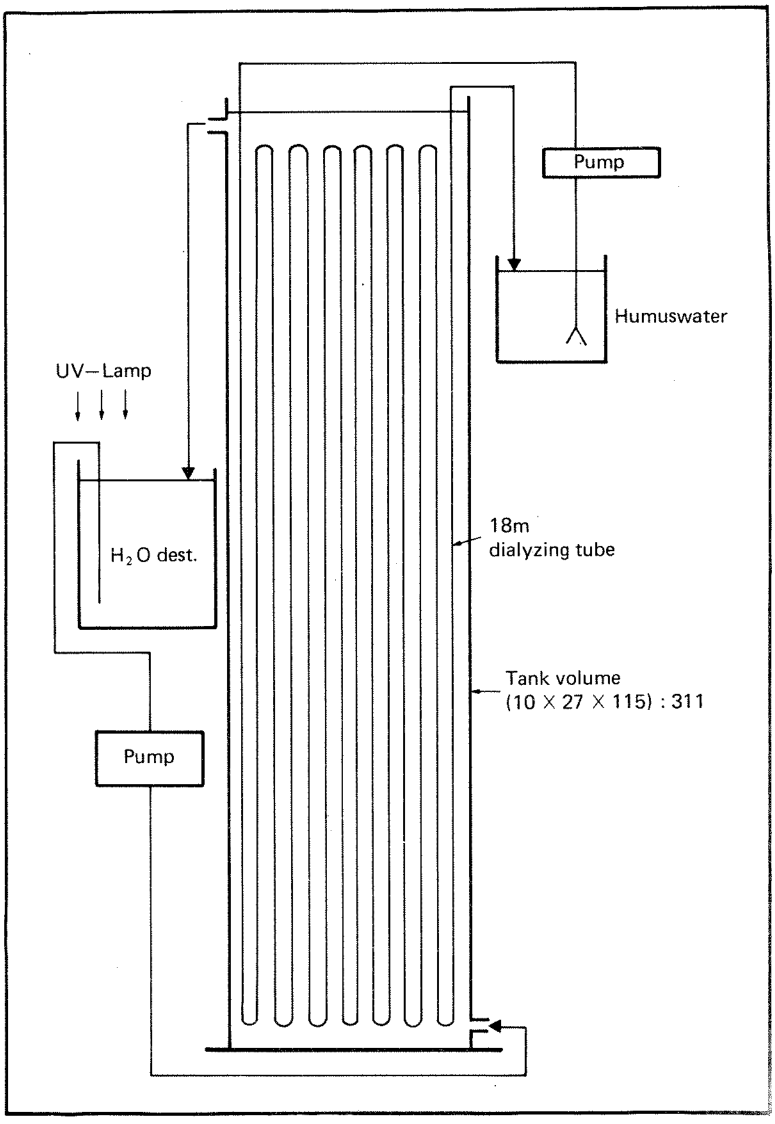
Acid Rain Research

REPORT 15/1988

Natural Organic Acids:

Their Role in Freshwater Acidification and Aluminium Speciation



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Report No.:

Sub-No.: 2108

Serial No.:

Limited distribution:

Report Title:

Natural organic acids: Their role in freshwater-acidification and aluminium speciation

Date: 11 March 1988

Prosject No 0-85244

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Topic group: Acid precipitation

Geographical area: Norway

Number of pages (incl. app.)

Contractor: Surface Water Acidification Program (SWAP)

Contractors ref. (or NTNF-No)

Abstract:
Samples containing humic substances, from an acidified area have been compared with corresponding samples from a less acidified area.
The studies are based on an equilibrium-dialyzation, using artifical membranes. The waters are thoroughly caracterized before and after dialyzation. Results may suggest that the sulphur reacts with the humus, to form a "sulfonic humus" having å lower pK-value.
Toxcity tests, using fish, suggest that dialyzed samples from acidified areas are more toxic than samples from less acidified areas.

4 keywords, Norwegian
1. Humus
2. Forsurning
3. Toksisitet
4. Dialyse

4 keywords, English
1. Hummic Substances
2. Acidification
3. Toxcity
4. Dialyzation

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For the Administration

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ISBN - 82-577-1387-2

Norwegian Institute for Water Research NIVA

0-85244

NATURAL ORGANIC ACIDS: THEIR ROLE IN FRESHWATER ACIDIFICATION AND ALUMINIUM SPECIATION

Oslo, 20. april 1988

Project leader: Egil T. Gjessing

CONTENTS

1. INTRODUCTION

Research on freshwater acidification and loss of fisheries have centered on clear waters. The role of natural organic acids and in particular the interaction between organic acids and the strong acids in soils and surface water is poorly understood. Weak acids in natural coloured waters are mainly weak organic acids and aluminum compounds. Other weak acids such as silica and ammonia usually play only a minor role, except at very low aluminum and organic matter concentrations.

The natural organic matter in water originates from the soil and is a result of chemical and microbiological decomposition of terrestrial plants. This organic matter is acidic and consists of slightly negatively charged macromolecules which are retained in the soil by adsorption to mineral surfaces (Kodama and Schnitzer 1968, 1969; Gjessing and Gjerdahl 1975; Gjessing 1976). The ability to be retained in the soil depends on pH and the nature of the mineral surfaces (Gjessing 1976). This suggests that acid precipitation will effect the release of the soil organic matter into surface water both quantitatively and qualitatively (Gjessing 1976).

The natural organic matter present in water, the aquatic humus, will also change with changes in water chemistry such as pH. A change in pH effects the colour, the molecular size, complexation, the degree of solubility in organic solvents and ion - fixation properties (Gjessing 1976). The bioavailability of inorganic and organic aluminum species, associated with humus, is thus changed.

The purpose of the work presented below is:

1. to introduce and test a modified method for determination of weak acids in water and to use this method to characterize the content of weak acids in coloured water from acidified and less acidified areas.
2. based on the assumption that the toxic effect of species in water is related to the ability to penetrate cell walls, studies on the dialyzability of different types of water, using artificial membranes, are performed.

2. METHODS AND EXPERIMENTAL APPROACH

2.1 Strong and weak acids

Normally, the determinations of strong and weak acids are based on Gran's method (Gran, 1952). The method includes potentiometic pH titration and transformation of titration data to a straight line, so called "Gran plot". Several variations of the Gran procedure have been reported, partly due to an overestimate of total acidity due to Co_2 contamination of the titrant, and partly due to an overestimate of strong acidity at the expense of an underestimate of the weak acidity due to dissosiated weak acids present in the low pH region of the titation curve.
From a critical survey of the literature the modified Gran procedure described by Molværsmyr and Lund (1983) seemed to be the best choice of method in order to avoid the most serious errors.

The titrations are carried out by coulometric generation of hydroxide ions, thus avoiding carbonate contamination of the titrant. A pH titration-range between 3.6 and 10.3 was assumed adequate for a majority of the fresh waters. With minor modifications this method was adapted for routine analysis of strong and weak acids (for details see Røgeberg, 1987).

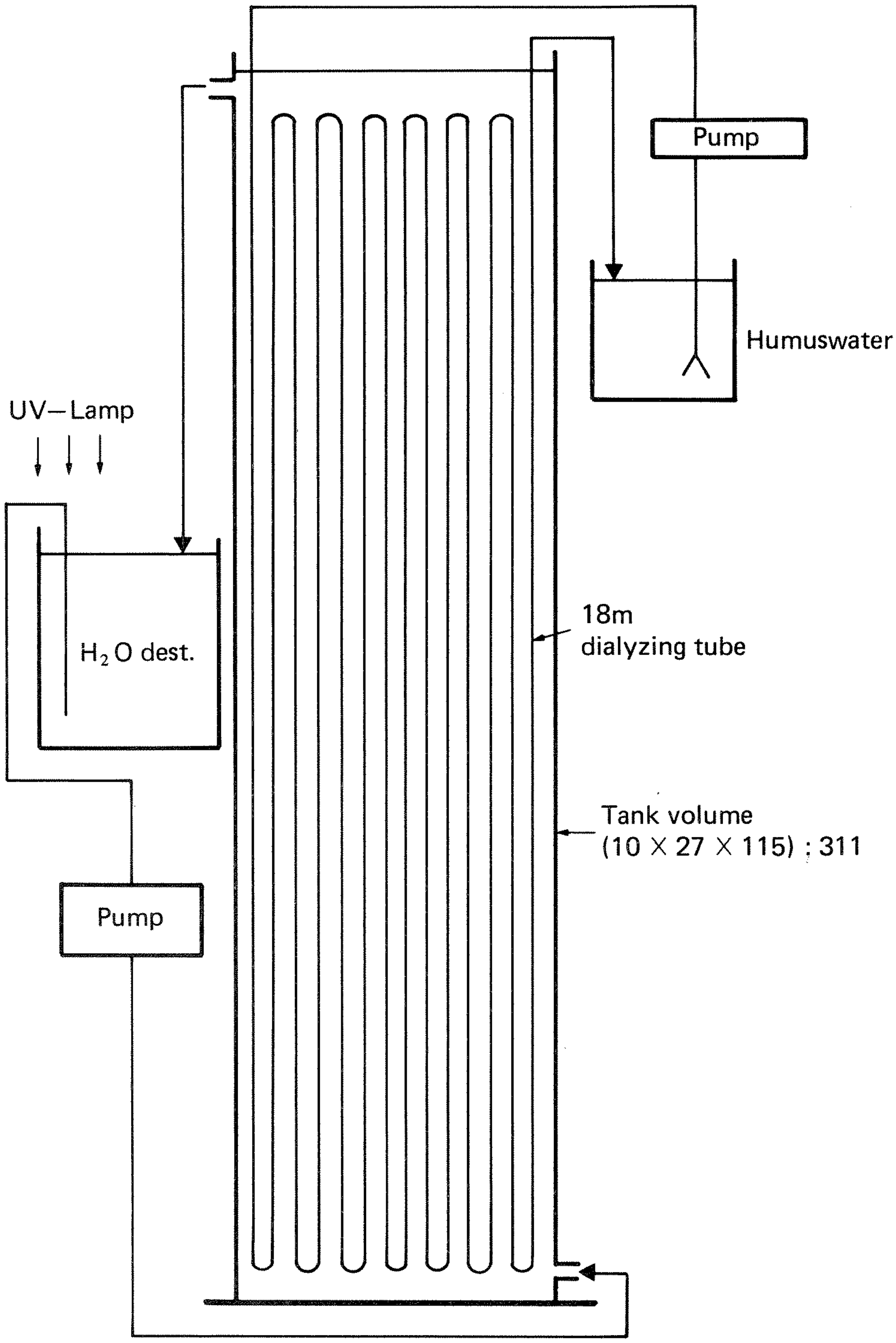


Figure 1.

System used for dialyzing humus water. The dialzing tube have a diameter of 16 mm and a theoretical "cut off" of about 12 000 MW. The purpose of the UV-radiation is to keep the system as sterile as possible.

2.1.1 Dialyzing technique

The equipment used for dialyzing the different water samples is illustrated on figure 1. The samples are dialyzed in distilled water. As can be seen at the upper right on the figure, the humus water is recirculated by a pump through several meters of a dialyzing tube (up to 18 meters in length) contained in a tank with a volume of approximately 30 liters. The dialyzing tube is surrounded by distilled water which is circulated in the tank and renewed several times during the run. The conductivity of this "washing water" never exceeded 0.4 mS/m, and before ending the run the conductivity of this water was below 0.15 mS/m. During the dialyzation the conductivity of the recirculated humus sample was measured. Some typical patterns of the reduction of conductivity of the water sample as a function of dialyzation time, are given in figure 2.

2.2 "Burning off"

The organic matter in the water samples is mineralized, using UV and H_2O_2.
Ultraviolet (UV) radiation of water, to which is added minute amounts of hydrogen peroxide (H_2O_2), will mineralize the organic matter nearly completely.
Some of the samples referred to below have been UV/H_2O_2 - treated and analyzed on relevant inorganic compounds.
The main purpose of this treatment is to see whether this is a possible approach to distinguish between inorganic and organic acids in water.

2.3 Toxicity tests with fish

Using Atlantic salmon (Salmo Salar L.), about one half of the samples are tested regarding fish toxicity (see table 7).

In these fish/water studies the toxicity of water is compared before and after membrane-dialyzation.
The screening test involves one liter of water, in which the survival of two small fishes (Atlantic Salmon about one gram each) is studied during a 96 hour period.

2.4 Samples

Hellerudmyra is a highly coloured water from a marsh area outside Oslo. This water source has been extensively used in our humus research during the last twenty years, and is apparently not affected by acid precipitation to any great extent. This water has also been the base for the Nordic Reference Humus and for the "NIVA-concentrate" (see table 3). The water used in the present experiment is the same water as that used for the isolation of the "Nordic" and the "NIVA-concentrate".
Artificial acidification is performed by adding either concentrated HCl or concentrated H_2SO_4. The Hellerudmyr-water is acidified to below pH 2 and stored for 24 hours before dialyzation.
"Egil" and "Kim" are samples from the RAIN-project-area at Risdalsheia, an acidified region in southern Norway.
"Kim" is water from the outlet of a small "roofed" catchment where all the acid is removed from the collected precipitation, before it is sprinkled back into the catchment.
"Egil" is the water from the reference-area, where the collected acid-precipitation is sprinkled back to the catchment without any treatment.
Artificial salt-solution is prepared from the following inorganic salts (regarding chemical composition of the solution see table 8): NaCl, Na_2SO_4, $Ca(NO_3)_2 \cdot 4H_2O$, $MgSO_4 \cdot 7H_2O$, K_2SO_4, H_2SO_4.

3. RESULTS

3.1 UV - H_2O_2-treatment

Seasonal samples from Hellerudmyra are compared. These four samples are also compared with one sample from "Egil". The results are summarized in table 1.
In general this treatment mineralizes essentially all the DOC (97%).
Comparing the pH in the water-samples from Hellerudmyra, with the pH of the sample from the Egil-catchment, it appears that essentially all the organic acid is removed from the Hellerudmyr samples whereas UV/H_2O_2-treated "Egil" retains a considerable concentration of H^+-ions.
With regard to aluminum this oxidation treatment removes most of the reactive aluminum (RAL) from Hellerudmyr-water, however little from the Egil-sample. All the "non labile" aluminum (ILAL), which consists of organically bound complexes, is removed, which is agrees with theory.
It should be emphasized that both the concentration of sulphate and in particular the concentration of nitrate are increased after oxidation with UV/H_2O_2. This increase might partly be due to organic nitrogen and sulphate connected to the humus molecule, but also due to a "complexation" of nitrate and sulphate to the humus molecule.

3.2 Dialyzation

The "membrane performance" is illustrated on figure 2. The dialyzation pattern on humus water (Hellerudmyra) is compared to salt and mineral acid solution.

According to the membrane specification (SPECTRATOR membrane tubing, SPECTRUM Medical Industries Inc.) the dialyzing tube operates in the molecular weight range of 12 000.

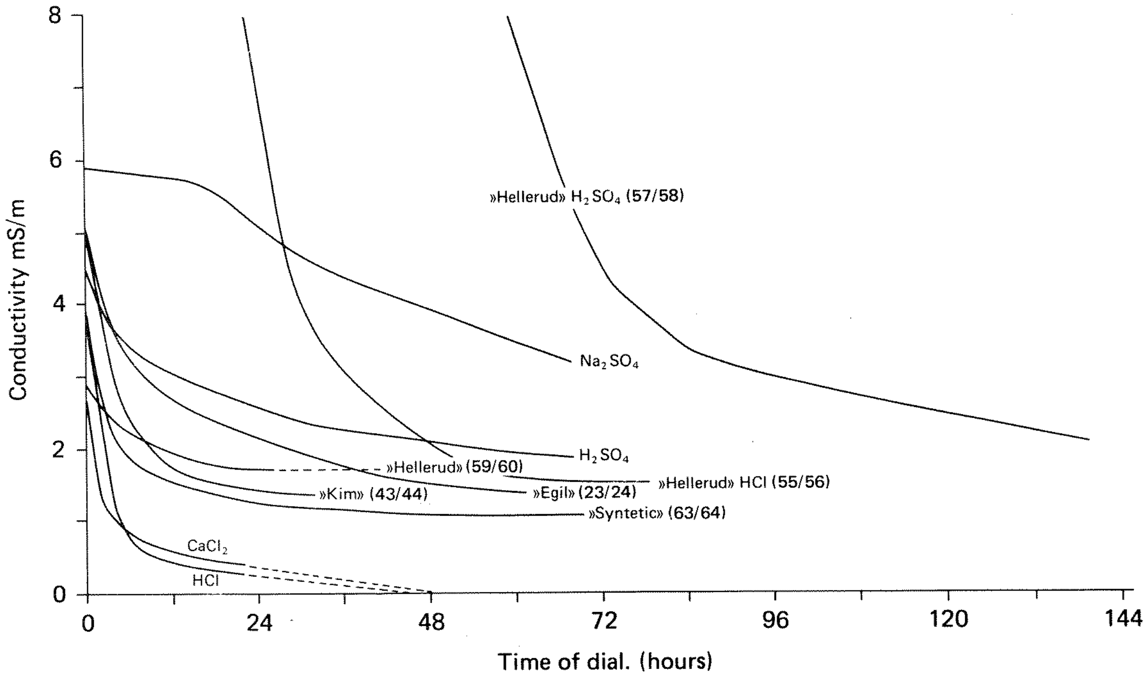


Figure 2

The change of conductivity of sample with time of dialyzation. The results suggest that SO_4-ions generally are "held back" by the membrane to a greater extent than the other inorganic ions.

As can be seen from figure 2 the discrimination of molecules is not only a matter of molecular size; most probably there is also an electrical charge effect, or a combination of size and charge. The results given in figure 2 indicate that sulphate ions are more resistant to penetrating the membrane than other anions, such as chloride. This again suggests that this artificial membrane surface, as natural membrane surfaces, has a net negative charge.
The chemical data of Humus water from Hellerudmyra, before and after dialyzation, are given in table 2 and table 3. Table 2 represents samples from four seasons and table 3 is based on water, sampled in July 1986. The results given in table 3 are partly "natural" Hellerudmyr-water, partly artificially acidified (HCl or H_2SO_4) and partly reference humus (Nordic fulvic acid and NIVA concentrate (before and after dialyzation).

Comparing column 6, 7, 8 and 9 in table 3, which is the same water dialyzed (and analyzed) in four different runs, there is generally good agreement in pH (H+), conductivity, aluminum and weak acid, regarding degree of retainment. The discrepancy regarding the other components is partly, probably mostly, due to analytical errors.

The middle section of table 3 represents acidified water from Hellerudmyra (using HCl or H_2SO_4), before and after dialyzation. As it appears from fig. 2 the dialyzing patterns are very different, comparing HCl and H_2SO_4. In addition to Cl and SO_4 it is in particular the pH of the dialysates that are significantly different; it should be emphasized that there is lack of agreement between the concentration of H^+ of the dialyzed "H_2SO_4-sample" and conductivity.

The right section of table 3 represents reference humus, the "Nordic fulvic acid reference humus" and "NIVA-concentrate". The former is isolated according to internationally accepted procedures, which involves adsorption of the organic matter to a synthetic adsorbant (XAD-8) and the "NIVA-concentrate", which is organic matter isolated from the same water as the "Nordic reference humus", however, by evaporation of membrane filtered water (0.45 μm) at reduced pressure and 30 ^{0}C.

Comparing the dialysates of the two "Reference humics," the lower content of weak acids of the "Nordic reference fulvic acid" should be emphasized. It is also remarkable that both dialysates, as also the dialysates of the "normal" Hellerudmyr-water, contain a significant amount of strong acids.

In table 4, 5 and 6 are the results of membrane filtered and dialyzed samples from the "Egil-area" (reference area of the RAIN-product at Risdalsheia) and the "Kim-area" (the catchment at Risdalsheia where the acid precipitation is removed). These are samples taken during summer and fall 1986. In general the results suggest relatively large differences between the samples. As the duplicate runs (column 16 and 17 in Table 4, and column 31 and 32 in Table 6) show essentially the same results, indicating reasonably good reproducibility, these differences are probably due to changes with time in the chemical composition; implying that there are episodic changes.

Neither "Egil nor Kim" (with a few exceptions) have any strong acids in the dialysate, in contrast to the sample from Hellerudmyra. As the biological "activity" of these waters is an essential part of the acidification problem, the toxicity of several of these waters have been tested, using fish. The results in table 7 indicate the time of survival. The dotted line indicates: 1 fish still living.

4. DISCUSSION

4.1 UV/H_2O_2

The oxidation process involved in this treatment, removes essentially all the organic matter.
Comparing the four seasonal samples from Hellerudmyra (table 1), the pH increases to above 5.8 (from less than 4.5). This suggests that organic acid dominates the acidic properties of these waters.

With regard to aluminum the results in table 1 show that the "non labile aluminum" (ILAL) is "removable", and suggests that most of the aluminum is hydrolyzed.
Comparing the anions chloride, sulphate and nitrate, before and after oxidation, it appears from table 1 that there is a general increase after UV/H_2O_2-treatment. For the summer-humus containing more than 22 mg of carbon pr. liter the increase in sulphate concentration is in the range of 15 µeq/l.
This might be organic sulphur oxidized to SO_4, SO_4 "complexed" with humus or sulphate liberated from a "sulphonic humus ester".
With regard to the NO_3 increase this is most probably due to oxidation of organically bound nitrogen.

The one sample from the "Egil-area" (ref.catchment at Rindalsheia), gives oxidation products which are similar to the Hellerudmyr-samples except from the pH. The pH of the oxidized sample from this acidified area is 4.8, which is more than a pH unit lower than in Hellerudmyr-water, indicating 15 µeq/l of mineral acids.

4.2 Dialyzation technique

The size of the pores of the dialyzing membrane is, according to the specification, equivalent to a molecular weight in the range of 12 000. Theoretically inorganic salt solutions should therefore easily penetrate through.
As shown in figure 2 this is not the case. It appears from the figure that $CaCl_2$ and HCl penetrate relatively easily, whereas Na_2SO_4 and the mixture of salts (see table 8) are resistant to penetrating the membrane.
Comparing the chemical composition of dialyzed inorganic salt-solution with that of natural water (Hellerudmyra) the results are relatively similar.
It should be emphasized that there are several uncertainties connected with the analytical results, as there is an ionic inbalance, particulary for the dialyzed inorganic salt solution.

Nevertheless, the performance of the dialyzing tube was unexpected regarding inorganic salts; in particular the penetration of sulphate ions, appeared to be slow. This suggests that the membrane surface has a negative charge, resulting in a rejection of anions. As SO_4-ions in aqueous solutions are relatively large, they are rejected to a greater extent than for instance the smaller chloride ions.

However, in spite of these unexpected properties, it is important to emphasize that cell membranes as such also generally have a negatively charged surface, so that the dialyzing experiments are valuable in interpreting the biological implications of surface waters containing humic substances.

4.3 Acidified surface waters

4.3.1 "Egil"-area

Samples from the "Egil-area" are representative for humus water from acidified waters. It appears indirectly from table 4 and 5 that in spite of pronounced differences in H^+-concentration (50-160 µeq/l) in the membrane filtered waters, the resulting H^+-concentration in the dialyzed water is relatively constant (10-20 µeq H^+/l). Sulphate in the sample-fraction that passes the dialyzing membrane also varies considerably (11-86 %, or 4-104 µeq SO_4/l). The SO_4-concentration in the dialyzed sample is also relatively constant (28-62 µeq SO_4/l, with exception of one value). However, as indicated earlier, there are generally remarkably high concentrations of sulphate in the dialyzed waters.

With regard to the penetration of SO_4 through the dialyzing membrane, a comparison of the results of the synthetic solution (see fig.2 and table 8) and the "Egil-water sample" (for instance No.23-24) reveals some interesting considerations:

Of the SO_4 in the synthetic water, only 23% (1.4 mg SO_4/l) has passed the dialyzing membrane at "steady state", whereas in the natural sample more than 60% (4.5mg SO_4/l) has passed the membrane under the same experimental conditions. This may imply that SO_4 is "helped" to the membrane when natural water is dialyzed, possibly together with the organic matter.

The aluminum results are very complex and confusing. Generally 50% of the total aluminium passes the dialyzing membrane, whereas roughly 1/4 to 1/2 of the labile form penetrates the membrane.
The lack of "persistent" aluminum results, reveals the complexity of the aluminum chemistry: During the dialyzation the chemistry will gradually change, and the pattern of these changes will depend on the chemistry of the original water. This implies that the concentration gradients of the different aluminum species during the dialyzation will differ and concequently the amounts that are penetratable through the dialyzing membrane depend on numerous conditional factors.

Essentially all the strong acids in the "Egil"-samples apparently penetrate through the membrane, suggesting that all mineral acids are removed from the dialyzates.
With regard to the weak acids the degree of penetration through the membrane varies considerably. In spite of the fact that the concentration of weak acids in the original samples is relatively constant, the degree of retainment by the membrane differs significantly. Any attempts to correlate these differences with other parameters have so far failed.

4.3.2 "Kim"-area

These samples are from the deacidified area at Risdalsheia, the area where the acids in the precipitation are removed.

PH in the dialyzed samples from the "Kim"-area is not significantly different from that of the "Egil"-area (in the range of 4.6 - 5.0).

The sulphate in the original samples from the "Kim"-area does not vary to any great extent (with one exception, within 2.0 - 2.7 mg SO_4/l), in contrast to the samples from the "Egil"-area. Only 1/4 the sulphate penetrates the membrane. Presently it is not known whether this resistance to dialysis is due to low concentration gradient, charge phenomena or humus complexation.

4.4 "Egil"-area/"Kim"-area/Hellerudmyra

Chemical composition before and after dialyzation.

4.4.1 H^+-strong and weak acids

In table 9 the results of the three different sample-types are summarized.
More H^+ and almost all strong acids (SA) are removed from the naturally acidified water-samples compared to water from Hellerudmyra where only 50% SA is removed. With regard to the total content of strong acid, the samples from the acidified areas do contain about twice as much as water from the less acidified area (Hellerudmyra). Comparing the content of weak acids in these two sample-sets, it appears from table 9 that there are insignificantly less weak acids in the water from Hellerudmyra. However, by relating the content of weak acids to that of organic matter (DOC) the results indicate that "Egil"-water contains two times more and "Kim"-water about 1 1/2 times more than Hellerudmyra. The same ratios are apparently valid for weak acids in dialyzed samples.

4.4.2 Aluminum

Significantly less aluminum passes through the dialyzing membrane in water from the "Kim"-area compared to the sample from the "Egil"-area.
With regard to RAL (Reactive aluminum) the results indicate a relationship between percent of membrane penetrateable aluminum and pH in the original water. In water from Hellerud-myra no LAL (Labile aluminum) apparently passes the membrane, whereas in acidified water ("Kim" and "Egil") significant amounts of LAL penetrate the dialyzing membrane.

4.4.3 Sulphate/chloride

Of the major anions, nitrate and chloride behave differently with regard to penetration through the membrane compared to the divalent sulphate. However, there is no significant difference between the three sample sets ("Hellerud", "Egil" and "Kim") in this respect. Generally most of the univalent anions (Cl and NO_3), passes the dialyzing membrane, whereas more than 1/2 of the sulphate is retained.
As indicated earlier, this difference in behaviour might be due to charge phenomena, molecular size or due to an association between sulphate and the humus molecule.

4.5 Artificially acidified Hellerudmyr water

The results from dialyzation of acidified humus water given in table 3 and in figure 2, clearly show that the addition of mineral acids to humus water does change the dialyzation behaviour dramatically and also the nature of the final dia-lyzation product:

Comparing HCl acidification (for instance, sample no 56, with dialyzed natural sample no 54), it appears from table 3 that all the components, including DOC and SO_4, pass the membrane to a significantly greater extent. There are several possible explanations for these important findings:

1. The molecular size of humus is reduced; the difference in DOC retainment between natural and HCl acidified water is, however, not remarkable (18.4 versus 16.1). This indicates that the transport of ions through the membrane is probably not by means of the organic matter.
2. The acidification results in a release of humus complexed cations; particularly Mg, ILAL and Fe apparently pass the membrane more easily.
3. The negative charge of the membrane-surface might be reduced (so also the charge of the humus molecule).

The conductivity of the HCl-sample (figure 2 "Hellerudmyra 55/56") apparently levels off at the same value as the natural sample, however, at a longer dialyzing time.

Comparing the dialyzing pattern of the H_2SO_4-acidified humus water, with that of HCl-acidified humus-water (figure 2), "Steady state" is apparently not reached after 6 days!

With regard to the composition of the final dialyzation product of this H_2SO_4 treated water sample, it appears from table 3 (sample no 58), that except for sulphate and DOC the results are not remarkably different from that of the HCl-treated sample (sample no.54). The relatively high concentration of SO_4 is probably due to, as indicated earlier, charge effects on the membrane, as the concentration of SO_4 in the dialysate is relatively high even at a late stage of the dialyzation run when the pH is relatively high.

4.6 Toxicity tests

As expected "Egil and Kim"-water (from Risdalsheia) are generally more toxic to yearlings of salmon than Hellerudmyr water. It can also be seen from table 7 that the waters are less toxic after dialyzation; which also should be expected. These experiments indicate, however, some results of significant importance: Dialysates of the most acidic waters (sample 33, 31, 29, 27, 23, 19 and 11) are apparantly more toxic than dialysates from less acidic samples.
It should also be pointed out that in 5 of these 7 apparantly toxic "dialysates" there has also been found a significant amount of strong acids.

5. CONCLUSION

* UV/H_2O_2 - treatment of natural water removes essentially all the organic matter. The composition of the "residual", such as pH, show differences between water from acidified and less acidified areas. This may indicate differences in the mineral acid/organic acids ratio.

* Membrane dialyzation, based solely on concentration gradient (sample/destilled water, without pressure) gives satisfactorily reproducible results and is apparently a more useful technique than most other dialyzation methods for estimating passage of compounds into organisms.

* Acid and acidified samples penetrate the membrane used more slowly than less acidified samples or deacidified samples.

* All the strong acids (SA), and most of the labile aluminum (LAL) pass the membrane from "natural" acidified waters. In contrast, only 50 per cent SA and essentially no LAL penetrate the membrane from the less acidified samples.

* There is no significant correlation between weak acids (WA) and DOC, either within sample types nor all samples considered.

* The sample from the acidified area apparently contains more weak acids (WA) per mg carbon (min, 20 µeq/mgC) than samples from the less acidified area (13 µeq/mgC).

* As the sulphate concentration per mg carbon in dialyzed samples are significantly higher in the acid waters compared to the less acidified, the results may suggest that the sulphur reacts with the humus, to form a "sulfonic humus" having a lower pK-value.

* Toxicity tests, using fish, suggest that dialyzed samples from acidified areas are more toxic than samples from less acidified areas.

5.1 Summary

Samples, containing humic substances, from an acidified area have been compared with corresponding samples from a less acidified area. Samples from a deacidified area (RAIN-project) and artificially acidified humus samples (laboratory acidified) are also included.
The studies are based on an equilibrium-dialyzation, using artificial membranes. The waters are thoroughly characterized before and after dialyzation. In the studies are also included toxicity tests of dialyzed and undialyzed water.
A potencial method (using UV/H_2O_2 mineralization) for estimating the content of mineral acids in waters is described.
The description of a modified method for the determination of weak and strong acids is also included.

The results suggest that the artificial dialyzation tubes have a negative surface-charge in the actual pH region, which hinders the penetration of anions, such as SO_4. However, as these properties are typical also for natural membranes, the technique may be valuable for the interpretation of biological effects.

Equilibrum dialyzation of three types of samples: acidified, non-acidified and deacidified humus water, show that even with considerable variance in the pH of the original samples, the pH of the dialyzed "product" are remarkably constant (pH 4.7 to 5.0).

The content of strong acid (SA) is, as expected, much higher in the water from the acidified area. In contrast to the non-acidified waters, the dialyzation removes almost all the SA from these waters.

In the dialyzed water of the non-acidified sample, there are apparently insignificantly less weak acids (WA). However, when related to DOC, the WA-content is one half compared to the acidified water.

Labile aluminum (LAL, the potencially most toxic Al-fraction to fish) does not penetrate the membrane from non-acidified waters, whereas in acidified waters, a significant fraction of LAL penetrates through the membrane.

Sulphate dialyzes differently compared to the other major anions, indicating a chemical association with the humic substances.

The fish toxicity of dialyzed acidified humus water is apparently higher than the corresponding non-acidified waters. The chemical parameters used to describe differences in the chemical composition of the various water samples, are apparently not sufficient to explain why this may be so.

6. References

Gjessing, E.T. and Gjerdahl, T.: (1975) "Electromobility of aquatic humus. Fractionation by the use of the isoelectric focusing technique". pp. 43-51 (1975). In: Povoledo, D. and Golterman, H.L. (ed.). "Humic substances - Their structure and function in the biosphere". Proceedings of an international meeting held at Nieuwersluis, the Netherlands May 29.-31., 1972. Pudoc, Wageningen 1975.

Gjessing, E.T.: (1976) "Physical and chemical characteristics of aquatic humus". Ann Arbor Science Publishers Inc. pp. 1-120. Ann Arbor, Mich.

Gran, G.: (1952) "Determination of equivalence point in potentiometric titrations". Part II. Analyst 17, 661-671.

Kodama, H. and Schnitzer, M.: (1968) "Effects of interlayer cations on the adsorption of a soil humic compound by montmorillonite", Soil.Sci. 106(1), 73-74.

Kodama, H. and Schnitzer, M.: (1969) "Thermal analysis of a fulvic acid-montmorillonite complex", Proceedings of the International Clay Conference, Tokyo, (Jerusalem: Israel University Press, 1969), pp. 765-774.

Molværsmyr, K. and Lund, W.: (1983) "Acids and bases in fresh-water. Interpretations of results from Gran plots". Water Res. 17, 303-307.

Røgeberg, E.: (1987) "A coulometric Gran titration method for the determination of strong and weak acids in freshwater". Acid Rain Res. Report 12/1987, (Norwegian Inst.Water Research, Oslo),28 pp.

Table 1. Membrane filtered (MF: 0.45 µm) and Mineralized (UV/H_2O_2) samples from Hellerudmyra and "Egil area".

	HELLERUDMYRA (less acidified area)																"Egil" - catchment acidified area			
	Winter				Spring				Summer				Fall				Fall			
	MF		UV/H_2O_2		MF		UV/H_2O_2		MF		UV/H_2O_2		MF		UV/H_2O_2		MF		UV/H_2O_2	
	conc	µeq /l	conc	µeq /l	conc	µeq /l	conc	µeq /l	conc	µeq /l	conc	µeq /l	conc	µeq /l	conc	µeq /l	conc	µeq /l	conc	µeq /l
pH	4.53	29	6.20	0	4.51	31	5.84	1	4.35	44	6.79	0	4.37	43	5.91	1	4.00	100	4.82	15
mS/m COND	2.77	-	1.82	-	2.15	-	1.34	-	2.88	-	1.56	-	3.28	-	2.04	-	7.19	-	4.38	-
µg/l Fe	300	-	190	-	260	-	180	-	713	-	530	-	306	-	195	-	240	-	220	-
µg/l Mn	21	-	15	-	15	-	15	-	13	-	12	-	17	-	12	-	12	-	18	-
mg Pt/Color	105	-	10	-	107	-	8	-	242	-	16	-	133	-	7	-	75	-	2	-
mg/l Ca	1.13	56	1.16	58	0.78	40	0.79	39	1.01	50	1.00	50	1.30	65	1.30	65	0.46	23	0.49	25
mg/l Mg	0.25	21	0.24	20	0.16	13	0.16	13	0.18	15	0.18	15	0.27	22	0.26	21	0.36	30	0.39	32
mg/l K	0.07	2	0.09	2	0.20	5	0.4	5	0.03	1	0.03	1	0.07	2	0.10	3	0.39	10	0.39	10
mg/l Na	1.01	44	1.05	46	0.64	28	0.63	27	0.75	33	0.72	31	0.98	43	1.02	44	2.62	114	2.69	117
µg/l Al	298	-	215	-	185	-	159	-	380	-	381	-	319	-	200	-	590	-	450	-
µg/l RAL	235	-	25	-	155	-	0**	-	304	-	46	-	268	-	19	-	500	-	390	-
µg/l ILAL	183	-	0**	-	114	-	0**	-	271	-	0**	-	204	-	0**	-	218	-	0**	-
µg/l LAL	52	6	25	3	41	5	0**	-	35	4	46	5	64	7	19	2	282	31	390	43
mg/l Cl	1.3	37	1.5	42	1.5	42	1.6	45	0.7	20	0.9	25	1.3	37	1.3	37	2.6	73	2.7	75
mg/l SO_4	3.5	73	3.7	77	3.5	73	3.4	71	1.5	31	2.2	46	4.6	96	4.5	94	4.4	92	4.8	100
µg N/l NO_3	15	1	93	7	9	1	82	6	7	1	54	4	5	0	91	7	620	44	685	49
mg C/l DOC	11.8	-	0.3	-	9.4	-	0.2	-	22.9	-	0.5	-	13.9	-	0.5	-	9.4	-	0.6	-
I/cm UV-abs	0.49	-	0.00	-	0.44	-	0.00	-	1.09	-	0.00	-	.615	-	0.00	-	0.39	-	0.00	-
ACID																				
Σ cations	-	158	-	129	-	122	-	85	-	147	-	102	-	182	-	136	-	308	-	242
Σ anions	-	111	-	126	-	116	-	122	-	52	-	75	-	133	-	138	-	209	-	224
Deficit	-	47	-	3	-	6	-	-37	-	95	-	27	-	49	-	-2	-	99	-	18

**) <10=0

Table 2. Membrane filtered (MF: 0.45 µm) and Dialyzed (MW 12.000) samples from Hellerudmyra and "Egil area".

Column No	1				2				3				4				5			
	HELLERUDMYRA (less acidified area)																"Egil" - catchment acidified area			
	Winter				Spring				Summer				Fall				Fall			
	MF*)		Dial		MF*)		Dial		MF*)		Dial		MF*)		Dial		MF*)		Dial	
	conc	µeq/l	conc	µeq/l	conc	µeq/l	conc	µeq/l	conc	µeq/l	conc	µeq/l	conc	µeq/l	conc	µeq/l	conc	µeq/l	conc	µeq/l
pH	4.53	29	4.91	12	4.51	31	4.87	14	4.35	44	4.67	21	4.37	43	4.86	14	4.00	100	4.78	14
mS/m COND	2.77	-	0.94	-	2.15	-	0.94	-	2.88	-	1.43	-	3.28	-	1.10	-	7.19	-	1.11	-
µg/l Fe	300	-	260	-	260	-	310	-	713	-	630	-	306	-	290	-	240	-	178	-
µg/l Mn	21	-	10	-	15	-	9	-	13	-	9	-	17	-	8	-	12	-	4	-
mgPt/Color	105	-	104	-	107	-	120	-	242	-	219	-	133	-	124	-	75	-	40	-
mg/l Ca	1.13	56	0.50	25	0.78	40	0.46	23	1.01	50	0.68	34	1.30	65	0.57	28	0.46	23	0.19	10
mg/l Mg	0.25	21	0.09	7	0.16	13	.008	7	0.18	15	0.12	9	0.27	22	0.11	9	0.36	30	0.11	9
mg/l K	0.07	2	0.02	1	0.20	5	0.05	1	0.03	1	0.01	0	0.07	2	0.04	1	0.39	10	0.05	1
mg/l Na	1.01	44	0.13	6	0.64	28	0.13	6	0.75	33	0.13	6	0.98	43	0.15	7	2.62	114	0.26	11
µg/l Al	298	-	240	-	185	-	205	-	380	-	347	-	319	-	258	-	590	-	263	-
µg/l RAL	235	-	178	-	155	-	146	-	304	-	283	-	268	-	197	-	500	-	219	-
µg/l ILAL	183	-	112	-	114	-	89	-	271	-	224	-	204	-	131	-	218	-	156	-
µg/l LAL	52	6	66	7	41	5	57	6	35	4	59	7	64	7	66	7	282	31	63	7
mg/l Cl	1.3	37	0.2	6	1.5	42	0.1	3	0.7	20	0.1	3	1.3	37	0.0	0	2.6	73	0.2	6
mg/l SO_4	3.5	73	1.1	23	3.5	73	1.1	23	1.5	31	0.5	10	4.6	96	1.1	23	4.4	92	1.7	35
µg N/l NO_3	15	1	3	0	9	1	3	0	7	1	8	1	5	0	7	1	620	44	5	0
mg C/l DOC	11.8	-	7.3	-	9.4	-	6.3	-	22.9	-	15.3	-	13.9	-	10.5	-	9.4	-	4.6	-
I/cm UV-abs	0.49	-	0.34	-	0.44	-	0.33	-	1.09	-	0.85	-	0.62	-	0.43	-	0.39	-	0.23	-
ACID																				
Σ cations	-	158	-	58	-	122	-	57	-	147	-	77	-	182	-	66	-	308	-	52
Σ anions	-	111	-	29	-	116	-	26	-	52	-	11	-	133	-	24	-	209	-	41
Deficit		47	-	29	-	6	-	31	-	95	-	66	-	49	-	42	-	99	-	11

*) Membrane filter (0.45 µm)

Table 3. Membrane filtered (MF:0.45µm) and Dialyzed (MW 12.000) samples from "Hellerudmyra", "Hellerudmyra" artificially acidified, "NIVA-CONC" and Nordic Fulvic acid", (sampled July -86) % denotes; passage through dialyzing membrane.

"HELLERUDMYRA"

Column No	6			7			8			9				
Sample No	15	16	-	17	18	-	37	38	-	53		54		-
	DUPLICATE													
	MF	DIAL	%	MF	DIAL	%	MF	DIAL	%	MF conc	MF µeq/l	DIAL conc	DIAL µeq/l	%
pH	4.3	4.9	74	4.3	4.8	68	4.3	4.9	74	4.40	40	4.92	12	70
mS/m COND	3.0	1.4	53	3.0	1.7	43	3.0	1.4	53	3.24	-	1.72	-	47
µg/l Fe	650	610	6	660	670	0	700	640	9	802	-	810	-	0
µg/l Mn	70	50	29	70	50	29	60	30	50	52	-	-	-	-
mgPt/Color	190	180	5	190	190	0	210	200	5	232	-	223	-	4
mg/l Ca	1.0	<1.0	-	1.0	1.0	-	1.0	<1.0	-	1.23	61	.96	48	22
mg/l Mg	.20	.20	0	.25	.20	20	.25	.15	40	.26	21	.24	20	8
mg/l K	<.1	.1	-	<.1	.1	-	.1	<.1	-	.05	1	.03	0	-
mg/l Na	1.2	.5	58	1.3	.6	54	1.3	.5	62	1.09	47	.46	20	58
µg/l Al	530	500	6	530	500	6	580	550	5	452	-	-	-	-
µg/l RAL	-	-	-	-	-	-	-	-	-	368	-	440	-	0
µg/l ILAL	-	-	-	-	-	-	-	-	-	284	-	323	-	0
µg/l LAL	-	-	-	-	-	-	-	-	-	84	9	117	13	0
mg/l Cl	2.0	.7	15	2.0	.8	10	2.0	.8	10	1.0	28	<.1	<3	>90
mg/l SO_4	3.0	2.5	16	3.0	3.0	0	3.0	2.5	16	1.98	41	1.20	25	39
µg N/l NO_3	<50	<50	-	<50	<50	-	<50	<50	-	10	1	4	0	-
mg C/l DOC	-	-	-	-	-	-	-	-	-	21.7	-	18.4	-	18
I/cm UV-abs	-	-	-	-	-	-	-	-	-	.950	-	.792	-	17
FTU TURB.	.25	.80	-	.25	.45	-	.25	.50	-	-	-	-	-	-
µg N/l AMMONIUM	10	110	-	10	10	-	10	240	-	-	-	-	-	-
µmol/l STRONG ACID	23	18	22	50	20	60	-	-	-	-	-	-	-	-
µmol/l WEAK ACID	283	211	25	281	233	17	-	-	-	-	-	-	-	-
Σ cations										-	179	-	113	-
Σ anions										-	69	-	26	-
Deficit										-	110	-	87	-

"HELLERUDMYRA" ARTIFICIALLY ACIDIFIED

Column No	10			11					12				
Sample No	19	20	-	55		56			57		58		
				HCl					H_2SO_4				
	MF	DIAL	%	MF conc	MF µeq/l	DIAL conc	DIAL µeq/l	%	MF conc	MF µeq/l	DIAL conc	DIAL µeq/l	%
pH	1.8	4.2	99	1.96	-	4.71	20	99	1.90	-	4.51	31	99
mS/m COND	650	2.40	99	628	-	1.63	-	99	691	-	2.39	-	99
µg/l Fe	740	290	61	850	-	440	-	48	840	-	370	-	56
µg/l Mn	70	20	71	-	-	-	-	-	-	-	-	-	-
mgPt/Color	140	150	0	165	-	182	-	0	168	-	151	-	10
mg/l Ca	1.0	<1	-	1.26	63	.59	29	53	1.26	-	.90	45	29
mg/l Mg	.25	<.1	-	.26	21	.06	5	77	.24	-	.09	7	71
mg/l K	.15	.10	33	.05	1	.03	0	40	.05	-	.03	0	40
mg/l Na	1.3	.5	62	1.11	48	.29	13	75	1.13	-	.13	6	88
µg/l Al	550	280	49	-	-	-	-	-	-	-	-	-	-
µg/l RAL	-	-	-	760	-	139	-	82	650	-	151	-	77
µg/l ILAL	-	-	-	15	-	130	-	0	25	-	131	-	0
µg/l LAL	-	-	-	745	83	9	1	99	625	-	20	2	97
mg/l Cl	640	.8	99	500	-	.6	17	[illegible]	4.1	-	<.1	<3	99
mg/l SO_4	4.0	2.0	50	2.4	50	.6	12	75	1030		4.1	85	99
µg N/l NO_3	<50	<50	-	5	0	5	0	100	5	0	4	0	20
mg C/l DOC	-	-	-	235	-	16.1	-	31	23.5	-	12.2	-	48
I/cm UV-abs	-	-	-	-	-	-	-	-	-	-	-	-	-
FTU TURB.	.50	1.1	-	-	-	-	-	-	-	-	-	-	-
µg N/l AMMONIUM	20	220	-	-	-	-	-	-	-	-	-	-	-
µmol/l STRONG ACID	-	100	-	-	-	-	-	-	-	-	-	-	-
µmol/l WEAK ACID	-	170	-	-	-	-	-	-	-	-	-	-	-
Σ cations				-	-	-	68	-	-	-	-	91	-
Σ anions				-	-	-	29	-	-	-	-	85	-
Deficit				-	-	-	38	-	-	-	-	6	-

"REFERENCE HUMUS"

	"NIVA CONC."			"NORDIC FUL."		
Column No	13			14		
Sample No	21	22	-	25	26	-
	MF	DIAL	%	MF	DIAL	%
pH	4.3	4.7	60	4.2	4.7	68
mS/m COND	3.27	1.76	46	2.11	1.08	49
µg/l Fe	650	590	10	<20	210	-
µg/l Mn	60	40	33	<20	<20	-
mgPt/Color	190	190	0	89	110	0
mg/l Ca	1.0	1.0	-	<1.0	<1.0	-
mg/l Mg	.25	.20	25	<.1	<.1	-
mg/l K	.10	<.1	-	<.1	-	-
mg/l Na	1.3	.5	62	.2	.3	0
µg/l Al	550	480	12	<20	140	-
µg/l RAL	-	-	-	-	-	-
µg/l ILAL	-	-	-	-	-	-
µg/l LAL	-	-	-	-	-	-
mg/l Cl	2.2	.0	64	.4	.	-
mg/l SO_4	3.0	2.5	17	1.0	1.0	0
µg N/l NO_3	<50	<50	-	<50	<50	-
mg C/l DOC	-	-	-	10.9	-	-
I/cm UV-abs	-	-	-	.487	-	-
FTU TURB.	.55	1.1	-	.30	.50	-
µg N/l AMMONIUM	30	210	-	5	260	-
µmol/l STRONG ACID	36	19	47	56	28	50
µmol/l WEAK ACID	272	243	11	143	154	0
Σ cations						
Σ anions						
Deficit						

Table 4. Membrane filtered (MF: 0.45μm) and Dialyzed (MW 12.000) samples from "Egil-area" ("natural acidified"). % denotes; passage through dialyzing membrane.

Column No	15			16			17			18			19		
Sample No	1	2		3	4		11	12		5	6		9	10	
				Duplicate											
	MF	Dial	%	MF	Dial	%	MF	Dial	%	MF	Dial	%	MF	Dial	%
pH	4.1	4.7	75	4.0	4.7	80	4.0	4.8	85	4.0	5.0	90	4.3	4.8	68
mS/m Cond	3.64	1.52	58	6.70	1.65	75	6.75	1.73	74	6.93	1.12	84	3.14	1.45	54
μg/l Fe	350	300	14	330	220	33	330	240	27	320	110	66	120	110	8
μg/l Mn	20	20	0	<20	20	-	20	20	0	20	<20	-	<20	<20	-
mgPt/Color	160	160	0	110	86	12	110	110	0	110	80	27	90	83	8
mg/l Ca	1.0	<1	-	<1	<1	-	<1	<1	-	<1	<1	-	<1	<1	-
mg/l Mg	0.15	0.20	-	0.30	0.20	33	0.30	0.20	33	0.30	0.10	66	0.10	<0.1	-
mg/l K	0.15	0.10	33	0.20	0.10	50	0.20	0.10	50	0.85	0.10	88	0.20	0.10	50
mg/l Na	1.1	0.4	64	2.0	0.6	70	2.60	0.7	73	3.0	0.2	93	1.2	1.1	?
μg/l Al	560	440	21	670	360	46	650	380	41	640	390	39	240	180	67
μg/l ILAL	370	340	8	320	110	66	310	120	61	290	120	59	60	30	50
μg/l LAL	190	100	47	350	250	29	340	260	24	350	270	23	180	150	17
mg/l Cl	2.0	0.6	70	3.0	0.2	93	3.0	0.3	90	5.0	0.4	92	1.7	0.4	76
mg/l SO_4	2.6	2.0	23	6.6	2.2	67	6.8	2.9	57	5.4	1.4	74	1.8	1.6	11
μg N/l NO_3	130	<50	-	220	<50	-	220	<50	-	530	<50	>91	110	<50	-
mg C/l DOC	17.7	16.3	-	13.8	9.3[1]	-	13.8	9.8[1]	-	13.7	8.6[1]	-	9.3[1]	8.8[1]	-
I/cm UV-abs	.785	.728	7	.613	.415	32	.613	.437	29	.610	.385	37	.417	.389	7
FTU	0.2	1.3	-	0.25	0.75	-	0.25	0.55	-	0.35	0.75	-	0.20	0.45	-
μgN/l Ammon	110	5	95	260	80	69	240	140	42	460	100	78	170	65	-
μmol/l Strong acid	37	-15	100	79	-12	100	85	-18	100	58	-30	100	3	-14	100
μmol/l Weak	249	199	20	274	171	38	263	187	29	292	166	43	193	149	23

Column No	20			21			22			23			24			25		
Sample No	13	14	-	23	24	-	27	28	-	31	32	-	35	36	-	29	30	-
	MF	Dial	%	MF	Dial	%	MF	Dial	%	MF	Dial	%	MF	Dial	%	MF	Dial	%
pH	4.3	4.7	60	4.0	4.9	87	3.9	4.9	90	3.8	4.8	90	4.1	4.8	79	3.8	4.9	92
mS/m Cond	3.54	1.59	55	6.23	1.70	73	7.60	1.63	79	8.81	1.77	80	4.80	1.44	70	8.10	1.31	84
μg/l Fe	430	410	5	210	200	5	170	120	29	170	130	24	130	120	7	170	100	41
μg/l Mn	20	<20	-	40	30	25	30	20	33	20	<20	-	<20	<20	-	<20	<20	-
mgPt/Color	180	180	0	110	90	18	70	55	21	64	55	14	87	86	1	60	50	17
mg/l Ca	<1	<1	-	<1	<1	-	<1	<1	-	<1	<1	-	<1	<1	-	<1.0	<1.0	-
mg/l Mg	0.20	0.15	25	0.40	0.25	38	0.40	0.20	50	0.50	0.30	40	0.20	0.15	25	0.45	0.15	67
mg/l K	0.70	0.20	71	0.25	<0.1	-	0.55	0.10	82	0.60	0.10	83	0.50	<0.1	>80	0.55	0.10	82
mg/l Na	1.8	0.8	56	2.4	0.5	79	3.3	0.7	79	2.9	0.6	79	2.3	0.7	70	2.9	0.5	83
μg/l Al	580	580	0	550	330	40	600	280	53	600	400	33	300	310	0	600	310	48
μg/l ILAL	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
μg/l LAL	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mg/l Cl	2.6	0.7	73	1.7	0.4	76	4.6	0.2	96	5.3	0.2	96	4.6	0.4	91	7.0	0.2	97
mg/l SO_4	3.0	2.0	33	7.0	2.5	64	8.0	3.0	63	8.0	4.0	50	2.5	2.0	-	5.0	2.0	60
μg N/l NO_3	250	<50	>80	920	<50	>95	670	<50	>93	700	<50	>93	180	<50	>72	440	<50	>89
mg C/l DOC	-	-	-	-	9.7[1]	-	9.2[1]	6.4[1]	-	8.6[1]	6.3[1]	-	9.7[1]	8.8[1]	-	7.8[1]	5.5[1]	-
I/cm UV-abs	-	-	-	-	.437	-	.412	.284	31	.378	.278	26	.428	.388	9	.347	.249	28
FTU	0.30	0.60	-	0.25	0.70	-	0.25	0.50	-	0.20	0.50	-	0.30	0.45	-	0.25	0.40	-
μgN/l Ammon	220	120	45	500	240	52	500	280	44	460	210	54	310	250	19	230	190	17
μmol/l Strong acid	29	-21	100	105	14?	87	105	27	74	135	3	98	72	21	71	141	-7	100
μmol/l Weak	275	253	8	244	182	24	272	144	47	250	186	26	189	162	13	223	171	23

*) TOT.AL - ILAL   1) Estimated from UV-abs.

ILAL is determined manually and both Al and ILAL is determined by atomic abs.

Table 5. Membrane filtered (MF: 0.45 µm) and Dialyzed (MW 12.000) samples from "Egil-area" ("natural acidified"). % denotes; per cent passage through dialyzing membrane.

Column No	26					27					28				
Sample No	41		42			47		48			49		50		
	MF		DIAL		%	MF		DIAL		%	MF		DIAL		%
	conc	µeq /l	conc	µeq /l		conc	µeq /l	conc	µeq /l		conc	µeq /l	conc	µeq /l	
pH	4.05	90	5.13	8	91	4.06	87	4.95	11	87	4.03	93	5.03	10	89
mS/m COND	8.05	-	1.29	-	84	7.41	-	1.36	-	82	8.57	-	1.30	-	85
µg/l Fe	148	-	66	-	55	166	-	126	-	32	116	-	74	-	36
µg/l Mn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mgPt/Color	56	-	47	-	16	72	-	61	-	15	53	-	38	-	28
mg/l Ca	0.52	26	0.47	23	10	0.39	19	0.28	14	28	0.46	23	0.33	16	28
mg/l Mg	0.42	35	0.18	15	57	0.23	27	0.19	16	42	0.44	36	0.22	19	50
mg/l K	0.50	13	0.10	3	80	0.46	12	0.09	2	80	0.52	13	0.08	2	85
mg/l Na	2.83	123	0.30	13	89	2.65	115	0.35	15	87	3.30	144	0.33	14	90
µg/l RAL	430	-	170	-	60	385	-	210	-	45	440	-	194	-	56
µg/l ILAL	94	-	99	-	0	118	-	125	-	0	91	-	94	-	0
µg/l LAL *)	336	37	71	8	79	267	30	85	9	68	349	39	100	11	71
mg/l Cl	4.8	135	<0.1	2	99	5.7	161	<0.1	2	99	6.8	192	<0.1	2	99
mg/l SO_4	6.2	129	2.5	52	60	4.5	94	2.3	48	49	5.6	117	2.7	56	52
µg N/l NO_3	930	66	6	0	99	575	41	4	0	99	725	52	4	0	99
mg C/l DOC	6.4	-	5.5	-	14	7.7	-	6.1	-	21	5.9	-	3.8	-	36
I/cm UV-abs	.284	-	.221	-	22	.331	-	.275	-	18	.224	-	.173	-	29
Σ cations	-	324	-	70	78	-	290	-	67	77	-	348	-	72	79
Σ anions	-	330	-	54	84	-	296	-	59	80	-	361	-	58	84
Deficit	-	-6	-	16	-	-		-	8		-		-	14	

*) RAL - ILAL

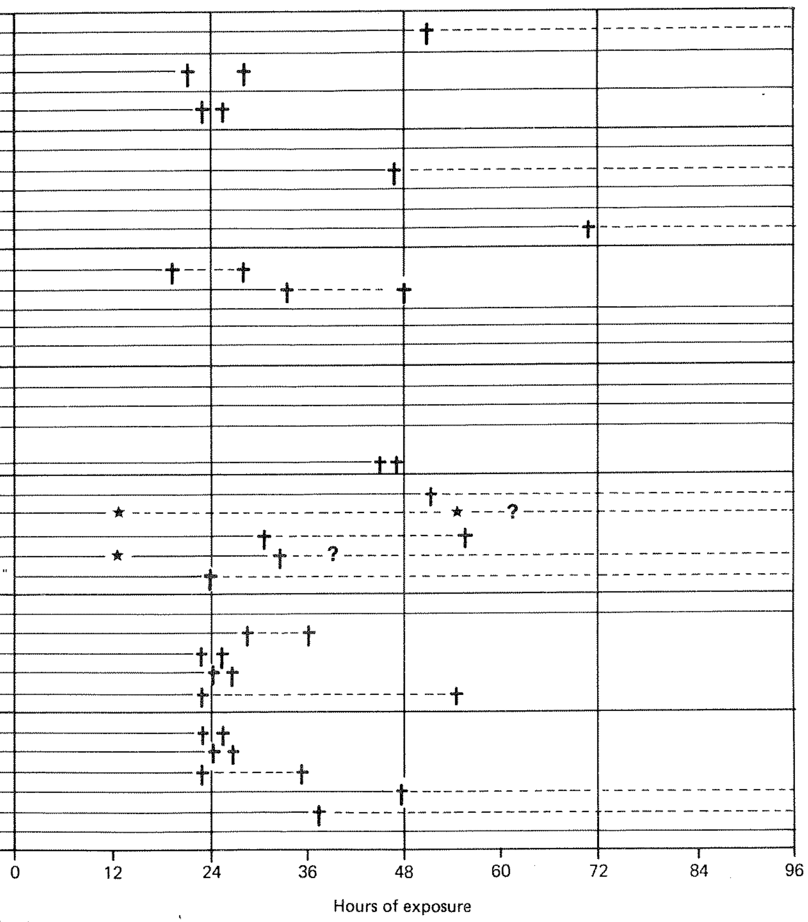
Table 6. Membrane filtered (MF: 0.45 µm) and Dialyzed (MW 12.000) samples from "Kim-area" ("artificially deacidified"). % denotes; passage through dialyzing membrane.

Column No	29			30			31					32					33					34				
Sample No	7	8		33	34		39		40			43		44			45		46			51		52		
							Duplicate																			
	MF	Dial	% pass	MF	Dial	% pass	MF conc	MF µeq /l	Dial conc	Dial µeq /l	% pass	MF conc	MF µeq /l	Dial conc	Dial µeq /l	%	MF conc	MF µeq /l	DIAL conc	DIAL µeq /l	%	MF conc	MF µeq /l	DIAL conc	DIAL µeq /l	%
pH	4.3	4.6	50	3.9	4.9	90	4.03	93	5.01	10	89	4.03	93	4.96	11	88	4.17	68	4.77	17	75	4.19	65	4.90	13	80
mS/m COND	3.57	1.62	55	6.78	1.04	85	7.89	-	1.47	-	81	7.89	-	1.32	-	83	4.99	-	1.59	-	68	5.03	-	1.30	-	34
µg/l Fe	340	300	12	200	160	20	182	-	104	-	44	182	-	104	-	44	310	-	2.60	-	16	270	-	210	-	22
µg/l Mn	< 20	< 20	-	20	< 20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
mgPt/Color	160	150	6	93	94	0	60	-	55	-	8	60	-	52	-	13	141	-	144	-	0	99	-	95	-	4
mg/l Ca	< 1	< 1		< 1	< 1	-	0.54	27	0.52	26	4	0.54	27	0.42	21	22	0.22	11	0.29	14	0	0.26	13	0.25	12	4
mg/l Mg	0.15	0.10	33	0.35	0.15	57	0.41	34	0.18	15	56	0.41	34	0.21	17	49	0.20	16	0.20	16	0	0.22	18	0.18	15	18
mg/l K	0.25	0.10	60	0.50	0.10	80	0.38	10	0.11	3	71	0.38	10	0.07	2	82	0.28	7	0.12	3	57	0.25	6	0.08	2	68
mg/l Na	2.1	0.9	57	2.5	0.5	80	2.6	113	0.37	16	86	2.6	113	0.28	12	89	1.77	77	0.50	22	72	1.91	83	0.43	19	77
µg/l RAL	-	-	-	-	-	-	370	-	140	-	62	370	-	189	-	49	415	-	355	-	14	385	-	313	-	19
µg/l ILAL	140	130	7	-	-	-	85	-	88	-	0	85	-	102	-	0	197	-	224	-	0	194	-	194	-	0
µg/l LAL *)	-	-	-	-	-	-	285	32	52	6	82	285	32	87	10	69	218	24	131	15	40	191	21	119	13	38
mg/l Cl	3.8	0.6	84	8.0	0.4	95	5.8	164	0.1	3	99	5.8	164	<0.1	3	99	3.2	90	<0.1	3	99	3.8	107	<0.1	3	99
mg/l SO_4	2.2	2.0	10	2.0	1.5	25	4.5	94	30	62	33	4.5	94	3.2	67	29	2.5	54	1.9	40	24	2.7	56	1.9	40	30
µg N/l NO_3	< 50	< 50	-	60	< 50	-	650	46	5	0	99	650	46	5	0	99	117	8	4	0	95	178	13	4	0	97
mg C/l DOC	18.7	16.7	-	-	9.7[1]	-	6.7	-	5.3	-	21	6.7	-	5.3	-	21	13.3	-	11.8	-	11	10.8	-	8.9	-	18
I/cm UV-abs	.861	.779	10	-	.445	-	.290	-	.247	-	15	.290	-	.232	-	20	.624	-	.569	-	9	.474	-	.420	-	11
FTU	0.30	0.60	-	0.30	0.45	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
µgN/l Ammonia	30	15	-	55	130	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
µmol/l Strong acid	29	-35	-	119	13	89	-	-	-	-	-	-	-			-	-	-	-	-	-			-	-	-
µmol/l Weak	283	253	10	210	189	10	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Σ cations	-	-	-	-	-	-	-	309	-	76	-	-	304	-	74	-	-	203	-	87	-	-	206	-	74	-
Σ anions	-	-	-	-	-	-	-	304	-	71	-	-	304	-	70	-	-	152	-	42	-	-	163	-	43	-
Deficit	-	-	-	-	-	-	-	5	-	5	-	-	0	-	4	-	-	51	-	45	-	-	43	-	31	-

*) RAL - ILAL 1) Estimated from UV-abs.

Table (7) Toxicity-test of membranefiltered and dialyzed water

SAMPLE	pH	mS/1	µg/1 TOT AL	µg/1 ILAL	µg/1 LAL x)	mg/1 SO_4	µgN/1 NO_3	UV-abs	µmol/1 Strong acid	µmol/1 Weak acid	FTU TURB.	TYPE xx)	REMARKS
1	4.2	3.64	560	370	190	2.6	130	0.785	37	249	0.20	Em	
2	4.7	1.52	440	340	100	2.0	<50	0.728	-15	199	1.3	Ed	
3	4.0	6.70	670	350	320	6.6	220	0.613	79	274	0.25	Em	
4	4.7	1.65	360	250	110	2.2	<50	0.415	-12	171	0.75	Ed	
5	4.0	6.93	640	350	290	5.4	530	0.601	58	292	0.35	Em	
6	5.0	1.12	390	270	120	1.7	<50	0.385	-30	166	0.75	Ed	
7	4.3	3.57	640	500	140	2.2	<50	0.861	29	283	0.30	Km	
8	4.6	1.62	610	480	130	2.0	<50	0.779	-35	253	0.60	Kd	
9	4.3	3.14	240	180	60	1.8	110	0.417	3	193	0.20	Em	
10	4.8	1.45	180	150	30	1.6	<50	0.385	14	149	0.45	Ed	
11	4.0	6.75	650	340	310	6.8	220	0.613	85	263	0.25	Em	
12	4.8	1.73	380	260	120	2.9	<50	0.437	-18	187	0.55	Ed	
13	4.3	3.54	580	-	-	3.0	250	-	29	275	0.30	Em	
14	4.7	1.59	580	-	-	2.0	<50	-	-21	253	0.60	Ed	
15	4.3	3.00	530	-	90	3.0	<50	-	23	283	0.25	Hm	
16	4.9	1.40	500	-	-	2.5	<50	-	18	211	0.80	Hd	
17	4.3	3.00	530	-	90	3.0	<50	-	50	281	0.25	Hm	
18	4.8	1.66	500	-	-	3.0	<50	-	20	233	0.45	Hd	
19	1.8	-	550	-	-	4.0	<50	-	-	-	0.50	-	HCl
20	4.2	2.40	280	-	-	2.0	<50	-	100	170	1.1	Hd	"
21	4.3	3.27	550	-	40	3.0	<50	-	36	272	0.55	Hm	"NIVA-CONC"
22	4.7	1.76	480	-	-	2.5	<50	-	19	243	1.1	Hd	"
23	4.0	6.23	550	-	-	7.0	920	-	105	244	0.25	Em	
24	4.9	1.70	330	-	-	2.5	<50	0.437	14	182	0.70	Ed	
25	4.2	2.11	20	0	0	1.0	<50	0.487	56	143	0.30	Hm	"NORDIC FULVIC"
26	4.7	1.08	140	-	0	1.0	<50	-	28	154	0.50	Hd	" "
27	3.9	7.60	600	-	-	8.0	670	0.412	105	272	0.25	Em	
28	4.9	1.63	280	-	-	3.0	<50	0.284	27	144	0.50	Ed	
29	3.8	8.10	600	-	-	5.0	440	0.347	140	223	0.25	Em	
30	4.9	1.31	310	-	-	2.0	<50	0.249	-7	171	0.40	Ed	
31	3.8	8.81	600	-	-	8.0	700	0.378	135	250	0.20	Em	
32	4.8	1.77	400	-	-	4.0	<50	0.278	3	186	0.50	Ed	
33	3.9	6.78	500	-	-	2.0	60	-	119	210	0.30	Km	
34	4.9	1.04	430	-	-	1.5	<50	0.445	13	189	0.45	Kd	
35	4.1	4.80	300	-	-	2.5	180	0.428	72	189	0.30	Em	
36	4.8	1.44	310	-	-	2.0	<50	0.388	21	162	0.45	Ed	



★ Fish jumped out
† 1 fish dead

x) TOT.AL - ILAL

xx) H = Hellerudmyra
E = "Egil-area"
K = "Kim-area"
m = membrane filtered
d = dialyzed

Table 8. Composition of a salt solution and sample from Hellerudmyra (July -86) before and after dialyzation.

Sample	61		62		59		60	
	Salt solution				Hellerudmyra			
	MF		DIAL		MF		DIAL	
	conc	μeq/l	conc	μeq/l	conc	μeq/l	conc	μeq/l
pH	4.22	60	4.89	13	4.39	41	4.91	12
COND mS/m	4.14	-	1.75	-	3.03	-	1.76	-
Colour mg Pt/l	-	-	-	-	188	-	176	-
DOC mg C/l	-	-	-	-	19.6	-	12.5	-
Fe μg Fe/l	-	-	-	-	570	-	480	-
Ca mg Ca/l	0.27	13	0.07	3	1.15	57	0.98	49
Mg mg Mg/l	0.32	26	0.25	21	0.24	20	0.24	20
RAL μg Al/l	-	-	-	-	274	-	237	-
ILAL - " -	-	-		-	190	-	196	-
LAL - " -		-	-	-	84	9	41	5
K mg K/l	0.29	7	0.09	2	0.04	1	0.07	2
Na mg NA/l	1.88	82	0.51	22	1.09	47	0.65	28
So_4 mg So_4/l	5.9	123	4.5	94	1.9	40	1.5	31
NO_3 μg N/l	44	3	2	-	2	-	5	-
Cl mg Cl/l	2.4	68	<0.1	2	1.7	48	0.8	23
UV abs. I/cm	.00	-	.00	-	.91	-	0.87	-
Σ cations		188		61		175		116
Σ anions		194		96		88		54

Table 9. Mean values from all tables (except for ionbalance, see foot notes).
% denotes; passing through membrane.

	HELLERUDMYRA					EGIL					KIM					EGIL, Samples corresponding with KIM				
	MF		DIAL			MF		DIAL			MF		DIAL			MF		DIAL		
	conc	1) µeq/l	conc	1) µeq/l	%	conc	3) µeq/l	conc	3) µeq/l	%	conc	5) µeq/l	conc	5) µeq/l	%	conc	6) µeq/l	conc	6) µeq/l	%
pH	4.38	37	4.84	14	67	4.03	93	4.83	14	85	4.08	80	4.82	15	82	3.98	90	4.92	12	87
mS/m Cond	2.92	-	1.33	-	54	6.50	-	1.46	-	78	6.03	-	1.39	-	77	7.35	-	1.41	-	81
µg/l Fe	549	-	528	-	4	227	-	167	-	26	247	-	190	-	23	148	-	101	-	32
µg/l Mn	40	-	23	-	-	<20	-	<20	-	-	<20	-	<20	-	-	<20	-	<20	-	-
mgPt/Color	175	-	170	-	3	94	-	81	-	14	102	-	98	-	4	66	-	56	-	15
mg/l Ca	1.09[1]	54	0.63[1]	31	42	0.46[3]	23	0.26[3]	13	43	0.39[5]	20	0.37[5]	18	51	0.47[6]	24	0.39[6]	19	21
mg/l Mg	0.26	18	0.14	9	46	0.39[3]	32	0.18[3]	15	53	0.31[5]	25	0.19[5]	16	39	0.40[6]	33	0.19[6]	16	52
mg/l K	0.08[1]	2	0.02[1]	0	75	0.47[3]	12	0.08[3]	2	83	0.32[5]	8	0.10[5]	3	69	0.50[6]	13	0.09[6]	2	82
mg/l Na	1.03	39	0.33	9	70	2.46	124	0.54	13	78	2.30	100	0.50	17	78	2.63	126	0.53	14	89
µg/l RAL	266[1]	-	249[1]	-	6	439[3]		198[3]	-	55	385[5]	-	249[5]	-	35	421[6]	-	186[6]	-	56
µg/l ILAL	211[1]	-	176[1]	-	17	130[3]	-	119[3]	-	9	140[5]	-	152[5]	-	0	99[6]	-	104[6]	-	0
µg/l LAL	55[1]	6	73[1]	8	0	309[3]	34	79[3]	9	74	245[5]	27	97[5]	11	60	322[6]	36	82[6]	9	75
mg/l Cl	1.48	33	0.38	4	74	4.03	140	0.3	3	93	5.07	131	0.1	<3	98	5.2	156	0.1	<3	98
mg/l SO_4	3.01	63	1.63	33	48	5.16	108	2.32	48	55	3.07	74	2.25	52	27	5.2	117	2.5	52	52
µg N/l NO_3	9	0	3	0	67	482	51	6	0	99	284	28	4	0	99	580	56	4	0	99
mg C/l DOC	15.9[1]	-	11.6[1]	-	27	6.6[3]	-	5.0[3]	-	24	9.4[5]	-	7.8[5]	-	17	6.5[6]	-	5.2[6]	-	20
I/cm UV-abs	.720	-	.550	-	24	.450	-	.342	-	24	.508	-	.449	-	12	.333	-	.264	-	21
µmol/l Strong acid	37[2]		19[2]		(49)	77[4])		5[4])		94	74		11		100					
µmol/l Weak	282[2]		222[2]		(21)	248[4]		179[4]		28	247		221		10					
Σ cations		156	-	72	-		318		63			260		78			322		69	
Σ anions		96	-	25	-		299		51			233		54			329		52	
Deficit		60		47			19		12			27		24			-7		17	

1) Column No 1, 2, 3, 4 & 9
2) column 6 & 8
3) column 5, 26, 27 & 28
4) " 15 - 25
5) column 31, 32, 33 & 34
6) " 20(×2), 27 & 28

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Acid Rain Research Reports

1/1982 Henriksen, A. 1982. Changes in base cation consentrations due to freshwater acidification. 50pp. Out of print.

2/1982 Henriksen, A. and Andersen, S. 1982. Forsuringssituasjonen i Oslomarkas vann. 45 pp. Out of print.

3/1982 Henriksen, A. 1982. Preacidification pH–values in Norwegian rivers and lakes. 24pp. Out of print.

4/1983 Wright, R.F. 1983. Predicting acidification of North American lakes. 165 pp.

5/1983 *Schoen, R.*, Wright, R.F. and *Krieter, M.* 1983 Regional survey of freshwater acidification in West Germany (FRG). 15 pp.

6/1984 Wright, R.F. 1984. Changes in the chemistry of Lake Hovvatn, Norway, following liming and reacidification. 68 pp.

7/1985 Wright, R.F. 1985. RAIN project. Annual report for 1984. 39 pp.

8/1985 *Lotse, E* and *Otabbong, E.* 1985. Physiochemical properties of soils at Risdalsheia and Sogndal: RAIN project. 48 pp.

9/1986 Wright, R.F. and Gjessing, E. 1986. RAIN project. Annual report for 1985. 33 pp.

10/1986 Wright, R.F., Gjessing, E., Semb, A. and Sletaune, B. 1986. RAIN project. Data report 1983–85. 62 pp.

11/1986 Henriksen, A., Røgeberg, E., Andersen, S., and Veidel, A. 1986 MOBILLAB–NIVA, a complete station for monitoring water quality. 44 pp.

12/1987 Røgeberg, E. 1987. A coulometric Gran titration method for the determination of strong and weak acids in freshwater. 28 pp.

13/1987 Wright, R.F. 1987. RAIN project. Annual report for 1986. 90 pp.

14/1988 Hauhs, M. 1988. Water and ion movement through a mini-catchment at Risdalsheia, Norway (RAIN–project). 74 pp.