Lake-wide assessment of trace elements in surface sediments and water of Lake Sevan

Gor Gevorgyan,[1*] Wolf von Tuempling,[2] Gayane Shahnazaryan,[3] Kurt Friese,[2] Martin Schultze[2]

[1]Scientific Center of Zoology and Hydroecology, National Academy of Sciences of Republic of Armenia, Yerevan, Armenia; [2]Helmholtz-Centre for Environmental Research – UFZ, Magdeburg, Germany; [3]Hydrometeorology and Monitoring Center, Ministry of Environment of Republic of Armenia, Yerevan, Armenia

ABSTRACT

Lake Sevan (Armenia) is one of the large freshwater high-mountain lakes of Eurasia. Detailed information about the extent and fate of trace elements on lake sediment and water quality has not been published yet. For this reason, surface sediment and water samples were collected from the southern and northern basins of Lake Sevan to determine trace element concentrations and assess the trace element behaviour. Geo-accumulation index, potential ecological risk index, and hazard index were calculated to estimate the environmental risk potential. In comparison to reference values, the investigated sediment samples contained elevated concentrations frequently for V, Cr, Co, Ni, Mo, Cd, Be, Ti, Rb, Sr, Se, Hf, and Th and occasionally for Cu, As, Li, B, Ag, Sb, Tl, Bi, U, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Tm. An overall potential ecological risk posed by all the investigated trace elements in the sediments was assessed to be moderate-considerable, however, Mo, Hg, and Cd were the elements with the highest ecological risk potential. The two basins of the lake showed significantly different behaviour according to the investigated trace element contents in the sediments to be higher in the bigger basin compared to the smaller basin. In comparison to reference concentrations in water samples according to the use of the adapted geo-accumulation index, elevated values for Ti, Cr, Cu, Cd, and Pb were observed. Elevated concentration was also observed in the case of B in nearly all water samples in comparison with literature values. Nevertheless, several water samples can be seen as not strongly anthropogenic influenced by Co, Ni, Sn, Sb, Ag, Hg, and Bi. The concentrations of trace elements in the lake water caused health risks to humans particularly children in the case of lake water used for drinking purposes, moreover, As was the main element posing health hazards. The results point out further attention to the sources of elevated trace elements in Lake Sevan, including anthropogenic influences and geological characteristics.

Corresponding author: gor.gevorgyan@sczhe.sci.am

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INTRODUCTION

Trace elements (TEs) are natural components of the earth's crust and therefore enter aquatic systems through natural processes such as weathering and erosions of soil, bed rocks and ore deposits (Drever, 2005; Chojnacka and Saeid, 2018; Gu *et al.*, 2020). Many of them are essential for organisms whereas others behave toxic. Often, TEs change from being essential to being toxic depending on concentration, speciation, and exposure (Pais and Jones, 1997; Chojnacka and Saeid, 2018; Kolarova and Napiorkowski, 2021). Anthropogenically, they can be introduced into an aquatic environment in different forms: dissolved as described for example by Ouyang *et al.* (2006), adsorbed on particles or bonded in particles through mining and industrial emissions, landfill and solid waste deposits, agrochemical and wastewater irrigation as well as urban and industrial (un)treated waste water (Gaillardet *et al.*, 2005; Kolarova and Napiorkowski, 2021). TEs adsorbed on particles or bonded in particles and accumulated in sediments can be a secondary anthropogenic source because of its potential for remobilization into the water column (Mondal *et al.*, 2018). In several cases, human impacts, mainly in the last two centuries, have led to the emission of TEs on excessive levels into the aquatic environment with the consequence of serious violation in its biogeochemical cycles on a regional and global level as described for example for European Russia and Western Siberia by Moiseenko *et al.* (2019), by Hua *et al.* (2016) for the Gan River, China, Santschi *et al.* (2001) and Bussan *et al.* (2017) for Mississippi River and Gulf of Mexico, Vignati *et al.* (2013) and Pavlović *et al.* (2016) for Danube River or Klein *et al.* (2023) for Rhine River and its German tributaries. In such cases, TEs reduce the aquatic biodiversity and abundance and pose even human health risks through the food chain due to their abundance, environmental toxicity, persistence, and bioaccumulation (Kumara *et al.*, 2010; Aksu *et al.*, 2014; Konieczka *et al.*, 2018). Among human activities, mining is particularly prone to mobilize TEs and cause enrichments and ecological damage in downstream water systems (Horowitz *et al*., 1995; Nordstrom, 2011; Tapia *et al*., 2018). Because of the use of highly toxic substances for the extraction of gold from the mined ore (mercury, cyanide), gold mining is not only forcing the mobilization of TEs occurring in the often polymetallic deposits but poses additional risks to the environment (von Tümpling *et al*., 1995; Müezzinoglu, 2003; Moreno-Bush *et al*., 2020). Almost all TEs tend to bond to particles often resulting in enrichment in sediments, particularly in the silt and clay fraction (Salomons and Förstner, 1984; Sigg, 1992; Gaillardet *et al.*, 2005; Dung *et al.*, 2013). Therefore, lake sediments often act as sinks for TEs and accumulate TEs (Förstner and Müller, 1981; Junge and Schultze, 2016; Baran *et al.*, 2019). Furthermore, modern approaches for assessment of contamination by TEs focus on the fraction of small particles. This makes the assessment more sensitive because of the mentioned affinity of TEs to these grain size fractions (Förstner and Müller, 1981; Dung *et al.*, 2013). Knowing the fate of TEs in water bodies and their catchment is essential for successful water quality management and informed decision-making.

Lake Sevan (Armenia), situated in the eastern part of the Republic of Armenia (Gegharkunik Province), is the largest freshwater resource in the Caucasus region and one of the great freshwater high mountain lakes of Eurasia. A freshwater lake began to form in the current Lake Sevan basin during late Miocene (Wilkinson 2020), and it became the current Lake Sevan (as existing until artificial water level draw down) in the Holocene due to damming of the Hazdan River by lava flows (Karakhanian *et al.*, 2001; Avagyan *et al.*, 2020). Lake Sevan is surrounded by mountain ranges and ridges (Gevorgyan *et al.*, 2016), and represents a tectonic basin influenced by grabens and faults (Wilkinson, 2020). The northern boundary of the watershed basin is 2–3 km away from Lake Sevan. All the other boundaries are 30 to 40 km away from the lake. The northern slopes are steep, the others are gentler. Lake Sevan basin is unique by its relatively high rate of endemism of flora and fauna (Babayan *et al.*, 2006). From the economical point of view, the lake provides a very important source of freshwater and freshwater fish in the South Caucasus region. For Armenia, the lake is a natural and cultural treasure, a major strategic resource for drinking water, an irrigation water and hydropower source, a recreation and tourism zone, and a habitat for rich and endemic biological species (Gevorgyan *et al.*, 2020; Gabrielyan *et al.*, 2022). Having such economic and strategic importance, Lake Sevan has been affected by various anthropogenic factors. Sevan basin drains 28 tributaries that flow through urban, agricultural, and industrial areas and transfer industrial, agricultural, and domestic waste into the lake causing changes in the lake ecosystem (Hovhannissian, 1994; Avalyan *et al.*, 2017). Hence, the Lake Sevan catchment basin management has always been an important environmental issue for investigators and decision-makers.

There is a lack of investigation on TEs in the aquatic ecosystems of Sevan basin. On an international level, only one publication on heavy metals in river waters (Gevorgyan *et al.*, 2016), one paper on tectonic influence, possible geological and anthropogenic impacts on TE content in the lake sediments (Karakhanian *et al.*, 2001) and two other articles for heavy metals in lake macrophytes (Vardanyan and Ingole, 2006; Vardanyan *et al.*, 2008) are known. There have been also some investigations on radioactive elements in the sediments of Lake Sevan (Nalbandyan *et al.*, 2004, 2006). When considering not only international publications but also publications in Russian, the studies of Jamgortzian and Chitchian (1962) and Kaplanyan *et al.* (1997) have to be mentioned. However, the used methodology of these two studies is comparable only to a limited extent with modern approaches. Therefore, and because of the changes that have taken place in the last almost 25 years (Gabrielyan *et al.*, 2022), an update was needed. Relevant changes were *e.g.*, the elevation of the water level of Lake Sevan and the substantial extension of the Sotk gold mine as visible from Google Earth since 2000.

The aim of the present study was to fill this gap. The overall status of TEs in Lake Sevan was investigated by sampling surface sediments and water. The results were evaluated based on international and national standards.

METHODS

Study site

Lake Sevan is located in the eastern part of Armenia, at 40°19’ north latitude and 45°21’ east longitude at an altitude of 1900 m above sea level. It has an elongated shape. By underwater thresholds and bilateral capes, the lake is divided into two unequal parts named Big Sevan (BS) and Small Sevan (SS) (Fig. 1). The water volume of the lake is about 37.9 km^3, the surface area – 1276.4 km^2 (HMCMERA, 2022) and the maximum and mean depths

– 81 m (Shikhani *et al.*, 2022) and 29.8 m (Gabrielyan *et al.*, 2022), respectively. For further details on Lake Sevan see Wilkinson (2020) and Gabrielyan *et al.* (2022).

Sampling of sediments and lake water

Thirteen sediment and 40 water samples were taken at different locations in both basins of Lake Sevan, in July and October 2017 (Fig. 1). The collection of sediment and water samples from Lake Sevan was done by the research vessel Yaroslavlec rm – 376. The lake surface sediment samples were collected with a Van Veen grab sampler, kept in plastic zip bags and stored in cool boxes under low-temperature conditions (4-8°C). The water samples were taken with a Molchanov bathometer (Sawod Gidrometribor) from different lake depths (surface, middle, and bottom layers), with simultaneous water temperature measurement and kept in polythene bottles after rinsing 3 times with some ml sample lake water. 10 drops of concentrated high-purity nitric acid (HNO_3) were added to each water sample for preservation. The bottles themselves were pre-washed with 20% HNO_3 and afterwards cleaned with distilled water in the laboratory before sampling.

Sample preparation and analysis of TEs

In the laboratory of the Scientific Center of Zoology and Hydroecology of NAS RA (Yerevan, Armenia), the sediment samples were frozen at -20°C until sample preparation. The water samples were stored at 4°C. For drying the frozen sediments, they were placed in Petri dishes in an incubator at 45°C until mass constancy. For further sample preparation, TE analysis and additional investigation, the sediment and water samples were transported cooled *via* air freight to the Central water laboratory of the Helmholtz-Centre for Environmental Research – UFZ in Magdeburg, Germany. Following the methodology described at Ribbe *et al.* (2021), dry sediments were sieved with a sieving machine (Vibratory Sieve Shaker Analysette 3, Fritsch, Germany) through a 63-µm mesh plastic sieve (Delrin®). The ≤63-µm sediment fraction was stored in sealable plastic containers at room temperature; 250 mg of each of the 13 sieved sediment samples were digested in quartz vessels with 6-mL 65% HNO_3 and 2-mL 37% HCl ("reverse aqua regia"; Suprapur® grade, Merck, Germany). The digestion was done in a pressure- and temperature-controlled microwave (Discover® SP-D, CEM Corporation, USA). The water samples were microwave digested with conc. HNO_3 and H_2O_2 (4:1).

All the reagents used for analysis were of analytical grade or higher. Element concentration (V, Cr, Co, Ni, Cu, As, Mo, Cd, Pb, Li, Be, B, Ti, Rb, Sr, Y, Se, Ag, Sn, Sb, Ba, Au, Tl, Bi, U, Hg, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, and Th) in the digested sediment samples and V, Cr, Co, Ni, Cu, As, Mo, Cd, Pb, Li, B, Ti, Rb, Sr, Ag, Sn, Sb, Ba, Bi, U, and Hg contents in the digested water samples were measured by inductively coupled plasma mass spectrometry (ICP-MS; Agilent 8800 Triple-Quadrupole, Agilent Technologies, Santa Clara, CA, USA) following the method EN ISO 17294-

Fig. 1. Location of Lake Sevan in Armenia and the lake monitoring sites as coded in Tab. S1.

2:2004 for application of ICP-MS (ISO 2004). High-purity water was used for the preparation of calibration standards and in the analyses. All the glassware used was pre-washed with 10% HNO_3, followed by rinsing with distilled water prior to use. To ensure that the ICP-MS/MS remained calibrated during the experiments, certified reference materials and a blank were analyzed for sediment and water samples every 20 samples.

Assessment of TE contamination and environmental risks for Sevan sediments and lake water

Obtained results of TE concentrations were compared with international regulations and literature data (Neal *et al.*, 1998; WHO, 1998; ANZECC and ARMCANZ, 2000; Vengosh *et al.*, 2002; Col and Col, 2003; Salminen *et al.*, 2005; CCME, 2009; Wenzel *et al.*, 2015; Paukstys, 2016) as well as the Armenian water quality norms for Lake Sevan (ARLIS, 2011). There are no Armenian environmental quality standards for sediments. TEs content in the surface sediments was assessed with geo-accumulation index (I_{geo}; Müller, 1979; Barbieri, 2016) developed based on a reference value:

$$I_{geo} = \log_2 \left(\frac{C_m}{1.5 C_b} \right), \qquad \text{(eq. 1)}$$

where C_m is the measured concentration of element in sediment samples, and C_b is the geochemical element reference value. The lowest registered value of each element was considered as reference. The world average concentration for shale from Turekian and Wedepohl (1961), which was used as C_b by Müller (1979) initially, exceeded the concentrations found in the sediment of Lake Sevan for almost all elements (see Fig. 2). Therefore we assume that the minimum of our own results represented the natural background much better than the values from Turekian and Wedepohl (1961). Contamination degree based on I_{geo} values was classified into the following categories: uncontaminated (contamination class 0; $I_{geo} <0$), uncontaminated to moderately contaminated (contamination class 1; $0 \leq I_{geo} <1$), moderately contaminated (contamination class 2; $1 \leq I_{geo} <2$), moderately to heavily contaminated (contamination class 3; $2 \leq I_{geo} <3$), heavily contaminated (contamination class 4; $3 \leq I_{geo} <4$), heavily to extremely contaminated (contamination class 5; $4 \leq I_{geo} <5$), extremely contaminated (contamination class 6; $I_{geo} \geq 5$; Müller, 1979).

Ecological risk of TEs (V, Cr, Co, Ni, Cu, As, Mo, Cd, Pb, Hg, Ti, Tl, Sb, Sr, Be) in the surface sediments was assessed with potential ecological risk index (PERI; Hakanson, 1980):

$$C_r^i = \frac{C_s^i}{C_n^i}, \qquad \text{(eq. 2)}$$

$$E_r^i = C_r^i . T_r^i, \qquad \text{(eq. 3)}$$

$$PERI = \sum E_r^i, \qquad \text{(eq. 4)}$$

where C^i_r is the pollution factor of single element in sediment, C^i_s is the measured concentration of single element in sediment, C^i_n is the background concentration of single

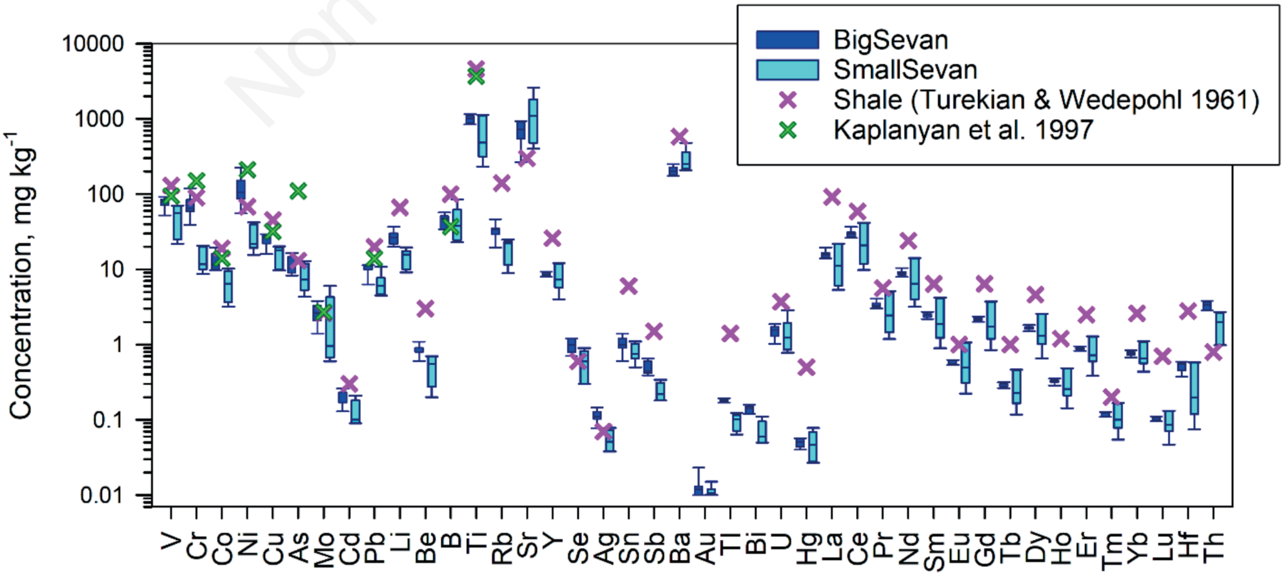

Fig. 2. Box and whisker plot of TE concentrations in surface sediments of Lake Sevan in comparison with the results of Kaplanyan *et al.* (1997) and data for shale from Turekian and Wedepohl (1961).

element in sediment, E^i_r is the potential ecological risk of single element, T^i_r is the toxic response factor for single element. The lowest registered value of each element was considered as background. T^i_r for V, Cr, Ni, Cu, As, Cd, Pb, Hg, and Ti was derived from Weissmannová *et al.* (2019) and for Co, Mo, Tl, Sr, Sb, and Be from Li *et al.* (2019). Potential ecological risk of single elements based on E^i_r values was classified into the following categories: low (E^i_r <40), moderate (40 ≤ E^i_r <80), considerable (80 ≤ E^i_r <160), high (160 ≤ E^i_r <320), very high (E^i_r ≥320; Hakanson, 1980). Overall potential ecological risk based on PERI values was classified according to Hakanson (1980): low (PERI <150), moderate (150 ≤ PERI <300), considerable (300 ≤ PERI <600), very high (PERI ≥600).

Health risks of TEs (V, Cr, Co, Ni, Cu, As, Mo, Cd, Pb, B, Sr, Sb, Ba, Hg) in Lake Sevan water were examined with the risk assessment methodology adopted from the U.S. Department of Energy (USDOE, 2011) and the U.S. Environmental Protection Agency (USEPA, 2011). The exposure doses through ingestion and dermal absorption were calculated using equations (5) and (6):

$$ED_{ing} = \frac{C \times IngR \times ED \times EF}{BW \times AT}, \quad \text{(eq. 5)}$$

$$ED_{derm} = \frac{C \times K_p \times ET \times ED \times EF \times SA \times CF}{BW \times AT}, \quad \text{(eq. 6)}$$

where ED_{ing} is exposure dose through the ingestion of water (mg kg^{-1} day^{-1}), ED_{derm} is exposure dose through the dermal absorption of water (mg kg^{-1} day^{-1}), C is measured TE concentrations in water (mg L^{-1}), IngR is the water ingestion rate for receptor (l day^{-1}), CF is the volumetric conversion factor (l cm^{-3}), ED is the exposure duration (year), EF is the exposure frequency (days year^{-1}), K_p is the dermal permeability coefficient (cm hour^{-1}), ET is the exposure time (hours day^{-1}), SA is the skin surface area available for exposure (cm^2), BW is the average body weight (kg), and AT is the averaging time for non-carcinogens (days).

The non-carcinogenic hazard quotient was calculated by equations (7) and (8):

$$HQ_{ing} = \frac{ED_{ing}}{RfD_{ing}}, \quad \text{(eq. 7)}$$

$$HQ_{derm} = \frac{ED_{derm}}{RfD_{derm}}, \quad \text{(eq. 8)}$$

where RfD_{ing} is the ingestion reference dose for water (mg kg^{-1} d^{-1}), and RfD_{derm} is the dermal reference dose for water (mg kg^{-1} d^{-1}). RfD_{ing} values for V, Cr, Fe, Mn, Co, Ni, Cu, Zn, As, and Mo were derived from USEPA (2003), and RfD_{derm} values for these elements were obtained from RfD_{ing} values by multiplying them with oral absorption efficiency for dermal absorption derived from USEPA (2004). $RfD_{ing/derm}$ values for Cd and Pb were derived from Liang *et al.* (2017).

Overall non-carcinogenic risks posed by all TEs, expressed as the hazard index (HI) *via* ingestion and dermal contact with water, were assessed by the following equations:

$$HI_{ing} = \sum_{i=0}^{n} HQ_{ing}, \quad \text{(eq. 9)}$$

$$HI_{derm} = \sum_{i=0}^{n} HQ_{derm}. \quad \text{(eq. 10)}$$

Statistical analyses

Basic statistical parameters (extremes, mean, median) were calculated, and cluster analyses were applied. For the multivariate chemometrical judgment and assessment, Statistica™, ver. 13.3 (StatSoft, Hamburg, Germany) was used. All univariate calculations have been made with Excel, ver. 2019 (Micorsoft, Redmond, USA). All graphs have been created with Grapher™, ver. 9 (Golden Software, Golden, CO, USA) and SigmaPlot, ver. 13 (Systat Software, Erkrath, Germany).

Comparison with river water

In order to identify potential main source areas for TEs in Lake Sevan, data from the monitoring of the water quality of the main surface inflows into Lake Sevan were used. This monitoring is operated by the Hydrometeorology and Monitoring Center of the Ministry of Environment of RA on a monthly basis with exception of the winter months (usually January, February, and March) when the sampling sites could not be accessed. We used the data received from river water samples collected from 2010 (implementation of the below-described methodology) to 2017 (year of sampling for sediments and lake water of the presented study) and measured by ICP-MS (ELAN® 9000, PerkinElmer, Waltham, MA, USA) according to the method EN ISO 17294-2:2004, 2016 (ISO, 2004, 2016).

RESULTS AND DISCUSSION

Assessment of TEs in surface sediments

Concentrations of the investigated TEs in the Lake Sevan surface sediments are given in Fig. 2, including a comparison with the TE concentrations found by Kaplanyan *et al.* (1997; average values taken from table 80) and Turekian and Wedepol (1961) in shale as the natural rock type that is most similar to aquatic sediments. Our results are in the same order of magnitude as the results of Kaplanyan *et al.* (1997) except for As and Ti. For both TEs, our results are less. The most probable reason for the differences is the heterogeneity of the lake sediments. The number of sampling sites in both our study and also the study of Kaplanyan *et al.* (1997) was quite limited allowing for substantial influence of local heterogeneity and single results on the calculated averages.

The dendrogram of the cluster analysis for the sampling locations showed that the sediments of the two basins were significantly different according to the investigated TEs. However, sampling site no. 8 in Small Sevan had the behaviour of both basins (Fig. 3) and is usually the reason for the much wider variety of the concentrations in Small Sevan compared to Big Sevan (Fig. 2). This can be explained by the fact that it is located close to the channel where Big and Small Sevan are mixed (Fig. 1). A further aspect might be that sampling site no. 8 falls into the small south-eastern part of Small Sevan which has a similar geological background as Big Sevan. According to Avagyan *et al.* (2020), the catchment of Small Sevan is dominated by i) basaltic andesites and andesites of the Upper Pleistocene-Holocene; and ii) volcanogenic/terrigenous sandy nummulitic limestones intercalated with basaltic and dacitic andesites of the Lower and Middle Eocene. In contrast, the catchment of Big Sevan is dominated by iii) basaltic andesites and andesites of the Upper Neogene to Quaternary; iv) trachybasaltic andesites, trachybasalts and their pyroclastic materials Neogene (reaching south-eastern part of the Small Sevan catchment); v) Campanian-Maastrichtian limestones, marls, and volcano-sedimentary formation (reaching north-eastern part of the Small Sevan catchment); vi) Middle Jurassic ultrabasites, periodotites, dunites, pyroxenites, lherzolites, and serpentinites; and vii) Middle Jurassic-Lower Cretaceous ophiolite complex. Almost all of those geologic formations and particularly the mafic and ultramafic magmatic rock among them are well known as sources of many TEs like B, Ba, Co, Cr, Li, Sr, and V

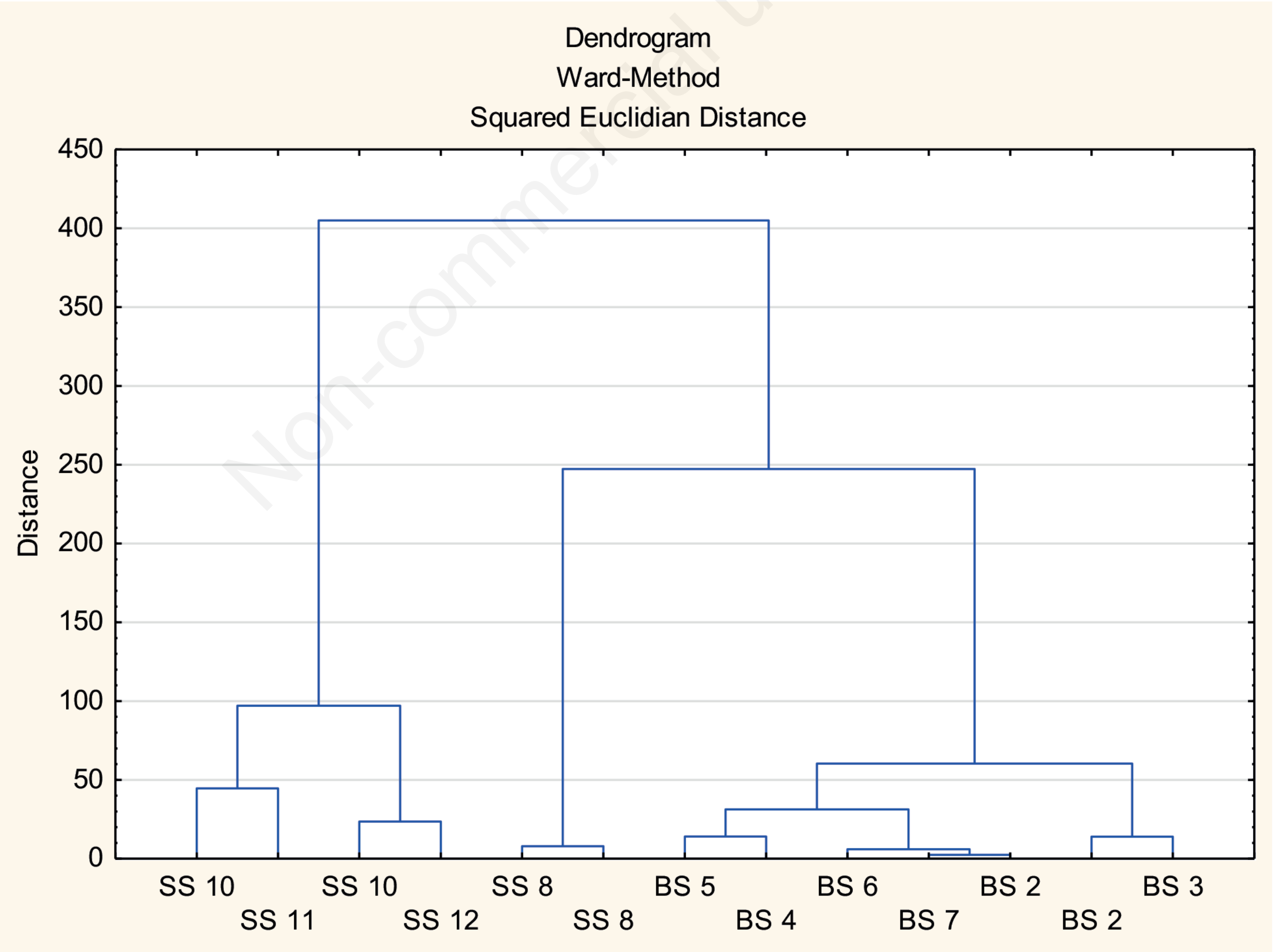

Fig. 3. Clustered sampling points according to the investigated TEs in the sediment samples (autoscaled data, ward method, squared Euclidian distance).

(Hem, 1985; Kaplanyan *et al*, 1997; Reimann and Birke, 2010). Furthermore, Kaplanyan *et al.* (1997) report on ore bodies in the catchment of Lake Sevan which are mainly located in the Sevan Mountains and, thus, along the eastern shore of Big Sevan. Three of these ore bodies have been mined: the famous Sotk gold deposit, the Tigranaberd copper deposit and the Shorzha chromium deposit. The area of the latter belongs to the catchment of Small Sevan and naturally dewaters to its southeast part around sampling site 8. However, all these mineralisations are basically polymetallic and have, thus, the potential to act as a source for many TEs.

The median contents for all the investigated TEs, except for Sr, Ba, Au, and Hg, were noticeably higher by factors in Big Sevan compared to Small Sevan (Fig. 2). This can be explained by higher anthropogenic influences of Big Sevan catchment basin since the degree of urbanisation and agricultural activities is much higher in this area and most of the inflowing rivers (24 out of 28 and Arpa-Sevan tunnel) enter this part of the lake (EUWI+, 2020a, 2020b). Also the geological composition of the catchments of Small and Big Sevan probably contributes to the observed differences. Furthermore, the Sotk gold mine operates in the catchment. The mined deposit is sulphidic and poly-metallic with an oxidized upper section and originally contained besides gold pyrite, arsenopyrite, sphalerite, tellurides, marcasite, and rhodochrosite (Konstantinov *et al*., 2010). Since the mined ore is processed in the Ararat Valley outside the catchment of Lake Sevan (Voigt *et al*., 2018), the risk of contamination of Lake Sevan by ore borne TEs is only given by natural weathering processes of the exposed ore deposits.

Observed As contents in all the sediment samples (Fig. 2) were less than the German Environmental Quality Standard (40 $\mu g\ g^{-1}$; Wenzel *et al*., 2015). According to Cr content (Fig. 2), all the sediments in Small Sevan and also some in Big Sevan fulfilled class 1 (60 $\mu g\ g^{-1}$), all others fulfilled class 2 (620 $\mu g\ g^{-1}$; acceptable good sediment quality; Wenzel *et al*., 2015). All the sediments had Cu contents (Fig. 2) less than the Predicted No Effect Concentration (87 $mg\ kg^{-1}$; Wenzel *et al*., 2015).

The results of the assessment of the single TEs content in the surface sediment samples with I_{geo} (Müller, 1979) are shown in Fig. 4. Pollution was considered for those cases which exceeded class 1. The results (Fig. 4) showed the lake sediment pollution with some TEs (V, Cr, Co, Ni, Mo, Cd, Be, Ti, Rb, Sr, Se, Hf, and Th). The degrees of elevated contents ranged between class 2 (moderately contaminated) and class 4 (heavily contaminated; applying only for Cr and Ni in one sample in Big Sevan in each case) (Fig. 4). However, the lake sediments showed mostly lower levels of elevation with Cu, As, Li, B, Ag, Sb, Tl, Bi, U, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Tm (Fig. 4). The assessment also showed higher content for main TEs in the sediments of Big Sevan (Fig. 4). The investigated TEs can be ranked according to contamination extent in decreasing order as follows: Cr>Ni>Hf>Co>Ti>Mo>V/Be/Rb>Se/Cd/Th>As/Ag/Li/Tl/Ce>Sr>Sb/La>Cu/Bi/Pr/Nd/Sm>Y/Eu/Gd/Tb/Dy/Ho/Er/Tm/Yb/Lu>U/Sn/Hg/Pb>B>Au>Ba for Big Sevan, and Sr>Hf>Mo>Eu/Gd/Tb/Dy/Ho/Er>V/Be/Ti/La/Ce/Pr/Nd/Sm>Tm>Co>B/U>Y/Lu>Hg/Sn/Rb/Se/Th/Cu/As/Li>Ba/Tl/Yb>Cr/Ni/Cd/Ag/Sb/Bi>Au>Pb for Small Sevan (Fig. 4). There was noticeable difference between the magnitudes of TE contamination of the sediments in Big Sevan and Small Sevan indicating contamination from sources of different nature.

One more possibility to describe the degree of contamination is the judgment and assessment of the PERI values. The PERI values, expressed as an overall potential ecological risk posed by all TEs, ranged between 342 and 498 with a median of 468 in Big Sevan (100% of the values express a considerable degree of contamination) and between 187 and 442 with a median of 280 in Small Sevan (more than 50% expresses a moderate degree of contamination) (Fig. 5). Once more a multivariate separation of Big and Small Sevan is given where the PERI values distribution with the median value was substantially higher for Big Sevan (Fig. 5).

The assessment of the potential ecological risk (E^i_r) of single TEs is shown in Fig. 6. Excluding Hg and Sr, all other elements had higher median E^i_r values in Big Sevan. This means for Hg that there was no essential direct influence visible from the catchment basin. The main pathway could be the atmospheric Hg washed out by rain entering the lake. Adsorbed on sedimented particles, similar contents were detectable in both basins. In more detail E^i_r values for V, Cr, Co, Cu, As, Pb, Ti, Be in both Big and Small Sevan sediments, Ni, Tl, Sb in Small Sevan sediments, as well as Sr in Big Sevan sediments were lower than 40 indicating a low risk (Fig. 6). E^i_r values for Ni in Big Sevan sediments (17.9-72.6), Cd in Small Sevan sediments (30-70), Tl in Big Sevan sediments (45.2-51.5), Sb in Big Sevan sediments (28.2-46.9), Sr in Small Sevan sediments (9.1-58.9) indicated a low-moderate risk, while Mo in Big Sevan (42-114) and Small Sevan (18-180) sediments, Cd in Big Sevan sediments (43.3-86.7), Hg in Big Sevan (59.3-84.4) and Small Sevan (40.0-115.6) sediments were of concern due to having either a low- and moderate-considerable risk or a low-high risk (Fig. 6). The potential ecological risk of single TEs can be ranked as Mo>Hg>Cd>Tl>Ni>Sb>As>Sr>Cr>Cu>Pb>V>Be>Ti>Co for Big Sevan and Mo>Hg>Cd>Sr>Tl>As>Sb>Ni>Cu>Pb>V>Cr>Be>Ti>Co for Small Sevan (Fig. 6). The first 3 elements with the highest ecological risk were the same for both basins (Mo, Hg, and Cd), therefore, more attention should be paid to these metals to prevent potential toxicity from these contaminants.

Assessment of TEs in lake water

In contrast to the sediments, no separation of the two basins could be observed by clustering the sampling points according to the measured concentration of the investigated elements in the water samples. This means that the water exchange and mixing were efficient in Lake Sevan in 2017. This was confirmed by comparing the concentrations of the lake water with those of the most relevant surface waters flowing into Lake Sevan (representing about 80% of surface inflows; see Fig. S1). For several TEs there were considerable differences between the concentrations of Lake Sevan and the rivers and between different rivers and the Arpa-Sevan tunnel, sometimes reaching more than one order of magnitude. For the evaluation of the latter, it has to be noted that the high concentrations occurred during low flow conditions. This means that the sampled water under these conditions was groundwater drained by the tunnel from the traversed mountains and not water diverted

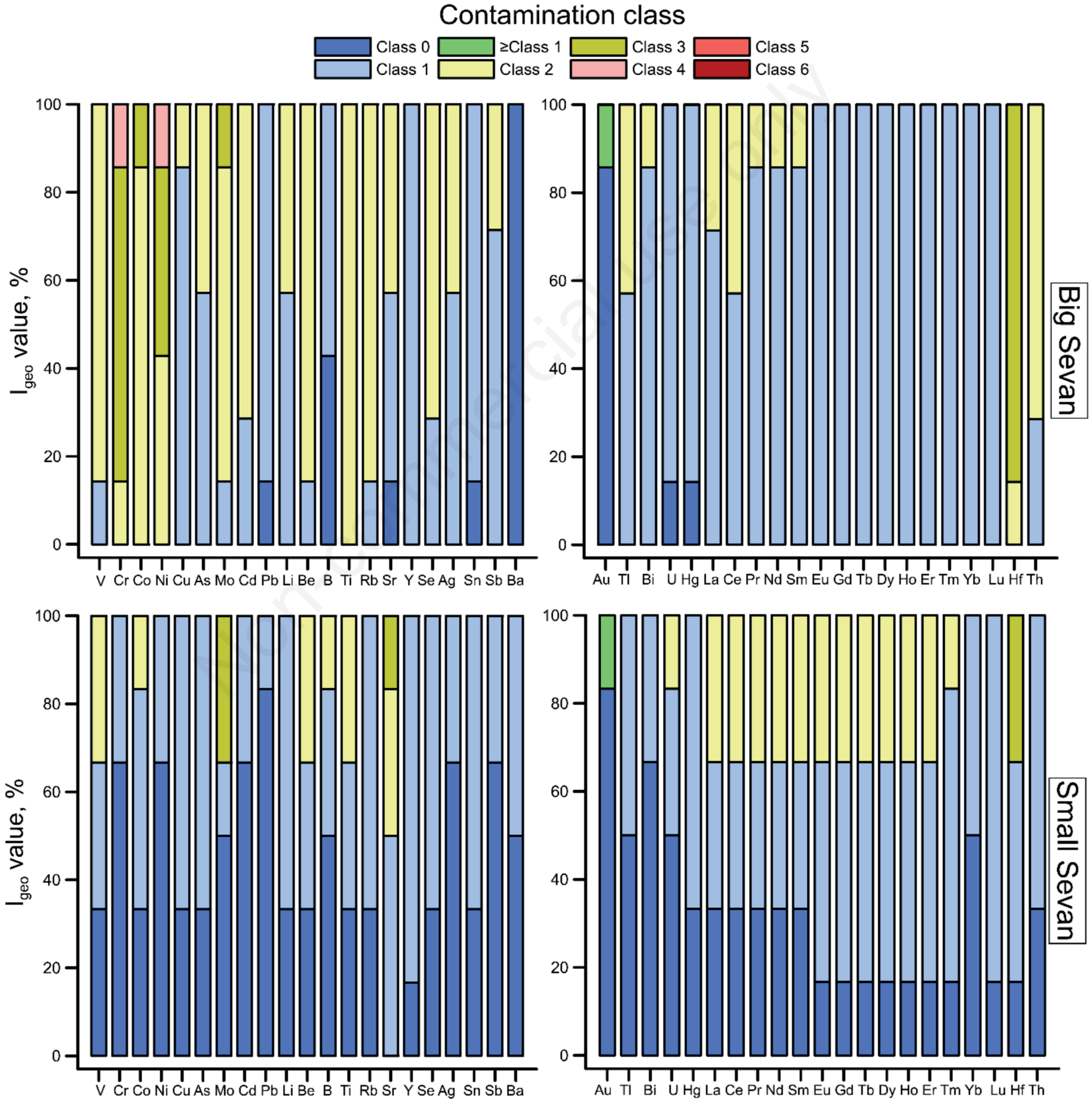

Fig. 4. Contamination classes of TEs in surface sediments of Lake Sevan.

from Arpa River. For many TEs, the concentrations of the lake water were higher or at the upper end of the overall concentration ranges. This is probably the result of enrichment of TEs in the lake water due to evaporation. The comparatively high concentrations of As and Sb in Masrik River probably reflected the influence of the ore deposits and the mining in the catchment of that river. The unexpectedly high concentrations of Cr in Tsakqar River are of not yet understood origin. Karakyan *et al.* (1997) mentioned enrichment of Cr around the lower stretch of Tsakqar River. However, even larger and stronger enrichments were mentioned by Karakyan *et al.* (1997) also for several other rivers.

In the following, the investigated elements will be discussed individually in more detail. Starting with As it can be stated that no lake water sample exceeded 8 μg L^{-1} (Fig. 7) indicating a good status in agreement with the strongest quality norm for freshwater with 24 μg L^{-1} (Wenzel *et al.*, 2015). Compared to the geochemical European Atlas (Salminen *et al.*, 2005), the As concentration in the water samples seems to be elevated (Fig. 7). 90% of the investigated European freshwaters have concentrations less than 2.45 μg L^{-1}. Cu concentrations in the lake water between 1 μg L^{-1} and 19 μg L^{-1} (Fig. 7) were in some samples higher than the Predicted No Effect Concentration (7.8 μg L^{-1}; Wenzel *et al.*, 2015). No lake water sample exceeded Cr of 3.3 μg L^{-1} (Fig. 7) indicating good agreement with the German standard of annual average background concentration (3.78 μg L^{-1}; Wenzel *et al.*, 2015). Ni and Pb in the lake water (Fig. 2) didn't exceed the German Environmental Quality Standard with 34 μg L^{-1} and 14 μg L^{-1}, respectively (Wenzel *et al.*, 2015). Detected values of B in the lake water between 0.4 mg L^{-1} and 0.6 mg L^{-1} (Fig. 7) were also elevated and higher than the described high-reliability trigger value for B of 0.37 mg L^{-1} in the Australian and New Zealand guidelines for freshwater quality (ANZECC and ARMCANZ, 2000). Reference values of B in non-polluted freshwaters are in the range of some 0.01 mg L^{-1} up to 0.1 mg L^{-1} (Neal *et al.*, 1998; WHO, 1998; Salminen *et al.*, 2005). Volcanic activity has been found to be one of the major sources of B in the hydrocycle (Argust, 1998; Coughlin, 1998). For example, Paukstys (2016) noticed B values near the

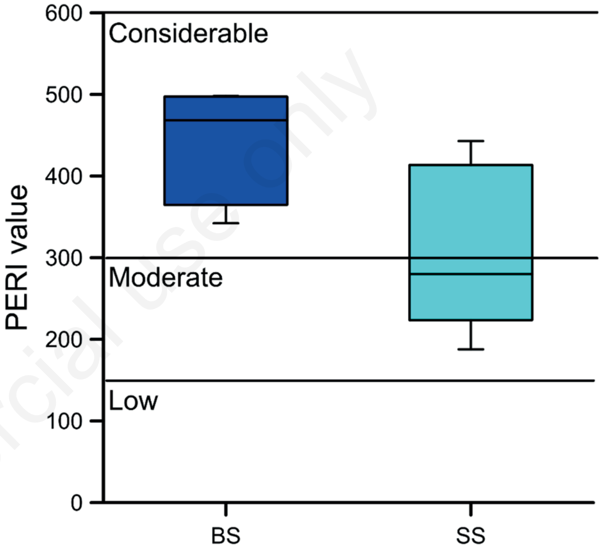

Fig. 5. Box and whisker plot of PERI values of TEs in surface sediments of Lake Sevan.

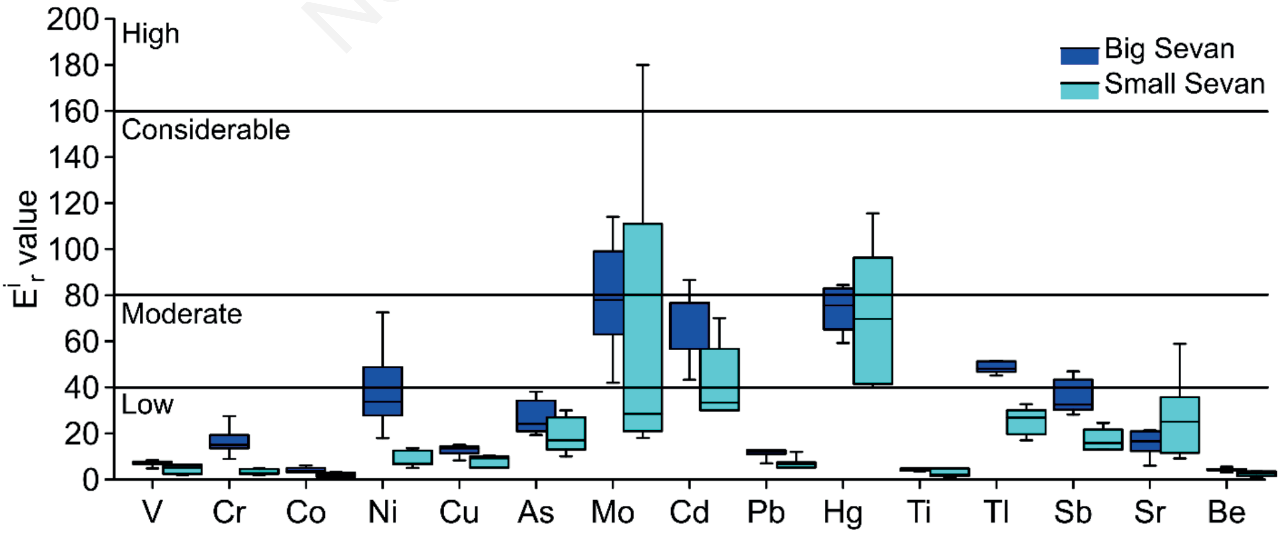

Fig. 6. Box and whisker plot of E^i_r values of TEs in surface sediments of Lake Sevan.

Ashotsq Spring (northwestern part of Armenia) in the range of 0.5 mg L^{-1}. High B concentration in groundwater was also found in Turkey (Vengosh *et al.*, 2002; Col and Col, 2003). In Kutahya Province in Turkey, the average B content in 382 water samples (tap water and natural springs) was 10 ± 4 mg L^{-1} (Col and Col, 2003). There are some thermomineral spring sources at the bottom of Lake Sevan which are related to degassing of volcanic chambers (Avagyan *et al.*, 2020). This allows to conclude about the volcanic nature of the relatively high natural background concentration of B in the lake water. However, many anthropogenic sources of B contamination of water are known as well (Parks and Edwards, 2005). Independent of the fact that elevated B concentration was detected, the long-term exposure for the protection of freshwater life with 1.5 mg L^{-1} for B, according to the Canadian environmental quality guidelines (CCME, 2009), was not exceeded. The comparison of some TEs (V, Cr, Co, Ni, Cu, As, Mo, Cd, Pb, Sn, Sb) with the Armenian water quality norms for Lake Sevan (ARLIS, 2011) showed concentrations for Sn which exceeded the II class of water quality (Fig. 7).

The investigated TEs can be ranked according to contamination extent in decreasing order as follows: Ti>Cd>Cu>Cr>Pb>Hg>Sb>Bi>Co>Ag>Sn>Ni>Mo>V/As/Ba/Li/B/Rb/Sr/U for Big Sevan, and Ti>Cd>Sn>Pb>Cr>Cu>Hg>Sb>Ag>Co>Bi>Ni>V>As/Mo/Ba/B/Li/Rb/Sr/U for Small Sevan. It is worth mentioning that there was a similarity between the orders of TE contamination extents in Big Sevan and Small Sevan water which indicates that both basins were influenced by TEs from sources of the same nature. It should be noted that there was a visible difference between the orders of TE contamination extents in Lake Sevan water and sediments which indicates that the TEs were accumulated in the sediments not only from the lake water but also from other sources, *e.g.*, groundwater. Further investigation should clarify the sources of contamination in the lake water and sediments.

Potential health hazards in the case of lake water use for drinking and domestic (bathing/showering) purposes according to the TEs also were assessed. The results showed that the HI through dermal contact with the lake water was noticeably lower than a threshold value of 1 (Fig. 8) which indicates that adverse health effects in the case of water used for domestic (bathing/showering) purposes were negligible. However, the investigations revealed non-carcinogenic health risks to children in the case of water used for drinking purposes. The values of HI through the ingestion of lake water by children were greater than 1 in all the investigated sites (Fig. 8). According to the average values of HQ, health hazard of single TEs was in the order of As>B>Mo>Sb>V>Co>Cr>Sr>Cu>Ba>Ni>Pb>Cd>Hg in Big Sevan and As>B>V>Sb>Mo>Co>Cr>Cd>Sr>Pb>Ni>Ba>Cu>Hg in Small Sevan (Fig. 8). There was no high contamination of water with As. However, the level of As exceeded threshold value of 1 in all the investigated sites during almost the whole investigation period (Fig. 8). This indicates, a serious risk cannot be excluded for children's health in the case of water use for drinking purposes. This is due to the fact that different elements have different toxicity levels and penetration capacities (Gevorgyan *et al.*, 2016) as a

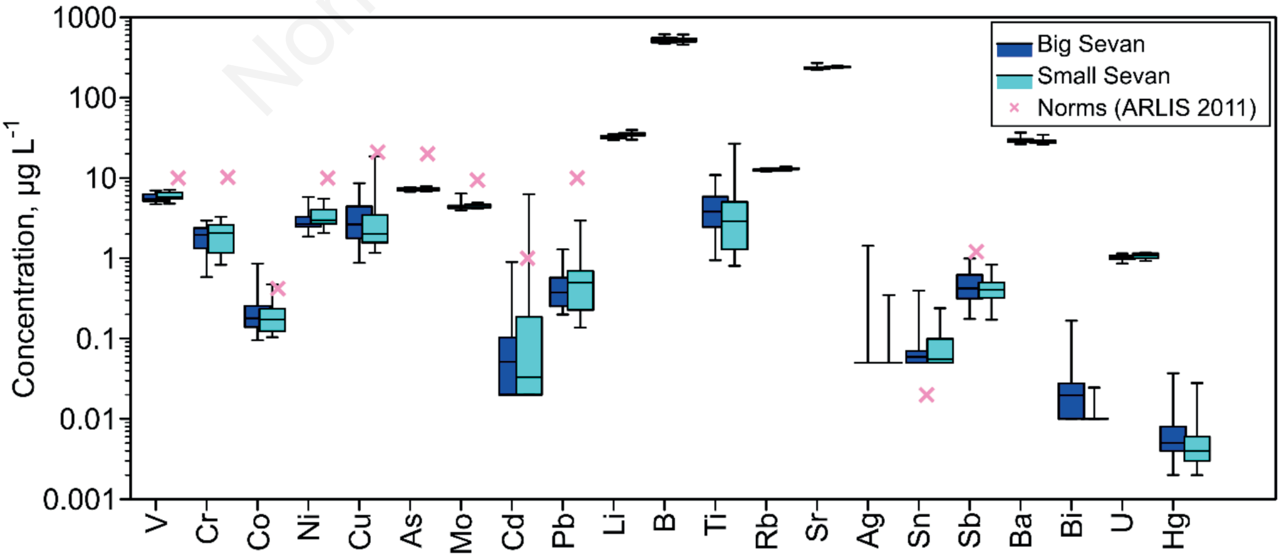

Fig. 7. Box and whisker plot of TE concentrations in Lake Sevan water in comparison with Armenian norms particularly II class of water quality from ARLIS (2011).

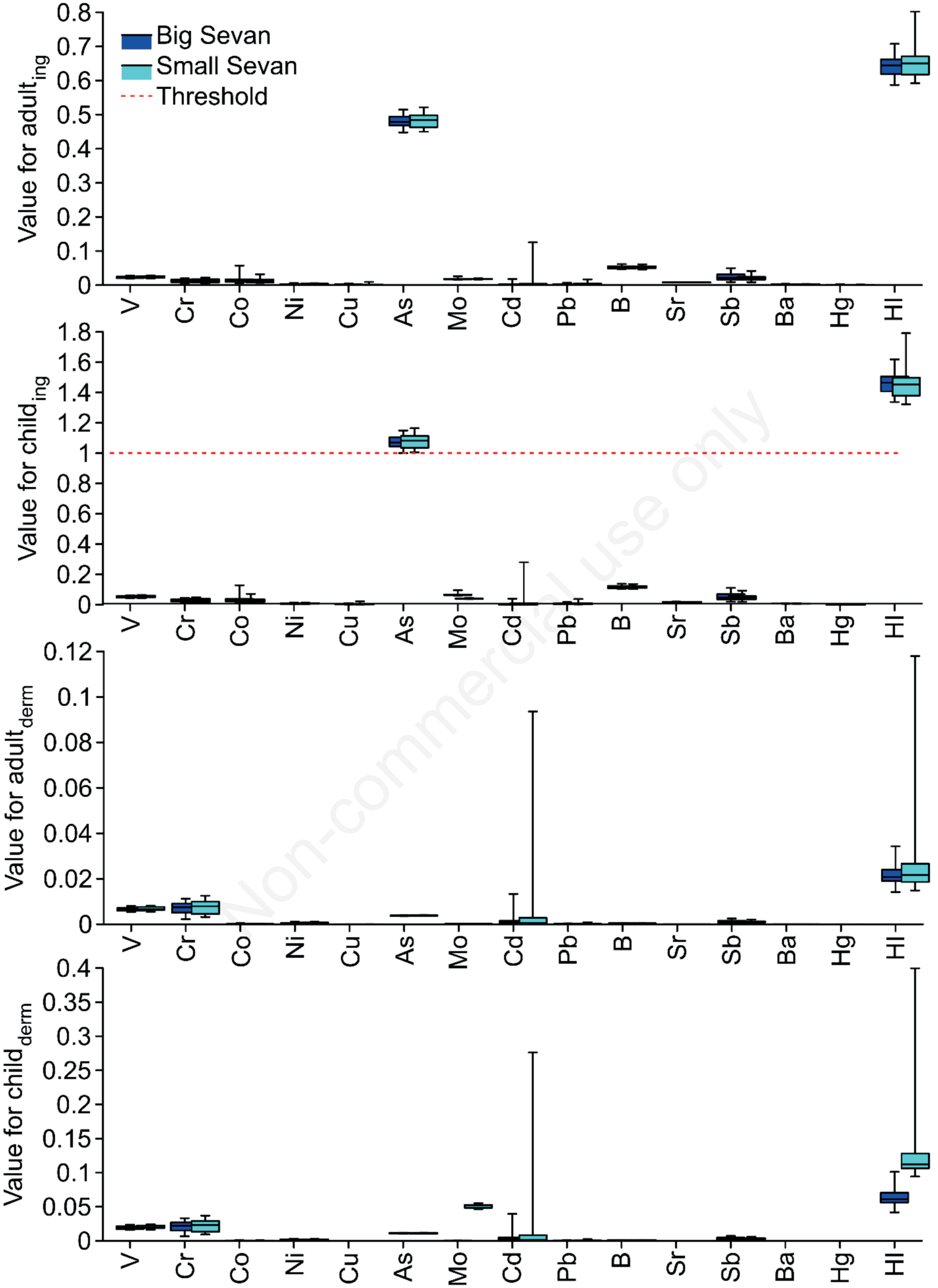

Fig. 8. Box and whisker plot of HQ (marked by relevant elements) and HI values of TEs in Lake Sevan water.

result of which As, which is considered to be quite toxic (USEPA, 2003), was risky for children's health even at low contamination degree. The higher vulnerability of children to exposure from TEs is explained by different physiological properties in contrast to adults (Weissmannová *et al.*, 2019).

Limitations of the present study and future research to overcome these limitations

Although we tried to cover the entire area of Lake Sevan, the limited number of samples did not allow for a more detailed exploration of lateral differences in the TE concentrations of the sediments. Such differences could be caused by i) different natural backgrounds of the inflowing rivers and the regional groundwater; ii) different deposition conditions due to sediment focusing; and iii) different TE-loading of all inflows by human activities. A much higher number of sampling sites is needed to overcome this limitation.

Only surface sediments were investigated and taken as grab samples. The found minimum concentrations were used as background concentrations. Much better would be the use of deeper layers of sediment, which were not influenced by human activities as proposed by Förstner and Müller (1981). This would require core sampling. A further advantage of core sampling would be that a detailed vertical separation could be done and dating of the sediment layers. Wilkinson (2020) mentioned a sedimentation rate of about one millimetre per year. Assuming the sampling depth of grab samples to be in the range of 5-10 cm, the investigated samples represented a period of 50 to 100 years, *i.e.*, the entire period of intense and increasing human impact on Lake Sevan.

The study could not identify the sources of the TEs found in the sediment. The catchment of Lake Sevan, including river water, river sediments, groundwater, and other potential sources of TEs, was out of the scope of the study and existing literature does not allow for overcoming this limitation. However, developing management measures to reduce the identified contaminations requires the identification of the sources and the quantification of their individual contributions. In summary, despite the valuable results the limitations underline the preliminary character of the study.

The achieved state of this investigation provides better knowledge about TE present status in Lake Sevan's surface sediments and water as well as its environmental hazards. This could be very useful for environmental monitoring and checking the health of Lake Sevan. However, the study outcomes leave some open lines of research and future developments. They can be divided into four directions: i) investigating TE contents in sediment depth profiles in the lake and TE concentrations in the water of inflowing rivers; ii) characterizing the geological status of the study area; iii) identifying the sources of TEs in the lake sediments and water; and iv) providing a more extensive assessment of TE-induced environmental hazards, including TE contents in the biological resources of the lake.

CONCLUSIONS

For the first time, TEs in a broad range and their behaviour have been investigated and assessed in Lake Sevan in surface sediments and water using modern approaches. For the judgment and assessment, at one hand, univariate chemometrical methods like median and percentile contents and concentrations as well as the Cluster analysis as a multivariate method were used. On the other hand, classifications and risk assessments were done according to the I_{geo}, PERI, E^i_r, and HI values.

The results of the assessment with I_{geo} have demonstrated that the lake had noticeably elevated content for V, Cr, Co, Ni, Mo, Cd, Be, Ti, Rb, Sr, Se, Hf, and Th in the sediments. Actual and overall potential ecological risk posed by all TEs in the lake sediments was assessed as moderate-considerable with the highest risk potential from Mo, Hg, and Cd. However, the southern and northern basins were significantly different according to the investigated TEs in the sediments. The median concentration for almost all the investigated TEs was substantially higher in Big Sevan which in turn posed higher ecological risk potential from the southern basin and can be explained by higher anthropogenic influences from Big Sevan catchment.

In comparison to reference concentrations in water samples according to the use of adapted geo-accumulation index, the lake also showed elevated values for Ti, Cr, Cu, Cd, and Pb in the water but no separation of the two basins according to the investigated TEs in the water. Elevated concentration was also registered for B in the lake water in comparison with international regulations. However, further investigations are required for the clarification of contamination sources. Moreover, the investigation revealed As-induced health risks, particularly to children in the case of lake water used for drinking purposes.

Beyond the results and conclusions regarding Lake Sevan, the study demonstrates how a preliminary assessment of TEs can be done for a large lake with quite limited effort and resources. This can be very helpful for water management and decision-making for so far widely unmonitored aquatic systems.

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