

Aqueous geochemistry of the Romerike area, southern Norway

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Jørgensen, P., Stuanes, A. O. & Østmo, S. R. 1991: Aqueous geochemistry of the Romerike area, southern Norway. *Nor. geol. unders. Bull.* 420, 57-67.

Groundwater flowing through the sandy glaciofluvial deposits at Romerike has an average residence time of 30 years. The most important processes taking place along its flowpaths are dissolution of low-Mg calcite and silicates. The decalcified zone which formed during postglacial time is about 10 m thick. The acid consumed in weathering processes is mainly CO₂ formed in the unsaturated zone. Oxidation of sulphides as well as leaching of old sea salt change the composition of the groundwater.

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Introduction

Maps of Pleistocene deposits and groundwater flow, together with a hydrological model for the Romerike area, were published by Østmo (1975, 1976) and Jørgensen & Østmo (1990). In this paper we are combining this hydrological model with hydrochemical data. The purpose is to describe the processes which take place along flowpaths in the groundwater reservoir. A description of these processes requires knowledge about the hydrological budget, the mineralogical composition of the sediments and the chemical composition of different watertypes.

The hydrological model

The area studied, Romerike, is located 40 km north of Oslo. Fig. 1 shows the groundwater flow pattern within the area studied. Shortly after the ice retreated after the last glaciation, the surface of the sandy sediments (Fig. 2) was lifted above sea level and chemical weathering could start. Immediately after deglaciation, the groundwater level was near to the surface and its gradient was low. Since isostatic rebound was initially fast, it took less than 400 years to establish a flow pattern similar to what we have today (Fig.1).

Fig. 2 shows the hydrological budget for the period 1965-1974. The size of the area is

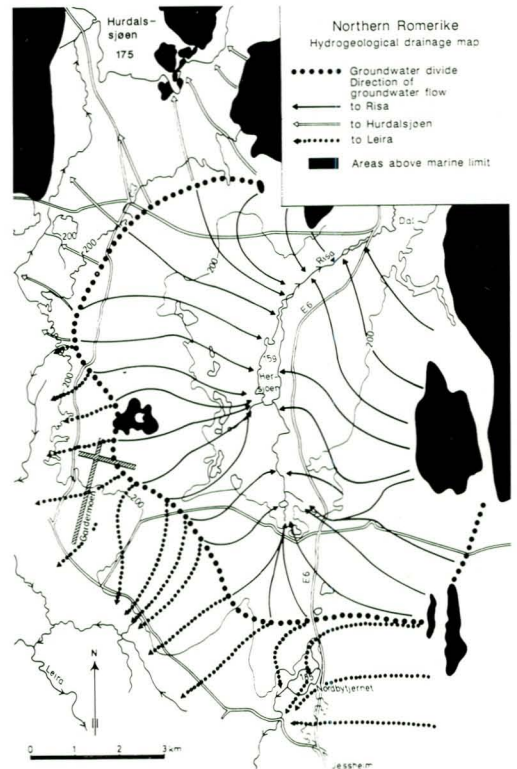


Fig. 1. Groundwater flow pattern within the studied area (Jørgensen & Østmo 1990).

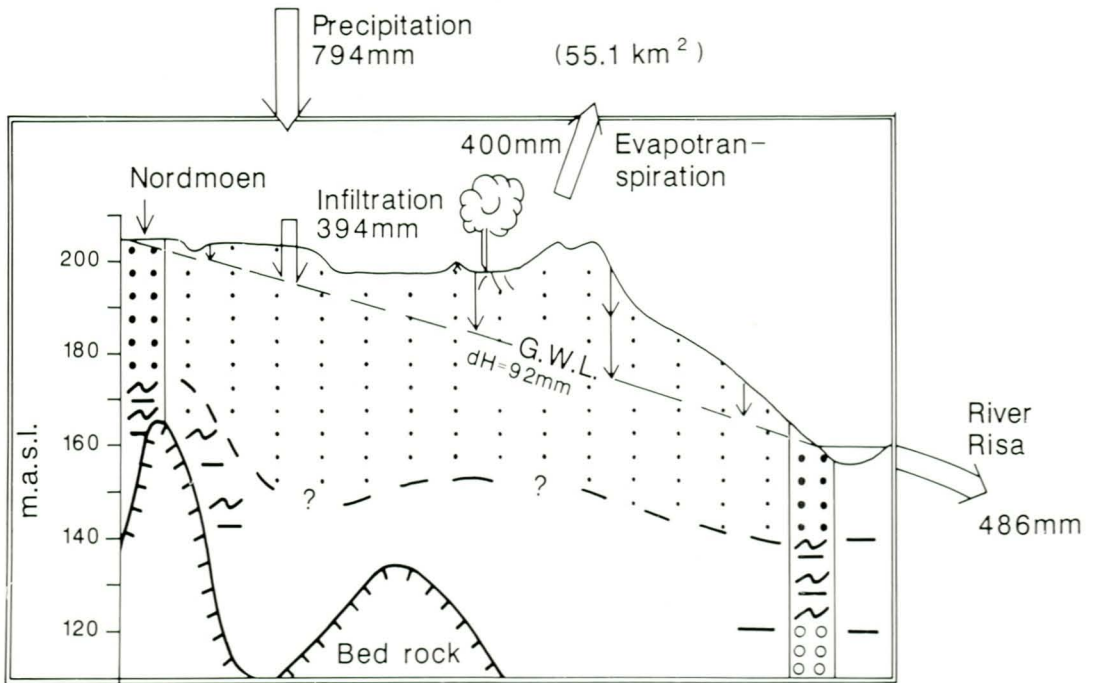


Fig. 2. Hydrological model for northern Romerike showing the average annual amounts over a decade. The size of the watershed is 55.1 km². dH is the decline in groundwater level. (Fig. 3 shows the geological legend).

55.1 km². Precipitation as well as discharge are given as mm or litres m⁻² which are identical values.

The model illustrates that 50% of the annual precipitation is lost due to evapo-transpiration. Annual average infiltration of new groundwater was equivalent to 394 mm of precipitation. There was a net lowering of the groundwater level (dH) during the decade 1965-74. The annual amount of water leaving the area with river Risa was equivalent to 486 mm. The average discharge with this river is 0.85 m³ s⁻¹ or 26.8 × 10⁶ m³ per year.

Mineralogical composition of sediments

The aquifer is composed mainly of sand underlain by silt and clay-bearing sediments (Fig. 3). Bulk samples collected at different depths down to 50 m were analysed chemically and by X-ray diffraction and microscopy. Sand samples collected below the soil profiles had almost the same composition with respect to silicate minerals (Table 1).

Table 1. Weight-% of silicate minerals in unweathered bulk samples of sand.

Amph.	Chlorite	Biotite	Muscovite	K-feld.	Plag.	Quartz
2	7	2	13	18	8	50

Amph. = Amphibole K-feld.= K-feldspar Plag.= Plagioclase

Calcite and pyrite in the sediments

Deep unweathered samples react strongly with dilute acid and CO₂ is released. Using a binocular lens we observed mainly a reaction with shale fragments containing calcite. A few grains of pure calcite were also observed.

Since most of the calcite was found in shale fragments, we used X-ray diffraction analyses to determine the amount of calcite in bulk samples collected at various depths. The amount of calcite in each sample was obtained by direct comparison with samples containing known amounts of calcite. The average calcite content in deep samples (Fig.4) is 2.4 ± 0.2%.

The samples were also analysed for their content of carbon and sulphur by igniting samples in a Leco oven. We know that the shale

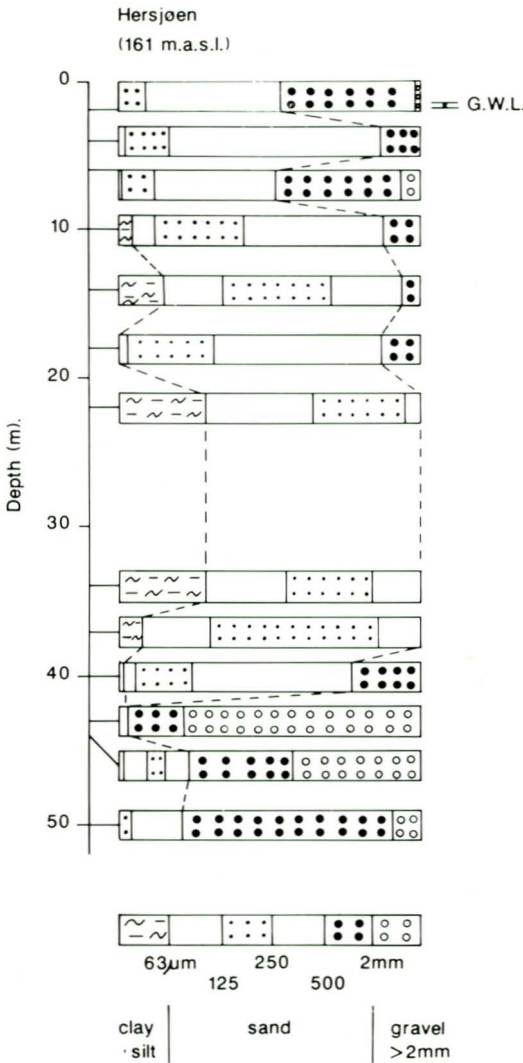


Fig. 3. Vertical section through the sandy deposits at lake Hersjøen.

fragments contain pyrite and calcite, and the sulphur and carbon data were used to calculate the possible maximum amounts of these minerals (Table 2).

The calculated amounts of calcite are higher than the amounts determined by X-ray diffraction. This is probably due to the following factors:

1. A part of the CO₂ produced under ignition is due to organic material in the shale fragments.
2. The crystallinity of our reference X-ray sample is probably better than the crystallinity of the calcite in our samples.

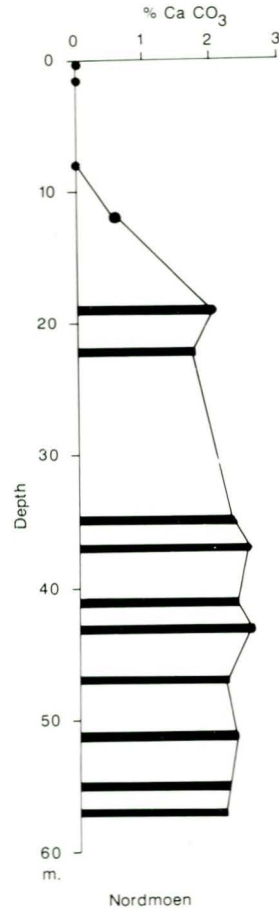


Fig. 4. Content of calcite at different depths in the aquifer.

Composition of the calcite

Isomorphous substitution of Mg²⁺ for Ca²⁺ will change the interplanar distances in the calcite. This is reflected in a change of the d-value for the strongest X-ray reflection. The exact Mg content was determined by using quartz as an internal standard and step-scanning with 0.02° intervals. The average value found for repeated scans on several samples is 0.3031 nm. This means that the calcite contains 2.5 mol% MgCO₃ (Goldsmith & Graf 1958).

Table 2. Calculated maximum amounts (weight%) of calcite and pyrite in the sediments.

Depth(m)	19	23	35	37	41	43	47	51	57
Calcite	3.50	3.80	3.80	3.60	4.10	4.70	3.90	3.10	3.80
Pyrite	0.43	0.39	0.47	0.46	0.69	0.51	0.58	0.62	0.48

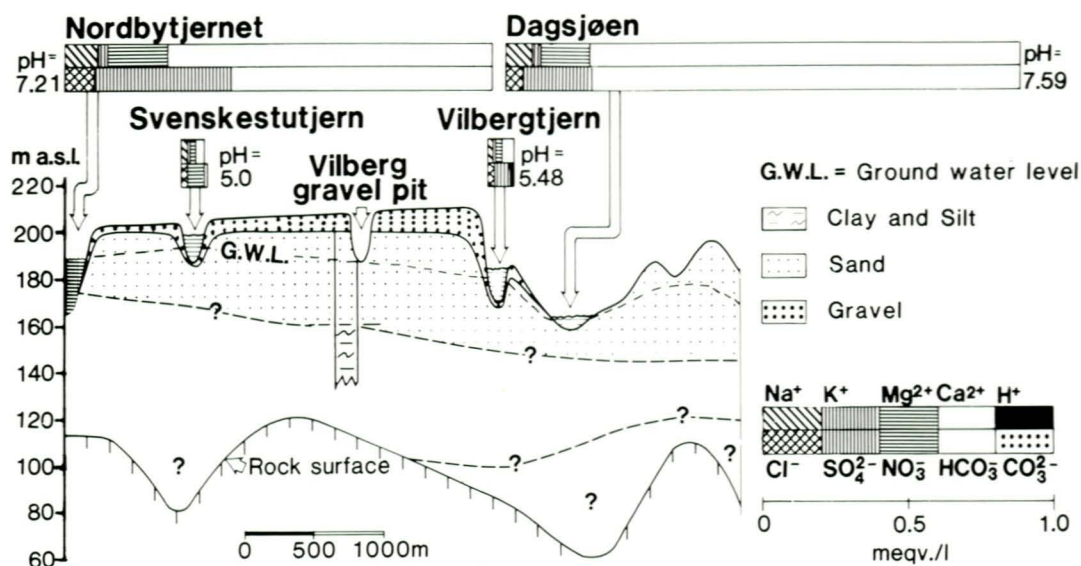


Fig. 5. Composition of different lakes in the watershed.

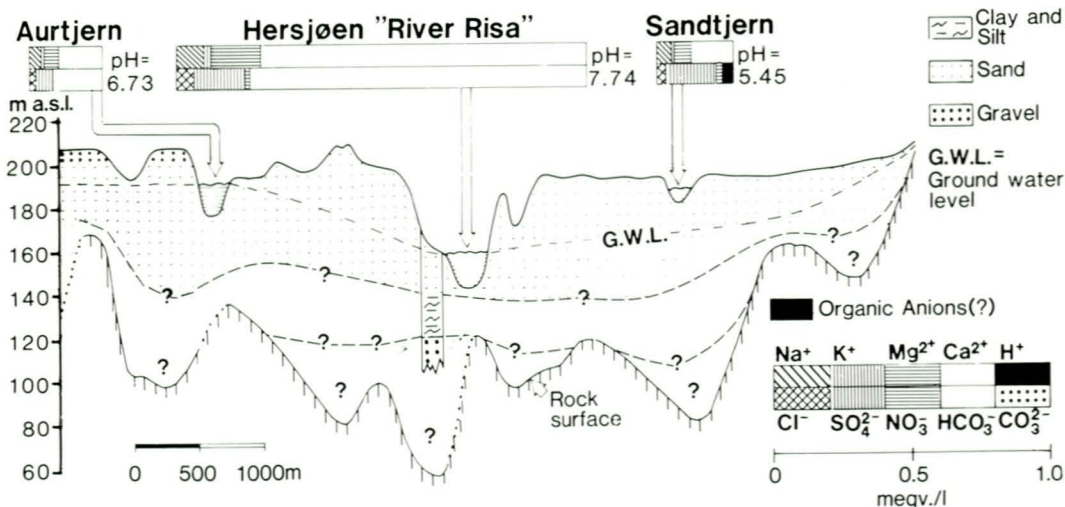


Fig. 6. Composition of different lakes in the watershed.

Lake chemistry

The depths and the positions of the different lakes in relation to the flow paths of groundwater are shown in Figs. 5 and 6.

The average chemical compositions of their water are given in Table 3. These compositions were calculated on the basis of 31 analyses from each lake. Samples were collected regularly during the International Hydrological

Decade (IHD) in the period 1967-1974 (Otnes 1975). The compositions of the lakes reflect the differences in groundwater composition.

As pointed out by Hongve (1977), lakes which are mainly fed with shallow groundwater have low ionic concentrations and may be characterised as acid sulphate lakes, while lakes fed with deeper going groundwater have high ionic concentrations and are classified as neutral bicarbonate lakes.

Table 3. Average chemical composition of the river Risa and the lakes Svenskestutjern (522), Vilbertjern (526), Aurtjern (500), Dragsjøen (504), Mjøntjern (513), Nordbytjern (514), Sandtjern (516), Transjøen (524) and a deep groundwater sample collected at 30 m depth at Furusmo (D.G.).

Lake	pH	spes. cond.	alk. (°)	Cl ⁻	Concentrations (mg/l)		Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
					SO ₄ ²⁻	NO ₃ ⁻				
522	5.00	13.54	0.01	0.90	3.65	0.02	0.54	0.37	0.29	0.65
526	5.48	11.94	0.01	0.85	2.77	0.12	0.53	0.49	0.37	0.75
500	6.73	29.7	0.26	1.13	3.66	0.12	1.41	0.46	0.81	3.73
504	7.59	187.8	1.88	2.75	14.83	0.36	2.80	1.65	2.69	37.88
513	7.68	226.9	2.38	4.61	14.12	0.10	4.93	1.47	3.90	45.56
514	7.21	161.6	1.16	4.70	29.45	0.27	3.40	1.53	3.31	28.70
516	5.45	35.2	0.03	1.44	11.60	0.12	1.45	0.48	1.02	4.06
524	7.77	254.5	2.61	6.19	18.30	0.11	5.77	1.51	4.65	50.94
Risa	7.71	171.6	1.60	2.86	12.10	0.11	3.12	1.24	2.86	31.39
D.G.	7.93	201.5	1.91	1.14	14.87	0.02	1.91	1.25	2.53	39.08

* alkalinity in mEq l⁻¹ and specific conductance in microsiemens cm⁻¹ at 20°C.

Inputs and Outputs

The volume weighed composition of wet deposition as well as the amount of dry deposition is based upon 2 years data from the Integrated Forest Study (Johnson & Lindberg 1991) while the hydrological budget, lake chemistry and river chemistry (discharge) are based upon data from the IHD-project (Otne 1973, 1975). We analysed 4 samples from the river Risa in 1989, and the composition was the same as during the IHD-period.

The river Risa, which is almost entirely fed by groundwater, has a stable discharge near its average value and an almost constant chemical composition through the year (Table 3). The composition is totally different from the input (wet and dry deposition), as illustrated by the Output-Input budget (Table 4).

This difference must be due to various geochemical processes along the flow paths in the aquifer. The annual input and output (river Risa) are divided by the total area (m²) of the catchment, and the values are given as mEq m⁻² yr⁻¹ (Table 4). Our budget calculations show that the most important processes taking place along groundwater flow paths are:

1. Leaching of old, probably diluted, seawater from deep sediments.
2. Oxidation of sulphides and precipitation of hydroxides.
3. Biological uptake of nitrogen and other nutrients and the formation of CO₂.
4. Weathering of carbonates.
5. Weathering of silicates.

Effect of old seawater

Our budget calculation shows that the output of chloride is higher than the input. Since the lowermost part of the aquifer was deposited

Table 4. Average annual input (wet and dry depositions, Johnson & Lindberg 1991) and annual output (river Risa). Last column shows Output-Input (mEq m⁻² yr⁻¹).

	Input (wet)	Input (dry)	Output	Output Input
H ⁺	41.51	6.49	0.01	-47.98
Ca ²⁺	3.47	5.34	761.27	752.47
Mg ²⁺	2.06	2.00	114.31	110.24
Na ⁺	7.71	7.30	65.95	50.94
K ⁺	1.45	4.25	15.41	9.71
NH ₄ ⁺	21.87	5.03	0	-26.90
Cl ⁻	9.62	9.70	39.22	19.90
NO ₃ ⁻	24.13	8.22	0.87	-31.47
SO ₄ ²⁻	34.45	12.49	122.42	75.48
HCO ₃ ⁻	0	0	777.60	777.60
Org.An.	9.87	0	16.83	6.96

Table 5. Composition of seawater with 19‰ chlorinity (25°C and pH = 8.15)

Cl ⁻	mEq l ⁻¹					
	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
560.0	56	2.9	480.0	10	108.0	20.0

under marine conditions, fossil seawater is probably leached from these marine deposits. This leaching is also reflected in the composition of lake water (Table 3) where concentrations as high as 6.2 mg l⁻¹ were found. By using the average composition of seawater (Table 5), we calculated that the discharge contains 2.61 mg l⁻¹ sea salt or 0.01% fossil seawater. Such a small contribution probably means that most of the old seawater, originally present in the underlying sediments, has been removed as a result of close to 9000 years with hydraulic flow, or that the flow through these sediments is very slow. The calculated contribution of different ions from old sea water is given in Table 6.

Oxidation of sulphides

There is a reasonable balance between input and output of SO₄²⁻ in the upper part of the

Table 6. Different components of the Output-Input budget ($\text{mEq m}^{-2} \text{ yr}^{-1}$).

	Sea water	Sulphide oxidation	Uptake of N	CO_2 consumed	Weathering Calcite	Silicates	Org. Acids
H^+		73.43	-4.57	400.46	-377.14	-147.13	6.96
Ca^{2+}	0.71				735.42	16.34	
Mg^{2+}	3.84				18.86	87.55	
Na^+	17.05					33.89	
K^+	0.36					9.35	
NH_4^+			-26.90				
Cl^-	19.90						
NO_3^-			-31.47				
SO_4^{2-}	2.05	73.43					
HCO_3^-	0.12			400.46	377.14		
Org.An.							6.96

soil profile (Johnson & Lindberg 1991). For the whole area the output of sulphate is higher than the input from wet and dry deposition.

The sediments contain considerable amounts ($\approx 20\%$) of shale fragments which are known to contain pyrite, and the pyrite content in unweathered samples is 0.4-0.7% (Table 2). Consequently, the most obvious explanation is that pyrite is weathered.

Sulphate will be reduced to sulphide in some of the lakes with anoxic bottom water and some sulphate is probably adsorbed in parts of the aquifer. The 'excess' sulphate is the net result of these three processes where sulphide oxidation is dominating. After correcting the Output-Input budget for the contribution from old seawater we are left with $73.4 \text{ mEq m}^{-2} \text{ yr}^{-1}$ 'excess' sulphate (Table 6).

The oxidation of pyrite can be described by the following equation:

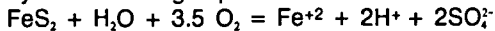
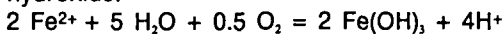


Table 7. Oxygen contents in lake Svenskestutjern and deep groundwater at Furusmo.

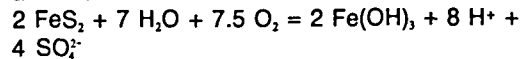
Locality	Depth (m)	No. of obs.	Average $\text{ml l}^{-1} \text{O}_2$
Svenskestutjern	Lake	29	6.2 ± 1.2
Furusmo	30	23	0.5 ± 0.4

Since the flow velocities are high in the coarse-grained sediments (Jørgensen & Østmo 1990) there is rapid throughflow, and even deep groundwater contains dissolved oxygen (Table 7).

Even after a long flow pathway, groundwater at 30 m depth in the Furusmo borehole contains 0.5 ml l^{-1} oxygen. Dissolved ferrous iron is unstable in such conditions, and is oxidized to produce a precipitate of ferric hydroxide:



The combination of these two reactions gives as a result:



The equation illustrates that the amount of oxygen dissolved in the groundwater will be reduced as distance along the flow path increases, as pyrite is oxidized, and protons are released.

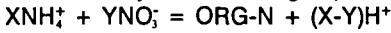
The difference in oxygen content between deep groundwater and surface water (Table 7) is 5.7 ml/l or 0.25 mmol/l . Again using 486 mm as the annual water flux, the total consumption of oxygen will be $121.5 \text{ mmol m}^{-3} \text{ yr}^{-1} \text{ O}_2$. According to the last equation, oxidation of pyrite to form $73.4 \text{ mEq m}^{-3} \text{ SO}_4^{2-}$ annually would require $68.8 \text{ mmol m}^{-3} \text{ O}_2$. The amount of sulphate formed is calculated for the whole drainage area (river Risa), while the observed reduction of oxygen is based on measurements from one groundwater well only. Consequently we only want to conclude that the observed reduction of oxygen in the groundwater is sufficient for the described sulphide oxidation.

This oxidation will produce $73.4 \text{ mEq m}^{-3} \text{ yr}^{-1}$ of protons, which are consumed in the weathering of calcite and silicates.

Biological uptake of nitrogen and other nutrients

We are only discussing the uptake of new nitrogen, from wet and dry deposition, added to the soils. In addition, there is a cycling of old nitrogen and old nutrients which will not influence our budget calculations under the assumption of no change in mineralization rates. Uptake of NH_4^+ is equivalent to release of H^+ from the biomass to the porewater, while uptake of NO_3^- is equivalent to release

of OH⁻. The net effect of these processes is described by the following equation:

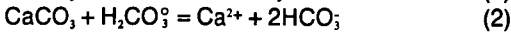


From our Output-Input budget we find that the annual input of new nitrogen compounds is equivalent to an annual input of 4.57 mEq m⁻³yr⁻¹ OH⁻ (or removal of H⁺) (Table 6). The uptake of new nitrogen is associated with the uptake of other new nutrients. The ratio (Ca+Mg+K):N is close to 0.6 for new biomass formed (Stuanes 1989). The uptake of these nutrients will add about 35.0 mEq m⁻³yr⁻¹ of H⁺. These protons are used for weathering, releasing equivalent amounts of new cations. Consequently, the uptake of these nutrients (Ca+Mg+K) and the consumption of the released protons will not be observed in our Output-Input calculations.

Weathering of calcite and silicates

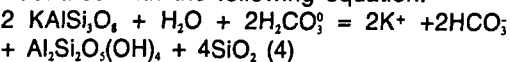
The high outputs of Ca²⁺, Mg²⁺ and HCO₃⁻ are largely due to carbonate weathering, while Na⁺, K⁺ (as well as parts of Ca²⁺ and Mg²⁺) must be due to silicate weathering.

According to Plummer et al. (1978) there are three weathering reactions for calcite which occur simultaneously:



The amount of annually formed bicarbonate, after correction for old seasalt, is 777.5 mEq m⁻². The amount formed from reactions 1 and 3 while pH increases from 5 to 7.7 is 4.86 mEq m⁻² (discharge is 486 mm). The pH in our groundwater is close to 5 when the weathering of calcite starts and the pH in river Risa is 7.7.

Consequently, we can conclude that reaction 2 reflects the most important process for calcite weathering in these deposits. Weathering of a simple silicate-like potassium feldspar is illustrated with the following equation.



Whether kaolinite (Al₂Si₂O₅(OH)₄) or other weathering products are formed is not important for this discussion. The important point is that feldspar weathering will only release 1 mEq K⁺ for each mmole of H₂CO₃^{*} that is consumed, while for carbonate weathering (Eq. 2) 2 mEq with Ca²⁺ are released for each mole of H₂CO₃^{*} consumed. Consequently, it is important to know how much of the bicarbonate in

our discharge comes from calcite and how much from CO₂. The amount from calcite will be between 0 and 50%, but groundwater flowing through calcite-bearing deposits will rapidly approach the higher value. If we knew this %-value we could calculate the amounts of Ca²⁺ and Mg²⁺ released from calcite. The remaining amounts of these two elements as well as Na⁺ and K⁺ must be due to silicate weathering.

The %-value which is assigned to calcite weathering will determine the amounts and the ratio of Mg:Ca ions released due to silicate weathering. We have assumed that this ratio shall be the same as the ratio determined for long-term weathering in this area (Tevelidal et al. 1990). The ratio of Mg:Ca released from silicates due to this weathering is 69.5:13.2 = 5.3. By using a spreadsheet program we found that reasonable Mg:Ca ratios were obtained if the amount of bicarbonate from calcite is between 48 and 49 %. We have used the value 48.5% in our calculations.

Using this value we find that the ratio of Mg:Ca released from silicates is 5.36 (Table 6). The annual weathering of calcite is 377.1 mmol m⁻² yr⁻¹, consuming an equivalent amount of CO₂. This weathering will release 735.4 mEq m⁻²yr⁻¹ Ca²⁺ and 18.9 mEq m⁻²yr⁻¹ Mg²⁺ (Table 6). For simplicity, we have assumed that CO₂ only was used for calcite weathering, while any remaining CO₂ and all other acids were used for silicate weathering. This assumption has no effect upon our budget calculations.

Silicate weathering

After subtracting the contributions from old seawater and calcite weathering we found the amounts of ions released due to silicate weathering or cationic exchange (Table 6). The protons needed for this weathering are from: pyrite oxidation: 73.4, acid Input-Output: 48.0, remaining CO₂: 23.3, 'organic acids': 6.96 and 'nitrogen uptake': -4.6. Sum = 147.1 (mEq m⁻²yr⁻¹) (Table 6).

Equilibrium calculations

An attempt was made to determine if there is equilibrium between deep groundwater and calcite. The state of equilibrium can be tested by calculating the saturation indices (SI):

$$\text{SI}_{\text{calcite}} = \log (\text{IAP}/K_{\text{eq}}) = \text{p}K_{\text{eq}} - \text{pIAP}$$

where IAP is the ion-activity product calculated

from analytical data and K_{eq} is the equilibrium constant. A saturation index of 0 means that there is thermodynamic equilibrium between calcite and water. The equilibrium constant for a calcite with composition

$Ca_{1-x}Mg_xCO_3$ is defined as:

$$K_{eq}(x) = [Ca^{2+}]^{1-x} \times [Mg^{2+}]^x \times [CO_3^{2-}]$$

and the value of $pK_{eq} = 8.48$ (Thorstenson & Plummer 1978). The constants used in the Debye-Hückel Equation are given in Garrels & Christ (1965), and the following activities were calculated for groundwater collected at 30 m depth at the southern fringe of the watershed (Furusmo):

$$[HCO_3^-] = 1.78 \times 10^{-3} \quad [Ca^{2+}] = 7.44 \times 10^{-4}$$

$$[Mg^{2+}] = 8.02 \times 10^{-5} \quad [H^+] = 10^{-7.93}$$

$$[CO_3^{2-}] = ([K_{HCO_3}^-] \times [HCO_3^-]) / [H^+]$$

$$[H_2CO_3] = ([H^+] \times [HCO_3^-]) / K_{H_2CO_3}$$

When we use the analysed values to solve these two equations (5°C and $x = 0.025$) we find:

$$[CO_3^{2-}] = 4.17 \times 10^{-6} \quad [H_2CO_3] = 7.0 \times 10^{-5}$$

The value of $IAP = 2.90 \times 10^{-9}$ and $pIAP = 8.54$.

The value for the saturation indices is: $SI_{calcite} = -0.06$ and we conclude that this deep groundwater is in equilibrium with the type of calcite found in these deposits.

The ionic strength of river Risa is close to the value found for deep groundwater (Table 3). This probably means that most of the water in this river has been flowing through calcite-bearing sediments.

Weathering rate of calcite

Plummer & Wigley (1976) have, on the basis of experimental data, calculated the rate of calcite dissolution in natural environments. The time needed to obtain 99% of saturation is given by the following equation for a system where the dissolution is transport controlled:

$$t_{99} = 4.6 \times V/A \times 1/k_T \text{ (sec.)}$$

where A is contact area between calcite and water (cm^2), V is volume of water in the system (cm^3) and k_T is the mass transport coefficient. In hydrologic environments the value of k_T is normally between 10^{-5} and $10^{-2} cm sec^{-1}$.

For reaction-controlled systems they obtained:

$$t_{99} = 1.6 \times 10^6 \times V/A$$

We have assumed that the contact area between water and calcite is proportional to the calcite content (2.4%). We determined the specific surface area for unweathered material ($1.58 m^2 g^{-1}$) and calculated the total surface

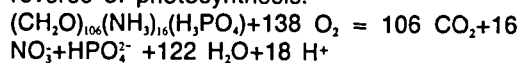
area for $1 m^3$ of material to $2.2 \times 10^6 m^2$. The contact area between calcite and water will then be $5.3 \times 10^4 m^2$. One m^3 of sediment contains 400 l of water ($n=0.4$). Consequently, the V/A ratio is given by:

$$V/A = 4 \times 10^3 / 5.3 \times 10^4 = 7.5 \times 10^{-4} \text{ (cm.)}$$

For a reaction-controlled system $t_{99} = 1200$ seconds, while the maximum value calculated for a transport-controlled system is 345 seconds. We only want to use these calculations to illustrate that calcite weathering is a very rapid process in these deposits compared with the contact time between water and calcite-bearing sediments.

Formation of CO_2 in the unsaturated zone

The results of respiration and bacterial decomposition of organic material are essentially the reverse of photosynthesis:



Later uptake of NO_3^- will release an equivalent amount of OH^- , which will react with H^+ . The result of this decay is mainly the formation of CO_2 . The CO_2 will dissolve in water percolating through the unsaturated zone, and later be consumed in weathering processes.

Carbonic acid in groundwater

The deep groundwater contains 1.91 mEq l^{-1} with HCO_3^- and 0.07 mmoles with CO_2 . We again assume that the amount of bicarbonate formed from calcite is 48.5% of the total amount. This means that the water, after percolating through the unsaturated zone but before the calcite weathering started, contained 1.05 mmole l^{-1} with CO_2 . The amount of CO_2 in this water was determined by the partial pressure of CO_2 in the soil atmosphere ($-p_{CO_2}$):

$$[CO_2] = K_{CO_2} \times P_{CO_2}$$

The value of K_{CO_2} at 5°C is $10^{-1.2}$ (Garrels & Christ 1965 p. 89).

The value of $[CO_2] = 1.05 \times 10^{-3} mol l^{-1}$ and the average p_{CO_2} must have been close to 0.017 atm or close to 1.7%. This is about 55 times higher than in water in contact with normal atmosphere.

Most values reported for CO_2 contents in soil atmospheres are in the range 0.5-3% (Gerstenhauer 1972), but the amounts vary

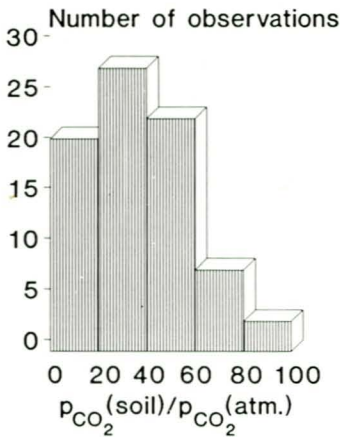


Fig. 7. Calculated values of pCO₂ in the soil atmosphere (BC-horizons).

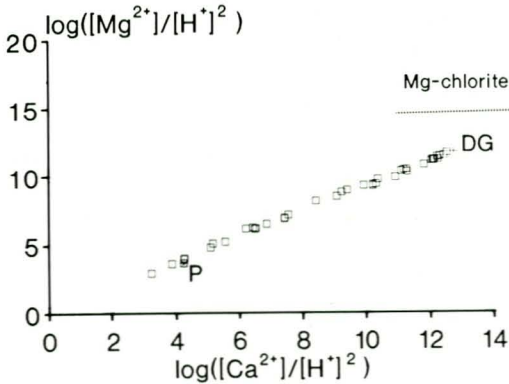


Fig. 8. Activity ratios for lake water. Data from Otnes (1973, 1975) and Hongve (1977).

considerably through the year and between years. The highest values are normally found in forest soils (Scheffer & Schachtschabel 1976). Our calculated average value falls within the values reported from a German forest soil (Gerstenhauer 1972) but they are higher than values reported from forest soils in Maine (Fernandez & Kosian 1987) and Ontario (Reardon et al. 1980). The high average CO₂ content was not expected, since 60% of new groundwater is formed during a short snow-melting period. This water percolates through the soil in a fairly cold period with low biological activity. Data for water collected by tension lysimeters at Nordmoen are used to calculate the CO₂ pressure in the soil atmosphere (BC-

horizon). The values vary through the year and between localities. The calculated values are shown in Fig. 7. The values calculated from soil lysimeter data must be minimum values and they support the calculated average value (1.7%) for the whole catchment.

Chemical evolution paths

The composition of the groundwater is gradually changing with increasing flow distances. This is reflected in the composition of the lakes. From the lake data we calculated the activity ratios:



The values are plotted in Fig. 8. In addition to data from the IHD-project we have used the data from Hongve (1977). The composition of lakes falls on an almost straight line between precipitation (P) and deep groundwater (D.G.), which is at equilibrium with calcite. Two lakes have lower activity ratios than precipitation, which means that the water was acidified by the soil before reaching the lake. Short contact with organic matter can explain the acidity of these two shallow lakes located in decalcified deposits.

The reaction between calcite and water is rapid compared to the residence time of the water in the catchment. As a result, these lakes are mixtures of groundwater which has been in contact with calcite-bearing deposits and water which has only been in contact with decalcified deposits.

Increasing [Ca²⁺]/[H⁺]² ratios (Fig. 8) are due mainly to the weathering of calcite while the increase in the [Mg²⁺]/[H⁺]² ratio can only be partly explained by this reaction. During weathering of the aquifer's calcite content, the increase in Ca²⁺ should be 40 times faster than the increase in Mg²⁺. The data in Fig. 8 show that the release of Ca²⁺ is only 5 times faster than the release of Mg²⁺. Consequently, a major part of the magnesium must come from other Mg-bearing minerals. This agrees with the data given in Table 1. There are several Mg-containing minerals in these deposits. Studies of soil profiles (Teveldal et al. 1990) have shown that breakdown of chlorite is the most important silicate-weathering reaction. A rapid weathering of chlorite in ion-rich water has also been described by Mackenzie & Garrels (1965).

The equilibrium line for Mg-chlorite (at quartz saturation) is shown in Fig. 8. Apparent-

ly the water has not reached equilibrium with this mineral. The chlorite found in our sediments has a composition near (microprobe data):



This chlorite will be in equilibrium at a lower $[\text{Mg}^{2+}]/[\text{H}^+]^2$ ratio. A higher silica content than the quartz equilibrium value will also lower the chlorite equilibrium line (Fig. 8). Consequently, we believe that the deep groundwater is near equilibrium with the low-magnesian calcite and the chlorite. The weathering of Mg-calcite and chlorite will rapidly retard the weathering of other silicates due to increased ionic activities and an increase in pH.

How much material has been removed during the postglacial period ?

If we assume that the deep weathering during the last 9000 years released annually the same amount of ions as today we can calculate the total depletion for this postglacial period.

The dry density of the sediments is close to 1.4 tons m^{-3} , and the mineralogical composition of 1 m^3 unweathered material is:

Amphibole: 27 kg	Muscovite: 176 kg	Quartz: 680 kg
Chlorite: 95 kg	K-feldspar: 245 kg	Calcite: 34 kg
Biotite: 27 kg	Plagioclase: 109 kg	Pyrite: 7 kg

The acid front — calcite weathering

Acid water, percolating through the unsaturated zone will rapidly dissolve calcite. As a result there will be a calcite depleted upper part with a fairly sharp boundary (the acid front) towards the underlying calcite-bearing sediments (Christensen 1962).

The depth of this decalcified zone depends upon the total amounts of strong and weak acids carried by the percolating water and the amount of calcite originally present in the sedimentary deposits.

The weathering budget showed that the amount of calcite dissolved each year was 377.1 mmol m^{-2} or 37.6 g m^{-2} . One m^3 with unweathered material contains 34 kg calcite and the acid front will move downward with slightly more than 1 mm per year. If the weathering of calcite through the postglacial period has been similar to what we observe to-

day, we would expect the thickness of the decalcified zone to be close to 10 m. This agrees very well with the observed thickness (Fig. 4). It also means that calcite weathering is a rapid process which takes place near the boundary between calcite-depleted and calcite-bearing deposits. Similar data have been reported by Reardon et al. (1980).

Annually, 36.7 $\text{mmol m}^{-2} \text{SO}_4^{2-}$ is formed from the oxidation of 18.4 mmol (or 2.3 g) of FeS_2 . If the oxidation rate has been the same during the last 9000 years 20.7 kg m^{-2} of FeS_2 has been oxidized to sulphate. One m^3 of unweathered sediment contains 7.0 kg of pyrite. The amount of pyrite oxidized during postglacial time corresponds to what is found in a 3 m-thick layer of unweathered material.

We will use potassium as an example for silicate-bound elements. One m^3 of unweathered sediment contains 54 kg K^+ . The amounts released during the last 9000 years are equivalent to 3.3 kg m^{-2} . The total amounts removed during the postglacial period are equivalent to all potassium found in a 6 cm-thick layer of unweathered deposits.

In addition, there is the amount stored temporarily in biomass, which has mainly been taken from the soil profile. Calculations showed that the water composition even for deep groundwater is nowhere near in equilibrium with K-feldspar.

Conclusions

Groundwater flowing through the deep glaciofluvial deposits has an average residence time of 30 years, and its composition is gradually changing along its flow paths.

The lakes are fed only with groundwater, and their compositions reflect the differences in groundwater composition. The most important acid for weathering is CO_2 formed in the unsaturated zone. The average CO_2 pressure in the lower part of the unsaturated zone must be about 55 times higher than in normal air.

A closed system dissolution of low-Mg calcite and silicates is important for the groundwater chemistry. Oxidation of sulphides and leaching of old sea salt also influence the groundwater chemistry.

Deep groundwater is at equilibrium with calcite and close to equilibrium with chlorite. Unweathered deposits contain about 2.4% calcite. The decalcified zone formed during

postglacial time (9400 years) is about 10 m deep.

The total amount of potassium removed during postglacial time is equivalent to all potassium in a 6 cm-thick layer of unweathered material. This illustrates the difference in susceptibility to weathering between calcite and some silicates.

Acknowledgements

The authors would like to express their appreciation to the referees for their useful comments and criticisms on earlier versions of this manuscript. Funds for this research were made available through The Agricultural Research Council of Norway (NLVF).

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Manuscript received November 1990: revises typescript February 1991: accepted March 1991.