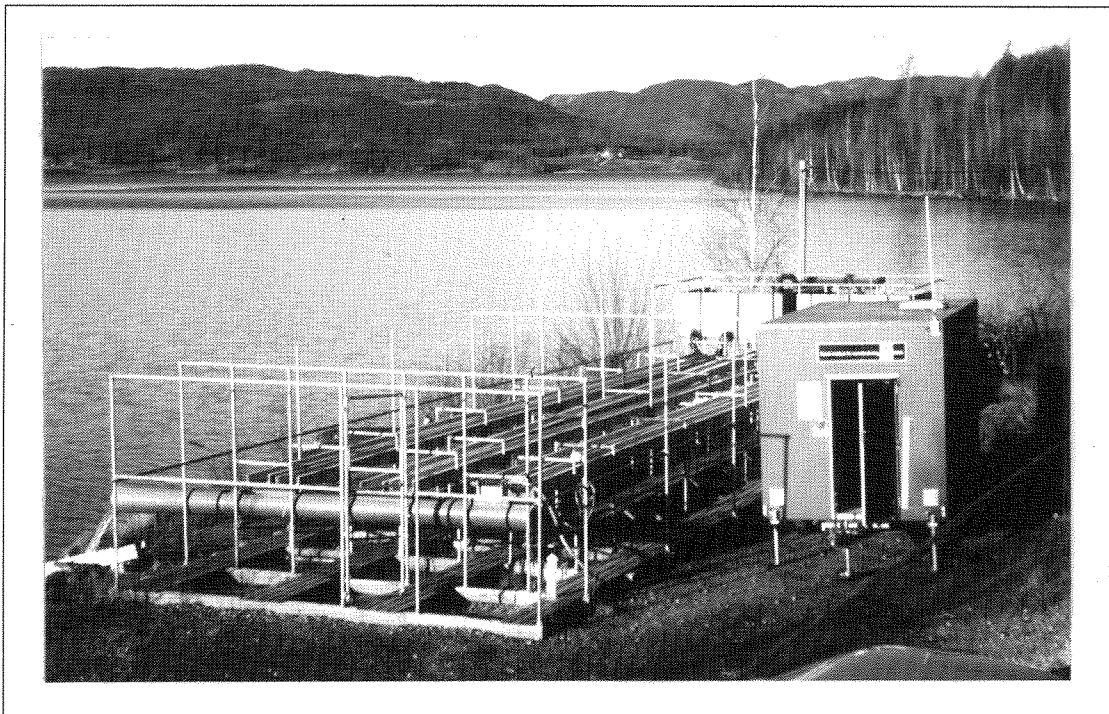


Acid Rain Research

REPORT 28/1992

Buffering Capacities and
Effects of River Substrates
during Acidic Episodes



Norwegian Institute for Water Research



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Report No.:

0-88018

Sub-No.:

Serial No.:

2718

Limited distribution:

Report Title:

**BUFFERING CAPACITIES AND EFFECTS OF RIVER
SUBSTRATES DURING ACIDIC EPISODES**

Date:

February 1992

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Topic group:

MILTEK

Geographical area:

Southern Norway

Number of pages (incl. app.)

24

Contractor:

Norwegian Institute for Water Research

Contractors ref. (or NTNF-No)

Abstract:

Experimental work in specially made channels has shown that moss (Nardia compressa and Fontinalis dalecarlica) exposed to running water act as buffering agents against pH variations, both up and down. Ion exchange (H^+ for cations) is responsible for the buffering. The most important cations in the buffering process are Ca and Al. Under less acidic to neutral conditions the moss regenerates its buffer capacity by adsorbing the same cations from the stream water.


4 keywords, Norwegian

1. Forsuring
2. Mose
3. Bufferkapasitet
4. Aluminium

4 keywords, English

1. Acidification
2. Moss
3. Buffer capacity
4. Aluminium

Project leader


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For the Administration


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ISBN 82-577 -2080-1


Bjørn Olav Rosseland

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INTRODUCTION

It has been well documented that aluminium (Al) concentrations in certain streams increase during episodes of low pH (Schofield 1977, Baker and Schofield 1982, Henriksen et al. 1984, Skogheim et al. 1984, Caines et al. 1985). Field experiments involving acidification of small brooks have shown release of large amounts of Al from stream substrates (Norton et al. 1987).

Experimental acidification to pH 4 of a small tributary of the river Vikedal was conducted in southwestern Norway. The tributary had pH-variations between 5 and 6. Large amounts of Al were released from moss growing on the stream bed during conditions of artificially lowered pH (Henriksen et al. 1988). The moss contained as much as 0.9% Al by dry weight. About 150 mg of Al were released per m² of stream surface during 6 hours of acidification.

Another experiment was carried out in the small brook Bonnabekken 10 km north of Oslo (Norton et al. 1987). Bonnabekken has a pH that ranges from 5 to 6. During episodic experimental acidification of Bonnabekken two Al sources were identified, a small reservoir of easily mobilized Al on stream bed substrates and a larger reservoir of slightly less soluble Al. About 1 g of Al was released per m² of stream surface over two days of acidification.

Tipping and Hopwood (1988) determined release rates for monomeric Al from streambed materials placed in a laboratory channel and exposed to acidic water. The values of the release rate coefficient (K) were estimated from results of the field experiments of Henriksen et al. (1988) and Norton et al. (1987). The values of K ranged from 0.1 to 3.2 $\mu\text{mol m}^{-2} \text{s}^{-1}$. K decreased with increasing pH and was greater for beds containing liverwort (Nardia compressa) than for mineral (pebbles/gravel) beds.

Using laboratory experiments Henriksen et al. (1988) and Wathne and Røgeberg (1988) also showed that acid treatment of stream bed substrates may release Al.

We conducted experimental work in six specially made channels. The water supply for the channels was taken directly from the lake Maridalsvannet, the water supply for Oslo. Acidification experiments using moss (Nardia compressa and Fontinalis dalecarlica), gravel, and sand as substrates investigated the release and uptake of Al and other cations during and between acid episodes.

MATERIALS AND METHODS

On the southeast shore of the lake Maridalsvannet the Norwegian Institute for Water Research (NIVA) has built an experimental set up with 6 plastic channels 15 m long, 20 cm wide, and with an adjustable flow and water depth (15 cm). Water from Maridalsvannet is pumped into a 1 m³ plastic reservoir where chemicals may be added. Water then flows through control weirs into the channels from the reservoir. The water inlet to the channels, where the "inlet samples" were taken, is placed 30 cm from the upper end of the channels. At the end of each channel is a second horizontal weir that controls the water depth in each channel. The "outlet" samples were taken close to this end of the channels. The residence time of water in the experimental channels will give a dilution effect during the experiment. This effect is considered while discussing the experimental results. The channels were scrubbed with stiff brushes to remove algal growth. (The mixing box was not effectively cleaned before the experiment was started.) For all experiments described in this report water flow was adjusted to 3.7 l/min. The residence time for water in the channels was about 1.3 minutes. Consequently we believe that mixing effects are largely over after 15 to 20 minutes.

The mosses (*Nardia compressa* and *Fontinalis dalecarlica*) used during the experiments were collected from Skarselva and Vikedalselva (Fig. 1). Moss was secured in the channels by means of ceramic tiles. Gravel and sand from Bonnabekken and Skarselva were placed in the channels without tiles. Currents were sufficiently low so that sediment transport was nil.

MOBILLAB-NIVA (Røgeberg and Henriksen 1985, Henriksen et al. 1986) was used for continuous measurement of pH, and reactive and labile Al at the inlet and outlet of the experimental channel. Thus the water was analyzed before and after passing the streambed substrates in the channel.

Al was measured continuously, with alternate measurements of reactive and non-labile Al occurring each 15 min. or just reactive Al every 15 min.

Individual water samples were collected and analyzed for other parameters at NIVA according to established procedures. The pH was determined with an Orion model 801-A meter with a radiometer combination electrode. Calcium, Mg, Na and K were determined by flame atomic absorption spectrophotometry (Perkin Elmer 560).

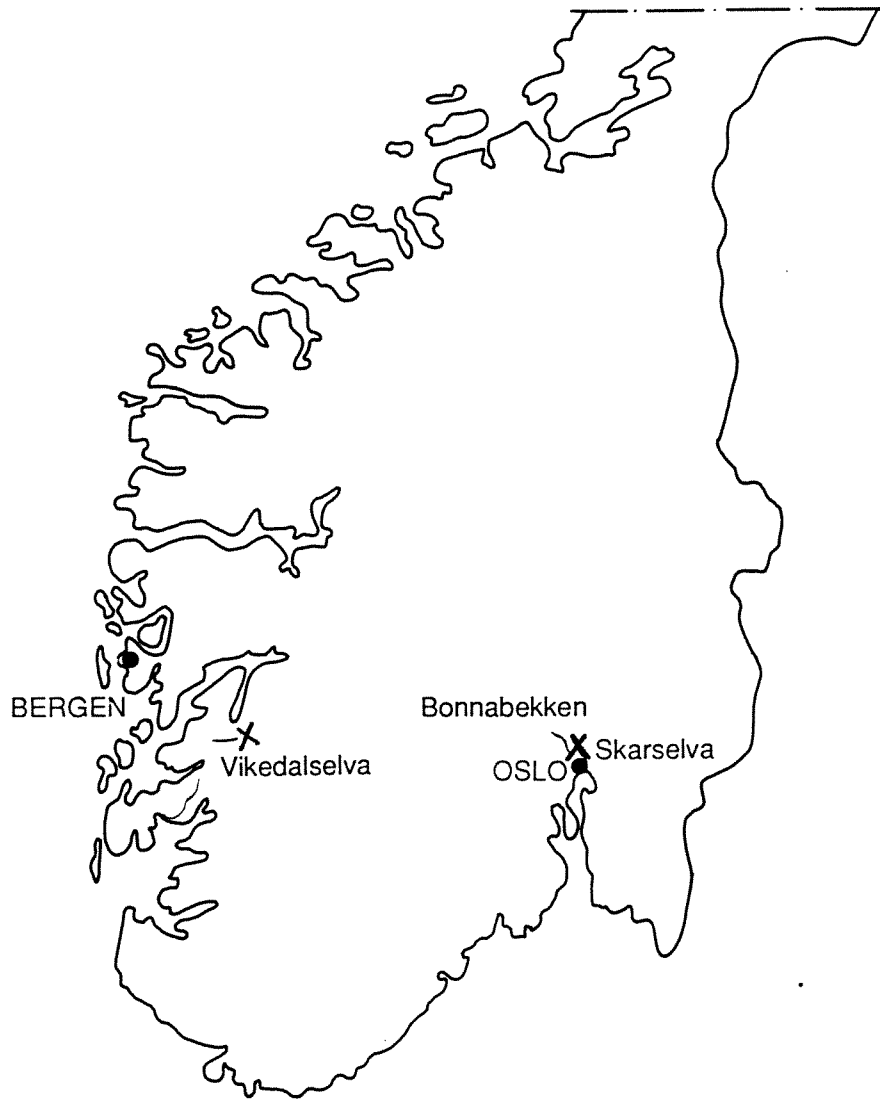


Fig. 1. Locations where samples of streambed substrates were taken (X).

Acid (added as 1N H_2SO_4) and Al (added as $[AlK(SO_4)_2 \cdot 12H_2O]$) were introduced with a peristaltic pump into the 1 m³ plastic box for mixing with water from Maridalsvannet. This system gave stable input water quality throughout the experiments.

The mass of moss in the experiments was determined by totaling harvesting it from the channels, drying it for approximately 18 hours at 105 °C, and weighing.

DESCRIPTION OF EXPERIMENTS

The conceptual drawings of the experiments are shown on figure 2.

A. Experiment # 1

This experiment was conducted to evaluate the effect on water chemistry of the experimental channel with bare ceramic tiles. The inflowing water was acidified to pH 4.0 (1A). After 24 hours Al-rich (~150 µg/l) water of pH 5.0 was introduced to the channel for 24 hours (1B), followed by water of pH 4.0 (with a lower Al-concentration, ~90 µg/l) (1C).

B. Experiment # 2

Sand and gravel from Bonnabekken (Fig. 1) (pH between 5 and 6), a small brook near Oslo (Norton et al. 1987, Henriksen et al. 1988, Wathne and Røgeberg 1988) were equilibrated with untreated water from Maridalsvannet for 48 hours (2A). The pH was then lowered to 4.0 for 48 hours (2B). The pH was then increased to ~5 and Al (~100 µg/l) was added for 48 hours (2C) (2 days). Then untreated water from Maridalsvannet (pH ~6.4, Al-conc. ~30 µg/l) was introduced for 2 days (2D), followed by acidification with H_2SO_4 to pH ~4.0 (2E).

C. Experiment # 3

Moss (Nardia compressa) from the river Skarselva (Fig. 1) in Maridalen was placed in the channel. Skarselva has a pH continuously above 5.5. Water from Maridalsvannet was pumped through the channel for 48 hours (3A). The water pH was 6.4 to 6.5 and reactive Al (RAL) was ~20 µg/l. The pH was lowered to 4.0 and kept constant for 48 hours (3B). Then the acid addition was stopped and water from Maridalsvannet with a pH of 6.4 was introduced for about 32 hours (3C). Then acidification was started again, with a constant pH of 4.0 for 24 hours (3D). Then acid

with dissolved Al ~100 µg/l was added for 24 hours at pH 4.0 (3E). The pH was raised to 5.0 for 24 hours and Al-concentration to ~200 µg/l (3F). Finally, the pH was lowered to pH=4, with ca. 100 µg Al addition (3G).

D. Experiment # 4

Stones from Skarselva (Fig. 1) and partly covered with moss (Nardia compressa) were subjected to water from Maridalsvannet for 24 hours (4A). The water was then acidified to pH 4.0. for 24 hours (4B).

E. Experiment # 5

Moss (Fontinalis dalecarlica) from the river Vikedalselva (Fig. 1) (pH between 5 and 6) was equilibrated with untreated water from Maridalsvannet for 48 hours (5A). Then the channel was acidified to pH 4.0 for 48 hours (5B), followed by 24 hours with water with pH 5 and Al of ~100 µg/l (5C). Then the pH was lowered to ~4.0 with no extra Al (5D).

F. Experiment # 6

One channel was not cleaned of algae. The channel had only been exposed to untreated water from Maridalsvannet before the pH was decreased to ~4 for 48 hours. After the experiment one tile (20 cm x 20 cm) in the channel was harvested for algae. The algae were dried overnight at 105°C to determine the dry weight.

RESULTS AND DISCUSSION

A. Experiment # 1

There was no significant buffering effect from the channel walls, ceramic tiles or remaining algae. The results for the first acidification to pH 4 are shown in Figure 3. This acidification was made with acid containing Al at a concentration of ~90 µg/l. The Al values and pH values at the inlet and outlet follow each other closely. The result was similar when Al-rich (~150 µg/l) water with pH 5 was submitted to the channel followed by a second acidification to pH 4 (see Figure 3). The rapid pH response at the outlet indicates that mixing of old and new water in the channels is minimal. Apparently much of the flow is "piston" flow. Steady state chemistry with conservative elements is achieved in <0.5 h.

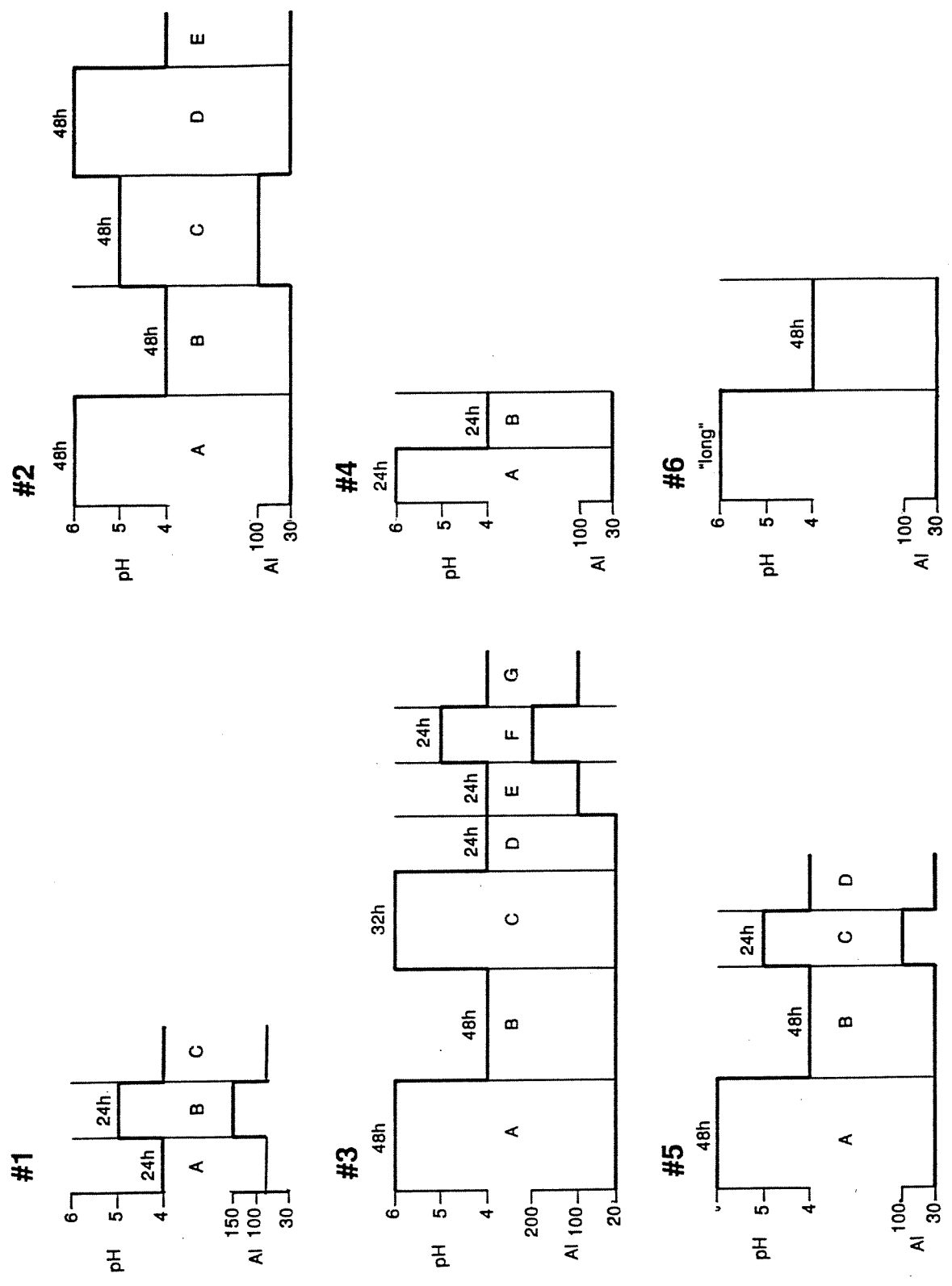


Fig. 2. Aluminium (Al) values and pH in inlet water during the experiments # 1 to # 6.

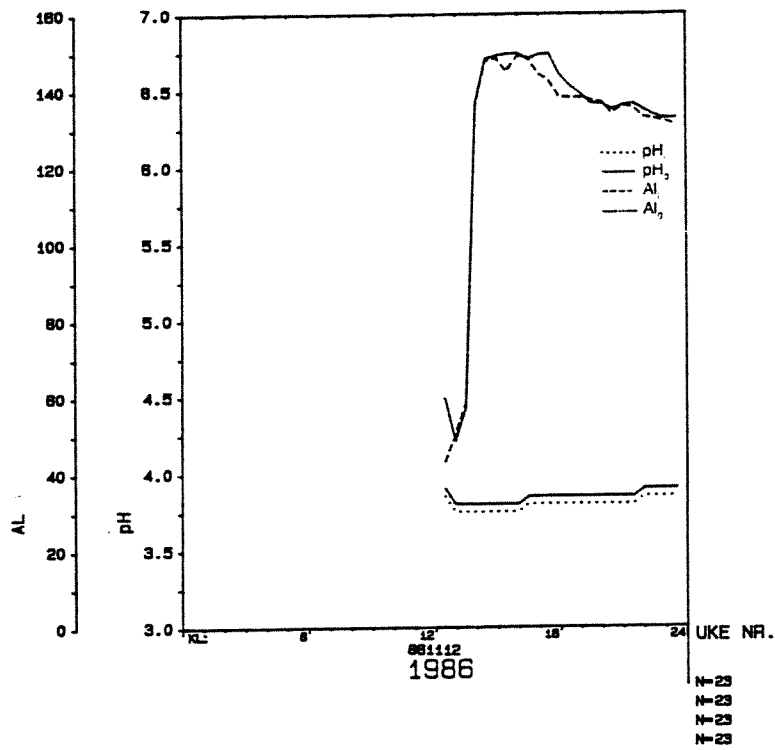
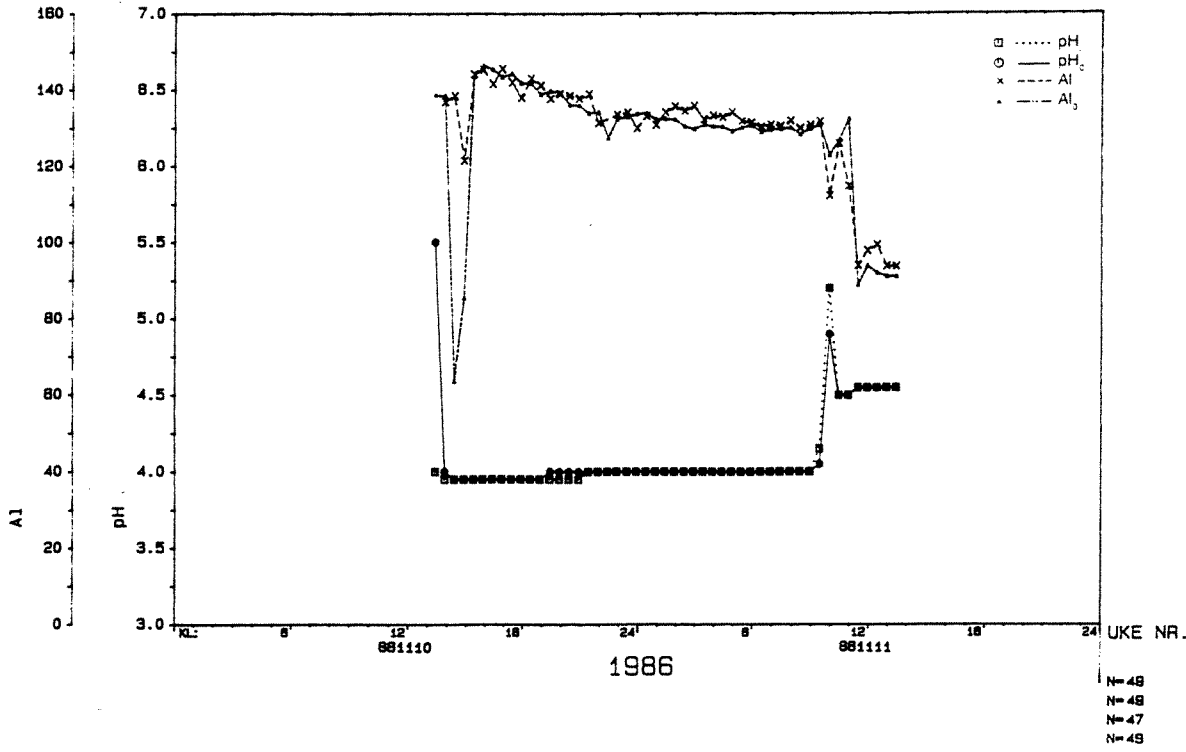


Fig. 3. Experiment # 1 (1A and 1C)(bare ceramic tiles). Aluminium (Al) and pH-values at the inlet (i) and outlet (o) of the experimental channel.

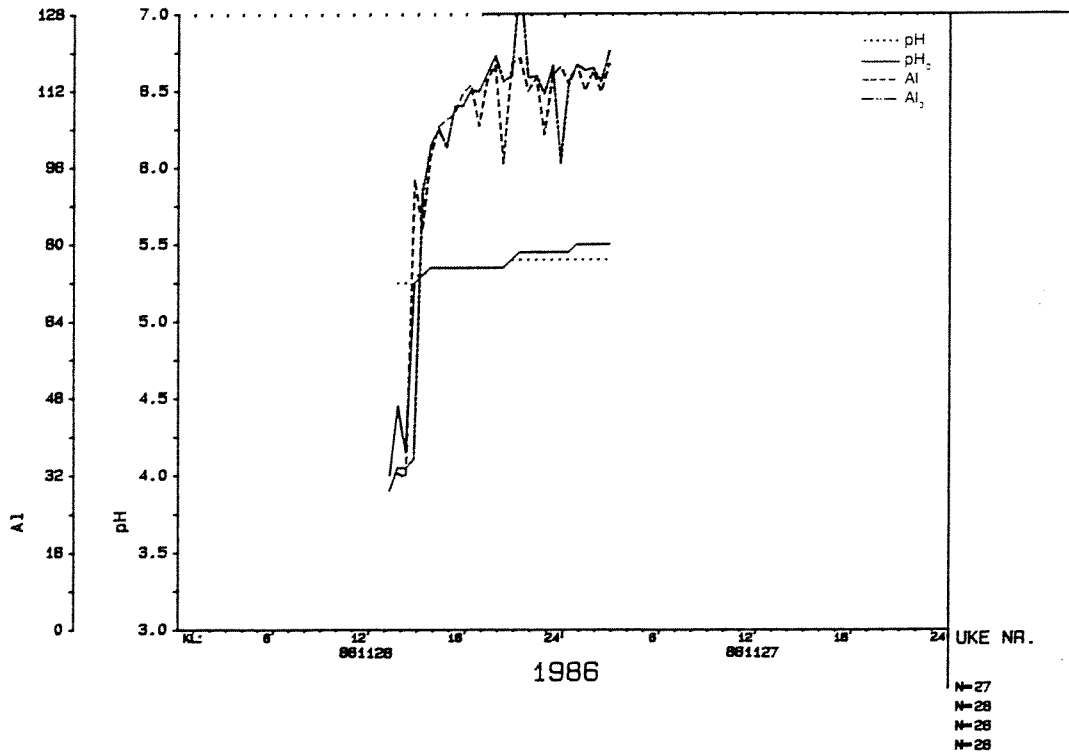


Fig. 4. Experiment # 2C (Bonnabekken, sand and gravel). Aluminium (Al) and pH-values at the inlet (i) and outlet (o) of the eksperimental channel.

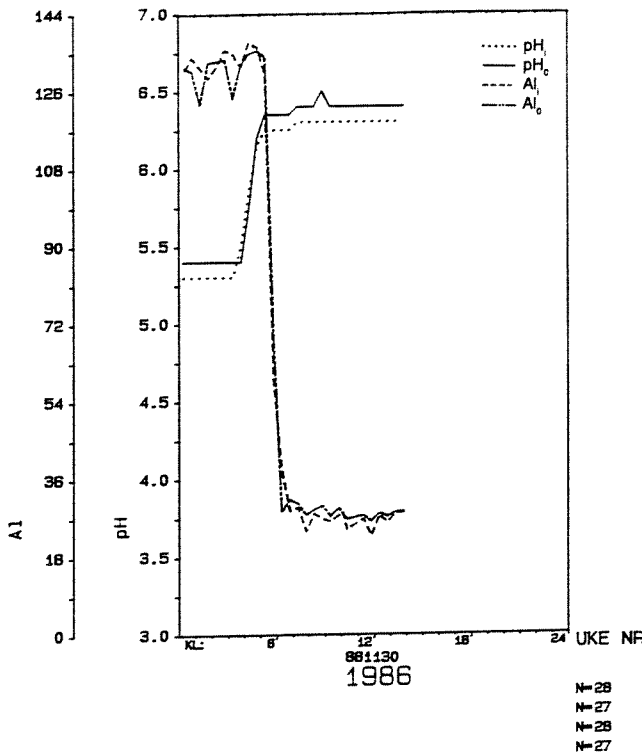


Fig. 5. Eksperiment # 2D (Bonnabekken sand and gravel). Aluminium (Al) and pH-values at the inlet (i) and outlet (o).

Water samples taken at the water reservoir before acid and Al addition and water samples from the outlet, taken 48 hours after the additions started, were analyzed for cations. The results are shown in table 1.

Table 1. Analysis of water samples from the mixing reservoir and the channel outlet during experiment # 1, acidification (1A) and Al addition (1B).

| | pH | Ca mg/l | Mg mg/l | K mg/l | Na mg/l |
|--------------|------|------------|------------|-----------|------------|
| a) Reservoir | 6.38 | 2.82 | 0.50 | 0.36 | 1.36 |
| Outlet | 4.32 | 2.88 | 0.49 | 0.51 | 1.33 |
| b) Reservoir | 6.49 | 2.77 | 0.48 | 0.36 | 1.31 |
| Outlet | 4.94 | 2.89 | 0.47 | 0.40 | 1.35 |

The results from this experiment show the small effect on input water chemistry caused by small amounts of algae and the tiles in the experimental channel. The increased K is due to the addition of Al as $AlK(SO_4)_2$ with acidification to both pH 4 and pH 5.

B. Experiment # 2

The analytical results for experiment 2C are shown in table 2.

Table 2. Analysis of water samples from the inlet and outlet during experiment # 2C with sand and gravel from Bonna-bekken. (Increased pH and Al after acidification.)
n = not measured.

| | | pH | Ca mg/l | Mg mg/l | K mg/l | Fe µg/l | Mn µg/l | Zn µg/l |
|-------|--------|------|------------|------------|-----------|------------|------------|------------|
| t=0 | Inlet | 4.28 | 2.79 | 0.53 | 0.40 | 102 | 19 | 20 |
| | Outlet | 4.27 | 2.80 | 0.50 | 0.39 | 59 | 18 | 20 |
| t=19h | Inlet | 5.61 | 2.80 | 0.50 | 0.48 | n | n | n |
| | Outlet | 5.61 | 2.83 | 0.50 | 0.49 | n | n | n |

The small increase in K is from the $\text{AlK}(\text{SO}_4)_2$ used for Al-addition. After 48 h, untreated water from Maridalsvannet (pH ~6.4) was introduced to the channel for 48 h (see Fig. 5). Then the pH was decreased to ~4 (Experiment 2E). Samples were taken at the inlet and outlet and results of the chemical analyses are shown in table 3.

Table 3. Analyses of water samples from the inlet and outlet during experiment # 2E with sand and gravel from Bonna-bekken.

| | | pH | Ca mg/l | Mg mg/l | K mg/l | Fe µg/l | Mn µg/l | Zn µg/l |
|----------|--------|------|------------|------------|-----------|------------|------------|------------|
| t=30min. | Inlet | 4.0 | 2.81 | 0.51 | 0.37 | 47 | 12.5 | 20 |
| | Outlet | 4.22 | 2.89 | 0.54 | 0.39 | 62 | 14.5 | 20 |
| t=50min. | Inlet | 3.70 | 2.88 | 0.54 | 0.38 | - | - | - |
| | Outlet | 3.87 | 3.04 | 0.55 | 0.39 | - | - | - |
| t=24 h | Inlet | 4.27 | 2.76 | 0.56 | 0.36 | | | |
| | Outlet | 4.22 | 2.82 | 0.52 | 0.36 | | | |

The samples taken after 50 min. showed that Ca 8 µeq were desorbed from the sand and gravel. The results for the pH and Al-measurements are shown in figures 4 and 5. The first part of figure 4 shows a slow rise in Al-concentrations compared to more rapid changes in pH. This indicates that Al changes are due not only to dilution flushing. No effect can be seen in outlet pH values as a result of increasing the inlet pH, but lowering the pH resulted in increased Al-values both at the inlet and at the outlet. This increase must be due to release of Al from algal growth in the plastic reservoir where chemicals were added (mixing box).

C. Experiment # 3

Chemical analyses of the inlet and outlet water gave the results shown in table 4; the results for the continuous measurements of Al and pH are shown in figure 6.

At t=0 no significant changes existed in the channel. After 20 min. of acidification there was a difference between intake and outlet chemistry. Sixteen µeq/l of H^+ -ions were taken up by the moss; the

release of Ca, Mg and K from the moss was 35 $\mu\text{eq/l}$, 6.7 $\mu\text{eq/l}$ and 0.77 $\mu\text{eq/l}$ respectively. The lack of charge balance may be due to non-steady state acid additions, i.e. pH and metals were not measured from the same sample. After 2.5 hours of acidification the moss reservoir of base cations for ion exchange was almost depleted. About 8 $\mu\text{eq/l}$ of H^+ -ions were taken up and amounts of Ca, Mg, and K desorbed were small. The release of Al had started and increased (Fig. 6).

Table 4. Analyses of water samples from the inlet and outlet of the experimental channel with moss from Skarselva at time $t=0$, 20 min., and 2.5 hours after the start of the acidification to pH 4.0. Experiment # 3B.

| | | pH | ΔH^+ | Ca | ΔCa | Mg | ΔMg | K | ΔK | Al* | ΔAl |
|-----------|--------|------|--------------------|------|-------------------|------|-------------------|------|------------------|-----------------|-------------------|
| | | mg/l | $\mu\text{eq/l}$ | mg/l | $\mu\text{eq/l}$ | mg/l | $\mu\text{eq/l}$ | mg/l | $\mu\text{eq/l}$ | $\mu\text{g/l}$ | $\mu\text{eq/l}$ |
| t=0 | Inlet | 6.51 | | 2.83 | | 0.49 | | 0.36 | | 20 | |
| | Outlet | 6.61 | -0.06 | 2.87 | +2 | 0.48 | -0.83 | 0.37 | +0.26 | 23 | + 0.33 |
| t=20 min. | Inlet | 4.46 | | 2.91 | | 0.48 | | 0.36 | | 21 | |
| | Outlet | 4.73 | -16 | 3.61 | +35 | 0.56 | +6.7 | 0.39 | +0.77 | 23 | + 0.22 |
| t=2.5 h | Inlet | 4.20 | | 2.91 | | 0.48 | | 0.36 | | 55 | |
| | Outlet | 4.26 | -8.1 | 2.99 | +4 | 0.49 | +0.83 | 0.36 | 0 | 62 | + 0.78 |

* Al-results taken from the continuous measurements in figure 5.

These results agree with earlier results from field and laboratory experiments, where neutralization by moss was initially dominated by release of Ca. The reservoir of Ca was quickly depleted, and the release of Al became increasingly important (Norton et al. 1987, Henriksen et al. 1988, Wathne and Røgeberg 1988). For experiment # 3B, the K- and Mg-reservoirs are depleted after 2.5 hours. The Ca-reservoir is almost depleted, but the Al-release is increasing, and the Al-reservoir is still releasing after 18 hours. If the ΔCa value at $t = 20$ min. is applied for 1h, the release of Ca is about 1000 $\mu\text{g/g}$ moss (DW).

Figure 6 shows an increase in Al from ~ 20 $\mu\text{g/l}$ to 65 to 70 $\mu\text{g/l}$ in 4 hours as the pH was decreased. Extra Al at the channel inlet must be due to Al from the mixing box. The concentration of Al at the outlet was approximately 5 $\mu\text{g/l}$ higher than the concentration at the inlet

for 13 hours before the acidification was stopped. With a flow of 3.7 l/min in the channel, ~14 mg Al were released. The dried weight (DW) of the moss was 145 g after the experiment was finished. The release of Al from the moss was thus ~100 µg/g DW or ~10 µeq/g DW after 18 hours of acidification. The moss was still releasing Al so this figure is a minimum amount expected to be released from this moss during an acid episode. We don't have reliable continuous measurements from this experiment after the first 18 hours. However, after 22.5 h and 26 h individual water samples were taken from the inlet and the outlet of the channel. They indicated no change of the water quality caused by the moss in the channel (see table 5).

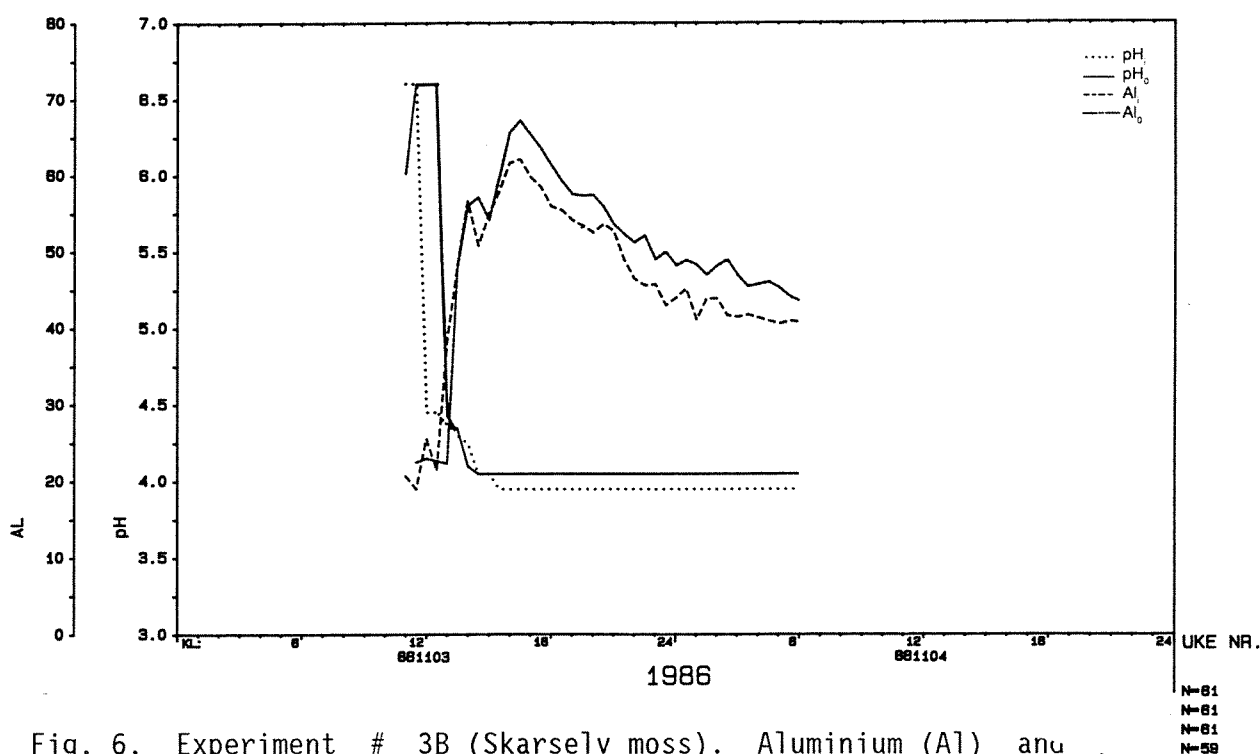


Fig. 6. Experiment # 3B (Skarselv moss). Aluminium (Al) and pH values at inlet (i) and outlet (o).

After acidification was stopped (h=0 in table 6) (Experiment 3C), samples taken at 1.5 h showed that the moss restored its buffer capacity by adsorbing primarily Ca. The pH was lowered from 6.47 at the inlet to 6.06 at the outlet resulting in 0.53 µeq/l of H⁺-ions desorbed to the water and a reduction of HCO₃⁻ alkalinity. The uptake of Ca, Mg, K and Al from the water were 19.5, 2.5, 1.0, and ca. 0.2-0.4 µeq/l respectively. Five hours after the acidification stopped the pH-, Ca-, Mg- and K-values at the outlet were back to inlet values.

Table 5. Chemical analyses of water samples taken at the inlet and the outlet of the channel with moss from Skarselva after 22.5 h and 26 h of acidification. Experiment # 3B.

| | | pH | Ca mg/l | Mg mg/l | K mg/l |
|------------|--------|------|------------|------------|-----------|
| t = 22.5 h | Inlet | 4.14 | 2.88 | 0.49 | 0.36 |
| | Outlet | 4.16 | 2.88 | 0.48 | 0.35 |
| t = 26 h | Inlet | 4.02 | 2.92 | 0.48 | 0.37 |
| | Outlet | 4.05 | 2.93 | 0.49 | 0.36 |

Table 6. Chemical analyses of water samples taken at the inlet and outlet of the experimental channel with moss from Skarselva at time = 0, 1.5 h and 5.0 h after stopping acidification, Experiment 3C.

| | | pH | ΔH^+ $\mu\text{eq/l}$ | Ca mg/l | ΔCa $\mu\text{eq/l}$ | Mg mg/l | ΔMg $\mu\text{eq/l}$ | K mg/l | ΔK $\mu\text{eq/l}$ | Al* $\mu\text{g/l}$ | ΔAl $\mu\text{eq/l}$ |
|---------|--------|------|--|------------|---------------------------------------|------------|---------------------------------------|-----------|--------------------------------------|------------------------|---------------------------------------|
| t=0 | Inlet | 4.30 | | 2.84 | | 0.48 | | 0.36 | | 41 | |
| | Outlet | 4.30 | 0 | 2.83 | -0.50 | 0.49 | +0.83 | 0.35 | -0.26 | 47 | + 0.67 |
| t=1.5 h | Inlet | 6.47 | | 2.87 | | 0.48 | | 0.36 | | 35 | |
| | Outlet | 6.06 | +0.53 | 2.48 | -19.5 | 0.45 | -2.5 | 0.32 | -1.0 | 33 | - 0.22 |
| t=5.0 h | Outlet | 6.46 | | 2.81 | | 0.48 | | 0.35 | | 33 | |

Acidification of the system was started again (Experiment 3D) (see Fig. 7). The Al (RAL) concentration increased both at the inlet (for reasons discussed previously) and somewhat more at the outlet. Release of Al from the moss in the channel resulted in approximately 6 $\mu\text{g/l}$ higher values at the outlet than at the inlet for 7 hours. The water flow in the channel was 3.7 l/min. yielding ~9 mg of Al (RAL) or 1000 μeq (60 μg Al/g DW).

Just prior to acidification, pH at the inlet and outlet was almost the same, 6.58 and 6.55 respectively. The pH at the inlet decreased faster than pH at the outlet because of dilution and because the moss was neutralizing some of the acid, as described earlier. After 7 hours, the pH at the inlet and outlet was 4.0.

For the first 6 hours the difference between inlet pH (4.1) and outlet pH (4.4) was approximately 39.6 $\mu\text{eq/l}$. The flow was still 3.7 l/min. giving ~50,000 $\mu\text{eq H}^+$ neutralized. About 1000 μeq of Al were released, or 2% of the 50,000 μeq of H^+ . Although part of the pH difference is due to the residence time of water in the experimental reach (and thus dilution effects), considerable neutralization by cation release is suggested. However, cations were not measured.

After 30 hours of acidification, Al (100 $\mu\text{g/l}$) was added to the system. The pH was kept at 4.0. The concentration of Al at the inlet and the outlet both increased to ~100 $\mu\text{g/l}$, but the concentration at the inlet increased faster than the outlet concentration as shown in figure 4. The difference between the two curves showing concentrations of Al gives an amount of ~8 mg Al taken up from the water during 7 hours, before the Al-concentrations at the inlet and outlet were equal and the moss was "saturated" with Al. The amount of Al taken up at pH 4.0 is then ~50 $\mu\text{g/g DW}$ or 0.6 $\mu\text{eq/g DW}$.

To be able to study the uptake and release of Al from/to water with another acidity, pH was then raised from 4.0 to 5.0 (Experiment 3F), while the Al-concentration was increased to ~290 $\mu\text{g/l}$ (see Figure 8). At $t = 0$ the water chemistry at the inlet and outlet was the same.

The pH at the inlet increased faster than at the outlet. This is consistent with dilution and the buffering effect of the moss. Similarly, the Al-concentrations showed higher values at the inlet for approximately 15 hours (Figure 8) whereas the pH values had converged after about 5 hours. The difference between inlet and outlet was approximately 10 $\mu\text{g Al/l}$. A water flow of 3.7 l/min. yields a calculated Al-uptake of ~30 mg, three times the uptake at pH 4.0 with Al-concentration in water ~100 $\mu\text{g/l}$. The total amount taken up by the moss was ~40 mg or 30 $\mu\text{eq/g DW}$ (~300 $\mu\text{g Al/g DW}$). The "storage" capacity for Al in the moss is 6 times higher at pH=5 and Al = 300 $\mu\text{g/l}$ than at pH 4 and Al-concentration ~ 100 $\mu\text{g/l}$ in the water.

After 24 hours the pH was reduced to 4 and Al decreased to 100 $\mu\text{g/l}$. Initially, there was a short-lived drop down to pH 3.9. The reduction in pH resulted in a rapid and high peak in the Al-concentration. The concentration at the outlet remained 10-20 $\mu\text{g/l}$ higher than at the inlet, due to Al released by the moss (figure 8).

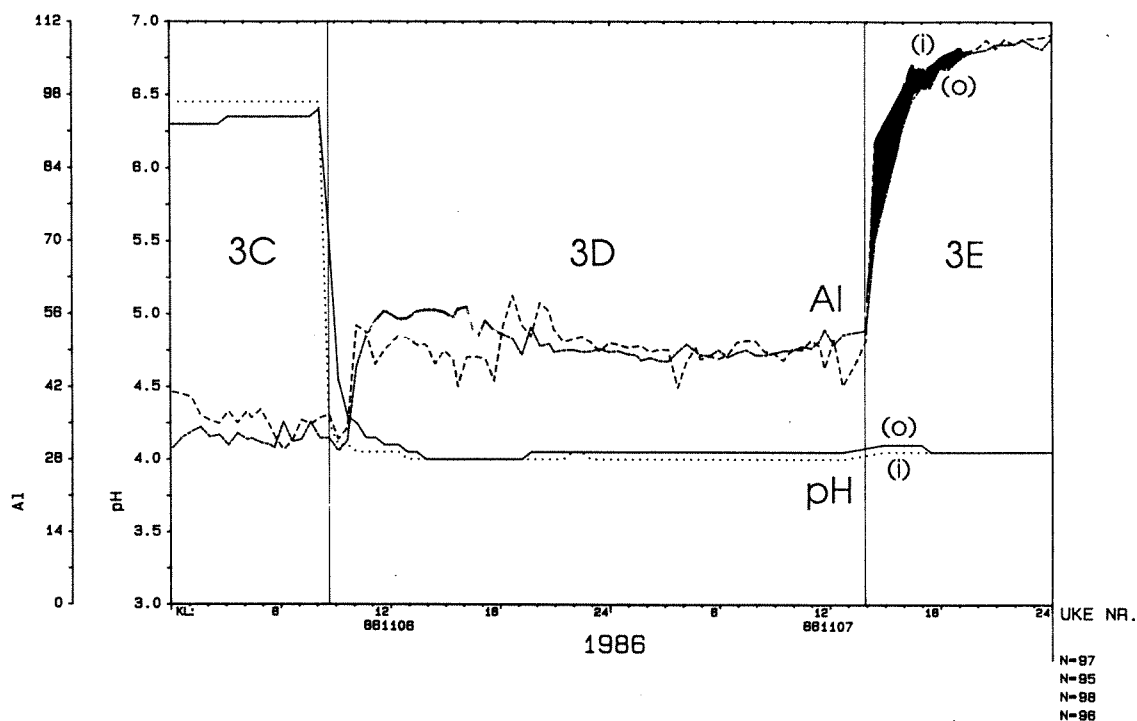


Fig. 7. Experiment # 3C,D,E (Skarselv moss). Aluminium (Al) and pH-values at inlet (i) and outlet (o). The "black" area representing the amount of Al taken up, the difference between the inlet and the outlet.

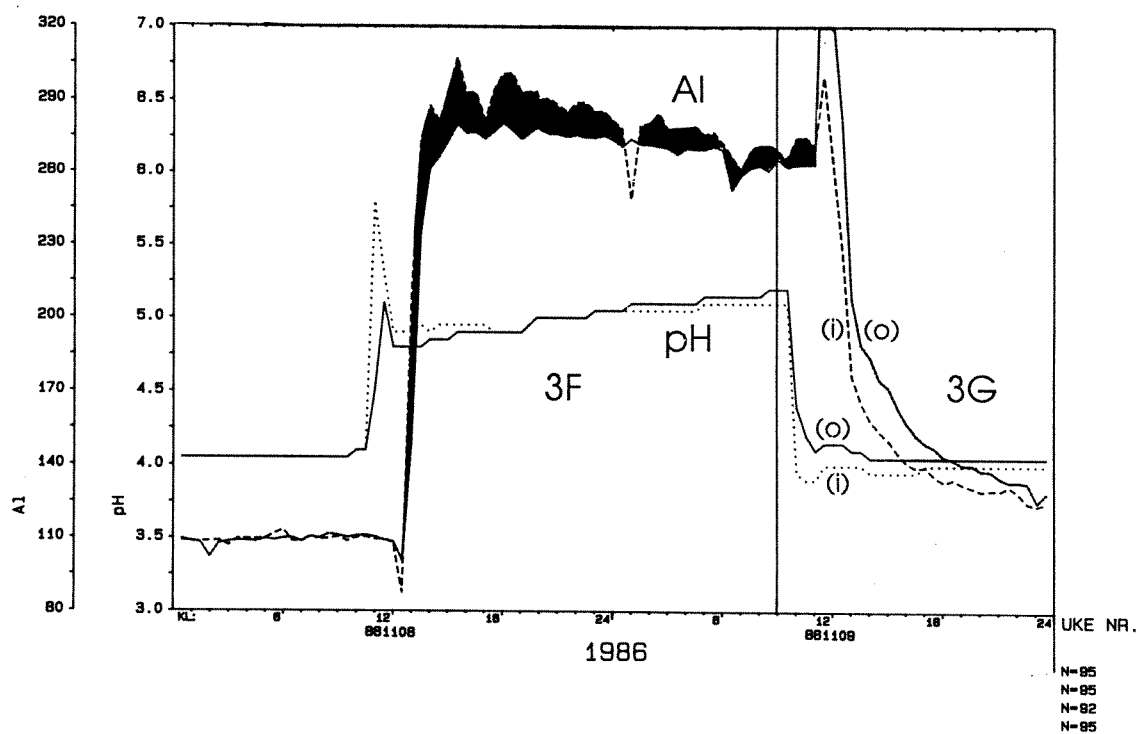


Fig. 8. Experiment # 3F and G (Skarselv moss) Aluminium (Al) and pH-values at inlet (i) and outlet (o). The "black" area representing the amount of Al taken up.

Before and after the lowering of pH from 5 to 4 and Al-concentration from ~290 µg/l to ~100 µg/l, samples were taken at the inlet and outlet of the channel. The results of analyses are shown in table 7. The elevated K-values at t=0 relative to t=1.5 hours are due to extra K in the water from the $AlK(SO_4)_2$.

Table 7. Analyses of water samples from the inlet and outlet of the experimental channel with moss from Skarselva before and after lowering of pH and Al-concentration from 5 to 4 and ~290 µg/l to ~100 µg/l. Experiment # 3G.

| | | pH | ΔH^+ µeq/l | Ca mg/l | ΔCa µeq/l | Mg mg/l | ΔMg µeq/l | Na mg/l | ΔNa µeq/l | K mg/l | ΔK µeq/l |
|---------|--------|------|-----------------------|------------|----------------------|------------|----------------------|------------|----------------------|-----------|---------------------|
| t=0 | Inlet | 5.18 | | 2.81 | | 0.49 | | 1.33 | | 0.72 | |
| | Outlet | 5.17 | ~ 0 | 2.84 | +1.5 | 0.49 | - | 1.32 | -0.43 | 0.73 | +0.26 |
| t=1.5 h | Inlet | 4.18 | | 2.87 | | 0.49 | | 1.31 | | 0.48 | |
| | Outlet | 4.37 | -23.4 | 2.98 | +5.5 | 0.51 | +1.7 | 1.33 | +0.87 | 0.51 | +0.77 |

At 1.5 h after the pH decrease, the buffering capacity of the moss resulted in an uptake of 23.4 µeq/l of H^+ -ions, the release of cations were 5.5 µeq/l for Ca, 1.7 µeq/l of Mg, 0.87 µeq/l for Na and 0.77 µeq/l for K. At this time the Al-concentrations were declining rapidly, and the precise concentrations of Al at 1.5 hours are not known.

The results from these experiments agree with the results from Caines et al. (1985) who used alternate additions of ammonium hydroxide and nitric acid to change pH in a water tank with Nardia compressa. The pH fluctuations lead to fluctuations in the aluminium concentration in the water, demonstrating a reversible ion exchange process on the moss.

D. Experiment # 4

The Al and pH values at the inlet and outlet for experiment # 4 are shown in figure 9. Water chemistry from the inlet and the outlet is shown in table 8. Only small variation existed for the concentrations of Al and base cations.

Table 8. Analyses of water samples from the inlet and outlet for Experiment # 4B.

| | | pH | Ca mg/l | Mg mg/l | K mg/l | Na mg/l | Al µg/l |
|-----------|--------|------|------------|------------|-----------|------------|------------|
| t=0 | Outlet | 6.44 | 2.92 | 0.48 | 0.37 | 1.37 | 50 |
| t=25 min. | Outlet | 5.26 | 2.94 | 0.49 | 0.35 | 1.32 | 49 |
| t=24 h | Inlet | 4.17 | 2.91 | 0.49 | 0.37 | 1.31 | 54 |
| | Outlet | 4.21 | 2.90 | 0.49 | 0.38 | 1.31 | 57 |

In figure 9 slightly but systematically higher (only 2 µg/l) Al-values are seen at the outlet for about 8 hours. With a water flow of 3.7 l/min. calculations give an amount of ~4 mg Al released from the moss and stones.

E. Experiment # 5

The values for pH and Al at the inlet and outlet for the initial acidification (Experiment 5B) are shown in figure 10. The same picture is seen as for experiment # 3B with moss (*Nardia compressa*) from Skarselva (fig. 5). The Al-values at the outlet average about 12 µg/l higher than at the inlet for at least 18 hours. The amount of Al released during these first 18 hours is ~50 mg. The dry weight of the moss was 121.45 g, giving a release of ~400 µg Al/g DW.

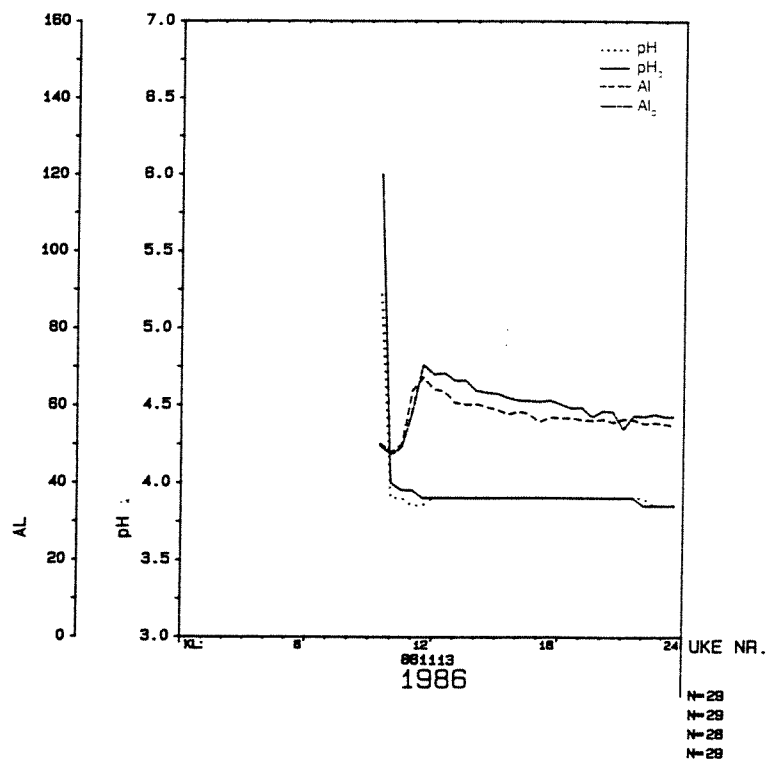


Fig. 9. Experiment # 4. (Stones partly covered with moss. Aluminium (Al) and pH-values at inlet (i) and outlet (o)).

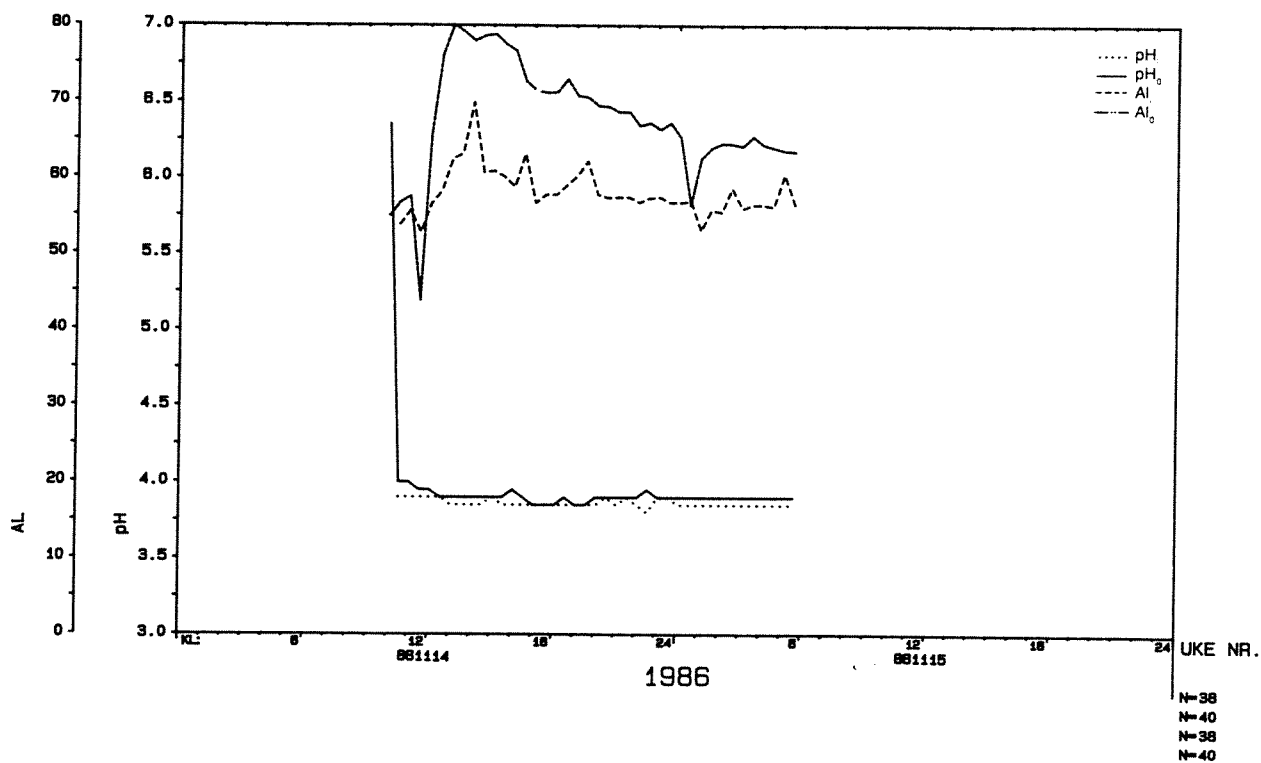


Fig. 10. Experiment # 5B (Vikedal moss). Aluminium (Al) and pH-values at inlet (i) and outlet (o).

Chemistry of water at the inlet and outlet is shown in table 9 together with the results from a water sample taken in Vikedalselva at the same time as the moss.

Table 9. Analyses of water samples from the river Vikedalselva and the inlet and outlet of the experimental channel with moss from Vikedalselva, during acidification. Experiment # 5B.

| | | pH | Ca mg/l | Mg mg/l | K mg/l | Na mg/l |
|-------------------------|--------|------|------------|------------|-----------|------------|
| Water from Vikedalselva | | 5.12 | 1.23 | 0.80 | 0.28 | 4.07 |
| h=0 | Inlet | 6.60 | 3.01 | 0.50 | 0.37 | 1.30 |
| | Outlet | 6.56 | 2.96 | 0.50 | 0.37 | 1.30 |
| h=25 min. | Outlet | 4.43 | 3.22 | 0.52 | 0.37 | 1.37 |

After 25 min. of acidification the pH at the outlet was depressed to 4.43 and the Ca-value had increased to 3.22 mg/l from 2.96 mg/l, an increase of 0.26 mg/l (13 μ eq/l).

The moss was treated with pH 5 water for 24 hours and Al-rich water (~100 μ g/l) for 24 hours (Experiment 5C) before acid water of pH 4 again was submitted to the channel (Experiment 5D). Problems with the acid dosing system gave rise to some unstable values, but the same tendencies as seen during experiment # 3 can be seen. (Table 10 and 11).

Table 10. Analyses of water samples from the inlet and outlet for experiment # 5C after acidification to pH 4 followed by increasing pH to 5. t=0 when water of pH 5 is introduced. n= not measured.

| | | pH | ΔH^+ $\mu\text{ekv/l}$ | Ca mg/l | ΔCa $\mu\text{ekv/l}$ | Mg mg/l | ΔMg $\mu\text{ekv/l}$ | K mg/l | ΔK $\mu\text{ekv/l}$ | Na mg/l | ΔNa $\mu\text{ekv/l}$ |
|-----------|--------|------|-----------------------------------|------------|--|------------|--|-----------|---------------------------------------|------------|--|
| t=0 | Inlet | n | | 2.84 | | 0.49 | | 0.39 | | 1.30 | |
| | Outlet | 4.18 | - | 2.83 | -0.5 | 0.49 | 0 | 0.37 | -0.5 | 1.32 | +0.9 |
| t=45 min. | Inlet | 5.16 | | 2.84 | | 0.49 | | 0.40 | | 1.30 | |
| | Outlet | 5.08 | +1.4 | 2.63 | -10.5 | 0.47 | -1.7 | 0.43 | +0.8 | 1.32 | +0.9 |
| t=24 h | Inlet | 5.37 | | 2.91 | | 0.49 | | 0.39 | | 1.32 | |
| | Outlet | 5.36 | +0.10 | 2.77 | -7.0 | 0.49 | 0 | 0.39 | 0 | 1.32 | 0 |
| t=48 h | Inlet | 5.50 | | 2.76 | | 0.50 | | 0.44 | | n | |
| | Outlet | 5.42 | | 2.76 | 0 | 0.51 | +0.8 | 0.44 | 0 | n | |

The results in table 10 show that when pH is increased to ~5 after acidification to ~4, the moss is recharging with Ca from the water over a period of at least 24 hours. At 48 h, no further uptake of Ca between the inlet and outlet occurred.

Table 11. Analyses of water samples from the inlet and outlet for Experiment 5D when the pH is decreased from 5 to 4 and Al is decreased from ~100 $\mu\text{g/l}$ to ~20 $\mu\text{g/l}$.

| | | pH | ΔH^+ $\mu\text{ekv/l}$ | Ca mg/l | ΔCa $\mu\text{ekv/l}$ | Mg mg/l | ΔMg $\mu\text{ekv/l}$ | K mg/l | ΔK $\mu\text{ekv/l}$ |
|-----------|--------|------|-----------------------------------|------------|--|------------|--|-----------|---------------------------------------|
| t=0 | Inlet | 5.50 | | 2.76 | | 0.50 | | 0.44 | |
| | Outlet | 5.42 | +0.64 | 2.76 | 0 | 0.51 | +0.8 | 0.44 | 0 |
| t=15 min. | Inlet | 4.15 | | 2.76 | | 0.51 | | 0.38 | |
| | Outlet | 4.35 | -26.1 | 3.03 | +13.5 | 0.55 | +3.3 | 0.38 | 0 |

The results in table 11 show that when pH is decreased the moss in the channel has a buffering effect. After 15 min. with water of pH ~4 the difference between inlet and outlet pH is 0.20 pH units showing that as much as (not considering dilution) 26.1 $\mu\text{eq/l}$ H^+ are neutralized by the moss. Ca accounts for 13.5 $\mu\text{eq/l}$ and (Ca + Mg) accounts for 16.8 $\mu\text{eq/l}$ of the H^+ neutralized.

F. Experiment 6

One of the experimental channels was not cleaned of algae. The water passing through the channel was acidified to pH 4. The results from samples taken at the inlet and outlet are described in table 12 and figure 11.

Table 12. Analysis of water samples from the inlet and outlet of an uncleaned experimental channel (Experiment 6) with algae growth.

| | | pH | ΔH^+ μeq | Ca mg/l | ΔCa μeq | Mg mg/l | K mg/l | Fe mg/l | Mn mg/l | Zn mg/l |
|----------|--------|------|--------------------------------------|------------|-------------------------------------|------------|-----------|------------|------------|------------|
| t=10min. | Inlet | 4.79 | | 2.77 | | 0.53 | 0.38 | 50 | 11.5 | 20 |
| | Outlet | 5.57 | -13.5 | 2.92 | +7.5 | 0.53 | 0.38 | 40 | 11.0 | 10 |
| t=2 h | Inlet | 4.19 | | 2.87 | | 0.54 | 0.38 | | | |
| | Outlet | 4.18 | 0 | 2.85 | -1 | 0.51 | 0.36 | | | |
| t=48 h | Inlet | 4.43 | | 2.72 | | 0.49 | 0.35 | | | |
| | Outlet | 4.44 | 0 | 2.69 | -1 | 0.47 | 0.37 | | | |

There is minor buffering from the algae in the channel. However, dried weight (DW) of algae in the channel was 23.25 g, small compared to the moss in experiments 3 and 5, which had DW-values of 122 g and 145 g respectively. If the ΔCa value is applied for 20 min., the release of Ca is about 500 μg Ca/g algae (DW).

CONCLUSIONS

Moss (*Nardia compressa* and *Fontinalis dalecarlica*) placed in experimental channels and exposed to running water act as buffering agents against pH variations, both up and down. Ion exchange (H^+ for cations) is responsible for the buffering. The most important cations in the buffering process are Ca and Al. Mg, Na and K contribute little. Under less acidic to neutral conditions the moss regenerates its buffer capacity by adsorbing the same cations from the stream water. The reactions are thus reversible.

The mosses can adsorb or desorb Al and Ca at least to the extent of 300 $\mu\text{g Al/g (DW)}$ and 1000 $\mu\text{g Ca/g (DW)}$. Similarly, algae can release at least 500 $\mu\text{g Ca/g (DW)}$. In agreement with earlier work (Norton et al. 1987, Henriksen et al. 1988, Wathne and Røgeberg 1988, Tipping and Hopwood 1988) we found that stones partly covered with moss, algae, sand and gravel also contribute some (but less) buffering against pH depression and recovery. Thus the buffering capacity of stream substrates depends largely on the living biomass.

The antecedent water chemistry and pH conditions seem to determine the size of the aluminium reservoir in the moss. Moss taken from Vikedalselva, a river subjected to acidic episodes with natural pH depressions down to about pH 5, released 4 times as much Al/g DW as moss taken from Skarselva, a river with pH always above 5.5.

After an artificial acidic episode with pH down to 4.0, the moss from Skarselva was able to adsorb (or regenerate) an amount of Al equivalent to the amount given off from the Vikedal moss.

At pH 5 and Al concentrations of $\sim 300 \mu\text{g/l}$ in the running water, the moss could take up Al amounting to 6 times the amount taken up at pH 4 and Al concentrations in water of $\sim 100 \mu\text{g/l}$.

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Postboks 69 Korsvoll, 0808 Oslo
ISBN 82-577-2080-1