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Soil response to a 3-year increase in temperature and nitrogen deposition measured in a mature boreal forest using ion-exchange membranes

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Abstract The projected increase in atmospheric N deposition and air/soil temperature will likely affect soil nutrient dynamics in boreal ecosystems. The potential effects of these changes on soil ion fluxes were studied in a mature balsam fir stand (*Abies balsamea* [L.] Mill) in Quebec, Canada that was subjected to 3 years of experimentally increased soil temperature (+4 °C) and increased inorganic N concentration in artificial precipitation (three times the current N concentrations using NH_4NO_3). Soil element fluxes (NO_3 , NH_4 , PO_4 , K, Ca, Mg, SO_4 , Al, and Fe) in the organic and upper mineral horizons were monitored using buried ion-exchange membranes (PRSTTM probes). While N additions did not affect soil element fluxes, 3 years of soil warming increased the cumulative fluxes of K, Mg, and SO_4 in the forest floor by 43, 44, and 79 %, respectively, and Mg, SO_4 , and Al in the mineral horizon by 29, 66, and 23 %, respectively. We attribute these changes to increased rates of soil organic matter decomposition.

Significant interactions of the heating treatment with time were observed for most elements although no clear seasonal patterns emerged. The increase in soil K and Mg in heated plots resulted in a significant but small K increase in balsam fir foliage while no change was observed for Mg. A 6–15 % decrease in foliar Ca content with soil warming could be related to the increase in soil-available Al in heated plots, as Al can interfere with the root uptake of Ca.

Keywords PRS probes · Podzol · Balsam fir · Aluminum · Soil warming · Base cations · Climate change

Introduction

Plant growth in boreal ecosystems is often constrained by nutrient availability (Hobbie et al. 2002). In the last decades, the human-induced increase in atmospheric N deposition has increased soil N availability (Driscoll et al. 2001) and improved the growth of many tree species in some regions of North America (Quinn Thomas et al. 2010) and Europe (Kenk and Fischer 1988). The global levels of atmospheric N deposition are projected to be 70 % higher in 2050 relative to that in 2000 (Galloway et al. 2004). In addition, boreal soils are also expected to undergo significant warming in the coming decades, with projected increases in mean annual temperature of 2.0–3.3 °C in 2070–2099 relative to the current 30-year average (1971–2000) for some sites in Eastern Canada (Houle et al. 2012). Many soil

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processes such as litter decomposition and mineralization of soil organic matter (SOM) are expected to proceed faster with such warming (Campbell et al. 2009). Because of the temperature dependence of enzymatic reactions in the soil, decay rates for the labile fraction of the SOM respond well to temperature increases (Davidson and Janssens 2006). A priori, these changes could have positive effects on the availability of N and base cations (K, Ca, and Mg). As boreal soils of the Canadian Shield generally have small reservoirs of available N (Tamm 1991) and base cations (Duchesne and Houle 2006), the combination of increased N deposition and warmer soils is expected to have beneficial effects on tree nutrition and growth in the Canadian boreal forest. Additive effects of these factors on plant productivity have been reported in temperate ecosystems (Hutchison and Henry 2010; Ma et al. 2011).

The soil nutrient response to increased temperature and N deposition may however be more difficult to predict than initially thought. For instance, the decomposition of more recalcitrant SOM fractions is relatively limited by other environmental factors such as physical aggregation or strong chemical bonds that can attenuate the positive effect of temperature on decomposition over time (see Davidson and Janssens 2006). Also, soil water content is projected to decrease in boreal forests during the growing season (Houle et al. 2012). Such changes could affect soil nutrient dynamics, as organic matter decomposition rates are affected by soil moisture (Swift et al. 1979). On the other hand, soil water content and temperature are projected to increase earlier in the season due to an earlier snowmelt (Houle et al. 2012). Changes in redox potentials associated with wetter and warmer soils early in the growing season could increase the amounts of Fe, Mn, PO₄, and SO₄ in soil solution (Darke and Walbridge 2000).

Increased soil temperature and atmospheric N deposition may also affect the acid–base status of soils. The higher SOM decomposition commonly observed in warming experiments (Rustad et al. 2001) is usually associated with increased releases of organic acids and can result in soil acidification (Van Cleve et al. 1990). Additional inputs from the atmosphere, namely NO_x, NH₃, and SO₄, also have the potential to increase soil acidity, a process that may have contributed to the decline of some fir and spruce forests of Germany and Eastern North America (Shortle and Smith 1988). In acidic soils with a low buffering capacity, acidic inputs can result in the dissolution of aluminum, a phytotoxic

ion that can inhibit root elongation and nutrient uptake (Cronan and Grigal 1995). Both Al and H ions can displace base cations from exchange sites resulting in increased leaching of these nutrients out of the soil rooting zone (Galloway et al. 1983).

Very few studies have been conducted to assess the combined effects of soil warming and increased N deposition in boreal forests, and in those that did, the focus was generally on N and C cycling (e.g., the study by Mäkipää et al. 1999 with Scots pine in Finland). Not only other nutrients (K, Ca, and Mg) but also elements potentially toxic to growth, Al for example, were not considered. Our objective is to characterize the potential effect of global changes on soil nutrient availability of a typical balsam fir (*Abies balsamea* [L.] Mill.) boreal forest of Quebec. For this purpose, we experimentally combined an increase in soil temperature (+4 °C) and length of growing season (earlier snowmelt, +2 to 3 weeks) with an increase in rain N concentration during the growing season (three times the current N concentration in the rain at the site), to study their effects on ion availability (NO₃, NH₄, PO₄, K, Ca, Mg, S, Fe, and Al). We hypothesized that (1) NO₃ and NH₄ availability will increase in the N deposition and the warming treatments, (2) NO₃ and NH₄ availability will be higher in the combined treatment (N deposition + warming soils), and (3) higher soil temperatures will increase base cation availability.

Materials and methods

Study area

The study site is located in the Lake Laflamme watershed north of Quebec City (47°17'N, 71°14'O; 800 m asl). The experimental plots were established in a 60-year-old even-aged balsam fir stand. The soil is an Orthic Ferro-Humic Podzol (Spodosol in the US soil taxonomic system), laying on a bedrock of Precambrian charnockitic gneiss and characterized by a sandy loam texture. The C and the N contents of the forest floor are 416 g C kg⁻¹ and 16.6 g N kg⁻¹, respectively, for a C/N ratio of 25 (unpublished data). The pH of the forest floor (at 5-cm depth) and mineral horizons (at 20–30-cm depth) is 3.0 and 4.1 (NH₄Cl-based), respectively. The climate is continental with cold winters and warm summers. Between 1981 and 2006, annual precipitation and mean air temperature averaged 1,535 mm and -0.4 °C,

respectively. Annual N deposition ($\text{NH}_4 + \text{NO}_3$) averages $5.7 \text{ kg N ha}^{-1} \text{ year}^{-1}$ (Houle and Moore 2008).

Experimental design

The experiment was set up in autumn 2008 and laid out according to a randomized split-plot design with two levels of warming (ambient and $4 \text{ }^\circ\text{C}$ above ambient) nested within two levels of artificial precipitation (no added NH_4NO_3 and three times the ambient NH_4NO_3 concentration in incoming precipitations, details below). Because of the intensive manipulations and sampling effort, we limited the experiment to 12 plots split up evenly into three blocks. The blocks were $12 \text{ m} \times 60 \text{ m}$ and laid out perpendicular to the slope with a 12-m buffer strip in between. Each block was divided in two $24\text{-m} \times 12\text{-m}$ plots separated by a $12\text{-m} \times 12\text{-m}$ buffer zone. Each plot was divided into two $12\text{-m} \times 12\text{-m}$ subplots. Within each subplot, a balsam fir tree was selected based on a visual estimation of good health and dominance or codominance in the canopy. The N deposition treatment was randomly distributed within the two plots of each block, and the soil warming treatment was randomly distributed within the two subplots of each plot.

Soil warming

In each plot, 70 m of heating cables (nonheating cables for the control) was buried in a spiral pattern 5–10 cm below the ground at the interface between the organic and mineral soil with an average distance between cables of approximately 30 cm. Great care was taken to minimize root damage, and roots $>5 \text{ mm}$ in diameter were bypassed by running the wire below or above the root. Soil temperature in each plot was measured continuously with thermistors (precision $\pm 0.2 \text{ }^\circ\text{C}$; model 107-L from Campbell Scientific Inc., Logan, UT, USA) buried between heating cables. The warming cables were activated and disabled when the average difference of soil temperature between heated and nonheated trees reached 3 and $5 \text{ }^\circ\text{C}$, respectively, in order to maintain an average difference of $4 \text{ }^\circ\text{C}$. This value was chosen based on climate simulations for the site for the period 2070–2099 (Houle et al. 2012). Storage of temperature data and control of warming were done with a CR1000 datalogger (Campbell Scientific, Inc., Logan, UT, USA). Soil heating was started in the spring of 2009. From the beginning of spring snowmelt

until the first autumn frost, the average soil temperature in heated plots was higher by 4.0 ± 0.4 , 4.1 ± 0.3 , and $3.7 \pm 0.9 \text{ }^\circ\text{C}$ in 2009, 2010, and 2011, respectively (Fig. 1).

In addition to the maintenance of a higher soil temperature during the growing season, the heating treatment was also designed to simulate an earlier snowmelt and an earlier snowpack disappearance. In 2009, soil warming was started on April 27 with a remaining snowpack of 0.75 m, with snowmelt in control plots ending 19 days later. A system malfunction caused an early interruption of the soil warming in mid-August that year. In 2010, soil heating was started on March 30 because of a warm spring. The snowpack was 0.85 m and the snowmelt was completed 28 days later. The treatment was stopped before the first freeze-thaw events, on October 19. The cold spring of 2011 delayed the start of soil heating to May 5. The snowpack was then 0.60 m and snowmelt was completed 16 days after the beginning of treatment. Heating was terminated on October 18.

Application of artificial rain

The protocol used to apply artificial rain was designed to simulate how natural atmospheric N is deposited on forest ecosystems. The rain solution (control and N-enriched) was applied on the tree canopy using nozzles set up above one tree in each plot, using a system of pumps and reservoirs. The composition of the artificial rain solution was based on the average concentrations of Na (0.046 mg L^{-1}), Ca (0.089 mg L^{-1}), Mg (0.018 mg L^{-1}), K (0.026 mg L^{-1}), H (0.014 mg L^{-1}), Cl (0.07 mg L^{-1}), and SO_4 (1.01 mg L^{-1}) in incoming precipitation measured at the site. Each year, from mid-June to mid-September, all 12 plots were simultaneously subjected to a weekly artificial precipitation of 70 L. For the six plots subjected to the N treatment, NH_4NO_3 was added to the rain solution to reach a final concentration of 1.0 and 3.4 mg L^{-1} of NH_4 and NO_3 respectively, which corresponds to approximately three times the concentrations measured in the local precipitation. The applications resulted in an increased N deposition of $1.544 \text{ g N tree}^{-1} \text{ year}^{-1}$, which was dispersed over an area estimated to $20\text{--}50 \text{ m}^2$, resulting in a rain event of 1.3–3.4 mm, or an additional $1.1\text{--}2.7 \text{ kg N ha}^{-1} \text{ year}^{-1}$. Watering was rescheduled to the next day on rainy days.

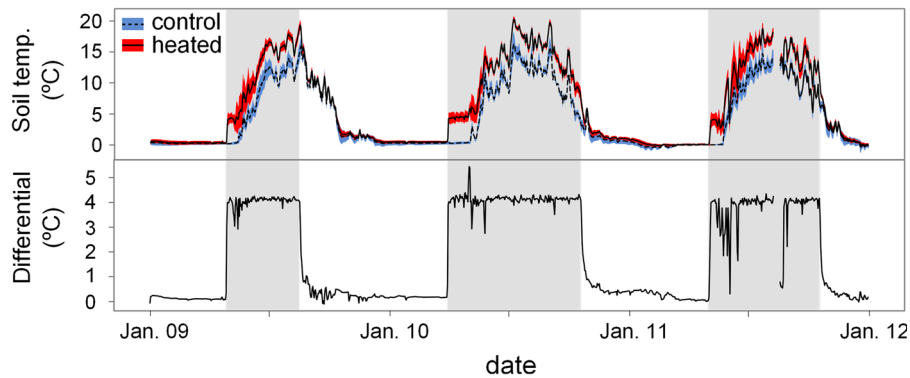


Fig. 1 Average soil temperature and the differential temperature between heated and control plots in 2009, 2010, and 2011. Colored ribbons are standard errors. The periods of soil warming are represented by the shaded areas

Soil sampling and analysis

Soil ion fluxes were determined during the 3 years of the study using ion-exchange membranes (PRSTTM probes, Western Ag Innovations Inc.; Saskatoon, SK, Canada). Ion-exchange membranes allow the assessment of nutrient supply rates by continuously adsorbing free ions on charged surfaces. Contrary to classical soil extractions or lysimeters, ion-exchange membranes simulate the action of plant roots that accumulate nutrients from soils through exchange reactions. At first, the probes typically adsorb the labile pool of ions until depletion, followed by measurements of ion supply rates through mineralization, leaching, or dissolution. Compared to traditional methods, several studies show that ion-exchange membranes may provide a better relative measure of nutrient availability and may be more sensitive to site conditions (see Szillery et al. 2006 for a review). The probe data will be referred to as “available nutrients” hereafter. Avoiding direct contact with heating cables, six pairs of probes—a pair consisting of one cation and one anion adsorbing membrane—were evenly distributed around the tree at a distance of 1.5 m from the stem, three pairs in the organic soil layer (approx. 5–10 cm deep) and three pairs in the mineral soil layer (approx. 10–20 cm deep). In 2009, the probes were replaced every 4 weeks to avoid potential saturation of the membranes, from May 21 to November 2. Based on these results, it was decided to replace the ion-exchange membranes every 6 weeks for the following years, each burial period corresponding to spring, summer, and autumn, and one set of probes was kept buried between the growing seasons to measure the nutrient availability during winter and the snowmelt period.

At the end of each burial period, the probes were removed and rinsed with deionized water to remove soil particles and then sent to the laboratory (Western Ag Innovations) for analysis. The probes were pooled per soil horizon for each tree. Membranes were eluted with 17.5 mL of 0.5 M HCl for 1 h. Concentrations of NH_4 , NO_3 , and PO_4 in the extract were determined colorimetrically using a Technicon AutoAnalyzer (Technicon AA2, Seal Analytical Inc., Mequon, WI, USA), while K, SO_4 , Ca, Mg, Al, and Fe concentrations were measured using inductively coupled plasma–atomic emission spectrometry (IPC–AES; Perkin Elmer Optima 3000-DV ICP; PerkinElmer, Inc., Shelton, CO, USA). Although sulfur levels measured with ICP are composed of SO_4 as well as dissolved organic S, they will be referred to as SO_4 as it is the most abundant fraction. The values are reported as micrograms per 10 cm² of resin surface. To compare seasonal or annual availability, values were divided by the duration of burial in days to account for the time differences between burial periods.

Soil water content

Volumetric soil water content (SWC) in the plots was measured weekly during the snow free period from 2009 to 2011. SWC was measured with a ThetaProbe ML1 (Delta-T Devices Ltd., Cambridge, GB) in 2009 and with a FieldScout TDR-300 device with 20-cm rods and standard calibration (accuracy ± 3 % vol; Spectrum Technologies, Inc., Plainfield, IL, USA) in 2010 and 2011. A broken rod delayed the start of the 2011 data collection. For each plot, nine measurements spaced

approximately 1 m apart were taken at a distance of 1.5 m from each tree and averaged.

Leaf chemistry

Current-year foliage was collected from the upper third of the canopy on three distinct branches of each tree. Sampling was done at the end of each growing season. Needles were oven-dried at 65 °C, ground at 250 µm, and digested with H₂SO₄. Nitrogen was determined with a Kjeldahl autoanalyzer (Kjeltec Auto model 1030 Analyzer, Tecator, UK), and P, K, Ca, and Mg were determined by ICP–AES (Perkin Elmer Optima 3000-DV ICP; PerkinElmer, Inc., Shelton, CO, USA).

Statistical methods

A linear mixed-model analysis of variance (ANOVA) with repeated measures was used to test for the effect of the soil warming treatment on SWC, considering soil warming, year, and sampling date as fixed factors and block as a random factor. Soil (per horizon) and leaf nutrient data were analyzed using a similar ANOVA model. When *treatment* and *treatment*×*time* interactions were significant, each time period was analyzed separately. Data were tested a priori to meet the assumptions of ANOVA and log-transformed when necessary, and Tukey's post hoc tests were used when needed to identify which means were significantly different from one another. Finally, principal component analyses (PCAs) were applied on the matrices of soil nutrients, with the soil warming treatment transformed to binary factor, for each soil horizon. The N deposition treatment was excluded because of the absence of significant effects measured with ANOVA. All statistical analyses and plots were done using the R software (R Development Core Team 2013).

Results and discussion

Initial soil disturbance effects

Except for Fe in the organic horizon, all ions measured with ion-exchange membranes displayed significant temporal fluctuations in both horizons ($P < 0.01$). In 2009, forest floor-available NH₄ and NO₃ were 9.5 and 3.2 times higher than the average of the following years, respectively (Table 1). With the exception of Fe

and SO₄, a similar pattern was observed for other ions in that horizon, with levels of Ca, Mg, K, PO₄, and Al being 1.6, 1.4, 3.1, 2.0, and 1.5 times higher, respectively, in 2009 relative to those in 2010–2011. In the mineral horizon, only NH₄, NO₃, and Al were highest in 2009, with levels 4.5, 7.4, and 1.4 times higher relative to those in 2010–2011. The high concentrations observed in 2009 in the forest floor for all elements were characterized by an early peak in the growing season followed by a marked decrease in autumn, particularly for NH₄ and K with a ten- and six-fold decrease, respectively (Table 1). In the mineral horizon, decreasing trends were also observed for NO₃, NH₄, PO₄, SO₄, and Al with levels 7.1, 4.8, 1.6, 3.8, and 1.7 times lower in autumn, respectively, while Mg, K, and Ca remained stable over the growing season.

The high levels of available soil nutrients observed in the first year of treatment are probably the result of the soil disturbance caused by the burial of the heating and control cables during the preceding fall. In boreal ecosystems, about 50 % of the fine root biomass (<2 mm in diameter) is located in the upper 10 cm of the soil profile, and up to 90 % can be found in the top 30 cm (Yuan and Chen 2010). The impact of the trenching on roots was minimized by running the cable below or above large roots. The effect of cable burial should therefore be mostly restricted to fine roots. In general, N mineralization rates are stimulated by the input of fresh organic matter or the mixing of the soil (Booth et al. 2006). The higher NH₄ concentrations measured in the forest floor early in the season were synchronous with increased NO₃ concentrations in the mineral horizon (Table 1), which suggests that some of the NH₄ was leached into the mineral soil where the higher pH could have allowed its transformation into NO₃ (Ste-Marie and Paré 1999). As for K, it cycles rapidly following ecosystem disturbance as it is found in living organisms as a soluble electrolyte and its concentration is relatively high in soil microbes and woody plants in comparison to other ions (Likens et al. 1994). Other elements like Ca or Mg are partly incorporated in cell organelles and plant tissue, for example Ca in cell wall. They also have a higher affinity for soil exchange sites because of their higher valence and are therefore more easily retained following soil disturbance. Similar nutrient pulses were observed in a hardwood forest of northeastern United States in the first year following cable burial (McHale and Mitchell 1996). During a spruce budworm outbreak in 1981–1984 at the site, N and K also displayed the

Table 1 Average daily soil element availability over the three growing seasons and per burial period in the organic and mineral horizons, as measured with ion-exchange membranes in $\mu\text{g } 10\text{cm}^{-2} \text{ day}^{-1}$ (PRS probes)

Organic horizon	Element	Overall														
		2009				2010				2011						
		May 21– Jun 25	Jun 25– Jul 21	Jul 21– Aug 24	Aug 24– Sep 22	Sep 22– Nov 2	May 12– Jun 30	Jun 30– Aug 12	Aug 12– Sep 30	Sep 30– May 30	May 30– Jul 20	Jul 20– Aug 29	Aug 29– Oct 7	Oct 7– Jun 7		
NO ₃	C	0.19	0.16	0.10	0.14	0.10	0.02	0.01	0.09	0.04	0.04	0.09	0.07	0.01	0.07	0.01
	N	0.17	0.28	0.07	0.11	0.07	0.01	0.02	0.07	0.01	0.11	0.03	0.07	0.02	0.07	0.02
	H	0.17	0.17	0.08	0.20	0.08	0.04	0.01	0.06	0.02	0.07	0.03	0.02	0.02	0.02	0.02
	HN	0.44	0.19	0.11	0.10	0.11	0.03	0.03	0.05	0.04	0.06	0.11	0.03	0.03	0.03	0.01
NH ₄	C	2.49	3.19	0.32	0.25	0.32	0.21	0.16	0.16	0.02	0.02	0.16	0.06	0.06	0.01	
	N	3.31	3.76	0.48	0.41	0.48	0.35	0.29	0.20	0.04	0.03	0.20	0.17	0.03	0.03	
	H	4.37	5.48	0.39	1.44	0.39	0.48	0.40	0.37	0.03	0.04	0.30	0.07	0.01	0.01	
	HN	1.67	3.62	0.37	0.57	0.37	0.31	0.33	0.48	0.04	0.03	0.25	0.08	0.08	0.08	
PO ₄	C	0.32	0.42	0.22	0.08	0.22	0.13	0.13	0.19	0.10	0.04	0.04	0.06	0.05	0.05	
	N	0.31	0.58	0.09	0.05	0.09	0.07	0.07	0.08	0.03	0.03	0.04	0.05	0.02	0.02	
	H	0.42	0.48	0.17	0.12	0.17	0.24	0.27	0.34	0.02	0.06	0.12	0.07	0.03	0.03	
	HN	0.33	0.34	0.16	0.11	0.16	0.19	0.10	0.14	0.03	0.06	0.23	0.11	0.02	0.02	
K	C	6.7	7.3 a	1.2	2.7	1.2	2.5 a	1.8	1.6	0.5	0.6	0.9	0.4 a	0.2	0.2	
	N	5.7	6.9 a	1.3	2.2	1.3	1.8 a	2.6	3.4	0.4	0.5	1.2	0.9 a	0.3	0.3	
	H	7.2	12.7 b	1.9	2.4	1.9	5.5 b	2.3	2.4	0.2	0.5	1.2	1.0 b	0.4	0.4	
	HN	7.7	14.3 b	2.6	4.0	2.6	2.8 b	2.1	2.0	0.4	1.0	1.8	1.8 b	0.3	0.3	
Ca	C	5.8	6.9	3.5	3.9	3.5	3.1	4.0	3.0	2.0	2.3	2.8	3.7	2.2	2.2	
	N	5.1	6.6	3.3	4.2	3.3	3.5	4.0	4.9	1.3	2.0	2.6	4.1	1.4	1.4	
	H	8.1	7.9	3.0	3.8	3.0	6.6	3.5	3.0	2.6	2.9	2.6	5.5	1.5	1.5	
	HN	8.2	8.3	3.5	3.7	3.5	3.8	4.7	3.3	2.4	3.7	2.8	5.3	2.2	2.2	
Mg	C	0.73 a	1.13	0.44	0.36 a	0.44	0.50 a	0.53	0.38	0.30 a	0.38	0.32 a	0.68	0.35	0.35	
	N	0.54 a	0.89	0.39	0.41 a	0.39	0.46 a	0.43	0.54	0.22 a	0.30	0.23 a	0.71	0.26	0.26	
	H	0.99 b	1.27	0.48	0.52 b	0.48	1.13 b	0.61	0.48	0.48 b	0.50	0.39 b	0.89	0.24	0.24	
	HN	1.25 b	1.21	0.54	0.53 b	0.54	0.66 b	0.70	0.45	0.53 b	0.77	0.44 b	0.91	0.41	0.41	
SO ₄	C	1.56	0.65	0.41	0.26 a	0.41	0.41	0.31 a	0.30	0.96 a	2.53	0.40	1.32	1.27	1.27	
	N	0.54	0.39	0.32	0.23 a	0.32	0.18	0.27 a	0.19	0.59 a	1.18	0.42	1.43	0.80	0.80	
	H	1.68	0.53	0.41	0.37 b	0.41	1.17	0.39 b	0.36	1.89 b	3.15	0.24	1.44	1.19	1.19	
	HN	3.60	0.96	0.39	0.40 b	0.39	1.37	0.37 b	0.26	1.72 b	4.27	0.23	2.44	1.55	1.55	
Al	C	1.05	1.04	0.85	0.94	0.85	0.53	0.51	0.42	0.23	0.46	0.77	0.84	0.38	0.38	
	N	1.07	0.89	0.85	1.06	0.85	0.49	0.60	0.48	0.21	0.66	0.80	0.95	0.34	0.34	
	H	1.18	1.26	0.77	0.97	0.77	1.06	0.58	0.37	0.38	0.54	0.70	0.81	0.25	0.25	

Table 1 (continued)

Mineral horizon		Overall											
		2009				2010				2011			
		May 21– Jun 25	Jun 25– Jul 21	Jul 21– Aug 24	Aug 24– Sep 22	Sep 22– Nov 2	May 12– Jun 30	Jun 30– Aug 12	Aug 12– Sep 30	Sep 30– May 30	May 30– Jul 20	Jul 20– Aug 29	Aug 29– Oct 7
HN	0.87	1.49	1.19	0.99	0.95	0.83	0.62	0.36	0.37	1.01	0.83	1.27	0.53
Fe	C	0.19	0.16	0.08	0.07	0.27	0.06	0.05	0.08	0.10	0.07	0.06	0.40
	N	0.14	0.10	0.08	0.05	0.28	0.04	0.05	0.19	0.14	0.08	0.08	0.11
	H	0.87	3.56	0.11	0.09	0.23	1.15	0.07	0.04	0.87	0.07	3.64	0.40
	HN	0.25	0.81	0.13	0.08	0.27	0.09	0.07	0.08	0.44	0.10	0.13	0.04
	C	0.12	0.57	0.29	0.13	0.13	0.02	0.03	0.01	0.07	0.06	0.07	0.03
	N	0.12	0.35	0.35	0.19	0.17	0.03	0.09	0.02	0.04	0.05	0.07	0.02
	H	0.36	1.39	1.39	1.13	0.11	0.02	0.06	0.02	0.08	0.14	0.10	0.03
	HN	0.17	0.76	0.65	0.25	0.03	0.06	0.06	0.04	0.08	0.07	0.05	0.03
	C	0.33	0.94	1.30	0.37	0.45	0.17	0.20	0.03	0.06	0.21	0.09	0.02
	N	0.30	0.75	1.10	0.47	0.30	0.19	0.26	0.04	0.05	0.15	0.08	0.01
	H	0.51	1.16	3.28	0.59	0.26	0.22	0.22	0.00	0.04	0.24	0.07	0.01
	HN	0.28	0.93	0.61	0.41	0.30	0.24	0.21	0.01	0.05	0.18	0.11	0.02
	C	0.17	0.32	0.11	0.10	0.27	0.21	0.24	0.03	0.13	0.17	0.31	0.04
	N	0.14	0.27	0.18	0.11	0.20	0.16	0.29	0.01	0.09	0.19	0.11	0.04
	H	0.19	0.30	0.36	0.15	0.16	0.18	0.49	0.01	0.23	0.16	0.12	0.03
	HN	0.17	0.37	0.19	0.14	0.13	0.30	0.36	0.01	0.07	0.17	0.14	0.02
	C	3.3	2.9	4.5	3.3	6.3	3.2	4.9	0.4	1.0	3.1	1.6	0.4
	N	3.0	2.7	3.9	4.2	3.4	2.6	7.2	0.5	0.7	4.3	1.8	0.6
	H	3.6	3.5	6.3	4.5	3.6	4.8	6.8	0.4	1.3	3.4	2.9	0.4
	HN	2.8	4.4	4.4	3.9	3.2	3.8	2.8	0.3	1.0	2.1	1.6	0.3
	C	5.6	5.7	5.5	6.4	6.1	3.6	12.7	3.2	3.4	5.6	7.4	2.9
	N	4.3	6.3	6.1	6.6	3.6	3.3	5.3	2.6	1.8	4.1	4.7	3.0
	H	5.1	5.5	7.3	6.7	4.9	5.3	8.2	3.3	3.4	5.3	6.1	2.3
	HN	5.6	5.8	6.5	9.3	4.8	7.2	6.5	3.9	4.6	4.4	6.1	3.0
	C	0.80 a	0.61	1.10	0.58	1.01	0.46 a	1.66	0.44 a	0.57	0.69 a	1.43	0.45
	N	0.58 a	0.57	0.74	0.73	0.54	0.53 a	0.78	0.40 a	0.46	0.52 a	0.68	0.49
	H	0.82 b	0.68	1.07	0.72	0.68	0.85 b	1.56	0.61 b	0.61	0.85 b	1.18	0.40
	HN	0.99 b	1.19	1.27	1.42	0.92	1.21 b	0.93	0.67 b	0.95	0.75 b	1.15	0.52
	C	0.92 a	1.28	0.68	0.37	0.63	0.40	0.64	1.14	2.73	0.56	1.37	1.39
	N	0.95 a	0.90	0.42	0.42	0.56	0.35	0.67	1.72	3.09	0.39	1.41	1.81
	H	1.53 b	2.20	1.09	0.81	0.33	1.15	0.80	2.38	3.51	0.42	3.85	2.48

Table 1 (continued)

	Overall	2009				2010				2011				
		May 21– Jun 25	Jun 25– Jul 21	Jul 21– Aug 24	Aug 24– Sep 22	Sep 22– Nov 2	May 12– Jun 30	Jun 30– Aug 12	Aug 12– Sep 30	Sep 30– May 30	May 30– Jul 20	Jul 20– Aug 29	Aug 29– Oct 7	Oct 7– Jun 7
HN	1.75 b	3.19	1.76	0.65	0.48	0.45	1.28	0.48	0.57	2.32	5.97	0.41	2.57	2.62
C	0.99 a	1.49	1.16	1.13	1.32	1.12	0.63	0.75	0.71	0.38	1.17	1.05	1.36	0.55
N	1.04 a	1.94	1.36	1.12	1.18	1.11	0.69	0.66	0.50	0.58	0.82	1.14	1.35	1.00
H	1.17 b	2.15	1.52	1.38	1.22	1.19	0.99	0.70	0.72	0.59	1.25	1.19	1.42	0.87
HN	1.31 b	2.23	1.74	1.61	1.47	1.12	1.53	0.91	0.65	0.62	1.60	1.19	1.34	1.00
C	0.31	1.02	0.26	0.18	0.33	0.37	0.13	0.16	0.13	0.38	0.44	0.24	0.28	0.11
N	0.28	0.76	0.25	0.21	0.44	0.35	0.09	0.10	0.08	0.31	0.27	0.16	0.33	0.25
H	1.97	10.05	0.72	0.44	0.42	0.31	1.06	0.18	0.11	0.18	7.13	0.34	4.19	0.52
HN	1.31	7.46	0.39	1.88	0.53	0.38	1.84	0.15	0.12	0.07	2.04	0.35	1.41	0.38

Different letters show significant differences between treatments ($P < 0.05$), as indicated by post hoc tests

highest leaching losses among soil nutrients in reaction to increased organic matter decomposition rates and reduced nutrient uptake (Houle et al. 2009).

Effects of treatments on soil N availability

Given that N is the most common growth-limiting nutrient in boreal ecosystems (Hobbie et al. 2002), increased N availability due to soil warming or additional N deposition has the potential to increase ecosystem productivity. However, contrary to our first two hypotheses, the treatments, alone or in combination, had no effect on N availability ($P > 0.05$, Table 1). This result is consistent with the absence of effects of both treatments on needle N concentration (Table 2) despite the fact that a fraction of the inorganic N in the artificial precipitation was immobilized in the foliage (see D’Orangeville et al. 2013a). A similar lack of response of soil N was also observed in a N fertilization experiment (18 and 60 kg N ha⁻¹ year⁻¹ added during 3 years) in a neighboring stand and was associated with high N retention in the upper soil profile with nearly no inorganic N in the soil solution at 30- or 60-cm depth (Houle and Moore 2008). This result suggests the presence of strong N sinks in the soil that may quickly immobilize the N input from the N deposition treatment (see Berg and Matzner 1997 for a review). Because of the temperature dependence of N mineralization (Rustad et al. 2001), the soil warming treatment was also expected to increase N availability. If SOM decomposition rates were indeed stimulated by the treatment, the resulting N compounds—including organic N, which can be taken up by ectomycorrhizal fungi (Chalot and Brun 1998)—could have been quickly immobilized due to the high competition mentioned earlier.

Response patterns to increased soil temperature

Soil warming significantly increased available K in the forest floor, Mg and SO₄ in both soil horizons, and Al in the mineral horizon ($P < 0.05$, Table 1). The cumulative amounts of forest floor-available K, Mg, and SO₄ were 43, 44, and 79 % higher in heated plots, respectively, relative to those in control plots. In the mineral horizon, available Mg, SO₄, and Al were 29, 66, and 23 % higher in heated plots, respectively. Exclusion of the first-year data from the calculations has negligible effects (± 3 %) on the cumulative values for all elements except for K, whose increase in the warming treatment went from 43

Table 2 Average nutrient concentration of balsam fir needles from control (C), fertilized (N), heated (H), and heated–fertilized (HN) plots from 2009 to 2011 and ANOVA treatment effects

	N (g kg ⁻¹)	P (g kg ⁻¹)	K (g kg ⁻¹)	Ca (g kg ⁻¹)	Mg (g kg ⁻¹)
C	12.7±0.74	2.05±0.16	5.1±0.19	4.1±0.42	0.94±0.07
N	13.1±0.39	2.11±0.07	6.1±0.27	4.4±0.54	0.95±0.08
H	12.4±0.44	1.96±0.05	5.3±0.12	3.9±0.48	0.90±0.09
HN	11.8±0.48	1.79±0.07	5.0±0.28	3.5±0.27	0.79±0.06
Statistical analyses					
Warming (H)	0.15	0.16	0.02*	<0.01**	0.14
Fertilization (N)	0.92	0.73	0.07	0.74	0.53
Year	0.02*	0.02*	0.18	<0.01**	<0.01**
H × N	0.36	0.38	<0.01**	0.07	0.33

Values are the mean±standard error. ANOVA interactions were removed when nonsignificant

P*=0.05; *P*=0.01 (significant treatment effects)

to 20 %. Therefore, we can assume for these elements that the influence of the initial disturbance on the soil warming response was limited.

The soil warming effect measured on available Mg and K is in agreement with our third hypothesis. Although the differences between treatments were not significant for Ca (*P*=0.11, Table 1), the PCA suggests that Ca behave similarly to Mg in the organic horizon (*r*=0.91, Fig. 2). The K response to the warming treatment was twofold stronger than Mg and Ca during the first year. As discussed above, the high mobility of K, as compared to Ca and Mg, probably increased its release following soil disturbance. In addition to the predicted

increases in base cations with warming, SO₄ and Al availability also increased in heated plots (Table 1). However, the soil warming effect for these elements was inconsistent and no common seasonal pattern emerged after 3 years of treatment. We can only speculate on the numerous environmental factors (e.g., precipitations, tree and microbial nutrient uptake, temperature) which could have interacted with the soil response.

Higher rates of litter decomposition and mineralization of organic compounds were probably responsible for the additional K, Mg, and SO₄ made available in the forest floor of heated plots. An incubation study using soil samples from the site after 3 years of treatment

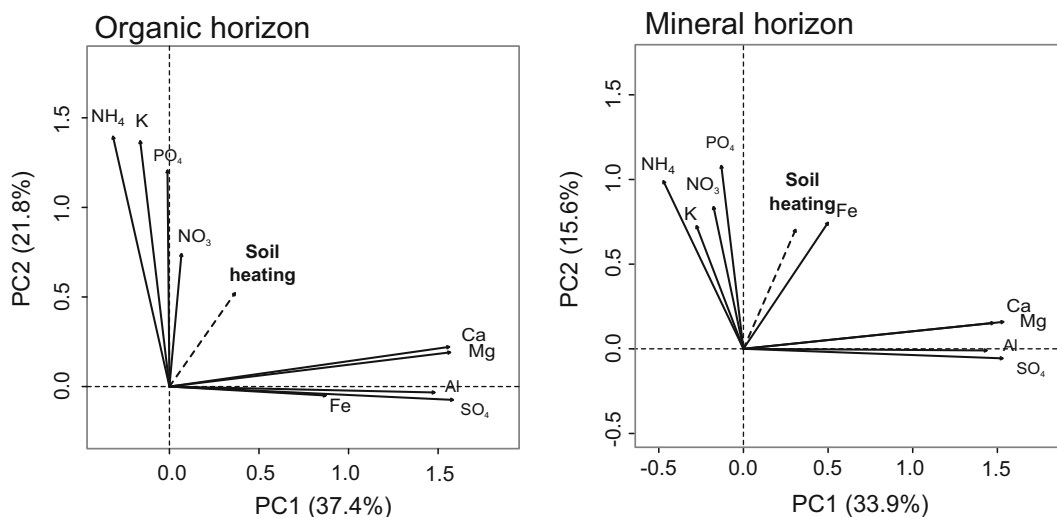


Fig. 2 Principal component analysis biplots of the soil warming treatment and available nutrients measured with ion-exchange membranes in the organic and mineral horizons. Values next to the axis captions show the fractions of variance accounted for by that axis

showed a 16–25 % reduction in mineralizable carbon in heated plots, therefore supporting the hypothesis of a greater microbial activity in heated plots (D'Orangeville et al. 2013b). The temperature dependence of these processes for base cations (Campbell et al. 2009) and S (MacDonald et al. 1995) are well known. Such positive temperature effects suppose that the warming treatment did not induce a water stress. The soil water content was not affected by heating in our plots ($P=0.08$, Table 3) which should have allowed the soil heating to produce the expected effects of increased decomposition and mineralization. The high correlation between Mg and SO_4 availability ($r \geq 0.72$ in both horizons, see Fig. 2) as well as the increase observed in the mineral horizon of heated plots for both elements support the possibility that the SO_4 liberated in soil solution was accompanied by Mg as a counterion and that both were leached together into the mineral horizon. As for Al, its proximity with SO_4 and Mg vectors in PCAs of both horizons (Fig. 2) suggests that the additional release of Al in the mineral soil could also be linked with the increased decomposition in the forest floor of heated plots. On the contrary, the lack of a warming effect on K availability in the mineral soil could suggest that K was not leached from the humus to the mineral soil horizons in greater amounts in heated plots.

Table 3 Average monthly soil water content (SWC) and standard error in control and heated plots in 2009, 2010, and 2011

		SWC (%)	
		Control	Heated
2009	May	27±1.2	28±1.5
	June	25.3±0.9	28±1.1
	July	29±1.1	28±1.0
	August	26.9±0.9	29.3±0.9
	September	28.2±0.6	32.5±0.6
2010	May	22.1±0.6	27±1.2
	June	21.6±0.4	25.6±0.5
	July	16.7±0.3	18.4±0.4
	August	20.3±0.5	22.6±0.5
	September	19.4±0.5	20.0±0.5
2011	June	28.9±0.7	35±1
	July	25.2±0.4	28.4±0.5
	August	24.9±0.4	24.8±0.4
	September	27.4±0.8	31±1.2

Effects of soil warming and soil water content on Fe availability

Peaks of available Fe were measured in the organic and mineral horizons of heated plots over the course of the experiment (Table 1), resulting in a significant interaction between time and soil heating ($P < 0.05$), but differences in cumulative fluxes between treatments were not significant ($P > 0.15$). The peaks in available Fe were exclusively observed in three of the six heated plots, with concentrations as high as 46- and 91-fold the average of other plots in the forest floor and mineral horizon, respectively. These extreme values were associated with elevated SWC ($> 30\%$) during spring or fall (Table 4). In the study of a floodplain forest soil in the USA, it was observed that Fe oxides were very sensitive to flooding-induced declines in soil redox potential (Darke and Walbridge 2000). Reducing soil conditions associated with prolonged periods of water saturation can lead to the dissolution of large amounts of Fe oxides through a temperature-sensitive reaction (Schwertmann 1991). Based on these observations, we suggest that the peaks of Fe were caused by the increased soil temperature at times of high soil moisture, in spring or fall. The soil temperature gradient between heating cables of heated plots could explain the variability of the response to warming at high soil moisture. As SO_4 is commonly adsorbed on Fe oxides in mineral podzolic horizons at the Lake Laflamme site (Houle and Carignan 1992), the dissolution of Fe oxides may have contributed to the higher SO_4 availability in the mineral horizon. In the future, the projected increases in soil temperature and water content in spring could favor similar changes in redox potential.

Table 4 Average daily available Fe and standard error relative to the soil water content in the organic and mineral horizon as measured with ion-exchange membranes (PRS probes)

Soil water content (%)	Available Fe ($\mu\text{g } 10 \text{ cm}^{-2} \text{ day}^{-1}$)			
	Organic		Mineral	
	Control	Heated	Control	Heated
15–20	0.05±0.01	0.07±0.01	0.13±0.02	0.17±0.03
20–25	0.12±0.05	0.08±0.01	0.23±0.03	0.49±0.20
25–30	0.17±0.05	0.37±0.20	0.27±0.03	0.95±0.29
30–35	0.37±0.12	1.5±0.8	0.65±0.18	3.8±1.8
35+	0.09±0.02	1.8±1.2	0.53±0.21	6.0±3.3

Consequences for tree nutrition and health

Like a majority of eastern Canada boreal forests, our study site rests upon shallow soils derived from granitic rocks with small exchangeable base cation reservoirs (Duchesne and Houle 2006). In the short term, the higher base cation availability (K and Mg) measured in the forest floor of heated soils could have a positive effect on tree nutrition. However, this possibility is not well supported by the measured foliar nutrient levels, as heated balsam fir trees only displayed a 3 % increase in K ($P=0.02$) while Mg levels remained unaffected by the treatment (Table 2). A more significant change in heated plots was the 6–15 % reduction in foliar Ca ($P<0.01$), an effect that could be related to the 23 % higher available Al measured in the mineral horizon of heated plots. Aluminum is known to produce antagonistic interference with Mg and Ca uptake as well as root damages from Al interactions with plant cell components (Cronan and Grigal 1995). The decline of spruce and fir in acid soils of the northeastern United States and in Germany (pH 3.0–4.5) has been attributed to Al-mediated impairment of Ca uptake by tree roots (Shortle and Smith 1988). In balsam fir, inhibition of root elongation is a primary effect of Al toxicity, but root deterioration and reduced uptake of essential nutrients have also been observed (Schier 1985). A Ca-to-Al molar ratio of ≤ 1 in the soil solution is commonly used as an indicator for potential toxicity (Cronan and Grigal 1995). Based on this threshold, the mean Ca/Al molar ratios of 3.1 ± 0.3 and 3.8 ± 0.2 measured in the mineral horizon of heated and control plots, respectively, with seasonal lows of 1.7 ± 0.3 in heated plots (Table 1), should not affect the tree health, but critical threshold values are difficult to establish as they show great variability between sites and species.

Conclusion

Climate manipulations of mature stands are an effective way of studying forest adaptation to climate change. In this study, a mature balsam fir stand was subjected to a 3-year manipulation of soil temperature and atmospheric N deposition, and the soil response was measured with buried ion-exchange membranes. The N deposition and soil warming treatments alone or together had no effect on inorganic N availability. Soil warming did increase forest floor Mg and K availability, which was

probably induced by increased rates of SOM decomposition, a temperature-dependent process. Three years of treatment had limited effects on leaf nutrition, with a 3 % increase in K and no changes in Mg in the needles of heated trees. Owing to the potential phytotoxicity of Al, the increased Al availability in the mineral soil caused by higher soil temperature could have significant consequences for ecosystem health. The higher soil Al could have interfered with the trees' Ca uptake capacity, which would explain the 6–15 % lower Ca content observed in needles from heated balsam fir trees. Although we observed significant and substantial effects on ion availability after 3 years of experimental manipulation, more time is necessary to verify if the observed effects will persist on the long term.

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