Liming freshwater systems in Norway by applying carbonate materials from geological deposits – a review

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Samandrag

Kalking av ferskvassystem i Noreg ved utnytting av karbonatiske materialar frå geologiske avsetningar – eit oversyn. Fennoskandia framviser generelt metamorfe, harde bergartar. Dei fleste områda er følsame mot forsurande forureiningar, og sur nedbør har gitt skadar i minst 150 år, og vil framleis vere eit problem. Men det finst karbonatbergartar i enkelte område, og utnytting av desse basiske sambindingane avhjelper dei giftige effektane av surt vatn, i innsjøar, elvar og terrestrisk i nedslagsfelt. Finland har vore tilbakehalden med desse kalkingstiltaka, mens Sverige og Noreg nytta desse økosystemressursane i omfattande grad sidan 1980, med stor suksess i vassystem. Noreg nyttar kalksteinar, kalksteinsmarmor, dolomittmarmor og skjelsand, årleg i mengder av 20.-40.000 tonn årleg, mest i ei rekke viktige lakseelvar. Kvalitetskrava er svært høge: reinleik av karbonat, derav høg kjemisk effektivitet, strenge øvre grenser for sporelement, tronge krav til partikkelstorleikar, d.v.s. mikronisert for innsjøar og elvesystem, selektivt grovt materiale for gytegrunn i elvar og bekkar.

Summary

The Fennoscandian region of North Europe generally presents a hard rock metamorphosed geology. Most areas are susceptible to acidifying pollution, with acid rain for more than 150 years, and still being a problem. However, certain areas contain carbonate rocks and deposits, and exploiting these basic compounds mediates toxic effects of acid water, in lakes, rivers and terrestrial parts of watersheds. Finland has been reluctant with these liming efforts, whilst Sweden and Norway extensively have applied these ecosystem resources since about 1980, with great success to water systems. In Norway limestones, marbles, marble dolomites and shell sand are applied, in recent years at an annual rate of 20-40 0000 tons, with priority to salmon rivers. Quality requirements are very high: purity of the carbonates, strict upper limits of trace elements, and tight particle size distribution, i.e., micronized for lake and river systems, selectively coarse for spawning grounds in rivers and creeks.

Introduction

Acidification of freshwaters comes from different sources, from natural ones like volcanic activity, aerosols from oceans with sulphur, excess of precipitation with carbonic acid from the atmosphere, to anthropogenic pollution by S and N compounds. This man-made acidification markedly increased since the industrial revolution from 1840 onward. Figure 1 shows critical loads of acid deposits to landside in 1980 and 2010, levels that would lead to the lowering of pH and alkalinity of soils and underlying sediments. This burden reached its maximum at about 1980-90, and then started to decline due to reduced emissions following international protocols on actions of cleaning. However, this constitutes still a negative impact on nature, acidifying many lake districts and river systems, and depleting nutrients from soils and impoverishing botany (Dahl et. al, 1967).

Carbonates applied for ecosystem services

Interaction with Fennoscandian geology

Europe displays a mosaic of different bedrocks; however, several countries on the continent have regions of buffered, alkaline rocks and soils. Parallelly, the weathering processes have been ongoing since and during the Tertiary era, and top sediments and soils may be depleted in nutrients, today harming forest vitality, as in Germany and the Czech Republic. Harmed lake districts are less frequent to find in all of Europe but occur in northern parts of Germany and Poland on poor geology.

However, Northern Europe with its Baltic shield profoundly differs with hard rock metamorphosed geology in most regions. This includes Norway, Sweden (except parts of Skåne in the South) and Finland, making the region very susceptible to the extra burden of man-made acidification, in particular freshwater systems, but also surrounding soils of the watersheds.

Figure 2 shows main features of the Norwegian bedrock geology and on to the border areas to Sweden.

Most geological units of Norway are classified as highly metamorphosed, with some exceptions mainly in south-eastern Norway: the Oslo Graben, and the Mjøsa region into its approximate valley and mountain areas in its north-western direction. Most rocks are weakly buffered silicate rocks, first of all the Sveco-Norwegian bedrocks (Precambrian basement) and the Western gneiss region and several sandstones in the Caledonian faults and basins.

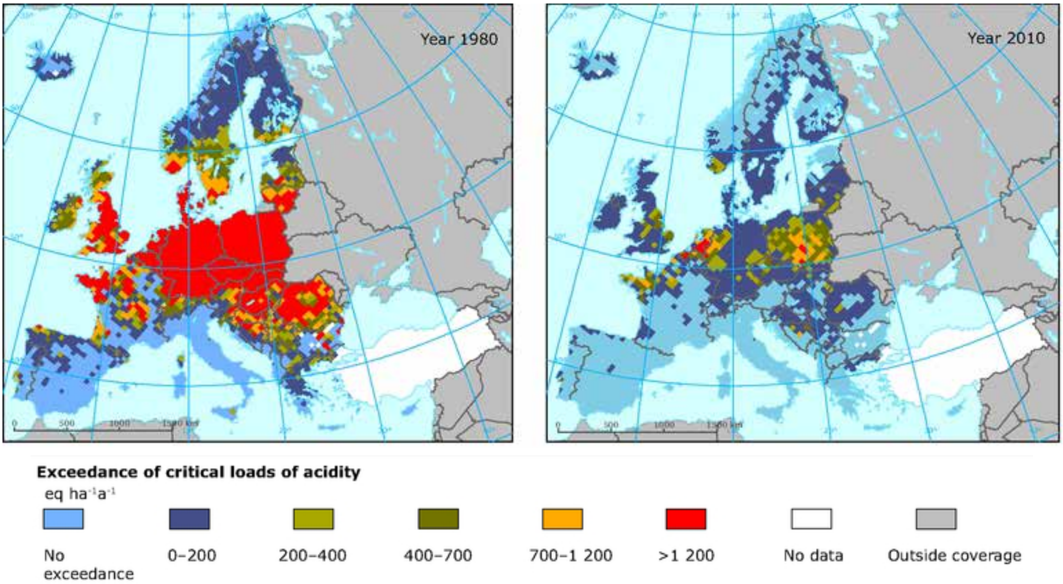

Figure 1. Exceedance of critical loads in Western and Central Europe 1980 and 2010, eq. ha^{-1} a^{-1} (European Environment Agency).

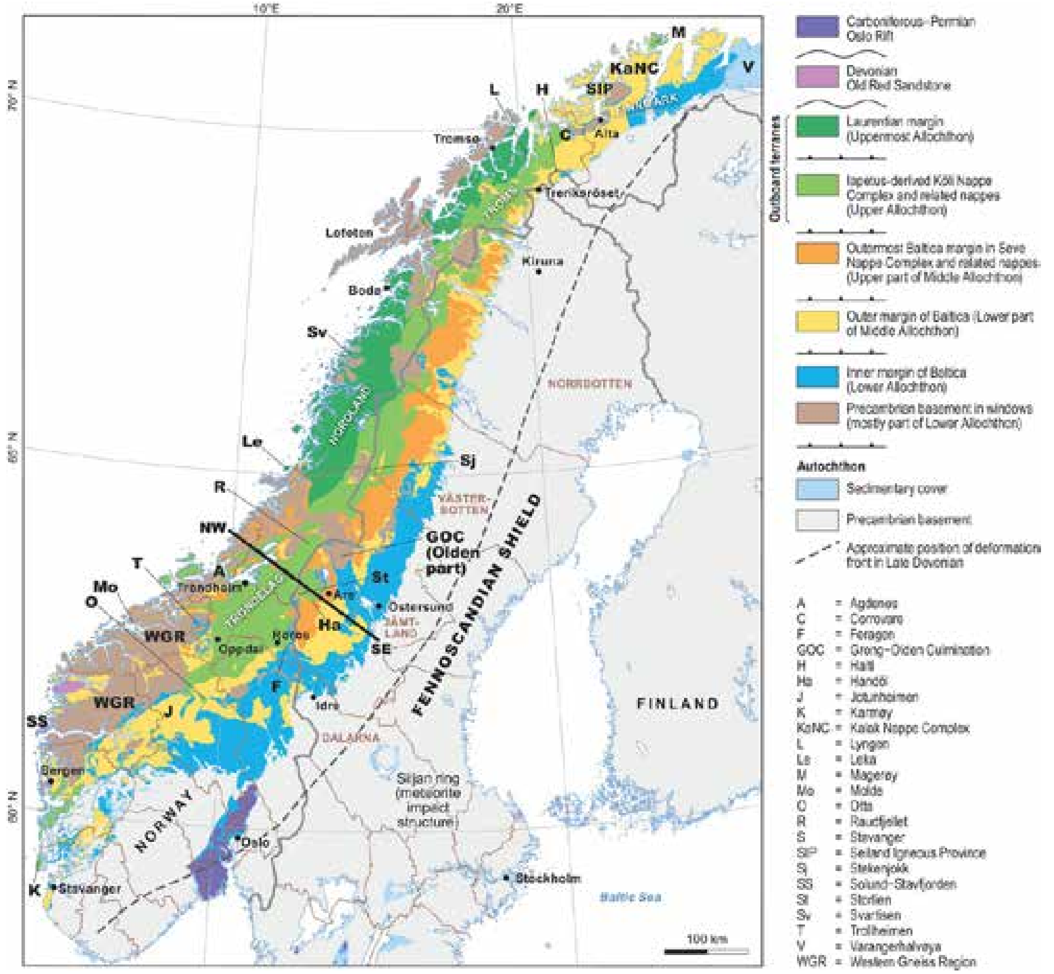

Figure 2. Main bedrock units of Norway including border regions of Sweden (The Geological Society of London, Memoirs – Lyell Collection).

However, limestones occur in parts of the South East, partly transformed in Trøndelag, marbles of limestone and dolomite in the Western gneiss region, but predominantly in vast massives in North Norway, in particular in the Laurentian margin of the Caledonides. Shell sand and coral sand are located as coastal sediments, the latter from Trøndelag to the North. All these carbonates play a vital role mitigating damages by acidification in other parts of Norway.

Research on acidification and freshwater liming

The first worries about fish death were evoked around the year 1900 at the Mandal River in southmost Norway, when dead salmons were detected. A slow decline in salmon population followed. From the 1920's reports from the interior low mountain areas of the same region came, saying that fishes became larger, but fewer and many lakes became empty (Dahl, 1921a,b; Dahl, 1926). Alarms were conveyed also from Sweden (Tamm, 1976), and research started there a little ahead of the Norwegian scientific institutes. 1972-80 a large state project was funded in Norway, SNSF (Effects of Acid Rain on Forest and Fish) (SNSF 1976, Overrein et al., 1981). Gradually it was confirmed that the low pH in the water itself did not kill biological life, but induced Al dissolution into toxic aluminium

(Al^{3+}) from sediments (Wright and Gjessing, 1976). The mechanisms were understood, and from 1983 the first freshwater liming projects in Norway started, and grew to be a part of the specialised liming effort, as research continued simultaneously. The Directorate of Nature Management (later The Environmental Protection Agency) in fact became the predominant customer, together with smaller projects at salmon breeding facilities (spawn production).

Lime industry for environment measures

With limited areas of carbonate rocks in Norway, these alkaline rocks of neutralising capacity have to be processed by milling for transport and use in the acidified regions, in order to yield ecosystem assistance against acid pollution in large parts for South Norway.

The total application of liming materials for rivers and lakes will be quite restricted as compared with other carbonate products for the industry, with annual variations in the range 20-40 000 tons, pending mainly on precipitation and runoff. Therefore, this production of fresh water liming materials has been concentrated to a few lime works.

Most nearby, the Ordovician-Silurian limestones of the Oslo Graben have historically been widely used, as in Bærum at Oslo, and Brevik of the cement industry further south. However, these were not always so concentrated on carbonates, often down to 80%, and in spite of good position for liming operations the Brevik limestone was cut off in the end because of repeatedly exceeding levels of several trace elements, as Cu, Ni and most seriously Hg.

The magnesian limestones in the Mjøsa region (Hole and Hamar works) were substantially purer, but the producer decided to stop delivering in recent years.

The final milling of one of the companies has been transferred to the southmost part of Norway, Eydehavn industrial site, in the core area of this liming. However, the Sveco-Norwegian Precambrian bedrock of this large region consists of mainly gneisses with intrusions of granites, almost without any carbonates, and the raw materials for this lime production in Eydehavn comes from Verdal in Trøndelag by ship. At Verdalskalk itself a backup production is secured, too, in case of delivery problems, but then with an expensive transport by cement tankers to the southmost part of the country. The raw material from Verdal must be monitored, because it contains hot spots of cinnabar (HgS), in order to keep detriments in nature low.

A large cluster of lime industry based on limestone marble is situated in Romsdal-Nordmøre close to Molde. Originally the marble was just local, but the main part is nowadays shipped from large quarries in Brønnøy in North Norway (Nordland) to Elnesvågen in Romsdal. These carbonates originate from the Caledonian thrust faults of Ordovician-Silurian age.

Similar carbonate rock massives, widely dolomitized, are located further North in Nordland, in Sørfold/Fauske, from which material is shipped to Knarrevik at Bergen, being micronised also for freshwater liming. In Ballangen at Narvik another dolomite ore is exploited, grinding into slightly coarser products for projects of catchment liming.

Shell sand and coral sand occur along the Norwegian wide coast and are classified as marine limestones of Quaternary age. These coarse materials are fit to improve the bottom substrate for spawning in small rivers and creeks.

Requirements to freshwater liming materials

Main requirements to freshwater liming materials in Norway, together with a Control system and analytical methods to be used, were proposed and launched in a publication asked for by the Directorate of Nature Management (Erstad, 1996). The directions are commented below.

Purity of carbonates (contents)

From the beginning, there was no definite lower limit of carbonate contents, but a minimum of 80% became usual and requested (DN, 1990; Fleischer et al. 1990). This reflected the competitiveness of products in the market, but also an awareness of avoiding acid insoluble fractions to cause sedimentation and sludge on bottom of rivers (back currents) and lakes. Later in practice, carbonate contents mostly lie in the range 95-99% carbonates. Main earth-alkali nutrient is Ca, but more or less content of Mg is also there. A stoichiometric dolomite has Ca : Mg = 1:1 on molar basis, Mg is also important for biological life, and increases effective neutralising value (EN 12945, 2014) to about 107 measured as $CaCO_3$ equivalents. The products shall not contain calcined residuals (Active CaO) from any process, because maximum pH may then come out of bicarbonate buffer control and induce toxic aluminate, $Al(OH)_4^-$ at pH>9.

Contamination by trace elements

Sedimentary carbonates contain substantially more trace elements than metamorphosed ones, which appear to have translocated these elements into surrounding rocks during recrystallization and crystal growth. Quite high levels of Al may still occur in marble, without doing much harm, except making the milling hard and energy consuming.

When liming fresh water this system is unbuffered, as compared with fixation to soil colloids, the requirements are strict with respect to Al and nine defined trace elements of concern (TABLE 1). All requirements are given as total contents; in spite that the entire number of confirmed elements will not be biologically available (EN 12485, 2017; NS 4770, 1994).

Importance of fineness

According to level of grinding and thereby their fineness fit for use, the freshwater liming materials are sorted into different categories, as given in TABLE 2.

The very coarse materials in category 8 are used for small rivers and creeks where spawning is assisted. Rather than a rapid lime dissolution, creation of a local alkaline environment for eggs and spawns has been the aim, normally with great success. These coarse carbonates must be loose in structure, allowing good circulation of oxygen rich water to biological life. A high inner porosity of these carbonates promotes a steady dissolution of lime into ambient water, and therefore, in recent years a sieved 2-8 mm shell sand (marine limestone) has been chosen.

However, for liming the bulk of water in lakes and rivers research and practice have shown the finer the better. The intention is rapid and efficient

Table 2. Liming materials in the market sorted into categories of fineness.

Category	50 % of the liming material finer than
1	0 – 3 mm*
2	4 – 9 mm
3	10 – 19 mm
4	20 – 39 mm
5	40 – 79 mm
6	80 – 199 mm
7	200 – 999 mm
8	Coarser than 1 mm

* 1 mm (micrometre) = 0,001 mm

Table 1. Requirements to contents of potentially harmful elements in freshwater liming materials.

Element	Concentration	Element	Concentration
Al *	<20 g/kg	Cu *	<20 mg/kg
Zn *	<50 mg/kg	V *	<20 mg/kg
Cr *	<50 mg/kg	Pb *	<20 mg/kg
Zn *	<20 mg/kg	Cd *	<0,5 mg/kg
Co *	<20 mg/kg	Hg **	<0,05 mg/kg

Determination of digests in solution: * NS 4770 (1994), ** NS 4768 (1989) dissolution, and simultaneously avoiding sedimentation of coarser particles that could create banks and backwaters of mud. Such sludge is not esthetical in water systems, and, even more important, it hampers biological life and diversity.

A fundamental research to measure the disintegration of ground carbonates in water was performed by Sverdrup (1985), describing calcite dissolution kinetics and lake neutralisation. Dolomite, tricalcium silicate, olivine and K-feldspar were also included in the studies. This should lead to tools of modelling a range of liming materials when dissolution properties have been experimentally determined.

Hence, the categories 2 and 3 are readily available in the market, and are normally chosen for these liming operations, in lakes by spreading with boat and helicopter, in rivers by dosage feeders. Limestones and marbles are used in both categories, dolomite with a slower kinetics, in category 2 to compensate for slow disintegration at equal particle size. A wet-ground marble in category 2, delivered as a slurry (colloidal solution), is also widely used. It dissolves instantly and completely. Powder limes are fiercely mixed into water in a drum in the spreading boats and dosage feeders before let into lakes and rivers, in order to disperse the particles and avoid agglomeration. Only by helicopter spreading dry powder is normally used, with exception of the marble slurry.

Water columns for dissolution tests

Warfvinge et al. (1984) described a method to assess the efficiency of different lake liming materials. This was based on 2 metres tall columns filled with ion-exchanged water.

The columns are filled with water of pH values 4,0, 4,5, 5,0, 5,5 and 6,0 respectively, and added 628 mg suspended lime (equal to 10 mg/l) into each column. Leaving undisturbed until 16 h, the columns are sampled through membranes at 40, 80, 120 and 160 cm depth, and Ca and Mg contents are measured. The test is repeated for the overdosing factor, the inclination of a liming material to be hampered by its own high concentration in water, and at water pH 4,6 lime doses of 10, 20, 35, 50 and 85 mg/l are added. Then, the procedure continues as above by sampling through the membranes.

These data allow calculation and modelling of the instant and long-term dissolution of the liming materials at different conditions as lake depth and run-off in freshwater systems, and to consider first time's liming and re-liming locations. The model has been verified and calibrated to hundreds of lakes in the county of Rogaland. Choosing an average and typical lake, comparison between different freshwater liming materials has also been established, and thus ranging products in the market in a situation of competition.

Figure 3. Water columns for instant dissolution test of freshwater liming materials.

Conclusion

In an Atlantic climate zone with excess of precipitation as compared with evapotranspiration, leaching from watersheds and their soil covers and rocks is a continuous process. When man-made acid rain comes on top of this load onto metamorphosed silicate rocks of Fennoscandia, ecosystem alleviation and mitigation measures are necessary by using alkaline rock mineral amendments. A recovery by nature itself is often incomplete or even impossible, because of previous depletion of base cations in the system. A well scheduled addition of manufactured carbonates from mine industry into acidified, poor watersheds may be considered as a geological translocation of materials to remediate endangered eco systems. It is proven to work perfectly according to intentions during 50 years and will continue far into future.

Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Author Contributions

KJE provided the main conceptual ideas and wrote the manuscript; HT worked on technical details, monitored the public (state) policy behind and revised the manuscript. Both authors contributed to the article and approved the submitted version.

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