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Research Article

Evaluation of some toxic metal levels in treatment waters

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Abstract

The quality of the water used and the aquatic environment are important factors that control the health and life of all organisms. Industrial development, excessive use of natural resources cause environmental pollution to increase rapidly and organic and inorganic substances, which are considered as the most important threatening factors of aquatic organisms, are spreading to the environment. Metals constitute the most important source of inorganic pollution in waters. In this study, the levels of some toxic metals in Karaman province and its surrounding settlements treatment waters were determined. For this purpose, the amounts of arsenic, cobalt, copper, zinc, cadmium, chrome and lead metals were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) method. According to Word Health Organization and Turkish Standard Institute-266 (TS-266), it was found that there was no pollution in terms of arsenic, cadmium, zinc, chrome, cobalt and lead in the water samples analyzed, but it was above the permissible limit values according to Turkish Standard Institute-266 for copper element.

Keywords: Treatment water, Toxic metal, ICP-OES.

Arıtma sularında bazı toksik metal seviyelerinin değerlendirilmesi

Öz

Kullanılan suyun kalitesi ve sucul çevre, tüm organizmaların sağlığını ve yaşamını kontrol eden önemli faktörlerdir. Endüstrinin gelişmesiyle doğal kaynakların aşırı kullanımı, çevre kirliliğinin hızla artmasına sebep olmakta ve suda yaşayan organizmaların en önemli tehdit edici faktörleri olarak kabul edilen organik ve inorganik maddeler çevreye yayılmaktadır. Metaller sulardaki en önemli inorganik kirlilik kaynağıdır. Bu çalışmada Karaman ili ve çevresindeki bazı yerleşim yerlerindeki arıtma sularında bazı toksik metallerin seviyeleri belirlenmiştir. Bu amaçla arsenik, kobalt, bakır, çinko, kadmiyum, krom ve kurşun metallerinin miktarları İndüktif Eşleşmiş Plazma Optik Emisyon Spektrometresi (ICP-OES) yöntemiyle analiz edilmiştir. Dünya Sağlık Örgütü ve Türk Standardı Enstitüsü-266'ya (TS-266) göre, analiz edilen su örneklerinde arsenik, kadmiyum, çinko, krom, kobalt ve kurşun açısından kirlenme olmadığı ancak bakır elementi için Türk Standardı Enstitüsü-266'ya göre izin verilen sınır değerlerin üstünde olduğu tespit edilmiştir.

Anahtar Kelimeler: Arıtma suyu, Toksik metal, ICP-OES.

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1. Introduction

Water is one of the basic elements in the life of all living organisms. It plays a key role in many ecosystems [1]. In recent years, tons of various pollutants (solid, liquid and gas) have been added to the environmental ecosystems due to the increase in urban and industrial activities and socio-economy. Trace element concentrations in the environment and waters increase due to anthropogenic activities such as mining, industrial production and medical waste incineration [2].

Chemical pollution of water resources in many parts of the world is an increasing problem [3]. More than 700 chemical contaminants that can be present in water have been identified [4]. Among these pollutants, trace metals are the most dangerous because of their high toxicity and carcinogenicity [5-6]. Although some trace elements are necessary for human health, their accumulation in natural waters can pose a threat to human health and ecological safety [7-8]. Among toxic metals, arsenic (As) is a predominant pollutant [9-10]. 1.85 million people in general drink water above 50 µg l^{-1} [11]. Lead (Pb), cadmium (Cd), mercury (Hg) and arsenic (As) do not have a known nutritional value for humans and are potentially toxic. These toxic elements are known to cause organ damage and their carcinogenicity is a concern for human health [12].

Among the commonly used spectrometric techniques, the inductively coupled plasma optical emission spectrometer (ICP-OES) is widely used in mineral analysis due to its high sensitivity, wide dynamic range and analysis speed and multi-element capabilities [13]. In this study, the levels of toxic metals in Karaman urban treatment waters were determined. For this purpose, the amounts of arsenic, cadmium, cobalt (Co), copper (Cu), zinc (Zn), chrome (Cr) and lead metals were analyzed by ICP-OES method. It was determined that there was no As pollution in the water samples analyzed, and the concentration values of Co, Cu and Zn elements were higher than World Health Organization (WHO) and Turkish Food Codex (TFC; TS-266) values in some seasons.

2. Material and Method

2.1. Materials

The place, time and shape of the water to be analyzed is important. Changes in these factors will directly affect the concentration of the analyzed water and cause errors. Samples were collected from treatment water centers which are frequently used as drinking water by the public in Karaman city center and its surrounding settlements (Figure 1). 12 important centers were selected for this purpose.

Figure 1. Map of sampling locations

2.2. Methods

Water samples were collected from mid-season to 4 seasons between 2011 and 2012. Samples were placed in polyethylene containers. The sample cups were first washed thoroughly with distilled water and then rinsed 3 times with the sample water. A 0.45µm fiber filter was used to filter all drinking water samples. Three filtered sub-samples were collected in 50 ml polyethylene bottles prepared separately by pre-washing to analyze toxic metals. These sub-samples were then protected with 10% ultra-pure HNO_3. The sampled water samples were then capped and stored in a refrigerator at 4 °C until further analysis. Inductively coupled plasma optical emission spectrometry (ICP-OES) (720, Agilent) was used for elemental analysis of the samples. ICP-OES is a multi-element atomic emission spectroscopic technique that allows the simultaneous and fast detection of both minor and major elements in complicated samples [14]. It is a widely used method for determination of elements in environmental and food analysis due to its wide working ranges and very good detection ability [15].

2.2.1. Evaluation of instrumental performance and calibration

The method and instrumental performance were evaluated by determining the detection limit (LOD) and the quantification limit (LOQ). LOD and LOQ were desciribed as the analyte concentration corresponding to 3 to 10 times the slope ratio of the standard deviation, respectively, and determined by the standard deviation of the six samples prepared by the slope of the calibration curves and nailing blank samples. Definite-concentration certificated standards have been used. 1000 mg kg^{-1} (Merck) standards have been used as main stock. From main stock solution as study standards; it has been prepared in HNO_3 (Merck) setting of 2 M 65% and as to be 100 ml. The performance and calibration procedure of various elements are presented in Table 1, 2.

The Agilent 720 (ICP-OES) properties a custom intended CCD detector, which ensures full simultaneous measure and wide wavelength coverage from 167 to 785 nm. The CCD detector includes constant angular arrays that are paired completely to the two-dimensional view from the echelle optics. The instrument operating conditions were given Table 3.

Table 1. LOD, LOQ and wavelength of determination of the different elements by ICP-OES (µg kg^{-1})

Element	LOD	LOQ	Wavelength
As	0.00712	0.02136	228.812
Co	0.00560	0.01698	235.341
Cu	0.00845	0.02535	324.754
Zn	0.00967	0.02932	213.857
Cd	0.00896	0.02714	226.502
Cr	0.00847	0.02567	267.716
Pb	0.00939	0.02847	220.353

Table 2. Calibration procedure (µg kg^{-1})

Element	Standart				
	1	2	3	4	5
As	0.4	0.8	1.6	2.4	3.2
Co	0.2	0.4	0.8	1.2	1.6
Cu	0.04	0.08	0.16	0.24	0.32
Zn	0.04	0.08	0.16	0.24	0.32
Cd	0.04	0.08	0.16	0.24	0.32
Cr	0.04	0.08	0.16	0.24	0.32
Pb	0.4	0.8	1.6	2.4	3.2

Table 3. Instrument operating conditions

Features	Value
Power	1.0 kW
Plasma gas flow	15 L min^{-1}
Auxiliary gas flow	1.5 L min^{-1}
Nebulizer flow	0.75 L min^{-1}
Pump speed	15 rpm
Stabilization time	15 sec
Rinse time	15 sec
Spray chamber type	Glass cyclonic
Torch	Standard one piece quartz axial
Nebulizer type	SeaSpray
Fast pump	On
Background correction	Left and right off peak

3. Results and Discussion

The concentrations of toxic elements in water samples are given in Table 4, 5, 6, 7, 8, 9 and 10.

Table 4. As concentrations in water samples (µg kg^{-1})

Sample	Autumn	Winter	Spring	Summer	Average±SD
1	2.135	2.277	3.407	2.081	2.475±0.627
2	2.249	2.498	3.823	1.280	2.463±1.048
3	2.328	2.307	2.390	1.689	2.179±0.328
4	2.101	3.085	2.813	1.771	2.443±0.610
5	1.364	2.263	2.794	2.919	2.335±0.707
6	2.073	2.704	2.443	2.108	2.332±0.299
7	3.112	2.178	2.431	2.163	2.471±0.445
8	2.531	2.664	2.086	2.080	2.340±0.302
9	3.126	3.038	3.683	2.572	3.105±0.456
10	3.621	5.408	3.763	3.752	4.136±0.850
11	3.772	2.656	2.398	2.147	2.743±0.717
12	3.333	0.303	2.658	3.371	2.416±1.446

Table 5. Pb concentrations in water samples (µg kg^{-1})

Sample	Autumn	Winter	Spring	Summer	Average±SD
1	*	*	0.314	*	0.31
2	*	*	*	0.011	0.011
3	*	0.192	*	*	0.192
4	*	*	27.89	*	27.89
5	0.261	*	6.889	*	3.575±4.687
6	0.559	*	*	*	0.559
7	*	0.073	*	*	0.073
8	4.245	*	*	0.409	2.327±2.712
9	5.495	*	*	*	5.495
10	0.081	0.563	*	2.178	0.941±1.098
11	3.009	*	0.187	4.049	2.415±1.998
12	*	*	*	*	*

Table 6. Cr concentrations in water samples (μg kg^{-1})

Sample	Autumn	Winter	Spring	Summer	Average±SD
1	1.017	0.869	1.649	1.057	1.148±0.344
2	0.883	1.001	1.414	0.161	0.865±0.521
3	0.666	0.770	0.630	0.800	0.717±0.081
4	0.977	1.103	0.990	1.152	1.056±0.086
5	0.832	0.840	1.343	1.113	1.032±0.245
6	0.819	0.977	1.044	1.047	0.972±0.107
7	1.047	1.042	0.961	1.196	1.062±0.098
8	0.946	0.799	0.855	1.232	0.958±0.192
9	1.018	0.934	1.052	0.941	0.986±0.058
10	1.101	1.460	1.115	1.562	1.310±0.236
11	1.228	0.941	0.897	1.205	1.068±0.173
12	0.951	*	1.012	1.463	1.142±0.282

Table 7. Cd concentrations in water samples (μg kg^{-1})

Sample	Autumn	Winter	Spring	Summer	Average±SD
1	0.006	0.047	*	0.003	0.019±0.025
2	*	0.012	*	0.021	0.017±0.006
3	*	0.102	*	0.007	0.055±0.067
4	*	*	1.349	*	1.349
5	0.078	0.008	0.147	*	0.078±0.070
6	0.067	*	*	*	0.067
7	*	*	*	0.006	0.006
8	0.192	0.006	0.012	*	0.070±0.106
9	0.372	*	*	*	0.372
10	*	0.045	*	*	0.045
11	0.246	*	0.006	0.015	0.089±0.136
12	0.008	*	0.006	0.015	0.010±0.005

Table 8. Zn concentrations in water samples (μg kg^{-1})

Sample	Autumn	Winter	Spring	Summer	Average±SD
1	2.631	1.053	6.884	1.549	3.029±2.653
2	2.233	2.745	6.701	5.579	4.315±2.167
3	2.176	8.690	18.50	6.682	9.011±6.885
4	2.736	1.199	4.936	5.312	3.546±1.934
5	4.546	0.665	6.582	4.179	3.993±2.458
6	3.145	1.437	1.512	1.554	1.912±0.823
7	22.39	22.25	27.78	25.70	24.53±2.692
8	14.73	9.362	33.88	114.9	43.22
9	8.755	4.449	7.759	3.853	6.204±2.417
10	5.361	8.916	5.249	9.353	7.220±2.219
11	20.16	1.182	1.128	119.7	35.53
12	3.898	0.189	8.982	32.76	11.46±14.65

Table 9. Co concentrations in water samples (μg kg^{-1})

Sample	Autumn	Winter	Spring	Summer	Average±SD
1	0.720	0.650	0.627	0.689	0.672±0.041
2	0.709	0.615	0.578	0.524	0.607±0.078
3	1.035	0.770	0.733	0.733	0.818±0.146
4	0.577	0.595	2.386	0.628	1.047±0.893
5	0.877	0.650	0.575	0.700	0.701±0.128
6	0.979	0.699	0.601	0.723	0.751±0.161
7	0.728	0.688	0.689	0.647	0.688±0.033
8	1.008	0.693	0.699	0.697	0.774±0.156
9	1.203	0.702	0.645	0.685	0.809±0.264
10	0.706	0.738	0.661	0.616	0.680±0.053
11	1.091	0.711	0.675	0.745	0.806±0.192
12	0.646	0.607	0.727	0.559	0.635±0.071

Table 10. Cu concentrations in water samples (μg kg^{-1})

Sample	Autumn	Winter	Spring	Summer	Average±SD
1	2.000	0.932	4.863	1.473	2.317±1.752
2	2.159	1.278	8.656	3.629	3.931±3.296
3	2.323	6.251	0.976	0.916	2.617±2.509
4	3.540	0.756	2.040	5.704	3.010±2.126
5	2.178	0.747	4.627	2.363	2.479±1.604
6	2.100	1.937	2.243	2.969	2.312±0.455
7	2.076	2.547	1.402	4.875	2.725±1.508
8	2.127	3.291	2.066	10.34	4.452±3.956
9	3.174	2.937	3.235	2.958	3.076±0.151
10	4.145	4.569	1.988	10.62	5.329±3.701
11	2.216	2.033	1.754	1.295	1.825±0.401
12	2.015	*	3.618	5.687	3.773±1.841

As a result of the measurements made for arsenic, it was observed that annual and seasonal results showed parallelism and the average concentration was consistent with seasonal measurements. As a result of the measurements made for Pb, although the water samples showed seasonal differences, generally reasonable levels of Pb concentrations were obtained. Cd was not detected in 60% of the water samples. Cd samples were also found to be low levels. According to Cr element measurement results, annual and seasonal results were found to be in parallel with each other. The metal concentrations of water samples collected in four seasons are shown in Figure 2, 3, 4 and 5.

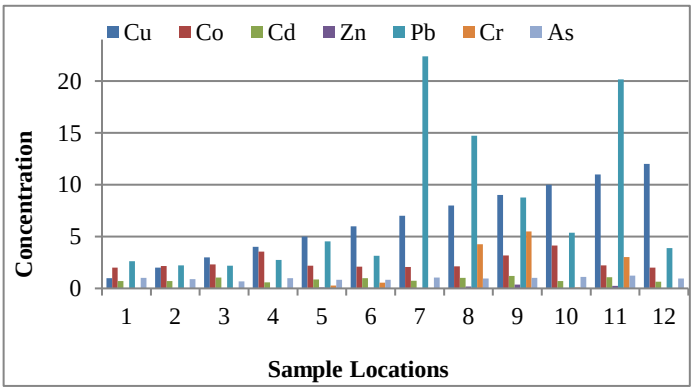

Figure 2. Metal concentrations of water samples collected in autumn season (μg kg^{-1})

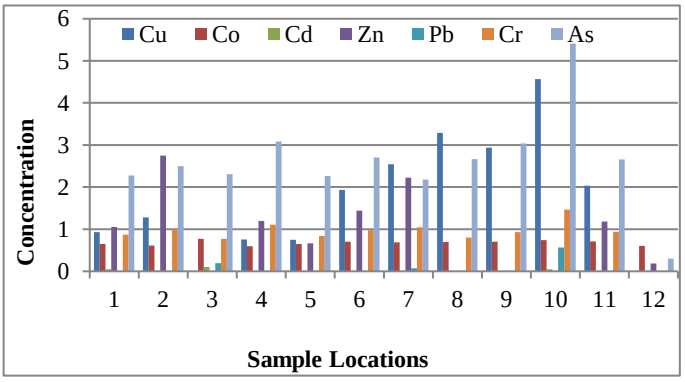

Figure 3. Metal concentrations of water samples collected in winter season (μg kg^{-1})

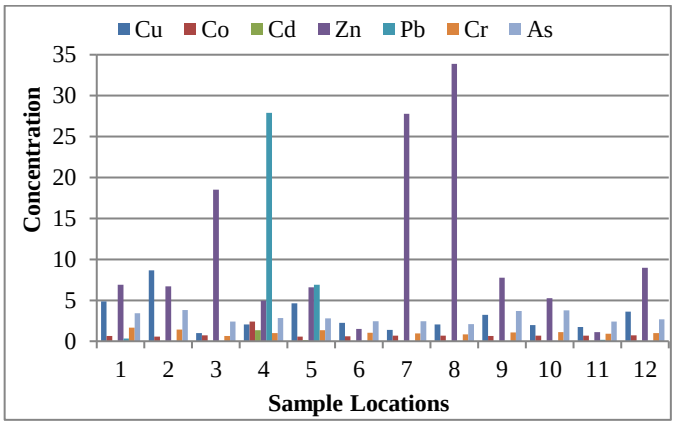

Figure 4. Metal concentrations of water samples collected in spring season (μg kg^{-1})

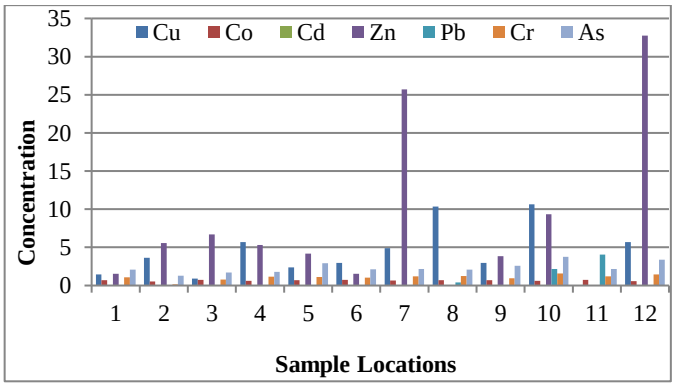

Figure 5. Metal concentrations of water samples collected in spring season (μg kg^{-1})

Lead is a toxic metal with multiple effects and can remain in the organism for a long time. Chronic lead poisoning can cause cognitive disorders such as depression, difficulty concentrating, peripheral neuropathies, and chronic interstitial nephropathy. Children are more sensitive to the effects of lead. Children are exposed to a small amount of lead for a long period of time due to physical and psychological development disorder, psychomotor disorders, learning difficulties and IQ [16]. It has a long half-life that varies depending on the tissue in which the lead is located. It is excreted for 28-36 days in blood, 40 days in soft tissue and more than 25 years in mineralized tissues [17]. Therefore, the increase in the total amount of lead accumulated in the body should be prevented. The upper limit value of lead that can be found in drinking water is 10 μg l^{-1} according to WHO and 50 μg l^{-1} according to TS-266. Only one of the

samples exceeded the limit value according to WHO. According to WHO and TS 266 standards, the amount of Pb in other samples is below the allowed limit values.

4. Conclusions and Recommendations

In recent years, the metal pollution in the water environment has attracted attention globally because of its persistence and environmental toxicity. Metals enter the aquatic environment with natural and anthropogenic sources. Heavy metals can enter the environment in different ways, do not biodegrade and show durability [18]. This study showed that there is Cu contamination in urban treatment waters, but this water can be used for very toxic elements such as As, Pb, Cr and Cd. Limit values determined for some elements according to Turkish Food Codex [19]; 10 μg kg^{-1} for As, 5 μg kg^{-1} for Cd, 50 μg kg^{-1} for Cr, 3 mg kg^{-1} for Cu, 10 μg kg^{-1} for Pb, 5 mg kg^{-1} for Zn. As a result of the analysis, it was determined that the results of As, Cd, Cr and Pb elements for TFC were below the allowed limit values and for Cu 68.75% of the samples were above the limit value. According to the World Health Organization [1], limit values of 10 μg kg^{-1} for As, 50 μg kg^{-1} for Cr and 10 μg kg^{-1} for Pb are given. It was determined that the water samples analyzed according to the limit values allowed by the World Health Organization are usable for As, Cr and Pb. The toxic metals determined in the waters will accumulate in the human body after a while [20]. In order to prevent the dispersion of copper pollution or to avoid exposure to pollution, risks must be calculated and an improvement plan is required.

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