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# Factors affecting leaching of dissolved organic carbon after tree dieback in an unmanaged European mountain forest

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**Abstract**– Forest disturbances affect ecosystem biogeochemistry, water quality and carbon cycling. We analysed water chemistry before, during and after a dieback event at a headwater catchment in the Bohemian Forest (central Europe), together with an unimpacted reference catchment, focusing on drivers and responses of dissolved organic carbon (DOC) leaching. We analysed data on carbon input to the forest floor via litter and throughfall, changes in soil moisture and composition, stream water chemistry, discharge and temperature. We observed that: (i) In the first three years following dieback, DOC production from dead biomass led to increased concentrations in soil, but DOC leaching did not increase due to chemical suppression of its solubility by elevated concentrations of protons and polyvalent cations, and elevated microbial demand for DOC associated with high ammonium ($NH_4^+$) concentrations. (ii) DOC leaching remained low during the next two years, because its availability in soils declined, which also left more $NH_4^+$ available for nitrifiers, increasing $NO_3^-$ and proton production that further increased chemical suppression of DOC mobility. (iii) After five years, DOC leaching started to increase as concentrations of $NO_3^-$, protons, and polyvalent cations started to decrease in soil water. Our data suggest that disturbance-induced changes in N cycling strongly influence DOC leaching via both chemical and biological mechanisms, and that the magnitude of DOC leaching may vary over periods following disturbance. Our study adds insights to why the impacts of forest disturbances are sometime observed at the local soil scale but not simultaneously on the larger catchment scale.

## INTRODUCTION

The susceptibility of forest ecosystems to large disturbance events such as insect infestations and wildfires is increasing globally.[1,2] Although such disturbances are to some extent natural, their frequency and/or severity has tended to be exacerbated by land-management factors such as single-species or single-age stand management, increased human presence (fires), and climate change.[3] Large-scale tree mortalities have recently occurred in Europe and the western USA and Canada, and have been shown to detrimentally impact downstream water quality.[4–6] Similar increases in frequency of occurrence and severity of impacts on water quality have been recorded for wildfires.[2] The impacts of such disturbances typically include temporally elevated leaching of ions and nutrients (notably nitrogen) to receiving waters. However, the impacts of disturbance on dissolved organic carbon (DOC) are less clear, despite its significance for ecosystem carbon budgets and (due to its high removal costs during treatment) for water supplies.[5–9]

Concentrations of dissolved organic carbon (DOC) have increased in numerous European and North American surface waters since the 1990s.[10–12] These increases have been attributed to: (i) declining atmospheric deposition of strong acid anions (SAAs, sum of $SO_4^{2-}$, $NO_3^-$, and $Cl^-$) and their effect on soil water pH and ionic strength;[13,14] (ii) factors related to climate change including warming, increased frequency of high precipitation events and rising atmospheric carbon dioxide concentrations;[15–17] and (iii) elevated N deposition.[18,19] These general long-term trends in DOC leaching can be further magnified or weakened by changes in land-use, disturbances, and management practice in catchments.[5–9,20,21]

Major sources of dissolved organic carbon (DOC) in forest soils are incomplete microbial decomposition of litter and dead biomass (roots, understory vegetation, microbes), root exudates, and leaching from canopies.[22–24] Major DOC sinks are mineralization, microbial and chemical immobilization in soils, and leaching to receiving waters. The proportion of DOC immobilized in new microbial biomass, oxidized to $CO_2$ or reduced to $CH_4$ depends on its composition (bio-availability), residence time in soils, availability of electron acceptors and nutrients, and soil temperature and moisture, all of which affect efficiency and pathways of C microbial use.[25–28] Chemical properties of DOC, soil water, and surfaces of soil particles further affect solubility and mobility of DOC via a complex of physico-chemical processes that affect DOC dissociation, coagulation, precipitation, and adsorption on Al and Fe hydroxides.[10,29–31] The amount of DOC leached from soils is further affected by soil hydrology and physical properties that control water residence time, moisture, hydraulic connection of DOC resources with their microbial sinks, and flow pathways through shallow *vs.* deep soil horizons.[23,33,34] Consequently, DOC fate in soils and its mobility and leaching from terrestrial to aquatic systems is controlled by a complex of biogeochemical factors, including plant productivity as the original source of organic C (ref. 35), hydrology, soil moisture and temperature, microbial activity, and chemical composition of soil and soil water.

Observed trends in DOC leaching from mountain catchments of the Bohemian Forest lakes (central Europe) combine most of the above causes.[36,37] The DOC concentrations have been increasing in the Bohemian Forest lakes since the late 1980s as a response to rapidly decreasing atmospheric deposition of $SO_4^{2-}$ and $NO_3^-$.[38] In addition, stream water DOC concentrations exhibit a pronounced seasonal variation and a high DOC leaching accompanying hydrological events.[36] In recent years, DOC concentrations have increased in some streams following insect infestation and tree dieback in their catchments.[37] The aim of this study is to evaluate mechanisms affecting terrestrial export of DOC following this forest disturbance. In particular, we evaluate changes in C input to the forest floor with litter and throughfall, soil moisture and composition, chemical properties of surface water, physico-chemical factors contributing to DOC variations in stream water, and possible effects of soil N cycle on DOC availability for leaching. Finally, we suggest a general conceptual model and evaluate risks of elevated DOC leaching from disturbed forests.

## METHODS

**Study site.** Plešné and Čertovo lakes are situated at 13.2–13.9 °E and 48.8–49.2 °N at elevations of 1,087 and of 1,027 m, respectively, in the Bohemian Forest (Supporting

Information, SI, Fig. SI-1). The Plešné and Čertovo bedrocks are formed by granite and mica-schist, their catchments are 64 and 89 ha in size and are steep, with maximum local relief of 291 and 316 m, respectively. Both catchments are mostly covered by shallow acidic forest soils (leptosol, podsol and dystric cambisol) and proportions of wetlands and bare rocks in their areas are <5%. Forest vegetation occupies >90% of both catchments and is dominated by Norway spruce (*Picea abies*). The catchments are part of a protected unmanaged area (Šumava National Park), with restricted access and land use activities. Both catchments were strongly acidified and N-saturated by high atmospheric deposition of $SO_4^{2-}$, $NO_3^-$ and $NH_4^+$ since the early 1960s.[39] Acidic deposition dramatically decreased in the 1990s, then its decline continued at a lower rate, and its present level (10, 31 and 37 mmol $m^{-2}$ $yr^{-2}$ for $SO_4^{2-}$, $NO_3^-$ and $NH_4^+$, respectively, in precipitation) is similar to the late 19th century for $SO_4^{2-}$ and $NH_4^+$, and to the 1960s for $NO_3^-$.[37,39] The Plešné and Čertovo lakes have three (PL-I to PL-III) and seven (CT-I to CT-VII) surface tributaries, respectively. These are small, first- to second-order streams, except for PL-III, which is partly subsurface and receives a high proportion of its flow from groundwater.

Between autumn 2004 and autumn 2008, almost all adult Norway spruce trees in the Plešné catchment were killed by a bark beetle (*Ips typographus*) outbreak.[37] Dead trees lost their needles during several months after infestation, and subsequently they continuously lost twigs, bark, and branches.[40] Most of the dead trees had been blown over by 2016, but all dead biomass has been left in place as part of the minimum-management policy within the area. Natural forest regeneration started within 1–3 years of tree dieback, and the average number of seedlings increased from 47 and 670 trees $ha^{-1}$ during the following decade.[37]

The Čertovo forest has experienced a low level of disturbance, limited to windthrows in 2007 and 2008 along the south-western ridge of the catchment, mostly in the upper parts of the CT-IV to CT-VII sub-catchments. Altogether, the total area of damaged forest (with > 50% dead trees) increased from ~4 to 18% in the whole Čertovo catchment between 2000 and 2015.[36]

**Soil, litterfall and throughfall.** In this study, we synthetize trends in soil chemistry, litterfall, and throughfall amount and composition that were published elsewhere. Sampling and analyses are described in detail in Part SI-1. Briefly:

(i) Soils were sampled from 9–21 pits in 1997–2001 and 2010 in both catchments, and in the Plešné catchment also in 2015. We use data on pH, exchangeable base cations (BCs, sum of $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, and $K^{+}$), $Al_i$, and $H^{+}$, and base saturation (percent proportion of BCs in the cation exchange capacity) in the upper soil horizons (O, litter; and A, the uppermost organic rich horizon). In addition, soils were sampled at 6-week intervals at one research plot in each catchment (PL-plot and CT-plot) from 2007–2017.[41,42] Trees at the PL-plot were killed by bark beetles in 2006–2007, while the control CT-plot was not affected. Trends in soil chemistry at the PL- and CT-plots are mass weighted means for O- and A-horizons. From this 6-week survey, we use data on soil moisture, exchangeable BCs, $Al_i$, and $H^{+}$, water extractable DOC, $NH_4^{+}$ and $NO_3^{-}$, and concentrations of C and N in microbial biomass ($C_{MB}$ and $N_{MB}$, respectively).

(ii) Litterfall was sampled at three and two plots in the Plešné and Čertovo catchments, respectively, from 2003 to 2016.[40] Trends in carbon fluxes associated with litterfall (the sum for needles, twigs, bark, cones, lichen and a mixture of poorly identifiable fragments) used in this study are averages for all plots in individual catchments. Large branches (> 2 cm in diameter), trunks and roots were not included in this flux.

(iii) Throughfall amount and chemical composition have been studied at two plots in each catchment since 1997.[36,37] Here, we use annual averages for amounts and concentrations of DOC and SAAs.

**Stream water.** Tributaries were sampled from May 1997 to April 2017 in three-week intervals. Discharge (Q, L $s^{-1}$) was estimated using a stopwatch and calibrated bucket at small natural waterfalls or rapids. Water temperature (T, °C) was measured during sampling.

Details on water analyses are given in Part SI-2. Briefly: DOC was analysed as $CO_2$ after sample mineralization in carbon analysers, with a detection limit of <4 µmol $L^{-1}$. Concentrations of $NH_4^+$, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $NO_3^-$, $Cl^-$, $SO_4^{2-}$, and $F^-$ were determined by ion chromatography. Concentrations of ionic Al and Fe forms ($Al_i$, $Fe_i$) were analysed colorimetrically after their fractionation.[43] Concentrations of organic acid anions ($A^-$) were calculated from concentrations of DOC and pH.[44]

Linear regression was used to evaluate the significance of relationships between concentrations of DOC and other water constituents, including ionic strength, in each tributary. We used the seasonal Mann-Kendall test[45] to determine if long-term trends in water chemistry were significantly different from zero. Multiple linear regression with forward stepwise selection (using SigmaPlot 11.0, Systat Software, San Jose, California, USA) was used to determine what variables explained variations in DOC concentrations. For this analysis, we selected seven variables (Q, T and concentrations of $SO_4^{2-}$, $NO_3^-$, $Cl^-$, $H^+$, and $Al_i$) that were previously shown to play important roles in seasonal and long-term variations in DOC concentrations.[13,34,38] We did not use ionic strength and concentrations of BCs as independent variables in the forward stepwise regression, because ionic strength mostly depended on the chemical variables already included in the statistical analysis, and concentrations of BCs mostly depended on concentrations of SAAs as counter-ions.[36,37] Concentrations of $H^+$ and $Al_i$ were considered as independent variables due to their important roles in DOC dissociation and coagulation.[29,31,46,47] Data on all tributaries were evaluated for the whole study period (May 1997 to April 2017) and also for periods prior to (1997–2003), during (2004–2008), and after (2009–2017) the bark beetle outbreak in the Plešné catchment. In the statistical tests, values of $p < 0.05$ were considered significant throughout the study.

## RESULTS

**Litterfall carbon and throughfall DOC fluxes.** Annual inputs of organic C to the Čertovo catchment were stable throughout the study, with average (± standard deviation) fluxes in litterfall and throughfall of 15 ± 2 and 0.80 ± 0.11 mol $m^{-2}$ $yr^{-1}$, respectively (Fig. 1). Throughfall fluxes of DOC were only slightly higher in the Plešné than Čertovo catchment prior to and during the tree dieback, but then rapidly decreased to ~0.15 mol $m^{-2}$ $yr^{-1}$ during 2014–2016. The litterfall fluxes of C were similar in both catchments prior to the bark beetle attack, then increased in the Plešné catchment in 2004 and peaked at 57 mol $m^{-2}$ $yr^{-1}$ in 2007. Since 2009, litterfall C fluxes have been similar in both catchments. The Plešné litterfall was dominated by needles, with a large proportion of green, non-senescent needles and bark in the first year after the tree infestation, and by twigs, small branches and bark in the following years. In contrast, composition of the Čertovo litter was stable throughout the study and was dominated by needles and twigs.[40]

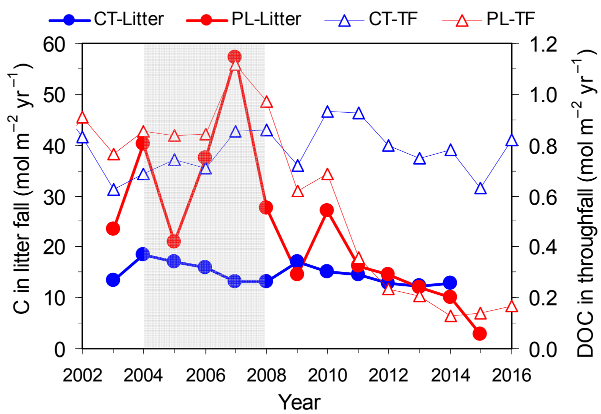


Fig. 1. Time series of inputs of organic carbon to the forest floor of Čertovo (CT) and Plešné (PL) catchments in litterfall (Litter) and throughfall (TF). Grey area indicates the period of bark beetle outbreak in the Plešné catchment.

The thinning of dead canopies caused significant changes in throughfall composition, leading to decreased fluxes of BCs and SAAs to forest floor; throughfall inputs of $SO_4^{2-}$, $NO_3^-$ and $Cl^-$ decreased on average by 41, 43, and 55%, respectively, in the Plešné relative to Čertovo catchment during 2009–2016 (Fig. SI-3).

**Throughfall amount, soil moisture and discharge.** Tree dieback affected throughfall amount and soil moisture (Fig. 2). Throughfall amounts were almost similar in both catchments till 2007, but then became consistently lower in the Plešné than Čertovo catchment (Fig. 2a). Soil moisture was similar at both research plots immediately after the tree dieback at the PL-plot in 2008, but became consistently higher than at the CT-plot from autumn 2009 (Fig. 2b), despite lower throughfall amounts in the Plešné catchment

(Fig. 2a). This difference was especially apparent in summer months and during years with low precipitation.

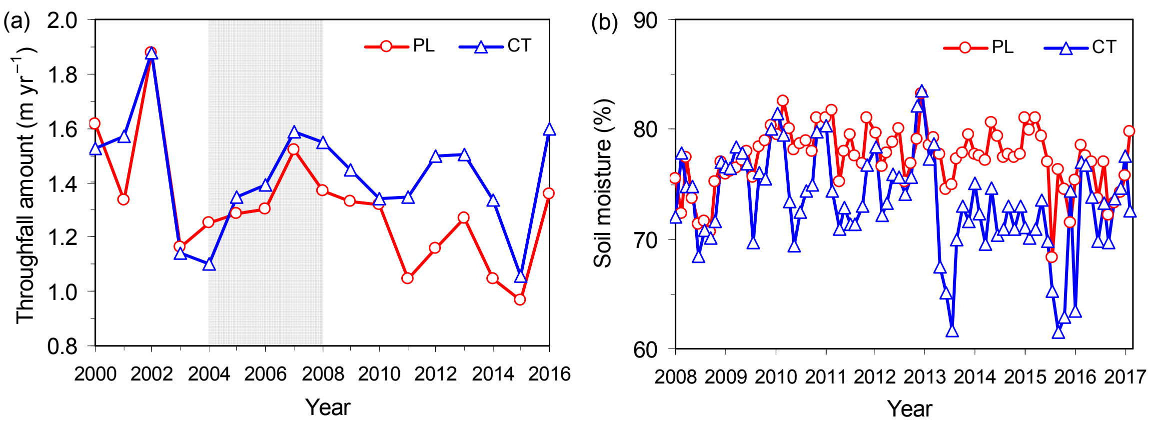


Fig. 2. Time series of (a) annual throughfall amount in Plešné (PL) and Čertovo (CT) catchments, and (b) soil moisture (mass weighted mean for O- and A-horizons) at the PL and CT research plots. Grey area indicates the period of bark beetle outbreak in the Plešné catchment (note that soil moisture data cover the post-disturbance period only).

The 1997–2017 average discharges of tributaries ranged over an order of magnitude with long-term averages from 0.6–11 L $s^{-1}$. During the study, water Q decreased in most tributaries due to decreasing precipitation (Fig. 2a), but this decrease only was significant in CT-VI, CT-VII, and PL-II (Table SI-3). Water discharge had no clear seasonality, except for elevated Q values during snowmelt periods.

**Soil chemistry.** Base saturation of the Plešné soils increased dramatically after the tree dieback, from 39 to 65% in the O-horizon, and from 21 to 38% in the A-horizon between 2000 and 2015 (Table SI-1). This increase in base saturation was accompanied by a decrease in concentrations of exchangeable $Al_i$, and also $H^+$ in the O-horizon. These changes were especially pronounced at the research PL-plot, while no significant long-term trends occurred in the control CT-plot (Fig. SI-3).

Concentrations of water extractable DOC and $NH_4^+$ were higher in the upper soil horizons at the PL- than CT-plot throughout 2008–2016, but this difference was most pronounced during the first three years after the tree dieback (Fig. 3a). In contrast, soil $NO_3^-$ concentrations were lower at the PL- than CT-plot until 2011, then abruptly increased (reciprocally to the DOC decline) and exhibited higher concentrations and variation than at the CT-plot until the end of study. Concentrations of $C_{MB}$ and $N_{MB}$ were higher in the Plešné than Čertovo soils until 2011, and generally lower thereafter (Fig. 3b). Microbial C to N ratios in soil exhibited similar molar averages (~12) and temporal patterns (not shown) at both research plots.

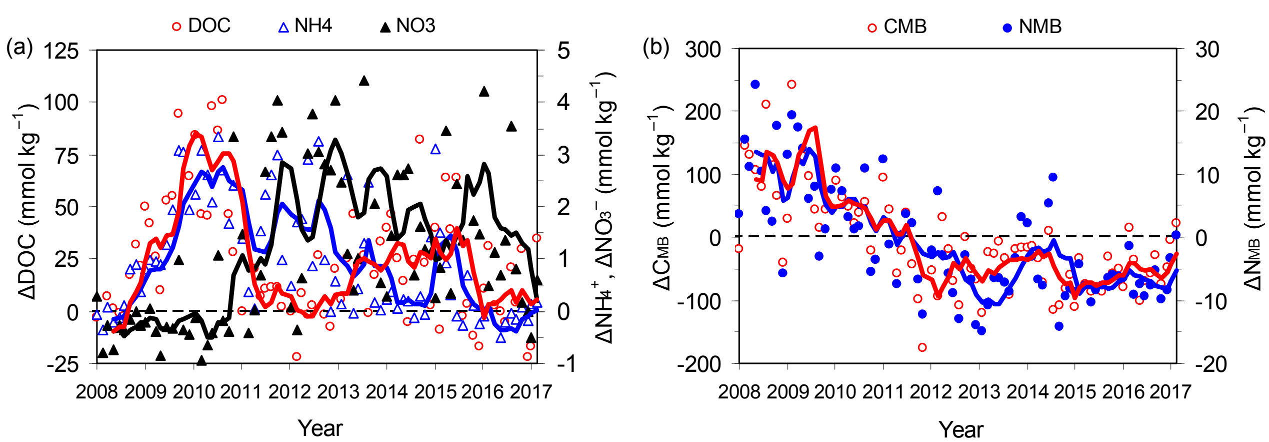


Fig. 3. Time series of differences (Δ) between soil properties observed at the Plešné (PL; beginning of tree dieback in 2007) and Čertovo (CT; unaffected control) research plots for: (a) concentrations of DOC, $NH_4^+$ and $NO_3^-$ in water extracts, and (b) concentrations of C and N in microbial biomass ($C_{MB}$ and $N_{MB}$, respectively). Lines are moving averages (n = 5). For absolute values see Fig. SI-4.

**Water chemistry.** The Čertovo and Plešné tributaries were strongly acidic, with 1997–2017 average pH values of 4.1–4.6. Concentrations of $SO_4^{2-}$ and $Cl^-$ varied in relatively narrow ranges, while those of $NO_3^-$ and DOC varied by an order of magnitude (Figs. 4 and SI-5).

Concentrations of DOC significantly increased in almost all Čertovo tributaries in 1997–2017. The only tributaries with no trends in DOC concentrations during 1997–2017 were CT-VI and CT-VII, where $NO_3^-$ concentrations increased following tree damage by windthrows in 2007 and 2008. The chemistry of Čertovo tributaries slowly recovered from atmospheric acidification during our study, exhibiting decreasing concentrations of $SO_4^{2-}$, $Cl^-$, $H^+$, $Al_i$ and ionic strength in all streams.

Chemistry of the Plešné tributaries exhibited similar trends to the Čertovo tributaries prior to the tree dieback (Tables SI-3 and SI-4), but strongly diverged thereafter (Fig. 4). In the period immediately following dieback there were increases in $NO_3^-$, $H^+$, $Al_i$, divalent base cations and ionic strength, whilst $SO_4^{2-}$ and $Na^+$ were unaffected. Concentrations of DOC did not immediately respond to dieback, but steep increases occurred from 2008–2017 as concentrations of initially affected ions and ionic strength decreased (Fig. 4).

Seasonal variations in water composition were highest for $NO_3^-$ and DOC (as well as $A^-$) concentrations and T, and exhibited inverse seasonal patterns, with the lowest $NO_3^-$ and the highest DOC concentrations and T values in the growing season. Concentrations of $Al_i$ and ionic strength (and also BCs, not shown) exhibited similar seasonal variations as SAAs, while the lowest seasonal variation occurred for $H^+$ concentrations (Fig. 4).

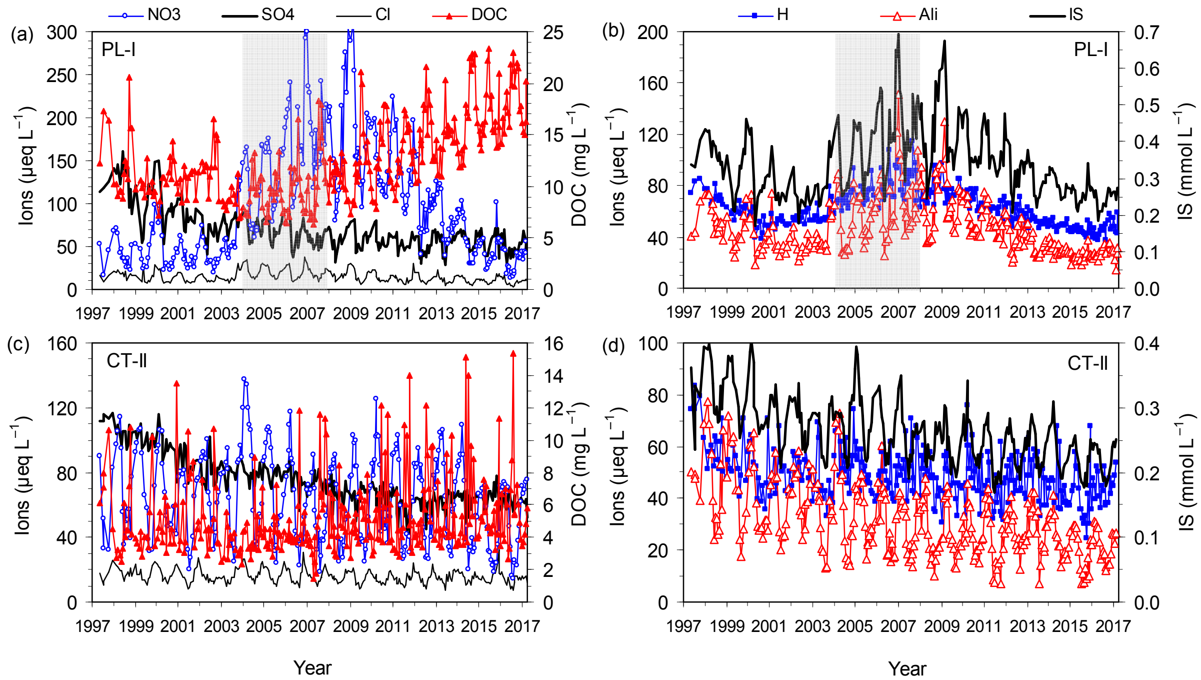


Fig. 4. Time series of concentrations of DOC, $NO_3^-$, $SO_4^{2-}$, $Cl^-$, $H^+$, ionic aluminium ($Al_i$), and ionic strength (IS) in the major surface tributary of (a, b) Plešné Lake (PL-I) and (c, d) Čertovo Lake (CT-II). Grey areas indicate the period of bark beetle outbreak in the PL catchment. For other tributaries see Fig. SI-5.

**Relationships between DOC and physico-chemical properties of stream water.** In the Čertovo catchment, concentrations of DOC correlated positively with Q and T, and negatively with BCs, $Al_i$, and ionic strength in most tributaries. Results of forward stepwise regression showed that majority of the long-term DOC variations in stream waters could be explained by 5–7 of the selected variables. Among them, either T or Q (climate variables) played the dominant role in the most Čertovo tributaries during the whole 2009–2017 period, while $SO_4^{2-}$, $NO_3^-$, and $H^+$ concentrations (i.e., chemical variables) contributed to explaining DOC variations in the CT-I and CT-II tributaries (Tables 1, SI-4, SI-5).

Table 1. Results of forward stepwise regression (FSR) between DOC *vs.* Q, T, and concentrations of $NO_3^-$, $SO_4^{2-}$, $Cl^-$, $H^+$, and $Al_i$ in major surface tributaries to Čertovo (CT-II, CT-VI and CT-VII) and Plešné (PL-I and PL-II) lakes, combined with correlation coefficients of linear regressions between DOC and these variables (Table SI-4). Values for DOC (given in brackets) represent Kendall's tau values of temporal trends for each time period (Table SI-3). Bold numbers indicate significant relationships at $p < 0.05$, negative values indicate inverse relationships. Asterisks indicate variables selected by the FSR. Coefficient of determination ($R^2$) of FSR are given for all variables selected by FSR (Table SI-5). The most important variable in FSR is given in the last row. All values are related to the given periods. For other tributaries and periods see Tables SI-3 to SI-5.

| | ----------------- 1997–2003 ----------------- | | | | | ----------------- 2009–2017 ----------------- | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | CT-II | CT-VI | CT-VII | PL-I | PL-II | CT-II | CT-VI | CT-VII | PL-I | PL-II |
| n | 74 | 67 | 67 | 74 | 56 | 144 | 143 | 144 | 143 | 123 |
| DOC trend | (0.07) | (0.10) | (–0.18) | (0.05) | (0.11) | (0.16) | (0.10) | **(0.26)** | **(0.58)** | **(0.37)** |
| Q | **0.54*** | **0.51*** | 0.16* | **0.55*** | 0.27* | **0.54** | **0.50*** | **0.43*** | 0.08 | **0.24*** |
| T | 0.14* | **0.39** | **0.66*** | **0.33*** | **0.44*** | **0.38** | **0.54*** | **0.63*** | **0.56*** | **0.51*** |
| $NO_3^-$ | **–0.51*** | **–0.49*** | **–0.60*** | **–0.35** | **–0.34** | **–0.48*** | **–0.43*** | **–0.61*** | **–0.75*** | **–0.81*** |
| $SO_4^{2-}$ | –0.21 | –0.11* | **–0.29** | –0.07 | –0.07 | **–0.59*** | –0.07* | **–0.54*** | **–0.63*** | **–0.45** |
| $Cl^-$ | –0.06 | **–0.31*** | 0.00* | –0.05 | –0.22 | **–0.20*** | **–0.22*** | –0.02* | **–0.72*** | **–0.74** |
| $H^+$ | **0.63*** | **0.33*** | 0.24 | **0.30** | **0.31*** | **0.54** | **0.22*** | 0.03 | **–0.45*** | **–0.49** |
| $Al_i$ | **–0.29** | –0.06 | **–0.43** | 0.01 | –0.11 | **–0.21** | –0.12 | –0.12 | **–0.58*** | **–0.70*** |
| FSR ($R^2$) | 0.84 | 0.70 | 0.73 | 0.54 | 0.43 | 0.81 | 0.75 | 0.83 | 0.81 | 0.83 |
| Variables | $H^+$ | Q | T | Q | T | $SO_4^{2-}$ | T | T | $NO_3^-$ | $NO_3^-$ |

Climate variables were also important for the Plešné tributaries during the whole study, but chemical variables dominated after the tree dieback (Tables 1, SI-5). During 1997–2003, most of DOC variation was explained by Q and T. During 2004–2008, $H^+$ and $Cl^-$ dominated in the relationships. DOC concentrations did not, however, exhibit significant trends during these two periods, and the selected variables mostly contributed to the explanation of seasonal DOC variations. In contrast, significant DOC increases during 2009–2017 were mostly explained by decreasing $NO_3^-$ and $Al_i$ concentrations (Table 1). A surprising positive correlation between DOC and $H^+$ occurred in Plešné tributaries during 1997–2008, but became negative in both PL-I and PL-II (the tributaries with the highest and most steeply increasing DOC concentrations) in 2009–2017 (Table 1). Relationships between DOC concentrations and SAAs, BCs, $Al_i$, and ionic strength were mostly negative and significant in all Plešné tributaries during all tested periods.

## DISCUSSION

**Effects of soil physico-chemical properties on DOC leaching.** Water discharge and temperature explained most of the DOC variations in most Čertovo tributaries, especially during 2009–2017, and also in Plešné tributaries prior to the tree dieback in its catchment (Table 1). These relationships reflected similar seasonality of DOC concentrations and water T, and elevated DOC leaching during high flow events, and thus do not indicate that climate variations are responsible for longer-term DOC trends. Decreasing concentrations of SAAs, $H^+$, and $Al_i$ contributed to the significant long-term increase in DOC concentrations in most Čertovo tributaries, especially during 1997–2008, with the exception of the two tributaries where $NO_3^-$ increases following windthrow events in 2007–2008 appeared to offset the rising DOC trend (Fig. SI-5).

The importance of Q and T in explaining DOC variation in the Plešné tributaries decreased after the tree dieback, while chemical variables became more important (Table 1). The close positive DOC *vs.* $H^+$ relationships prior to and immediately after the tree dieback probably resulted from a coincidence, because it is not probable that decreasing pH would elevate DOC mobility; more likely, variations in $H^+$ concentrations were affected by variations of $A^-$ leaching. The most plausible reasons for the absence of trends in DOC leaching immediately after the tree dieback are increased concentrations of $H^+$ and polyvalent cations (especially $Al_i$), which increase protonation and coagulation of DOC and thereby reduce its mobility[29,46], and elevated microbial DOC uptake (see next section). Chemical suppression was also found to reduce DOC leaching from a Northern Irish moorland catchment during several years following a wildfire[9], suggesting that this mechanism may be a consistent short-term response to ecosystem disturbances in acidic catchments.

The increase in $H^+$ concentrations in soil water and streams was fast (preceded peaks in BCs and $Al_i$)[37], and peaked ~3 years after the tree dieback (Fig. 4), as $H^+$ was displaced from the soil sorption complex by other cations in the upper (mostly O) horizons, and leached to surface waters along with $NO_3^-$.[41]

The steepest increasing trends in DOC leaching occurred in the Plešné tributaries during 2009–2017, some years after the initial dieback event. During this time, the amount of litter in the catchment was still high, but concentrations of $NO_3^-$, $H^+$ and $Al_i$ in stream water had declined, perhaps enabling more of the DOC produced through decomposition to leach to surface waters. The negative correlations between DOC and $H^+$, $Al_i$ and $NO_3^-$ in the surface Plešné tributaries during this period (Table 1) are all consistent with an effect of decreasing soil water acidity and/or ionic strength on DOC mobility. Because changes in Q and T were negligible in the Plešné tributaries during 2009–2017 *vs.* previous periods, we conclude that these climatic variables did not contribute to the observed DOC increase in the latter phase following tree dieback. Our data thus support the idea of multiple temporal scale drivers involved in trends of DOC leaching, indicating that seasonal and inter-annual variation can be explained by climate variables whereas long-term variation are more probably associated with changes in soil biogeochemistry.[11,34,48,49]

**Effects of soil microbial community on DOC leaching.** Changes in soil microbial biomass and tight links between C and N cycling could also have contributed to low DOC leaching immediately after the tree dieback, which occurred despite elevated DOC concentrations in soils (Fig. 3a), and to the subsequent increase as $NO_3^-$ leaching declined (Fig. 4a). Štursová et al.[50] have shown that soil microbial community significantly changed in the Plešné catchment after the tree dieback, which has also been observed elsewhere.[51] At Plešné, fungal community biomass decreased, despite a relative increase in saprotrophic taxa, due mostly to the disappearance of mycorrhizal fungi following tree death. In contrast, bacterial biomass increased or remained unaffected after the disturbance, which resulted in a substantial decrease in the soil fungi-to-bacteria ratio.[50] Bacteria are distributed heterogeneously in small-scale habitats, physically connected by water, or along preferential flow paths, and their growth depends on DOC and nutrients passively transported to their surfaces.[23,52] This causes bacteria to be more dependent on water content and the presence of soluble compounds in soil than hyphal fungi.[23] The elevated soil moisture after the tree dieback (Fig. 2b) thus probably further supports development of bacterial *vs.* fungal biomass and their increasing role in soil C and N cycling.

The Plešné catchment was already N-saturated, and exhibited significant $NO_3^-$ leaching, even before forest disturbance (Fig. 4). The elevated $NH_4^+$ concentrations in soils immediately after the tree dieback (Fig. 3a) further increased availability of inorganic N for microbial and plant communities. Consequently, N saturation in the Plešné catchment rapidly progressed to an advanced stage in which excess $NH_4^+$ leads to elevated nitrification.[53] The supply of the surplus $NH_4^+$ to nitrifiers may, however, have remained relatively low immediately after the tree dieback due to elevated soil concentrations of bio-available DOC from decaying dead biomass (e.g., fine roots), enabling immobilization of DOC and $NH_4^+$ into $C_{MB}$ and $N_{MB}$ (Fig. 3b). This situation lasted for ~3 years, until DOC availability in soils decreased (Fig. 3a). The absence of elevated DOC leaching despite its production from dead biomass was therefore probably partly related to its immobilization into soil microbial biomass (as well as to the solubility controls discussed above) during this period. Even though stream water $NO_3^-$ concentrations increased immediately after the three dieback (Fig. 4), this trend might have been steeper without abundant bio-available DOC in soils.

When C and N immobilization in microbial biomass decreased, more $NH_4^+$ remained for nitrifiers, and soil water $NO_3^-$ concentrations rapidly increased (Fig. 3a).[42] This $NO_3^-$ production increased concentrations of electron acceptors in the system, available for $NO_3^-$ reducing microbes (denitrification and dissimilatory nitrate reduction to ammonium) in anoxic soil micro-sites, which could further reduce the pool of DOC available for leaching.[25,26,38]

Decreasing $NO_3^-$ availability in soils due to reduced excess N supply from mineralization of dead biomass and increasing N uptake by re-growing vegetation, and the reduced $SO_4^{2-}$ and $NO_3^-$ throughfall deposition could contribute to the reduced availability of these electron acceptors for DOC mineralization in anoxic soil micro-sites and the increasing DOC leaching during 2009–2017 (Fig. 4). Moreover, the elevated DOC leaching also could be associated with lower DOC bioavailability, connected with reduced input of fresh dead biomass.

**Effects of catchment characteristics and soil moisture on DOC leaching.** Long-term increasing trends in DOC leaching after tree dieback caused by bark beetle attack occurred in mountain catchments with > 50% impacted stands in western North America.[8] DOC concentrations increased in soil water of dead (compared to intact) mountain Norway spruce stands in Germany, as well as in streams draining clear-cut Norway spruce forests in Finland.[4,21] In contrast, some other studies (for review see ref. 7) found negligible effects of forest disturbance on DOC exports from soil to streams. Piirainen et al.[20] observed elevated DOC leaching from the organic soil horizon, but effective DOC retention in the mineral soil horizons. The spatial differences in DOC leaching after forest dieback thus also seem to reflect differences in catchment characteristics. The effect of forest dieback on DOC leaching is probably smaller when vertical water flow through well developed mineral soil horizons represents the dominant water pathway. In contrast, steep catchments (like that of Plešné Lake), with young organic-rich soils, poorly developed mineral horizons, and short water residence time in soils are more sensitive to elevated DOC leaching after tree dieback.

This leaching is further magnified by lateral flows during high-flow events, when water passes horizontally through the organic rich soil horizons. The probability of lateral flows and the associated risk of elevated DOC leaching increase during high precipitation and runoff events.[17,54] This may have been amplified following tree dieback by reduced water uptake and evapotranspiration beneath dead trees[55,56], leading to increased soil moisture

(Fig. 2b), shallower groundwater, and therefore greater water fluxes through shallow, organic-rich soils.[5,6]

Another factor potentially affecting DOC leaching after tree dieback is pre-disturbance soil base saturation, which also appears to influence DOC response to wildfire.[9] In poorly buffered catchments, increases in $NO_3^-$ (and $H^+$) are likely to exceed the increases in BCs, thereby acidifying soil water and reduce DOC mobility, whereas in well-buffered catchments, acidity may be unchanged or even decrease (if BC increases exceed acid anion increases).

**Interplay of soil C and N responses to tree mortality.** Our data suggest a complex contribution of chemical and microbial variables to ecosystem responses to tree dieback, manifested by initial $NO_3^-$ leaching followed by increased DOC leaching. We observed a stable level of DOC leaching in the first years after the tree dieback (Fig. 4a), despite the rapid increase in litter available for decomposition (Fig. 1) and elevated DOC concentrations in soil water (Fig. 3a). In contrast, DOC leaching increased from the system in the latter phase, when litter input to the forest floor had already ceased. These trends can be explained by changes in soil water chemistry, soil microbial community, and links between C and N cycles. Our data suggest that changes in N cycling could play an important role in DOC leaching. We conceptualise ecosystem C and N responses to tree mortality in three stages (Fig. 5):

*Stage 1*: Immediately after tree dieback, tree-associated fungi decline, and bacterial populations increase. Elevated N availability for free bacteria enables them to utilize available DOC for transformation into bacterial biomass (Fig. 3b) and energy (mineralization to $CO_2$). DOC mobility is suppressed by increasing soil water acidity due to

$H^+$ displacement from the soil sorption complex by other cations, and by microbial $NH_4^+$ use (Fig. 4b). Nitrification remains low relative to $NH_4^+$ availability, and $NO_3^−$ leaching is therefore limited despite a steep increase in soil $NH_4^+$ concentrations after tree dieback (Fig. 3a). Elevated microbial DOC utilisation and chemical suppression of its mobility restrict DOC leaching to waters (Fig. 4a).

*Stage 2*: In the second stage, microorganisms became C-limited as litter inputs decrease, and their capacity to assimilate $NH_4^+$ becomes saturated. At this point, nitrification rates increase, reducing the pool of available $NH_4^+$ and increasing $NO_3^−$ production and leaching. The associated production of $H^+$ and mobilisation of polyvalent cations (including $Al_i$ from dissolution of soil $Al(OH)_3$) maintain suppression of DOC mobility. In addition, nitrification increases the availability of electron acceptors for $NO_3^−$ reducing microorganisms. These processes together act to delay DOC leaching despite its continued liberation from the dead biomass.

*Stage 3*: In the final stage of ecosystem response to forest dieback, the available N pool begins to decline as the supply of $NH_4^+$ from organic matter mineralisation is exhausted, and N uptake by re-growing trees begins to occur. During this phase, DOC leaching increases due to: (i) reduced chemical suppression of DOC mobility as soil solution $H^+$ and $Al_i$ decline, following the decrease in $NO_3^-$ production and leaching (Fig. 5c); (ii) decreasing availability of $NO_3^−$ (Fig. 5b) for DOC mineralization by $NO_3^−$ reducing microorganisms in anoxic soil micro-sites; and (iii) decreasing DOC immobilization in microbial biomass (Fig. 5a). The elevated DOC production can be considered as the net difference between ongoing DOC production from dead wood biomass by saprotrophic fungi, and the decreasing utilisation of DOC by free bacteria as the N supply declines. To the extent that the increase in DOC leaching is due to the alleviation of chemical suppression, we would expect DOC concentrations to return to the 'baseline' concentrations represented by the Čertovo reference site (note that DOC has been increasing in both catchments due to the ongoing decline of atmospheric S and N deposition[38], therefore this baseline is not flat). However, the enhanced production of DOC from dead biomass has the potential to increase DOC leaching above this reference level, and previous work has suggested that this production can continue (albeit with decreasing intensity) for up to three decades after a mortality event.[57,58]

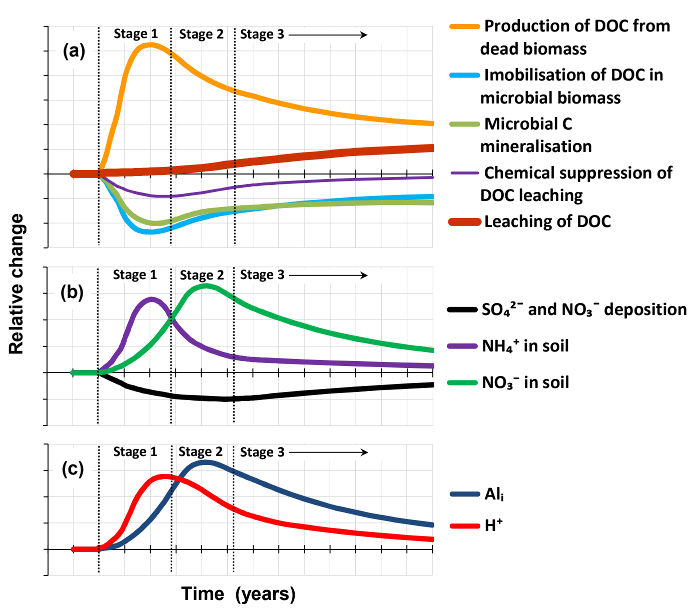


Fig. 5. Conceptual graph showing significant processes and chemical changes that can influence DOC leaching during forest dieback, based on observations from the Plešné catchment: (a) Changes in production, microbial use, chemical suppression and leaching of DOC. (b) Changes in availability of inorganic N and electron acceptors ($NO_3^-$ and $SO_4^{2-}$) for microbial C mineralization in anoxic soil micro-sites. (c) Changes in soil water $H^+$ and

$Al_i$ concentrations that affect chemical suppression of DOC mobility. Grey areas indicate period of tree dieback.

Our results contribute to the growing body of evidence[25,38,59,60] that an integrated understanding of ecosystem C and N cycles is required in order to evaluate and predict DOC and $NO_3^-$ leaching from terrestrial ecosystems, especially their responses following forest disturbances.

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## ASSOCIATED CONTENT

**Supporting Information Available**

Part 1: Detailed description of the Plešné and Čertovo catchments, including details on soil, throughfall and litter sampling and composition; Part 2: Details on water sampling and analyses; Part 3: Details on water composition and statistics. This information is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interests.

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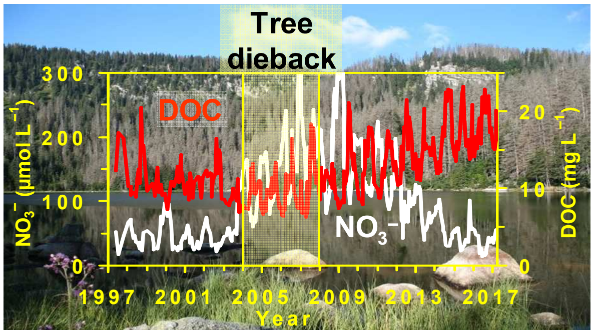
Tree
dieback
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NO3-
300
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20
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0
NO3- (µmol L-1)
DOC (mg L-1)
1997 2001 2005 2009 2013 2017
Year