

Comparison of soil and seepage water properties in the limed and not-limed spruce forest stands in the Beskydy Mts.

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The study deals with evaluation of a liming experiment carried out in spruce stands situated near Bílý Kříž in Moravian-Silesian Beskydy Mts. at an altitude of 908 m. Soil type was humo-ferric podzol with mor-moder humus form and low content of nutrients. Soil properties and soil solution composition from two research plots with *Picea abies* [L.] Karst. monoculture aged 28 in 2006 were compared. One of the plots was limed by dolomitic limestone at a total dose of 9t ha⁻¹ in the 80s of the 20th century the second plot was a not-limed control. Sampling of sub-surface seepage water was carried out in fortnight intervals on the both plots during 2001–2006. Statistically significant differences between the limed and control plot were found in soil solution concentrations of Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺, HPO₄²⁻, SO₄²⁻, dissolved organic carbon (DOC) and pH. Significant differences were not observed between the plots in NO₃ concentrations. Soil samples taken from the both plots in 2003 were analyzed and the results have shown that changes induced by liming could be detected even after 16 year after the last liming event. Increased pH values in the entire soil profile, and changes in the composition of soil sorption complex and increased base saturation in the forest floor horizons were found on the limed plot.

Keywords: soil solution, calcium, magnesium, lysimetric water, liming, forest soil, Moravian-Silesian Beskydy Mts.

Introduction

Liming of forest soils has a long history (Materna 2001). At the beginning it had been expected that liming would have positive influence on tree growth but the results were rather controversial: both growth stimulation (Hausser 1958, Schairer 1958, Spiecker et al. 1996, Spiecker 1999) and growth reduction (Saarsalmi, Mälkönen 2001, Nilsen 2001) were reported or no influence on tree growth and vitality was observed (Huber et al. 2004). The last trials from Jizerské hory Mts. (in the Czech Republic) demonstrate positive influence of liming on beech growth (Balcar et al. 2011) and spruce plantation prosperity (Kuneš 2003) when lime was applied in planting holes (in the first case) or on the soil surface around the each tree (in the second case).

Liming started to be viewed from a new perspective as a remedy to prevent acidification and degradation of forest soils since 1970s when the so called new forest decline (a phenomenon which affected forests in Europe and in the North America during the 1970s and 1980s) was studied. It was discovered that acid depositions caused an accelerated acidification of forest soils (Meiwes et al. 1986) and leaching of base cations (Ca, Mg, K) which are inevitable for the good development and nutrition of plants. The increase in soil acidity led also to solubilization of Al (Mulder, Stein 1994) which (in the form of Al³⁺) can have detrimental effects on root growth and impedes base cation uptake (Godbold et al. 1988). Calcium is being exhausted from the surface soil horizons more rapidly under shallow rooted trees including Norway spruce (Dijkstra, Smits 2002, Berger et al. 2006) but spruce monocultures have been grown, from economical reasons, at many places throughout the Czech Republic already in the second generation (Tesař, Klimo 2004, Balcar et al. 2008). Methods of harvesting, when not only stems but also branches with assimilatory organs are removed from the forest, contribute to lowering the content of base cations in forest soils (Rothe et al. 2002, Klimo et al. 2010). The new aims of forest liming were newly formulated as follows (see e.g. Materna, Skoblík 1988 or Badalík, Řezáč 2001):

- to compensate the acid input from depositions;
- to lower soil acidity;
- to decrease the solubility and mobility of certain elements in soil (Al, Mn) and to protect the root of trees;
- to supplement stock of nutrients (Ca and Mg) and improve the stand nutrition status;
- to improve condition for the activity of soil organisms.

Large-scale liming always represents a serious intervention and entails also potential risks for the ecosystem. Accelerated decomposition of organic matter caused by liming can enhance nitrification and in localities with high nitrogen load nitrate leaching can be observed (Hüttl, Zöttl 1993, Marschner et al. 1989). Changes induced by liming and their merits for soil and forest management are always dependent on site characteristics, particularly on soil properties, the amount and composition of depositions, climate and main forest tree species (Kreutzer 1995).

In the Czech Republic extensive forest areas in Krušné hory Mts., Beskydy Mts., Jizerské hory Mts. and in Krkonoše Mts. have been limed since 1970s (Hruška, Cienciala 2002, Balek et al. 2001). Dolomitic limestone was usually applied because magnesium had been found to be one of the deficient elements in tree nutrition. Published liming studies were aimed at individual localities: Orlické hory Mts. (Podrázský 1993, Podrázský 2006), Krušné hory Mts. (Lettl 1991, Lettl 1992), Šumava Mts. (Lettl 1991), Jizerské hory Mts. (Peřina, Podrázský 1988, Lettl 1992), Beskydy Mts. (Klimo, Vavříček 1991, Orlová, Stalmachová 1991). The form and composition of applied limestone and also the way of application (aerial or on surface) (Pavlíček, Musil 1988, Peřina, Podrázský 1988) can be crucial for the final effect of liming. Therefore it is very difficult to derive unequivocal conclusions from all these studies. A project for long-term evaluation of liming effectiveness was prepared in 2001 (Balek et al. 2001) after a new wave of liming (supported by Ministry of Agriculture of the Czech Republic, see the Resolution No. 532/2000) had been launched and some results are already available (Šrámek et al. 2003, Šrámek et al. 2006) but any complex evaluation have not been published yet.

This study is aimed at the comparison of soil properties and of the soil solution composition on limed and not-limed plots situated in the Moravian-Silesian Beskydy Mts. at the border of the Czech Republic and Slovakia not far from the Polish frontier. The results can contribute to understanding of liming influence in the region which belongs among the sites with the highest concentrations of air pollutants in Europe and can be referred to as a "black triangle II" (Markert et al. 1996).

Material and Methods

Research plots at Bílý Kříž are situated at an altitude of 900±8 m. Climatically, it refers to a moderately cool, humid and precipitationrich climatic zone. Mean annual air temperature reaches 4.9 °C, mean relative air humidity is 80% and mean annual total precipitation is 1100 mm (Kulhavý et al. 2009). The Norway spruce stands are grown here in the 2nd generation. The 1st generation of spruce stands was prematurely felled after the frost disaster potentiated by imissions in 1978/1979 (Raška 1985).

The limed stand (FD) was established in 1981 by the row planting of 4-year saplings of Norway spruce (*Picea abies* [L.] Karst.) at $2 \times 1 \text{ m}$ spacing and the N-S orientation of rows. The position of the site is given by geographic co-ordinates 49° 30' N and 18° 32' E. The mean inclination of a slope where the stands are planted is 13.5° and its aspect is SSE. The age of the stands reached 25 years in 2006 and the age of trees was 29 years. In 1983, 1985 and 1987, the stand on this plot was limed with dolomitic limestone 3 t ha⁻¹ at each of these years, what makes the total amount of 9 t ha-1. According to the control measurements the real dose having met the ground was only 6.76 t ha-1 (Klimo, Vavříček 1991). The not-limed control stand (FK) is situated in the

cadastre of Makov Forest Administration (49°29' N, 18°32'E) and arouse from natural regeneration of Norvay spruce (*Picea abies* [L.] Karst.). The mean inclination of a slope where the stand lies is 30° and its aspect is SE. The age of trees was 30 years in 2006. The area of each experimental plot is 50×50 m (i.e. 0.25 ha). Stand density was the same for the both stands: 2600 tree per ha in 1999. Since 1999 only natural thinning occurred (Kulhavý et al. 2009).

The soils in the studied stands are of moderate depth, sandy loam to sandy clay loam, the soil texture being characteristic for sandy flysh sediments with 15–35% of clay fraction, highly skeletal in the depth. High content of organic matter in the upper part of soil profiles (0–10 cm) is apparent. Geological bedrock in the both stands consists of flysh layers with the predominance of sandstone; typical humo-ferric podzol with the mor-moder form of surface humus is the soil type. *Abieto – Fagetum acidophilum* (Acidic Fir – Beech) is the forest type. The sequence of soil horizons and their depths are given in Tab. 1.

The soil sampling was carried out in July 2003 at the both plots. Soil samples were taken from five spots at each plot (FD and FK) and mixed samples of individual horizons were prepared. The samples were dried and processed to obtain fine earth according to Zbíral (2002). Acidity of soil samples was measured using digital pH meter (Radelkis, OP-208/1) with a combination pH electrode (THETA '90, HC-103) in the soil sample suspensions both in H₂O and in KCl (1 mol l⁻¹), extraction ratio was 1:5 (by volume). Available nutrients were determined in macroelement soil extracts prepared according to Mehlich (1978) by standard methods described by Zbíral (2002).

Exchangeable Al was determined in soil extracts in 1M KCl solution (100g of soil was shaken 1 hour with 250ml of 1M KCl and filtered after 16 hours). The exchangeable acidity was determined by the titration of the extract aliquot with 0.01NaOH using phenolphtalein as indicator, then the concentration of Al³⁺ was obtained by the back titration of the same extract after the acidification with a drop of HCl and addition of 3.5% solution of NaF.

Effective cation exchange capacity (CEC) was calculated as the sum of base cations and exchangeable acidity according to the formula:

CEC=Ca/20.039+Mg/12.153+K/39.098+Ae+ +Na/22.99+Al/8.994+Fe/18,616+Mn/27.469

Where CEC is cation exchange capacity and Ae is the exchangeable acidity both in milimols of chemical equivalents per kilogram and Ca, Mg, K, Na, Al, Fe, Mn represent contents of individual elements in soil samples in mg kg⁻¹.

Base saturation in % was calculated as the share of base cations (Ca^{+2} , Mg^{+2} , K^+ , Na^+) in CEC.

Total nitrogen (N_{tot}) and carbon (C_{tot}) were measured by high-temperature $(1000 \,^{\circ}\text{C})$ dry combustion method with automatic analyzer LECO CNS 2000. All samples were ground manually using an agate mortar and pestle and dried (for 1 hour at 105 $\,^{\circ}\text{C}$) and cooled in exsiccator before total nitrogen and carbon analysis.

The results of soil $pH(H_2O)$ and pH(KCl) measurements from the time before liming were taken from Klimo, Vavříček (1991). They took soil samples in 1983 before the first liming event in the newly afforested FD plot.

On FD and FK plots, zero-tension lysimeters (three per plot) of the area of 550 cm² were installed under the surface humus horizon to monitor the flow of substances with seepage water. The samples of seepage water were taken biweekly. Sampling period started in the end of March and ended in the end of November every year during the period of 2001–2006. pH was measured in all water samples (method described in ČSN ISO 10523 1996) with pH meter JENWAY 4320 and a combination pH electrode (THETA '90, HC-103). Concentrations of cations were analysed within a week after sampling using the flame atomic absorption spectrophotometry for Ca and Mg determination and flame atomic emission spectrophotometry in case of Na and K (spectrometer AA 30 F4 VARIAN, airacetylene flame). The sub-sample for the determination of anions was deep frozen and kept in freezer until the analyses could be done. Anions, i.e. sulphate, nitrate, phosphate were analysed using ion exchange chromatography with KOH gradient elution (DX-600 ion chromatographic system equipped with a GP50 gradient pump, an ED50 electrochemical detector, an EG40 eluent generator and an IonPac® AS11-HC AS11 HR $(250 \times 2 \text{ mm})$ analytical column with an AG11 HR $(50 \times 2 \text{ mm})$ guard column, operated under PeakNet 6.0 software, all parts Dionex Corp.). For the determination of ammonium manual spectrometric method was used as described in ČSN ISO 7150-1 (1994). Dissolved organic carbon (DOC) concentration were determined in subsamples filtered through 0.45 µm membrane filter using TOC analyser Shimadzu TOC5000 which works on the principle of high temperature catalytic combustion (680 °C) with infrared detection of CO₂ evolved from sample. The analytical procedure is described in the Czech standard (ČSN EN 1484, 1998).

Concentrations of Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺, HPO₄²⁻, SO₄²⁻, NO₃⁻, DOC and the pH values of the seeapage water samples from the limed plot were compared with corresponding ion concentrations and pH of the seeapage water samples from the control plot by a two-sample t-test using Microsoft Office Excel 2007.

Results and Discussion

The contents of C_{tot} , nitrogen, calculated C/N ratios, and results of pH(H₂O) and pH(KCl) measurements in individual soil horizons at both studied plots in 2003 are summarized in Tab.1. Results of pH(H₂O) and pH(KCl) measurements and total carbon content from the time before liming are shown in Tab. 2.

In the results of soil acidity determination apparent differences were found between the limed and not-limed stands (Tab. 2). In all examined horizons, lower acidity (i.e. higher pH(H₂O) and pH(KCl) values) were found in soil samples taken from the limed plot FD. This difference was the highest in the forest floor horizons where it reached even one pH unit. In the organomineral horizon Ae, the difference in pH(KCl) was about 0.4 pH units and the difference in pH(H₂O) was about 0.7 pH units. In lower soil horizons, the differences were smaller. Presupposing similar conditions on the both plots before liming we can see that a distinct positive influence of liming (with reference to soil acidification) has been outlasting for 15 years (since the last liming event).

This can be derived also from the comparison with soil acidity values measured before liming (see Tab. 2) which we could regard as initial for the both studied plots. While the not limed FK plot had been a subject of an ongoing acidification the acidity on the limed plot FD was decreased in all but the top (Ol) horizon in the comparison with values before liming. In the Ol horizon on the FD reacidification is apparently under way. It is necessary to realize that acid inputs in the Czech Republic have been really high and considering the data published by Kopáček and Veselý (2005) we can derive the value of cumulative acid emissions between 1850 and 2000 of 494 kmol of H⁺ per ha in the Czech Republic and Slovakia. We can calculate that dolomitic limestone applied at the Bílý Kříž site contained approximately 98.5% (Klimo, Vavříček 1991) of $CaMg(CO_3)_2$ and suppose simplifiedly that the dose of 6.76t ha-1 has been (during the years) completely dissolved and used to neutralize the acid input according to the following equation:

$$CaMg(CO_3)_2 + 4H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2CO_2 + 2H_2O$$

Then the amount of protons neutralized by this process should be about 144.4 kmol H^{+} per ha (molar weight of CaMg(CO₃)₂ being 184.401g mol⁻¹) what makes only 29.2% from the total anthropogenic acid input between the years 1850 and 2000. In this context one can see

Plot	Horizon	Depth (cm)	$pH(H_2O)$	pH(KCl)	$C_{tot} (g kg^{-1})$	$N_{tot}(g kg^{-1})$	C/N
	Ol	0-2	4.78	4.34	464	13.6	34.2
	Of	2-3	4.65	3.94	210	10.3	20.3
	Oh	3-8	4.32	3.43	190	9.4	20.3
гD	Ae	8-10	4.23	3.18	54	2.8	19.1
rυ	Ep	10-15	4.06	3.21	11	0.6	17.7
	Bh	15-20	4.30	3.69	39	1.5	26.5
	Bsl	20-30	4.05	3.29	38	2.0	19.7
	Bs2	30-50	4.69	4.29	10	0.4	23.1
	Ol	0-2	4.13	3.54	493	16.7	29.5
	Of	2-5	3.66	2.95	362	16.7	21.7
FK	Oh	5-9	3.36	2.71	213	10.8	19.7
	Ae	9-12	3.55	2.81	63	3.3	19.2
	Ep	12-25	3.78	3.04	8	0.4	21.6
	Bhs	25-65	4.16	3.60	26	1.2	21.2

Tab. 1: Soil horizons, their depths and chosen chemical properties of soil horizons before liming in the limed (FD) and not limed (FK) forest stands at Bílý Kříž in Beskydy Mts. in 2003.

tot - denotes total nutrient content in soil horizons

Plot	Horizon	pH(H ₂ O)	pH(KCl)
	Ol	5.07	4.52
	Of	4.21	3.38
	Oh	3.58	2.66
FD before liming	Ae	3.43	2.56
	Ep	3.40	2.92
	Bh	4.00	3.33
	Bs	4.40	4.11

Tab. 2: Soil pH at the Bílý Kříž site before liming. Results published by Klimo, Vavříček (1991).

Tab. 3: Soil sorption complex characteristics for samples taken from limed (FD) and not-limed (FK) experimental plots at Bílý Kříž in 2003.

Chan d	Horizon	Ca	Mg	К	Na	Aex	Al	Fe	Mn	CEC	BS	Ca/Al
Stand			mmol _c kg ⁻¹							%		
	Ol	166.9	27.6	13.5	0.68	94	8.8	0.8	2.54	314.7	66.3	19.0
FD	Of	131.0	59.7	4.6	0.12	168	8.0	0.8	1.16	373.4	52.3	16.4
	Oh	89.4	60.6	3.7	0.10	262	19.6	1.4	0.28	437.1	35.2	4.6
	Ae	23.3	17.9	1.5	0.04	102	36.4	25.7	0.02	206.9	20.7	0.6
	Ep	9.3	3.7	0.7	0.04	74	44.4	15.3	0.02	147.4	9.3	0.2
	Bh	15.7	5.7	1.1	0.09	154	93.5	9.9	0.06	280.0	8.1	0.2
	Bsl	16.5	9.8	1.3	0.29	209	111.9	8.6	0.04	357.4	7.8	0.1
	Bs2	14.9	3.9	1.1	0.27	78	18.3	2.7	0.07	119.3	16.9	0.8
FK	Ol	63.9	14.6	10.7	0.64	120	14.3	1.4	3.19	228.7	39.3	4.5
	Of	55.9	17.0	16.4	1.53	249	60.7	3.0	1.43	404.9	22.4	0.9
	Oh	25.7	10.5	6.3	0.95	372	85.1	2.2	0.40	503.1	8.6	0.3
	Ae	16.0	5.6	2.0	0.32	143	53.5	6.8	0.10	227.2	10.5	0.3
	Ep	11.4	4.0	0.9	0.27	47	31.1	6.7	0.04	101.5	16.4	0.4
	Bhs	11.8	4.7	1.4	0.28	130	81.2	10.3	0.11	239.7	7.6	0.1

mmol_c – milimols of chemical equivalents, Aex – milimolar content of exchangeable acidity, CEC – cation exchange capacity, BS – base saturation, Ca/Al – molar ratio of Ca and Al

that the applied dose of limestone could have compensated not a third of acid inputs at the site. It was also shown that low doses of dolomitic limestone (2t per ha) had had almost no influence on pH both of humus layer and of A horizon having been aerially applied on various sites in Jizerské hory Mts. (Peřina, Podrázský 1988). Generally it is possible to say that when the liming dose is sufficient and the form of lime appropriate (i.e. fine-grained) then the induced pH increase can be observed at first only in the upper horizons (forest floor) and after about 8-10 years the effect is measurable in A horizon and deeper (Kuneš, Podrázský 2003). The increase in soil pH can be apparent after 28 years (Lettl 1991, Lettl 1992) and even after longer time as

reviewed by Lundström et al. (2003a). The results from Bílý Kříž fit in this pattern.

We can see also differences between the limed and not-limed plots in C_{tot} and N_{tot} contents (Tab. 3), especially in the humus horizons and in the A horizon, the C_{tot} and N_{tot} content being lower on the limed plot. The drop in C_{tot} and N_{tot} content in the humus horizons or even in the entire soil profile was reported in the majority of published studies as reviewed by Lundström et al. (2003a). It was demonstrated that liming stimulates soil respiration and microbial activity Kreutzer, Zelles (1986), Lettl (1991), Lettl (1992), Podrázský (1992a), Podrázský (1992b) and accelerated humus turnover results in decrease of C_{tot} and N_{tot} stock on limed sites (Kreutzer, 1995). Through these processes the loss of organic matter could occur.

Differences were also found between the limed and not-limed plots in the composition of soil sorption complex and its base saturation at the Bílý Kříž site. The base saturation of the soil sorption complex was higher on the limed plot in forest floor horizons by 26 to 27% and in the organomineral horizon Ae by 15% when compared with the control plot. On the contrary, the sorption complex of Ep horizon was more saturated by bases on the control plot and in the Bhs horizon differences were not noted while comparing the sorption complex saturation on the limed and control plot (see Tab. 3). The soil sorption complex was saturated only in Ol and Oh horizons on the limed plot. The exchangeable Ca content in humus layers (Ol, Of, Oh) was more than doubled on the limed plot when compared with the not limed control (Tab. 3) in 2003; higher contents of exchangeable Ca on the limed plot were found also in organomineral and mineral horizons with the exception of Ep horizon. Contents of exchangeable Mg in the humus layers and in the organomineral horizon were also higher on the limed plot. Increased contents of Ca an Mg and higher base saturation of CEC on the limed plot can be expected and the effects may be observed after several decades (Nihlgård et al. 1988). Lower concentrations of available K, Na, Mn were measured in Of, Oh, Ae, Ep and B horizons on the limed plot (Tab. 3). This can be explained by the accelerated consumption of these elements by boosted microbial community on the limed plot.

Considerable differences between the limed and control plot were also found in the

composition of soil water sampled by (subsurface) lysimeters. It is evident from data in Tab. 4 that the average pH value of soil water (calculated from the concentration of H^+ ions for the whole monitored period) on the limed plot is about 0.6 units higher than the average pH value of seepage water on the control plot. Significantly higher concentrations of calcium, magnesium, phosphates, ammonium nitrogen, sulphates, sodium and DOC were measured in seepage water on the limed plot during the monitored period Tab. 4).

Concentrations of potassium, on the contrary, were higher on the not limed plot FK, and significant difference was not observed between the nitrate concentrations on the both studied plots. The increased leaching of DOC from humus layer on the limed plot is well documented (Lundström et al. 2003a). This effect is caused by increased microbial activity and mineralization of soil organic matter induced with liming (see also Persson et al. 1991) as was mentioned above while discussing the contents of C_{tot} and N_{tot}. Kreutzer (1995) observed increased leaching of nitrates during 8 year period after liming at Högwald site (Germany) and expressed concern about possible undesirable rise of nitrate concentrations in ground water caused by liming. But this effect, most probably, is site specific (Nohrstedt 2002) and at Bílý Kříž the nitrate concentrations were not elevated in soil solution on the limed plot. The increased leaching of sulphates after liming, observed at Bílý Kříž (Tab. 4), was described e.g. by Lundström et al. (2003b) for Hasslöv site (Sweden) or by Huber et al. (2006) for Högwald forest (Germany).

significance of differences between particular plots by a t-test.								
Parameter	FD plot	FK plot	Difference between plots (FD–FK) and its statistical significance					
рН	4.96	4.32	0.64	p=2.5E-13				
$Ca^{2+}[mgl^{-1}]$	1.71	1.06	0.65	p=9.4E-06				
$Mg^{2+}[mgl^{-1}]$	2.52	0.27	2.25	p=1.2E-23				
$K^{+}[mg l^{-1}]$	1.20	1.82	-0.61	p=0.003				
$NO_{3}^{-}[mgl^{-1}]$	2.28	2.04	0.25	p=0.3				
$HPO_{4}^{2-}[mgl^{-1}]$	0.21	0.09	0.12	p=0.01				
$NH_{4}^{+}[mgl^{-1}]$	0.28	0.16	0.12	p=0.007				
$SO_4^{2-}[mgl^{-1}]$	6.69	5.46	1.23	p=0.03				
$Na^{+}[mgl^{-1}]$	0.34	0.25	0.08	p=3.8E-05				
DOC [$mg l^{-1}$]	32.18	23.77	8.41	p=0.0003				

Tab. 4: Average concentrations of various ions in mg l⁻¹ and average pH values (average of H⁺ concentrations converted to pH) in lysimetric waters on limed (FD) and non-limed (FK) plots, Bílý Kříž, sampling in 2002–2006. In the last column, results are given of the statistical comparison of the significance of differences between particular plots by a t-test.

Conclusion

Even after 16 years from the last liming, changes induced by liming were demonstrated by the analysis of forest soils sampled from the limed and control plots at the Bílý Kříž locality. Increased pH values in the entire soil profile, changes in the composition of soil sorption complex in the forest floor horizons were found on the limed plot. Lower content of carbon and nitrogen was determined in forest floor at the limed site. Long-term monitoring (2001–2006) of the soil solution composition also proved significant differences between the limed and not-limed plots. On the limed plot, there were

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significantly higher concentrations of Ca²⁺, Mg²⁺, HPO₄²⁻, NH₄⁺, SO₄²⁻, Na⁺, DOC and also pH values of the soil solution sampled on the limed plot were higher than pH values of the soil solution taken from the non-limed control plot. Concentrations of K⁺ in soil solutions were, on the contrary higher in the soil solution sampled from the not-limed plot FK. Significant differences were not observed between the plots in NO₃⁻ concentrations in soil solution.

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