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## Research Article

### THE EFFECT OF WATER TREATMENT ON CALCIUM AND BERYLLIUM LEVELS OF WATER IN KARUN RIVER AND BYBLUS AND ANAHITA COMPANIES IN AHVAZ CITY, IRAN

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#### Abstract

**Introduction:** Water quality is an important issue for human health management. The aim of this research was to compare calcium and beryllium levels in the water of Karun river at the influent stream of the water treatment plant number two (WTP2) in Ahvaz city and Byblus and Anahita companies and their outlet water after the water treatment process. **Materials and Methods:** Fourteen samples of Karun river water at the inlet of AhvazWTP2 and Byblus and Anahita companies and their outlet water after the water treatment process were collected during five months (September 2013, and January - April 2014). Samples were taken fourteen times, each time; five, one liter samples were collected. The samples were then mixed and one liter composite sample was isolated and transported to laboratory. The collected samples were filtered through filter paper (0.45 µm). For their fixation and protection by nitric acid the pH adjusted 2 and was analyzed by ICP-MS. **Results:** it was shown that average of Calcium in water at the inlet of AhvazWTP2 and Byblus and Anahita companies and their outlet water after the water treatment process were 164.714, 94.571, 111.714, 54.485, 124.571, and 17.528 µg/l, respectively. Also, average of Beryllium in water at the inlet of AhvazWTP2 and Byblus and Anahita companies and their outlet water after the water treatment process were 15.142, 5.714, 8.714, 2.571, 9.428 and 2.285 µg/l, respectively. **Conclusion:** The results showed that the purification process causes reduction in content of metals in waters

**Keywords:** Karun River, beryllium, calcium, water treatment process, ICP-MS.

#### Introduction

Currently, Because of increasing world population and increase in per capita consumption along with economic development demand for water has been reached to very high level. To respond to this demand in our country, indiscriminate harvesting of water resources along with natural events like drought caused qualitative and quantitative resumption in the drinking water resources in many areas which water supply had become serious challenge in many region of country (J.salvato 1992).

Using bottled water for drinking is a good choice, especially in cities which had no access to water in good quality or had not enough fund and knowledge for water transport and full filtered water. Dispensation of bottled water among accident victims in disasters is a healthy

option. Because of public demand for healthy and soft water, bottled water industry has a high growth world widely (Alsohaimi, Alothman et al. 2012).

People in many countries use bottled water for its health and safety but there are some reports on contamination in bottled water with Chemical and microbial contaminants (APHA 1992, Andra and Makris 2014).

Calcium and Beryllium are elements which are in water. Beryllium is a micronutrient which has a important role in body but in some cases it can enter the body and cause toxicity. This ion could be found in environmental pollution and is an occupational hazard (Holzer, Midasch et al. 2008).

Components by beryllium sources are very toxic(Ito, Kawaguchi et al. 2008).

Mammalian tissues cannot secrete this ion, so by the accumulation of this ion, toxicity would be appearing which cause damage to the skin and mucosa(Krachler and Shotykh 2009).

Calcium is the other ion which has an important role in regulating muscles and nerves(Ling, Li et al. 2001).

Calcium loss would inhibit Ossification(Lopez-Darias, Pino et al. 2010).

Low calcium in diets will increase 1,25Dihydroxy vitamin D3, interfering calcium to adipocytes, increasing or decreasing lipogenesis and increasing in triglyceride storage in fat tissue. It had been predicted that by decreasing 1,25 Dihydroxy vitamin D3 by calcium increasing in tissue will cause decreasing weight and fat production(Majumder, Islam et al. 2011).

## Materials and Methods

### Chemicals, Reagents and Materials

Mix standard solution containing Calcium and Beryllium were obtained from Perkin Elmer Co. (USA) at concentration 10 µg/ml, HNO<sub>3</sub>, Whatman filter papers (0.45µm)

### Cleaning glassware

All glassware was cleaned by soaking in 10% (v/v) acid nitric for 24 h, rinsing five times with Milli-Q water and dried in oven at 450 °C temperature.

### Apparatus

Inductively Coupled Plasma – Mass Spectrophotometric devices (Perkin Elmer ELAN DRC 6000, USA). Typical daily instrumental used parameters are given in table 1.

### Sampling

Sampling is one of the most important stages of the study. By using G power software the number of samples required for each inlet and outlet WTP2, by blus and Anahita was determined (14 water samples). Samples were taken fourteen times, each time; five, one –liter samples were collected. The samples were then mixed and one liter composite sample was isolated and transported to laboratory. The collected water samples were filtered by passing through filter papers (0.45µm). To protect and stabilize them, pH were adjusted <2 by concentrated HNO<sub>3</sub> and were kept at 4 °C before the analysis.

By preparing zinc and copper standards solutions in 1, 10, 25, 50, 75 and 100 ppb concentrations and measuring their concentrations with ICP-MS, calibration curves for copper and zinc were plotted. <sup>40</sup>Ca and <sup>9</sup>Be isotopes were chosen. Copper and zinc levels in collected water samples without any dilution or adding any materials were measured by ICP-MS method and their concentrations were calculated by calibration curves. Results were analyzed by Excel and SPSS 20 software.

Table 1- ICP-MS operating conditions

Spray Chamber	Cyclonic
Nebulizer	Meinhard
RF power (W)	1500
Argon flow rate	
Plasma	15 l/min
Auxiliary	0.8 l/min
Nebulizer	0.7-0.9 l/min
Detector multiplier	Dual-stage discrete dynode electron
Mass filter	Quadrupole
Dynamic range	8
Scan mode	peak hopping
Resolution (amu)	0.7
Replicate time(s)	1
Dwell time (s)	50
Sweeps/reading	20
Integration time (ms)	1000
Replicates	3
Isotopes	<sup>40</sup> Ca, <sup>9</sup> Be

**Results**

Lines equations with correlations for Calcium and Beryllium were  $y=17.897x+128.15$ , with the coefficient of determination (R<sup>2</sup>) 0.9995 and  $y=11.298x+50.985$ , 0.9995 respectively

**Statistical analyses**

By using SPSS software version 20, average mean of calcium and beryllium was measured for each samples and showed them by Mean±SEM. One sample T-test was used for comparison of calcium and beryllium for Permissible limit. To compare calcium and beryllium levels in samples Kruskalwalis and Man whitney test was used. P<0.05 was proposed as a significant level. All recoveries were more than 95%,

indicating the high accuracy of the method. The limit of quantification (LOQ) for calcium and beryllium were 10 ppm and 1 ppb.

The results of this study shown that average of Calcium in water at the inlet of Ahvaz WTP2 and Byblus and Anahita companies and their outlet water after the water treatment process were 167.714, 94.571, 111.714, 54.485, 124.571, and 17.528 mg/l, respectively (Table 2).

Also, average of Beryllium in water at the inlet of Ahvaz WTP2 and Byblus and Anahita companies and their outlet water after the water treatment process were 15.142, 5.714, 8.714, 2.571, 9.428 and 2.285 µg/l, respectively (Table 3).

**Table 2. Minimum, Maximum, Average and etc. for calcium concentration in water samples**

		Type of water					
		Karun at inlet to water treatment plant No.	Karun at outlet from water treatment plant No.	water at inlet of Byblus factory	water at outlet from Byblus factory	water at inlet of Anahita factory	water at outlet from Anahita factory
Con.Ca	Mean	164.7143	94.571	111.7143	54.4857	124.571	17.2857
	95% Confidence Interval for Mean	146.9268	71.5500	51.5455	-5.2318	87.8567	5.7626
	Statistic Median	182.5018	117.5928	171.8831	114.2032	161.2862	28.8088
	Variance	178.0000	113.0000	149.0000	17.0000	137.0000	10.0000
	Std. Deviation	369.905	619.619	4232.571	4169.318	1575.952	155.238
	Minimum	19.23291	24.89215	65.05822	64.57026	39.69827	12.45946
	Maximum	140.00	67.00	16.00	16.00	36.00	9.00
	Range	181.00	116.00	152.00	150.00	148.00	36.00
	SEM	41.00	49.00	136.00	134.00	112.00	27.00
			7.26936	9.408	24.58969	24.40526	15.004

**Table3. Minimum, Maximum, Average and etc.for Beryllium concentration in water samples**

		Type of water					
		Karun at inlet to water treatment plant No.	Karun at outlet from water treatment plant No.	water at inlet of Byblus factory	water at outlet from Byblus factory	water at inlet of Anahita factory	water at outlet from Anahita factory
Con.Be	Mean	15.142857	5.714286	8.714286	2.571429	9.428571	2.285714
	95% Confidence Interval for Mean	1.651214	4.330692	7.834582	-.090732	6.766411	1.586597
	Statistic Lower Bound	28.634500	7.097879	9.593989	5.233589	12.090732	2.984832
	Upper Bound	10.000000	6.000000	9.000000	2.000000	10.000000	2.000000
	Median	212.810	2.238	.905	8.286	8.286	.571
	Variance	14.5879925	1.4960265	.9511897	2.8784917	2.8784917	.7559289
	Std. Deviation	8.0000	4.0000	7.0000	1.0000	3.0000	2.0000
	Minimum	48.0000	8.0000	10.0000	9.0000	11.0000	4.0000
	Maximum	40.0000	4.0000	3.0000	8.0000	8.0000	2.0000
	Range		5.5137429	.5654449	.3595159	1.0879676	1.0879676
SEM							

**Table 4. Compression of concentration mean of calcium and Beryllium in water samples by national and WHO standard limit by one-sample T-test**

Type of water	Ca.Sig. (2-tailed) test value=250ppm	Be.Sig. (2-tailed) test value=4ppb
Karoun at inlet of WTP2*	.000	.090
Karoun At outlet of WTP2	.000	.023
Byblus at inlet	.001	.000
Byblus at outlet	.000	.237
Anahita at inlet	.000	.002
Anahita at outlet	.000	.001

## Discussion

The highest average of calcium concentration (164.714 ppm) was related to water at the inlet of Ahvaz WTP2. There were no significant differences between water at the inlet of Ahvaz WTP2 and Byblus ( $P>0.05$ ) but there were differences with other water samples ( $P<0.05$ ).

Average of calcium concentration of filtered water in Ahvaz WTP2 (94.571 ppm) had no significant differences with average of calcium concentration in water at the inlet and outlet water of Byblus company ( $P>0.05$ ) but it had significant differences with water at the inlet of Ahvaz WTP2 and water at the inlet and outlet water of Anahita company ( $P<0.05$ ).

Average of calcium concentration in water at the inlet of Byblus company (111.714 ppm) has significant differences with calcium concentration in outlet water of Anahita company ( $P<0.05$ ) but there were significant no differences with other water samples ( $P>0.05$ ).

Significant differences was found between Average of calcium concentration in outlet water of Byblus company (54.485 ppm) with Average of calcium concentration in water at the inlet of Ahvaz WTP2 ( $P<0.05$ ) but there were no significant differences with other water samples ( $P>0.05$ ).

There were significant differences with water at the inlet of Anahita company (124.571 ppm) with average of calcium concentration of water at the inlet and in outlet water of Anahita Company and Ahvaz WTP2 ( $P<0.05$ ) but there were no significant differences with average of calcium concentration of water at the inlet and in outlet water of Byblus Company ( $P>0.05$ ).

There were no significant differences with Average of calcium concentration in outlet water of Anahita Company (17.528 ppm) and average of calcium concentration in outlet water of Byblus Company ( $P>0.05$ ), but there were significant differences with other water samples ( $P<0.05$ ).

The highest average of Beryllium concentration (15.142 ppm) was related to water at the inlet of Ahvaz

WTP2. There were no significant differences between water at the inlet of Byblus and Anahita companies ( $P>0.05$ ) but there were differences with other water samples ( $P<0.05$ ).

There were significant differences with average of Beryllium concentration in filtrated water of Ahvaz WTP2 (5.714 ppm) and average of Beryllium concentration of other samples ( $P<0.05$ ).

There were no significant differences between average of Beryllium concentration in water at the inlet of Byblus company (8.714 ppm) and average of Beryllium concentration in water at the inlet of Ahvaz WTP2 ( $P>0.05$ ) but there were significant differences with other water samples ( $P<0.05$ ).

There were no significant differences in average of Beryllium concentration in outlet water of Byblus Company (2.571 ppm) with average of Beryllium concentration in outlet water of Anahita Company ( $P>0.05$ ) but there were significant differences with other water samples ( $P<0.05$ ).

There were no significant differences in average of Beryllium concentration between water at the inlet of Anahita company (9.428 ppm) and water at the inlet of Ahvaz WTP2 ( $P>0.05$ ) but there were significant differences with other water samples ( $P<0.05$ ).

There were no significant differences in average of Beryllium concentration between outlet water of Anahita Company (2.285 ppb) and outlet water of Byblus Company ( $P>0.05$ ) but there were significant differences with other water samples ( $P<0.05$ ).

Shabankareh et al (2012) conducted a study on evaluation of physical and chemical quality on drinking water in Boushehr city. They found calcium concentration on 156.38 ppm which was higher than all of our samples except water at the inlet of Ahvaz WTP2 but in both studies mount of calcium was lower than national and WHO permissible limit (Makris, Andra et al. 2013).

Rajaei et al (2010) conducted a study on evaluation of chemical quality on drinking water in Birjand and Qaen city. They found calcium concentration on 62.60 ppm which was lower than all of our samples except outlet water of Anahita and Byblus companies but in both studies amount of calcium was lower than national and WHO permissible limit (McLaughlin, Carter et al. 2006).

Loloyi and Zolala (2009) conducted a study on evaluation of quality on drinking water in Kerman city. They found calcium concentration on 45.55 ppm which was lower than all of our samples except outlet water of Anahita company but in both studies amount of calcium was lower than national and WHO permissible limit (Miranzadeh, Ehsanifar et al. 2011).

Samaee et al (2006) conducted a study on evaluation of physical and chemical quality on drinking water in Yazd city. They found calcium concentration on 104.94 ppm which was lower than water at the inlet of Ahvaz WTP2 and Anahita Company and higher than other samples except but in both studies amount of calcium was lower than national and WHO permissible limit (Mousa, Basheer et al. 2013).

J. Klaus et al (1994) in South America at State of Nevada conducted a study on evaluation of Beryllium and some other materials by Beryllium ICP-MS device in underground water. They found Beryllium concentration on 0.018 ppm which was lower than our samples and outlet water of Anahita and Byblus companies are in national and WHO permissible limit (Moxley, Ashwal et al. 2005).

D. Cichella et al (2010) in Italy conducted a study on evaluation of concentration of Beryllium, calcium and some other materials by ICP-MS device in 158 different brands of bottled water. They found Beryllium and calcium concentration on 0.018 ppm and 69.41 ppm, respectively, in which Beryllium concentration was lower than our samples and outlet water of Anahita and Byblus companies are in national and WHO permissible limit. Also, calcium concentration was lower than our samples except outlet water of Anahita and Byblus companies. In both studies calcium concentration was lower than national and WHO permissible limit (Pal and Bakshi 1992).

## Conclusion

Level of calcium in this study was lower than national and WHO permissible limit but beryllium level in outlet water of Anahita and Byblus companies were at national and WHO permissible limit and other water samples such as outlet water of Ahvaz WTP2 which is piped water of city, were higher than national and WHO permissible limit which should be noticed by government because this level of beryllium could cause serious risks and damages by long term.

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