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Elemental composition, fractions and balance of nutrients in an Andic Gleysol under a long-term fertilizer experiment in Iceland

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ABSTRACT

Soil samples from a long-term fertilizer experiment, testing different types of N fertilizer, were analysed for total chemical composition, slowly releasable fractions by boiling ignited soil samples in hydrochloric acid, and exchangeable cations and available phosphorus by the AL method. The total chemical composition reveals that the soil mineral material resembles that of basaltic rocks. The Ca and Mg contents are lower than the common range for basalt, indicating that these elements have weathered and leached from the soil. The use of acidifying ammonium sulphate reduces the more readily available reserves and exchangeable Ca and Mg but does not appear to have influenced the HCl-soluble and exchangeable K contents. The input – output balance of K was negative and a resulting depletion was observed in the total content of the soil rather than in the HCl-soluble fraction and the exchangeable fraction. This indicates that the total K content of the soil is an important measure of the long-term fertility of the soil. The annual negative input – output balance was 30 – 40 kg K ha^{-1} and the remaining K reserves in the top 600 t soil ha^{-1} would only last for another 60 – 100 years at this rate. The positive input – output balance of P has led to an increase in the P content basically confined to the top 5 cm of the soil. The AL-soluble P increased but P was mainly soluble in hydrochloric acid, indicating that it was moderately strongly bound.

Key words: Long-term fertilizer experiment, N fertilizers, elemental composition, nutrient balance, potassium, phosphorus

YFIRLIT

Samsetning steinefna og jafnvægi næringarefna í gljáajörð í lok langtímatilraunar með áburð

Jarðvegssýni úr langtímatilraun, þar sem mismunandi tegundir nituráburðar voru bornar saman, voru efnagreind með þremur mismunandi aðferðum. Gerð var heildargreining á sýnunum auk mælinga á veðranlegum forða (HCl-lausn) og auðleysanlegum forða (AL-lausn). Heildargreiningin sýnir að steinefnahluti jarðvegsins hefur svipaða samsetningu og basalt. Kalsíum- og magnesíumhlutfall er heldur lægra en algengt er í basalti sem sýnir að þessi efni hafa veðrast og skolast úr jarðveginum. Notkun á sýrandi ammonsúlfati minnkar veðranlegan forða þessara efna og jafnframt skiptanlegt Ca og Mg en virðist ekki hafa haft áhrif á veðranlegt og skiptanlegt K. Ræktunarjöfnuður kalís var neikvæður. Við það minnkaði heildarforðinn fremur en veðranlegur og skiptanlegur forði kalís. Þetta gefur vísbendingar um að heildarmagn kalís í jarðvegi megi nota sem mælikvarða á frjósemi jarðvegsins til lengri tíma. Að jafnaði voru 30 – 40 kg ha^{-1} af kalí fjarlægð árlega umfram það sem var í áburðinum. Á þeim hraða myndi forðinn í efstu 10 sm jarðvegsins (600 tonnum) einungis endast í 60 – 100 ár enn. Meira hefur verið borið á tilraunina af fosfór en það sem hefur verið fjarlægt. Aukning á fosfórforða jarðvegsins takmarkast að mestu leyti við efstu 5 sm jarðvegsins. AL-leysanlegur, en einkum þó HCl-leysanlegur fosfór, hefur aukist og er því sá fosfór, sem safnast hefur, hóflega fast bundinn.

INTRODUCTION

A large number of investigations on the effect of fertilizers on soils have been performed during the last century. Primarily the research has concentrated on exchangeable cations and soluble phosphorus, whereas only few investigations have looked at the total storage in the soil and release of cations through weathering or the transfer between different pools of phosphorus (Johnston 1998, Holmquist et al. 2003). Potassium and phosphorus are of greatest interest because of their high fertilizer demand. Where, over a prolonged period, less K is being applied than harvested, as in the experiment reported here, the question arises if this will influence the long-term soil fertility and sustainability. In order to answer this question both the total source and the rate of release need to be better known (Holmquist et al. 2003). In Iceland this is of particular interest since the parent material is very low in K and there are no phyllosilicates in the soil that fix or build a slowly releasable source of potassium. In Iceland more P is generally applied than taken away through harvest. This has led to a build-up of P that is believed to be fixed, immobile and practically unavailable to the ecosystem, as reported for Andosols in general (Dahlgren et al. 2004). On the other hand Helgason (2002) has shown that a relatively high proportion of the soil P is bound in the organic matter that theoretically would mean that it could be transformed to the readily available pool.

Previous studies have shown that long-term use of different N fertilizers has a large effect on pH, organic matter content and exchangeable nutrients (Helgason 1975). A major investigation of soils at the long-term experimental site at Skriðuklaustur, East Iceland, has recently been carried out (Thorvaldsson et al. 2003, Gudmundsson et al. 2004). A pH decrease to below 4 was observed after 43 years of ammonium sulphate application, whereas the pH was at or above 7 in plots which received calcium nitrate as N fertilizer. Changes in the main nutrient composition were found in the nutrient fraction extracted by boiling the samples in 30% HCl after ignition. This showed that especially in the acid plots the mineral fraction was acting as a buffer and nutrients were released. There was also a general decrease in the K content of the harvested grass from the early years of the experiment until the end of experimentation in 1996.

The hypothesis was therefore that there would also be changes in the total elemental composition as a result of the long-term use of different types of N fertilizers. This is of particular interest for potassium as basalt has a low potassium content and over the experimental period of 43 years the potassium balance was negative. Also of interest was to determine from which fractions calcium and magnesium were released. To gain more information on changes in the total elemental composition compared with other fractions, samples from one replicate (row) of experimental plots were chosen for the total chemical analyses.

Table 1. Plots and treatments used in the study. Application of N, P, K, Ca and S per annum and accumulated over 43 years, kg ha^{-1}.

Treat-ment	Nitrogen	Phosphorus		Potassium		Calcium		Sulphur	
	In 43 y	Yearly	In 43 y	Yearly	In 43 y	Yearly	In 43 y	Yearly	In 43 y
B 120 NH_4NO_3	5160	30.6	1316	74.4	3199	19.8	851	0	
C 120 $(NH_4)_2SO_4$	5160	30.6	1316	74.4	3199	19.8	851	137	5891
D 120 $Ca(NO_3)_2$	5160	30.6	1316	74.4	3199	191	8213	0	
No fertilizer		0	0		0		0		0

In this paper we report on the total chemical composition of the soil, the amount of the slowly releasable fraction of the main nutrients Ca, Mg, K and P, and the amount of these main nutrients as determined by the AL method which is used by the advisory service in Iceland.

MATERIALS AND METHODS

The experiment at Skriðuklaustur

The experimental farm at Skriðuklaustur is situated in a glacial valley about 50 km inland in East Iceland. The annual precipitation is about 500 mm with 174 mm falling between May and September. The annual mean temperature is 4.1°C, the mean July temperature is 11°C and for January –1.3°C.

The field experiment number 19-54 at Skriðuklaustur was intended to compare different types of N fertilizers. It was run from 1954 to 1996 when the soil was sampled and subsequently analysed. The experimental plots were square, 50 m^2 in area, arranged systematically in a knight's move variant of the 5x5 Latin square design. The plots received a basic annual application of P (30.6 kg ha^{-1}) and K (74.7 kg ha^{-1}). The five experimental treatments received the following N fertilizer in kg ha^{-1}:

A	0	N
B	120	N as NH_4NO_3
C	120	N as $(NH_4)_2SO_4$
D	120	N as $Ca(NO_3)_2$
E	75	N as NH_4NO_3

The input of major elements with fertilizers is shown in Table 1. The input – output balance of the nutrients (Table 2) was obtained by adding the fertilizer input and input through precipitation and subtracting the amount taken away through the harvest. Nutrients lost through leaching cannot be taken into account as no information on leaching is available. The annual input through precipitation was estimated using annual rainfall and composition of rainwater in Iceland as follows (Thorvaldsson et al. 2003): Ca and Mg 2 kg ha^{-1} each, K 1.5 kg ha^{-1}, Na 30 kg ha^{-1} and P approximately zero.

Comprehensive data on the soils, sampling and data from three of five replicates are given by Thorvaldsson et al. (2003) and some data

Table 2. Input – output balance over 43 years. Input from fertilizers and precipitation minus output through harvest, kg ha^{-1}. Mean of five replicates for the treatments, no fertilizer assessed.

	Ca	Mg	K	Na	P
Treatment B	– 412	– 637	– 1770	947	357
Treatment C	122	– 386	– 1589	956	541
Treatment D	6555	– 541	– 1857	931	393
No fertilizer	– 430	– 172	– 1226	1161	– 215

Table 3. Soil pH (in water), organic carbon and total nitrogen of the soil (g kg^{-1} DM), volume weight of samples, kg l^{-1}. Mean of three replicates (Thorvaldsson et al. 2003).

Depth, cm		**No fertilizer**	**B 120 N NH_4NO_3**	**C 120 N $(NH_4)_2SO_4$**	**D 120 N $Ca(NO_3)_2$**
0 – 5	pH	6.3	5.8	3.8	6.9
	C	120	146	229	151
	N	9.3	11.2	15.2	12.8
	C/N	12.9	13.0	14.9	11.8
	vol.w.	0.55	0.48	0.30	0.54
5-10	pH	6.8	7.0	4.4	7.2
	C	42	61	85	66
	N	3.5	5.0	6.3	5.3
	C/N	12.0	12.3	13.5	12.5
	vol.w.	0.77	0.70	0.60	0.69
10-20	pH	7.0	7.3	6.2	7.2
	C	37	40	52	48
	N	2.8	3.2	4.3	4.0
	C/N	13.0	12.6	12.2	12.1
	vol.w.	0.78	0.78	0.69	0.70

on the treatments are given in Table 3. There has been a general increase in organic matter depending on N fertilizer but also in the unfertilized area (Gudmundsson et al. 2004). The pH in plots with ammonium sulphate as N fertilizer has decreased to below 4 in the top 5 cm and at the same time the organic matter has increased. A high pH and an increase in organic matter with the lowest C/N ratio characterise the plots with calcium nitrate as N fertilizer, whereas ammonium nitrate has had little effect on the pH.

Sampling and analyses

The soil sampling and the determination of bulk density, soil pH, organic C and total N has been described (Thorvaldsson et al. 2003, Gudmundsson et al. 2004). Plots with no P and K were not included in the experiment. However, to obtain information on unfertilized soil, samples were taken just outside the experimental field adjacent to the rows that were sampled. In this study samples from the central row plots B, C and D that lie next to each other and from the adjacent unfertilized area were selected for total chemical analysis. Results from earlier analyses on the exchangeable and slowly releasable fractions from these plots were used to provide direct comparison. Plots E and A lie between plot D and the unfertilized area.

Exchangeable cations and phosphorus were extracted in ammonium lactate (AL method) according to Egner et al. (1960). The slowly releasable reserve or the “weatherable” fraction was determined according to Schlichting et al. (1995). The samples were ignited at 500 °C for 1 hour and then boiled in 30% HCl using a water bath. In both extracts Ca and Mg were determined by atomic absorption, K and Na using flame photometry and P photometrically. For the total elemental analysis, samples of 0.125 g were melted with 0.375 g $LiBO_2$ and dissolved in HNO_3. The concentration of elements (metals) was measured by Plasma-emission spectrometry (ICP-AES) and a Plasma mass spectrometer (ICP-QMS).

Table 4. Elemental composition of the soil, calculated as % of the mineral fraction. Mean values from four plots and three depths (0– 5, 5– 10 and 10– 20 cm) and standard deviations (s.d.) of the observations, n=12. Range in Icelandic rocks adapted from Jakobsson (1980).

Element	Mean	s.d.	Common range in Icelandic Basalt	Common range in Icelandic Rhyolite
SiO_2	52.2	1.21	48 – 50	74 – 74
$A_{l2}O_3$	14.3	0.99	14 – 16	13 – 14
CaO	8.0	1.04	9.5 – 11.6	0.5 – 1.3
Fe_2O_3	14.6	0.81	9.7 – 16.8	3.1 – 3.5
K_2O	0.7	0.08	0.3 – 0.8	3.0 – 4.7
MgO	4.0	0.18	6.0 – 9.1	0.1 – 0.4
MnO	0.25	0.05	0.20 – 0.25	1.06
Na_2O	2.1	0.13	2.0 – 3.1	4.8 – 5.6
P_2O_5	0.87	0.71	0.2 – 0.5	0.01 – 0.05
TiO_2	2.2	0.09	1.5 – 3.1	0.25 – 0.31
Sum	99.2	0.53		

RESULTS

The total elemental composition was calculated on the basis of the residue after ignition (Table 4 and Figure 1 and 2). The results are presented in the oxide form in Table 4 for comparison with basalt and rhyolite but elsewhere in elemental form. The use of the residue after ignition as a measure of the inorganic fraction allowed comparison with the elemental composition of Icelandic rocks. It also avoided apparent differences between plots and depths induced by different amounts of organic matter. However, it did include the organically bound elements, including phosphorus. The contents of the total soil (Figure 3) were based on a fixed amount of soil, 600 t ha^{-1}, which corresponds approximately to the top 10 cm. This is the most active rooting zone in Icelandic grassland. The differences between columns in Figure 3 are interpreted as non-weatherable (total amount minus HCl-soluble) and slowly releasable reserves (HCl-soluble minus AL-exchangeable and extractable), respectively.

The low silicon, manganese and sodium content on the one hand and the high content of iron, and titanium on the other are indicative of the basaltic origin of the inorganic soil material (Table 4). The contents of calcium, magnesium, potassium, sodium and phosphorus were to a greater extent influenced by weathering and fertilization but also showed a marked resemblance to the basaltic rocks.

Calcium

The mean Ca content was slightly lower than common in Icelandic basalt and the effects of different fertilizers were reflected in the fairly high standard deviation (Table 4). The total content in the top 5 cm was clearly lowest in the acid plot and highest in the plot that received calcium nitrate as N fertilizer. At 10–20 cm depth these changes were no longer evident (Figure 1). In the acid plot C the HCl-soluble fraction was only 16–17 % of the total compared with 40–50 % in other plots and depths. The exchangeable fraction was most sensitive to changes in pH. On the acid plot C the loss of calcium apparently exceeded the exchangeable fraction and the acid soluble fraction had also decreased substantially. The top soil of plot D with calcium nitrate had a very high exchangeable Ca of about 20 mg kg^{-1} (on mineral bases) and the acid plot C only 1.35 mg kg^{-1} in the top 5 cm compared with 9.9 and 7.2 mg kg^{-1} in the ammonium nitrate plot and the unfertilized area, respectively. These findings show the

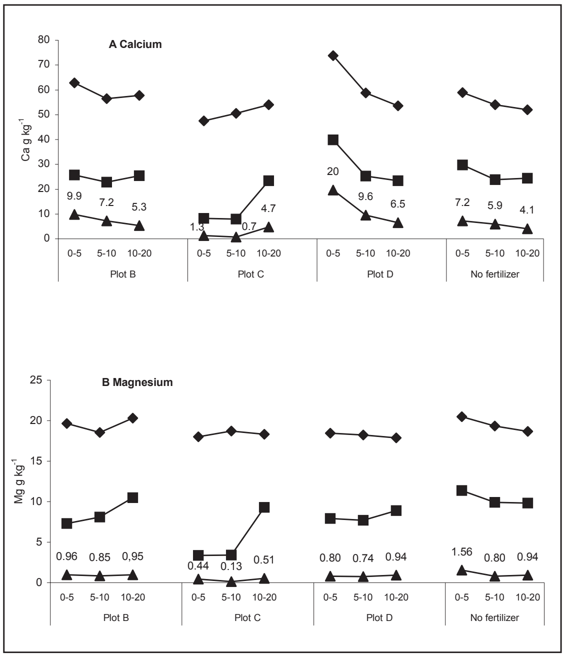

Figure 1. Fractionation of A) Calcium and B) Magnesium at 0-5, 5-10 and 10-20 cm depths. Showing ◆=total amounts, ■=HCl soluble and ▲= AL-soluble Ca and Mg. Calculated in g kg^{-1} of the inorganic component of the soil.

impact of different N fertilizers.

The soil had large reserves of calcium, 23–30 t ha^{-1} in the top 600 t of soil (approximately the top 10 cm). Where Ca-rich N fertilizer was used the reserves were highest, and lowest where acidifying N fertilizer was applied (Figure 3). The positive Ca balance explains the high Ca in the calcium nitrate plot. Compared with the zero plot and the ammonium nitrate plot the reserves were about 5 t ha^{-1} less in the acid plot on the basis of the total soil, and after correcting for organic matter and balancing on the mineral basis the difference was still 2 – 3 t ha^{-1}. The differences in the HCl-soluble fraction and in exchangeable Ca showed that these fractions shouldered the greatest burden of buffering the acid input.

Magnesium

The magnesium content of the soil was clearly lower than the common range in basalt (Table 4). As Mg was not applied in fertilizers there was a negative input – output balance, not accounting for leaching, and depletion of magnesium in the profile would be expected. The differences between plots and depths were small and did not seem to indicate a regular pattern (Figure 1). Differences showed up in the HCl-soluble and AL-extractable fractions where there was a depletion of Mg in the top 0 – 5 and 5 – 10 cm of the soil in the acid plot and in the AL-fraction also at 10 – 20 cm depth. Other plots and depths varied only slightly but the zero fertilizer plot had the highest values. As with Ca, the buffering of the acid input affected the weatherable and exchangeable fractions.

The total Mg content in the top 600 t soil ha^{-1} (~ top 10 cm) was high with 8.5–9.8 t

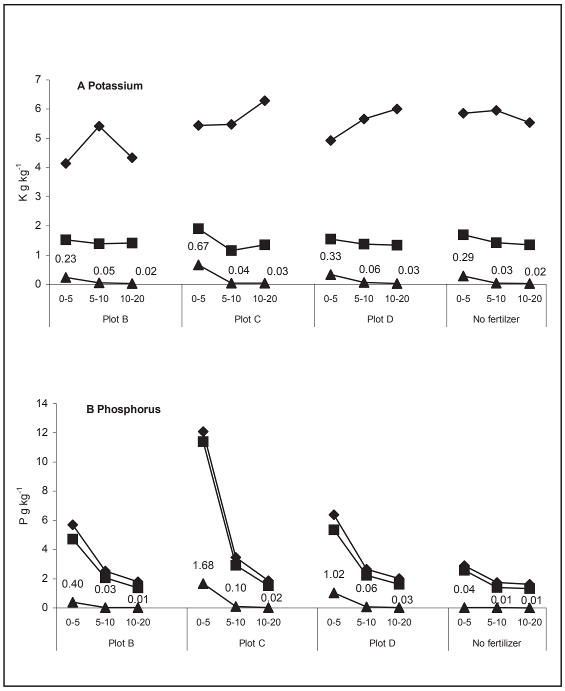

Figure 2. Fractionation of A) Potassium and B) Phosphorus at 0-5, 5-10 and 10-20 cm depths. Showing ◆=total amounts, ■=HCl soluble and ▲= AL-soluble Ca and Mg. Calculated in g kg-1 of the inorganic component of the soil.

ha^{-1}, the lowest value being in the acid plot and the highest in the unfertilized area. As in the case of Ca, the differences showed up in the HCl- and AL-fractions. The Mg values were lower where acidifying fertilizer was used, in particular exchangeable Mg. There was only 131 kg ha^{-1} in the acid plot compared with 550 kg ha^{-1} in the unfertilized area and 427 and 355 kg ha^{-1} in the ammonium nitrate and calcium nitrate plots, respectively.

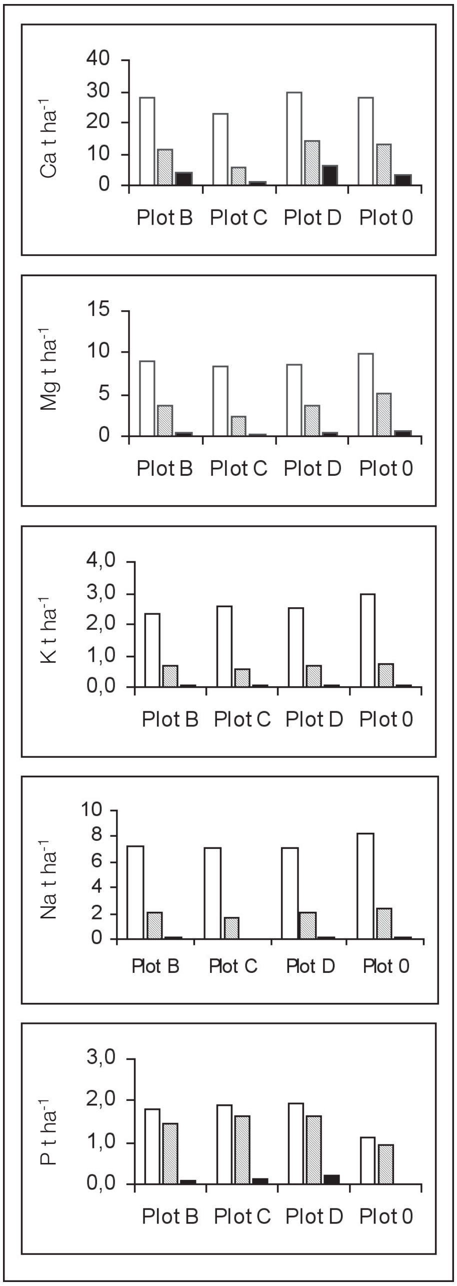

Figure 3. Fraction of the main nutrients in t ha^{-1} in plots B, C and D and the unfertilized area O. Showing □ =total amounts, ▨ =HCl soluble and ■ = AL-exchangeable or extractable fractions in the top 600 t soil ha^{-1} (corresponding approximately to the top 10 cm).

Potassium

The mean potassium content was in the upper range for basalt (Table 4). Considering the negative input – output balance and some leaching this indicated an admixture of rhyolitic material. The most recent contribution was rhyolitic volcanic ash from the volcano Askja in 1875. As rhyolite contains 5 – 10 times more potassium than basalt only a small addition of rhyolitic ash would increase the K content of the soil. The lowest values were in plot B and highest at 10 – 20 cm depth in plots C and D. These differences were likely to have been inherited from the parent material due to varying amounts of rhyolitic ash. Only 21 – 37 % of the total potassium was HCl-soluble, the highest proportion being in the top 0 – 5 cm. Neither the HCl-soluble nor the AL-exchangeable K seemed to be related to different treatments.

The total K in the top 600 t soil ha^{-1} (~ top 10 cm) was only 2.3 – 2.9 t ha^{-1}, highest in the unfertilized area, which may be attributed to the lowest output. Potassium was characterised by low solubility. Only about 600 – 770 kg ha^{-1} were soluble in HCl and the exchangeable AL-fraction was in the range 58 – 78 kg ha^{-1}. These low values may be interpreted as a result of the negative input – output balance ranging from 1226 to 1857 kg ha^{-1} over the 43 years of the experiment or 28 – 43 kg ha^{-1} per annum. It is noticeable that the total negative balance was 2 – 3 times higher than the HCl-soluble fraction that is considered to be a measure of the weatherable fraction.

Phosphorus

The mean total phosphorus in the soil was higher than expected given the basaltic origin (Table 4) and the variation was high, reflecting heterogeneity of the samples. The highest total P was in all plots in the top 5 cm of the soil and in the fertilized plots it decreased sharply with depth. The HCl-soluble P ranged from 77 – 94 % of the total content with no obvious relation to treatment or depth. Thus the HCl-extraction was higher for P than for the other elements. The AL-extractable fraction ranged from 0.4 to 1.7 g kg^{-1} in the top 5 cm in the fertilized plots compared with 0.036 in the unfertilized area. The P content decreased very rapidly with depth so that at 10 – 20 cm depth the same low content of soluble P was reached in the unfertilized area as in the fertilized plots.

The total P in the top 600 t soil ha^{-1} (~ top 10 cm) was 1786, 1875 and1908 kg ha^{-1} in the fertilized plots B,C and D, respectively, compared with 1122 kg ha^{-1} in the unfertilized area. The differences in total soil P between the fertilized plots and the unfertilized area of 664, 753 and 786 kg ha^{-1} compared reasonably well with the positive input – output balance of the fertilized plots (Table 2). The input – output balance, taking the negative balance of the unfertilized area into account, gives a surplus loss of 572, 756 and 608 kg ha^{-1} for plots B, C and D respectively.

Sodium

The sodium content fell within the common range in basalt. Within the plots the total content calculated on the mineral bases was irregular but the lowest value, found in the top 5 cm of the acid plot, was consistent with the same observation for calcium. The HCl-soluble fraction was in the range of 21 – 30 % of the total Na, or similar to that for potassium, but proportionately lower than for both calcium and magnesium. The AL-fraction ranged from 0.11 to 0.37 g kg^{-1}, with the highest values in the surface layer.

With 7.1 – 8.1 t Na ha^{-1} in the top 600 t soil ha^{-1} the reserves of Na were 2 – 2.5 times higher than the potassium reserves. The HCl-soluble and AL-fractions were smallest in the acid plot, as was the case for the other cations. Due to the high input through precipitation the input – output balance was positive and sodium had to leach out in considerable quantities.

DISCUSSION

A characteristic of the Icelandic long-term experiments on permanent lay is that after the onset of the experiment the soil has remained undisturbed, no cultivation or resowing has taken place. This provides the opportunity to study differences in soil formation where the conditions in different plots have developed in different ways or even in opposite directions. At Skriðuklaustur this is the case for pH and organic matter. However, this also imposes new difficulties in ascertaining nutrient balances and comparing plots when large differences in organic matter accumulation and corresponding changes in bulk density occur. To counter these differences Gudmundsson et al. (2004) used soil weight rather than a fixed depth as a reference when balancing and comparing differences in organic matter accumulation.

In this study the inorganic component was chosen as a reference and elemental composition calculated as % or g kg^{-1} based on the mineral material. The inorganic material was determined by using the residue upon ignition. With this method the sum of the main elements as oxides totalled about 99 % (Table 4), indicating that this was a relatively stable size. Using this method, apparent differences in elemental composition due to differences in organic matter are diminished. This allows a comparison between plots as well as between different depths.

Calculation of the total amount of elements in the top 600 t soil ha^{-1} was carried out in the same way as Gudmundsson et al. (2004) had applied for C and N. This corresponded reasonably well with the top 10 cm of the soil. Alternatively the top 500 t ha^{-1} inorganic material could have been used as a reference.

However the differences in the end were not too big as the "thinning" effect of organic material in the top 5 cm of the soil was compensated by additions from the soil below a depth of 10 cm to get to the reference size of 500 t inorganic soil material per ha.

As shown in previous papers (Thorvaldsson et al. 2003, Gudmundsson et al. 2004) there is a trend within the experimental site which influences the amount of organic matter and extracted elements and this was corrected for by using a simple regression. In this study total analysis was added but only to one row, i.e., samples only from one plot of each treatment at different depths. The fertilized plots lie close to each other but the unfertilized area is two plots or 14 m away. This makes corrections due to inherited differences within the experimental site difficult but by using the mineral material as reference differences induced by different contents of organic matter, both inherited and as a result of the different treatments, were eliminated. The low variability of both Si and Al (Table 4) is an indication of a fairly uniform parent material. Gudmundsson et al. (2005) show that the stable elements Ti and Zr are within a narrow range and conclude that variations in other elements within the area can be interpreted as a result of fertilizer treatment.

Earlier studies on the influence of different types of N fertilizer on nutrients in soils used exchangeable cations only but not the other fractions used in the present study (Helgason 1975, Ólafsson 1978). Their results show that ammonium nitrate and ammonium sulphate fertilizers reduce exchangeable Ca and Mg where precipitation is high. Where precipitation is low there is no or only a minor effect from ammonium nitrate on exchangeable Ca and Mg. Helgason's study included Skriðuklaustur and the present study on samples taken 23 years later confirmed his observations.

Calcium and Magnesium

The total content of both Mg and Ca were lower in the soil than the common range of both basalt and rhyolite. This suggests that these elements play a major role in buffering the soil pH. However with about 22 – 30 t Ca ha^{-1} and 8 – 10 t Mg ha^{-1} in the top 600 t soil ha^{-1} (top 10 cm of the soil) the reserves were very large. Upon acidification by fertilizers Ca appears to be affected to a greater extent than Mg. This was reflected in both lower concentrations in the acid plot of Ca as well as in lower total amounts in the top 600 t ha^{-1} than in the unfertilized area and in the ammonium nitrate plot. A corresponding change in total Mg between treatments did not occur. However, in the acid soluble fraction and the AL-fraction both Ca and Mg were significantly lower in the acid plot than in other treatments to a depth of 10 cm. In the calcium nitrate plot the input of 6.5 t Ca ha^{-1} as a surplus over the output was only found in the AL-exchangeable fraction. Thus the depletion reached the reserve fractions that acted as a buffer in the soil system, whereas the addition remained in the most soluble fraction.

By comparing the ammonium nitrate plot and the unfertilized area with the calcium nitrate plot which received a surplus of 6.5 t Ca ha^{-1} it was possible to assess the amount of leaching. Using the total amounts showed that there were about 2 t Ca ha^{-1} more in the calcium nitrate plot than in the others, indicating a loss of 4 – 4.5 t Ca ha^{-1} through leaching or a yearly loss of about 100 kg Ca ha^{-1}. This was somewhat more than the annual loss of 70 kg ha^{-1} that Thorvaldsson et al. (2003) found when balancing the whole experiment and using the HCl-soluble fraction.

Potassium and sodium

The inherited low K content of Icelandic soils and a high uptake of both the natural vegetation and of crops make it a particularly interesting element. The negative balance of 1.22 – 1.86 t ha^{-1} was large considering the total reserves of only 2.33 – 2.95 t ha^{-1} in the top 600 t soil ha^{-1}. In contrast the inherited sodium content was about 3 times higher and input through precipitation exceeded the removal through harvesting by about 1000 kg Na ha^{-1} over the 43 years of the experiment. The acidification appeared not to have affected either the concentration of K and Na in the different fractions nor the total amounts in the top 600 t soil ha^{-1}. The high variability of K, especially in plot B (Figure 2), can be attributed to variations in the parent material as only small amounts of rhyolitic ash would affect the K content considerably. The total amount of K in the top 600 t soil ha^{-1} was highest in the unfertilized area that was also the one with the least losses in the input – output balance. In plots B, C and D 544, 363 and 631 kg ha^{-1} respectively more K had been removed through harvesting than in the unfertilized area. This compared reasonably well with the lower total K in these same plots compared with the unfertilized area; 625, 384 and 461 kg ha^{-1} K in the same plots, respectively. Although these figures are only based on one set of plots it is tempting to conclude that the harvested K has effectively reduced the total reserve. In the HCl-soluble fraction, the supposedly weatherable fraction, these differences were much smaller and led Thorvaldsson et al. (2003) to conclude that K must either have been released from the slowly weatherable fraction or taken up from greater depths. This suggest that K is released from the slowly weatherable reserve. This would mean that a total K analysis is necessary to access the reserves of K in this soil. The rate of release can be estimated from the negative input – output balance. Losses through leaching are not known but are probably very low as potassium is lacking. This would give a release of 28 – 43 kg ha^{-1} per annum. This is a large amount although it is within the weathering rate of 3 – 80 kg K ha^{-1} in a range of northern European soils (Holmquist et al. 2003). If the annual negative input – output balance of 30 – 40 kg K ha^{-1} remained, the reserves in the top 600 t soil ha^{-1} would last for another 60 – 100 years.

The exchangeable K fraction was in all cases highest in the top 5 cm of the soil and decreased to very low values as soon as at a depth of 5 – 10 cm. Similarly the fertilizer application had not resulted in differences in exchangeable K which may be explained by the fact that in all cases less K was applied than removed by the crop. However, high exchangeable K in the top few cm of the soil and low below seems to be characteristic of Icelandic soils as similar results have frequently been reported (Helgason 1975, Ólafsson 1978, Gudmundsson & Sigvaldason 2000). The exchangeable Na was of a similar magnitude in the top 5 cm as exchangeable K and changed only slightly with depth, and in lower horizons it was substantially higher than exchangeable K. This finding is again consistent with earlier findings in Icelandic soils. The relatively high exchangeable Na can be associated with the high inputs through precipitation as well as a large reserve in the soil.

Potassium was measured in the harvest at irregular intervals from 1959 – 1996. The K content of the harvested grass was highest in the early years ranging form 2.0 – 2.7 %, depending on treatment. From 1985 values above 2% K in the harvest have been rare and the mean in all plots had decreased to 1.75 % in 1996. Thus the depletion of potassium from the soil has apparently affected the uptake and content in the grass. This is a clear indication that a long- term negative potassium balance in Icelandic hay fields will not only reduce the potassium reserves in the soil but also affect the quality of the yield. This raises the question of how to sustain the soil fertility and ensure that the soils will not be degraded in terms of potassium reserves and availability.

Phosphorus

The positive P balance in the fertilized plots has led to a substantial build-up of phosphorus in the soil. This build-up, which was greatest in the top 5 cm and leveled out at 10 – 20 cm depth, showed how strongly the P was bound in the soil. After balancing the P by comparing the content in the fertilized plots with the unfertilized area, the surplus P can be accounted for by using the HCl-soluble fraction (Thorvaldsson et al. 2003). Under permanent grassland surplus P is apparently always associated with the very top few cm of the soil (Gudmundsson & Sigvaldason 2000). The present results show that it is bound in the HCl-soluble fraction. Helgason (2002) showed that up to 70% of phosphorus in the soil is organically bound. At Skriðuklaustur with 120 – 229 g C kg^{-1} soil the organic binding of P is likely to play a major role, together with amorphous allophane and iron or iron aluminium complexes, which are known to have high affinity for binding P (Dahlgren et al. 2004).

CONCLUSIONS

Long-term use of acidifying ammonium sulphate not only reduces the pH and increases the organic matter but has a considerable effect on the Ca and Mg content. The long-term buffering in the soil is through release of calcium, where both the HCl-soluble reserve and the HCl-insoluble reserve make a contribution. However, magnesium is only released from the HCl-soluble pool. The potassium reserves were very small and the total K was the long-term reserve in the soil. The negative input – output balance and a reduction in total K did not show up in less exchangeable K or in less HCl-soluble K compared to the unfertilized area. However there was a reduction in the uptake of potassium with time suggesting that a long term negative potassium balance had reduced the rate of transfer from the reserve to the readily available fraction. The limited K reserves did not allow a long-term negative input – output balance of potassium. Surplus fertilizer was either weakly or moderately strongly bound. The surplus calcium was exchangeable, whereas the surplus phosphorus was AL-extractable only to a small extent. The phosphorus was mainly HCl-soluble and thus in a reserve that should be releasable and accessible for the ecosystem.

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