

Analysis, Assessment and Principal Component Analysis of Heavy Metals in Drinking Waters of Industrialized Region of Turkey

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Received 21 Feb. 2014;

Revised 23 April 2014;

Accepted 5 May 2014

ABSTRACT: Since they may expose to inorganic pollutants, drinking waters should be investigated and monitored in industrialized regions. In this study, drinking water samples taken from eight different locations in heavily industrialized region of Turkey, namely Marmara region, were analyzed to determine heavy metal and harmful trace element (Fe, Co, Cd, Hg, Pb, Zn, Sb, Cu, Ba, Mo, Cr, Mn and V) concentrations. Besides analytical analysis, principal component analysis (PCA) technique, spatial relationships related to these metal elements were also examined. Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used to determine the metal concentrations. The average concentrations in μgL^{-1} were as follows: Hg. Cd and Co BDL; Pb 0.18 ; Zn 27.32 ; Sb 0.04 ; Cu 6.35 ; Mn 2.15 ; Cr 1.07 ; V 1.86 ; Mo 0.52 ; Ba 35.22 ; Sr 252. The obtained results indicated that the heavy metals concentrations in drinking water samples did not exceed the limits values declared in the guidelines of WHO (World Health Organization), EPA (Environment Protection Agency) and TSE-266 (Turkish National Standards). However, some V and Cu concentrations found to be very close to tolerable limits declared by EPA.

Key words: Hazardous element, PCA, drinking water

INTRODUCTION

Water is doubtless main constituent to human since it plays a key role in body functions. Along with the development of science and technology, a number of metal have been used for different scientific, industrial, various purposes and they are unfortunately discharged into the environment. Hence, there has been tremendous increase observed levels in heavy metals and harmful trace elements in nature. Heavy metals pollution in aquatic environments especially in drinking water not only pose a severe threat to health but also led to unfavorable and unwanted results in ecological systems as well as tendency to bioaccumulation (Leeuwen, 2009; Symon, 1986). Since water pollution is one of the most serious environment problems confronting the modern human society those particularly inhabiting close to industrialized areas as they are highly affected by effluents of industrial facilities, domestic wastes as well as crowded population characteristics, heavy metal concentration in drinking water should be kept in tolerable limits determined by international authorities such as WHO and EPA (Koul *et al.*, 2012).

In order to investigate the spatial variability of heavy metals a principal component analysis (PCA) followed by a varimax rotation of the normally distributed means were employed (Ouyang, 2005; Ouyang *et al.*, 2006; Simeonova *et al.*, 2003). PCA is designed to reduce the number of variables to a small number of indices (i.e. principal components or factors) while attempting to preserve the relationships present in the original data. It offers a statistical way to the interpretation of complex data matrices and a better understanding of water quality and ecological status of the studied systems. The method allows the identification of the possible factors affecting the water systems.

Although concentrations of some heavy metals have been measured in tap, surface and other water samples in Turkey, drinking waters consumed in Marmara region have not been conducted in a similar way (Moskalyk *et al.*, 2003; Topçuođlu, 2004; Yalçýn, 2001). Determining the concentrations of heavy metals in tap water samples collected from different location within Marmara region is extremely important for proper assessment of the hazards associated with their intake

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because of intensive industrialization. As part of this study, tap water samples were taken from eight different locations in Marmara region covering the industrial zones connected to residential areas. The main aim of the present study were to investigate concentrations of Fe, Co, Cd, Hg, Pb, Zn, Sb, Cu, Ba, Mo, Cr, Mn and V in drinking water and to assess whether metal concentrations in household drinking water in Marmara region may pose risks to public health considering tolerable limits given.

MATERIALS & METHODS

The Marmara region with a surface area of 67000 km² is the smallest but most densely populated part of Turkey. It represents approximately 8.6% of the Turkish national territory and about 30% of its population. The region with its total population of more than 20 million inhabitants is the economic and cultural center of Turkey and represents 60% of the country's economy. It is Turkey's leading region from many aspects including industrial facilities, energy consumption, large transportation network, tourism incomes and population density. Locations in this region are biggest and most industrialized places (Istanbul, Kocaeli and Tekirdağ) and they are located in the region as shown in Fig. 1. Activities in the places are processed food items, textiles, ready-to-wear clothing, cement, paper, petrochemical products, durable household

items, ships. As it was seen from the activities Marmara region cover almost many industrial facilities. Hence, this study is mostly conducted in the northern part of the region covering these provinces.

Tap water samples were collected from eight different locations showed in Fig.1. then taken to 50 ml polythene bottles. The samples transferred to laboratory and were stored at +4 °C until analyses. All the water samples immediately acidified with 67% (v/v) suprapure nitric acid to bring down the pH level to 2. All prepared stock solutions used were of analytical grade. Calibration standards of Fe, Co, Cd, Hg, Pb, Zn, Sb, Cu, Cr, Mo, Ba, Mn and V prepared from 1000 mgL⁻¹ stock solutions. The solutes were analyzed by Thermo X2 ICP-MS by using EPA 6020 standard methods. A Fischer Scientific Accumet 15 model pH-meter with a combined glass electrode was used for pH measurements. LGC ERM-CA 011b hard drinking water UK metals was used as certified material to evaluate accuracy of analytical performance.

RESULTS & DISCUSSION

Analytical performance is important that give precision and accuracy of device. Hence, the certified reference material has been used to observe accuracy. The concentrations of elements were given as the average of three analysis and in the form of mean±SD.

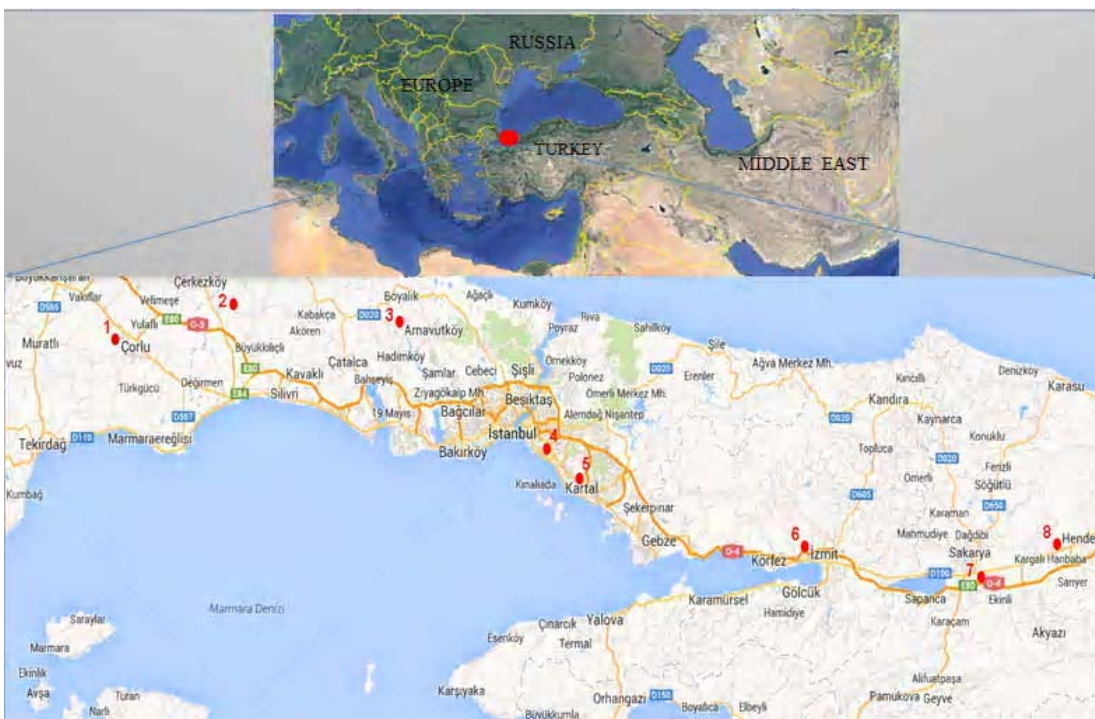


Fig. 1. Locations of drinking water samples from the northern part of Marmara Region

Analytical performance as accuracy was considerable high since the concentrations of all the element analyzed were fall in the range of given certified value, as shown in Table 1.

Another important factor effecting the analytical performance is precision. Limit of detection and correlation coefficient values given in Table 2. Their results were also in a good agreement that display a good analytical precision. The R² value of the calibration curve was e'' 0.99 for each element. Results we obtained in good agrement with procedure of EPA (EPA 6020).

The results for heavy metal concentrations in drinking water samples by locations were shown in Table 3. The mean concentration of elements were considered as two parts which are the elements with relatively low concentrations (< 50 in µg/L) and relatively high concentrations (> 50 in µg/L). Concentrations of these elements were plotted in Fig. 2(a) and (b), respectively. It was noticed that only the elements Fe, Ba, Zn and Sr were generally higher. Table 3 and Table 4 show concentrations of the elements analyzed and explanatory statistics result. Sr, had the highest concentrations in the analyzed samples

Table 1. Comparison of certified values and measured values

Sample	Element	Certified concentration (µg/L) ^a	Measured concentration (µg/L) ^a
LGC ERM-CA011b Hard Drinking water UK-Metals	Sb	5.11±0.23	4.95±0.15
	Zn	597±19.47	576±7.48
	Cd	4.88±0.19	4.71±0.11
	Cr	48.20±1.60	45.20±0.70
	Pb	24.51±0.52	25.70±1.15
	Mn	48.30±1.61	46.60±0.58
	Mo	5.45±0.33	5.49±0.09
	Ni	19.27±0.68	17.05±0.24
	Sr	471±21.23	491±5.12
	V	4.75±0.34	4.83±0.08

^aMean±SD, n=3

Table 2. Limit of dedection, correlation coefficient of calibration curve and linear study range

Element ^a	LOD (µgL ⁻¹)	Correlation coefficient	Linear Study Range (µgL ⁻¹)
⁵¹ V	0.024	0.99931	5-50
⁵² Cr	0.003	0.99965	5-50
⁵⁵ Mn	0.012	0.99961	5-50
⁵⁶ Fe	0.18	0.99923	50-500
⁵⁹ Co	0.003	0.99940	5-50
⁶⁵ Cu	0.027	0.99984	5-50
⁶⁶ Zn	0.151	0.99917	50-500
⁸⁸ Sr	0.003	0.99975	50-500
⁹⁵ Mo	0.009	0.99994	5-50
¹¹⁴ Cd	0.006	0.99921	5-50
¹²³ Sb	0.003	0.99971	5-50
¹³⁸ Ba	0.006	0.99943	5-50
²⁰² Hg	0.057	0.99893	0.5-5
²⁰⁸ Pb	0.015	0.99951	5-50

Table 3. Concentrations of heavy metal elements in drinking water samples by locations

Element	Concentrations (μgL^{-1}) by Sampling Locations							
	1	2	3	4	5	6	7	8
V	0.41±0.01	0.75±0.01	0.52±0.01	0.25±0.001	1.17±0.02	0.28±0.02	0.17±0.02	8.08±0.08
Cr	0.38±0.01	0.78±0.02	0.4±0.01	0.24±0.01	3.14±0.04	0.51±0.01	0.06±0.01	3.1±0.02
Mn	6.32±0.03	5.2±0.64	1.8±0.04	1.87±0.04	BDL**	1.6±0.03	0.02±0.01	BDL
Fe	13.33±0.53	7.31±1.64	15.81±1.37	0.69±0.65	BDL	50.57±7.19	21.05±0.51	BDL
Co	BDL	BDL	BDL	BDL	0.09±0.01	BDL	BDL	BDL
Cu	10.7±0.04	5.97±0.24	18.98±1.71	11.32±0.24	0.42±0.02	2.48±0.01	0.88±0.04	0.07±0.01
Zn	32.16±0.65	9.8±1.02	60.11±7.15	31.14±0.66	1.09±0.12	84.33±0.92	BDL	BDL
Sr	174.5±1.19	334.4±1.08	157.7±0.39	55.65±0.34	300±1.96	247.8±0.48	358±0.03	387.4±2.26
Mo	0.31±0.01	0.8±0.07	0.19±0.01	0.11±0.01	0.79±0.02	1.71±0.20	BDL	0.28±0.01
Cd	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Sb	0.06±0.01	0.08±0.01	0.04±0.01	0.02±0.01	BDL	0.14±0.01	BDL	BDL
Hg	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb	0.3±0.01	BDL	1.01±0.08	BDL	BDL	BDL	0.17±0.01	BDL
Ba	31.08±0.27	28.47±0.09	32.59±0.05	32.17±0.12	82.99±0.22	58.91±0.19	2.99±0.019	12.71±0.12

*Mean±SD, n=3, BDL**= Below Detection Limit

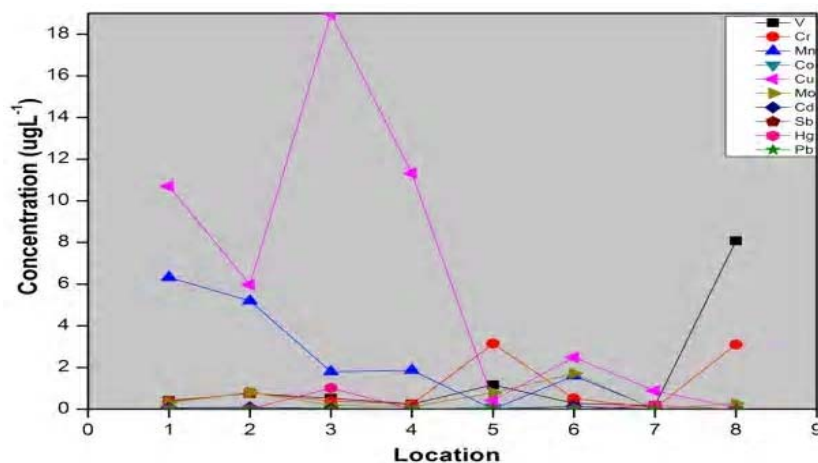


Fig. 2(a). The elements with low concentrations

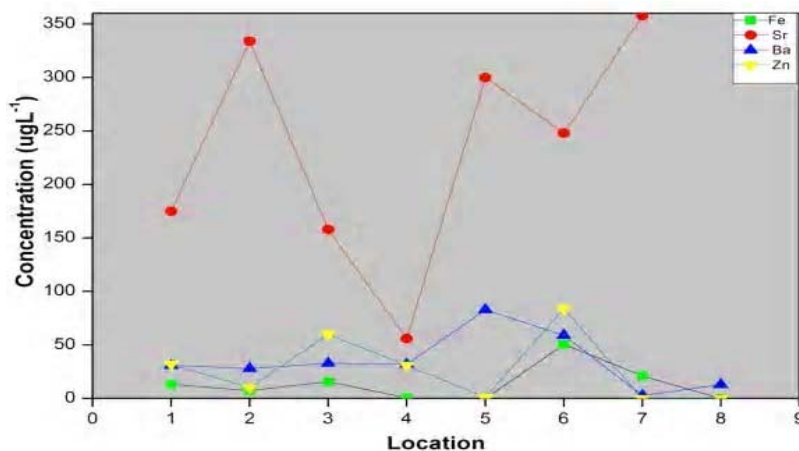


Fig. 2(b). The elements with high concentrations

Table 4. Explanatory statistics of heavy metal concentrations

Element	Range	Minimum	Maximum	Mean	Std. Deviation	Variance
V	7.910	0.170	8.080	1.453	2.697	7.274
Cr	3.080	0.060	3.140	1.076	1.278	1.634
Mn	6.320	BDL	6.320	2.101	2.418	5.851
Fe	50.570	BDL	50.570	13.595	16.917	286.199
Co	0.090	BDL	0.090	0.011	0.032	0.001
Cu	18.910	0.070	18.980	6.352	6.791	46.112
Zn	84.330	BDL	84.330	27.329	31.285	978.724
Sr	331.750	55.650	387.400	251.931	114.724	13161.798
Mo	1.710	BDL	1.710	0.523	0.563	0.317
Cd	BDL	BDL	BDL	BDL	BDL	BDL
Sb	0.140	BDL	0.140	0.042	0.049	0.002
Hg	BDL	BDL	BDL	BDL	BDL	BDL
Pb	1.010	BDL	1.010	0.185	0.351	0.124
Ba	80.000	2.990	82.990	35.239	25.263	638.226

with a mean concentration of 252 µg/L. The element concentrations in descending order were Sr> Ba> Zn> Fe> Cu> Mn> V> Cr> Mo> Pb> Sb> Hg, Cd.

The concentrations of Hg and Cd were found below detection limits in all the samples.

V (vanadium) concentrations in the analyzed drinking water samples were found in the range of 0.17-8.08 µg/L⁻¹ with the mean of 1.45 µg/L⁻¹. The mean concentration of V were found higher than a similar study conducted in Italy (Tamasi and Cini, 2004). The highest V concentration was 8.08 µg/L obtained at the location 8 which were very close to the tolerable limits by declared EPA (10 µg/L). The location 8 is characterized by intensive automotive and metal industries. Therefore, one can think that the leaks of the effluents from this location to water distribution system may lead to this level. V has been evaluated in carcinogen class (Group I) as well as Hg, Cd and Cr(VI) by International Agency for Research on Cancer (IARC). In low levels, V reflects irritative on the upper respiratory tract, however, uptaking at high concentrations result in bronchitis and pneumonitis beyond lung cancer (Högbergj and Alexanderj, 1986). It is also used in the form of ferrovanadium to improve steel (Moskalyk and Alfantazi, 2004). V levels in all the samples analyzed were below reported WHO limits. Hg (Mercury) and Cd (cadmium) concentrations in all the drinking water samples were found below detection limit. Hg and Cd are both of the most hazardous elements to human. After long term intake, it is seen neurological disorders and beyond lung cancer (Jarup, 2003). Over exposure to Cd may result in kidney lesions.

itai-itai disease and osteopose (Duruibe, 2007; Jarup, 2003; Jarup, *et al.*, 2000; Makino, 2012). The concentrations of Pb (Lead) in the samples varied in the range of <BDL – 1.01. The mean Pb concentrations obtained from other similiar studies were also lower, such as 2 µg/L⁻¹ in Italy (Tamasi and Cini, 2004), 20 µg/L in Egypt (Bahnasawy, 2011) and 27 µg/L in India (Buragohain *et al.*, 2009). Acceptable Pb limits reported by WHO in drinking water is 10 µg/L (WHO, 1995). Pb is classed in Group 2A that means probably carcinogenic to humans. Exposure to Pb result in stomachache, central nervous system disorders (Jarup, 2003). The levels of Zn varied up to 84.33 µg/L with the mean of 27.33 µg/L. The average Zn (Zinc) concentrations studies given in some studies. (Tamasi and Cini, 2004; Bahnasawy, 2011). Obtained results with 101-320 µg/L were found lower. However, it was higher from the results of a study conducted Norway with a mean of 14 µg/L. According to WHO Zn level in drinking water should not be exceed 5000 µg/L. Over exposure of Zn result in bloody urine and liver functional disorder (Duruibe, 2007; Nolan, 2003). Observed Co (Cobalt) levels in water samples was below limit of dedection such as Cd and Hg. WHO established 5 µg/L the maximum permissible limits for Sb (Antimony) in drinking water. Sb results in this survey were in the range of BDL-0.02 µg/L which was lower than the limits. Cu (Copper) concentration of our samples were in the range of 0.07-18.98 µg/L. All the samples had lower Cu levels compared to the limits declared by EPA (20 µg/L). We also found lower Cu concentrations given in the studies (Bahnasawy, M.,

2011; Tamasi G. and Cini R. 2004) in which Cu levels were in the range of 10-50 µg/L (Chaitali and Dhote, 2001; Ehi-Eromosele, 2012; Luza and Speisly, 1996; Janus and Krajnc, 1990; Okiei, 2012). Excessive amount of Cu uptake in drinking water may lead to chronic anaemia, coronary heart diseases and high blood pressures. Cu concentration should be regularly checked to prevent unfavorable effect to human. Mn (Manganes) levels in analyzed samples varied in the range of BDL-6.32 µg/L of which tolerable limit declared by WHO is 100 µg/L. Obtained Mn levels remain below some studies in the world such as 6 µg/L in Norway (Flaten T. P. 1991) . 27 µg/L in Italy (Tamasi and Cini, 2004) and 170 µg/L in India (Buragohain *et al.*, 2009). Health effects over uptake of Mn led to muscle weakness. sensory problems and inadequate testosterone levels. (Lakshmi *et. al.*, 2012). Cr (Chromium) concentrations in analyzed samples were found in the range of 0.06-3.14 µg/L⁻¹. In our study. Cr concentrations exceed Italy concentration >0.8 µg/L⁻¹ (Tamasi and Cini 2004). EPA reference chromium concentration is 100 µg/L⁻¹. Cr poses potential health risks and it may pose stomach upsets and ulcers. After exposing over many years occur allergic dermatitis. The greatest usage of Cr is in the metal alloys, paints, cements, paper, rubber, leather, dyes and ceramic industry. Mo (Molibdenium) concentrations in analyzed samples were 0.52 µg/L⁻¹. Mo limit in drinking water declared by EPA is 90 µg/L⁻¹. Oral exposures can result in gastrointestinal disturbances, growth retardation, anemia, hypothyroidism. Mo and its

compounds are used primarily in the production of metal alloys as well as in thermo-couples, dyeing silk, leather and rubber (Afkhami and Norooz-Asi, 2009; Namasisvayam and Sangeetha, 2006).

Ba (Barium) levels in analyzed samples varied in the range of 2.99- 35.22 µg/L which is lower compared to EPA limit of 2000 µg/L. Ba is generally present in air in particulate form as a result of industrial emissions particularly from combustion of coal and diesel oil. At high exposure to Ba causes vasoconstriction and hypokalemic paralyses (Stockinger, 1981; Shankle and Keane, 1988). The concentration of Fe in drinking water samples ranged in <BDL-50.57 µg/L with the mean of 13.63 µg/L. The permissible limit of Fe concentration in drinking water reported by EPA is 300 µg/L. The ingestion of Fe in large quantities results in hemochromatosis that may inactive to liver. General symptoms include abdominal pain, fatigue, joint pains, loss of body hair (Bacon, 2007).

We employed PCA on the results to compare the spatial and compositional patterns between the examined drinking water samples and to identify the latent factors. The elements Hg, Cd and Co which concentrations usually lower than the limit of detection of the method were excluded. The dataset was treated after data scaling by z-transformation by PCA by applying varimax rotation with Kaiser Normalization as principal component extraction method. The correlation coefficients tabulated in Table 5 were used in PCA runs. Rotated factors with loading scores ≥ 0.7 were interpreted in the evaluations.

Table 5. Cross-correlations between the variables in the dataset

	V	Cr	Mn	Fe	Cu	Zn	Sr	Mo	Sb	Pb	Ba
V	1.000										
Cr	0.720	1.000									
Mn	-0.352	-0.446	1.000								
Fe	-0.379	-0.481	0.017	1.000							
Cu	-0.393	-0.540	0.445	-0.066	1.000						
Zn	-0.395	-0.491	0.182	0.746	0.482	1.000					
Sr	0.508	0.512	-0.310	-0.002	-0.776	-0.547	1.000				
Mo	-0.148	0.110	0.063	0.639	-0.339	0.513	0.158	1.000			
Sb	-0.369	-0.426	0.494	0.766	0.124	0.762	-0.159	0.788	1.000		
Pb	-0.222	-0.338	0.102	0.082	0.786	0.389	-0.356	-0.354	-0.037	1.000	
Ba	-0.281	0.361	-0.081	0.123	-0.101	0.288	-0.180	0.647	0.269	-0.151	1.000

Four principal components with eigenvalues ≥ 1.0 were extracted by PCA which were sufficient to cover 87.42% of the total variance from 11 elements. Factor loadings of these elements onto the principal components with eigenvalues and explained variances were given in Table 6. Here, significant factor loadings were bold faced. The principal components PC-1 to PC-4 (Fig 3) accounted for 28.50%, 25.84%, 17.95% and 15.13% of the total variance in the dataset, respectively. Therefore, our discussions should focus only on the first four components extracted which cover the total variation in the dataset adequately.

The elements Hg, Cd and Co which exhibited values usually lower than the detection limit of the

method were excluded. Principal component analysis used here as a tool to understand latent correlations between unexpected heavy metals and drinking water. Fe, Zn, Sb and Mo were loaded onto PC-1. These metals may be caused from particularly industrial activities such as steel and construction industry, vehicle traffic as well as domestic wastes. It's known that Mo and Sb among these metals have been mainly used in steel production to indure steel. Therefore, brasion of metal alloys and migration of effluents from metal industry may give rise to elevated levels in drinking waters in study region. Sb in this group has been used in the home goods like cradles. As to Zn, it has been originated from natural and anthropogenic sources such as

Table 6. Extracted principal components by PCA using varimax rotation for the whole dataset

Elements	Principal Components			
	PC-1	PC-2	PC-3	PC-4
V	-0.314	-0.374	-0.586	-0.142
Cr	-0.418	-0.432	-0.575	0.460
Mn	0.044	0.060	0.887	-0.065
Fe	0.978	0.019	0.000	-0.073
Cu	-0.044	0.899	0.347	-0.073
Zn	0.788	0.518	0.108	0.198
Sr	0.007	-0.757	-0.425	-0.242
Mo	0.731	-0.359	0.050	0.554
Sb	0.843	-0.046	0.426	0.171
Pb	0.064	0.855	-0.127	-0.226
Ba	0.174	0.012	-0.019	0.965
Eigenvalue	3.135	2.843	1.975	1.664
% of variance	28.500	25.841	17.953	15.130
Cumulative %	28.500	54.341	72.294	87.424

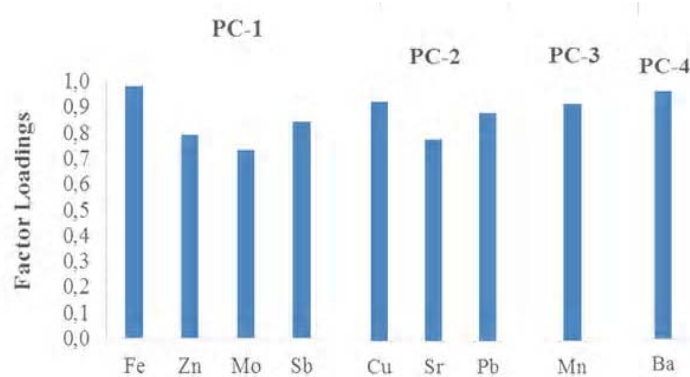


Fig. 3. Component loadings for the four components from PC1 to PC-4

agricultural practices, fertilization and use of fungicides. Many industrial facilities located around the study region, particularly around the locations 6 to 8 where the metal concentrations on PC-1 were relatively high, thus PC-1 can be mainly considered as the effect of industrial activities.

The second principal components, PC-2 grouped Cu, Sr and Pb. These heavy metals is mainly correlated with intensive vehicle traffic causing the elevated emission levels around the highway. Particularly, elevated Cu and Pb levels were identified in road runoff that can easily immigrate to drinking water distribution system (Boyacioglu and Boyacioglu, 2011). It's known that Cu pipes used in plumbing may cause to elevated Cu levels in drinking water. PC-2 also showed a negative correlation between Sr and the other metals in the study region. Because Turkey has the third biggest reserve in terms of Sr after China and Mexico (BGS, 2009). It's straightforward to express that Sr may migrate from soil to drinking water distribution system, so PC-2 can be named as the effect of vehicle traffic.

PC-3 was responsible for the impact of Mn. Industrial activities and domestic wastes are the major sources for Mn. It has been used in batteries, glass in the form of manganese dioxide, cleaning and bleaching products as potassium permanganate as well as fertilizers, varnish and fungicides. Mn related effluents and domestic wastes may reach to water distribution system by migrating through infiltration of surface water, so PC-3 can be named as domestic effect.

The effect of Ba was seen in PC-4 which may be arised from dust air. The study area, due to its heavily industrialized character and intensive vehicle traffic, led to elevated Ba levels in the atmosphere, which can reach to soil as settled dust by dry and wet deposition mechanisms. So, PC-4 is related to effect of atmospheric pollution.

CONCLUSION

Marmara region in Turkey covers very important transition line that is intersected between east and west, and industrial areas. It thus has a huge economic potential and every kind of industry get along together in the region. Inevitably, heavy metals may migrate to drinking waters in a way. As a result, twenty million people may exposure to the heavy metals in Marmara region with different pathways. The result of present study clearly demonstrate that heavy metals analyzed (V, Zn, Cu, Cr, Pb, Hg, Ba, Mo, Fe, Mn, Sb, Cd) in drinking water samples were under permissible limits declared by authorities such as WHO and Water Pollution Control Regulation of

Turkish Authorities. However, V and Cu concentrations in particular were found to be close to the threshold limits, due to intensive industrial activities in the region. In order to understand spatial distribution of heavy metals in drinking water samples with latent factors behind, PCA were employed. Four principal components by PCA showed that spatial distribution of analyzed heavy metals affected by very different pathways which were named as industrial activities, vehicle traffic, domestic effect and effect of atmospheric pollution.

The results obtained in this study promote that heavy metal concentrations analyzed in drinking water in some countries which has intensive industrial characteristics like Italy and Turkey present similar values to each other. In addition, vehicle traffic and air pollution may mediate influence on drinking water system due to the leaks in the system which is very difficult to identify. Heavy metal concentrations analyzed depicted that the effect of industrial activities were dominated in the region following by the effect of vehicle traffic. In conclusion, the concentrations of analyzed heavy metals in drinking water samples explain that drinking water treatment system applied provides the necessary water quality in terms of reported standards, however, the water distribution system is influenced by environmental conditions in the region.

ACKNOWLEDGEMENT

This work was partly supported by Duzce Universty Research Fund (Project No: 2103.6.2.203), and the authors wish to thank to Central Research Laboratory of Duzce Universty as well.

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