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THE EFFECTS OF LIME ON pH VALUES OF SOIL AT DIFFERENT pH LEVELS

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ABSTRACT

An experiment on nitrogen fertilization (60-240 kg N/ha) was carried out for 42 years (1964-2005) at Sámsstaðir in Southern Iceland. Application of N during this period resulted in a decrease of soil pH, especially in plots that received high doses of nitrogen. These plots with variable pH values were used for a new experiment with different types and amounts of lime application, implemented in 2008. It included four treatments on each nitrogen plot: zero lime, 2 and 4 tons of lime with 35% Ca and 1.4% Mg and 4 tons of lime with 20% Ca and 12% Mg. Soil samples were collected in 2012. It was revealed that soil pH had increased in non-limed plots, especially in the most acid plots (240 N). In 7 years it increased by 0.44-0.86 pH units, probably due to the intense mineralization process in the soil. Additionally, liming application increased soil pH significantly at 0-5 cm soil depth ($p<0.001$). The pH increased linearly by 0.1 pH unit for each ton of lime applied and the lime effects were similar in all nitrogen plots. Only a very little effect of liming could be found at a 5-10 cm depth.

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1. INTRODUCTION

Soil pH represents the degree of soil acidity and alkalinity in a soil solution. It is below 6.5 in acid soils and above 7.0 in alkaline soils (Rowell 1994). The soil pH is naturally affected by climatic condition, soil parent material and vegetation cover, whereas acid-rain, fertilization and irrigation are considered as human-induced factors (Brady & Weil 2008). In acidic soils base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and nutrients (P, N, S) are less available, whilst in alkaline soils minor elements (Zn, Cu, B, Mn, Fe) become less soluble. Plant communities and living organisms can be depleted or deteriorated in soils with very low or very high pH levels (Brady & Weil 2008).

In general, soil pH (measured in H_2O) in Icelandic soils is above 4.9, though it can fluctuate from 4.0 to 7.9. The pH of Andosols (FAO 2006), which cover 86% of Icelandic soils, is in the range of 5.5-6.5. It can be very low (pH 4.5-5.5) in Histosols (FAO 2006) in the western part of Iceland because of high precipitation and the least input of ash and aeolian deposition, while the pH of Vitrisols is almost 7.0 (Arnalds 2004, 2008). The soil pH can significantly increase due to aeolian flux and deposition of volcanic ash, or can decrease due to revegetation, drainage and cultivation activities (Arnalds & Kimble 2001; Gudmundsson et al. 2004; Arnalds 2008).

During the 1930-70s many experiments on different types and amount of fertilizers in grass fields were established in Iceland. A number of the experiments became long term, with the same amount and type of fertilizers for decades (Thorvaldsson et al. 2008). Some of these experiments showed acidification effects of certain types of nitrogen fertilizer, especially ammonium sulphate. However, long-term application of ammonium nitrate also decreased soil pH in small pH units, while calcium nitrate increased soil pH (Gudmundsson et al. 2004; Brynjolfsson 2008).

One of these experiments (No.147-64) was performed with an increased amount of ammonium nitrate (from 60-240 kg N/ha per year) and was run for 42 years (1964-2005). In 2005, soil samples were collected from the experiment and the results of soil pH analysis showed a pH decrease in topsoil layers, especially in the plots with high doses of ammonium nitrate (Thorvaldsson et al. 2008). In 2008, a new experiment with lime treatment was designed in the same field to research the effect of lime on soil pH. The results from this new experiment are presented in this study.

The main objective of this study was to assess the effect of different types and amounts of lime treatment on soil pH in the topsoil layers. The research questions were:

- How is soil pH affected if fertilization treatment is stopped?
- How does different lime treatments affect soil pH?
- What is a favourable lime treatment for soil pH adjustment?

2. LITERATURE REVIEW

2.1 Classification of soil pH and its variation in soils

Soil pH can be arranged into five classes based on soil acidity or alkalinity level. Each class has a certain variation of soil pH. The first class includes acid sulphate soils which are below 4.5 and therefore extremely acid. In the second class, the pH varies from 4.5 to 5.5 and is considered very acid. The most favourable pH condition for nutrient availability is in the range of 5.5 and 7.2 referred to as acid and neutral soils, respectively. The fourth class is for alkaline soils with a pH level of 7.2-8.5 found in carbonate rich soils. The last class contains pH levels above 8.5, indicating sodic[1] or saline-sodic soils where sodium carbonates become dominant (Thomas 1996; FAO 2012).

A classification or interpretation of soil pH is based on established pH methods (Thomas 1996; Brady & Weil 2008). The values of pH for the same soil sample can differ by up to 1 pH unit depending on the method used. The most used methods for soil pH measurements are to make soil suspensions with: i) water (distilled, deionized), or ii) an unbuffered solution such calcium chloride (0.01 M $CaCl_2$), and iii) with potassium chloride (1 M KCl) (Thomas 1996; Elberling & Matthiesen 2007; Brady & Weil 2008).

Soil pH varies considerably in soils. It can vary naturally from 7.6 to 8.3 in Calcisols (FAO 2006) due to an abundance of $CaCO_3$ (Thomas 1996), while soil pH in Durisols can be as low as 5.0 or as high as 10, but the pH values are typically between 7.5 and 9.0 (FAO 2006). However, soil pH can change more or less due to vegetation cover. For instance, soil $pH_{(H2O)}$ in grass and shrub pastures was found to be from 4.4 to 4.9 in Umbrisol (FAO 2006, Dümig et al. 2008). The $pH_{(H2O)}$ was 4.3 and 4.7 for pasture and forest (*Cryptomeria japonica*), respectively (Bartoli et al. 2007), while it was 5.6 in a crop field in Silandic Andosols (Kusa et al. 2006).

2.2 The negative effects of high and low pH values in soils

Soils with $pH_{(H2O)}$ above 8.5 are toxic to many plants (Brady & Weil 2008) due to dominance of alkaline salts such as sodium carbonate (Na_2CO_3) or sodium bicarbonate ($NaHCO_3$) which can cause depletion of plant growth, damage in photosynthesis and imbalance of nutrients (Chen et al. 2011). For example, in China, a reduction in the survival rate of salt tolerant grass species (*Aneurolepidium chinense*) was observed at a pH above 8.8 (Shi & Wang 2005).

Micronutrients such as iron (Fe), zinc (Zn), and manganese (Mn) can be reduced to yield-limiting levels at high pH levels (Sims 1996). Boron (B^-) deficiency is common in alkaline soils because it is tightly bound in the clay part. In contrast, molybdenum (Mo) solubility is high and can exceed toxicity level in alkaline soils. Phosphorus (P) can also be deficient in alkaline soils due to an abundance of calcium and magnesium. It can react with cations, particularly with calcium, by forming calcium-phosphate compounds that become increasingly insoluble in alkaline soils (Brady & Weil 2008).

Soils with low pH suffer from deficiency of nutrients such as calcium (Ca^{2+}), magnesium (Mg^{2+}) and phosphorus (P). A pH below 5.0 inhibits availability of phosphorus (Haigh 1998; Kaihura et al. 1998) and the activity of cation exchange capacity (Baumann et al. 1998;

[1] According to Brady & Weil (2008): It is also called *alkali* soil which in most cases is confused with *alkaline* soil. "*Alkali"* is an obsolete term for what is now called *sodic* or *saline-sodic*.

Berthrong et al. 2009). Soil acidity can also have a negative effect on living organisms in soils. For instance, in the Czech Republic, a body mass decrease of Enchytraeidae worm (*Cognettia sphagnetorum*) was found after two years in soil with a pH level of 4.3 (Sustr et al. 1997).

Iron (Fe^{3+}) can reach toxic levels for plants at pH lower than 4.0, while hydrogen (H^+) can damage root membranes at pH levels between 4.0 and 4.5 (Brady & Weil 2008). In very acidic soils (pH 4.5-5.5) aluminium (Al^{3+}) toxicity affects plant metabolism where roots containing Al become shortened and thickened and unable to adequately take up water and nutrients, particularly phosphate (Rowell 1994). Like aluminium, manganese can be very soluble as pH drops, but its toxicity level in soils increases at a pH as high as 5.6 (Brady & Weil 2008).

Factors affecting soil acidification

Soil acidification can occur due to high precipitation in humid regions, leaching or washout of base cations, high elevation and vegetation growth (Smith et al. 2002). Several internal factors can cause soil acidity, such as released hydrogen (H^+) during decomposition of organic matter and nitrification, organic acids discharged from vegetation and plant roots, carbonic acid (H_2CO_3) derived from CO_2 emitted by roots, and microbial respiration (Rowell 1994; Oh and Richter 2004).

Soil acidification can also be induced by afforestation with pine trees of the genus *Pinus* and other conifers (Farley & Kelly 2004; Berthrong et al. 2009), use of sludge amendment in crop fields (Brallier et al. 1996), application of N-containing fertilizers, such as ammonium sulphate in grass fields under long-term use (Gudmundsson et al. 2004), ammonium nitrate under greenhouse conditions (Zhou et al. 2010), and urea in forest surface soils (Mitchell & Smethurst 2004).

Gases such as sulphur dioxide (SO_2) and oxides of nitrogen (NO_x) emitted from industries react with substances in the atmosphere to form nitric (HNO_3) and sulphuric acids (H_2SO_4) that return to the land surface with precipitation; so called acid rain. The pH of the acid rain is between 4.0 and 4.5 while normal rainwater has a pH of 5.5. The dissociation of these acids into H^+ cations and NO_3^-, SO_4^{2-} anions causes acidification in soils (Brady & Weil 2008).

2.4 The pH adjustment ways in acid soils

Soil acidity is an unfavourable condition for most plants to grow in. Even though some plants, such as potato, blueberry, shrubs and a large number of grass species, are acid tolerant and can grow at pH levels of 5.0-5.5, most crops such as corn (*Zea mays* L.), soybean (*Glycine max* L. Merr.) and wheat (*Triticum aestivum*) are most productive at a soil pH of 6.0 (Sims 1996).

Soil acidity has been controlled since the Renaissance (14^{th}-17^{th} centuries) in Europe (Christie et al. 2001). People tried to control soil acidification based on optimum plant growth, not knowing the precise chemical characteristics of lime. At present, limestone such as calcite ($CaCO_3$) or dolomite ($Ca{\bullet}MgCO_3$) is mostly recommended to adjust acid soil pH because of its effectiveness and because it is financially economical (Sims 1996). Calcium and magnesium bicarbonates are much more soluble and quite reactive in soils when it comes to replacing acid cations such as hydrogen (H^+) and aluminium (Al^{3+}) in colloidal complexes

(Brady & Weil 2008). For instance, calcitic limestone (5% $CaCO_3$) can neutralize 1 g H^+ kg^{-1} or 2500 kg H^+ ha^{-1} in topsoil layers (Rowell 1994). It is advised to break down the limestone finely and sieve it through a 60-mesh screen (<0.25 mm in diameter), as larger lime aggregates react slowly with soil particles. In humid regions limestone should be regularly applied every 3 to 5 years (Brady & Weil 2008).

The pH of acid soils can be partly controlled by applying by-product material with alkaline properties. For example, in England defecation lime from sugar processing factories is commonly used in farming to balance soil acidity (Masharipova 2006), or linz-donawitz slag produced by the iron and steel industry is applied on pastures in northern Spain to increase soil pH (Pinto et al. 1995). In Australia, red lime and alkaloam waste-derived products are used to adjust soil pH and to reduce the mobility of toxic elements (Carter et al. 2009). In addition, biochar (or charcoal), which is alkaline, can also be used to raise soil pH and exchangeable base cations in acid soils (Yuan & Xu 2011).

2.5 Liming rate applied in grassland

Different liming rates are used in grassland to target suitable pH levels. The liming rate of 3.7 t ha^{-1} was established to adjust soil to pH 5.5 (0.01 M $CaCl_2$) over a 6 year period on pasture land sown with ryegrass and subterranean clover (*Trifolium subterraneum*) in south-east Australia (Ridley et al. 2001). In England, Wales and Scotland the liming rate was at 2.5 t ha^{-1} for grassland to maintain soil acidity and to avoid yield loss (Chalmers 2001), whilst in Ireland for grassland with mineral soils the it was advised target was $pH_{(H_2O)}$ 6.2, incorporated with a liming rate of 6.7 t ha^{-1} during a 4- to 5-year liming cycle (Tunney et al. 2010).

2.6 Positive and negative effects of liming on soil properties

It is well established that liming has positive effects on soil properties (Rowell 1994; Sims 1996; Brady & Weil 2008). As an example, dolomitic lime applied at 6 t ha^{-1} enriched organic carbon (TOC) in the topsoil 0-2.5 cm layer (Briedis et al. 2012). Soil respiration and content of nutrients (Ca^{2+}, Mg^{2+} and P) including pH level were increased linearly with increased liming rates and reduced acid cations (H^+, Al^{3+}) (Marcelo et al. 2012). Liming treatment (80%, $CaCO_3$) significantly elevated the pH level in acid soil from 3.5 to 6.5 by immobilizing heavy metals in ryegrass (*Lolium perenne* L.) (Antoniadis et al. 2012).

Grassland with the species *Agrostis* and *Festuca* was limed with $CaCO_3$ at a rate of 600 g m^2 which resulted in higher biomass production and carbon flux in shoots compared to unlimed plots (Castro et al. 2004, 2005). A similar result on carbon accumulation by shoots was observed in limed grassland with a strong relationship ($P<0.008$) between shoot biomass and excess of carbon (^{13}C) in shoots (Johnson et al. 2002).

However, in some cases liming can disturb living organisms or induce nutrient leaching in soils. For example, liming performed in two catchments in a forest area at a dose of 2.5 t ha^{-1} (dolomite with 70% $CaCO_3$ and 17% $MgCO_3$) significantly lowered the total number of micro-invertebrate species in both catchments (Auclerc et al. 2012). Another study revealed leaching of nitrate (NO_3^--N) associated with liming at a rate of 3.7 t ha^{-1} in pastures containing annual (*Lolium rigidum*) and perennial grasses (*Phalaris aquatica* and *Dactylis glomerata*). The highest loss of N was 9 and 15 kg N ha^{-1} for non-limed and limed annual pastures, respectively (Ridley et al. 2001).

3. MATERIALS AND METHODS

3.1 General information about study area

The study area is located at the Sámsstaðir farm in Fljótshlíð, East Rangárþing municipality, south Iceland (N63°44'06'', W20°06'25'', 60 m.a.s.l.) (Fig. 1). The soil is Silandic Andosol (Thorvaldsson et al. 2008; Gudmundsson 2008; Gudmundsson et al. 2008). The experiment was located on a south facing slope. Mean annual temperature 1931-1962 was 5.0^{o}C and precipitation was 1103 mm per annum (Veðráttan 1962).

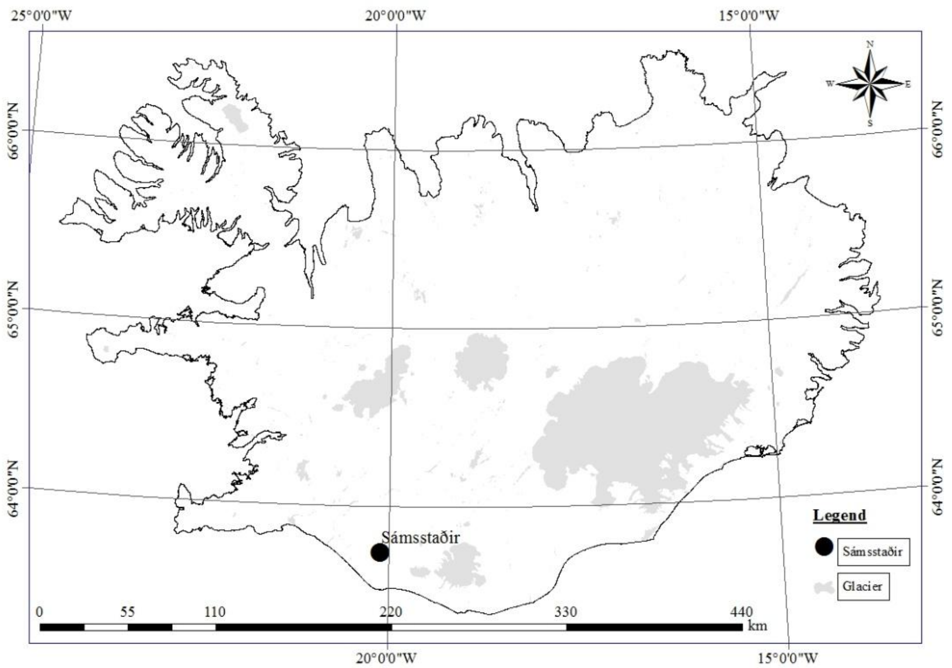

Fig.1. *Location of study area at Sámsstaðir farm in south Iceland.*

3.2 Experiment with nitrogen fertilizer

In 1964 an experiment with increasing amounts of nitrogen was established at Sámsstaðir. This experiment was fertilized and harvested for 42 years (1964-2005). The experimental design is shown below as well as the nitrogen treatments (Fig. 2).

Plot size was 36 m^2 (6x6 m). Each treatment was replicated 4 times and fully randomized within each block of the experiment. Additional fertilizer was 26.2 kg of phosphorus and 49.8 kg of potassium per hectare every year. There was no ploughing introduced during the experimental period. The grass was cut two times annually after being fertilized.

In 2005, soil samples were taken from all plots in the experiment. Different analyses were performed on these samples, for example measurement of pH. The mean values of soil pH are given in Table 1. The effect of nitrogen treatment on soil pH in the topsoil was significant ($p<0.001$). See table A in the appendices. The pH data were obtained from Guðni Thorvaldsson (unpublished).

- 60 kg N/ha = **A**
- 120 kg N/ha = **B**
- 150 kg N/ha = **C**
- 180 kg N/ha = **D**
- 240 kg N/ha = **E**

E	**C**	**A**	**D**
D	**B**	**E**	**C**
C	**A**	**D**	**B**
B	**E**	**C**	**A**
A	**D**	**B**	**E**

Fig. 2. *Design of nitrogen experiment at Sámsstaðir farm in south Iceland.*

The main grass species in the plots in the year 2005 was *Agrostis capillaris*. Other important species were *Festuca rubra*, *Alopecurus pratensis*, *Poa pratensis* and *Taraxacum officinale*. The plots with the highest rate of nitrogen had much more *Agrostis capillaris* than the other plots, or 86% (Guðni Thorvaldsson, unpublished data). The experimental area was not fertilized and harvested after the soil sampling in 2005.

Table 1. *Mean values of soil* $pH_{(H2O)}$ *after treatment with ammonium nitrate* (NH_4NO_3) *for 42 years, data from 2005.*

Nitrogen treatment kg N ha^{-1}	Topsoil layers 0-5 cm	5-10 cm
Unfertilized (Zero)	5.93	6.02
60	5.49	5.73
120	5.47	5.76
150	5.41	5.66
180	5.37	5.54
240	4.93	5.03

Monthly temperature and precipitation of the study area from 2005 are given in Tables 2 and 3.

Table 2. *Monthly and annual temperature at Sámsstaðir in 2005-2011.*

Year	Average temperature, ^oC												
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Yearly
2005	-0.1	1.2	3.6	4.3	5.8	10.3	11.8	10.7	6.1	3.2	2.1	2.5	5.1
2006	2.0	3.6	0.9	2.0	6.5	9.7	11.2	11.6	10.6	5.4	1.5	2.6	5.6
2007	-0.6	1.1	2.0	5.9	6.2	10.8	12.1	11.3	7.9	6.0	2.7	1.4	5.6
2008	-0.2	-0.2	0.8	4.3	9.1	10.5	12.7	11.0	9.3	2.5	2.2	1.0	5.2
2009	2.2	0.9	0.7	5.7	7.5	10.3	12.2	11.4	8.1	5.9	3.7	0.9	5.8
2010	2.2	0.3	3.2	2.7	8.6	10.9	12.9	11.9	10.4	6.5	1.1	0.2	5.9
2011	1.7	2.2	0.4	4.5	7.2	8.7	12.0	11.1	9.5	5.3	4.6	-2.0	5.4

Table 3. *Monthly and annual rainfall at Sámsstaðir in 2005-2011.*

Year	Average precipitation, mm												
	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Total
2005	78	91	25	16	17	82	103	67	112	73	87	113	864
2006	219	85	39	100	53	72	56	32	120	77	141	145	1137
2007	67	53	172	70	52	23	47	98	167	290	161	201	1401
2008	85	158	60	30	25	67	38	75	230	77	122	139	1106
2009	136	81	60	92	74	27	19	67	162	120	26	67	931
2010	136	25	95	60	52	37	34	105	84	40	24	72	763
2011	62	102	97	168	25	44	48	35	70	138	113	62	964

3.3 Experimental design for the liming treatment

In spring 2008 (May 13), a new experiment with lime treatment was started on the same nitrogen experimental plots at Sámsstaðir. Each plot (36 m^2) was divided into four 9 m^2 subplots (6 x 1.5 m). Four different lime treatments, including control (no lime), were introduced in the subplots. The lime treatment scheme and design are shown in Fig. 3. Two types of limestone (Granukal 35% Ca, 1.4% Mg and Dolomite 20% Ca, 12% Mg) were applied in the experiment.

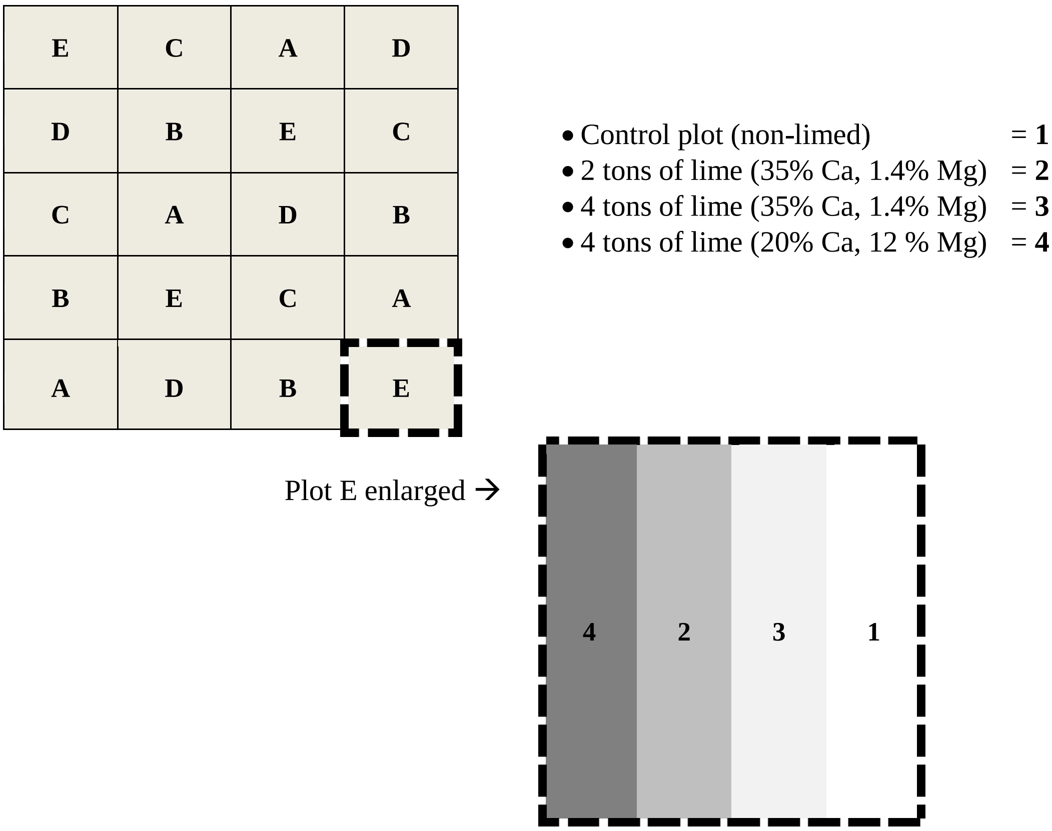

Fig. 3. *The scheme of liming treatments superimposed on the nitrogen experiment.*

3.4 Soil sampling 2012

On the 3rd of July, 2012, soil samples were collected from all subplots in the experiment with an Eijkelkamp core auger (3 cm in diameter), 6 cores from each plot. Grass was removed and the soil samples were divided into two depths, 0-5 and 5-10 cm with the help of knife and ruler (Fig. 4).

Fig. 4. *The experimental field at Sámsstaðir where subplots were bordered by rope (left). Soil samples from a subplot (middle). Cutting process of soil sample (right).*

3.5 Laboratory work and pH analysis

All 160 soil samples were transported from the field to the laboratory of the Soil Conservation Service of Iceland (SCSI) in Gunnarsholt on the 3rd of July, 2012. The soil samples were air-dried at room temperature for a week and kept in a thermostat (Avesta Sheffield) at 30±3^{o}C. The larger roots of grasses were removed and soils were sieved through 2 mm size mesh before pH measurements.

The pH analysis was implemented in the laboratory of the Agricultural University of Iceland at Hvanneyri.

A subsample of soil was placed into a 25 ml glass beaker (2-3 teaspoonfuls). Distilled water was added to the soil and mixed with a spoon until it was like a thin pudding. After 60 minutes standing time, the mixture was stirred again before introducing a pH electrode into it. Two buffers 4.0 and 7.0 were used for calibration of the electrode. Soil samples with known pH were used as reference samples.

3.6 Statistical analysis

To test whether the lime and nitrogen treatments had had an effect on soil pH, a multi-factor analysis of variance (ANOVA) was carried out. The factors included in the model were: nitrogen treatment, lime treatment, soil depth and replicates along with interactions. Factors not found significant at α=0.05 were removed from the model. All pairwise comparisons were done using the Tukey test (α=0.05). Regression was done to investigate the relationship between pH level and amount of lime (35% Ca, 1.4% Mg) applied. All statistical analysis was carried out using the statistical software R, version 2.15 (R Development Core Team 2012).

4. RESULTS

Multi-factorial ANOVA was performed on the data set (Table 4) and the main results of the experiment are presented in Tables 5 and 6. The pH was significantly affected by nitrogen treatments in the old experiment, by lime treatment in the new experiment and by soil depth. Significant interactions between soil depth and lime treatment, and between soil depth and nitrogen treatment were also found. That is, the effects of lime and nitrogen were not the same in both soil layers.

Table 4. *The significant differences of soil pH values with soil depth, nitrogen and lime treatment factors and its interaction level in multi-factorial ANOVA.*

Factors	Df	SS	MS	F	P-value
Replication	3	0.031	0.010	1.539	0.207
Soil depth	1	2.500	2.500	374.137	< 0.001
Nitrogen treatment	4	1.441	0.360	53.911	< 0.001
Lime treatment	3	1.407	0.469	70.188	< 0.001
Soil depths * Lime treatment	3	0.837	0.279	41.751	< 0.001
Soil depths * Nitrogen treatment	4	0.097	0.024	3.621	0.007
Residuals	141	0.942	0.007		

Table 5. *Soil pH at 0-5 cm depth in plots with different lime and nitrogen treatments.*

Nitrogen (kg/ha)	0-5 cm layer Liming treatment			
NH_4NO_3	Zero	2 tons[a]	4 tons[a]	4 tons[b]
60	5.93	6.18	6.37	6.37
120	5.98	6.26	6.35	6.38
150	5.98	6.18	6.39	6.36
180	5.92	6.20	6.34	6.31
240	5.79	6.05	6.26	6.07
Average	5.92	6.17	6.34	6.30
SD	0.08			

[a] Granukal lime contained 35% Ca, 1.4% Mg
[b] Dolomite lime contained 20% Ca, 12% Mg.

Table 6. *Soil pH at 5-10 cm depth in plots with different lime and nitrogen treatments.*

Nitrogen (kg/ha)	5-10 cm layer Liming treatment			
NH_4NO_3	Zero	2 tons[a]	4 tons[a]	4 tons[b]
60	5.98	6.09	5.99	5.99
120	5.98	6.04	6.02	6.08
150	5.96	5.95	6.04	5.98
180	5.87	5.96	5.95	5.97
240	5.67	5.72	5.76	5.67
Average	5.89	5.95	5.95	5.94
SD	0.08			

[a] Granukal lime contained 35% Ca, 1.4% Mg
[b] Dolomite lime contained 20% Ca, 12% Mg.

Therefore, ANOVA analysis was done separately for each depth of soil layers (Tables B and C in appendices). The pH values were affected by nitrogen treatment in both soil layers ($p<0.001$), while liming effect was only significant in the 0-5 cm soil layer ($p<0.001$), though it was not far from being significant ($p = 0.07$) in the 5-10 cm soil layer. The Tukey test showed significant differences between all lime treatments, except the two treatments with 4 tons of lime (different percentages of calcium and magnesium). There was a significant difference among nitrogen treatments as well. The highest amount of nitrogen (N240) was significantly different from all the other nitrogen treatments in both soil layers ($p<0.001$). There were no significant differences among the other nitrogen treatments, except between N180 and N120 treatments in the 5-10 cm soil layer ($p = 0.01$).

Soil pH did not differ considerably among nitrogen treatments in non-limed plots, except for the highest treatments (N180 and N240). The pH values in the 0-5 cm layer ranged from 5.92-5.98 for treatments with 60, 120, 150 and 180 kg N/ha but was 5.79 in plots that received 240 kg N/ha (Table 5). In the 5-10 cm soil layer the pH was 5.87 and 5.67 respectively in plots that received 180 and 240 kg N/ha (Table 6).

4.1 Change in pH with time in unlimed plots

According to the data from 2005 there was a significant effect of nitrogen treatments on soil pH ($p<0.001$). After 42 years of fertilization the pH results were 5.49, 5.47, 5.41, 5.37 and 4.93 in plots treated with 60, 120, 150, 180 and 240 kg N/ha, respectively, in the 0-5 cm soil layer. It dropped with increased amounts of nitrogen in the 5-10 cm soil layer as well. In non-fertilised soil outside the experiment, the mean values of soil pH were 5.93 and 6.02 in the 0-5 and 5-10 cm soil layers, respectively (Table 1).

A considerable increase in soil pH was revealed in untreated plots from 2005 to 2012 (Figs. 5 and 6). Soil pH in the 0-5 cm layer increased by 0.4, 0.5, 0.6, 0.6 and 0.9 units in plots that had recieved 60, 120, 150, 180 and 240 kg N/ha, respectively. It did not increase as much in the lower layer. The most increase in the pH was in plots with the lowest pH values in both soil layers (Figs. 5 and 6). After seven years without any fertilization the pH level of the soil had recovered to its natural state, except in the most acid plots. The soil pH in non-fertilized soil was 5.93 and 6.02 in 0-5 and 5-10 cm soil layers, respectively in the 2005 data (Table 1). The results in 2012 showed 5.92 and 5.89 to be the average values for non-limed plots of the different nitrogen treatments in the 0-5 and 5-10 cm soil layers, respectively (Tables 5 and 6).

4.2 Liming effect on soil pH values

Lime treatment performed four years ago significantly affected soil pH in addition to the natural changes through time ($p<0.001$) in the 0-5 cm soil layer. Soil pH changed slightly in the 5-10 cm soil layer as well. Soil pH increased with the rate of lime applied. The average pH of soil in the 0-5 cm layer increased by 0.25 units (5.92 - 6.17) in plots receiving 2 tons of lime, whilst it resulted in 0.42 units (5.92 - 6.34) in plots which received 4 tons of lime per hectare (Tables 5 and 6).

There was a linear relationship between pH and amount of lime which showed an increase in pH with increasing lime, but the relationship was different between the two soil layers ($p<0.001$). The increase in pH by lime amount was higher in the 0-5 cm soil layer than the 5-10 cm, as mentioned earlier. In the 0-5 cm topsoil layer the pH increased by 0.1 unit for each ton of lime ($p< 0.001$) and in the 5-10 cm soil layer the increase in pH was 0.01 with each ton increase in lime (p = 0.017). The relationship between pH and lime was the same for all N treatments (Figs. 7 and 8).

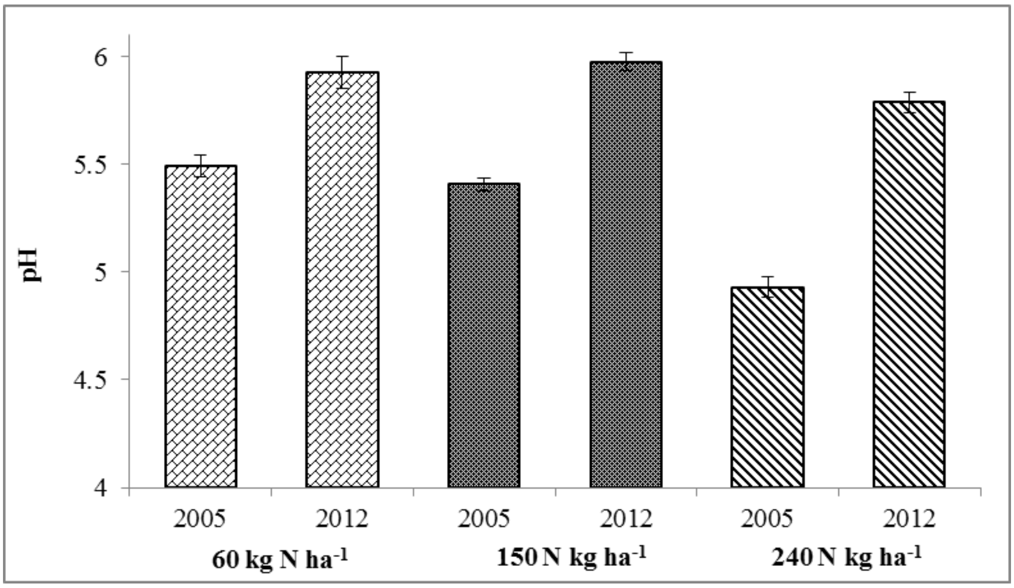

Fig. 5. *Change in soil pH from 2005-2012 in 0-5 cm soil layer in unlimed plots at three different nitrogen treatments.*

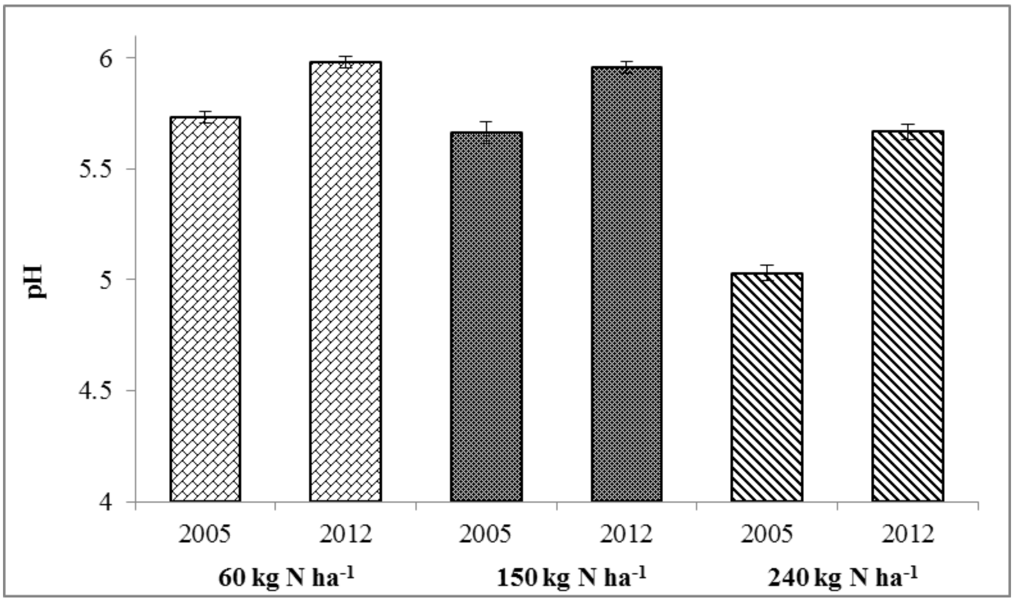

Fig. 6. *Change in soil pH from 2005-2012 in 5-10 cm soil layer in unlimed plots at three different nitrogen treatments.*

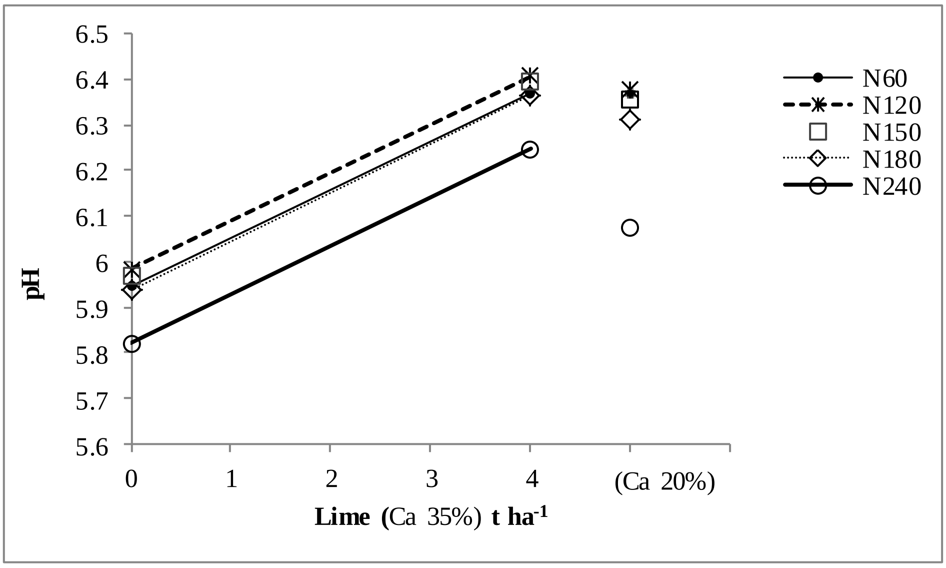

Fig. 7. *Predicted pH values for lime (35% Ca, 1.4% Mg) and average pH values for lime (20% Ca, 12% Mg) at 0-5 cm soil layer.*

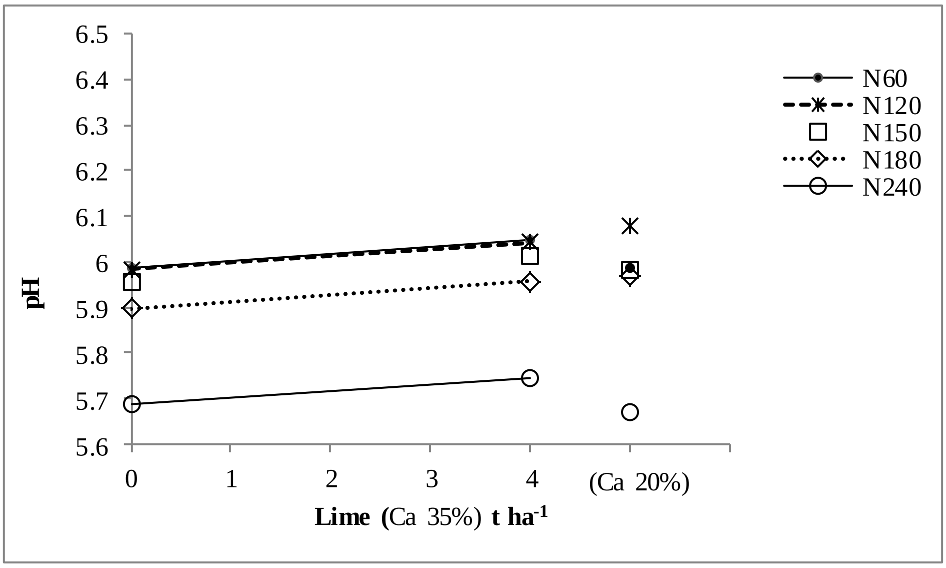

Fig. 8. *Predicted pH values for lime (Ca 35%, 1.4% Mg) and average pH values for lime (Ca 20%, Mg 12%) at 5-10 cm soil layer.*

5. DISCUSSION

5.1 Soil pH changes in non-limed plots

After seven years without nitrogen fertilization the soil pH level had increased in all non-limed plots, especially in the most acid plots. The experiment was implemented on Silandic Andosol (Thorvaldsson et al. 2008; Gudmundsson 2008) which is rich in rock minerals (Arnalds 2004). The unexpected increase in the pH of the topsoil was probably due to mineralization of the basic cations from rock minerals such as olivine and apatite induced by

H^+ which was released from the nitrogen treatment. This mineralization process was likely more intense in the plots with the lowest pH because the acid environment stimulated the mineralization process. The soil system controls the released H^+ by alkalinizing processes where H^+ ions are consumed in the system (Brady & Weil 2008).

However, it should also be mentioned that there was a volcanic eruption in Eyjafjallajökull in 2010, close to the study area. Ash did not fall in that area but ash particles might still have come, blown by wind. In this part of Iceland it is common that dry winds bring soil particles over the area. This could have contributed to the pH increase. Aeolian particles weathered from basaltic tephras would increase soil pH by charging the soil system with basic cations in the topsoil (Arnalds 2004; 2008). It is remarkable how much the soil pH had increased by mineralization and the possible effect of ash and aeolian particles. These effects were even higher than the lime effects.

5.2 Liming effect on soil pH in topsoil

The positive effect of liming on soil pH in topsoil is well known (Poozesh et al. 2010; Higgins et al. 2012; Marcelo et al. 2012). In this experiment each ton of lime increased the soil pH by 0.1 pH units. The effect of liming on soil pH was linear up to 4 tons. Jóhannesson and Kristjánsdóttir (1954) studied bogs in northern and southern Iceland and found a linear increase in pH up to high pH levels with increased lime. The increase in pH in their study was 0.12 pH units per ton lime in the north but 0.15 in the southern part of Iceland. The northern soil showed a greater exchange capacity than the southern one. A recent study on liming showed a linear effect up to 3.6 ton ha^{-1}, and the increase in pH was 0.2 pH units per ton of lime (Marcelo et al. 2012).

6. CONCLUSIONS

This study showed positive changes in soil pH after nitrogen fertilization was stopped. The soil pH increased considerably in non-limed plots. A certain break time after N fertilization could therefore be a natural solution to low pH if funds for liming are not available.

Liming application had significant effects on soil pH in the 0-5 cm soil layer, and it had started to affect the pH in the 5-10 cm layer as well. Soil pH increased by 0.1 units per ton applied. From this experiment, performed on Silandic Andosol, application of 1 ton of lime is recommended to increase soil pH in the 0-5 cm soil layer by 0.1 pH units.

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APPENDIX 1

***A)** Result of ANOVA of pH values in 0-5 and 5-10 cm soil layer in 2005.*

Topsoil at 0-5 and 5-10 cm layers					
Factors	Df	SS	MS	F	P-value
Replication	3	0.024	0.008	1.157	0.342
Soil depth	1	0.438	0.438	62.626	< 0.001
Nitrogen	4	2.247	0.561	80.155	< 0.001
Residuals	31	0.217	0.007		

***B)** Result of ANOVA of pH values in 0-5 cm soil layer in 2012.*

0-5 cm soil layer					
Factors	Df	SS	MS	F	P-value
Replication	3	0.053	0.017	2.766	0.048
Lime	3	2.195	0.731	113.558	< 0.001
Nitrogen	4	0.409	0.102	15.883	< 0.001
Residuals	69	0.444	0.006		

***C)** Result of ANOVA of pH values in 5-10 cm soil layer in 2012.*

5-10 cm soil layer					
Factors	Df	SS	MS	F	P-value
Replication	3	0.023	0.007	1.196	0.318
Lime	3	0.048	0.016	2.484	0.068
Nitrogen	4	1.128	0.282	43.115	< 0.001
Residuals	69	0.451	0.006		

***D)** Results of regression analysis of pH value at 0-5 cm soil layer.*

R^2 = 0.83	Topsoil at 0-5 cm layer			
N-treatment	Estimate	Std. Error	t value	P-value
Intercept	5.944	0.027	219.73	< 0.001
N120	0.037	0.033	1.118	0.268
N150	0.025	0.033	0.745	0.459
N180	-0.005	0.033	-0.174	0.862
N240	-0.124	0.033	-3.7	< 0.001
Slope	0.106	0.006	16.389	< 0.001

***E)** Results of regression analysis of pH value at 5-10 cm soil layer.*

R^2 = 0.69	Topsoil at 5-10 cm layer			
N-treatment	Estimate	Std. Error	t value	P-value
Intercept	5.988	0.025	236.558	< 0.001
N120	-0.005	0.031	-0.186	0.853
N150	-0.035	0.031	-1.115	0.269
N180	-0.091	0.031	-2.919	0.005
N240	-0.303	0.031	-9.661	< 0.001
Slope	0.015	0.006	2.467	0.016