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Heavy metal distribution and chemical partitioning in Lake Saimaa (SE Finland) sediments and moss *Pleurozium schreberi*

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This paper presents data on the concentration and chemical partitioning of four heavy metals, iron (Fe), copper (Cu), cadmium (Cd) and lead (Pb) in Great Lake Saimaa (Finland) sediments and moss (*Pleurozium schreberi*). Elemental analysis was performed by Flame Atomic Absorption Spectrometry and (FAAS) and anodic stripping voltammetry, using multi-element standard solutions. Results showed that the highest metal concentrations of Fe in sediments were recorded for Partakoski village, Mikkeli city and Ristiina with values of 86 mg/kg, 67.1 mg/kg and 63.8 mg/kg, respectively. The highest Cu concentration was observed in Anttola and Partakoski village sediments with values of 8.1 mg/kg and 7.3 mg/kg, respectively. On the contrary, the highest Cd concentration was found in Tetriniemi village and Puumala harbour sediments (0.6 mg/kg and 0.4 mg/kg, respectively) and the highest Pb concentrations were found in Puumala (2.2 mg/kg) and Ristiina (1.7 mg/kg) sediments. On average, the total metal contamination followed the order Partakoski > Mikkeli city > Ristiina > Anttola harbour > Imatra > Puumala harbour > Astuvansalmi > Tetriniemi. The highest amount of Fe was found in moss samples (85.4 mg/kg) from Ristiina and Cu was found to be the chiefly accumulated in moss (10.2 mg/kg) from Anttola. There was negligible amount of Cd and Pb found in all the moss samples. Partitioning of Fe, Cu, Cd and Pb showed that more than 90% of metal was associated with residual fraction in sediments, with an exception of Cu that was significantly (20% of the total) associated with an organic/sulfide fraction and Fe (22% of the total) was associated with exchangeable/carbonate fraction as well. On the other hand, chemical partitioning of metals in moss samples showed that Cu (up to 90%), Pb (up to 80%) and Fe (up to 60%) were strongly associated with extracellular fraction and Cd showed the highest affinity towards intracellular fraction (up to 70%). Statistical analyses carried out with principal component analysis and cluster analysis methods showed good correlation between Pb, Fe and Cu content and moss as well as sediments. Significant relationship ($p < 0.05$) between different metals was observed for Cu – Cd (0.88), Fe – Pb (0.65), Fe – Cu (0.68), Cu – Pb (0.47) in sediments and moss samples. The metal content in exchangeable and extracellular fractions in sediments and moss samples showed that Cu, Pb and Fe were the most bioavailable elements.

Keywords: heavy metals; distribution; lake sediments; chemical partitioning; *Pleurozium schreberi*

1. Introduction

The emission of heavy metals is one of the most serious environmental problems and the amount of these elements tends to increase in the environment [1]. Metal aerosols pollute soil and plants.

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Excessive amounts of heavy metals interfere with plant metabolism and retards shoot and root growth [2]. However, critical toxicity levels (above 20–30 mg kg⁻¹ dry weight in leaves) of heavy metals in plants usually depend on species, plant organ, development stage and nutrient status [3]. Higher plants not only intercept pollutants from atmospheric deposition but also accumulate metals from the soil. Heavy metal deposits are generally taken up from the soil by plants via their root system and transferred to other regions of the plant.

Sediments are a very important compartment in the freshwater ecosystem as it is the final destination for many heavy metals as a result of adsorption, desorption, precipitation, diffusion processes, chemical reactions, biological activity and combination of these phenomena [4]. Contaminated sediments are a significant environmental problem affecting many marine, estuarine and freshwater environments throughout the world. Most assessments of, for example, water quality have mostly focused on water-soluble compounds, with relatively little attention paid to sediment – a repository for adsorbed contaminants. Therefore, heavy metal distribution in vegetation and sediments in particular and their bioavailability has to be considered to obtain a better understanding of a potential threat to the environment.

Anthropogenic compounds enter the aquatic environment mainly via fluvial or atmospheric input. Depending on their physical and chemical properties some substances remain dissolved in the soluble phase whilst others bind onto particles, sink to the ground and become part of the sediment. In this way, an accumulation of many hydrophobic (and in general strongly adsorbing compounds) takes place. Due to resuspension processes, changes in pH and redox potential, contaminants can be remobilised again, thus the sediments can also act as a source for contaminants.

As stated by Fernández et al. [5], the best way to determine the extent and a threat of contamination in the environment for organisms is by measurement of the levels of contaminants in the organisms themselves for example in mosses. In fact, mosses or bryophytes are known as being able to intercept, retain and accumulate pollutants. This phenomenon was first described by Rühling and Tyler in 1968 [6] and they concluded that the accumulation ability of mosses in particular is of vital importance as they may take up metals to levels exceeding their own physiological needs. Mosses, such as *Pleurozium schreberi* are slow growing and assimilate metals at a rapid rate but release them at a low rate [7]. They were first used as bioaccumulative indicators in relation to point emission sources, where decreasing metal concentrations in species correlated with increasing distance from the source [8]. Mosses have also been used to assess deposition patterns and heavy metal burdens for larger scale monitoring purposes. In mosses, metals can accumulate to high levels by trapping insoluble particles, extracellular ion exchange processes, adsorption and active uptake [9].

The analysis of total metal concentrations provides only information on metal enrichment of the sediment and moss samples, but not direct information on the biological effects of the metals [10]. Hence, the chemical partitioning of metals between different fractions is very important in determining the bioavailability of metals as well as potential threat to the environment [11]. Sequential extraction procedures have been developed predominantly to determine the amounts and speciation of metals present within plants, soils or sediments samples, sewage sludge and sludge treated soils [12]. Moreover, sequential partitioning can provide useful information on metal distribution in different medias, particularly for comparative purposes [13].

Saimaa Lake lies in the western margin of the Eurasian taiga with two boreal subzones included, forming a unique ecological complex introducing the post-glacial forest revival. It is extremely valuable and important for recreation as well as an economic zone. It is a mosaic-like, complex lake system with exceptionally high shoreline/area ratio and high number of islands with boreal forest [14]. There is also a diversity of different landforms of glacial origin like complex esker systems and vast end-moraines.

The main aim of this study was to assess the distribution, chemical partitioning and potential bioavailability of Fe, Cu, Cd and Pb in sediments and *Pleurozium schreberi* samples of Lake

Saimaa region in South East Finland. Multivariate analytical techniques to interpret the results were also introduced.

2. Materials and methods

2.1. Study area

Figure 1 presents the general map of Finland and a detailed presentation of Saimaa Lake region. Eight sampling points were chosen along the Saimaa Lake during October–November 2004 and July–August 2005 to evaluate the contamination of sediments and mosses *Pleurozium schreberi* with heavy metals. Sampling point 1 was collected close to Mikkeli, sample 2 was collected in close proximity from a plywood factory in Ristiina, sample 3 was from Partakoski village farmlands, sample 4 was collected from the nature reserve close to the rock paintings at Astuvansalmi, sample 5 was from Anttola harbour, sample 6 from Puumala harbour, sample 7 was collected from Tetriniemi village and sample 8 was collected close to the town of Imatra.

2.2. Equipment and procedures

2.2.1. Sampling and total metal determination

Each sampling site consisted of a square of 2 m × 2 m within which three samples of the moss *P. schreberi* were collected. Mosses were collected as proposed by UNECE [15]. The stones, soil and other particles were manually removed from samples onsite. Mosses were not washed before the analysis in order not to flush any heavy metals attached to the most labile water soluble

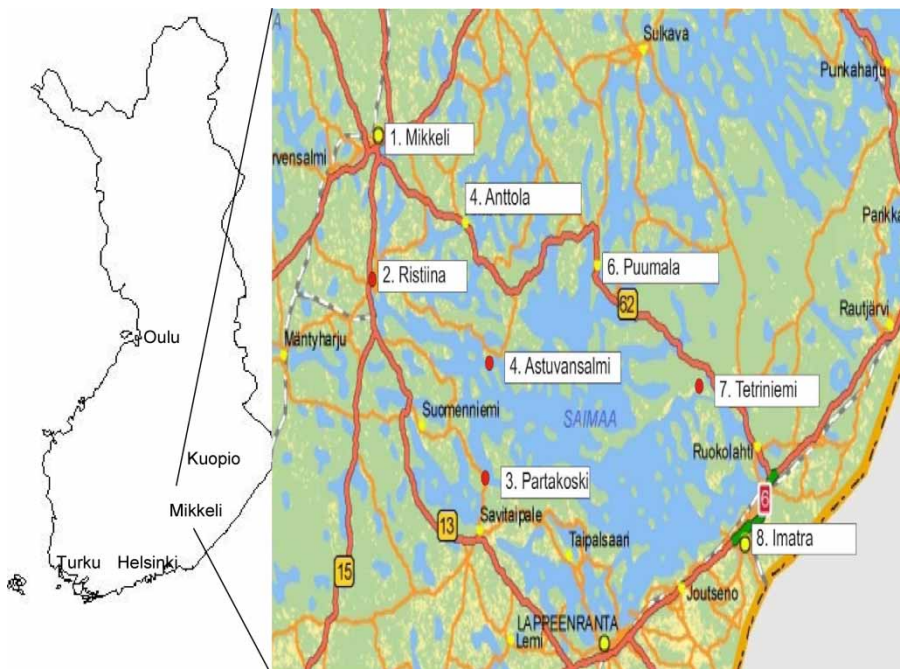


Figure 1. Sampling area of Lake Saimaa region (SE Finland).

phases. Despite the fact it may retain locally produced contamination, it was assumed that such contamination did not alter the final results and therefore was neglected. The moss samples were then dried to a constant weight in an air oven at 50°C for 48 h.

Sediment and top soil (0–5 cm) samples were collected at the same sites or nearby the moss samples as proposed by Fernández and Caballeira [5]. Because of the heterogeneity of the substrate, a number of sub-samples (5–10) were collected and later combined at the laboratory to give a single sample. At the laboratory, samples were sieved and the fraction smaller than 2 mm was used for experiments. Prior to the experiments, samples were homogenised manually with a pestle and mortar.

The total metal concentration in the homogenised samples (5 g dry weight each) was determined after aqua regia (HCl/HNO₃, 3 : 1, 10 ml) microwave assisted digestion (Matthews CEM 2100, North Caroline, USA) as described by Virkutyte and co-authors [12]. Analytic grade chemicals were used throughout the analyses. After the digestion, sediment and moss samples were analysed for Fe, Cu, Cd and Pb using Flame Atomic Absorption Spectrometer (FAAS, Analyst 800) and anodic-stripping voltammetry (Metrohm 797 VA computer, Metrohm Nordic, Finland). All elements were determined against standards (Merck, pro analyse quality) containing the same matrix as samples [16]. The results were calculated on a dry weight basis.

2.2.2. Enrichment factor

To investigate the behaviour of *P. shreberi* as a potential bioindicator, enrichment factor (EF) was calculated as suggested by [17]:

$$EF = \frac{(X/Ti)_{moss}}{(X/Ti)_{soil}}$$

where X is the concentration of element of interest and Ti is an amount of reference metal in the soil. $EF \leq 1$ indicates that there is no enrichment of metal of interest in the moss sample, while $EF > 1$ shows that there is enrichment of metal of interest relative to its level in the soil. To avoid analytical errors, Dongarrá and Varrica [18] proposed that elements were enriched when the average $EF > 3$, and at least 30% of the samples had $EF > 3$.

2.2.3. Chemical fractionation in sediments and moss samples

The analytical performance of the laboratory procedures was evaluated by analysis of Certified Reference Material BCR-701 and CRM 146R [19]. A two-sided *t*-test was used to check for significant differences from the reference content. Uncertainty was expressed as standard deviations; the values obtained were not significantly ($p > 0.05$) different from the certified values. The data for total concentrations were obtained from triplicates ($n = 3$) with mean standard deviation. The reliability of the analytical methods was assessed through recovery studies. Recoveries were done by three replicate determinations of the selected trace metals in three different CRM samples and the range of recoveries was 95–106%.

The revised BCR scheme [20,21] was designed based on an acetic acid extraction of approximately 1 g total suspended solids (TSS) of sample (step 1), hydroxylamine hydrochloride extraction (step 2) and hydrogen peroxide oxidation and ammonium acetate extraction (step 3). To extract the residual phase (step 4), a mixture of 2.5 ml HNO₃ (65%) and 7.5 ml HCl (37%) (*Aqua regia* digestion) was added to the fraction 3 residue. The microwave digestion procedure was carried out in three steps (15 min at 100°C, 15 min at 150°C and 30 min at 200°C). After microwave digestion, the samples of step 4 were paper filtered and diluted to 100 ml with ultra pure water. Compared to the original BCR procedure, the revised protocol involved the use of an increased concentration of NH₂OH·HCl and lower pH as described by [21].

Table 1. Chemicals used for the sequential extraction to determine the chemical speciation in sediment and moss samples.

Fraction	Extracting agent	Extraction conditions	
		Shaking Time ¹	Temp
Sediments			
1* Water soluble	20 ml H ₂ O	16 h	20°C
1. Exchangeable + carbonate	40 ml CH ₃ COOH (0.11 M, pH = 7)	16 h	20°C
2. Fe and manganese oxides	40 ml NH ₂ OH-HCl (0,1 M, pH = 1.5)	16 h	20°C
3. Organic Matter and sulfides	20 ml H ₂ O ₂ (30% pH = 2) and then 40 ml CH ₃ COONH ₄ (1 M, pH = 2)	1 h 2 h	20°C 85°C
4. Residual	10 ml demineralised water and 10 ml Aqua regia (HCl/HNO ₃ , 3:1)	26 min	Microwave oven ²
Moss samples			
Extracellular	10 ml EDTA	30 min	20°C
Intracellular	10 ml 1 M HNO ₃	30 min	20°C
Residual	4 ml HNO ₃ ; 10 ml demineralised water ¹	Until material was completely digested	100°C, microwave oven

¹Shaking was applied at 30 (sediments) and 3000 (moss) rpm. ²Extraction of the residual fraction in the microwave was equal with the pseudo-total extraction method.

Heavy metals from moss samples were extracted using sequential elution technique (SET) procedure as proposed by Vasquez et al. [22]. To extract metals from extracellular fraction, 10 moss apical segments were subjected to 10 ml EDTA and then incubated for 30 min with constant shaking. After extraction, moss samples were dried in an oven at 50°C for 48 h to rupture the cell membranes. Then in order to extract metals from intracellular metal fraction, samples were subjected to 10 ml of 1 M HNO₃ for 30 min with constant shaking. The residual fraction was determined by placing the remaining segments in a glass tube with 4 ml of 70% HNO₃ and placed in a water bath (100°C), until the material was completely digested. Then tubes were centrifuged at 3000 rpm for 5 min and supernatant was used to determine the residual fraction of metals in moss (Table 1).

2.2.4. Statistical analyses

Principal components analysis (PCA) and hierarchical Cluster Analysis (CA) were used to assess the relationships between variables and possible patterns in the distribution of the measured data by StatistiXL (Excel™ add-in, 2007). PCA is unsupervised multivariate technique that defines the quantitative relationships among the variables in groups (metal concentrations in the current study) within the data using a smaller number of linearly independent new variables, called principal components (PC) that have two main features [20]: (a) they are uncorrelated between themselves; (b) the first PCs calculated keep the main part of the variance of the original data set. Eigenvalues and varimax rotation method were used to extract and represent principal components (PCs).

$$PC1 = \sum_{j=1}^p a_{1j}X_j$$

where PC1 is principal component and a_{1j} = Linear coefficient – eigen vectors. The plot of loadings (correlation coefficients between the PC scores and the original variables) measures the importance of each variable in accounting for the variability in the PC. It is possible to interpret the

first few PCs in terms of ‘overall’ effect or a ‘contrast’ between groups of variables based on the structures of PC loadings. High correlation between PC1 and a variable indicates that the variable is associated with the direction of the maximum amount of variation in the dataset. The plot of scores (the derived composite scores computed for each observation based on the eigenvectors for each PC) gives information about similarities among samples. The means of PC scores are equal to zero, as these are the linear combination of the centered variables. In PCA, relationships between PC scores and PCA loadings associated with any two PCs can be illustrated in a bi-plot display.

CA is an unsupervised method that is used to identify and categorise subsets of objects that are, more often than not, continuously distributed. A dendrogram is the most commonly used method of summarising the hierarchical clustering results. Technique, which was used in the current study to evaluate the similarities between samples, was agglomerative hierarchical clustering method, in which Euclidean distance between normalised data in order to measure similarity between samples, and both average linkage between groups and Ward’s method to establish different clusters was applied.

2.2.5. QC/QA analysis

The analysis of samples followed the standard quality assurance and control (QA/QC) procedures [19]. To assure the reproducibility of testing procedures, the following precautions were taken into consideration: (1) new sampling bottles and other experimental ware were used for each test, (2) to prevent the sample contamination with trace metals, all the glassware and plastic containers were treated with 0.01 M HNO₃ and rinsed with ultra-pure water, (3) all chemical analyses were performed in triplicate, (4) the FAAS calibration was checked after five standard solutions, and (5) a mass balance was calculated for each test.

3. Results and discussion

3.1. Metal accumulation in sediments and vegetation

The concentrations of selected heavy metals (http://www.sciencedirect.com.ezproxy.uku.fi:2048/scidirimg/sci_dir/nextterm.gif) isn’t in document in lake sediments expressed as threshold effect level (TEL) values are presented in Table 2 [23]. The results for the selected heavy metals in sediments and moss samples are presented in Table 3.

The number of samples was insufficient to perform a detailed mapping of the contamination or heavy metal distribution in sediments and moss, however, the data still allows us to obtain a great insight into the potential extent of contamination in Lake Saimaa region.

High levels of heavy metals in sediments do not always indicate similar high concentrations in plants. The extent of accumulation is highly dependent on the vegetation species itself and the heavy metal under observation. The interpretation of analytical data may be complicated by many

Table 2. Sediment quality guidelines for selected metals that reflect TECs (i.e. below which harmful effects are unlikely to be observed) [23].

Metal	TEC (mg/kg dw)	Background concentration in clayey soils (mg/kg dw)
Cd	0.6	0.17
Cu	35.7	19
Pb	91.3	8.1
Fe	NA	41000

Table 3. The distribution of selected heavy metals in sediments and moss samples.

	Mikkeli	Ristiina	Partakoski	Astuvansalmi	Anttola	Puumala	Tetriniemi	Imatra
Concentration in sediments (mg/kg dry weight except for Fe- g/kg dry weight)								
Fe	67.1 ± 2	63.8 ± 2	86 ± 5	12.2 ± 0.5	35.5 ± 1.5	17.5 ± 0.5	14.5 ± 0.5	21.2 ± 1.5
Cu	3.6 ± 0.05	1.4 ± 0.05	7.3 ± 0.05	1.8 ± 0.05	8.1 ± 0.2	0.9 ± 0.005	0.9 ± 0.005	1.2 ± 0.05
Cd	0.2 ± 0.001	0.05	0.05	0.05	0.07	0.4 ± 0.001	0.6 ± 0.001	0.05
Pb	0.9 ± 0.005	1.7 ± 0.001	0.4 ± 0.001	1.2 ± 0.001	0.2 ± 0.001	2.2 ± 0.005	0.2 ± 0.001	0.2 ± 0.001
Concentration in moss (mg/kg dry weight except for Fe- g/kg dry weight)								
Fe	72.1 ± 2	85.4 ± 2	60.2 ± 2	27.4 ± 2	15.1 ± 0.5	7.8 ± 0.05	7.1 ± 0.05	5.4 ± 0.05
Cu	8.2 ± 0.05	8.8 ± 0.05	6.7 ± 0.05	3.3 ± 0.01	8.8 ± 0.05	3.4 ± 0.01	2.1 ± 0.01	2.1 ± 0.01
Cd	<0.001	<0.001	<0.001	<0.001	0.02	0.03	0.03	0.02
Pb	0.2 ± 0.001	0.3 ± 0.001	0.05	0.01	0.3 ± 0.001	0.2 ± 0.001	<0.001	0.03

factors, thus total metal accumulation in sediments and moss samples can only reflect the relative extent of the contamination and its bioavailability.

3.2. Total metal concentrations

The elements present in the Lake Saimaa sediments originate either from geochemical environment or from anthropogenic activities. Usually, the increased concentrations of heavy metals in sediments are mainly a result of increased anthropogenic activities [11]. In particular, Yilmaz and Zengin [24] suggest that elevated concentrations of Cu and Pb in vegetation indicate air contamination with these elements.

According to Table 2, none of the metals of interest exceeded the TEC in sediments (Table 3), however, Cd concentration in Puumala and Mikkeli harbour and Tetriniemi sediments was one order of magnitude higher than the background concentration. This may be considered to be detrimental to sediment-dwelling organisms as indicated by [25]. It suggests that if the load of Cd continues to increase, mainly due to phosphate-containing fertilisers spread onto the fields close to Tetriniemi village, the contamination problem will occur shortly. In all the sampling areas, total Cd concentration was the lowest (0.05 to 0.6 mg/kg), followed by Pb (0.4 to 2.2 mg/kg), Cu (0.8 to 8.1 mg/kg) and Fe (6 to 86 mg/kg) (Table 3).

In terms of metal distribution in moss, the lowest concentrations were observed for Cd (0.03 mg/kg), Pb (0.05 mg/kg), Cu (10.2 mg/kg) and Fe (85.4 g/kg), respectively (Table 3). In general, the contamination in sediments and moss followed the order of Fe > Cu > Cd > Pb. Also, the total heavy metal concentrations in sediments followed the order of Partakoski > Mikkeli > Ristiina > Anttola harbour > Imatra > Puumala harbour > Astuvansalmi > Tetriniemi.

Iron: The highest amount of Fe (86 g/kg, 67.1 g/kg and 63.8 g/kg) was found close to Partakoski village farmlands, Mikkeli and Ristiina, respectively (Table 3). This may be due to the combustion of fossil fuels, especially close to Partakoski village where heavy traffic is present during the harvesting periods. However, it is assumed that Saimaa region peaty sediments may also contain natural elevated amounts of Fe. Indeed, as reported by [5], iron, bound to soil particles, may be present naturally or be omitted during the combustion of fossil fuels such as coal and thus deposited in the sediments. The excess of Fe in collected sediment samples shows that reactive iron being mainly retained in the upper sediment layers. The retention may result from the interaction of Fe (II) with O₂ and MnO₂ at the topmost sediment layer that works as a chemical barrier slowing down the movement of Fe(II) exported from sediments to the water column [26]. Nonetheless, there were rather insignificant amounts of Fe (up to 35.5 g/kg) in Anttola and Puumala harbour sediments where it was expected to find elevated concentrations of Fe due to the natural conditions and heavy boat traffic during the spring – autumn months. The moss analysis determined that

Ristiina had the highest concentrations of Fe (85.4 mg/kg), followed by Mikkeli (72.1 mg/kg) and Partakoski (60.2 mg/kg) sampling areas (Table 3).

In general, sediment contamination with Fe was in the order of Partakoski > Mikkeli > Ristiina > Anttola > Imatra > Puumala > Astuvansalmi > Tetriniemi. However, Fe distribution in moss is not uniform. It implies that Fe is not entirely taken up by plants from the soil or sediments but may reach the vegetation via atmospheric deposition when prevailing winds are from Russia, where smelting and refinery industries are present. Indeed, Nyarko and co-authors [27] found that numerous industries release Fe into the atmosphere and subsequent Fe deposition in vegetation occurs.

Copper: The highest amount of copper (8.1 mg/kg and 7.3 mg/kg) was found in Anttola harbour and Partakoski sediments and Cu-enriched moss in Ristiina and Mikkeli (8.8 mg/kg and 8.2 mg/kg), respectively (Table 3). Adriano [28] claimed that enrichment of Cu in soils may also due to the input of airborne pollutants. However, it is assumed that the main source of Cu in sediments and moss samples is the combustion of oil for boat and car traffic (Anttola and Puumala harbour, Mikkeli) and the possible use of Cu-containing pesticides in a close proximity of Ristiina and Partakoski village. The same patterns were observed by Gerdol and co-authors [29], where the monitoring of heavy metal deposition by moss was performed. In addition, Derome and Nieminen [30] determined that significant amount of copper deposits in sediments from copper (copper sulfate) fertilisers.

Lead: It is evident from Table 3 that the most Pb-enriched sediments were found in Puumala harbour (2.2 mg/kg), Ristiina (1.7 mg/kg) and Astuvansalmi (1.2 mg/kg). It is important to note that Ristiina – Astuvansalmi – Puumala area is the most important touristic attraction that has a great number of visitors every year. According to Gerdol and co-authors [29], Pb mainly comes from motor vehicles using leaded gasoline, therefore elevated concentrations of Pb in the areas may possibly be attributed to the increased, especially during spring-autumn, traffic from neighbouring Russian Federation where leaded gasoline is still being used. Also, it could be the consequence of a long deposition process during the past when leaded gasoline was used [31]. The highest Pb concentration in moss was observed in Ristiina (0.3 mg/kg), Mikkeli and Puumala (0.2 mg/kg) (Table 3). This could be attributed to the fact that usually the highest concentrations of Pb are found near highways (Mikkeli and Puumala) and farmlands (Ristiina). Also, Pb occurrence in sediments and vegetation in the area may be due to the production and use of phosphate fertilisers, leaching from auto-repair shops and building industries that use Pb-based compounds. According to the data, Lake Saimaa is not polluted by Pb and the concentration of this particular metal is considered as a natural background level.

Cadmium: the highest concentrations of Cd in sediments were found close to the Tetriniemi village (0.6 mg/kg), Puumala harbour (0.4 mg/kg) and Mikkeli (0.2 mg/kg) (Table 3). These values are higher than background values reported in Table 2 and they may be caused by phosphate fertilisers usage and leaching from the construction sites, especially if cement is used for the building purposes. There were insignificant amounts of Cd in moss, indicating that Cd contamination was not recent in Great Saimaa lake region (Table 3).

The positive, statistically significant correlations ($p < 0.05$) were found for the following heavy metal pairs in sediments: Fe – Cu (0.65) and Cd – Pb (0.4) and mosses: Fe – Cu (0.68), Fe – Cd (0.57), Fe – Pb (0.65), Cu – Cd (0.88), Cu – Pb (0.37) and Cd – Pb (0.47), suggesting that these metals are derived from a common origin [10]. Therefore, there is a strong association of Fe and Cu in sediments and mosses. This might be explained by the morphology of Lake Saimaa sediments. The sediments in Lake Saimaa are mainly derived from the weathering products of bedrock. Similar observations were made by [11] where association between Fe, Cu, Co and Ni in sediments was discussed. There was a significant association between Fe and Pb and Cu and Cd in moss. However, the relation between Fe and Cd as well as Pb is negative, indicating different sources and geochemical behaviour of Pb and Cd in sediments than Fe [11].

Table 4. Enrichment factors.

	Mikkeli	Ristiina	Partakoski	Astuvansalmi	Anttola	Puumala	Tetriniemi	Imatra
Fe	1.1	1.4	0.7	3.2	0.5	0.7	1.1	0.3
Cu	3	2.1	0.9	1.2	1.3	1.2	1.3	1.8
Cd	0.1	0.1	0.1	0.1	0.4	0.1	0.1	0.1
Pb	0.2	0.2	0.01	0	0.02	0.1	0.1	0.01

3.3. Enrichment factor

In order to evaluate whether metal content in soil derives from natural or anthropogenic sources, the enrichment factor was calculated. Table 4 shows the Enrichment Factor using Ti as reference element.

The highest EF was observed for Fe (3.2), followed by Cu (3), Cd (0.4) and insignificantly for Pb (0.2). This is in a good agreement with [29] where the distribution of selected heavy metals in soils and sediments was determined. Significant EF of Fe and Cu was observed in Mikkeli, Ristiina and Astuvansalmi suggesting that these were supplied from anthropogenic sources rather than from the soil itself as sampling sites were close to industrial activities (Ristiina), busy roads (Mikkeli) and, surprisingly, a nature reserve with well developed touristic boat traffic (Astuvansalmi). Indeed, according to [32], elements with EF higher than 1 can be considered not to have originated from the local soil background and may be attributed to the anthropogenic sources.

3.4. Statistical analysis

Principal Component Analysis was applied to the samples, using the average concentrations of heavy metals calculated in sediments and moss. PCA with eigenvalues higher than one for heavy metals showed that two components (PCs) accounted for approximately 80% and 95% of the variance in heavy metals concentration in sediments and moss, respectively (Figure 2).

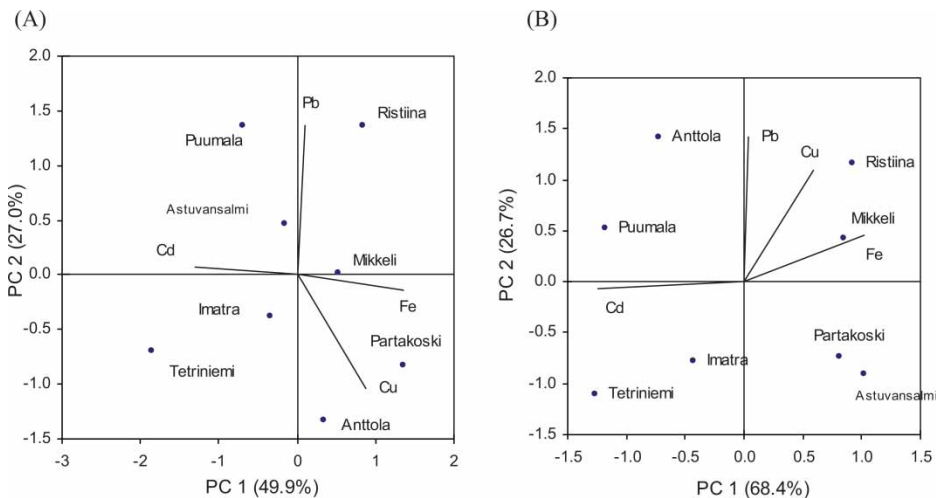


Figure 2. Combined plot of PC1 vs. PC2 loadings on (A) sediments and (B) moss samples.

In sediments, PC1 alone accounted for almost 52% of the variation, was highly correlated with Pb concentration. On the other hand, negative values were mainly determined by redox-sensitive Fe and Cu concentrations (Figure 2a). PC2 was mainly determined by anthropogenic origin Cd concentrations. Moreover, Pb, Fe and Cu are correlated and more abundant in sites where pollution was found to be the highest: Mikkeli, Ristiina and Partakoski village. Additionally, in moss, PC1 alone was almost 70% of the variation and was highly correlated with Pb, Cu and Fe and yet again, negative values in PC2 were determined by Cd (Figure 2b).

Results from the hierarchical cluster analysis (HCA) for each site are reported in the form of dendrograms. On the basis of the connecting distances between the locations and their positions on the dendrograms, distinctive clusters of the variables are defined along the Lake Saimaa sampling site. Despite the procedure is subjective, the distinction between clusters in this analysis is quite clear from the dendrograms. The hierarchical cluster analysis pointed out a clear distinction among several locations regarding heavy metals in sediments (Figure 3). Two main groups were identified. Strong similarity was observed between Ristiina and Mikkeli in one as well Tetriniemi and Astuvansalmi in a second group of sediment samples (Figure 3b). These similarities may probably be attributed to similar environmental and anthropogenic conditions. However, Partakoski and Astuvansalmi sites are isolated from all other sites. Figure 3b shows results from heavy metal in moss as dendrogram. Strong similarities are exhibited between Tetriniemi and Puumala as well as Partakoski and Mikkeli sites. Nonetheless, Astuvansalmi and Ristiina sites were detached from the rest of sampling locations.

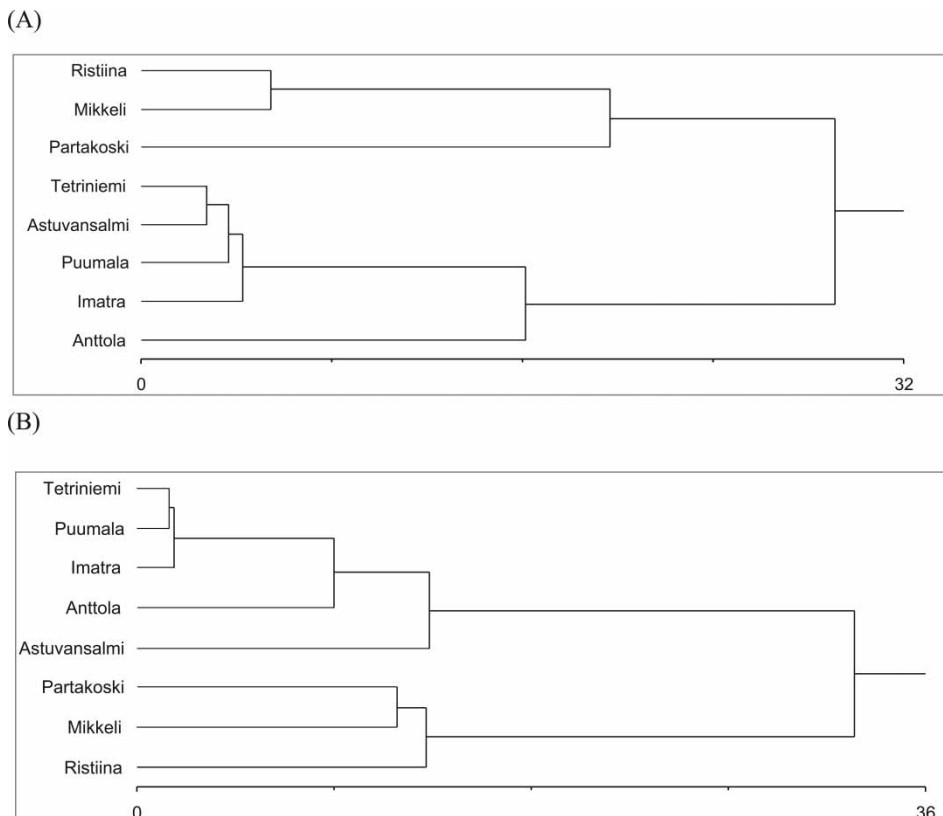


Figure 3. Dendrogram obtained with hierarchical agglomerative cluster analysis where (A) is data from the sediments and (B) shows the moss samples.

3.5. Metal distribution in different chemical fractions

In all sediments, the total amount of the extracted fractions was within 20% of the total metal concentration determined independently (pseudo-total metal concentration), supporting the accuracy and reliability of the extraction process. Metals bound to different fractions will behave differently in sediments and thus have different potentials for remobilisation and for uptake by biota [33]. Partitioning of Fe, Pb, Cd and Cu in sediments and moss are presented in Figures 4 and 5.

3.5.1. Sediments

All four metals were mainly (more than 80% of the total) associated with the residual fraction in sediments (Figure 4). Similar results were observed by Fernández and co-authors [4] where it was found that more than 90% of Cd, Fe, Mn, Ni, Pb and Zn were found in the residual fraction of sediments.

Fe was significantly associated with exchangeable/carbonate fraction, indicating that Fe input may be recent. There was no significant difference between sampling sites as all four metals followed similar fractionation pattern. Also, Cu attached to reducible (Fe/Mn oxides) fraction was different throughout the sampling area from 8% of the total in Anttola and Puumala harbors to 1% in Patrakoski, Astuvansalmi and Imatra (Figure 4). This Cu attachment to Fe/Mn oxides can be explained by the common origin of Fe and Cu as discussed above. Also, Fernández and co-authors [4] found that local topography may play a significant role in increasing Cu deposition to the sediments, i.e. attachment to the organic/sulfide and residual and partly to Fe/Mn oxide fraction.

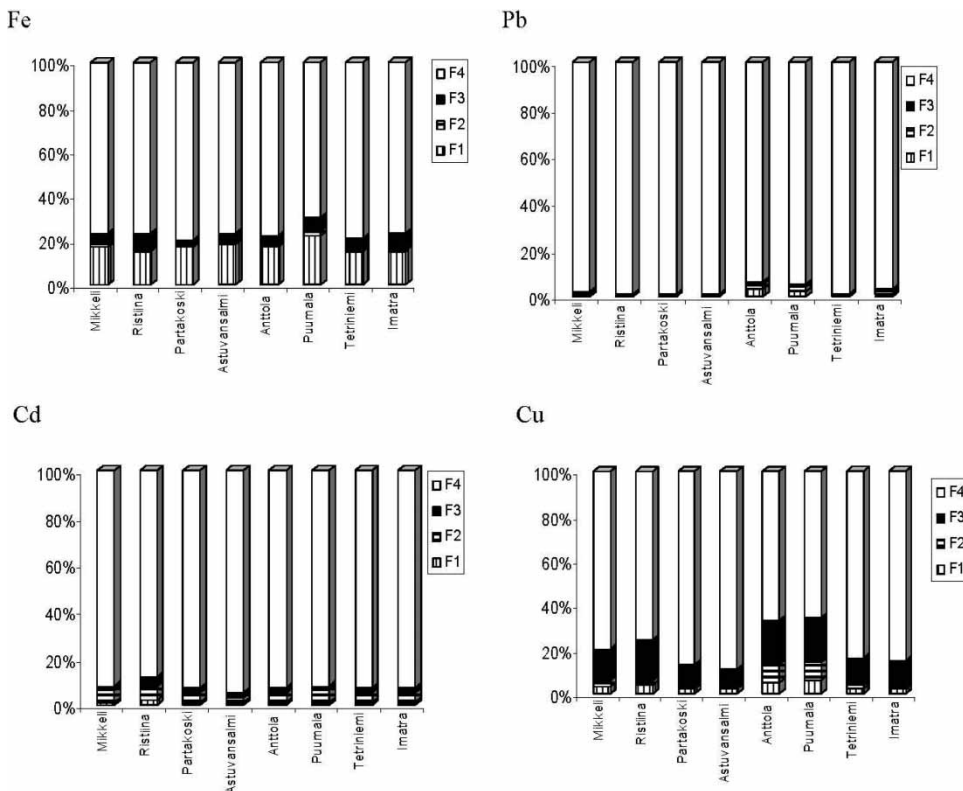


Figure 4. Chemical partitioning of selected metals in sediments (F1 exchangeable/carbonate; F2 Fe/Mn oxide; F3 organic/sulfide and F4 residual fractions).

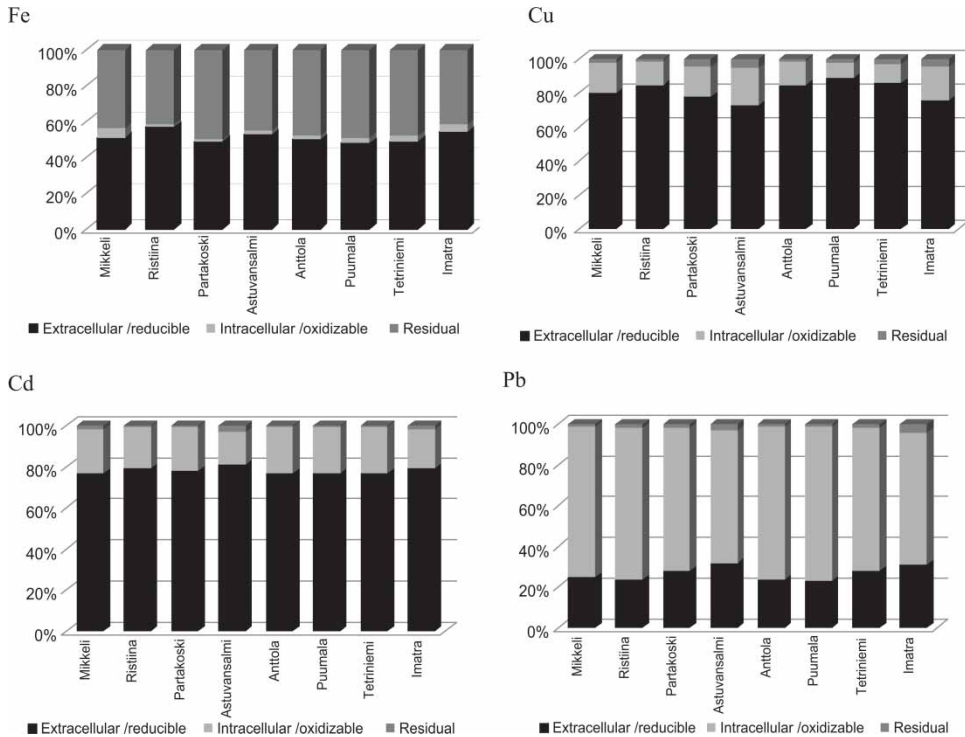


Figure 5. Chemical partitioning of metals in moss samples.

On the other hand, Cu showed a significant affinity (20% of the total) towards organic/sulfide fraction (Figure 4). It was discussed by Marschner [3] that when copper ends up in soil, it strongly attaches to organic matter and minerals. In addition, Fytianos and Lourantou [33] found that Cu has high affinity to humic substances in particular, which are a fraction of natural organic matter very chemically reactive in complexing Cu. As a result of microbial oxidation of the organic substrate within the sediments, Cu may be released from this particular fraction and become bioavailable [34]. Cu fractionation presents some differences between the samples, for instance the organic/sulfide fraction is 20% of the total in Puumala and Anttola harbour sediments, while it is only 8% in Astuvansalmi and 10% in Partakoski sediments (Figure 4).

Also, there was some affinity of Cd towards Fe/Mn oxides in Anttola and Puumala harbors as well as Ristiina (Figure 4). Interestingly, in the sample taken from Ristiina, Cd was associated (4%) with the organic/sulfide fraction, which is the second highest for Cd apart from the residual fraction (Figure 4). According to Marin and co-authors [35], this is due to the possible formation of CdS in the lake sediments.

There was some insignificant (3% of the total) of Pb associated with exchangeable/carbonate fraction (Figure 4), which can be explained by the recent atmospheric deposition [36]. Also, similar results were obtained by Marin and co-authors [35], who studied Lake Balaton sediments and determined Pb association with exchangeable and organic fraction.

3.5.2. *Pleurozium schreberi*

In addition to atmospheric deposition, dust originating from the forest floor and nearby roads may also be trapped by vegetation and affect the chemical composition of plants [37]. However, samples were not washed prior the analysis, therefore they contain considerable amounts of dust attached to them (exchangeable and extracellular fractions of a metal) and the actual concentration

(intracellular and residual fractions in particular) that may have harmful metabolic effects are much lower than those reported in field conditions [38].

Extracellular fraction was found to be substantial for Cu (up to 90%), Pb (up to 80%) and in lesser extent for Fe (up to 60%) regardless sampling area (Figure 5). This indicates that Cu, Pb and Fe can easily be leached from moss by rain and thus these metals can be easily introduced to the surface waters and sediments. In addition, significant intracellular fraction was observed for Cd, indicating that if the optimum pH, redox and climatic conditions prevail, Cd may be leached from moss and therefore poses a risk to the environment [7]. On the contrary, Fe showed the tendency to remain incorporated in the moss structure – residual fraction (Figure 5).

3.6. Potential bioavailability

Exchangeable and extracellular fractions are potentially toxic for the biota because it may be easily removed and consumed by organisms present in sediments. Figures 4 and 5 show the potential bioavailability of selected heavy metals. It is evident that only Fe and in some extent Cu (up to 22% and up to 6%, respectively) from sediments (Figure 4) and Cu, Pb and in lesser extent Fe (90%, up to 80% and up to 60%, respectively) from moss are bioavailable and therefore can pose a threat to the biota if concentrations exceed the background as well as maximum allowed concentrations (Table 2).

4. Conclusions

The current study showed that none of Fe, Cu, Cd and Pb analysed in sediments exceeded the maximum allowed concentration. However, it was found that Cd exceeded the background concentration in some sediments three-fold, which may pose a significant threat to microorganisms present in sediments. The contamination in sediments and moss samples followed the order of Fe > Cu > Cd > Pb. Also, the total heavy metal concentrations in sediments followed the order of Partakoski > Mikkeli > Ristiina > Anttola harbour > Imatra > Puumala harbour > Astuvansalmi > Tetriniemi. Significant relationship ($p < 0.05$) between different metals was observed for Cu – Cd (0.88), Fe – Pb (0.65) and Fe – Cu (0.68) in sediments and moss samples. Fe, Cu, Cd and Pb found in sediments showed the strongest affinity towards the residual fraction. Also, significant amount of Cu, Pb and Fe found in moss are bound to extracellular fraction and therefore are bioavailable and can pose a threat to the biota if concentrations exceed the background as well as maximum allowed concentrations.

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