Health Risk Assessment for Trace Metals, Polycyclic Aromatic Hydrocarbons and Trihalomethanes in Drinking Water of Cankiri, Turkey

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Abstract: Lifetime exposure to trace metals, pesticides, polycyclic aromatic hydrocarbons (PAHs), trihalomethanes (THMs), and the other chemicals in drinking water through ingestion, and dermal contact may pose risks to human health. In this study, drinking water samples were collected from 50 sampling sites from Cankiri and its towns during 2010. The concentrations of all pollutants were analyzed, and then compared with permissible limits set by Turkish and WHO. For health risk assessment of trace metals, chronic daily intakes (CDIs) via ingestion and dermal contact, hazard quotient (HQ), and hazard index (HI) were calculated by using statistical formulas. For ingestion pathway, the maximum HQ values of As-non cancer in central Cankiri and Kursunlu town were higher than one. Considering dermal adsorption pathway, the mean and maximum HQ values were below one. HI values of As-non cancer in central Cankiri and Kursunlu town were also higher than one. Each trace metal (As-non cancer, B, Cd, Cr, Pb, and Sb) of the mean HI values were slightly below unity. Risks of As, PAHs, THMs, and benzene on human health were then evaluated using carcinogenic risk (CR). It is indicated that CRs of As and THMs were also found >10⁻⁵ in drinking water of Cankiri might exert potential carcinogenic risk for people. These assessments would point out required drinking water treatment strategy to ensure safety of consumers.

Keywords: Trace metal, Polycyclic aromatic hydrocarbons, Trihalomethanes, Drinking water, Risk assessment, Cancer.

Introduction

Supplying safe and good quality drinking water to humans has been the most important duty of all governments. Main drinking water pollutants are trace metals, pesticides, polycyclic aromatic hydrocarbons (PAHs), trihalomethanes (THMs) and the other organic chemicals such as benzene. The contamination of water with these pollutants is related to natural processes such as atmospheric deposition, erosion and mineral weathering as well as
anthropogenic activities such as urban, industry and agriculture is of great concern worldwide\textsuperscript{15}.

Firstly, the present study was conducted to investigate trace metal (As, B, Cd, Cn, Cr, Cu, Cl, Hg, Ni, Pb, Se, and Sn) concentrations of drinking water samples in Cankiri, Turkey. Some of these trace metals in drinking water as copper (Cu) are essentially required for normal body growth and functions of living organisms, while the high concentrations of other metals like arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), and lead (Pb) are considered highly toxic for human and animals\textsuperscript{6}. Prolonged periods of exposure of trace metals via ingestion, and dermal contact (i.e. showering, and bathing) of contaminated water can cause serious diseases such as, reproductive, cardiovascular and neurological diseases or various cancers\textsuperscript{7-9}.

Secondly, this study aimed to measure the levels of organophosphate or organochlorine pesticides in drinking water. These pesticides are currently used for agricultural and vector control purposes all over the world, and they contaminated soil, water, and air\textsuperscript{10}. Prolonged exposure to pesticides in humans can lead to severe disorders in reproductive, nervous and immune system and in can even lead to cancer\textsuperscript{11}.

Thirdly, this study was carried out to determine the levels of PAHs in the drinking water of Cankiri. Most PAHs polluted the water sources via anthropogenic inputs or biological conversion of the fossil fuel products. The presence of PAHs in drinking water represents a hazard to human health including mutagenic, carcinogenic and toxicological effects\textsuperscript{12}.

Fourthly, in the present study, it was investigated the contents of THMs and chemical pollutants in drinking water samples. The surface and groundwater always contains pathogenic microorganisms. Disinfection using such as chlorine is essential to protect the public from waterborne diseases and to ensure the water quality during water distribution. However, chlorine reacts with natural organic matters and/or inorganic substances in water to form various chlorination by-products such as THMs, and the others\textsuperscript{13}. In several epidemiological studies, these THM species are considered as probable carcinogens for humans\textsuperscript{14}. Other chemical pollutants such as benzene, 1,2-di / tri / tetra / chloroethane, epichloridine, vinyl chloride, and acrylamide have been reported in drinking water, which are suspected to be human carcinogens. These chemicals used in water treatment and drinking water storage and distribution components such as pipes, joining and sealing materials\textsuperscript{15}.

Several methods have been proposed to estimate the potential health risks of pollutants in drinking water, dividing the effects into non-carcinogenic and carcinogenic. Non-carcinogenic risk assessments are typically based on the use of the hazard quotient (HQ), a ratio of the estimated dose of a contaminant to the dose level below which there will not be any appreciable risk (Reference dose, RfD). On the other hand, carcinogenic risks (CRs) assessments are the incremental probability of an individual developing any type of cancer over a lifetime due to carcinogenic exposure\textsuperscript{16}.

In this study, the HQ values for ingestion route and dermal absorption, and HI were calculated to evaluate the non-carcinogenic health effects of trace metals in drinking water. Furthermore, this study aimed to ascertain the potential health risk of PAHs, THMs and the other organic chemicals with carcinogenic risks in Cankiri, Turkey.

**Experimental**

The chemical dataset of 50 different waterworks were obtained from the Health Directorate of Cankiri for this study. Drinking water samples were collected from central Cankiri and towns during 2010. Samples were collected from residential tap water according to correct sampling techniques to analyze their chemical contents.
All filtered and acidified water samples were analyzed for trace metals (Cd, Cr, Cu, Hg, Ni, Pb, Se, Sn) using Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES) (Varian Vista, Australia). As concentration in samples was measured using atomic absorption spectrophotometer (Perkin Elmer HGA 700, USA). B was analyzed by using Ion Chromatography technique (Dionex DX-600, USA). CN was analyzed colorimetrically (Hach DR/2500 Spectrophotometer, USA). In view of data quality assurance, each sample was analyzed in triplicate and after every 10 samples two standard; one blank and another of 2.5 μg/L of respective metal were analyzed on atomic absorption. The reproducibility was found to be at 95% confidence level. Therefore, the average value of each water sample was used for further interpretation.

The determination of level of pesticides such as, organophosphates (azinphos-methyl, azinphos-ethyl, demethon, diazinon, disulfoton, ethion, malathion, parathion-ethyl, parathion-methyl, methamidophos, chlorpyrifos-ethyl, chlorpyrifos-methyl) or organochlorines (hexachlorobenzene-HCB, α-/γ-hexachlorocyclohexane (HCH), heptachlor, aldrin, heptachlor epoxide, dieldrin, β-endosulfane, total dichlorodiphenyl trichloroethane-DDT) in drinking water was performed by using gas chromatography [HP Agilent 6890N series II - USA, with nitrogen–phosphorus (GC-NPD and electron capture detector (GC-EC)] with the USEPA Method 507 and 508, respectively.

The levels of PAHs including benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[g,h,i]perylene (B[g,h,i]P), indeno[1,2,3-cd]pyrene (I[cd]P), benzo[a]pyrene (B[a]P) were investigated in the samples of drinking water. Analyses have been performed by high performance liquid chromatography with fluorescence detection- HPLC/FD (Shimadzu LC-10 HPLC and RF-10AXL Shimadzu fluorescence detector, Japan) with the USEPA Method 550.

The most dominant THM compounds are chloroform (CHCl₃), bromodichloromethane (CHBrCl₂), dibromochloromethane (CHBr₂Cl) and bromoform (CHBr₃) in Cankiri drinking water. THM and benzene, 1,2-di/tri/tetra/ chloroethane, acrylamide concentrations were determined by gas chromatography with electron capture detector (GC-ECD, HP Agilent 6890N series II – USA), using EPA Method 551. Other chemical pollutants (epichloridine, vinyl chloride) in drinking water samples were measured by purge and trap GC/MS (HP Agilent 6890N series II – USA), using EPA Method 524.2.

All these analyses were performed in the laboratory of the Refik Saydam National Public Health Agency at Ankara, Turkey. The all data were analyzed descriptive statistically by software program (SPSS 15.0 for Windows).

Human Health Risk Assessment

1. Chronic Daily Intake (CDI) Indices

In the risk assessments, CDI of contaminants in drinking water are estimated from different exposure scenarios through ingestion¹⁷, inhalation and dermal contact pathways¹⁸. In this paper, the basic equations for ingestion and dermal contact pathways are provided.

**Oral Exposure (Ingestion)**

CDI through ingestion of some trace metals, PAHs, THMs and benzene with drinking waters are typically predicted¹⁷ as:

\[
CDI_{ing} = \frac{C_w \times IR \times EF \times CF1}{BW \times AT}
\]  

(1)
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(1) \[CDI_{ing} = \text{chronic daily intake via ingestion (mg/kg day)}, \ Cw = \text{concentration of As in drinking water (μg/L)}, \ IR = \text{drinking water ingestion rate (L/day)}, \ EF = \text{exposure frequency (days/year)}, \ ED = \text{exposure duration (year)}, \ BW = \text{body weight (kg)}, \ AT = \text{averaging time (days)}, \ \text{and} \ CF1 = \text{mass conversion factor from μg to mg (0.001).}\]

**Dermal Contact Exposure**

CDI from some trace metals exposure with drinking water through dermal contact can be estimated as:

\[
CDI_{derm} = \frac{Cw \times SA \times Kp \times ET \times EF \times ED \times CF1 \times CF2}{BW \times AT}
\]

(2) \[CDI_{derm} = \text{chronic daily exposure dose through dermal contact of water (mg/kg day)}, \ Cw = \text{concentration of As in drinking water (μg/L)}, \ SA = \text{drinking water exposed skin area (cm²)}, \ Kp = \text{dermal permeability coefficient (cm/hr)}, \ ET = \text{exposure time during bathing and shower (min/day)}, \ EF = \text{exposure frequency (days/year)}, \ ED = \text{exposure duration (year)}, \ BW = \text{body weight (kg)}, \ AT = \text{averaging time (days)}, \ CF1 = \text{mass conversion factor from μg to mg (0.001)}, \ \text{and} \ CF2 = \text{unit conversion factor (L/1,000 cm³) (0.001). According to USEPA database Kp values are 1.10^{-3} \text{ cm/hr for As, Cd, Cu, Se and Sb; 2.10^{-3} cm/hr for Cr; 1.3.10^{-4} cm/hr for Pb; and 2. 10^{-4} cm/hr for Ni}.\]

2. **Hazard Quotient (HQ) and Hazard Index (HI) Indices**

The HQ (ingestion and dermal contact) and HI for non-carcinogenic risk of some trace metals in drinking water can be calculated using Eqs. (3), (4), and (5). If the HQ exceeds 1, there might be concern for non-carcinogenic effects. To evaluate the total potential non-carcinogenic risks posed by more than one pathway, the hazard index HI was introduced, which was the sum of the HQs from all applicable pathways. HI > 1 indicated a potential for an adverse effect on human health or the necessity for further study.

\[
HQ_{ing} = \frac{CDI_{ing}}{RfD}
\]

(3)

\[
HQ_{derm} = \frac{CDI_{derm}}{RfD}
\]

(4)

\[
HI = HQ_{ing} + HQ_{derm}
\]

(5)

(3), (4), (5) \[CDI_{ing} = \text{chronic daily intake via ingestion \times 10^{-3} (μg/kg day)}; \ CDI_{derm} = \text{chronic daily exposure dose through ingestion of water (μg/kg day)}; \ RfD = \text{the reference dose of the contaminant (μg/kg day)}. \text{The ingestion reference dose (RfD}_{ing}\) values were obtained from the USEPA\textsuperscript{21}. The RfD\textsubscript{ing} was multiplied by a gastrointestinal absorption factor (ABSg) to yield the corresponding dermal absorption reference dose (RfD\textsubscript{derm})\textsuperscript{19}.\]
3. Carcinogenic Risk (CR) Indices

Carcinogenic risks through ingestion of PAHs, THMs and benzene with drinking waters are typically predicted by the following equation using Eq. (6)\(^6\). Under most regulatory programs, a CR value over 1.00E-05 indicates potential carcinogenic risk\(^2\).

\[
CR = CD_{\text{ing}} \times SF
\]  

(6) \([CD_{\text{ing}} = \text{chronic daily intake via ingestion (mg/kg day)}; SF = \text{the carcinogenic slope factor of the contaminant (mg/kg/day)}]^{14}\)

Results and Discussion

A large variability in concentrations of trace elements has been observed in drinking water samples of Cankiri. Results of Cankiri centre and its towns are summarized in Table 1, together with the Turkish Imperative\(^22\) and WHO Guideline\(^15\) values for drinking water. Table 1 shows that the toxic elements as Hg occur at very low concentrations, mostly below detection limits in the studied drinking water samples. The highest As values were detected in Kursunlu town (mean, 10.47 \(\pm\) 12.91; ranged <1.0\(^d\)-37.3 \(\mu g/L\)), significantly higher than the upper value (10 \(\mu g/L\)) set in accordance with legislations\(^15,22\) (\(d\) identified below detection limits of the method). The values of central Cankiri [maximum value (MaxV) 12.5 \(\mu g/L\), Cerkes (MaxV 9.45 \(\mu g/L\), and Orta (MaxV 8.15 \(\mu g/L\) were slightly below that limits. Concentrations of As in drinking water samples were found to be ranging between 10 and 50 \(\mu g/L\) in 22 points and >50\(\mu g/L\) in 5 stations of Aksaray in Turkey\(^3\). B concentrations in Kizilirmak town’s samples analyzed were found to range from 130 to 1050 \(\mu g/L\) (mean, 417.5 \(\pm\) 428), significantly higher than the limits of Turkish (1000 \(\mu g/L\)) and WHO (500 \(\mu g/L\)) recommended values for drinking water\(^15,22\). It is followed by recorded in central Cankiri (MaxV 360 \(\mu g/L\) and Kursunlu (MaxV 230 \(\mu g/L\). Cöl and Cöl\(^23\) found higher B levels in waters of Kutahya-Turkey resulted from rich boron mine areas. The highest Sb concentrations were found in samples from Korgun town (mean, 2.65 \(\pm\) 2.18; ranged <2.0\(^d\)-5.60 \(\mu g/L\)) followed by those determined in Bayramoren town (MaxV 3.0 \(\mu g/L\) and Sabanozu town (MaxV 2.5 \(\mu g/L\). The maximum Sb value of Korgun town was exceeded according to legislation of Turkish and WHO (5 \(\mu g/L\))\(^15,22\). The highest Pb concentrations were determined in Orta town (mean, 3.32 \(\pm\) 4.63; ranged <7.0\(^d\)-10.20 \(\mu g/L\), significantly higher than the limit of WHO (10 \(\mu g/L\)) recommended values for drinking water\(^15\). The levels of Pb in Korgun town (mean, 6.19 \(\pm\) 2.39; ranged <7.0\(^d\)-8.70 \(\mu g/L\) were slightly below the recommended limit of WHO\(^15\). Cd values of Yapraklı town were ranged from 0.36 to 3.38 \(\mu g/L\) (mean, 2.18 \(\pm\) 1.64), the maximum value of it significantly higher than the limit according to legislation of WHO (3 \(\mu g/L\))\(^15\). Significant higher values of Cd and Pb were detected specifically in samples of Korgun and Yapraklı towns attributed to the storage and distribution system of drinking water in these towns.

In the risk assessment process, IR, EF, ED, BW, AT, and SA were calculated according to the data of local residents obtained from the Ministry of Health of the People’s Republic of Turkey, and they directly adapted from the reference values of USEPA\(^24\). The mean values of population parameters are shown in Table 2.
| Location Metal | Central Cankiri n° = 8 | Atkaralar n° = 3 | Bayramoren n° = 1 | Cerkes n° = 4 | Eldivan n° = 2 | Ilgaz n° = 2 | Kızılirmak n° = 4 | Korgun n° = 4 | Kursunlu n° = 7 | Orta n° = 6 | Sabanozu n° = 4 | Yapralı n° = 5 |
|----------------|------------------------|------------------|-------------------|---------------|---------------|--------------|------------------|---------------|------------------|-------------|----------------|----------------|
| As | ±SD | 8.03 ± 2.88 | <1.0d | <1.0d | 5.44 ± 3.78 | 1.37 ± 1.24 | <1.0d | 1.67 ± 1.52 | 1.6 ± 1.33 | 10.47 ± 12.91 | 2.16 ± 1.34 | 1.11 ± 1.44 | 1.87 ± 2.97 |
| TRa = 10 | WHOb = 10 | Range | 3.36-12.50 | <1.0d | <1.0d | <1.0d | <1.0d | <1.0d | <1.0d | <1.0d | <1.0d | <1.0d |
| B | ±SD | 220 ± 96 | 120 ± 23 | <60d | 140 ± 39 | <60d | 417.5 ± 428 | 94 ± 98 | <60d | 74 ± 73 | 3.01 | 3.39 |
| TRa = 1000 | WHOb = 500 | Range | <60d | 90-130 | <60d | 80-160 | <60d | 130-1050 | <60d | 60d | 200 |
| Cd | ±SD | 1.18 ± 0.94 | <1.4d | 2.0 | <1.4d | <1.4d | 0.55 | <1.4d | <1.4d | <1.4d | <1.4d | <1.4d | 1.64 |
| TRa = 5 | WHOb = 3 | Range | <1.4d | 2.0 | <1.4d | <1.4d | 0.55 | <1.4d | <1.4d | <1.4d | <1.4d | <1.4d | 3.38 |
| CN | ±SD | 9.55 ± 5.63 | <7.0d | <7.0d | <7.0d | <7.0d | <7.0d | <7.0d | <7.0d | <7.0d | 1.13 ± 2.24 | <7.0d |
| TRa = 50 | WHOb = 50 | Range | <7.0d | <7.0d | <7.0d | <7.0d | <7.0d | <7.0d | <7.0d | <7.0d | 1.13 ± 2.24 | <7.0d |
| Cr | ±SD | 4 ± 2 | <3.0d | <3.0d | <3.0d | 3.0d | 6.50 ± 3.11 | 3.50 ± 1.91 | 9.50 ± 2.94 | 110.6 ± 240 | |
| TRa = 2000 | WHOb = 2000 | Range | 1-6 | <3.0d | <3.0d | <3.0d | <3.0d | <3.0d | <3.0d | 15.2 | 3.0d | 3.0d |
| Hg | ±SD | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d |
| TRa = 1 | WHOb = 1 | Range | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d | <0.2d |
| Ni | ±SD | 5.57 ± 3.7d | <3.7d | <3.7d | 7.33 ± 3.90 | 4.65 ± 3.48 | <3.7d | <3.7d | <3.7d | <3.7d | 4.91 ± 2.73 |
| Definition                          | Units    | Mean     |
|------------------------------------|----------|----------|
| Ingestion rate (IR)                | L/day    | 2        |
| Exposure frequency (EF)            | day/year | 365      |
| Exposure duration (ED)             | year     | 70       |
| Body weight (BW)                   | kg       | 90       |
| Average time (AT)                  | day      | 25550    |
| Skin surface area (SA)             | cm²      | 18000    |
| Exposure time during bathing and shower (ET) | h/event | 0.25     |

*Adapted from USEPA*[^24].

[^24]: Adapted from USEPA.
Considering significantly and slightly important concentration of trace metal in drinking water samples of Cankiri (Table 3), the HQ and HI values are calculated. The reference dose (RfD), HQs (ingestion and dermal contact) and HI for non-carcinogenic risk of some trace metals in drinking water of Cankiri are listed in Table 4. In this study, the mean and the maximum values were used as high-end estimates in the risk characterization. In general, if HQ or HI value is greater than one, it indicates potential adverse health effects and needs for further study. For ingestion pathway, the maximum HQ values of As-non cancer in central Cankiri (1.190) and Kursunlu (3.352) town were higher than one. These trace metal of the mean HQ values (ranged 1.057E-01–9.970E-01) were slightly below unity (As-non cancer: Cerkes, Orta, Sabanozu, Yapraklı; Cd: Bayramoren, Yapraklı; Pb: Korgun; and Sb: Bayramoren, Korgun). Considering dermal adsorption pathway, the mean and maximum HQ values were also below one. Only, the maximum HQ value of Kursunlu for As-non cancer was slightly below unity (1.345E-01). On the other hand, HI values of As-non cancer in central Cankiri (maxV, 1.235) and Kursunlu (mean, 1.347; maxV, 3.686) town were higher than one. These results indicate that measured trace metals in drinking water may pose little health risk for local consumers through ingestion and dermal contact, except As for central Cankiri and Kursunlu town.

Table 3. The most important water quality variables for each location of Cankiri, Turkey.

| Location            | Important variables | Slightly important variables |
|---------------------|---------------------|-----------------------------|
| Cankiri Centre      | As                  | B, Cd, Cr, Ni, Se           |
| Atkaracalar         | -                   | -                           |
| Bayramoren          | -                   | Cd, Sb                      |
| Cerkes              | -                   | As, B                       |
| Eldivan             | -                   | -                           |
| Ilgaz               | -                   | Ni, Se                      |
| Kizilirmak          | B                   | As, Ni                      |
| Korgun              | Sb                  | Ni, Pb                      |
| Kursunlu            | As                  | B                           |
| Orta                | Pb                  | As                          |
| Sabanozu            | -                   | As, Sb                      |
| Yaprakli            | Cd                  | As, B, Cu, Ni, Se           |

Table 5 shows that the concentration of pesticides, PAHs, THMs and benzene in drinking water samples of Cankiri. All organophosphate and organochlorine pesticides, bromoform as THM, other chemical pollutants (1,2-di/tri/tetra–chloroethane, acrylamide, epichloridine and vinyl chloride) occur at very low concentrations, mostly below detection limits in drinking water samples of Cankiri. The PAH concentrations were in the range of <0.0003–0.0329 μg/L, while the mean values of central Cankiri (0.00695 ± 0.00875 μg/L), Kizilirmak (0.0151 ± 0.00219 μg/L), Korgun (0.01645 ± 0.00050 μg/L), and Kursunlu (0.00826 ± 0.0118 μg/L) were slightly below than the limits of Turkish (0.1 μg/L) and WHO (0.2 μg/L) recommended values for drinking water.15,22 On the other hand, the highest mean THM levels (ranged <1.0–38.926 μg/L) were found in Atkaracalar, Orta, Sabanozu, and central Cankiri (13.235 ± 8.259; 9.86 ± 14.79; 6.34 ± 11.60; 6.322 ± 4.119, respectively), whereas
those measured values were slightly below than the recommended limits of Turkish (150 μg/L)\textsuperscript{22}. The benzene content of the samples was in the range of <0.1–0.799 μg/L. The measured mean benzene levels were in central Cankiri, Ilgaz, Yapraklı, and Kursunlu (0.337 ± 0.041; 0.295 ± 0.008; 0.119 ± 0.118; 0.081 ± 0.213, respectively), while those values were not exceeded according to legislation of Turkish (1 μg/L) and WHO (10 μg/L)\textsuperscript{15,22}. The study results showed that people living in Cankiri have not the health risk due to the pesticides, PAHs, THMs and benzene exposure in drinking water.

Cancer risk (CR) can be defined as the upper bound lifetime probability of an individual’s developing cancer because of exposure to a potential carcinogen. The range of carcinogenic risks acceptable or tolerable by the US EPA was 10–6 to 10–4 \textsuperscript{19}. In this paper, the CDI equations for ingestion pathway are used to ascertain the potential health risk of these pollutants (PAHs, THMs and benzene) with CRs. Furthermore, the CR values over 1.00E-05 are estimated as an indicator for potential carcinogenic risk.

The carcinogenic risk assessment indicated (Table 4) that As was the most important pollutant in central Cankiri (mean CI 1.564E–04), Cerkes (mean CI 1.051E–04), and Kursunlu (mean CI 2.023E–04), similar to the result compared to water drinking guidelines (Table 1). It is known that long time absorption of arsenic can cause cancers of liver, lung, bladder, kidney and skin, and other adverse health effects including hypertension, neuropathy, diabetes, shin lesions, and cardiovascular and cerebrovascular diseases\textsuperscript{25}. Therefore, special attention should be paid to arsenic in drinking water for local residents particularly for the sensitive children, and measures needed to be taken for sustaining the healthy aquatic ecosystem.

The estimated cancer risks from exposure to PAHs through ingestion for Cankiri and its towns are shown in Table 6. The overall cancer risks have been predicted to be in the range of non-detectable (ND) to 5.40E–07. In a recent study, CR values of PAHs were all lower the 1.00E-05 for ingestion pathway, too\textsuperscript{4}. The obtained results indicate that the CR values of PAHs in all water samples were lower than 1.00E-05 indicating that PAHs cause no adverse biological effects.

Results in Table 7 show that the values of investigated drinking water of Cankiri ranged from ND to 8.27E-06 for the THMs with the mean. Considering the carcinogenic health risk, the maximum values of central Cankiri were higher than 1.00E-05 for CHBr2Cl (1.27E-05) and for CHBrCl2 (2.15E-05). Furthermore, the maximum CR values of central Cankiri, Atkaracalar, Cerkes, Kursunlu, Orta, and Sabanozu were also higher than 1.00E-05 for total THM (4.03E-05, 1.05E-05, 1.44E-05, 1.74E-05, 1.38E-05, 1.90E-05; respectively). These results showed that total THM pose little cancer risk to Cankiri residents through ingestion exposure. The higher TSM concentrations with CR assessment were also reported in drinking water in Istanbul, Turkey\textsuperscript{26} and 19 cities of Canada\textsuperscript{5}, before.

There was no important high CR value for benzene in drinking water samples in Cankiri (Table 7), indicating no adverse health effects and potential carcinogenic concern. The risk assessments at above, chronic daily intakes (CDI) of contaminants are estimated from different exposure scenarios, which are multiplied by the slope factors\textsuperscript{14} to obtain CRs (Table 8).
| Trace Metal   | Location            | HQ\text{ing} | Max       | HQ\text{derm} | Max       | HI=ΣHQs | Cancer Risk |
|--------------|---------------------|--------------|-----------|---------------|-----------|----------|-------------|
|              |                     | Mean         | Max       | Mean          | Max       | Mean     | Max         |
| As-cancer (1500/3660) | Cankiri Centre     | 1.529E-04    | 2.381E-04 | 2.257E-06     | 3.513E-06 | -        | -           |
|              | Cerkes              | 1.036E-04    | 1.798E-04 | 1.528E-06     | 2.653E-06 | -        | -           |
|              | Kizilirmak         | 2.895E-05    | 7.428E-05 | 4.271E-07     | 1.096E-06 | -        | -           |
|              | Kursunlu           | 1.994E-04    | 7.104E-04 | 2.942E-06     | 1.048E-05 | -        | -           |
|              | Orta                | 4.114E-05    | 1.552E-04 | 6.071E-07     | 2.290E-06 | -        | -           |
|              | Sabanozu           | 2.114E-05    | 5.733E-05 | 3.113E-07     | 8.459E-07 | -        | -           |
|              | Yapraklı           | 3.561E-05    | 6.457E-05 | 5.254E-07     | 9.527E-07 | -        | -           |
|              |                     | Mean         | Max       | Mean          | Max       | Mean     | Max         |
| As-noncancer (0.3/0.285) | Cankiri Centre     | 7.645E-01    | 1.190     | 2.898E-02     | 4.511E-02 | 7.934E-01 | 1.235       |
|              | Cerkes              | 5.180E-01    | 8.990E-01 | 1.962E-02     | 3.407E-02 | 5.376E-01 | 9.330E-01  |
|              | Kizilirmak         | 1.447E-02    | 3.714E-01 | 5.484E-03     | 1.407E-02 | 1.818E-02 | 3.855E-01  |
|              | Kursunlu           | 9.970E-01    | 3.552     | 3.778E-02     | 1.345E-01 | 1.347    | 3.686       |
|              | Orta                | 2.057E-01    | 7.760E-01 | 7.796E-03     | 2.941E-02 | 2.135E-01 | 8.054E-01  |
|              | Sabanozu           | 1.057E-01    | 2.866E-01 | 3.997E-03     | 1.086E-02 | 1.097E-01 | 2.975E-01  |
|              | Yapraklı           | 1.781E-01    | 3.228E-01 | 6.747E-03     | 1.189E-02 | 1.848E-01 | 3.347E-01  |
| B (90/-)    | Cankiri Centre     | 6.984E-02    | 1.142E-01 | -             | -         | 6.984E-02 | 1.142E-01  |
|              | Cerkes              | 4.444E-02    | 5.079E-02 | -             | -         | 4.444E-02 | 5.079E-02  |
|              | Kizilirmak         | 1.325E-01    | 3.333E-01 | -             | -         | 1.325E-01 | 3.333E-01  |
|              | Kursunlu           | 2.984E-02    | 7.301E-02 | -             | -         | 2.984E-02 | 7.301E-02  |
|              | Yapraklı           | 2.349E-02    | 6.349E-02 | -             | -         | 2.349E-02 | 6.349E-02  |
| Cd (0.5/0.025) | Cankiri Centre     | 6.743E-02    | 1.143E-01 | 3.035E-03     | 5.144E-02 | 7.046E-02 | 1.657E-01  |
|              | Bayramoren         | 1.143E-01    | 1.143E-01 | 5.144E-02     | 5.144E-02 | 1.657E-01 | 1.657E-01  |
| Element   | Location            | RfD<sub>mg</sub> (μg/kg day) | RfD<sub>derm</sub> (μg/kg day) | Cancer Slope Factor |
|-----------|---------------------|-------------------------------|---------------------------------|---------------------|
| Cr (3<sup>g</sup>/0.075<sup>h</sup>) | Cankiri Centre       | 9.095E-02                    | 3.774E-02                     |                     |
| Cu (40<sup>g</sup>/8<sup>h</sup>)   | Yaprakli             | 7.900E-02                    | 1.184E-04                     |                     |
| Ni (20<sup>g</sup>/0.8<sup>h</sup>) | Cankiri Centre       | 8.952E-05                    | 5.027E-03                     |                     |
| Pb (1.4<sup>g</sup>/0.42<sup>h</sup>) | Korgun               | 6.883E-06                    | 1.154E-05                     |                     |
| Se (5<sup>g</sup>/0.15<sup>h</sup>) | Cankiri Centre       | 2.240E-02                    | 2.033E-02                     |                     |
| Sb (0.4<sup>g</sup>/0.06<sup>h</sup>) | Bayramoren           | 4.000E-01                    | 4.060E-01                     |                     |

<sup>g</sup> RfD<sub>mg</sub> (μg/kg day),  <sup>h</sup> RfD<sub>derm</sub> (μg/kg day),  <sup>i</sup> - " indicate that a cancer slope factor or RfD has not been established.
Table 5. Concentration of pesticides, PAHs, THMs and benzene in drinking water samples from central Cankiri and its towns, Turkey (µg/L).

| Location      | Cankiri Centre n=8 | Atkaracalar n=3 | Bayramoren n=1 | Cerkes n=4 | Eldivan n=2 | Ilgaz n=4 | Kizilirmak n=4 | Korgun n=4 | Kursunlu n=7 | Orta n=6 | Sabanozu n=4 | Yaprakli n=5 |
|---------------|---------------------|------------------|-----------------|------------|-------------|-----------|----------------|-----------|--------------|-----------|-------------|-------------|
| **Organochlorine pesticides** | TR=0.5 WHO<sup>p</sup>=10 | | | | | | | | | | | | |
| χ±SD<sup>e</sup> | <0.01<sup>d</sup> | <0.01<sup>d</sup> | <0.01<sup>d</sup> | <0.01<sup>d</sup> | <0.01<sup>d</sup> | <0.01<sup>d</sup> | <0.01<sup>d</sup> | <0.01<sup>d</sup> | <0.01<sup>d</sup> | <0.01<sup>d</sup> | <0.01<sup>d</sup> | <0.01<sup>d</sup> | |
| Rang e | | | | | | | | | | | | | |
| **Total PAHs** | TR=0.1 WHO<sup>p</sup>=0.2 | | | | | | | | | | | | |
| χ±SD<sup>e</sup> | 0.00695 ± 0.00055 | 0.0077 ± 0.00205 | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | 0.0151 ± 0.00219 | 0.01645 ± 0.00118 | 0.00826 ± 0.00764 | 0.00423 ± 0.00064 | 0.00488 ± 0.01376 | 0.00052 ± 0.00055 | |
| Rang e | | | | | | | | | | | | | |
| **B[b]F** | | | | | | | | | | | | | |
| χ±SD<sup>e</sup> | 0.00088 ± 0.0006 | 0.0004 ± 0.00158 | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | 0.0004 ± 0.00176 | 0.0004 ± 0.00019 | 0.00021 ± 0.00014 | 0.00012 ± 0.00015 | 0.00038 ± 0.00016 | 0.00014 ± 0.00026 | <0.0003<sup>d</sup> ± 0.0003<sup>d</sup> | |
| Rang e | | | | | | | | | | | | | |
| **B[k]F** | | | | | | | | | | | | | |
| χ±SD<sup>e</sup> | 0.00062 ± 0.0004 | <0.0003<sup>d</sup> | 0.0004 ± 0.0006 | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | 0.0011 ± 0.00021 | 0.0015 ± 0.00057 | 0.0004 ± 0.00008 | <0.0003<sup>d</sup> ± 0.0003<sup>d</sup> | <0.0003<sup>d</sup> ± 0.0003<sup>d</sup> | |
| Rang e | | | | | | | | | | | | | |
| **B[ghi]P** | | | | | | | | | | | | | |
| χ±SD<sup>e</sup> | 0.0010 ± 0.0004 | 0.0003 ± 0.0006 | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | 0.0005 ± 0.00019 | 0.0012 ± 0.00108 | 0.0006 ± 0.00005 | 0.0026 ± 0.00004 | 0.00435 ± 0.00052 | <0.0003<sup>d</sup> ± 0.0003<sup>d</sup> | |
| Rang e | | | | | | | | | | | | | |
| **I [cd]P** | | | | | | | | | | | | | |
| χ±SD<sup>e</sup> | 0.00009 ± 0.00001 | 0.00010 ± 0.00004 | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | <0.0003<sup>d</sup> | |
| Substance          | Mean ± SD | Rang ± SD | WHO | TR | e |
|--------------------|-----------|-----------|-----|----|---|
| Benzene            | 0.0019 ± SD | <0.0003<sup>d</sup> | 0.0019 | 10 | 1 |
| CHBrCl             | 0.0014 ± SD | <0.0003<sup>d</sup> | 0.0006 | 22 | 1 |
| CHBrCl             | 0.0003 ± SD | <0.0003<sup>d</sup> | 0.0004 | 22 | 1 |
| CHCl               | 0.0010 ± SD | <0.0003<sup>d</sup> | 0.0006 | 22 | 1 |
| TR                 | 0.0026 ± SD | <0.0003<sup>d</sup> | 0.0062 | 22 | 1 |
| Total trihalometans | 0.0002 ± SD | <0.0003<sup>d</sup> | 0.0042 | 22 | 1 |
| B[a]P              | 0.0003 ± SD | <0.0003<sup>d</sup> | 0.0004 | 22 | 1 |
| TR<sup>a</sup>     | 0.00059 ± SD | <0.0003<sup>d</sup> | 0.00007 | 22 | 1 |
| WHO<sup>b</sup>    | 0.0018 ± SD | <0.0003<sup>d</sup> | 0.0010 | 22 | 1 |
| TR<sup>c</sup> ≥ 150 | 4.119 ± SD | 13.235 ±<sup>1.0</sup> | 0.366 | 3 | 1 |
| CHCl<sub>3</sub>   | 3.892 ± 10.776 ±<sup>1.0</sup> | 2.002 ±<sup>1.0</sup> | 1.809 ±<sup>1.0</sup> | 8.195 ±<sup>1.0</sup> | 4.478 ±<sup>1.0</sup> |
| CHBr<sub>2</sub>Cl | 1.324 ± 1.087 ±<sup>1.0</sup> | 1.291 ±<sup>1.0</sup> | 0.501 ±<sup>1.0</sup> | 0.629 ±<sup>1.0</sup> | 0.629 ±<sup>1.0</sup> |
| CHBrCl<sub>2</sub> | 2.247 ± 5.306 ±<sup>1.0</sup> | 1.453 ±<sup>1.0</sup> | 1.093 ±<sup>1.0</sup> | 1.293 ±<sup>1.0</sup> | 1.641 ±<sup>1.0</sup> |
| Benzene            | 0.337 ± 0.041 ±<sup>1.0</sup> | 0.295 ±<sup>1.0</sup> | 0.081 ±<sup>1.0</sup> | 0.0012 ±<sup>1.0</sup> | 0.0012 ±<sup>1.0</sup> |

<sup>a</sup> Imperative values established by Turkish legislation for drinking water<sup>14</sup>. <sup>b</sup> Guideline values established by the World Health Organization for drinking water<sup>15</sup>. <sup>c</sup> The number of water sample, <sup>d</sup> Below detection limits of the method, <sup>e</sup> Mean ± SD.
### Table 6. Cancer Risk assessment for PAHs in the drinking water samples of central Cankiri and its towns, Turkey.

| Location         | B[b]F Mean | B[b]F Max | B[k]F Mean | B[k]F Max | B[ghi]P Mean | B[ghi]P Max | I[cd]P Mean | I[cd]P Max | B[a]P Mean | B[a]P Max | ΣPAHs Mean | ΣPAHs Max |
|------------------|------------|-----------|------------|-----------|---------------|-------------|-------------|------------|-------------|-----------|-------------|-----------|
| Cankiri Centre   | 5.76E-09   | 2.63E-08  | 4.07E-09   | 7.88E-08  | 1.27E-09      | 6.24E-09    | 6.37E-09    | 1.27E-07   | 9.20E-08    | 5.52E-07  | 1.09E-07    | 7.90E-07  |
| Kizilirmak      | 5.91E-09   | 1.75E-07  | 7.23E-09   | 7.88E-09  | 6.70E-09      | 7.62E-09    | ND          | ND         | 1.74E-07    | 5.81E-07  | 1.94E-07    | 7.50E-07  |
| Korgun           | 2.73E-08   | 2.83E-08  | 9.86E-08   | 1.25E-07  | 7.10E-09      | 7.69E-09    | ND          | ND         | 4.07E-07    | 5.59E-07  | 5.40E-07    | 7.20E-07  |
| Kursunlu         | 3.68E-09   | 9.02E-09  | 2.63E-09   | 7.88E-09  | 4.36E-09      | 1.93E-08    | 6.51E-09    | 2.10E-08   | 3.35E-08    | 1.18E-06  | 5.07E-08    | 2.01E-06  |
| Orta             | 2.63E-09   | 6.66E-09  | ND         | ND        | 1.71E-09      | 9.00E-09    | 6.66E-09    | 1.91E-08   | 1.84E-07    | 6.57E-07  | 4.05E-07    | 6.92E-07  |
| Sabanozu         | ND         | ND        | ND         | ND        | 2.86E-09      | 9.53E-09    | 4.14E-09    | 1.38E-08   | 2.63E-08    | 7.88E-08  | 3.33E-08    | 8.11E-08  |

\(^{3)}\) not determined.

### Table 7. Cancer Risk assessment for THMs and benzene in the drinking water samples of central Cankiri and its towns, Turkey.

| Location         | CHCl\(_3\) Mean | CHCl\(_3\) Max | CHBr\(_3\) Mean | CHBr\(_3\) Max | CHBr\(_2\)Cl Mean | CHBr\(_2\)Cl Max | CHBrCl\(_2\) Mean | CHBrCl\(_2\) Max | ΣTHMs Mean | ΣTHMs Max | Benzene Mean | Benzene Max |
|------------------|-----------------|---------------|-----------------|---------------|-------------------|-----------------|-----------------|-----------------|------------|-----------|--------------|-------------|
| Cankiri Centre   | 1.11E-06        | 6.13E-06      | ND\(^{3)}\)     | ND            | 3.18E-06         | 1.27E-05        | 3.98E-06        | 2.15E-05        | 8.27E-06    | 4.03E-05  | 5.22E-07     | 5.67E-07    |
| Atkaracalar      | 3.01E-06        | 5.68E-06      | ND              | ND            | ND                | ND              | 4.35E-06        | 4.84E-06        | 7.36E-06    | 1.05E-05  | ND           | ND          |
| Cercyes          | 5.72E-07        | 1.51E-06      | ND              | ND            | 3.10E-06         | 7.22E-06        | 2.57E-06        | 5.69E-06        | 6.24E-06    | 1.44E-05  | ND           | ND          |
| Ilgaz            | ND              | ND            | ND              | ND            | ND                | ND              | ND              | ND              | ND         | ND        | 4.57E-07     | 4.65E-07    |
| Kursunlu         | 5.17E-07        | 2.91E-06      | ND              | ND            | 1.20E-06         | 4.74E-06        | 1.93E-06        | 9.77E-06        | 3.65E-06    | 1.74E-05  | 1.25E-07     | 8.74E-07    |
| Orta             | 2.34E-06        | 7.91E-06      | ND              | ND            | 2.29E-06         | 5.91E-06        | 4.11E-06        | 1.38E-05        | 0.78E-07    | 1.24E-06  | ND           | ND          |
| Sabanozu         | 1.28E-06        | 4.65E-06      | ND              | ND            | 1.51E-06         | 4.55E-06        | 2.90E-06        | 9.81E-06        | 5.69E-06    | 1.90E-05  | ND           | ND          |
| Yaprakli         | ND              | ND            | ND              | ND            | ND                | ND              | ND              | ND              | ND         | ND        | 1.85E-07     | 5.05E-07    |

\(^{3)}\) not determined.
Table 8. Human health toxicological data for PAHs, THMs and benzene\textsuperscript{14}.

| Compounds          | USEPA Slope factor (SF) [mg/kg/day]\textsuperscript{-1} |
|--------------------|------------------------------------------------------|
| B(p)F              | 0.23                                                 |
| B(k)F              | 0.23                                                 |
| B(ghi)P            | 0.023                                                |
| I(cdP              | 0.23                                                 |
| B(aP)              | 2.3                                                  |
| CHCl\textsubscript{3} | 0.01                                                |
| CHBr\textsubscript{3} | 0.0079                                               |
| DBCM               | 0.0084                                               |
| BDCM               | 0.062                                                |
| Benzene            | 0.055                                                |

Conclusion

This study estimated human health and cancer risk through exposure to trace metals, pesticides, PAHs, THMs and the other organic chemicals in drinking water for regions of Cankiri, Turkey. The concentrations of As, B, Cd, Pb and Sb were higher than their respective permissible limits in drinking water samples. The health risk assessments like CDI and HQ\textsubscript{mg} indices indicated that the As, B, Cd, F, Pb and Sb levels in drinking water is not safe for human consumption, while HQ\textsubscript{dern} indices indicated the only As levels is dangerous. In addition, the carcinogenic risk assessment indicated that As is the most important trace metal in drinking water of Cankiri, Turkey. Therefore, it suggested that, the water from contaminated sites should not be used for drinking without treatment and Government of Turkey may provide drinking water alternatives to these areas. Investigating the all the cancer risk assessment for pesticides, PAHs, and the other organic chemicals concentrations, there is no chronic health risk for assumption. However, the results show that THMs in drinking water of Cankiri might exert potential carcinogenic risk for local residents. Concentration of THMs can be reduced by improving pretreatment processes in the water supply systems and/or introducing alternative disinfectants, which often require trade off studies between risk and cost. Health and carcinogenic risk assessments may be a very useful tool to reveal the true meaning and relevance of pollutants in drinking water. These results can be useful for guiding the researchers to perform risk assessments from exposure to pollutants trough drinking water and giving the consumers information on the safety of the water supplied to them for domestic purposes.

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