ELSEVIER

A health risk assessment for exposure to trace metals via drinking water ingestion pathway

Pınar Kavcar[a,1], Aysun Sofuoglu[b], Sait C. Sofuoglu[b,*]

[a]*Environmental Engineering M.Sc Program, İzmir Institute of Technology, Gülbahçe, Urla, 35430 İzmir, Turkey*
[b]*Department of Chemical Engineering and Environmental Research Center, İzmir Institute of Technology, Gülbahçe, Urla, 35430 İzmir, Turkey*

Abstract

A health risk assessment was conducted for exposure to trace metals via drinking water ingestion pathway for Province of İzmir, Turkey. Concentrations of 11 trace metals were measured in drinking waters collected from 100 population weighted random sampling units (houses). The samples were analyzed in atomic absorption spectrometry for arsenic, and inductively coupled plasma-optical emission spectrometry for Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn. Questionnaires were administered to a participant from each sampling unit to determine drinking water consumption related information and demographics. Exposure and risks were estimated for each individual by direct calculation, and for İzmir population by Monte Carlo simulation. Six trace metals (As, Cr, Cu, Mn, Ni, and Zn) were detected in $>50\%$ of the samples. Concentrations of As and Ni exceeded the corresponding standards in 20% and 58% of the samples, respectively. As a result, arsenic noncarcinogenic risks were higher than the level of concern for 19% of the population, whereas carcinogenic risks were $>10^{-4}$ for 46%, and $>10^{-6}$ for 90% of the population.

Introduction

Although some metals such as iron (Fe), copper (Cu), manganese (Mn), and zinc (Zn) are essential for living organisms at specific concentrations, toxic effects are observed when concentrations increase. Ingestion of drinking water containing significant amounts of metals may result in adverse health effects varying from shortness of breath to several types of cancers (Cantor, 1997; Calderon, 2000; Xia and Liu, 2004; Dogan et al., 2005). One of the most hazardous trace metals found in drinking waters is arsenic being both toxic and carcinogenic. Long term intake of arsenic (As) may give rise to skin lesions at concentrations $\leqslant 50\,\mu g/l$ (WHO, 2001). Arsenic was also reported to cause cancers of the skin, lung, bladder, and other internal organs along with numerous noncancer diseases (Tsai et al., 1999; Ritter et al., 2002).

The major source of arsenic and other trace metals, in general, is chemical weathering of rocks. Furthermore, trace metals may accumulate in water bodies as a result

*Corresponding author. Tel.: +90 232 750 6648; fax: +90 232 750 6645.

E-mail addresses: cemilsofuoglu@iyte.edu.tr, saitcemil@iit.edu (S.C. Sofuoglu).

[1]Current address: Department of Chemical Engineering, İzmir Institute of Technology, Gülbahçe, Urla, 35430 İzmir, Turkey.

of industrial wastewater discharges and atmospheric deposition. Other important sources of trace metals include smelters and mines (Cantor, 1997), agricultural runoff (Ritter et al., 2002), leakage into the groundwater supplies from heavily contaminated areas, and geothermal waters (Buchet and Lison, 2000). Corrosion of household plumbing systems is also an important source of trace metals found in tap waters (Calderon, 2000; Tamasi and Cini, 2004). Significant levels of trace metals may be detected after stagnation of the water in distribution systems, especially during night-time (van Dijk-Looijaard and van Genderen, 2000; Seifert et al., 2000).

The concentrations of trace metals reported in drinking waters usually lie well below standards as in the examples of EPA Region V (Thomas et al., 1999), Maryland, USA (Ryan et al., 2000), South Tuscany, Italy (Tamasi and Cini, 2004), and Shanghai, China (Xu et al., 2006). However, arsenic concentrations as high as 36.7 and 40 μg/l have been detected in Arizona, USA (O'Rourke et al., 1999) and Chilean (Caceres et al., 2005) tap waters, respectively. Health risk levels associated with trace metals in Arizona drinking water were reported for the ingestion pathway (Sofuoglu et al., 2003); 90th percentile noncarcinogenic risk values were less than the respective acceptable levels for As, Cd, and Ni, whereas the median, mean, and 90th percentile carcinogenic risks for arsenic were all $> 10^{-6}$. Although concentrations of some of the trace metals have been measured in tap and surface waters in Turkey (Divrikli and Elci, 2002; Soylak et al., 2002; Gülbahar and Elhatip, 2005), exposure and associated health risk levels of the Turkish population have not been investigated.

It was suspected that drinking waters in İzmir may contain high trace metal levels due to several factors: (1) There are a number of industrial zones with a variety of industries around City of İzmir. (2) High atmospheric trace metal concentrations were measured in İzmir (Odabasi et al., 2002). Therefore, atmospheric deposition may be a source of surface water contamination. (3) İzmir is located on a land of long extinct volcanoes, with vast areas of lava ground suitable for agriculture, and there are high thermal activity areas such as hot springs and thermal baths, in and around the city (Ulman et al., 1998). (4) Metal (galvanized iron) pipes were widely used in water distribution systems in Turkey. (5) Although drinking water in the metropolitan area is mainly provided from surface waters, ground waters are also used both in the city and throughout the province. Therefore, the objectives of this study were set as to measure the concentrations of trace metals in İzmir drinking waters, determine demographics and drinking water consumption levels of İzmirians, and estimate the individual and population based exposure and associated risk levels for Province of İzmir.

Materials and methods

Study area

İzmir, the third largest province in Turkey with a population of approximately 3.5 million, is located on the Aegean Sea shore (Fig. 1). The majority of the population resides in the metropolitan area where drinking water is supplied by İzmir Metropolitan Municipality from Tahtalı Dam as the primary source. Balçova Dam and several groundwater wells are the secondary sources (see Fig. 1). As observed during this study, bottled spring water consumption is widespread amongst metropolitan İzmirians due to concerns about the quality of the tap water.

Sampling design and questionnaires

Drinking water samples taken from drinking water treatment plant effluents or points throughout the waterworks may not represent the level of exposure to trace metals accurately because water may be enriched/contaminated until it reaches the consumer tap, or use of bottled water may be overlooked. Therefore, 100 houses were visited in different districts of İzmir to collect drinking water samples from consumer taps or other sources (generally bottled water) in order to estimate the exposure and risk levels for İzmir population associated with ingestion of trace metals in drinking water. A population weighted random sampling was used. The number of samples to be collected from each district in the province was calculated according to the geographical population distribution (Fig. 1). Houses (sampling units) to be visited in each district were selected randomly on the day of sampling.

For each sampling unit, one person was requested to be the primary participant, and administer the questionnaires.
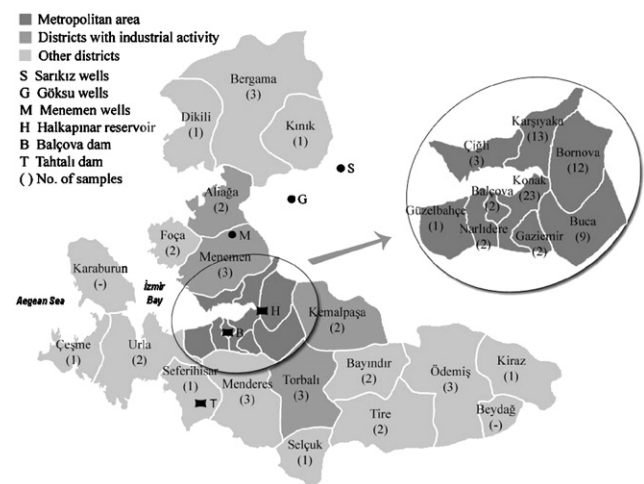

Fig. 1. Location of Province of İzmir, its districts, and sample sizes.

The first questionnaire, which inquired about demographics of occupants, was administered by the authors during the visit. The participant was asked to declare personal information such as body weight (BW), gender, age, education and income level, and homeland information, as well as information on the drinking water such as type and source. The second questionnaire was self-administered by the primary participant, for 7 consecutive days starting on the day of the visit. The participant was asked to count the number of standard glasses (200 ml) of water consumed during each day at home and away from home (e.g., at work) separately, remember the numbers before going to sleep, and fill it in the corresponding fields in the questionnaire. However, since contaminant levels were not measured in water drunk away from home, exposure away from home was estimated by assuming equal concentrations at home and away. Dietary exposure due to use of drinking water in hot or cold beverages and food items such as soups was not determined. The questionnaires used in this study were modified from the Baseline, Descriptive and Time – Activity Questionnaires used in the National Human Exposure Assessment Survey (NHEXAS) – Arizona study (Lebowitz et al., 1995) taking the lifestyle of Turkish people into consideration (Kavcar, 2005).

Drinking water sampling

For all analyses, cleaning, and sampling procedures, trace organic and chemical free MilliQ water (Millipore Elix 5) and high-purity solvents were used. All glassware and HDPE bottles (Sigma) were washed once with tap water and three times with MilliQ water and were kept in 20% nitric acid bath (Merck 65%) for at least 3 h. After being dried in the hood at room temperature, the HDPE bottles were tightly capped.

In each sampling unit, the primary participant was asked about the main drinking water source, and samples were accordingly collected from tap or other sources. Tap water samples were collected after 3-min flushing. The flow rate was reduced before sampling, and the samples were filtered (0.45 µm, Schleicher and Schuell) into 60-ml HDPE bottles. Bottled water samples were directly taken from containers and filtered. Five drops of 1:3 diluted nitric acid (Fluka, >69%) was added to acidify the sample (pH < 2). All samples were transported to the laboratory in cooled containers and stored in the fridge at 4 °C until analyses. Blanks and replicates were collected for over 10% of the samples.

Analytical methods

Drinking water samples were analyzed for 11 trace metals. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was used for the analyses of beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, vanadium, and zinc, whereas arsenic analyses were performed by atomic absorption spectrometry (AAS).

ICP-OES (Perkin-Elmer, Optima 2100 DV) was calibrated daily with a certified standard solution (Merck ICP Multi-element standard solution XIII). The R^2 value of the calibration curve was > 0.99 for each trace metal. The calibration was checked after every 15 samples using a control solution and if the deviation was $> 10\%$, the device was recalibrated. Repeatability was checked with the calibration check solution and the deviation was found to be $< 10\%$. The following analytical wavelengths were used for analysis: Be, 234.861 nm; Cd, 228.802 nm; Co, 228.616 nm; Cr, 267.716 nm; Cu, 224.700 nm; Mn, 257.610 nm; Ni, 221.648 nm; Pb, 220.353 nm; V, 292.464 nm; Zn, 213.857 nm. Method detection limit for each trace metal was calculated as 0.05 µg/l for Be, 0.35 µg/l for Cd, 0.44 µg/l for Co, 0.28 µg/l for Cr, 0.93 µg/l for Cu, 0.10 µg/l for Mn, 3.32 µg/l for Ni, 2.49 µg/l for Pb, 2.01 µg/l for V, and 3.90 µg/l for Zn.

For a better detection limit, arsenic was analyzed by AAS (Thermo Elemental Solar M6 Series) with an air–acetylene burner. Arsenic concentrations were determined by hydride generation atomic absorption spectrometry (HGAAS) method using hollow cathode lamps at 193.7 nm wavelength as described by Yersel et al. (2005). The operating conditions for the HGAAS system are listed in Table 1. The instrument detection limit for this system was 0.05 µg/l.

Statistical methods

Since all trace metals were not detected in all drinking water samples, concentration data had to be censored to avoid overestimation of population exposure and risk. A robust method (Helsel, 1990) was used to censor the data. Probability distributions were fitted to the detected concentrations of each metal. Values were generated by randomly sampling from BDL section of the fitted distribution, and randomly assigned to the nondetects.

Statistical analyses were performed using SPSS (Release 12.0); Monte Carlo simulations were performed using Crystal Ball (v 4.0e). Monte Carlo

Table 1. HGAAS operating conditions

Carrier gas	N_2
Carrier gas flow rate	200 ml/min
HCl concentration	0.12 M
HCl flow rate	6.1 ml/min
NaBH$_4$ concentration	1% (m/v) stabilized with 0.1% (m/v) NaOH
NaBH$_4$ flow rate	3.0 ml/min

simulation is a computer-based method of analysis that uses statistical sampling techniques in obtaining a probabilistic approximation to the solution of a mathematical equation or a model (USEPA, 1997). For each variable in an equation, the possible values are defined with a probability distribution. The probability distributions were determined by fitting distribution functions to measured/surveyed data by the help of goodness-of-fit tests which were chi-square, Kolmogorov–Smirnov, and Anderson–Darling (AD) tests. The fitting process was as follows: (1) determine the best fitting distribution according to AD test, (2) check if any of the remaining two tests show the same distribution as the best fitting, (3) if yes, proceed with the identified distribution, if no, repeat the process with the second best fitting distribution according to AD test. The beta, exponential, gamma, normal, lognormal, logistic, pareto, and Weibull distributions were considered. Definition of the distribution functions can be found elsewhere (Oracle, 2007). The simulation software is used in fitting distributions, which provides values of the test statistics, and allows the user to determine the best fitting distribution. These probability distributions are used as the input distributions for exposure model parameters. During a single trial, values are randomly selected according to the defined distribution for each uncertain variable and then the output of the model is calculated. If a simulation is run for 10,000 trials, 10,000 forecasts (or possible outcomes) are calculated compared to the single outcome obtained in the deterministic approach. Exposure and risk distributions of İzmir population were estimated using the simulated values ($n = 10,000$).

Kruskal–Wallis and Mann–Whitney tests were used to determine whether the concentrations of trace metals found in drinking water and risk associated with exposure to these trace metals differed across population subgroups. The Kruskal–Wallis test was applied to the data sets with more than two subgroups to test the null hypothesis that all subgroups have identical distribution functions against the alternative hypothesis that at least two of the samples differ only with respect to location (median), if at all. On the other hand, Mann–Whitney test was used to test for difference between the medians of two subgroups. In this study, p-values < 0.05 were considered to indicate a significant difference between the compared subgroups.

Exposure and risk assessment

In order to estimate the daily exposure of an individual, USEPA (2005) suggests the Lifetime Average Daily Dose (LADD) as the exposure metric. The following equation is a similar representation of daily exposure for ingestion route modified from USEPA (1992) and Chrostowski (1994):

$$CDI = \frac{C \times DI}{BW}, \tag{1}$$

where CDI is the chronic daily intake (mg/kg/d), C is the drinking water contaminant concentration (mg/l), DI is the average daily intake rate of drinking water (l/d), and BW is body weight in (kg). Deterministic exposure assessment involved using Eq. (1) to estimate individual exposures to each trace metal.

Cancer risk associated with ingestion exposure is calculated using the following equation (Patrick, 1994):

$$R = CDI \times SF, \tag{2}$$

where R is the excess probability of developing cancer over a lifetime as a result of exposure to a contaminant (or carcinogenic risk), CDI is the chronic daily intake (mg/kg/d), and SF is the slope factor of the contaminant $(mg/kg/d)^{-1}$.

To estimate noncarcinogenic risk, the hazard quotient (HQ) is calculated using the following equation (USEPA, 1999):

$$HQ = \frac{CDI}{RfD}, \tag{3}$$

where RfD is the reference dose (mg/kg/d). SF and RfD values employed in this study were obtained from the USEPA (IRIS, 2005).

Results and discussion

Trace metal concentrations

Concentrations of trace metals found in İzmir drinking water ranged from BDL to 2319 µg/l (Zn). At least one trace metal was detected in all of the drinking water samples. The maximum number of trace metals detected in a single sample was nine ($n = 1$). Four to seven trace metals were detected in the majority (84%) of the samples. The detection frequency of the analyzed contaminants, in descending order, were nickel (97%), arsenic (89%), manganese (83%), zinc (75%), copper (68%), chromium (53%), cobalt (29%), vanadium (26%), lead (15%), beryllium (13%), and cadmium (2%). Taking 50% detection frequency as the lower limit, exposure and risk assessment was carried out only for 6 of the 11 trace metals (As, Cu, Cr, Mn, Ni, and Zn).

Trace metal concentrations, except for As and Ni, were below the WHO guideline values (WHO, 2004) and Turkish (Ministry of Health, 2005), American (USEPA, 2002a, b), and European (SI No.:439, 2000) standards. Descriptive statistics of trace metal concentrations after censoring are presented in Table 2 along with the parameter values of the fitted probability distributions,

AD statistic values, and rank of the selected distribution by all three goodness-of-fit tests. Arsenic concentration exceeded the standard level of 10 μg/l in 20% of the drinking water samples; considering both carcinogenic and noncarcinogenic effects of arsenic, it can be classified as the most hazardous among the studied contaminants. In addition, attention should be paid to Ni since the Turkish standard of 20 μg/l was exceeded in 58% of the samples.

Median and mean values for As, Cr, Cu, and Zn concentrations lie within the range of concentrations reported in the literature (O'Rourke et al., 1999; Thomas et al., 1999; Seifert et al., 2000; Divrikli and Elci, 2002; Sofuoglu et al., 2003; Tamasi and Cini, 2004; Gülbahar and Elhatip, 2005; Xu et al., 2006). In the case of Mn, the mean concentration obtained in this study was about seven times smaller than the value reported by Thomas et al. (1999). This number would drop to five if only the mean Mn concentrations of flushed tap water samples were taken into consideration for both studies. In the same manner, Tamasi and Cini (2004) measured a very high concentration in a spring water that is approximately 9 times and 1.7 times the measured maximum concentrations in this study in nontap and tap samples, respectively. Ni concentrations found in İzmir drinking waters were the highest (O'Rourke et al., 1999; Thomas et al., 1999; Divrikli and Elci, 2002; Sofuoglu et al., 2003; Tamasi and Cini, 2004). In short, inclusion of drinking water sources other than tap water would play an important role in characterization of population exposure.

Information gathered from questionnaires was used in statistical tests in order to determine whether trace metal concentrations in drinking water samples differed across subgroups in İzmir population. The questionnaire data were summarized elsewhere (Kavcar et al., 2006). Population subgroups were investigated in six categories; gender, area, water source, education level, homeland, and income level. Mann–Whitney test results revealed that the concentration of trace metals did not differ between the gender categories ($p > 0.5$). Each district of İzmir was placed in one of the following subgroups: (1) metropolitan area in which tap water is supplied by İzmir Metropolitan Municipality, and (2) other districts (Fig. 1). Ni concentrations found in metropolitan area were significantly less than those in other districts (Fig. 2a). For the other trace metals, the differences were not significant. The drinking water source of each participant was classified as (1) tap water or (2) nontap water, which included purchased bottled water, water pumped from private wells, and water collected into bottles from close-by springs. Thirty-five percent of the participants, overall, consumed nontap water among which 80% was bottled water. The percent of bottled water use was found as 36% in the metropolitan area. All trace metals, excluding Ni,

Table 2. Descriptive statistics of metal concentrations in İzmir drinking water

Metal	Minimum	Median	Mean	S.D.	90th percentile	95th percentile	Maximum	Fitted distribution	Distribution parameters	AD**	Rank** AD	KS	CS
Arsenic	9.72E−05	1.15	6.47	10.91	24.24	34.85	46.00	Gamma	Scale: 17.09, shape: 0.3782*	1.77	1	1	1
Chromium	0.08	0.39	1.30	2.62	2.86	4.10	21.30	Lognormal	Mean: 1.15, S.D.: 2.08	2.83	1	2	1
Copper	6.99E−04	2.37	7.66	12.05	23.64	38.05	59.76	Gamma	Scale: 16.47, shape: 0.4649*	0.76	2	1	2
Manganese	0.02	0.57	1.95	3.82	5.49	7.99	27.68	Lognormal	Mean: 2.15, S.D.: 8.05	0.64	2	1	2
Nickel	2.68	23.30	31.37	42.82	68.39	95.15	388.4	Lognormal	Mean: 30.03, S.D.: 29.57	0.87	1	1	2
Zinc	0.01	56.24	150.3	295.8	431.5	713.2	2318	Gamma	Scale: 434.33, shape: 0.3460*	0.31	1	1	1

$N = 100$, all concentrations are in μg/l. *Location = 0.00. **AD: Anderson–Darling, KS: Kolmogorov–Smirnov, CS: Chi-square test.
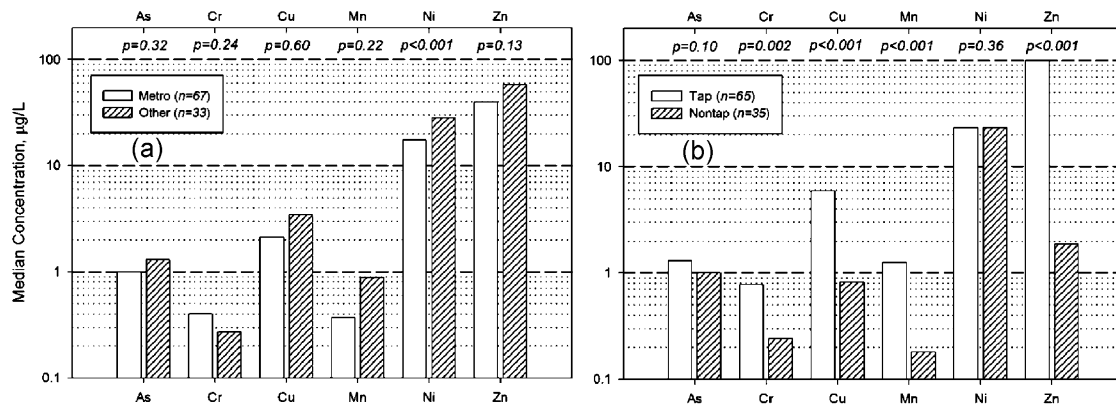
Fig. 2. Comparison of median trace metal concentrations for (a) area and (b) source categories (*p*-values indicate Mann–Whitney test results)

were detected in higher concentrations in tap water (Fig. 2b). The differences were significant at the selected significance level except for As. The difference was significant at $\alpha = 0.10$ for As.

When concentration data were stratified according to area, it was revealed that arsenic concentrations in nontap water were higher than in tap water in other districts as opposed to metropolitan area. Data showed that outside the metropolitan area, where tap water is supplied by local municipalities, lower levels of arsenic were present in tap water. Median arsenic concentrations in tap water were 2.90 μg/l for metropolitan area and 1.30 μg/l for other districts. In addition, nontap water arsenic concentrations in other districts (median = 1.50 μg/l) were higher than those in metropolitan area (median = 0.95 μg/l). This was due to the fact that in metropolitan area most of the nontap samples (83%) were commercial bottled waters containing small amounts of arsenic, and that in other districts, use of water pumped from private wells or water from close-by springs was more frequent (40%).

The median arsenic concentration for İzmir tap water was lower than the concentrations reported by Sofuoglu et al. (2003) for Arizona. For İzmir nontap water, on the other hand, greater values were calculated for both median and mean arsenic concentrations. In the case of Cr, median and mean concentrations in Arizona (Sofuoglu et al., 2003) were higher than those found in İzmir tap and nontap waters. However, Ni was detected in much higher levels in İzmir for both drinking water sources.

All trace metal concentrations measured in the surface water used as the source of drinking water in Yatagan (Demirak et al., 2005) were below the WHO recommended levels. Cu, Mn, and Ni concentrations in İzmir tap water were compared with the values reported by Soylak et al. (2002) for Yozgat, Turkey which is located in central Anatolia 800 km away from İzmir. Mean Cu

and Mn concentrations found in this study were almost 18 and 5 times greater than those calculated for Yozgat tap water, respectively. Ni was not detected in any of the Yozgat tap water samples.

Education level was investigated in three subgroups; (1) up to high school, (2) high school graduate, and (3) technical school/college graduate. Results of Kruskal–Wallis tests presented in Table 3 show that the differences in concentrations were significant only for Cu, subgroup-1 being the highest, and subgroup-3 the lowest. Although there were participants with homelands of seven different geographical regions, the majority were from three regions. Therefore, statistical tests were applied to only these homeland subgroups due to sample size limitations: (1) Aegean Region, (2) Central Anatolia Region, and (3) Eastern Anatolia Region. Across these subgroups, Cr concentrations were significantly higher for Eastern Anatolia Region compared to the other subgroups. No significant difference was observed for the rest of the trace metals. In order to determine the income level of a household, monthly income of each individual living in that house was summed up. The income level was examined in three subgroups; (1) low, 0–600 YTL; (2) medium, 600–2000 YTL, and (3) high, >2000 YTL (1 USD = 1.30 YTL). For As, Cr, Mn, and Ni, the concentrations did not differ across these subgroups. However, the concentrations for Cu and Zn were significantly lower for the high-income subgroup.

Average daily intake rate and body weight

The number of standard (200 ml) glasses of water drunk per day for 7 consecutive days in the week of sampling was reported by the participants in the second questionnaire. Then, these data were converted into liters and averaged to calculate individual DI. The fitted

Table 3. Results of Kruskal–Wallis tests on subgroups for metal concentrations

Category	Education level	Homeland	Income level
Subgroups	Up to high school/high school graduate/technical school or college	Aegean/Central Anatolia/ Eastern Anatolia	0–600 YTL/600–2000 YTL/2000+ YTL
Sample sizes	34/30/36	63/12/15	34/55/11
p-values			
Arsenic	0.908	0.363	0.314
Chromium	0.058	*0.035*	0.575
Copper	*0.002*	0.234	*0.002*
Manganese	0.156	0.483	0.415
Nickel	0.327	0.935	0.254
Zinc	0.069	0.154	*0.018*

p-values in *italics* indicate significant difference.

probability distribution for DI was lognormal with 1.99 l/d mean and 1.39 l/d standard deviation. DI statistics for İzmir population with median and mean values of 1.80 and 1.95 l/d, respectively, were found to be almost half a liter greater than the corresponding statistics of the American adults (USEPA, 1997), and are in agreement with values reported in the literature. DI varies in the population with 90th and 95th percentile values of 3.2 and 4.4 l/d, respectively. The sampling campaign was carried out from September 2004, to January 2005, which covered both summer and winter conditions because summer temperatures, although not the peak ones, generally last until mid-October. Actually, both peak high and low temperature days in summer and in winter, respectively, were not included in the campaign. Therefore, the authors believe that the calculated statistics can be used as estimations of annual average values for İzmir population. Furthermore, the use of a probability distribution for average daily intake rate of drinking water instead of assuming a point estimate for the whole population, as practiced in many risk assessment studies (Lee et al., 2004; Tokmak et al., 2004; Uyak, 2006), has eliminated the probability of over/underestimation of exposure and risk.

The BW of each participant was declared by himself/herself during the administration of the first questionnaire. BW data followed a lognormal distribution with mean and standard deviation values of 65.56 and 13.02 kg, respectively. BWs of 62% of the participants were between 50 and 70 kg, while the portion of participants with a BW between 70 and 90 kg was 23%. The median (64.5 kg) and mean (65.6 kg) BWs for İzmir population were found to be less than the value, 70 kg, suggested by the USEPA and used in the literature (Lee et al., 2004). If the BW were assumed to be 70 kg for İzmir population, exposure and risk would have been underestimated for female participants (median = 58 kg) and overestimated for male participants (median = 74.5 kg). Detailed information regarding DI and BW were reported elsewhere (Kavcar et al., 2006).

Exposure assessment

Amongst three main routes of exposure (ingestion, inhalation, and dermal absorption), only ingestion route was taken into consideration in this study. Ingestion was reported to be the most important route for exposure to trace metals (O'Rourke et al., 1999). Exposure and risk assessments were carried out by deterministic and probabilistic approaches for the most frequently detected six trace metals due to statistical limitations. In deterministic exposure assessment, CDI values were calculated for each participant. The statistics are presented in Table 4. The deterministic CDI statistics for As, Cr, and Ni reported by Sofuoglu et al. (2003) were compared to the values calculated in this study. The median, mean, and 90th percentile CDI values of As and Ni calculated in this study were much greater than those found in NHEXAS-Arizona study for both Arizona (2–3 times for As, 20–32 times for Ni) and the border (18–39 times for As, 200–357 times for Ni) populations. Cr CDI statistics for İzmir were greater than Arizona and less than the border population CDI values. Ryan et al. (2000) reported median and 95th percentile daily intakes of 0.52 and 2.65 μg/d for As, 0.05 and 0.12 μg/d for Cd, and 0.33 and 2.78 μg/d for Pb from drinking water in Maryland, USA. When the daily intake values of arsenic were converted to exposures with the assumption and utilization of 70 kg BW, median and 95th percentile values are approximately 5 and 21 times less than the respective statistics in this study. Assessment of exposure based on measured contaminant levels and assumed DI and BW values for an average adult would provide deficient estimations as discussed in Section "Average daily intake rate and body weight".

Aiming to estimate exposure probabilistically, Monte Carlo simulation was run using the fitted probability distributions for trace metal concentrations, DI, and BW as the input variables. In Table 4, the statistics extracted from Monte Carlo simulation are shown. The median, mean, and 90th percentile CDI values for As and Ni were much greater than the values reported by Sofuoglu et al. (2003) for the probabilistic approach (2–3 times for As, 12–40 times for Ni). On the other hand, Cr CDI statistics for the NHEXAS-Arizona study were 1.36–1.97 times greater than the values obtained in this study.

Risk assessment

Both deterministic and probabilistic approaches were used to assess carcinogenic and noncarcinogenic risks attributable to trace metals for which RfD and SF values were available. Risk (R) values greater than one in a million (10^{-6}) are generally considered unacceptable by the USEPA. However, this acceptable level may change according to national standards and environmental policies and may be as high as 10^{-4} (Health Canada, 1998; USEPA, 2000; WHO, 2004). HQs>1 indicate a potential for an adverse effect to occur or the need for further study. For İzmir drinking water, the deterministically calculated HQ values pointed out negligible noncarcinogenic risks, except for As, as presented in Table 5. Calculated HQ values were >1 for 17% of the participants with a maximum HQ of 5.77. When the median and 90th percentile HQ values for As, Cr, and Ni were compared to those reported in NHEXAS-Arizona study (Sofuoglu et al., 2003), similar levels were observed for Cr. However, in the case of As and Ni, much higher noncarcinogenic risk levels were associated with İzmir drinking water (2–41 times for As, 23–356 times for Ni).

Similar results were obtained from the probabilistic approach as presented in Table 5. Probabilistic/

Table 4. Descriptive statistics of exposure assessment

Metal	Minimum	Median	Mean	S.D.	90th percentile	95th percentile	Maximum
Deterministic approach ($N = 100$)							
Arsenic	4.46E−06	0.035	0.151	0.268	0.423	0.783	1.729
Chromium	1.10E−03	0.011	0.039	0.084	0.090	0.150	0.702
Copper	2.47E−05	0.060	0.193	0.298	0.598	0.860	1.775
Manganese	3.52E−04	0.019	0.055	0.112	0.168	0.233	0.830
Nickel	2.28E−02	0.607	1.015	1.419	2.795	3.802	9.888
Zinc	4.95E−05	0.945	3.403	5.377	9.539	17.07	29.47
Probabilistic approach ($N = 10,000$)							
Arsenic	6.68E−07	0.053	0.208	0.448	0.571	0.926	9.686
Chromium	1.00E−04	0.014	0.035	0.078	0.080	0.135	2.371
Copper	5.20E−06	0.076	0.238	0.474	0.641	1.001	11.47
Manganese	2.75E−05	0.014	0.067	0.217	0.142	0.280	6.575
Nickel	1.02E−02	0.557	0.961	1.325	2.110	3.114	27.27
Zinc	1.31E−11	1.122	4.809	10.75	12.95	22.29	263.2

All values are in μg/kg/d.

Table 5. Descriptive statistics of noncarcinogenic risk assessment

Metal	Minimum	Median	Mean	S.D.	90th percentile	95th percentile	Maximum
Deterministic approach ($N = 100$)							
Arsenic	1.49E−05	0.1156	0.5018	0.8925	1.411	2.609	5.765
Chromium	3.68E−04	0.0037	0.0129	0.0280	0.030	0.050	0.234
Manganese	2.52E−06	0.0001	0.0004	0.0008	0.001	0.002	0.006
Nickel	1.14E−03	0.0303	0.0508	0.0710	0.140	0.190	0.494
Zinc	1.65E−07	0.0032	0.0113	0.0179	0.032	0.057	0.098
Probabilistic approach ($N = 10,000$)							
Arsenic	2.23E−06	0.1760	0.6930	1.4936	1.904	3.087	32.29
Chromium	3.49E−05	0.0046	0.0117	0.0261	0.027	0.045	0.790
Manganese	1.97E−07	0.0001	0.0005	0.0016	0.001	0.002	0.047
Nickel	5.09E−04	0.0279	0.0480	0.0662	0.106	0.156	1.363
Zinc	4.35E−14	0.0037	0.0160	0.0358	0.043	0.074	0.877

deterministic ratio ranged between 0.90 and 1.25 for Cr, Cu, Mn, and Ni, while it was 1.4 for both As and Zn, when mean values of exposure (Table 4) and risk (Tables 5 and 6) were utilized. Probabilistically estimated median, mean, 90th and 95th percentile HQ values for arsenic were 1.18–1.52 times greater than those calculated deterministically. The maximum HQ estimated using the Monte Carlo simulation was 5.6 times greater than the value calculated from deterministic approach; this indicates that the probabilistic approach covers all possible scenarios including extremes which might not

have been encountered during sampling. However, unrealistic values might have been picked from the probability distributions of DI and BW, since correlation between the two could not be taken into consideration in the simulation. Therefore, some of the highest modeled values may be overestimations. In accordance, decision makers should use the 90th or 95th percentile values as high-end estimates instead of the maxima.

Lifetime carcinogenic risk was calculated for only arsenic since the SF values were not available for the

Table 6. Descriptive statistics of carcinogenic risk assessment for arsenic

Method	Minimum	Median	Mean	S.D.	90th percentile	95th percentile	Maximum
Deterministic ($N = 100$)	6.69E−09	5.20E−05	2.26E−04	4.02E−04	6.35E−04	1.17E−03	2.59E−03
Probabilistic ($N = 10,000$)	1.00E−09	7.92E−05	3.12E−04	6.72E−04	8.57E−04	1.39E−03	1.45E−02

Table 7. Uncertainty in distributional statistics of simulated exposure

Metal	Statistic	Minimum	Median	Mean	S.D.[†]	Maximum
Arsenic	Median	0.0478	0.0588	0.0583	0.0048	0.0736
	Mean	0.1866	0.2135	0.2146	0.0122	0.2520
	S.D.	0.3152	0.4090	0.4107	0.0314	0.4818
	90th percentile	0.4026	0.5306	0.5288	0.0509	0.6913
	95th percentile	0.7057	0.7983	0.7991	0.0406	0.9334
Chromium	Median	0.0113	0.0139	0.0137	0.0009	0.0153
	Mean	0.0297	0.0386	0.0388	0.0037	0.0495
	S.D.	0.0628	0.1165	0.1154	0.0300	0.1904
	90th percentile	0.0754	0.0858	0.0862	0.0061	0.1083
	95th percentile	0.1235	0.1450	0.1483	0.0161	0.1902
Copper	Median	0.0604	0.0749	0.0736	0.006	0.0920
	Mean	0.1872	0.2155	0.2164	0.0114	0.2519
	S.D.	0.3110	0.3753	0.3761	0.0243	0.4619
	90th percentile	0.5220	0.6369	0.6498	0.0541	0.8045
	95th percentile	0.8849	1.0395	1.0460	0.0938	1.4827
Manganese	Median	0.0108	0.0133	0.0134	0.0009	0.0155
	Mean	0.0603	0.0845	0.0861	0.0126	0.1253
	S.D.	0.1808	0.3728	0.3675	0.1189	0.6437
	90th percentile	0.1044	0.1319	0.1340	0.0117	0.1840
	95th percentile	0.1915	0.2611	0.2651	0.0321	0.3911
Nickel	Median	0.4939	0.5491	0.5535	0.0236	0.6173
	Mean	0.8292	0.9127	0.9152	0.0355	1.0281
	S.D.	0.8665	1.1105	1.1032	0.0755	1.2791
	90th percentile	1.8475	2.1221	2.1427	0.1440	2.4167
	95th percentile	2.5850	3.1188	3.1484	0.2340	3.6177
Zinc	Median	1.0301	1.2679	1.2661	0.0809	1.5492
	Mean	4.0736	4.7080	4.6936	0.2782	5.4333
	S.D.	7.3053	8.9279	8.9021	0.7182	10.789
	90th percentile	11.070	13.907	13.899	1.3267	17.697
	95th percentile	19.900	23.912	23.931	2.1997	29.334

Number of bootstrap samples = 200.
Number of trials per sample = 1000.

other trace metals. Deterministic and probabilistic approaches produced similar results with deterministic R values being slightly lower. While the median lifetime carcinogenic risks were less than 10^{-4}, the mean, 90th percentile and 95th percentile R values exceeded this level, as presented in Table 6. Risks reported for NHEXAS-Arizona (Sofuoglu et al., 2003) were 2–40 times less than those calculated for İzmir, with both median and mean R values $< 10^{-4}$.

In this study, 91% of the individuals had lifetime carcinogenic risks $> 10^{-6}$, whereas 41% had R values $> 10^{-4}$. This striking result shows that an important portion of the population is at risk, even if only drinking water ingestion pathway is taken into consideration. It is evident that the situation would be worse when aggregated exposure over all pathways/routes is considered.

The results of Mann–Whitney and Kruskal–Wallis tests used to compare the CDI, HQ, and R values across subgroups were in total agreement with the p-values reported for trace metal concentrations. Significant differences discussed for trace metal concentrations for all categories were valid for exposure and risk. This indicates that the differences in exposure to trace metals were mainly due to concentration differences, and that body weight and average daily intake rate of drinking water did not differ significantly within categories. Statistical analyses regarding the differences in BW and DI values across subgroups also supported this inference pointing out significant differences only for the gender category.

Uncertainty analysis

Uncertainty analysis was conducted for population exposure distributions using the boot-strapping method. Uncertainty in statistics of simulated exposure is shown in Table 7. Environmental managers and policy makers would be better equipped with these ranges in decision making. This analysis was applied only to exposure statistics because estimation of carcinogenic and non-carcinogenic risk involves multiplication/division of exposure with a factor value specific for each of the trace metals.

In addition to the quantified uncertainty in the simulation results, there is uncertainty due to some methodological aspects that could not be quantified: (1) seasonal variation in contaminant concentrations and daily water intake rate were not investigated, (2) contaminant concentrations were measured only in the primary source, (3) the exposure in the morning from the all night standing water was not considered, (4) body weights were acquired, not measured, (5) sampling biases due to recall and determination of primary respondent, and (6) uncertainty in the best fitting distributions.

Summary and conclusions

The concentrations of beryllium, cadmium, chromium, cobalt, copper, lead, manganese, vanadium, and zinc were in attainment of drinking water standards, whereas 20% and 58% of the samples exceeded the standard levels of arsenic and nickel, respectively. The data collected in this study showed that drinking water intake and body weight characteristics of the Turkish people are different from the American counterparts, and that assumptions for these two variables should be avoided, when possible, in risk assessment studies to avoid under/overestimation of population risks. Non-carcinogenic risks attributable to ingestion of trace metals in İzmir drinking water were found to be negligible, except for arsenic. Arsenic HQ values were > 1 in 19% of the population, which indicates a potential for toxic effects that calls for attention and further investigation. While median lifetime carcinogenic risk for arsenic was $< 10^{-4}$, this level was exceeded for 46% of the population. The fraction of population with carcinogenic risk $> 10^{-6}$ was 90%. Sources of this contaminant and precautions to be taken should be investigated. Aggregated exposure over all pathways/routes and associated risks should be estimated for a complete assessment.

Acknowledgments

References

Buchet, JP., Lison, D., 2000. Clues and uncertainties in the risk assessment of arsenic in drinking water. Food Chem. Toxicol. 38, S81–S85.

Caceres, DD., Pino, P., Montesinos, N., Atalah, E., Amigo, H., Loomis, D., 2005. Exposure to inorganic arsenic in drinking water and total urinary arsenic concentration in a Chilean population. Environ. Res. 98, 151–159.

Calderon, RL., 2000. The epidemiology of chemical contaminants of drinking water. Food Chem. Toxicol. 38, S13–S20.

Cantor, KP., 1997. Drinking water and cancer. Cancer Causes Control 8, 292–308.

Chrostowski, PC., 1994. Exposure assessment principles. In: Patrick, D.R. (Ed.), Toxic Air Pollution Handbook. Van Nostrand Reinhold, New York, NY, p. 154.

Demirak, A., Balci, A., Dalman, O., Tufekci, M., 2005. Chemical investigation of water resources around the Yatagan thermal power plant of Turkey. Water Air Soil Pollut. 162, 171–181.

Divrikli, Ü., Elci, L., 2002. Determination of some trace metals in water and sediment samples by flame atomic absorption spectrometry after coprecipitation with cerium(IV) hyroxide. Anal. Chim. Acta 452, 231–235.

Dogan, M., Dogan, A.U., Celebi, C., Baris, Y.I., 2005. Geogenic arsenic and a survey of skin lesions in the Emet region of Kutahya, Turkey. Indoor Built Environ. 14, 533–536.

Gülbahar, N., Elhatip, H., 2005. Estimation of environmental impacts on the water quality of the Tahtalıdam watershed in Izmir, Turkey. Environ. Geol. 47, 725–728.

Health Canada, 1998. Assessment and Management of Cancer Risks from Radiological and Chemical Hazards. 98-EHD-216 AECB INFO-0684(E) AC-5.

Helsel, D.R., 1990. Less than obvious – statistical treatment of data below the detection limit. Environ. Sci. Technol. 24, 1766–1774.

IRIS (Integrated Risk Information System), 2005. US Environmental Protection Agency, Cincinnati, OH. Accessed at: ⟨http://www.epa.gov/iris⟩, September 2005.

Kavcar, P., 2005. Assessment of exposure and risk associated with trihalomethanes and other volatile organic compounds in drinking water. M.Sc. Thesis, İzmir Institute of Technology, İzmir, Turkey.

Kavcar, P., Odabasi, M., Kitis, M., Inal, F., Sofuoglu, S.C., 2006. Occurrence, oral exposure and risk assessment of volatile organic compounds in drinking water for İzmir. Water Res. 40, 3219–3230.

Lebowitz, M.D., O'Rourke, M.K., Gordon, S., Moschandreas, D.J., Buckley, T., Nishioka, M., 1995. Population-based exposure measurements in Arizona: a phase I field study in support of the National Human Exposure Assessment Survey. J. Expo. Anal. Environ. Epidemiol. 5, 297–325.

Lee, S.C., Guo, H., Lam, S.M.J., Lau, S.L.A., 2004. Multipathway risk assessment on disinfection by-products of drinking water in Hong Kong. Environ. Res. 94, 47–56.

Ministry of Health, 2005. İnsani tüketim amaçlı sular hakkında yönetmelik (in Turkish). Resmi Gazete, 25730, Ankara, Turkey.

Odabasi, M., Muezzinoglu, A., Bozlaker, A., 2002. Ambient concentrations and dry deposition fluxes of trace elements in Izmir, Turkey. Atmos. Environ. 36, 5841–5851.

Oracle, 2007. Crystal Ball Reference Manual. Oracle Inc., USA.

O'Rourke, M.K., van de Water, P.K., Jin, S., Rogan, S.P., Weiss, A.D., Gordon, S.M., Moschandreas, D.J., Lebowitz, M.D., 1999. Evaluations of primary metals from NHEXAS Arizona: distributions and preliminary exposures. J. Expo. Anal. Environ. Epidemiol. 9, 435–445.

Patrick, D.R., 1994. Risk assessment and risk management. In: Patrick, D.R. (Ed.), Toxic Air Pollution Handbook. Van Nostrand Reinhold, New York, NY, p. 347.

Ritter, L., Solomon, K., Sibley, P., Hall, K., Keen, P., Mattu, G., Linton, B., 2002. Sources, pathways, and relative risks of contaminants in surface water and groundwater: a perspective prepared for the Walkerton Inquiry. J. Toxicol. Environ. Health Part A 65, 1–142.

Ryan, P.B., Huet, N., MacIntosh, D.L., 2000. Longitudinal investigation of exposure to arsenic, cadmium, and lead in drinking water. Environ. Health Perspect. 108, 731–735.

Seifert, B., Becker, K., Helm, D., Krause, C., Schulz, C., Seifert, M., 2000. The German Environmental Survey 1990/1992 (GerES II): reference concentrations of selected environmental pollutants in blood, urine, hair, house dust, drinking water and indoor air. J. Expo. Anal. Environ. Epidemiol. 10, 552–565.

SI No.:439, 2000. The European Communities (Drinking Water) Regulations, Dublin, Ireland.

Sofuoglu, S.C., Lebowitz, M.D., O'Rourke, M.K., Robertson, G.L., Dellarco, M., Moschandreas, D.J., 2003. Exposure and risk estimates for Arizona drinking water. JAWWA 95, 67–79.

Soylak, M., Armagan Aydin, F., Saracoglu, S., Elci, L., Dogan, M., 2002. Chemical analysis of drinking water samples from Yozgat, Turkey. Pol. J. Environ. Stud. 11, 151–156.

Tamasi, G., Cini, R., 2004. Heavy metals in drinking waters from Mount Amiata (Tuscany, Italy): possible risks from arsenic for public health in the province of Siena. Sci. Total Environ. 327, 41–51.

Thomas, K.W., Pellizzari, E.D., Berry, M.R., 1999. Population-based dietary intakes and tap water concentrations for selected elements in the EPA Region V National Human Exposure Assessment Survey (NHEXAS). J. Expo. Anal. Environ. Epidemiol. 9, 402–413.

Tokmak, B., Capar, G., Dilek, F.B., Yetis, U., 2004. Trihalomethanes and associated potential cancer risks in the water supply in Ankara, Turkey. Environ. Res. 96, 345–352.

Tsai, S.M., Wang, T.N., Ko, Y.C., 1999. Mortality for certain diseases in areas with high levels of arsenic in drinking water. Arch. Environ. Health 54, 186–193.

Ulman, C., Gezer, S., Anal, O., Tore, I.R., Kirca, U., 1998. Arsenic in human and cow's milk: a reflection of environmental pollution. Water Air Soil Pollut. 101, 411–416.

USEPA, 1992. Guidelines for Exposure Assessment. EPA/600/Z-92/001. US Environmental Protection Agency, Risk Assessment Forum, Washington, DC.

USEPA, 1997. Exposure Factors Handbook. EPA/600/P-95/002Fa. US Environmental Protection Agency, Office of Research and Development National Center for Environmental Assessment, Washington, DC.

USEPA, 1999. Guidance for Performing Aggregate Exposure and Risk Assessments. US Environmental Protection Agency, Office of Pesticide Programs, Washington, DC.

USEPA, 2000. Water Quality Standards, Establishment of Numeric Criteria for Priority Toxic Pollutants for the State of California. Accessed at: ⟨http://www.epa.gov/fedrgstr/EPA-WATER/2000/May/Day18/w11106.htm⟩, September 2006.

USEPA, 2002a. Code of Federal Regulations, 40CFR141.62. Title 40 – Protection of Environment, Chapter 1 – Environmental Protection Agency, Part 141 – National Primary Drinking

Water Regulations, 141.62 – Maximum Contaminant Levels for Inorganic Contaminants.

USEPA, 2002b. Code of Federal Regulations, 40CFR143.3. Title 40 – Protection of Environment, Chapter 1 – Environmental Protection Agency, Part 143 – National Secondary Drinking Water Regulations, 143.3 – Secondary Maximum Contaminant Levels.

USEPA, 2005. Guidelines For Carcinogen Risk Assessment. EPA/630/P-03/001F. US Environmental Protection Agency, Risk Assessment Forum, Washington, DC.

Uyak, V., 2006. Multi-pathway risk assessment of trihalo-methanes exposure in Istanbul drinking water supplies. Environ. Int. 32, 12–21.

van Dijk-Looijaard, A.M., van Genderen, J., 2000. Levels of exposure from drinking water. Food Chem. Toxicol. 38, S37–S42.

WHO, 2001. Environmental Health Criteria 224: Arsenic and Arsenic Compounds, second ed. World Health Organization, Geneva.

WHO, 2004. Guidelines for Drinking-Water Quality, third ed., vol. 1. Recommendations. World Health Organization, Geneva.

Xia, Y., Liu, J., 2004. An overview of chronic arsenism via drinking water in PR China. Toxicology 198, 25–29.

Xu, P., Huang, S., Wang, Z., Lagos, G., 2006. Daily intakes of copper, zinc and arsenic in drinking water by population of Shanghai, China. Sci. Total Environ. 362, 50–55.

Yersel, M., Erdem, A., Eroğlu, A.E., Shahwan, T., 2005. Separation of trace antimony and arsenic prior to hydride generation atomic absorption spectrometric determination. Anal. Chim. Acta 534, 293–300.