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Original Research

Concentrations and Human Health Risk Assessment of Selected Heavy Metals in Surface Water of the Siling Reservoir Watershed in Zhejiang Province, China

Naveedullah[1], Muhammad Zaffar Hashmi[1], Chunna Yu[2], Hui Shen[1], Dechao Duan[1], Chaofeng Shen[1]*, Liping Lou[1], Yingxu Chen[1]

[1]Department of Environmental Engineering, College of Environmental and Resource Sciences,
Zhejiang University, Hangzhou 310058, P. R. China
[2]Center for Biomedicine and Health, Hangzhou Normal University,
Hangzhou 311121, P. R. China

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Abstract

Anthropogenic and agricultural activities are deteriorating drinking water quality of the Siling reservoir. Spatio-temporal variations and risk assessment of select heavy metals (Zn, Cu, Mn, Fe, Cr, Cd, and Pb) were investigated in water samples. During summer Mn (37.32 μg/L), Fe (41.0 μg/L), and Cd (1.18 μg/L) concentrations were higher in the water samples, while the concentrations of Zn (86.12 μg/L), Fe (42.0 μg/L), and Pb (30.82 μg/L) were dominant in winter. However, Cr exhibited elevated concentrations in both seasons. The health-risk assessment revealed that hazard quotient (HQ_{ing}) and hazard index (HI_{ing}) values were near to the acceptable limit, indicating non-carcinogenic risk to the recipient via oral intake of water. The calculated values for chronical daily intake (CDI) were found in the order of Cr > Fe > Mn > Zn > Cd in summer and Zn > Fe > Cr > Pb > Mn > Cu during winter. The carcinogenic risk (CR_{ing}) via ingestion route for Cr, Cd, and Pb were noted higher than the acceptable limit (10^{-6}). Multivariate statistical analysis such as cluster analysis (CA) and principal component analysis (PCA) results revealed that natural processes and anthropogenic activities were the main sources of water contamination. The data provided in this study are considered essential for reservoir remediation. The results suggested that quick action should be taken to protect the drinking water integrity of the Siling reservoir watershed from the different nonpoint pollution sources, especially the application of agricultural fertilizers.

Keywords: health risk assessment, heavy metals pollution, source apportionment, surface water, Siling reservoir watershed, environmental health

Introduction

Water is an essential element for life. Fresh water comprises 3% of the total water on earth. For human use only 0.01% of this freshwater is available [1]. Unfortunately, even this small proportion of fresh water is under gigantic stress due to lithogenic and anthropogenic sources, particularly from rapid population growth, urbanization, and unsustainable consumption of water in industry and agricultural activities [2-4]. Predominant are the heavy metal

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*e-mail: ysxzt@zju.edu.cn

high concentrations that accumulated in the aquatic system via several pathways, e.g. variety of bedrock, atmospheric deposition, water drainage, runoff from agricultural and urban areas, and industrial effluents [4-6]. Furthermore, heavy metals contaminate the surface water and ground water, resulting in deterioration of drinking and irrigation water quality affecting human health as well as the health of the aquatic ecosystem [7, 8]. Eminent metals concentration in different water systems may pose a risk of adverse effects such as deformities, cancer, and health of aquatic animals together with their terrestrial predators [9-11]. Some heavy metals at lower concentrations like copper (Cu) and zinc (Zn) play an important role in the metabolic activities of living organisms, while the high concentrations of other metals like cadmium (Cd), chromium (Cr), manganese (Mn), and lead (Pb) are considered highly toxic for human and aquatic life [12], including liver and kidney problems and genotoxic carcinogens [13, 14].

Heavy metals enter the human body through several pathways such as food chain, direct ingestion, dermal contact, fume inhalation, and particles through mouth and nose. Siling reservoir has four main functions: drinking water supply for water works, releasing flood water, irrigation, and supplying water for tourism and landscape. Therefore, in surface water environment ingestion and dermal absorption are the main routes of exposure [15, 16-18]. For effective assessment of water quality it is important to identify potential human health effects of pollutants in drinking water. The traditional method for evaluating health effects is to directly compare the measured values with permissible limits, but it is not sufficiently reliable to provide detailed hazard levels and identify contaminants of the most concern. Health risk assessment is an important tool for estimating the potential health impact in aquatic ecosystems caused by various contaminants [19, 20]. This method has been applied to evaluate the potential adverse health effects by exposure to contaminated water [11, 21, 22]. Although ingestion is considered to be the primary route of exposure to chemical contaminants in drinking water sources, likewise inhalation and dermal absorption are also increasingly taken into account as important exposure pathways. Seasonal succession of different elements can be a key factor in determining seasonal variation of metal concentrations in different water sources and its relationships with environmental factors. Furthermore, seasonal variations play an important role in metal concentration in soil and water dynamics.

Siling reservoir watershed is one of the typical small watersheds in Tiaoxi River watershed. Tiaoxi River is the main source of Taihu Lake, which is one of the most polluted lakes in China. The present study investigated the concentrations of various pollutants in drinking water and health risk in Siling reservoir watershed Hangzhou, Zhejiang, China. It is evident that anthropogenic and agricultural activities are generally responsible for deterioration of surface water quality of aquatic systems in watersheds [23]. However, there is limited information on the effect of different anthropogenic and agricultural activities on the water quality of Siling reservoir. Safeguarding the water quality in the watershed of the Siling reservoir is of great importance for conserving water quality in the reservoir. In the study area of the Siling watershed, so far no research work has been conducted on heavy metal contamination in drinking water source and their effects on human health. Our study aims to determine the concentrations of the selected metals (Zn, Cu, Mn, Fe, Cr, Cd, and Pb) in drinking water of the Siling reservoir and to evaluate health risk associated with exposure to these trace metals via oral ingestion and absorption through skin. Agriculture is the dominant land use in this region and large amounts of agrochemicals have been applied to the farming areas of the Siling reservoir watershed. We selected these seven heavy metals as major contributors to soil pollution from the application of fertilizers and pesticides in the watershed of the reservoir. These seven heavy metals are important from a health perspective, which relates to the leaching of these metals into water sources and ultimately reaches the food chain from the drinking of water in such sources [24]. The Multivariate statistical techniques were used to identify the source apportionment of metals in the drinking water reservoir. The selections of metals were based on the detailed baseline questionnaire survey previously made in the study area. It is expected that the data will serve as an important reference for the management of the drinking water in the target area of the Siling watershed.

Materials and Methods

Study Area

Siling reservoir is located in the ecology town of Luniao, Yuhang district, Hangzhou city, belonging to the Taiping river, Northern Tiaoxi tributaries, East Tiaoxi river, Taihu Basin (Latitude 30.419~30.434, Longitude 119.706~119.782) (Fig. 1). The storage capacity of the reservoir is 30 million m^3 with a total catchments area of 80 km^2 (approx.), while the length is 25 km (approx.), with maximum height of 600 m. The designed capacity of the reservoir is 2.8×10^7 m^3; with a depth of 78.0 meters. Siling reservoir is surrounded by Jurassic mountains comprised of rhyolite porphyry, tuff and siltstone rocks. The water of the reservoir is grade-one and is the main source of drinking and irrigation water of Jingshan town and Hangzhou city. In the surrounding of the reservoir, there are many scenic spots providing recreational facilities for the local public. The inhabitants of the study area are enjoying four seasons in a year, namely summer, autumn, winter, and spring with an average rainfall of 1,450 millimeters (57.1 in). In the last few years the applications of agrochemicals and fertilizers in the vicinity of Siling reservoir have deteriorated the quality of water. Episodic runoff events from the agricultural and forest areas also drain into the reservoir [24]. Algal bloom in the Siling reservoir has therefore extended coverage and persists throughout the summer season, which seriously affects the reservoir as a service of drinking water supply. Water samples were collected from the selected points upstream of the reservoir in different times of year.

The choices of the locations were made at the exit of the different potential agricultural fields in the local area.

Sampling and Analysis

Several sampling campaigns were carried out at the Siling watershed during 2011 and 2012 from 11 selected points (Fig. 1). pH was measured on the spot using a Water Quality Checker Model U-52, Horiba Ltd. Kyoto JAPAN. Water samples were collected in pre-cleaned high-density polyethylene bottles in triplicate and subsequently well-mixed in situ following standard methodology [25]. The samples were filtered through pre-washed 0.45 μm Millipore nitrocellulose filters to remove any remaining suspension, acidified with ultra-purified 6 M HNO_3 (2 mL/L) to keep pH < 2, and stored at -4ºC for elemental analysis [26]. The concentrations of zinc (Zn), copper (Cu), manganese (Mn), iron (Fe), chromium (Cr), cadmium (Cd), and lead (Pb) were analyzed using a graphite furnace atomic absorption spectrometer (Perkin Elmer, AAS-PEA-700) under optimum analytical conditions [27, 28].

Quality Control

The quality of the analytical data was guaranteed through the implementation of laboratory quality assurance and quality laboratory methods, including the use of standard operating procedures, calibration with standards, analysis of reagent blanks, and analysis of replicates. Each sample was analyzed in triplicate and after every 3 samples two standard; one blank and another of 2.5 μg/L of respective metal were analyzed on atomic absorption. Recoveries were done by three replicate determinations of the select heavy metals in three water samples and the range of recoveries was 90±0.78-95±0.23%. Calibration curves were optimized by the application of quality control standards at every step of sample measurement. All chemicals and reagents used in the study were of analytical grade and procured from Merck (Germany) or BDH (UK) with 99.9% certified purity. Glassware was from Pyrex, washed with deionized H_2O, dipped in 10% NHO_3 overnight, rinsed with deionized H_2O, and dried finally in an oven at 60ºC. The polyethylene bottles were tightly caped before proceeding to analysis.

Data Treatment and Multivariate Statistical Analysis

Analytical data were processed using STATISTICA software. Basic statistics such as min., max., mean, and relative standard deviation (RSD) were computed, along with the multivariate statistics. Principal component analyses (PCA) was used to identify the possible heavy metal sources. PCA was performed by the method of Varimox normalized rotation on the dataset. It is mainly used to explain the major variation within the data. Hierarchical methods, which form clusters sequentially, beginning with the most similar pair of objects and forming higher clusters stepwise. Cluster analysis (CA) was applied to produce a dendrogram that provide a visual summary of the clustering process, describing clustering groups with a reduction in dimensionality of the original data [15, 29].

Human Health Risk Assessment Indices

Risk assessment is defined as the processes of estimating the probability of occurrence of any given probable magnitude of adverse health effects over a specified time period and is a function of the hazard and exposure. Health risk assessment of the metals in surface water was examined via ingestion and dermal routes to the recipients based on the USEPA risk assessment methodology [17, 18]. In light of the two pathways discussed above, the exposure doses are calculated using equations (1) and (2) adopted form the US environmental Protection Agency [18, 20].

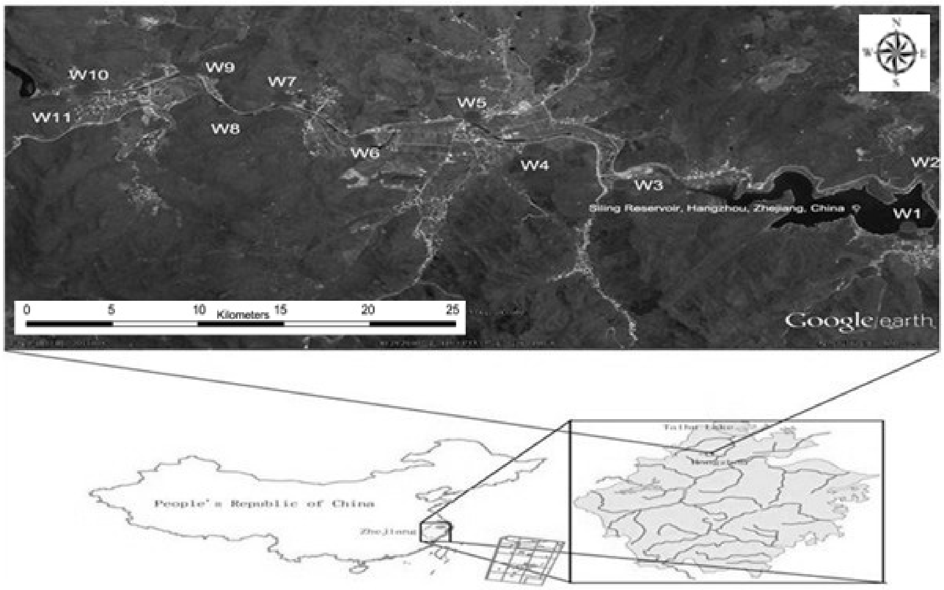


Fig. 1. The Siling reservoir watershed showing water sampling points, China.

Table 1. Parameters for estimating exposure assessment of metals in water samples used in the present study [16, 20, 30, 31].

Exposure factors	Unit	Values
Concentration of metals in water (C_{water})	µg/L	-
Water ingestion rate (IR)	L/day	2.2
Exposure frequency (EF)	days/year	360
Exposure duration (ED)	year	30
Average body weight (BW)	kg	70
Averaging time (AT)	days	10,950
Exposed skin area (SA)	cm^2	28,000
Exposure time (ET)	h/day	0.6
Unit conversion factor	L/cm^3	0.001
Dermal permeability coefficient (K_p)	cm/h	
Zn		0.0006
Cu		0.001
Mn		0.001
Fe		0.001
Cd		0.001
Cr		0.002
Pb		0.004

$$Exp_{ing} = \frac{C_{water} X\, IR\, X\, EF\, X\, ED}{BW\, X\, AT} \tag{1}$$

$$Exp_{derm} = \frac{C_{water} X\, SA\, X\, K_p X\, ET\, X\, EF\, X\, ED\, X\, CF}{BW\, X\, AT} \tag{2}$$

...where Exp_{ing} – exposure dose through ingestion of water (µg/kg/d); Exp_{derm} – exposure dose through dermal absorption (µg/kg/d). The parameters for estimating human health risk assessment through different pathways are listed in Table 1.

The human health risk assessment for metals and potential non-carcinogens were performed by comparison of the calculated contaminant from each exposure route (ingestion, dermal) with the reference dose (RfD) in order to develop hazard quotient (HQ), using equation (3) [15, 18]. HQ > 1, there might be concern for non-carcinogenic effects.

$$HQ_{\frac{ing}{derm}} = \frac{Exp_{\frac{ing}{derm}}}{RfD_{\frac{ing}{derm}}} \tag{3}$$

...where $HQ_{ing/derm}$ – hazard quotient via ingestion or dermal contact (unit less); and $RfD_{ing/derm}$ – oral/dermal reference dose (µg/kg/d) [15, 16, 20].

Hazard index (HI) was introduced to evaluate the total potential for non-carcinogenic effects posed by more than one pathway, which was the sum of the HQs from all applicable pathway equations (4). HI > 1 showed a potential for adverse effect on human health [15, 18].

$$HI_{\frac{ing}{derm}} = \sum_{i=0}^{n} HQ_{\frac{ing}{derm}} \tag{4}$$

...where $HI_{ing/derm}$ – hazard index via ingestion or dermal contact (unit less).

Chronic daily intake (*CDI*) was calculated using equation (5) modified from [16, 27, 32].

$$CDI = C \times \frac{DI}{BW} \tag{5}$$

...where, *C*, *DI*, and *BW* represent the concentration of heavy metal in water (µg/L), average daily intake rate (2.2 L/day), and body weight (70 kg), respectively.

Carcinogenic risks (CR) were estimated using Eq. (6) and the detailed calculating process was followed by [16, 20, 33]. The incremental probability of an individual developing cancer over lifetime as a result of exposure to a potential carcinogen. The range of carcinogenic risks acceptable or tolerable by [34] was 1.0E-06 to 1.0E-04.

$$CR_{ing} = \frac{Exp_{ing}}{SF_{ing}} \tag{6}$$

...where CR_{ing} is carcinogenic risk via ingestion route (unit less); SF_{ing} is the carcinogenic slope factor, ingestion $(µg/g/d)^{-1}$. In order to show the lifetime carcinogenic risk to the local people, CR_{ing} values were calculated for Cd, Cr, and Pb. The SF_{ing} values for Cd, Cr, and Pb are 6.1E+03, 5.0E+02, and 8.5E+00, respectively [18, 35, 36]. SF_{ing} values for the rest of the metals were not available.

Results and Discussion

Spatiotemporal Variation

In the aquatic environment chemical and biological processes can be affected by pH. Even though human health cannot be directly affected by pH, an elevated range of pH attributes a bitter taste to drinking water [27]. Mean pH of the Siling water was 7.43 in winter and 9.74 during summer, which showed a significant temporal variation. pH variability due to seasonal contamination has been reported previously [37]. Distribution of the select metals level (Mean ± SE) in water samples from Siling watershed in comparison to national/international standards are given in Table 2. The concentrations of the variables Zn, Mn, Cr, Cd, and Pb have shown significant temporal variability in both seasons. In summer on average basis metals Mn (37.32 µg/L), Cr (44.71 µg/L), and Cd (1.18 µg/L) showed higher concen-

Table 2. Summary of metals concentration (Mean±SE) in water samples from Siling watershed during summer and winter, and comparison with world values and national/international standards (µg/L).

Sites	Zn	Cu	Mn	Fe	Cr	Cd	Pb	Reference
Siling watershed (Summer)	37.0±24.90	BDL	37.32±11.82	41.0±21.50	44.71±17.63	1.18±0.53	BDL	Present study
Siling Watershed (Winter)	86.12±31.78	1.37±2.05	2.07±1.47	42.0±16.71	30.50±19.25	BDL	30.82±22.16	Present study
p-value	0.00	0.00	0.00	8.38E-01	0.00	0.00	0.00	
Han River, China (Dry season)	–	7.76	42.20	40.66	5.89	3.21	7.37	[3]
Han River, China (Rainy season)	–	18.97	18.79	20.63	10.32	1.38	11.02	[3]
Yangtz River, China	9.40	10.70	5.40	239.80	20.90	4.70	55.10	[4]
Stream rivers, Ghana	138.00	2.65	682.00	–	0.52	0.04	0.85	[58]
Odiel River, Spain	24.23	7.60	13.70	23.47	–	0.08	0.21	[38]
Hindon River, India	833.20	4390.20	857.90	1229.2	332.10	24.00	901.20	[59]
Warri River, Nigeria	87.60	47.20	244.20	2558.40	10.60	7.20	0.10	[60]
Tigris River, Turkey	37.00	165.00	467.00	388.00	< 5	1.37	0.34	[39]
Khanpur Lake, Pakistan	15	9	11	51	46	20	221	[20]
Simly Lake, Pakistan	25	22	14	60	75	17	200	[20]
Surface water standards (China)								
Class I	50	10	–	–	10	1	10	[40]
Class II	1000	1000	100	300	50	5	10	[40]
Class III	1000	1000	100	300	50	5	50	[40]
Class IV	2000	1000	–	–	50	5	50	[40]
Class V	2000	1000	–	–	100	10	100	[40]
Guidelines for Drinking Water Quality	3000	2000	500	1000	50	3	10	[61]
Drinking Water Directives (DWD)	100	2000	50	200	50	5	10	[62]
Guidelines for Drinking Water Quality	5000	1300	50	300	100	5	15	[63]
Freshwater aquatic life	120	13	–	1000	–	2	–	[64]

BDL – below detection limit

tration followed by Zn (37.0 μg/L) and Fe (41.0 μg/L). The concentrations of metals recorded during summer and winter in our study were lower than the concentrations of metals from the Han and Yangtz rivers [15, 16]. Similarly, metals concentrations in our study were also lower from the Odiel River, Spain [38]; Khanpur and Simly lakes, Pakistan [28] and Tigris River, Turkey [39]. However, Cu and Pb were below the detection limits during summer. The peak values for Zn, Cu, Fe, and Pb appeared in winter, followed by Mn and Cr. The concentration of Cd was below the detection limit during winter. Zn, Cu, and Pb revealed higher concentrations in water samples from Siling reservoir during winter as compared to summer. The metals concentrations were also compared with permissible limits set by the USEPA/WHO for non-carcinogenic effects. The mean level of Pb (30.82 μg/L) in water samples from the Siling watershed during winter was significantly higher, while the rest of the metals were within the acceptable levels. Moreover, Zn, Cr, Cd, and Pb exhibited higher concentrations when compared with the Chinese surface water standards (Class I) [40]. In general, the mean value of Pb was found to be elevated over the permissible limits of USEPA/WHO, signifying gross contamination of the drinking water source (Table 2). The level of Pb was below the detection limit during summer and reaches its maximum during winter. In the aquatic environment Pb comes from automotive exhaust deposition and non-point sources [41]. During winter the decreased level of water in the reservoir due to low rainfall results from low dilution of chemicals in water [42], hence increasing the level of Pb.

The total concentrations of seven metals in surface water at different points from Siling watershed during summer and winter seasons ranged from 98.74 μg/L (P-1) to 247.33 μg/L (P-2) and 83.90 μg/L (P-8) to 250.06 μg/L (P-2), respectively (Fig. 2). However, there were significant differences observed among the total concentrations in different points during summer and winter. During winter P-2, P-3, P-4, and P-11 showed higher concentrations of total metals as compared to the other points. The lowest total metals concentrations were noted for point 8 during winter. While in summer P-2, P-9, and P-11 showed relatively higher concentrations of total metals than the other points. Generally, total metals concentration showed an increasing trend from upstream point P-11 toward P-1, explaining the accumulation of metals in the main reservoir during both times of the year (Fig. 2). The phenomenon of heavy metals accumulation along the watershed was earlier reported by Ntakirutimana et al. and Xu et al. [23, 43]. Trace metals in an aquatic environment are derived both from atmospheric deposition and from weathering of bedrock and soil within the catchment [44]. Since Siling water reservoir is located in a remote mountain region and is an important drinking water source, until now there have been few local point pollution sources [24]. The watershed of Pyramid Lake, Nevada, receives anthropogenic trace metals solely from atmospheric deposition and agrochemicals [45].

Multivariate Analysis for Source Apportionment

Cluster analysis identified two main groups of metals for winter; cluster 1 comprised Zn, Fe, Cr, and Pb, and cluster 2 consists of Cu, Mn, and Cd (Fig. 3). Two clusters were also identified for summer season; cluster 1 has Zn, Mn, Fe, and Cr, while Pb and Cd in cluster 2. Factor analysis for summer resulted in two factors with total 73.87 variance and eigen value > 2 (Table 3 and Fig. 4a). PCA/FA 1 and 2 accounted for 47.77 and 26.10% of total variance. In winter season factor analysis resulted in three factors with the eigen value >2. Factor 1, 2, and 3 explained 39.93, 21.62, and 18.78% of the total variance (Fig. 4b). Correlation analysis exhibited that in summer, metals Mn was positively correlated with Zn (r=0.42) and Fe (r=0.74) (Table 4). Cr was negatively correlated with Zn (r= -0.47), Mn (r= -0.40), and Cd (r= -0.48). In winter Cu was negatively correlated with Zn (r=-0.43) and positively correlated with Fe (r= 0.50) and Mn (r=0.62). Fe was negatively correlated with Zn (r= -0.39) and positively correlated with Mn (r=0.37), while Pb was negatively correlated with Fe (r= -0.41).

Inter associations between elements preserve more information about the pathways and heavy metals sources [46]. In the present study, the results of the PCA/FA showed that concentrations of Mn and Fe in PC1 during summer were

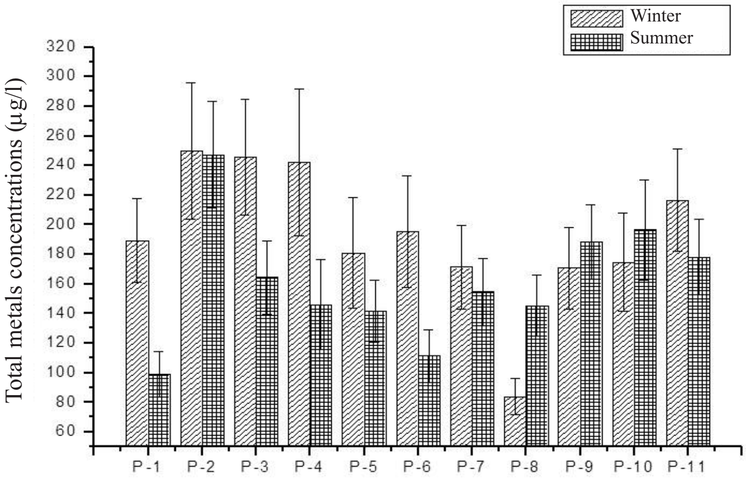


Fig. 2. Total concentrations of seven metals in different points during summer and winter at Siling watershed (μg/L).

Table 3. Factor loading for select heavy metals in water samples from Siling watershed during summer and winter.

	Summer		Winter		
	PC 1	PC 2	PC 1	PC 2	PC 3
Zn	0.53	0.45	-0.37	0.63	-0.37
Cu	–	–	**0.88**	-0.25	0.00
Mn	**0.88**	0.20	**0.89**	0.17	0.09
Fe	**0.92**	-0.10	0.50	-0.26	0.62
Cr	-0.39	**-0.78**	0.09	**0.91**	0.15
Cd	-0.15	**0.88**	–	–	–
Pb	–	–	0.07	-0.12	**-0.94**
Eagen value	2.39	1.31	2.40	1.30	1.13
% Total variance	47.77	26.10	39.93	21.62	18.78
% Cumulative variance	47.77	73.87	39.93	61.54	80.32

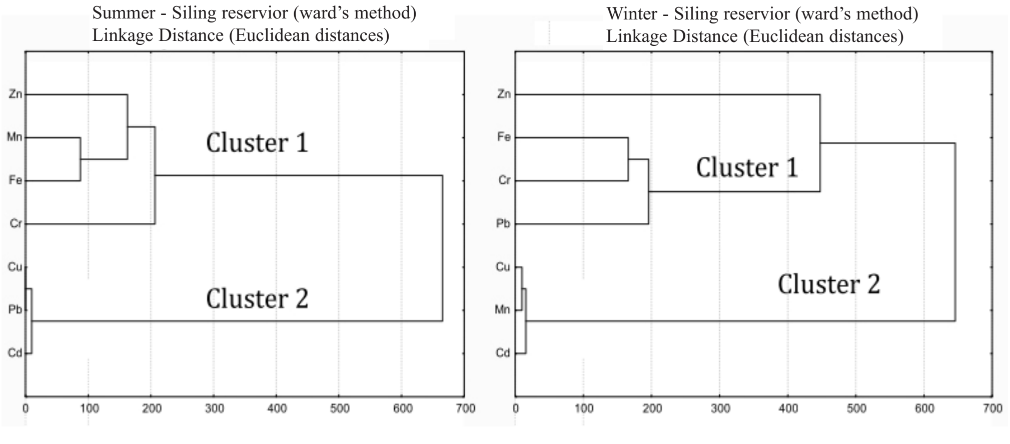
Marked loadings are significant at > 0.70

Table 4. Correlation matrix of select heavy metals in water samples during summer (above the diagonal) and winter (below the diagonal) n=39.

	Zn	Cu	Mn	Fe	Cr	Cd	Pb
Zn	1	0	**0.42**	0.28	**-0.47**	0.14	0
Cu	**-0.43**	1	0	0	0	0	0
Mn	-0.26	**0.62**	1	**0.74**	**-0.40**	0.15	0
Fe	**-0.39**	**0.50**	**0.37**	1	-0.29	-0.12	0
Cr	0.33	-0.14	0.15	-0.12	1	**-0.48**	0
Cd	0	0	0	0	0	1	0
Pb	0.22	0.05	-0.09	**-0.41**	-0.18	0	1

Bold correlations are significant at the 0.05 level

strongly correlated with each other. These results were also supported by cluster analysis and correlation. The results suggest that these metals are mainly to serve as an indirect marker of Fe/Mn oxide content in soils, which are known to affect the retention and chemical behavior of heavy metals in soil and water [47]. PC2 showed a significant negative correlation between Cr and Cd, indicating their input sources from different activities. The presence of Cr during summer in the drinking water may be due to natural processes like weathering [48]. Agricultural practices such as fertilization and use of fungicides tended to increase the concentration of Cd and other metals in surface runoff [49].


Summer - Siling reservior (ward's method)
Linkage Distance (Euclidean distances)

Winter - Siling reservior (ward's method)
Linkage Distance (Euclidean distances)

Fig. 3. Dendogram showing clustering of Siling watershed during summer and winter seasons.

PCA/FA identified three principle components (PC) for the winter. In PC1, Cu and Mn exhibited close associations. Correlation analysis and cluster analysis also verified the positive correlation and stronger cluster between these two metals. The results suggest that these metals are from the same source, which may be attributed to the use of agrochemicals, herbicides, and run-off from extensive farmed areas [50]. In PC 2 the only Cr was positively significant with the eigen value 1.30. Correlation analysis also showed no correlation of Cr with any other metals. However, cluster analysis exhibited a weak cluster of Cr with Fe. Our results suggest that the concentration of Cr in winter may be due to large amounts of particulate matter in the reservoir, which retained Cr as adsorbed ion. Acute toxicity of Cr to invertebrates is highly variable upon species [51, 52], and the concentration may create a toxic effect on aquatic organisms. While the Pb in PC 3 was negatively significant with the eigen value 1.13. There was no strong cluster observed for Pb with other metals. However, correlation analysis verified a negative correlation between Pb and Fe. Like Cr, Pb in winter was alone and without the cluster with other metals. It might be due to the high atmospheric air deposition of lead in recent times, which mixed with rain water during the monsoon and finally reached the water bodies through precipitation [53]. Another reason might be the pesticide application to the farmer's field in the vicinity of the Siling reservoir as the covered areas of the watershed are mostly agricultural crops [24].

Human Health Risk Assessment

Levels of the selected metals in water via ingestion and dermal routes from the Siling reservoir during summer and winter are summarized in Table 5. During summer, the levels of Exp_{ing} and Exp_{derm} from Siling reservoir were observed in the order: Cr > Fe > Mn > Zn > Cd and Cr > Fe > Mn > Zn > Cd, respectively, while Cu and Pb were not detected. In winter the order of the average values of Exp_{ing} and Exp_{derm} were Zn > Fe > Pb > Cr > Mn > Cu and Pb > Cr > Zn > Fe > Mn > Cu, respectively. The concentration of Cd was below the detection limit. These results suggest that Cr, Fe, Mn, Zn, and Pb were the main contributors for ingestion and dermal exposures to the human environment in the watershed of the Siling reservoir. In the present study the levels of HQ_{ing} for all the metals during summer and winter were smaller than unity (Table 5), which indicates that these metals could pose minimum hazard to local residents [16]. However, Cr in summer and Pb in winter exhibited near unity, reflecting that they could have harmful effects on human health [50-52]. The HQ_{dermal} values were also found to be less than unity, which means that the dermal adsorption of the metals in the watershed of the Siling may have little or no health threat. The current study findings are in agreement with the results of the reported studies [16, 54]. During summer and winter seasons the mean levels of HI_{ing} were found to be 0.554 and 0.985, respectively (Table 5), while the observed values for HI_{dermal} were 2.95E-04 and 2.21E-06, respectively. It is obvious from the results that in both cases the observed values are below the safe limit unity, which clearly indicates that there was no cumulative potential of adverse health risks in water samples via direct ingestion or dermal ingestion to the inhabitants of the drinking water source [20]. However, in the present investigations the main contributors to non-carcinogenic health risks were Cr and Pb.

The average CDI values in summer season for the selected heavy metals (Zn, Mn, Fe, Cr, and Cd) were 1.161, 1.173, 1.287, 1.405, and 0.037, respectively. Similarly, during winter the average CDI indices for the selected heavy metals (Zn, Cu, Mn, Fe, Cr, and Pb) were calculated to be 2.707, 0.043, 0.065, 1.318, 0.959, and 0.097, respectively. Therefore, CDI indices for heavy metals in the study area during summer and winter were found in the order: Cr > Fe > Mn > Zn > Cd and Zn > Fe > Cr > Pb > Mn > Cu, respectively (Table 5). In drinking water of the Siling reservoir, the high CDI values were of Cr, Zn, Fe, and Mn. He et al. and Wu et al. [49, 50] suggested that domestic sewage and agricultural practices such as fertilization and use of fungicides and run-off from these extensive farmed areas intended to increase the

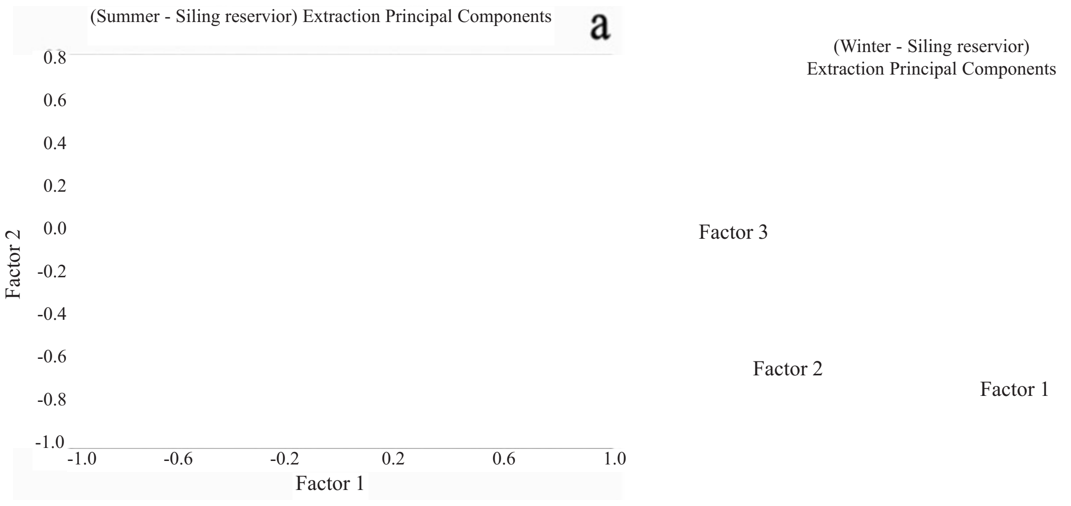


Fig. 4. Factor analysis of the water samples of the Siling reservoir during summer (a) and winter (b).

Table 5. Summary of health risk assessment for metals in water samples from Siling watershed through ingestion and dermal absorption pathways during summer and winter.

Element	$RfD_{ingestion}$ (μg/kg/d)	RfD_{dermal} (μg/kg/d)	Ex_{ping}	Exp_{derm}	$HQ_{ingestion}$	HQ_{dermal}	$\sum HQ_s$	CDI
Summer								
Zn	300	60	1.01	5.10E-06	0.003	8.50E-08	3.37E-03	1.161
Cu	40	8	ND	ND	ND	ND	ND	ND
Mn	24	0.96	1.02	8.58E-06	0.043	8.94E-06	4.25E-02	1.173
Fe	700	140	1.12	9.43E-06	0.002	6.74E-08	1.60E-03	1.287
Cr	3	0.075	1.22	2.06E-05	0.407	2.75E-04	4.07E-01	1.405
Cd	0.5	0.025	0.03	2.71E-07	0.10	1.08E-05	1.00E-01	0.037
Pb	1.4	0.42	ND	ND	ND	ND	ND	ND
$\sum HI_{ing/derm}$					0.554	2.95E-04		
Winter								
Zn	300	60	2.60	8.28E-06	0.009	1.38E-07	8.67E-03	2.707
Cu	40	8	0.04	1.84E-06	0.001	2.30E-07	1.00E-03	0.043
Mn	24	0.96	0.06	2.21E-07	0.003	2.30E-07	2.50E-03	0.065
Fe	700	140	1.26	3.22E-05	0.002	2.30E-07	1.80E-03	1.318
Cr	3	0.075	0.92	3.45E-08	0.307	4.60E-07	3.07E-01	0.959
Cd	0.5	0.025	ND	ND	ND	ND	ND	ND
Pb	1.4	0.42	0.93	3.87E-07	0.664	9.21E-07	6.64E-01	0.097
$\sum HI_{ing/derm}$					0.985	2.21E-06		

ND – not detected

concentration of Zn, Fe, and Mn, and were suspected to affect water quality and ecosystem biodiversity [55]. Public health concerns are centered on the presence of hexavalent Cr, which is classified as a known human carcinogen via inhalation. Cr has high environmental mobility and can originate from anthropogenic and natural sources [5, 56] such as weathering of rock constituents, wet precipitation, and dry fallout from the atmosphere, and runoff from terrestrial systems [57]. In summer the average levels of carcinogenic risk via ingestion exposure CR_{ing} for Cr and Cd were 2.44E-03 and 4.92E-06 in water samples from Siling, respectively. During winter the CR_{ing} for Cr and Pb were calculated to be 1.84E-03 and 1.52E-04, respectively. In most cases the results slightly exceeded the target remedial goal of 1.0E-06 [20]. This indicated that the carcinogenic risk was found to be higher than the non-carcinogenic risk to the inhabitants via ingestion route of water from the reservoir.

Conclusions

It is concluded from this study that, in both seasons (summer and winter), the heavy metals concentrations were within permissible limits, while the concentrations of Zn, Cr, Cd, and Pb were above the Chinese class I surface water standards. The health risk assessment indices like HQ_{ing} and CDI for a few metals were found to be near the safe limit (unity), whereas the levels on HQ_{derm} were less than unity, indicating that risk may occur via the ingestion route only. In general the overall non-carcinogenic health risk assessment HI_{ing} near unity indicated significant risk via the ingestion route, while the dermal contact of water from the reservoir was much lower than unity and considered to be safe ($HI_{derm} < 1$). Risk assessment indicated that Cr and Pb were the major contributors to non-carcinogenic health risks. In the water samples from the Siling reservoir carcinogenic risk (CR_{ing}) was found to be associated with the slight elevated values of Cr, Cd, and Pb. Multivariate analysis confirmed both geogenic and anthropogenic contributions of the metals in the reservoir. Finally, the present study suggests that special attention must be paid to the application of agro-chemicals and anthropogenic activities in the watershed of the Siling reservoir in order to provide safe drinking water to the local people. Furthermore, precautionary measures needed to be taken for sustaining a healthy aquatic ecosystem. This study provides preliminary information of different heavy metals status in Siling reservoir with different techniques, which can be used for future drinking water quality monitoring and planning elsewhere.

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