SEASONAL VARIATION IN LAKE SEDIMENT GEOCHEMISTRY IN AN ACTIVE MINE AREA (PYHÄSALMI, FINLAND)

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Abstract
The focus of the study was on the seasonal variation of sediment geochemistry in the Lake Junttiselkä in Finland. The lake is loaded mainly by the Pyhäsalmi Zn-Cu-mine waters and municipal sewages of Pyhäsalmi town. The sulphate load released by the mine is more than 10000 t/a. Lake water quality varies markedly during the autumn-winter (oxic/anoxic) period and thus the sediment composition was also expected to show corresponding seasonal variations.
Lake sediment samples were collected in November 2005 and in March 2006 by Limnos corer from 32 points. The sediment core was partitioned into 0-2 cm, 2-4 cm and 4-6 cm slices. The sediment samples were freeze-dried and multielement determinations were performed using ICP-MS on nitric acid extracts (EPA 3051). Results show that geochemical composition of sediment varies strongly within the autumn-winter period. In autumn the Ca and S concentrations in the 0–2 cm layer were 1.0 wt.% and 0.2 wt.% but concentrations increased during winter to 1.3 wt.% and to 0.4 wt.% respectively. Increased concentrations of Fe, C, N, Cr, Cu, V, La, P, Li, Sc, U, As, Sr, Na, Pb and Se were also found in sediments deposited during wintertime compared with autumn. Conversely, in autumn the Mn concentration in the 0–2 cm layer was 516 mg/kg but in winter the corresponding value was 414 mg/kg. Sediments were also depleted in Cd, Zn and Co in the winter period compared with autumn. The greatest enrichment/depletion of elements occurred within the 0-2 cm sediment layer, but was also discernible in the 4-6 cm sediment layer. Thus the elements migrated within the sediment layer and considerable amounts of element exchange across the sediment/water interface was observed during the brief time oxic/anoxic period.

Introduction
Pyhäsalmi Zn-Cu ore is located on the northeastern edge of the Svecofennian domain and the volcanic host rocks belong to the paleoproterozoic island arc succession (1.9 Ga, Saltikoff et al., 2006). Supracrustals are situated between Archean tonalitic gneisses in the northeast and Svecofennian granitic rocks in the southwest. The hydrothermally-altered host rocks are composed of acid and mafic metavolcanics. The mine has been in operation since 1962 and refined effluents have since then been released into Lake Junttiselkä (Fig. 1).
Junttiselkä is a separate northern part of Lake Pyhäjärvi and both are headwater lakes of the Pyhäjoki river system. Junttiselkä has an area of 570 ha and a mean depth of 2.5 m. At the deepest point the height of the water column is 8 m. Junttiselkä receives refined effluents from both Pyhäsalmi mine and the municipality of Pyhäsalmi. The mine waters are refined by lime treatment/precipitation and thus the effluents contain significant quantities of Ca and sulphate. The mine sulphate loading to Lake Junttiselkä is more than 10000 t/a. As the mine effluents have also contained Cu and Zn, the concentrations of these metals in Lake Junttiselkä are much higher than in natural sediments. The mine effluents enter the southern part of the lake and the municipal effluents enter the northern part.
The seasonal variation in water quality in Junttiselkä is pronounced, because in winter the electrolyte concentration in the water becomes high and the hypolimnion becomes anoxic. After melting of the ice cover and the spring overturn the water suddenly becomes acidic. The variation in water quality suggests a strong external and/or internal load on the lake. It has been supposed that seasonal variation in the water column is linked to sediment quality. The aim of this study was therefore to examine the seasonal variation in sediment composition. As the most significant difference in water quality is between winter and summer/autumn periods, sampling was carried out in the autumn and winter.

Methods
Sampling was performed at 32 points during November 2005 and March 2006 using a Limnos corer. The aim of the study was to compare sediment composition within different seasons (autumn/winter samples). The core was partitioned into 0 to 2 cm, 2 to 4 cm and 4 to 6 cm slices and the material was placed in plastic bags. The samples were frozen within one day and after that the samples were freeze-dried and homogenized. The weight of the sample was determined before and after drying. The samples were digested in hot nitric acid (EPA 3051) and the supernatant analyzed by multielement ICP-MS. Carbon and N analyses were performed using a CN analyzer. The data were statistically analyzed using SPSS 14.0 software.

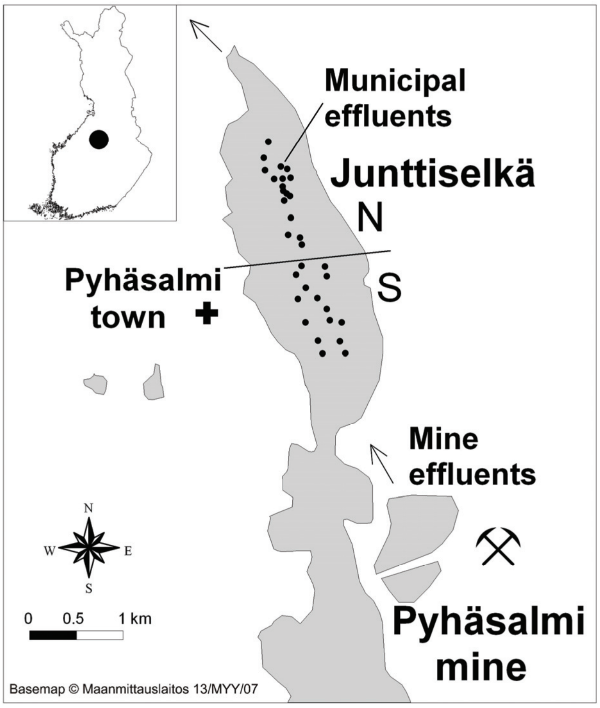

Figure 1. Pyhäsalmi mine and Pyhäsalmi town are situated in the vicinity of Lake Junttiselkä. The samples from Junttiselkä are divided into northern (N) and southern (S) groups.

Results and Discussion

Because the composition of the Junttiselkä surface sediment (0 to 2 cm) varies between northern and southern parts of the lake, the data were divided into two parts (N and S, Fig. 1). The elements showing the greatest difference between the N and S parts of the lake are presented in Table 1. According to the results, sediments in the N part of the lake contained more As, Co, Fe, Mn, P, Zn, C and N, while those in the S part of the lake had the highest concentrations of Ca, Cu, Pb and S.

The results indicate that sediment metal concentrations depend on both the distance from the effluent source and on the physicochemical properties of the system. In the vicinity of the mine loading point in the southern part of the lake, the sediment is enriched in Ca, Cu, Pb and S. However Co, Fe, Mn and Zn are enriched in the N part of the lake, although Zn loading has been most significant in the S part. This reflects metal transportation in a soluble form and the adsorption of metals to organic/oxic phases.

Table 1. Mean concentration of selected elements in Junttiselkä sediment (0 to 2 cm) in northern and southern part of the lake. Composition in winter 2006.

	As	Co	Fe	Mn	P	Zn	C	N	Ca	Cu	Pb	S
Area	mg/kg	mg/kg	%	mg/kg	mg/kg	mg/kg	%	%	%	mg/kg	mg/kg	mg/kg
North	**17**	**15**	**5.8**	**494**	**1886**	**466**	**7.4**	**0.7**	1.2	141	28	3051
South	15	14	4.7	381	1576	423	6.7	0.6	**1.4**	**180**	**38**	**5545**

There was significant seasonal variation in the sediment composition according to the Wilcoxon signed-rank test and graphically the variation can be expressed as a concentration ratio between winter and autumn sediment samples (C_{winter}/C_{autumn}) (Fig. 2). The concentration ratios were separately computed from 0 to 2 cm, 2 to 4 cm and 4 to 6 cm sediment slices.

Elemental enrichment or depletion in winter was most significant in the top sediment layer (0–2 cm) and was revealed in several element ratios. The most pronounced enrichment in the sediment in winter was for Ca and S, which clearly reflects mine effluent loading to the lake. The enrichment of Ca and S was greatest in the southern part of the Junttiselkä, near the outlet of the mine effluent channel. In winter the average Ca and S concentrations in the 0 to 2 cm layer were 1.3 wt.% and 0.4 wt.%, but concentrations in autumn were 1.0 wt.%

and 0.2 wt.%, respectively. Enrichment during the winter was also apparent for the following elements: Se, Pb, Na, Sr, As, U, Sc, Li, P, La, V, Cu, Cr, N, Ni, C and Fe. In autumn the average Mn concentration in the 0 to 2 cm layer was 516 mg/kg, but in winter the corresponding value was 414 mg/kg. The depletion of Mn was most notable in the northern part of Lake Junttiselkä. The concentrations of Cd, Zn and Co also decreased during the winter. The most probable reason for the depletion of Mn and other metals from the sediment was the formation of sulphides during anoxic conditions, which in turn decreases the stability of Fe-Mn oxides.

In the depth layer 2 to 4 cm the pattern of enrichment/depletion was similar, but not as pronounced as in the 0 to 2 cm layer. The concentrations of S, Ca, Na, Sc, Ni, V, Cu, P, Se and Cr in sediment were higher in the winter than the autumn. However, the respective concentrations of K, Ba, Al, As and Mn decreased.

Statistically significant seasonal composition differences in the 4 to 6 cm sediment layer were only observed in the southern part of Lake Junttiselkä. In winter, enrichment was only observed for S, Ca, N, Sr, K, Ba, Al, Mn, Fe and Mg. The concentrations of Cd and As decreased.

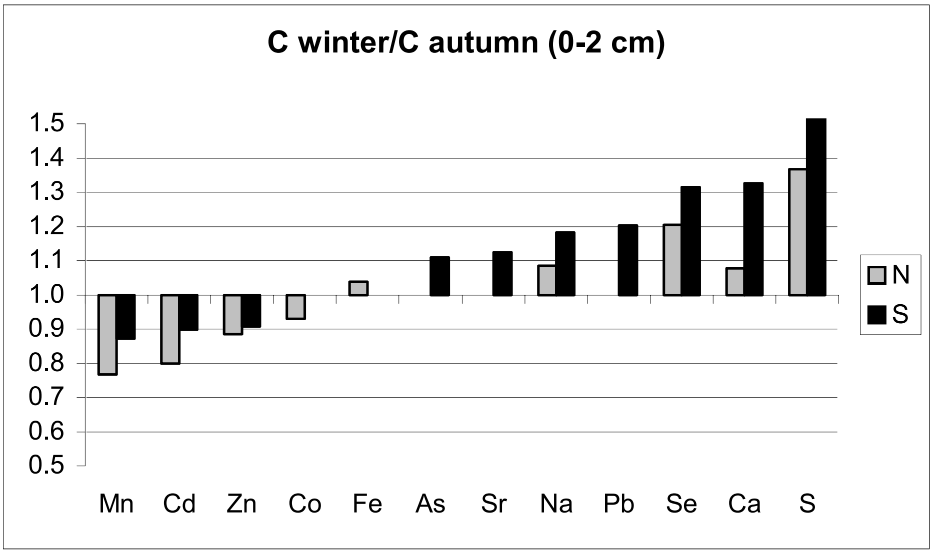

Figure 2. The mean winter-to-autumn element concentration ratios in the upper 0 to 2 cm sediment layer (C winter/C autumn). The element ratios are expressed separately for samples from the northern (N) and southern (S) part of Lake Junttiselkä. The winter:autumn ratio for S in the southern part of Junttiselkä is 2.32.

Conclusion

The seasonal variation of sediment composition in Junttiselkä is pronounced. In the winter the sediment is enriched in Ca and S, which are derived from the mine effluents. The winter anoxic conditions in the hypolimnion decreases the solubility of Cd, Co, Mn and Zn, which are diffused from the sediment to the overlying water. Enrichment/depletion of elements can be found within 0–6 cm of the sediment surface.

References

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