

Mechanisms for metal nodule formation on sediment surfaces of limed lakes



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<p>Abstract</p> <p>The water chemical and biological effects of liming have been fairly well documented. One of the research projects revealed relatively large (up to 1-3 cm in diameter) metal nodules on the sediment surface of some of the limed lakes. Here, we report on results for sediment and porewater metal content and densities of profundal macroinvertebrates from an in-depth investigation of two of 17 previously examined limed lakes. Trace element concentrations (especially of Mo and U) in Djupøyungen sediments are especially high, probably caused by the sulphide-containing bedrock, typical for the area. The metals in the sediment porewater are characterised by their association with Fe and Mn oxides and sulphides (Co, As and Mo) or S (U) and diagenetic separation (Cd and Mn). Significant Mn enrichment is probably due to facilitated precipitation of Mn oxides at the increased pH after liming. Gentle flushing of grab samples revealed a total dominance of Mn and Fe nodules on the sediment surface in some parts of Breisjøen. Although comparisons with Norwegian and other guidelines for sediments indicate that the measured concentrations for some of the metals are significantly above acceptable limits, data from only one of the sampling sites indicate effects on invertebrates. Residual Ca from the liming may protect the biota from negative effects.</p>

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surfaces of limed lakes**

Preface

Lack of documentation of the amount and effects of residual limestone powder on lake sediments after several years of liming initiated this project. Preliminary results and results from the main project revealed significant amounts of metal nodules on the sediment surface. As this was interpreted as partly a result of liming, there was a need to examine the mechanisms behind their formation.

This project is a follow-up on the main project. The focus has been to link pore water and sediment chemistry to nodule formation and possible ecological effects in two limed lakes. Based on recent research the team of authors developed the set of sampling techniques and methods used. The group has also conducted all the field work. Water chemistry and sediment analyses were by the NIVA laboratory in Oslo.

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Contents

Summary	5
Sammendrag	6
1. Background	7
2. Material and methods	7
2.1 The lakes and the sampling stations	8
2.2 Water sampling and methods	10
2.3 Sediment characterization	10
2.4 Sediment sampling and analytical methods	11
2.5 Invertebrate sampling and analyses	12
3. Results	13
3.1 Water chemistry and temperature	13
3.2 Sediment characteristics	16
3.3 Sediment chemistry	20
3.4 Invertebrates	25
4. Discussion	27
4.1 Liming residuals	27
4.2 Trace element dynamics	28
4.3 Major element enrichments	30
4.4 Invertebrates	31
5. References	33

Summary

Liming of acidified lakes and rivers is relatively extensive in southern Norway, and comprised 2500 lakes and 21 rivers in 2009-2010. The water chemical and biological effects of liming have been fairly well documented by the research and monitoring projects associated to the operational liming programme.

One of these projects was aimed at the quantification of limestone powder residuals in the lake sediments after several years of lake-liming (Hindar et al. 2013). As relatively large (up to 1-3 cm in diameter) metal nodules were discovered on the sediment surface of some of the limed lakes in 2011, this project was expanded. Several issues were addressed; how wide-spread may this be, is it related to the liming, what are the sources for metals and mechanisms behind their presence, and do the metal nodules/enrichment affect the bottom-dwelling invertebrates?

Hindar et al. (2013) examined 17 limed lakes for limestone powder residuals and sediment metal content, and related these results to data from 20 un-limed, reference lakes of a previous study. Here, we report on results for sediment and porewater metal content from the more in-depth investigation of two of the 17 limed lakes. Metal enrichment and metal nodules had already been documented in these two lakes, and a closer examination was expected to shed more light on metal sources and mechanisms.

Several methods were used in this project. First of all, we used Rizons to extract porewater from intact sediment cores. Porewater and sediment slices from the same sediment core were analysed for metal content. We also recorded the sediment surface by lowering a video-camera with external light source down to the sediment surface in order to document surface sediment structures that might contain metal nodules. An important part was also to examine the lake sediments, shore areas and outlet streams for invertebrates in order to reveal any impacts from the metal enrichment and nodules in the sediment.

We found that trace element concentrations (especially of Mo and U) in both the sediment porewater and solid phase at Djupøyungen are high compared to literature values for lakes, at the level of mining-contaminated sediments. The metal source is probably the metal-rich and easily weathered sulphide-containing bedrock in parts of the area, which provided basis for extensive mining until about hundred years ago. Estimates based on known metal concentrations in limestone powders show that the liming material is an insignificant source for sediment metals in both lakes.

The metals in the sediment porewater are characterised by their association with Fe and Mn oxides and sulphides (Co, As and Mo) or S (U) and diagenetic separation (Cd and Mn). The Fe and Mn oxides (in the upper oxidised parts) and sulphides (reduced conditions) are key carrier phases for trace metals due to adsorption. Significant Mn enrichment was found in many cores, probably due to facilitated precipitation of Mn oxides at the increased pH after liming. In un-limed, reference lakes of a previous study, such enrichment was only associated with extensive sediment Fe enrichment, and probably caused by co-precipitation of Mn oxides with the Fe oxides.

We found metal nodules on the sediment surface in both lakes, in accordance with the previous study. Video-recordings and grab-samples clearly indicated and showed, respectively, aggregates of metal nodules in Lake Breisjøen. Gentle flushing of grab samples revealed a total dominance of metal nodules in some parts of Breisjøen. Nodules were found in the grab samples from Lake Djupøyungen also, but were relatively small and fewer than in Breisjøen. The sediment surfaces of Djupøyungen were smooth, with no indication of nodules from the video-recordings.

Although comparisons with Norwegian guidelines for marine sediments indicate that the measured concentrations for some of the metals are significantly above acceptable limits, data from only one of the sampling sites indicate effects on invertebrates. Work by others indicates that residual calcium from the liming, still present in the sediments, may protect the biota from metal effects.

Sammendrag

Kalking av innsjøer og elver i Norge er omfattende, og omkring 2500 innsjøer og 21 laksevasdrag ble kalket i 2009-2010. Effekter på vannkjemi og biologi er forholdsvis godt kjent gjennom overvåkingsprogrammer og FoU-prosjekter. Ett av disse prosjektene hadde som mål å kvantifisere rester av kalk på sedimentoverflater etter mange års innsjøkalking (Hindar et al. 2013). Prosjektet ble utvidet etter funn av relativt store metall-noduler på sedimentoverflaten til flere av innsjøene i 2011. Flere forhold burde avklares; hvor utbredt var dette, er det knyttet til kalking, hva er kilden for metaller og hvordan dannes nodulene? Det var også viktig å avklare om metallanrikning og utfellingene hadde biologiske effekter.

Hindar et al. (2013) undersøkte 17 kalkede innsjøer og sammenliknet resultatene med data fra 20 ukalkede referanseinnsjøer fra en tidligere undersøkelse. To av de 17 kalkede innsjøene er undersøkt nærmere i dette prosjektet. Metallanrikning og metallnoduler var allerede dokumentert, og det ble antatt at nærmere undersøkelser ville belyse forhold omkring metallkilder og dannelsesmekanismer.

Flere metoder ble tatt i bruk, og en viktig del var bruk av Rizons for å trekke ut porevann fra intakte sedimentkjerner. Metallkonsentrasjon i porevann og sediment fra samme sedimentkjerner ble analysert. Vi gjorde også video-opptak av sedimentoverflatene for å undersøke om det var overflatestrukturer som indikerte metallnoduler. En viktig del av prosjektet var å undersøke invertebrater i bunnsedimenter, strandsonen og i utløpet av innsjøene for å se om det var effekter av den antatte metallanrikningen.

Konsentrasjonen av spormetaller, særlig Mo og U, var svært høy i både porevann og sediment i Djupøyungen, på linje med funn i innsjøer påvirket av gruveavrenning. Kilden er trolig lett nedbrytbare (høy forvittringshastighet) sulfidmineraler med forholdsvis høy metallkonsentrasjon, typisk for dette tidligere gruveområdet. Beregninger viste at kalkens innhold av metaller ikke kan være en viktig kilde for metaller i sedimentene i de to innsjøene.

Metaller i sedimentene er karakterisert av deres assosiasjon til oksider og sulfider av Fe og Mn i hhv. øvre oksiderte og underliggende reduserte sedimentsjikt (Co, As og Mo) og til S (U) og av diagenetisk separasjon (Cd og Mn). Dette siste viser at Cd ikke er knyttet til dannelse av Mn-utfellinger. Betydelig Mn-anrikning skyldes trolig økt pH som følge av kalking og dermed bedre forhold for Mn-utfelling. I ukalkede innsjøer skjer dette først og fremst som felling sammen med på Fe-oksider, og er dermed mindre utbredt.

Vi fant metallnoduler i sedimentene i begge innsjøene. Dette var mest utbredt i Breisjøen og syntes tydelig på video-opptakene. Sedimentprøver i Breisjøen hentet med bunndyrgrabben inneholdt stedvis nesten utelukkende metallnoduler. Slik var det ikke i Djupøyungen, der videopptakene ikke viste strukturer som indikerte metallnoduler. Prøver tatt med bunndyrgrabben inneholdt imidlertid slike kuler, men de var mindre og færre enn i Breisjøen.

Selv om metallkonsentrasjonene i sedimentene fra begge innsjøer var betydelig høyere enn retningslinjer for marine sedimenter, var det bare en stasjon i Djupøyungen som hadde lavere innhold av invertebrater enn forventet i upåvirket tilstand. Andre arbeider viser at kalsium beskytter biota mot gifteffekter av metaller. Det indikerer at kalsium fra kalken, som fortsatt finnes i sedimentene, kan være med å forklare hvorfor invertebrater ikke viser en større negativ respons på de høye metallkonsentrasjonene som ble målt i sedimentene.

1. Background

Acid deposition due to emissions of sulfuric and nitrous gases to the atmosphere has affected lakes and rivers in vulnerable areas in Northern Europe (Skjelkvåle et al. 2003). In Scandinavia several thousand populations of fish, among them valuable populations of Atlantic salmon (*Salmo salar*), have been eradicated (Sevaldrud et al. 1980; Hesthagen and Hansen 1991). However, emissions have been reduced substantially over the last few decades, and the affected water bodies show clear-cut signs of recovery (Skjelkvåle et al. 2003; Hesthagen et al. 2011).

Large-scale liming of lakes, rivers and catchments has been carried out to counteract the ecological and commercial setbacks in affected areas (Clair and Hindar 2005; Henrikson et al. 2005). In Norway, about 2500 lakes and 21 salmon rivers were limed in 2009-2010 (DN, 2011). Water chemistry and biological effects of liming are fairly well documented from the associated research and monitoring projects (Hindar and Clair 2005). To ensure a combination of rapid and long-lasting effect on pH after lake liming, use of fine-grinded (90 % < 0.1-0.2 mm) calcite powder (80-99 % CaCO₃) has been recommended (Hindar and Hegna 1990). Model calculations indicate that most of the particles will dissolve as they sink to the lake bottom, although a significant fraction may end up on the sediment surface (Sverdrup 1985, 1986; Sverdrup and Bjerle 1982).

One important question related to the liming practice in Norway have been left unanswered; to what extent are surface sediments enriched in limestone powder residuals after several years of liming? In a previous study we therefore sampled lake sediments in 17 limed lakes and compared the results with corresponding data from 20 non-limed reference lakes. The conclusion from the project was that after ordinary lake liming the occurrence of residuals were relatively low (Hindar et al. 2013). However, the discovery of large amounts of relatively large (up to 1-3 cm) metal nodules at the sediment surface in two limed lakes was un-expected.

Metal precipitation after liming has been documented, but metal nodules have not been reported. In a Norwegian study it was found that Al, Fe, Mn, Cd, Cu, Ni and Zn were enriched in the sediment during the liming period 1980-1991, and precipitation of Al, Fe and Mn was ascribed to production of oxyhydroxides at the increased pH after liming (Andersen and Pempkowiak 1999). In a Swedish study it was found that direct lake liming increased the sediment loading of Cd and Pb, probably also As, Co and Zn in Swedish lakes (Wällstedt and Borg 2005; Wällstedt et al. 2008).

The large metal nodules we found on the sediment surface arised new questions; what are the mechanisms behind their formation, can lake liming facilitate metal enrichment, and is there any reason for concern when it comes to ecological effects? The present study was designed to answer these questions.

2. Material and methods

An important part of the project was to develop a relevant sampling strategy (lakes, matrix, sampling techniques and analyses). We decided to examine two limed lakes with metal nodules from the previous study relatively closely. An un-limed reference lake and/or a limed lake without nodules could have been included, but with examining sediment cores down to 10 cm depth we believed that we would get sufficient information on the pre-liming situation in the selected lakes. A national study of sediments in 2010 lakes showed that the sedimentation rate in Nordic forest lakes were generally 1.2 ± 0.5 mm yr⁻¹ (ref. cited in Rognerud and Fjeld, 2001). However, close to the water/sediment interface the sediment growth can be higher due to higher water content. With a net sediment increase rate of 2 mm/yr, 20-30 years of liming will mainly affect the upper 4-6 cm of the sediment.

2.1 The lakes and the sampling stations

Lake Djupøyungen and Lake Breisjøen are located in forested areas in Akershus and Hedmark counties, respectively, in southeastern Norway. Lake Breisjøen has the largest catchment and lake area, and shortest residence time (*Figure 1, Table 1*). The sampling sites and locations data are given in *Figure 2 and Table 1*. The catchment area of Lake Djupøyungen is dominated by porphyritic granite, whereas granite and gneiss dominates the catchment of Lake Breisjøen (Sigmond et al. 1983).

Several abandoned mining sites (active until 1915) are located in the surrounding area of Djupøyungen. Aanes (2011) examined several streams in the area and found high concentrations of Zn (260 µg/L), Mo (8.4 µg/L) and Cd (0.8 µg/L) in association with elevated concentrations of sulphate (13.9 mg/L) in a stream draining a waste-rock dump at a former sphalerite (ZnS) mine 5-6 km north-west of Djupøyungen. This stream drains to Storøyungen west of the Djupøyungen catchment, but we cannot exclude that easily-weathered sulphides with several associated metals also may be found in the Djupøyungen catchment.

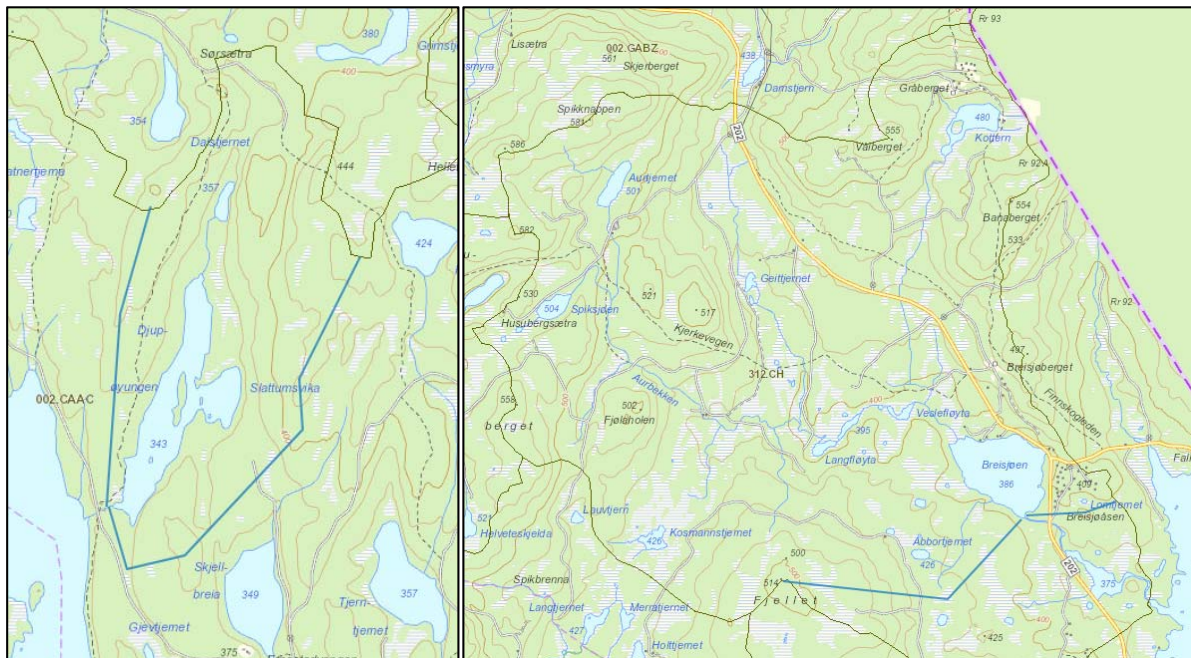


Figure 1. The catchment areas of Lake Djupøyungen (left), and Lake Breisjøen. Delimitation is partly from NVE Atlas, partly drawn with blue lines from the outlet. Lake data are given in Table 1.

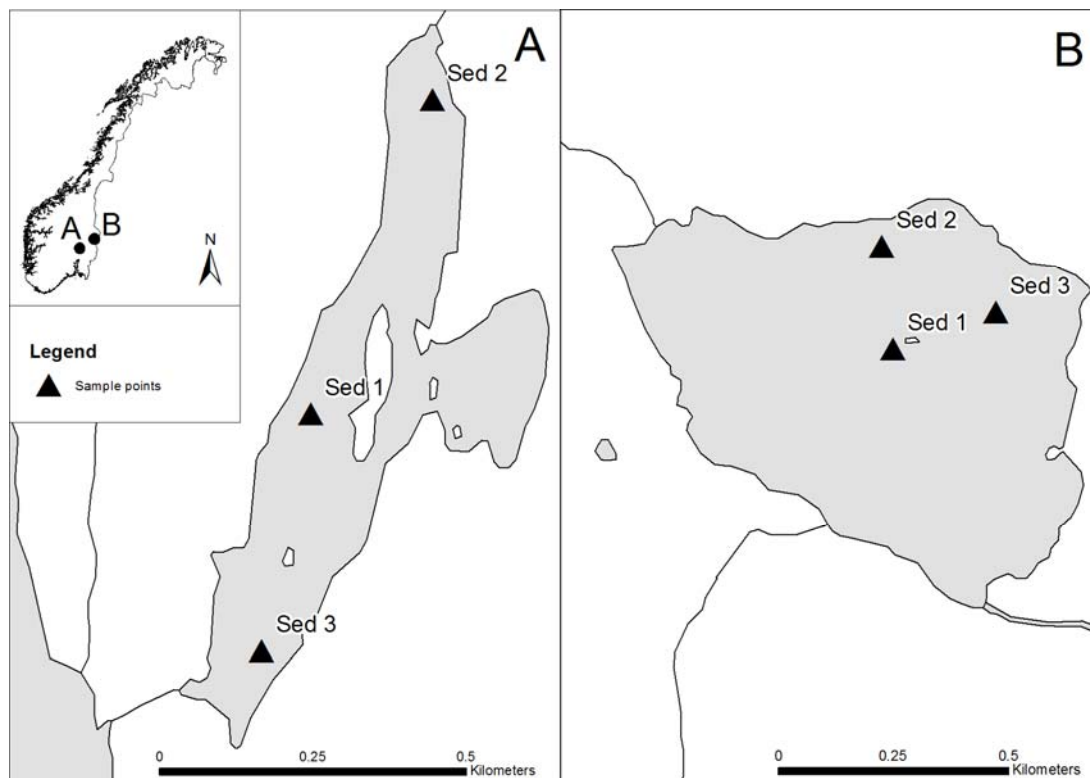


Figure 2. Location of sediment sampling in Lake Djupøyungen (A) and Lake Breisjøen (B).

Table 1. Lake data for Lake Djupøyungen and Lake Breisjøen. Coordinates are from the lake outlet and the sampling sites for sediments.

Location	NVE ID	EU89		Depth	Hasl	Area km ²	Volume mill m ³	Md depth m	Catchment km ²	Discharge L/s/km ²	Ret.time yr
		Lat	Long								
Breisjøen, outlet	3820	60,5533	12,5299	0							
Breisjøen, sed 1		60,5582	12,5260	20							
Breisjøen, sed 2		60,5602	12,5254	13							
Breisjøen, sed 3		60,5590	12,5308	6							
Djupøyungen, outlet	5026	60,1585	10,8975	0							
Djupøyungen, sed 1		60,1627	10,9010	20							
Djupøyungen, sed 2		60,1674	10,9040	10							
Djupøyungen, sed 3		60,1592	10,9000	12							
Breisjøen	386	0,590	2,20	3,7	27,20	13,28	0,28				
Djupøyungen	343	0,207	1,55	7,5	1,16	21,49	2,03				

Lake Djupøyungen was limed from 1995 until 2011 with about 6 tonnes/yr over the last years, whereas Lake Breisjøen was limed each year in the period 1993-2001 with an amount of 33-80 tonnes/yr. Although the lake area and volume of Breisjøen is larger than for Djupøyungen, these amounts of limestone powders clearly show that the lime dose, when related to lake volume (25 vs 4 g/m³) or lake area (0.9 vs 0.3 t/ha), was significantly higher for Breisjøen. This difference may be due to three important features; 1) the short retention time of Breisjøen demands for a relatively large dose to keep the pH high until re-liming the next year, 2) Breisjøen has probably served as a limestone reservoir for downstream parts of the watercourse, whereas Djupøyungen drains directly to a large, also formerly limed lake

(Storøyungen), and 3) Lakes limed from the Swedish side, such as Breisjøen, may have been limed with higher doses.

The limestone powder used at Djupøyungen was Sa-3 from Verdal (2008-2011), and probably HO-3 from Hole/Reinsvoll and NK3 from Brevik before that. Metal content of these limestone powder qualities were obtained from product data sheets and listed in *Table 2*. We have not been able to get limestone product data for Sweden used at Breisjøen, but the metal content is probably in the range of the data in *Table 2*. Metal content in Norwegian limestone powders used for acid waters is also regularly analysed as part of a control programme for these products (e.g. DN 2012), and the metal content of such random samples may differ from the figures in the table due to the analytical variability and local differences in mineralogy at the quarries. The NK3 was withdrawn from the market in 2012 due to large product variability.

Table 2. Metal content (mg/kg limestone powder) together with CaCO₃ - content (%) of limestone powders used at Djupøyungen. Abbreviations and quarry sites are given for each powder. All data are from product data sheets from the producer (Franzefoss Miljøkalk AS).

		Sa 3* Verdal	HO 3 Hole	NK3** Brevik
Co	mg/kg	0,3	1,4	5
Cu	mg/kg	<0,5	2,4	13
Zn	mg/kg	6	15,6	19
Ni	mg/kg	2	4,7	21
Cr	mg/kg	0,2	3,8	25
V	mg/kg	1	5,3	18
Hg	mg/kg	0	<0,01	0,04
Pb	mg/kg	1	7	5
Cd	mg/kg	0,1	0,1	<0,5
Al	%	0,05	0,4	0,5
CaCO ₃	%	98	86	89

*from 2008

**not from 2012 due to unstable quality

2.2 Water sampling and methods

Water samples were collected in 2011, and analysed for pH, conductivity, alkalinity, all major ions, aluminium fractions and total organic carbon (TOC) by use of standard methods at the NIVA laboratory in Oslo (Hindar et al. 2013).

As a part of the field work we used a YSI 6600 V-2 multiparameter sonde for measuring water column profiles of pH, temperature and oxygen saturation.

2.3 Sediment characterization

A video camera equipped with a light source was used in order to visually characterize the surface of the sediments. The camera rig was lowered from a boat down to a few decimetres above the sediment, and then the boat was moved slowly while recording. The sediment surfaces were inspected for nodule structures *in situ* from the screen on board of the boat and later from the recorded film. All film sequences were recorded and later transferred to a PC compatible format. For presentation in the report the PC-film was stopped and still pictures copied by use of Snipping Tool. The colour of the pictures is partly affected by the artificial light source.

Nodules captured with the grab sampler for invertebrates were documented by pictures and by counting.

2.4 Sediment sampling and analytical methods

Sediments. Sediments were sampled from three different locations and depths in each lake (*Figure 2, Table 1*). We used a modified Kajak-Brinkhurst gravity-type corer with acrylic tubes of inner diameter 8.3 cm for sediment sampling (*Figure 3*). Only sediments with an undisturbed sediment-water interface were used in the study. The cores were extruded and sectioned (2 cm slices) in the field. The homogenized 0-2 cm samples for metal analysis included all the nodules that were found in the layer. The samples were placed in acid-washed polyethylene cups and processed further in the laboratory. Sediments were dried, homogenized, and the <0.070 mm fractions, were used for analysis of metals. All metal analyses, including nodules were carried out at NIVA by ICP-MS after standard methods.

Porewater sampling. The key parts of our sampling method are Rhizons (*Figure 3*), distributed by Rhizosphere Research Products (NL-6706 Wageningen). They are made of a hydrophilic porous polymer tube, with a typical pore diameter of 0.1 μm , extended with a polyvinyl chloride tube. The pore size (mean 0.1 μm , max. 0.2 μm) ensures the extraction of the “truly dissolved” fraction. The outer diameter of a Rhizon is 2.4 mm, and the filter section has a length of 5 cm. To support the polymer, a nylon wire is fixed to one end of the porous polymer. The fluid sampled from the sediment flows into the space between the porous tube and the supporting wire.

A Rhizon has several advantages compared with other sampling devices: low mechanical disturbance of the sediment due to small diameter (2.4 mm), low dead volume (0.5 mL including standard tubing) and minimized sorption processes on the inert polymer. It is faster and less expensive to deploy than diffusion peeper (which require typical deployment period of 21 days). In addition, Rhizons allows preservation of the samples immediately, unlike centrifugation and filtration, which induces artefacts due to sample manipulation in the laboratory.

The key drawback of Rhizon is that the pumping of the porewater might induce a field flow around the Rhizon which might perturb the porewater profile. To overcome this limitation, Seeberg-Elverfeldt et al. (2005) have performed numerical modelling of the flow field and the catchment areas around Rhizons. These authors have shown that even for low porosity, a porewater volume of 6 mL can be extracted without bias between adjacent sediment layers to obtain porewater profiles with 1 cm vertical resolution. Consequently, we defined a 1 cm vertical resolution, and used vacuum tubes to extract ~4-6 ml of porewater. Porewater samples were acidified at 2% HNO_3 before analysis by ICP-MS.

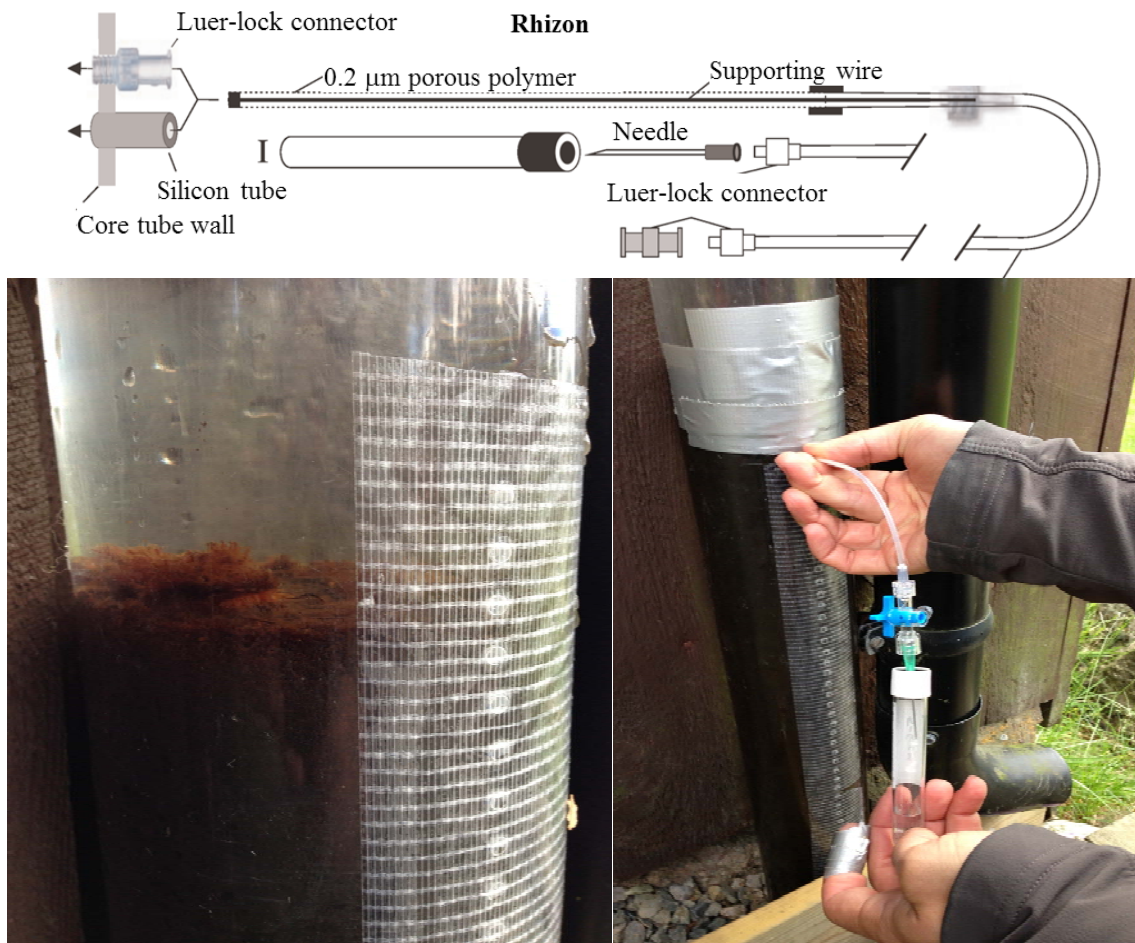


Figure 3. Rhizon assembly (top) and picture of intact sediment core with holes for syringe and vacuum based collection of pore water through plastic tubing Rhizons.

2.5 Invertebrate sampling and analyses

Benthic macroinvertebrates were collected from littoral zone, the profundal zone and the outflowing streams of both lakes. Both aerial and aquatic sampling methods were applied in order to detect both aquatic instars as well as terrestrial stages. The objective of including lake littoral and riverine invertebrates, in addition to profundal communities, was to provide a broad characterization of the fauna and to document natural variability between lakes, as well as any anthropogenic impairment.

Macroinvertebrates in the profundal zone were sampled using a 12.5 x 14.5 cm van Veen grab sampler (Downing and Rigler (eds) 1984). Three sampling locations from different depths were investigated in each lake. From each sampling location, three sampling stations were chosen, and from each sampling station, nine parallel samples were collected. Thus a total of 27 van Veen grab samples were collected from each sampling location. The quality of each sample was examined before including the data. Samples were discarded if the sampler had not closed correctly. The collected material was carefully sieved through a net with 250-µm mesh sizes. Only bottom dwelling macroinvertebrates were included in estimates of densities. Any pelagic living invertebrates, such as Chaoborus (phantom midges), were therefore not included in the analysis.

Aquatic macroinvertebrates from the littoral lake zone were collected using kick sampling (frame opening of 25 x 25 cm and 250 µm mesh sizes) in addition to a shafted hand sieve (1000 µm mesh sizes). The kick sample was taken by walking slowly backwards 1 m and stirring the bottom substrate with the feet for 20

seconds. This procedure was repeated 9 times and the samples were then pooled into one. Hand sieve sampling was standardized to approximately 30 minutes catch per unit effort sampling (CPUE) in littoral habitats that were reachable and not covered by the kick sampling. Aerial sweeps were conducted from a shoreline section of approximately 25 m length in each lake. In the outflowing streams kick sampling was conducted. Sampling was standardized to 3 minutes sampling time and 2.25 m² area of river bottom.

All biological samples were stored in glass jars and preserved by adding 96% ethanol and were later sorted in a laboratory using magnification for reliable identification and counting. Ephemeroptera, Plecoptera, Trichoptera, Hirudinea, Heteroptera, Gastropoda, Coleoptera and Odonata were identified to species level when possible. Other taxa were identified to family or subfamily level only. Characterization of the sediment particles from each invertebrate sample was also conducted in the laboratory. The nodules content in the macroinvertebrate samples were measured and grouped as follows (cm³): No, few < 20, moderate 20.1 – 60 and high > 60.1.

Plots of benthic densities (violin plots) were made using the statistical software R (R Development Core Team 2013) and ggplot2 (version 0.9.0).

At present, there are no inter-calibrated national acidity index systems for benthic macro-invertebrates in humic lakes and rivers (colour > 30 mg Pt l⁻¹). It is however possible to differentiate acidity impacts also in humic streams, based on presence and dominance of acid intolerant species, such as the mayflies *Baetis*. This genus is sensitive to both chronic and episodic acidification but survival is dependent on humic content in the water. *Baetis* is not expected to be found in humic streams with prolonged episodes of pH < 5 (Aanes and Baekken, 1995). Any red or black listed species were documented following the criteria given by International Union for Conservation of Nature (IUCN) (Gederaas et al., 2012; Kålås et al., 2010).

3. Results

3.1 Water chemistry and temperature

Lake Djupøyungen is a moderately humic lake, with relatively high pH, Ca concentration and Ca/Mg ratio (above 20 on a weight basis) in 2011, clearly a result of the on-going lake liming programme at the time of sampling (Table 3). Lake Breisjøen on the other hand is humic and was relatively acid in 2011, with a low Ca/Mg ratio (4.4), about 10 years after terminated liming operations. The sulphate concentration and toxicity indicators, such as ANC (Acid Neutralising Capacity) and LAl (labile aluminium), indicate that acidification of Breisjøen due to anthropogenic influence is minor. The low pH is a result of the relatively high concentrations of weak organic acids, indicated by a total organic carbon concentration (TOC) of 13 mg/L.

Table 3. Water chemistry from the studied lakes sampled in June and October 2011.

Lake:	Date	pH	Cond mS/m	ALK-E µeqv/L	TotN µg/LN	NO ₃ -N µg/LN	TOC mg/LC	Cl mg/L	SO ₄ mg/L	Al/R µg/L	Al/II µg/L	LAL µg/L	Ca mg/L	K mg/L	Mg mg/L	Na mg/L	ANC µeqv/L
Breisjøen	16.06.2011	5,51	1,45	24	455	21	13	0,72	1,09	75	61	14	1,06	0,33	0,24	1,02	81
Djupøyungen	13.10.2011	6,86	2,80	170	325	51	5,3	0,96	2,02	40	26	14	4,76	0,33	0,22	1,01	235

The probe profiles for pH, temperature and oxygen saturation are shown in Figure 4 and Figure 5. pH was about 6.3 in the circulating 4-5 m epilimnion of Djupøyungen, decreasing to as low as 5.3 in the hypolimnion at the deepest point. The still relatively high pH-values reflect a relatively low dilution rate due to the lake-water retention time of 2 years, but may also be a result of the long-term dissolution of

sedimented limestone powder. The temperature profiles show a relatively shallow thermocline at about 5 meters depth and a decline of the oxygen content to about 60 % in the deepest parts.

In contrast, pH was about 5.0 in the circulating 4-5 m epilimnion of Breisjøen, decreasing to 4.45-4.6 in the hypolimnion. Both the time elapsed after termination of liming operations and the short retention time (0.28 years) ensure that the pH is probably back at pre-liming levels. This was probably also the case in 2011 (pH was 5.51 in October), however, and indicates that the pH from the probe may have been too low. The temperature profiles are similar to those of Djupøyungen, but the oxygen saturation was slightly higher (about 70 %) in the deepest parts.

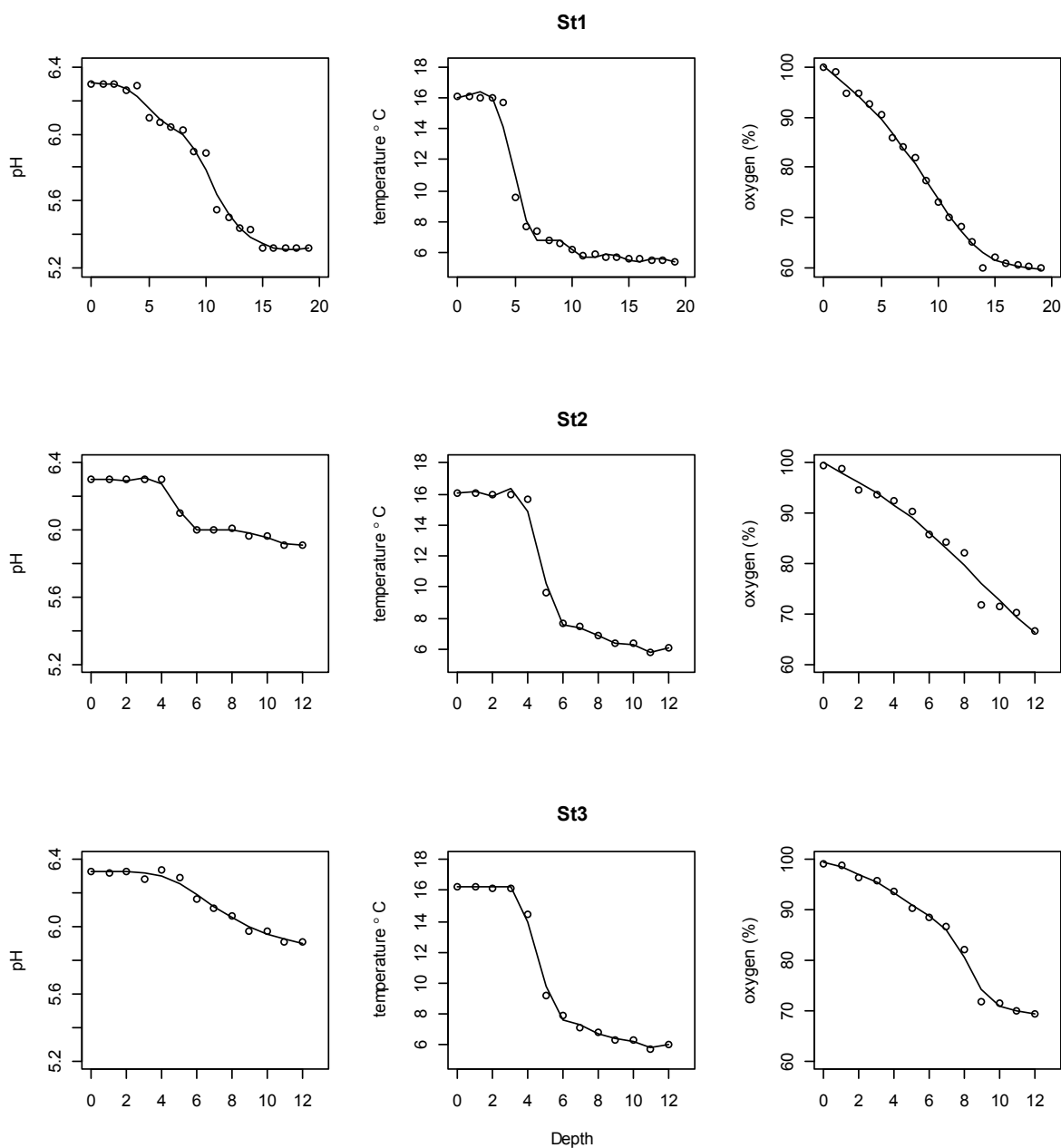


Figure 4. Lake water profiles for pH, temperature and oxygen saturation at the sediment sampling stations in Djupøyungen on June 22, 2014. Depth in meters from the surface.

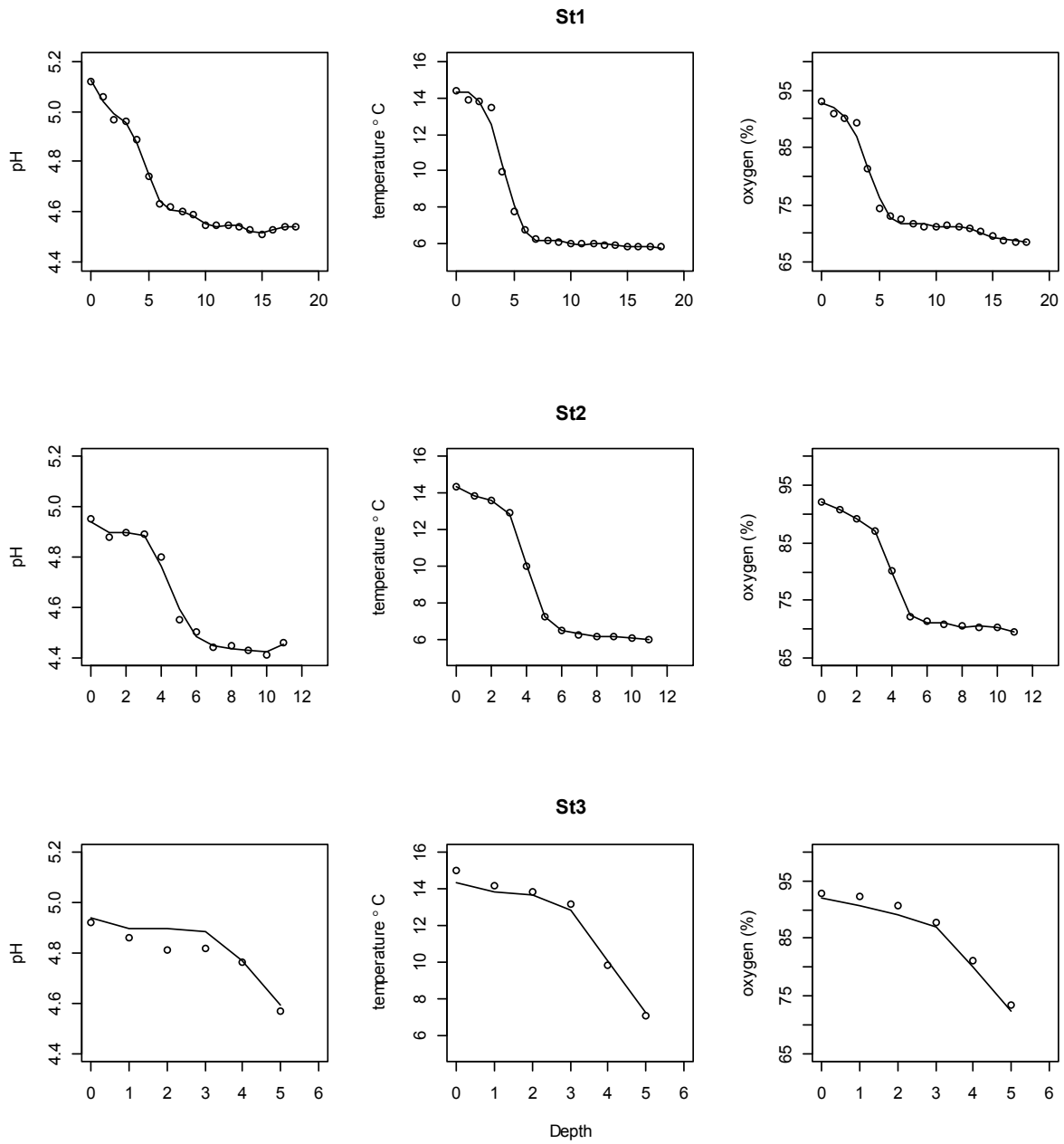


Figure 5. Lake water profiles for pH, temperature and oxygen saturation in Breisjøen on June 23, 2014. Depth in meters from the surface.

3.2 Sediment characteristics

Inspection of the sediment surfaces by video camera gave relatively contrasting results for the two lakes. In Lake Djupøyungen clear-cut nodules were hard to see, and the lake bottom was dominated by single vegetation structures with attached algae (*Figure 6*). The lake bottom was relatively smooth, but some areas were obviously affected by visible liming residuals (white spots in *Figure 7*).

Large areas of the Lake Breisjøen surface sediment were dominated by, what we believe are structures of metal nodules, in relatively large aggregates. The structuring material of the surface, although covered by a thin layer of organic matter, gave therefore a gnarled and knotted appearance (*Figure 8*). After a gentle wash off of the organic material medium sized metal nodules appeared in the invertebrate sediment grab sampler (*Figure 9*). Other areas, especially in the northern part, were obviously affected by use of fish nets, as we found long narrow trenches (furrows) on the sediment surface (not shown here).

More on nodule characterisation (size and form) is given in the invertebrate section, as these nodules are an important part of the microenvironment for bottom-dwelling organisms.



Figure 6. Generally, a relatively homogenous surface with single vegetation structures, are typical for the sediment in Lake Djupøyungen.

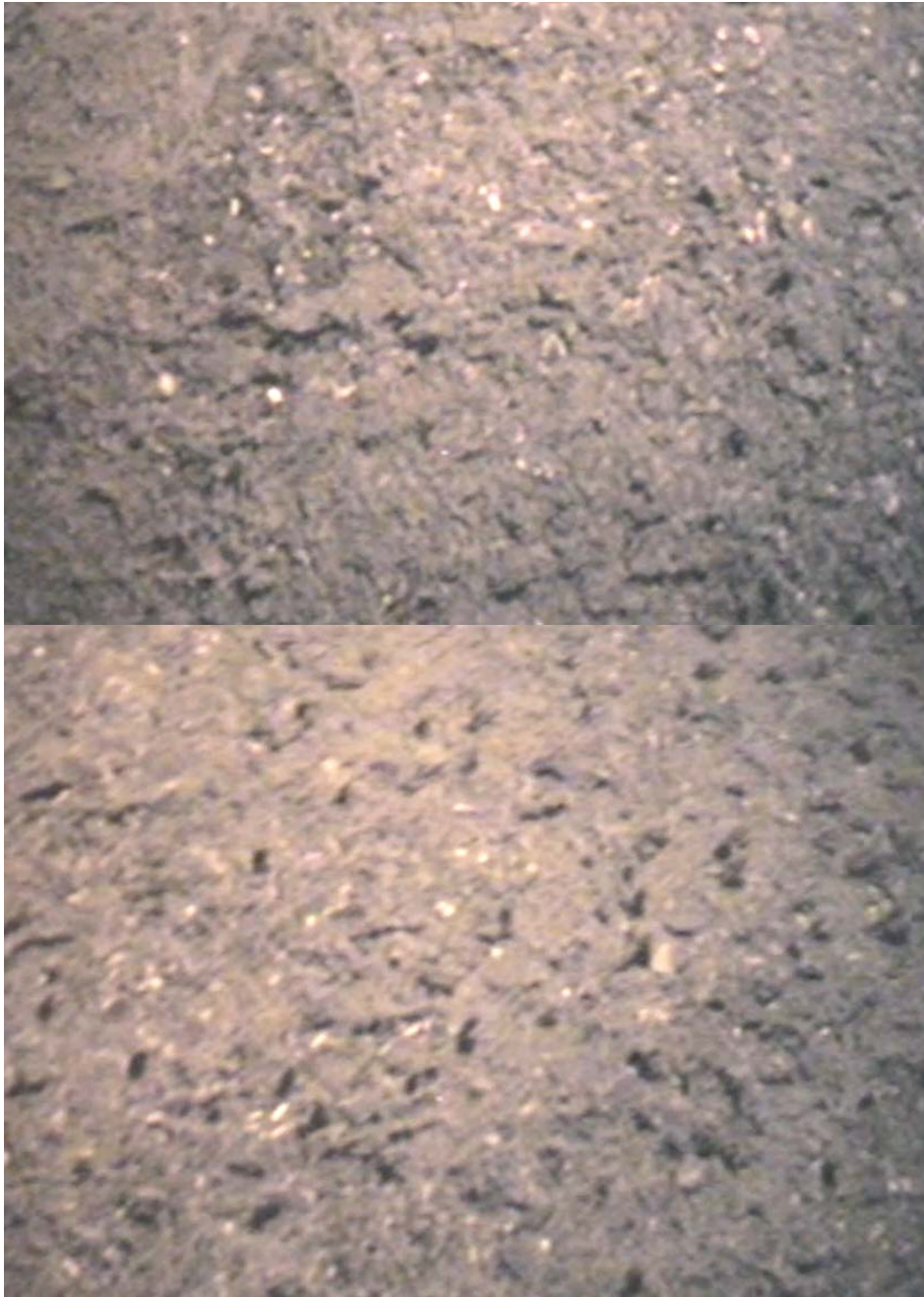


Figure 7. Some areas with white, relatively coarse particles were observed on top of the sediment at Lake Djupøyungen, interpreted as residuals from the liming.

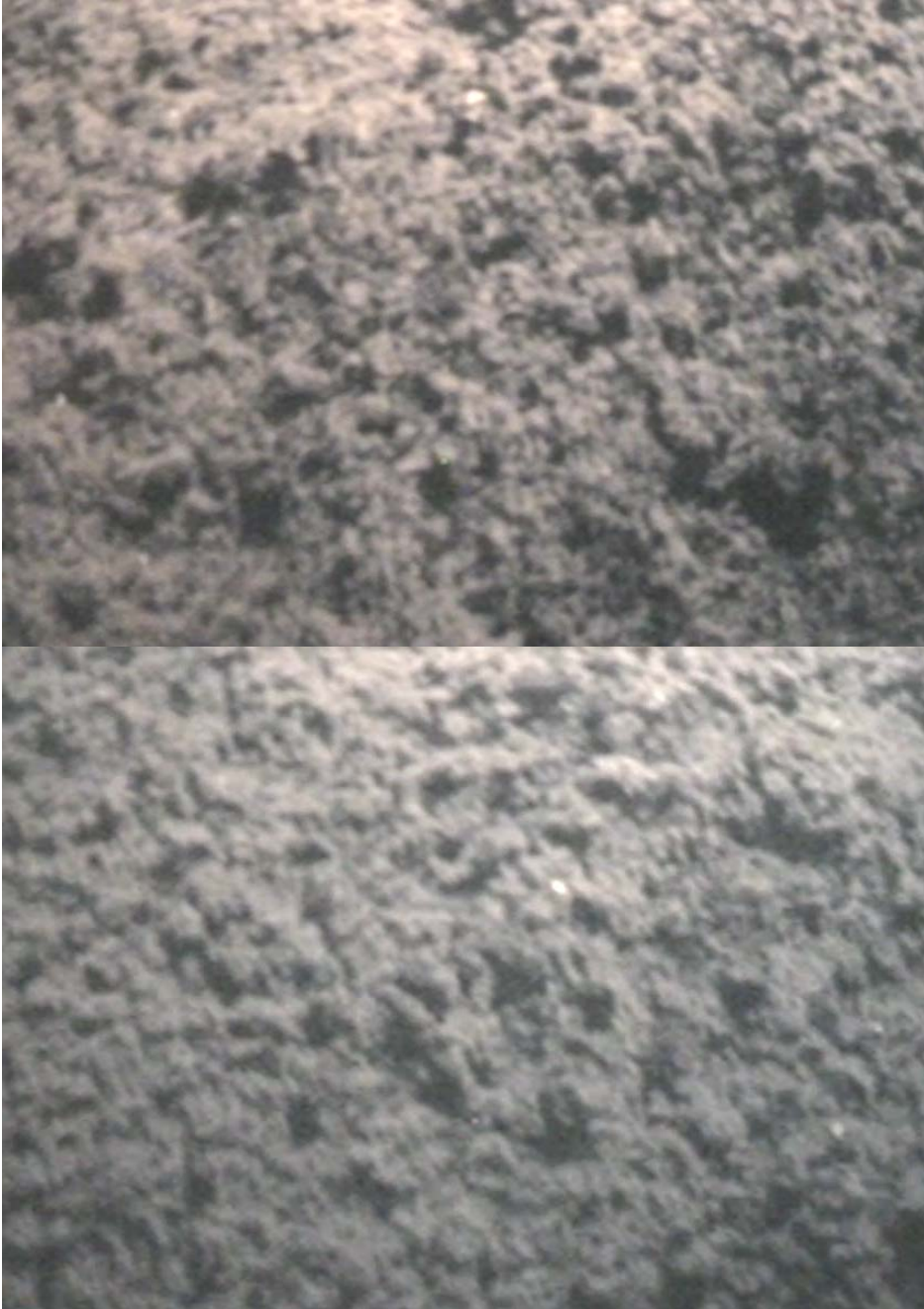


Figure 8. The surface sediment in parts of Lake Breisjøen was clearly more uneven than the sediments of Lake Djupøyungen. Samples collected with the grab sampler for invertebrates showed that this pattern was caused by loose aggregates of metal nodules (Figure 9).



Figure 9. Fresh sediment collected with the grab sampler for invertebrates at Lake Breisjøen. Loose organic material was removed by gentle flushing, in order to visualize that the vast majority of the sample was metal nodules. The black colour is caused by Mn oxides and the brown-orange of oxidized Fe.

3.3 Sediment chemistry

Locations within the lake were defined/ranked as littoral (shallowest), intermediate and profundal (deepest), although two of the depths at Djupøyungen are close, 10 and 12 m.

Major elements. Manganese (Mn) concentrations in the solid phase decrease with distance from shore. While Mn depth profiles are constants with depth at the deepest sites, they show strong subsurface enrichment in the cores from littoral sites, peaking at 80 and 300 mg/g in Breisjøen and Djupøyungen, respectively (*Figure 10* and *Figure 11*). Porewater Mn depth profiles show strong gradient just below the sediment-water interface (SWI), then remain constant with depth. High concentrations of ~10 mg/L are measures in the shallow cores at both sites.

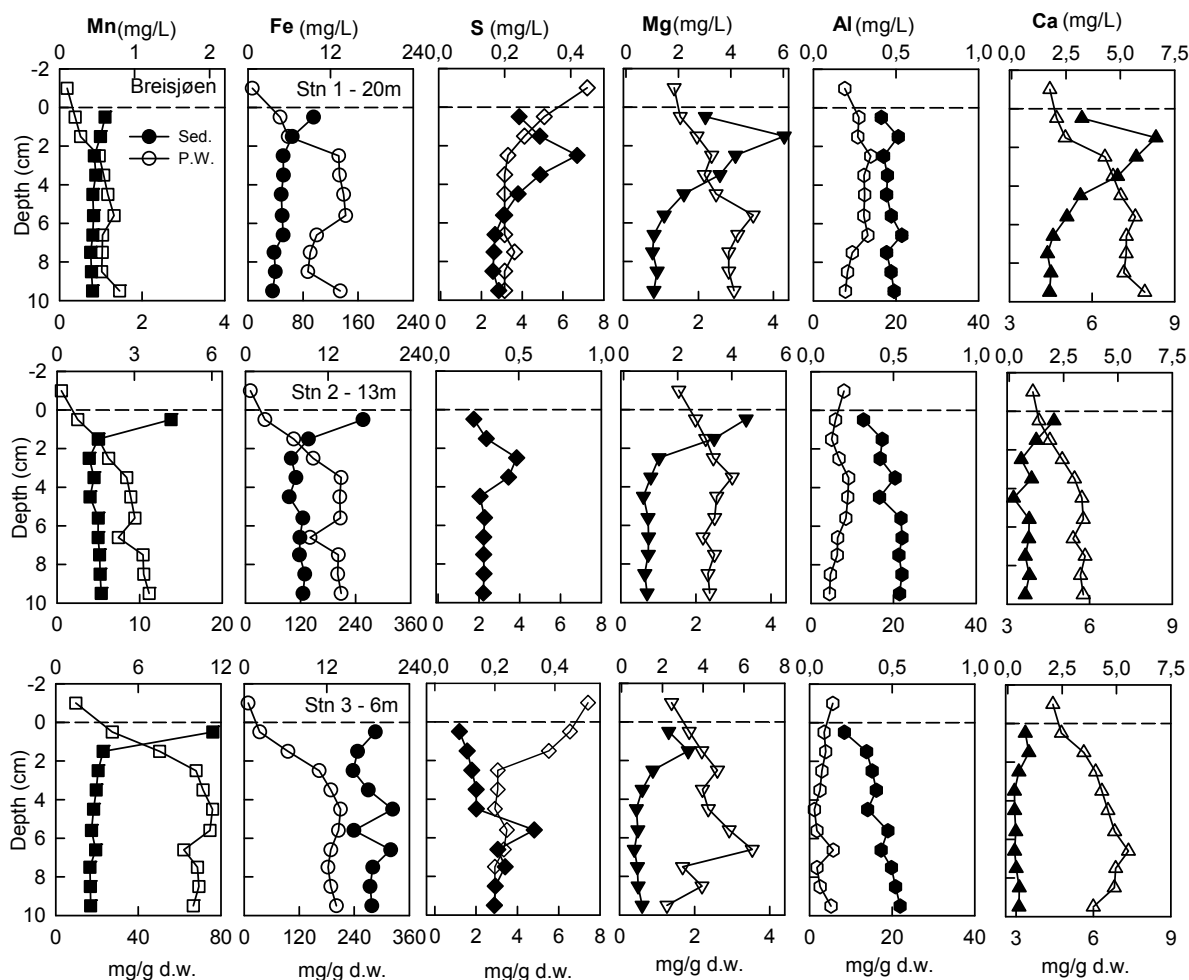


Figure 10. Sediment (solid symbols) and pore water (open symbols) concentration profiles of the major elements Mn, Fe, S, Mg, Al and Ca in the sediments of Lake Breisjøen at 20m (st.1), 13m (st.2), and 6m depth (st.3). The horizontal dashed line indicates the sediment-water interface.

Similarly to Mn, Fe concentrations are higher in the littoral sediments than in the profundal sediments. However, there are no systematic subsurface enrichments in solid-phase Fe. At all sites, porewater Fe concentration profiles display strong subsurface gradients, although the concentrations plateaus is twice as high at Breisjøen than at Djupøyungen, reaching 10 mg/L in and 5 mg/L, respectively.

Total solid-phase S display sub-surface peaks of 6-10 mg/g at 3-5 cm at all profundal and intermediate sites, while they increase with depth a littoral sites. At all sites, porewater S decreases from the highest values in the overlying waters, (0.5 mg/L at Breisjøen and 0.8 mg/L in Djupøyungen), to a lower values becoming constant with depth 2-4 cm below the SWI. The sample preservation techniques by acidification likely released volatile hydrogen sulphides, such that the measured S likely represents sulphates (SO_4^{2-}).

Ca and Mg solid-phase depth-profiles are contrasting with those of solid-phase Mn, as both elements are enriched in cores taken at the deepest sites. Subsurface Mg concentrations are similar in both lakes (6 mg/g), while Ca is twice higher at Djupøyungen than at Breisjøen. At all sites, porewater Ca and Mn increase with depth from below the SWI to about 4-6 cm depth.

At the littoral sites of both lakes Al is lower just below the SWI, then increase with depth to reach the background concentrations. Background (e.g., downcore) Al is of 40 mg/g at Djupøyungen and 20 mg/g at Breisjøen.

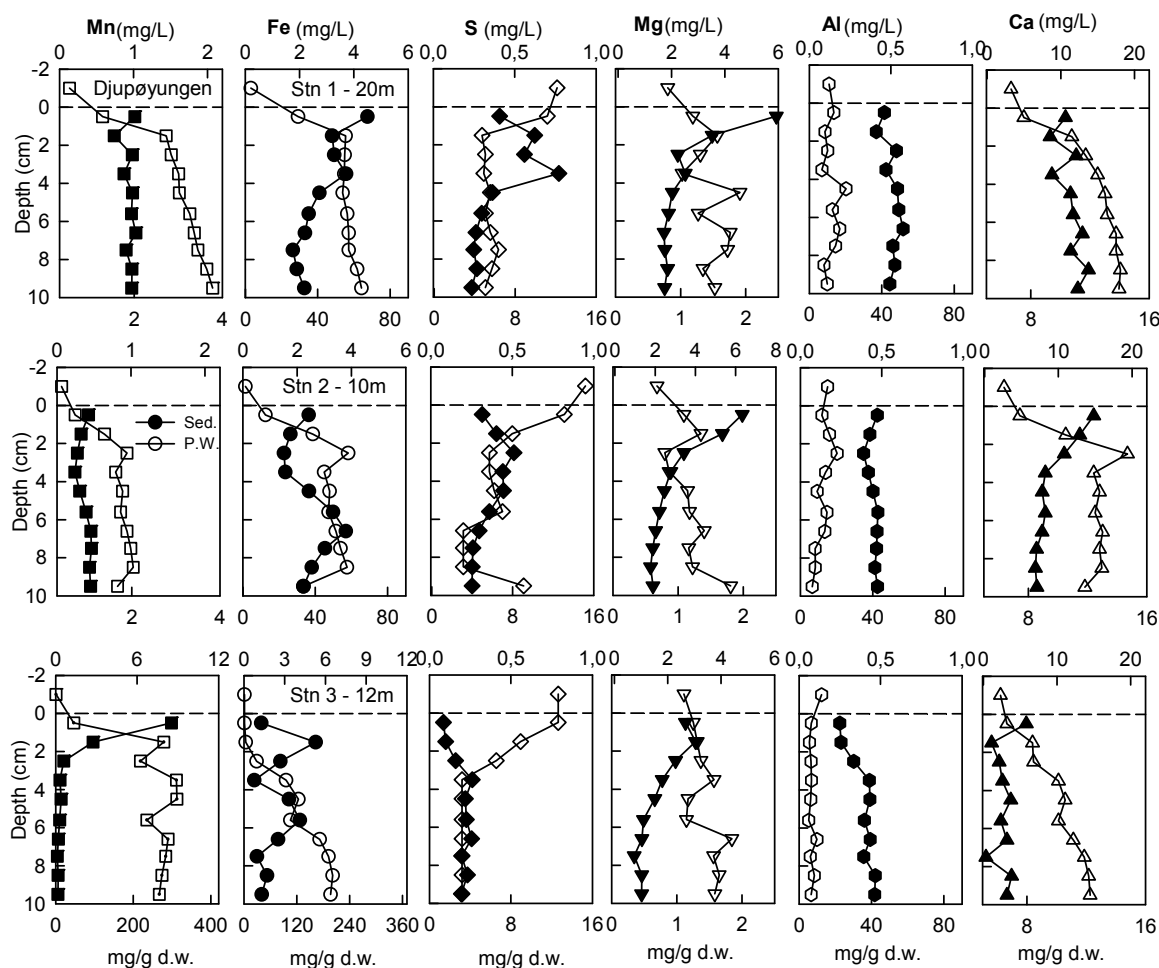


Figure 11. Sediment (solid symbols) and pore water (open symbols) concentration profiles of the major elements Mn, Fe, S, Mg, Al and Ca in the sediments of Lake Djupøyungen at 20, 12, and 10m depth. The horizontal dashed line indicates the sediment-water interface.

Phosphorus and trace-elements. Phosphorus profiles differ sharply between sites and lakes. At all sites in Lake Breisjøen solid-phase P is lowest at the SWI, and then increasing with depth to reaching 3000 $\mu\text{g/g}$ (Figure 12 and Figure 13). SWI concentrations are lowest (30 $\mu\text{g/g}$) at the shallow site, and highest at the deep site (2100 $\mu\text{g/g}$). Porewater P also increases with depth in all cores at Breisjøen, reaching 100, 50 and 20 $\mu\text{g/L}$ at the deep, intermediate and shallow site, respectively. In contrast to the systematic trends observed at Breisjøen, depth-profiles of P concentrations at Djupøyungen display much less difference between the SWI and the down-core values.

Solid-phase As display sub-surface peaks of 20-30 $\mu\text{g/g}$ at 3-5 cm depth at all sites, with the exception of the intermediate site at Breisjøen which shows a constant decrease from the SWI. Porewater As concentration profiles are relative consistent across sites and lakes, with subsurface maxima of 0.7 $\mu\text{g/L}$ at 2-7 cm depth.

With the exception of As, Co and Cd, trace-element contents in sediments are systematically higher at Djupøyungen than at Breisjøen, by factors ranging from 2-fold (Cu and Ni) to 100- (Zn) and 1000-fold (Mo).

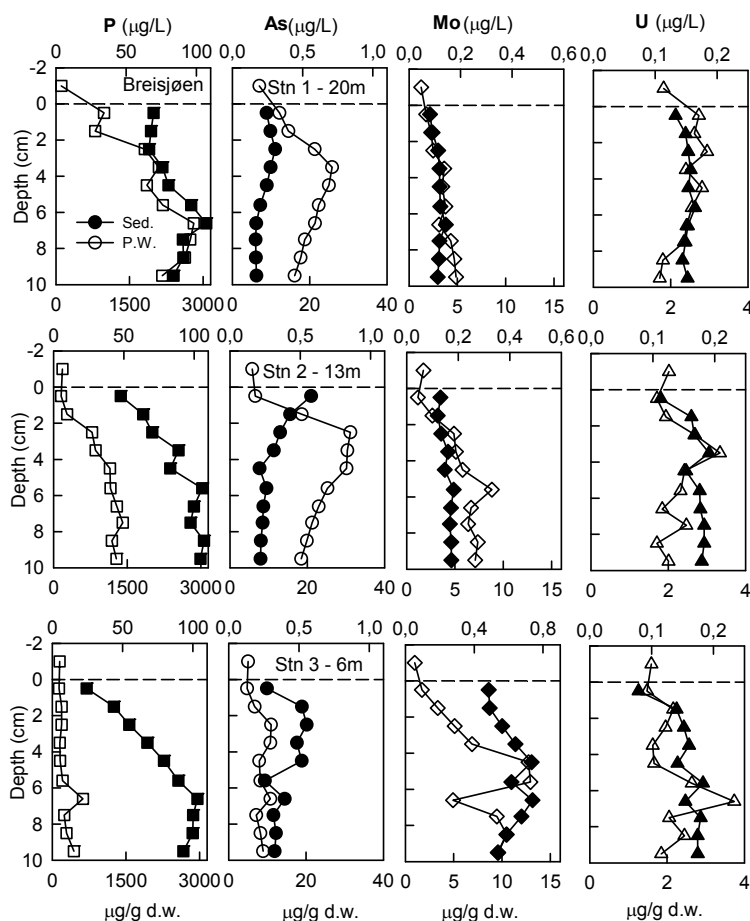


Figure 12. Sediment (solid symbols) and pore water (open symbols) concentration profiles of the oxyanions P, As, Mo and U in the sediments of Lake Breisjøen at 20m, 13, and 6m depth. The horizontal dashed line indicates the sediment-water interface.

Mo and U concentrations are sharply contrasting between lakes. Solid-phase Mo decrease with the distance from shore at both sites, but maximum Mo at Djupøyungen (1500 $\mu\text{g/g}$) is 3 orders of magnitude higher than maximum Mo at Breisjøen (12 mg/g). Similarly, maximum U at Djupøyungen (100 $\mu\text{g/g}$) is 2 orders of magnitude higher than at Breisjøen (3 $\mu\text{g/g}$). Meanwhile, porewater Mo peaks at 120 $\mu\text{g/L}$ at the shallow site of Djupøyungen, and at 0.5 $\mu\text{g/L}$ at the shallow site of Breisjøen. Porewater U concentration profiles are relative constant with depth at all sites, although 5-fold higher at Djupøyungen (0.5 $\mu\text{g/L}$) than at Breisjøen (0.1 mg/L).

Despite the concentrations being systematically higher at Djupøyungen than at Breisjøen, the features of the depth profiles of Co, Cd, Ba and Pb are similar across lakes (Figure 14 and Figure 15). Concentration of solid-phase profiles of Co show a sub-surface maximum at 2-4 cm depth at the profundal sites, and two maxima at the littoral sites. Solid-phase Cd concentrations peak at 2-4 cm at all sites, although the peaks are more sharply defined at Breisjøen. Solid-phase Pb concentrations also peak at 2-4 cm depth at all site, and despite solid-phase concentrations of Pb being 2-fold higher at Djupøyungen than at Breisjøen, porewater Pb is relatively constant at ~ 0.25 $\mu\text{g/L}$ at all sites. In most cores, Ni, Cu, Zn and Sn are higher at the SWI, while Sb, along with Co, Cd and Pb, displays a sub-surface maximum.

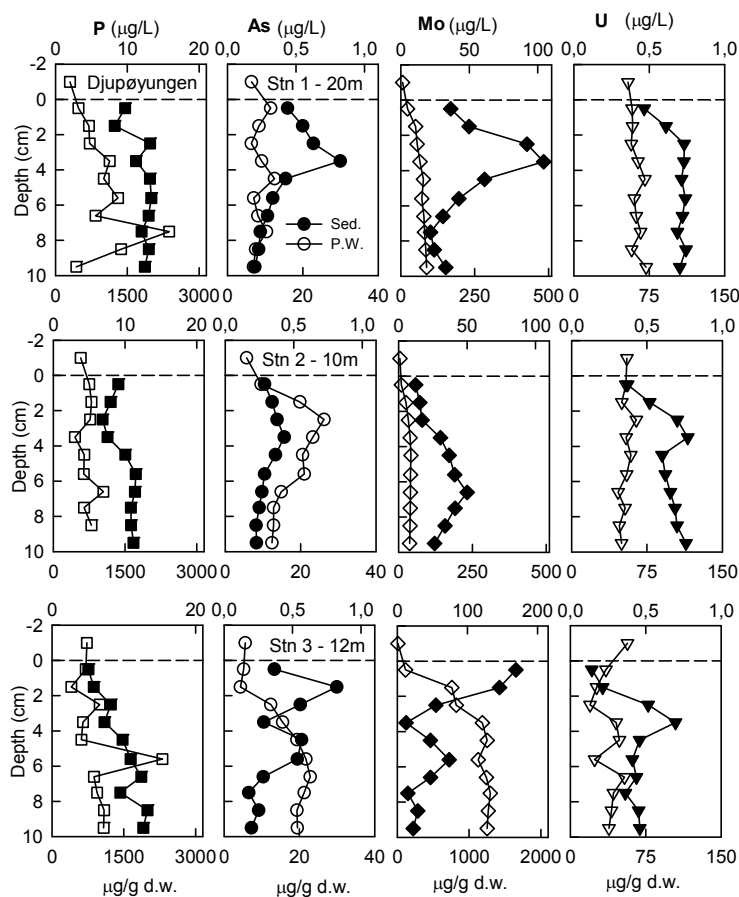


Figure 13. Sediment (solid symbols) and pore water (open symbols) concentration profiles of the oxyanions P, As, Mo and U in the sediments of Lake Djupøyungen at 20, 12, and 10m depth. The horizontal dashed line indicates the sediment-water interface.

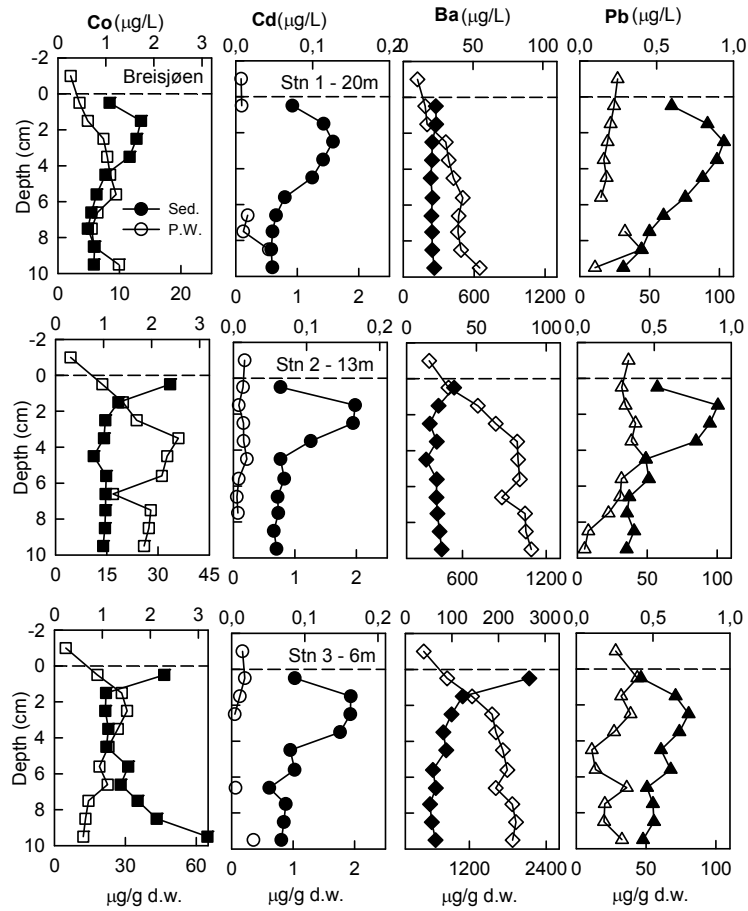


Figure 14. Sediment (solid symbols) and pore water (open symbols) concentration profiles of the trace elements Co, Cd, Ba and Pb in the sediments of Lake Breisjøen at 20m, 13, and 6m depth. The horizontal dashed line indicates the sediment-water interface.

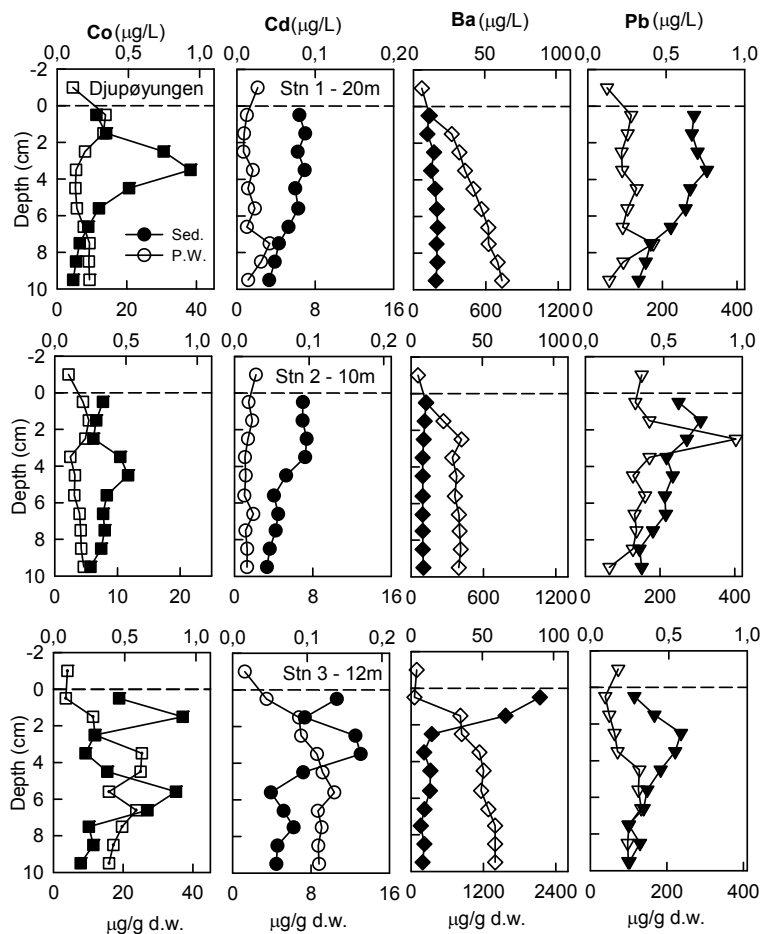


Figure 15. Sediment (solid symbols) and pore water (open symbols) concentration profiles of the trace elements Co, Cd, Ba and Pb in the sediments of Lake Djupøyungen at 20, 12, and 10m depth. The horizontal dashed line indicates the sediment-water interface.

3.4 Invertebrates

Lake littoral and riverine macroinvertebrates

The faunal composition and food chains were similar and typical for acidified and humic boreal lakes: species poor, detritus based, and with a low number of herbivores relative to predators. The acid sensitive genus *Baetis* was recorded in low numbers from the outlet stream of Lake Djupøyungen, but not from Lake Breisjøen. This indicates that both streams were acidified, periodically or chronically, and also that there is a relatively higher acid stress in Lake Breisjøen. No red or black listed species were recorded.

Sediment characteristics

Sediment nodules were found in the grab samples in Lake Djupøyungen from depths 20, 12 and 10 meters. The amount collected in the grab samples, along with samples of benthic macroinvertebrates, varied between stations. Few, moderate and high amounts of nodules were recorded from depths 20, 12 and 10 m, respectively. The nodules had in general an orange coloured surface and black core (Figure 16). The forms varied from oblong to round. No nodules were found from the outlet river station or in the eulittoral zone from Lake Djupøyungen.

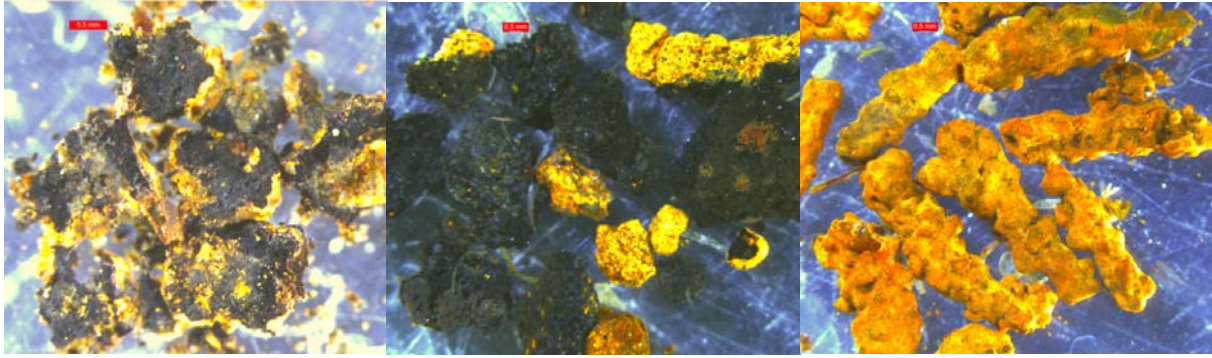


Figure 16. Nodules collected together with van Veen grab samples from Lake Djupøyungen. Samples are from depths 20 m (left), 12 m (middle) and 10 m (right). Scale bars (marked red) denote 0.5 mm length.

Sediment nodules were found from depths 13 and 6 m in Lake Breisjøen as well as in the outlet river. The amount of nodules collected in the grab samples (together with samples of benthic macroinvertebrates) varied between stations. Moderate and high amounts of nodules were recorded from depths 13 and 6 m, respectively. The nodules had in general an orange colour, speckled surface and black cores (Figure 17).

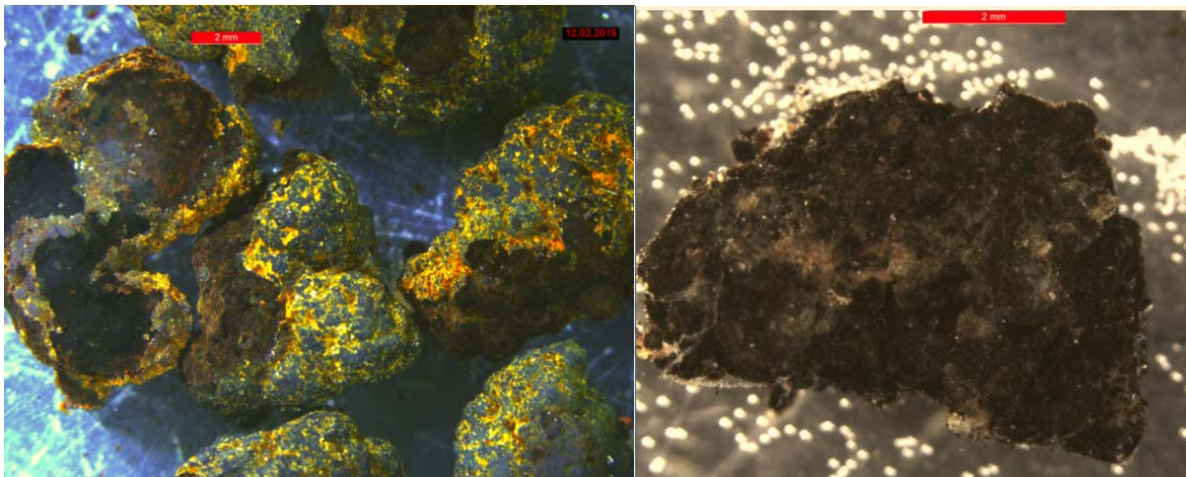


Figure 17. Nodules collected with van Veen grab from Lake Breisjøen. Samples collected from 13 m and 6 m depths together (left) and in the outlet river (right). Scale bars (marked red) denote 2 mm length. In Lake Breisjøen no nodules were found from 20 m depth or in the eulittoral zone.

Lake profundal macroinvertebrates

Profundal macroinvertebrates samples comprised of Chironomidae, Oligochaeta and Sphaeriidae. Nodules were recorded in varying amounts from all lake locations except from Breisjøen from 20 meters depth. There was no clear evidence that the amount of nodules affected densities of macroinvertebrates more than did depth (Figure 18). Densities from 12 m depth in Lake Djupøyungen were lower than from 20 m depth in the same lake, and also lower than 13m depth in Lake Breisjøen.

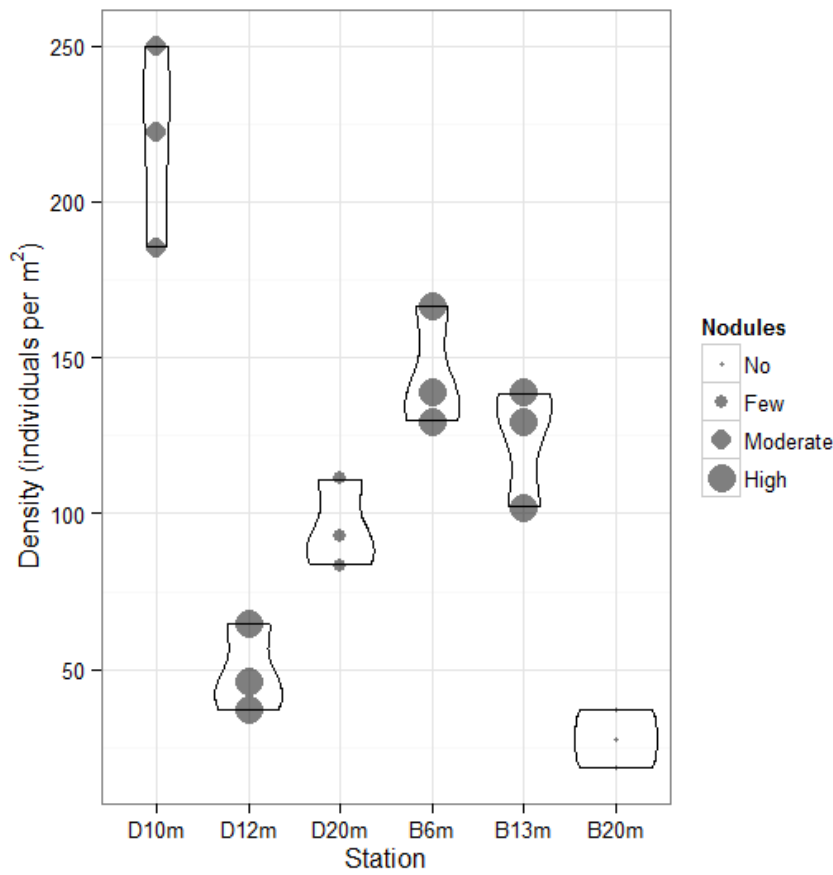


Figure 18. Total densities of profundal macroinvertebrates (*Chironomidae*, *Oligochaeta* and *Sphaeriidae*), in relation to depth and amount of nodules. D denotes Lake Djupøyungen and B denotes Lake Breisjøen followed by the sampling depth (m). The shape of the plot outline illustrates the distribution of data and each black dot denotes the median density. The amount of nodules in each invertebrate sample is denoted by the size of the black dots, see legend.

4. Discussion

4.1 Liming residuals

Both lake sediments are affected by previous liming operations, indicated by higher sediment and porewater Ca concentrations than would be expected if left un-limed. The sediments at shallow and intermediate lake depth had also significantly lower Ca concentrations in the sediment than the cores from larger depths, indicating the typical higher area-specific lime-doses in areas of larger lake depths. At Breisjøen the 20 m sediment still had a significantly higher Ca concentration in the uppermost part of the sediment, probably due to residuals from the heavy liming (high doses) of this lake. The Ca level of both sediment and porewater was significantly lower at Breisjøen than at Djupøyungen, however, probably due to the relatively long re-acidification time after liming and depletion of the Ca-source due to long-term dissolution at Breisjøen.

The porewater Ca concentration tended to be lower in the upper parts of all sediments, resembling that of the lake water immediately above the sediment surface. This is a result of the tendency to establish an

equilibrium between the solid-phase and water-phase Ca, and also due to the smooth and hard-to-define delimitation of porewater and lakewater at the sediment-water interface.

The almost identical vertical distribution of sediment Ca and the relatively high concentrations of both sediment and porewater Ca in Djupøyungen indicate that sediment perturbation may be important or that the sediment accumulation rate is higher than the 2 mm/year we anticipated. Liming may be a reason for this by the addition of un-dissolved limestone powder at each liming occasion and the likely co-precipitation of metals and organic matter due to the pH-increase. On the other hand increased pH due to liming also should facilitate microbial breakdown of organics due to anticipated increased bacterial activity and thereby prevent the accumulation of organic matter on the sediment surface. The mineralization process could be relatively slow, however, if the organic material is dominated by less attractive lignins.

4.2 Trace element dynamics

Sources of trace elements. Wällstedt and Borg (2005) and Wällstedt et al. (2008) examined metal accumulation in the lake sediments after liming of Swedish lakes. They found that direct lake liming increased the sediment concentration of Cd and Pb, probably also As, Co and Zn.

Here, the results show that Mo and U concentrations in the sediments of Djupøyungen are 2-3 orders of magnitude higher than in Breisjøen, high compared to literature value for lakes, and at the level of mining-contaminated sediments. One reason for this might be that Djupøyungen is situated in a previous mining area (Aanes, 2011), indicating metal sources in the bedrock. The high weathering rate and metal content of the sulphide-containing bedrock of the area may be a source for these metals.

One important question emerges though, and needs to be answered: could the limestone powder be a significant source of metals to the lake sediments?

According to *Table 2*, Norwegian limestone powders obviously contain trace metals. Whereas the Sa-3 from Verdal is a high-grade calcite low in metals, HO-3 from Hole intermediate in metal content, the NK3 is more enriched, and the quality also more variable.

We combined the data for NK3 with sediment data for trace metals (*Table 4*) for both lakes in order to estimate the maximum possible trace metal content that may originate from the powders used (or a corresponding powder for Breisjøen). First, we calculated the maximum potential flux brought about by the addition of lime powder NK3. We used typical amounts of powder applied each year over the liming periods (6 tonnes for Djupøyungen and 50 tonnes for Breisjøen), and assumed that 50% of the powder was dissolving before reaching the sediment surface. Accounting for the surface-area of the lake basin, we obtained the fluxes given in *Table 4* for each element. This calculation reveals that <50% of the CaCO₃ indeed reached the sediment surface. The fluxes brought about by the addition of lime are at least 2 orders of magnitude lower than the calculated present-day inventories of trace-elements (in mg dry weight of trace element per m² of sediment area, for a 10 cm sediment core) at Djupøyungen, and by at least 1 order of magnitude lower at Breisjøen. This suggests that liming is not a significant source of metals to the sediments.

Table 4. Maximum metal flux contributed to the sediment-water interface by the NK3 powder, compared to present-day inventory of trace-elements in a 10 cm sediment column at Lake Djupøyungen (upper part) and Lake Breisjøen (lower part). All units in mg/m².

Element	Ca	Co	Cu	Zn	Ni	Pb	Cd	Sn	Sb	U	As	Se	Mo
Flux from NK3	2.4×10 ⁵	1.2	3.2	4.7	5.0	1.2	0.2						
Inventory DI	1.4×10 ⁵	195	270	8980	200	3121	72	19	10	1309	198	49	2939
Inventory DII	1.4×10 ⁵	110	325	8144	219	3107	77	14	13	1304	157	53	1867
Inventory DIII	1.1×10 ⁵	318	248	18540	402	2581	130	26	8	998	257	49	11357
Flux from NK3	3×10 ⁶	1.7	4.4	10.5	11.5	4	0.4						
Inventory BII	5×10 ⁴	73	121	1333	72	632	9	8	4	23	73	16	29
Inventory BII	5×10 ⁴	233	192	2263	104	850	15	20	6	38	159	32	58
Inventory BIII	4×10 ⁴	428	157	2183	121	799	16	19	6	30	195	30	136

We also calculated the most likely metal concentrations in the lake-water as a result of the 50 % dissolution of the limestone powder at each liming occasion, assuming that the 50 % dissolution resulted in a corresponding fraction of dissolved metals. The potential maximum increase in metal concentration (will be diluted according to the lake retention times) was 0.04 and 0.2 µg/L for Djupøyungen and Breisjøen, respectively, after use of NK 3 or corresponding powders, and significantly lower after use of the other two powders of Table 2. This also clearly indicates that metals originating from the limestone powders are not a significant source for metals in the lake-waters and sediments. Therefore, trace-elements are from geogenic origins.

Below, we discuss specific trace elements that are notably enriched and propose mechanisms responsible for those enrichments.

Arsenic. The concentrations of As at all sites are close to mean level for Norwegian surface sediments (Rognerud and Fjeld, 2001). Porewater As is a sensitive indicator of redox reactions; it is mobile at the redox transition between stable metal oxides, and mostly stable in the presence of sulfides (Couture et al., 2010). Here, the porewater As profiles display this classical dynamics, by which As sorbed on Fe-Mn oxides is released during the dissolution of those carrier phase, and precipitate at depth during the formation of sulfides (Figure 12 and Figure 13). This result in a sub-surface maxima in As due to diagenetic enrichments.

Cobalt. Co in sediment is 3-6 fold higher than values for industrially contaminated sediment reported in France (Rigaud et al., 2013). At the deepest site (Djupøyungen-1) solid-phase Co, As and Mo both display a sharp subsurface peak at 4 cm depth, suggesting association with sulfides, likely amorphous Fe and Mn sulfides. These elements are frequently associated with sulfides, such as pyrite, when these phases are actively forming in the sediments. In contrast, at shallow sites where Fe and Mn oxides are strongly enriched at the sediment-water interface, Co, As and Mo clearly associate with those phases while total S concentration are low (e.g. Figure 13).

Cadmium. Cd in porewater and in the sediments at Djupøyungen-3 is twice higher than in the sediment from a comparable oligotrophic, acidic lake in Canada (Alfaro-De la Torre and Tessier, 2002). Similarly, Cd concentrations are twice and 3-fold higher than those reported for lakes that have been limed in the past by Andersen and Pempkowiak (1999) and Wällstedt et al. (2008), respectively. These authors observed higher concentrations of Cd in the overlying water than in the porewater, however at Djupøyungen-3 Cd is produced to the porewater, below the peak of solid-phase Cd. This suggests that a Cd-bearing phase is dissolving at depth, or that Cd-rich water is inflowing from groundwater seepages. In the case of the latter, dissolved Cd would then be precipitating below the depth of Mn reduction. Indeed, at the shallow sites of both lakes, it is clear that Cd accumulation in the sediments starts only after Mn

oxides are reduced (Figure 19). Such diagenetic separation of Cd and Mn was previously described as a result of the interplay between surficial Mn oxides and profundal Cd-sulfides, driven by carbon fluxes from the water column (Gobeil et al., 1997). Although the same process is likely in play at Breisjøen, Cd concentrations in the pore water at that site was below detection limit.

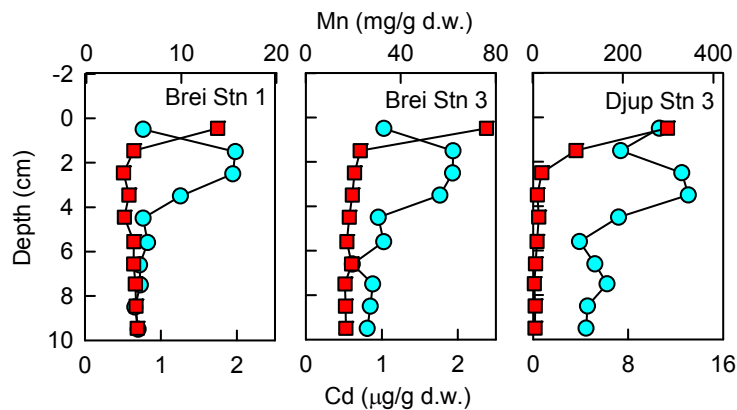


Figure 19. Close-ups of solid-phase Mn (squares) and Cd (circles) concentration depth profiles at three stations where sharp Mn surface enrichments are followed, at depth, by Cd peaks.

Molybdenum. Mo concentrations in Djupøyungen are high at all sites, with Djupøyungen -3 being the highest. Although Mo at Breisjøen is close to the Norwegian average for surface sediments (Rognerud and Fjeld, 2001), it reaches 340-fold that values in Djupøyungen-3. Comparing these values to a comprehensive study of Mo in Canadian lakes, comprising results from both pristine and contaminated lakes, reveals that Mo in the porewater of Djupøyungen-3 are 3 orders of magnitude higher than in the pore water of lakes under the influence of a metal smelter (Chappaz et al., 2008a), and 1 order of magnitude higher in the sediments. At all sites porewater Mo concentration profiles indicate remobilization to the porewater, the magnitude of remobilization closely following that of Mn and Fe, to which Mo is likely associated (Chappaz et al., 2008b; Sundby et al., 2004). Remobilized Mo then precipitates during the formation of Fe and Mn sulfides, as evidenced by solid-phase Mo peaks at depths (e.g. Figure 13).

Uranium. U levels in Breisjøen are close to the baseline reported in the literature for surface sediments, while those at Djupøyungen are between 1 and 2 orders of magnitude higher than the reported levels for smelter-impacted lakes (Chappaz et al., 2010). Solid-phase U exhibit a subsurface maximum in all cores, associated with S rather than Fe or Mn. Contrary to Mo, As and Cd, which were enriched with high Fe and Mn in the littoral cores and with sulfides in the deepest cores, U appears enriched only in the deepest core, indicating different mechanisms of diagenetic enrichments (Figure 13). The sharp contrast between Mo and U distribution is evident at Djupøyungen-3 (Figure 13), testifying of a strong redox control on both elements, as was observed in estuarine sediments (Sundby et al., 2004).

4.3 Major element enrichments

Both as oxides and as sulphides, Fe and Mn minerals are key carrier phases for trace metal(loid)s onto which they sorb (e.g., Linge, 2008). Major elements describe marked sub-surface enrichments in the solid phase, accompanied with the porewater remobilization diagnostic of dynamic geochemical cycling. Such significant Mn enrichment in the top sediment was found in many of the cores. Iron enrichment was significantly less pronounced. In contrast, marked Mn-enrichment in the top sediment was found in only three of the 20 non-limed reference lakes of the previous study (Hindar et al. 2011). These three lakes (two clear-water and one humic) had lake-water pH in the range 5.48- 5.88, but at the same time very high

concentrations of surface sediment Fe, corresponding to 20-25 % of the dry weight. Co-precipitation of Mn on Fe oxy-hydroxides may therefore explain the elevated Mn concentrations in non-limed lakes.

Together, this strongly indicates that increasing pH after liming of acid lakes stimulates processes that result in Mn precipitation, as was also found by Andersen and Pempkowiak (1999). Precipitation of Al, Fe and Mn was ascribed to production of oxy-hydroxides at the increased pH after liming

Dissolved Fe and Mn display sharp increasing gradients below the sediment-water interface, suggesting the dissolution of metal oxides (*Figure 10, Figure 11*). It is also important to notice the clear patterns in S distribution, systematic in all cores. Dissolved S describes an opposite trend to Fe and Mn, with sharp decrease below the sediment-water interface, likely due to microbial sulfate reduction. Evolving sulfides then form fresh metal-sulfides by precipitation with Fe and Mn released to the aqueous phase, responsible for the observed solid-phase S enrichments (*Figure 10, Figure 11*). These phases are known to sequester trace elements (Morse, 1994), as well as Fe and Mn, although we cannot exclude that Fe and Mn also precipitates as carbonates upon reduction of their oxides.

As we have shown the interfaces of water/sediment surfaces may be a likely site for these processes, as also shown by Tebo et al. (2005). Mn-oxides also form more easily at pH > 7-8, especially in the presence of Mn-oxidizing bacteria and other microorganisms in soil and waters (Morgan 2005; Tebo et al. 2005; Silber et al 2008). The combination of increased pH after liming and humic water with available carbon sources may ensure good growing conditions for these bacteria and thereby for nodules. Acidified lakes have probably not experienced pH above 6.5, even prior to acidification, and many may have had pre-acidification pH down to 5.0 (Wright and Cosby 2012). Liming of lakes to historically high pH values (pH > 6.5), and probably even higher at the sediment surface, represents a new chemical environment that make Mn oxidation and precipitation more likely.

Formation of Fe-Mn nodules is known to be enhanced by particles of different kinds, among them fragments of carbonates (Post 1999). Initial steps may be metal precipitation around un-dissolved limestone particles. These calcite particles may dissolve over time thus explaining the low nodule concentrations of both Ca and Mg (Hindar et al. 2011).

Studies of a total of 1500 sediment samples from three national surveys of non-limed lakes (Rognerud and Fjeld 1993, 2001 and Rognerud et al. 2008) revealed no metal nodules of any significant sizes, although small grains were found. The relatively large metal nodules in sediments of limed lakes are therefore uncommon and, as shown, probably related to the liming. However, similar nodules and even significantly larger metal precipitates are described from Lake Baikal (Vodyanitskii, 2009) and several lakes in North America (Edgington and Callender 1970; Pecher et al 2003; Asikainen and Werle 2007).

4.4 Invertebrates

Guidelines for environmental quality of freshwater and freshwater sediment are not available for all elements studies. Arp et al. (2014) provides tentative guidelines for Cd, Pb, As, Cu, Ni and Zn. Comparing maximum observed concentrations at each site with these guidelines reveals that Cd, Pb and Zn are systematically above toxicity thresholds in the solid phase at all sites. Only Zn and Cu are above the toxicity thresholds for the porewater. Zn crosses thresholds at all sites, while Cu is above the thresholds at Bresjøen-1 and -3, and at Djupøyungen-1. As and Ni are consistently below toxicity thresholds in both sediment and porewater. We further compared the measured concentrations with the more comprehensive criteria for marine sediment. Although not strictly applicable to freshwater sediments, Norwegian guidelines for marine sediments reveal that most of the sites reach concentrations above thresholds that induce toxic effect to benthic fauna (*Table 5*). Concentrations of Mn and Mo indicate very bad condition in both lakes, and those of U, Cd, Pb and Zn moderate conditions in Djupøyungen. Concentrations of As, Ni and Cu are at acceptable levels according to these guidelines.

As the concentrations of several metals in the Djupøyungen and Breisjøen sediments were significantly above critical limits set for marine sediments, one might expect effects on invertebrates in these lakes. Station Djup3 (Djupøyungen at 12 m) had lower densities of macroinvertebrates than expected, and compared to station Djup1 (20 m) and Djup2 (10 m). Station Djup-3 also had the highest recorded level of Mn in the porewater. No effects on invertebrates in the littoral and outlet of Djupøyungen and no effects at all in Breisjøen were found.

Although we cannot exclude the possibility that the result at 12 m depth in Djupøyungen may be related to natural patchiness of invertebrates across the lake, the combination of low densities, high porewater Mn and high levels of some of the trace metals indicates negative effects on biota at this depth. The combined effect on biota is lower than indicated by the metal concentrations, however.

Table 5. Classification, according to published total sediment concentration criteria, of the maximum metal content found in the sediments of each sampling sites. Criteria are for marine sediments and cannot therefore be directly applied as indicator of potential toxicity in lakes.

Site Element (ref)	Breisjøen			Djup.		
	1	2	3	1	2	3
Mn ¹	Red	Black	Black	Red	Red	Black
As ²	Blue	Blue	Blue	Green	Blue	Green
Mo ¹	Black	Black	Black	Red	Red	Black
U ¹	Blue	Blue	Blue	Yellow	Yellow	Yellow
Co ²						
Cd ²	Green	Green	Green	Yellow	Yellow	Yellow
Pb ²	Yellow	Yellow	Yellow	Yellow	Yellow	Yellow
Ni ²	Blue	Blue	Blue	Blue	Blue	Blue
Cu ²	Blue	Blue	Blue	Blue	Blue	Blue
Zn ²	Green	Green	Green	Yellow	Yellow	Yellow

Legend
Black
Red
Yellow
Green
Blue

>10 × Very Bad
Very bad
Bad
Moderate
Good
Baseline

¹Thompson et al. (2005), ²Bakke et al. (2010)

High levels of Mn is usually associated with elevated concentrations of other metals (e.g. Fe and Cu), which may also have deleterious effects on invertebrates. It is thus difficult to isolate the effect of Mn, and Mn tolerances to invertebrates reported in the literature varies widely. The lowest toxic concentrations are reported from watersheds with low water hardness and high pH (Kleinmann and Watzlaf, 1988). Elevated Ca and Mg seem to have a protective effect on Mn toxicity for invertebrates, while concentrations of dissolved organic carbon (DOC) have little protective effect (Peters et al., 2011). Liming, in terms of increased concentrations of Ca in the sediments, may thus explain why the effects on invertebrates are lower than indicated by the metal concentrations.

However, there is limited information about trace metal effects on macroinvertebrates and freshwater ecosystems. Type of food items and their respective metal content is important, and thus how increased sediment concentrations influence the concentration in these food items. (Goodyear & McNeill, 1999). If communities of macroinvertebrates are dominated by Chironomidae and Oligochaeta, it may take extreme levels of sediment pollution to get significant changes in ecosystem functionality, although the species composition may shift (Canfield et al., 1996). Sediment pollution may however lead to sub-lethal effects through e.g. physiological deformities, for instance mouthparts that do not develop correctly (Meregalli et al., 2000; Ochieng et al., 2008; Warwick, 1991; Canfield et al., 1996), although this is not always the case (Canfield et al., 1994).

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