Sediment And Pore Water Properties Across The Chemocline Of A Mine Water-Impacted Boreal Lake During Winter Stagnation And Autumn Overturn

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Abstract Discharge of mine waters into the typically dimictic lakes in the Nordics may cause meromixis in which complete overturns no longer happen. Water column properties were measured from the mining-meromictic Lake Valkjärvi and sediments and pore waters were sampled below, at, and above the chemocline during winter stratification and autumn overturn. Element concentrations were elevated in pore and overlying waters during the overturn. Sediment bulk concentrations showed an opposite behavior. The results demonstrate the importance of the chemocline fluctuation zone on the annual cycle of elements and trace metal concentrations of the sediment compartment.

Introduction

Northern European countries remain a major source of metals with more mines to be opened in the coming years. In countries such as Finland and Sweden, it is often dimictic lakes that receive the effluent waters from the mining operations. In dimictic lakes, thermal stratification is interrupted twice a year by periods of overturn, i.e. mixing of the surface and deeper waters. Mine waters, even those that come from closed mines or that are discharged with strict permit conditions, typically contain high concentrations of electrolytes that increase the density of the waters. In extreme cases, mine waters may cause a condition called meromixis in which complete overturns no longer happen and a permanently stratified monimolimnion forms at the bottom, separated from the overlying mixolimnion by a chemocline.

When mining-induced disrupted annual stratification patterns have started, they may persist even if loading from the mine decreases. This is especially true for meromixis because permanent stratification typically also causes a redox gradient with reducing conditions in the monimolimnion. This redox stratification may contribute to biogeochemical cycling processes at the chemocline (the transitional layer between the upper and deeper water) that work to maintain the permanent stratification. The sediments and their immediate overlying waters also take part in this cycling if processes at the sediment water interface return dissolved constituents into water instead of permanently removing them from circulation.

Lake bottom sediments are a crucial compartment in the lake system, especially regarding the ecological risks of mine waters. This is because harmful concentrations of metals may accumulate in sediments even in cases when concentrations in the water column are not at harmful levels (Väänänen et al. 2016). In the case of metals as hazards, bioavailability is of crucial importance and geochemical conditions play a major role in determining the speciation and bioavailability. In Nordic climates, seasonality modifies these conditions and in meromictic lakes this is further influenced by the features of the stratification and the migration of the chemocline.

This study examined the chemical properties of the sediment compartment (pore water, immediate overlying water, and bulk sediment) of a mining-impacted meromictic boreal lake. Samples were cored above, at, and below the chemocline at the end of the winter stagnation period (March) and near the end of the open water season during autumn overturn (November) in 2014. Water column properties were measured at both sampling occasions as well. The aim was to study the geochemical properties of the biologically active top layer of the sediments across the chemocline in both winter stagnation and autumn overturn conditions. These data can be useful for the estimation of the ecological risks of metals in the sediments of mining impacted lakes, especially at the zone of seasonal chemocline fluctuation.

Material and methods

Lake Valkeinen is located just south of the closed Kotalahti nickel-copper mine at Oravikoski in Leppävirta, Finland. The mine was in operation between 1959-1987. Waters from the mine site are primarily discharged to a larger lake east of the mine and only a small ditch drains a natural wetland close to the tailings pond towards Lake Valkeinen (Figure 1). Other streams enter the lake from the SE. The lake has a surface area of 19.5 ha and a maximum depth of 16 m.

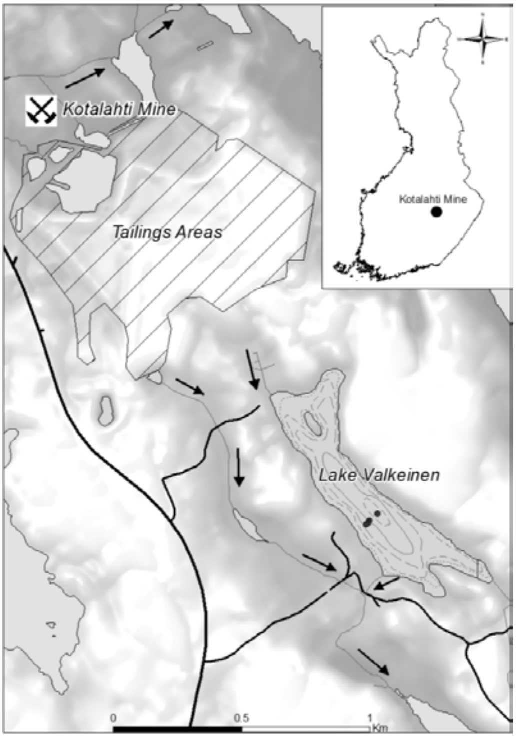

***Figure 1**. Map of Lake Valkeinen and its location in Finland. Coring sites (8, 10, 14, and 16 m) are marked with dots.*

Lake Valkeinen was cored from the ice in late March in 2014 (17.-24.3.2014) and from a boat in early November (3.-6.11.2014). The coring sites form a transect towards the deepest part of the lake: 8 m (above the chemocline), 10 m (near the chemocline), 14 m (below the chemocline), and 16 m (deepest part). The sediments were cored with a Kajak-type corer that closes at the upper end. This preserves the water overlying the sediment during the withdrawal of the corer. A limiter was used to limit the penetration depth of the corer in the sediments to ensure that enough of overlying water was obtained in all cases. Artificial roots ('rhizons') of a nominal pore diameter of 0.2 µm were used to sample both the overlying water and the pore waters (top 5 cm) into pre-vacuumed test tubes. The test tubes for elemental analyses were opened in the field and nitric acid was added for preservation.

The water samples, including water column samples from 2, 10, and 14 m, were analyzed for element concentrations with ICP-AES/MS, major anions with IC (SFS-EN-ISO 10304-1:en), and DOC according to SFS-EN 1484 in the accredited (FINAS T025) testing laboratory of Labtium Ltd. Every tenth sample or at least one in every batch were analyzed as laboratory duplicates and reference materials and field blanks also were analyzed.

The top sediments corresponding to the pore water samples (5 cm) were freeze dried for geochemical analyses with ICP-MS and ICP-AES from microwave-assisted HNO_3 leachates (US EPA 1994). The digestion breaks down sulphides, most salts (e.g., apatite), carbonates, trioctahedral micas, and 2:1 and 1:1 clay minerals but does not appreciably dissolve major silicates. A CN-analyzer was used to determine carbon concentrations. Laboratory duplicates and internal standards were employed for the sediment analyses as well.

Water column properties were measured using a Yellow Springs Instruments XL600 and Professional Plus multiparameter sondes. The variables included depth, temperature, specific conductance (conductivity), pH, reduction potential (ORP), and oxygen. Measurements were also made from the water overlying the sediments in the Kajak corer, and directly from the sediments by pushing the electrodes into the soft sediment. The variables measured from the cores included temperature, pH, ORP, and conductivity. The meters and electrodes were from WTW and Mettler Toledo.

Results

Water column properties

Water column properties show that a monimolimnion devoid of oxygen exists below 10 m also during the autumnal overturn. The mixolimnion remained well aerated (O_2 saturation > 80 %, O_2 11 mg/L) all the way to 9 m where the first small decline was recorded during the overturn. In contrast, O_2 concentration and saturation declined gradually with depth in the mixolimnion during winter stagnation with steeper decline starting at 9 m. There was a decline in O_2 between 2.5 and 3 m during the winter sampling, accompanied with a slight but distinct increase in temperature and a barely detectable drop in pH. The change in temperature at the chemocline was steeper during the overturn with a rapid transition from the stable 3.4 C to the warm (4.7 C) upper part of the monimolimnion. The specific conductivity of the mixolimnetic water was 460 µS/cm for both autumn and winter down to 6 m. Below this level the conductivity started to gradually increase towards the chemocline during winter stagnation. Conductivity increased to 700 µS/cm in the monimolimnion in both periods with a layer of even more electrolyte rich waters below 14 m (up to 1000 µS/cm). Water column pH was higher throughout during the overturn declining from 8.0 at the surface to 7.5 at 9 m and then dropping to 7.0 below the chemocline. There was a layer of higher pH near the lake bottom during both periods and another layer of elevated pH at the rapid decline in ORP at 10.5 m during the winter stagnation. Above this layer, there was a zone of lower pH between 9 and 10 m. Corresponding ORP-pH zoning was not observed during the overturn.

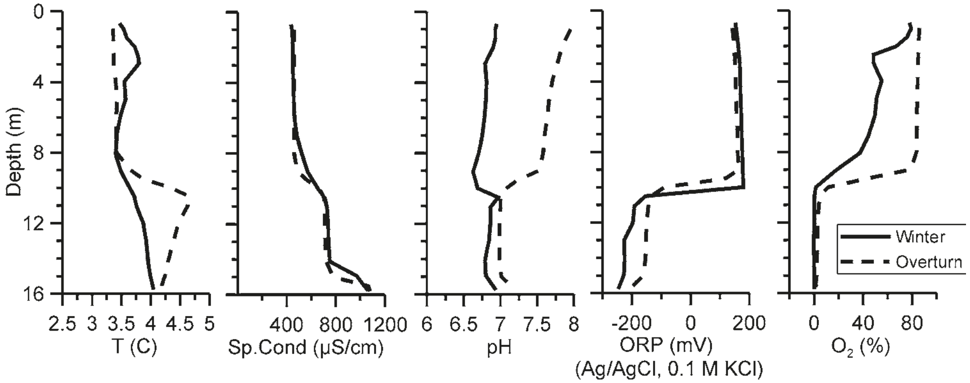

***Figure 2**. Water column properties at the deepest part of the lake, at the end point of the coring transect. Solid line = winter stagnation, dashed line = autumn overturn.*

In accordance with the conductivity results, element concentrations in the water column (results not shown) were higher in the monimolimnion than in the upper part of the mixolimnion during both occasions. Concentrations in the transitional zone were in general between these two extremes. However, Mn, Ni, Co, and Zn concentrations were elevated at the chemocline. Manganese in particular was found at 10 m during the overturn whereas Fe concentrations were conspicuously low in all samples. Similar to most elements, sulfur and SO_4 concentrations increased with depth. Total sulfur and SO_4 molarities coincided at 2 m and 10 m but there was a 2-2.5 mmol/l excess of sulfur at 14 m.

Pore waters and overlying waters

During late winter stagnation, the waters overlying the sediment (10 cm layer) were oxidizing at 8 m (+184 mV using Ag/AgCl, 0.1 M KCl electrode) and turned more reducing at the deeper sites (Table 1). Within the top sediment (at 3 cm), pore waters were reducing at all sites (~ -250 mV). There was a gradual increase in SO_4 concentrations with depth in both the overlying and pore waters. When compared with total S concentrations, SO_4 accounted for most of the sulfur at 8 and 10 m but there was an excess of sulfur (i.e. other species) below the chemocline, especially in the overlying waters at 16 m. In all cases, there was more sulfur in the waters overlying the sediment than in the pore water.

***Table 1**. Selected properties of pore waters (bottom) and the waters overlying sediments (top). Winter values are on the right, overturn values on the left.*

Depth (m)	ORP (mV)	EC (µS/cm)	Al µg/L	Fe mg/L	Mn µg/L	Ni µg/L	Zn µg/L	S mg/L	SO4 mg/L	DOC mg/L	ORP (mV)	EC (µS/cm)	Al µg/L	Fe mg/L	Mn µg/L	Ni µg/L	Zn µg/L	S mg/L	SO4 mg/L	DOC mg/L
8	184	219	8.74	<0.05	20.5	7.99	5.51	82.7	200	5	82	15	<1	0.95	619	7.13	5.28	60.0	180	2.6
10	-10	350	14.6	<0.05	405	10.6	8.46	103	249	3.2	-111	306	12.3	0.52	2780	7.84	16.0	89.0	240	3.1
14	-245	417	37	0.1	2460	5.98	4.86	157	306	5.5	-243	447	32.0	0.07	2030	5.09	1.56	651	400	5.3
16	-208	558	38.8	<0.05	1040	4.47	4.11	380	417	3.5	-364	640	26.0	<0.05	1120	4.60	2.46	808	410	12
8	-220	330	131	7.24	3190	6.72	7.56	71.4	199	9.1	-110	250	28.6	5.26	2980	3.82	7.88	58.0	170	8.1
10	-248	310	170	0.07	3450	3.29	1.45	71.9	207	11	-280	300	35.4	0.08	3060	3.99	10.7	74.6	210	11
14	-290	400	170	<0.05	2230	4.34	4.66	118	243	18	-292	376	53.5	<0.05	1480	3.50	0.59	278	310	12
16	-260	560	154	<0.05	1060	5.53	3.22	161	361	20	-364	640	74.7	<0.05	1180	5.26	0.75	355	330	13

Iron concentrations were again negligible in the pore and overlying waters in the winter with the exception of the pore waters of the shallowest site (7 mg/L). In contrast, Mn concentrations were relatively high in especially the pore waters of the two shallowest sites, declining below the chemocline. In the overlying waters, Mn was all but absent at 8 m and at the highest at 14 m. Here again, Ni and Zn concentrations in the overlying waters were highest at 10 m, accompanied with low pore water concentrations. The highest concentrations of these elements in pore water were found at the shallowest site (8 m). There was more DOC in the pore waters than in the waters overlying the sediment with an increasing trend with depth (from 9 to 20 mg/L).

The autumnal overturn did not result in more oxidizing conditions in either the overlying waters or pore waters at any depth. In fact, overlying water remained more reducing than during the winter at the chemocline (10 m). Similar to the winter stagnation, SO_4 concentrations increased with depth in both the overlying and pore waters with higher concentrations above the sediment than in pore waters. Here again, SO_4 accounted for most of the sulfur at the mixolimnetic sites but the proportion of excess sulfur over SO_4 was higher in both the overlying water (16-21 mmol/l) and pore water (5.5-7.7 mmol/l) than in late winter.

Iron concentrations were very low also during the overturn, with some Fe detected in the shallowest sites. Mn concentrations were highest in the pore waters of the 8 m and 10 m sites while the highest concentrations in the overlying water were measured at 10 m, in line with the water column results. The same was true for Zn and Ni in the overlying waters but, in contrast to winter stagnation, pore water concentrations at the chemocline (10 m) were not conspicuously low. The increasing trend in pore water DOC concentrations with depth was similar to the late winter conditions but this time there was a similar and even more pronounced trend in the overlying water as well. Electrical conductivity increased with depth as in winter and in the water column but the conductivity in the overlying water at 8 m was very low at 15 µS/cm. This general trend was seen in major cations as well.

When the major winter-to-overturn differences in pore waters and overlying waters were examined at different sampling depths, they mostly consisted of cases where concentrations were higher during the overturn. However, there were cases in which concentrations were higher in the winter at the monimolimnetic sites (14 m and 16 m) such as Cr in the overlying water at 16 m, Se in pore water at 14 m and 16 m, and Zn in both water fractions at 14 m and 16 m. In addition, Al concentrations were higher during the winter at all depths. In general, however, concentrations were higher in the autumn and this was especially true for the 10 m coring site which is located close to the chemocline. At this site, especially the concentrations in the waters overlying sediment showed higher element concentrations during the overturn. Concentrations of total sulfur were exceptions to this rule with high autumnal concentrations only in the monimolimnion.

Sediments

As is common for any lake, mining impacted or not, there were trends in sediment element concentrations with depth. These trends stem from the physical and geochemical processes that sort the materials between the shallower and deeper areas of a lake basin. At Lake Valkjärvi as well, elements typical to silicate minerals had higher concentrations in the shallower sediments (Al, Cr, K, Ti, V). In addition, Mn and Pb declined with depth. Elements with higher concentrations deeper in the lake included Co, Fe, S, Ni, and P and also alkaline and alkaline earth metals Ca, Mg, Na, and Sr. As usual, carbon concentrations were higher in the deep water sites, also affecting element concentrations in sediments.

***Table 2**. Concentrations of selected elements in the sediments (in mg/kg, C in %). Upper panel = winter, lower panel = overturn.*

Depth (m)	Al	As	Ba	Ca	Co	Fe	K	Mg	Mn	Na	Ni	P	Pb	S	Sr	Ti	V	Zn	C
8	17200	15	378	10200	104	48500	2360	7230	2260	317	1120	2250	73	15900	51.6	784	50.9	329	20.4
10	13900	13	234	8870	130	52500	1960	6130	1390	268	979	1930	56	48100	44	623	35.7	187	19.8
14	13500	15	202	11100	216	72100	2130	7400	1230	423	1930	1900	53	71700	55.5	578	31.7	262	21.8
16	13500	16	439	12100	321	103000	1820	7230	2150	347	2050	3620	36	108000	71.7	467	24.9	276	20.3
8	16500	7	241	8820	65	45800	2040	6120	1430	260	560	1580	68	18400	40	709	46	241	19.1
10	13700	7	200	9490	91	45300	2180	6650	1420	313	710	1680	62	42400	43	679	36	181	20.1
14	12200	9	221	11300	265	67900	1800	7060	1130	356	1970	2190	46	70600	51	466	24	251	20.9
16	10100	8	234	11200	230	78600	1740	6990	1150	354	1930	2260	37	84100	53	454	20	256	21.5

Understandably, changes in sediment concentrations were less pronounced than those in the water phases of the sediment realm. In general, concentrations were slightly higher in the winter than in during the overturn (the opposite was true for the waters). The change, although slight, was strongest at the deepest (16 m) and shallowest (8 m) sites. In particular, the concentrations of Fe, Mn, As, and S were higher at 16 m in winter. Fe and S were elevated also at the chemocline zone (10 m) in winter whereas Al and the alkaline and alkaline earth metal concentrations were lower at that depth. At the shallowest site, above the chemocline fluctuation zone, winter concentrations were higher for e.g. Ba, Ca, Mg, and also Mn, Ni, and Zn.

Discussion

The results show that Lake Valkeinen indeed is meromictic and autumnal overturn is unable to mix the monimolimnion. However, mixing erases the zonation in the mixolimnion seen during winter stagnation with a zone of oxygen consumption, higher temperature, and lower pH at the interface between fresh water from the top at 3 m and the slightly oxygen deficient deeper mixolimnetic water. Mixing also erases the zone of redox reactions at the chemocline with a decline in pH above the redoxcline, presumably due to reprecipitation of the diffused reduced species, and elevated pH immediately below the redoxcline in the reducing monimolimnion. Chemical analyses of the 10 m water column sample suggest that species of Mn, Ni, Co, and Zn play a role here and these same metals also showed high concentrations in the water overlying the sediment at the same depth. Seasonality also affects the monimolimnion, especially the temperature profile, but also the pH and redox conditions to some degree. However, it doesn’t erase the layer of high electrolyte content and low ORP at the deepest part of the lake, presumably formed due to reactions at or near the sediment water interface that may also involve redissolution of precipitates settling through the water column. There also was an excess of other, presumably more reduced, sulfur species over SO_4 in the water column, pore waters, and the overlying waters in the monimolimnion, especially during the autumn overturn.

Seasonality had an effect on the element concentrations of the pore waters and the waters overlying the sediments especially at the chemocline. In general, concentrations were higher during the overturn, particularly in the waters overlying the sediments. Major increases at the chemocline compared to winter conditions were seen in Ba, Co, Mn, P, Pb, V, and Zn. In the winter, pore water concentrations of e.g. Zn and Ni were low at 10 m, suggesting binding to sediments may be more efficient. At this time, the ORP values increase rapidly above the chemocline while the O_2 concentrations are low compared to the overturn conditions, suggesting other oxidizing species are present.

In contrast to waters, sediments had slightly higher concentrations of HNO_3 soluble elements in the winter than during the overturn, especially at the deepest and shallowest sites. At the deep, this may be due to precipitation as sulfides because the effect was strongest for Fe, Mn, As, and S. Iron and sulfur also showed higher sediment concentrations at the chemocline in winter.

Conclusions

The results show that seasonality may have an effect on the chemical conditions of the sediment compartment of mining-impacted meromictic lakes. The effect varies with depth and across the chemocline. Furthermore, the response differs between individual elements and also between pore waters and the waters overlying the sediments. Even when the monimolimnion remains stable, conditions change in this reducing, high electrolyte part of the system as well.

Acknowledgements

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