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The sensitivity of water chemistry to climate in a forested, nitrogen-saturated catchment recovering from acidification

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ABSTRACT

Fluxes of major ions and nutrients were measured in the N-saturated mountain forest catchment-lake system of Čertovo Lake (Czech Republic) from 1998 to 2014. The lake has been rapidly recovering from atmospheric acidification due to a 90% decrease in sulphate (SO_4^{2-}) deposition since the late 1980s and nitrate (NO_3^-) contribution to the pool of strong acid anion and leaching of dissolved organic carbon (DOC) have increased. Present concentrations of base cations, phosphorus (P), total organic N (TON), and ionic (Al_i) and organically bound (Al_o) aluminium in tributaries are thus predominantly governed by NO_3^- and DOC leaching. Despite a continuing recovery lasting 25 years, the Čertovo catchment is still a net source of protons (H^+), producing 44 mmol m^{-2} yr^{-1} H^+ on a catchment-area basis (corresponding to 35 μmol L^{-1} on a concentration basis). Retention of the deposited inorganic N in the catchment averages 20%, and ammonium consumption (51 mmol m^{-2} yr^{-1}) and net NO_3^- production (28 mol m^{-2} yr^{-1}) are together the dominant terrestrial H^+ generating processes. In contrast, the importance of SO_4^{2-} release from the soils on terrestrial H^+ production is continuously decreasing, with an average of 47 mmol m^{-2} yr^{-1} during the study. The in-lake biogeochemical processes reduce the incoming acidity by ~40%, neutralizing 23 μmol L^{-1} H^+ (i.e., 225 mmol m^{-2} yr^{-1} on a lake-area basis). Denitrification and photochemical and microbial decomposition of DOC are the most important in-lake H^+ consuming processes (50 and 39%, respectively), while hydrolysis of Al_i (from tributaries and photochemically liberated from Al_o) is the dominant in-lake H^+ generating process. Because the trends in water chemistry and H^+ balance in the catchment-lake system are increasingly related to variability in NO_3^- and DOC leaching, they have become sensitive to climate-related factors (drought, elevated runoff) and forest damage that significantly modify the leaching of these anions. During the study period, increased exports of NO_3^- (accompanied by Al_i and base cations) from the Čertovo catchment occurred after a dry and hot summer, after forest damage, and during elevated winter runoff. Increasing DOC export due to decreasing acid deposition was further elevated during years with higher runoff (and especially during events with lateral flow), and was accompanied by P, TON, and Al_o leaching. The climate-related processes, which originally "only" confounded chemical trends in waters recovering from acidification, may soon become the dominant variables controlling water composition in N-saturated catchments.

1. Introduction

After decades of atmospheric acidification of waters in acid sensitive regions, the adoption of international protocols to reduce sulphur (S) and nitrogen (N) emissions led to a significant decrease in acidic deposition and enabled the recovery of numerous European and North American surface waters (e.g., Stoddard et al., 1999; Evans et al., 2001). Observed chemical changes in recovering waters are not universal, however, and differ between regions (e.g., Garmo et al., 2014). The most common confounding factors in chemical recovery from acidification are usually climate-related, and are associated with the increased frequency and severity of droughts, changes in the terrestrial cycling of N, S and organic carbon, elevated weathering and leaching of base cations, and also (especially in coastal regions) with the increasing frequency of sea salt episodes (e.g., Webster and Brezonik, 1995; Skjelkvåle et al., 2003; Rogora et al., 2003). Further uncertainties arise from the progressing N-saturation of some terrestrial ecosystems at stable or even decreasing N deposition (Wright et al., 2005; Rogora, 2007), as well as from elevated leaching of dissolved organic carbon (DOC) accompanying decreasing acidic (mostly sulphate, SO_4^{2-}) deposition (Monteith et al., 2007), elevated runoff and

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forest dieback (Hejzlar et al., 2003; Hongve et al., 2004; Mikkelson et al., 2013).

These factors, confounding the trends in water chemistry anticipated by available models on the basis of acidic deposition, introduce a significant degree of uncertainty to predictions on the future development of recovering aquatic ecosystems. Most of this uncertainty is related to the future behaviour of N in catchments and the effects of climate change on N leaching (Skjelkvåle et al., 2003; Curtis et al., 2005). Nitrogen deposition in Europe has recently become more important than that of S on a molar basis, because S emissions have decreased more rapidly (Wright et al., 2005; Tørseth et al., 2012). After the rates of decreasing trends in SO_4^{2-} deposition and lake water concentrations slowed down, trajectories of water recovery became more complex and started to exhibit clear variations with weather and climate (e.g., Dillon et al., 1997; Rogora, 2007). The effect of climatic factors on recovery trends of surface waters became especially evident in N-saturated sites, with a high proportion of NO_3^- in the total concentrations of strong acid anions (Murdoch et al., 2000; Rogora, 2007). Such areas also sensitively react to various disturbances in the catchment vegetation by elevated NO_3^- leaching (Goodale et al., 2000; Oulehle et al., 2013). The elevated concentrations of NO_3^- in soil solutions mobilize H^+, base cations (especially K^+, Mg^{2+}, and Ca^{2+}), and ionic aluminium forms (Al_i) (Likens and Bormann, 1995; Houlton et al., 2003; McHale et al., 2007), which may further confound the long-term trends in water chemistry.

In this study, we use a 17-year long mass balance of major ions and nutrients in the strongly acidified and N-saturated catchment-lake system of Čertovo Lake (Czech Republic) to evaluate how climate-related factors (drought, elevated runoff) and forest damage affect stream and lake water chemistry. The lake is one of the most strongly atmospherically acidified mountain lakes in the world, but has also exhibited rapid recovery due to the most pronounced declines in S and N deposition among all European lake districts (Evans et al., 2001). Sea salt inputs do not influence water chemistry in the lake (Kopáček et al., 2009), and the most confounding factors thus arise from climatic effects on catchment processes and forest vigour that primarily affect NO_3^- and DOC leaching. The aims of this study are to quantify (1) changes in water composition resulting from elevated concentrations of NO_3^- and DOC, (2) the net effect of these changes on proton (H^+) production in the catchment, and (3) the ability of in-lake processes to neutralize these terrestrial acidity sources.

2. Methods

2.1. Description of the study site

Čertovo Lake is situated in the Bohemian Forest at the Czech-German border (13°12′ E, 49°10′ N) at an elevation of 1028 m (Fig. 1); for its image see Supplementary Information (SI), Fig. SI-1. It is a dimictic, oligotrophic lake of glacial origin, with surface area of 10.7 ha and maximum depth of 36 m (Vrba et al., 2003). Anoxia only occurs in a thin (~1–2 m) layer above the bottom in the deepest part of the lake during the late stages of winter and

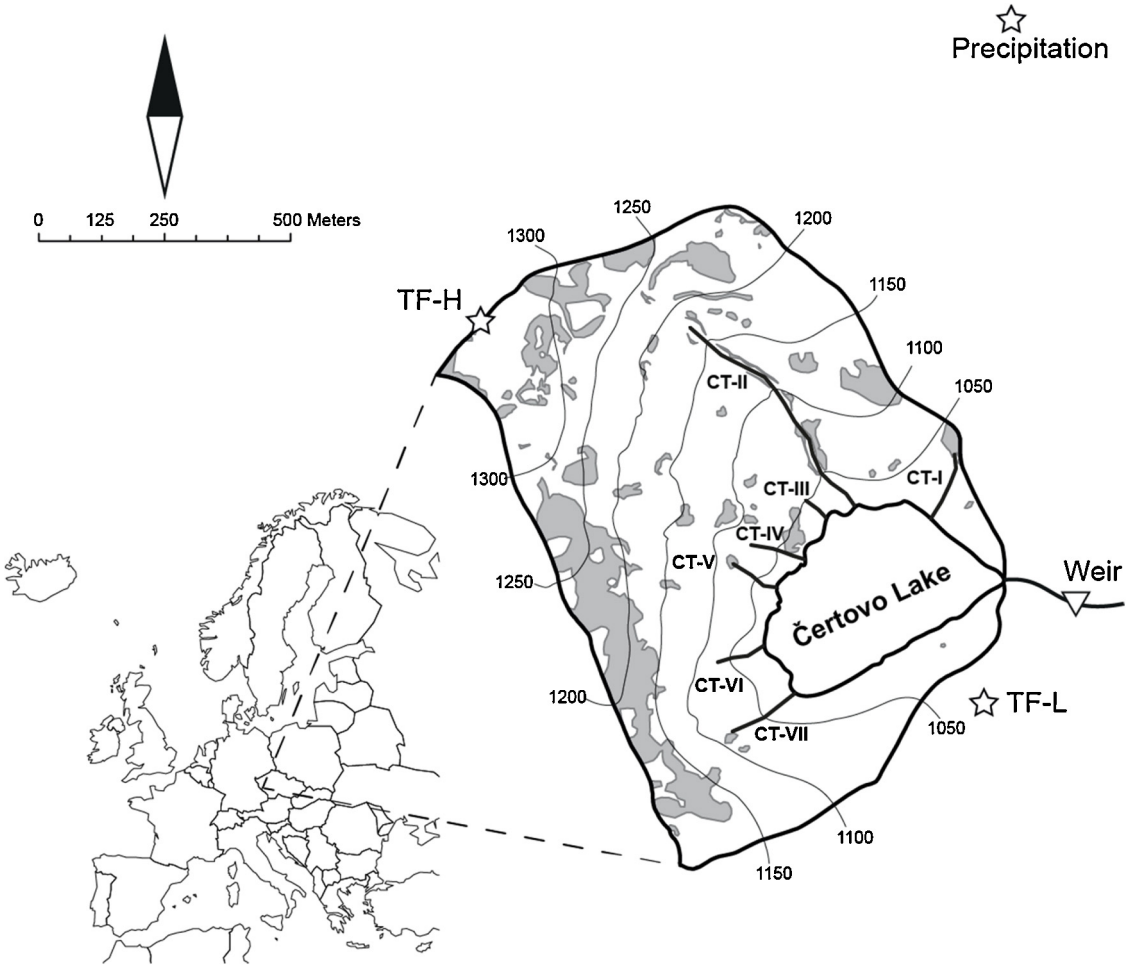

Fig. 1. Location of Čertovo Lake in Europe. The detail shows positions of lake tributaries (CT-I to CT-VII), precipitation and throughfall (TF) plots, weir, and areas with >50% reduction of living trees due to windthrows in 2007 and 2008 and the following bark beetle infestation (grey areas); the rest of the catchment is covered with healthy forest.