

Prague July 3, 2019

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RE: Manuscript resubmission (ref. # soil-2019-9)

Dear Prof. Dr. Miano,

We thank the Editorial Board of SOIL for the opportunity to provide a revised version of our SOILD manuscript  
15 titled "*Spatially resolved soil solution chemistry in a central European atmospherically polluted high-elevation  
catchment*". The revised version enclosed benefited significantly from the interactive review process, which  
allowed for progressively restructuring, clarifying and addressing flaws of the original paper. We highly value the  
reviewers' insights and criticisms and provide below point-by-point response to both of the reviews, together with  
a list of all relevant changes made in the manuscript and marked-up manuscript version. We express our  
20 gratitude to the reviews for their insight that considerably improved our manuscript and your editorial handling on  
the topic.

On behalf of all authors,

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## Reviewer 1

**RC1.1** In the paper, hydrological problems rather than soil properties are discussed.

We have confidence that the “hydrological problems” considered in our *SOILD* are relevant for soil systems scientists focused on studying atmospheric-derived soil pollution and the detrimental propagation effects to contiguous ecosystems. See also response to RC1.3 below.

**RC1.2** Unfortunately, the paper is not generally well written, organized and balanced. The introduction is very short and quite approximate. A real state of the art is completely missing. Introduction should more concisely lead to the objectives of the work. Usually, a general rationale is needed. What is the purpose of the study?

We thank the reviewer for thoughtful criticism and kindly pointing out weakness of our original manuscript with regard to organization, balance, revision of pre-established concepts, and for carefully going through the text. A revised introduction addressing the reviewer's concerns was made available to the *SOILD* forum on Monday 04.05.19, with only minor editions made in the revised version of the manuscript. In addition, and as described below, by addressing each of the reviewer's concerns, requests for clarification and suggestions we have made every attempt to improve our report and look forward to the opportunity to submit the revised version of the *SOILD*.

**RC1.3** Methods, results and discussion of soil properties are poor. Authors indicated that soil profiles were described according to FAO guidelines, but no descriptions are included in the paper. They investigated Podzols, but soil properties are described and discussed referring only to a layer of a depth of 40-80 cm, without taking into account soil genetic horizons.

Descriptions of the soil profiles in UDL and their classification were published elsewhere (e.g., Novak et al. 2005; Oulehle et al. 2017). This fact has been made clearer in the revised version of the manuscript. Constituents of the layer referred by the reviewer are necessarily mentioned since their mineralogy, granulometry (particulate surface area), variable organic content and weathering paths are considered to affect (or be reflected by) the spatial variability of the chemical composition of the subsoil pore waters collected via lysimeters in our small mountain catchment. With regard to soil texture, we have modified the manuscript as follow:

page 3, lines 32-33; 4 lines 1-4 (Study Site: Background Information): *“A detailed description of the soils occurring on this watershed has been previously reported (Novak et al. 2005; Oulehle et al. 2017). Accordingly, the soil in the catchment are mostly acidic Podzols developed on orthogneiss to which only the Entic qualifier applies. Low base status soils have developed at expense of the mineralogy of the orthogneissic bedrock, and given the lack of lithological discontinuities, pedodiversity is low across the catchment area with Mor being the most common humus.”*

page 7, lines 17-20 (Results): *“In the eastern part of the catchment, coarse soil particles (gravel and stones) accounted for 24 % in the hillslope and 62 % of total soil granulometry at the hilltop, whereas in the western part of the catchment the soil particles above 10 cm in size accounted only for ~12 % (Table 2). The soil texture is loamy sand, with presence of authigenic clays (7-15 %) as weathering-induced alteration products of the orthogneiss parental material. [...]”*

**RC1.4** In two different sites on each hilltop and slope only one profile was investigated, and they are compared with the properties of only one soil profile located in a valley. All together, five soil profiles were investigated, and soil properties were compared. Soils are very different in their properties, especially in a mountain areas, so the number of soil profiles was not sufficient to compare and to conclude on differences in such soil properties as

carbon content, pH, cation exchangeable capacity, base saturation, etc. This, in addition to ignoring soil genetic horizons of Podzols investigated, is a reason of the weakness of data interpretation.

We respectfully disagree with the reviewer in his/her assertion that one soil profile for sampling area is insufficient for discussing the likely effect of soil textural features on the variability of the parameters listed above vs. legacy pollutants and nutrients imbalances. Previous, more detailed soil profile analyses in UDL has consistently show low pedodiversity (see note above on this regard).

**RC1.5** Soil properties, especially pH, changes in time through a year. It seems that soil samples were collected only once (in October 2010?).

We thank the reviewer for carefully going through the paper and for requesting sound clarifications. The soil samples were obtained in July 2015. This is now mentioned in page 5, line 17. On the other hand, we intended to compare pH values measured in stream water vs. pH of soil solutions. The confusing typo has been corrected as follow (page 4, line 24-26): “[...] during the decade 1994-2014, the median pH in the stream water remained stable in the range  $5.2 \pm 0.4$ , while over the same period, median pH levels measured in water percolating through the canopy (i.e., throughfall) increased from 4.1 to 5.2 (Oulehle et al., 2017).”

**RC1.6** Why [soil] pH values are compared to pH values of water collected during a whole year (page 5 lines 25-26)?

In the revised text, the lines highlighted here now read (page 6, lines 13-16): “Table 2 lists physical data for mineral soil and chemical data for soil extracts from the 40-80 cm depth layer and data for soil solutions collected by suction lysimeters (50 cm depth). As described above, the dataset is grouped according to sampling position within the catchment area (i.e., hilltops, slopes and valley; Fig. 1).” **That is, for the pH parameter there is no reference to the table directly serving for comparison purposes between discrete samples.**

**RC1.7** It is not clear what data were measured by authors and what data were cited from the literature (Oulehle et al. 2017).

To make clearer this key aspect highlighted by the reviewer, we have restructured the manuscript. Accordingly, the revised introduction now includes the following lines (page 3, lines 22-24): “This paper addresses primarily soil solutions chemistry in the UDL catchment. Supporting data on the chemistry of spruce canopy throughfall and stream runoff—parameters which are used here for comparison purposes, are accessible in Oulehle et al. (2017).”

Also, the first call to pre-existing data used for comparison purposes in the text is made in the new section 2 *Study Site and Background Information* (i.e., Fig. 2 and Table 1)

**RC1.8** It is not clear how authors define runoff and throughfall (amount of water versus chemistry of water) and how these parameters were measured. These parameters should be defined.

Following this important reviewer’s request for clarification, the word “runoff”, when originally and unclearly referring to runoff water samples, has been substituted for “stream water(s)” and a brief definition of throughfall water is now provided in page 4, lines 25-26: “[...] measured in water percolating through the canopy (i.e., throughfall) [...]”

**RC1.9** Conclusions summarize obtained results, but not contain real conclusions. Authors did not underline any innovative aspect that this article provides with respect to what is already present in literature.

The Conclusions section has been rewritten taking in consideration this concern of the reviewer and additional suggestions to improve the section provided by Reviewer 2.

**RC1.10** Several sentences are hard to follow, thus English proofreading is necessary.

Careful proofreading have been conducted to avoid runoff sentences.

- 5 **RC1.11** Summarizing, I do not consider this paper as relevant enough that deserves publication in the Soil journal.

We have made every attempt to address the reviewer's criticism and requests for clarification, elucidated its importance to the SOIL journal' readership in the Introduction and Discussion section, and, thus, hope that the revised version of our SOILD could be considered for publication in the EGU SOIL.

- 10 **RC1.12** After a major revision it would be considered for publication in a journal dealing with hydrology.

Please see to the author's reply to RC1.1 and RC1.11.

#### Detailed comments

**RC1.13** page 4, line 1: "A total of 15 replicates (3 per sampling location) were collected monthly". What replicates were collected? Does that mean water samples collected from 5 sites, each 3 times monthly?

- 15 This request of clarification of the reviewer has been addressed as follow (page 5, lines 7-8): *"[...] Each nest consisted of 3 lysimeters, and thus produced equal number of monthly replicates per sampling location. [...]"*

**RC1.14** page 4, lines 6-7: soil material from the depth 40-80 cm was collected. What soil horizons corresponded to this depth

- 20 This request of clarification of the reviewer has been addressed as follow (page 5, lines 25-26): *"Only results from the 40-80 cm soil level are considered here. This level is in chemical equilibrium with waters collected by our 50 cm depth lysimeter nets and correspond to horizon Bs2 in all plots."*

**RC1.15** page 4, line 16: "Runoff samples were collected monthly at the limnigraph location". How these samples were collected?

- 25 To address this reviewer's query, the revised text now reads (page 6, lines 1-2): *"Stream water samples and runoff flux estimations were collected monthly at a V-notch weir in the limnigraph location (Fig. 1b) according to methods outlined in Kram et al. (2003)."*

- 30 **RC1.16** page 4, line 4: " After centrifugation and filtration through 0.45 um cellulose–acetate filters, the filtrates were analyzed for cations" - this is not clear. Do these data refer to exchangeable cations? If so, the method was described in a wrong way. If not, what these data were measured for? Where these data were presented in the paper?

- 35 To address this flaw of the methods description kindly pointed out by the reviewer, the revised text has been streamlined as follow (page 6, lines 7-11): *"Exchangeable cations in soils were analyzed in 0.1 M BaCl<sub>2</sub> extracts by atomic absorption spectrophotometry (AAS, AAnalyst Perkin Elmer 200). Exchangeable acidity was determined by titration of the extracts. Cation exchange capacity (CEC) was calculated as the sum of exchangeable base cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>) and exchangeable acidity. Base saturation (BS) was determined as the fraction of CEC associated with base cations"*

**RC1.17** page 5, lines 25-26: "Table 2 lists physical data for mineral soil and chemical data for soil extracts from the 40-80 cm depth layer and compares them with data for soil solutions collected by suction lysimeters (50-cm depth)" - what does mean "soil extracts"? Were they obtained as described on page 4, line 4?

Please see note above.

- 5 **RC1.18** page 6, line 3: "characterized by acidic pH". Reaction can be acidic, but pH may be high or low.

The offending line highlighted by the reviewer now reads (page 7, line 23): *"The soil at the 40-80 cm depth was characterized by  $pH_{H_2O} < 5$ "*

- 10 **RC1.19** page 6, lines 4-5: "The mean pH of soil solutions ranged similarly between the first and the second year, except for the valley (pH valley of 4.1 in year 1, and 4.5 in year 2; Table 2). The two-year averages of soil solutions were", - this part of the text belongs to the paragraph 3.1. (Soil texture and pH). Does this data refer to soil extracts (page 4 line 4)? It seems that soil samples were collected just once in 2010, so how was it possible to obtain two-years averages? If these data refer to soil solutions obtained from lysimeters (page 3, line 28), they should be included in paragraph 3.3. (Solute concentrations in soil waters).

- 15 The data refer to soil water solutions obtained from lysimeters, not to soil extracts. As per reviewer's suggestion the text has been moved to subsection "4.2.1 pH, CEC and BS" of the restructured manuscript

**RC1.20** page 6, lines 9-10: how 33 meq and 58 meq can give mean 32 meq?

We thank the reviewer for highlighting the lack of clarity of the initial data description. The revised text now reads (page 8, line 2): *"[...] which is within the mean CEC values measured at all of the plots at UDL:  $32 \pm 7$  meq  $kg^{-1}$  (Table 2)."*

- 20 **RC1.21** page 6, lines 10-17: usually cation exchange capacity differ significantly through Podzol profiles, from ectohumus through albic and spodic horizons. The same concerns base saturation. I have a doubt if these values may be compared without referring to given soil horizon.

- 25 To address this important observation of the reviewer. The following feature was added to our description of Soil Samples (page 5, line 25-26): *"Only results from the 40-80 cm soil level are reported in this work. This level is considered in chemical equilibrium with waters collected by our 50 cm depth lysimeter nets and corresponds to horizon Bs2 in all plots."*

**RC1.22** page 6, line 26: authors used different terms to characterize chemical properties of water, namely: soil water, soil solution, mineral soil solution. It is not clear to what data refer concentration in soil water? Are they data from lysimeters?

- 30 A unification of equivalent terms referring to soil water from lysimeters has been implemented in this revision, and are now only referred to as "soil solutions"

**RC1.22** page 7, line 2: how was runoff measured?

Please refer to author's answer to RC1.15 above

**RC1.23** Were data in table 1 obtained by authors?

- 35 Table 1 is comprised of background information and this has been now made clearer. Please see author's response to RC1.7 (above)

**RC1.24** page 7, lines 10-11: "Our results for NO<sub>3</sub><sup>-</sup> across the lysimeter network also show that this chemical species was readily bioavailable along mostly in the valley, where its concentrations were one order of magnitude higher than in the upslope soil solutions" - it is not clear how this was deduced.

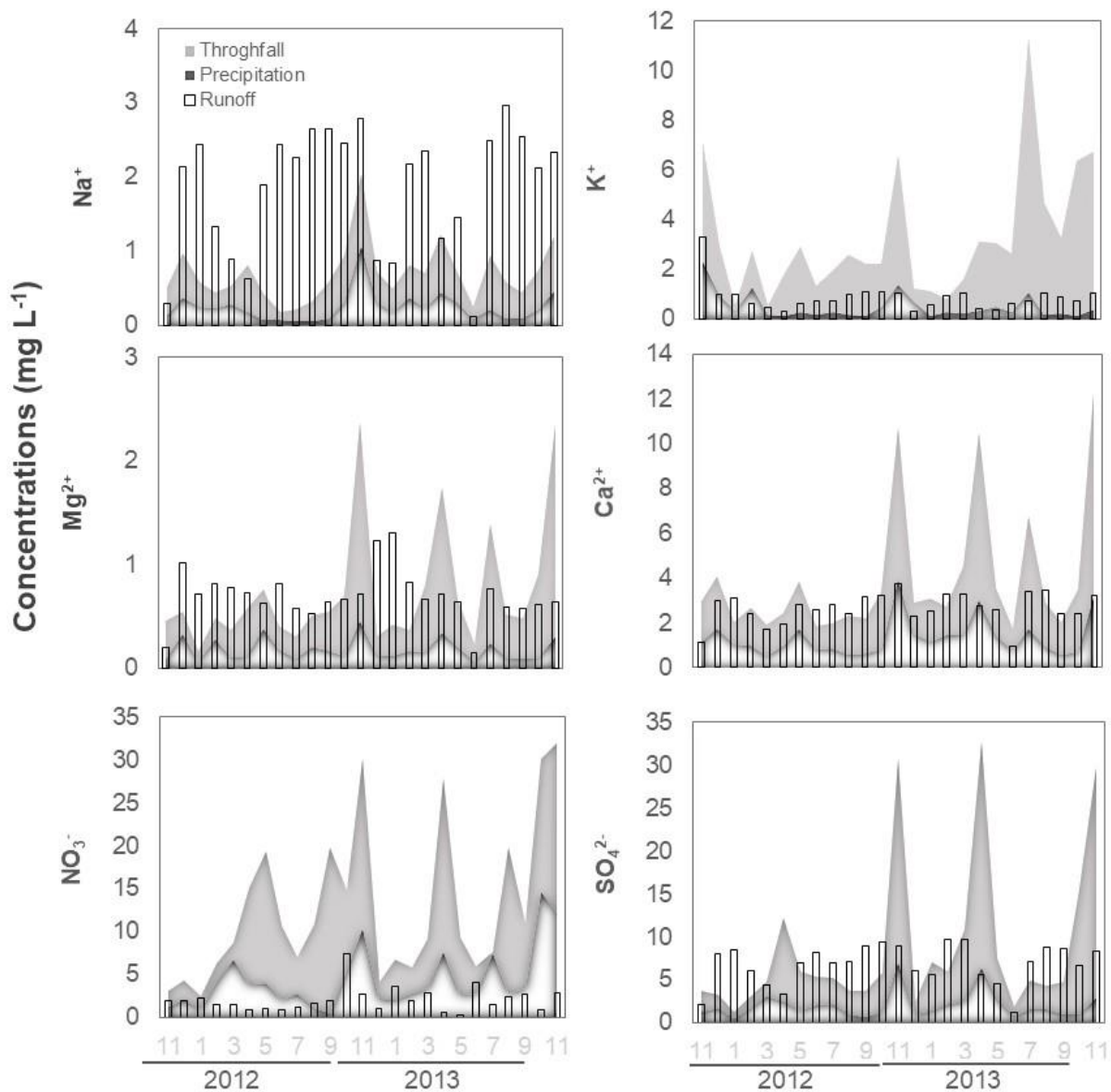
- 5 The revised text (page 8, 33 and 9, 1-2) now reads: *"Our results for NO<sub>3</sub><sup>-</sup> across the lysimeter network also show that this chemical species was readily bioavailable along the study site but mostly in the valley, where its concentrations were one order of magnitude higher than in the upslope soil solutions (Fig. S1)."*

**RC1.25** page 10, line 3: table 2 does not provide sufficient information on soil textures heterogeneity

Table 2 only presents the available relevant information on soil texture for comparison purposes in the studied low pedodiversity, UDL catchment area.

- 10 **RC1.26** Figure 2 is unreadable due to unclear crosshatch. Does it present data obtained by authors?

As per reviewer request the crosshatch has been removed from the revised version of Figure 2 thus making it clearer. Figure 2 is background information and in consequence is first called in section 2, *Study Site and Background Information*.



**RC1.27** Table 1. In Hydrology, throughfall is the process which describes how wet leaves shed excess water onto the ground surface. Was throughfall measured by authors? If so, how it was measured?

Generally accepted definition as used in our manuscript and related literature is the water percolating through the canopy (please see also author's response to RC1.8).

**RC1.28** Table 2. Why (and how) soil particulate size (> 10 cm) were expressed in t/ha?

From the methods of estimation outlined in section 3.2. Soil Samples, where the weighted material from a given area. To address this concert, this parameter in Table 2 is now expressed in kg instead of ton.

**RC1.29** Figure S2. What does mean the following: "hydrochemical data for runoff, atmospheric in lysimeters"?

We thank the reviewer for carefully going throughout the manuscript. The offending line caption now reads: [...] *"Non-parametric multidimensional scaling ordination of time-series hydrochemical data for stream water, rainwater and soil solutions collected in lysimeters."*



## Reviewer 2

**RC2.1** Petrash et al. present an interesting study on the spatial heterogeneity of soil solution in a central European high-elevation catchment which formerly received high loads of atmospheric pollutants. The topic is highly relevant for SOIL and the data gathered for the study are considered worth being published. However, with respect to the structure of the manuscript as well as the presentation of the methods and the data the manuscript seems to need major revisions.

We thank the constructive criticism of reviewer 2, Prof. Dr. Meesenburg, and have made every attempt to address each of his concerns and suggestions for improvement.

**RC2.2** The introduction reflects the history of atmospheric pollution in the “Black Triangle” The last paragraph of the introduction needs to be completely rewritten as it contains little information concerning the design of the study, but methodological issues, results and even concluding statements. No objectives neither hypotheses are given in the introduction. Please amend accordingly.

To address this concern of the reviewer, the introduction section has been significantly rewritten and expanded to now provide a brief review of background information and relevance, objectives and hypotheses of the study.

**RC2.4** Otherwise, assessments are mentioned (i.e. soil moisture determination), which value for the study remains unclear.

Unused information such as unrelated soil moisture measurements has been now removed from the revised methods.

**RC2.5** According to Figure 1, sampling plots for soil solution and solid soil are up to more than 200 m apart. However, no information is given with respect to the comparability of the respective plots. Please give a rationale for this approach as the results from either solid soil or soil solution are related to the respective slope position.

The revised version of the MS page 5, rows 19-19 now clarifies this aspect: *“Five 0.5 m<sup>2</sup> soil pits were excavated in July 2015 at some distance to the previously installed suction lysimeter nests to avoid disturbances to the zero tension soil solution collection systems (Fig. 1b) while preserving a soil profile equivalent to the one at the nearby nest and also the relative position within the catchment area.”*

**RC2.6** The contents of the results section are structured differently as the methods section.

The revised results section of our MS has been restructured to address this flaw of the original submission kindly pointed out by the reviewer.

**RC2.7** Some parameters, which are displayed in the tables and figures aren’t mentioned in the text body of the results section.

Conductivity parameter has been removed from Table 2. The rest of the parameters listed are either mentioned/discussed in the main text, or are needed for calculations (e.g., Al<sub>ox</sub>, Fe<sub>ox</sub>)

**RC2.8** For soil solution, different units are reported in the text and in table 2.

Now all in-text mentions to soil solution concentrations are referred to Table 2, where concentrations units are expressed in ppb.

**RC2.9** The last part of the results (i.e. page 8, row 6-11) seems to be more suitable for the discussion.

The misplaced text kindly highlighted by the reviewer was moved and integrated to the discussion section (page 12, rows 16-21).

**RC2.10** The integration of the assessment of P availability into the study appears a little bit weak as no relation to either soil solution or runoff P concentrations is given. Also, a discussion on the role of P availability for tree nutrition is missing. A convincing evidence for the “de-coupling” of P availability and organic carbon is missing. At least, an explanation should be given, why a “coupling” of P availability and organic carbon should be expected.

There is no further reference in the revised text to coupled/decoupled cycling of nutrients, but to the role of P in belowground C allocation and base cation imbalance. With regard to our P measurements, the revised text (page 12, rows 23-34) now reads: *“Soil P sorption saturation is often used as an environmental indicator of soil P availability to runoff. Phosphorus losses from soils not subjected to an augmented erosional process are generally small (see Heuck and Spohn, 2016) [...]. It is possible that P limitation has developed because of the legacy of anthropogenic N deposition in this region. The homogenous pattern of low P availability contrasts with elevational differences in DOC concentrations in soil solutions (Fig. S1), which points to variable belowground leaching and allocation of C or could be reflective of variable inputs of C from regenerating vegetation in the N-saturated, P-limited forest ecosystem. Conifer tree species are generally more tolerant to P limitations, which in turn make them more susceptible to nutrient depletion following losses from harvesting and exacerbated rates of nutrient export (Hume et al., 2018). We attribute the variable belowground allocation of C in UDL to spatially variable Mg<sup>2+</sup> and/or K<sup>+</sup> deficiencies (e.g., Rosenstock et al., 2016) rather than to P imbalances within the catchment since we detected no spatially contrasting P deficiencies exerting influence over the contrasting patterns of nutrient limitation and subsoil nutrients leaching observed across the studied forested landscape.”*

**RC2.11** The conclusion contains issues, that haven't been discussed before (e.g. the role of drought and torrential rains, isotope investigations). This should be avoided.

The flaws on the original conclusions kindly pointed out by the reviewer are now avoided and the conclusion section have been streamlined, with no reference to undiscussed aspects.

**RC2.12** The last three points of the conclusions resembles a collection of keywords more than elaborated findings.

The last three points indicated by the reviewer were removed from the text, and the section rewritten as follows:

*“The hydrochemical comparisons implemented here were aimed at evaluating spatial and temporal concentration patterns on the water chemistry among the subsoil compartment of the critical zone in a temperate forest. Because of landscape and lithological simplicity, which facilitates discerning flow paths without variability effects introduced by differential bedrock weathering, it was possible discussing what factors in association to soil N-saturation affect the soil solution chemistries of a small mountainous catchment area reforested by Norway spruce after acidification-related spruce die-back. By combining soil solution chemical measurements and establishing comparisons with published hydrochemical data, this work provides evidence pointing to substrate variability, and C, but not P bioavailability, as major controls over the flux of base metal leached into the subsoil level and across the elevation gradient. Soil solutions at the 50 cm depth were generally more diluted than stream waters due to lateral surface runoff of solutions originating in the litter and humus enriched in SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>. Increased concentrations are linked to anthropogenic atmosphere-derived pollution affecting natural (bio)geochemical processes. Differences between chemistry of soil solution and runoff could have been also caused by a direct contribution of throughfall, which scavenged atmospheric chemicals of the canopy and leached nutrients from inside the foliage, or by polluted open-area precipitation. Soil solutions had lower pH in the valley than at upslope locations, being more diluted in the valley than on hilltops in the case*

of DOC, Ca<sup>2+</sup> and Mg<sup>2+</sup>. Both NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in soil solutions exhibited a clear seasonality that can affect base metal leaching, with maximum concentrations in the growing and dormant season, respectively.

The observed temporal trends amongst strong anion inputs and leaching of base metals and acid anions reflect that at the time of sampling nutrient imbalances in UDL were linked to groundwater carrying legacy pollutants. A complementary isotope modelling show that the responses of the studied mountain catchment to precipitation are fast, i.e., within the monthly sampling interval, with direct precipitation contributing 20 to 40% of the discharge and the rest being the contribution of local groundwater. When evaluated with regard to stream water chemistries and previously published input and fluxes, the dataset in this study provides insights into the localized controls and effects of acidification disturbances at a catchment-scale and offers a perspective of the spatially and temporally variable nutrient concentrations in soil solutions that is relevant for (i) more effectively designing stream water chemical analyses aimed at understanding the coupling of soil development processes and hydrology over variable time scales, and between deep and shallow weathering processes in mountain catchments; and (ii) for evaluating soil recovery processes after atmospherically induced perturbations that affected other catchments analogue to UDL."

- 15 **RC2.13** The chapter on <sup>18</sup>O/<sup>16</sup>O modelling in the Appendix seems not very well integrated in the study.

We added the following lines to the rewritten introduction to address this concern of the reviewer (page 3, lines 16-18): *"In addition, the contribution of groundwater vs. runoff infiltration is further evaluated by mean of a supplementary isotopic runoff model, which provides evidence for a likely contribution of groundwater enriched in selected chemical species due to sufficiently long water-saprolite interactions."*

- 20 Also the revised discussion text (page 12, lines 4-12) now reads: *"On this note, we followed the modelling approach implemented by Buzek et al. (1995, 2009) to provide further insight on the mean residence time of soil solutions—calculated across all sampling locations— which was estimated in approximately 8.3 months (Appendix A). In consequence, the runoff water at UDL is a mixture of direct precipitation with older soil solutions containing admixed with even older shallow groundwater. The supplementary isotopic modelling implemented here also shows that direct precipitation contributes between 20 and 40% of the discharge, with the rest being local soil pore and ground waters (Appendix A). The combination of all these three water types is called "mobile water", defined as the sum of all water pools and fluxes that respond to changing precipitation amounts. This mobile water transiently increases soil solution saturation and concomitantly with such an increase, the hydrologic connectivity of soil pore waters to the stream can cause a heterogeneous distribution of dissolved ions in soil solutions at the catchment-scale (Basu et al., 2010)."*

**RC2.14** The references are mostly relevant for the study and up-to-date. However, some citations aren't very specific to the referenced issues.

The reference have been revised as per reviewer indications (see below under Specific comments).

- 35 **RC2.15** The publication of the manuscript can only be recommend after a major revision considering the above mentioned concerns

We thank the reviewer for providing generous indications, guidance and sound revisions/ suggestions that significantly improved the original submission.

## **R2. Specific comments**

- 40 **RC2.16** page 2, row 1 "Blazkova et al., 1996" -> "Blazkova, 1996"

Done

**RC2.17** page 2, row 3 “Blazkova et al., 1996” -> “Blazkova, 1996”

Done

- 5 **RC2.18** page 2, row 6 “Fen et al. 1998” doesn’t appear in the references. Is “Fenn et al. 1998” meant? If so, this citation doesn’t support the before stated sentence, because it mainly reflects the situation in North America.

Done.

**RC2.19** page 2, row 6 “Hruska et al. 2003” -> “Hruska and Kram, 2003”

Done.

**RC2.20** page 2, row 8 “Gradowski et al., 2008” -> “Gradowski and Thomas, 2008”

- 10 Done.

**RC2.21** page 2, row 9 “Matschullat et al., 1998” -> “Matschullat et al., 1992”. This citation doesn’t give relevant information on the bioavailability of phosphorus. Please replace accordingly.

Reference removed as per reviewer indication.

**RC2.22** page 2, row 10-11 This sentence isn’t relevant for the introduction. It may be shifted to section 2.1.

- 15 Text was removed as part of the editions implemented to the Introduction.

**RC2.23** page 2, row 10-18 “For this aim, a nests of suction lysimeters was installed ...” -> “For this aim, nests of suction lysimeters were installed ...”

Done

**RC2.24** page 2, row 30 Would this kind of orthogneiss with the reported composition really be termed “alkaline”?

- 20 Word “alkaline” removed. The term apply to granite protolith over the base of the observed gneiss composition.

**RC2.25** page 3, row 1 “... m, UDL’s ...” -> “... m a.s.l., UDL’s ...”

Done

**RC2.26** page 3, row 2 At page 2, row 30, the parent material was named “alkaline gneiss”. Is this the same as “porphyric granite”? Please clarify!

- 25 The first is the metamorphic product of the latter. We thank the reviewer for noticing the lack of clarity of the text. This has been now clarified (page 4, row 2-3): *“Low base status soils have developed at expense of the mineralogy of the porphyritic granite that served as protolith to the orthogneissic bedrock [...]”*

**RC2.27** How can Podzols develop on “alkaline gneisses”?

- 30 The unclear statement was corrected as per note above. In igneous petrology, the composition of the igneous-metamorphic bedrock falls within alkaline granite in a compositional diagram.

**RC2.28** page 3, row 4 Are the given figures the runoff for one month? Please clarify!

We have clarified the text as per reviewer request (page 4, row 6): “ [...] the monthly highest stream water runoff flow is usually recorded ( $\sim 162 \pm 29$  mm).”

**RC2.29** page 3, row 9 I wouldn't consider saplings trees up to 40 yrs.

True. The revised text now refers these to as “trees < 40 yrs” (page 4, row 8)

- 5 **RC2.30** page 3, row 12 Please delete “The.”

Deleted.

**RC2.31** page 3, row 12-13 Please give the depth interval for the pH figures.

The revised text now reads (page 7, row 23): “The soil at the 40-80 cm depth was characterized by  $pH_{H_2O} < 5$  (Table 2).”

- 10 **RC2.32** page 3, row 13 “... a pH increases in throughfall measurements ...” -> “... a pH increase in throughfall ...”.

The revised text now reads (page 4, row 25-26): “[...] while over the same period, median pH levels measured in water percolating through the canopy (i.e., throughfall) increased from 4.1 to 5.2 (Oulehle et al., 2017).”

**RC2.33** page 3, row 13-14 Two times the same citation in one sentence isn't necessary.

- 15 The doubled citation referred by the reviewer is now removed from text.

**RC2.34** page 3, row 14-15 A comparison of pH(H<sub>2</sub>O) and pH(KCl) doesn't makes much sense.

Agreed. The offending text pointed out by the reviewer was removed.

**RC2.35** page 3, row 15 “Hruska, 2000” -> “Hruska, pers. comm.” (unpublished data weren't published in 2000).

Reference removed as per note above.

- 20 **RC2.36** page 3, row 16-26 The content of this paragraph may be better placed in the results section. In addition figures presented should be given with standard deviation. Presented figures are a strange mixture of 13 or 14 catchments. Please revise consistently!

As suggested by the reviewer, a new section 2, titled *Study Site and Background Information*, now contains this information. There are 14 catchments in the Geomon network, this has been revised for consistency in page 4, line 32: “[...], which is far in excess of the atmospheric inputs observed in the remaining 13 GEOMON's monitored catchments across the Czech Republic”.

- 25

**RC2.37** page 3, row 27 Section “2.2.1” follows “2.1”. Please check for consistency.

Consistency of section and subsection numbering and general manuscript structure has been revised as per reviewer's suggestion.

- 30 **RC2.38** page 3, row 28 “... at a 50-cm depth below ...” -> “... at 50 cm depth below ...”. Please change consistently throughout the manuscript.

Done.

**RC2.39** page 3, row 28 Were the lysimeters installed 50 cm below soil surface or below forest floor? Please clarify!

Done. The revised text now reads (page 5, row 6): *“were installed at 50 cm depth below soil surface”*

**RC2.40** page 4, row 6 the sampled depth intervals aren't horizons. Please specify!

5 Now these are referred to as soil levels (e.g., page 10, row 20; page 11, row 13).

**RC2.41** page 4, row 8 the given citation (FAO 2006) isn't about soil description. Please give correct citation!

FAO, 2006 removed from references.

**RC2.42** page 4, row 19 Please specify the relation of soil to water for pH measurement.

10 Done. The revised text now reads (page 6, row 5-6): *“A Radiometer TTT-85 pH meter with a combination electrode was used to measure  $pH_{H_2O}$  of soil (soil–water suspension ratio = 1 : 2.5).”*

**RC2.43** page 4, row 19-20 Please specify the meaning of soil moisture determination for the study, if any.

Any reference to soil moisture in text is now removed.

**RC2.44** page 4, row 22 “5 ° C” -> “5°C”

Done.

15 **RC2.45** page 4, row 23-27 The sequence of the determination of exchangeable cations seems in an incorrect order. Where NO<sub>3</sub> and SO<sub>4</sub> determined in the BaCl<sub>2</sub> extracts?

20 We thank the reviewer for kindly pointing out this flaw in our original methods description. The text has been revised as follow (page 6, row 9-11): *“[...] The concentrations of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> from the soil extracts described above were determined by ion chromatography (HPLC Knauer 1000), with limit of quantification (D.L.) of 0.1 and 0.3 mg L<sup>-1</sup>, [...]”*

**RC2.46** page 4, row 28 Consider “For a phosphorus (P) release estimation, ...” -> “For a estimation of phosphorus (P) availability, ...”

Following the reviewer suggestion page 6, row 13 now reads: “For an estimation of phosphorus (P) release [...]:

**RC2.47** page 4, row 28-29 Please specify the soil:solution relation and the concentration of the solution.

25 Done. The revised text (page 6, row 13-18) now reads: *“[...], ammonium oxalate extractions were performed by following the protocol described in Schoumans (2000). In short, a reagent solution consisting of (COONH<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and (COOH)<sub>2</sub>·2H<sub>2</sub>O was used to dissolve 1 g of the <2 mm soil fraction. Extractable phosphorus (P<sub>ox</sub>), iron (Fe<sub>ox</sub>), and aluminium (Al<sub>ox</sub>) were determined by shaking for 2 h in the dark duplicate samples of soils with 30 mL of 0.5 M reagent in 50 mL centrifuge tubes. [...]”*

30 **RC2.48** page 5, row 1 “DPSox” in table 2.

Corrected as per Table 2.

**RC2.49** page 5, row 3 “Beauchemin et al., 1999” -> “Beauchemin and Simard, 1999”

Done

**RC2.50** page 5, row 4 “Borovec et al., 2018” -> “Borovec and Jan, 2018” page 5, row 11

Done

**RC2.51** Please introduce the meaning of D.L. at the first appearance! If detection limit is meant, consider to use “limit of quantification” instead.

5 Done (page 6, row 10): “*with limit of quantification (D.L.)*”

**RC2.52** page 5, row 14 Please explain the meaning of “non-parametric data”.

Done (page 7, row 2): “The non-normally distributed (*i.e.*, non-parametric) data [...]”

**RC2.53** page 5, row 14-22 The description of the factor analysis resembles - in my view as a nonstatistician – a parametric method. Please specify the non-parametric component of the statistical analysis.

10 Done. Please see note above.

**RC2.54** page 5, row 20 Please check the grammatical structure of the sentence.

The revised text now read (page 7, row 9-11): “*The variables can then be plotted in groups with correlation among them being determined by their position (e.g., proximity, distance, orthogonality,). The two-dimensional plane where the rotated, normalized data were plotted can be interpreted in terms of the main controls over the general variance of the dataset (see Vega et al., 1998 for details).*”

15

**RC2.55** page 5, row 24 The reporting of results for soil texture and pH in one subchapter appears strange to me. Why not report pH together with other soil chemical variables?

This flaw in our original manuscript structure has been corrected (see new subsection in *4.2 Soil Chemical Characterization*)

20 **RC2.56** page 5, row 26-28 This sentence is more or less a repetition from section 2.2.1. Accordingly, it may be omitted.

The text was omitted as per reviewer’s suggestion.

**RC2.57** page 6, row 1 Please give a definition of “pebbles” and “cobbles”.

In the revised text (page 7, row 17) we now use “coarse soil particles (gravel and stones)”

25 **RC2.58** page 6, row 4-7 Consider to shift this part to section 3.3.

Moved to equivalent section 4.2.1 in the restructured manuscript.

**RC2.59** page 6, row 10 Is the mean given for all five sampling plots?

This revised text was clarified in this matter as follow (page 7, rows 28-29; 8, 1-2): “*In the eastern part of the catchment, the cation exchange capacity (CEC) of the mineral soil at 40-80 cm depth was up to 33 meq kg<sup>-1</sup> on the slope and 58 meq kg<sup>-1</sup> on the hilltop (Table 2). By contrast, in the western part, the CEC was 22 and 19 meq kg<sup>-1</sup>, which is lower than the mean CEC values measured at all of the plots at UDL, whilst CEC in the valley was 27 meq kg<sup>-1</sup>, which is within the mean CEC values measured at all of the plots at UDL: 32 ± 7 meq kg<sup>-1</sup> (Table 2).*”

30

**RC2.60** page 6, row 16 Please check “twice larger” for correctness.



Done. Revised text (page 8 row 11-12) now reads: *"The BS at UDL is twofold higher than the BS determined at similar soil depths in the leucogranitic catchment LYS [...]"*

**RC2.61** page 6, row 17 "Hruska et al., 2001" isn't in the references. Please check.

Revised. It is Hruska et al., 2000 (page 8, row 10)

- 5 **RC2.62** page 7, row 4-6 Water volumes haven't been mentioned before. This sentence may be omitted or the relevance of water volumes for the study should be emphasized.

This information was removed as is not further used in our results or discussions

**RC2.63** page 7, row 9 "... to be higher at ..." -> "... to be highest at ..."

Done.

- 10 **RC2.64** page 8, row 2 According to figure S2, explained variance is 24%

True. Corrected.

**RC2.65** page 8, row 3 According to figure S2, explained variance is 18%

True. Corrected.

**RC2.66** page 8, row 3 Is "Fig. S2" meant here?

- 15 Correct. Revised (now page 9, row 11)

**RC2.67** page 8, row 6-11 This part seems rather to be dedicated to the discussion. However, logical and grammatical consistency should be checked.

- 20 The text moved as per reviewer suggestion to discussion and also revised for grammatical correctness (page 12, rows 16-21): *"Finally, given the complexity of the possible interrelations among the environmental variables considered here, there was an apparent generally poor correlation between solute concentrations measured in the soil in 2012-2013 and decadal runoff and atmospheric deposition data compiled in Table 1 (after Ouhlele et al., 2017). Such a result in turn points to a major control exerted by groundwater chemistry over soil solution chemistry, and also to soil organic and inorganic ligand properties also exerting a control over the residence time of each of the measured components."*

- 25 **RC2.68** page 8, row 7 Please explain the meaning of "apparent insignificant correlation".

See note above: *i.e.*, poor correlation

**RC2.70** page 8, row 23-24 "Manderscheid et al., 1995" -> "Manderscheid and Matzner, 1995"

Done.

**RC2.71** page 8, row 24 "Hruska et al., 2000" appears twice in the references. Which one is meant?

- 30 Corrected as per RC2.61

**RC2.72** page 8, row 24 "Armbruster et al., 2004" -> "Armbruster and Feger, 2004"

Done.



**RC2.73** page 9, row 9 “Meyer et al., 2001” is missing in references.

Done.

**RC2.74** page 9, row 12-14 Please check grammatical consistency of the sentence.

5 Done. Now page 11, row 14-16: *“The latter effect seems to be critical in the variability in soil solution chemistry at the hilltops, where the subsoil level contain significant amounts of coarse parental-rock material (Table 2).”*

**RC2.75** page 9, row 20 Is “Novak et al., 2005 meant here?

Right.

**RC2.76** page 10, row 4 What is meant with “areal control” here?

10 Text edited as follow (page 11, row 17-18): *“For Na<sup>+</sup> and K<sup>+</sup> ions in soil solutions, our spatially resolved time-series observations (Fig. 3) show that their concentrations defined patterns and trends largely derived from heterogeneity in soil granulometry (Table 2), with seasonality [...]”*

**RC2.77** page 10, row 4-6 I can’t follow this statement.

Corrected. Please see note above.

**RC2.78** page 10, row 8-9 What is the rationale behind the comparison of K and Na outputs?

15 The revised text (page 11) clarify the rationale and provide further information.

**RC2.79** page 10, row 14-15 To which other period is the spring season of 2013 compared here?

The request for clarification of the reviewer has been addressed as follow (page 11, row 29-30): *“[...] a seemingly more rapid response of Na<sup>+</sup> leaching to soil solutions could result from strong anion belowground episodic accumulation (Fig. 3; e.g., Spring 2013)*

20 **RC2.80** page 10, row 21 “Heuck et al., 2016” -> “Heuck and Spohn, 2016”

Done.

**RC2.81** page 10, row 23 “... in the 50 cm-depth ...” -> “... in the 40-80 cm depth ...”?

Done.

**RC2.82** page 12, row 5 “... these periods ware compared.” -> “... these periods were compared.”

25 Done.

**RC2.83** page 12, row 11 Figure A1a isn’t visible in the manuscript. If “Figure 2A is meant, it should be corrected throughout Appendix A. page 12, row 26 Consider “... in soil pore spaces ...” -> “... in soil pores ...”

Done.

30 **RC2.84** page 12, row 28 What is meant with “direct precipitation”? If the “contribution of direct runoff (or “event water” as in eq. 2) to total runoff” is meant, a clear definition of “direct runoff” should be given.

The originally unclear text now reads “bulk precipitation” (page 15, line 1); “direct” removed

**RC2.85** page 15, row 21 “Fenn, E.M.,” -> “Fenn, M.E.,”

Reference removed.

**RC2.86** page 15, row 22 “Stottlemeye, R.” -> “Stottlemyer, R.”

Done.

5 **RC2.87** page 15, row 24-25 “FAO: Guideline for soil description; Rome, Italy, 2006” should be cited here.

Reference removed given that soil profile descriptions were done in previous works. See also reply to RC2.4.

**RC2.88** page 15, row 32-16/2 Please give correct title of the reference.

Done.

10 **RC2.89** page 16, row 3-7 “Hruska et al., 2000” appears twice. Please indicate the respective citations with “a” and “b”. page 16, row 13 This line should be deleted.

Done.

**RC2.90** page 16, row 22 “Ma, L; Teng, F.-Z.; Lin, L.,” -> “Ma, L; Teng, F.-Z.; Lin, L.; et al.,” page 18, row 2 “Soiling” -> “ Solling”

Done.

15 **RC2.91** page 19, Figure 1 (b) Please consider to shift the sentence starting with “in the studied UDL ...” to the text body of section 2.1.

Caption edited as suggested.

**RC2.92** page 23, Figure 2A The content of this figure relates to Appendix A and should be placed in the supplements accordingly?

20 Done.

|

# Spatially resolved soil solution chemistry in a central European atmospherically polluted high-elevation catchment

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**Abstract.** We collected soil solutions by suction lysimeters in a central European temperate forest with a history of acidification-related spruce die-back in order to interpret spatial patterns of soil nutrient partitioning, compare them with stream water chemistry. ~~To interpret spatial patterns of soil nutrient partitioning and compare these with runoff in a temperate forest with a history of acidification-related spruce die-back, the chemistry of mineral I<sub>i</sub> soils and evaluate both of these these parameters relative to concurrent loads of anions and cations in precipitation, soil solutions were collected by suction lysimeters in a central European temperate forest with a history of acidification-related spruce die-back and evaluated relative to concurrent loads of anions and cations in precipitation.~~ Lysimeters nesties. Five lysimeter nests were installed in the 33-ha U dvou loucek (UDL) mountain catchment at different topographic positions (hilltops, slopes and valley). Following equilibration, monthly soil solution samples were ~~collected~~ interrogated over a 2-year period with regard to their over a 2-year period. ~~In the vicinity of each lysimeter nest, soil pits were excavated for constraining to also constrain soil chemistry. Soil solutions were analyzed for~~ SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and total dissolved Al concentrations, organic carbon (DOC), and pH. ~~Soil pits were excavated in the vicinity of each lysimeter nest to also constrain soil chemistry. For an estimation of phosphorus (P) availability~~ For a P-release estimation, ammonium oxalate extraction of soil samples was performed. ~~Comparison of soil watersolution data with other previously acidified monitored European sites indicated that most of the environmentally relevant chemical species investigated at UDL had concentrations similar to median concentrations observed in sites with similar bedrock lithology and vegetation cover.~~ Cation exchange capacity (CEC ≤ 58 meq kg<sup>-1</sup>) and base saturation (BS ≤ 13 %) ~~, however,~~ were found to be significantly lower at UDL than in other monitored central European small catchments areas, documenting incomplete recovery from acidification. Spatial trends and seasonality in soil ~~watersolution~~ chemistry support belowground inputs from mineral-stabilized legacy pollutants. Overall, the soil solution data suggest the 30 years after peak acidification the ecosystem is was still out of balance chemically, relative to the ~~present concurrent~~ loads of anions and cations in precipitation, documenting incomplete recovery from acidification. Nearly 30 years after peak acidification, UDL exhibited similar soil solution concentrations of SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> as median values at the Pan-European International Co-operative Program (ICP) Forest sites with similar bedrock lithology and vegetation cover, yet NO<sub>3</sub><sup>-</sup>

concentrations were an order of magnitude higher. Higher-When concentrations of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and base cations in runoff than in are compared to soil pore waters are explained by, higher concentration in runoff point to lateral surficial leaching of pollutants and nutrients from in excess than from topsoil to subsoil. With P availability being below the lowest range observed in soil plots of the Czech Republic, the managed forest ecosystem in UDL probably reflects growing inputs of C from regenerating vegetation in the N-saturated soil, which leads to P depletion in the soil. Nearly 30 years after peak acidification, UDL exhibited similar soil solution concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as median values at the Pan-European International Co-operative Program (ICP) Forest sites, yet  $\text{NO}_3^-$  concentrations were an order of magnitude higher. In addition, the observed spatial variability provides evidence pointing to substrate variability, C and P bioavailability, and landscape as major controls over base metal leaching toward the subsoil level in N-saturated catchments.

## 1 Introduction

During the second half of the 20th century, atmospheric deposition of reactive nitrogen (N) and sulfate ( $\text{SO}_4^{2-}$ ) caused persistent perturbations in temperate forest soils and water sheds across Europe (Blazkova, 1996; Alewell et al., 2001; Verstraeten et al., 2017). Reaction of sulfur dioxide ( $\text{SO}_2$ ) and nitrogen oxides ( $\text{NO}_x$ )  $\text{SO}_2$  and  $\text{NO}_x$  gases with water molecules in the atmosphere produced sulfuric and nitric acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ) which were then entering mountain forest ecosystems via wet and dry deposition. Intergovernmental cooperation to significantly abate detrimental sulfur dioxide ( $\text{SO}_2$ ) and nitrogen oxides ( $\text{NO}_x$ ) emissions was implemented during the 1980s and resulted in a significant decrease in the atmospheric deposition of soil-acidifying species. Reaction of  $\text{SO}_2$  and  $\text{NO}_x$  gases with water molecules in the atmosphere produced sulfuric and nitric acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ) which were then entering mountain forest ecosystems via wet and dry deposition. Industry restructuring and installation of scrubbers in power plants significantly reduced industrial  $\text{SO}_2$  emission rates by more than 90% in one of the most polluted industrial regions of Central-central Europe, known as the “Black Triangle”, which includes mountainous border regions of three countries, Czech Republic, East Germany and Poland (Fig. 1a; Blazkova et al., 1996; Novak et al., 2005). A decrease in soil solution  $\text{SO}_4^{2-}$  concentrations followed, and has progressively lowered soil solution ionic strengths while contribution contributing to a progressive raise in soil pH, which may have in turn increased organic matter leaching by lowering the soil solution concentrations of aluminum ions ( $\text{Al}^{3+}$ ) (e.g., Monteith et al., 2007). Although also significantly decreased (Waldner et al., 2014), atmospheric inputs of reactive N species in excess to the nutritional demands of plants and microorganisms have prevailed across central Europe (Waldner et al., 2014, 2015). These have resulted in forest ecosystem perturbations consisting on a cascade of biogeochemical reactions linked to soil N-saturation (Galloway et al., 2003). For instance, despite a ~40 % reduction in atmospheric N inputs (Kopáček-Kopacek et al., 2013), in the Czech Republic alone the value of the total nitrogen deposition remained—during the last decade—in the range of 70,000–80,000 t per year as a result of the production of  $\text{NO}_x$   $\text{NO}_x$ -emissions from transport, industrial production and energy generation (CENIA, 2017). The unchanged figures, despite significant efforts for controlling industrial emissions over the

same period, is a societal concern since there is growing uncertainty on whether or not central European temperate forest ecosystems—~~some of which are displaying signs of N saturation (Oulehle et al. 2017),~~ will be in capacity to continue acting as major sinks for a 15-20% intensification in anthropogenic emissions of reactive N to the atmosphere (Galloway et al. 2008). A detrimental effect ~~for the environment~~ of unmanaged soil N-saturation in catchment areas ~~would be~~ the propagation of environmental effects to nearby lacustrine ecosystems—increased seasonal water reservoir eutrophication linked to augmented N-exports (Kopáček-Kopacek et al. 1995).

N-saturation in soils is indicated by leaching and losses of nitrate ( $\text{NO}_3^-$ ) below the rooting zone (Aber et al., 1989; Perakis and Hedin, 2002). Continuing mineralization of soil organic N pools has been pointed out as the most probable reason for ~~N~~ high N fluxes. Yet, the fate of excess  $\text{NO}_3^-$  is not only controlled by belowground biogeochemical N-cycling and remineralization processes, but also by site-specific characteristics, such as the size and quality of subsoil carbon pools, bedrock lithology, differential weathering and hydrological conditions (Lovett and Goodale, 2011). Altogether these parameters affect soil solution chemistries to produce complex spatial and temporal trends at a catchment scale.

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

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

small catchment has a low pedodiversity as it is situated entirely on base-poor gneissic bedrock in the north-eastern part of Czech Republic (Fig. 1a). This peculiarity simplifies our interpretations (cf. Kram et al., 2012). In addition, the contribution of groundwater vs. runoff infiltration is further evaluated by mean of a supplementary isotopic runoff model, which provides evidence for a likely contribution of groundwater enriched in selected chemical species due to sufficiently long water-saprolite interactions.

Amongst 14 multi-decadal monitored small forested catchments of the Czech' GEOMON network, UDL received the highest bulk atmospheric loads of a nitrogen and sulfur. As a result, the catchment is P limited and purportedly N saturated, with the ongoing pollution recovery process apparently altering concentrations and surface fluxes of other solutes via runoff (Oulehle et al., 2017). This paper addresses primarily soil solutions chemistry in the UDL catchment. Supporting data on the chemistry of spruce canopy throughfall and stream runoff—parameters which are used here for comparison purposes, are accessible in Oulehle et al. (2017). The combined dataset documents spatial heterogeneity of soil solutions in the form of variable nutrient imbalances and offers further information to improve interpretations on the dynamics and catchment-scale patterns of soil solutions in temperate forests undergoing recovery after peak acidification.

## 2 Study Site and Background Information

This study was conducted in the UDL catchment, NE Bohemia, Czech Republic. Located in the Eagle Mountains (Orlické hory) at coordinates 50°13' N, 16°29' E (Fig. 1a), UDL is a 33-ha, V-shaped valley with a medium-gradient sloping land (Fig. 1b); incised within orthogneiss ( $\text{SiO}_2 = 75$  wt. %;  $\text{Na}_2\text{O} + \text{K}_2\text{O} = 8$  wt. %;  $\text{MgO} + \text{CaO} < 0.5$  wt. %). This acid metamorphic lithology comprise the Orlica-Snieznik Massif of Cambro-Ordovician age, together with blue schists of Neoproterozoic sedimentary protoliths that the granitic protolith intruded (Winchester et al., 2002; Don et al., 2003). A detailed description of the soils occurring on this watershed has been previously reported earlier (Novak et al. 2005; Oulehle et al. 2017). Accordingly, the soil in the catchment are mostly acidic Podzols developed on orthogneiss to which only the Entic qualifier applies. Low base status soils have developed at expense of the mineralogy of the porphyritic granite that served as protolith to the orthogneiss bedrock, and given the lack of lithological discontinuities, pedodiversity is low across the catchment area, with Mor being the most common humus.

With an elevation of 880-950 m a.s.l., UDL's climate is characterized as humid temperate. The mean precipitation is 1500 mm  $\text{yr}^{-1}$ , and the mean annual air temperature is 5.0 °C. In the mid 20th century, high anthropogenic emissions An ephemeral snow cover lasts from late November to late March, when the monthly highest stream water runoff flow is usually recorded ( $\sim 162 \pm 29$  mm). Vegetation cover complexity is low, and essentially consist in Norway spruce (*Picea abies*, L. Karst). Following reforestation, its current vegetation cover includes approximately 27% of trees < 40 yrs. in age, with 1.7 out of 33 ha remaining non-forested.

Historically, the site was influenced by emissions from nearby large industrial complexes. From the early 1970s, high anthropogenic discharges of sulfur dioxide ( $\text{SO}_2$ ) and nitrogen oxides ( $\text{NO}_x$ ) produced sulfuric and nitric acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ) that affected the temperate forest ecosystem via wet and dry deposition. The largest point sources of these compounds were coal-burning power plants (Blazkova et al., 1996; Kolar et al., 2015). In central Europe alone, acid rain killed spruce stands over an area of approximately 1000 km<sup>2</sup> in the so-called “Black Triangle”; alone (Novak et al. 2005). Emissions of acidifying compounds in these centrally planned economies peaked in the late 1980s; installation of desulfurization units in coal-burning power plants started in 1987 and was completed in the mid-1990s in the Czech Republic and Germany, and several years later in southern Poland (Fen et al., 1998; Alewell et al., 2001; Hruska et al. and Kram, 2003;

Novak et al., 2005). As in other coniferous-forest ecosystems negatively affected by acid rain, in the Black Triangle area the productivity of temperate forests was likely perturbed by (i) enhanced leaching of base cations, such as potassium ( $K^+$ ), calcium ( $Ca^{2+}$ ) and magnesium ( $Mg^{2+}$ ) (e.g., Gundersen et al., 2006;), (e.g., Gradowski et al., 2008, Kopacek et al., 2015;) and (ii) decreased bioavailability of phosphorous (P) (Gradowski and Thomas, 2008).

- 5 UDL is also one of only three monitored catchments in the Czech Republic whose forests were also affected by massive acidification-related spruce dieback at elevations > 700 m a.s.l. between approximately 1975 and 1996. After spruce defoliation, liming by aircraft was performed three times to raise the soil pH. Liming took place in 1986, 2002 and 2007, introducing three metric tons of ground dolomitic limestone per hectare into the mountain ecosystem on each occasion. ~~(*Picea abies*, L. Karst)~~ Accordingly, during the decade 1994-2014, the median pH in the soilstream-pH<sub>H2O</sub> water in UDL remained
- 10 stable in the range  $4.92 \pm 0.40$ . Over the same period, median pH levels measured in water percolating through the canopy (i.e., throughfall) increased from  $4.07$  to  $5.49$  was registered across the Czech Republic (Oulehle et al., 2017). ~~At times of peak soil acidification, recorded, yet unpublished pH<sub>KCl</sub> measurements were below 3 units (Hruska, 2000).~~
- ~~Annual hydrochemical input-output mass balances for this site have been recently revised and compared with those of other monitored catchments in the Czech Republic (Oulehle et al., 2017).~~ Historical input-output hydrochemical data are summarized
- 15 in Table 1, and time-series of input-output concentration data for base cations, nitrate ( $NO_3^-$ ) and sulfate ( $SO_4^{2-}$ ) are shown in Figure 2. ~~The~~ According to Oulehle et al. (2017), UDL stream's pH was consistently acidic ( $< 5.5$ ) during the studied period.
- For most elements (except for  $Na^+$ ), the highest concentrations were observed in spruce canopy throughfall, followed by ~~runoff~~ stream water ( $SO_4^{2-}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ) and open-area precipitation ( $NO_3^-$ ). The average (1994-2014) sulfur (S) bulk atmospheric input was  $\sim 1.6 \text{ g m}^{-2} \text{ year}^{-1}$ , which is far in excess of the atmospheric ~~input~~ inputs observed in the remaining ~~43~~ 13
- 20 GEOMON's monitored catchments (Oulehle et al., 2017) across the Czech Republic ( $0.75 \text{ g m}^{-2} \text{ year}^{-1}$ ). Dissolved inorganic nitrogen (DIN) deposition input was  $11.7 \text{ mg m}^{-2} \text{ year}^{-1}$ , thus exceeding the value observed at other monitored sites. The  $Ca^{2+}$  input of  $2.5 \text{ g m}^{-2} \text{ year}^{-1}$  largely exceeded the average  $Ca^{2+}$  input into other monitored catchments ( $0.6 \text{ g m}^{-2} \text{ year}^{-1}$ ). The  $Mg^{2+}$  catchment input into UDL was  $0.3 \text{ g m}^{-2} \text{ year}^{-1}$  (the average for all sites of the monitoring network was  $0.1 \text{ g m}^{-2} \text{ year}^{-1}$ ). Inputs of  $Na^+$  and  $K^+$  were  $0.6$  and  $1.3 \text{ g m}^{-2} \text{ year}^{-1}$ , respectively (averages across ~~44~~ GEOMON' sites were  $0.2$  and  $0.5 \text{ g m}^{-2} \text{ year}^{-1}$ ).

## 25 2.23 Materials and Methods

### 3.1 Soil solution samples

- In October 2010, five nests of Prenart suction lysimeters were installed at ~~a~~ 50-cm depth below soil surface in a V-shaped arrangement as follows: hilltop west, hilltop east, slope west, slope east, and valley (filled circles in Figure-Fig. 1b). Each nest
- 30 consist of 3 lysimeters, and thus produce equal number of monthly replicates per sampling location. The lysimeter distributions along the V-shaped Shale Hills Critical Zone Observatory (Pennsylvania, USA) ~~(see~~ Ma et al., 2015; Brantley et al., 2018 for
- a review) inspired our sampling design at UDL. Each nest consisted of three lysimeters, 6 to 10 m apart. The lysimeters were
- pressurized at the beginning of each sampling using an electrical vacuum pump period to 750 Bar below the atmospheric
- pressure at the time of sampling. During the first 12 months, soil solutions were collected each month and discarded. Monthly



~~hydrochemical monitoring of soil solutions was then~~The soil solutions were collected in 2 L PE bottles placed in a shallow soil pit. Monthly hydrochemical sampling of the lysimeters was performed during the following two hydrological years, i.e., from November 2011 to October 2013.~~A total of 15 replicates (3 per sampling location) were collected~~ The collected soil solutions include both capillary and percolating water in the mineral soil (e.g., Nieminen et al., 2011).~~monthly.~~

## 5 ~~2.23.2~~ Soil Samples

~~Five 0.5 m<sup>2</sup> soil pits were excavated~~Five 0.5 m<sup>2</sup> soil pits were excavated in July 2015 at some distance ~~off~~to the previously installed suction lysimeter nests to avoid disturbances to the zero tension soil solution collection systems ~~previously installed~~ (Fig. 1b) while preserving a soil profile equivalent to the one at the nearby nest and also the relative position within the catchment area. The pits were excavated and processed by using the methodology described by Huntington et al. (1988) along both slopes of the UDL catchment (open circles in Figure 1b). Forest floor and mineral soil were removed to a depth of  $\geq 80$  cm below surface, and separated into ~~topsoil in which plants have their roots, and which is comprised of the Oi/(L) + Oe(F) and Oa(H) as well as the top soil layers defined by depth (0-10, 10-20 cm) (not investigated here);~~ and subsoil ~~and comprised by four the 20-40 and 40-80 cm mineral soil horizons~~layers defined by depth (0-10, 10-20, 20-40, and 40-80 cm). Soil profiles were described following the guidelines of the Food and Agriculture Organization of the United Nations (FAO, 2006).~~The soil layers were weighed in the field, processed by sieving to stones; coarse roots; and the > 1 cm soil fraction; and the < 1 cm soil fraction.~~ Two kg of the < 1 cm soil fraction were transported to the laboratory. Only results from the 40-80 cm ~~mineral layer, which are considered soil level~~ are reported in this work. This level is considered in chemical equilibrium with waters collected by our 50 cm depth lysimeter nets and corresponds to ~~be~~horizon Bs2 in all plots in chemical equilibrium with our 50 cm depth lysimeters, were further processed as part of this research.

## 20 ~~2.23.3~~ Bulk ~~atmospheric~~ Atmospheric deposition Deposition and Stream Water Samples

Atmospheric deposition was sampled in ~~an open areas~~open areas (“rainfall”), with ~~–~~sampling sites being 20 m apart among them and 1.2 m above ground (open square in Fig. 1b). Cumulative ~~monthly~~rainfall was collected ~~monthly~~ in three replicates. ~~For oxygen isotope analyse.~~ The rainfall sampling sites are 20 m apart among them and 1.2 m above ground (open squares in Fig. 1b). ~~D~~diffusive and evaporative losses from narrow-mouth bulk rain collectors were avoided by keeping precipitation under a 5-mm layer of chemically stable mineral oil. ~~Runoff~~Stream water samples and runoff flux estimations were collected monthly at a V-notch weir in the limnigraph location (Fig. 1b) according to methods outlined in Kram et al. (2003)(Fig. 1b).

## ~~2.3.4~~ Analyses

### ~~2.3.4.1~~ Soil Characterization

A Radiometer TTT-85 pH meter with a combination electrode was used to measure pH<sub>H2O</sub> of soil.~~Soil moisture was determined in the laboratory by difference of weights after 24 hrs of oven drying at 105 °C. (soil–water suspension ratio = 1 : 2.5).~~ Soil

texture was analyzed by the hydrometer method (ISO 11277 2009). Following air drying, the mineral substrate was sieved through a 2-mm sieve. The sieved samples were kept at  $5^{\circ}\text{C}$  before chemical analysis.

Exchangeable cations in soils were analyzed in 0.1 M  $\text{BaCl}_2$  extracts by atomic absorption spectrophotometry (AAS, Analyst Perkin Elmer 200). Exchangeable acidity was determined by titration of the extracts of 0.1 M  $\text{BaCl}_2$  extracts. Cation exchange capacity (CEC) was calculated as the sum of exchangeable base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Na}^{+}$ ) and exchangeable acidity. Base saturation (BS) was determined as the fraction of CEC associated with base cations. The concentrations of  $\text{NO}_3^{-}$  and  $\text{SO}_4^{2-}$  from the soil extracts described above were determined by ion chromatography (HPLC Knauer 1000; detection limits), with limit of detection/quantification (D.L.) of 0.1 and 0.3  $\text{mg L}^{-1}$ , respectively.

For an estimation of phosphorus (P) release estimation, ammonium oxalate extraction was performed by following the protocol described in Schoumans, (2000). In short, a reagent solution consisting of  $(\text{COONH}_4)_2 \cdot \text{H}_2\text{O}$  and  $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$  was used to dissolve 1 g of the <2 mm soil fraction. After shaking, extractable phosphorus ( $\text{P}_{\text{ox}}$ ), iron ( $\text{Fe}_{\text{ox}}$ ), and aluminium ( $\text{Al}_{\text{ox}}$ ) were determined by shaking for 2 h in the dark duplicate samples of soils with 30 mL of 0.5 M acidified (pH 3.0) reagent in 50 mL centrifuge tubes. After shaking, centrifugation and filtration, the soil solutions were analyzed for total dissolved oxalate extractable phosphorus (examined through inductively coupled plasma-atomic emission spectroscopy). The  $\text{P}_{\text{ox}}$ , iron ( $\text{Fe}_{\text{ox}}$ ), and aluminium ( $\text{Al}_{\text{ox}}$ ). These concentrations were used to estimate the degree of P saturation of the soil [ $\text{DPS}_{\text{ox}} = \text{P}_{\text{ox}} * (0.5 * (\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}})^{-1})$ ], which accounts for the P available to be released into solution in relation to the remaining binding capacity of soil and, thus, allows identifying areas in the catchment with relatively higher potential for P export (Beauchemin et al., and Simard, 1999; Borovec et al., and Jan, 2018). For calculations of the amount of P sorbed by soil particles (Borovec et al., and Jan, 2018), the average runoff stream water P concentration, measured during our two years monitoring period (i.e.,  $27.9 \pm 6.5 \mu\text{g L}^{-1}$ ), was used as an input for calculating the equilibrium P concentration in the catchment area.

### 2.3.4.2. Soil Solutions

Concentrations of  $\text{NH}_4^{+}$  and total phosphorus ( $\text{P}_{\text{tot}}$ ) were measured spectrophotometrically (Perkin-Elmer Lambda 25; > 20 and 6  $\mu\text{g L}^{-1}$ , respectively). Concentrations of  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were determined by electrothermal atomic absorption (Analyst 200; > 5  $\mu\text{g L}^{-1}$ ). Concentrations of aluminium ( $\text{Al}^{3+}$ ) were also measured by electrothermal atomic absorption instrument with a graphite furnace (D.L. < 0.01  $\text{mg L}^{-1}$ ). Concentrations of DOC and total dissolved nitrogen (TN) were determined on a combustion analyzer (Torch, Teledyne Tamar; D.L. < 0.1 and 0.5  $\text{mg L}^{-1}$ ).

### 2.3.4.3 Statistical Analysis

The non-normally distributed (i.e., non-parametric) data were evaluated by factor analysis. Empirical data were implemented in the computer code XLSTAT following the protocol by Vega et al. (1998). In short, data were normalized to zero and unit variance, and a covariance matrix of the normalized species was generated. For this analysis, the covariance matrix was diagonalized and the characteristic roots (eigenvalues) were obtained. The transformed variables, or principal

components (PCs), were obtained as weighted linear combinations of the original plotted multidimensional variables. A rotation of principal components allowed simpler and more meaningful representation of the underlying factors by decreasing the contribution of each variables to the two-dimensional plane. ~~Variables~~The variables can then be ~~then~~ plotted in groups with correlation among them being determined by their position (*e.g.*, proximity, distance, orthogonality.). The two-dimensional plane where the rotated, normalized data were plotted can be interpreted in terms of the main controls over the general variance (see Vega et al., 1998 for details).

### **3.4 Results**

#### **3.1. Soil Texture and pH**

Table 2 lists physical data for mineral soil and chemical data for soil extracts from the 40-80 cm depth layer and ~~compares~~ ~~them with~~ data for soil solutions collected by suction lysimeters (50-cm depth). ~~Following the conceptual sampling purposed in Shale Hills Critical Zone Observatory, our~~As described above, the dataset is grouped according to sampling<sup>2</sup> ~~geographic location and position in within~~ the catchment area (i.e., hilltops, slopes and valley; Fig. 1). ~~In the eastern part of the catchment, a coarse soil granulometry comprised of pebbles and cobbles accounted for 24 % of soil particle size in the hillslope and 62 % at the hilltop, whereas in the western part of the catchment, the soil was sandy, with pebbles and cobbles accounting only for~~ 12 %-1).

#### **4.1. Soil Textural Characterization**

In the eastern part of the catchment, coarse soil particles (gravel and stones) accounted for 24 % in the hillslope and 62 % of total soil granulometry at the hilltop, whereas in the western part of the catchment the soil particles above 10 cm in size accounted only for ~12 % (Table 2). The soil texture is loamy sand, with presence of authigenic clays (7-15 %) as weathering-induced alteration products of the orthogneiss parental material. The groundwater table is shallow.

#### **4.2 Soil Chemical Characterization**

##### **4.2.1 pH, CEC and BS**

The soil at the 40-80 cm ~~soil~~ depth was characterized by ~~acidic~~  $\text{pH}_{\text{H}_2\text{O}} < 5$  (Table 2). ~~Mineral~~This mineral soil layer had pH ~~was~~ higher in the valley (4.7), compared to the hilltop (~~4.2 to 4.4~~ to 4.2 units). The mean pH of soil solutions ranged similarly between the first and the second year, except for the valley (pH ~~valley of = 4.1 in year 1, and to 4.5 in year 2~~; Table 2). The two-year averages of soil solutions were 5.2, 4.7, and 4.3 pH units on the hilltops, slopes, and valley, respectively. Therefore, the solid substrate extracts and soil solutions were characterized by an opposite elevational pH trend; *i.e.*, more acidic ~~substrates~~soil extracts uphill, more acidic soil watersolution downhill.

### 3.2. Basic Soil Chemical Characterization

- In the eastern part of the catchment, the cation exchange capacity (CEC) of the mineral soil at 40-80 cm depth was up to 33 meq kg<sup>-1</sup> on the slope and 58 meq kg<sup>-1</sup> on the hilltops (mean 32 meq kg<sup>-1</sup>; hilltop (Table 2). By contrast, in the western part, the CEC was 22 and 19 meq kg<sup>-1</sup>, which is lower than the mean CEC values measured at all of the plots at UDL, 22 and 19 meq kg<sup>-1</sup> on the slope and hilltops whilst, respectively. CEC in the valley was 27 meq kg<sup>-1</sup>, which is within the mean CEC values measured at all of the plots at UDL:  $32 \pm 7$  meq kg<sup>-1</sup> (Table 2). The range of base saturation (BS) values in the soil varied between 6 and 13 %, with higher BS observed in the east (> 9 %) as compared to the west (< 8 %). The CEC in the studied soil depth at UDL was dominated by exchangeable Al. Consequently, the soil base saturation (BS) and soil pH<sub>H2O</sub> values were also low (Table 2). In summary, cation exchange capacity in UDL soils developed on base-poor orthogneiss ranged between 19 and 58 meq kg<sup>-1</sup>, base saturation was 6 to 13 %. Both parameters had lower values than median values at the European LTER sites (84 meq kg<sup>-1</sup> and 30 %, respectively). With regard to other analogous central European forest ecosystems, soil solution solute concentrations in UDL were found above values reported throughout the evaluation of temporal changes in inputs, runoff and fluxes (e.g., Manderscheid and Matzner, 1995a,b; Wesselink et al., 1995, Hruska et al., 2000; Armbruster and Feger, 2004; Oulehle et al., 2006; Navratil et al., 2007).
- BS at UDL was classified as poor with the dominant equivalent proportion of divalent base cations  $\text{CaCa}^{2+}$  (mean 46 %) and  $\text{MgMg}^{2+}$  (mean 24 %). The BS at UDL was twice larger than is twofold higher than the BS in determined at similar soil depths in the leucogranitic catchment LYS (Kram et al., 1997; Hruska et al., 2001, 2000), which is the most acidified catchment of the Czech monitoring network (Oulehle et al., 2017). Holmberg et al. (2018) evaluated BS and CEC of numerous forest sites of the LTER (Long-Term Ecological Research) network in nine European countries, with calculated median BS of 30 % and CEC of 84 meq kg<sup>-1</sup>. From the European perspective, the soil BS and CEC values at the UDL were low.

#### 4.2.2 Solute Concentrations

- Mean concentrations of individual chemical species, such as DOC, sulfate, nitrate, base cations, aluminium, chloride and pH values in soil solutions collected at the 50 cm depth are listed separately for the years 2012 and 2013 (Table 1), whilst Figure S1 shows their spatial variability of the statistical distribution (minimum, first quartile, median, third quartile and maximum; (in mg L<sup>-1</sup>). Coefficients of variation within individual nests of lysimeters are listed in Table S1.
- Concentrations of organic C ( $\text{C}_{\text{org}}$  DOC) ranged between 0.40 and 1.81 wt. %, while concentrations of total nitrogen (TN) were between 0.02 and 0.10 wt. %, with concentrations being highest on hilltop east, and lowest on hilltop west (Table 2). Oxalate-extractable P was the lowest in the valley (334 mg kg<sup>-1</sup>), and highest on hilltop east (536 mg kg<sup>-1</sup>). The degree of P saturation varied between 0.08 (valley) and 0.16 (hilltop east). These values fall below the lowest range observed in soil plots of the Czech Republic (see Borovec et al., 2018). and Jan, 2018 Concentrations of organic C ( $\text{C}_{\text{org}}$ ) ranged between 0.40 and 1.81 wt. %, while concentrations of total nitrogen (TN) were between 0.02 and 0.10 wt. %. Concentrations of both  $\text{C}_{\text{org}}$  and TN were the highest on hilltop east, and the lowest on hilltop west (Table 2), pointing to a potential ecosystem P deficit.

### 3.3 Solute Concentrations in Soil Waters

Table 2 lists mean concentrations of major anions and cations in soil solutions, grouped according to sampling location and position in the catchment area (cf., Fig. 1). Mean concentrations of individual chemical species in soil solutions are listed separately for the years 2012 and 2013; whilst Figure S1 shows the spatial variability of the statistical distribution (minimum, first quartile, median, third quartile and maximum) for soil solutions concentrations of dissolved organic carbon, sulfate, nitrate, base cations, aluminum, chloride (in  $\text{mg L}^{-1}$ ) and pH values at the 50 cm depth at UDL. Coefficients of variation within individual nests of lysimeters are listed in Table S1.

Our combined dataset (*i.e.*, Tables 1 and 2) show that six of the studied chemical species were more diluted in 50 cm soil waters than in runoff. Sulfate concentrations in soil watersolutions were, on average, 37 % lower than those in runoffstream water, while, relative to runoffstream waters,  $\text{NO}_3^-$  concentrations in soil watersolutions were 14 % lower ~~than those measured in runoff.~~ Similarly, the concentrations of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were lower in soil watersolutions by 73, 63, 79 and 4 %, respectively. ~~Water volumes collected by suction lysimeters differed among sampling locations, decreasing from the hilltops to the slopes to the valley (means of 1.13, 0.99 and 0.38 L per lysimeter per month, respectively).~~ The combined dataset (*i.e.*, Tables 1 and 2) show that except for DOC and  $\text{Al}^{3+}$  the rest of the studied chemical species were more diluted in the 50 cm' soil solutions than in stream waters.

#### 3.3.1. Anion Concentrations

A time-series plot reveals that  $\text{SO}_4^{2-}$  concentrations in the valley were higher in winter than in summer (Figure 3). The mean  $\text{SO}_4^{2-}$  concentrations in soil watersolution during the monitored period were found to be higherhighest at the slopes (East > West), followed by the valley and hilltops (East  $\approx$  West) (Table 2, Fig. S1). Our results for  $\text{NO}_3^-$  across the lysimeter network also show that this chemical species was readily bioavailable along the study site but mostly in the valley, where its concentrations were one order of magnitude higher than in the upslope soil solutions (Fig. S1). For this anion, the dataset also shows a high temporal variability, and in both years,  $\text{NO}_3^-$  concentrations in the valley peaked by late spring (Fig. 3). By comparison, the belowground  $\text{NH}_4^+$  concentrations were found to be low (usually below the detection limit, Table 2), a result that is consistent with previous observations at a soil research plot in north-western Czech Republic (Oulehle et al., 2006). For  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , coefficients of variation were between 2 and 17 %, with no clear-cut differences within the sampling locations (Table S1).

#### 3.3.2 Cation Concentrations

Mean  $\text{Na}^+$  and  $\text{K}^+$  concentrations in soil solutions were the highest on slope east, ~~close to 1.0 and 0.4  $\text{mg L}^{-1}$ , respectively~~ (Table 2; Fig. S1). For these cations, coefficients of variation (Table S1) were between 9 and 55 %, with the hilltop soil watersolutions exhibiting the largest variation in  $\text{K}^+$  concentrations. The second year was characterized by generally lower

K<sup>+</sup> concentrations in soil solutions collected in the valley, compared to the first year. Na<sup>+</sup> concentrations in soil solutions in the valley started to decrease only in the second half of the second year (Fig. 3). ~~The~~  
 As shown in Table 2, the highest mean Mg<sup>2+</sup> concentrations were observed on hilltop west (~~0.95 mg L<sup>-1</sup>~~), while the highest mean Ca<sup>2+</sup> concentrations were measured on slope east (~~0.83 mg L<sup>-1</sup>~~). The lowest mean Mg<sup>2+</sup> ~~concentrations were found in~~  
 5 the valley (~~0.41 mg L<sup>-1</sup>~~). ~~The lowest mean~~ and Ca<sup>2+</sup> concentrations were found also in the valley (~~0.48 mg L<sup>-1</sup>~~; Table 2, Figure S1). Coefficients of variations for Mg<sup>2+</sup> and Ca<sup>2+</sup> in soil solutions were relatively low, between 6 and 21 % (Table S1). The time series of Ca<sup>2+</sup> concentrations exhibited localized maxima in spring/early summer of the second year in soil solutions collected in most locations. Except for slope east, most locations also exhibited indistinct maxima in Mg<sup>2+</sup> concentrations in soil solutions in the spring/early summer of the second monitored year (Fig. 3).

#### 10 4.3.4 Statistical Analysis

Several spatial trends are evident by evaluating the statistical distribution of anions and cations in the soil solutions (Table 2; Fig. S4S1). ~~Throughout the monitored period t~~ There was a weak correlation between atmospheric deposition, ~~runoff~~ stream water and soil solution concentrations ~~throughout the monitored period~~ (Fig. S2). The first factor of our explorative factor analysis, D1, exhibited a maximal overall variance that explained ~~1924~~ % of total inter-correlated variance of collected data.  
 15 The second factor, D2, had maximal variance amongst all unit length linear combinations that were uncorrelated to D1 and explained ~~1218~~ % of variance within the dataset (Fig. S1). Based on the weights of the parameters, correspondence to each of these factors, and their cluster distribution, intrinsic properties of the soil, such as its DOC and clay contents (i.e., ~~D1~~), ~~determined the variance on the soil water solute concentration to a higher degree (i.e., 19 %) than seasonal inputs (i.e., D2). In summary, given the complexity of the possible interrelations among the environmental variables considered, there was an~~  
 20 ~~apparent insignificant correlation between solute concentrations measured in the soil in 2012–2013, runoff and atmospheric deposition data. Such a result in turn points to a major control exerted by groundwater chemistry over soil water~~ D1) determined the variance on the soil solution solute concentration to a higher degree than seasonal inputs (i.e., D2), ~~chemistry, and also to soil organic and inorganic ligand properties that also exert a control over the residence time of each of the measured component. The contribution of groundwater vs. runoff infiltration is further evaluated by mean of an isotopic runoff model in the Appendix~~  
 25 A.

### 4.5 Discussion

#### 45.1 Comparison with Other European Forests

A comparison of previous studies with data presented here is not straightforward due to differences in sampling and analytical strategies, dissimilar and heterogeneous bedrock lithologies, variable soil buffering capacities, and other factors, such as  
 30 canopy density, inter-annual water influx variability, and tree species diversity. Nonetheless, insights from ~~the previous related~~ studies provide the framework for our interpretations. Johnson et al. (2018) have recently published soil solution data from

162 plots monitored as part of the (ICP) Forest monitoring network, including median concentrations of environmentally relevant chemical species for the years 1998-2012. Soil solutions in the 40-80 cm deep mineral subsoil across Europe typically contained  $6.3 \text{ mg SO}_4^{2-} \text{ L}^{-1}$ ,  $1.0 \text{ mg NO}_3^- \text{ L}^{-1}$ ,  $1.9 \text{ mg Ca}^{2+} \text{ L}^{-1}$ , and  $0.7 \text{ mg Mg}^{2+} \text{ L}^{-1}$ . ~~It (i.e., median values). Considering those values alone, it~~ follows that soil solutions at UDL in 2012-2013 were characterized by similar analogue concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  as the ICP sites, and by about an one order of magnitude higher  $\text{NO}_3^-$  concentrations than the ICP sites. Solute Increased nitrate leaching toward the mineral soil in the UDL' forest ecosystems clearly reflects its N-saturated state (Aber et al., 1989; MacDonald et al., 2002). ~~concentrations in UDL are also above those observed in other studies that evaluated temporal changes in inputs, runoff and soil solution chemistry and fluxes in analogous forest ecosystems (e.g., Manderscheid et al., 1995a,b; Wesselink et al., 1995; Hruska et al., 2000; Armbruster et al., 2004; Oulehle et al., 2006; Navratil et al., 2007).~~

## 45.2 Recovery from Acidification as Observed in the Spatial and Temporal Variability in UDL of Soil Water Chemistry

In all studied soil solutions, ~~an elevational trend was found in soil water parameters, such as pH, DOC and the concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . All these parameters showed a decreasing trend downhill, with evident spatial trends in the soil solution chemistries~~ was found in pH, DOC and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations (Table 2; Figures 3 and S1). Amongst ~~these such~~ trends were, those ~~for of~~ pH (~~a—exhibiting a downhill 0.6 units difference~~), and DOC (~~with concentrations on the hilltop of approximately  $14 \text{ mg L}^{-1}$ , lower lower by a factor of 2 to 3 in the valley~~). ~~In as compared with hilltops, contrast, the decrease in—~~ with a rather moderate downslope decrease in soil solution'  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentration trends, which difference within the catchment area do not exceed  $1 \text{ mg L}^{-1}$ . Our time series data shows that  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ~~concentrations~~ in soil solutions defined a general trend likely reflective of the balance between evapotranspiration and biological inputs, with a punctual and correlative shift recorded in concentrations measured during mid-2013 (Table 2). This punctual correlative increase of these ions can be linked to an increase in strong anions inputs (Fig. 2), ~~yet i~~ Increased leaching of these macronutrients could also be regulated by temporary changes in the soil nitrate abundances (Oulehle et al., 2006; Wesselink et al., 1995; Akselsson et al., 2007, 2008). For DOC, the high variability on the slopes may reflect preferential flow paths. ~~downslope was small, within  $1 \text{ mg L}^{-1}$ .~~ A relatively higher DOC belowground leaching on the eastern hilltop can be inferred from the data, which suggests that C partitioning is site-specific, with little lateral redistribution from upslope organic soil levels toward the valley. Higher than topsoil mobilization of DOC below the rooted soil levels is proxy for an incomplete recovery from acidification (Verstraeten et al., 2017).

Clear-cut seasonal concentration trends in soil solutions were recorded for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (valley and slope west; Table 2). The underlying mechanism may be different for both anions.

A The co-evaluation of peak nitrate levels in soil solutions and precipitation inputs during the monitoring period (Fig. S3) ~~does~~ not suggest a cause effect-relation linked to atmospheric deposition. Thus, higher abundance of  $\text{NO}_3^-$  in soil



solutions in the growing season may be related to higher rates of nitrification of organically cycled  $\text{NH}_4^+$ -N during summer (e.g., van Miegroet and Cole, 1984). Higher abundance of  $\text{SO}_4^{2-}$  in soil solutions in winter remains unexplained. Historically, more soil S pollution was caused by higher  $\text{SO}_x$  emissions from nearby coal-burning power plants during the heating cold season, but such seasonality was no longer seen for the years 2012-2013 (Fig. 2). Hence, it is thought that nitrate in soil solutions during summer originated during the dormant season, and, whilst high sulfate concentrations observed during winter times originate from organic S being recycled and accumulated during the summer (Novak et al., 2001). As shown by Novak et al. (2005) using sulfur isotope ratios ( $^{34}\text{S}/^{32}\text{S}$ ), cycling of the high amounts of deposited  $\text{SO}_x$  at UDL occurred not only by adsorption/desorption of  $\text{SO}_4^{2-}$  onto soil particles, but, to a great extent also by cycling through the soil organic matter. As consequence acidification and export of  $\text{SO}_4^{2-}$ , and for that matter legacy reactive N, may prevail for several decades in the UDL and similarly polluted mountain catchments (Novak et al., 2000; Armbruster et al., 2003; Mörtz et al., 2005). Similarly, in UDL decreased runoff  $\text{NO}_3^-$  export seems to be rather controlled by biological processes than by catchment hydrology (Oulehle et al., 2017), but in association to increased organic productivity due to excess N, the managed restoration of hardwood species to UDL following spruce die-back, along with an increase in total (aboveground) biomass immobilize a large proportion of the deposited  $\text{NO}_3^-$  and  $\text{NH}_4^+$  (e.g., McDowell et al., 2001), the winter, originating from recycled organic S during the summer (Meyer et al., 2001; Novak et al., 2001-2004), also increased the demand of P, leading to an apparent general ecosystem deficiency on this macronutrient.

~~Toward the hilltops.~~ Due to pollution abatement policies, atmospheric input has decreased since peak acidification, yet UDL has been previously characterized by higher export of  $\text{SO}_4^{2-}$ , DOC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  than their atmospheric input. In this regard, biogeochemical process within the soil seem to release more non-conservative ions than received from the atmosphere. Interestingly, export of total inorganic N from UDL via stream runoff continues to be significantly lower than its atmospheric input, but our results show that N leaching toward the subsoil levels is much higher than runoff. Toward the hilltops differences in porosity and greater fluid-rock-derived particle interactions, together with higher reactive surface area and solute flux may, might as well exert a control over the measured soil solution chemical variability (Godsey et al., 2009). The latter effect seems to be critical in the variability in soil solution chemistry as at the hilltop lower soil horizons hilltops, which where the are sandy and subsoil level contain significant amounts of coarse parental-rock material (Table 2).

~~For  $\text{Na}^+$  and  $\text{K}^+$  ions in soil solutions. For DOC, the high variability on the slopes may reflect preferential flow paths. The higher DOC belowground leaching on the eastern hilltop suggest that C partitioning is site specific, with little lateral redistribution from upslope organic soil horizons toward the valley.~~

~~Due to successful pollution abatement strategies, atmospheric input has decreased since peak acidification, and UDL has been characterized by higher export of  $\text{SO}_4^{2-}$ , DOC,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$  than their atmospheric input. Conversely, export of total inorganic N from UDL via stream runoff continues to be significantly lower than its atmospheric input (Oulehle et al., 2017). As shown by Novak et al. (2004) using sulfur isotope ratios ( $^{34}\text{S}/^{32}\text{S}$ ), cycling of the high amounts of deposited  $\text{SO}_x$  at UDL occurred not only by adsorption/desorption of  $\text{SO}_4^{2-}$  on soil particles, but, to a great extent, also by cycling through the soil organic matter, which may prevail for several decades (Novak et al., 2000; Armbruster et al., 2003; Mörtz et al., 2005).~~



In UDL, decreased  $\text{NO}_3^-$  export is controlled by biological processes, rather than catchment hydrology (Oulehle et al., 2017). Invasion of hardwood species to UDL following spruce die back, along with an increase in total (aboveground) biomass, continue to immobilize a large proportion of the deposited  $\text{NO}_3^-$  and  $\text{NH}_4^+$  (see McDowell et al., 2004). This is nicely illustrated by limited presence of dissolved inorganic N forms in our soil solution chemistries (Table 2; Figure 3).

5 Within our time series,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in soil waters defined a general trend that likely reflect the balance between evapotranspiration and biological inputs, with a punctual, correlative shift recorded in concentrations measured during mid 2013 (Table 2). These seemed coeval to increased inputs in strong anions (Fig. 2). Increased leaching of these macronutrients could also be regulated by temporary changes in soil nitrate abundances (Oulehle et al., 2006; Wesselink et al., 1995; Akselsson et al., 2007, 2008). Whilst factor analysis did not reveal significant relationships between measured UDL parameters (Fig. S1), cross-plots in Figure 4 show a relatively strong pH-Mg/Al correlation. Both variables in each cross-plot reached the highest values on slope east and the lowest values in the valley. Thus, correlations seem to follow a trend determined by the higher Al solubility at lower pH (Palmer et al., 2005).

#### 4.3 Retreat of Acidification

Our spatially resolved, time-series observations (Fig. 3) for soil solution  $\text{Na}^+$  and  $\text{K}^+$  (Fig. 3) show that their concentrations of these ions defined patterns and trends largely derived from heterogeneity in soil textures/granulometry (Table 2), with seasonality and pulses in atmospheric inputs also exerting a likely areal some control over average and peak their concentrations (is soil solutions (cf. Fig. 2 and Fig. 3). For  $\text{K}^+$ , and to a minor extent for  $\text{Na}^+$ , soil waters/solution concentrations recorded peaks that are more or less correlative to  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  inputs (cf., Figs. 2 and 3), again pointing to lapses in which the atmospheric contributions of strong anions exerted a significant control over the weathering and leaching of plagioclase and K-feldspars feldspar minerals in the underlying crystalline rock; for example (e.g., Moore et al., 2012). In this regard, Oulehle et al. (2017) reported that  $\text{K}^+$  average annual runoff through runoff was two to three times higher than that of  $\text{Na}^+$  (Table 1), with both cations exceeding runoff concentrations values measured in other monitored catchments.

When the realized spatial variations in  $\text{Na}^+$  and  $\text{K}^+$  at the 50 cm-depth soil solutions at UDL are also evaluated, a deep flow path within the eastern slope to the valley seems possibly augmented as a response of either atmospheric S inputs or solubilization of the  $\text{SO}_4^{2-}$  stored in the weathering zone below the rooted soils, due to soil water saturation of the soil. Because  $\text{Na}^+$  has low affinity toward organic and inorganic ligands in soil, and thus behaves relatively conservatively (McIntosh et al., 2017), a seemingly more rapid response of  $\text{Na}^+$  than  $\text{K}^+$  leaching to soil solutions could be interpreted as the result from of the episodic accumulation of strong anions belowground accumulation toward the relatively more humid spring season of 2013 (cf. Fig. 2 and Fig. 3; e.g., Spring 2013). From this result, it can be argue that localized and punctual chemical analyses of runoff waters in mountain catchments might not directly reflect nutrient partitioning trends along elevation gradients, but temporal variations of the strong anion content of the water table, which has implications for the design of studies centered centered in stream water analyses for understanding the coupling of soil development processes and hydrology over variable time scales, and between deep and shallow weathering processes.

Such-The observation-behaviour of  $\text{Na}^+$  vs.  $\text{K}^+$  ions can ~~in turn~~ also be interpreted as a decrease in water residence time from the slope to the valley. On this note, we followed the ~~modeling~~modelling approach implemented by Buzek et al. (1995, 2009) to provide further insight on the mean residence time of soil solutions—calculated across all sampling locations— which was estimated in approximately 8.3 months (Appendix A); ~~indicating that the volume of the entire mobile water at UDL is larger than the volume of soil solution transported the 50 cm subsoil levels and below (see Appendix A).~~ In consequence, the runoff water at UDL is a mixture of direct precipitation with older soil solutions containing admixed with even older shallow groundwater. The supplementary isotopic modelling implemented here also shows that direct precipitation contributes between 20 and 40% of the discharge, with the rest being local soil pore and ground waters (Appendix A). The combination of all these three water types is called “mobile water”, defined as the sum of all water pools and fluxes that respond to changing precipitation amounts. This ~~effect is probably linked to mobile water transiently increased~~ soil ~~watersolution~~ saturation and concomitantly ~~with an~~ increase ~~in~~ the hydrologic connectivity of soil pore waters to the stream, ~~with a cause a~~ heterogeneous distribution of dissolved ions in soil solutions at the catchment-scale (Basu et al., 2010).

Whilst factor analysis did not reveal significant relationships between measured UDL parameters (Fig. S2), ~~yet~~ cross-plots in Figure 4 show a relatively strong pH–Mg/Al correlation. Both variables in each cross-plot reached the highest values on slope east and the lowest values in the valley. Correlations seem to follow a spatial trend determined by the higher Al solubility at lower pH (Palmer et al., 2005). Finally, given the complexity of the possible interrelations among the environmental variables considered here, there was an apparent generally poor correlation between solute concentrations measured in the soil in 2012–2013 and decadal runoff and atmospheric deposition data compiled in Table 1 (after Ouhlele et al., 2017). Such a result in turn points to a major control exerted ~~over the soil solution chemistry both by groundwater chemistry-carrying legacy pollutants and by over soil solution chemistry, and also to spatially variable soil organic and inorganic ligand properties content, that also exerting a control over which likely determine the the residence time of each of the measured components. The contribution of groundwater vs.~~ 4.4 Phosphorus Availability and Belowground Organic Matter

### 5.3 Phosphorus Availability and Belowground C Allocation

Soil P sorption saturation is often used as an environmental indicator of soil P availability to runoff. Phosphorus losses from soils not subjected to an augmented erosional process are generally small (see Heuck ~~and Spohn, 2016), with several factors determining which fractions are transported in streams. Among them hill slopes, climate and soil type features are the most relevant determinants of the preferential transport of mainly fine-size fractions and associated elements, such as P typically associated to Al- and to a minor extent in UDL, Fe- (oxyhydr)oxide fractions (Borovec and Jan, 2018, and references therein).~~ Our calculation of P sorbed by the soil particles, as determined by oxalate extraction, shows that between 22 and 29 mg of P per kg of soil was sorbed ~~in the 40–80 cm depth~~ at the time of sampling, with insignificant difference between hilltops, slopes and valley. ~~It is possible that P limitation has developed because of the legacy of anthropogenic N deposition in this region. That-The homogenous pattern of low P availability~~ contrasts with elevational differences in DOC concentrations in soil solutions ~~seen in~~-(Fig. 3; P and  $C_{\text{org}}$  in UDL soils at the studied depth are de-coupled S1)3, ~~pointing which points to a variable~~

belowground leaching and allocation of C or could be reflective of variable inputs of C from regenerating vegetation in the N-saturated, P-limited forest ecosystem, with significant P lost through runoff (Table 2). ~~that is~~ Conifer tree species are generally more tolerant to P limitation, which in turn make them more susceptible to nutrient depletion following losses from harvesting and exacerbated rates of nutrient export (Hume et al., 2018). We attribute the variable belowground allocation of C in UDL to ~~more probably controlled by spatially variable Mg<sup>2+</sup> and/or K<sup>+</sup> deficiencies (e.g., Rosenstock et al., 2016) rather than by P imbalances within the catchment since we detected no spatially contrasting P deficiencies exerting influence over the contrasting patterns of nutrient limitation and subsoil nutrients leaching across the studied forest landscape. As previously discussed, the homogeneity of the gneissic bedrock in which the UDL valley was incised, such localized, nutrient deficiency could probably be linked to differences in weathering and leaching potential of the parental granite across the topographic gradient of UDL or spatial [Mg] ion variabilities resulting from liming.~~

## 5. Conclusions ~~and Summary Observations~~

The hydrochemical comparisons implemented here were aimed at evaluating spatial and temporal ~~alterations~~ concentration patterns on the water chemistry among the subsoil compartment of the critical zone in temperate forest, ~~and calculated transit times within the soil.~~ Because of landscape and lithological simplicity, which facilitates discerning flow paths ~~and prevent without -variability effects derived from introduced by differential bedrock weathering of the bedrock,~~ it was possible discussing what factors ~~in addition, or in association,~~ to soil N-saturation affect the soil solution chemistries ~~in a of a small mountainous catchment area reforested by Norway Sspruce after acidification-related die-back.~~ By combining soil solution chemical measurements and establishing comparisons with published hydrochemical data, this work provides evidence pointing to substrate variability, C ~~and but not -perhaps- P bioavailability, and landscape~~ as major controls over the flux of ~~water and base metal leached toward into the subsoil level and across the elevation gradient in our small, N-saturated catchment. Such factors are reflected in the chemistry of the soil solutions.~~ Cation exchange capacity in UDL soils developed on base poor orthogneiss ranged between 19 and 58 meq kg<sup>-1</sup>, base saturation was 6–13 %. Both parameters had lower values than median values at the European LTER sites (84 meq kg<sup>-1</sup> and 30 %, respectively).

Soil solutions at ~~the the~~ 50-cm depth were generally more diluted than stream ~~runoff waters.~~ This can be explained by ~~due to~~ lateral surface runoff of solutions originating in the litter and humus, enriched in SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, ~~due to~~ ~~Increased concentrations are linked to anthropogenic atmosphere-derived pollution and/or as a result of affecting~~ natural (bio)geochemical processes. Differences between chemistry of soil solution and runoff could have been also caused by a direct contribution of throughfall, which scavenged atmospheric chemicals ~~due to a large surface area of the canopy and leached nutrients from inside the foliage, or by polluted open-area precipitation, such surface water trend has been documented especially along slopes considerably steeper than those at UDL, that can be enhanced by increased periods of drought and more frequent torrential rains.~~ Soil solutions ~~also~~ had lower pH in the valley than at upslope locations, ~~and were more being more~~ diluted in the valley than on hilltops in the case of DOC, Ca<sup>2+</sup> and Mg<sup>2+</sup>. ~~Both In the valley,~~ NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in soil solutions

exhibited a clear seasonality that can affect base metal leaching, with maximum concentrations in the growing and dormant season, respectively.

~~Phosphorus availability appeared to be decoupled from DOC. Differences between chemistry of soil water and runoff could have been caused by: (i) a direct contribution of throughfall, which scavenged atmospheric chemicals due to a large surface area of the canopy and leached nutrients from inside the foliage, or (ii) by polluted open area precipitation, such surface runoff has been documented especially along slopes considerably steeper than those at UDL.~~

~~Biogeochemical process within the soil which release more non-conservative ions than received from the atmosphere.~~

~~A contribution of groundwater enriched in selected chemical species due to sufficiently long water-rock interaction.~~

~~Finally, isotope investigations would be needed for better identification of dispersion pathways of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the stressed ecosystem.~~

The observed temporal trends amongst strong anion inputs and leaching of base metals and acid anions reflect that at the time of sampling nutrient imbalances in UDL were linked to groundwater carrying legacy pollutants. A complementary isotope modelling show that the responses of the studied mountain catchment to precipitation are fast, i.e., within the monthly sampling interval, with direct precipitation contributing 20 to 40% of the discharge, and the rest being the contribution of local groundwater. When evaluated with regard to stream water chemistries, and previously published input and fluxes data, this study provide insights into the localized controls and effects of acidification disturbances at a catchment-scale and offer a perspective of the spatially and temporarily variable nutrient concentrations in soil solutions that is relevant for more effectively designing stream water chemical analyses aimed at understanding the coupling of soil development processes and hydrology over variable time scales, and between deep and shallow weathering processes in mountain catchments and for evaluating soil recovery processes after atmospherically induced perturbations that affected the UDL catchment.

**Supplementary Materials:** The following are available online at \_\_\_, Figure S1 Descriptive statistics (2012- 2013) for soil watersolution concentration values of dissolved organic carbon, sulfate, nitrate, base cations, Al and chloride (in  $\text{mg L}^{-1}$ ) and pH values at ~~the~~ 50-cm depth at UDL. Figure S2: Non-parametric multidimensional scaling ordination of time-series hydrochemical data for runoff, atmospheric in lysimeters. Figure S3: Comparison of monthly precipitation volumes at UDL during the monitoring period (2012-2013) vs. the hydrologic years 2016-2017. Table S1: Coefficient of variation ( $\text{Cv} = 100\sigma/\mu$ ) of inorganic species across our lysimeter network.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## 5 Appendix A

### A1 Hydraulic insights from $^{18}\text{O}/^{16}\text{O}$ isotope modeling

Aiming at constraining the hydraulic parameters of the catchment under evaluation, a runoff generation model based on the water years 2016-2017, i.e., on a later time period, was constructed as we believe it compares to the soil solutions during 2012-2013. To constrain the limitation of this approach, monthly precipitation among these periods ~~warewere~~ compared. As seen in Figure S3, annual precipitation are comparable, with totals 1236, 1388, 1110, and 1284 mm in the hydrological years 2012, 2013, 2016 and 2017, respectively. Precipitation in the driest year 2016 corresponded to 80 % of precipitation in the wettest year 2013. Across this period, the mean monthly precipitation consistently peaked in December, May and September. Methodological details and mathematical components used to construct the isotopic  $^{18}\text{O}/^{16}\text{O}$  model are provided in the Appendix B (below).

Figure A1a shows that the  $\delta^{18}\text{O}$  values of atmospheric input did not follow a canonical sinusoidal curve—isotopically heavy rainfall O in summer and isotopically light rainfall O in winter. Isotopically lighter  $\text{H}_2\text{O}$ -O in soil solutions relative to runoff in the spring of both years (Fig. A1b) indicate that water derived from the snowmelt predominates in soil pores several months toward summer. Isotopically heavier  $\text{H}_2\text{O}$ -O in soil ~~watersolution~~, common in summer of the first year and in autumn of the second year, more closely corresponded to high  $\delta^{18}\text{O}$  values of the instantaneous precipitation. Interestingly,  $\delta^{18}\text{O}$  values of soil solutions in the valley (solid circles in Fig. A1) often departed from  $\delta^{18}\text{O}$  values of runoff (thick solid line in Fig. A1b), despite the very small distance between the two sampling sites (70 m). Despite interpretative limitations imposed by different monitored periods, the runoff generation model can be generalized for the catchment interrogated here. Accordingly:

The response of the within-catchment hydrological system to precipitation is fast.

~~Runoff water at UDL is a mixture of direct precipitation with older soil water and even older shallow groundwater. The combination of all these three water types is called “mobile water”, defined as the sum of all water pools and fluxes that respond to changing precipitation amounts.~~

~~The mean residence time of soil solutions calculated across all sampling locations indicate that the volume of the entire mobile water at UDL is larger than the volume of soil water transported under low vacuum to lysimeters 50 cm below surface.~~

The hydrochemistry at the ~~50-5-~~ cm soil depth reflected ~~a number of~~ preceding precipitation events, modified by ~~evapotranspiration~~ evapo-transpiration and, to a much smaller extent, mineral dissolution; the mixture mostly remained in soil ~~pore spaces~~ pores until saturation was reached and leaching initiated; cf. Siegenthaler (1999).

The contribution of [directbulk](#) precipitation to runoff is relatively low: 5 to 35 % (Fig. A1c).

The mean residence time of water in the UDL catchment (~8.3 months) was shorter than in three previously studied catchments in the Czech Republic. Lysina (LYS) catchment in the western Czech Republic (elevation of 830-950 m) was characterized by a mean water residence time of 15.2 months (Buzek [et al.](#) 2009). Dehtare and Jenin catchments in the central Czech Republic (elevations of 500-640 and 640-880 m) had a mean water residence time of 12.5 and 9.3 months, respectively (Buzek et al., 1995). A fourth small catchment located in a spruce die-back affected area near Jezeri (northwestern Czech Republic; elevation of 540-750 m) exhibited just slightly lower mean water residence time of 7.2 months than UDL (Maloszewski and Zuber 1982). While the bedrock at Jezeri and UDL was similar (gneiss), the steepness of both catchments differed (elevational span of 210 m at Jezeri vs. mere 70 m at UDL). The mean residence time of water at Jezeri and UDL was similar despite contrasting catchment areas (2.6 vs. 0.3 km<sup>2</sup>).

## Appendix B

### B1 O isotope analyses

Atmospheric deposition was sampled in an open area (“rainfall”). Cumulative monthly rainfall was collected in three replicates, 20 m apart, 1.2 m above ground. Diffusive and evaporative losses from narrow-mouth rain collectors were avoided by keeping precipitation under a 5-mm layer of chemically stable mineral oil. Grab samples of runoff were collected monthly at the closing profile. The  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  values were obtained by off-axis integrated cavity output spectroscopy (OA-ICOS; Liquid Water Isotope Analyzer, Model 3000, LGR Inc., Mountain View, Ca, U.S.A.). One  $\mu\text{L}$  of water was injected through a port heated to 80°C. The vapor was transported into a pre-evacuated cavity and analyzed for the  $^{18}\text{O}/^{16}\text{O}$  ratio. The reproducibility of  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  determinations was better than 0.20 ‰.

### B2. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ modeling approach

A two-component model of runoff generation was produced using oxygen isotope ratios of  $\text{H}_2\text{O}$  ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ ) of open-area precipitation, runoff and suction lysimeters water. The model is derived from a general isotope mass balance calculated following Eq. (1):

$$\delta^{18}\text{O}_{\text{tot}} = \frac{\sum \delta^{18}\text{O}_i * Q_i}{Q_{\text{tot}}} \quad [\text{‰}], \quad (1)$$

where  $i$  is an individual water source,  $Q_i$  is its mass flow [ $\text{m}^3$ ] and  $Q_{\text{tot}}$  is the total flow [ $\text{m}^3$ ]. This mass balance is typically used for the separation of stormflow hydrograph into its event and pre-event components (Eq. (2)):

$$\delta_t Q_t = \delta_p Q_p + \delta_e Q_e \quad [\text{‰. m}^3 \cdot \text{s}^{-1}], \quad (2)$$

where  $Q_t$  is streamflow [ $\text{m}^3 \cdot \text{s}^{-1}$ ],  $Q_p$  and  $Q_e$  are contributing pre-event water (groundwater) and event water (rainfall, snowmelt) [ $\text{m}^3 \cdot \text{s}^{-1}$ ], and  $\delta_t$ ,  $\delta_p$  and  $\delta_e$  are the corresponding isotopic compositions [‰]. Equation 2 can be solved parametrically for the contribution of the event water  $p$  and of the pre-event water ( $1-p$ ) as shown in Eq. (3):

$$p = \frac{Q_e}{Q_t} = \frac{\delta_t - \delta_p}{\delta_e - \delta_p} \quad (3)$$

- 5 The mass balance (1) is valid for any period of time if the isotope composition of all the components is known, for example for winter and summer. The mean annual  $\delta^{18}\text{O}$  isotope composition (mean groundwater input),  $\delta_{\text{in}}$ , was estimated as the mean  $\delta^{18}\text{O}_{\text{tot}}$  of the runoff.

A simple method of estimating the turnover time (mean age) of the subsurface reservoir employs an exponential model approximation; the distribution of transit times of water in the outflow is exponential and likely corresponds to permeability decreasing with the aquifer depth (Maloszewski and Zuber, 1982; Buzek, 1991). In case of stable isotopes, Siegenthaler (1979) demonstrated that the input (*i.e.*, precipitation) can be approximated by a sinusoidal function with a one-year period as per Eq (4):

$$\delta_{\text{precip}} = D + A \sin(2\pi t), \quad (4)$$

where  $D$  = constant,  $A$  = amplitude of  $\delta^{18}\text{O}$  variation in precipitation,  $t$  takes values 0-1 for a full-year period. Under a simplifying assumption of constant filtration and discharge, this input appears in discharge from the system as approximated by the factor  $B/A$  (Eq(5)):

$$\delta_{\text{discharge}} = D + B \sin(2\pi t + \delta), \quad (5)$$

where  $B$  is the amplitude of  $\delta^{18}\text{O}$  variation in output (discharge) a  $\delta$  is the time shift of output variations in relation to input. The mean transit time ( $T$ ) in years can be determined using Eq. (6) either the damping factor  $B/A$  or the phase shift  $\delta$ :

$$20 \quad T = 1/2 \delta ((B/A)^{-2} - 1)^{1/2}. \quad (6)$$

A similar approach can be applied also to lysimeters;  $\delta_{\text{precip}}$  represents the input, and infiltrated soil [watersolution](#) ( $\delta_{\text{inf}}$ ) is used instead of  $\delta_{\text{discharge}}$ .

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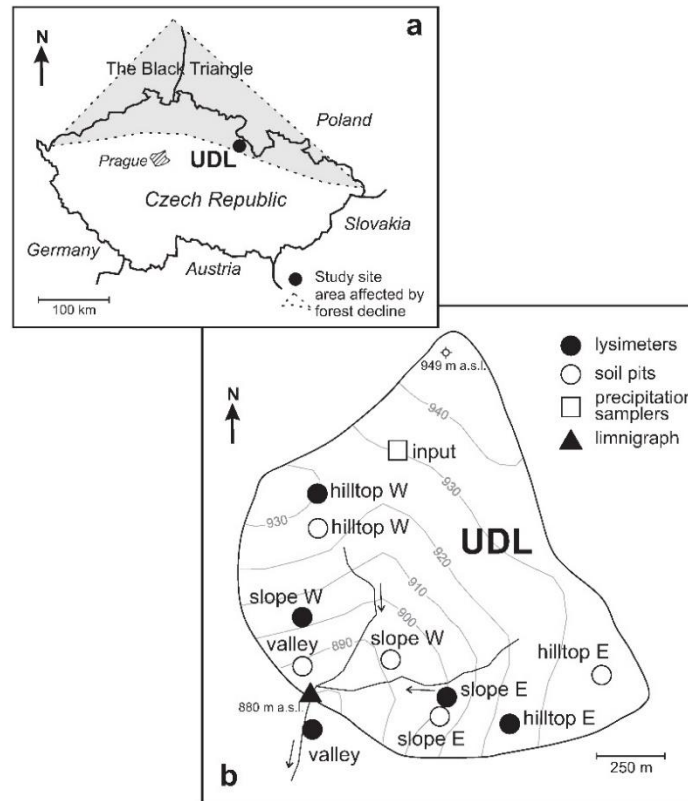


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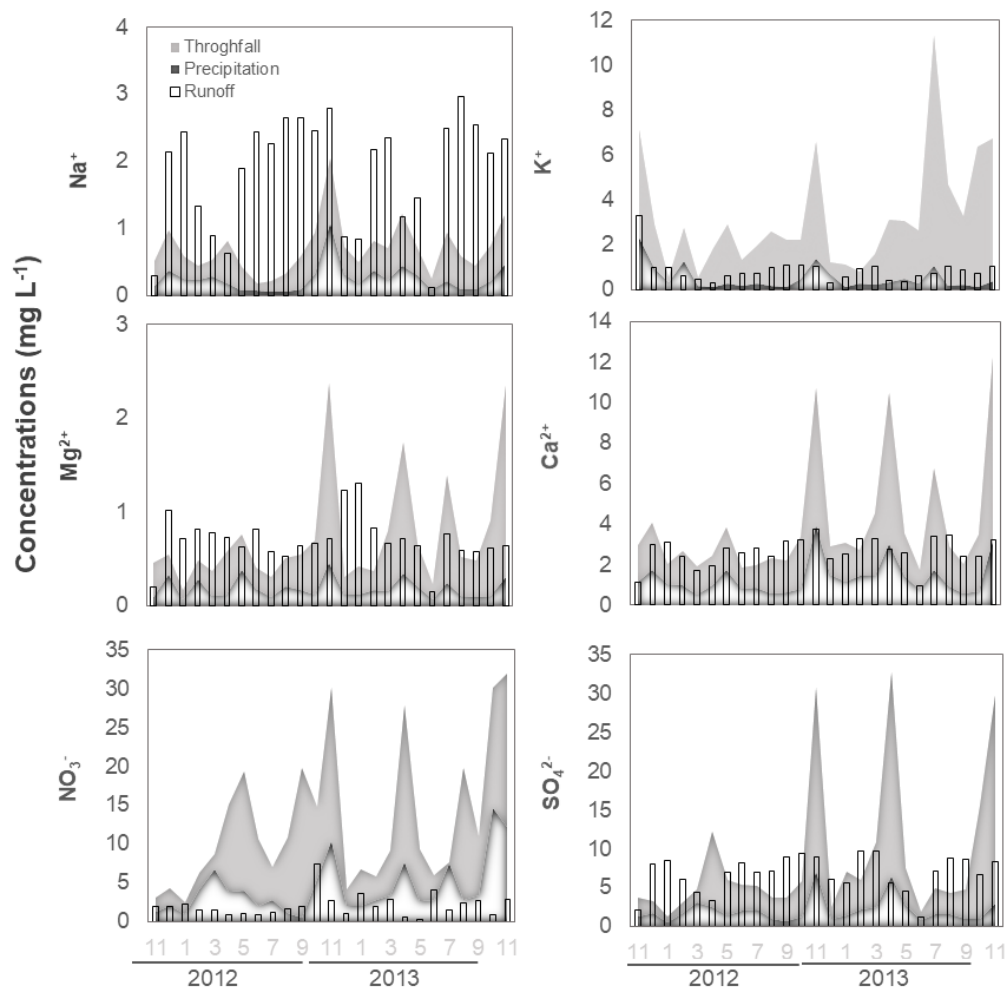
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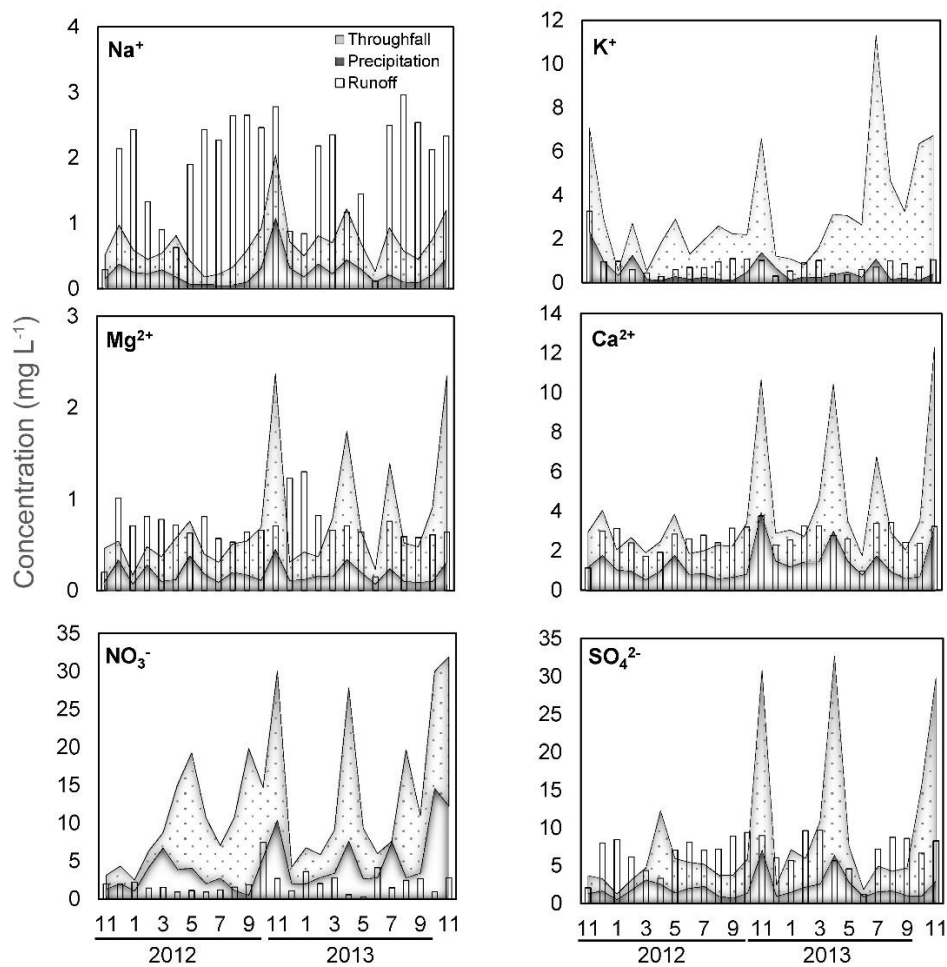
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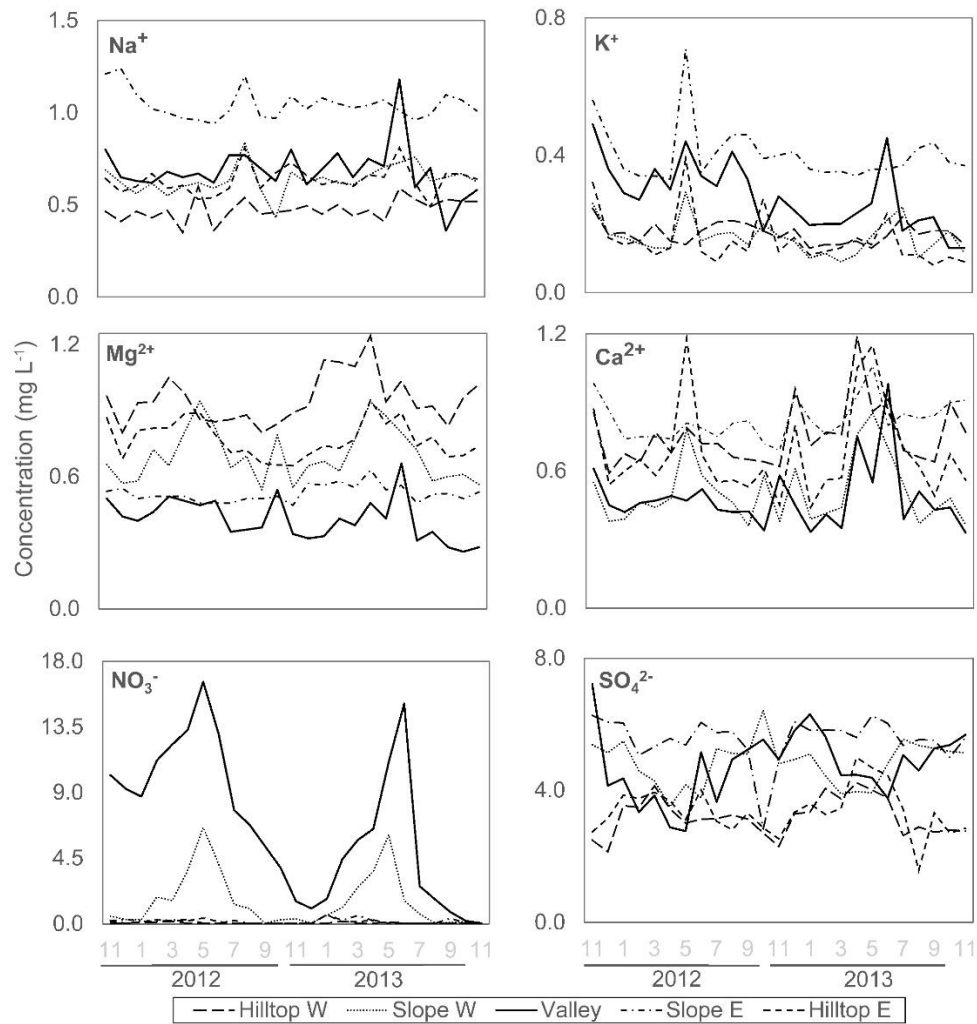


**Figure 1:** Study site location: (a) The shaded area shows the so-called "Black Triangle", (b) Sampling setup. In the studied UDL site, spruce stands die back at elevations > 700 m a.s.l. due to acid rain between approximately 1975 and 1996.



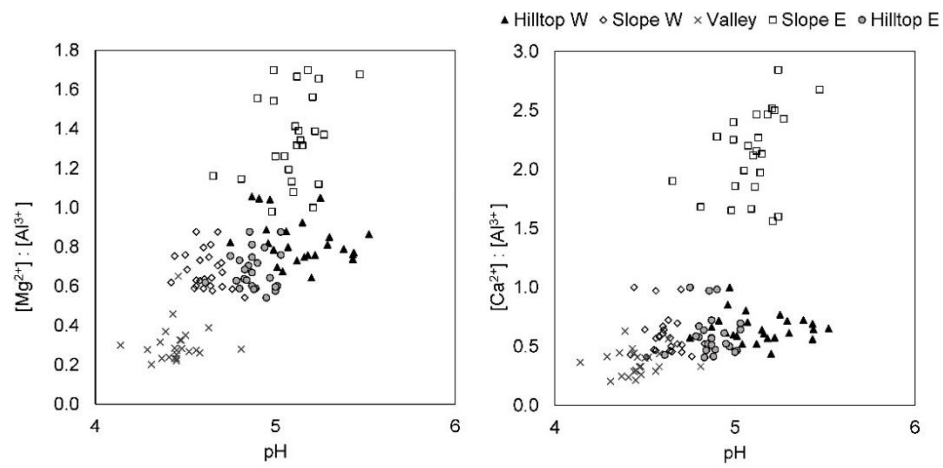


**Figure 2:** Hydrochemical data relevant for the monitoring period (2012-2013). X-axis shows months and hydrological year; concentrations after Oulehle et al. (2017).

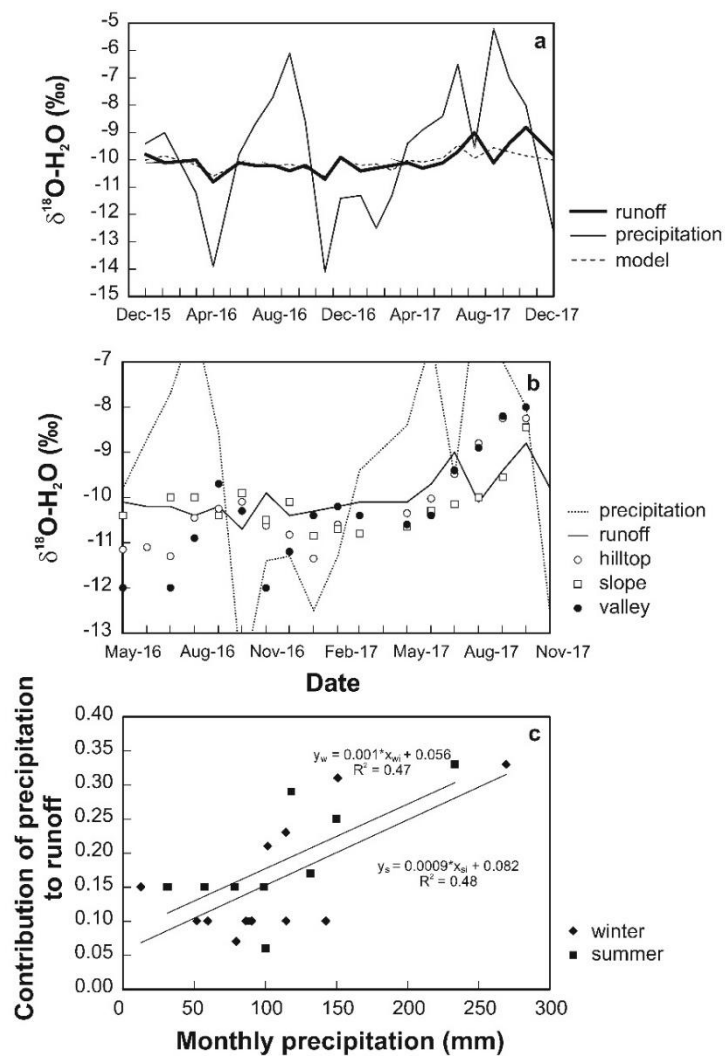


**Figure 3:** Spatially resolved, time-series soil [watersolution](#) concentration values of base cations, sulfate and nitrate at 50-cm depth. X-axis shows months and hydrological year.





**Figure 4:** Comparison of Ca/Al and Mg/Al vs. pH.



**Figure 2AA1:** Time series of  $\delta^{18}\text{O}$ : (a) input-output model. (b) Areal distribution across the UDL catchment. (c) Estimated contribution of precipitation in runoff.

**Table 1.** Average hydrochemical data 2012-2013 (after Oulehle et al., 2017)

	pH	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	DOC	Na <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Al <sup>3+</sup>	TP
		μg L <sup>-1</sup>								mg L <sup>-1</sup>	
Rainfall	5.7	2000	4400	700	2200	250	500	180	1350	NM	< 20
Throughfall	5.5	6600	8500	1950	7900	450	2760	550	2600	NM	< 20
Runoff <sup>‡</sup>	5.9	6840	2070	40	7240	1850	840	700	2660	<u>293</u>	<u>21.48</u>
<b>Standard Error (σ/√25)</b>											
<u>Rainfall</u>	<u>0.2</u>	<u>300</u>	<u>720</u>	<u>170</u>	<u>250</u>	<u>40</u>	<u>110</u>	<u>20</u>	<u>170</u>	=	=
<u>Throughfall</u>	<u>0.2</u>	<u>1550</u>	<u>1350</u>	<u>370</u>	<u>1400</u>	<u>40</u>	<u>470</u>	<u>100</u>	<u>430</u>	=	=
<u>Runoff<sup>‡</sup></u>	<u>0.1</u>	<u>460</u>	<u>290</u>	<u>10</u>	<u>850</u>	<u>170</u>	<u>110</u>	<u>50</u>	<u>140</u>	<u>37</u>	<u>6</u>

<sup>‡</sup>Average runoff flux during the monitoring period was 9.4 L s<sup>-1</sup>, with maximums recorded in April (76.9 ± 4.0 L·s<sup>-1</sup>) and minimums in August (0.5 ± 0.1 L s<sup>-1</sup>). NM: not measured

**Table 2.** Spatially resolved physical and geochemical data for solid substrate (40-80 cm depth) and annual average soil [watersolution](#) chemistries at the 50-cm depth

Measurement	Hilltop W		Slope W		Valley		Slope E		Hilltop E	
Soil										
CEC (meq kg <sup>-1</sup> )	19.4		22.6		27.2		33.4		58.4	
BS (%)	7.5		6.4		7.7		9.2		12.5	
>10 cm ( <del>kg</del> ha <sup>-1</sup> ) <sup>†</sup> <del>·10<sup>3</sup></del>	0		75		0		141		2038	
< 2-mm ( <del>kg</del> ha <sup>-1</sup> ) <sup>†</sup> <del>·10<sup>3</sup></del>	4707		2842		2199		3726		1102	
pH <sub>H2O</sub>	4.2		4.6		4.7		4.7		4.4	
Na <sup>+</sup> (mg kg <sup>-1</sup> )	3		6		17		6		34	
K <sup>+</sup> (mg kg <sup>-1</sup> )	30		19		4		29		7	
<del>Mg</del> Mg <sup>2+</sup> (mg kg <sup>-1</sup> )	2		8		4		9		27	
<del>Ca</del> Ca <sup>2+</sup> (mg kg <sup>-1</sup> )	7		27		20		26		78	
C <sub>org</sub> (%)	0.40		0.81		0.99		0.45		1.81	
TN (%)	0.020		0.037		0.045		0.032		0.101	
Al <sub>ox</sub> (mg kg <sup>-1</sup> )	3880		5490		4390		2550		2370	
Fe <sub>ox</sub> (mg kg <sup>-1</sup> )	1040		2500		3950		2810		4150	
P <sub>ox</sub> (mg kg <sup>-1</sup> )	352		421		334		450		536	
DPS <sub>ox</sub> <sup>#</sup>	0.14		0.10		0.08		0.17		0.16	
Measurement	2012	2013	2012	2013	2012	2013	2012	2013	2012	2013
Soil solution*										
pH	5.4	5.5	4.6	4.4	4.1	4.5	5.0	4.8	4.9	4.9
SO <sub>4</sub> <sup>2-</sup>	3132	3270	4850	4770	4420	5000	5440	5640	3360	3400
NO <sub>3</sub> <sup>-</sup>	63	58	1800	1300	9870	4040	155	181	149	117
NH <sub>4</sub> <sup>+</sup>	< 20	< 20	< 20	< 20	< 20	30	< 20	< 20	< 20	70
DOC	13500	NA	8440	NA	4510	NA	4230	NA	15100	NA
Al <sup>3+</sup>	1130	1170	945	859	1590	1280	396	394	1130	1150
Na <sup>+</sup>	455	493	611	662	683	687	1050	1040	618	649
K <sup>+</sup>	184	161	177	145	340	225	430	378	179	128
Mg <sup>2+</sup>	897	1000	700	699	445	378	505	539	775	764
Ca <sup>2+</sup>	699	806	498	531	459	514	794	851	668	697
Conductivity	18.8	19.8	27.0	26.5	43.0	33.2	23.6	22.5	20.6	20.6

<sup>†</sup>Soil particulate size. <sup>#</sup>Degree of P Saturation (DPS = P<sub>ox</sub>·(0.5·(Fe<sub>ox</sub> + Al<sub>ox</sub>)<sup>-1</sup>). \*Concentrations in µg L<sup>-1</sup>; ~~conductivity in µS cm<sup>-1</sup>~~.  
NA: not measured; ~~variation coefficients are given in the supplementary material.~~