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Physiochemical properties of soils at Risdalsheia and Sogndal: RAIN project.

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Norwegian Institute for Water Research NIVA

Royal Norwegian Council for Scientific and Industrial Research

Address:
Postbox 333, Blindern
Oslo 3
Norway

Telephone:
47 2 23 52 80

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Author(s):

Erik Lotse
Erasmus Otabbong

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Abstract:

The RAIN project investigates the interactions between acid deposition, vegetation, soil and water. This report present physical and chemical properties of soil samples collected in the fall of 1982. These are background data before the artificial acidification at Sogndal and the exclusion of acid rain at Risdalsheia started.

The Risdalsheia soils are strongly acid with pH (H_2O) values ranging from 3.7 to 4.7. The Sogndal soils are weakly acid with pH (H_2O) values varying between 4.2 and 5.8. The base satruation is lower and the aluminum saturation higher at Risdalsheia than at Sogndal. The Al-pH relationship is also different in the two soils. The concentration of water-soluble SO_4-S is higher and the concentration of adsorbed SO_4-S lower at Risdalsheia than at Sogndal.

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Physicochemical Properties of Soils at Risdalsheia and Sogndal: RAIN Project

Erik Lotse and Erasmus Otabbong
Department of Soil Science
Swedish University of Agricultural Sciences
Box 7014, 750 07 Uppsala

Oslo, 20 May 1985

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1. INTRODUCTION

The physicochemical and biochemical reactions between water, bedrock, soil, sediment, and gases, as influenced by vegetation and microorganisms, produce or consume chemical components. The mechanisms for these processes include dissolution, precipitation, complex formation, hydrolysis of metal complexes, production and decomposition of organic acids, oxidation-reduction, adsorption and desorption, evaporation, nutrient uptake, mineralization, nitrification and denitrification, and transport. Each of these processes occurs with a characteristic rate.

Acidification of soil and water by biological acid formation, atmospheric deposition, oxidation of S, Fe and N, and (when applicable) fertilization is counterracted by weathering and ion exchange. In order to understand and describe the acidification process, and the opposite process when the acid deposition is reduced, we need not only to make a total budget of input and output of various elements but also to quantify the processes in soil and vegetation that are responsible for the difference between input and output. The rate of the physicochemical and biochemical reactions determines the time lag in the acidification and the return to a less acid state, respectively.

The interactions between atmospheric deposition, vegetation, soil and water are studied in the RAIN project (Wright, 1985). The objectives are to describe the processes and mechanisms of acidification and to predict the changes in the biogeochemical processes and the time lag for improvement of the surface water chemistry, after the acid disposition has been reduced, with the help of models.

Two small catchments at Sogndal, which up to a year ago were not subject to strong acidification, are now acidified by irrigation with acid "rain". One catchment receives H_2SO_4 and another a 1:1 mixture of H_2SO_4+HNO_3. Two strongly acidified catchments at Risdalsheia have been shielded from acid deposition by means of roofs. The effects of changed deposition on vegetation, soil, and water are being studied on these four catchments and control catchments in the close vicinity. The proton production and proton consumption of the biogeochemical processes, the export of base cations to the runoff waters, and the decrease in acid neutralizing capacity of the soils are being investigated.

Two key processes that have been studied are cation exchange and sulfate adsorption. The results discussed pertain to soil samples collected in the fall of 1983 and represent the starting-point before the manupulation of the environment. Samples of soils and plants were collected again in August 1984 and will be collected and analyzed each year. In this way it will be possible to quantify the leaching of base cations and acid cations, the decrease in base saturation, the selectivity of ion exchange, the change in CEC through sulfate adsorption and other factors, the weathering, and the mineralization of organic substances.

2. MATERIALS

2.1. Sogndal

The catchments at Sogndal are underlain by siliceous gneiss covered with thin poorly-developed soils.

The vegetation consists mainly of Betula verrucosa, Betula nana, Juniperus communis, Salix hastata, Empetrum nigrum, Vaccinium Myrtillus, Vaccinium uliginosu,, Vaccinium Vitis-idaea, Calluna vulgaris grasses, mosses and lichens. A typical profile is described below.

Classification: Lithic Haplumbrept, sandy, siliceous, frigid
Location: Sogndal, Sogn and Fjordane country, Norway
Physiographic position: Top of a mountain ridge.

OO 12-5 cm. Mat of Calluna vulgaris, Empetrum nigrum, Vaccinium Myrtillus, Vaccinium uliginosum, Vaccinium Vitis-idaea, mosses and lichens, clear boundary.

O1 5-10 cm. Black (10YR 2/1) mat of partly decomposed roots and other plant parts; abundant roots; very strongly acid; clear boundary.

A11 0-6 cm. Very dark brown (10YR 2/2) sandy loam; very fine, weak, crumb, soft; abundant roots; very strongly acid; gradual boundary.

A12 6-11 cm. Very dark brown (10YR 2/2) and light gray (10YR 7/1) loamy sand; very fine, weak, crumb; loose; abundant roots; very strongly acid; gradual boundary.

A/B 11-15 cm. Dark yellowish brown (10YR 3/4) loamy sand; single grain; loose; many roots; strongly acid; gradual boundary.

B21 15-20 cm. Dark reddish brown (5YR 3/3) loamy sand; single grain; loose; many roots; strongly acid; gradual boundary.

B22 20-23 cm. Reddish brown (5YR 4/3) gravelly sand; single grain; loose; few roots; medium acid.

R 23 cm. Siliceous gneiss.

2.2. Risdalsheia

The area is underlain by granitic rocks covered by thin soils.

The vegetation at Risdalsheia is similar to that of Sogndal except that here pine (*Pinus sylvestris*) and spruce (*Picea abies*) are also present. The soils are also similar except that the pH is almost one unit lower at Risdalsheia than at Sogndal.

3. METHODS

3.1. Sample collection

The sampling at Risdalsheia was designed to minimize the standard error of the spatial component. Samples were collected at 1 m intervals along transects across each catchment. A fixed number of soil cores were taken from each point. A 25-mm diameter auger was used. The cores were split into 3 levels - 0-15, 15-30, and >30 cm. The soil from each transect were composited into 3 samples, one from each depth.

At Sogndal samples were collected from 11 pits and split into 3 levels - 0-15, 15-30 and > 30 cm.

3.2. Analytical procedures

3.2.1. Sample preparation

Samples were weighed and subsamples taken out for determination of the dry matter content. The samples were passed through a 4-mm sieve and homogenously mixed. The coarse and 4 mm fractions were weighed and the dry weight of each fraction calculated. Organic material was ground in a mixer as necessary. One fourth of each sample was dried at 35°C and stored in a closed plastic container. The remainder of the sample was placed in a plastic container and stored at +3°C.

3.2.2. Soil pH

Weigh in duplicate 10 g of the undried 4-mm fraction and place each replicate in a 30-ml centrifuge tube. Add 10 ml of deionized H_2O. A little more water may be required in case of humus. Mix thoroughly with a glass rod. Close the tubes and let stand overnight. Mix again and measure pH using a glass electrode compared to a calomel electrode. The pH values of the standard buffer solutions and the slurry are recorded to an accuracy of ±0.01 pH units. The pH (H_2O) of a sample obtained in that way is abbreviated pHw in the determinations following the present one. Obtain the pH in 1M KCl in a similar way as described above.

3.2.3. Exchangeable (KCl) acidity, exchangeable alumium and hydrogen (Yuan, 1959, 1963)

3.2.3.1. Exchangeable (KCl) Acidity

3.2.3.1.1. Reagents

1M KCl - Dissolve 74.56 g KCl (pro.anal.) in 800 ml of deionized H_2O and make to volume (1,000 ml) using deionized water.

0.1N HCl - Dilute 100 ml of 1N HCl stock solution to 1 liter using deionized H_2O. The solution is standardized against sodium oxalate using methyl orange as an indicator.

0.1N NaOH - Dilute 100 ml of 1N NaOH solution to 1 liter using deionized H_2O. The solution is standardized against the standard 0.1N HCl using phenolphthalein as indicator. Connect a soda-lime tube to the air inlet to prevent CO_2 absorption.

3.2.3.1.2. Extraction

Weight in pairs 5 g of the undried <4 mm fraction and place each sample into a 50 ml centrifuge tube. Add 25 ml of 1M KCl solution to each tube. Close the tubes with rubber stoppers and shake, first by hand (to make sure the contents are mixed) and then on a shaker for 30 minutes. Centrifuge the (opened) tubes at 5,000 r.p.m. for 5 minutes. Carefully decant through a funnel into a 100 ml volumetric flask. Repeat the operations 3 more times, collecting the extract in the same flask each time. Bring the contents of the flask to the 100 ml mark using the extractant. Pressure filter the extract first through a Whatman 44 ashless filter paper and then through an 0.45 µm millipore filter. (The filters are rinsed with 10 ml of 0.01N HCl followed by 2x200 ml deionized H_2O prior to filtration.) 1M KCl blank is also filtered and analyzed. Measure the pH of the KCl extract. Store the extracts in clean polypropylene bottles at +4°C.

3.2.3.1.3. Determination of exchangeable (KCl) acidity

Take 50 ml of the KCl extract and place into a 150 ml Erlenmeyer flask. Add 2 drops of phenolphthalein solution (1 % phenolphthalein prepared using 95 % ethanol as a solvent). Swirl the flask. Bubble N_2 into the extract (Fig. 1). Titrate to a permanent pink endpoint using the standardized 0.1N NaOH. The reactions involved in determining total exchangeable acidity by titration of the extract with base are:

$H^+ + OH^- = H_2O$
$Al^{3+} + 3OH^- = Al(OH)_3$

The exchangeable (KCl) acidity is calculated using the following equation:

$$X = (S-B)cNV100/vg;$$

where
x = meq exchangeable (KCl) acidity/100 g d.m.
B = ml of 0.1N NaOH consumed during titration of 50 ml of blank, 1M KCl
S = ml of 0.1N NaOH consumed during titration of 50 ml of test solution
c = coef. to convert X to content of the acidity per unit d.m. (subheading 9)
N = normality of NaOH
V = total volume of extract
100 = coef. to convert acidity/gram d.m. to acidity/100 g d.m.
v = volume of extract taken
g = wt of sample

3.2.3.2. Exchangeable Al^{3+}

3.2.3.2.1. Determination of Al^{3+} by titration

Add 1 drop of 0.1N HCl to bring the solution back to the colorless condition. Add 2 ml of 4 % NaF (40 g NaF/liter deionized H_2O) to the titrated KCl extract. Al in the $Al(OH)_3$ is converted to a stable complex of fluoraluminate, Na_3AlF_6, and NaOH is produced. Using 0.1N HCl solution, titrate the NaOH to a colorless endpoint. The reactions are as follows:

$Al(OH)_3 + 6NaF = 3NaOH + Na_3AlF_6$
$NaOH + HCl = H_2O + NaCl$

Compute exchangeable aluminum as shown for exchangeable (KCl) acidity. Alternatively, exchangeable Al may be determined photometrically according to the procedure described under 3.2.3.2.2 (Dougan and Wilson 1974) or by atomic absorption spectrophotometry.

3.2.3.2.2. Determination of Al by photometry

3.2.3.2.2.1. Reagents

Solution 1 - 140 g hydroxylammonium chloride ($HONH_3Cl$) and 14 g 10-phenanthroline monohydrate ($C_{12}H_8N_2 \cdot H_2O$) is dissolved in deionized H_2O and made to 1,000 ml using the H_2O. The solution is stable for at least 3 months.

Solution 2 - Dissolve 0.21g 3,3,4-trihydroxofucson-2-sulfonacid (pyrocatechol violet) $C_{19}H_{14}O_7S$ in deionized H_2O and bring to 1,000 ml using the H_2O and filter the solution. The solution is stable for at least 3 months.

Solution 3 - 390 g hexamethylenetetramine $(CH_2)_6N_4$ is dissolved in 600 ml deionized H_2O. Add 22.8 g NaOH or 10 ml NH_4OH (s.p. 0.900) and make to 1 liter using deionized H_2O. This solution is stable for at least 3 months.

Al-standard - Dissolve 1.757 g $KAl(SO_4)_2 \cdot 12\,H_2O$ (pro. anal.) in 90 ml deionized H_2O. Bring the solution to 100 ml using the H_2O. This is Al-standard - A and contains 1 mg Al/ml. Dilute 1 ml of Al-standard A to 100 ml using deionized H_2O. This is Al-standard B and contains 0.01 mg Al/ml. Dilute 10 ml of Al-standard B to 100 ml using deionized H_2O. This is Al-standard C and contains 0.001 mg Al/ml.

3.2.3.2.2.2. Determination of Al

From the extract, measure 25 ml and place in a 50 ml volumetric flask. From Al-standard C, measure 0, 2, 4, 10, 20 and 30 ml, placing each amount into a 50 ml flask. Bring the standard flasks to 40 ml using 1M KCl solution. Now add to each flask (including the one containing the extract) 2 ml of 0.1N HCl, 0.5 ml of Solution 1, 1 ml of solution 2 and 5 ml of solution 3, mixing the contents after every addition. Solution 3 is added so that pH 6.0-6.2 is achieved. Make the flasks to 50 ml using 1N HCl. Read the absorbance at 585 nm on a Vitatron or Beckman Model B spectrophotometer, the reference cuvette being filled with deionized water.

$X \quad = 100\ abc/9g$

X = meq Al/100 g d.m.
a = mg Al from calibr. curve
b = dilution factor
c = coef. to convert X to content of Al per unit d.m.
100 = coef. to convert meq/g d.m. sample to meq/100 g d.m.
9 = equivalent wt of Al
g = wt of sample used

3.2.3.3. Exchangeable H^+

Exchangeable H^+ is calculated by subtracting exchangeable Al^{3+} from the exchangeable (KCl) acidity. It is also obtained from the pH of the KCl extract.

3.2.4. Exchangeable acidity ($BaCl_2$-TEA) (Peech 1965)

3.2.4.1. Reagents

0.5N $BaCl_2$. Dissolve 61 g $BaCl_2$ (pro. anal.) in 800 ml deionized H_2O. Mix 28 ml of 7.5N triethanolamine (TEA) with 4 ml of 6N HCl. The solution obtained is added to the $BaCl_2$ solution. Adjust the $BaCl_2$-TEA solution to pH 8 ± 0.02 using 2N TEA solution or 0.1N HCl. Make the solution to 1 liter using deionized H_2O. Connect a sodalime tube to the air inlet to prevent CO_2 absorption.

Mixed indicator. Dissolve 0.22 g bromcresol green and 0.075 g methyl red in 96 ml of 95 % ethanol containing 3.5 ml of 0.1N NaOH. Make to 100 ml using ethanol.

2N TEA. Dilute 133 ml of 7.5N TEA to 500 ml using deionized H_2O. Standardize against 0.1N HCl to the endpoint (pink) of the mixed indicator.

3.2.4.2. Extraction

Weigh in duplicates 5 g of the undried <4 mm fraction and place each replicate in a 50ml centrifuge tube. Add 25 ml of $BaCl_2$-TEA solution, mix the contents with a glass rod, close the tubes and shake for 30 minutes. Centrifuge at 5,000 r.p.m. for 5 minutes and decant the supernatant into a 100ml volumetric flask. Repeat the operations 3 times. Make the contents of the flasks to the 100ml mark using the extractant. Then filter the extract and 100ml blank as described under subheading 3.2.3.1.2.

3.2.4.3. Determination

Transfer quantitatively the extract to a 200 ml E flask and add 5 drops of the mixed indicator solution. Titrate to the pink endpoint with 0.1N HCl. Titrate the blank to the same endpoint.

$$X = (B-S)100\ cN/g$$

where

X = meq exchangeable ($BaCl_2$-TEA) acidity/100 g d.m.
B = ml of 0.1N HCl expended in titrating blank $BaCl_2$-TEA
S = ml of 0.1N HCl expended in titrating extract
c = coef. to convert X to content of the acidity per unit d.m.
N = normality of HCl
100 = coef. to convert meq/d.m. to meq/100 g d.m.
g = wt of sample taken

3.2.5. Cation exchange capacity measured at pH 7 (CEC pH 7)

3.2.5.1. Reagents

1N $CA(OAc)_2$-pH 7 - Dissolve 79 g $Ca(OAc)_2$ (pro.anal.) in 800 ml of deionized H_2O. Add 3 drops of toluine. Adjust the solution to pH 7 using 0.04N $Ca(OH)_2$ or 1N HOAc. Make the solution to 1 liter using deionized water.

1N NH_4OAc-pH 7 - Dissolve 77 g NH_4OAc (pro. anal.) in 800 ml deionized H_2O. Adjust to pH 7 using 1N NH_4OH. Bring the solution to 1 liter using deionized H_2O.

Ca-standard - Empty the contents of 1 ampule of $CaCl_2$ (1,000 ml Ca) in a 1 liter flask. Dilute the solution to 1 liter using 1 % HCl. Designate the solution Ca-standard A. The solution contains 1,000 ppm Ca or 1 mg Ca/ml. Dilute 20 ml of Ca-standard A to 1 liter using the acid. The new solution contains 20 ppm Ca or 0.02 mg Ca/ml. Designate the solution Ca-standard B.

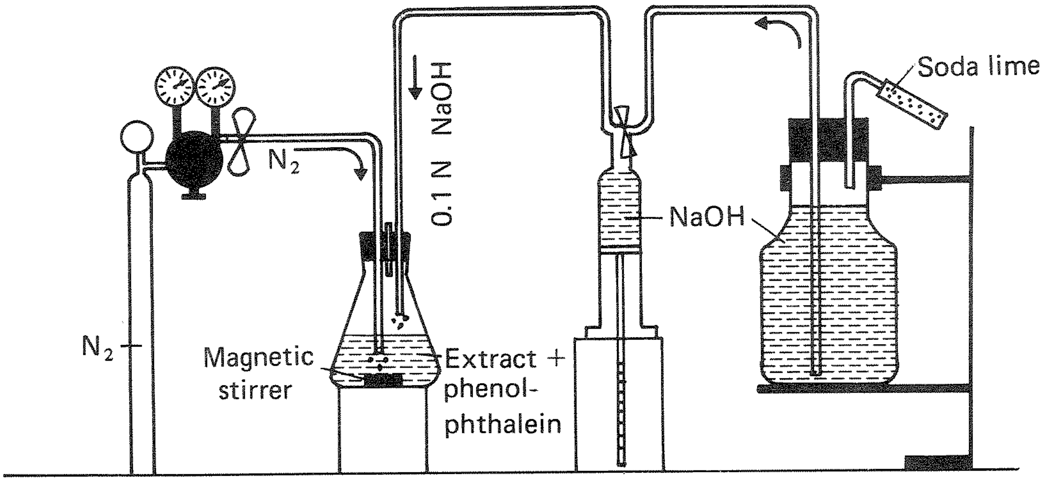

Figure 1. Scheme for titration of total exchangeable acidity.

<u>0.05M $LaCl_3 \cdot 7\ H_2O$</u> - Dissolve 18.57 g $LaCl_3 \cdot 7\ H_2O$ (pro. anal.) in 40 ml 12N HCl. Make solution to 1 liter using deionized H_2O.

3.2.5.2. Extraction

Measure in pairs 5 g of the undried <4 mm fraction, placing each replicate into a 50 ml centrifuge tube. Add 25 ml of 1N $Ca(OAc)_2$-pH 7 solution. Mix the contents using a glass rod. Close the tube using a plastic stopper, shake for 30 minutes, centrifuge at 5,000 r.p.m. for 5 minutes and discard the extract. Repeat the operations 3 more times. Now add 25 ml deionized H_2O, mix the contents, shake for 30 minutes, centrifuge at 5,000 r.p.m. for 5 minutes and discard the supernatant. After washing the sample 5 times with H_2O and methanol, add 25 ml of 1N NH_4OAc-pH 7 solution and follow the above procedure up to centrifuging. At this point, the supernatant is carefully decanted through a funnel into a 100ml volumetric flask. Repeat the operation 3 more times and collect the washings in the same flask each time. Make up the contents of the flask to the 100 ml mark using

1N NH_4OAc-pH 7 solution. Should the extract be unclear or contain suspended matter, filter as described under subheading 3.1.2.

3.2.5.3. Measurement of Ca

Depending on the type of sample take a known volume of the extract and dilute. Transfer 50 ml of mineral soil extract or 10 ml of organic soil extract into a 100-ml volumetric flask, add 2 ml of 0.05M $LaCl_3$ solution and bring the solution to 100 ml using 1N NH_4OAc-pH 7 solution. From the Ca-standard B take 0, 2, 4, 6, 10, 40 and 80 ml and add 2 ml of the 0.05M $LaCl_3$ solution to each aliquot. Bring the contents of the flasks to the 100 ml mark using the 1N NH_4OAc-pH 7 solution. Determine Ca by atomic absorption spectrophotometry at 422.7 nm.

Comments: The $LaCl_3$ and LiCl mixture (7.2) may be used instead of $LaCl_3$ alone. This could not only economize chemicals but also time and space.

$X = 100abc/20g$

where

X = meq Ca adsorbed per 100 g d.m. and equals CEC pH 7
a = mg Ca obtained from the calibration curve
b = dilution factor
c = coef. to convert X to Ca content per unit d.m.
20 = equivalent wt of Ca
g = wt of sample used
100 = coef. to convert meq/g d.m. to meq/100 g d.m.

3.2.6. Cation exchange capacity measured at soil pH (KCl) and pH 8

The cation exchange capacity at the soil pH (KCl) is calculated as the sum of milliequivalents of exchangeable (KCl) acidity and exchangeable base cations per 100 g of soil.

The CEC pH 8 is calculated as the sum of milliequivalents of exchangeable ($BaCl_2$-TEA) acidity and exchangeable base cations per 100 g of soil.

3.2.7. Exchangeable cations (Thomas 1982)

3.2.7.1. Extraction

The exchangeable basic cations (Ca, Mg, K and Na) are extracted using 1N NH_4OAc adjusted to pH 7. Pairs of 5 g of the undried <4 mm fraction are taken from each sample and extracted successively 4 times using 25 ml of 1N NH_4OAc pH 7 each time. The same procedures as those described for the extraction of adsorbed calcium during the measurement of CEC pH 7 are followed.

3.2.7.2. Standard reagents

Ca - Use Ca-standard B prepared as described under subheading 5.1.

Mg - Empty quantitatively 1 ampule of $MgCl_2$ in 1-liter flask. Bring the flask to 1 liter mark using 1 % HCl. This is Mg-standard A. It contains 1,000 ppm Mg or 1 mg Mg/ml. Dilute 10 ml of Mg-standard A to 1 liter using 1 % HCl. This is Mg-standard B and contains 10 ppm Mg or 0.01 mg Mg/ml.

K - Empty 1 ampule of KCl into a 1-liter flask. Dilute to 1 liter using deionized H_2O. This is K-standard A. It contains 1,000 ppm K or 1 mg K/ml. Dilute 20 ml of K-standard A to 1 litre using deionized H_2O. This is K-standard B and contains 20 ppm K or 0.02 mg K/ml.

Na - Empty 1 ampule of NaCl in a 1-liter flask and dilute to 1 liter using deionized H_2O. This is Na-standard A, and it contains 1,000 ppm Na or 1 mg Na/ml. Now dilute 20 of Na-standard A to 1 liter using deionized H_2O. The solution contains 20 ppm Na or 0.02 mg Na/ml. This is Na-standard B.

$LaCl_3$ + LiCl - Dissolve 18.57 g $LaCl_3 \cdot 7\ H_2O$ (pro. anal.) in 40 ml of 12N HCl. Make the solution to 500 ml using deionized H_2O. Dissolve 6.36 g $LiCl_3$ (suprapur) in 40 ml 12N HCl and make to 500 ml using deionized H_2O. Now mix the $LaCl_3$ and LiCl solutions. The mixture contains 0.05M $LaCl_3$ and 0.15M LiCl.

3.2.7.3. Measurement of cations

Take 20 ml of the extract and 0, 2, 4, 6, 10, 20, 60 and 80 ml from each of the B standard solutions for Ca, Mg, K and Na. Add 2 ml of the $LaCl_3$ and LiCl mixture to the extract and 8 ml of the mixture to the standard aliquots. Make the standard solutions to 100 ml and the extract to 25 ml using 1N NH_4OAc pH 7. The cations are measured by atomic absorption spectrophotometry at 422.7, 285, 765 and 589 nm for Ca, Mg, K and Na, respectively. Prepare a calibration curve for each cation. Finally, determine exchangeable ammonium by ion chromatography using an aliquot from the KCl extract described under 3.1.2.

Comments: If the extract requires dilution, measure the cation in a separate aliquot diluted to the required concentration.

X = 100 abc/dg

where

X = meq cation/100 g d.m.

a = mg cation on calibration curve

b = dilution factor, if dilution is made

c = coef. to convert X to meq cation per unit d.m.

d = equivalent wt of cation

g = wt of sample used

100 = coef. to convert d.m. of sample to 100 g d.m.

3.2.8. Total nitrogen and carbon

Total nitrogen and carbon are determined simultaneously by a Carlo Erba Elemental Analyzer Model 1106. The method is based on dry combustion of the sample (ground to pass through a 0.08 mm sieve) in an oxygen-helium atmosphere, reduction over copper, and gas chromatographic separation and determination of the combustion products.

3.2.9. Coefficient c

The content of a substance or element in a soil is usually expressed per unit wt of 105°C oven dried matter (d.m.) of the soil. The multiplying factor (coefficient) is designated here as c and is obtained as described below.

Dry two small glass cups with covers at 105°C, cool in a desiccator and weigh. Place in each cup 5 g of the undried <4 mm fraction. Denote the weight of the undried sample a. Allow the samples to dry at +35°C in the open cups. Now place the cups (+ sample) in an electric oven set to 105°C and allow to stand there for 5 hrs. (The covers of the cups should also be in the oven.) Close the cups and cool in an desiccator. Weigh the sample + the covered cup and obtain the weight of the dry soil by subtracting the weight of the cup + cover from the total weight. Designate the weight of the dry soil b.

$X = 100\ (a-b)/c$

where

X = % water in the soil

$a-b$ = wt of water

c = $(100 + X)/100$

3.2.10. Loss on ignition

Weigh in duplicate 1 g of air-dried and finely ground (<0.08 mm) soil into two tared porcelain crucibles with covers. The weight of crucible + sample is denoted (a). Place the crucibles in an electric oven adjusted to 105°C. Dry the samples for 6 hrs. Fit the covers on the crucibles, cool in a desiccator and weigh the crucible + cover + dried soil. Denote the weight (b). The weight of dry matter (c) = a-b.

Place the crucible + dried soil in an electric oven and raise the temperature gradually to 600°C. Keep the sample at that temperature for 2 hrs, cover the crucible, cool in a desiccator and weigh. Repeat the operations until a constant weight is achieved. Denote the final weight (d).

The weight of ignited soil (e) = b-d. The loss on ignition (f) = c-e grams. The loss on ignition in percent (g) = f/c x100.

3.2.11. Water-soluble sulfur

3.2.11.1. Apparatus

200-ml centrifuge tubes, 100-ml conical flasks, 150-ml funnels, millipore filters (<.22 µm) and a temperature-controlled centrifuge.

3.2.11.2. Extraction (Freney 1958)

Weight in duplicate undried (<4 mm sieved) soil equivalent to 4 g dry matter into 40-ml centrifuge tubes.

Add 20 ml deionized H_2O, stopper the tubes (plastic stoppers) and shake them on a reciprocating shaker for 30 minutes.

Centrifuge the suspension at 4,000 r.p.m. for 5 minutes. Filter the supernatant through a millipore filter (<.22μm) which has previously been washed 3 times with deionized H_2O. Preserve the soil residue for the determination of adsorbed S as described under the next subheading. In order to check if the pad adsorbed some S, take 2 equal known volumes of deionized H_2O, add 20 μg S to each and filter in the same way as for the soil extracts. Determine S in the soil extracts as well as in the check samples. Correct the results for the S held, if any, by the filter pad. The results are expressed per unit weight of oven-dried (105^oc) samples. If the determination is not performed immediately after extraction, store samples in tightly closed plastic bottles at 3^oC.

3.2.11.3. Determination (Dick and Tabatabai 1979)

Determine SO_4^{2-} in the extract by ion chromatography.

3.2.12. Adsorbed sulfur

3.2.12.1. Background

Different solutions (NH_4OAc-HOAc, KH_2PO_4, $Ca(H_2PO_4)_2$, $Ca(C_2H_3PO_4)_2$, KCl, LiCl, $NaHCO_3$, etc) have been used to obtain soil-sorbed S. However, many researchers prefer using a solution of calcium monophosphate monohydrate - $Ca(H_2PO_4)_2 \cdot H_2O$. The Ca ion flocculates soil colloids and PO_4^{2-} displaces the sorbed SO_4^{2-}. In contrast, KH_2PO_4 usually produces turbid extracts difficult to filter. Therefore, Dick & Tabatabai (1979), and others, recommended a solution of $Ca(H_2PO_4)_2$ for the extraction of SO_4^{2-} from soils.

3.2.12.2. Reagents

Dissolve 0.407 g $Ca(H_2PO_4)_2 \cdot H_2O$ (pro. anal.) in 700 ml of deionized H_2O. Adjust the solution to 1 liter using H_2O. This solution contains 100 ppm P.

3.2.12.3. Extraction

Add 25 ml of $Ca(H_2PO_4)_2$ solution to the soil residue obtained after the removal of water-soluble S as described under the previous subheading.

Stopper the tube, mix the contents, shake, centrifuge and filter the supernatant as described earlier. Repeat the operation 3 times, collecting the supernatant in a 100-ml volumetric flask. Bring the contents of the flask to 100 ml using the extractant. Carry through the operations with two check solutions as described under 3.2.11.2.

3.2.12.4. Determination

Determine SO_4^{2-} in the extract by ion chromatography (Dick and Tabatabai 1979).

3.2.13. Total sulfur

Total sulfur in soils and plants is determined by the LECO SC-32 Sulfur Analyzer. The performance of this instrument has been evaluated by The South Midlands Area Laboratory, Great Britain. The results obtained from the instrument show good reproducibility and good agreement with British Standard methods (BS 1016 Part 6) as shown in Tables 3 and 4 which are copied from the South Midlands Area Laboratory report.

3.2.14. Sulfate adsorption isotherms

Wash undried <4mm soil equivalent to 5 g of oven-dried material once with deionized water in a weighed centrifuge tube. Weigh tube + soil. Shake the soil with 50 ml of a K_2SO_4 solution of known concentration for 24 h at $20^{\circ}C$. The S concentrations to be used are 1, 2, 3, 4, 5, 10, 20, 40, 60 and 100 mg per liter. Centrifuge the suspension at 4,000 r.p.m. for 5 minutes by a temperature-controlled contrifuge. Filter the supernatant through a millipore filter (<.22µm) which has previously been washed 3 times with deionized H_2O. Check the filter for S adsorption as described under 11.2 and correct for the S held, if any.

Determine the concentration of S in solution by ion chromatography. Calculate the amount of S adsorbed as the difference between the initial and final concentration (the latter corrected for dilution). Express the results in mg of S adsorbed per kg of oven-dried (105^{o}C) soil.

4. RESULTS AND DISCUSSION

4.1. Total Elemental Carbon, Nitrogen and Sulfur

The contents of total carbon, nitrogen and sulfur are given in Tables 1 and 2. The carbon content is high for both soils. The average C contents are 17.52 and 7.59 per cent at depths 0-15 and 15-30 cm, respectively, in Risdalsheia soils and 15.13 and 9.59, respectively, in Sogndal soils.

The nitrogen contents vary between 0.16 and 1.28 per cent and decrease with depth. The carbon:nitrogen ratios vary between 15 and 26 and are about the same in Risdalsheia and Sogndal soils.

The contents of total sulfur vary between 0.031 and 0.161 per cent in the Risdalsheia soils and between 0.010 and 0.107 in the Sogndal soils. On an average the sulfur content at 0.15 cm depth is slightly highter in Risdalsheia soils (0.080 per cent) than in Sogndal soils (-0.061 per cent). The carbon:sulfur ratio varies between 101 and 320 and is slightly higher in Sogndal than in Risdalsheia soils.

4.2. pH and Exchangeable Acidity

The pH (H_2O) and the exchangeable acidity are given in Tables 1 and 2, and the pH (KCl) is given in Tables 3 and 4. The Risdalsheia soils, which have received very acid deposition, are stongly acid with pH (H_2O) values ranging from 3.70 to 4.71 and pH (HCl) values ranging from 2.95 to 4.16. The Sogndal soils, which receive a relatively clean precipitation, are weakly acid with pH (H_2O) values varying between 4.16 and 5.80 and pH (KCl) values varying between 4.13 and 5.03. The pH increases with increasing depth in both soils.

The exchangeable acidity is very high in the Risdalsheia soils. On average it is 80 and 88 per cent of the CEC at pH (KCl) at depths 0-15 and 15-30 cm, respectively. It increases with increasing pH and is on an average 95.5 and 97 per cent of the CEC at pH 8 at depths 0-15 and 15-30 cm, respectively. The average value of the exchangeable acidity, exchangeable (KCl)H^++Al^{3+}, for field 1 (KIM), 0-15 cm, is 14.0 meq $100g^{-1}$.

In the Sogndal soils the exchangeable acidity is on an average 73 and 76 per cent of the CEC at pH (KCl) and 92 and 95 per cent of the CEC at pH 8 at depth 0-15 and 15-30 cm, respectively. The average value for field 2, 0-15 cm, is 6.8 meq 100 m^{-1}, i.e., less than half of the exchangeable acidity of the Risdalsheia, field 1 soil.

The sources of exchangeable acidity are mainly organic matter, organometallic complexes, aluminosilicate clay minerals, hydroxy compounds of iron and aluminum oxides and oxidation of N, S and Fe.

The organic matter not only furnishes acidity by dissociating hydrogen from functional groups, but also complexes metal ions such at iron and aluminium. Hydrolysis of these organometallic complexes contributes to acidity. In addition as organic matter decomposes, acid-forming ions (hydrogen, aluminum, iron and sulfur) are liberated into solution and increase soil acidity.

Protons attack aluminosilicate minerals and release aluminum and iron ions which compete for cation-exchange sites. The buffering intensity - the amount of strong acid or base required to change the pH of a system by a given amount - of minerals depends on their respective solubilities at different pH levels (van Breemen and Wielemaker, 1974). The clay minerals montmorillonite and kaolinite are strong buffers in the pH range of 3 to 4. At pH 4.5 to 6.0, minerals such as microcline feldspar, gibbsite, and clay micas are strong buffers.

Presence of hydroxyaluminum interlayers and coatings strongly affect the solubility of aluminum and the soil acidity, especially in the pH range of 4.5 to 6.5. Further studies are nedded in order to elucidate the relative contribution of each of the above sources to soil and water acidity and to soluble aluminum.

4.3. Exchangeable Cations, CEC, and Base Saturation

The concentrations of exchangeable cations and the base saturation are given in Tables 1 and 2. The sum of exchangeable base cations, S_B, is on an average 3.1 meq 100 g^{-1} at 0-15 cm depth and 0.9 meq

100^{-1} at 15-30 depth in the Risdalsheia soils. The corresponding figures for the Sogndal soils are 2.6 meq 100 g^{-1} at 0-15 cm depth and 1.2 meq 100 g^{-1} at 15-30 cm depth.

The average CEC at the pH (KCl) is 18.2, 8.6 and 8.0 meq 100 g^{-1} at the depth 0-15, 15,30, and >30 cm, respectively, for Risdalsheia, field 1 (KIM). At pH 7 the CEC is 49.1, 22.4, and 16.4 meq 100 g^{-1} and at pH 8 65.5, 33.2, and 28.3 meq 100 g^{-1} at the depth 0-15, 15-30, and >30 cm, respectively. The corresponding figures for Sogndal, field 2, are at pH (KCl) 9.2, 5.8, and 2.4 meq 100 g^{-1}, at pH 7 21.5, 14.8 and 5.7 meq 100 g^{-1} and at pH 8 34.9, 26.7, and 9.0 meq 100 g^{-1}. The much lower CEC of the Sogndal soil than the Risdalsheia soil is mainly due to a lower organic matter content in the former than in the latter.

As can be expected the base saturation is lower in the Risdalsheia than in the Sogndal soils. The average value for the Risdalsheia, field 1 (KIM), soil is 22 per cent at pH (KCl) and for the Sogndal, field 2, soil 28 per cent at the 0-15 cm depth. The cation saturations in per cent of the CEC at pH 7 for the Risdalsheia, field 1, soil at the 0-15 cm depth are 3.6 Ca, 2.1 Mg, 1.1 K, 0.7 Na, and 1.2 NH_4. The corresponding figures for the Sogndal, field 2, soil are 5.6 Ca, 2.5 Mg, 1.4 K, 1.0 Na, and 0.5 NH_4. Of the base cations, Ca has experienced the largest loss through leaching and acidification.

The exchangeable aluminum Al_T, in per cent of the CEC at pH (KCl) is on an average 54 in the surface 15 cm at Risdalsheia and 50 in the surface 15 cm at Sogndal. In per cent of the exchangeable acidity at pH (KCl) it is 68 for Risdalsheia soils and 67 for Sogndal soils at 0-15 cm depth.

The natural logarithm of exchangeable aluminium as a function of pH is shown in Figures 1 and 2. It is evident that the Al-pH relationship for Risdalsheia soils is different from that of Sogndal soils. The Risdalsheia soils are on the borderline between the cation exchange buffer range (pH 4.2-5.0) (Ulrich et al., 1979). The Sogndal

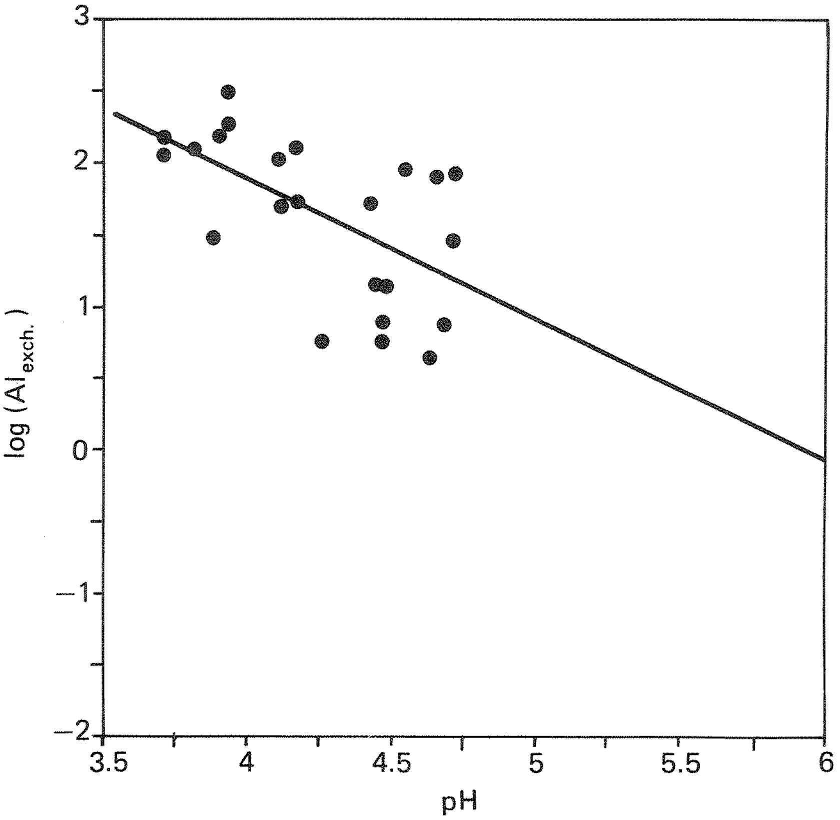

Figure 2. The natural logarithm of exchangeable aluminum as a function of pH for Risdalsheia soils. Least-squares regression gives log(Al exch.) = 5.7-0.96 pH, r = 0.58, n = 23.

soils, on the other hand, are in the carbonic acid/silicate neutralization range (pH 5.0-6.2). A mineralogical investigation is needed in order to explain more fully the differences between the Risdalsheia and the Sogndal soils with respect to the Al-pH relationships.

4.4. Organic Carbon and Exchangeable Aluminum

Organic acids, released by the decomposition process, complex aluminum and facilitate its transport. The carbon:aluminum ratio of the complexes usually decreases during the transport through the soil profile (due to microbial oxidation of organic matter and complexation of mineral aluminum by organic matter). This trend, common for podzolized soils, is not evident, however, for the soils at Risdalsheia and Sogndal (one exception being field 1 at Sogndal). Table 5 shows that the average organic carbon:exchangeable aluminum ratio is practically constant for fields 1 and 2 at Risdalsheia and increases with depth for fields 1, 2 and 4 at Sogndal. Apparently the transport of complexed Al and the oxidation of organic matter are not extensive in these soils.

4.5. Ratios between Exchangeable Cations

The ratios between exchangeable cations are given in Tables 1 and 2. It is interesting to note that the H:Ca, K:Ca, Na:Ca, and NH_4:Ca ratios are high, especially in the very acid Risdalsheia soils, and that the ratios increase with increasing depth. Apparently the selectivity for monovalent cations as compared to that for divalent cations increases with decreasing base saturation. On the other hand, the monovalent cation:aluminum ratio decreases with decreasing base saturation and is lower for the Risdalsheia than for the Sogndal soils. The selectivity for aluminium increases with decreasing pH.

The divalent cation:aluminum ratio depends on per cent organic matter, mineralogical composition, and pH. Hydroxyaluminum polymers neutralize a large part of the permanent charges.

4.6. Water-soluble and Adsorbed SO_4-S

The concentration of water-soluble SO_4-S is higher and the concentration of adsorbed SO_4-S is lower in the Risdalsheia than in the Sogndal soils. The average concentrations of water-soluble SO_4-S are 18.5, 10.9, and 9.0 mg kg^{-1} at the depths 0-15, 15-30, and >30 cm, respectively, at Risdalsheia, field 1 (KIM). The average concentrations of adsorbed SO_4-S are much lower at 2.39, 1.45, and 1.96 mg kg^{-1}, respectively, at the depths 0-15, 15-30, and >30 cm. The corresponding values for Sogndal, field 2, are 6.3, 8.8, and 2.0 mg kg^{-1} of water-soluble SO_4-S and 9.3, 8.9, and 10.6 mg kg^{-1} of adsorbed SO_4-S.

Since the Risdalsheia soils have received much higher deposition of SO_4-S than the Sogndal soils, is is not surprising that the concentrations of water-soluble SO_4-S is higher at Risdalsheia than at Sogndal. The higher concentrations of adsorbed SO_4-S in Sogndal soils than in Risdalsheia soils is partly due to the higher sulfate sorption capacity of the Sogndal soils (see below). A more complete elucidation of the differences in SO_4-S adsorption requires mineralogical analyses and determination of the sulfate output:input ratio for the Risdalsheia and Sogndal soils.

4.7. Sulfate Adsorption Isotherms

Sulfate adsorption isotherms for two soil samples from Risdalsheia and two soil samples from Sogndal are given in Figure 3. The adsorption data did not fit the Langmuir equation. It is not, therefore, possible to calculate the sulfate adsorption maximum for the soils. The adsorption isotherms show, however, that the Sogndal soils have a much higher sulfate adsorption capacity than the Risdalsheia soils and that the adsorption capacity increases with decreasing organic matter content. The Risdalsheia soil, 0-15 cm, appears to be saturated with SO_4-S at a final concentration of about 40 mg S l^{-1} in solution. The other soil samples did not reach the adsorption maximum at the concentrations used in the experiment.

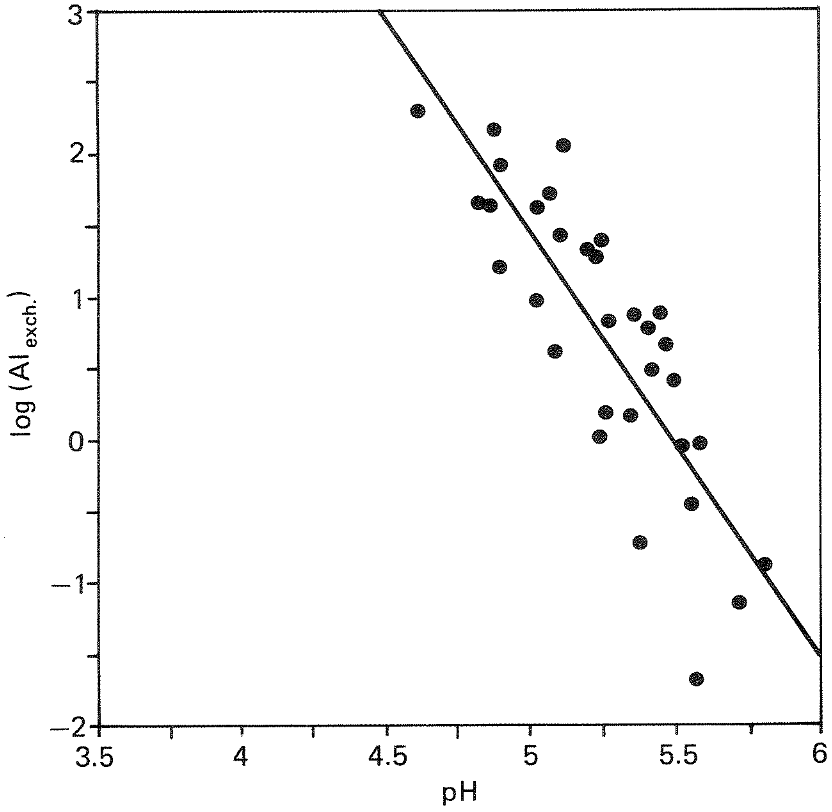

Figure 3. The natural logarithm of exchangeable aluminium as a function of pH for Sogndal soils. Least-squares regression gives log(Al exch.) = 16.2-2.95 pH, r = 0.84, n = 31.

5. ACKNOWLEDGEMENTS

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Table 1. Chemical data for soil samples from Risdalsheia.

Site No.	Depth (cm)	pH (H_2O)	Loss on ign. (%)	C (%)	N (%)	S (%)	C/N	C/S	Exch. (KCl) acidity (meq 100 g^{-1})	Exch. ($BaCl_2$-TEA) acidity (meq 100 g^{-1})
					FIELD 1 (KIM)					
5	0-15	3.89	29.3	15.77	.67	.067	24	235	12.15	48.39
5	15-30	4.67	6.5	4.05	.27	.031	15	131	5.32	16.34
8+9	0-15	4.10	24.6	13.61	.63	.062	22	220	9.88	41.97
9	15-30	4.70	11.6	5.05	.35	.031	14	163	5.18	28.09
10	0-15	3.92	57.7	29.60	1.14	.125	26	237	18.70	85.41
10	15-30	4.25	30.4	16.71	.78	.089	21	188	8.13	39.10
11	0-15	3.70	36.6	21.50	.87	.084	25	256	11.44	62.99
11	15-30	4.54	14.8	8.17	.44	.053	19	154	10.61	36.05
11	>30	4.65	13.2	8.76	.52	.067	17	131	9.72	32.93
12	0-15	3.70	35.6	21.54	.86	.070	25	308	13.05	49.92
12	15-30	4.41	21.5	6.15	.36	.036	17	171	7.25	22.01
12	>30	4.63	10.6	6.97	.40	.058	17	120	5.64	12.40
13+14	0-15	3.92	47.9	26.51	1.28	.161	21	165	18.56	81.74
13+14	15-30	4.11	28.9	15.49	.94	.107	16	145	9.40	51.89
13+14	>30	4.44	22.1	11.19	.72	.111	16	101	6.98	37.88
Ave	0-15	3.87	38.6	21.42	.91	.095	24	237	13.96	61.74
	15-30	4.45	19.0	9.22	.52	.058	17	159	7.65	32.25
	>30	4.57	15.3	8.97	.55	.079	17	117	7.45	27.74
					FIELD 2 (EGIL)					
16A	0-15	3.81	23.9	13.01	.61	.065	21	200	12.41	38.77
16A	15-30	4.47	18.3	7.76	.48	.060	16	129	6.37	28.68
17-19	0-15	3.87	25.5	14.99	.68	.067	22	224	8.21	46.96
17-19	15-30	4.46	12.3	6.22	.41	.042	15	148	5.12	19.51
20-22	0-15	4.16	22.5	12.90	.62	.061	21	211	7.65	35.85
20-22	15-30	4.46	8.1	4.41	.25	.024	18	184	3.10	17.23
23-25	0-15	4.16	23.6	13.53	.68	.068	20	199	10.75	43.90
23-25	15-30	4.71	17.8	5.44	.36	.042	15	130	4.26	19.41
Ave	0-15	4.00	23.9	13.61	.65	.065	21	209	9.76	41.37
	15-30	4.53	14.13	5.96	.38	.042	16	148	4.71	21.21

Table 1. Continued.

Site No.	Depth (cm)	Exchangeable cations (meq 100 g^{-1})								Al_T (% of exch. acid.)	S_B (meq 100 g^{-1})
		Ca	Mg	K	Na	NH_4	H	Al_{AAS}	Al_T		
					FIELD 1 (KIM)						
5	0-15	1.13	.60	.32	.33	.39	3.09	9.42	9.06	75	2.77
5	15-30	.37	.13	.17	.23	.13	2.89	2.63	2.43	46	1.03
8+9	0-15	.59	.26	.28	.18	.55	2.23	7.65	7.65	77	1.86
9	15-30	.06	.07	.06	.28	.14	.83	4.35	4.35	84	.61
10	0-15	4.22	2.43	1.17	.25	.82	8.99	9.93	9.71	52	8.89
10	15-30	.44	.33	.32	.29	.58	5.98	2.42	2.15	26	1.96
11	0-15	.71	.77	.68	.40	.57	3.44	7.84	8.00	70	3.13
11	15-30	.11	.08	.22	.12	.15	3.43	7.24	7.18	68	.68
11	>30	.11	.08	.07	.13	.16	2.92	6.78	6.80	70	.55
12	0-15	2.43	1.19	.48	.39	.57	4.27	8.83	8.78	67	5.06
12	15-30	.15	.08	.12	.08	.14	1.65	5.66	5.60	77	.57
12	>30	.07	.07	.07	.16	.11	3.71	2.20	1.93	34	.48
13+14	0-15	1.40	.85	.41	.36	.57	6.40	12.16	12.16	66	3.59
13+14	15-30	.19	.19	.18	.16	.28	3.89	5.51	5.51	59	1.00
13+14	>30	.06	.08	.09	.12	.20	3.76	3.41	3.22	46	.55
Ave	0-15	1.75	1.02	.56	.32	.58	4.74	9.31	9.23	68	4.22
	15-30	.22	.15	.17	.19	.24	3.11	4.35	4.54	60	1.00
	>30	.08	.08	.08	.14	.16	3.46	4.13	3.98	50	.53
					FIELD 2						
16A	0-15	.68	.35	.36	.20	.36	4.17	8.39	8.24	66	1.95
16A	15-30	.18	.13	.12	.24	.32	3.19	3.05	3.18	50	.99
17-19	0-15	.73	.47	.29	.26	.36	3.80	4.41	4.41	54	2.11
17-19	15-30	.09	.07	.06	.12	.13	2.64	2.48	2.48	48	.47
20-22	0-15	.89	.53	.21	.17	.37	1.97	5.75	5.68	74	2.17
20-22	15-30	.15	.06	.07	.09	.14	.92	2.23	2.18	70	.51
23-25	0-15	.50	.13	.44	.21	.40	2.52	8.24	8.23	77	1.68
23-25	15-30	.28	.19	.15	.17	.12	1.30	3.16	2.96	69	.91
Ave	0-15	.70	.37	.33	.21	.37	3.12	6.70	6.64	68	1.98
	15-30	.18	.11	.10	.16	.18	2.01	2.73	2.70	59	.72

Table 1. Continued.

Site No.	Depth (cm)	CEC (meq 100 g^{-1})			V (%)		
		pH (KCl)	pH 7	pH 8	pH (KCl)	pH 7	pH 8
		FIELD 1 (KIM)					
5	0-15	14.92	40.84	51.15	19	7	5
5	15-30	6.35	10.81	17.37	16	10	6
8+9	0-15	11.74	33.45	43.83	16	6	4
9	15-30	5.79	16.70	28.70	10	4	2
10	0-15	27.59	74.54	94.30	32	12	9
10	15-30	10.09	41.36	41.06	19	5	5
11	0-15	14.57	42.15	66.12	21	7	5
11	15-30	11.29	21.11	36.73	6	3	2
11	>30	10.27	16.88	33.48	5	3	2
12	0-15	18.11	37.00	54.98	28	14	9
12	15-30	7.82	10.76	22.58	7	5	3
12	>30	6.12	7.72	12.88	8	6	4
13+14	0-15	22.15	66.83	85.33	16	5	4
13+14	15-30	10.40	33.44	52.89	10	3	2
13+14	>30	7.53	24.73	38.43	7	2	1
Ave	0-15	18.18	49.09	65.45	22	8	6
	15-30	8.62	22.36	33.22	11	5	3
	>30	7.97	16.44	28.26	7	4	2
		FIELD 2 (EGIL)					
16A	0-15	14.36	32.50	40.72	14	6	5
16A	15-30	7.36	22.12	29.67	13	5	3
17-19	0-15	10.32	34.86	49.07	20	6	4
17-19	15-30	5.59	12.52	19.98	8	4	2
20-22	0-15	9.82	27.22	38.02	22	8	6
20-22	15-30	3.61	11.95	17.74	14	4	3
23-25	0-15	12.43	31.17	45.58	14	5	4
23-25	15-30	5.17	11.44	20.32	18	8	4
Ave	0-15	11.73	31.44	43.35	18	6	5
	15-30	5.43	14.51	21.93	13	5	3

Table 1. Continued.

Site No.	Depth (cm)	Ratios between exchangeable cations									
		H/Ca	K/Ca	Na/Ca	NH_4/Ca	H/Al_T	K/Al_T	Na/Al_T	NH_4/Al_T	Ca/Al_T	Mg/Al_T
FIELD 1 (KIM)											
5	0-15	2.73	.28	.29	.35	.34	.04	.04	.04	.12	.07
5	15-30	7.81	.46	.62	.35	1.19	.07	.09	.05	.15	.05
8+9	0-15	3.78	.47	.31	.93	.29	.04	.02	.07	.08	.03
9	15-30	13.83	1.00	4.67	2.33	.19	.01	.06	.03	.01	.02
10	0-15	2.13	.28	.06	.19	.93	.12	.03	.08	.43	.25
10	15-30	13.59	.73	.66	1.32	2.78	.15	.13	.27	.20	.15
11	0-15	4.46	.96	.56	.80	.43	.09	.05	.07	.09	.10
11	15-30	31.18	2.00	1.09	1.36	.48	.03	.02	.02	.02	.01
11	>30	26.54	.63	1.18	1.45	.43	.01	.02	.02	.02	.01
12	0-15	1.76	.20	.16	.23	.49	.05	.04	.06	.28	.14
12	15-30	11.00	.80	.53	.93	.29	.02	.01	.03	.03	.01
12	>30	53.00	1.00	2.29	1.57	1.92	.04	.08	.06	.04	.04
13+14	0-15	4.57	.29	.26	.41	.53	.03	.03	.05	.12	.07
13+14	15-30	20.47	.95	.84	1.47	.71	.03	.03	.05	.03	.03
13+14	>30	62.67	1.50	2.0	3.33	1.17	.03	.04	.06	.02	.02
Ave	0-15	3.24	.41	.27	.49	.50	.06	.04	.06	.19	.11
	15-30	16.31	.99	1.42	1.29	.94	.05	.06	.07	.07	.05
	>30	47.40	1.04	1.82	2.12	1.17	.03	.05	.05	.03	.02
FIELD 2 (EGIL)											
16A	0-15	6.13	.53	.29	.53	.51	.04	.02	.04	.08	.04
16A	15-30	17.72	.67	1.33	1.78	1.00	.04	.08	.10	.06	.04
17-19	0-15	5.21	.40	.35	.49	.86	.07	.06	.08	.17	.11
17-19	15-30	29.33	.67	1.33	1.44	1.06	.02	.05	.05	.04	.03
20-22	0-15	2.21	.24	.19	.42	0.35	.04	.03	.01	.16	.09
20-22	15-30	6.13	.47	.60	.93	.42	.03	.04	.06	.07	.03
23-25	0-15	5.04	.88	.42	.80	.31	.05	.03	.05	.06	.02
23-25	15-30	4.64	.54	.61	.43	.44	.05	.06	.04	.09	.06
Ave	0-15	4.65	.51	.31	.56	.51	.05	.04	.05	.12	.07
	15-30	14.46	.59	.97	1.15	.73	.04	.06	.06	.07	.04

Table 2. Chemical data for soil samples from Sogndal.

Site No.	Depth (cm)	pH (H_2O)	Loss on ign. (%)	C (%)	N (%)	S (%)	C/N	C/S	Exch. (KCl) acidity (meq 100 g^{-1})	Exch. ($BaCl_2$-TEA) acidity (meq 100 g^{-1})
FIELD 2										
1	0-15	4.89	28.4	16.23	.71	.060	23	271	5.92	47.76
1	15-30	5.35	18.4	8.14	.35	.035	23	233	3.21	36.04
1	0-15s.s.	5.23	26.5	10.92	.42	.046	26	237	4.34	23.60
1	15-30s.s.	5.37	22.7	6.64	.35	.046	19	144	3.81	17.62
1	30-40s.s.	5.71	8.6	3.29	.16	.019	21	173	2.48	10.31
2	0-15	4.86	27.0	12.74	.48	.053	27	240	8.91	34.50
2	15-30	5.34	16.8	6.95	.32	.031	22	224	3.38	13.81
2	0-15s.s.	5.08	23.7	11.52	.48	.042	24	274	6.47	27.51
3	0-15wt.v.	5.57	7.1	2.90	.19	.025	15	116	1.37	9.61
3	0-15w.v.	5.02	15.2	7.41	.33	.037	22	200	4.55	21.11
4	0-15	5.57	9.1	3.15	.17	.025	19	126	2.76	10.96
5	0-15	4.87	39.9	20.71	1.12	.104	18	199	16.12	51.46
5	>15	5.02	34.5	15.99	.90	.105	18	152	9.90	43.10
6	0-15	4.89	33.3	16.38	.64	.065	26	252	11.32	50.51
6	>15	5.27	18.4	7.48	.30	.033	25	227	3.84	24.50
6	0-15s.s.	5.19	27.8	12.79	.49	.050	26	256	5.60	30.20
6	15-30s.s.	5.52	13.3	5.06	.22	.025	23	202	2.51	16.20
6	>30s.s.	5.80	10.1	3.08	.15	.010	21	308	1.27	6.70
7	0-15	5.06	32.6	16.86	.75	.071	22	237	7.70	51.20
7	>15	5.44	17.4	7.69	.36	.035	21	220	4.79	26.50
Ave	0-15	5.11	24.6	11.96	.53	.053	23	219	6.82	32.58
	15-30	5.39	17.7	7.24	.35	.039	19	175	3.93	22.22
	>30	5.76	9.4	3.19	.16	.015	21	241	1.88	8.51
FIELD 4										
8	0-15	5.22	26.8	12.22	.62	.060	20	204	4.02	35.16
8	>15	5.49	18.4	8.02	.40	.042	20	191	2.40	22.25
8	0-15s.s.	5.11	34.4	23.07	1.00	.072	23	320	10.79	46.50
8	15-30s.s.	5.40	23.1	16.96	.71	.057	24	298	5.62	26.51
8	>30s.s.	5.46	12.7	10.82	.57	.098	19	110	3.84	29.80
9	0-15	4.61	51.8	28.79	1.13	.107	25	269	14.29	59.60
9	>15	4.82	35.4	19.66	.72	.068	27	289	7.43	17.51
Ave	0-15	4.98	37.7	21.36	.92	.080	23	264	9.70	47.09
	15-30	5.24	25.6	14.88	.61	.056	24	259	5.15	22.09
	>30	5.46	12.7	10.82	.57	.098	19	110	3.84	29.80

Table 2. Continued.

Site No.	Depth (cm)	pH (H_2O)	Loss on ign. (%)	C (%)	N (%)	S (%)	C/N	C/S	Exch. (KCl) acidity (meq 100 g^{-1})	Exch. ($BaCl_2$-TEA) acidity (meq 100 g^{-1})
					FIELD 1					
10	0-15	5.10	28.9	13.68	.63	.051	22	240	5.53	33.94
10	>15	5.56	15.8	7.11	.33	.028	22	254	1.26	14.52
11	0-15	5.24	21.9	10.43	.48	.044	22	237	5.68	21.70
11	>15	5.42	16.4	6.20	.28	.027	22	230	3.58	12.80
Ave	0-15	5.17	25.4	12.06	.56	.051	22	239	5.61	27.82
	>15	5.49	16.1	6.66	.31	.028	22	242	2.42	13.66

Table 2. Continued.

Site No.	Depth (cm)	Exchangeable cations (meq 100 g^{-1})								Al_T (% of exch. acid.)	S_B (meq 100 g^{-1})
		Ca	Mg	K	Na	NH_4	H	Al_{AAS}	Al_T		
					FIELD 2						
1	0-15	2.07	.64	.48	.17	.10	2.61	3.30	3.31	56	3.46
1	15-30	1.06	.20	.08	.33	.10	.83	2.47	2.38	74	1.77
1	0-15s.s.	.21	.15	.13	.13	.08	3.31	.98	1.03	24	.70
1	15-30s.s.	.18	.06	.04	.13	.07	3.33	.35	.48	13	.48
1	30-40s.s.	.17	.04	.08	.06	.08	2.16	.21	.32	13	.43
2	0-15	1.23	.86	.37	.15	.08	3.83	6.12	5.08	57	2.69
2	15-30	.22	.05	.11	.11	.07	2.21	1.24	1.17	35	.56
2	0-15s.s.	1.02	.67	.16	.11	.09	4.62	1.95	1.85	29	2.05
3	0-15wt.v.	.67	.04	.43	.12	.07	1.18	.10	.19	14	1.33
3	0-15w.v.	.85	.13	.29	.18	.07	1.89	2.65	2.66	58	1.52
4	0-15	.20	.09	.10	.21	.07	1.79	.90	.97	35	.67
5	0-15	1.05	.67	.36	.31	.19	7.36	8.86	8.76	54	2.58
5	>15	.47	.22	.25	.26	.13	4.81	5.21	5.09	51	1.33
6	0-15	2.52	1.34	.38	.26	.12	4.49	6.92	6.83	60	4.62
6	>15	.59	.20	.61	.37	.09	1.57	2.29	2.27	59	1.86
6	0-15s.s.	1.71	.43	.25	.34	.10	1.78	3.85	3.82	68	2.83
6	15-30s.s.	.18	.10	.14	.20	.07	1.56	.97	.95	38	.69
6	>30s.s.	.20	.07	.10	.09	.06	.86	.40	.41	32	.52
7	0-15	1.68	.87	.45	.33	.15	2.09	6.00	5.61	73	3.48
7	>15	.23	.15	.32	.07	.11	2.41	2.47	2.38	50	.88
Ave	0-15	1.20	.54	.31	.21	.10	3.18	3.78	3.65	48	2.36
	15-30	.42	.14	.22	.21	.09	2.39	2.02	2.10	46	1.58
	>30	.19	.06	.09	.08	.07	1.51	.31	.37	23	.48
					FIELD 4						
8	0-15	.77	.44	.42	.17	.10	.37	3.67	3.65	91	1.90
8	>15	.23	.13	.14	.10	.11	.90	1.53	1.50	63	.71
8	0-15s.s.	3.50	1.22	.51	.34	.10	2.97	7.71	7.82	72	5.67
8	15-30s.s.	.22	.11	.22	.12	.19	3.42	2.20	2.20	39	.86
8	>30s.s.	1.40	.44	.39	.39	.22	1.88	2.12	1.96	51	2.84
9	0-15	1.11	.69	.52	.43	.25	4.24	10.06	10.05	70	3.00
9	>15	.45	.24	.38	.13	.14	2.14	5.18	5.24	71	1.34
Ave	0-15	1.79	.78	.48	.31	.15	2.53	7.15	7.17	78	3.52
	15-30	.30	.16	.25	.12	.15	2.15	2.97	2.98	58	.97
	>30	1.40	.44	.39	.39	.22	1.88	2.12	1.96	51	2.84

Table 2. Continued.

Site No.	Depth (cm)	Exchangeable cations (meq 100 g^{-1})								Al_T (% of exch. acid.)	S_B (meq 100 g^{-1}
		Ca	Mg	K	Na	NH_4	H	Al_{AAS}	Al_T		
					FIELD 1						
10	0-15	.73	.56	.38	.17	.12	1.35	4.00	4.18	76	1.96
10	>15	.16	.06	.09	.18	.09	.61	.52	.64	51	.58
11	0-15	.73	.43	.29	.25	.13	1.66	4.32	4.02	71	1.83
11	>15	.86	.32	.21	.21	.08	1.98	1.58	1.60	45	1.68
Ave	0-15	.73	.50	.34	.21	.13	1.51	4.16	4.10	74	1.90
	>15	.51	.46	.15	.20	.10	1.30	1.05	1.12	48	1.13

Table 2. Continued.

Site No.	Depth (cm)	CEC (meq 100 g^{-1})			V (%)		
		pH (KCl)	pH 7	pH 8	pH (KCl)	pH 7	pH 8
		FIELD 2					
1	0-15	9.38	30.78	51.22	37	11	7
1	15-30	4.98	22.71	37.81	36	8	5
1	0-15s.s.	5.04	13.41	24.30	14	5	3
1	15-30s.s.	4.29	9.33	18.10	11	5	3
1	30-40s.s.	2.91	7.41	10.74	15	6	4
2	0-15	11.60	24.66	37.19	23	11	7
2	15-30	3.94	8.97	14.37	14	6	4
2	0-15s.s.	8.52	14.63	29.56	24	14	7
3	0-15wt.v.	2.70	5.35	10.94	49	24	12
3	0-15w.v.	6.07	17.59	22.63	25	9	7
4	0-15	3.43	5.35	11.63	20	13	6
5	0-15	18.70	32.31	54.04	14	8	5
5	>15	11.23	24.22	44.43	12	5	3
6	0-15	15.94	36.50	55.13	29	13	8
6	>15	6.03	14.88	26.69	36	13	7
6	0-15s.s.	8.43	28.07	33.03	34	10	9
6	15-30s.s.	4.10	7.84	17.79	39	9	4
6	>30s.s.	1.79	3.97	7.22	29	13	7
7	0-15	11.18	28.13	54.68	31	12	6
7	>15	5.67	15.56	27.38	16	6	3
Ave	0-15	9.18	21.52	34.94	28	12	9
	15-30	5.75	14.77	26.65	23	7	4
	>30	2.35	5.69	8.98	22	10	6
		FIELD 4					
8	0-15	5.92	21.00	37.06	32	9	5
8	>15	3.11	13.62	22.96	23	5	3
8	0-15s.s.	16.46	29.45	52.17	34	19	11
8	15-30s.s.	6.48	18.42	27.37	13	5	3
8	>30s.s.	6.68	16.47	32.64	43	17	9
9	0-15	17.29	36.32	62.60	17	8	5
9	>15	8.77	11.63	18.85	15	12	7
Ave	0-15	13.22	28.93	51.61	28	12	7
	15-30	6.12	14.57	23.06	17	7	4
	>30	6.68	16.47	32.64	43	17	9

Table 2. Continued.

Site No.	Depth (cm)	CEC (meq 100 g^{-1})			V (%)		
		pH (KCl)	pH 7	pH 8	pH (KCl)	pH 7	pH 8
		FIELD 1					
10	0-15	7.49	20.97	39.90	26	9	5
10	>15	1.84	7.16	15.10	32	8	4
11	0-15	7.51	13.27	23.53	24	14	8
11	>15	5.26	7.24	14.48	32	23	12
Ave	0-15	7.50	17.12	31.72	25	13	7
	>15	3.55	7.20	14.79	32	16	8

Table 2. Continued.

Site No.	Depth (cm)	Ratios between exchangeable cations									
		H/Ca	K/Ca	Na/Ca	NH_4/Ca	H/Al_T	K/Al_T	Na/Al_T	NH_4/Al_T	Ca/Al_T	Mg/Al_T
		FIELD 2									
1	0-15	1.26	.23	.08	.05	.79	.15	.05	.03	.63	.19
1	15-30	.78	.08	.31	.09	.35	.03	.14	.04	.45	.08
1	0-15s.s.	15.76	.62	.62	.38	3.21	.13	.13	.08	.20	.15
1	15-30s.s.	18.50	.22	.72	.39	6.94	.08	.27	.15	.38	.13
1	30-40s.s.	12.71	.47	.35	.47	6.75	.25	.19	.25	.53	.13
2	0-15	3.11	.30	.12	.07	.75	.07	.03	.02	.24	.17
2	15-30	10.05	.50	.50	.32	1.89	.09	.09	.06	.19	.04
2	0-15s.s.	4.53	.16	.11	.09	2.50	.09	.06	.05	.55	.36
3	0-15wt.v.	1.76	.64	.18	.10	6.21	2.26	.63	.37	3.53	.21
3	0-15w.v.	2.22	.34	.21	.08	.71	.11	.07	.03	.32	.05
4	0-15	8.95	.50	1.05	.35	1.85	.10	.22	.07	.21	.09
5	0-15	7.01	.34	.30	.18	.84	.04	.04	.02	.12	.08
5	>15	10.23	.53	.55	.28	.94	.05	.05	.03	.09	.04
6	0-15	1.78	.15	.10	.05	.66	.06	.04	.02	.37	.20
6	>15	2.66	1.03	.63	.15	.69	.27	.16	.04	.26	.09
6	0-15s.s.	1.04	.15	.20	.06	.47	.07	.09	.03	.45	.11
6	15-30s.s.	8.67	.78	1.11	.39	1.64	.15	.21	.07	.19	.11
6	>30s.s.	4.30	.50	.45	.30	2.10	.24	.22	.15	.41	.17
7	0-15	1.24	.27	.20	.09	.37	.08	.06	.03	.30	.16
7	>15	10.48	1.39	.30	.48	1.01	.13	.03	.05	.10	.06
Ave	0-15	4.42	.34	.29	.14	1.67	.29	.13	.75	.63	.16
	15-30	8.77	.65	.59	.30	1.92	.11	.14	.06	.27	.08
	>30	8.51	.49	.40	.39	4.43	.25	.21	.20	.47	.15
		FIELD 4									
8	0-15	.48	.55	.22	.13	.10	.12	.05	.03	.21	.12
8	>15	3.91	.61	.43	.48	.60	.09	.07	.07	.15	.09
8	0-15s.s.	.85	.15	.10	.03	.38	.07	.04	.01	.45	.16
8	15-30s.s.	15.55	1.00	.55	.86	1.55	.10	.05	.09	.10	.05
8	>30s.s.	1.34	.28	.28	.16	.96	.20	.20	.11	.71	.22
9	0-15	3.82	.47	.39	.23	.42	.05	.04	.02	.11	.07
9	>15	4.76	.84	.29	.31	.41	.07	.02	.03	.09	.05
Ave	0-15	1.72	.39	.24	.13	.30	.08	.04	.02	.26	.12
	15-30	8.07	.82	.42	.55	.85	.09	.05	.06	.11	.06
	>30	1.34	.28	.28	.16	.96	.20	.20	.11	.71	.22

Table 2. Continued.

Site No.	Depth (cm)	Ratios between exchangeable cations									
		H/Ca	K/Ca	Na/Ca	NH_4/Ca	H/Al_T	K/Al_T	Na/Al_T	NH_4/Al_T	Ca/Al_T	Mg/Al_T
					FIELD 1						
10	0-15	1.85	.52	.23	.16	.32	.09	.04	.03	.17	.13
10	>15	3.81	.56	1.13	.56	.95	.14	.28	.14	.25	.09
11	0-15	2.27	.40	.34	.18	.41	.07	.06	.03	.18	.11
11	>15	2.30	.24	.24	.09	1.24	.13	.13	.05	.54	.20
Ave	0-15	2.06	.46	.29	.17	.37	.08	.05	.03	.18	.12
	>15	3.06	.40	.69	.33	1.10	.14	.21	.10	.40	.15

Table 3. Physical and chemical data for soil samples from Risdalsheia

Site No.	Depth (cm)	Bulk density (g cm^{-3})	pH (KCl)	Water-soluble SO_4-S		Adsorbed SO_4-S	
				(mg kg^{-1})	(meq kg^{-1})	(mg kg^{-1})	(meq kg^{-1})
FIELD 1 (KIM)							
5	0-15	.79	3.13	35.8	2.23	1.68	.11
5	15-30	1.35	3.94	14.4	.90	.95	.06
8+9	0-15	.77	3.37	9.9	.62	3.45	.22
9	15-30	.96	3.95	9.1	.57	1.68	.11
10	0-15		2.98	15.5	.97	2.30	.14
10	15-30		3.58	13.2	.83	2.08	.13
11	0-15	.64	3.00	11.6	.73	2.05	.13
11	15-30	1.57	3.89	6.4	.40	1.15	.08
11	>30		3.63	5.9	.37	.75	.05
12	0-15	.67	2.95	13.2	.82	1.73	.11
12	15-30	1.70	3.69	6.1	.39	.98	.06
12	>30	1.74	4.15	6.6	.41	2.70	.17
13+14	0-15		3.41	24.7	1.54	3.15	.20
13+14	15-30		3.63	16.0	1.00	1.83	.12
13+14	>30		3.93	14.6	.91	2.42	.15
Ave	0-15		3.14	18.5	1.15	2.39	.15
	15-30		3.78	10.9	.68	1.45	.09
	>30		3.90	9.0	.56	1.96	.12
FIELD 2 (EGIL)							
16A	0-15	.63	3.17	10.7	.67	1.16	.08
16A	15-30		3.90	7.2	.45		
17-19	0-15	.71	3.16	9.3	.58	1.32	.09
17-19	15-30	1.39	3.79	15.2	.95	.80	.05
20-22	0-15	.68	3.33	9.0	.56	1.20	.08
20-22	15-30		3.74	4.8	.30		
23-25	0-15	.63	3.53	11.5	.72	1.37	.09
23-25	15-30	1.02	4.16	8.9	.56	2.05	.13
Ave	0-15		3.30	10.1	.63	1.26	.09
	15-30		3.90	9.0	.57	1.43	.09

Table 4. Physical and chemical data for soil samples from Sogndal

Site No.	Depth (cm)	Bulk density (g cm^{-3})	pH (KCl)	Water-soluble SO_4-S		Adsorbed SO_4-S	
				(mg kg^{-1})	(meq kg^{-1})	(mg kg^{-1})	(meq kg^{-1})
FIELD 2							
1	0-15	.52	4.16	6.8	.42	4.0	.25
1	15-30	.56	4.41	29.1	1.81	3.9	.24
1	0-15 s.s.		4.60	4.1	.25	10.6	.66
1	15-30 s.s.		4.63	6.7	.42	6.3	.39
1	30-40 s.s.		4.87	2.8	.17	11.1	.69
2	0-15	.44	4.18	8.9	.56	8.2	.51
2	15-30	.61	4.70	8.2	.51	16.5	1.03
2	0-15 s.s.		4.32	7.0	.44	5.2	.33
3	0-15 wt.v.		5.01	2.0	.12	6.9	.43
3	0-15 w.v.			3.0	.19		
4	0-15	.84	5.03	1.6	.10	32.1	2.00
5	0-15	.82	4.15	5.8	.36	2.3	.14
5	>15		4.35	2.9	.18	5.1	.32
6	0-15	.77	4.16	10.1	.63	6.5	.41
6	>15		4.49	5.6	.35	11.3	.71
6	0-15 s.s.			13.4	.84	8.0	.50
6	15-30 s.s.		4.77	2.4	.15	17.3	1.08
6	>30 s.s.		4.95	1.2	.07	10.1	.63
7	0-15	.67	4.25	6.9	.43	9.0	.56
7	>15		4.49	6.8	.42	1.7	.11
Ave	0-15		4.43	6.3	.39	9.3	.50
	15-30		4.55	8.8	.55	8.9	.55
	>30		4.91	2.0	.12	10.6	.66
FIELD 4							
8	0-15	1.05	4.39	6.8	.42	2.1	.13
8	>15		4.70	8.4	.52	12.5	.76
8	0-15 s.s.		4.16	8.6	.54	6.2	.38
8	15-30 s.s.		4.63	5.9	.37	7.2	.45
8	>30 s.s.		4.58	5.1	.32	3.4	.21
9	0-15	.61	4.88	6.2	.39	4.6	.29
9	>15		4.13	3.3	.21	2.0	.13
Ave	0-15		4.48	7.2	.45	4.3	.27
	15-30		4.49	5.9	.37	7.2	.45
	>30		4.58	5.1	.32	3.4	.21
FIELD 1							
10	0-15	.85	4.27	6.3	.40	4.2	.26
10	>15		4.75	8.5	.53	7.5	.46
11	0-15	.85	4.40	7.2	.45	6.2	.39
11	>15		4.65	2.9	.18	7.3	.45
Ave	0-15		4.34	6.8	.43	5.2	.33
	>15		4.70	5.7	.36	7.4	.46

Table 5. The average organic carbon:exchangeable aluminum ratio for Risdalsheia and Sogndal soils

Depth (cm)	C (%)/Al_T (meq 100 g^{-1})				
	Risdalsheia		Sogndal		
	Field 1	Field 2	Field 1	Field 2	Field 4
0-15	2.3	2.1	2.1	3.3	3.0
15-30	2.0	2.2	6.0	3.5	5.0
>30	2.3	-	-	8.6	5.5

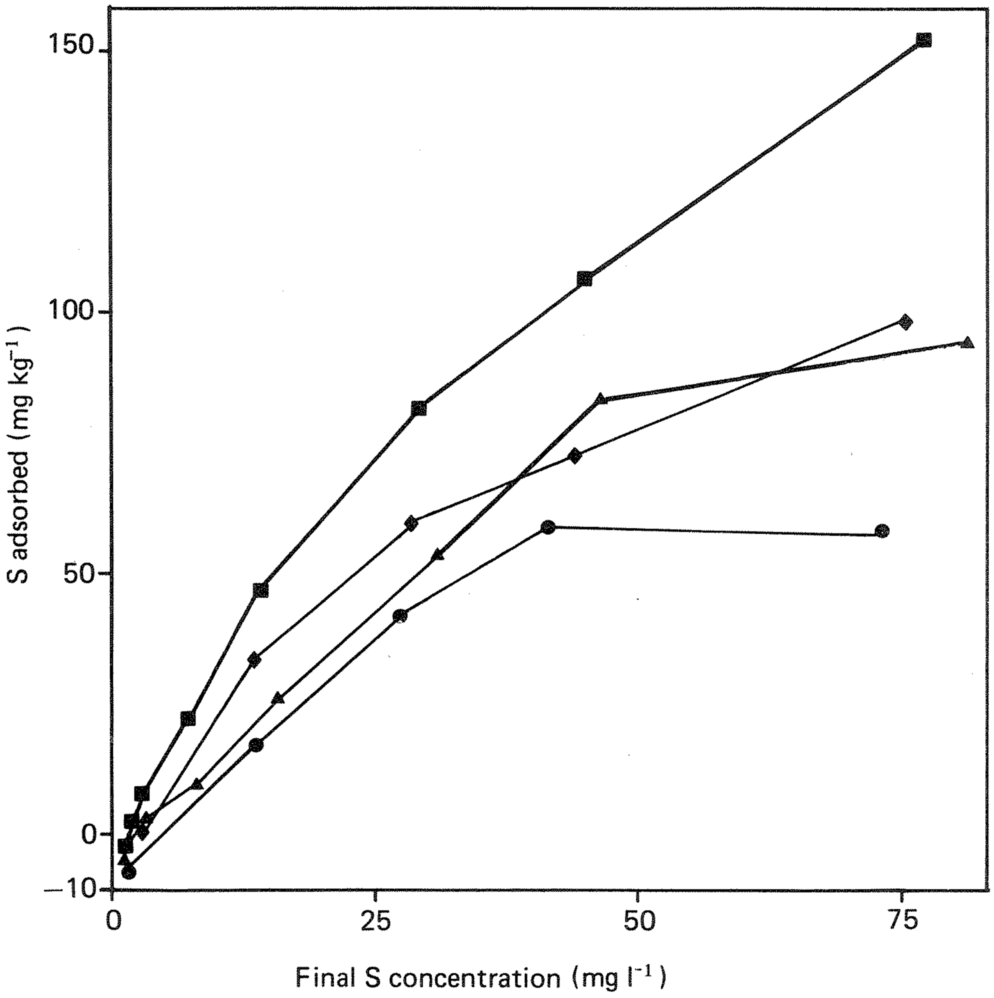

Figure 4. Sulfate adsorption isotherms. ● - Risdalsheia (KIM), site 12, 0-15 cm. ▲ - Risdalsheia (KIM), site 12, 15-30 cm. ◆ - Sogndal, field 2, site 2, 0-15 cm. ■ - Sogndal, field 2, site 2, 15-30 cm.

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APPENDIX. Maps of RAIN project sites and soil sampling points.

Figure A1. Location of the experimental catchments in project RAIN. Areas within the pH 4.7 isoline receive precipitation with a yearly weighted average pH below 4.7 (from Wright 1985).

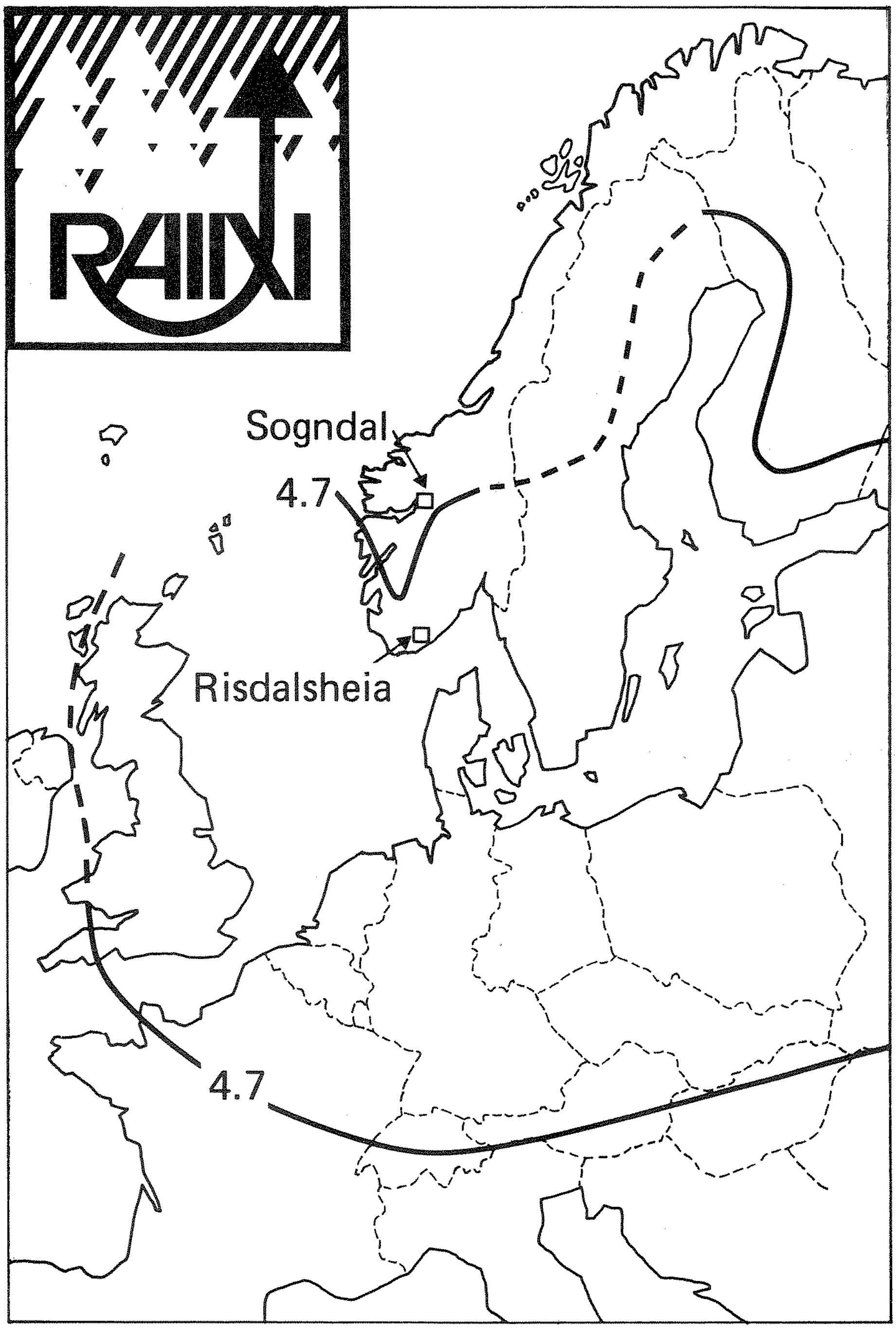


Figure A2. Overview map of the 4 catchments at Sogndal. Catchments 1 and 3 are controls while catchment 2 receives H_2SO_4 and catchment 4 H_2SO_4+HNO_3 (from Wright 1984).

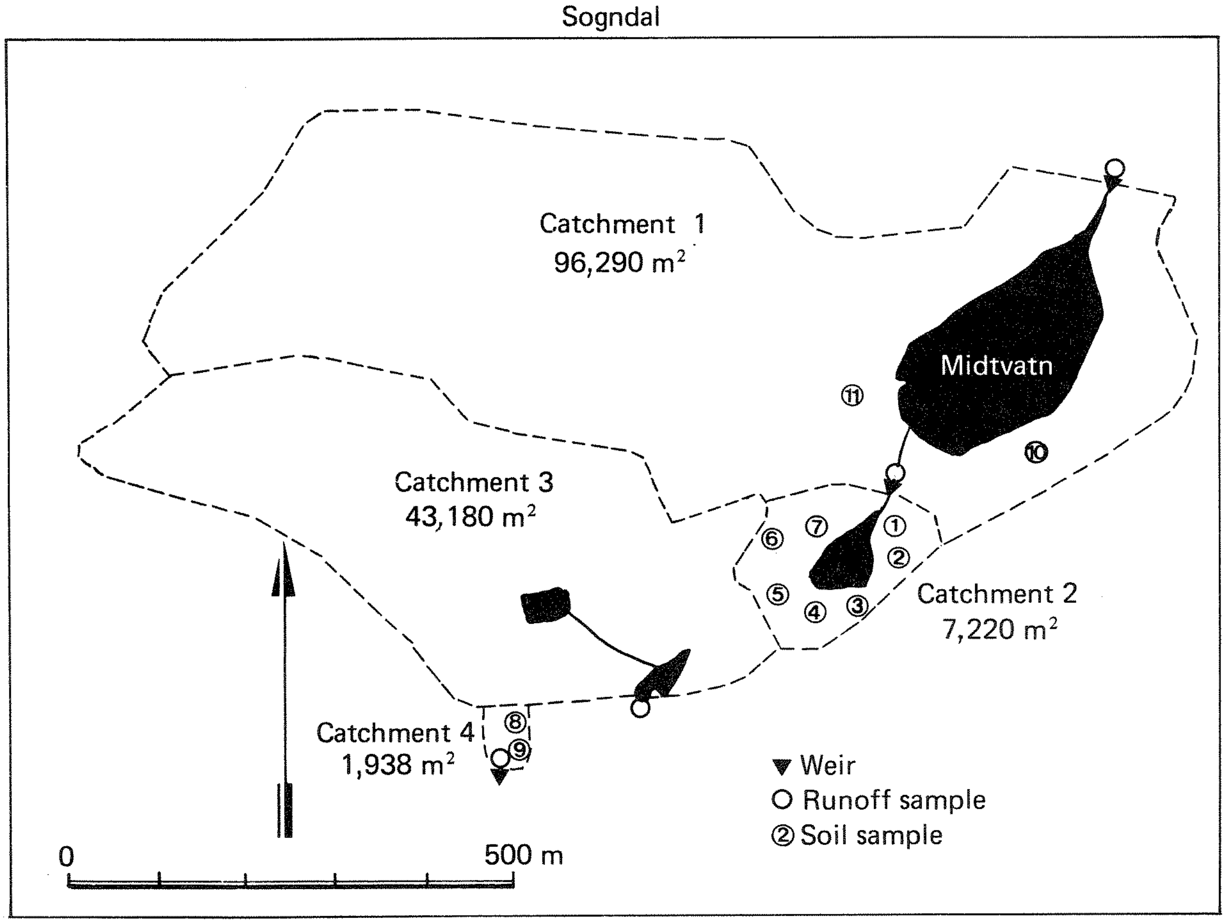


Figure A3. Map of KIM catchment at Risdalsheia showing soil sampling points (hatched areas are soil covered) and soil depth in cm.

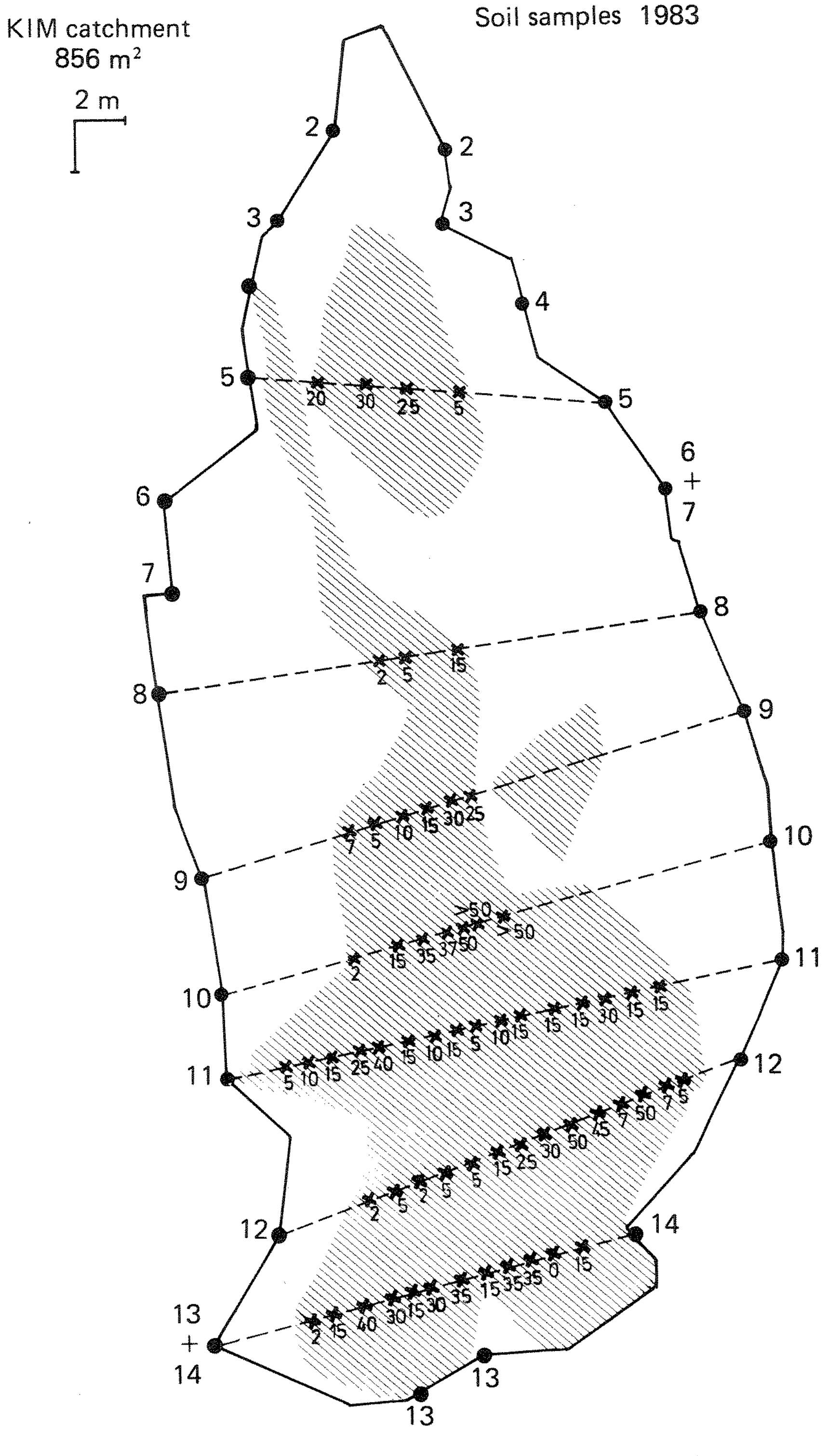
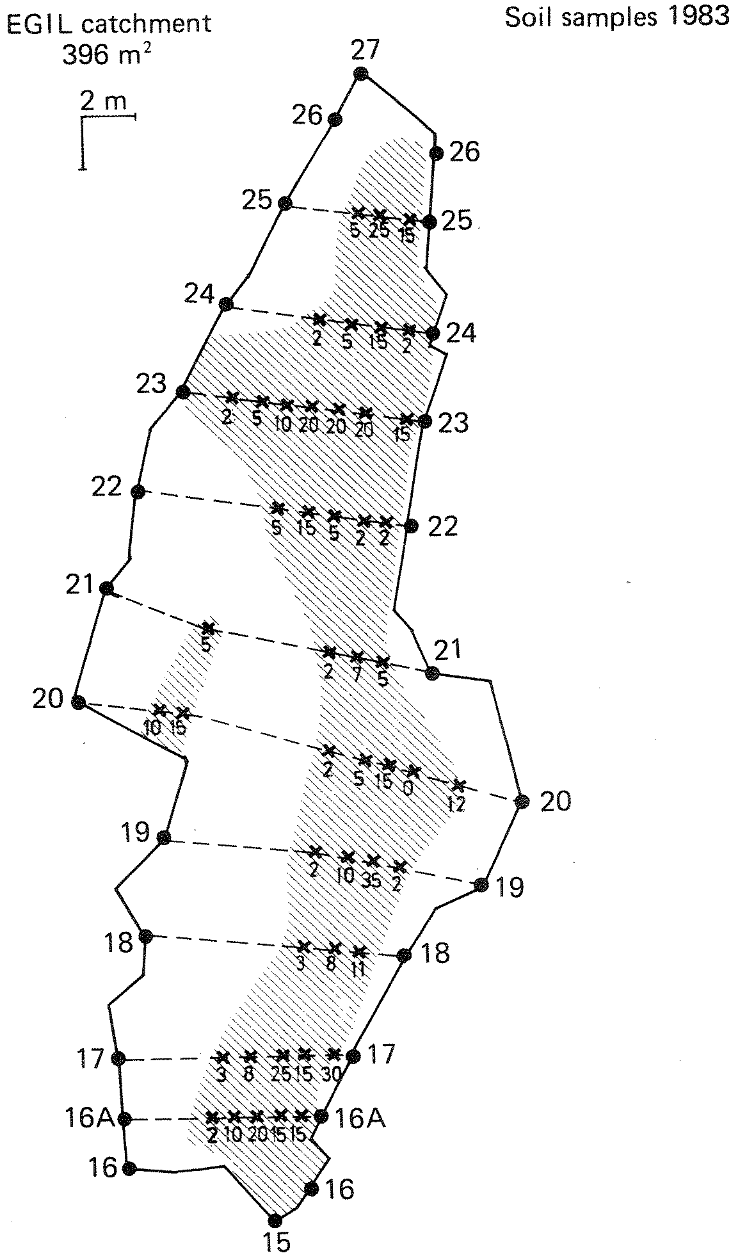


Figure A4. Map of EGIL catchment at Risdalsheia showing soil sampling points (hatched areas are soil covered) and soil depth in cm.



WRI/LIS
DISK:WRI2
Jnavn:r/8207