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Quality of drinking water of Canakkale Province, Turkey

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Abstract

Concentrations of arsenic cadmium, copper, lead, and zinc in the first flush and post-first flush of tap water were determined. Further, the tap water was allowed to run at least 3 minutes and samples were analyzed for bacteriological quality. The analysis showed that Cd and Pb concentrations in the first and second forty samples collected were under the detection limits of the analytical method employed. The concentration ranges of As, Cu, and Zn in the first forty samples were 0.95-11.9 µg/L, 0.011-0.58, and 0.04-5.29 mg/L, respectively. Lower ranges of Cu and Zn levels of 0.010-0.343 and 0.008-4.546 mg/L, respectively, were found in the second forty samples. Total aerobic mesophilic bacteria, total coliform and *Escherichia coli* were detected in 28, 18 and 1 out of 40 water samples, respectively. Our results show that some of the water samples that contained high levels of bacterial colonies were collected from four buildings, situated at two faculties of the university, a cafeteria and a bakery. These findings indicate that the distribution system and drinking water of Canakkale needs improvement.

Keywords: Bacteriological quality, heavy metal, contamination, water quality.

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Çanakkale İçme Suyu Kalitesi

Özet

Açılır açılmaz ve belir süre akıtıldıktan sonra alınan musluk suyu örneklerinde arsenik, kadmiyum, bakır, kurşun ve çinko konsantrasyonları belirlenmiştir. Bununla birlikte musluk suyunun 3 dakika akıtılmasından sonra alınan su örneklerinin bakteriyolojik analizi yapılmıştır. Elde edilen sonuçlar, açılır açılmaz alınan 40 örnekte ve belli bir süre akıtıldıktan sonra alınan 40 örnekte Cd ve Pb konsantrasyonlarının çalışmada kullanılan analitik metodun deteksiyon limitinin altında olduğu görülmüştür. As, Cu ve Zn'nun konsantrasyon aralıkları sıra ile 0.95-11.9 µg/L, 0.011-0.58 ve 0.04-5.29 mg/L olarak bulunmuştur. Cu ve Zn'nun en düşük konsantrasyonları belli bir süre akıtıldıktan sonra alınan 40 örnekte saptanmış ve sıra ile 0.010-0.343 ve 0.008-4.546 mg/L olarak bulunmuştur. Bakteriyolojik analiz için alınan 40 örneğin 28'inde aerobik mezofilik bakteri, 18'inde coliform ve 1'inde *Escherichia coli* saptanmıştır. Yüksek seviyede bakteri kolonileri oluşturan örneklerin 2 fakülteden, 1 kafeteryadan ve 1 ekmek fırınından alındığı saptanmıştır. Bu sonuçlar, Çanakkale içme suyu ve şebekesinin iyileştirme gereksinimi olduğunu göstermiştir.

Anahtar Kelimeler: Bakteriyolojik kalite, ağır metal, kontaminasyon, su kalitesi.

Introduction

Pollution created by human activities is a consequence of urban life and increases in parallel with industrial development. Environmental pollution accelerated especially during the second half of the 20th century. Rapid industrial developments and use of chemicals in many industrial activities have resulted in contamination of many natural sources. Among these, contamination of the water sources has particular importance for human and environment health. Many natural and man-made activities pollute water sources and decrease the quality of the drinking water. Detecting and controlling contamination of water pollutants are important prerequisites for taking further precautionary measures to protect human health.

Natural impurities in drinking water arise from many factors. Snow and rainwater contain particulate mineral and some gaseous pollutants from the atmosphere and can affect impurity levels of drinking water (Weiner 2000). Besides such natural phenomena human activities such as industrial waste, petroleum discharges, agricultural application, fallout etc. also affect the type and level of water impurities. Because of its ability to dissolve many chemicals, water can retain and carry many pollutants such as organic materials, industrial wastes, petroleum derivatives, agricultural synthetic manures, detergents, radionuclides, pesticides, inorganic salts, chemical and organic synthetic materials (Calderon 2000).

Many nonessential elements from natural or artificial sources such as lead (Pb) are toxic to living organisms even in trace levels. On the other hand, high concentrations of essential elements are also toxic, while their deficiency can lead to health problems for humans. Such deleterious effects can manifest themselves as various types of cancers, adverse reproductive outcomes, cardiovascular disease, and neurological disease (Calderon 2000). At present, human populations could be exposed to high metal concentrations from different sources. One major source of such exposure is drinking water (Matte and Jacobs 2000). Heavy metals may enter drinking water via debris, geological formation, urban and rural run-off, drinking water distribution materials, and the drinking water treatment process (Calderon 2000). Furthermore, many materials resulting from corrosion or leaching of pipeline materials can enter potable water as chemical contaminants. Drinking water in houses can also be contaminated by corrosion of the plumbing materials used to supply the houses (Gardels and Sorg 1989).

Apart from many inorganic- and organic pollutants found in water, bacteriological pollution is another factor that affects water quality raising major health concerns. The contamination of natural water with fecal material, domestic and industrial sewage, and agricultural and pasture runoff is likely to result in increased risk of disease transmission to humans who consume these waters (Nogueira et al. 2003). Some waterborne disease carrying pathogens potentially indicated by the presence of coliform bacteria may cause infection, resulting in diarrhea, cramps, nausea, jaundice, headaches, and fatigue (EPA 2001). Although coliform organisms might not always be directly related to the presence of fecal contamination or pathogens in drinking water, the coliform test is still useful for monitoring the microbial quality of treated piped water supplies (Nogueira et al. 2003).

The main aim of this study was to check whether the heavy metals and bacteriological pollution levels comply with national and international standards for drinking water and to show whether metals and bacteriological pollution in the drinking water in Canakkale constitute a risk to public health. The results obtained will also contribute to the baseline data of heavy metal and bacteriological pollution in Canakkale, Turkey.

Materials and methods

Water samples were collected from 40 sampling stations attached to the main water system of Canakkale city center. Two different water samples were collected for comparison after standing overnight in water pipes using 500 ml capacity sterile bottles from each station, for determining content of As, Cd, Cu, Pb and Zn. The first samplings were done as soon as the tap was opened. The second samplings were done after the tap was allowed to run for 3 min. Thus, 80 drinking water samples, forty each of the first and second samples, were collected and analyzed for heavy metal levels. The field blank utilized was deionized water (18.2 M Ω cm^{-1}) which was treated as a sample and used for eliminating possible air contamination during sampling and to measure contamination from containers and reagents added to samples during the digestion procedure in the laboratory. Collected samples were acidified by adding 1 ml of concentrated HNO_3 for further analysis. Gloves were used during sampling and preparation of water samples for heavy metal analysis. In addition, all glassware were washed with detergent solution, three times rinsed by tap water, soaked in 6M HNO_3 for 2 days, rinsed five times with deionized water, dried and stored in polyethylene bags. All works were carried out in a specially designed fume cupboard.

A 100-ml water sample was placed in a beaker, 5 ml of concentrated HNO_3 was added and then the sample was evaporated using a hot plate until 2-3 ml of water remained. The concentrated sample was placed in a volumetric flask; subsequently, the material was diluted with deionized water to a final volume of 10 ml. The concentrations of Cd, Cu, Pb, and Zn were determined using ICP-AES, Varian *Liberty Series II* ICP-AES with *axially*- viewed plasma. The accuracy of measurements was checked using Trace Element in Drinking Water Standard A (CRM-TMDW-A). The difference between the certified and obtained values was insignificant and at a reasonable level. The certified, measured, recovery and RSD % values are presented in Table 1. The concentrations of metals in each sample were measured in triplicate and the results recorded were the mean values of these three measurements. Mean value of metals obtained for blank was deducted from concentration of metals measured for drinking water samples. All the relative standard deviations (RSD) for replicates were less than 5%. SPSS 10.0 for Windows was used for the data analysis.

Table 1. Results of certified reference material analysis (mg/L).

	Measured	Certified	Recovery, %	ᵃSD	ᵇRSD %
Al	0,117	0,120	0,97	0,0028	2,35
Cd	0,009	0,010	0,90	0,0004	4,80
Cr	0,022	0,020	1,08	0,0010	4,60
Cu	0,022	0,020	1,10	0,0007	2,80
Fe	0,087	0,090	0,97	0,0009	1,05
Mg	8,014	8,000	1,00	0,0842	1,05
Mn	0,039	0,040	0,97	0,0002	0,40
Ni	0,062	0,060	1,03	0,0010	1,70
Pb	0,017	0,020	0,85	0,0008	4,60
Zn	0,067	0,075	0,89	0,0023	3,45

[a] SD= Standard Deviation
[b] RSD=Relative Standard Deviation

Concentrations of As in the 80 drinking water samples were analyzed on a 757 VA Trace Analyzer. A gold electrode (ϕ = 3 mm) was used as the working electrode, while Ag/AgCl (KCl 3M) and platinum wire electrodes were selected as reference and counter electrodes, respectively. As_2O_3 was used for calibration of voltammetry. *Differential* pulse *anodic stripping voltammetry* (DPASV) was chosen for measuring As because of the low detection limits. Britton-Robinson (BR) (pH=8.50) buffer solution was used as supporting electrolyte for the stripping voltammetric measurements. For the determination of As, 10 mL of supporting electrolyte was transferred to the cell, the stirrer was switched on and the solution was degassed with pure nitrogen for 5 minutes. Subsequently, 10 ml of water sample was pipetted into the voltammetric cell and the mixture solution was degassed with pure nitrogen for 2 minutes. The pH of the mixture was adjusted to pH 8.50 using 0.2 M NaOH. The voltammograms were recorded after the accumulation period (of 60 s) at -1.2V.

Forty samples of tap water were analyzed once for bacteriological pollution according to EPA (EPA 2002). The samples were collected in sterilized 500-ml glass bottles containing 0.2 ml/L of sterile sodium thiosulfate ($Na_2S_2O_3$). The tap water was allowed to run at least 3 minutes and then the taps were closed and sterilized by a flame up to one minute. Subsequently, the mouth of a bottle was flamed and the water samples were then collected. All precautions were taken to prevent any bacteriological contamination occurring during sampling. The water samples after collection were brought to the laboratory without exposing them to daylight or heat and then stored in the refrigerator at the +4°C until analysis. The samples were subjected to bacteriological analysis within 12 hours. A Membrane Filtration (MF) system (Sartorius) is used for the bacteriological analysis of drinking water for many decades. This method enables the analysis of large-volume samples with low microbial counts (Wang and Fiessel 2008). The membrane filter system was sterilized in an autoclave at 121ºC for 20 min. 100 ml water samples were filtered using the Millipore membrane filters (0.45 μm) and nutrient pad sets (Standard Triphenyltetrazoliumchloride [Standard Triphenyltetrazoliumchloride (TTC, TMSartorius 14055) for total aerobic mesophilic bacteria and Tergitol TTC (TMSartorius 14056) for total coliform and E.coli] were moistened with sterile and demineralized water. The filters with the microorganisms were removed and placed on the nutrient pad and incubated at 36ºC for 24 hours, after which the culture medium was examined for the count of total aerobic mesophilic bacteria, total coliform, and *E.coli*. Brown-colored colonies were taken to represent total aerobic mesophilic bacteria in Standard TTC. Colonies that were yellow-orange and brown in color were taken to represent *E.coli* and total coliform, respectively, in Tergitol TTC.

Results and discussion

Heavy metals

Descriptive statistics of results obtained for heavy metals in the two sample types are presented in the Table 2. Pearson correlation analysis was applied to both the Cu- and Zn concentrations set of samples, and the results obtained are given in Table 3. The detection limits, calculated as three times the standard deviations of the blank measured ten replicates, of Cd, Cu, Pb, and Zn for the method employed were 0.003, 0.01, 0.02, and 0.004 mg/L, respectively, while the detection limit of As obtained by voltammetry was 0.5 μg/L. Levels of As, Cd, and Pb obtained from the supply reservoir in the first forty samples were below the detection limits of the instrument, while the concentrations of Cu and Zn were 0.024 and 0.05 mg/L, respectively.

Table 2. Descriptive statistics of heavy metals in the first and second sampled water samples and their permissible limits given by authorities.

		As (µg/L)	**Cd**(mg/L)	**Cu**(mg/L)	**Pb**(mg/L)	**Zn**(mg/L)
First forty samples	Mean	4.49	nd	0.065	nd	1.48
	Median	2.90	nd	0.021	nd	0.65
	[a]SD	3.19	nd	0.135	nd	1.64
	N	15	-	34	-	40
	Max	11.9	nd	0.584	nd	5.29
	Min	0.95	nd	0.011	nd	0.04
First forty samples	Mean	[b]nd	nd	0.023	nd	0.652
	Median	nd	nd	0.009	nd	0.256
	SD	nd	nd	0.056	nd	1.056
	N	-	-	19	-	38
	Max	nd	nd	0.343	nd	4.546
	Min	nd	nd	0.010	nd	0.008
	TS266[c]	10	0.05	2	0.01	-
	WHO[d]	10	0.003	2	0.01	-
	EPA[e]	10	0.005	1	0.02	5
	EU[f]	10	0.005	2	0.01	-

[a]SD is refer to standard deviation, [b]nd is less than the detection limit of the method employed.
[c] TS266 (2005), [d] WHO (2006), [e] EPA (2003), [f] EU (1998)

Table 3. Pearson correlation between Cu and Zn in the first and second sampling water.

		First forty samples		**Second forty samples**	
		Cu	Zn	Cu	Zn
First forty samples	Cu	1			
	Zn	-0.08	1		
Second forty samples	Cu	[a] 0.79	-0.18	1	
	Zn	-0.10	[a] 0.56	-0.09	1

[a]P< 0.01

As was detected in 37.5 % of the first forty samples and not detected in the second forty samples nor in the supply reservoir of the city. After excluding the highest value observed (that was above the maximum allowed by standards), the As concentrations observed were below the drinking water standards of TS266 (2005), WHO (2006), EPA (2003), and EU (1998). The EPA cautions that changes in water chemistry arising from the use of new sources can affect water quality of the distribution system, causing an increase in arsenic levels (EPA, 2007). Copeland et al. (2007) also indicate that iron-based solids, such as corrosion deposits present in the drinking water distribution system, have adsorptive properties and could therefore concentrate As and potentially release it back into the distribution system. The As content of solids collected from the drinking water system were significant. Significant amounts of As were even found in solids present in the systems that were exposed to relatively low concentrations of As (<10 µg/L) dissolved in the water (Copeland et al. 2007). This finding could explain the measurable concentrations of As in the first forty samples.

Cd contamination of drinking-water could be due to the presence of Cd as an impurity in the zinc of galvanized pipes or Cd-containing solders in fittings, water heaters, water coolers and taps (WHO 2004). All Cd concentrations of the first- and second forty samples were below the detection limit of the instrument (< 0.003 mg/L), which corresponds to the non-polluted natural waters whose Cd content is usually considerably lower than 1 µg/L (EPA, 2003).

The results obtained are in accordance with the findings of Tamasi et al. (2004), who found that all Cd concentrations in drinking water except one were below the detection limit of the method employed.

Because of the widespread use of copper pipes, drinking water could significantly contribute to the daily Cu intake (Nordberg et al. 2007). Cu was detected in 85 % of the first forty samples and 47.5 % of the second forty samples. The minimum and maximum concentrations of Cu were found to be 0.011-0.584 mg/L in the first forty samples and 0.010-0.343 mg/L in the second forty samples. The Cu concentrations were considerably lower in the second forty samples. In all except four samples among the first forty, the Cu concentrations were <0.079 mg/L. The highest concentration of Cu in the first forty samples was below the drinking water quality standards specified by the authorities. Consequently, it was concluded that no Cu contamination was found in the current study. This is in agreement with the findings of Asubiojo et al. (1997); Soylak et al. (2002); Tuzen and Soylak (2006), whose investigations of drinking water samples revealed low levels of Cu.

Pb is rarely present in the tap water because it originates from natural sources; to be more precise, it arises primarily from household plumbing systems that contain lead in the pipes, solder, and fittings or from the service connections to homes. Contrary to the findings of many studies which reported a high content of Pb in the first flush of drinking water (Gulson et al. 1994; Rajaratman et al. 2002), Pb was not detected in both sets of samples.

The EPA requires that Pb and Cu are regulated by a treatment technique that controls the system level of a contaminant in drinking water (EPA 2003). For Cu, the action level is 1.3 mg/L and for Pb is 0.015 mg/L. If more than 10% of tap water samples exceed the action level, water systems must take additional steps. In this study, none of the measurements was in excess of the action levels for Cu and Pb.

Zn was detected in all of the first forty samples and 95 % of the second forty samples. The minimum and maximum concentrations of Zn in the first forty samples were found to be in the ranges 0.04-5.29 mg/L and 0.008-4.55 mg/L, respectively. According to WHO (2006), drinking water containing Zn at levels above 3 mg/L may not be suitable for consumption. In this context, 22.5% of the first forty samples and 5 % of the second forty samples exceeded the value (3 mg/L) specified by WHO (2006). Despite the low Zn value in the supply reservoir (0.05 mg/L), these high values should be taken into consideration for public health purposes. Only one sample among the first forty contained Zn level above the EPA specified limit of 5 mg/L (EPA 2007). The difference between the concentrations of first- and fully flushed drinking water samples was discovered by Rajaratnam et al. (2002), who showed that Zn levels in first flush water were significantly higher than those in either post-first flush or fully flushed samples.

Comparison of the results of heavy metal content in our study with permissible limits specified by TS266 (2005), WHO (2006), EPA (2003), and EU (1998) shows that there was no significant contamination in the Canakkale water system, apart from two of the first forty water samples, one of Zn and the other of As. The Zn value exceeding the EPA's permissible limit was found in only one sample, representing 2.5% of all the samples tested. We conclude that this high value most probably arose from the design of the water system of the building. On the other hand, the low Zn level in the supply reservoir indicated that the higher concentrations of Zn in the drinking water were from other sources. Cu- and Zn levels in the first forty samples were significantly higher than those in the second forty samples ($p<0.05$, *t*-test).

Pearson correlation analysis showed that Cu levels of the first forty and second forty samples were significantly correlated ($p<0.01$). Similarly, Zn levels in the first forty and second forty samples also revealed significant correlation at the $p<0.01$ level. The results we obtained are in agreement with the findings of Rajaratnam et al. (2002). Elevated concentrations of Cu and Zn in tap water are usually due to corrosion of the pipes and plumbing (Asubiojo et al. 1997). These results suggest that differences in concentration between the two water samples collected from the same sampling stations originate from the water pipes and/or fittings. We conclude that standing time is an important factor in leaching Cu and Zn from the tap water distribution system.

Bacteriological analysis

The results of bacteriological analysis obtained from the drinking water samples are given in Table 4. In all the samples, total aerobic mesophilic bacteria counts in 100 mL varied between 0 and 1000, total coliform counts between 0 and 898, and *E.coli* colonies between 0 and 2. Total aerobic mesophilic bacteria were detected in 28 water samples (70 %), total coliform were found in 18 water samples (45 %), and 1 (2.5 %) water sample was contaminated with *E.coli*. The results obtained are in agreement with findings reported by Nogueira et al. (2003) and Chaidez et al. (2008), where they were observed that some samples of tap water were contaminated with *E.coli*. Similarly, Amanatidou et al. (2007) reported that total coliform, *E. coli* and total aerobic mesophilic bacteria of potable water samples collected in Western Macedonia exceeded the limits. Considering the TS266 (2005), WHO (2006) and EU (1998) water standard limits which refer to 0 colonies/100 mL for coliform and *E.coli*, these water samples were contaminated with the bacteria groups named. Besides, 2 colonies/100 mL of total aerobic mesophilic bacteria were also found in the Canakkale supply reservoir. According to WHO (2006), *E. coli* or thermotolerant coliform bacteria in treated water in the distribution system must not be detectable in a 100-mL water. The above findings indicate that the water supplied did not measure up to the required health standards with respect to bacteriological contamination. In this context, it can be concluded that the treatment procedures of the water in the supply reservoir need to be examined and additional treatment needs to be carried out by the municipality. On the other hand, no coliform bacteria contamination was found in the water sample collected from the water treatment station. However, up to 1000 bacterial colonies/100 mL were counted at locations away from the supply reservoir.

Table 4. Microbiological quality of the drinking water (colonies/100 mL)

Station number	Total aerobic mesophilic bacteria	Total coliforms	*Escherichia coli*
1	2	0	0
2	4	0	0
3	0	0	0
4	4	0	0
5	32	0	0
6	0	0	0
7	8	0	0
8	0	0	0
9	10	0	0
10	8	6	0
11	20	6	0
12	2	2	0
13	0	0	0
14	800	718	0
15	870	6	0
16	1000	898	0
17	32	0	0
18	0	0	0
19	0	0	0
20	118	38	2
21	10	8	0
22	10	6	0
23	700	652	0
24	480	434	0
25	4	0	0
26	420	180	0
27	0	0	0
28	0	0	0
29	52	28	0
30	176	62	0
31	134	126	0
32	170	4	0
33	0	0	0
34	0	0	0
35	2	0	0
36	8	6	0
37	0	0	0
38	0	0	0
39	106	12	0
40	4	0	0

The detection of *E. coli* contamination reveals that the water samples may be contaminated with feces or sewage water flowing into the drinking water. In addition, the presence of coliform bacteria could be indicative of the presence of other microorganisms (viruses, and protozoa) capable of causing serious illnesses. Traditionally, the presence of coliform bacteria in drinking water has been viewed as an indicator of fecal contamination through cross connections, inadequate treatment, or inability to maintain adequate residual concentration of disinfectant in the water distribution system. The higher level of bacteriological pollution in these stations might come from storage tanks and the aging water system of the buildings. Generally, some offices and buildings have water storage tanks for the storage of water as a precaution against the water scarcity in Canakkale. These tanks are mostly made of inappropriate materials, and are significant sources of pollutants. Our results show that some of the water samples that contained high levels of bacterial colonies were collected from four buildings, situated at two faculties of the university, a cafeteria and a bakery.

Conclusions

Summing up, no significant heavy metal contamination, in excess of national- and international standards, was found in the main water supply source of Canakkale province. Furthermore, heavy metal concentrations in the running water were lower than those found in the water stored for prolonged periods in the distribution system. Some water samples showed unacceptably high levels of bacteriological pollution according to TS266 (2005), WHO (2006) and EU (1998) water standards, probably as a result of problems in the water systems of specific buildings. Therefore, to ensure adequate public health protection, it is important to routinely monitor heavy metal concentrations and bacteriological pollution of the water in the supply reservoir to living units.

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