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Effects of rockfill dams and rock dumps on downstream water chemistry

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ABSTRACT

A number of potential negative effects on aquatic environments are associated with rockfills. However, in southwestern Norway, lakes and rivers downstream from large rockfills were among the very few sites where trout survived the acidification period. In this study, twelve rockfill dams, three rockfill dumps, several downstream locations and references were surveyed. The seepage water from the dams were found to have considerably elevated concentration of ions compared to the reservoir water. Despite a loss of alkalinity from oxidation of sulphide minerals, a net positive contribution to the downstream lakes was established. Simulations demonstrate a positive effect on the water chemistry downstream of the rockfills. The study suggest that this buffering effect has contributed to the survival of trout populations.

PREFACE

First and foremost, I am forever grateful for the help and guidance from my supervisor, Espen Enge. You're involvement and help with fieldwork, analysis and corrections have been vital for the project.

The fieldwork was comprehensive and included 400 km of driving each 12 samplings. Analyses were preformed manually, with a considerable time-consume. The 130 sulphate analysis required approximately one hour per sample.

I want to thank Mike, Magnus, Sigurd, Fredrik, and Samuel for their assistance in the field and lab work. I also want to thank especially Trond Erik Børresen (Lyse) and Lars Jakob Gjemlestad (Sira Kvina) for providing info and data necessary for this study.

The thesis included a published article (Appendix A)

Stavanger, September 2019
Christine Stølen

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1 INTRODUCTION

Rockfills are associated with many different kinds of pollution, such as particles, nitrogen compounds and metals. Moreover, rockfills are a potential source of sulfuric acid through the oxidation of sulphide minerals. This effect is common in the mining industry (Snoeyink and Jenkins 1980), where it is referred to as Acid Mine Drainage (AMD). Adverse effects of sulphide-oxidation have also been linked to other engineering and construction activities (Sørensen 1988, Hindar and Lydersen 1994, Hindar et al. 2015). Furthermore, acidification effects have also been reported from rockfill dams. Fell et al. (2014) list several examples of acidic seepage caused by the oxidation of pyrite (FeS_2).

Acidification is not restricted to local sources. During the past century, atmospheric deposition of long-range transported sulphur- and nitrogen-compounds has severely affected surface waters throughout southern Norway. Waters in Sirdal and adjacent mountain areas in Rogaland are dilute and unbuffered and are therefore particularly sensitive to acidification (Enge 2013). In Sirdal, an emerging decline of the trout (Salmo trutta) populations was observed as early as during the late 1800s, possibly caused by effects of acidification (Enge et al. 2017). After the mid 1900s, the population decline accelerated, and in the late 1970s the vast majority of trout populations in Sirdal and adjacent mountain areas were considered lost due to acidification (Sevaldrud and Muniz 1980).

Surveys from southwestern Norway (Sevaldrud and Muniz 1980, Gunnerød et al. 1981) revealed that all trout populations adjacent to rock dumps and rockfill dams survived the acidification. Sporadic water chemistry measurements from dam leakages in the past decades showed higher pH, alkalinity- and conductivity-values than in the corresponding reservoirs (Enge 2009).

Seek to understand the potential chemical effects from usage and disposal of blasted rocks in aquatic environments, and evaluate if these effects may explain the observed survival of trout.

2 THEORY/BACKGROUND

2.1 General Water Chemistry/Chemistry and composition of natural waters

95-99% of the total dissolved inorganic solute composition of natural surface waters consists of four cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and three anions (HCO_3^-/CO_3^{2-}, SO_4^{2-}, Cl^-), listed in order of abundance (Brezonik and Arnold, 2011). However, there are many exceptions to this general composition.

The sources of the ions are primarily bedrock, atmosphere, and may also include anthropogenic contribution. When passing through a catchment, the chemical composition is modified by several chemical, physical and biological processes.

2.2 Atmospheric contribution and processes

Atmospheric deposition processes of aerosols can be divided into two types: dry deposition and wet deposition. These include marine (sea salts) and continental components (terrestrial soil dust and anthropogenic pollution)(Eby 2004). The transportation distance and deposition are influenced by particle size, wind direction and velocity, but are also geographically restricted and limited by topographic barriers.

2.2.1 Precipitation chemistry

Evaporated water can be transported over long distances and deposited as rain, snow, hail or any other form of wet precipitation. Various chemical components are incorporated into the water as it condenses. This dilute solution of dissolved salts can be further transformed by natural and anthropogenic chemical processes in the atmosphere (Snoeyink and Jenkins 1980).

Water equilibrates with the gases in the lower atmosphere, which can significantly influence the chemistry of the precipitation. Some of the minor constituent, such as CO_2 and SO_2, are very soluble compared to the other major atmospheric constituents like N_2 and O_2 (Snoeyink and Jenkins 1980). In an unpolluted atmosphere, the pH of precipitation is 5.7, a result of the equilibrium with the weakly acidic dissolved CO_2 (Stumm and Morgan 1996). Any small amounts of the acid-producing SO_2 and NO_x will lower the pH even further. These gases primarily originate from fossil fuel combustion and react with the precipitation water to form sulphuric and nitric acid (H_2SO_4 and HNO_3).

The concentration of ions in precipitation decrease with increasing distance from the coast. This coastal gradients are seen in the geographical distribution of sodium and chloride concentrations in lakes in Norway (Wright and Henriksen 1978).

2.2.2 Marine contribution

In lakes with limited non-marine contribution combined with high precipitation and runoff rates, the composition of the precipitation can have a significant influence on the ionic concentration. As the water passes through the catchment, the ionic composition is modified by a range of interrelated processes.

When investigating the chemical effect from the bedrock and anthropogenic sources, the marine contribution of ions must be subtracted to correct for the sea-salt effect. Cl^- and SO_4^{2-}, both major components of sea-water, are mobile ions. Precipitation input and hydrological output Cl^- and SO_4^{2-} in the catchment is close to balanced making them suitable as tracers in the catchment (Skartveit 1981). In addition to the marine source, SO_4^{2-} has a number of both natural and anthropogenic sources. Due to minimal anthropogenic and terrestrial sources of Cl^-, the concentration of Cl^- can serve as an indicator of the sea-salt influence.

Assuming that all chloride is exclusively of marine origin and that the ionic proportions of the marine contribution in the atmospheric deposition are of the same ratio as sea-water (Table 2.1) the marine fraction of ions can be estimated from chloride. The non-marine concentration (denoted with an asterisk) of any ion ("X") in a sample can be calculated with the following formula:

$$[X]^* = [X]_{sample} - \left[\frac{X}{Cl^-}\right]_{sea} \times [Cl^-]_{sample}$$

Table 2.1 Primary ionic composition of seawater

Ion	Seawater (g/kg[1])	Ratio to Cl^-
Na^+	10.77	0.556
Mg^{2+}	1.29	0.067
Ca^{2+}	0.4121	0.021
K^+	0.399	0.021
Cl^-	19.354	1.000
SO_4^{2-}	2.712	0.140

[1] Stumm and Morgan (1996)

2.3 Hydrogeochemical contribution and processes

The proportions of the solutes in natural waters depend highly on the local geochemical conditions (Brezonik and Arnold, 2011). The concentration is influenced a range of hydrogeochemical processes, including dissolutions and precipitation, redox reactions, hydrolysis, ion exchange and complexing. Chemical weathering is the alteration and decomposition of the rock material through hydrogeochemical processes.

The primary chemical weathering agent is water and carbonic acid derived from atmospheric CO_2 (Stumm and Morgan 1996). Carbonic acid acts as a proton donor and reacts with the bases of the minerals. CO_2 is protolyzed in two steps:

$$CO_{2(g)} \rightleftarrows CO_{2(aq)}$$

$$CO_{2(aq)} + H_2O \rightleftarrows H^+ + HCO_3^-$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$$

Calcite being a good example of this kind of weathering:

$$CaCO_3 + H^+ \rightleftarrows Ca^{2+} + HCO_3^-$$

$$CaCO_3 + H_2O \rightleftarrows Ca^{2+} + HCO_3^- + OH^-$$

$$CaCO_3 + H_2O + CO_2 \rightleftarrows Ca^{2+} + 2HCO_3^-$$

This is a relatively fast reaction that produce calcium- and bicarbonate-ions and has a significant effect on the ionic concentration in water.

The alumino-silicate minerals are a complex group. In general, they weather to form a base cation, bicarbonate, dissolved silica, and a variety of clay mineral products. Albite, a common feldspar it a good example:

$$NaAlSi_3O_{8(s)} + CO_2 + 5\tfrac{1}{2} H_2O \rightarrow Na^+ + HCO_3^- + 2H_4SiO_4 + \tfrac{1}{2} Al_2Si_2O_3(OH)_4$$

Even though these minerals don’t contain any carbonate, the chemical reaction of hydrolysis between water and the mineral consumes acid and form bicarbonate from CO_2 (Brezonik and Arnold, 2011). This has been shown with minerals containing calcium and magnesium like dolomite and olivine as well (Sverdrup, 1985). However, the feldspar reactions proceed much slower due to kinetic constraints and provide a much smaller contribution to the bicarbonate concentration in the water compared to the dissolution of carbonate minerals. Consequently, surface water underlain by granitic bedrocks comprised of quarts and feldspar minerals have a very low buffer capacity.

The various minerals weather at different rates. The solubility of the material are dependent on factors such as the pH, oxidation-reduction potential, ionic strength of solution, temperature and pressure (Eby 2004)

The interaction between water and gases and the rock material is dependent on the surface are and the kinetics of the geochemical reactions. The chemical weathering processes can be induced by the physical weathering, which increase the surface-to-volume ratio and expose fresh mineral surfaces, and biotic processes which increase the rate of reaction (Eby 2004)

While most weathering reactions produce alkalinity, several exceptions exists e.g. the oxidation of metal sulphide minerals such as pyrite (FeS_2). The overall sequence of reactions can be summarized as follows:

$$FeS_{2(s)} + \frac{15}{4}O_2 + 3\frac{1}{2}H_2O \rightarrow Fe(OH)_{3(s)} + 4H^+ + 2SO_4^{2-}$$

The oxidation and following reactions of pyrite and other sulphide minerals are complex. Exposure of the mineral to air (oxygen) and water can result in a large number of different reactions paths. The rate of the process is biologically mediated by e.g. *Thiobacillus ferroxidans*, an acid-tolerant, iron oxidizing bacteria. Overall, pyrite oxidize rapidly and result in the production of sulphuric acid (Snoeyink and Jenkins 1980).

2.4 Alkalinity and acidification

The pH of natural waters is determined by the balance between the acids from the atmosphere, primarily CO_2, and the contribution of bases from the bedrocks. The waters buffer and neutralization capacity is referred to as the alkalinity which is, for many aqueous systems, controlled primarily by carbonate chemistry (Stumm Morgan 1996). In a carbonate system, the alkalinity is defined as:

$[ALK] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$

This equation can be simplified depending on the chemical conditions since the concentration of the carbonate species varies with pH. At pH under 8.3 the carbonic species are present as CO_2 and HCO_3^{2-}.

$$\frac{[H^+][HCO_3^-]}{[CO_{2(aq)}]} = K_{a1}$$

$$pH = pK_{a1} + \log\left(\frac{[HCO_3^-]}{[CO_{2(aq)}]}\right)$$

Oligotrophic waters are generally oversaturated with CO_2 (Norton and Henriksen 1983). Despite this, the concentration of dissolved CO_2 is relatively stable compared to the HCO_3^-. Subsequently, the pH is practically a function of a HCO_3^-. Calcium and bicarbonate are normally present in equivalent amounts (Wright and Henriksen 1978). Therefore, pH can be estimated using Ca values.

The Acid-neutralizing capacity, ANC, is an alternative definition of alkalinity. The term is often referred to as the "calculated alkalinity" and takes into account the sum of a wide range of proton-accepting and proton-donating species:

$ANC = \Sigma(\text{proton acceptors}) - \Sigma(\text{proton donors})$

This can require a number of individual ion determinations depending on the system. Proton acceptors such as NOM^- (organic anions), aluminium, boron, silicon, phosphorous and sulphur species can contribute to the acid-neutralization capacity (Snoeyink and Jenkins 1980). In most cases, the contribution of these species are minimal because their concentrations are generally too small to have a significant effect. The estimation of ANC is often simplified as the strong cations and strong acid anions. The ions included in the equation for most natural waters usually comprise:

$ANC = [Ca^{2+}] + [Mg^{2+}] + [Na^+] + [K^+] - [SO_4^{2-}] - [Cl^-] - [NO_3^-]$

The alkalinity produced in the weathering reactions are equivalent to the cations that are produced (Wright and Henriksen 1978). In many water bodies, primarily with low concentration of organic matter, the alkalinity is approximately equal to the ANC. Titration does not distinguish species, measurements of alkalinity are actually measurements of ANC.

Acidification is defined as a loss of alkalinity and can be estimated by the difference between pre-acidification, the original alkalinity, and the current alkalinity (Henriksen 1980).

$[ALK]_{loss} = [ALK]_0 - [ALK]$

In natural oligotrophic water, it is the non-marine cations that contribute to the alkalinity.

$[ALK]_0 \approx \Sigma[\text{base cations}]^*$

The sum of non-marine calcium and magnesium, marked with an asterisk (*), is approximately equivalent to the pre-acidification alkalinity (Henriksen 1980):

$[ALK]_0 \approx 0.91 \times ([Ca]^* + [Mg]^*)$

A simpler equations has also been proposed:

$[ALK]_0 \approx 1.21 \times [Ca]^*$

The acidification is approximately the sum of non-marine sulphate and nitrate. Therefore,

$[ALK] = [ALK]_0 - \sum \text{Acidification} = [ALK]_0 - [SO_4^{2-}] - [NO_3^-]$

Surface waters with low alkalinity is susceptible to changes in pH. In mountain lakes in Rogaland, the median alkalinity is 7 μeq/L, making them highly sensitive to acidification.

2.5 Study Area/site description

The study area is located at altitudes of 560-930 m a.s.l. in south western Norway, within the counties of Rogaland and Agder (fig x). The forest vegetation reaches an altitude of 600-700 m a.s.l, and the area is characterized by barren rock with limited vegetation and soil cover.

2.5.1 Climate

The region has a continental subarctic climate to alpine tundra above the tree line and is prone to large rainfalls and runoff. The annual average temperature and precipitation recorded at Tjørhom weather station, located in the valley bottom 5 km south of Valevatn at 500 m a.s.l, is 3.2°C and 1760 mm, respectively. Monthly normals (1961-1990) show peaks in precipitation from September to January with a maximum in October (232 mm) and a minimum in April (67 mm). The precipitation normally falls as snow from November to April. Snow-accumulation ranges from 290 at Tjørhom (500 m a.s.l) to 1420 mm at Auråhorten (1200 m a.s.l) (Enge et al. 2016). The snow primarily melts during April to June.

Although the spring and summer are the driest periods, the runoff rates are high due to snowmelt. Daily streamflow is measured continuously at a station by Jogla river, located 2 km east from Valevatn at an altitude of 610 m. The catchment of 31.1 km2 drains mountain areas up to 1209 m a.sl. and is characterized by a mixed snowmelt/rainfall regime (Vormoor et al. 2016). Monthly average (1973-2007) runoffs in May and June illustrates the magnitude of the snowmelt from the accumulated snow and ice (Figure 2.1 b).

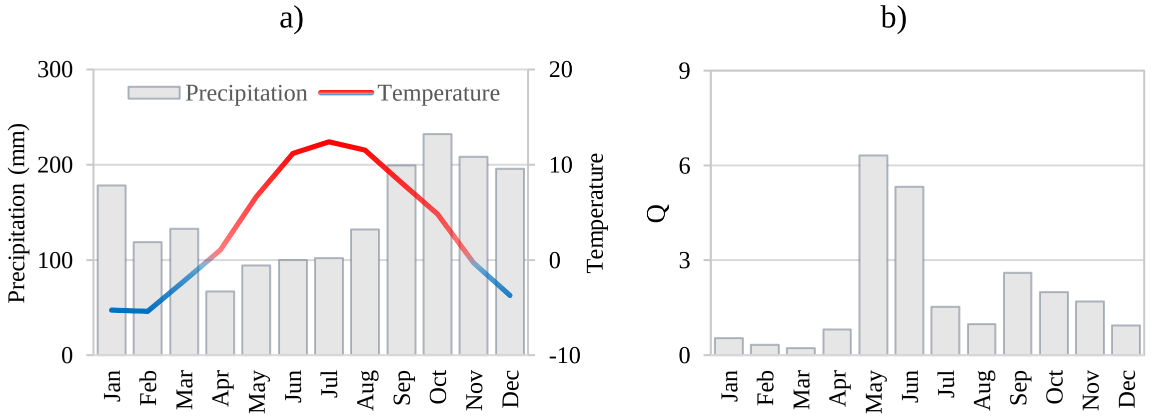

Figure 2.1 Meteorological and hydrological data from the study area. Precipitation and temperature is presented with monthly normals recorded Tjørhom from the period of 1961 to 1990 (a), and the monthly average flowrate at Jogla from 1973 to 2007 (b)

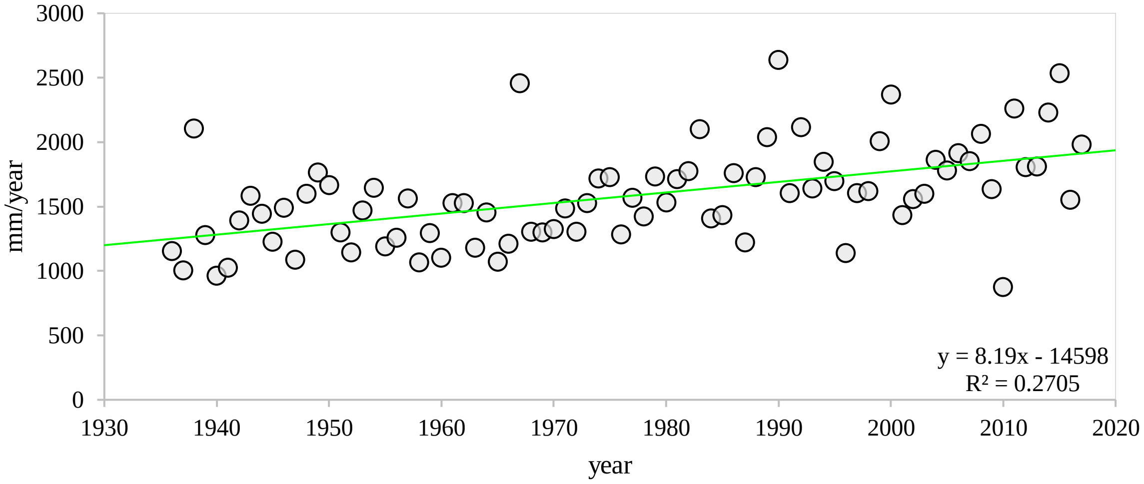

Figure 2.2 Increase in precipitation the last 90 years illustrated by regression line (green) of the precipitation data from the meteorological station «Øvre Sirdal».

Data from 1930 up to today recorded at the meteorological station "Øvre Sirdal" show an 8 mm increase in precipitation per year ($p<0.001$) (Figure 2.2) (eKlima.no). This trend is also persistent in the runoff data, demonstrated by an increase of 32% and 24% in the nominal runoff from 1930-1960 to 1961-1990 at Jogla and Tjørhom, respectively.

2.5.2 Geology

The bedrock in the mountain areas of the southern part of Norway is of Precambrian origin and comprises primarily gneiss and granite with little carbonate minerals (ngu.no). These rock types are slow weathering silicate minerals, and are poor contributor to ions in natural waters. Waters associated with such geology are dilute and have low buffer capacity. Glacial deposits are scarce and mainly located in the valley bottom.

Biotittic gneiss is somewhat less resistant to weathering. Patches of this type of rock are found distributed in the area, contributing to slightly higher values for pH and calcium in adjacent waters. This was suggested to be the cause of better fish status in the otherwise extremely dilute waters in the area. (L'Abée-Lund, 1985).

Pyrite (FeS_2) is the most abundant of the sulphide minerals found in a variety of geological formations, including the metamorphic and igneous rocks such as gneiss and granite. Positive detection of chalcopyrite has been reported from this area (Urdal, 2018). Small quantities of another less common sulphide mineral, molybdenum disulphide (MoS_2), can be found in granite. Large deposits of this is spread in a region from Numedal to Ørsdalen (Nystuen, 1972).

2.5.3 Dams and rock dumps

There are 345 large dams (exceeding 15 m in height) in Norway and over 185 of these are embankment dams (Lia et al. 2015) of which the vast majority is of the rockfill type. An embankment dam is defined as "*any dam constructed of excavated natural materials or of waste materials*" (ICOLD 1978). If more than 50% of the total volume comprises of natural or crushed stone, the dam is classified as "rockfill" (ICOLD 1978). Most of these dams were built between 1950 and 1990 during Norway's most intense hydropower development period. The Sira-Kvina hydropower development is one of the largest in Norway, generating 6300 GWh yearly, accounting for 5% of Norway's total power production. The development of the seven power stations started in 1967 with numerous dams being constructed between 1960 to 1980 for regulation and storage of the water in the Sira catchment area. Svartevatn dam is the largest of these standing 130 m tall and regulating a reservoir volume with a retention time of three years (Table 2.2)

Table 2.2 Rockfill dams in south western Norway

Name		Constructed	Maximum height	Crest length	Base width
Used name	Official name	Year	m	m	m
Deg	Deg	1970	92	390	290
Roskrepp A	Roskreppfjord	1968	48	360	140
Roskrepp B	Roskreppfjord secondary dam	1968	28	225	89
Svartevann	Svartevatn dam	1976	128	410	400
Tolvkjørheller	Deg Secondary dam 2	1970	36	390	113
Ripledal	Deg Secondary dam 4	1970	26	90	83
Gravann	Gravann	1971	29	270	200
Flothøl	Flåthølmyra main dam	1970	26	215	83
Akslarå	Akslaråtjørn	1984	33.5	165	100
Flørli	Dam St.Flørli	1999	35	200	120
Lyngsvatn S	Lyngsvatn South	1964(1)	37	660	110
Lyngsvatn N	Lyngsvatn North	1975	17	185	50

(1) Reconstructed/built 10 m taller in 1975

Excess of rockfills are also deposited in the terrain or in lakes. An example of this is lake Listølvatn. The water in the lake was drained and large amounts of rock mass from the inlet tunnel to Tjørhom Kraftverk was placed in the lake. The water level was re-established afterwards.

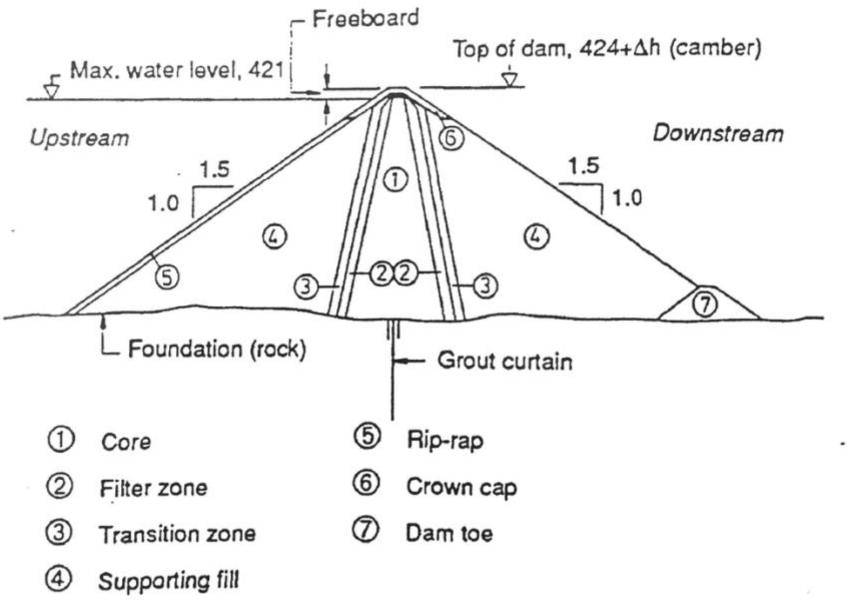

Figure 2.3 Cross section of a typical rockfill dam with a central moraine core (Retrieved from Höeg et al. 1993)

Every dam is unique and various types and design exists. The dams typically consist of a main impervious central core of moraine, sandy gravel filter, transitioning zone of finer rockfill followed by supporting rockfill (Figure 2.1). The dams are constructed of quarried gneiss and granite from an nearby areas.

Although the central core is impervious and considered practically "water-tight", all dams experience loss of water through seepage. Seepage is defined as "*an interstitial movement of water though the construction itself or the dams foundation or abutments*" (ICOLD 1978). This is accounted for in the design of the dams to limit the seepage.

2.5.4 Acidification, water quality and survival of fish

The region is prone to large rainfalls and runoff, but receives little marine addition/contribution of ions due to its geographical location (elevation and distance to sea). Combined with a slow weathering bedrock, the surface waters have low ionic strength with a low buffer capacity. Fish populations in such dilute water qualities is primarily restricted by pH and conductivity (Enge and Kroglund 2011). Brown trout was formerly highly prevalent in the majority of lakes in Sirdal and adjacent mountain areas, but the populations appeared to decline in the 1960s and 1970s (Sevalrud and Muniz 1980).

The region was particularity vulnerable to acid input due to the low buffer capacities of the water. An increase in sulphate and nitrate concentrations in the precipitation in Norway was consistent with the increase of fossil fuel consumption in a long term precipitation quality data dating back to 1955 (Joranger et al. 1980). Consequently, the considerable deposition of acid precipitation in the mid 1900´s had a significant effect on pH values in the lakes.

At the end of the 1970’s, 75% of the fish populations in the lakes was considered extinct or severely damaged. The majority of the lakes was registered to have a pH under 5 during this period (Sevaldrud and Muniz 1980). However, a few trout populations survived despite the acidification (Table 2.3)

While test-fishing in Valevatn reservoir was found to be negative, several surveys have established that the populations in Lake Fidjelandsvatn, downstream the Deg dam, survived the acidification (Larsen et al. 1989, Sevalrud Muniz 1980). Lake Ortevatn, upstream of Lake Fidjelandsvatn, was found to support a sparse population.

Most of the fish populations in the lakes now included in the Svartevatn reservoir were extinct except for three lakes in the eastern part which had sparse populations. The fish populations in most lakes and tributaries downstream the Svartevatn dam were extinct, except sparse populations registered in Lake Godfarlonene and the downstream Lake Grauthellervatn. During a survey in Lake Grauthellervatn in 1986, a sparse population was found, establishing that the trout survived.

In addition to these two major study sites, fish populations were also registered in neighbouring areas associated with dams and rockfills (Table 2.3).

Since the late 1980´s the sulphur emissions in Europe declined considerable as a result of several international agreements (Figure 2.4) . In mountain lakes in south-west Norway, the water chemistry is close to pre-acidification state (Enge 2013). The trout populations have recovered correspondingly.

Table 2.3 Fish population status in registered in various waters in Sirdal. Population status expressed as follows: 1: Dense population, 2: Sparse population and 3: Extinct.

Area	Lake	m a.s.l.	Year	Status	pH	Cond
Gravvatn dam	Sandvatn (1)	574		1		
	Gravvatn (1)	660	> 1970	3		
Deg dam	Valevatn (1)(2)	660	> 1970	3		
	Ortevatn (1)(2)	565	1960-1970	2		
	Fidjelandsvatn (1)(2)	565		1		
Rockfills	Ognheller (1)(3)	765	> 1970	1	4,95(1), 5.00(2)	12,7
	Håhellervatn (1)(3)	868	> 1970	1	6,10(1), 5.30	9.80
Svartevatn (reservoir pre-dam construction)	Store Auråvatn (1)	834	1960-1970	3	5,33	9,9
	Lonevatn (1)	825	1960-1970	3		
	Svartevatn (1)	781	1960-1970	3		
	Ytre Storvatn (1)	889	1950-1960	3	4,93	4,7
	Hyttevatn (1)	865		2	5,19	6,4
	L.Auråvatn (1)	835		2		
	Såtjørn (1)	873		2	5,26	7,1
Downstream Svartevatn dam	S.Godfartjørn (tributary) (1)	769	1960-1970	3		
	L.Godfartjørn (tributary) (1)	770	1960-1970	3		
	Godfarlonene (1)	760	1960-1970	2		
	Grauthellervatn (1)(4)	754	1960-1970	2		
	Salomonsvatn (1)	697	1960-1970	3		
	Dyngjanvatn (1)	681	1960-1970	3		

(1) (Sevalrud and Muniz 1980)
(2) (Larsen et al. 1989)
(3) (Gunnerød et al. 1981)
(4) (Enge 1987)

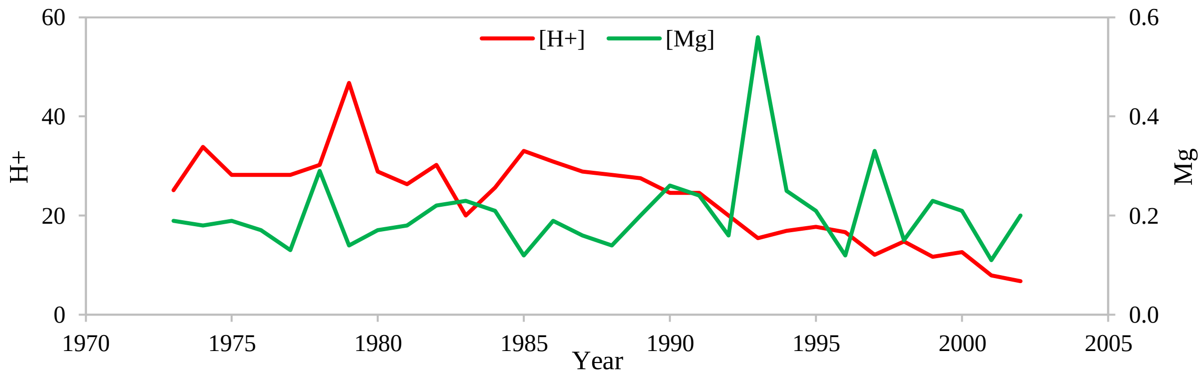

Figure 2.4 Yearly average of $[H^+]$ and [Mg] measured in precipitation at Skreå in Sirdal. The marine ion contribution is represented by [Mg].

3 METHODS

3.1 Sample collection/locations/data collection/sampling

The study comprised of rockfill dams and rockfill dumps within Rogaland and Agder counties. The most comprehensive sampling was performed in Sirdal, within the Sira and Kvina watersheds. The samples were collected at 13 sites, with a total of 33 sampling locations categorized into four groups:

- References
- Seepage water from rockfill dams
- Lakes with rockfill dumps
- Downstream locations

The references included primarily the reservoirs, but also pristine water bodies were included. The downstream locations comprised of rivers, outlets and lakes, with distance ranging from 350 m to 1.5 km from the dams. These locations were included to study the mixing of the seepage water with other unaffected water bodies and examine/investigate the degree/possible effects of the seepage water in downstream locations/water bodies.

With a frequency of 2-4 weeks, the sampling was distributed throughout June 2018 to March 2019. Samples were collected at the surface of the locations in 500 ml LDPE bottles, occasionally supplemented with 2 × 250 ml HDPE bottles. The bottles were primarily new. Used bottles were washed with acid, followed by thorough wash with distilled water. Before collecting the samples, all bottles were washed by vigorously shaking with four consecutive portions of sample water. The bottles were completely filled to reduce gas exchange.

Some of the locations were ice-covered in December to March. The water was collected using a “Ruttner” sampler at 0.5m depth from a drill hole in the ice.

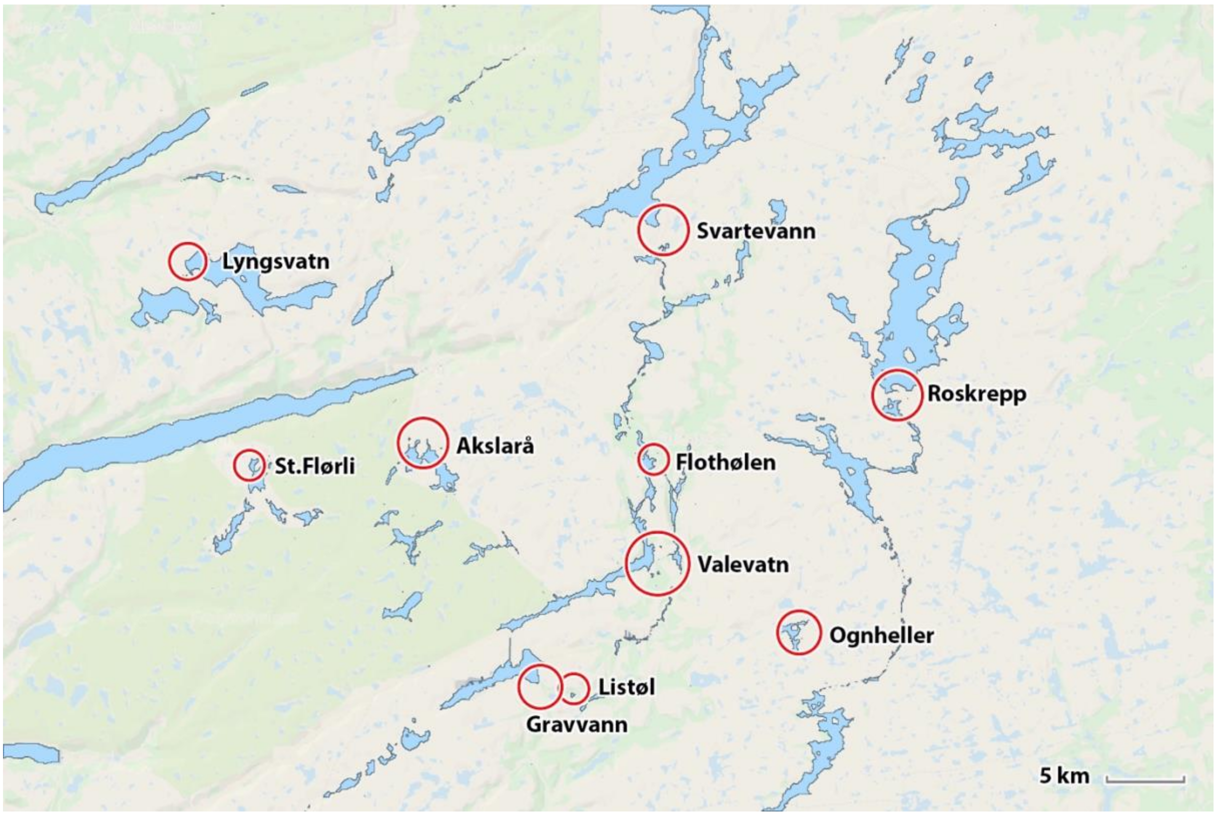

Figure 3.1 Map of study area. The circles include several sampling locations.

3.2 Analytical methods

The water chemistry was characterized by a total of 15 parameters. The nine parameters, temperature, pH, conductivity, colour, alkalinity, calcium, chloride, sodium, magnesium, were determined for all samples, while sulphate, “total cations” and fluoride were measured for 2/3 of the samples. Iron, aluminium, and nitrate were included occasionally. Hardness was measured in 27 samples for quality control purposes, only.

Parameters considered as non-preservable were measured within 48 hours (pH, conductivity, alkalinity and colour). pH was measured immediately after uncapping the bottle to minimise possible CO_2-exchange.

Due to the lack of required instrumentation, frequently used methods (Craft 2005) were not applicable for several parameters. Consequently, rarely used methods were applied, e.g. conductometric titration of sulphate.

3.2.1 pH

pH was measured potentiometrically according to “Standard Methods”, 4500-H+ pH Value (Eaton et al. 1995). A Cole Parmer pH meter equipped with a Radiometer pHC4001 electrode was applied. The instrument was calibrated using standard buffers (pH 4.01 and pH 6.86).

3.2.2 Conductivity

Conductivity was determined according to “Standard Methods” 2510, using a VWR CO310 conductivity meter for field measurements, and an Amber Science instrument for lab measurements. Conductivity is an indirect measure of total ionic content, determined as the electrical current between two inert plates of known geometry. The field and lab instruments were calibrated with solutions of KCl 718 µS/cm and NaCl 210 µS/cm, respectively. The two locations Deg dam and its down-stream location, Jorunnshølen, were equipped with a HOBO U24 Conductivity Logger (U24-001) programmed to record every six hours.

3.2.3 Alkalinity

Alkalinity was determined by titrating the sample with 0.01 N H_2SO_4 (diluted from Merck “Titrisol” 0.1 N). Samples with expected low alkalinity were titrated using 0.0025 N acid. A full titration curve was recorded for each of the samples, and interpolation of the curves yielded the titration volumes corresponding to the applied endpoint of pH = 4.5.

For low alkalinity values, the direct use of this endpoint yields an overestimation of the true equivalence alkalinity (Snoeyink and Jenkins 1980). To adjust for this over-titration, a formula derived by Henriksen (1982) was applied:

$$ALK_E = ALK_{pH=4.5} - 32 + 0{,}646 \cdot \sqrt{ALK_{pH=4{,}5} - 32}$$

(ALK_E is the equivalence alkalinity, $ALK_{pH=4.5}$ is the alkalinity corresponding to an endpoint of pH=4.5, units: µeq/L).

3.2.4 Colour

Colour was determined according to ISO (7887:2011) and expressed in mg Pt/L. The recommended filtration step was omitted due to the low content of particles in the water. Absorption was measured at 410 in 40 mm glass cuvettes using a Shimadzu spectrophotometer (UV-120-01). The result is expressed as mg Pt/L, as first proposed by Hazen (1892). The colour produced by platinum (as K_2PtCl_6) tinted with cobalt chloride is close to the natural yellow-brownish colour produced by humic substances.

3.2.5 Calcium, sodium, chloride

Calcium, sodium and chloride were measured potentiometrically using Radiometer ion-selective electrodes (ISE) according to the manuals (Table 3.1). Combined with a reference electrode, the electrode potentials were measured using a VWR pHenomenal pH1000 H in mV-mode. The uncertainty limit for the analysis of sodium and chloride are 15% and ± 0.1 mg/L for calcium (Espen Enge, pers. com.).

Table 3.1 Experimental set up for determination of calcium, sodium and chloride

Ion	ISE	Reference electrode	Membrane	Sample	ISA	
				mL	mL	Solution
Ca^{2+}	ISE25Ca	Ref201, single junction, saturated with KCl	Polymeric membrane	12.5	0.5	3 M KCl with 12.5 mg/L Ca^{2+} *
Na^{+}	ISE21Na	Ref201, single junction, saturated with KCl	Glass membrane	10	5	7.5% Ethanolamine, adjusted to pH 10 with HNO_3
Cl^{-}	ISE/HS25 Cl	VWR, double junction, 0.1 M KNO_3 outer chamber	Solid state	10	1	1 M KNO_3 0.004 M HNO_3

* added as $CaCl_2$

3.2.6 Total cations

The determination of total cations was based on the ion exchange method described by Vogel (1961). The method recommends H^+ ion exchange, followed by strong base titration, and subsequently adjusting the result for the loss of alkalinity. In this study, a sodium ion exchanger was applied (Amberlite IR120 Na^+), obviating the need for alkalinity adjustments. Sodium was measured potentiometrically (Table 3.1).

3.2.7 Sulphate

Sulphate was determined by conductometric titration with barium acetate, modified after Vogel (1961). The samples were pretreated by Na^+ cation exchange (as described for Σcations) to eliminate interferences from divalent cations. Isopropanol (p.a.) was added to reduce the solubility of the precipitation product (v/v = 2:1). A conductivity titration curve was recorded using a Greisinger GLF 100 RW conductometer. Linear regression was applied to the linear segments of the curve before and after the equivalence point, and the volume was determined by the intercept between the two regression lines (Appendix C)

3.2.8 Magnesium

Magnesium was measured by atomic absorption according to “Standard Methods” (3111 B. Direct Air-Acetylene Flame Method). An atomic absorption spectrophotometer AA-6200 Shimadzu was used to read the absorption.

3.2.9 Aluminium

Aluminium was determined photometrically with Eriochrome Cyanine R according to “Standard Methods” (3500-Al D). The colour was measured with a HACH DR/3 spectrophotometer at 530 nm in 1” cuvettes.

3.2.10 Iron

Samples for determination of iron was collected in separate bottles. Iron in water: The samples were preserved by the addition of H_2SO_4 to a pH of 1.4. Iron was measured photometrically with thiocyanate, after oxidising all iron to ferric state with ceric ammonium sulphate (Goswami and Kalita 1988). The absorbance at 480 nm was measured in 10 mm polystyrene cuvettes, using a UVmini-1240 Shimadzu spectrophotometer.

3.2.11 Fluoride

Fluoride was measured photometrically with SPANDS according to «Standard Methods» (4500-F- D). The principle of the determination is that fluoride bleaches the red colour of the reagent. The absorbance was measured at 570 nm in 10 mm polystyrene cuvettes with a Shimadzu spectrophotometer (UV-120-01).

3.2.12 Hardness

Hardness was determined according to "Standard Methods" (2340 C. EDTA Titrimetric method).

3.2.13 Nitrate

Nitrate was measured photometrically, modified after "Standard methods" (45090 E). For reducing nitrate to nitrite, cadmium was substituted with zinc because of lower environmental toxicity and similar chemical properties. Nitrite was diazotized with sulphanilamide coupled with N-(1-naphtyl)-ethylenediamine dihydrochloride and the colour of the azo dye was measured at 550 nm in 4 cm cuvettes with a Shimadzu spectrophotometer (UV-120-01).

3.3 External data

In addition to water chemistry data from field measurements and sample analysis, several external sources have been used. Meteorological data registered at the stations "Tjørhom" and "Øvre Sirdal" were retrieved from eklima.met.no. Catchment area, average annual runoff and daily measurements of water flowrate from the limnigraph "Jogla" were retrieved from nve.no.

Supplementary water chemistry data were retrieved from Enge (2009). Data of leakage flow rates from the dams, water level in the reservoirs, and design and construction/structural properties of the dams were provided by Sira-Kvina Kraftselskap AS and Lyse Produksjon AS.

3.4 Statistical methods

Paired t-tests were used for analysing significant difference between duplicates and other sets of water chemistry values. Estimated and simulated values were compared with observed values using the paired t-test as well. In addition, simple linear regression analysis followed by a standard t-test of the slope and intercept coefficients were used to test for linear 1:1 relationships of the regression line of these data sets.

Simple and multiple linear regression was also used for analysing significant relationships between variables.

All statistical analysis were performed with Microsoft Excel. For analytes measured to be under the detection limit of the chemical analysis, values half of the detection limit was used in statistical analysis.

3.5 Quality control

3.5.1 Precision and accuracy

Table 3.2 Overview of quality control analysis

Parameter	Internal standard	Precision	Other controls
pH	Dist. water & Merck cert. buffer		
Alkalinity	Na_2CO_3		
Conductivity	KCl	"Duplicates"	
Na^+	Diluted seawater		
Cl^-	Diluted seawater		
Ca^{2+}	Diluted seawater		Hardness
Mg^{2+}	Diluted seawater		Hardness
SO_4^{2-}	Diluted seawater	Duplicates	
F^-		Duplicates	
Total cations		"Duplicates"	

General verification of the methods and instrument performance was controlled using internal standards, certified reference material and measuring duplicates. The pH-meter and its calibration was controlled with an independent buffer within current measuring range (pH =5.00, Merck “CertiPur”, NIST- and PTB-traceable). The normality of the sulphuric acid used in alkalinity determination was verified by titration with sodium carbonate (Merck «CertiPur», NIST-traceable). Furthermore, distilled water was used as an internal standard for 35 pH measurements and the certified sodium carbonate was used to make a synthetic sample (360 μeq/L) for the control of the alkalinity measurements.

Calibration solutions and an internal standard of diluted seawater was included in every test series performed of calcium, sodium, chloride as a control. Each test series consisted of around 60-90 samples in which the calibration solution and the seawater sample was measured between every fifth and 30th sample, respectively. Control charts with the seawater measurements were constructed. Two dilutions of the seawater standard was also applied in the verification of the sulphate analysis (Appendix C) and at the end of the sample series of magnesium. Furthermore, The individual measurements of Ca^{2+} and Mg^{2+} was tested by determining hardness on a random selection of 27 samples.

The conductivity was controlled by using different instruments at two environmental conditions: one in the field and the other in the lab. Temperatures were noted for both conditions and representative data from the measurements was compared with the paired t-test. Additionally, the lab conductivity meter was controlled twice a month with an independent calibration solution (KCl 147 μS/cm).

To test the precision of the analysis, a random selection of samples were used for duplicate measurements of F^- and SO_4^{2-}. The duplicates were controlled by calculating the standard deviation according to “Standard methods” (1030 C.).

Control of the ion exchange pretreatment was performed by running the exchange at 35-40 mL/min, a flowrate ten times faster than the recommended flowrate of 4 mL/min (Vogel 1961). The two treatments samples were compared using the paired t-test.

3.5.2 Evaluation of calcium estimations from historical data

The applicability of older/historical Ca^{2+} data was evaluated/verified by testing the equation derived for Ca^{2+} estimations/determinations (Enge 2009):

$$Ca_{Estimated} = 0.71 \times \text{Hardness} - 0.026 \times \text{Conductivity}^* + 0.03$$

(H^+-corrected conductivity: 1 µeq/L H^+ = 0.35 µS/cm)
(Hardness as mg CaO/L and Ca as mg/L)

Ca^{2+} and Mg^{2+} was not measured separately, but determined as hardness in older data. The equation was derived/formulated for the purpose of converting the older data to Ca^{2+} from the measured hardness and conductivity. The equation is empirical in nature, based on and calibrated for Ca^{2+} values under 1 mg/L. Ca^{2+} in the seepages were estimated to be as high as 35.2 mg/L in 1986. To verify if the equation “accurately” estimates higher values as well, the equation was applied for/to the current data-set and compared with the measured Ca^{2+}.

3.5.3 Correctness of analysis

Calculations of the cation-anion balance was performed using the added sum of the measured anions and total amount of cations determined by the ion-exchange method. The latter omit the need for a separate K^+ measurement. NO_3^- is not included, but is assumed to have a negligible impact on the anion sum due to the general low concentrations previously found in the area (Enge 2009). The cation-anion balance criteria was 0.2 meq/L, according to “Standard Methods” (1030 F.).

The cation sum was also compared to the measured conductivity. According to “Standard Methods” (1030 F.), 100 × Σcations (meq/L) should be within 90-110% of the conductivity value (µS/cm).

3.6 Loss of alkalinity

The original alkalinity "ALK_0" was calculated as the sum of non-marine base cations using the data from direct determination of Σcations. ALK_0 may also be estimated by the sum of non-marine calcium and magnesium ($ALK_0 = 0.91 \times (Ca^* + Mg^*)$) or by the approximation $ALK_0 = 1.21 \times Ca^*$ (Henriksen 1980). The three methods were used and compared. The loss of alkalinity was calculated as the difference between the measured and original alkalinity (ALK_0), with the latter being based on the calculations using then Σcations. The marine ion contributions were estimated using the ions relative ratio to chloride (Cl^-) (Skartveit 1981).

3.7 Simulations

Models were used to evaluate the water chemistry downstream dams with respect to the suitability for brown trout. The leakages from the dams Deg and Svartevatn were used as a case studies. Calculations were made for Jorunnshølen and Grautheller, located 350 m and 1.5 km downstream of the dams, respectively.

The simulations were performed according to Enge and Hemmningen (2010), using flowrate data and mass flux of calcium based on the mass balance:

$$Q_{Total} \times Ca_{Total} = Q_{Leakage} \times Ca_{Leakage} + Q_{Runoff} \times Ca_{Runoff}$$

Since $Q_{Leakage}$ << $Q_{Runnoff}$, the second term of the equation can be simplified to only include Ca_{Runoff} (which is close to constant) in the following equation:

$$Ca_{Total} = \frac{Q_{Leakage} \times Ca_{Leakage}}{Q_{Total}} + Ca_{Runoff}$$

Jorunnshølen has a catchment of 2.91 km$_2$ with an annual average runoff of 125 L/s, while Grautheller has a catchment of 13.92 km$_2$ and 1141 L/s annual runoff (nve.no). To calculate the actual flowrate from the local catchments downstream of the two dams, the daily measurements from the adjacent limnigraph "Jogla" (nve.no) were scaled with respect to the average runoffs from the catchments.

Empirical relations were used to estimate pH from calcium values. The simulated values were compared to observations. Here, data from the 1980s (retrieved from Enge 2009) was included. To achieve comparable periods including all observations, the periods of March 1986-1988 and March 2017-2019 were chosen. The first period represents a period highly affected by acidification, while the latter period represents the most recent data.

The simulations were based on the daily flow while all the other input variables were kept constant in the simulations. The $Q_{Leakage}$, $Ca_{Leakage}$ and Ca_{Runoff} were based on average values from all years with available data and were equal for both periods. The leakage flow from Deg and Svartevatn was calculated to be 3.6±0.9 L/s (n=305) and 2.8 ± 1.0 L/sec (n = 501), respectively (Per-Magne Sinnes, Sira-Kvina, pers.comm.)

A second simulation was performed to estimate a "worst case scenario", lowering the input values in the model to the lowest of the measured values from the simulation-periods.

Figure 3.2 Overview of Deg area.

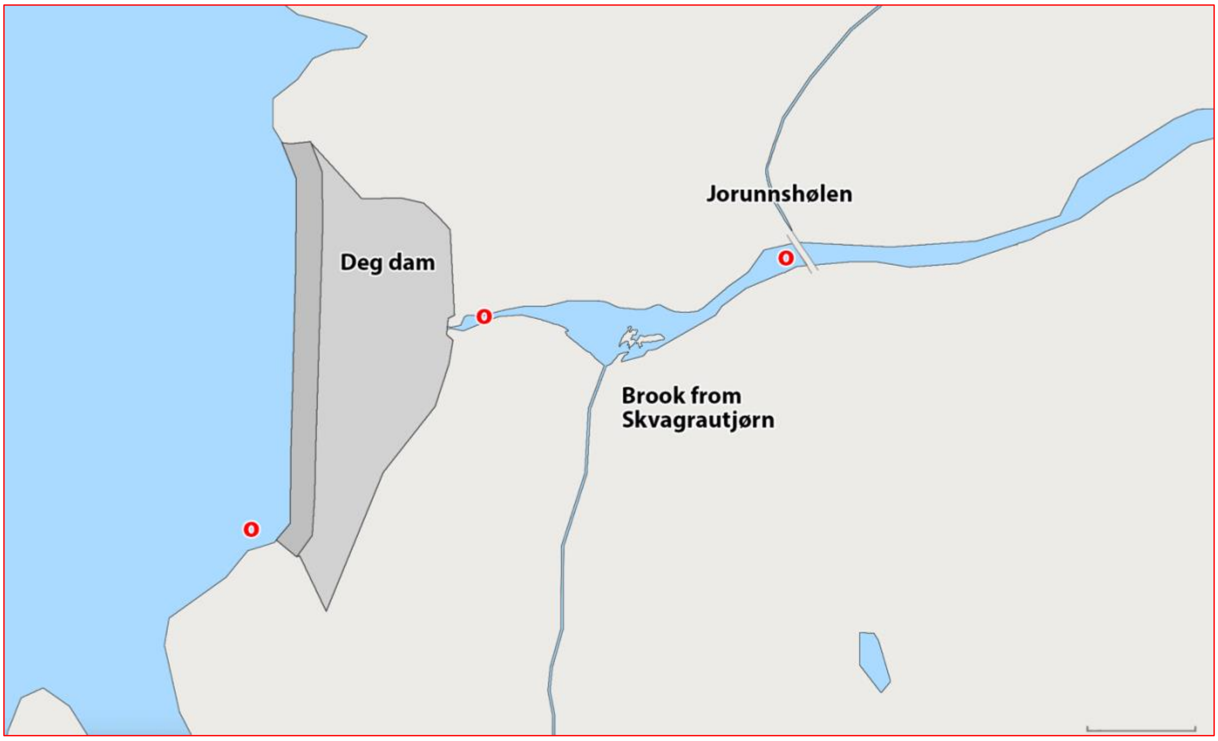

Figure 3.3 Detailed map of sample locations at Deg dam.

Figure 3.4 Detailed map of sample locations at Svartevatn dam.

4 RESULTS

4.1 Quality control

4.1.1 Precision and accuracy

The replicate pH-measurements of distilled water showed high precision (pH = 5.54 ± 0.05, n = 35). The averages of Ca^{2+}, Na^{+}, Mg^{2+}, Cl^{-} and SO_4^{2-} measured in diluted seawater were close to the known concentrations and showed low standard deviations (Table 4.1). All individual control measurements for Ca^{2+}, Cl^{-} and Na^{+} (Figure 4.1) were within the uncertainty limit for each parameter analysis (Chapter 3.2.5)

Table 4.1. Control determinations using diluted seawater as an internal standard

Parameter	Known concentration [mg/L]	n	Average	Standard deviation
Ca^{2+}	0.32	21	0.33	± 0.03
Na^{+}	2.14	24	2.14	± 0.03
Mg^{2+}	0.10	9	0.11	± 0.02
	0.83	3	0.86	± 0.04
Cl^{-}	3.86	25	3.79	± 0.10
SO_4^{2-}	10.8	5	10.6	± 0.2
	5.4	5	5.3	± 0.1

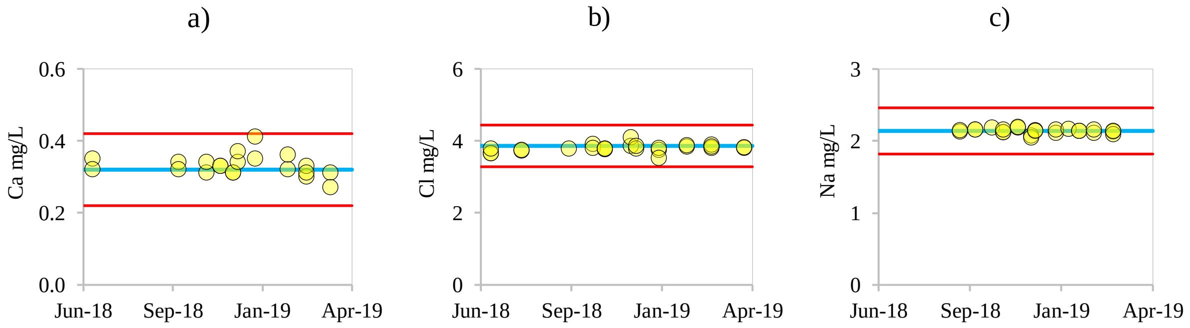

Figure 4.1 Control charts of measured Ca^{2+} (a), Cl^{-} (b), and Na^{+} (c) from samples of diluted seawater marked as yellow dots (included in all measuring series). The blue and red lines representing the theoretical values for each ion and the uncertainty of the analysis, respectively.

The certified sodium carbonate was used to make a synthetic sample (360 µeq/l) for ten replicate measurements of alkalinity. The result showed high precision but was found to give 3.3% higher values (372 ± 3 µeq/l) than the "true" alkalinity (360 µeq/l). The ALK_E approach systematically overestimates alkalinity (Espen Enge, pers com.)

Duplicate measurements of sulphate performed for five random samples in the concentration range 2.65-55 mg/L showed a low standard deviation of ± 0.1 mg/L. Similarly, fluoride showed a low standard deviation, ± 0.03 mg/L (n = 5). Re-measurements of total cations using different flowrates for the ion exchange pretreatment showed no difference ($p < 0.05$, n = 7).

Up to 5 times higher values were found in the field measurements of conductivity compared to the laboratory. The outliers were found in locations with stratification (Chapter 4.5.3). All measurements of conductivity from these locations with apparent outliers excluded in statistical analysis. A significant difference was found ($p < 0.001$, n = 126) between the two measurements. The lab measurements were higher than the field measurements in 88% of the samples. However, only a small deviation was found (0.7 ± 1.2 µS/cm) (Figure 4.2 a)

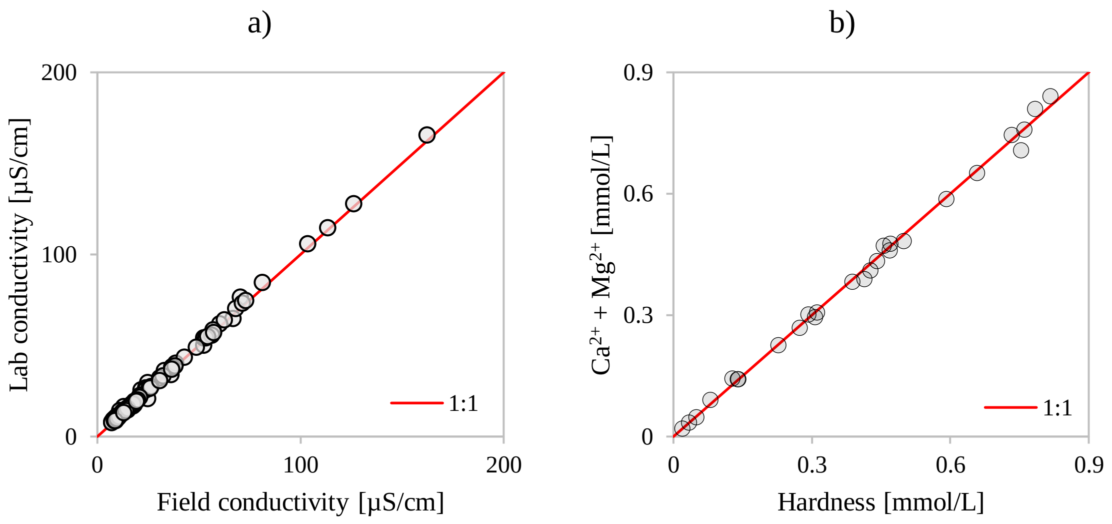

Figure 4.2 Comparison of conductivity measured in the field and in the lab (a). Calculated hardness (the sum of Ca^{2+} and Mg^{2+}) plotted against measured hardness (b).

No difference was found between hardness calculated as the sum of Ca^{2+} and Mg^{2+} and the measured hardness ($p > 0.05$, n = 27) (Figure 4.2 b). Linear regression analysis also showed a high correlation ($r^2 = 0.99$) and a 1:1 regression line with a intercept not different from 0 and a slope not different for 1 ($p > 0.05$).

4.1.2 Evaluation of calcium estimations from historical data

The estimated Ca^{2+}, calculated from the measured hardness and conductivity, correlated highly with the measured Ca^{2+} ($r^2 = 0.99$) (Figure 4.3). However, the estimations were significantly lower than the measured Ca^{2+} ($p < 0.001$, n = 27). The equation underestimated primarily the higher values of Ca^{2+}. The difference increased with increasing values.

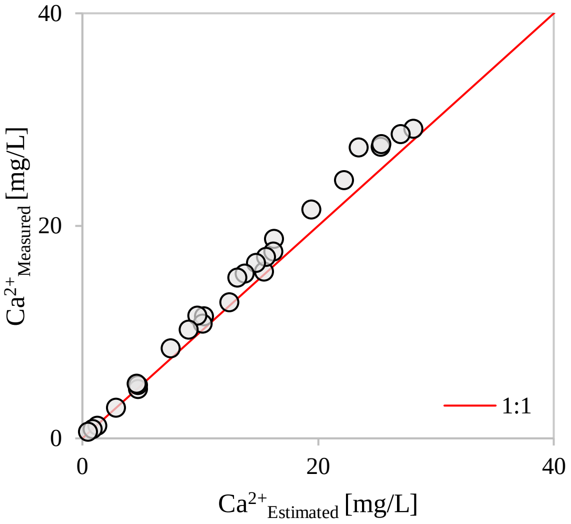

Figure 4.3 Ca^{2+} calculated from measured hardness and conductivity using the equation derived by Enge (2009)(b).

4.1.3 Correctness of analysis

The cation-anion balance was within the acceptable limit of ± 0.2 meq/L for all individual samples (Figure 4.4 a). When checking the total cations with the measured conductivity, 26% of the individual samples deviated slightly from the acceptance criteria (Figure 4.4 b). These deviations were primarily samples with lower cation values compared to conductivity, predominated by locations most extensively affected by acidification.

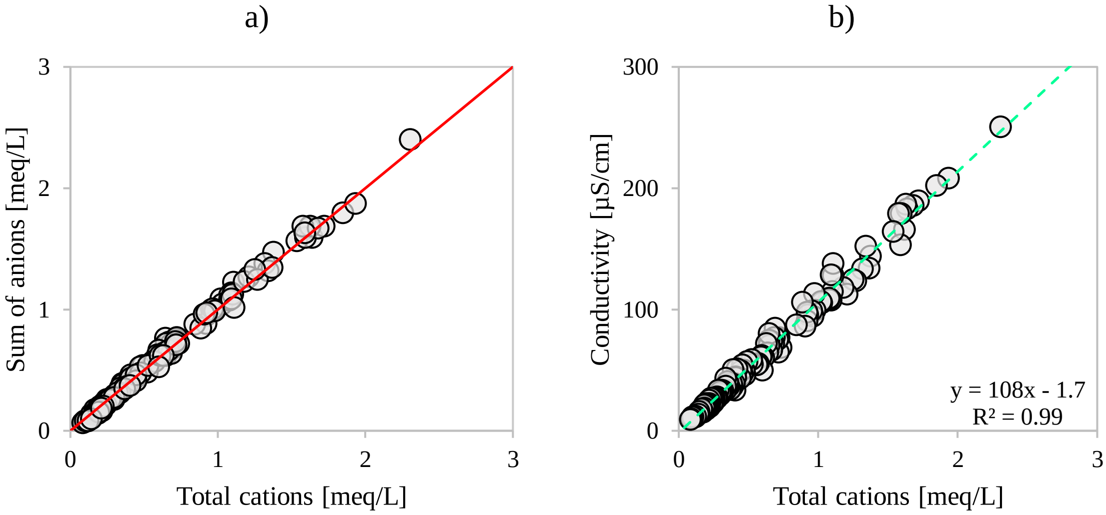

Figure 4.4 The sum of cations (measured as total cations) plotted against the sum of the measured anions (SO_4^{2-}, Cl^-, and alkalinity). The red line represents a 1:1 relationship. (b) Comparison between the total cations and the conductivity, with regression line (green).

4.2 Water Chemistry

The study included 217 water samples (table x) with a total of 2371 chemical analysis. The data material comprised of 44 references, 88 seepages, 72 downstream, and 13 samples of water from lakes with rock dumps (Table 4.2, Appendix B)

The reference samples had an uniform water chemistry; slightly acidic and extremely dilute (pH = 5.64 ± 0.18, Cond = 9.9 ± 1.2 μS/cm, Ca = 0.25 ± 0.14 mg/L, n = 44). Higher values for all parameters were found in the seepage samples compared to the references, except for colour and chloride in a few samples. The alkalinity and calcium concentrations in the seepages were particularly elevated, with average values of approximately 50 times that of the references.

Several relations and variations in the chemistry of the seepage water was observed/noticed. The seepages showed a large range in concentration between the different dams. Most prominent was the high values of SO_4^{2-} observed at two of the dams, Svartevatn and Roskrepp secondary dam. Based on their general cation concentration, these dams had significantly lower alkalinity values than expected.

The seepage concentrations also fluctuated throughout the study-period, at each individual dam. Flothølen, Ripledalen, Gravvann and Tolvkjørheller A showed large ranges in concentrations in particular. General patterns were observed as well. All locations showed generally higher concentrations throughout the summer and a notable decrease in samples collected in the autumn associated with heavy rain.

Additionally, some of the dams had more than one seepage location. Three seepage locations at Tolvkjørheller was observed. Seepage location B and C were particularly higher in concentration compared to location A. Slightly different concentrations were also observed at the two adjacent drainage pipes at Svartevatn collecting water from the left and right side of the dam, respectively. These differences were constant though-out the sample period.

Three of samples deviated from the rest of the samples from the individual dam. These particular samples were collected at a different location than normally, or altered by temporary changes in the environment of the location.

Downstream sites and lakes with rock dumps were sufficiently buffered to sustain pH-values of about 6. However, the latter is a non-homogeneous group, including lakes with Ca-values ranging from 0.33 ± 0.03 mg/L, n = 4 (Ognhellervatn) to 5.0 ± 0.3 mg/L, n = 3 (lake at Kvinen power station). The average values of the downstream samples generally decreased with increasing distance from the dams and the rockfill dumps.

Table 4.2 The average water chemistry at each sampling location, grouped by area. Parameters not measured on all samples: in brackets.

Area	**Sample location**	**Type**	**n**	**pH**	**Cond. µS/cm**	**Colour mg Pt/l**	**ALKe µeq/L**	**Ca^{2+} mg/L**	**Na^{+} mg/L**	**Mg^{2+} mg/L**	**Cl^{-} mg/L**	**SO$_4^{2-}$ mg/L**	**Tot-cat. mgNa/L**	**F^{-} mg/L**	**NO$_3^{-}$ mgN/L**	**Fe^{2+} mg/L**	**Al µg/L**
Akslarå	Reservoir	Ref.	3	5.74	10.6	4	7	0.20	1.2	0.14	2.0	(0.67)	(2.8)	(<0.05)			
	Dam	Leak.	3	7.59	110	4	755	18.0	1.4	0.68	2.6	12.0	24.1	0.21		(0.24)	(5)
	Small brook	Ref.	4	5.63	8.7	8	8	0.22	0.94	0.09	1.2						(28)
	Pond outlet	Down.	4	6.08	10.2	7	19	0.35	1.1	0.14	1.7						(27)
Svartevann	Reservoir	Ref.	9	5.64	10.0	5	6	0.24	1.1	0.13	1.7	(0.75)	(2.2)	(0.03)			(24)
	Dam	Leak.	15	7.32	167	13	441	23.6	2.6	1.5	1.9	48.5	34.3	0.67		0.22	(5)
	Godfarlonene	Ref.	8	5.70	8.3	16	11	0.25	0.84	0.12	1.3	(0.80)		(<0.05)			
	Grautheller innlet	Down.	9	5.99	11.0	16	18	0.56	0.88	0.13	1.4						(48)
Roskrepp	Reservoir	Ref.	3	6.01	10.1	14	23	0.5	0.81	(0.10)	1.2	(0.8)	(2.1)	(<0.05)			
	Dam main	Leak.	5	7.32	67.0	9	276	9.9	1.2	0.38	1.4	11.7	13.5	1.0			
	Dam sec.	Leak.	3	6.10	106	10	75	13.1	1.3	1.4	1.3	35.1	20.6	1.6			
	Håheller innlet	Down.	3	6.88	31.9	23	130	3.9	0.95	0.23	1.4	4.7	6.9	0.39			
Gravvann	Reservoir	Ref.	8	5.49	11.1	11	4	0.20	1.2	0.16	1.9	(0.87)	(2.7)	(<0.05)			
	Dam	Leak.	8	7.02	53.4	53	320	7.0	1.8	0.56	2.4	7.2	11.9	0.06			
	Sandvann innlet	Down.	8	5.43	14.8	59	15	0.47	1.5	0.23	2.1						
	Sandvann outlet	Down.	8	5.70	13.8	38	13	0.33	1.5	0.21	2.3						

Table 4.1 Continued

Area	Sample location	Type	n	pH	Cond. µS/cm	Colour mg Pt/l	ALKe µq/L	Ca^{2+} mg/L	Na^{+} mg/L	Mg^{2+} mg/L	Cl^{-} mg/L	SO_4^{2-} mg/L	Tot-cat mgNa/L	F^{-} mg/L	NO_3^{-} mgN/L	Fe^{2+} mg/L	Al µg/L
Valevatn	Reservoir	Ref.	9	5.57	10.2	13	7	0.25	1.1	0.12	1.7	(0.87)	(2.3)	(<0.05)			(41)
	Deg dam	Leak.	3	7.34	94.1	9	704	15.2	1.8	0.96	2.9	6.3	19.9	0.51			
	Deg	Down.	11	6.69	39.1	55	256	5.1	1.7	0.44	2.2	3.7	9.0	0.10	(0.15)	(0.59)	
	Jorunnshølen	Down.	13	6.16	22.1	64	90	1.9	1.6	0.30	2.2	3.0	5.4	0.07	(0.04)	(0.39)	(94)
	Skvagrautjørn	Down.	12	5.19	16.3	61	4	0.42	1.5	0.22	2.2	(3.1)	(4.4)	(0.04)	(0.04)	(0.37)	(110)
	Tolvkjørheller A	Leak.	9	7.29	68.4	39	555	10.9	1.8	0.5	2.3	4.4	15.6	0.14			(12)
	Tolvkjørheller B	Leak.	10	7.38	100	8	871	16.6	1.6	0.67	2.6	4.1	22.9	0.19		(0.23)	(4)
	Tolvkjørheller C	Leak.	11	7.38	107	23	945	17.9	1.8	0.84	2.5	4.2	25.0	0.20		(4.1)	(5)
	Flothøl dam	Leak.	9	6.65	29.0	36	152	3.2	1.4	0.25	1.8	3.2	6.5	<0.05			(30)
	Ripledal dam	Leak.	9	6.94	36.6	28	240	4.7	1.7	0.25	2.4	2.4	8.4	0.13			(14)
Ognheller	Lake Kvinen ps.	Dump.	3	6.99	37.0	48	211	4.9	1.0	0.32	1.6	4.5	8.0	0.34			(33)
	Ognheller innlet	Down.	4	5.41	8.8	15	2	0.17	0.87	0.08	1.4	(0.82)	(1.9)	(0.03)			(59)
	Ognheller	Dump.	4	5.60	10.0	29	13	0.33	0.97	0.11	1.5	(1)	(2.3)	(<0.05)			(58)
Listøl	Lake Listøl	Dump.	6	6.16	18.6	38	50	1.0	1.6	0.26	2.3	2	4.3	<0.05			(66)
Dam St.Flørli	Dam	Leak.	1	6.04	24.6	2	63	1.2	2.4	0.47	3.6	2	5.0	<0.05			
Lyngsvatn	Dam north	Leak.	1	6.48	21.9	22	72	1.8	1.7	0.24	2.1	2	5.0	<0.05			
	Dam south	Leak.	1	6.40	20.6	16	51	1.7	1.4	0.23	2.0	3	4.9	<0.05			

High concentrations of non-marine sodium were observed in the seepages, while the downstream locations and references had considerable lower concentrations (Figure 4.5)

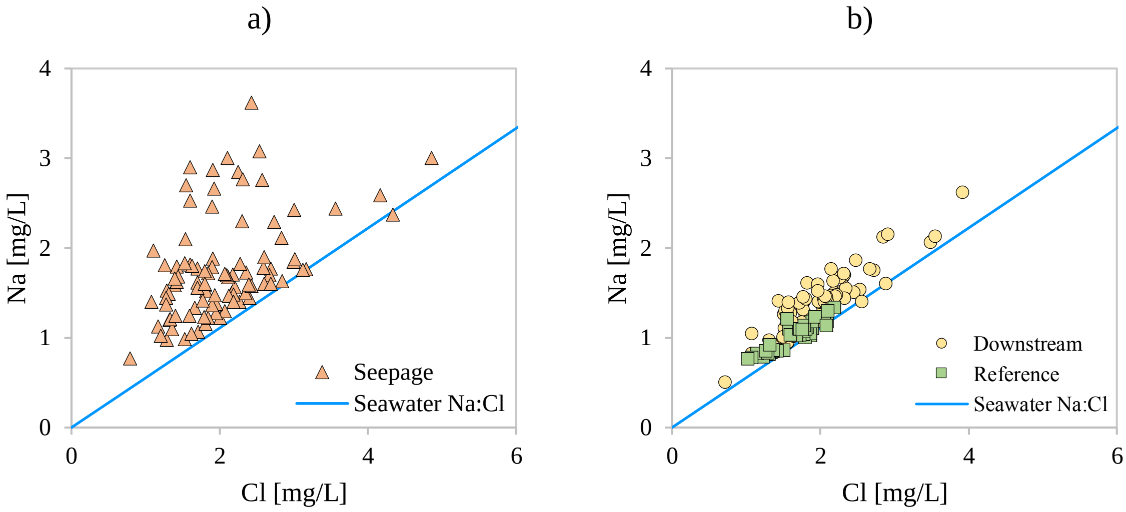

Figure 4.5 Measured sodium versus chloride. The blue line representing the ratio between sodium and chloride in seawater.

Aluminium was found to be generally low in the seepages. Except for Flothølen (Al = 30 µg/L), all seepages had aluminium values below 15 µg/L. The highest aluminium values were measured at low pH and high colour values. Multiple linear regression (r_2 = 0.92, n = 18) showed that aluminium was positively correlated to colour ($p < 0.001$) and negatively correlated to pH ($p < 0.001$) (Figure 4.6).

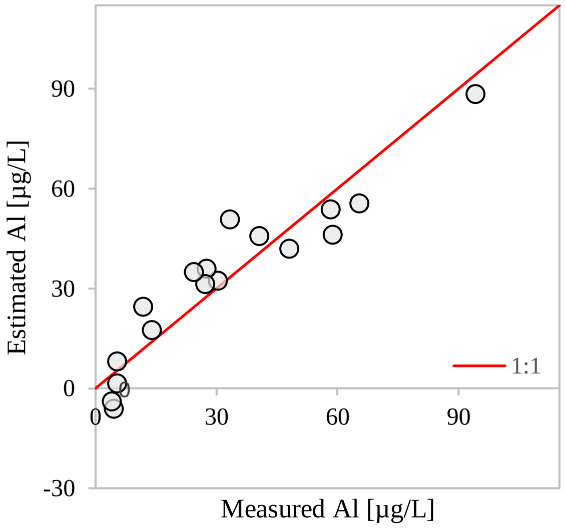

Figure 4.6. Relation between measured aluminium and estimated aluminium from colour and pH values ($Al_{estimated}$ = 131 + 0.92 x colour – 18 x pH) . Aluminium concentrations increased with increasing colour (a) and with decreasing pH (b).

Except for one sample at Tolvkjørheller C, the concentrations of iron were below 1 mg/L (n = 13). The referred sample had an iron concentration of 4.05 mg/L and was collected in January.

4.3 ACIDIFICATION

Three methods for estimating ALK_0 were compared. No difference was detected between ALK_0 determined as sum of non-marine cations and as 1.21 × non-marine Ca ($p > 0.05$, $n = 135$), (Figure 4.8a). The third method, estimating ALK_0 using the formula $ALK_0 = 0.91 \times (Ca^* + Mg^*)$, showed lower values ($p < 0.001$) than the two other methods (Figure 4.7).

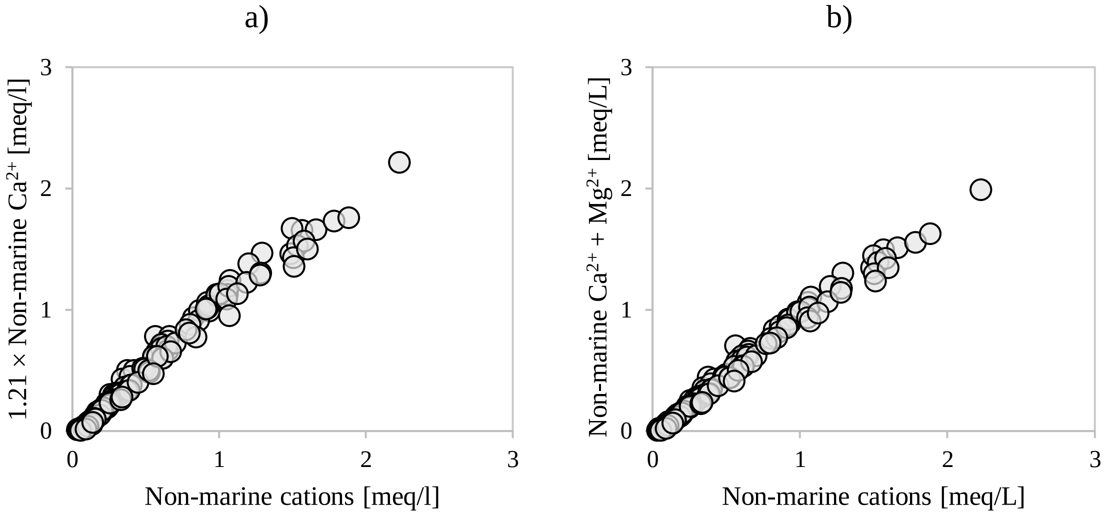

Figure 4.7 Comparison of three methods of estimating ALK_0. There was no difference between non-marine cations and 1.21× non-marine Ca (a). The sum of non-marine Ca and Mg was showed distinct lower and significantly different from the other two methods of determining ALK_0 (b).

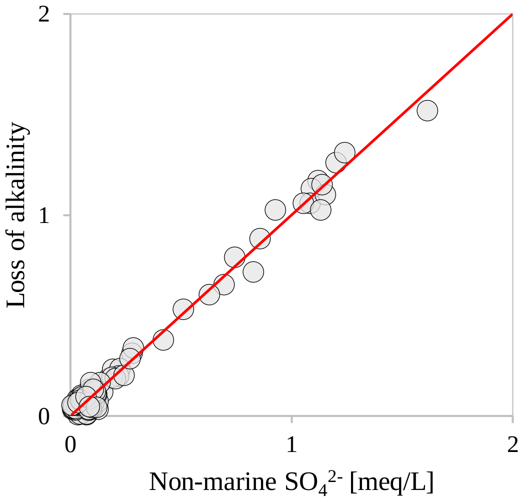

Figure 4.8 A 1:1 relation between non-marine sulphate and loss of alkalinity was found.

No difference was detected between the loss of alkalinity and the non-marine sulphate ($p > 0.05$) (Figure 4.8) . Furthermore, regression analysis revealed a high correlation ($r^2 = 0.99$, $p > 0.001$, $n = 135$), with a slope and intercept of the regression line not different from 1 ($p > 0.05$) and 0 ($p > 0.05$), respectively. The 1:1 relationship suggesting that the acid causing the loss of alkalinity was sulphuric acid.

Considerable differences in alkalinity and alkalinity loss were found between the dams (Figure 4.9). Regression analysis showed that non-marine total cations increased with increasing sulphate ($r_2 = 0.58$, $p < 0.001$, $n = 88$), suggesting that the acid induces the mobilization of cations. The overall contribution from weathering of dam material exceeded the acidification. The remaining alkalinity was sufficient to sustain a pH > 6.5 in 77 of the 88 samples from the dam.

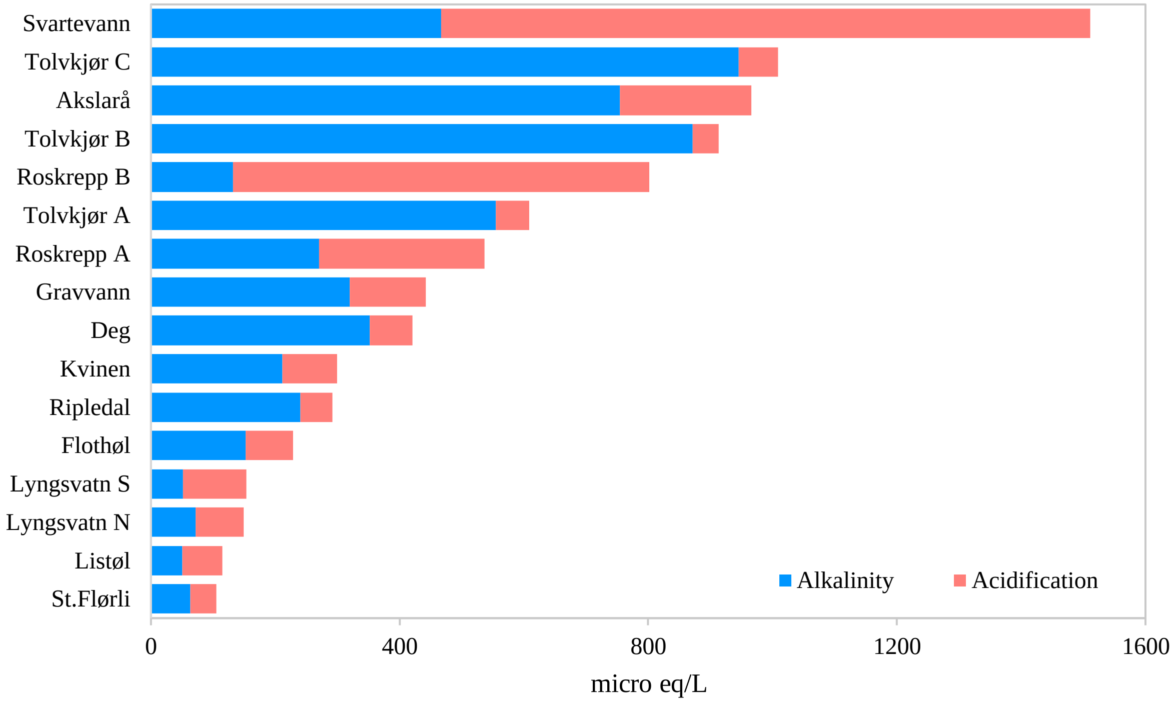

Figure 4.9 Considerable differences in alkalinity were detected. The figure shows the original alkalinity (ALK_0) as sum of measured alkalinity and the calculated alkalinity loss.

4.4 Simulations

4.4.1 Quality of model

Statistical analysis showed no significant difference between the simulated and observed values ($p > 0.05$), with the exception of two of the simulations at Jorunnshølen ($p < 0.05$) (Table 4.3).

Low precision was observed for the simulation at Jorunnshølen 1986-1988. Four of the observations were particularly elevated, being 9.8 to 21.2 mg/L higher in observed Ca than the simulated Ca.

While there were limited deviation from August to November in the simulation of Jorunnshølen 2017-2019, a larger deviation was observed the rest of the year. These large differences were primarily cases of sharp climbs and drops in the simulated Ca.

Table 4.3 Statistical analysis of the model, comparing simulated and observed values of Ca and pH

Location	Period	n	Diff. Ca [mg/L](1)		Diff. pH*	
			average	p	average	p
Jorunnshølen	1986-1988	9	-5.8 ± 9.1	n.s.	-0.65 ± 0.81	< 0.05
	2017-2019	13	1.3 ± 2.0	< 0.05	0.16 ± 0.70	n.s.
Grautheller	1986-1988	12	0.02 ± 0.79	n.s.	0.05 ± 0.26	n.s.
	2017-2019	9	0.84 ± 2.40	n.s.	0.09 ± 0.28	n.s.

(1) Difference = Simulated value minus observed value

4.4.2 Simulation results

The simulation at Jorunnshølen showed a pH increase of about 0.3 units from the period of 1986-1988 to 2017-2019. The fraction of pH-values < 5.5 were 24% and 14%, respectively, with only negligible differences between the minimum values (Table 4.4)

For Grautheller, the simulations showed a large increase in pH between the two time periods (± 0.7 unit difference). Furthermore, the minimum pH value during 2017-2019 were 0.8 units higher than during 1986-1988. While none of the simulated values were below 5.5 during 2017-2019, 67% were below 5.5 and 14% were below 5.0 during 1986-1988.

The simulated pH in Jorunnshølen was generally higher with larger variations than Grautheller (Figure 4.10). While the Ca was also highest at Jorunnshølen, the standard deviation/variation was generally large for all simulations. Furthermore, both locations had negligible difference in average Ca between the two simulation periods.

Table 4.4 Results from the simulations of water chemistry at Jorunnshølen and Grautheller downstream the dams Deg and Svartevatn, respectively (n = 732).

			pH		Ca [mg/l]	
Location	Period	Flow [l/s]	average	min.	average	min.
Jorunnshølen	1986-1988	103	5.98 ± 0.53	5.13	2.87 ± 2.69	0.34
	2017-2019	113	6.25 ± 0.67	5.16	2.77 ± 2.85	0.33
Grautheller	1986-1988	935	5.34 ± 0.36	4.96	0.84 ± 0.69	0.31
	2017-2019	1030	6.07 ± 0.31	5.76	0.90 ± 1.19	0.30

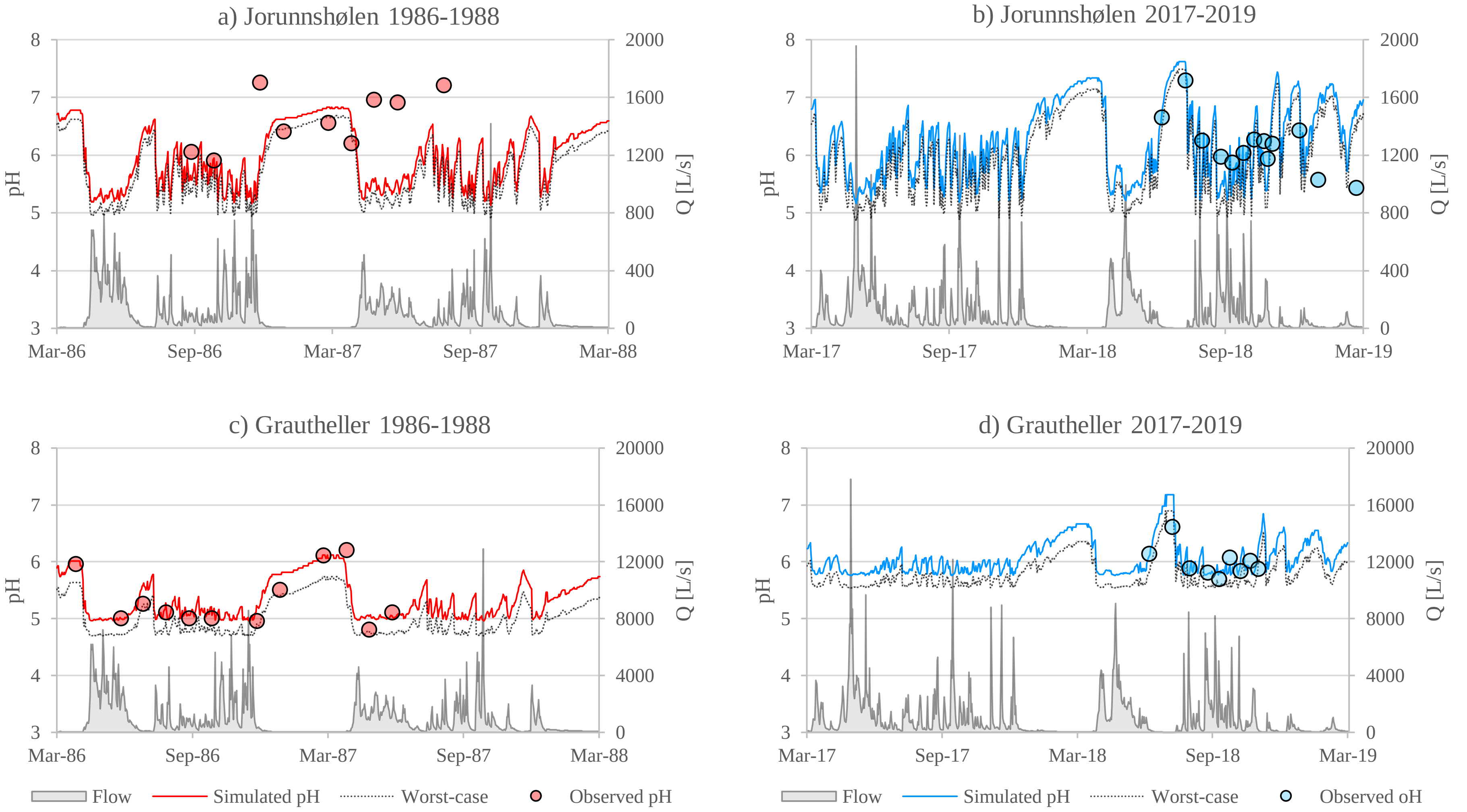

Figure 4.10. Comparative plot of Simulated and observed pH at Jorunnshølen (a&b) and Grautheller (c&d). The pH is shown as lines (simulated) and dots (observed) with red and blue colours representing data from 1986-88 and 2017-19, respectively. The grey lines represent a worst case scenario of the pH. The area graph represents the flowrate from Jogla dilated according to each location.

4.5 Other observations

4.5.1 Logger

Conductivity and temperature was measured by a logger placed at Jorunnshølen and inside of the Deg dam, between November and May (Figure 4.11)

At Jorunnshølen, the logger showed steep declines in conductivity during flow peaks followed by a slow increase. Large temporal variations/fluctuations in temperature was registered/found starting in April.

The logger at Deg showed a more stable conductivity and temperature from November to the end of January. The declines registered during flow peaks were less pronounced with rapid recovery. From February, the logger revealed large changes in the conductivity (ranging from 65 to 125 µS/cm) of the seepage water, which did not appear to follow the flow pattern.

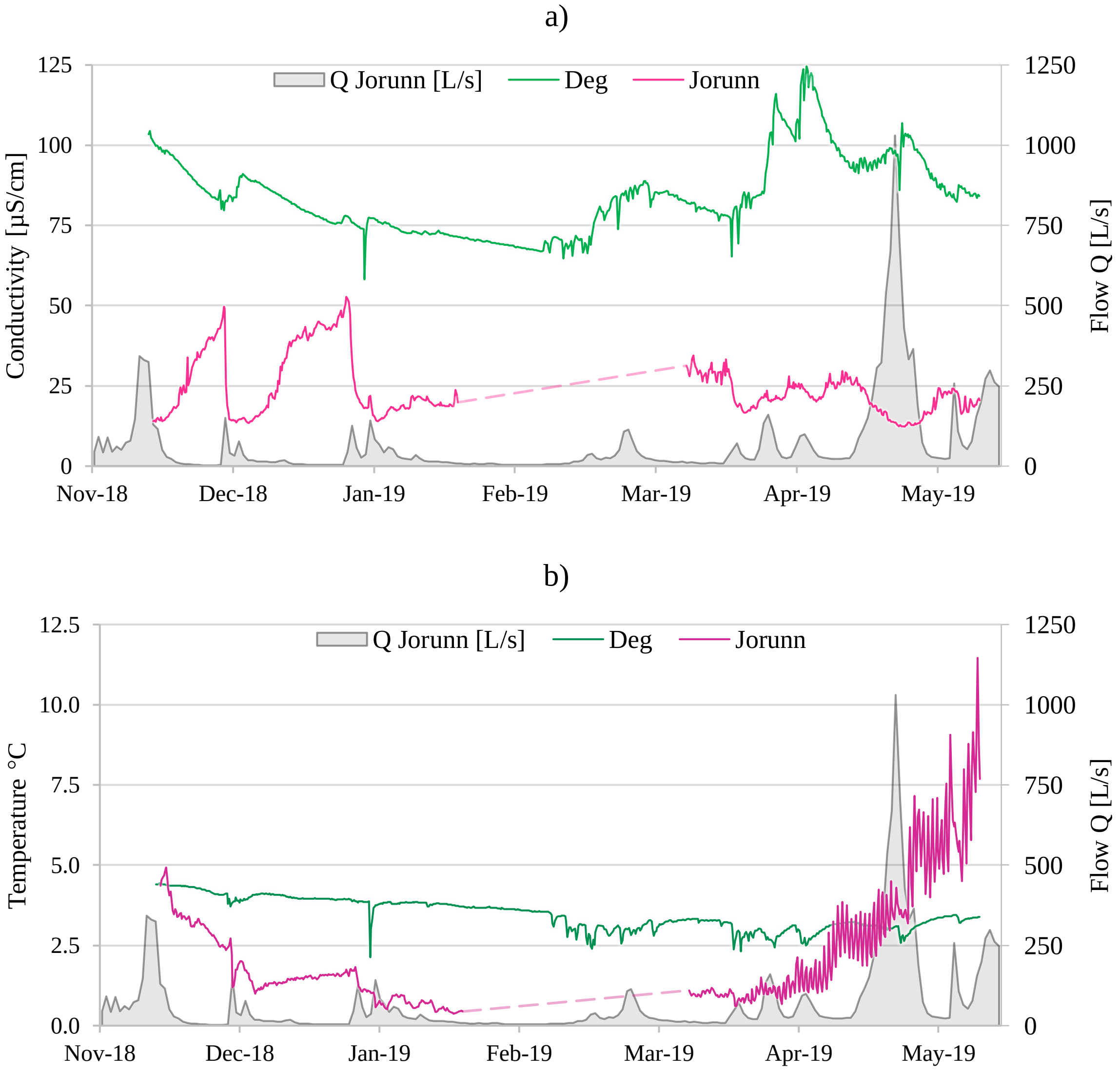

Figure 4.11 Measurements of conductivity (a) and temperature (b) at Deg and Jorunnshølen marked with green and purple, respectively (stippled line: no measurements). The grey area represents the flowrate from Jogla dilated according to/in respect to the catchment at Jorunnshølen.

4.5.2 Leakage flowrate

The seepage flow was highly correlated with the water level of the reservoir at all the dams (Table 4.5) and negative correlations with time were found at Svartevann and Roskrepp secondary dam. Additionally, the flowrates at the two Roskrepp dams were significantly correlated with the flowrate registered at Jogla.

Table 4.5 Regression analysis of leakage flowrate against time, water level of the reservoir and flowrate at Jogla.

	Variables		
Dam	time	Water level	Q Jogla
Svartevatn dam	< 0.001	< 0.001	n.s.
Deg dam	n.s.	< 0.001	n.s.
Roskrepp main dam	n.s.	< 0.001	< 0.001
Roskrepp sec. dam	< 0.05	< 0.001	< 0.05

4.5.3 Stratification

A notable increase in conductivity and temperature with depth was observed at three of the sampling locations (Deg, Tolvkjørheller B and C) (Figure 4.12). The field determinations were performed at somewhat deeper levels than the lab measurements of the water samples collected at the surface.

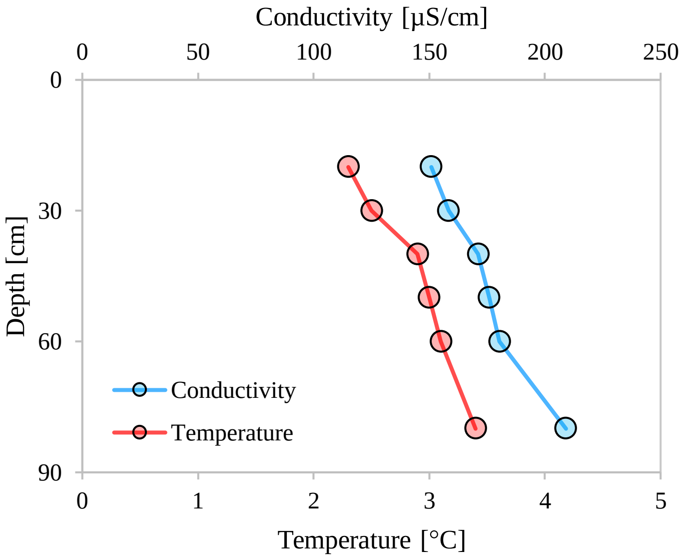

Figure 4.12 Field measurements of conductivity and temperature at Tolkjørheller B (20.november) recorded at different depths

5 DISCUSSION

5.1 Water chemistry

This study established that the surveyed dams and rock dumps had a net buffering effect on adjacent waters and suggest that this effect has saved trout populations from acidification.

The slow weathering bedrock in the area normally leads to a highly dilute water chemistry with low levels of calcium. In Rogaland County, lakes located at an altitude of > 500 m a.s.l. showed a median calcium value of 0.23 mg/L (Enge, 2013), fairly equal to the average calcium of the reservoirs (0.25 mg/L). The long residence time of the reservoir water reduces the variation in water chemistry over the year as well as between years. Thus, the water represents a mix of water chemistries over several years. This is apparent in the results which show a uniform, stable and extremely dilute water chemistry in all the reservoirs and is consistent with previous observations (Enge, 2015, 2017, 2018).

The dam leakages, exposed to the same geology as the reservoirs, showed an average Ca^{2+} of 12.9 mg/L. Rock dumps also showed higher Ca^{2+}-values than the references. This effect is assumed to be a result of enhanced weathering rates. Particle breaking and fracturing of the rocks increase the surface area and expose fresh mineral surfaces to air and water (Price, 2009).

Water infiltrates and flows through the foundation beneath the dam or abutments at the end of the dam, or through the structure. The leakage or seepage is generally a result of the hydraulic head pressure and the permeability of the structure and foundation (Craft, 2005). The significant effect of the pressure exerted by the water level of the reservoir was found on the leakage flow rate (Table 4.5). The permeability depends on the geology and associated porosity. The path of the water depends on the permeability and pressure as well. The flow of the water may be diffuse, direct and confined, or more circuitous and meandering with corresponding transit times. The terms “leakage” and “seepage” take on different meanings and are differentiable by these factors and variables (Contreras and Hernádez, 2010). However, distinguishing between the two terms requires more detailed data. Therefore, the general term "seepage" is consequently used in this study.

Slightly higher values of Cl^- were found in the leakage compared to the reservoir samples. Due to mixing of the water caused by the regulating of the reservoir, the reservoir water is close to homogenous (Enge, 2015, 2017, 2018). Samples collected at the surface in the reservoirs can be assumed to reflect the chemistry at all depths, the increase in Cl^- cannot be explained by stratification of the reservoir water. Since Cl^- is not commonly found in the mineral composition of the bedrock in the area, the increase is not a result of weathering. Varying concentrations and high colour value suggest that the leakage water is mixed with foreign water from downstream of the dam. The leakages at Flothølen, Ripledalen and Gravvann appeared to be particularly affected by foreign water, evident by the range of the fluctuations of colour and chloride throughout the sampling period. These locations have a comparatively large catchment downstream the dam. This mixing of waters also dilutes the liming effect of the leakages.

Although an inverse relationship has been found between colour and marine-salts (Hindar and Enge, 2006), no such correlation was found in the current study. This can be explained by the narrow measuring range of Cl^-.

Eight high alkalinity samples were reanalysed for Cl^- using a ISA-solution five times higher in $[H^+]$. These measurements were, on average, 1.8 ± 0.4 mg/L lower in Cl^- than the initial analysis. The largest differences were observed for the highest alkalinities. This indicates that the original ISA-solution was not sufficient to neutralize the alkalinity in the samples with the highest alkalinity. Cl^- had a limited contribution to the overall ion sum. Therefore, none of the established relationships were affected by replacing these eight original values.

Titration of 10 samples of 360 μeq/L showed a 3.3% overestimation of alkalinity. This overestimation is expected when using the ALK_E approach (Neal, 1988). Although the method introduces a positive bias, the difference is small and is assumed to have negligible effect on the overall result.

The quality control showed high precision and accuracy for the other methods. The slightly higher conductivity values measured in the lab compared to the field (+ 0.7 ± 1.2) can be explained by the differences in temperature at measurement. All ions have their own respective temperature coefficients (McCleskey et al,. 2012) which the various instrument brands handle in different ways (McCleskey et al., 2012). The uncertainty introduced by the temperature correction is the most likely cause to this difference, and can be reduced by measuring samples at the same temperature. Therefore, the lab measurements have been used in further calculations.

The quality criteria based on the sum of cation and conductivity is based on empirical relations. Samples deviating from the acceptance criteria for the ratio of cation sum and conductivity can be explained by different ionic and chemical composition of the samples. The contribution to the overall conductivity of an ion is relative to its concentration and ionic molar conductivity (McCleskey et al., 2012), which is not accounted for in the acceptance criteria. The equivalent conductance of HCO_3^- and SO_4^{2-} is 44.5 and 80.0 μS/cm per meq/L, respectively. Consequently, a sample being acidified, e.g., by substitution of HCO_3^- with sulphate, will experience an increase in conductivity.

The deviations from the criteria were primarily seen in the leakage samples from the Roskrepp dams and Svartevann (the most northern dams), the three locations with the highest measured SO_4^{2-}. These locations were observed to have a considerably low alkalinities compared to their cation values. The leakage water at Roskrepp B was estimated to have lost as much as 90.1% of its alkalinity. Sulphuric acid, concluded to be the cause of this alkalinity loss, most likely originates from pyrite. This mineral can be found in both gneiss and granite and is the most abundant of the sulphide minerals. Furthermore, positive detection of chalcopyrite has been reported at Roskrepp (Urdal, 2018). Iron was not observed due to the insolubility of the iron(III)-compounds formed in the oxidation processes.

Estimations of the original alkalinity and acidification (ALK_0 and ALK_{loss}) was calculated from the non-marine cations. The equation calculating the original alkalinity as 1.21 × Ca* was included for comparability with a large study from the area (Enge, 2013). Although this is a simpler equation, the estimation was found to be a better fit than the more advanced formula 0.91 × (Ca*+Mg*). The estimates of the original alkalinity assumes that the cations concentrations do not change in response to acidification.

The positive correlation found between sulphate and non-marine cations suggests that sulphuric acid has accelerated the mobilization of cations. Acid increases the rate of chemical weathering, even for slow weathering rocks such as granite (Webb, 1980). Relatively high concentrations of cations were found even at low sulphate levels as well, suggesting that the presence of sulfuric acid is not a critical factor in the observed weathering.

Differences in water chemistry enrichment between the dams, such as the increase in cation concentrations, depend on factors such as geology, size and geometry of the dams. These factors indirectly determine the pathway and consequently the residence time of the water.

The three separate leakages from the Tolvkjørheller dam differed in the concentration. The leakage associated with the longest base width had twice the alkalinity than the leakage with the shortest width. The same trend was observed after calculating the non-marine concentrations, confirming/indicating that dilution from other water sources was not the cause. The longer pathways can be assumed to have a longer residence time, contact time and overall increase in rock surfaces. At Svartevatn, the two pipes were also found to have slightly different chemistries. Identifying a possible cause for this difference would require more detailed data from the dam construction and is beyond the scope of this study.

The substantial differences in acid production detected between the dams does not entirely depend on the presence and availability of sulphides in the dam material. Since sulphide minerals such as pyrite oxidize rapidly (Eby, 2004), the difference may also be linked to the age of the dam. A gradual decrease in acidity has been observed after the construction of Corin dam in Australia, which contains about 1% pyrite (Fell et al. 2014). Except for the Flørli dam, all dams in our study were built throughout the same period, about 50 years ago, indicating that ageing does not explain the differences in acidity between the dams. Considering that the acidification at Roskrepp B was measured to be critically close to exceeding the alkalinity, the leakage could potentially have been acidic the first years after construction like Corin dam. However, the acidification from all dams in this study appear to have been neutralized since construction, with the excess alkalinity buffering the water downstream. This is evident in historical data regarding the chemistry and surviving fish populations through the acidification period (Sevaldrud and Muniz, 1980).

5.2 Simulations

Although the seepage rates are approximately equal, Jorunnshølen showed a higher pH and Ca values compared to Grautheller, as well as larger variations in water chemistry. This variation is primarily a result of the size and nature of the downstream catchment. Grautheller inlet covers an area nearly 5 times larger than Jorunnshølen, and consequently has an average runoff flowrate almost 10 times larger. This leads to a greater stability in terms of the water chemistry at Grautheller inlet and larger variations in pH and Ca at Jorunnshølen.

Except for the catchment runoff flow, the input variables in the simulations were kept constant. The constant Ca_{Runoff} entails a limitation in the simulation by fixing the background concentration of Ca and consequently predefine a lower level for the simulated pH. The leakage flowrate varies and the conductivity logger revealed fluctuations in the conductivity, which is highly correlated with Ca (Enge et al., 2016). To check the effects of these variations, the input values were changed to the lowest measured values. However, the simulated "worst case scenario" is relatively improbable. Considering the inverse relation between calcium concentration and flowrate, it is highly unlikely that the input variables would be simultaneously low.

The method for estimating Ca based on hardness and conductivity used by Enge (2009) showed good precision and accuracy in the measuring range < 1 mg/L, but slightly higher values in the more concentrated samples with hardness above this range. The deviation was overall relatively small, but could mean that the simulated Ca values in 1986-1988 were underestimated.

In general, the model/simulation is subject to uncertainties associated with temporal and spatial differences of the catchments. At higher elevations, the snow accumulates earlier in the year followed by a later snowmelt. While the catchment area at Jorunnshølen reaches an altitude of 842 m a.s.l., the limnigraph at Jogla drains a larger catchment area which/and covers altitudes between 600-1208 m a.s.l. This furthers the differences in the hydrological regimes between the two catchments areas. In addition, the size and nature of the surface lead to some differences in catchment dynamics and consequently response-time and retention of the peak discharge.

This also includes the water storage and discharge from the mixing sites; in this case, Jorunnshølen and Grautheller. The model simulates the mixing of water chemistries only and does not take into account the levelling effect, caused by an eventual water volume. These factors may explain some of the differences between observed and simulated pH which appear to be temporally deviated by ± 1-2 days during rapid increases and decreases in runoff. Accounting for temporal variability allows for close alignment between simulated and observed pH values.

Some uncertainties are specifically associated with the 1986-1988 simulations. The lack of exact dates registered for the observations may account for some of the difference between the simulated and observed values in the 1986-1988 simulations. These samples were catalogued using month and year. For this reason, all observations were assigned/given the 15th of its reported month for a full date when listing the values in the simulation.

Between the two simulation periods, 1986-1988 and 2017-2019, the water level and subsequently the water volume at Jorunnshølen has been altered by a weir at the sampling location 350 meters downstream of the dam. The levelling effect associated with retained water volume and has resulted in a more stable water chemistry relative to that of the simulation of Jorunnshølen in 2017-2019. In contrast, Jorunnshølen was not dammed by this weir prior to 1988. During the summer and winter or other "dry" periods, the water at Jorunnshølen would primarily consist of leakage water from the dam and would result in higher peak values in pH. This is a possible reason for the considerably high values of Ca and pH observed during 1986-1988. However, the effect of this is negligible for the overall water quality at Fidjeland. Relatively large differences between the simulation and observation at Jorunnshølen in 2017-2019 during summer and winter as well. During the field surveying/measurements in these periods, stratification at Deg and Jorunnshølen was observed. Sampling done at the surface of such waters is not representative of the overall chemistry and may cause discrepancies between the observations and simulations.

Considerations can be made in regards to the water volumes or the temporal and spatial differences between the fields. However, a more advanced hydrological model would be required to capture the catchment dynamics and is beyond the scope of this research.

Higher precision and accuracy might be achieved by the use of conductivity-loggers in both the dam leakage and in the sidestream-river. This would lower the uncertainty associated with the constant input values and more frequent recordings of the leakage flowrate. However, the model was developed with applicability for historical events with less hydrological and chemical data. Additional instruments and data would be unnecessary in this case. As such, the model provides reasonable approximation, requires few input data and is fit for its purpose.

Due to an almost steady leakage rate from the dams, and a highly variable flowrate from the Skvagrau and Godfarlonene catchments, the mixing ratio ranged from 0.2% - 86% and 0.02% - 35% leakage water at Jorunnshølen and Grautheller, respectively. When the water from dams predominates, high calcium-values are measured at the downstream locations. For these high calcium-values, a substantial increase in pH and alkalinity have been observed throughout the past 30 years. presumably due to declining acidification from the dam (c.f. Fell et al., 2014). Low calcium-values, in contrast, indicate the dominance of dilute water from the Skvagrau and Godfarlonene catchments. In case of low calcium-values, a moderate improvement in the water chemistry has been observed, in line with the general improvement of the water chemistry in this area during the past decades (Enge, 2013).

Prior to the Sira-Kvina regulation, Storå contributed 3/4 of the total runoff from Valevatn. Therefore, the water chemistry in Storå is most likely representative for Valevatn. Storå has been monitored for 35 years. During the five-year period from 1985 to 1989, pH was 4.77 ± 0.12, n=26 (Enge et al., 2016). Without regulation and "liming-effect" from the dam, we may assume that such detrimental water chemistry would have dominated the entire river stretch from the dam and downstream to Fidjelandsvatn during the 1980s.

A fish survey in 1987 found that the trout population in Valevatn was extinct while Ortevatn had a reduced population (Larsen et al., 1989). However, the lake downstream of these two, Fidjelandsvatn, had a dense population of trout. Recruitment in the river downstream Jorunnshølen was also established. Young trout were hardly detected elsewhere in this part of Sira.

The reservoir at Svartevatn comprised of several smaller lakes prior to the construction of the dam. Fish populations, surveyed between 1950-1970, were found to be sparse in the inner part and extinct in the outer part of the reservoir (Sevalrud and Muniz, 1980). All tributaries and lakes downstream of the dam, which was built in 1976, were extinct with the exception of sparse populations registered at Lake Grauthellervatn and Lake Godfarlonene. Test-fishing conducted at Lake Grauthellervatn in 1986 found a sparse, but self-reproducing, population of good quality. No fish were caught in the stream located below Lake Godfarlonene and Lake Grauthellervatn (Enge, 1987). Between the dam and Lake Godfarlonene, the physical conditions are not suitable for repoduction (Espen Enge pers. comm)

The simulations showed pH = 5.98 ± 0.53 and pH_{min} = 5.13 in Jorunnshølen during 1986-1988 (Table 4.4). Even the minimum pH was not critical for trout. pH measured down to 5.0 were found to have no effect in a fish survey during late snowmelt in the region (Enge et al., 2017). The simulation at Lake Grauthellervatn during 1986-1988 were slightly lower, showing pH = 5.34 ± 0.36 and pH_{min} = 4.96. This pH is not critical for the survival of adult fish, but is not optimal and could limit reproduction.

The worst-case scenario resulted in an overall drop in pH of 0.2-0.3 units (relative to the “original” simulation). In these simulations, pH_{min} were calculated to be 4.90 and 4.69 during 1986-1988 in Jorunnshølen and Lake Grauthellervatn, respectively. For Jorunnshølen, this pH was still not critical for adult/older fish. The minimum pH of 4.69 at Lake Grauthellervatn in this scenario is detrimental for younger life stages while older fish would most likely survive. However, this is somewhat dependent upon other chemical parameters, including Al, Ca^{2+} and conductivity. The sample with the lowest observed pH (4.8) in this period has a conductivity of 18.8 μS/cm (H^+-corrected). A minimum of 15 μS/cm is needed for the fish to tolerate this pH (Enge and Kroglund, 2011). While no fry were observed in the inlet to Lake Grauthellervatn during a fish survey in 1988, fish have been caught every year since 1990.

Fish actively avoid adverse water chemistry and migrate towards better water chemistry (Peterson et al., 1988). Even if temporally detrimental water chemistry had occurred due to acidic water from the local catchment (Skvagrautjørn and Lake Grauthellervatn), the trout could easily have migrated closer towards the Deg leakage. Between Jorunnshølen and Lake Fidjelandsvatn there are excellent spawning sites for trout. Subsequently, the effects of the dam may also have sustained the dense population of trout in Lake Fidjelandsvatn at a time when neighbouring lake populations were either extinct or reduced.

In lakes affected by rock dumps, the liming effects are often diluted due to large lake volumes. The survival of the trout in such lakes, e.g. Lake Ognhellervatn, is probably due to slightly better water chemistry around the dumps.

Even though pronounced acidification was detected inside the dams, the net effects on pH and alkalinity were positive. Downstream sites and lakes affected by rock dumps had also satisfactory water chemistry, suggesting that the populations downstream of the dams survived due to the water chemistry effects of the dam. Therefore, rockfills should be subjected to careful and individual evaluation, rather than be viewed as inherently detrimental. However, it should be noted that despite the positive effects on fish, the dams and rockfills have created an "unnatural" water chemistry with considerably higher calcium-values than the adjacent waters.

The study established a net buffering effect of the dams and rock dumps. Variations in the water chemistry of the dam seepages show that many factors affect the ionic contribution. The current study suggest that the effect of the rockfills on the water chemistry has contributed to the survival of trout populations.

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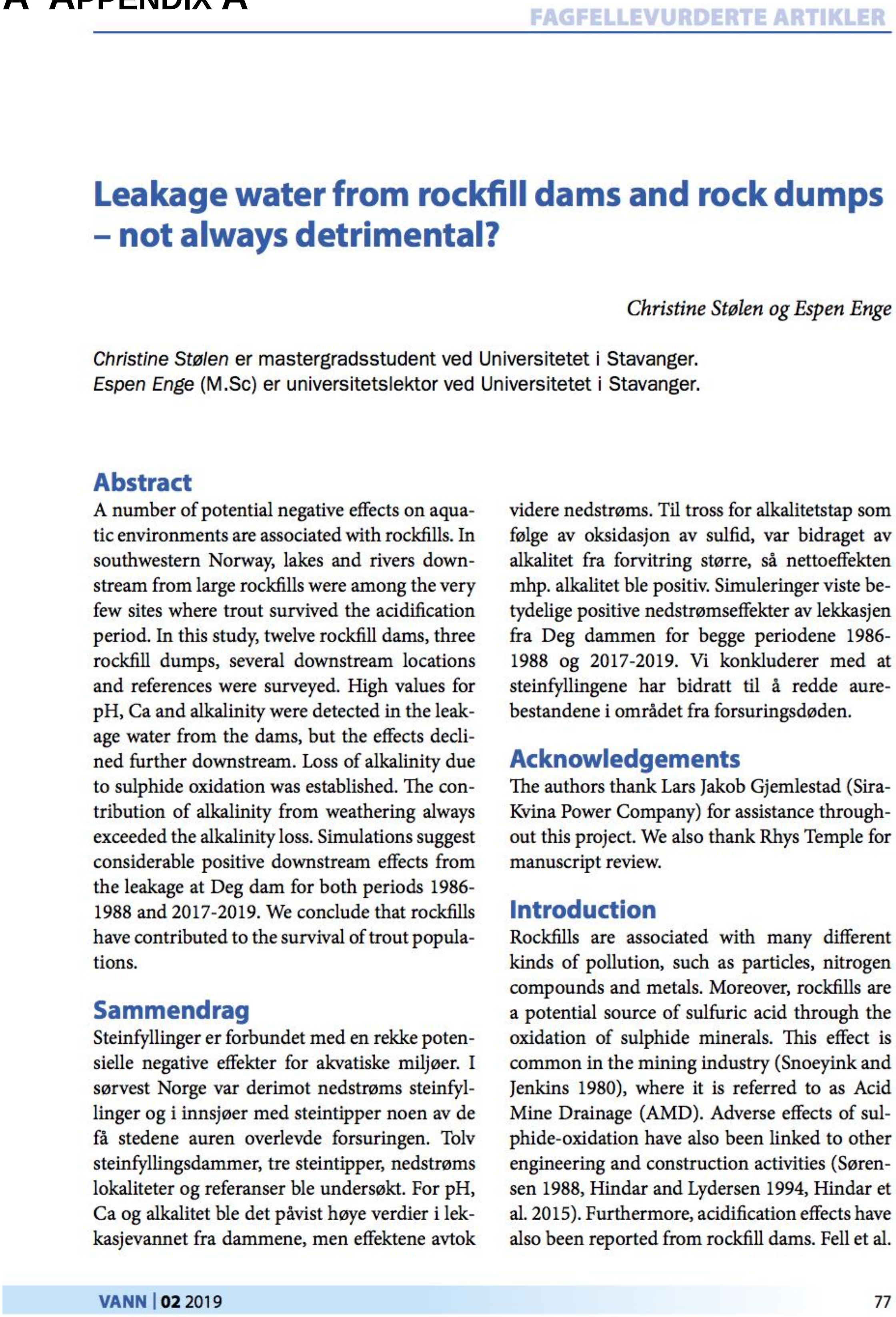
A APPENDIX A



Leakage water from rockfill dams and rock dumps – not always detrimental?

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Abstract

A number of potential negative effects on aquatic environments are associated with rockfills. In southwestern Norway, lakes and rivers downstream from large rockfills were among the very few sites where trout survived the acidification period. In this study, twelve rockfill dams, three rockfill dumps, several downstream locations and references were surveyed. High values for pH, Ca and alkalinity were detected in the leakage water from the dams, but the effects declined further downstream. Loss of alkalinity due to sulphide oxidation was established. The contribution of alkalinity from weathering always exceeded the alkalinity loss. Simulations suggest considerable positive downstream effects from the leakage at Deg dam for both periods 1986-1988 and 2017-2019. We conclude that rockfills have contributed to the survival of trout populations.

Sammendrag

Steinfyllinger er forbundet med en rekke potensielle negative effekter for akvatiske miljøer. I sørvest Norge var derimot nedstrøms steinfyllinger og i innsjøer med steintipper noen av de få stedene auren overlevde forsuringen. Tolv steinfyllingsdammer, tre steintipper, nedstrøms lokaliteter og referanser ble undersøkt. For pH, Ca og alkalitet ble det påvist høye verdier i lekkasjevannet fra dammene, men effektene avtok videre nedstrøms. Til tross for alkalitetstap som følge av oksidasjon av sulfid, var bidraget av alkalitet fra forvitring større, så nettoeffekten mhp. alkalitet ble positiv. Simuleringer viste betydelige positive nedstrømseffekter av lekkasjen fra Deg dammen for begge periodene 1986-1988 og 2017-2019. Vi konkluderer med at steinfyllingene har bidratt til å redde aurebestandene i området fra forsuringsdøden.

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Introduction

Rockfills are associated with many different kinds of pollution, such as particles, nitrogen compounds and metals. Moreover, rockfills are a potential source of sulfuric acid through the oxidation of sulphide minerals. This effect is common in the mining industry (Snoeyink and Jenkins 1980), where it is referred to as Acid Mine Drainage (AMD). Adverse effects of sulphide-oxidation have also been linked to other engineering and construction activities (Sørensen 1988, Hindar and Lydersen 1994, Hindar et al. 2015). Furthermore, acidification effects have also been reported from rockfill dams. Fell et al.

(2014) list several examples of acidic seepage caused by the oxidation of pyrite (FeS_2).

Acidification is not restricted to local sources. During the past century, atmospheric deposition of long-range transported sulphur- and nitrogen-compounds has severely affected surface waters throughout southern Norway. Waters in Sirdal and adjacent mountain areas in Rogaland are dilute and unbuffered and are therefore particularly sensitive to acidification (Enge 2013). In Sirdal, an emerging decline of the trout (*Salmo trutta*) populations was observed as early as during the late 1800s, possibly caused by effects of acidification (Enge et al. 2017). After the mid 1900s, the population decline accelerated, and in the late 1970s the vast majority of trout populations in Sirdal and adjacent mountain areas were considered lost due to acidification (Sevaldrud and Muniz 1980).

Surveys from southwestern Norway (Sevaldrud and Muniz 1980, Gunnerød et al. 1981) revealed that *all* trout populations adjacent to rock dumps and rockfill dams survived the acidification. Sporadic water chemistry measurements from dam leakages in the past decades showed higher pH, alkalinity- and conductivity-values than in the corresponding reservoirs (Enge 2009).

The primary aim of our study has been to establish the water chemistry effects of rockfill dams and rock dumps, and evaluate if these effects may explain the observed survival of trout.

Material and methods

Study area

The study comprises of rockfill dams and rock dumps within Rogaland and Agder counties that were built in the 1960s and 1970s in association with hydroelectric power development. The most comprehensive sampling was performed in Sirdal, within the Sira and Kvina watersheds. Two of the dams are among the largest in Norway, Svartevassdammen (120 m) and Deg (90 m).

Locations & sampling

Distinguishing between "leakage" and "seepage" requires more detailed data. Therefore, the general term "leakage" is consequently used in this study.

The survey included i) references, primarily sampled in the reservoirs, ii) leakage samples from 12 rockfill dams, iii) samples from downstream locations and iv) samples from three lakes affected by rock dumps.

With a frequency of 2-4 weeks, the sampling was conducted throughout June 2018 to March 2019. LDPE bottles (500 ml) were used for sampling, but were occasionally supplemented with HDPE bottles (250 ml). Samples were collected at the surface of the locations (lakes) or in flowing water (rivers&brooks). In December and January, some of the locations were ice-covered. Here, the water was sampled at 0.5m depth from a drill hole in the ice, using a "Ruttner" sampler.

Water chemistry analyses

pH was determined potentiometrically according to "Standard Methods", 4500-H^+ pH Value (Eaton et al. 1995). A Cole Parmer pH-meter equipped with a Radiometer pHC4001 electrode was used. The instrument was calibrated with standard buffers (pH 4.01 & 6.86). *Conductivity* was measured according to "Standard Methods" 2510, using a VWR CO310 conductometer for field measurements, and an Amber Science instrument was used for lab measurements. The two instruments were calibrated with solutions of KCl 718 µS/cm and NaCl 210 µS/cm, respectively. *Alkalinity* was determined by titrating the sample with 0.01 N H_2SO_4 (diluted from Merck "Titrisol" 0.1 N, verified by titration of certified Na_2CO_3). Samples with expected low alkalinity were titrated using 0.0025 N acid. A full titration curve was recorded for each of the samples, and interpolation of the curves yielded the titration volumes corresponding to the applied endpoint pH=4.50. For low alkalinity values, direct use of this endpoint causes an overestimation of the true equivalence alkalinity (Snoeyink and Jenkins 1980). To adjust for this overtitration, the formula derived by Henriksen (1982) was applied:

$$\mathbf{ALK_E = ALK_{4.5} - 32 + 0.646 \times SQRT(ALK_{4.5} - 32)}$$

(ALK_E is the equivalence alkalinity, $ALK_{4.5}$ is the alkalinity corresponding to an endpoint of pH=4.5, units: µeq/L)

Calcium, sodium and chloride were measured potentiometrically using Radiometer ionselective electrodes (ISE) according to the manuals. The determination of *Σcations* was based on the ion exchange method described by Vogel (1961), which recommends H^+ ion exchange followed by strong base titration, and subsequently adjusting the result for the loss of alkalinity. In this study, sodium ion exchange was used (Amberlite IR120 Na^+), removing the need for alkalinity adjustment. *Sulphate* was determined by conductometric titration with barium acetate, modified from Vogel (1961). The samples were pretreated by sodium cation exchange to eliminate interferences from divalent cations. Isopropanol (p.a.) was added to reduce the solubility of the precipitate (v/v=2:1). The conductivity titration curve was recorded using a Greisinger GLF 100 RW conductometer. *Fluoride* was measured photometrically using the SPANDS-method ("Standard Methods" 4500-F^- D). Absorbance was measured at 570 nm in 10 mm polystyrene cuvettes with a Shimadzu spectrophotometer (UV-120-01). *Quality:* Quality controls were performed using i) internal standards (pH, Ca, Na, Cl & SO_4), ii) certified reference material (ALK & Na), and iii) measuring duplicates (conductivity, F & SO_4). Based on the 130 samples with sufficient data, cation-anion balance for

Dam at Roskreppfjord

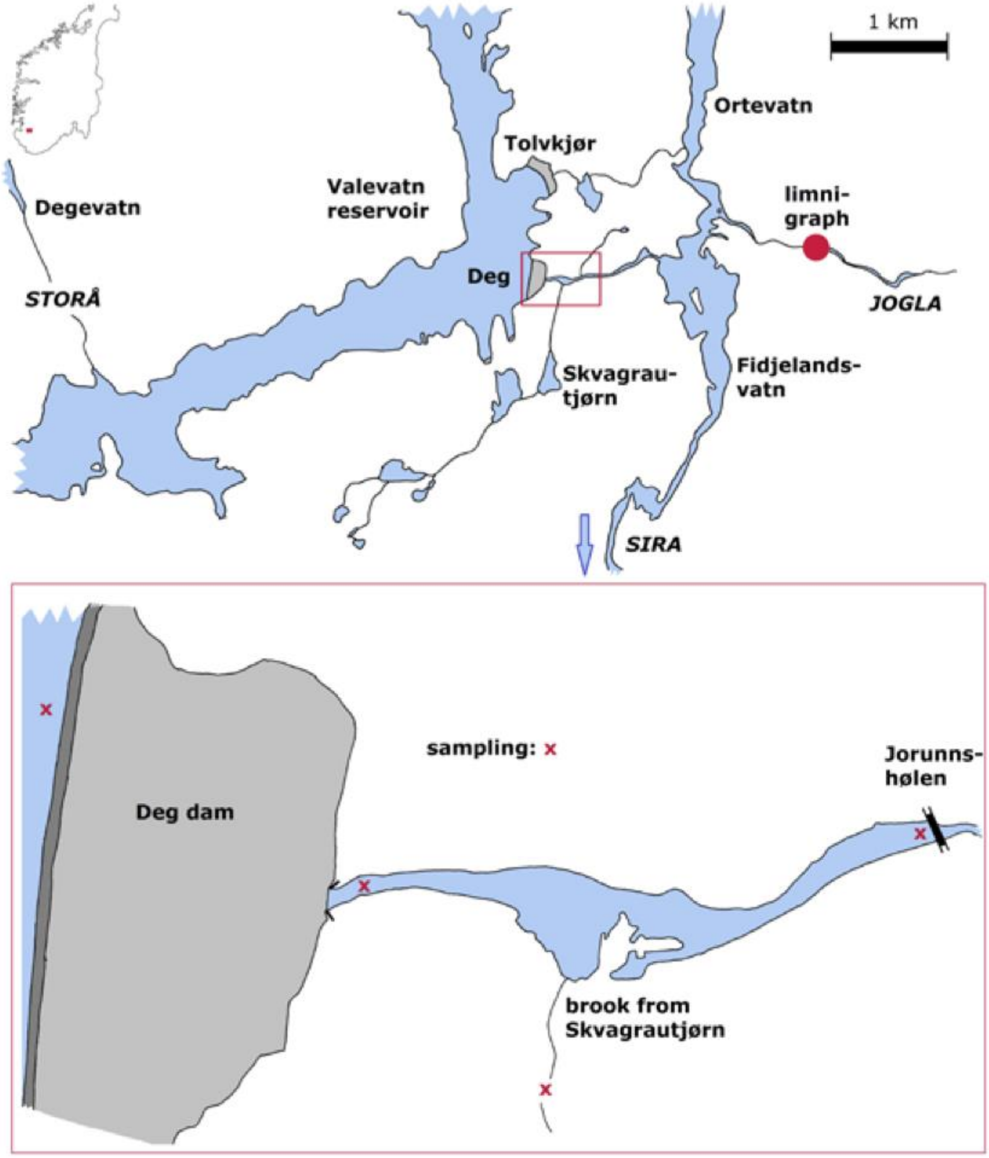

Figure 1. Deg dam and adjacent areas

all of them was well within the acceptance limits given by Eaton et al. (1995).

Alkalinity calculations

The original alkalinity "ALK_0" was calculated as the sum of non-marine base cations. The data from the direct determination of *Σcations* were applied. Here, the marine ion contribution was estimated using the relative ratio to chloride (Skartveit 1981). ALK_0 may also be estimated by the approximation $ALK_0 \approx 1.21$ x non-marine calcium (Henriksen 1980). These two methods were compared. The loss of alkalinity was calculated as the difference between original and measured alkalinity.

Simulations of water chemistry

Models were used to evaluate the suitability of the water chemistry for brown trout downstream from dams. Here, the leakage from the Deg dam was used as a case (fig. 1). Calculations were made for Jorunnshølen, located 350 m downstream of the dam. Jorunnshølen has a local catchment of 2.91 km^2 with an annual average runoff of 125 L/sec (nve.no), while the leakage contributes with 3.6±0.9 L/sec, n=305 (Per-Magne Sinnes, Sira-Kvina Power Company, pers.com.).

The simulations were performed according to Enge and Hemmingsen (2010), using flowrate data and mass flux of calcium. To calculate the flowrate at Jorunnshølen, the daily measurements from the adjacent limnigraph "Jogla" (nve.no) were downscaled with respect to average runoffs from the two catchments. Empirical relations were used to estimate pH from calcium values. The simulations were compared to observations. Here, data from the 1980s, retrieved from Enge (2009), was also included. To achieve comparable periods which include all observations, the periods March 1986-1988 and March 2017-2019 were chosen. The first period represents a period highly affected by acidification, while the latter period represents the most recent data.

Results

General water chemistry

The study included a total of 217 water samples (tab. 1). The reference samples had an uniform water chemistry; slightly acidic and extremely dilute (pH=5.64±0.18, Ca=0.25±0.14 mg/L, n=44). For all parameters, higher values were found in the leakage water compared to the references ($p<0.001$). With average values of approximately 50 times the references, alkalinity and calcium concentrations were particularly elevated compared to the references. Three of the samples from the Deg dam were collected inside the dam, in the concentrated leakage. Average pH and calcium were 7.34±0.10 and 15±2 mg/L, respectively. This average value of calcium was used in the simulations. Downstream sites and lakes with rock dumps were sufficiently buffered to sustain pH-values of about 6 (tab. 1). However, the latter is a non-homogeneous group, including lakes with Ca-values ranging from 0.33±0.03 mg/L, n=4 (Ognhellervatn) to 5.0±0.3 mg/L, n=3 (lake at Kvinen power station).

Acidification

No difference was detected between ALK_0 determined as the sum of non-marine cations and determined as 1.21 x non-marine calcium ($p>0.05$), (fig. 2a). The loss of alkalinity was highly correlated with non-marine sulphate ($r^2=0.99$, $p<0.001$, n=130). The perfect 1:1 relationship (fig. 2b) suggests that sulfuric acid was causing the loss of alkalinity.

Considerable differences were observed between the dams regarding alkalinity and alkalinity loss (fig. 3). Despite this loss, the overall contribution of alkalinity from weathering of dam material exceeded the acidification. The remaining alkalinity was sufficient to sustain a pH>6.5 in 77 of the 88 samples from the dams. The sum of non-marine cations increased with increasing sulphate ($r^2=0.57$, $p<0.001$, n=85).

Table 1. Average values for all samples

Sample type	n	pH	Cond.	ALKe	Ca	Cl	Na	SO_4	F	ΣCAT
	samples		µS/cm	µeq/L	mg/L	mg/L	mg/L	mg/L	mg/L	meq/L
Dams & leakages	88	7.13	87.0	412	12.9	2.2	1.8	13.5	0.33	0.82
Downstream dams	72	5.91	19.6	68	1.5	1.9	1.4	(3.4)	(0.10)	(0.28)
Lakes (rock dump)	13	6.18	20.2	76	1.7	1.9	1.3	2.9	0.12	0.23
References	44	5.64	9.9	8	0.25	1.6	1.0	(0.8)	(0.03)	(0.11)

Brackets (): Parameter analyzed for 1/3 of the samples

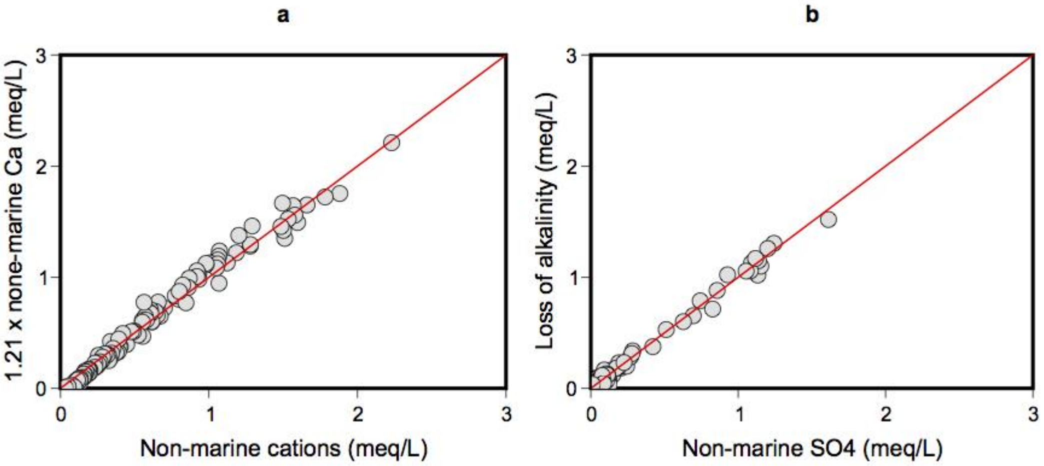

Figure 2. There was no difference between non-marine cations and 1.21 x non-marine Ca (a). A 1:1 relation between non-marine sulphate and loss of alkalinity was found (b). (Lines=1:1)

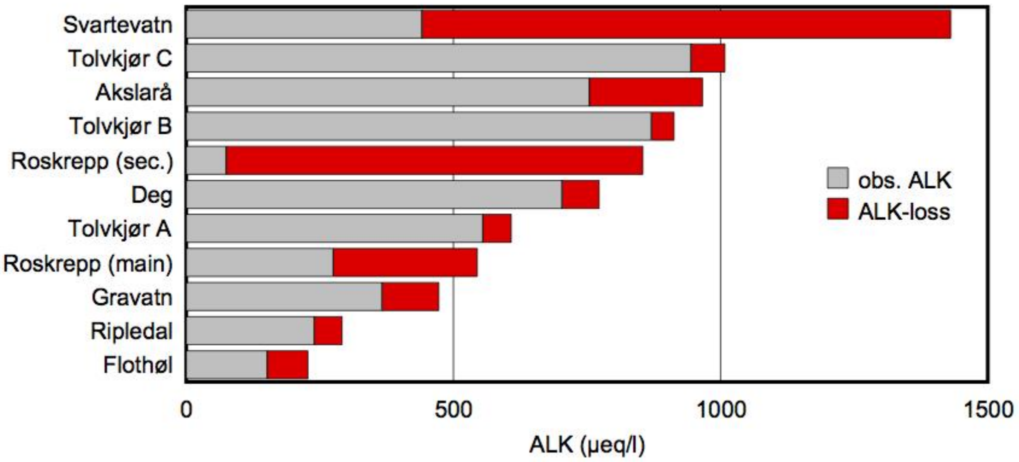

Figure 3. Considerable differences in alkalinity were detected, exemplified by dams in Sira and Kvina. The figure shows the original alkalinity (ALK_0) as the sum of present alkalinity and alkalinity loss.

Both pH and alkalinity-values have increased in the past 30 years. For calcium-values of 1 and 10 mg/L in Jorunnshølen, the increases in alkalinity were 11 and 162 µeq/l, respectively (fig. 4a). The corresponding values were +0.24 and +0.53 for pH (fig. 4b).

Simulations

No differences between simulated and observed pH were found (fig. 5) ($p>0.05$). The simulations showed a pH increase of about 0.3 units from the period of 1986-1988 to 2017-2019 (tab. 2). The fraction of pH-values <5.5 were 24% and 14%, respectively. Only negligible differences were found between the minimum values. Limited differences for calcium between the two periods were observed (tab. 2).

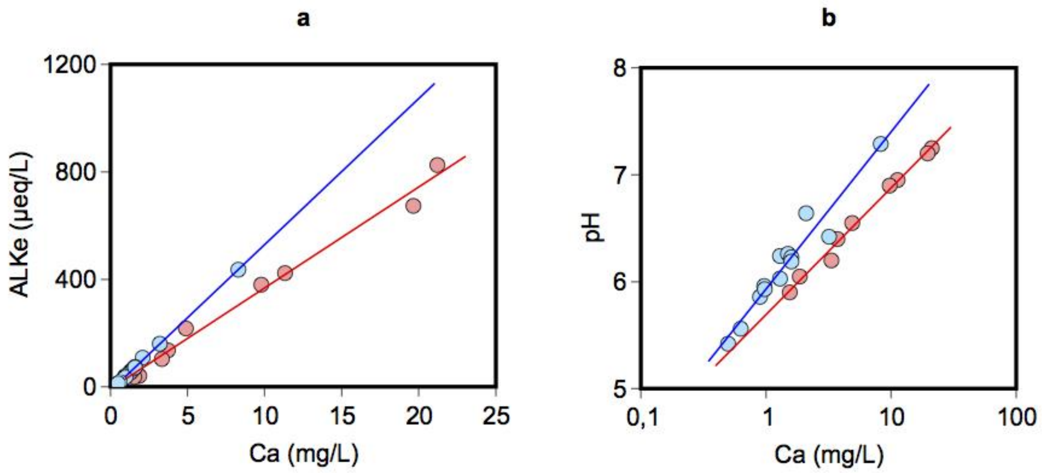

*Figure 4. pH, Ca and alkalinity data from Jorunnshølen. Red and blue colours represent data from 1986-1988 and 2017-2019, respectively. The differences (blue-red) in the empirical relations ALK vs. Ca (**a**) and pH vs. Ca (**b**) reflects reduced acidification between the two periods.*

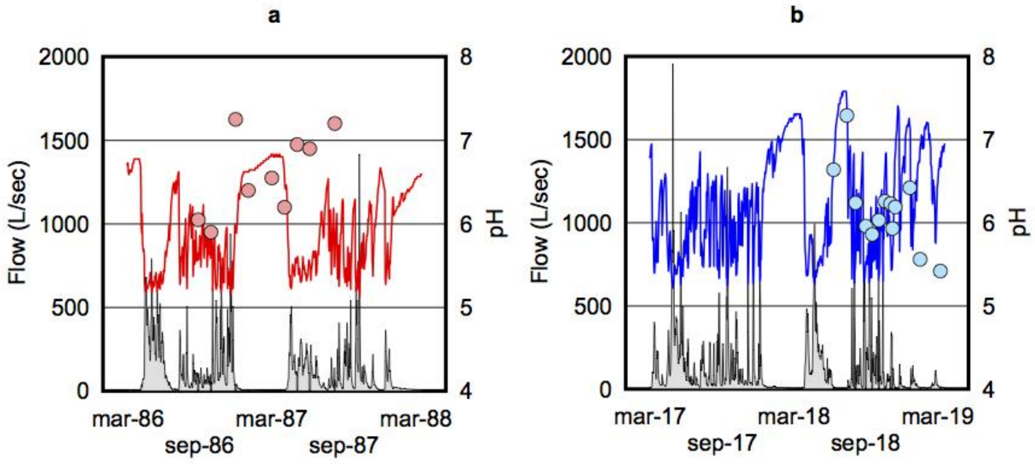

*Figure 5. Simulations of pH-values at Jorunnshølen. Figures **a** (red) and **b** (blue) blue represent data from 1986-1988 and 2017-2019, respectively. In figs. **a&b** lines, dots and "area" represent simulated pH, observed pH and flowrates, respectively.*

Table 2: Results from simulations of water chemistry at Jorunnshølen.

Parameter		**1986-1988**	**2017-2019**
Flow (L/sec)		103	113
pH	Average	5.98 ± 0.53	6.27 ± 0.64
	Minimum	5.13	5.22
Ca (mg/L)	Average	2.87 ± 2.69	2.77 ± 2.85
	Minimum	0.34	0.33

Discussion

This study established that the surveyed dams and rock dumps had a net buffering effect on adjacent waters.

The bedrock in the mountain areas of southernmost Norway consists mainly of slow weathering rock types such as gneiss and granite (ngu.no). Normally, this leads to highly dilute water chemistry with low levels of calcium. In Rogaland County, lakes located at an altitude of > 500 m a.s.l. showed a median calcium value of 0.23 mg/L (Enge 2013), fairly equal to the results from the current study (tab. 1). The dam leakages, exposed to the same geology, showed an average of 12.9 mg/L. This effect is probably due to the processing of the rock used in the dams. Particle breaking and fracturing enhance weathering rates by increasing the surface area and exposing fresh mineral surfaces to air and water (Price 2009).

The positive correlation found between sulphate and non-marine cations suggests that sulphuric acid has accelerated the mobilization of cations. Acid increases the rate of chemical weathering, even for slow weathering rocks such as granite (Webb 1980). However, relatively high concentrations of cations were found even at low sulphate levels, suggesting that the presence of sulfuric acid has not been critical for the observed weathering.

Differences in water chemistry enrichment between the dams, such as increases in cation concentrations, depend on factors such as geology, size and geometry of the dams. The latter two factors indirectly determine contact time and path length of the leakage. Tolvkjør dam (fig. 1) has a complicated geometry. Three separate leakages from this dam were surveyed. The leakage associated with the longest base width had twice the alkalinity than the leakage with the shortest width (fig. 3).

Substantial differences in acid production were detected (fig. 3). This does not entirely depend on the presence and availability of sulphi-

Deg dam March 2019. (illustrasjonsbilde) des in the dam material, but may also be linked to the age of the dam. A gradual decrease in acidity has been observed at Corin dam in Australia, which contains about 1% pyrite (Fell et al. 2014). Except for the Flørli dam, all dams in our study were built throughout the same period, about 50 years ago, indicating that ageing does not explain the differences in acidity between the dams.

Due to a constant leakage rate from Deg, and a highly variable flowrate from the Skvagrau catchment, the mixing ratio ranged from 0.2%-88% Deg-water at Jorunnshølen (fig. 1). When the water from Deg predominates, high calcium-values are measured at Jorunnshølen. For these high calcium-values, a substantial increase in pH and alkalinity have been observed throughout the past 30 years (fig. 4), presumably due to declining acidification from the dam (c.f. Fell et al. 2014). Low calcium-values, in contrary, indicate the dominance of dilute water from the Skvagrau catchment. In case of low calcium-values, a moderate improvement in the water chemistry has been observed (fig. 4), in line with the general improvement of the water chemistry in this area during the past decades (Enge 2013).

Prior to the Sira-Kvina regulation, Storå (fig. 1) contributed 3/4 of the total runoff from Valevatn. Therefore, the water chemistry in Storå is most likely representative for Valevatn. Storå has been monitored for 35 years. During the five-year period from 1985 to 1989, pH was 4.77±0.12, n=26 (Enge et al. 2016). Without regulation and "liming-effect" from the dam, we may assume that such detrimental water chemistry would have dominated the entire river stretch from the dam and downstream to Fidjelandsvatn during the 1980s.

A fish survey in 1987 (Larsen et al. 1989), found that the trout population in Valevatn (fig. 1) was extinct while Ortevatn had a reduced population. However, the lake downstream of these two, Fidjelandsvann (fig. 1), had a dense population of trout. Recruitment in the river downstream Jorunnshølen was also established. Young trout were hardly detected elsewhere in

Leakage from Svartevassdammen. (illustrasjonsbilde) this part of Sira. The simulations showed pH=5.98±0.53 and pH_{min}=5.13 in Jorunnshølen during 1986-1988 (tab. 2). Even the minimum pH was not critical for trout. Moreover, this is a "worst-case scenario". The applied model simulates mixing of water chemistries only (Enge and Hemmingsen 2010), and does not consider the levelling effect, caused by an eventual water volume at the mixing site; in this case Jorunnshølen.

Fish actively avoid adverse water chemistry and migrate towards better water chemistry (Peterson et al. 1988). Even if detrimental water chemistry had occurred due to acidic water from the local catchment (Skvagrau), the trout could easily have migrated towards Deg (fig. 1). Therefore, we suggest that the population downstream of Deg survived due to the water chemistry effects of the dam. Between Jorunnshølen and Fidjelandsvatn there are excellent spawning sites for trout. Subsequently, the effects of the dam may also have sustained the dense population of trout in Fidjelandsvatn at a time when neighbouring lake populations were either extinct or reduced.

In lakes affected by rock dumps, the liming effects are often diluted due to large lake volumes. The survival of the trout in such lakes, e.g. Ognhellervatn, is probably due to slightly better water chemistry around the dumps.

Even though pronounced acidification was detected inside the dams, the net effects on pH and alkalinity were positive. Downstream sites and lakes affected by rock dumps had also satisfactory water chemistry. Therefore, rockfills should be subjected to careful evaluation, rather than be viewed as inherently detrimental. However, it should be noted that despite the positive effects on fish, the dams and rockfills have created an "unnatural" water chemistry with considerably higher calcium-values than the adjacent waters.

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B APPENDIX B

Table 0.1 Chemical analysis

Temp. °C	Type	Sample location	Dato	pH	Cond. µS/cm	Colour mgPt/L	ALK_E µevk/L	Ca^{2+} mg/L	Cl^- mg/L	Na^+ mg/L	Mg^{2+} mg/L	SO_4^{2-} mg/L	Tot-cat mgNa/L	F^- mg/L	NO_3^- mgN/L	Hard. mM	Al µg/L	Fe^{3+} mg/L
2.5	Leak.	Akslarå dam	26-Jun-18	7.34	50.8	0	334	7.4	0.79	0.77	0.28	4.2	9.6	0.01				
3.1	Leak.	Akslarå dam	09-Nov-18	7.64	115	6	810	18.8	3.0	1.6	0.74	10.9	25.4	0.27		0.48		
2.0	Leak.	Akslarå dam	20-Nov-18	7.80	165	5	1121	27.7	3.9	1.7	1.0	20.8	37.2	0.33		0.74	5	0.24
14.0	Down.	Akslarå pond outlet	26-Jun-18	6.09	10.8	0	19	0.38	2.0	1.2	0.16							
20.7	Down.	Akslarå pond outlet	27-Jul-18	6.30	10.2	8	22	0.35	1.7	1.2	0.14							
2.3	Down.	Akslarå pond outlet	09-Nov-18	5.92	10.3	9	14	0.30	1.6	1.0	0.16							
2.9	Down.	Akslarå pond outlet	20-Nov-18	6.00	9.3	10	21	0.38	1.3	0.87	0.10						27	
10.7	Ref.	Akslarå reservoir	26-Jun-18	5.79	10.2	1	8	0.25	1.8	1.1	0.16							
19.3	Ref.	Akslarå reservoir	27-Jul-18	5.86	10.4	4	8	0.26	2.1	1.3	0.15							
2.8	Ref.	Akslarå reservoir	09-Nov-18	5.57	11.3	6	6	0.10	2.1	1.1	0.12	0.67	2.8	0.00				
14.6	Ref.	Akslarå small brook	26-Jun-18	5.67	5.6	0	8	0.08	0.72	0.50	0.05							
18.6	Ref.	Akslarå small brook	27-Jul-18	5.78	8.8	11	12	0.22	1.1	1.1	0.09							
2.2	Ref.	Akslarå small brook	09-Nov-18	5.39	9.8	11	1	0.38	1.5	1.0	0.12							
2.6	Ref.	Akslarå small brook	20-Nov-18	5.69	10.4	9	9	0.20	1.6	1.2	0.10						28	
8.1	Dump.	Lake Listøl	28-Sep-18	6.13	18.2	38	40	1.0	2.6	1.6	0.28	2.3	4.3	0.03				
9.3	Dump.	Lake Listøl	13-Oct-18	5.91	15.3	40	28	0.60	2.2	1.5	0.19	2.0	3.3	0.03				
4.5	Dump.	Lake Listøl	27-Oct-18	6.37	22.0	39	65	1.2	2.4	1.6	0.30	2.7	4.4	0.02				
4.2	Dump.	Lake Listøl	09-Nov-18	6.29	19.7	37	61	1.2	2.4	1.6	0.25	2.5	4.9	0.02				
2.2	Dump.	Lake Listøl	20-Nov-18	6.33	19.1	43	58	1.2	2.1	1.5	0.22	2.7	4.4	0.00			66	
1.6	Dump.	Lake Listøl	26-Dec-18	5.92	17.2	31	48	0.84	2.1	1.7	0.31	2.3	4.6	0.03		0.03		
2.1	Dump.	Lake Kvinen ps.	27-Oct-18	7.03	36.6	48	206	4.7	1.6	1.0	0.30	4.6	7.7	0.32		0.14		
3.0	Dump.	Lake Kvinen ps.	09-Nov-18	6.99	38.1	45	218	5.2	1.7	1.1	0.30	4.5	8.1	0.36		0.14		
3.3	Dump.	Lake Kvinen ps.	20-Nov-18	6.95	36.2	50	210	5.0	1.5	0.99	0.35	4.4	8.3	0.35		0.14	33	
7.7	Down.	Ognheller	13-Oct-18	5.53	10.8	36	13	0.32	1.5	1.1	0.13							

Temp. °C	Type	Sample location	Dato	pH	Cond. µS/cm	Colour mgPt/L	ALK_E µevk/L	Ca^{2+} mg/L	Cl^- mg/L	Na^+ mg/L	Mg^{2+} mg/L	SO_4^{2-} mg/L	Tot-cat mgNa/L	F^- mg/L	NO_3^- mgN/L	Hard. mM	Al µg/L	Fe^{3+} mg/L
3.1	Down.	Ognheller	27-Oct-18	5.62	9.5	25	14	0.29	1.5	0.96	0.13							
3.9	Down.	Ognheller	09-Nov-18	5.64	9.9	26	12	0.34	1.6	0.95	0.13	1.0	2.3	0.02				
2.3	Down.	Ognheller	20-Nov-18	5.62	9.6	27	14	0.37	1.4	0.89	0.06						58	
7.4	Down.	Ognheller innlet	13-Oct-18	5.36	8.8	17	5	0.12	1.3	0.89	0.07							
3.1	Down.	Ognheller innlet	27-Oct-18	5.45	8.7	13	-2	0.19	1.4	0.88	0.11							
3.3	Down.	Ognheller innlet	09-Nov-18	5.40	8.8	15	2	0.15	1.5	0.87	0.07	0.82	1.9	0.00				
2.3	Down.	Ognheller innlet	20-Nov-18	5.44	8.7	15	4	0.24	1.4	0.84	0.06						59	
	Leak.	Lyngsvatn dam N	30-Nov-18	6.48	21.9	22	72	1.8	2.1	1.7	0.24	2.0	5.0	0.00				
	Leak.	Lyngsvatn dam S	30-Nov-18	6.40	20.6	16	51	1.7	2.0	1.4	0.23	2.6	4.9	0.00				
	Leak.	St.Flørli dam	08-Aug-18	6.04	24.6	2	63	1.2	3.6	2.4	0.47	1.5	5.0	-0.03		0.05		
8.8	Leak.	Gravvann dam	27-Jun-18	7.29	75.1	6	433	10.0	3.0	2.4	0.66	10.3	16.3	0.00				
10.1	Leak.	Gravvann dam	27-Jul-18	6.94	95.0	21	595	13.4	4.2	2.6	0.98	12.3	21.3	0.06				
9.8	Leak.	Gravvann dam	19-Aug-18	7.32	55.3	75	334	8.0	1.5	1.8	0.57	9.2	13.2	0.05				
8.8	Leak.	Gravvann dam	13-Sep-18	7.09	43.5	84	283	6.0	1.7	1.6	0.50	6.2	9.4	0.12				
6.6	Leak.	Gravvann dam	28-Sep-18	7.02	38.5	72	227	5.1	2.7	1.6	0.44	4.8	8.7	0.03				
7.5	Leak.	Gravvann dam	13-Oct-18	6.17	16.4	84	60	1.3	1.6	1.2	0.16	3.2	3.8	0.14				
2.8	Leak.	Gravvann dam	27-Oct-18	7.16	48.9	43	289	5.5	1.8	1.7	0.49	5.5	10.3	0.04				
4.4	Leak.	Gravvann dam	09-Nov-18	7.16	54.8	35	338	6.6	2.6	1.8	0.68	6.0	12.2	0.06				
14.3	Ref.	Gravvann reservoir	27-Jun-18	5.46	11.9	1	5	0.23	2.2	1.3	0.21							
16.7	Ref.	Gravvann reservoir	27-Jul-18	5.57	10.3	11	6	0.24	1.9	1.2	0.15							
13.8	Ref.	Gravvann reservoir	19-Aug-18	5.57	10.5	15	4	0.20	1.8	1.1	0.17							
12.1	Ref.	Gravvann reservoir	13-Sep-18	5.54	10.5	11	4	0.23	1.7	1.1	0.17							
9.4	Ref.	Gravvann reservoir	28-Sep-18	5.50	10.9	12	4	0.23	1.8	1.1	0.11							
8.1	Ref.	Gravvann reservoir	13-Oct-18	5.43	11.5	12	0	0.17	1.9	1.2	0.15							
6.6	Ref.	Gravvann reservoir	27-Oct-18	5.44	11.7	12	4	0.13	2.1	1.2	0.20							
5.6	Ref.	Gravvann reservoir	09-Nov-18	5.40	11.4	14	2	0.13	2.1	1.2	0.15	0.87	2.7	-0.01				
20.8	Down.	Sandvann innlet	27-Jun-18	5.93	14.1	11	26	0.60	2.1	1.5	0.27							
23.8	Down.	Sandvann innlet	27-Jul-18	5.76	15.3	45	33	0.57	1.8	1.6	0.22							

Temp. °C	Type	Sample location	Dato	pH	Cond. µS/cm	Colour mgPt/L	ALK_E µevk/L	Ca^{2+} mg/L	Cl^- mg/L	Na^+ mg/L	Mg^{2+} mg/L	SO_4^{2-} mg/L	Tot-cat mgNa/L	F^- mg/L	NO_3^- mgN/L	Hard. mM	Al µg/L	Fe^{3+} mg/L
13.6	Down.	Sandvann innlet	19-Aug-18	5.32	13.9	97	13	0.55	1.4	1.4	0.26							
10.4	Down.	Sandvann innlet	13-Sep-18	5.23	13.6	94	8	0.46	1.5	1.3	0.21							
7.3	Down.	Sandvann innlet	28-Sep-18	5.14	17.4	57	3	0.49	2.9	1.6	0.26							
8.8	Down.	Sandvann innlet	13-Oct-18	5.25	15.2	70	7	0.39	2.2	1.5	0.18							
3.7	Down.	Sandvann innlet	27-Oct-18	5.31	14.4	40	12	0.32	2.6	1.4	0.24							
4.4	Down.	Sandvann innlet	09-Nov-18	5.53	14.5	61	15	0.40	2.3	1.4	0.22							
17.2	Down.	Sandvann outlet	27-Jun-18	5.84	12.9	7	13	0.35	2.3	1.5	0.20							
20.9	Down.	Sandvann outlet	27-Jul-18	6.07	14.6	28	26	0.44	2.3	1.7	0.25							
14.9	Down.	Sandvann outlet	19-Aug-18	5.88	12.9	36	15	0.35	2.2	1.5	0.21							
11.6	Down.	Sandvann outlet	13-Sep-18	5.67	13.2	44	12	0.34	2.0	1.4	0.19							
7.9	Down.	Sandvann outlet	28-Sep-18	5.50	14.1	41	9	0.34	2.3	1.5	0.20							
7.5	Down.	Sandvann outlet	13-Oct-18	5.52	14.2	41	11	0.30	2.3	1.6	0.22							
5.3	Down.	Sandvann outlet	27-Oct-18	5.57	14.2	61	10	0.27	2.5	1.5	0.21							
5.1	Down.	Sandvann outlet	09-Nov-18	5.55	14.3	43	9	0.26	2.5	1.5	0.22							
4.5	Down.	Håheller innlet	28-Sep-18	6.85	30.6	24	120	3.9	1.5	0.96	0.21	4.3	6.9	0.35				
6.4	Down.	Håheller innlet	13-Oct-18	6.89	33.1	22	137	4.0	1.3	0.97	0.25	5.0	7.1	0.36				
0.1	Down.	Håheller innlet	27-Oct-18	6.91	32.1	24	132	3.7	1.4	0.92	0.24	4.8	6.9	0.46				
	Leak.	Roskrepp dam A	24-Jul-18	7.34	71.5	3	296	10.2	1.6	1.2		13.2	14.5	0.90				
3.5	Leak.	Roskrepp dam A	28-Sep-18	7.29	58.5	16	247	8.5	1.4	1.1	0.38	9.4	12.0	0.69		0.23		
2.3	Leak.	Roskrepp dam A	13-Oct-18	7.22	53.9	15	235	8.2	1.2	1.0	0.27	8.5	10.5	1.0				
2.2	Leak.	Roskrepp dam A	27-Oct-18	7.37	74.4	5	296	11.2	1.3	1.2	0.40	13.6	14.9	1.0				
	Leak.	Roskrepp dam A	29-Oct-18	7.36	76.6	5	303	11.5	1.4	1.3	0.46	13.9	15.8	1.2		0.29		
2.5	Leak.	Roskrepp dam B	28-Sep-18	6.05	106	9	56	12.8	1.3	1.2	1.7	35.9	20.4	1.6		0.38		
2.9	Leak.	Roskrepp dam B	13-Oct-18	6.22	84.3	13	123	10.9	1.2	1.1	1.1	24.8	15.9	1.4				
0.9	Leak.	Roskrepp dam B	27-Oct-18	6.04	128	7	46	15.7	1.3	1.4	1.5	44.8	25.5	1.8		0.47		
7.1	Ref.	Roskrepp reservoir	28-Sep-18	6.04	11.0	16	29	0.63	1.3	0.82	0.08			0.06		0.02		
6.3	Ref.	Roskrepp reservoir	13-Oct-18	6.05	10.1	14	23	0.52	1.1	0.82	0.10							
4.4	Ref.	Roskrepp reservoir	27-Oct-18	5.93	9.2	12	15	0.33	1.2	0.79	0.11	0.83	2.1	0.02				

Temp. °C	Type	Sample location	Dato	pH	Cond. µS/cm	Colour mgPt/L	ALK_E µevk/L	Ca^{2+} mg/L	Cl^- mg/L	Na^+ mg/L	Mg^{2+} mg/L	SO_4^{2-} mg/L	Tot-cat mgNa/L	F^- mg/L	NO_3^- mgN/L	Hard. mM	Al µg/L	Fe^{3+} mg/L
2.8	Leak.	Svartevann dam (big pipe)	26-Jun-18	7.38	179	2	482	23.6	2.3	2.8	1.6	54.8	36.2	0.60				
3.1	Leak.	Svartevann dam (big pipe)	27-Jul-18	7.33	185	13	449	24.8	2.6	2.8	1.5	55.1	38.6	0.58				
3.6	Leak.	Svartevann dam (big pipe)	19-Aug-18	7.36	164	14	429	24.2	1.6	2.5	1.8	52.3	35.3	0.66				
6.9	Leak.	Svartevann dam (big pipe)	13-Sep-18	6.58	50.4	9	83	5.1	2.4	1.4	0.49	11.2	9.0	0.04				
	Leak.	Svartevann dam (big pipe)	19-Sep-18	7.18	138	13	345	19.2	1.5	2.1	1.3	40.0	25.4	0.53				
4.0	Leak.	Svartevann dam (big pipe)	13-Oct-18	7.15	113	15	332	16.3	1.3	1.8	0.94	30.4	22.4	0.50				
2.7	Leak.	Svartevann dam (big pipe)	27-Oct-18	7.43	202	14	524	28.6	2.1	3.0	1.7	58.0	42.5	0.81		0.81		
	Leak.	Svartevann dam (big pipe)	09-Nov-18	7.30	152	11	400	21.5	1.9	2.5	1.3	41.4	30.8	0.60		0.59		0.21
2.6	Leak.	Svartevann dam (big pipe)	20-Nov-18	7.42	179	13	477	25.3	1.9	2.7	1.7	50.9	36.6	0.72			5	0.23
	Leak.	Svartevann dam (inside)	29-Oct-18	7.27	182	8	397	27.3	2.3	2.8	1.7	54.1	37.7	0.59		0.71		
	Leak.	Svartevann dam (small pipe)	19-Sep-18	7.37	187	17	479	25.9	1.5	2.7	1.7	55.6	37.4	0.75				
2.6	Leak.	Svartevann dam (small pipe)	28-Sep-18	7.52	208	16	576	29.1	1.6	2.9	2.2	59.9	44.4	1.1		0.84		
3.5	Leak.	Svartevann dam (small pipe)	13-Oct-18	7.38	128	17	404	18.6	1.1	2.0	1.1	33.6	25.1	0.61				
2.1	Leak.	Svartevann dam (small pipe)	27-Oct-18	7.60	250	21	711	36.7	2.4	3.6	2.1	77.9	53.0	1.1				
	Leak.	Svartevann dam (small pipe)	09-Nov-18	7.48	189	18	531	27.4	1.9	2.9	1.8	52.7	39.5	0.85		0.76		0.22
10.2	Ref.	Svartevann reservoir	26-Jun-18	5.62	9.7	0	6	0.19	1.8	1.1	0.16							
16.8	Ref.	Svartevann reservoir	27-Jul-18	5.72	9.4	2	5	0.19	1.8	1.1	0.13							
12.5	Ref.	Svartevann reservoir	19-Aug-18	5.66	9.6	3	3	0.23	1.7	1.0	0.12							
10.2	Ref.	Svartevann reservoir	13-Sep-18	5.65	9.9	2	4	0.23	1.7	1.0	0.13							
7.0	Ref.	Svartevann reservoir	28-Sep-18	5.60	10.3	8	8	0.25	1.7	1.1	0.09							
6.7	Ref.	Svartevann reservoir	13-Oct-18	5.68	9.9	6	8	0.31	1.6	1.0	0.15							
5.9	Ref.	Svartevann reservoir	27-Oct-18	5.62	11.1	6	8	0.26	1.8	1.0	0.17	0.75	2.2	-0.01				
5.4	Ref.	Svartevann reservoir	09-Nov-18	5.59	10.3	8	5	0.28	1.9	1.0	0.12							
4.5	Ref.	Svartevann reservoir	20-Nov-18	5.65	10.0	7	7	0.26	1.8	1.0	0.08						24	
18.8	Ref.	Godfarlonene	26-Jun-18	5.91	7.6	2	13	0.24	1.3	0.83	0.10							
22.2	Ref.	Godfarlonene	27-Jul-18	6.25	9.3	7	17	0.42	1.3	0.92	0.13							
12.9	Ref.	Godfarlonene	19-Aug-18	5.74	7.4	17	11	0.22	1.1	0.78	0.11							

Temp. °C	Type	Sample location	Dato	pH	Cond. µS/cm	Colour mgPt/L	ALK_E µevk/L	Ca^{2+} mg/L	Cl^- mg/L	Na^+ mg/L	Mg^{2+} mg/L	SO_4^{2-} mg/L	Tot-cat mgNa/L	F^- mg/L	NO_3^- mgN/L	Hard. mM	Al µg/L	Fe^{3+} mg/L
9.6	Ref.	Godfarlonene	13-Sep-18	5.65	7.7	19	10	0.29	1.0	0.76	0.11							
6.1	Ref.	Godfarlonene	28-Sep-18	5.55	8.5	18	7	0.28	1.4	0.86	0.10							
7.1	Ref.	Godfarlonene	13-Oct-18	5.44	8.7	26	10	0.18	1.3	0.85	0.13	0.80		0.00				
3.0	Ref.	Godfarlonene	27-Oct-18	5.55	8.6	19	9	0.18	1.4	0.86	0.14							
2.8	Ref.	Godfarlonene	09-Nov-18	5.54	8.8	21	8	0.18	1.5	0.86	0.10							
18.5	Down.	Grautheller innlet	26-Jun-18	6.13	8.1	1	15	0.33	1.3	0.86	0.10							
24.6	Down.	Grautheller innlet	27-Jul-18	6.60	17.4	9	30	1.3	1.7	1.2	0.21							
12.7	Down.	Grautheller innlet	19-Aug-18	5.88	8.9	18	12	0.34	1.0	0.77	0.14							
9.2	Down.	Grautheller innlet	13-Sep-18	5.80	9.2	20	15	0.40	1.2	0.83	0.16							
5.9	Down.	Grautheller innlet	28-Sep-18	5.69	9.1	18	17	0.35	1.3	0.85	0.10							
7.7	Down.	Grautheller innlet	13-Oct-18	6.07	11.7	19	22	0.71	1.1	0.82	0.12							
2.1	Down.	Grautheller innlet	27-Oct-18	5.83	9.7	18	16	0.33	1.5	0.87	0.13							
3.0	Down.	Grautheller innlet	09-Nov-18	6.01	14.0	19	22	0.75	1.6	0.95	0.15							
2.2	Down.	Grautheller innlet	20-Nov-18	5.87	10.7	19	16	0.55	1.4	0.85	0.08						48	
18.7	Down.	Deg	27-Jun-18	6.81	24.3	11	132	2.6	2.0	1.5	0.30	2.6	5.9	0.04				
19.9	Down.	Deg	28-Jul-18	7.45	60.4	33	448	8.6	2.9	2.2	0.63	4.4	13.6	0.20				
14.5	Down.	Deg	19-Aug-18	6.39	22.0	66	102	2.2	1.8	1.5	0.25	2.9	5.6	0.05				
10.0	Down.	Deg	13-Sep-18	6.34	23.3	90	109	2.4	1.6	1.4	0.30	3.7	5.7	0.07				
5.8	Down.	Deg	28-Sep-18	6.64	46.0	80	306	6.3	2.3	1.7	0.47	5.0	10.9	0.06				
7.1	Down.	Deg	13-Oct-18	6.73	38.8	94	269	5.3	1.8	1.4	0.48	4.8	9.2	0.20				
2.9	Down.	Deg	27-Oct-18	6.68	44.2	70	277	5.3	2.3	1.7	0.43	4.4	9.4	0.16				
5.0	Down.	Deg	09-Nov-18	6.73	49.5	56	371	6.2	2.3	1.7	0.59	4.1	10.8	0.16				
0.2	Down.	Deg	26-Dec-18	6.60	42.8	38	283	5.4	2.2	1.8	0.52	3.1	10.2	0.06				
2.1	Down.	Deg	20-Jan-19	6.71	32.8	29	195	3.5	2.2	1.6	0.35	2.5	7.4	0.06				0.41
	Down.	Deg	11-Mar-19	6.48	46.1	39	323	8.3	2.5	1.9	0.53	2.9	10.5	0.05	0.15			0.76
	Leak.	Deg dam	29-Oct-18	7.31	97.2	6	707	15.5	3.0	1.9	0.98	7.5	21.1	0.62		0.41		
	Leak.	Deg dam	14-Nov-18	7.45	105	11	827	17.1	3.1	1.8	1.0	6.1	23.6	0.51		0.46		
	Leak.	Deg dam	20-Feb-19	7.26	79.7		577	12.9	2.6	1.9	0.88	5.2	14.9	0.41				

Temp. °C	Type	Sample location	Dato	pH	Cond. µS/cm	Colour mgPt/L	ALK$_E$ µevk/L	Ca^{2+} mg/L	Cl$^-$ mg/L	Na$^+$ mg/L	Mg^{2+} mg/L	SO$_4^{2-}$ mg/L	Tot-cat mgNa/L	F$^-$ mg/L	NO$_3^-$ mgN/L	Hard. mM	Al µg/L	Fe^{3+} mg/L
17.2	Down.	Jorunnshølen	27-Jun-18	6.64	20.8	11	108	2.1	2.1	1.5	0.31	2.0	5.1	0.04				
20.0	Down.	Jorunnshølen	28-Jul-18	7.29	59.8	37	436	8.3	2.8	2.1	0.48	4.7	14.0	0.22				
13.8	Down.	Jorunnshølen	19-Aug-18	6.24	16.6	67	57	1.3	1.7	1.4	0.19	2.6	4.3	0.03				
10.5	Down.	Jorunnshølen	13-Sep-18	5.96	15.1	89	40	0.97	1.6	1.3	0.21	3.2	4.0	0.09				
6.9	Down.	Jorunnshølen	28-Sep-18	5.86	16.0	76	34	0.90	2.1	1.4	0.23	2.9	3.9	0.06				
8.2	Down.	Jorunnshølen	13-Oct-18	6.03	17.8	87	53	1.3	2.1	1.5	0.21	3.1	4.5	0.13				
3.6	Down.	Jorunnshølen	27-Oct-18	6.26	19.2	75	67	1.5	2.1	1.4	0.24	2.8	4.3	0.07				
4.7	Down.	Jorunnshølen	09-Nov-18	6.23	19.9	72	74	1.6	2.2	1.5	0.27	3.0	4.7	0.07				
	Down.	Jorunnshølen	14-Nov-18	5.93	15.0	77	36	0.98	1.8	1.3	0.25	2.8	4.0	0.04				
3.1	Down.	Jorunnshølen	20-Nov-18	6.19	19.4	76	72	1.6	2.1	1.4	0.29	3.3	5.1	0.10			94	
1.1	Down.	Jorunnshølen	26-Dec-18	6.42	29.4	57	160	3.2	2.0	1.6	0.46	3.7	6.9	0.01				
0.4	Down.	Jorunnshølen	20-Jan-19	5.56	17.3	63	18	0.63	2.7	1.8	0.30	2.8	4.4	0.03				0.38
0.7	Down.	Jorunnshølen	11-Mar-19	5.42	20.7	51	13	0.77	3.6	2.1	0.42	2.2	4.6	0.05	0.04			0.39
17.2	Down.	Skvagrautjørn	27-Jun-18	5.62	10.9	9	12	0.30	1.8	1.3	0.14							
15.3	Down.	Skvagrautjørn	28-Jul-18	5.92	32.9	18	40	1.8	3.9	2.6	0.45	4.9	6.5					
14.5	Down.	Skvagrautjørn	19-Aug-18	5.24	12.3	61	5	0.30	1.6	1.3	0.13							
10.9	Down.	Skvagrautjørn	13-Sep-18	5.04	13.2	86	-2	0.23	1.5	1.3	0.17	2.7	3.2	0.07				
7.2	Down.	Skvagrautjørn	28-Sep-18	4.99	14.9	74	-2	0.25	2.0	1.4	0.15			0.01				
7.9	Down.	Skvagrautjørn	13-Oct-18	4.95	15.0	78	-4	0.19	2.0	1.4	0.15							
4.5	Down.	Skvagrautjørn	27-Oct-18	5.06	14.4	73	-1	0.19	2.0	1.3	0.18							
4.1	Down.	Skvagrautjørn	09-Nov-18	5.07	14.6	74	-2	0.27	2.1	1.4	0.19							
2.4	Down.	Skvagrautjørn	20-Nov-18	5.13	14.1	77	0	0.31	2.0	1.3	0.16						110	
0.3	Down.	Skvagrautjørn	26-Dec-18	5.17	14.2	70	4	0.32	1.8	1.4	0.27							
0	Down.	Skvagrautjørn	20-Jan-19	5.06	17.6	60	3	0.43	2.7	1.8	0.31	2.9	3.8	0.01				0.41
0	Down.	Skvagrautjørn	11-Mar-19	5.02	21.2	48	-3	0.50	3.5	2.1	0.38	2.0	4.3	0.00	0.04			0.32
8.3	Leak.	Flothøl dam	26-Jun-18	7.04	43.0	4	196	4.2	1.8	1.4	0.26	3.1	7.8	0.00				
21.5	Leak.	Flothøl dam	27-Jul-18	7.05	35.6	20	260	5.0	1.9	1.5	0.35	2.5	8.8	0.01				
9.7	Leak.	Flothøl dam	19-Aug-18	6.52	33.7	85	163	4.2	1.4	1.7	0.27	6.6	8.5	0.09				

Temp. °C	Type	Sample location	Dato	pH	Cond. µS/cm	Colour mgPt/L	ALK_E µevk/L	Ca^{2+} mg/L	Cl^- mg/L	Na^+ mg/L	Mg^{2+} mg/L	SO_4^{2-} mg/L	Tot-cat mgNa/L	F^- mg/L	NO_3^- mgN/L	Hard. mM	Al µg/L	Fe^{3+} mg/L
8.0	Leak.	Flothøl dam	13-Sep-18	6.66	27.3	52	139	3.2	1.3	1.4	0.28	4.4	6.3	0.07				
7.6	Leak.	Flothøl dam	28-Sep-18	6.57	26.3	45	131	2.8	2.2	1.4	0.21	2.8	6.2	0.00				
8.3	Leak.	Flothøl dam	13-Oct-18	6.44	25.4	43	131	2.8	1.9	1.4	0.20	3.3	5.7	0.00				
4.7	Leak.	Flothøl dam	27-Oct-18	6.64	26.5	29	126	2.5	1.8	1.2	0.21	2.4	5.3	0.04				
4.8	Leak.	Flothøl dam	09-Nov-18	6.48	22.3	25	113	2.1	1.8	1.2	0.20	2.0	5.1	0.02				
2.8	Leak.	Flothøl dam	20-Nov-18	6.49	21.2	21	107	2.2	1.8	1.2	0.23	2.1	4.9	0.10			30	
4.5	Leak.	Ripledal dam	20-Nov-18	6.91	26.6	13	159	3.1	2.0	1.2	0.21	1.6	6.3	0.17			14	
12.5	Leak.	Ripledal dam	27-Jun-18	6.91	33.2	2	225	4.5	1.8	1.5	0.25	1.8	7.8	0.07				
16.9	Leak.	Ripledal dam	28-Jul-18	6.55	33.3	78	272	4.6	2.1	1.7	0.22	1.9	9.3	0.07				
8.5	Leak.	Ripledal dam	19-Aug-18	7.11	49.8	36	390	7.8	1.4	1.7	0.34	4.6	13.8	0.13				
8.4	Leak.	Ripledal dam	13-Sep-18	7.09	57.0	36	327	7.1	4.9	3.0	0.39	3.4	11.3	0.17				
7.3	Leak.	Ripledal dam	28-Sep-18	7.09	37.7	24	244	4.9	2.3	1.5	0.23	3.2	8.2	0.12				
7.5	Leak.	Ripledal dam	13-Oct-18	7.02	40.0	35	248	5.0	3.0	1.9	0.24	2.6	8.1	0.15				
6.0	Leak.	Ripledal dam	27-Oct-18	6.98	26.6	13	159	2.9	2.0	1.3	0.21	1.4	5.9	0.13		0.09		
6.2	Leak.	Ripledal dam	09-Nov-18	6.82	25.4	13	139	2.6	2.1	1.3	0.18	1.4	5.4	0.12				
17.2	Ref.	Valevatn reservoir (Deg)	27-Jun-18	5.66	9.2	2	7	0.20	1.6	1.0	0.12							
17.6	Ref.	Valevatn reservoir (Deg)	28-Jul-18	5.76	10.1	8	15	0.30	1.7	1.1	0.10							
13.3	Ref.	Valevatn reservoir (Deg)	19-Aug-18	5.66	10.3	14	6	0.31	1.6	1.1	0.09							
10.6	Ref.	Valevatn reservoir (Deg)	13-Sep-18	5.55	10.0	12	4	0.23	1.6	1.0	0.13							
9.0	Ref.	Valevatn reservoir (Deg)	28-Sep-18	5.54	10.2	14	6	0.25	1.6	1.1	0.10							
8.5	Ref.	Valevatn reservoir (Deg)	13-Oct-18	5.44	10.2	17	4	0.19	1.6	1.1	0.10							
6.8	Ref.	Valevatn reservoir (Deg)	27-Oct-18	5.51	10.6	15	8	0.24	1.8	1.1	0.17							
5.7	Ref.	Valevatn reservoir (Deg)	09-Nov-18	5.47	11.1	16	5	0.22	1.9	1.1	0.13	0.87	2.3	0.01				
4.6	Ref.	Valevatn reservoir (Deg)	20-Nov-18	5.51	10.5	16	5	0.28	1.9	1.0	0.15						41	
6.1	Leak.	Tolvkjørheller dam A	27-Jun-18	7.25	65.9	5	533	10.0	1.6	1.8	0.60	4.0	15.3	0.15				
11.9	Leak.	Tolvkjørheller dam A	28-Jul-18	6.90	85.6	31	730	13.9	4.3	2.4	0.64	5.2	20.9	0.16				
8.5	Leak.	Tolvkjørheller dam A	19-Aug-18	7.16	64.5	51	544	10.8	1.4	1.8	0.44	5.7	16.5	0.16				
7.0	Leak.	Tolvkjørheller dam A	13-Sep-18	7.42	61.8	60	515	9.9	1.4	1.6	0.46	5.0	13.7	0.07				

Temp. °C	Type	Sample location	Dato	pH	Cond. µS/cm	Colour mgPt/L	ALK_E µevk/L	Ca^{2+} mg/L	Cl^- mg/L	Na^+ mg/L	Mg^{2+} mg/L	SO_4^{2-} mg/L	Tot-cat mgNa/L	F^- mg/L	NO_3^- mgN/L	Hard. mM	Al µg/L	Fe^{3+} mg/L
5.4	Leak.	Tolvkjørheller dam A	28-Sep-18	7.43	64.0	46	493	10.2	2.7	1.7	0.46	3.5	14.6	0.13		0.27		
6.8	Leak.	Tolvkjørheller dam A	13-Oct-18	7.32	54.1	66	424	8.5	2.2	1.6	0.42	3.8	12.9	0.18				
?	Leak.	Tolvkjørheller dam A	27-Oct-18	7.45	70.1	31	569	10.8	2.4	1.7	0.58	3.9	14.9	0.18		0.30		
3.6	Leak.	Tolvkjørheller dam A	09-Nov-18	7.31	73.0	31	577	11.5	2.3	1.8	0.60	4.0	15.4	0.16		0.31		
	Leak.	Tolvkjørheller dam A	20-Nov-18	7.38	76.4	30	613	12.3	2.2	1.7	0.70	4.5	16.5	0.10			12	
2.9	Leak.	Tolvkjørheller dam B	27-Jun-18	7.75	123	0	1056	20.3	2.7	1.8	0.82	5.4	29.2	0.21				
5.1	Leak.	Tolvkjørheller dam B	28-Jul-18	8.05	125	6	1084	18.8	4.0	1.8	0.71	6.2	28.7	0.24				
4.1	Leak.	Tolvkjørheller dam B	19-Aug-18	7.23	68.5	12	629	12.0	1.1	1.4	0.36	2.7	16.9	0.06				
4.5	Leak.	Tolvkjørheller dam B	13-Sep-18	7.17	86.9	9	765	14.5	1.3	1.5	0.52	3.4	19.4	0.06				
4.4	Leak.	Tolvkjørheller dam B	28-Sep-18	6.85	71.8	7	603	11.8	2.3	1.4	0.55	2.0	15.6	0.07				
4.5	Leak.	Tolvkjørheller dam B	13-Oct-18	6.24	27.4	20	193	3.8	1.3	0.98	0.21	1.5	6.3	0.04				
4.0	Leak.	Tolvkjørheller dam B	27-Oct-18	7.66	118	6	1036	19.8	3.5	1.8	0.67	4.5	27.1	0.34				
4.0	Leak.	Tolvkjørheller dam B	09-Nov-18	7.54	106	7	914	17.6	3.2	1.8	0.76	3.9	23.5	0.28		0.48		0.22
3.1	Leak.	Tolvkjørheller dam B	20-Nov-18	7.73	133	6	1175	22.9	3.7	1.8	0.87	4.7	30.3	0.35			4	0.23
0.3	Leak.	Tolvkjørheller dam B	26-Dec-18	7.54	144	6	1258	24.3	2.7	2.3	1.2	6.4	31.7	0.31		0.65		
2.9	Leak.	Tolvkjørheller dam C	27-Jun-18	7.39	134	0	1184	21.3	2.8	2.1	1.1	3.8	31.4	0.16				
8.6	Leak.	Tolvkjørheller dam C	28-Jul-18	7.48	112	11	1073	20.6	4.4	2.3	1.2	3.4	27.8	0.16				
5.2	Leak.	Tolvkjørheller dam C	19-Aug-18	7.59	94.2	11	851	16.7	1.4	1.6	0.52	5.4	22.2	0.18				
6.4	Leak.	Tolvkjørheller dam C	13-Sep-18	7.51	107	8	931	18.0	1.3	1.5	0.52	5.6	25.1	0.09				
5.3	Leak.	Tolvkjørheller dam C	28-Sep-18	7.57	99.3	7	842	16.6	2.2	1.5	0.38	4.0	22.5	0.28				
5.4	Leak.	Tolvkjørheller dam C	13-Oct-18	7.40	76.1	13	641	12.9	1.7	1.3	0.52	3.2	16.4	0.13				
4.2	Leak.	Tolvkjørheller dam C	27-Oct-18	7.58	109	6	925	18.7	3.1	1.6	0.84	4.7	24.8	0.29				
4.5	Leak.	Tolvkjørheller dam C	09-Nov-18	7.47	98.3	7	832	16.5	2.8	1.6	0.75	4.0	22.0	0.22		0.43		
3.8	Leak.	Tolvkjørheller dam C	20-Nov-18	7.48	108	7	909	18.5	3.1	1.6	0.83	3.8	24.8	0.36			5	
0.5	Leak.	Tolvkjørheller dam C	26-Dec-18	6.95	90.2	7	743	15.1	1.9	1.9	0.92	4.1	21.2	0.03		0.39		
1.9	Leak.	Tolvkjørheller dam C	20-Jan-19	6.77	153	172	1465	22.4	2.5	3.1	1.6	4.5	36.6	0.28				4.1

Table 6.1 Input values of the simulations

Location	**Simulation**	**Input variables**		
		$Q_{Leakage}$	**$Ca_{Leakage}$**	**Ca_{Runoff}**
Jorunnshølen	Average	3.6	15.0	0.3
	Worst case	2.7	12.9	0.19
Grautheller	Average	2.8	23.5	0.3
	Worst case	1.8	16.3	0.18

C APPENDIX C

Quantitative Analysis of low concentrations of Sulphate by Conductometric titration

Christine Stølen

Introduction

Sulfate is one of the major constituents in natural waters. It is present in varying amounts and is recognized to be a possible indication of acidification. A number of methods for determining sulfate have been developed with varying degrees of sensitivity, accuracy and measuring ranges. One of the most commonly used method at present time is ion chromatography. A major drawback of this method and other instrumental methods in general is the considerable cost of the equipment/expensive. There are few methods that are simple and sufficiently sensitive for quantitative analysis of low levels of sulfate.

Except for precipitation of insoluble sulfate with barium or lead, few reactions can be used for quantitative determination of sulfate (Hwang, 1983). This type of reaction is utilized in methods such as gravimetric, turbidimetric and nephelometric and a number of different titrimetric techniques. The measuring ranges is a particular issue when analyzing natural waters with low sulfate concentrations. The gravimetric method has a lower limit of 10 mg/l and the turbidimetric method can be applied to sulfate levels between 1-40 mg/l. Although the latter can measure quite low, the method lacks in precision in the lower regions (Eaton et al. 1995).

Conductometric titration can be applied for reaction products with a solubility of less than 5% (Vogel, 1989). Barium sulfate, with a solubility of $1 \cdot 10^{-5}$ mol/l (Hwang, 1983) equal to 0,96 mg/l, is suitable precipitate for this titration and the method is often chosen for determining sulfate in drinking water (Kirowa-Eisner et al. 2007). Even though the method is simple, large errors can occur when analyzing low concentrations of sulfate. Pretreatment of the titrated solution and carefully chosen reagents can minimize these errors.

One way of minimizing the errors for conductometric titration is to add an organic solvent.

Mixing alcohols with the water sample are often used when determining sulfate through any precipitation reactions. The organic solvent reduces the solubility of the precipitation product, enhancing the sensitivity of the method. Addition of an organic solvent also increases the rate of precipitation, especially for micro-crystalline precipitates. Acetone, ethanol and isopropanol are the preferred solvents for this with no significant difference in solubility and cost between the three. Based on volatility, isopropanol is chosen to minimize changes in concentration during titration. A 50 % mixture of isopropanol lowers the solubility to $6,4 \cdot 10^{-7}$ mol/l (Hwang, 1983) equal to 0,06 mg/l. An 80% solution of alcohol was recommended by Hwang, while Vogel recommends addition of 30-40% (Vogel, 1989; Hwang, 1983).

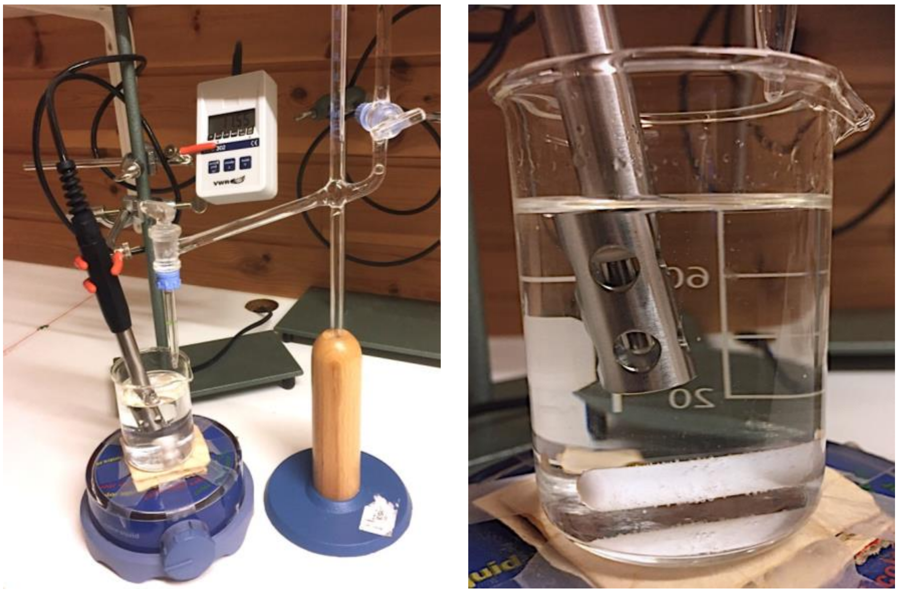
Another way of minimizing errors in this type of analysis is to decrease the angle between the two branches of the curve to as small as possible. A very obtuse angle can result in large deviations with only small errors in the conductance reading. To obtain a small and sharp angle, the reagent should be selected considering the relative mobility of its ionic species. When measuring anions, the conductivity of reagents anion should be lower than that of the anion to be determined in order to produce a steep curve, while the conductivity of cation of the reagent should be large in comparison (Vogel, 1989). Sulfate has a conductance of 80,0 µS/cm per meq/l, and barium 63,6 µS/cm per meq/l. Acetate is often recommended as the counter anion of the titrant when determining anions like sulfate, and has a conductance of 40,9 µS/cm per meq/l (Vogel, 1989).

When determining sulfate by condutometric titration interference caused by anionic and cationic species must be considered. Interference of H^+, coprecipitation of Ca^{2+} and Mg^{2+} and precipitation of bicarbonates and carbonates as $BaCO_3$ is of special concern. Interferences can be solved by pretreating the water samples by cation exchange resin, replacing the interfering of Ca^{2+} and Mg^{2+} with another cation (normally H^+) (Kirowa-Eisner et al. 2007).

Methods

Diluted seawater was chosen as the sample solution for a representative experiment. The diluted seawater was pretreated by ion exchange with Na^+ to remove inferences. The pretreated sea water was weighed to 25 ml and isopropanol was added as an organic solvent to reduce the solubility of the precipitation product. In order to get a 1:3 solution of sea water and isopropanol, about 50 ml (40 g) Isopropanol (p.a.) was added and thoroughly mixed in with a magnetic stirrer.

The conductivity of the mixture was measured while stirring. 0,001 M Barium acetate was added from a glass microburette with 0,01 ml readability. Experimental set up shown in figure 1. Volumes of 0,25 or 0,5 ml of barium acetate was added subsequently between each reading until close to the equivalence point. Four to five readings with additions of 0,25 ml was done after the equivalence point. Conductivity was read while stirring between each addition.



Known concentrations of 10,8 ± 0,2 and 5,4 ± 0,1 mg/l was used, with five replicate measurement for each. Barium acetate was chosen as the titrant and the concentration was standardized against a solution of sodium sulfate of known concentration.

Interferences can be solved by pretreating the water samples by cation exchange resin, replacing the interfering of Ca^{2+} and Mg^{2+} with another cation (normally H^{+}). Exchanging to Na^{+} ions works as a neutralization step as this approach also exchange H^{+}. This reduce background conductance, discard any carbonates and bicarbonates and enable the use of acetate as the titrant (Kirowa-Eisner et al. 2007). Further treatment to remove carbonates was deemed unnecessary and omitted. At pH<8 the carbonic species exist as CO_2 and HCO_3^-.

Results and discussion

Each reading from the replicate measurements gave clean and straight lines as seen in Figure 1 taken from measurement number 4 of the 5,4 mg/l seawater sample. Before reaching equilibrium, there was only a slight decrease or no change in conductivity for some samples, seen in measurement 4. After equilibrium, the conductivity increased to give a steep, straight line for all replicate measurements.

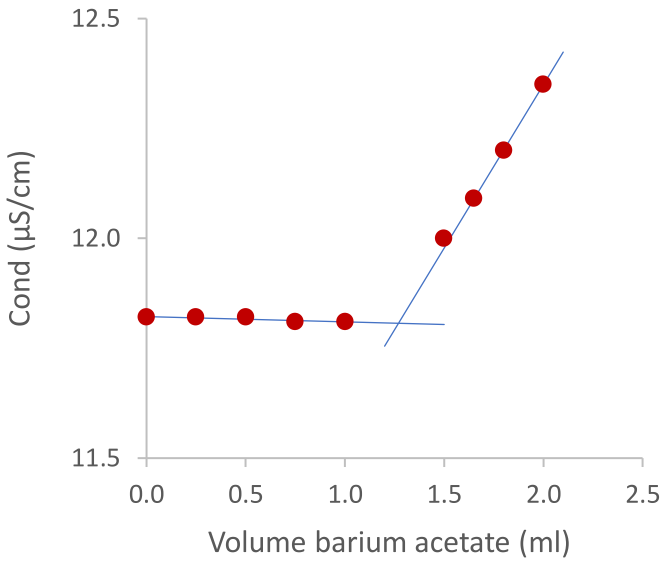


Figure 1. Illustration of curve of measurement number 4 for the 5,4 mg/l seawater sample

With many readings and little variation in the rate of these, we can rule out major deviations. This is also supported by the measured concentration for each replicate as seen in table 1. For the 10,8 mg/l seawater sample, the average of the replicates was calculated to be 10,64 mg/l with a standard deviation of 0,21. With an uncertainty of ± 0,2 for the concentration of the seawater, the method shows good results. This is further supported by the results from the replicates of the 5,4 mg/l seawater sample which had an average of 5,31 mg/l and standard deviation of 0,07. The uncertainty of the concentration for this solution was ± 0,1.

Table 1. Measured concentrations of sulfate compared to known solutions of seawater

Measurement	**Known concentration (mg/l)**	
	10,8 ± 0,2[a]	5,4 ± 0,1[a]
1	10,76	5,44
2	10,45	5,28
3	10,89	5,28
4	10,39	5,29
5	10,73	5,28
Average	**10,64**	**5,31**
Standard deviation	0,21	0,07

[a] Uncertainty as 95% confidence interval

A possible reason for errors can be due to occlusion during precipitation. However, this type of error won't have huge effects after pretreating the sample by ion exchange, and the result indicates little interferences. A test of the same method without ion exchange of the sample would have been a good comparison to check and validate the effect of the pretreatment.

Conclusion

The averages of the measurements were within the uncertainty of concentration of the seawater sample. These results indicate that the condutometric titration method can be applied for measuring low amounts of sulfate in natural water. Pretreatment of the sample minimized possible interferences that might be present in natural waters.

References

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