INVESTIGAÇÃO DE ALGUNS AGENTES PERIGOSOS E TRAÇOS DE ELEMENTOS NA ÁGUA POTÁVEL DA REGIÃO DE KOCAELI

INVESTIGATION OF SOME HAZARDOUS AGENTS AND TRACE ELEMENTS IN DRINKING WATER OF KOCAELI REGION

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RESUMO

Todas as questões estão relacionadas com a ecologia ambiental, a qualidade da água potável obtém uma importância particular agora, no século XXI. Como um estudo de caso, o artigo discute a qualidade da água potável na região de Kocaeli, na Turquia. A análise foi feita para revelar o principal agente poluente na água potável. Investigou-se a presença de metais como Al, Cu, Zn, Fe, Cd, Pb, Mn, Ni, Na e Hg. Não Metais como B, F, Cl, Cl Livre, NH_4, Amônia, Nitrogênio (NH_3-N). Os metais pesados incluíram Cd, Pb, Mn, Ni, Hg, Cu, Fe e Zn. E agentes orgânicos, como Beta-Endosulfato, Benz(a)antraceno, Benz(a)pireno, Benzeno, Bromodiclorometano, Carbaril e Fenantreno. Separadamente foi investigada a concentração de iodo na água potável devido à água que vinha das montanhas e o iodo pode ser lavado das rochas e penetrado na água. Os resultados estão discutindo. Segundo a pesquisa é claro que a água na região de Kocaeli, a Turquia é limpa e segura para beber. Existe alguma quantidade de iodo, mas a sua quantidade depende das estações. Foi elaborada fórmula para contagem da concentração média de iodo no organismo humano após um mês de consumo de água.

Palavras-chave: *Poluição da água, Agentes poluentes; Metais pesados em água, Quantidade de iodo; Equação para contagem de iodo.*

ABSTRACT

All the issues are related to environmental ecology, drinking water quality obtains particular importance in the 21st century. As a case study, the article discusses the drinking water quality in Kocaeli region, Turkey. The analysis was done for revealing the main pollutant agent in the drinking water. It was investigated the presence of metals such as Al, Cu, Zn, Fe, Cd, Pb, Mn, Ni, Na, and Hg. Following Non-Metals : B, F, Cl, Free Cl, NH_4, Ammonia, Nitrogen (NH_3-N). Heavy metals ions included Cd, Pb, Mn, Ni, Hg, Cu, Fe, and Zn. And Organic agents such as Beta-Endosulfan, Benzo(a)pyrene, Benzene, Bromodichloromethane, Carbaryl, and Fhenanthrene. Separately was investigated Iodine concentration in the drinking water due to water came from mountains and Iodine can be washed out from the rocks and entered in the water. The results are discussing. According to the research is clear that water in the Kocaeli region, Turkey is cleaned and safe for drinking. There is some amount of Iodine but its quantity depends on the seasons. Was elaborated formula for counting average concentration of Iodine in the human body after one-month drinking water.

Keywords: *Water pollution, Pollutants agents; Heavy metals in water, Quantity of Iodine; Equation for counting Iodine.*

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INTRODUCTION

Water quality issues are a major challenge that humanity is facing in the twenty-first century. Throughout history, the quality of drinking water has been the main factor to determine human welfare. Different pollution of drinking water has frequently caused waterborne diseases that have decimated the populations in the cities [1]. Unwholesome water, polluted by natural sources, has caused great hardship for people forced to drink it or use it for irrigation. Accessing to safe drinking water has improved over the last decade in almost every part of the world, but approximately one billion people still lack accessing to safe water and over 2.5 billion lack accessing to adequate sanitation. There are general types of drinking water pollutants (see Table 1).

Nowadays among pollutants most dangerous and spreading heavy metals, which reach water systems in natural and anthropogenic ways. Trace elements are essential for human life but they can be toxic depending on the concentration [2].

Some trace elements can be met in water [3].

In the article, we are providing research on drinking water in Kocaeli region. The research was done during 2017 and in the first part of 2018. Was measured almost all importance hazardous elements and among them was done microbiological analyzes.

Kocaeli region is located in the easternmost end of the Marmara Sea around the Gulf of Izmit. Kocaeli is bordered by the province of Istanbul and the Marmara Sea to the west, the Black Sea to the north, the province of Sakarya to the east, the province of Bursa to the south and the province of Yalova to the southwest.

Drinking water in Kocaeli province is received from Yuvacık Dam, Namazgah Dam, and local resources. In Kocaeli, 160.822.229 m^3 of drinking water provided in 2017 and 2018 was provided from 132.241.452 m^3 of the dam and 28.580.777 m^3 from local sources. Therefore, all water samples were taken from this area (see Figure 1). Generally, in Kocaeli region, there is a lot of different type of water cleaning systems, among them Natural treatment systems and water can be used as drinking from the tap [4].

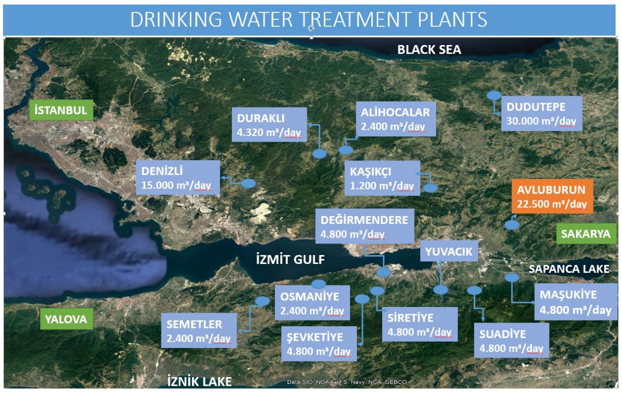

Figure 1. Avluburun drinking water treatment plant

EXPERIMENTS AND METHODS

Water samples were collected from Avluburun drinking water treatment plant which is treatment capacity 22.500 m^3/day. Local sources formed by the precipitation of snow and rainwater are used as a raw water source and extra raw water is made from Sapanca lake in the summer. As soon as the raw water arrives, it is passed through the phases in a controlled and supervised manner and conducted to the network for human consumption purposes. These phases respectively; Blower, flocculation- coagulation, sedimentation, filtration, neutralization and in case of needing disinfection, conditioning. The monitoring of the control is carried out by taking the samples from the predetermined points of the network at weekly periods. Samples which both in and out of the plant as well as instantly in accordance with the technique of the specific points in the network are taken by specialist team weekly. In addition, measurement is carried out for parameters such as free chlorine.

Almost every major pollutants in the water were examined: Metals and heavy metals among them, Non-metals, cations and anions, total dissolved solids and organic meter. Also, the bacteriological examination was done. Frequent bacteriological examinations are essential for hygienic control. Methods used by us are more relevant for water with chlorine disinfection. All used measurement methods are under Turkish Standards Institution (TSE) [5] and EU (European Association) standards [6].

The following parameters were measured in the laboratory: cations, anions, nutrients, BOD5, heavy metals. Field analysis of physical-chemical (dissolved oxygen, pH, temperature, salinity) parameters were determined on the sampling site with the mobile devices; Laboratory analysis of samples, in particular, cations, anions, nutrients were made in accordance with the following methods: SM 2540 D; TS EN ISO 11885; Membrane Filtration; TS EN ISO 10304-1; SM 2510 B;_SM 5220 B; SM 2120 C;_SM 2550 B; EPA 200.8;_SM 4500 Sulphate-D; TS EN ISO 14911; TS EN ISO 9308-1;_TS EN ISO 7899-2;

The received results see in Table 2, 3, 4, 5, 6, 7.

We must especially emphasize the matter of iodine in drinking water. In terms of the effect of iodine deficiency on intellectual development, there has been a growing wealth of literature from different parts of the world including both developed and developing countries[7]. The detrimental effects of iodine deficiency on intellectual development, particularly in terms of the intelligence quotient (IQ) as a common assessment of intelligence, in children, have been demonstrated in all studies.

It is well known, that in the regions where drinking water contains 0.0001-0.001mg I_2 e.g. 0.1-1.0 micro/gram per litter water, from 1000 habitants 15-30 suffers from an illness of Goiter[8]. Where Iodine content per litter water is 0.001-0.01 mg, was registries one case of Goiter from 1000 habitants. In the modern worlds there is a solution to this problem with Iodized salt but its contents in water, even in small quantity, also is very important.

Iodine in water is normally determined by a titrimetric procedure which can be used for solutions containing 2–20 mg of iodine per liter. A leuco crystal violet method may be used for the determination of iodide or molecular iodine in water. This photometric method is applicable to iodide concentrations of 50–6000 µg/ liter; the detection limit for iodine is 10 µg/ liter [9]. We used TS EN ISO 10304-1 methodology for more exact determination iodine in our samples. The received results see in Table 8.

RESULTS AND DISCUSSION:

According to the research conducted, the metals in Kocaeli region are within the norm. Within the Turkish drinking water quality standards[5,] the maximum number of **aluminum** is 1-200 µg/L per liters of water. Generally, Al in the surface water can appear after using from population cheap detergents, shampoos and Dushe Gels[10]. In this type of home chemistry, Al is as aluminum sulfate $Al_2(SO_4)_3$. Removing it from water is quite problematic. According to the result of our research, the number of it is always low.

According to Turkish standards, the maximum number of **Manganese** per liters of water is 50 µg/L. According to our research to quantity is always under the norm and at the end of 2017. Its contents in the water decrease sharply. During the first part of 2018, it is under the limit. This indicates reliable protection of the environment.

Ni is quite poisoning metal which in the surface water appears from Industry. According to Turkish standards, the maximum number of **Nickel** in liters of water is 20 µg/L. In our research was used two type of methods for measurement: TS EN ISO 7294-2 and TS EN ISO 11885. According to the two methods in the water is the minimum number of Ni. In the second part of 2017, its quantity was equal to zero. During the first part of 2018, it is under the limit.

Sodium is light metal in the water it can appear from detergents. According to Turkish standards, the maximum number of Na in liters of water is 0.1 mg/l. After our research is clear that maximum number was found only in August 2017. During the first part of 2018, it is under the limit.

Cu, Zn, Fe, Cd, Pb are very **dangerous heavy** metals. Most of them have a tremendous affinity for sulfur and disrupt enzyme function by forming bonds with sulfur groups in enzymes.

According to Turkish standards, the maximum number of **Copper** per liters of water is 100µg/L. According to our research, it was within limits and in the second part of 2017, it was totally removed from the water. During the first part of 2018, it is under the limit.

According to Turkish standards, the maximum number of **Zinc** per liter of water is 1 µg/L. According to our research, it was totally removed from the water.

According to Turkish standards, the maximum number of **Iron** per liter of water is 0.2 µg/L (0.0002mg/l). According to our research, it was within limits.

Cadmium as mentioned above a heavy metal. Mainly, it is spreading with zinc extract from its extraction deposits. Also, it may arise from industrial discharges and mining wastes. According to Turkish standards, the maximum number of Cd per liters of water is 5 µg/L (0.005 mg/l). According to our research, it was totally removed from the water. This refers to reliable clean water because it is well known that even ecologically very cleaned soil contains ions of Cd from where it can appear in the surface water.

According to Turkish standards the maximum number of **Lead** per liters of water is10 µg/L. In our research, two type of methods were used: TS EN ISO 7294-2 and TS EN ISO 11885. According to to the first method, it is under the limit and the second method reveals that there is no Pb in the water.

Mercury is the most dangerous heavy metal. Toxicological data indicate that mercury is a cumulative poison. Mercury enters the environment from a large number of miscellaneous sources related to human use of the element. According to researches, Hg is within limits.

All heavy metals can be appeared in the water due to human activities.

According to the investigation [2] by using equation (1) can be calculated the possible impact of heavy metals on human health.

$$ADIW_{ing}=C\times IR\times EF\times ED/BW\times AT \qquad \text{(Eq.1)}$$

Were:

$ADIW_{ing}$ is the average daily intake of heavy metals ingested from water (mg/kg-day);
C is the heavy metal concentration in water (µg/L).
IR is the daily intake of water, approx. 2L/day.
ED is the exposure duration, approx. 70 years.
EF is the exposure frequency, 365 days/year.
AT is the time period over which the dose is averaged, 365×70=25.550 days. BW is the body weight of the exposed individual (70kg approx.) [2].

At the same time can be calculated e.g. "Hazard quotient" (HQ) by equation (2).

$$HQ=ADI/RfD \qquad \text{(Eq.2)}$$

Were:

ADI is a value obtained from the previous equation.
RfD is chronic reference dose values are generally calculated [2].
For our water samples, the values calculated from equation (1) and (2) is given in Table 9.

The research of nonmetals B, F, Cl_2 was done.

According to Turkish standards, the maximum number of **Boron** per liters of water is 1.0 mg/L. The maximum number of **F** is 4.0 mg/L and a number of free **Cl_2** is 250 mg/L. According to our research, all of them were under the limit.

The research of **nitrite, nitrate** and **sulfate** ions were done. Generally, Nitrite and nitrate ion occurs in water as an intermediate oxidation state of nitrogen. Nitrite is added to some industrial process water to inhibit corrosion. The sulfate ion is found in some industrial wastewaters. Sodium sulfate is commonly added to boiler feed waters as an oxygen scavenger. According to Turkish and European standards, the maximum number of Nitrite in liters of water is 50 µg/L, nitrate 3 µg/L, sulfate 250mg/l. According to our research, all parameters were under the limit.

The water pH value was also measured in this study. According to standards it equals 6.5-8.5 and is under the limit. According to the same research was done an analysis of some organic agents (Table 7) which also were under regulations.

Regarding **Iodine,** we got very interesting results. As previously it was mentioned, the content of iodine in water prevents the population from illness of Goiter. In our samples, there were found some quantity of Iodine (Table 9). Maximum of them we found in samples collected in the springtime. We can explain this by the fact that it often rains in Kocaeli region in springtime. Because of rains Iodine in rocks is washes out in large quantities and enters in the water.

Among Kocaeli, population illness of Goiter is very low. Of course, we can think that this is due to Kocaeli location near seaside and Iodine evaporation from the seaweed in the air[9]. But iodine-containing water factor also very important.

To finding out how many Iodine can be arrived in the human body after one monthly regular drinking water from Kocaeli, by us was developed the following equation (3).

Suppose a person's weight is 70kg, he/she drink 2-liter water per day, where is some quantity of Iodine (see Table 9). We calculated for maximum indexes-4.19 µg/L (2017 springtime) and 3.89 µg/L (2018 springtime) (see Table 9).

Than:

Continuance time= Total mass of Iodine/rate of intake (Eq.3)

The rate of intake can be calculated with the following way:

The rate of intake *= amount of water, drinking by person per day × amount of Iodine measured in the water samples × water drinking duration (number of days).*

E.g:

Rate of intake = 2000 g water (2 liter = 2000 ml = 2000 g) × 4.19 µg/L **or** 3.89 µg/L × 7day = 5.866×10^4 **or** 5.446×10^4 (Eq.4)

Continuance time *(in our case one month = 30 Day) = Total mass of Iodine/5.866×10^4* ***or*** *5.446×10^4* (Eq.5)

From equation (5):

The total mass of Iodine *= Continuance time × Rate of intake* (Eq.6)

E.g:

The total mass of Iodine = 30 Day × 5.866×10^4 ***or*** *5.446×10^4*

The total mass of Iodine is then:

For maximum indexes for 2017: 1.7598×10^6 and for the first part of 2018: 1.6338×10^6.

For person daily intake of iodine by an individual amount is 500 micrograms [11], monthly is 1.5×10^4

So, if the person will drink Kocaeli water regularly some average amount of Iodine will be arrived in his/her body. Another part of Iodine he/she can take from the food and iodized salt.

The different problem appears in the water with Bacterial organisms. Throughout any year, 95% of samples should not contain any coliform organisms in 100 ml. No sample should contain *E. coli* in 100 ml. Coliform organisms should not be detectable in 100 ml of any two consecutive samples[12,13,14]. According to our research drinking water is totally free from bacterial organisms.

CONCLUSIONS:

Thus, according to measurements of different hazardous agents, trace elements and bacterial organisms in the drinking water we can conclude that all of them are under the EU and Turkish standards.

Among trace elements, the main attention was paid to the measurement of Iodine in the water because nowadays, lack of Iodine among the population is the international problem. We find out that in the water of Kocaeli region there is some amount of Iodine. It is of course, not enough for daily demands of this element but a regular drink of water will take part for prevention of Goiter disease.

Besides this, in the scope of the investigation was developed a formula for calculated theoretically how many Iodine could arrive in the human body after one-month drinking water from Kocaeli region.

Thus, we can conclude that the Kocaeli region the tap water is useful and safe for drinking.

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Table 1. General types of water pollutants

Class of pollutant	Significance
Trace elements	Health, aquatic biota
Heavy metals	Health, aquatic biota
Organically-bound metals	Metal transport
Radionuclide	Toxicity
Inorganic pollutant	Toxicity, aquatic biota
Asbestos	Human health
Algal nutrients	Eutrophication
Acidity, alkalinity, salinity	Water quality, aquatic life
Trace organic pollutant	Toxicity
Polychlorinated biphenyls	Possible biological effects
Pesticides	Toxicity, aquatic biota, wildlife
Petroleum wastes	Effects on wildlife, esthetics
Sewage, human, animal wastes	Water quality, oxygen levels
Biochemical oxygen demand	Water quality, oxygen levels
Pathogens	Health effects
Detergents	Eutrophication, wildlife, esthetics
Chemical carcinogens	Incidence of cancer
Sediments	Water quality, aquatic biota, wildlife
Taste, odor and color	Esthetics

Table 2. Content of metals in drinking water

Metals	Methods	Unit	Standard	2017		2018 (first period)	
				Max	Min	Max	Min
Al	TS EN ISO 7294-2	µg/L	1-200	180	10	140	15
Cu	TS EN ISO 7294-2	µg/L	100	12	0	11	0
Zn	TS EN ISO 11885	µg/L	1	1	0.01	1	0.01
Fe	TS EN ISO 7294-2	mg/L	0.2	0.13	0.01	0.11	0
Cd	EN ISO 7294-2	mg/L	0.005	0.001	0	0.002	0
Pb	TS EN ISO 7294-2	µg/L	10	0.8	0	2	0
Mn	TS EN ISO 7294-2	µg/L	50	20	0,5	15	0,1
Ni	TS EN ISO 7294-2	µg/L	20	0.38	0.01	0.96	0.01
Na	EPA 200.8	mg/L	0.1	18.13	6.08	22.14	4.03
Hg	EPA 200.8	µg/L	0.1	0.05	0	0.04	0

Table 3. Content of non-metals in drinking water

Non-Metals	Methods	Unit	Standard	2017		2018 (first period)	
				Max	Min	Max	Min
B	TS EN ISO 17294-2	mg/L	1	0.001	0	0	0
F	TS EN ISO 10304-1	mg/L	4	0.07	0.02	0.08	0.04
Cl	TS EN ISO 10304-1	mg/L	250	1.08	0.12	1.24	0.08
Free Cl	Hack	mg/L	=0.5	0.82	0.55	0.78	0.52
NH_4	Hack	mg/L	0.2	0.08	0.01	0.12	0.02
Ammonia Nitrogen (NH_3-N)	Hack	mg/L	0.2	0.1	0.01	0.1	0.01

Table 4. Content of some anions in drinking water

Anions	Methods	Unit	Standard	2017		2018 (first period)	
				Max	Min	Max	Min
Nitrate (NO_3)	TS EN ISO 10304-1	mg/L	0.5	0.1	0.01	0.13	0.01
Nitrit (NO_2)	TS EN ISO 10304-1	mg/L	3	-	-	-	-
Sulfat (SO_4)	TS EN ISO 10304-1	mg/L	250	-	-	-	-

Table 5. Different characteristics of drinking water

Others	Methods	Unit	Standard	2017		2018 (first period)	
				Max	Min	Max	Min
Blurs	Hack	NTU	<1	0.56	0.10	0.65	0.14
Conductivity		µS/cm	<2500	120	70	145	63
PH	SM 4500 H + B	-	6-9	7.9	7.4	8.1	7.3
Color	SM 2120 C	Pt-Co	<10	0	0	0	0
Temperature ºC	SM 2550 B	ºC	-	16	8	17	7
Suspended Solid	SM 2540 D	mg/L	-	-	-	-	-
Total Hardness	Hack	mg/L	°Fr	9.0	7.6	10.2	8.1

Table 6. Organic pollutants

Organic Agents	Methods	Unit	Standard	2017		2018 (first period)	
				Max	Min	Max	Min
Beta-Endosulfan	EPA 538	mg/L	>1	0	0	0.01	0
Benzo (a)antracene	EPA 538	mg/L	mg/L	0	0	0	0
Benzo (a) pyrene	EPA 538	mg/L	>1	0	0	0.01	0
Benzene	EPA 538	mg/L	>0.01	0	0	0	0
Bromodichloromethane	EPA 538	mg/L	>1<4	0	0	0	0
Carbaryl	EPA 538	mg/L	---	0	0	0	0
Fhenanthrene	EPA 538	mg/L	---	0.001	0	0	0

Table 7. Bacterial characteristics of drinking water

Bacterial analysis	Methods	Unit	Standard	2017		2018 (first period)	
				Max	Min	Max	Min
E-Koli	TS EN ISO 9308-1	kob/ 100ml	0	0	0	0	0
Enterococcus	TS EN ISO 7899-2	kob/ 100ml	0	0	0	0	0
Coliform Bacteria	SM 9222 D	kob/ 100ml	0	0	0	0	0
Colony Count 22°C	TS EN ISO 6222	kob/ml	<20	0	0	0	0
Total Coliform	TS EN ISO 9308-1	kob/ 100ml	0	0	0	0	0

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Table 8. Iodine in drinking water

Seasons	Methods	Unit	Standard	2017		2018 (first period)	
				Max	Min	Max	Min
Winter	TS EN ISO 10304-1	μg/L	4-18	3.01	1.08	Not Measured	Not measured
Spring	TS EN ISO 10304-1	μg/L	4-18	4.19	2.25	3.89	1.58
Summer	TS EN ISO 10304	μg/L	4-18	2.07	0.01	1.93	0.78
Autumn	TS EN ISO 10304	μg/L	4-18	1.08	0.14	1.74	0.22

Table 9. ADIW and HQ values for some hazardous metals in Kocaeli region

Heavy metals ions	ADIWing		HQ	
	2017	2018	2017	2018
Cd	0.029	0.057	58	114
Pb	22.8	57.1	651.4	325.7
Mn	57.1	42.8	40.7	30.5
Ni	10	27	500	135
Hg	1.4	1.1	1400	1100
Fe	3.7	3.1	123.3	103.3
Zn	0.28	2.8	0.93	9
Cu	34.2	31.4	85.5	78.5

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