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Assessment of drinking water quality in Tirana city, Albania

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Abstract – The analysis of drinking-water for metal contamination is an important step in ensuring human and environmental health. Samples were analyzed in order to determine the water quality in 30 tap from Tirana, Albania during the year 2018. The concentrations of 26 metals (µg/L) in drinking-water samples were determined using ICP-MS for all samples collected from different sites. With purpose to see if the concentrations of these elements in water have a negative impact on health problems, the results obtained were compared with the standard classification proposed by the WHO. From the comparison is obviously that the drinking water of Tirana is within the permitted norms regarding the metal content. The data set obtained was subjected to the FA analysis to identify water quality variables. Four dominant factors were extracted. FA1 represent the association of Na, Mg, Al, K, V, As, Se, Mo, Sb and Ba with lithogenic and anthropogenic emission (elements derived from traffic), and FA3 (Ni, Cu, Zn, Hg and Pb) is probably related to the influence of the old pipelines or their aerial deposition at the source.

Keywords – Drinking Water, Assessment, Heavy Metals, ICP-MS, Factor Analysis

I. INTRODUCTION

Environmental protection is an important factor in ensuring a functional and balanced ecosystem. Its pollution is caused by any discharge of substances into the air, water or soil which creates or may create acute or chronic deterioration in the physical, chemical and biological quality of the environment, damage to the Earth's ecological balance or negative effects on the quality of life [1]. In general, environmental pollutants lead to the degradation of ecosystems, especially on land [2].

In nature metals play an important role not only as an integral part of the geological and geochemical structure of the surrounding environment, but also as essential elements for the life of many organisms. They have the property of environmental persistence and bioaccumulation, and these heavy metals enter in the aquatic system through various routes, where not only impair the quality of the aquatic ecosystem but also human health. On the other hand, they are quite toxic and cause serious disorders in living organisms when there is an insufficiency or large amount of them in the organism [3], [4].

The availability or presence of heavy metals in the ecosystem derives from various sources that are either natural or anthropogenic. Important sources include geological erosion, mineral exploration, soil erosion, industrial discharge, use of agricultural chemicals, etc., [5]. Meanwhile, the existence of heavy metals in water environments can have different origins, among which the main role is played by anthropogenic sources and to a lesser extent their origin from the leaching of ores that contain them.

Some metals found in water of aquatic ecosystem interact with the biomolecules of the human body to generate biotoxic compounds that are extremely stable with low dissociation ability [6].

Through the heavy metals, Mn, Hg, Pb, and Si can interfere with the central nervous system. Similarly, Hg, Pb, Cd and Cu cause problems for the secretory organs, especially the kidneys, while bone or tooth formation is sensitive to the effects of Ni, Cd, Cu and Cr [7]. The elements with the highest toxicity are arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cu), copper (Cr), manganese (Mn) and nickel (Ni) [8]. However, other heavy metals are also carcinogenic or toxic and can cause serious health effects [7].

Although the world concern about the impact of heavy metals on health has increased during the last decades and their negative effects have been thoroughly studied, this pollution is still one of the main environmental problems all over the world. Many regulations in this field during the last years have contributed to reducing the emission of heavy metals; however, this type of pollution still poses a threat to health, especially in developing countries. Following the report of World Health Organization (WHO), access to safe drinking water has been acknowledged as being essential to health and a component of effective policy for health protection ([9]-[10]).

The purpose of the work carried out is to evaluate the quality of Tirana's drinking water through the measurement or determination of trace metals by means of the analysis performed with an inductively coupled plasma mass spectrometer (ICP-MS).

This study presents a picture that includes the study of 26 chemical elements (Hg, Ca, Fe, K, Mg, Na, Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb , Sb, Se, Th, Tl, U, V, Zn) in the drinking water of a big city like Tirana. Since for 5 of these elements, such as Ag, Be, Cd, Th, and Tl the results we obtained were below the detection limit, we managed to study only 21 of these metals.

II. Materials and Method

A. Water sampling

The study area is Tirana, the capital city of the Republic of Albania. It is located in the center of Albania, about 35 km to the east of Durres and about 40 km to the north-west of Elbasan, in a valley surrounded by Dajti Mountain to the east, the hills of Kërraba and Sauk to the south, the hills of Vaqarri and Yzberishti in the west and those of Kamza in the north, with an area of approximately 1100 km².

Water sampling was carried out during the first two weeks of December 2018, at 30 areas unevenly distributed over the territory of Tirana as is shown in figure 1. The latter were taken in 50 mL plastic tubes, filled directly from the tap.

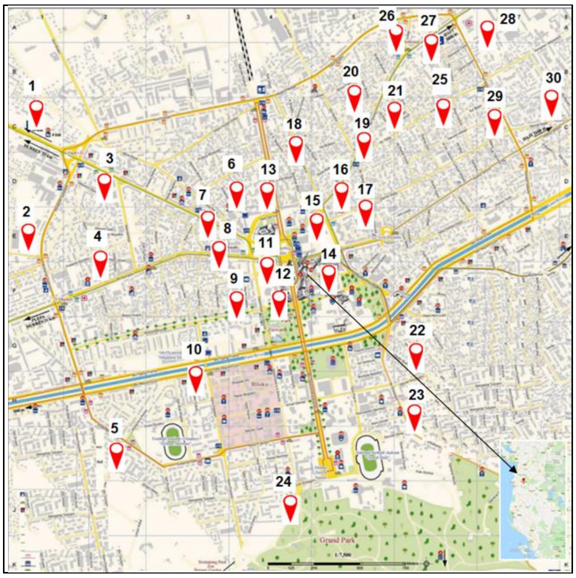

Fig. 1 Tirana city map. Area of study with location of sampling stations (http://www.maphill.com/albania/tirane/):

B. Methodology:

B.1. Water analysis

The contents of 26 chemical elements (Hg, Ca, Fe, K, Mg, Na, Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb , Sb, Se, Th, Tl, U, V, Zn) were determined by applying *inductively coupled plasma mass spectrometry ,ICP-MS* using the 4th generation octopole-based collision cell in the Agilent 7900 Series ICP-MS in He-mode with kinetic energy discrimination (KED) for the elimination of polyatomic ions that are the main source of spectral interferences during the analysis of numerous elements, such as V, Cr, Fe, Co, Ni, Cu, As, Se, etc. The Agilent 7900 ICP-MS is a flexible single quadrupole ICP mass spec instrument that provides the industry's best matrix tolerance, most effective helium collision mode, lowest detection limits, and widest dynamic range. Accuracy of the method was checked by use of standard addition method. The ICP-MS analysis was done at the *Food Safety and Veterinary Institute, Tirana, Albania.*

Before being placed in the auto sampler of the instrument, the water samples were pre-acidified to 2% concentration (v/v, 20 ml water + 400 µl HNO3 67%). After acidification the samples were transferred to the ICP/MS auto sampler tubes and thus made ready for analysis.

B.2. Statistical analyzes

Descriptive statistics were used to the data onto the elements measured at multiple locations. To detect the relationships between the element concentrations in water samples and to determine the potentially influencing environmental factors, the correlation and FA were used. The relationships of data were tested using, Spearman correlation confirmed by the statistical significance level for p <0.05, p <0.01, and p <0.001.The FA analysis is used as an extension of correlation analysis that explores the data onto hidden multivariate structures and explains their different means. The most important factors were determined and discussed. Statistical analyses were conducted using the MINITAB 17 software package.

III. RESULTS

A Descriptive Statistics analysis

The results of descriptive statistic analysis onto concentration data of the samples taken in the study are shown in Table 1. For the calculation effect, the elements that have concentrations below the dictation level were not included in the processing, while for Pb for 6 different areas, values which were below the dictation level, again for effect of calculations were obtained 0.0008 μg/L.

From the results presented in Table 1, it is noted that the content of elements based on their medians in water samples follows the trend: Ca> Na> Mg> K> Al> Zn> Ba> Fe> Cu> Ni> Se> Mo > V> Mn> Cr> As= U> Sb> Pb> Co= Hg. We also see that the median values are not close to the mean values, which indicates that our data does not follow a normal distribution.

Almost half of the elements taken in the study have a moderate coefficient of variance (CV% from 25% to 75%), indicating that they are relatively stable elements. While the elements Cr, Mn, Fe, Co, Ni, Cu, Zn, Hg, Pb and U show high values of the coefficient of variation (Cr: 142%, Mn: 234%, Fe: 170%, Co: 378%, Ni: 120%, Cu: 191%, Zn: 169%, Hg: 95.5%, Pb: 223% and U: 118%), which shows that they are influenced by many factors and as a result will also show high values of statistical parameters Skewness (> 2) and Kurtosis (> 3), which indicates that they have a positive distribution tendency.

B Multivariable analysis

In order to observe the association of elements with similar properties or of close origin, the analysis results are subjected to correlation analysis. Since our data do not obey the normal distribution, Spearman correlation was performed and values of $r^2 > 0.4$ and $P < 0.05$ were considered.

Very strong and significant positive correlations $r^2 > 0.8$; $p < 0.001$ were found among the pairs of 10 elements (Na, Mg, Al, K, V, As, Se, Mo, Sb and Ba) in drinking water samples. These findings are probably showing their ions are associated with geogenic and/or anthropogenic emission. Strong and significant correlation ($0.8 > r^2 > 0.6$; $p < 0.01$) were found between Na, Mg, Al, Ca, Cr, Mn, Co, Ni and U elements in drinking water samples that are probably related to the geogenic source. Moderate significant correlation ($0.6 > r^2 > 0.4$ $p < 0.05$) were found between K, Ca, Cr, Ni, Cu, Zn, Hg and Pb elements in drinking water samples that are probably related to the influence of the old pipelines or their aerial deposition at the source.

In order to observe more clear the source of the elements in the samples taken, factorial analysis was carried out, the results of which are given in the following table 2 and figure 2. The data were subjected to Varimax rotation, which made it possible to simplify the interpretation of the results by grouping them into four essential factors, which according to the Kaiser criterion are the factors with Eigen values > 1, and also for each factor the values were taken into consideration of load (Loadings) > 0.4.

Table 1. Results of Descriptive Statistics analysis of the concentration of 26 elements in drinking water

Elements	N	Mean	SD	CV%	Min.	Q1	Median	Q3	Max.	Skewness	Kurtosis
23Na	30	13787	7344	53.3	1063	11021	15408	16577	29742	-0.05	0.37
24Mg	30	8577	4342	50.6	944	6831	9832	10388	18581	-0.26	0.36
27Al	30	49.53	25.80	52.1	5.280	20.38	61.91	70.14	80.44	-0.68	-1.25
39K	30	2094	1226	58.6	281	1576	2220	2483	5979	1.05	3.18
44Ca	30	48355	19279	39.9	36858	39761	41481	44866	121113	**2.86**	**7.88**
51V	30	0.624	0.227	36.5	0.090	0.603	0.710	0.760	0.860	-1.53	0.96
52Cr	30	0.675	0.961	**142**	0.210	0.250	0.280	0.445	3.990	**2.56**	**5.74**
55Mn	30	0.966	2.263	**234**	0.070	0.248	0.385	0.598	12.45	**4.86**	**24.88**
56Fe	30	11.23	19.04	**170**	1.000	3.400	4.730	9.490	93.54	**3.58**	**13.33**
59Co	30	0.276	1.043	**378**	0.010	0.010	0.020	0.040	5.720	**5.24**	**28.12**
60Ni	30	1.468	1.764	**120**	0.070	0.838	0.910	1.163	8.680	**3.10**	**10.32**
63Cu	30	10.67	20.33	**191**	0.170	0.810	2.120	7.090	81.48	**2.60**	**6.29**
66Zn	30	122.0	206.1	**169**	2.100	24.20	36.60	179.3	1084	**3.79**	**16.97**
75As	30	0.155	0.058	37.5	0.040	0.105	0.185	0.200	0.210	-0.86	-0.82
78Se	30	0.699	0.321	45.9	0.080	0.513	0.840	0.933	1.040	-0.93	-0.52
95Mo	30	0.609	0.356	58.4	0.020	0.203	0.805	0.883	1.040	-0.67	-1.25
121Sb	30	0.128	0.060	46.8	0.010	0.088	0.150	0.160	0.240	-0.53	-0.25
137Ba	30	25.10	11.18	44.6	3.330	22.10	28.36	30.53	45.44	-0.85	0.07
202Hg	30	0.027	0.025	**95.1**	0.010	0.01	0.020	0.033	0.130	**2.67**	**8.97**
208Pb	30	0.346	0.771	**223**	0.001	0.017	0.100	0.270	3.640	**3.40**	**12.11**
238U	30	0.260	0.307	**118**	0.040	0.153	0.185	0.200	1.400	**2.75**	**7.29**

Min. minimum ; Max. maximum

Table 2. Factorial analysis results for the 21 elements determined in the water samples (Varimax rotation).

Elements	Factor1	Factor2	Factor3	Factor4	Summary
23Na[He]	**0.729**	-0.525	0.386	0.189	0.992
24Mg[He]	**0.774**	-0.560	0.227	0.161	0.989
27Al[He]	**0.818**	0.472	-0.224	-0.027	0.943
39K[He]	**0.609**	-0.330	0.633	0.258	0.947
44Ca[He]	-0.045	**-0.737**	0.632	0.164	0.970
51V[He]	**0.921**	-0.158	0.112	0.139	0.906
52Cr[He]	-0.002	**-0.868**	0.445	0.007	0.952
55Mn[He]	-0.025	**-0.922**	-0.158	-0.239	0.933
56Fe[He]	-0.086	-0.074	0.196	**-0.859**	0.789
59Co[He]	-0.024	**-0.941**	-0.137	-0.118	0.920
60Ni[He]	0.127	-0.500	**0.806**	-0.006	0.917
63Cu[He]	-0.361	-0.098	**0.784**	-0.137	0.774
66Zn[He]	-0.128	-0.241	**0.871**	-0.097	0.843
75As[He]	**0.925**	0.168	-0.287	-0.057	0.968
78Se[He]	**0.954**	0.230	-0.133	0.035	0.983
95Mo[He]	**0.850**	0.375	-0.326	-0.137	0.989
121Sb[He]	**0.891**	-0.262	-0.127	-0.009	0.878
137Ba[He]	**0.862**	-0.371	0.252	0.172	0.974
202Hg[He]	-0.030	-0.194	**-0.435**	-0.235	0.283
208Pb[He]	-0.033	0.045	**0.689**	-0.225	0.529
238U[He]	0.183	**-0.896**	0.368	0.155	0.997
Variance	7.253	5.574	4.452	1.195	18.474
Variance %	0.345	0.265	0.212	0.057	0.880

IV. DISCUSSION

The median concentrations elements in drinking water in public water system in Tirana 2018 were compared with the maximum contaminant level recommended by World Health Organization (WHO, 2022), selected as a drinking water standards can cause health hazard as the Table 3.

Table 3. The comparison of median concentrations of metals in drinking water in public water system in Tirana and the maximum contaminant level recommended by World Health Organization (WHO, 2022)

Elements	Median of drinking water (μg/L)	WHO, 2022 (μg/L)
52Cr	0.675	50
55Mn	0.966	80
56Fe	11.23	NGL*
59Co	0.276	NGL*
60Ni	1.468	70
63Cu	10.67	2000
66Zn	122.0	NGL*
75As	0.155	10
78Se	0.699	40
95Mo	0.609	10
121Sb	0.128	20
137Ba	25.10	1300
202Hg	0.027	6
208Pb	0.346	10
238U	0.260	30

NGL* No Guideline

The concentration of heavy metals in drinking water beyond the recommended limit prescribed by various national and international organization causes acute and choric diseases. From the comparison of the metal content in the samples taken in the study with the maximum allowed levels given by the WHO (Table 2), it can be seen that the drinking water of Tirana is within the permitted norms regarding the metal content.

According to the results obtained from the analysis, it turns out that 4 main factors representing 88% of the total variance were extracted. The number of factors was selected based on the Controlled Decline Test (SCREE Plot) (Fig. 2).

Factor 1. This factor is the main factor which represents 34.5% of the total variance and has high positive loadings (> 0.5) for the elements Na, Mg, Al, K, V, As, Se, Mo, Sb and Ba. High values of these elements indicate the influence of similar factors and similar sources of origin. The presence of Sb in this group indicates the lithogenic nature of this factor, because it is an element contained in the soil. Also the elements Sb, Se, Mo are added to the group of elements derived from traffic.

Factor 2. This is the second strongest factor, representing 26.5% of the total variance. The presence of elements such as Ca, Cr, Mn, Co and U is related to the geogenic contribution.

Factor 3 represents 21.2% of the total variance and the presence of the elements Ni, Cu, Zn, Hg and Pb are probably related to the influence of the old pipelines or their aerial deposition at the source.

Factor 4. This is the weakest factor which represents only 5.7% of the total variance and the presence of Fe may be related to the passage of particles in suspension and since Fe is in high content it can be captured.

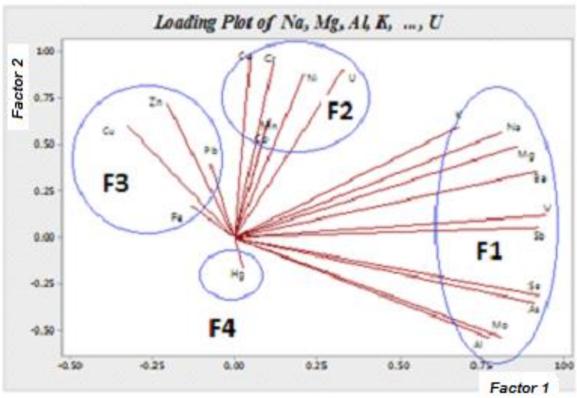

Fig. 2 Loading plot of two importatnt factor of elemenets in drinking water samples

To see the obbservations that have influenced the association of elements in different factors and the correlation between them we established the score plot graphs of the first of two important factor for the concentration elements in drinking water samples.

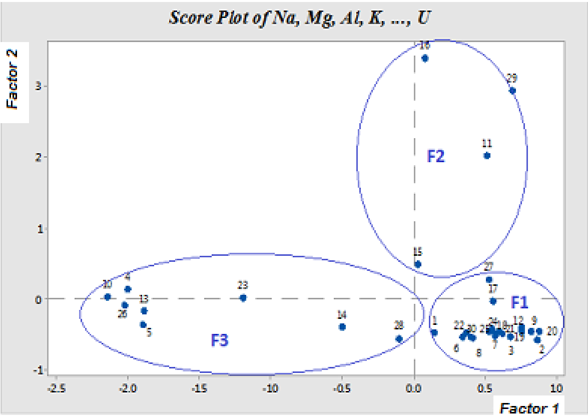

Fig. 3 Score plot graphs of two importatnt factor of elemenets in 30 drinking water samples sites

The data plot according to the "scores plot" (Fig.3) method makes it possible to highlight the samples (areas) that have influenced the association of elements in different factors and the correlation between elements.

V. CONCLUSION

This research was conduct to assess the quality of Tirana's drinking water on period December 2018, through the determination of trace metals by means of the analysis performed with ICP-MS. At the end of its we reached in this conclusions:

- ✓ ICP-MS analysis resulted successful even for low content of elements in drinking water samples
- ✓ Multi-element analysis combined with statistical processing makes it possible to carry out a fairly complete study regarding the content level of the elements taken in the study and the study of the factors that have influenced their content levels.
- ✓ From the comparison of the metal content in the samples taken in the study with the maximum allowed levels given by the WHO, it can be seen that the drinking water of Tirana is within the permitted norms regarding the metal content
- ✓ The "outlier" values and high variability of concentration data for certain elements indicate that the monitoring of these parameters should be continuous.

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