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Measurement of Heavy Metals Concentration in Drinking Water from Source to Consumption Site in Kermanshah - Iran

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Abstract: Nowadays water pollution is one of the most important environmental health concerns. Quality of drinking water is affected by conditions of water supply system and presence of contamination sources. In this study a total number of 165 water samples were collected from water supply resources (128 wells), 25 water reservoirs and water distribution network (tap water) of Kermanshah City (with a population of about one million). Heavy metals concentrations (Aluminum, Arsenic, Cadmium, Lead, Chromium, Mercury, Copper, Cobalt, Iron, Manganese, Selenium, Molybdenum, Vanadium, Antimony, Nickel and Zinc) in all samples were measured by the Varian atomic absorption device. Results indicated that concentrations of all measured metals (except the amount of Aluminum, Iron and Manganese in some samples of water resources, distribution network and water reservoirs) were lower than the national standards and guidelines recommended by the World Health Organization (WHO). Continuous monitoring of heavy metals concentrations in urban water systems from source of production to consumption site is recommended to identify the source of pollution.

Key words: Heavy metals · Drinking water · Water resources · Water quality · Kermanshah

INTRODUCTION

Nowadays water pollution is one of the most important environmental problems [1]. Among the wide variety of contaminants affecting water supplies, heavy metals deserve specific attention regarding their high toxicity even at low concentrations [2]. Drinking safe water with desired quality is an essential part of human health and assessment of trace heavy metals is a main part of public health research works [3-7]. Heavy metals are elements with atomic weights between 63.546 and 200.590 g/mol and density more than 4.0 g/cm^3. Heavy metals in the water are in colloidal, particulate and dissolved forms [8]. Sources of heavy metals in water comprise natural sources including eroded minerals within sediments, leaching of ore deposits and volcanic materials and anthropogenic sources such as solid waste disposals, industrial or municipal effluents and wharf channel dredging [2].

Heavy metals in nature are not usually hazardous to the environment and human health as the amounts of them are not significant; furthermore some heavy metals are required at low concentrations as catalysts for enzyme activities in human body. Some of these metals are vital to keep up life such as Calcium, Magnesium, Potassium and Sodium, which are necessary for common body functions

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and others including Cobalt, Copper, Iron, Manganese, Molybdenum and Zinc is needed at low levels as catalysts for enzyme activities [8-10]. However if the level of these metals are elevated to higher than the normal ranges, they cause malfunction and result in toxicity to human body.

Heavy metals possess serious effects on human health and might cause various symptoms depending on the type and amount of the metal involved [11]. Their toxicity is made by forming complexes with proteins where they contain carboxylic acid (–COOH), amine ($–NH_2$) and thiol (–SH) groups. These modified biological molecules lose their proper functions and consequently lead to breakdown or cell death. As heavy metals combine with these groups, they inhibit vital enzymes or may disturb the formation of some proteins necessary for catalytic functions of enzymes. In addition to that some of these heavy metals can incite the production of harmful radicals and result in oxidation of biological molecules [12].

Aluminum (Al), Arsenic (As), Cadmium (Cd), Lead (Pb) Chromium (Cr) and Mercury (Hg) are common heavy metals, which humans are exposed to. Al is associated with Alzheimer's and Parkinson's diseases and senile and pre-senile dementia. One of the most hazardous trace metals found in drinking waters is as being both toxic and carcinogenic. Long term exposure to the concentration of 50 mg/L can cause skin damages [13]. Cd may cause diseases including hypertension, arteriosclerosis, cancer, etc. [14, 15]. Maximum acceptable concentration for Cd is recognized to be 3 µg/L or 5 µg/L by World Health Organization (WHO) and Environmental Protection Agency (EPA) respectively [13, 16]. Pb is a toxin and probably a human carcinogen [17]. WHO identified 10 µg/L as the maximum permissible limit for Pb in drinking water [18]. Hg is also poisonous and might be associated with deterioration of mental status and disorders of speech, hearing, vision and movement [19]. Pb as well as Hg may result in autoimmunity in which immune system of the body attacks its own cells. This might cause the development of joint diseases and malfunction of kidneys, cardiovascular system and neurons. At higher concentrations, Pb and Hg can cause permanent brain damages.

Cr is a trace metal essential for humans and animals but in higher concentrations especially in the more toxic Chromium VI valence state, it will impair human health as it may be involved in pathogenesis of some diseases such as lung and gastrointestinal cancers [20]. Abundant levels of copper (Cu) in drinking water can be neurotoxic and result in mental diseases like Alzheimer's disease [21]. In conclusion, the concentration of heavy metals in drinking water should be maintained within the standard range.

Water demand in Kermanshah City (with a population of approximately one million people) is provided by underground water. Since the level of toxic and heavy metals in Kermanshah's drinking water has not been investigated yet, measurement of heavy metals concentrations in different water resources of Kermanshah is of great concern for proper assessment of drinking water quality and possible hazards to public health.

In this study, water samples were collected from water supply resources (wells) of Kermanshah, water reservoirs and water distribution network (tap water). The aim of this study was to measure the concentrations of heavy metals including Al, As, Cd, Pb, Cr, Hg, Cu, Co, Fe, Mn, Se, Mo, V, Sb, Ni and Zn in Kermanshah's drinking water to detect any pollution sources and any possible threats to public health due to high concentration of heavy metals in household drinking water.

MATERIALS AND METHODS

Kermanshah City is located in the west part of Iran. Water demand in Kermanshah is supplied by underground water (128 wells). Produced water is transmitted and stored in 25 water reservoirs.

Heavy metals in samples were detected by the Varian atomic absorption device (Varian Spect AA-220, Australia). We utilized the AA device equipped with a hydride generator (Varian VGA-77) and generation of hydride with sodium borohydride for measurement of concentration of As, Se and Sb. Hg was detected by cold vapor production using SnCl2. Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd and Pb were also detected using the graphite furnace (GTA 110 Varian Australia). All utilized lamps were hollow cathode. Graphite Tubes used for analysis were pyrolitic-type with the platform. Specific interferences from medium were not observed in all of the samples and the continuum condition correction was adequate for detection of all specific absorption [22-24].

Reagents and Chemicals: All reagents and chemicals were of analytical reagent grade. De-ionized double distilled water was used all through the testing procedure. The standard solutions contained 1 g/L of all elements and were purchased from Merck (Germany) and prepared by proper dilution of 1000 parts per million (ppm) of stock standard with de-ionized double distilled water. For analysis of all other elements no modified medium was used. The control of analytical quality has been down included daily analysis of standard and replicate analysis of samples and blanks. All solutions were prepared with de-ionized water and the daily standards were prepared. The stock solution of all metals, containing 1000 ppm (of selected heavy metals) and nitric acid was used without additional purification.

Sampling and Analysis: Totally 109, 23 and 33 samples were collected from water supply sources (wells), water reservoirs and water distribution network, respectively. Sampling and analysis were carried out carefully to minimize any external contamination with metals. That is a very important point in evaluation of trace metals as there are many metals containing substances (including dust, car exhaust particulate, rust) in the environment and samples may be contaminated in the laboratory. Polyethylene bottles were used for collecting water samples. The bottles were prewashed with detergent, double de-ionized distilled water, diluted HNO_3 and again with double de-ionized distilled water, consequently. Samples were taken directly from the water pump after allowing the water run for a while (at least 10 minutes). The samples were acidified with nitric acid to reach a concentration of 0.1% v/v. Before delivery to the laboratory we stored the samples at 4°C for as short time as possible to minimize physicochemical alterations [25]. Regarding the existence of very few visible particles in the samples filtering was not considered to be necessary. No further sample digestion was performed. Therefore the results reflect total dissolved and easily extractable metal concentrations.

Statistical Analysis: According to lack of normal distribution (p-value<0.05), One-Sample kolmogorov Smirnov test was used for comparison of data analysis with the standard amounts. U Mann-Whitney tests were used for comparison of the means of obtaining results between two studies groups, using SPSS – Ver. 16 with a significance level of $P<0.05$.

RESULTS

Heavy metals concentrations in samples collected from water supply sources (wells), water reservoirs and distribution network and comparison of mean concentrations in different locations are depicted in Tables 1-7.

DISCUSSION

Results of data analysis demonstrated that concentrations of all measured metals (except the amount of Al in three samples collected from two water resources and one from the distribution system, the amount of Fe in two samples collected from one water resource and one water reservoir and the amount of Mn in one sample collected from one water resource) were less than the national standards [26] and guidelines recommended by WHO [27]. In conclusion regarding toxic heavy metals concentrations, consumption of the water, that was studied on, does not possess any health concerns.

Results revealed that the average amount of Al, As, Co and Cr in water resources out of the city were significantly more than the water resources within the city but concentrations of Fe, Ni, Pb and Ti were not different. That difference could be due to the effect of agricultural

Table 1: Toxic heavy metals concentrations (µg/l) in drinking water collected from water resources (wells) of Kermanshah.

Heavy metal	Number of samples	Mean	Standard deviation (SD)	*Min	**Max
Al	109	64.650	63.64	1.7	321.91
As	109	0.990	2.18	0	9.3
Cd	109	0.060	0.17	0	1.5
Co	109	0.210	0.33	0	1.7
Cu	109	4.910	14.72	0.1	145.7
Fe	109	37.070	55.50	1.6	342
Hg	109	0.084	0.12	0	1
Mn	109	2.070	10.95	0	113.3
Mo	109	1.100	1.40	0	7.8
Ni	109	1.880	2.05	0	13
Pb	109	1.280	1.35	0	8.36
Sb	109	0.020	0.08	0	0.5
Se	109	0.180	0.33	0	2
V	109	6.120	7.13	0	56
Zn	109	15.880	30.71	0.3	254
Cr	109	4.790	3.49	0	15.2

Table 2: Toxic heavy metals concentrations (μg/l) in drinking water collected from water reservoirs of Kermanshah

Heavy metal	Number of samples	Mean	Standard deviation (S.D)	Min	Max
Al	23	18.730	15.030	0.66	67.2
As	23	0.320	0.770	0.03	3.84
Cd	23	0.070	0.057	0	0.2
Co	23	0.580	0.510	0	1.49
Cu	23	6.570	10.870	0.8	55
Fe	23	53.680	62.740	15.6	325.44
Hg	23	0.003	0.014	0	0.07
Mn	23	1.990	2.200	0.3	10.84
Mo	23	0.310	0.620	0	3.02
Ni	23	2.370	1.770	0	7
Pb	23	1.350	1.620	0	7.5
Sb	23	0.040	0.113	0	0.46
Se	23	0.200	0.438	0	1.89
V	23	4.730	2.880	0	2.9
Zn	23	16.500	20.060	1.1	67.28
Cr	23	4.160	2.400	0	11.19

Table 3: Toxic heavy metals concentrations (μg/l) in drinking water collected from a water distribution network of Kermanshah

Heavy metal	Number of samples	Mean	Standard deviation (S.D)	Min	Max
Al	33	40.540	60.740	2	329.8
As	33	0.328	0.700	0.03	4.12
Cd	33	0.072	0.123	0.01	0.71
Co	33	2.250	8.220	0	48
Cu	33	6.790	4.210	0.27	14.66
Fe	33	55.660	52.580	17.9	281.83
Hg	33	0.006	0.021	0	0.1
Mn	33	1.450	1.360	0.11	6.23
Mo	33	0.280	0.278	0	1.09
Ni	33	1.680	1.140	0	4.7
Pb	33	2.220	1.970	0	8.76
Sb	33	0.000	0.000	0	0
Se	33	0.004	0.200	0	0.11
V	33	5.740	5.160	0	21.5
Zn	33	45.290	72.800	0	320.53
Cr	33	3.860	3.010	0	12.84

Table 4: Toxic heavy metals concentrations (μg/l) in tap water (the last part of the distribution system) of Kermanshah

Heavy metal	Number of samples	Mean	Standard deviation (S.D)	Min	Max
Al	165	53.43	60.850	0.66	320.1
As	165	0.77	1.840	0	9.3
Cd	165	0.06	0.150	0	1.5
Co	165	0.67	3.730	0	48
Cu	165	5.52	12.750	0.1	145.7
Fe	165	43.11	56.300	1.6	347
Hg	165	0.05	0.109	0	1
Mn	165	1.93	8.940	0	113.3
Mo	165	0.82	1.230	0	7.8
Ni	165	1.91	1.870	0	13
Pb	165	1.48	1.560	0	8.76
Sb	165	0.02	0.080	0	0.5
Se	165	0.15	0.320	0	2
V	165	5.85	6.320	0	56
Zn	165	21.85	42.980	0.3	320.53
Cr	165	4.52	3.270	0	15.2

Table 5: Comparison of mean concentrations of toxic heavy metals in water collected from reservoirs with water collected from water resources and water distribution network of Kermanshah

	P value			
Heavy metal	Water reservoirs compared to water resources	Water distribution network compared to water reservoirs	North water reservoirs compared to north water resources within the city	South water reservoirs compared to south water resources within the city
Al	0.033	0.064	0.264	0.055
As	0.509	0.085	<0.0001	0.005
Cd	<0.0001	0.226	0.056	0.176
Co	<0.0001	0.062	<0.0001	0.007
Cu	0.003	0.085	0.051	0.126
Fe	<0.0001	0.659	0.005	0.57
Hg	<0.0001	0.933	0.001	0.003
Mn	<0.0001	0.224	0.002	0.11
Mo	0.001	0.368	0.018	0.019
Ni	0.047	0.132	0.118	0.319
Pb	0.907	0.039	0.612	0.499
Sb	0.589	0.014	0.921	0.467
Se	0.459	0.004	0.188	0.193
V	0.907	0.809	0.488	0.393
Zn	0.883	0.028	0.634	0.477
Cr	0.827	0.629	0.033	0.67

Table 6: Comparison of mean concentrations of toxic heavy metals in water collected from the water distribution network with water collected from reservoirs and water resources in Kermanshah

	P value			
Heavy metal	Water resources compared to distribution network	Water distribution network compared to water reservoirs	North water resources within the city compared to north water distribution network	South water resources within the city compared to south water distribution network
Al	0.003	0.064	0.427	0.581
As	0.509	0.085	<0.0001	0.001
Cd	<0.0001	0.226	0.418	0.054
Co	<0.0001	0.062	<0.0001	0.002
Cu	0.003	0.085	0.006	0.001
Fe	<0.0001	0.659	0.022	0.897
Hg	<0.0001	0.933	0.002	<0.0001
Mn	<0.0001	0.224	0.149	0.581
Mo	0.001	0.368	0.179	0.005
Ni	0.047	0.132	0.934	0.758
Pb	0.907	0.039	0.062	0.211
Sb	0.589	0.014	0.144	0.01
Se	0.459	0.004	0.112	0.012
V	0.907	0.809	0.846	0.82
Zn	0.883	0.028	0.064	0.355
Cr	0.827	0.629	0.313	0.673

activities (such as using fertilizers and chemical pesticide containing As, Co and Cr) on water resources out of the city. Discharging wastewater of workshops and small industrial units to the environment inside the city as well as vehicle traffics could be other reasons of water resources pollution within the city [27].

Statistical results also showed that average concentrations of Al, Hg, Mn and Mo in all samples collected from water resources were more than those samples collected from water reservoirs with significant differences, but the concentrations of Cd, Co, Cu, Fe and Ni were not different. Probably the main reason of these differences is precipitation of some metals at the bottom of the reservoirs which lead to decreased concentrations of some metals within the reservoirs water. Urban activities such as discharging wastewater of small industrial units to the environment could be a significant reason for the existence of some metals such as Hg and

Table 7: Comparison of mean concentrations of toxic heavy metals in water collected from reservoirs and water resources with water collected from the water distribution network in Kermanshah in different locations

Heavy metal	P value: Water resources within the city compared to water resources outside the city	North water resources within the city compared to south water resources within the city	Western water resources within the city compared to eastern water resources within the city	North water reservoirs compared to south water reservoirs	North water distribution network compared to south water distribution network
Al	0.04	0.803	<0.0001	0.483	0.644
As	<0.0001	0.497	<0.0001	0.946	0.207
Cd	0.122	0.813	<0.0001	0.84	0.159
Co	0.018	0.623	0.001	0.592	0.056
Cu	0.063	0.051	0.71	0.161	0.036
Fe	0.001	0.02	0.326	0.443	0.916
Hg	0.818	0.568	0.593	0.228	0.312
Mn	0.576	0.016	0.093	0.301	0.585
Mo	0.052	0.236	0.84	0.814	0.449
Ni	0.43	0.64	<0.0001	0.894	0.629
Pb	0.001	0.101	0.954	0.203	0.101
Sb	0.005	0.965	0.924	0.427	1
Se	0.469	0.298	<0.0001	0.124	0.07
V	0.752	0.828	<0.0001	0.474	0.817
Zn	0.242	0.595	<0.0001	0.385	0.324
Cr	<0.0001	0.473	0.13	0.92	0.883

Mo in underground water rather than the water reservoirs. In contrast, pipelines type and their corrosion could be the reason for the existence of some metals in water of the inlet pipelines to reservoirs. As a result concentration of these elements would be increased within the water of reservoirs [28]. In addition, statistical test results demonstrated that average concentrations of Hg, Mn, Mo, Ti and Se in water supply resources were more than the water in the distribution network with significant differences meanwhile concentrations of Cd, Co, Cu and Fe were not different. Cause of this difference could be the precipitation of some elements in water of reservoirs and entrance of some other elements to the water distribution system as a result of steel pipe corrosion with impurities such as Co and Cu to the distribution network water. Also mean concentrations of Pb and Zn in water distribution system were more than the water reservoirs with significant differences but concentrations of Ti and Se in water distribution system and water reservoirs were not different. It could be due to the corrosion of distribution pipelines and entrance of Pb and Zn to the distribution network and precipitation of Ti and Se in water reservoirs. Consequently the amounts of these elements are decreased in the distribution system [29, 30]. Mean concentrations of the studied elements in water reservoirs and water distribution network in south and north parts of the city were not significantly different. Meanwhile the amounts of Fe and Mn in water supply resources of the south part of the city were significantly more than the northern part. Reasons for increased Fe and Mn in underground water resources of the southern region could be presence of workshops in the southern part, its wider area, geological texture and the point that the south part of the city is much older than the north part [28].

Comparison of the elements concentrations in water resources outside the city showed that the mean concentrations of Al, Co, Fe, Mn, Mo, Ni, Se and V in western resources were more than the eastern ones and the difference was statistically significant. The difference could be due to the geological texture and more agricultural activities (Such as utilization of fertilizers and chemical pesticides containing metals such as cobalt) around water wells in the city's western region [30-32].

CONCLUSION

The amount of heavy metals in different parts of the urban water supply system could be different. The concentration of some elements was higher in water resources, which was reduced following entrance to the water reservoirs. Meanwhile concentration of some metals was invariable through the supplying system. Those metals could find their way to the consumption site and may create health hazards for consumers. Besides, the material used in the pipelines plays a significant role in increasing the concentration of some metals to the upper standard limits. In conclusion continuous monitoring of heavy metals in urban water systems from source of production to the site of consumption is recommended to identify sources of possible pollutions in water resources or in the distribution network. In this manner changes in metals concentrations from water resources to the consumption site are determined and required protecting and controlling procedures are carried out.

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