Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting Information to "Geochemistry of trace elements associated with Fe and Mn nodules in the sediment of limed boreal lakes"

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10 pages, 4 figures, 5 Tables

Table SI-1. Name, number (referring to Fig. 1 in the main text) and coordinates of the 17 survey lakes.

Lake name	Lake no	Latitude °N	Longitude °E
Limed lakes			
Breisjøen	1	60.558395	12.526743
Kalsjøen	2	60.368757	12.543140
Terjevatn	3	58.093726	7.902653
Selura	4	58.311277	6.706695
Fallsjøen	5	60.545165	12.574386
Rotbergsjøen	6	60.499243	12.542902
Nøklevatnet	7	60.348251	12.539608
Djupøyungen	8	60.161772	10.901568
Storøyungen	9	60.152747	10.894002
Bjertnessjøen	10	60.194749	10.882297
Råsjøen	11	60.203746	10.816771
Hølvatnet	12	59.772077	11.912573
Stangebrot	13	59.748974	11.886595
N. Boksjø	14	59.059991	11.669727
Holtetjern	15	59.277231	11.382737
Ljosevatn	16	58.865666	8.749462
Trælevatn	17	58.862084	8.779809

Table SI-2. Summary characteristics and water chemistry of the 17 survey lakes.

Limed lakes (n=17)					
Variable	Mean	SD	Min	Max	Median
m.a.s.l.	286	124	22	436	335
Lake surface area, km^2	1.56	1.88	0.06	6.01	0.69
Catchment area, km^2	23.6	33.4	1.2	128.5	12.1
Max. depth, m	31	25	11	118	27
pH	6.26	0.55	4.88	6.86	6.26
Conductivity, $mS\ m^{-1}$	2.59	1.34	1.45	6.42	2.33
Nitrate, $\mu g\ N\ L^{-1}$	60	52	15	220	42
TOC, $mg\ C\ L^{-1}$	8.9	4.9	2.0	24.8	7.9

Table SI-3. Reactions for the formation of the various Fe, Mn, P, As and Mo species and their corresponding equilibrium constants added to the MINTEQ database.

Reaction	Log K	Reference
Ionization		
$AsO_3^{3-} + H^+ \leftrightarrow HAsO_3^{2-}$	15.0	Nordstrom and Archer (2003)
$AsO_3^{3-} + 2H^+ \leftrightarrow H_2AsO_3^-$	29.2	Nordstrom and Archer (2003)
$AsO_3^{3-} + 3H^+ \leftrightarrow H_3AsO_3^0$	38.3	Nordstrom and Archer (2003)
$AsO_4^{3-} + H^+ \leftrightarrow HAsO_4^{2-}$	11.80	Nordstrom and Archer (2003)
$AsO_4^{3-} + 2H^+ \leftrightarrow H_2AsO_4^-$	18.79	Nordstrom and Archer (2003)
$AsO_4^{3-} + 3H^+ \leftrightarrow H_3AsO_4^0$	21.09	Nordstrom and Archer (2003)
Sulfidation		
$AsO_3^{-3} + HS^- + 4H^+ \leftrightarrow H_3AsSO_2^0 + H_2O$	45.7	Helz and Tossell (2008)
$AsO_3^{-3} + HS^- + 3H^+ \leftrightarrow H_2AsSO_2^- + H_2O$	42.0	Helz and Tossell (2008)
$AsO_3^{-3} + 2HS^- + 3H^+ \leftrightarrow HAsS_2O^{2-} + 2H_2O$	44.2	Helz and Tossell (2008)
$AsO_3^{-3} + 3HS^- + 4H^+ \leftrightarrow HAsS_3^{2-} + 3H_2O$	56.7	Helz and Tossell (2008)
$AsO_3^{3-} + 3HS^- + 3H^+ \leftrightarrow AsS_3^{3-} + 3H_2O$		Helz and Tossell (2008)
$AsO_3^{3-} + 4HS^- + 6H^+ \leftrightarrow As(SH)_4^- + 3H_2O$		Helz and Tossell (2008)
$AsO_3^{-3} + 2HS^- + 5H^+ \leftrightarrow H_3AsS_2O^0 + 2H_2O$	56.5	Helz and Tossell (2008)
$AsO_3^{-3} + 3HS^- + 6H^+ \leftrightarrow H_3AsS_3^0 + 3H_2O$	69.0	Helz and Tossell (2008)
$AsO_4^{-3} + HS^- + 4H^+ \leftrightarrow H_3AsSO_3^0 + H_2O$	39.1	Helz and Tossell (2008)
$AsO_4^{-3} + 2HS^- + 5H^+ \leftrightarrow H_3AsS_2O_2^0 + 2H_2O$	46.2	Helz and Tossell (2008)
$MoO_4^{2-} + H^+ + HS^- = MoO_3S^{2-} + H_2O$	12.21	Erickson and Helz (2000)
$MoO_4^{2-} + 2H^+ + 2HS^- = MoO_2S_2^{2-} + 2H_2O$	24.03	Erickson and Helz (2000)
$MoO_4^{2-} + 3H^+ + 3HS^- = MoOS_3^{2-} + 3H_2O$	36.05	Erickson and Helz (2000)
$MoO_4^{2-} + 4H^+ + 4HS^- = MoS_4^{2-} + 4H_2O$	47.95	Erickson and Helz (2000)
Precipitation		
$2AsO_3^{3-} + 9H^+ + 3HS^- \leftrightarrow As_2S_{3(s)} + 6H_2O$	122.8	Nordstrom and Archer (2003)
$2AsO_3^{3-} + 9H^+ + 3HS^- \leftrightarrow As_2S_{3(am)(s)} + 6H_2O$	121.4	Nordstrom and Archer (2003)
$AsO_3^{3-} + 4H^+ + HS^- - 0.25O_2 \leftrightarrow AsS_{(s)} + 2.5H_2O$	36.9	Nordstrom and Archer (2003)
$Fe^{+2} - H^+ + HS^- \leftrightarrow FeS_{m(s)}$	3.5	Davison (1991)
Adsorption reaction		
$\equiv MnOH_{(s)} + H_2AsO_4^- + H^+ \leftrightarrow \equiv MnH_2AsO_4 + H_2O$	3	Ying et al. (2012)
$\equiv MnOH_{(w)} + H_2AsO_4^- + H^+ \leftrightarrow \equiv MnH_2AsO_4 + H_2O$	-3	Ying et al. (2012)
$\equiv MnOH + MoO_4^{2-} + 2H^+ \leftrightarrow \equiv MnHMoO_4 + H_2O$	18.7	Balistrieri and Chao (1990)
$\equiv MnOH + PO_4^{3-} + 2H^+ \leftrightarrow \equiv MnHPO_4^- + H_2O$	25	Balistrieri and Chao (1990)

Table SI-4. Proportion (%) of species of the element Ba, Co, Cd, P, As, Mo, Pb and Zn calculated by Visual MINTEQ v3.1 at the sediment-water interface of each site. The dominant species for each element is indicated in bold. ≡ denotes a surface complex.

	Lake 1			**Lake 8**		
	6m	13m	20m	10m	12m	20m
Ba						
$\equiv MnO\text{-}Ba^{+}$	**100**	**100**	**100**	**99**	**100**	**100**
Co						
$\equiv Mn\text{-}Co^{+}$	**99**	**99**	**99**	**93**	**76**	**74**
$\equiv MnO\text{-}Co(OH)$				7	23	26
Cd						
$\equiv FeO\text{-}Cd^{+}$				42	5	13
$\equiv MnO\text{-}Cd^{+}$	45	10			**84**	5
DOC-Cd	**52**	**86**	**96**	**53**	11	**79**
P						
$\equiv Fe\text{-}H_2PO_4$	**53**	**66**	30	11	26	4
$\equiv Fe\text{-}HPO_4^{-}$	29	32	32	26		17
$\equiv Fe\text{-}PO_4^{2-}$	17		**37**	**63**	**72**	**80**
As						
$\equiv Fe\text{-}HAsO_4^{-}$	**59**	**61**	**60**	**49**	41	36
$\equiv Fe\text{-}AsO_4^{2-}$	12	22	24	45	**55**	**60**
Mo						
$\equiv FeO\text{-}Mo(OH)_5$	5	13	36	11	6	**66**
$\equiv MnO\text{-}HMoO_4$	**95**	**87**	**63**	**89**	**94**	34
Pb						
$\equiv FeO\text{-}Pb^{+}$				3		1
$\equiv MnO\text{-}Pb^{+}$	**97**	**98**	**97**	**76**	**75**	**91**
$\equiv Mn\text{-}PbOH$	3	1	2	22	25	8
Zn						
$\equiv FeO\text{-}Zn^{+}$				**44**		7
$\equiv MnO\text{-}Zn^{+}$	**97**	**98**	**96**	29	47	**74**
$\equiv MnO\text{-}Zn(OH)$	3	0	3	27	**52**	17

Text SI-1. Metal content of the limestone used for liming

The limestone powder used at Djupøyungen was of type SA-3 from 2008-2011 and HO-3 and NK3 before that both from produced Franzefoss Miljøkalk AS (Norway). Metal content of these limestone powders were obtained from product data sheets and compiled in Hindar et al. (2013). These authors report not being able to get limestone product data used at Breisjøen, but its metal content is likely in the range found for the NK3 product. We combined the data for NK3 with sediment data trace element inventories in Lakes 1 and 8 in order to estimate the maximum possible trace element content that may be ascribed from the powders used. We used typical amounts of powder applied each year over the liming periods 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 SI-6. The calculated 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 m^2 of sediment area, for a 10 cm sediment core) at Lake 8, 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 SI-5. Estimated maximum metal flux contributed to the SWI by the NK3 powder, compared to present-day inventory of trace-elements in a 10 cm sediment column at Lakes 1 and 8.

	Ca (×10$^{5)}$	**Co**	**Cd**	**As**	**Mo**	**Pb**	**Zn**
				mg/m^2			
Fluxes to Lake 8	**2.4**	1.2	0.2	-	-	1.2	4.7
10 m	1.4	110	77	157	1867	3107	8144
12 m	1.1	318	130	257	11357	2581	18540
20 m	1.4	195	72	198	2939	3121	8980
Fluxes to Lake 1	**30**	1.7	0.4	-	-	4	10.5
6 m	0.4	428	16	195	136	799	2183
13 m	0.5	233	15	159	58	850	2263
20 m	0.5	73	9	73	29	632	1333

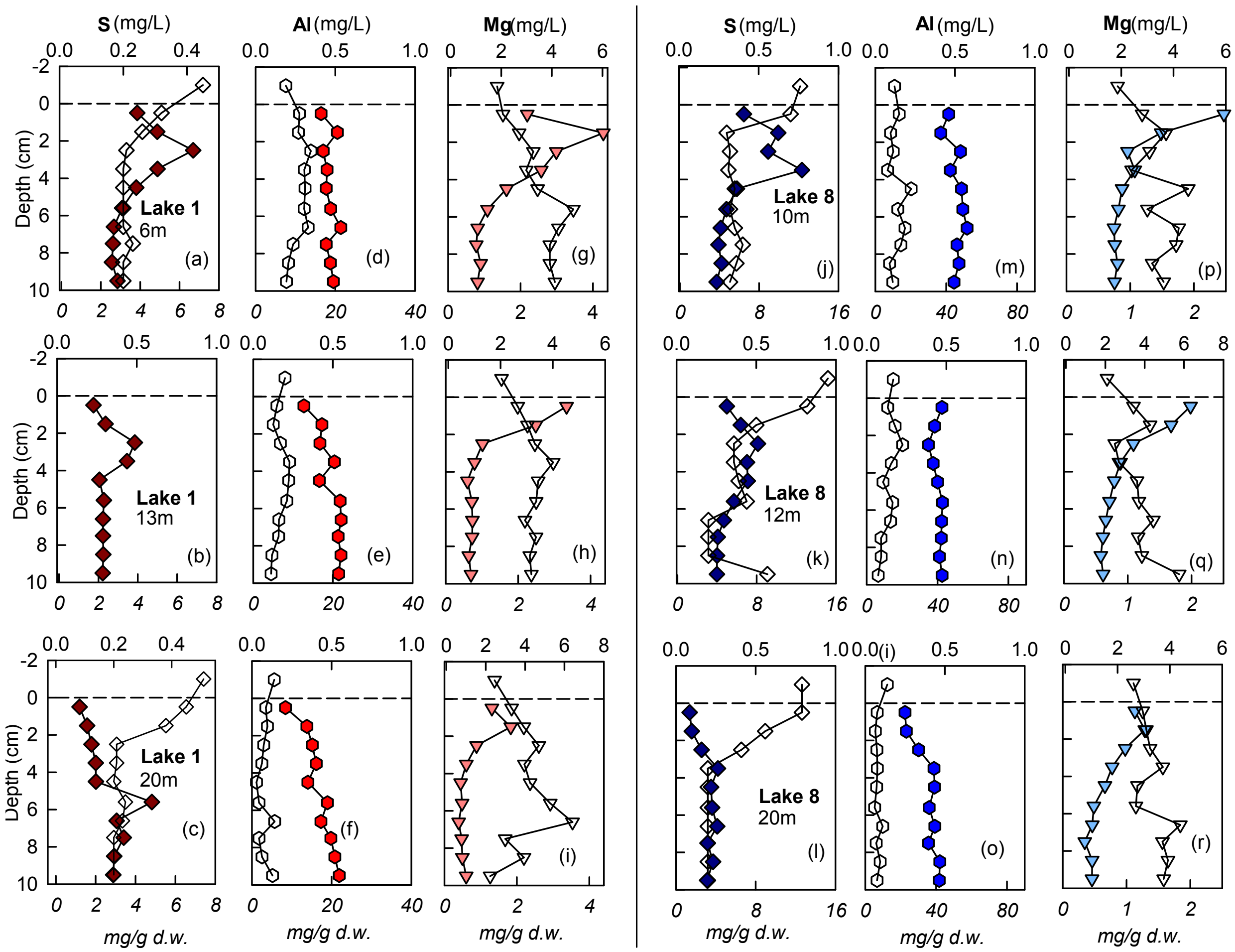

Figure SI-1. Depth profile of sedimentary (closed symbol, scale on lower X-axis) and porewater (open symbol, scale on upper X-axis) S (a-c, j-l), Al (d-f, m-o), and Mg (g-i, p-r) in Lake 1 (left panels a-i) and Lake 8 (right panels j-r). Horizontal dashed lines indicate the sediment-water interface.

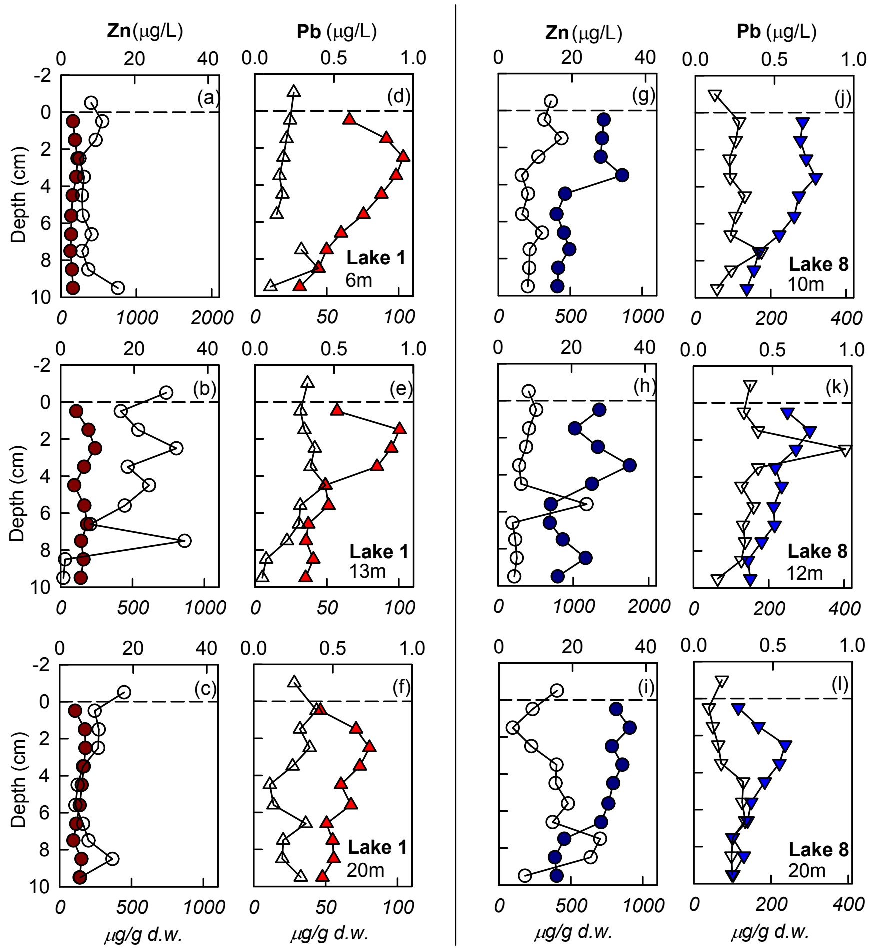

Figure SI-2. Depth profile of sedimentary (closed symbol, scale on lower X-axis) and porewater (open symbol, scale on upper X-axis) Zn (a-c, g-i) and Pb (d-f, j-l) in Lake 1 (left panels a-i) and Lake 8 (right panels j-r). Horizontal dashed lines indicate the sediment-water interface.

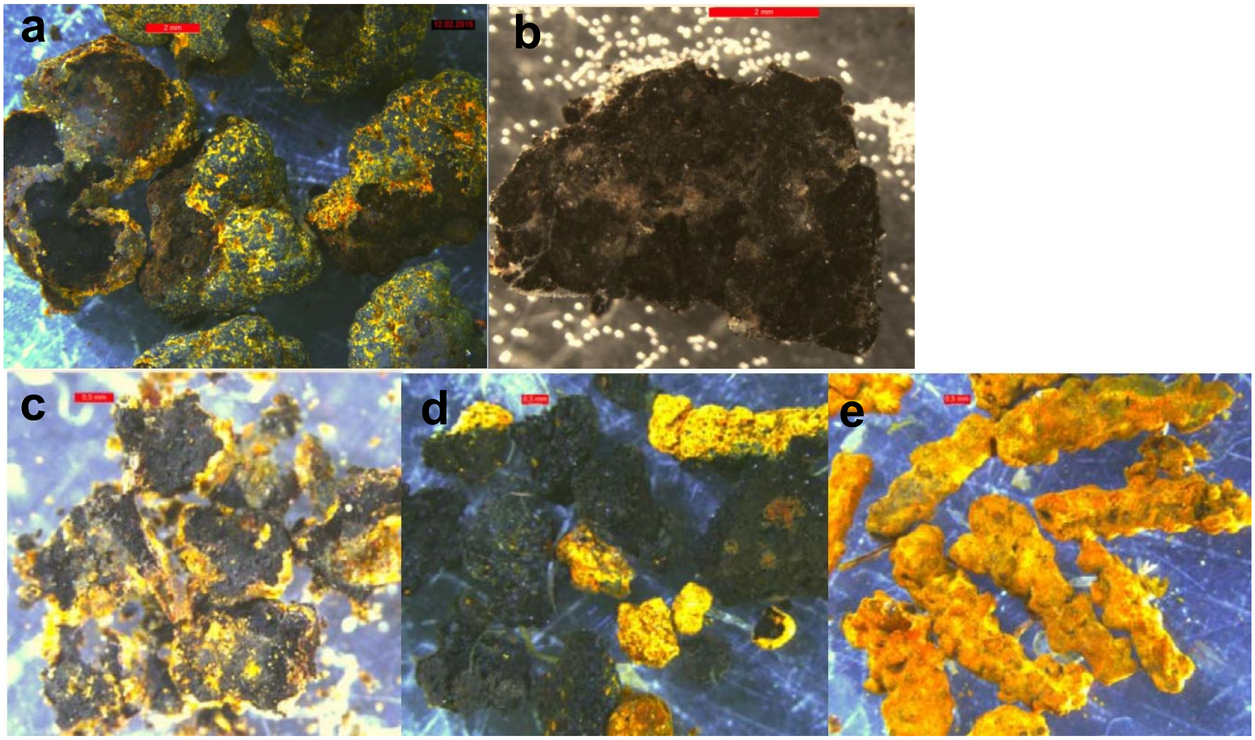

Figure SI-3. Photograph of washed nodules sampled at 13m and 6m depth in Lake 1 (panel a-b, red scale = 2mm) and from 20m, 12, and 10m depth in Lake 8 (panel c-e; red scale = 0.5 mm). No nodules were found at 20 m depth in Lake 1.

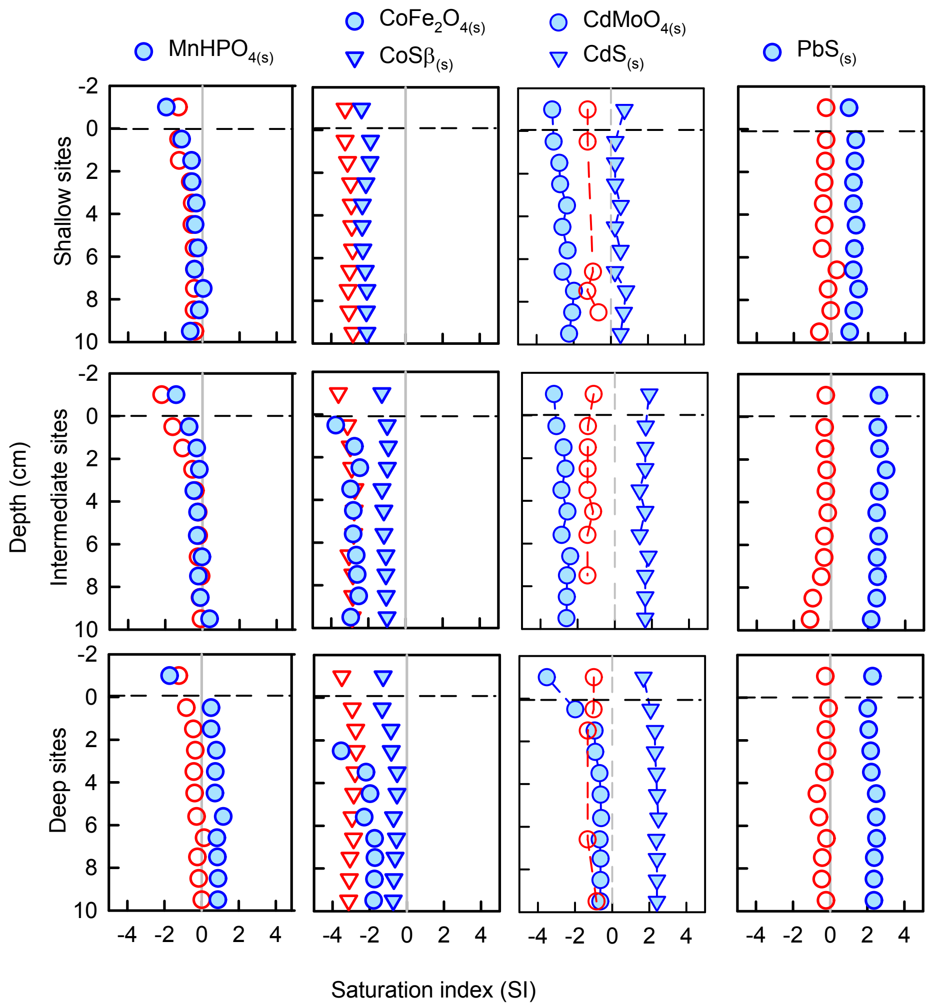

Figure SI-4. Depth profile of saturation indices (SI) for solid phases with SI ± 4 as calculated with PHREEQC v.3 and the Minteq v.4 database. Open symbols refer to Lake 1 and solid symbols to Lake 8. Horizontal dashed lines indicate the sediment-water interface and the vertical line indicate SI = 0 (i.e. pore water are at saturation with respect to the indicate mineral).

Litterature cited

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