

Liming of the acidified River Storå, southwestern Norway - the world's first conductivity-controlled liming station?

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Sammendrag

Kalking av den forsurede Storåa; verdens første kalkdoserer styrt av elvevannets ledningsevne?

Dagens kalkdoserere er vanligvis styrt av en kombinasjon av vannføring og pH. Imidlertid er pH-måling i ionevakt vann utfordrende, noe som forsterkes av krevende miljøforhold. Her viser vi at ionebytteeffektene som skjer i nedslagsfeltene i kystnære områder kan benyttes til å styre doserere ved hjelp av konduktiviteten. Dette systemet har vist seg å være robust og krever lite tilsyn og vedlikehold. Til tross for høyst varierende vannføring og vannkjemi har den konduktivitetsstyrte dosereren i Bjordal produsert stabil vannkvalitet i Storå i 10 år. Episoder med lave pH-verdier har stort sett blitt forårsaket av tekniske forhold, ikke av selve styringssystemet.

Summary

Modern liming stations are usually controlled using a combination of water discharge and pH. However, measuring pH in low-conductivity water under harsh environmental conditions is demanding. Moreover, the electrode requires frequent services, such as e.g. calibration, refill of KCl-solution, and cleaning. In the current work, we demonstrate that ion exchange effects occurring in coastal watersheds may be applied to control liming using conductivity. This system

has shown to be robust and requires a minimum of services. Despite highly variable discharge and water chemistry, the conductivity-controlled Bjordal liming station has produced stable water chemistry in River Storå for the past 10 years. Incidents with low pH were largely attributed to technical issues, not to the control system itself.

Introduction

Southern Norway was severely affected by acidification and fish death during the mid and late 1900s (Jensen & Snekvik 1972, Wright & Snekvik 1978, Sevaldud & Muniz 1980, Hesthagen et al. 1999). In the short term, liming was applied as a "first aid" while waiting for emission reductions. In the beginning, this included lake liming. River liming was included in the national liming program from the mid-1980s and expanded in volume from the mid-1990s.

The first liming station in Norway, the Audna station, was established in 1985. Initially, the dosing was controlled by water discharge only. Later, the station was modified, and pH was included as a control variable. Today, the majority of the liming stations in Norway are controlled either by a combination of water discharge and upstream pH or by downstream

pH. Here, lime dosing is regulated to maintain a seasonally stratified target pH.

Numerous studies have emphasized the challenges associated with determining pH in low-conductivity waters, even when performed in a controlled laboratory environment (e.g. Covington et al. 1983, Hindar 1984, Covington et al. 1985, Neal & Thomas 1985, Busenberg & Plummer 1987). Variable temperatures and harsh environmental conditions enhance these problems. Furthermore, the pH-electrode requires frequent services such as recalibration, refill of KCl-solution, and cleaning. Finally, according to the manufacturers, a pH electrode has a typical shelf life of 1-2 years. Therefore, a more robust and less service-requiring alternative to pH control is desirable.

Episodes of high sea salt exposure may greatly increase conductivity and consequently also the Na^+ concentrations in surface waters. During

such episodes, H^+ and Al^{3+} adsorbed to soil-colloids are exchanged by Na^+ , causing acidic runoff (Hindar et al. 1994). This is referred to as a “sea salt episode”. The consequence is a negative correlation between pH and conductivity (Enge & Hemmingsen 2010, Enge 2022), a relationship which is used for estimating the required lime dose.

The Bjordal liming station has recently been the focus of a MSc thesis (Mo 2020), primarily borrowing data from “our” monitoring program, sampled during the six years 2014-2020. Briefly, the study concluded that the station produced a stable pH, and explained deviant values by technical issues.

The current study has a broader objective. Data from the 10 years 2014-2024 were compiled. Topics such as declining acidification, the effects of “brownification”, and the effects of reduced deposition of sea salts are thoroughly discussed.

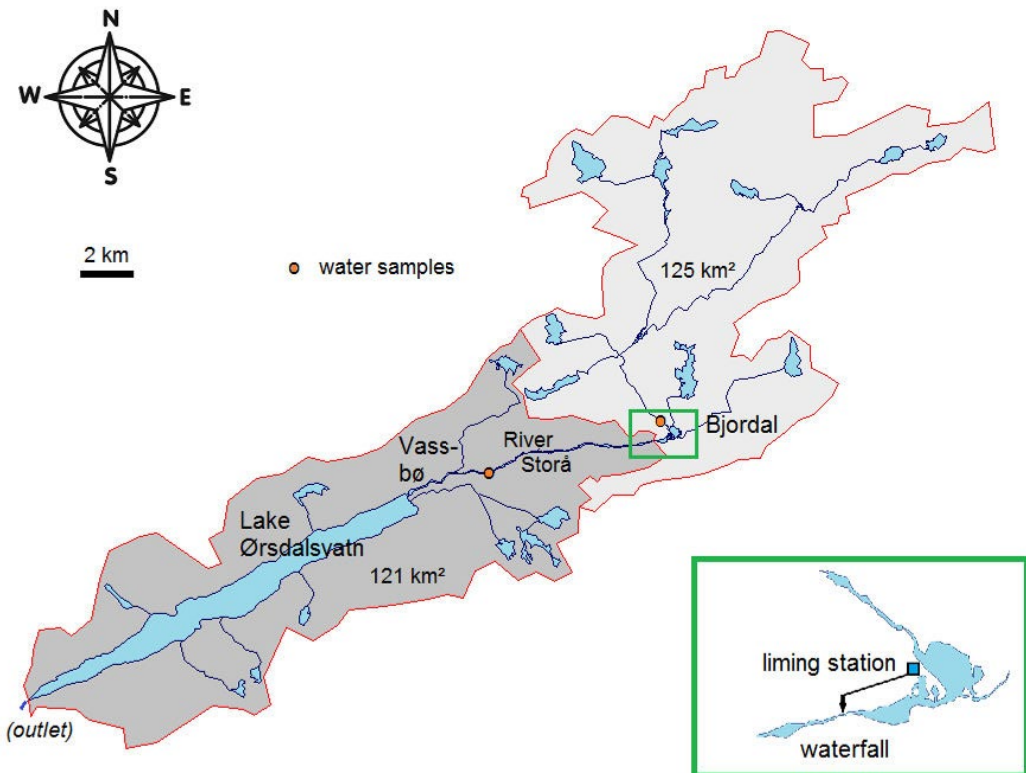


Fig. 1. Overview of the total watershed to Lake Ørsdalsvatn. The light grey area represents the watershed upstream of the Bjordal liming station. The detailed map (green frame) shows the location of the liming station. In a 500 m plastic pipe, the lime slurry is led to the top of the Bjordal waterfall.

Based on 10 years of data, our study will try to answer the following two questions: i) Does the Bjordal liming station produce a stable water chemistry suitable for salmon? ii) Is this control system capable of handling declining acidification? Answering these questions require a comprehensive analysis of water chemistry trends.

Study area

Lake Ørsdalsvatn (63 m a.s.l.) and the upstream River Storå (Fig. 1) represent a tributary to the River Bjerkreim. The watershed upstream of the liming station ranges from 209 m a.s.l. at Bjordal to 985 m a.s.l. at Myrfjell. The bedrock weathers slowly and is mainly comprised of gneiss and granite (ngu.no). Most of the watershed consists of barren mountains, but in the major valleys, scattered birch woods are found.

River Storå at Bjordal has a watershed of 125 km². The annual runoff is 363 Mm³/yr, equal to an average discharge of 11.5 m³/s (nevina.nve.no). The average discharge during the 10 years 2014-2024 was 11.8 m³/s, equal to 372 Mm³/yr (sildre.nve.no).

The large Lake Ørsdalsvatn (area=12 km², max depth=243m), located seven km downstream of Bjordal, represents a total watershed of 246 km², and the annual runoff is 683 Mm³ (nevina.nve.no). Thus, the Bjordal watershed represents 53% of the total runoff from Lake Ørsdalsvatn.

The area is characterized by highly unstable hydrology. Maximum discharge during the study period was measured at 329 m³/s (06.12.2015), 30 times the average discharge. The lowest measured discharge, 0.22 m³/s (27.07.2018), equals 2% of the average discharge. Subsequently, the factor Q_{MAX}/Q_{MIN} was approximately 1500.

Due to acidification, the brown trout (*Salmo trutta*) populations in most of the lakes in the Bjordal watershed became extinct during the 1960s and 1970s (Sevaldrud & Muniz 1980). In the 1980s, most of the lakes in the Bjordal watershed had pH values <5.0 (Enge 2013a). In River Storå, the salmon (*Salmo salar*) had been absent ever since the late 1800s.

Due to a combination of declining acidification (Enge 2013a) and upstream lake liming, pH and alkalinity in River Storå at Vassbø was 5.59±0.34 and 8±9 µeq/l (n=46), respectively, in 2012 (Enge 2013b).

The liming station is located at Bjordal, and the outlet is led to the top of the Bjordal waterfall (Fig. 1). When the liming station was established, many of the upstream liming projects were either reduced or terminated.

The liming station

The Bjordal liming station was designed to use lime slurry as the liming agent. This liming agent is easily soluble. The station was built during the autumn of 2013, and the liming started in November. Maximum capacity equals a water discharge of 105 m³/s at maximum lime dose.

Using data from 2011 and 2012, Enge (2013b) established the following relationship between alkalinity and conductivity (units: µeq/l, µS/cm):

$$ALK_E = 65.2 - 19.6 \times \ln(\text{Conductivity}) \quad (r^2=0.35, n=88)$$

The difference between the conductivity-estimated alkalinity and target alkalinity determines the lime dosage. Initially, an alkalinity, ALK_E (Henriksen 1982), of 25 µeq/l was applied as the target alkalinity, corresponding to a pH-value of 6.1 (Enge 2013b). Recalculated to the currently used “ ALK_{02} ” (Enge & Garmo 2021), this equals 23 µeq/l. The preliminary dose table, made in 2013 (Enge 2013b), has been used ever since.

The control system has shown to be robust and reliable and has required a minimum of services. The conductivity data is available online, and the result is consecutively checked with data from the weekly sampling. During the 10 years 2014-2024, the conductivity cell has been calibrated twice, and the total adjustment was 5%. To our knowledge, this liming station, controlled by conductivity, is one of a kind.

Material and methods

The monitoring program

The water chemistry monitoring program was intended to check the functionality of the liming station and simultaneously ensure a suitable water chemistry for salmon. Therefore, the parameters pH, Ca, alkalinity, Al, and color were included in the program. Moreover, for checking the control system, conductivity, Cl, and Na were also included. In retrospect, we realize that analysing all major ions would have been recommendable.

In the current study, we used data from the liming period (2014-2024) from the two locations “Vassbø”, and “Bjordal”, the latter upstream of the liming (Fig. 1). A third location, located one km downstream of the liming station, was discontinued in 2022 and will not be referred to further herein.

Sampling

Water was sampled weekly in 250 ml acid-washed HDPE bottles. The samples were mailed to the laboratory in Stavanger. In 2022 and 2023, the average time from sampling to arrival was 2.9 ± 1.4 days. For most parameters, this delay is acceptable (Enge 2019, Enge et al. 2021b), but may cause 1-2 $\mu\text{g/l}$ underestimation of LAl (Hana 2024).

Water chemistry measurements

pH and conductivity were determined according to “Standard Methods” (Eaton et al. 1995). The pH-electrodes used throughout the period, Radiometer GK2401C and Hamilton LIQ-Glass, are both suitable for low ionic strength measurements. The color was measured photometrically according to the previous Norwegian Standard 4722. Due to low turbidity, the samples were measured without filtration. A wavelength of 445 nm and 20 mm glass cuvettes were used. Alkalinity was determined by single endpoint acidimetric titration to pH=4.50. Until recently, the ALK_E approach (Henriksen 1982) was applied for the subsequent calculation of the alkalinity. However, ALK_{02} (Enge & Garmo 2021) has shown to be a more accurate representation

of carbonate alkalinity in low-buffered waters and has been applied in recent years. Previous ALK_E data were recalculated to ALK_{02} using an empirical relationship based on 2022 and 2023 data (unit: $\mu\text{eq/l}$):

$$\text{ALK}_{02} = 0.943 \times \text{ALK}_E - 0.56 \quad (r^2=1.000, n=212)$$

Al was determined according to “Standard Methods” (ECR method). Labile Al was calculated as the difference between Al measured with/without ion exchange (Amberlite IR120, Na^+). Ca, Na, and Cl were determined using Radiometer ion selective electrodes, according to the electrode manuals. For documentation of quality and accuracy, see e.g. Enge et al. (2021a).

To estimate the “original” alkalinity, i.e. the alkalinity without any acidification, Henriksen (1980) suggested the formula $\text{ALK}_0 = 1.21 \times \text{Ca}^*$. Here, Ca^* is the sea salt adjusted Ca-concentration (all concentrations in $\mu\text{eq/l}$). The applicability of this formula to waters in this part of Norway was verified by Stølen & Enge (2019).

Data sets

The total data set comprises a total of 1032 samples, of which 516 samples were collected from each of the locations Bjordal and Vassbø. However, due to a few missing results from single parameters, 496 samples from Bjordal and 502 samples from Vassbø include the common parameters pH, conductivity, color, alkalinity, Ca, Na, and Cl. To ensure comparability, all water chemistry *calculations* were performed using this data set.

In addition to our monitoring, Vassbø is also included in the national monitoring program by the Norwegian Environment Agency (NEA). Beyond establishing an empirical relationship between TOC and color, data from this program has not been used.

Results

Water chemistry upstream of the liming station

The marine ion contribution, represented by Cl, dominated the water chemistry in River Storåna (Fig. 2a). The coefficient 3.8 $\mu\text{S/cm}$ per mg Cl/l is

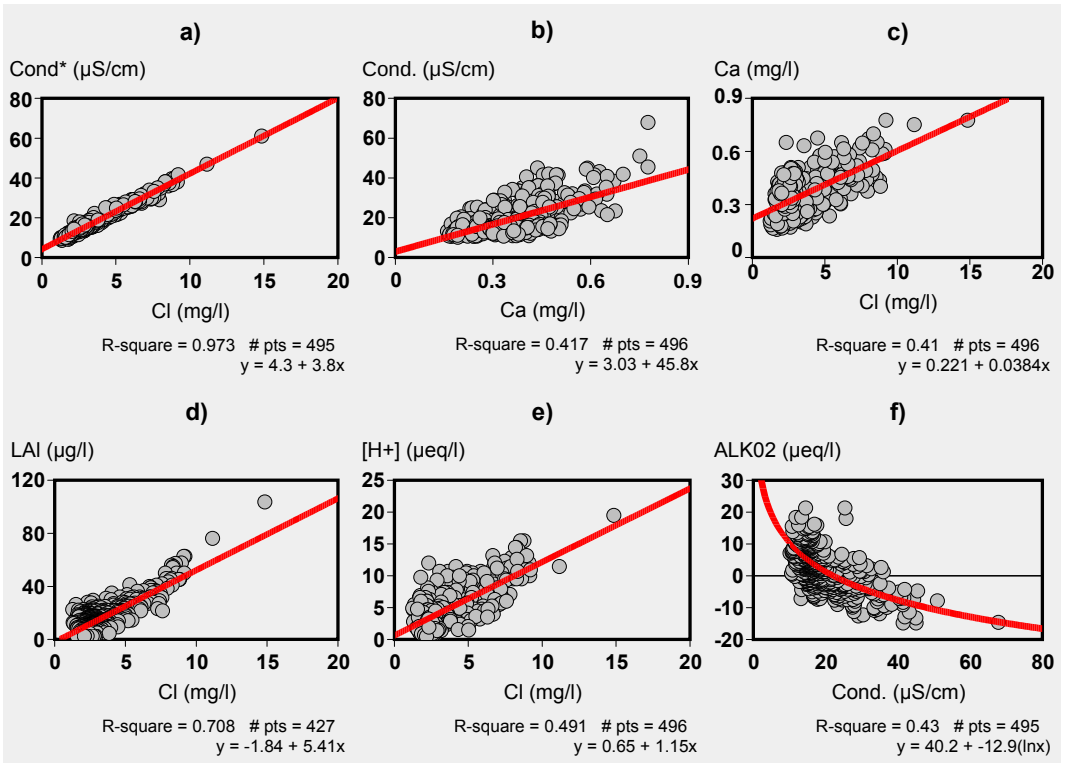


Fig. 2. Linear regressions of conductivity (*: adjusted for the H⁺-contribution) vs. Cl (a), and Ca (b). Effects of Cl (“sea salt exposure”) on parameters such as Ca (c), LAl (d), and H⁺ (e). Curve (f) shows the relationship between ALK₀₂ and conductivity.

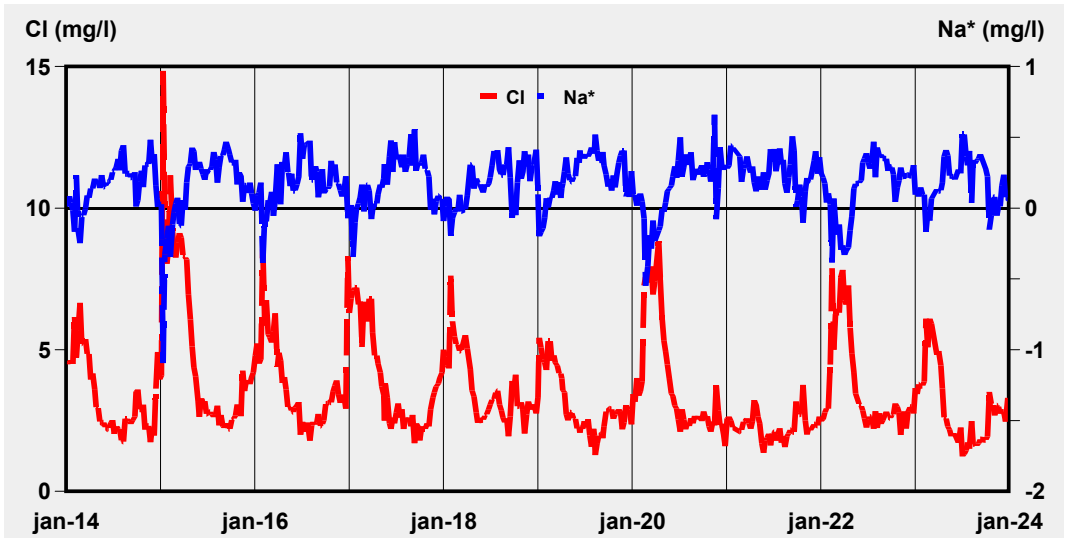


Fig. 3. Demonstration of ion exchange effects (Bjoldal-data): High Cl-values are associated with low values for Na* (non-marine Na), and vice versa ($n_{Cl}=n_{Na^*}=512$). Notice the severe sea salt episode in Jan. 2015 (Cl=14.8 mg/l, Na*=-1.1 mg/l).

close to the theoretical conductivity/Cl ratio in seawater when recalculated to current ionic strength. The geological contribution, represented by Ca, was less prominent (Fig. 2b). This is also supported by a multiple regression of conductivity vs. both Cl and Ca. Here, Ca did not improve the regression significantly ($r^2=0.973$ to 0.976).

Due to ion exchange effects, marine ions indirectly determined the concentrations of many of the other ions (Fig. 2c, 2d, 2e), effects that are crucial for understanding the conductivity regulation of the liming station. All the referred relationships (Fig. 2) were significant ($p<0.001$).

Alkalinity was negatively correlated with conductivity ($r^2=0.43$) (Fig. 2f), a relationship used to regulate the liming. A slightly better regression was obtained by including time (date) in the regression ($r^2=0.47$), demonstrating the effect of declining acidification. The sea salt exposure, expressed as Cl, was most prominent during winter, causing low Na^+ values (Fig. 3).

Water chemistry and salmon

92% of the pH values from Vassbø were fully acceptable for salmon, i.e. >6.0 (Fig. 4a). The lowest value, $\text{pH}=5.26$, was dated 09.05.2016. 15% of the LAI-values (Fig. 4b) were $>10 \mu\text{g/l}$, which is potentially detrimental to salmon. The maximum value for LAI was registered on 28.03.2017, being $25 \mu\text{g/l}$. These two incidents were associated with technical issues in the liming station.

Time trends and declining acidification

Selected parameters were tested for time trends (Tab. 1). Increasing pH (+0.38) and alkalinity (+9.5 $\mu\text{eq/l}$) and a decline in Ca (-0.08 mg/l), Al (-17.2 $\mu\text{g/l}$), and LAI (-12.4 $\mu\text{g/l}$) were registered at Bjordal during the 10 years 2014-2024 (Tab. 1), being typical for water chemistry recovering from acidification. Based on the difference between estimated original ALK and current ALK, the acidification status recovered by 12.2 $\mu\text{eq/l}$ during the period (Fig. 5), approximately equal to the observed increase in alkalinity.

Tab. 1. Time trends for selected parameters. (*: see explanations in the text)

Site	Parameter	Constant	Coefficient yr^{-1}	r^2	p	n
Bjordal	pH	0.8833	0.0380	0.1647	0.0000	496
Bjordal	ALK_{02}	-110.6367	0.9524	0.1775	0.0000	495
Bjordal	Ca	1.3330	-0.0082	0.0491	0.0000	496
Bjordal	Recovery*	-156.9261	1.2241	0.2231	0.0000	496
Bjordal	LAI	165.7337	-1.2403	0.0731	0.0000	412
Bjordal	Al	256.9060	-1.7152	0.0571	0.0000	412
Bjordal	Conductivity	114.1989	-0.7977	0.0918	0.0000	496
Bjordal	H^+ -conductivity	19.4025	-0.1493	0.1754	0.0000	496
Bjordal	Cl	21.5232	-0.1514	0.0598	0.0000	496
Bjordal	Na	11.5635	-0.0793	0.0725	0.0000	496
Bjordal	Color	-229.4542	2.1480	0.1553	0.0000	496
Vassbø	pH	7.4451	-0.0100	0.0210	0.0011	502
Vassbø	ALK_{02}	96.7913	-0.5529	0.0221	0.0008	502
Vassbø	Ca	5.2727	-0.0367	0.1173	0.0000	502
Vassbø	LAI	-14.8007	0.1739	0.0128	0.0210	416
Vassbø	Al	93.3146	-0.4416	0.0057	0.1219	416
Vassbø	Color	-193.8329	1.8557	0.1183	0.0000	502

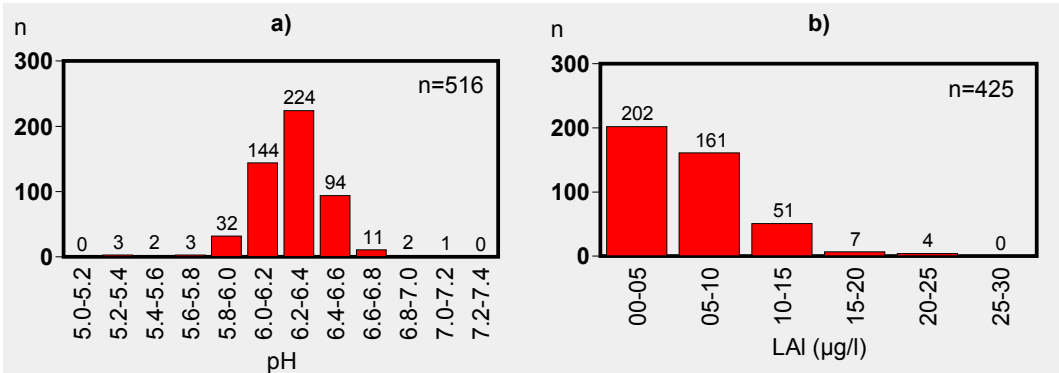


Fig. 4. pH (a) and LAI-values (b) in River Storå at Vassbø 2014-2024.

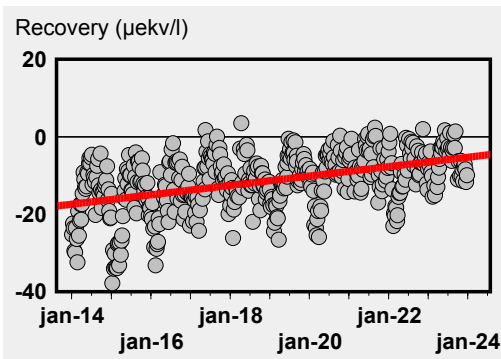


Fig. 5. Recovery from acidification, here estimated as the difference between the original alkalinity and the observed alkalinity (n=496). Note the very strong acidification associated with the sea salt episode in January 2015.

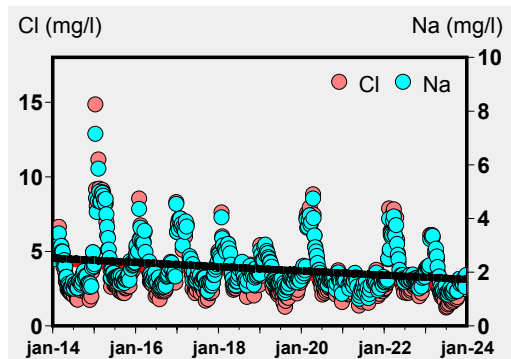


Fig. 6. Plot of Cl and Na during 2014-2024. The axes are scaled relatively to the Cl/Na ratio in seawater. The trend line includes two overlapping regression lines.

During the study period, Cl and Na at Bjordal decreased by 1.51 mg/l and 0.79 mg/l, respectively. The ratio Na-decrease/Cl-decrease was 0.53, close to the Na/Cl ratio in seawater (0.56). In a time plot, the two regression lines, scaled relatively to the Na/Cl ratio in seawater, were close to overlapping (Fig. 6).

Upstream of Bjordal, termination of lake liming, equal to 27 t of “BioKalk”/yr, represents a Ca-decrease of 0.02 mg/l. Therefore, 0.06 mg/l of the observed reduction (-0.08 mg/l) is attributable to reduced mobilization of Ca from the catchment, being effects of “recovery” from acidification. At Vassbø, a decrease in the liming parameters pH (-0.10), Ca (-0.37 mg/l), and alkalinity (-5.5 µeq/l) was registered. In these changes, a 0.08 mg/l reduction in Ca and an

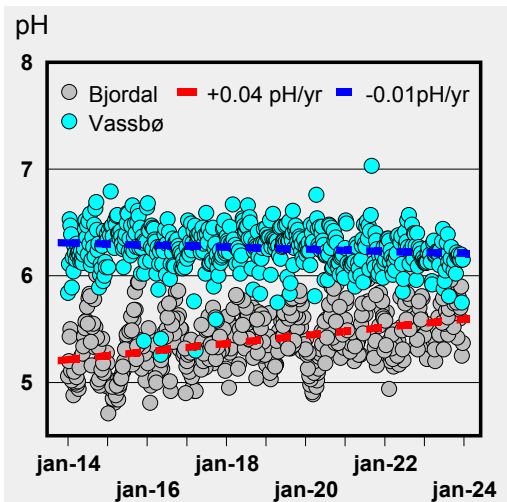


Fig. 7. pH values at Bjordal (n=496) and Vassbø (n=502) during 2014-2024.

increase in alkalinity of 9.5 $\mu\text{eq/l}$ at Bjordal is included. Thus, reduced liming represents -0.29 mg/l (-14.5 $\mu\text{eq/l}$) of Ca and -15.0 $\mu\text{eq/l}$ of alkalinity.

Despite the reduced liming, only a limited reduction in pH was registered at Vassbø (Fig. 7). However, a distinct increase in pH occurred upstream of liming. Apparently, the liming station has compensated for the reduced acidification.

At Vassbø, a limited increase in LAI during the study period, was found (+1.74 $\mu\text{g/l}$) (Tab. 1). This effect may be attributable to slightly decreasing pH. No trend in AI was observed ($p>0.05$).

In total, conductivity at Bjordal declined by 7.98 $\mu\text{S/cm}$ during the study period. The decrease in conductivity, caused by decreasing Cl (“sea salts”), was calculated to 5.75 $\mu\text{S/cm}$, using the annual decrease in Cl $\times 10 \text{ yr} \times$ the Cl/conductivity ratio (Fig. 2a). The decrease in $[\text{H}^+]$ caused a conductivity reduction of 1.49 $\mu\text{S/cm}$. The difference, 0.74 $\mu\text{S/cm}$, may be attributed to reduced mobilization of ions from the watershed and reduced deposition of acidic components, indicating that direct and/or indirect effects of declining acidification accounted for about 30% of the reductions in conductivity. Therefore, declining acidification is only partly the cause of the reduction in lime dose.

Color

A considerable increase in color was observed (Tab. 1). Furthermore, color was distinctly correlated to Cl ($r^2=0.423$, $n=998$) (Fig. 8).

Color had a pronounced effect on the pH values. Half of the samples at Vassbø with $\text{pH}<6.00$ had color $>40 \text{ mg Pt/l}$. In a multiple regression on pH vs. date, $\log(\text{Ca})$, conductivity, and color, the first two parameters contributed positively ($p<0.001$), while a negative contribution ($p<0.001$) from the two latter parameters was established ($r^2=0.854$, $n=997$). The coefficient for color was determined to be $-0.0033 \pm 0.0005 \text{ pH/color unit}$. Consequently, the 18.6 mg/l increase in color (Vassbø) corresponds to a reduction of 0.06 pH units during the study period. The maximum registered color

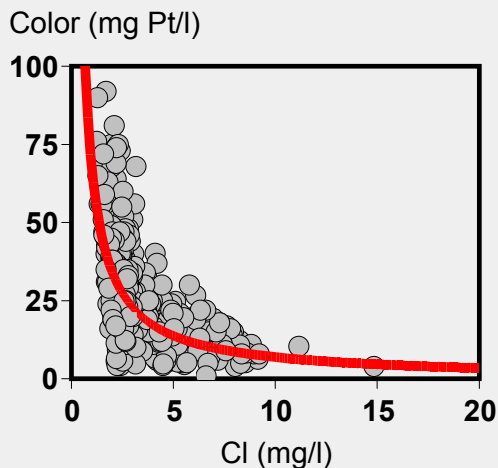


Fig. 8. Color vs. Cl. Data from Bjordal ($n=496$) and Vassbø ($n=502$) from the 10 years 2014-2024.

value (89 mg Pt/l) represents a theoretical depression of 0.29 pH.

Multiple regression on ALK_{02} vs. date, Ca, conductivity, and color ($r^2=0.918$, $n=997$) yielded fairly the same result as for pH, except that no effect of color was detected ($p>0.05$). However, if Cl replaced conductivity in the same regression, color contributed negatively ($p<0.05$) to alkalinity.

TOC was included in the official monitoring at Vassbø (NEA). Because TOC is currently the preferred measure of organic matter in natural waters, a comparison to the parameter “color” is relevant. TOC was highly correlated to our concurrent (± 3 days) measurements of color ($r^2=0.838$, $n=38$). Here, we use data from August 2020 - 2024 (MDIR 2020, MDIR 2021, MDIR 2022, MDIR 2024) which originate from the same laboratory (change of laboratory in Aug. 2020).

The intercept was not significant ($p>0.05$). A regression line “forced” through zero yielded (units: mg C/l, mg Pt/l):

$$\text{TOC} = 0.080 \times \text{Color}$$

Based on the total material from both locations ($n=998$), the color was $26 \pm 16 \text{ mg Pt/l}$, corresponding to $\text{TOC} = 2.1 \pm 1.3 \text{ mg C/l}$.

Discussion

The Bjordal liming station has produced stable water chemistry in River Storå for the past 10 years. At Vassbø, the vast majority of the pH and LAl-values have been >6.0 and $<10 \mu\text{g/l}$, respectively. It is important to emphasize that the target pH in River Storå, presented in the official reports from MDIR, is not correct. A target *alkalinity* has been defined, not a pH value (Enge 2013b).

Even severe acidification episodes have effectively been ameliorated. During the sea salt episode in January 2015, pH and LAl at Bjordal were measured at 4.71 and $104 \mu\text{g/l}$, respectively. At Vassbø, downstream of liming, the corresponding values were 6.08 and $9 \mu\text{g/l}$, demonstrating perfect detoxification of the acidic water.

During the study period, ion strength and acidification decreased at Bjordal while color and pH increased. In the past decades, such effects have also been registered globally (Monteith et al. 2007). Improvements in acidity parameters were caused by the decline in S and N deposition, while the observed dilution of the water chemistry was caused primarily by a reduced supply of marine ions. The latter appears as declining values for Cl, Na (Fig. 6) and/or conductivity, effects also found in other studies (Hessen et al. 2016, Enge et al. 2021a, de Wit et al. 2023). During the 10 years 2014–2024, the Cl and Na-values in River Storåna were reduced by 35% and 31%, respectively. The increase in color is also explainable by the reduced supply of marine ions. In the Cl-range $<5 \text{ mg/l}$, even insignificant changes in Cl may cause substantial changes in color (Fig. 8). It should be mentioned that in Sira, the neighbouring watershed east of Bjordal, similar color changes have been observed (Enge, unpublished data).

Organic matter in pristine surface waters is largely comprised of brownish-tinted humic substances. Empirically, the TOC/color ratio was determined to be 0.080, being close to the color/TOC ratio of 10, as suggested by Wright et al. (2011) for tributaries to the adjacent Lake Byrkjeldsvatn. Due to the relatively high

content of carboxyl groups (Snoeyink & Jenkins 1980), humic substances have an acidic nature. This explained the distinct negative effect of color on pH found in our data material. During the study period, the color increase in River Storåna at Vassbø represented a reduction of 0.06 pH. This demonstrates that the ongoing “brownification” restricts the return to the pre-acidification state, as also recently found in a large national study (de Wit et al. 2023).

Lake Ørsdalsvatn, located 7 km downstream of Bjordal, was limed for the first time in 1995 using 4000 tons of limestone powder. In the following years, 1000 tons were used annually. When the liming station in Bjordal was established, the liming of Lake Ørsdalsvatn was discontinued. However, there was a concern that the liming in Bjordal was insufficient to meet the requirement for lime in Lake Ørsdalsvatn. In a few years, it became evident that the Bjordal-liming provided sufficient effect in the downstream Lake Ørsdalsvatn.

Three causes of low or lack of dosing were discovered. Several incidents of pump failure have been registered during the study period. Moreover, episodes with foreign objects blocking the water intake pipe have also been registered. In December 2015, low pH was caused by an extreme water discharge, beyond the capacity of the liming station. Incidents with very high values for Ca and pH (Fig. 7) were also registered. On three occasions, pump and/or valve failure caused river water to be pumped into the lime tanks (Svein Olav Tengedal, pers. comm.). To discard the diluted lime, the dosage was increased considerably, which caused high values for pH, Ca, and alkalinity in the river. Occasionally, another problem occurred during winter, causing the same effect. The liming station determines the water discharge using the water level in the river. During hard winters, ice may raise the water level, causing the liming station to overestimate the discharge and, subsequently, overestimate the lime dosage. Therefore, the episodes with severely deviant water chemistry were attributed to technical issues, not to the regulation system itself.

In coastal watersheds, variations in the Na/Cl ratio caused by ion exchange largely determine the seasonal variations in pH (Enge 2022), while the pH level primarily is determined by the acidification status. Therefore, the conductivity control system is less effective in cases where these variations are levelled out, as in lake systems. A regulation based solely on discharge may work adequately in such stable systems. Consequently, conductivity control is primarily applicable in coastal river systems, especially in acidic systems where H^+ makes up an appreciable part of the conductivity.

Acknowledgements

The authors thank Fredrik Berg-Larsen and Henrik van der Hoeven for participating in the water chemistry analysis and Tor Sigve Hovland and Josef Malmei for water sampling throughout the project period. We also thank Øyvind Garmo for valuable comments to the manuscript and Malcolm Kelland for improving the language. Last but not least, we thank Svein Olav Tengesdal (Bjerkreim Kommune) who has administered the liming all these years.

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