







**Materials and Method**

**Sampling and Analysis**

A 72 cm-long sediment core was taken from Lake Tortum using a Kajak gravity core sampler (coordinates 40°36'57.64"N - 41°38'8.43"E; Figure 1).

The sample obtained was cut into 2 cm-thick slices for heavy metal and organic carbon analysis. The samples were dried at 60oC in a drying oven and grounded to fine powder with a mortar to determine the percentage of organic carbon in the sediment based on the Wakley-Black titration method (Gaudette et al., 1974).

The heavy metal content in the powder products of the sub-samples was determined using ICP-MS at Bureau Veritas Mineral Laboratory (Canada). The samples were first kept in a heating block in a mixture of HCl, HNO3 and DI H2O for an hour to achieve disintegration, which was followed by processing with diluted HCL. Quality control of the results was conducted using repetitions, blank samples, and internal standard reference material (STD OREAS45EA). The results obtained from the reference sample are shown in Table 1.

Table 1. Values obtained from reference sample.

Element	Observed Value	Expected Value	Measurement Limits
<b>Cu</b>	696,39	709	0.01
<b>Pb</b>	14,3	14,3	0.01
<b>Zn</b>	30,7	31,4	0.1
<b>Ni</b>	397,2	381	0.1
<b>Mn</b>	379	400	1
<b>Fe</b>	20.4%	23.51%	0.01%
<b>As</b>	9,9	10,3	0.1
<b>Cd</b>	0,03	0,03	0.01
<b>Cr</b>	751,8	849	0.5
<b>Al</b>	3.26%	3.13%	0.01%

To determine metal enrichment in the lake sediments, enrichment and contamination factors were calculated. The enrichment factor (EF) determines the anthropogenic contribution to the heavy metal concentration. It is obtained by dividing the ratio between the current metal concentration and Al by the ratio of Al in the metal concentration in uncontaminated sediments pertaining to the pre-contamination period (Zhang et al., 2007). The metal concentration that displayed the lowest metal/Al value in the core sample obtained from Lake Tortum was used as the background value for metals. The enrichment factor was evaluated in consideration of Sutherland’s scale (Sutherland 2000), as follows:

- EF<2, minimal enrichment or no enrichment
- EF=2-5, moderate enrichment
- EF=5-20, significant enrichment
- EF=20-40, high enrichment
- EF>40, extremely high enrichment

Another method that was used to determine contamination levels was the Contamination Factor (CF), which is the ratio of metal concentration to background metal concentration. CF is calculated using the following formula (Hakanson 1980):

$$C_f^i = C_d^i / C_b^i \tag{Eq.1}$$

- $C_f^i$ : Contamination factor
- $C_d^i$ : Concentration value measured in lake sediment
- $C_b^i$ : Background metal concentration rate

The contamination value is classified into four groups (Hakanson 1980):

- CF<1, low contamination
- 1≤CF<3, moderate contamination
- 3≤CF<6, high contamination
- CF>6, very high contamination

The Integrated Pollution Load Index (PLI) was calculated in consideration of all metals present in the sediment for the purpose of determining the environmental quality of the sediments and the level of toxicity in the materials examined. The Pollution Load Index was determined by the following formula (Eq.2) (Suresh et al., 2011):

$$PLI = \left[ (CF)_1 \times CF_2 \times \dots \times CF_n \right]^{\frac{1}{n}}$$

The potential ecological risk index (PERI) developed by Hakanson (1980) was used to determine the toxic effects of the metals. The risk factor of each metal is applied as per the formula below:

$$Er^i = Tr \times C \tag{Eq.2}$$

Tr<sup>i</sup>: Toxic Reflection Factor of Each Metal (Reaction Coefficient)

C<sub>f</sub><sup>i</sup>: Contamination Factor

The coefficients corresponding to the toxicity of metals are as follows:

Hg=40, Cd=30, As=10, Cu=Pb=Ni=5, Cr=2, Zn=1 (Guo et al., 2010).

The following formula was used in calculating the ecological risks that could be caused by the combined effect of the metals:

$$PER = \sum Er^i \tag{Eq.3}$$

The following classifications were used to determine the risk factor:

- Er<sup>i</sup><40, low ecological risk
- 40 ≤ Er<sup>i</sup><80, moderate ecological risk
- 80 ≤ Er<sup>i</sup><160, significant ecological risk
- 160 ≤ Er<sup>i</sup><320, high ecological risk
- Er<sup>i</sup> ≥ 320, very high ecological risk
- PER < 150, low potential ecological risk
- 150 ≤ PER < 300, moderate potential ecological risk
- 300 ≤ PER < 600, significant potential ecological risk
- PER ≥ 600, very high potential ecological risk

## Results and Discussion

The vertical distribution of heavy metals is given in Figure 2. The minimum, maximum and average values pertaining to these metals (+/- standard error) are shown in Table 2. Analysis of the change in heavy metals along the core sample revealed this to be between the level of 2-20 cm, except for Pb, Mn and Hg. On the other hand, the highest concentration is observed in the 36-50 cm range for metals other than Pb, Mn, Hg and Ni. Cu concentration generally displays an increasing trend, although it shows some small fluctuations as we move deeper from the current lake bottom. The change in Pb concentration is different in comparison to the other elements, except for Mn and Hg. In this context, Pb reaches its maximum around the 42-44 cm level and displays a decrease as the bottom of the core sample is reached. The shallow-sediment core sample of Lake Tortum reveals a significant increase of Zn at 32 cm. It must also be pointed out that the Ni concentration is high in the 32-52 cm range.

The vertical distribution of Mn proceeds in waves, but in general displays a decrease from the surface of the core sample down to its deeper sections. Fe is observed in similar values, both on the surface and in deeper sections. However, significant increases were determined in the amount of Fe at the levels of 24-26, 34-42, and 48-50 cm. The value of As, which is an important pollutant agent, is irregular along the core sample, but displays high levels in the 18-42 cm range. The vertical distribution of Cd has similar close values at all levels. Cd concentration shows an increasing trend as we move deeper than the current lake bottom. It was determined that Cr reaches its maximum level in the 36-40 cm range. Al concentration generally displays an increasing trend as we move from the surface to deeper sections of the core sample. Al concentration was determined to be at its lowest in the 12-14 cm range (23400 µg/g) and highest in the 36-38 cm range (30400 µg/g). Vertical distribution of the Hg concentration displays a considerably irregular trend and is comparatively the lowest at the surface.

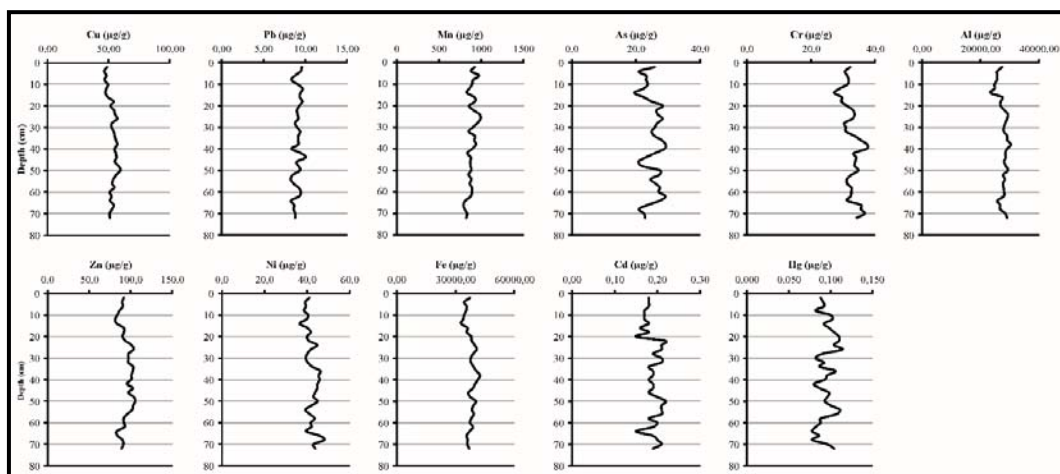


Fig. 2. Vertical distribution of heavy metals in core samples.

Table.2. Heavy metal concentrations, minimum, maximum, and average values for organic carbon and calcium carbonate in current sediment of Lake Tortum (µg/g).

	Cu	Pb	Zn	Ni	Mn	Fe	As
<b>Min.</b>	46,47	8,26	81,60	36,50	789,00	32800,00	19,50
<b>Max.</b>	59,78	10,05	105,60	48,10	992,00	42500,00	29,30
<b>Average</b>	53,03	9,07	94,39	42,11	885,22	37719,40	25,12
<b>Median</b>	53,57	9,15	93,20	41,80	881,50	37850,00	25,80
<b>St. Error</b>	0,56	0,07	1,14	0,44	8,06	369,34	0,45
	Cd	Cr	Al	Hg	OC	CaCO3	
<b>Min.</b>	0,15	27,30	23400,00	0,08	0,00	14,05	
<b>Max.</b>	0,22	37,60	30400,00	0,11	1,68	23,01	
<b>Average</b>	0,19	32,68	27650,00	0,09	0,54	18,07	
<b>Median</b>	0,19	32,60	28000,00	0,09	0,44	17,83	
<b>St. Error</b>	0,00	0,39	256,27	0,00	0,06	0,41	

The heavy metal concentration values obtained from the Lake Tortum core sample were compared to concentrations obtained in various studies of lakes globally and in different regions of Turkey (Table 3). Accordingly, the Cu value of Lake Tortum was observed to be higher in comparison to the lakes of Uluabat, Kovada, Kapulukaya, Beyşehir, Çamlık, Sapanca, Chapala, Çıldır, Dongting and Dongping but lower in comparison to Yedigöller, Veeranam, Baihua and Kapulukaya. The Cu value of the sediment in Lake Tortum is in the same range as the value for Lake Hazar while the Pb value is higher in comparison to Uluabat and Kovada. The Pb concentration of the lake is lower than the values obtained for Sapanca, Çıldır, Veeranam, Yedigöller, Dongping, Dongting and Chapala but displays conformity with the Pb concentration of Lake Kapulukaya.

The Zn value of Lake Tortum is higher than other lakes in Turkey except for Kapulukaya, Yedigöller and Hazar. On the other hand, the Zn concentrations observed in other countries are higher than those of Lake Tortum. The Ni value is lower in comparison to the lakes Çıldır, Yedigöller and Veeranam but higher than Kovada, Sapanca and Chapala and in the same range as the Ni value for Kapulukaya and Hazar lakes. The Mn average of Lake Tortum is only lower than Baihua Lake. This average for Lake Tortum is in conformity with the Mn value ranges for Beyşehir and Kapulukaya. The As concentration was determined to be higher than that of Lake Çıldır. The Cd values of lakes other than Uluabat are higher than Lake Tortum while the Cd concentration of Lake Tortum lies in a similar range to Lake Kovada. The Cr concentration of Lake Tortum Lake is in the

Table 3. Current sediment heavy metal concentrations for Lake Tortum, other lakes in Turkey, and world-wide ( $\mu\text{g/g}$ ).

Name of Lake	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Al	Hg
Chapala, Mexico <sup>a</sup>	29,26	81,74	102,75	32,24	-	3,97%	-	-	66,12	4,5%	-
Hazar, Turkey <sup>b</sup>	10-64	ND	46-210	38-130	85-625	3650-30000	-	-	17-79	-	-
Uluabat, Turkey <sup>c</sup>	0,75	1,42	3,89	-	-	-	-	0,078	2,95	-	-
Çamlık Lagoon, Turkey <sup>d</sup>	19,15-32,23	35,96-67,29	27,58-67,41	-	-	15778,30 - 30441,70	-	1,33-1,66	-	-	-
Sapanca, Turkey <sup>e</sup>	26,68	15,20	62,00	26,72	337,81	-	-	0,29	19,09	-	-
Kovada, Turkey <sup>f</sup>	4,65-13,77	1,74-4,42	12,82-33,42	9,13-25,93	61,19-165,96	3006-7345	-	0,19-0,27	6,63-17,59	3780-9990	-
Beyşehir, Turkey <sup>g</sup>	5,44-10,47	-	10,3-58,05	-	57,665-1029	3466-15136	-	-	-	-	-
Yedigöller, Turkey <sup>h</sup>	67,80-68,53	30,67-32,67	68,47-104,13	59,87-60,33	466,8-510,8	18303-48701	-	ND	43,20-43,93	11572,2 - 13705,6	ND
Veeranam, India <sup>i</sup>	94,12	30,06	180,08	63,61	-	-	-	0,81	88,20	-	-
Baihua, China <sup>j</sup>	102,71	-	184,3	-	1780	5,39	-	-	-	3,08	-
Kapulukaya, Turkey <sup>k</sup>	5-29,3	8,6-34,0	14,8-124,2	24,7-127,1	326,6-1053	0,92-3,48%	9,1-69,7	0,5-1,8	98-1116	1,47-4,64%	1-1,6
Dongting, China <sup>l</sup>	47,48	60,99	185,25	-	-	-	29,71	4,65	88,29	-	0,157
Dongping, China <sup>m</sup>	52,00	35,5	100,5	-	-	-	25,30	0,285	89,3	-	0,055
Çıldır, Turkey <sup>n</sup>	30,11	18,85	64,52	50,12	781,5	21000	3,27	0,38	39,57	22,583	0,07
<b>Tortum<sup>o</sup></b>	<b>53,3</b>	<b>9,07</b>	<b>94,39</b>	<b>42,11</b>	<b>885,22</b>	<b>37719,4</b>	<b>25,12</b>	<b>0,19</b>	<b>32,68</b>	<b>27650</b>	<b>0,09</b>

(ND: not detected; a: Rosales-Hoz et al., 2000; b: Özmen et al., 2004; c: Barlas et al., 2005; d: Dural and Göksu 2006; e: Duman et al., 2007; f: (Kır et al., 2007; g: Tekin-Özan and Kir 2008; h: Arslan et al., 2011; i: Suresh et al., 2012; j: Yi Wang et al., 2012; k: Kankılıç et al., 2013; l: F. Li et al., 2013; m: Yunqian Wang et al., 2015; n: Kükreer et al., 2015; o: this study)

same range as Lake Hazar but lower than that of Çıldır, Yedigöller, Chapala, Veerenam, Dongting, Dongping and Kapulukaya and higher than that of Uluabat, Kovada and Sapanca lakes. The Hg value was determined to be higher in Lake Tortum in comparison to Dongting and Kapulukaya but lower in comparison to Dongping and Çıldır.

**Enrichment (EF) and contamination factor (CF) values**

According to calculations made to determine the presence of any anthropogenic effect, enrichment in all the shallow-sediment core sample elements of Lake Tortum is at minimal levels. However, the enrichment factor for elements As, Hd and Hg approaches moderate levels (EF>2), (Figure 3).

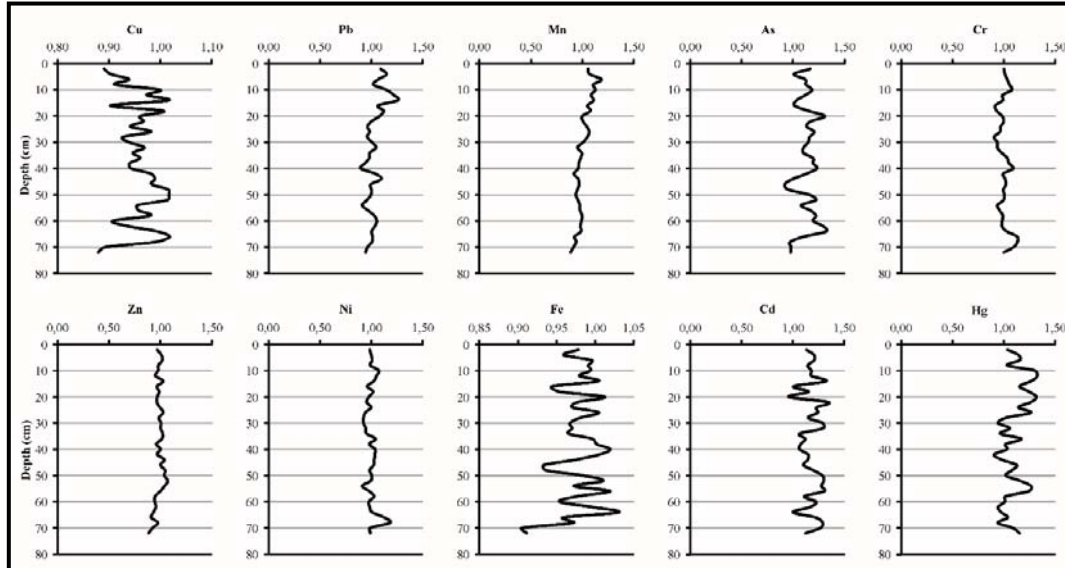


Fig.3. Vertical changes in enrichment factor values of heavy metals found in shallow sediment core sample from Lake Tortum.

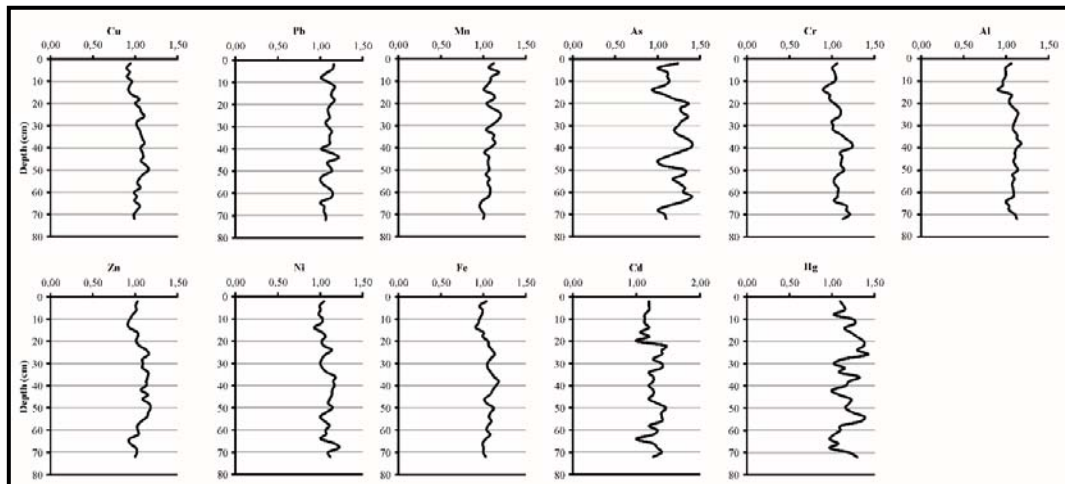


Fig.4. Vertical changes in contamination factor values of core sample from Lake Tortum.



Examination of the contamination factor reveals moderate levels of contamination for all elements; however, all of these values are close to '1', which distinguishes low and moderate levels of concentration from each other. The elements with the highest contamination value are As, Cd and Hg. In all elements the contamination value either falls below or approaches '1', which is a low contamination value, at the levels of 0-20 cm and 60-70 cm (Figure 4).

It is our opinion that the waste produced by the local use of fossil-based fuels for heating plays an important role in contamination of the lake due to the fact that winter is long and harsh (Rodríguez Martín et al., 2006; Hou et al., 2013; Kükreer 2016; Kükreer 2017). Chemical fertilizers used in agricultural fields are also significant sources of heavy metal enrichment, especially where Zn and Cd concentrations are concerned (Micó et al., 2006; Rodríguez Martín et al., 2006; S. Li and Zhang 2010; Sundaray et al., 2011; Cai et al., 2012; Varol and Şen 2012). However, because the surroundings of Lake Tortum are mountainous and have steep slopes,

agricultural activity is limited. In this context, the restricted extent of fields limits the effect of contaminating agricultural activities (use of fertilizers, etc.).

### Potential Ecological Risk (PER) and Contamination Load (PLI) Indices

When the potential ecological risk status of the metals in Lake Tortum are evaluated one by one, all elements other than Cd and Hg display *low levels of ecological risk*. For this reason, these elements do not constitute an ecological risk for the ecosystem (Figure 5). However, evaluation of Cd and Hg revealed that Hg in particular is an ecological risk factor for the ecosystem. Hg displays a moderate level of potential ecological risk, except at the levels of 62-64 cm and 66-68 cm. Where Cd is concerned, the *ecological risk approaches the moderate level limit with moderate levels of ecological risk* observed at levels of 20-26, 28-32, 46-56, 58-60 and 66-70 cm. However, in consideration of the general potential ecological risk, Lake Tortum can be classified in the low ecological risk group.

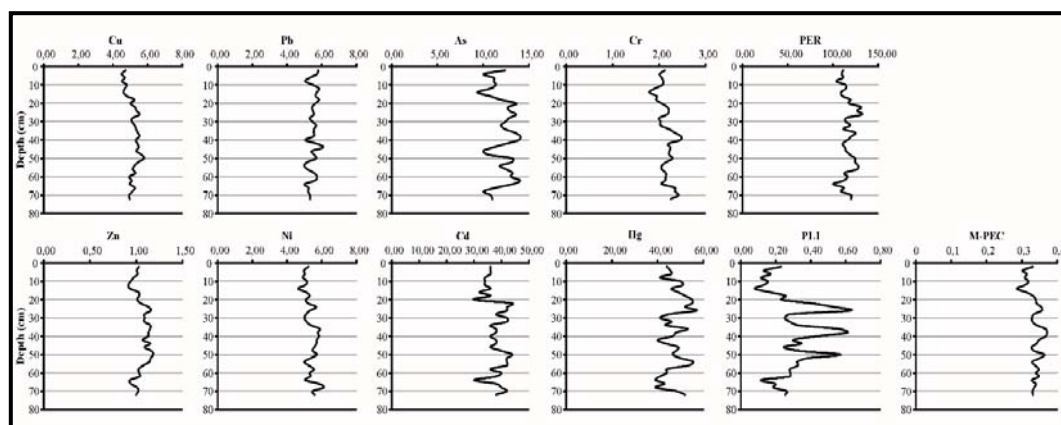


Fig.5. Vertical changes in integrated potential ecological risk (PER) and contamination load index of metals present in sediment of Lake Tortum.

The ideal value of the contamination load index used for the purpose of determining the contamination level in a lake's sediment is 0. On the other hand, '1' is a reference level for contamination load. The contamination increases for values higher than '1', and thus a high level of degradation becomes a consideration (Suresh et al., 2011).

The contamination load index is less than '1' along the entire length (i.e. 72 cm) of the core sample taken from Lake Tortum (Figure 5). In the core sample, the level that most closely approaches the reference value lies in the 24-26 cm range (0.63).

Table 4. Pearson's correlation coefficients between variables (dark colors are coefficients significant at 95% confidence interval).

	Cu	Pb	Zn	Ni	Mn	Fe	As	Cd	Cr	Al	Hg	PER	PLI	OC	CaCO <sub>3</sub>
<b>Cu</b>															
<b>Pb</b>	0,0317														
<b>Zn</b>	<b>0,7947</b>	0,0338													
<b>Ni</b>	<b>0,6527</b>	-0,0208	<b>0,4064</b>												
<b>Mn</b>	0,0961	0,1628	<b>0,4244</b>	-0,1319											
<b>Fe</b>	<b>0,7634</b>	-0,0936	<b>0,8003</b>	<b>0,5228</b>	<b>0,3517</b>										
<b>As</b>	<b>0,4635</b>	-0,0949	<b>0,4154</b>	0,2192	<b>0,3468</b>	<b>0,7913</b>									
<b>Cd</b>	<b>0,5187</b>	-0,0756	<b>0,5724</b>	0,2805	0,0828	<b>0,3992</b>	0,1373								
<b>Cr</b>	<b>0,5547</b>	-0,2461	<b>0,4294</b>	<b>0,8511</b>	-0,0816	<b>0,5698</b>	0,2887	0,3194							
<b>Al</b>	<b>0,7665</b>	-0,0105	<b>0,8196</b>	<b>0,6121</b>	0,3004	<b>0,8627</b>	<b>0,5406</b>	<b>0,5183</b>	<b>0,6649</b>						
<b>Hg</b>	0,1777	0,0056	0,2466	-0,0954	0,3188	0,1531	0,1192	0,2079	-0,0718	0,1844					
<b>PER</b>	<b>0,5536</b>	-0,0191	<b>0,5973</b>	0,2091	0,3241	<b>0,5152</b>	<b>0,3623</b>	<b>0,7050</b>	0,2407	<b>0,5603</b>	<b>0,8038</b>				
<b>PLI</b>	<b>0,7979</b>	0,0456	<b>0,8149</b>	<b>0,5425</b>	<b>0,4624</b>	<b>0,8674</b>	<b>0,6301</b>	<b>0,5672</b>	<b>0,5754</b>	<b>0,8160</b>	<b>0,4103</b>	<b>0,7511</b>			
<b>OC</b>	0,0592	-0,1244	-0,0949	-0,0041	0,0520	0,0290	0,2158	-0,0593	-0,0281	-0,0964	<b>0,3692</b>	0,2545	0,1058		
<b>CaCO<sub>3</sub></b>	<b>-0,7492</b>	0,1136	<b>-0,4940</b>	<b>-0,5787</b>	0,1998	<b>-0,6721</b>	<b>-0,5533</b>	-0,3241	<b>-0,5396</b>	<b>-0,6340</b>	0,0749	-0,2795	<b>-0,5175</b>	-0,0311	

Table 5. Factor loading matrix after varimax rotation.

	<i>Factor 1</i>	<i>Factor 2</i>	<i>Factor 3</i>	<i>Factor 4</i>
<b>Cu</b>	<b>0,800992</b>	0,348634	0,213591	0,0349651
<b>Pb</b>	-0,17826	0,0390251	0,200435	<b>0,583456</b>
<b>Zn</b>	<b>0,615756</b>	0,463025	0,407192	0,273561
<b>Ni</b>	<b>0,848679</b>	0,0216625	-0,125391	-0,014724
<b>Mn</b>	-0,150633	0,282086	<b>0,785141</b>	0,231383
<b>Fe</b>	<b>0,751309</b>	0,190749	<b>0,5827</b>	-0,0330242
<b>As</b>	0,450105	-0,0250043	<b>0,743691</b>	-0,29817
<b>Cd</b>	0,442825	<b>0,688394</b>	-0,13396	0,182071
<b>Cr</b>	<b>0,851883</b>	0,0356948	-0,0923997	-0,102158
<b>Al</b>	<b>0,78682</b>	0,320478	0,358821	0,150947
<b>Hg</b>	-0,180877	<b>0,816428</b>	0,217814	-0,278537
<b>PER</b>	0,26863	<b>0,910683</b>	0,225147	-0,128308
<b>PLI</b>	<b>0,645761</b>	0,521452	0,494317	0,0294497
<b>OC</b>	-0,124919	0,218458	0,17631	<b>-0,784346</b>
<b>CaCO<sub>3</sub></b>	<b>-0,83001</b>	0,0260218	-0,11247	0,171859

### Correlation Test

According to the correlation analysis, Pb and Hg do not appear to be correlated with any other metals and this indicates that their processes are quite separate from other metals. While Hg is not related to any other metal, it displays a weak correlation with OC. A weak correlation was also determined between Mn-Fe and Zn-As. While Fe is correlated with all metals other than Pb and Hg, Al is correlated with all metals other than Pb, Mn and Hg. This shows that the majority of the metals were transferred in compounds that contain both Al and Fe, while Mn was brought in along with compounds containing only Fe. On the other hand, CaCO<sub>3</sub> displays a negative correlation with Cu, Zn, Ni, Fe, As, Cr and Al. This could point to the fact that metal transfer occurs in humid periods (Matthiesen 1998; Özkan 2012; Kükürer et al., 2015). While all metals other than Pb and Cr contribute to PER, all metals other than Pb contribute to PLI. Accordingly, it could be said that Pb does not have an adverse effect on sediment quality (Table 4).

### Factor Analysis

Four factors explain 79.08% of the changes (Table 5). The first factor is responsible for 46.24% and indicates the transfer of metals under continental climate conditions during humid periods. The second factor explains 15.29% and represents potential ecological risks. This factor contains Hg and Cd, which make the highest contribution to PER. The third factor explains 9.21%, as well as the fact that elements Fe, Mn and As are transferred together. The fourth factor explains 8.34% of the changes, with the dominant effect of Pb and OC, that have very little/no correlation with other variables.

### Conclusion

Heavy metal accumulation intensifies in the 36-50 cm range of the core sample in all metals other than Ni. Except for Pb and Hg, the depth where the metal accumulation is low in the core sample is between 10 and 18 cm. In all metals, the enrichment value is at minimal levels at  $EF < 2$ . Because the contamination factor is (CF)  $1 \leq CF < 3$  for all elements, a moderate contamination level of the sedimentation is

deduced. The ideal contamination load index value is '0'. A degradation in the lake is said to be taking place when the contamination load index values along the 72 cm core sample from Lake Tortum are higher than '0'. However, the values do not exceed '1', which would indicate an advanced level of degradation. Upon evaluating the ecological risk of each metal ( $Er^i$ ) other than Hg, these could all be said to display a low ecological risk value as all have  $Er^i < 40$ . Although the ecological risk value for Cd exceeds the lower limit in some places ( $40 \leq Er^i < 80$ ), in general it does not pose a risk. On the other hand, Hg poses a moderate level of ecological risk as its risk value lies in the general range of  $40 \leq Er^i < 80$ . The integrated potential ecological risk (PER) of all metals is low since PER is  $< 150$  along the entire length of the core sample, starting from the current lake bottom. However, the PER values closely approach the moderate potential ecological risk limit ( $150 \leq PER < 300$ ). The long harsh winter in the region increases fossil-based fuel consumption and this most likely affects the contamination. However, due to the mountainous terrain agricultural fields are few in number which limits the effect of contaminating agricultural pesticides and suchlike.

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