ASSESSMENT OF EXPOSURE AND RISK ASSOCIATED WITH TRIHALOMETHANES AND OTHER VOLATILE ORGANIC COMPOUNDS IN DRINKING WATER

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ABSTRACT

Concentrations of 54 volatile organic compounds (VOCs) were measured in İzmir drinking water, and associated health risks due to ingestion of these compounds were investigated using a semi-probabilistic sampling design. 100 houses were visited in different districts of İzmir and drinking water samples were collected from consumer taps and bottled waters. Using questionnaires, demographics and drinking water consumption rates were determined. Individual and population based exposures and risks were estimated by employing deterministic and probabilistic approaches, respectively.

Trihalomethanes (THMs) (i.e., chloroform, bromodichloromethane, dibromochloromethane, and bromoform), benzene, toluene, p-xylene, and naphthalene were the most frequently detected VOCs in İzmir drinking water with concentrations ranging from below detection limit to 35 μg/l. None of the samples exceeded the maximum contaminant levels stated in the Turkish, European, and American drinking water regulations. For all VOCs, the concentrations measured in metropolitan area were greater than those in other districts. All THM species were detected in higher concentrations in tap water.

Noncarcinogenic risks attributable to ingestion of VOCs in İzmir drinking water were negligible whereas the mean carcinogenic risk estimates for bromodichloromethane and dibromochloromethane were above the acceptable level of one in a million (10^{-6}). Deterministic approach revealed that 23%, 29%, and 2% of individuals had lifetime cancer risks greater than 10^{-6} associated with ingestion of bromodichloromethane, dibromochloromethane, and bromoform, respectively. The results of this study show that exposures to drinking water contaminants and associated risks may be higher than the acceptable level even if the concentrations fall below the drinking water standards.

ÖZET

İzmir ilinde, yarı probabilistik yöntem kullanılarak belirlenen 100 evden alınan içme suyu örneklerinde 54 uçucu organik maddenin derişimleri ölçülmüş, ve bundan kaynaklanan maruziyet ve risk seviyeleri değerlendirilmiştir. Her evden bir katılımcıya anket uygulamak yoluyla demografik veriler ve günlük su tüketim oranları belirlenmiş ve her bir katılımcı ve İzmir halkı için sırasıyla deterministik ve probabilistik yaklaşımlar kullanılarak maruziyet ve risk seviyeleri tespit edilmiştir.

İzmir içme suyunda, trihalometan (THM) bileşikleri (kloroform, bromodiklorometan, dibromoklorometan ve bromoform), benzen, toluen, p-ksilen, ve naftalin en sık belirlenen uçucu organik maddeler olmuş ve belirleme sınırının altından 35 µg/l'ye kadar değişen derişimlerde ölçülmüştür. Hiç bir uçucu organik madde hiç bir örnekte İnsani Tüketim Amaçlı Sular Hakkında Yönetmelik ve Avrupa Halkları İçme Suyu Yönetmeliği'nde belirtilen değerler ya da Amerikan Çevre Koruma Ajansı sınır değerleri ve Dünya Sağlık Örgütü rehber değerlerinin üzerinde ölçülmemiştir. Metropol alanda ölçülen derişimler bütün uçucu organik maddeler için diğer ilçelerde ölçülenlerden daha yüksektir. Bütün THM bileşikleri musluk suyunda daha yüksek derişimlerde ölçülmüştür.

İzmir içme suyundaki uçucu organik maddelerden kaynaklanan kanser harici riskler çok düşük seviyelerde iken bromodiklorometan ve dibromoklorometan için ortalama kanser riski kabul edilebilir seviye olan milyonda bir (10^{-6}) seviyesinin üzerinde bulunmuştur. Bromodiklorometan, dibromoklorometan, ve bromoform için birey bazında yapılan hesaplar, katılımcıların anılan sıraya göre %23, %29 ve %2'sinin kabul edilebilir seviyenin üzerinde kanser riski bulunduğunu göstermiştir. Sonuç olarak, kirletici derişimleri sınır değerler altında bile olsa oluşan kanser risklerinin kabul edilebilir seviyenin üzerinde olabileceği görülmüştür.

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CHAPTER 1

INTRODUCTION

Water is one of the most important compounds to sustain life, but it may also be the source of many illnesses. Volatile organic compounds (VOCs) may be present in drinking waters at levels high enough to cause adverse health effects. Ingestion of drinking water containing these contaminants may lead to liver and kidney damage, immune system, nervous system, and reproductive system disorders as well as several types of cancers (Cantor 1997, Calderon 2000, Fawell 2000, IRIS 2005).

VOCs are released into the environment during their production, storage and use, and can enter both groundwater supplies and surface water bodies from point and/or nonpoint sources. VOCs are of great concern because once these compounds are in gaseous state, they are much more mobile, and therefore, more likely to be released to the environment (Tchobanoglous and Burton 1991). In urban areas, VOC concentrations in drinking water may be high due to oil spills and leakage from underground fuel/chemical storage tanks whereas in rural areas, agricultural activities may lead to increased VOC levels. VOCs may also be released from the components of home distribution systems due to leaching of the plastic piping used in plumbing or from adhesives used in the construction of the system (Hofer and Shuker 2000, Squillace et al. 2002). Furthermore, the processes practiced in drinking water treatment plants (i.e., disinfection) and the chemicals added to the water for specific treatment goals may result in production of specific VOC species such as trihalomethanes (THMs). THMs are by-products of disinfection, produced in drinking water treatment plants by the reaction between the natural organic matter present in raw water and the chemicals added as disinfectants, especially chlorine.

VOCs are mostly found in groundwaters whereas THM levels are higher in disinfected surface waters (Kostopoulou et al. 1999, Hsu et al. 2001). Also, highest THM concentrations are observed at the end of drinking water distribution systems since the reaction between free residual chlorine and natural organic matter continues throughout the distribution system and chlorine is dosed at certain intervals as a protection against waterborne diseases (Gelover et al. 2000, Golfinopoulos 2000). Despite drinking water regulations and control practices, THM concentrations may be as high as 300 μg/l

(Fawell 2000). Other VOCs, on the other hand, are usually detected at concentrations below the maximum contaminant levels, although greater values such as 38 μg/l have been reported for benzene (Gelover et al. 2000).

Several researchers have studied THM and other VOC concentrations in drinking waters and estimated the health risks through ingestion route (Hsu et al. 2001, Sofuoglu et al. 2003, Lee et al. 2004). While all estimates for noncarcinogenic risk were found to be less than the demarcation value of 1, carcinogenic risk estimates both below and above the acceptable level of 10^{-6} have been reported. Although the effects of various parameters on THM formation and seasonal and spatial variations in THM concentrations have been studied in treatment plant effluents and at points throughout the drinking water distribution systems (Çapar and Yetiş 2002, Toroz and Uyak 2005), exposure and associated health risk levels of the Turkish population have not been investigated at the time this study began. Despite the cancer risk estimates reported recently by Tokmak et al. (2004) for Ankara residents, there is still insufficient information concerning VOC levels in both tap and bottled waters in Turkey and associated exposures and risks.

The objectives of this study are to measure the concentrations of THMs and other VOCs in İzmir drinking water, determine demographics and drinking water consumption rates, and estimate the individual and population based exposure and associated risk levels for İzmir population. In the following chapters, information regarding VOCs and discussion of drinking water VOC concentrations in the literature (Chapter 2), background on exposure and risk assessments, and analysis of the literature pertaining to drinking water exposure and risk assessment (Chapter 3), material and methods employed in this study (Chapter 4) are presented. Results and discussion (Chapter 5) is followed by the conclusions (Chapter 6).

CHAPTER 2

TRIHALOMETHANES AND OTHER VOLATILE ORGANIC COMPOUNDS IN DRINKING WATER

2.1. Volatile Organic Compounds

Volatile organic compounds (VOCs) are carbon-based chemicals that easily evaporate into gaseous state at room temperature. The sources of VOCs found in the environment may be natural processes or human activities. VOCs are found in everyday household items such as paints, glues, fuels, paint strippers, aerosols, varnishes, lacquers, wood preservatives, craft kits, cleaners, pesticides, cigarette smoke and dry-cleaned clothes. VOCs are of great concern because once such compounds are in gaseous state, they become much more mobile, and consequently, more likely to be released to the environment (Tchobanoglous and Burton 1991).

2.1.1. General Properties of VOCs

Physical and chemical properties of some of the VOCs most commonly found in drinking water are presented in Table 2.1. Although VOCs have a wide range of physical and chemical properties, they share some general characteristics. Their relatively high vapor pressures and low solubilities allow them to move between air and water.

Amongst the VOCs listed in Table 2.1, benzene, toluene, ethylbenzene, and xylene are known as the BTEX compounds. These compounds are used as antiknock compounds in gasoline, and therefore, are found in manufactured gas plant wastes. They are commonly found as groundwater contaminants near gas stations, manufactured gas plant sites, and other industrial facilities.

Chloroform, bromodichloromethane, dibromochloromethane, bromoform, benzene, toluene, p-xylene, and naphthalene are the most frequently detected VOCs in our samples. Therefore, the following sections will focus on these VOCs.

Table 2.1. Physical and Chemical Properties of Some VOCs

Compound	Molecular Weight (g/mol)	Melting Point (^{o}C)	Boiling Point (^{o}C)	Density at 20^{o}C (g/ml)	Solubility in Water at 25^{o}C (mg/l)	Vapor Pressure at 20^{o}C (mm Hg)	Henry's Law Constant at 25^{o}C (atm.l/mol)
Benzene	78.10[a]	5.5[a]	80.1[a]	0.879[b]	1789[a]	75.0[b]	5.50[b]
Toluene	92.10[a]	-95.0[a]	110.6[a]	0.867[c]	518[a]	27.7[c]	5.94[c]
Ethylbenzene	106.20[a]	-95.0[a]	136.2[a]	0.867[d]	168[a]	7.0[d]	7.90[d]
p-Xylene	106.20[a]	13.2[a]	138.0[a]	0.861[e]	180[a]	6.50[e]	7.66[e]
Carbon tetrachloride	153.80[a]	-22.9[a]	76.5[a]	1.594[f]	970[a]	90.0[f]	29.4[f]
Naphthalene	128.2 [a]	80.6[a]	217.9[a]	1.145[g]	31.5[a]	0.087[g]	0.46[g]
Styrene	104.16[h]	-30.6[h]	145.2[h]	0.906[h]	300[h]	5.0[h]	2.61[h]
Chloroform	119.40[a]	-63.5[a]	61.7[a]	1.483[i]	7709[a]	160[i]	4.06[i]
Bromodichloromethane	163.83[j]	-57.1[j]	90.0[j]	1.980[j]	4500[j]	50.0[j]	2.41[j]
Dibromochloromethane	208.28[k]	-20.0[k]	120.0[k]	2.451[k]	2700[k]	76.0[k]	0.99[k]
Bromoform	252.80[a]	8.3[a]	149.5[a]	2.899[k]	3110[a]	5.0[k]	0.56[k]

a. Schwarzenbach (1993)
b. ATSDR (1997a)
c. ATSDR (2000)
d. ATSDR (1999)
e. ATSDR (1995)
f. ATSDR (2003a)
g. ATSDR (2003b)
h. ATSDR (1992)
i. ATSDR (1997b)
j. ATSDR (1989)
k. ATSDR (2003c)

Benzene is a colorless liquid with a sweet odor. Although volcanic eruptions and forest fires contribute to benzene in the environment, industrial processes are the main sources. Benzene is a major industrial chemical made from coal and oil, and also a component of gasoline. It is used primarily as a solvent in the chemical and pharmaceutical industries to make plastics, nylon, synthetic fibers, rubber products, dyes, detergents, and pesticides; and also as a starting material and intermediate in the synthesis of numerous chemicals (ATSDR 1997a).

Toluene is a clear, colorless liquid with a distinctive smell. Toluene occurs naturally in crude oil and in the tolu tree. It is also produced in the process of making gasoline and other fuels from crude oil and making coke from coal. Toluene is used in making paints, paint thinners, fingernail polish, lacquers, adhesives, and rubber and in some printing and leather tanning processes (ATSDR 2000).

Xylene is a colorless, sweet-smelling liquid that catches on fire easily. It occurs naturally in petroleum and coal tar and is formed during forest fires. Chemical industries produce xylene from petroleum to be used as a solvent. It is used in printing, rubber, and leather industries, as a cleaning agent, a thinner for paint, and in paints and varnishes. It is found in small amounts in airplane fuel and gasoline (ATSDR 1995).

Naphthalene is a white solid that evaporates easily. It is used as an intermediate in the production of phthalic anhydride, which is an intermediate in the production of phthalate plasticizers, pharmaceuticals, insect repellents, and other materials. It is also used as an intermediate in the production of 1-naphthyl-Nmethylcarbamate insecticides, beta-naphthol, synthetic leather tanning chemicals, surfactants, moth repellents, and toilet bowl deodorants (ATSDR 2003b).

Chloroform, bromodichloromethane, dibromochloromethane, and bromoform (i.e., trihalomethanes), by-products of drinking water disinfection, are detailed in Section 2.2.

2.1.2. Sources of VOCs in Drinking Water

VOCs are released into the environment during their production, storage and use. They can enter both groundwater supplies and surface waters from point and/or nonpoint sources. There are four main routes through which VOCs can enter the drinking water supply system: **(1)** A water source may be contaminated due to oil spills

or leakage from underground fuel/chemical storage tanks or as a result of agricultural and industrial activities. **(2)** VOCs released to the atmosphere may accumulate in water bodies. **(3)** VOCs may be produced during the processes practiced in drinking water treatment plants (i.e., disinfection) and from chemicals added to the water for specific treatment goals. **(4)** VOCs may also come from the components of home distribution systems due to leaching of the plastic piping used in plumbing or from adhesives used in the original construction of the system

2.2. Trihalomethanes

Disinfectants have been added to drinking waters since the early 1900s to kill disease causing microorganisms in order to control the spread of typhoid, cholera, and other diseases. The addition of chlorine to drinking water is an effective, simple and economic means of providing primary and secondary disinfection to public water supplies. However, in 1970s it was discovered that chlorine reacts with natural organic matter (NOM), mainly humic and fulvic acids from decomposed vegetation and algae, in water to produce disinfection by-products (DBPs), several of which are proven or suspected carcinogens (Bellar et al. 1974, Rook 1974, Cantor 1997). Among DBPs, trihalomethanes (THMs), which comprise chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform, attract special attention as these contaminants are detected in high quantities and due to their suspected carcinogenic nature.

2.2.1. Formation of THMs

As chlorine gas is added to water, hypochlorous acid (HOCl) is formed which reacts with natural organic matter (also called precursors) resulting in the formation of THMs and other DBPs. When natural bromide is present in the source water, however, hypobromous acid is formed during disinfection which causes a shift in distribution of DBPs to more highly brominated species (Richardson et al. 2000, Sadiq et al. 2002). These reactions can be depicted as follows:

$$Cl_2 + H_2O \rightarrow HOCl \tag{2.1}$$

$$HOCl \mid HOBr + NOM \rightarrow THMs\ and\ other\ DBPs \tag{2.2}$$

THM formation in drinking water is dependent on several factors as described in many studies (Peters et al. 1980, Garcia-Villanova et al. 1997, Golfinopoulos et al. 1998, Shin et al. 1999, Sohn et al. 2001, Gallard and von Gunten 2002). These are: characteristics of the source water, chlorine dose and residual chlorine, contact time, temperature, pH, bromide levels, and water storage and distribution conditions.

Since groundwater rarely contains high levels of organic matter, chlorinated private water supplies and public wells are less susceptible to the formation of THMs. In fact, THMs are most often found in chlorinated surface waters used for public drinking water supplies as reported by Golfinopoulos (2000) and Nissinen et al. (2002).

Besides the addition of chlorine in drinking water treatment plants for primary disinfection, chlorine is also dosed at certain intervals throughout water distribution systems to maintain some chlorine residual. In this way, the drinking water is protected from re-growth of microorganisms and re-appearance of waterborne diseases. However, this residual chlorine will favor THM formation as long as NOM is present in the distribution system and until the free chlorine residual is depleted (Golfinopoulos 2000). Because of these continuing reactions, drinking water samples taken from plant effluents or points throughout the distribution system may not represent the exact concentrations of THMs in tap water (Cohn et al. 1999, Shin et al. 1999, Hofer and Shuker 2000, Sohn et al. 2001).

2.3. Drinking Water Regulations

In the United States, The Safe Drinking Water Act (SDWA) was passed by Congress in 1974 to protect public health by regulating public drinking water supplies. The law was amended in 1986 and 1996 and requires many actions to protect drinking water and its sources: rivers, lakes, reservoirs, springs, and groundwater wells. SDWA authorizes the United States Environmental Protection Agency (USEPA) to set national health-based standards for drinking water to protect against both naturally-occurring and man-made contaminants that may be found in drinking water (USEPA 2004).

The USEPA has two main categories for drinking water standards, Primary and Secondary. Primary standards or Maximum Contaminant Levels (MCLs) are the enforceable standards for public water supplies. These standards are based on health considerations in order to protect the public from pathogens, toxic chemicals,

radionuclides, and other health effects. Laws and regulations require that consumers be notified if chemicals appear at levels above the standard, and action must be taken to reduce the contaminant.

Federal regulations controlling THMs in drinking water were established in 1979 setting a MCL of 100 µg/l (ppb) for total THMs (TTHMs) for systems serving populations of greater than 10,000 people. Since then, the increasing awareness of microbial risks in drinking water has resulted in increased levels of disinfection, and thus caused DBPs to become more of an issue. In 1998, TTHM regulatory limit was lowered to 80 µg/l by the Stage 1 Disinfection By-Products Rule (63-FR-69389).

The MCLs for THMs and other VOCs of concern are presented in Table 2.2 along with guideline values suggested by the World Health Organization (WHO) and those included in the European Communities (EC) drinking water regulations. In addition to these regulations, strict treatment requirements for surface waters are imposed by the USEPA to reduce DBP precursors.

Naphthalene was not included in any of these regulations since when average daily intakes from drinking water are compared with intakes from food, air, and soil, drinking water accounts for a relatively small proportion of total naphthalene intake (USEPA 2003a). Therefore, regulation of naphthalene in drinking water was thought to be unlikely to represent a meaningful opportunity for health risk reduction.

Table 2.2. Maximum Contaminant Levels in Drinking Water

Contaminant	**Guideline Values / Maximum Contaminant Levels (µg/l)**		
	WHO [a]	USEPA	EC[d]
Chloroform	200	-	-
BDCM	60	-	-
DBCM	100	-	-
Bromoform	100	-	-
TTHMs	‡	80[b]	150[†]
Benzene	10	5[c]	1
Toluene	700	1000[c]	-
Xylenes (total)	500	10000[c]	-
Naphthalene	-	-	-

- Not included in regulations

‡ The sum of the ratio of the concentration of each THM to its respective guideline value should not exceed 1, WHO (2004)

† 100 µg/l must be met by 25 December, 2008.

a. WHO (2004)
b. 40CFR141.64 (2002)
c. 40CFR141.61 (2002)
d. SI No:439 (2000)

None of the VOCs listed in Table 2.2 took part in former Turkish drinking water standards (TS 266 1997). This year, however, the Ministry of Health published the "Regulation Concerning Water Intended for Human Consumption" regulating TTHMs at a MCL of 150 µg/l which will be lowered to 100 µg/l by the end of 2012 (Ministry of Health 2005). Benzene concentration was also set at a MCL of 1 µg/l in order to comply with the EC standards.

The MCL is set as close as feasible to the Maximum Contaminant Level Goal (MCLG), the level at which no known or anticipated adverse health effects occur. However, in addition to health effects, the USEPA considers the feasibility and combined cost of analyzing water for a contaminant and for treating water to remove the contaminant. Therefore, the MCLs are usually less stringent than the MCLGs which are shown in Table 2.3.

Table 2.3. Maximum Contaminant Level Goals in Drinking Water

Contaminant	Maximum Contaminant Level Goals (µg/l)
Chloroform	70[a]
BDCM	0[b]
DBCM	60[b]
Bromoform	0[b]
Benzene	0[c]
Toluene	1000[c]
Xylenes (total)	10[c]
Naphthalene	-

- Not included in regulations
a. USEPA (2003b)
b. 40CFR141.53 (2002)
c. 40CFR141.50 (2002)

2.4. VOC Levels Reported in Literature

Since drinking water is almost always disinfected before consumption, presence of THMs is reported in many studies. Despite drinking water regulations and control practices, THM concentrations may be as high as 300 µg/l (Fawell 2000). Among THMs, chloroform is usually the most frequently detected compound and it also points out the presence of other DBPs.

Gelover and co-workers (2000) analyzed samples from five Mexican cities to determine the presence of VOCs in drinking water and found that benzene was present in 88% of the samples. They have related the frequent occurrence of benzene in drinking water to leaks from underground petroleum storage tanks and accidental spills

of these products; however, the concentrations were rarely above 0.66 µg/l. Chloroform and DBCM were the third and fifth mostly detected compounds with concentration ranges given in Table 2.4.

Table 2.4. Contaminant Levels in Tap Water Reported in Literature

Study	Measured Concentration Ranges (µg/l)						
	Chloroform	BDCM	DBCM	Bromoform	TTHM	Benzene	Toluene
Gelover et al. (2000)	0.4 - 12.14	-	1.25 - 17.00	-	-	0.19 - 38.00	-
Weisel et al. (1999)	0.04 - 200.00	0.06 - 48.00	0.14 - 9.70	0.03 - 4.21	0.03 - 260.00	-	-
Simpson & Hayes (1998)	-	-	-	-	6.00 - 191.00	-	-
Kuo et al. (1997)	<0.36 - 99.00	<0.02 - 66.46	<1.36 - 73.21	<0.10 - 11.71	3.53 - 191.13	<0.58 - 4.09	<0.04 - 63.12

Although individual THM species reported in previous studies usually do not exceed the maximum contaminant levels, some of the TTHM concentrations found in tap water in New Jersey (Weisel et al. 1999), Australia (Simpson and Hayes 1998), and Taiwan (Kuo et al. 1997) were above the MCLs specified in Table 2.2. On the other hand, benzene and toluene concentrations usually fell below the MCLs given by the stated agencies as in the case of Arizona (Sofuoglu et al. 2003) and Taiwan (Kuo et al. 1997) studies.

Weisel et al. (1999) analyzed water samples collected from the kitchen faucet for DBPs and reported median concentrations of 16, 2.6, 1.4, and 0.45 µg/l for chloroform, bromodichloromethane, dibromochloromethane, and bromoform, respectively. Mean concentrations for the same compounds were 31, 5.7, 2, and 0.73 µg/l with concentration ranges given in Table 2.4.

DBP concentrations in chlorinated and chloraminated drinking water samples from different locations across five states of Australia were determined by Simpson and Hayes (1998). THMs were the predominant DBPs in the majority of chlorinated waters ranging between 25 and 191 µg/l. In chloraminated waters, both THM concentrations and overall DBP production were much lower compared to chlorinated samples.

Kuo et al. (1997) analyzed tap water and boiled water collected from 29 districts in the three major metropolitan areas in Taiwan. Mean TTHM concentrations were 37.61, 104.12, and 49.93 µg/l in tap waters of Taichung, Kaohsiung, and Taipei, respectively. Following boiling, the mean TTHM concentrations decreased to 7.44,

21.30, and 19.66 μg/l. Except for THMs, toluene was the most frequently detected compound with mean concentrations of 4.00, 15.88, and 6.20 μg/l for the three cities; and unlike THMs, toluene concentration did not decrease significantly after boiling.

Chloroform was detected in 80.7% of tap water samples collected from USEPA Region 5 (Illinois, Indiana, Ohio, Michigan, Minnesota, and Wisconsin) as part of the National Human Exposure Assessment Survey (NHEXAS) Phase I field study (Clayton et al. 1999). Median, mean, and 90th percentile concentrations reported for chloroform were 5.15, 15.19, and 47.04 μg/l, respectively. On the other hand, benzene was detected in only 5.9% of tap water samples; therefore, statistics were not calculated for this compound. NHEXAS-Arizona Study (Robertson et al. 1999) reported similar results, such that the 50th percentile benzene concentration was below the detection limit of 0.03 μg/l while 90% of the drinking water samples had benzene concentrations less than 0.04 μg/l.

In another study, conducted by Sofuoglu et al. (2003) as part of the NHEXAS-Arizona, VOC concentrations in drinking water samples from tap and nontap sources were compared for Arizona and border populations. Median, mean, and 90th percentile chloroform concentrations were reported to be 0.03, 2.60, and 2.04 μg/l for Arizona tap water; 0.05, 1.30, and 2.00 μg/l for Arizona nontap water; 0.11, 0.39, and 1.19 μg/l for border population tap water; and 0.15, 0.74, and 0.87 μg/l for border population nontap water respectively. In the same manner, median, mean, and 90th percentile toluene concentrations were found as 0.22, 2.14, and 4.51 μg/l for Arizona tap water; 0.57, 2.35, and 6.78 μg/l for Arizona nontap water; 0.49, 1.54, and 5.71 μg/l for border population tap water; and 0.50, 1.21, and 2.67 μg/l for border population nontap water respectively. As the results imply, chloroform concentrations were at about the same levels for tap and nontap water for Arizona and border populations. The Mann-Whitney test, however, pointed out a significant difference in toluene concentrations for tap and nontap water.

CHAPTER 3

HUMAN HEALTH RISK ASSESSMENT

3.1. Health Effects of VOCs

Contaminants in drinking water can cause either acute or chronic health effects. Acute effects usually occur immediately after ingestion of a large dose. This may be due to chemical spills or leaks (Calderon 2000). Common acute effects include irritation of the eyes, nose, throat and skin. Vomiting, headache, nausea and dizziness may occur, as well as fatigue and shortness of breath. These effects are usually temporary and improve once the source of the exposure is identified and removed.

Normally, the levels of contaminants in drinking water are not high enough to cause acute health effects. Instead, chronic effects are usually observed which occur after exposure to small amounts over long periods of time. Chronic health effects include nervous system disorders, liver and kidney damage, leukemia, reproductive system and immune system deficiencies as well as several types of cancers (Cantor 1997, Calderon 2000, Fawell 2000, IRIS 2005).

Possible outcomes of ingestion of drinking water containing volatile organic compounds, especially DBPs, have been investigated by toxicological and epidemiological means since the discovery of these compounds in drinking water in 1970s. Animal studies have demonstrated that liver, kidney, and intestinal tumors have a positive association with chronic ingestion of THMs (Dunnick and Melnick 1993).

Numerous toxicological studies have shown several DBPs (e.g., bromodichloromethane, bromoform, chloroform) to be carcinogenic in laboratory animals. These findings of carcinogenicity influenced EPA to promulgate the TTHM Rule (44-FR-68624) in 1979 and the Stage 1 DBP Rule (63-FR-69389) in 1998. The Stage 1 DBP Rule primarily addressed possible carcinogenic effects (e.g., bladder, colon, and rectal cancers) reported in both human epidemiology and laboratory animal studies. Since the Stage 1 DBP Rule, new health studies continue to support an association between bladder, colon and rectal cancers from long-term exposure to chlorinated surface water (USEPA 2003b).

As summarized by Calderon (2000), epidemiological studies suggest a relationship between consumption of DBPs and adverse reproductive and developmental outcomes such as stillbirths, neonatal deaths, miscarriage, low birth weight, preterm delivery, intrauterine growth retardation, short body length, and birth defects such as major cardiac defects and oral clefts. Short-term, high-dose animal screening studies on individual by-products (e.g., BDCM) have also reported adverse reproductive and developmental effects, such as whole litter resorption and reduced fetal body weight, that are similar to those reported in the human epidemiology studies (USEPA 2003b).

3.2. Exposure and Risk Assessment

Risk assessment is an attempt to identify and quantify potential risks to human health resulting from exposure to various contaminants. It involves evaluation of toxicity data for chemicals to which humans are exposed, and estimation of potential exposure levels.

The four-component paradigm described by the National Research Council (NRC) of the National Academy of Sciences (NAS) involves the following steps: hazard identification, dose-response assessment, exposure assessment, and risk characterization (NRC 1983). Among these steps, the first two are concerned primarily with the properties of particular chemicals and the characterization of expected toxicological effects under a variety of circumstances. On the other hand, the second two steps, exposure assessment and risk characterization, are specific to the particular exposure scenario. Specialists in toxicology (the study of the toxic effects of chemicals) and epidemiology (the study of the distribution of diseases in populations) take part in different steps of the risk assessment process as well as physicians, biologists, chemists, and engineers.

3.2.1. Hazard Identification

In the hazard identification step, scientists determine various health problems a chemical could cause by examining the available scientific data about its effects in humans and laboratory animals. Depending on the chemical, these health effects may

include short-term ailments such as headaches, nausea, and eye, nose, and throat irritation; or chronic diseases, such as cancer.

The potential health effects of noncarcinogens range from irritation to life-shortening. Data on the noncarcinogenic effects of chemicals are used to estimate reference dose values which is explained in the dose-response assessment step.

In order to determine whether a chemical poses a carcinogenic hazard in exposed humans, USEPA (1992b) examines the results from both human studies of the association between cancer incidence and exposure to the chemical of concern and long-term animal studies under controlled laboratory conditions. Since cancer is a collection of several diseases that develop through cell and tissue changes over time (USEPA 2005), supporting evidence such as short-term tests for genotoxicity, metabolic and pharmacokinetic properties, toxicological effects other than cancer, structure-activity relationships, and physical/chemical properties of the chemical are also considered. A weight-of-evidence approach is used by the USEPA to classify the likelihood the chemical of concern is a human carcinogen and as a result each chemical is placed into one of the five categories presented in Table 3.1.

Table 3.1. USEPA's Carcinogenicity Classification of Chemicals*

Group	Category
A	Human carcinogen
B	Probable human carcinogen
	B1 indicates limited human evidence
	B2 indicates sufficient evidence in animals, inadequate/ no evidence in humans
C	Possible human carcinogen
D	Not classifiable as to human carcinogenicity
E	Evidence of noncarcinogenicity for humans

* USEPA (1992b)

As listed in Table 3.2, USEPA has classified chloroform, BDCM and bromoform as probable human carcinogens, Group B2, based on sufficient evidence of carcinogenicity in animals and inadequate human data. DBCM and toluene are not classifiable as to human carcinogenicity, Group D, based on the lack of data regarding the carcinogenicity of these compounds in humans or animals. Benzene is characterized as a known human carcinogen for all routes of exposure based upon convincing human evidence as well as supporting evidence from animal studies. Adequate human data on the carcinogenicity of xylenes are not available, and the available animal data are

inconclusive as to the ability of xylenes to cause a carcinogenic response. Therefore, p-xylene could not be placed into any category. Naphthalene is classified in Group C, a possible human carcinogen based on inadequate data of carcinogenicity in humans and the limited evidence of carcinogenicity in animals.

Table 3.2. USEPA's Carcinogenicity Classification of VOCs*

Contaminant	Group
Chloroform	B2
Bromodichloromethane	B2
Dibromochloromethane	D
Bromoform	B2
Benzene	A
Toluene	D
p-Xylene	†
Naphthalene	C

* IRIS (2005)
† Inadequate evidence of carcinogenicity

3.2.2. Dose-Response Assessment

Dose is the amount of a substance available for interaction with metabolic processes or biologically significant receptors after crossing the outer boundary of an organism (USEPA 2005). Dose-response assessment is the determination of the relationship between the magnitude of dose and a specific biological response. Response can be expressed or measured as observed number of incidences, percent response in groups of subjects or populations, or the probability of occurrence of a response in a population (USEPA 1997b).

The mathematical relationship between the amount of chemical to which a person is exposed and the risk that there will be an unhealthy response to that dose is schematically represented in Figure 3.1. For non-carcinogens, it is assumed that there is a reference dose (RfD) below which no adverse effects are observed. RfDs are calculated by determining the No-Observed-Adverse-Effect-Level (NOAEL) or bench-mark dose (BMD) point of departure from either acute or chronic toxicity studies and dividing it by the appropriate uncertainty factors.

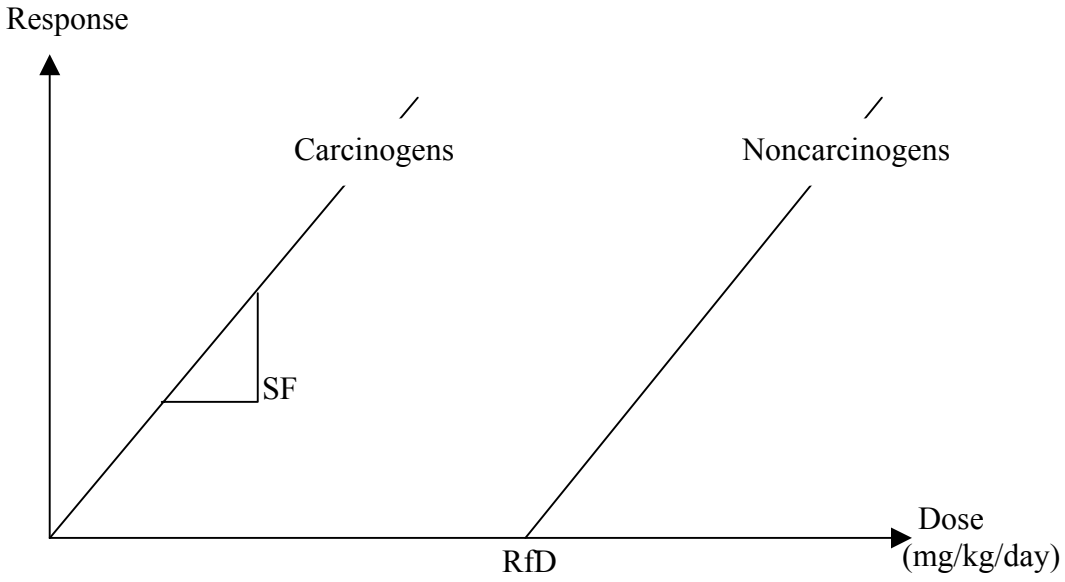

Figure 3.1. Dose-Response Curve for Carcinogenic and Noncarcinogenic Compounds

The NOAEL is defined as the highest dose or concentration of a chemical that causes no detectable adverse health effect (WHO 2004). If a NOAEL is not available, a LOAEL (Lowest-Observed-Adverse-Effect Level) may be used, which is the lowest observed dose or concentration of a substance at which there is a detectable adverse health effect (WHO 2004). An alternative way of calculating RfD values is the BMD approach which is the lower confidence limit of the dose that produces a small increase in the level of adverse effects (WHO 2004).

Typically, an uncertainty factor is applied to account for: variation within the human population (i.e., intraspecies), the differences between humans and animals as the animal data are extrapolated to humans (i.e., interspecies), the duration of the study, the end point used in the calculation (NOAEL or LOAEL), and the completeness of the database (USEPA 2003c).

For carcinogens, on the other hand, it is assumed that any exposure will create some likelihood of cancer. As shown in Figure 3.1, the slope of the dose-response curve is called the potency factor (PF) or the slope factor (SF) and it is defined by the USEPA (1992b) as the cancer risk per unit of dose. Both reference dose and slope factor values are unique for each chemical and the values suggested by the USEPA (IRIS 2005) are listed in Table 3.3.

Table 3.3. Reference Doses and Slope Factors for VOCs*

Contaminant	RfD (mg/kg/d)	SF (mg/kg/d)$^{-1}$
Chloroform	1.00E-02	W
Bromodichloromethane	2.00E-02	6.20E-02
Dibromochloromethane	2.00E-02	8.40E-02
Bromoform	2.00E-02	7.90E-03
Benzene	4.00E-03	1.50E-02 to 5.50E-02
Toluene	2.00E-01	NA
p-Xylene	2.00E-01	†
Naphthalene	2.00E-02	‡

* IRIS (2005)
W. Withdrawn
NA. Not available
† Inadequate evidence of carcinogenicity
‡ Lack of data

The USEPA (IRIS 2005) indicates that chloroform is considered likely to be carcinogenic to humans by all routes of exposure under high-exposure conditions that lead to cytotoxicity and regenerative hyperplasia in susceptible tissues. However, chloroform is not likely to be carcinogenic to humans by any route of exposure under lower exposure conditions that do not cause cell toxicity and abnormal growth/regeneration. Therefore, former oral slope factor of 0.031 (mg/kg/d)$^{-1}$ was withdrawn and a dose of 0.01 mg/kg/day (equal to the RfD) was considered protective against cancer risk.

Adequate human data on the carcinogenicity of xylenes are not available, and the available animal data are inconclusive as to the ability of xylenes to cause a carcinogenic response. Evaluations of the genotoxic effects of xylenes have consistently given negative results (IRIS 2005). As a result, a slope factor could not be derived for p-xylene. In the same manner, an oral slope factor for naphthalene was not derived because of a lack of chronic oral naphthalene studies (IRIS 2005).

3.2.3. Exposure Assessment

Exposure assessment is the qualitative and quantitative determination of the magnitude, frequency, and duration of exposure and internal dose (USEPA 1992a). Exposure may occur via three main routes; ingestion, inhalation, and dermal absorption. In this study, only the ingestion route was taken into consideration in order to assess exposure associated with THMs and other VOCs in drinking water.

In order to estimate the daily exposure of an individual, USEPA (1999a) 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 (1992a) and Chrostowski (1994).

$$CDI = \frac{C * DI}{BW} \tag{3.3}$$

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 the body weight (kg). Values of these three input variables, specific to each subject, are used to estimate the subject individual's chronic daily exposure level.

The original equation used by the USEPA to estimate average daily dose includes two more variables, exposure duration (ED) and lifetime (LT), in the numerator and denominator, respectively. When oral ingestion is considered as the only route of exposure, these variables may be omitted since they can be assumed to be equal.

3.2.4. Risk Characterization

The last step in risk assessment involves bringing all the previous steps together to define an overall risk to a specific population. The data obtained in the dose-response assessment is combined with that obtained in the exposure assessment to yield a numerical estimate of risk (USEPA 1992b).

Lifetime cancer risk associated with ingestion exposure is calculated using the following equation (Patrick 1994, USEPA 1999a):

$$R = CDI * SF \tag{3.4}$$

where, R is the probability of excess lifetime cancer (or simply risk), CDI is the chronic daily intake (mg/kg/d), and SF is the slope factor of the chemical $(mg/kg/d)^{-1}$.

Risk values greater than 1 in a million (10^{-6}) are generally considered unacceptable by the USEPA (2000b). 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 2000c, WHO 2004).

When promulgating water quality standards, USEPA intends to use a 10^{-6} cancer risk level for all priority toxic pollutants regulated as carcinogens, which they believe reflects an appropriate target risk level for the general population. States and authorized Tribes, USEPA (2000b) expresses, have the flexibility to adopt water quality criteria that result in a risk level higher than 10^{-6}, ensuring that highly exposed groups do not exceed a target 10^{-4} risk level.

To estimate non-carcinogenic risk, the hazard quotient (HQ) is calculated using the following equation (USEPA 1999b):

$$HQ = \frac{CDI}{RfD} \tag{3.5}$$

where RfD is the reference dose (mg/kg/d). HQ values greater than 1 indicate a potential for an adverse effect to occur or the need for further study.

3.3. Deterministic vs. Probabilistic Approach

Depending on the objectives of the assessment, exposure may be calculated deterministically or probabilistically (stochastically). In deterministic approach, exposure and risk are estimated individually for each subject using Equations (3.1), (3.2), and (3.3). Using these point estimates, a risk distribution is derived for the general population. The uncertainty related to the variables included in the above equations can not be calculated since **(1)** the contaminant concentration found in subject's drinking water (C) is a single value resulting from instrumental analysis and **(2)** the values used for body weight (BW) and average daily intake rate of drinking water (DI) are based on subject's statement.

On the other hand, probabilistic approach involves using probability distributions to represent each variable in exposure and risk equations. Probabilistic techniques can enhance risk estimates by more fully incorporating available information concerning the *range* of possible values that an input variable could take, and weighing these values by their *probability* of occurrence. This approach requires more time and effort; therefore, computer-based methods such as Monte Carlo Simulation are needed.

3.3.1. Monte Carlo Simulation

Monte Carlo Simulation is a computer-based method of analysis developed in the 1940's that uses statistical sampling techniques in obtaining a probabilistic approximation to the solution of a mathematical equation or model (USEPA 1997a). For each uncertain variable in the equation, C, DI, and BW in the case of exposure (CDI) estimation, the possible values are defined with a probability distribution as shown in Figure 3.2. These probability distributions are used as the input distributions for exposure model parameters. During a single trial, values are randomly selected from the defined possibilities (the range and shape of the 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 created compared to the single outcome obtained in the deterministic approach.

The probability distribution obtained for exposure to each compound is then used to estimate HQ and R values. Using Equations (3.2) and (3.3), probability distributions similar to the outcome presented in Figure 3.2 are created.

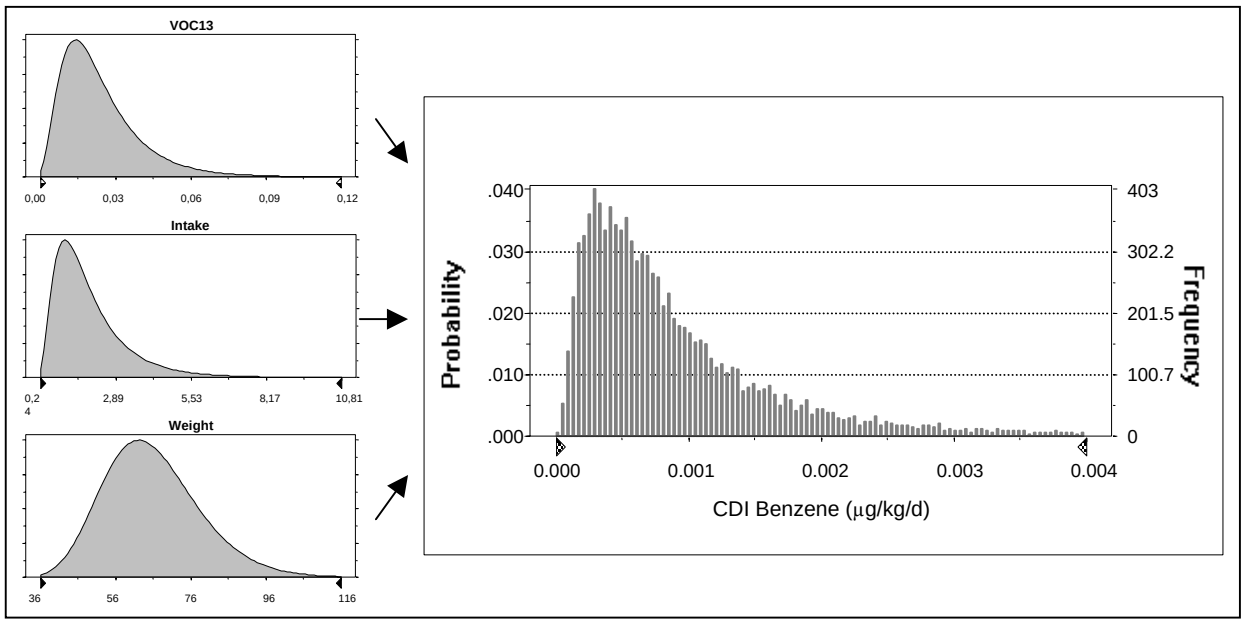

Figure 3.2. Schematic Representation of Monte Carlo Simulation

The principal advantage of the Monte Carlo method is its very general applicability. There is no restriction on the form of the input distributions or the nature

of the relationship between input and output; computations are also straightforward (USEPA 1992a).

The USEPA recommends that all risk assessment activities include some degree of uncertainty analysis to provide proper perspective to risk management decision-makers. Since full ranges of model and parameter assumptions are combined to calculate the entire probability distribution of the exposure variables, rather than just the upper-bound single-point estimation or default values, a complete distribution of risk is derived in Monte Carlo Simulation. In this way, the probability of each outcome and underlying uncertainties can be clearly stated.

3.4. Drinking Water Exposure and Risk Assessment Studies in the Literature

Williams and co-workers (2002) evaluated the relative cancer risks of six VOCs in drinking water sources in California from 1995 to 2001 using the contaminant concentrations reported in the California Department of Health Services water quality monitoring database. Exposure calculations were based on point estimates with the mean detected concentration of each VOC and standard USEPA default values, such as 70 kg body weight and 2 l/day water intake, being the input parameters. For each VOC, cancer slope factor obtained from California's Office of Environmental Health Hazard Assessment (OEHHA) was multiplied by the calculated lifetime average daily dose (LADD) to estimate the individual lifetime cancer risk from exposure to contaminated drinking water. Since the database contained both detect and nondetect data, as Williams et al. state, it was not possible to calculate an actual population risk. Therefore, rather than absolute risk estimates, relative risks were reported; benzene ranking second and chloroform ranking fourth. However, when the detection frequencies were taken into account for each VOC, adjusted lifetime cancer risk for chloroform was the greatest; because benzene was detected in less than 1% of the samples whereas 12-14% of the samples contained detectable levels of chloroform.

Potential lifetime cancer risks from consuming chlorinated drinking water in Taiwan were estimated for THMs (Hsu et al. 2001). THM concentrations in drinking water were obtained from the annual reports of the Environmental Protection Administration of Taiwan from 1994 to 1997 to estimate cancer risks using the

methodology provided by the USEPA. Risks varied with different water sources, water supply areas, and intake rates; but in all cases, 10^{-6} level was exceeded by each THM species. The highest risk was calculated as $1.8x10^{-4}$ for chloroform in tap water from water supply plants of South Taiwan assuming 3 l/day daily intake. Using an additive model to estimate lifetime cancer risks for TTHMs, the risks for 2 l/day daily intake rate were reported as presented in Table 3.4.

As part of the NHEXAS-Arizona study, Sofuoglu et al. (2003) assessed exposure to VOCs for Arizona and Arizona-Mexico border populations. Using the body weight and daily intake data obtained from the NHEXAS questionnaires and the slope factors taken from USEPA, exposure and risk were estimated both deterministically and probabilistically. In addition to carcinogenic risks, noncarcinogenic risks were reported by calculating the hazard quotient for each compound. As shown in Table 3.4 all risks were below the acceptable risk level, i.e., 10^{-6} for carcinogenic risk and 1 for noncarcinogenic risk, and probabilistic approach resulted in higher risk estimates when compared to deterministic approach. In general, risks attributable to oral exposure from tap water were greater than those attributable to nontap water, but the differences were not significant for VOCs. In spite of the concern that exposures of the border communities may be higher than those of other parts of the state, risk estimates pointed out the opposite.

Lee et al. (2004) estimated the lifetime cancer risk and hazard quotient for THMs through exposure from tap water using data collected in 1997 and the USEPA guidelines for human health risk assessment. Body weight and daily intake were taken as 70 kg and 4.48 l/day based on lifestyle of Hong Kong residents. The average lifetime cancer risks were ranked in descending order as BDCM, chloroform, DBCM, and bromoform for ingestion route with percentage contributions of 59, 24, 17, and 0, respectively. In all districts, cancer risk for bromoform was below 10^{-6} whereas the other THM species exceeded this level. The lifetime cancer risks calculated for TTHMs were in the range $4.5x10^{-5}$ - $1.15x10^{-4}$ with an average value of $7.55x10^{-5}$. Hazard quotient ranges given in Table 3.4 indicate that all noncarcinogenic risk estimates were below the level of concern.

The occurrence of THMs in Ankara drinking water was investigated by Tokmak and co-workers (2004) and lifetime cancer risk was estimated using the methods developed by the USEPA and adopted by other researchers. Consumer tap water samples were collected from 22 districts and analyzed for THM content.

Table 3.4. Estimated Lifetime Cancer Risks Reported in Literature for Drinking Water Ingestion Route

Study	Description	Chloroform		BDCM		DBCM		Bromoform		TTHMs		Toluene	
		C	NC	C	NC	C	NC	C	NC	C	NC	C	NC
Hsu et al., 2001	North Taiwan, tap water	9.23E-5	-	4.74E-6	-	2.63E-6	-	8.9E-8	-	9.98E-5	-	-	-
	Central Taiwan, tap water	9.32E-5	-	2.99E-6	-	7.92E-7	-	3.4E-8	-	9.71E-5	-	-	-
	South Taiwan, tap water	1.79E-4	-	5.87E-6	-	4.91E-6	-	2.87E-7	-	1.9E-4	-	-	-
	South Taiwan, well water	2.72E-5	-	1.01E-7	-	3.88E-7	-	-	-	2.76E-5	-	-	-
Sofuoglu et al., 2003	Arizona, deterministic, median	2.6E-9	4.2E-5	-	-	-	-	-	-	-	-	-	1.7E-5
	Arizona, deterministic, mean	1.5E-7	2.5E-3	-	-	-	-	-	-	-	-	-	1.3E-4
	Arizona, probabilistic, median	6.9E-9	1.1E-4	-	-	-	-	-	-	-	-	-	2.0E-5
	Arizona, probabilistic, mean	2.1E-7	3.5E-3	-	-	-	-	-	-	-	-	-	1.9E-4
	Border, deterministic, median	2.2E-9	3.6E-5	-	-	-	-	-	-	-	-	-	5.5E-6
	Border, deterministic, mean	4.5E-9	7.3E-5	-	-	-	-	-	-	-	-	-	1.4E-5
	Border, probabilistic, median	3.0E-8	4.8E-4	-	-	-	-	-	-	-	-	-	3.5E-5
	Border, probabilistic, mean	8.6E-8	1.4E-3	-	-	-	-	-	-	-	-	-	8.7E-5
Lee et al., 2004	Highest estimates	-	4.81E-1	-	5.50E-2	-	1.78E-2	-	2.94E-3	-	5.19E-1	-	-
	Lowest estimates	-	3.65E-2	-	1.61E-2	-	2.66E-3	-	ND	-	6.89E-2	-	-
	Average	-	3.02E-1	-	3.55E-2	-	7.75E-3	-	1.79E-4	-	3.45E-1	-	-

C. Carcinogenic risk (R values)

NC. Noncarcinogenic risk (HQ values)

Daily intake rate was taken as 2 l/day and body weight was assumed to be 72 kg for males and 65 kg for females in the study conducted for Ankara (Tokmak et al. 2004). The average risk due to chloroform was the highest among the THM species followed by BDCM and DBCM in descending order since 90-95% of all halogenated compounds was chloroform in all samples and bromoform was not detected at all. Cancer risk estimates were not reported for exposure routes separately, but Tokmak et al. stated that the major cancer risk for both male and female residents was through oral ingestion and that the total risks were greater than the USEPA's acceptable risk level of 10^{-6} for TTHMs for all districts when the risk for each exposure route was summed.

CHAPTER 4

MATERIALS AND METHODS

4.1. Sampling Design and Questionnaires

The dynamics of drinking water treatment and delivery can change the concentrations of VOCs such that samples taken from plant effluents or points throughout the distribution system may not represent the level of exposure to these compounds. Therefore, 100 houses were visited in different districts of İzmir to collect drinking water samples from consumer taps and bottled waters in order to estimate the exposure and risk levels for İzmir population associated with ingestion of VOCs in drinking water.

USEPA (2000a) defines probability samples as samples in which every member of the target population (i.e., every potential sampling unit) has a known probability of being included in the sample. A semi-probabilistic sampling design was used in this study, and the number of samples to be collected from each district was calculated according to geographical population distribution as presented in Figure 4.1. Houses to be visited in each district were selected randomly on the day of the sampling.

For each sampling unit, one person was asked to be the primary participant and administer the questionnaires. The first questionnaire (see Appendix A), which inquired about demographics of occupants, was administered by the author during the visit. The second questionnaire (see Appendix B) was self-administered by the primary participant, for seven consecutive days starting on the day of the visit, in order to determine the average daily intake rate of drinking water as well as frequency and longevity of activities that could be determinant to exposure to subject contaminants. The questionnaires used in this study were modified from the Baseline, Descriptive and Time-Activity Questionnaires used in NHEXAS-Arizona study (Lebowitz et al. 1995) taking the lifestyle of Turkish people into consideration.

Data collected from questionnaires such as body weight and daily intake rate, the two most important parameters to be used in estimating chronic daily exposure, were helpful in predicting more accurate risk levels compared to making assumptions, as usually practiced in risk assessment studies. Other key data included sex, age, education

and income level, and homeland which made comparison of exposure and risk for different subgroups possible.

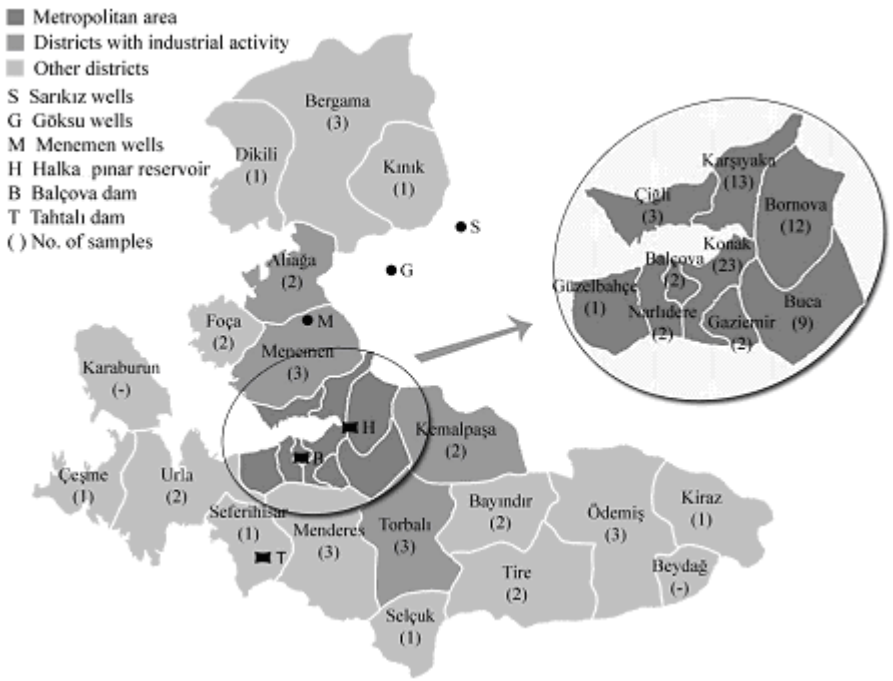

Figure 4.1. Districts and Drinking Water Sources of İzmir

4.2. Drinking Water Sampling

For all analyses and during sampling and cleaning procedures, trace organic and chemical free MilliQ water (Millipore Elix 5) and high purity solvents were used. All glassware were washed with methanol (Merck, ≥99.9%) and water prior to use and dried in the oven for an hour at 105^{o}C.

In each sampling unit, the primary participant was asked about the main drinking water source and samples were collected from tap or bottled waters accordingly. Duplicate samples were collected from each sampling unit in 20-ml headspace vials (Agilent). Tap water samples were collected after allowing the system to flush for 3 minutes. Then the flow rate was reduced to avoid introducing bubbles and 10 ml of water was collected in the sampling vial. Bottled water samples were directly taken from containers. 6.25 mg ascorbic acid (Fluka) was added to the vial as the quenching agent to prevent further reactions leading to changes in VOC concentrations. A drop of 1:3 diluted hydrochloric acid (Merck, 37%) was added to decrease the pH of the sample below 2. Residual chlorine concentration was determined using a DPD (diethyl-p-

phenylene-diamine) test kit (Riedel-de Haën) prior to sampling and another 6.25 mg ascorbic acid was added if the residual chlorine exceeded 5 mg/l.

The vials were immediately sealed with 20-mm aluminum crimp caps (Agilent) with Teflon faced septa (Agilent) and shaken to mix the content. All samples were transported in cooled containers and stored in the dark at 4^{o}C for a maximum of 5 days.

4.3. Analytical Methods

Drinking water samples were analyzed for VOCs using an automated headspace sampler (Agilent 7694) followed by a gas chromatograph (GC) (Agilent 6890N). The GC was equipped with a mass spectrometry (MS) detector (Agilent 5973Nms) to identify and quantify VOCs. EPA Method 524.2 (USEPA 1992c) was followed.

"Liquid Volatile Organic Compound Mixture" (ChemService, LVOC-1JM) containing 54 VOCs was used as the stock standard solution which was purchased as 2000 µg/ml in methanol. Primary dilution standards were prepared at concentrations which could be easily diluted to prepare aqueous calibration solutions that would bracket the working concentration range. These standards were prepared in methanol in 2-ml crimp capped vials to achieve minimum headspace and stored in the dark in a freezer at -27^{o}C. Aqueous calibration standards were prepared by injecting appropriate volumes of primary dilution standards into headspace vials containing 10 ml acidified (pH 2) pure water and 6.25 mg ascorbic acid. The final concentration of the calibration standards were 1, 5, 25, 50, and 100 µg/l. The R^2 values for the linearized calibration curves were between 0.996 and 0.999 for all VOCs of interest.

In the static headspace method, the water sample is placed in a headspace vial and an aliquot of the closed airspace above the water phase is sampled directly to the gas chromatographic column with split injection. The samples were heated and shaken for 15 minutes in the headspace sampler to achieve volatilization of VOCs present in water. The operating conditions for the headspace sampler and the GC/MS system are shown in Table 4.1. The column was temperature programmed to facilitate the separation of compounds which are then detected with the mass spectrometer.

Table 4.1. Gas Chromatography and Headspace Conditions

Instrument / Condition	Description
Gas Chromatography	
Carrier flow rate	0.9 ml/min
Split ratio	40:1
Injection volume	1 µl
Column	Agilent 19091S-433 30m x 0.25 mm x 0.25 µm HP-5MS
Temperature program	3 min at 40°C 40 to 100°C at 5°C per min 2 min at 100°C 100 to 120°C at 5°C per min 2 min at 120°C 120 to 150°C at 10°C per min
Headspace	
Oven temperature	90°C
Loop temperature	95°C
Tr. Line temperature	100°C
GC cycle time	50 min
Vial equilibration time	15 min
Pressurizing time	0.05 min
Loop fill time	0.05 min
Loop equilibration time	0.05 min
Inject time	3 min

Identification of the compounds eluting from the GC column was accomplished by comparing their measured mass spectra and retention times to reference spectra and retention times in a database (ChemStation, Agilent). Selective ion monitoring (SIM) program was employed to increase instrument sensitivity which is essential for drinking water samples since the concentrations are in the low µg/l range. Two ions per compound were chosen for data acquisition, one being the target ion and the other qualifier ion, as presented in Table 4.2 along with the retention time for each compound.

In order to determine the detection limits (DLs) of the VOCs, aqueous solutions were prepared with concentrations close to the expected DLs. 14 solutions with varying concentrations between 0.01 and 0.5 µg/l were analyzed and the DLs presented in Table 4.2 were calculated from those peaks for which the signal-to-noise ratio was at least 3:1.

Table 4.2. Retention Times, Reference Mass Spectra and Detection Limits for VOCs

Compound	Retention Time (min)	Target Ion	Qualifier Ion	Detection Limit (µg/l)
1,1-dichloroethene	1.88	61	63.1	0.05
dichloromethane	1.94	84	86	0.03
trans-1,2-dichloroethene	2.06	61	96	0.04
1,1-dichloroethane	2.14	63	65.1	0.05
1,2-dichloropropane	2.14	62	64.1	0.40
cis-1,2-dichloroethene	2.34	96	98	0.07
2,2-dichloropropane	2.39	77	79.1	0.04
bromochloromethane	2.41	130	127.9	0.05
chloroform	2.41	83	85	0.02
1,1,1-trichloroethane	2.68	97	99	0.02
1,2-dichloroethane	2.71	62	64.1	0.10
1,1-dichloropropene	2.79	75	77.1	0.04
benzene	2.86	78.1	77.1	0.02
carbontetrachloride	2.86	119	117	0.02
trichloroethene	3.38	130	132	0.02
dibromomethane	3.41	174	171.9	0.07
bromodichloromethane	3.49	83	85	0.03
cis-1,3-dichloropropene	4.14	75	77.1	0.08
toluene	4.72	91.1	92.1	0.01
1,1,2-trichloroethane	4.84	97	99	0.06
1,3-dichloropropane	5.18	76	78.1	0.07
dibromochloromethane	5.41	128.9	126.9	0.04
1,2-dibromoethane	5.70	107	109	0.05
tetrachloroethene	5.80	166	163.9	0.02
chlorobenzene	6.86	112	114	0.02
1,1,1,2-tetrachloroethane	6.98	131	134.9	0.04
ethylbenzene	7.33	91	106.1	0.01
p-xylene	7.58	91.1	106.1	0.01
bromoform	8.01	172.9	170.9	0.09
styrene	8.24	104	103.1	0.01
o/m-xylene	8.31	91	106.1	0.01
1,1,2,2-tetrachloroethane	8.96	83	85	0.07
trans-1,3-dichloropropene	9.18	75	77.1	0.09
1,2,3-trichloropropane	9.19	97	99	0.30
isopropylbenzene	9.34	105	120.1	0.01
bromobenzene	9.48	77	156	0.05
2-chlorotoluene	10.17	91	126.1	0.02
n-propylbenzene	10.28	91	120.1	0.01
4-chlorotoluene	10.36	91	126.1	0.02
1,2,4-trimethylbenzene	10.76	105	120.1	0.01
tert-butylbenzene	11.55	119	134.1	0.02
1,3,5-trimethylbenzene	11.56	105	120.1	0.01
1,4-dichlorobenzene	11.91	146	148	0.02
sec-butylbenzene	12.13	105	134.1	0.01
1,2-dichlorobenzene	12.14	146	148	0.02
p-isopropyltoluene	12.58	119	134.1	0.01
1,3-dichlorobenzene	12.85	146	148	0.02
n-butylbenzene	13.58	91	92.1	0.01
1,2-dibromo-3-chloropropane	14.40	157	155	0.30
1,2,4-trichlorobenzene	17.67	180	182	0.02
naphthalene	17.91	128.1	127.1	0.01
1,2,3-trichlorobenzene	18.99	180	182	0.02
hexachloro-1,3-butadiene	19.19	225	222.9	0.02

4.4. Quality Assurance / Quality Control

Quality Assurance / Quality Control evaluations included initial demonstration of laboratory accuracy and precision; continuing calibration checks; and analysis of field duplicates, laboratory reagent blanks, field reagent blanks, and laboratory fortified blanks as proposed by the USEPA (1992c). In addition, MS autotune was performed every day before introducing the samples.

Field duplicates are two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Both laboratory reagent blanks and field reagent blanks were prepared with an aliquot of reagent water and treated exactly as a sample including the addition of HCl and ascorbic acid. Laboratory reagent blanks were prepared in the laboratory whereas field reagent blanks were prepared during the visits while drinking water samples were being collected.

For initial demonstration of laboratory accuracy and precision, replicates of a laboratory fortified blank containing each analyte of concern at a known concentration were analyzed. On a routine basis, laboratory fortified blanks were prepared and treated like samples to determine if the methodology was in control and if the laboratory was still capable of making accurate and precise measurements. For each analyte, the mean accuracy and relative standard deviation were checked to be between 80 to 120% and less than 20%, respectively.

Calibration curves were prepared throughout the linear response range and were routinely checked during analysis of samples using laboratory fortified blanks at different concentrations.

With each batch of samples processed as a group, a laboratory reagent blank was analyzed to determine the system background contamination. In the same manner, with each set of drinking water samples, a field reagent blank was analyzed to define contamination resulting from field sampling procedures and transportation activities. None of the laboratory reagent blanks or field reagent blanks showed contamination.

4.5. Statistical Methods

4.5.1. Goodness-of-Fit Tests

Goodness-of-fit tests, as defined by the USEPA (1997b), are formal statistical tests of the hypothesis that the set of sampled observations are an independent sample from the assumed distribution. The null hypothesis is that the randomly sampled set of observations is independent, identically distributed random variables with distribution function F.

Commonly used goodness-of-fit tests include the chi-square test, Kolmogorov-Smirnov test, and Anderson-Darling test. The chi-square test is based on the difference between the square of the observed and expected frequencies. It is highly dependent on the width and number of intervals chosen and is considered to have low power. It is best used to reject poor fits. The Kolmogorov-Smirnov Test is a non-parametric test based on the maximum absolute difference between the theoretical and sample cumulative distribution functions (CDFs). The Kolmogorov-Smirnov test is most sensitive around the median and less sensitive in the tails and is best at detecting shifts in the empirical CDF relative to the known CDF. It is less proficient at detecting spread, but is considered to be more powerful than the chi-square test. The Anderson-Darling test is designed to test goodness-of-fit in the tails of a probability density function (PDF) based on a weighted-average of the squared difference between the observed and expected cumulative densities (USEPA 1997b).

4.5.2. Variability and Uncertainty Analyses

Variability, also called natural or stochastic uncertainty, is due to variation or heterogeneity among different members of a population. For example, there are differences between people in the amount of water they drink; therefore, the risk associated with exposure to a certain compound takes the form of a range of possible values, most commonly described in terms of statistics such as the mean, median, etc.

Uncertainty results from lack of knowledge about the parameters of a model or system. It is possible to only provide a range of alternative estimates of the true (but unknown) value of a parameter. Examples of knowledge uncertainties in this study

include uncertainty around the true mean and the standard deviation of variables such as VOC concentrations in water. Unlike variability, uncertainty can be reduced by gathering better data.

Monte Carlo Simulation and bootstrapping are frequently used methods to determine variability and uncertainty in risk assessment processes. Monte Carlo Simulation, as detailed in Section 3.3.1, involves placing model variables into an algorithmic loop and allowing them to change based on probability distributions. Classical methods used to estimate the reliability or accuracy of forecast statistics obtained by Monte Carlo Simulation rely on mathematical formulas to describe the accuracy of sample statistics. These methods assume that the distribution of a sample statistic approaches a normal distribution, making the calculation of the statistic's standard error or confidence interval relatively easy. However, when a statistic's sampling distribution is not normally distributed or easily found, these classical methods are difficult to use or are invalid. In contrast, bootstrapping analyzes sample statistics empirically by repeatedly sampling the data and creating distributions of the different statistics from each sampling.

To generate a bootstrap uncertainty estimate for a given statistic from a set of data, a subsample is generated from the data, and the statistic is calculated. This process is repeated for many subsamples, typically between 500 and 1000, and the computed values for the statistic form an estimate of the sampling distribution of the statistic (NIST / SEMATECH 2005).

These two methods were employed as a two-step process in this study. After the distribution of exposure to each VOC was estimated using the Monte Carlo Simulation, the uncertainty associated with these distributions was estimated by bootstrapping.

4.5.3. Kruskal-Wallis and Mann-Whitney Tests

To determine whether the concentrations of VOCs found in drinking water and risk associated with exposure to these VOCs differed across population subgroups, Kruskal-Wallis and Mann-Whitney Tests were used. 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, also known as the Wilcoxon Rank Sum Test, was used to test for difference between the medians of two subgroups.

Kruskal-Wallis Test is the analogue to the F-test used in analysis of variance whereas Mann-Whitney Test is the nonparametric equivalent of the two sample t-test (Montgomery and Runger 1999). While analysis of variance tests depend on the assumption that all populations under comparison are normally distributed, Kruskal-Wallis and Mann-Whitney Tests place no such restriction on the comparison. In addition, nonparametric tests give more powerful results compared to parametric tests when data has been measured on an ordinal scale (e.g. yes/no answers in questionnaires), sample size is small (<30), variances across subgroups are unequal, and data includes outliers.

Resultant p-values of Kruskal-Wallis and Mann-Whitney Tests were examined for different subgroups, such as income and education level, in İzmir population. Large p-values indicate a high probability that an observed difference is due to sample variation, or *chance*, whereas small p-values indicate a real or *significant difference* between means. USEPA (1997b) defines significant difference as an inference that the probability is low that the observed difference in quantities being measured could be due to variability in the data rather than an actual difference in the quantities themselves. In this study, p-values smaller than 0.05 were considered to point a significant difference between the compared subgroups.

CHAPTER 5

RESULTS AND DISCUSSION

The results are discussed under two main sections: Exposure Assessment and Risk Assessment. The first section includes the results obtained for each of the variables used in the chronic daily intake equation as well as the estimated values of exposure using both the deterministic (individual) and the probabilistic (population based) approaches. In the same manner, carcinogenic and noncarcinogenic risk estimates are presented in the second section including the results obtained from both approaches.

5.1. Exposure Assessment

5.1.1. VOC Concentrations

Drinking water samples were analyzed for 54 VOCs using the headspace autosampler - GC/MS system. VOC concentrations ranged from below detection limit to 35 μg/l with none of the samples exceeding the guideline values / maximum contaminant levels presented previously in Table 2.2. However, when total THM concentrations were calculated using an additive model, i.e., the concentrations for the four individual THM species were summed up, one of the drinking water samples exceeded the TTHM MCL of 80 μg/l established by the USEPA (40CFR141.64). All VOC concentrations were found to be below the Turkish drinking water regulations recently published by the Ministry of Health (2005).

At least one VOC was detected in all of the drinking water samples. 69% of the samples contained up to eight different VOC species whereas nine or more VOCs were detected in 31% of the samples. The maximum number of VOCs detected in a single sample was 15, which was encountered in only three samples.

In addition to the four THM species (i.e., chloroform, bromodichloromethane, dibromochloromethane, and bromoform), benzene, toluene, p-xylene and naphthalene were the most frequently detected VOCs. The numbers of samples in which these VOCs were detected are shown in Table 5.1. Since a large proportion of the rest of the 54

VOCs were below the detection limits, exposure and risk assessments were carried out for only these eight VOCs due to statistical limitations.

Table 5.1. Detection Frequencies of the VOCs of Concern

VOC	Frequency (%)	VOC	Frequency (%)
Chloroform	71	Benzene	47
Bromodichloromethane	46	Toluene	96
Dibromochloromethane	47	p-Xylene	74
Bromoform	45	Naphthalene	70

Extreme outliers are measurements that are extremely large or small relative to the rest of the data and, therefore, are suspected of misrepresenting the population from which they were collected. Box and whisker plots were constructed to identify the extreme outliers. Four of these plots are presented in Figure 5.1. The concentration values marked by an asterisk (*) indicate outliers.

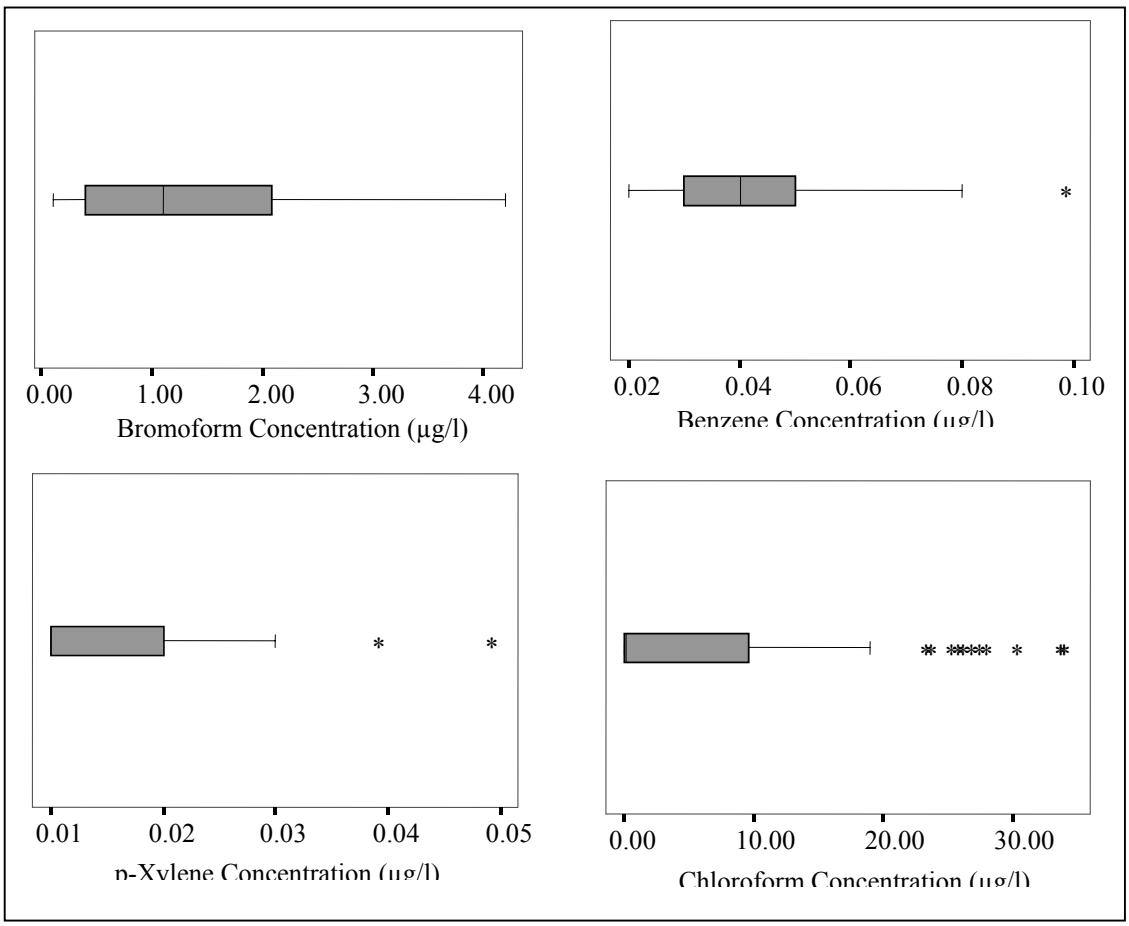

Figure 5.1. Box and Whisker Plots for Selected VOCs

Even though some outliers were detected in some of the concentration data, as seen in the examples of benzene, p-xylene and chloroform, none of them was an extreme outlier; therefore, all of the measured concentrations were included in the data set.

5.1.1.1. Probability Distributions

Goodness-of-fit tests, i.e., the chi-square test, Kolmogorov-Smirnov test, and Anderson-Darling test, were applied to the concentration data to obtain the best fitted distribution for each VOC. These tests are used to test whether data follow a specific distribution, i.e., how *good* a specified distribution fits the data (USEPA 2000a).

Due to the fact that none of the VOCs were detected in all of the samples, concentration data had to be adjusted, using censoring techniques, in order to obtain a concentration value for each individual sample, to equate the sample sizes of all VOC data sets for comparison purposes, and to avoid overestimation of exposure and risk. While the concentration may be highly uncertain for the contaminants below the detection limit (DL), it does not necessarily mean that the concentration is zero. Exposure assessors are often faced with the problem of having to estimate values for the censored data. Simple substitution methods are commonly practiced; and frequently used values include zero, the DL, DL/2, and DL/$\sqrt{2}$ (USEPA 1992a).

Distributional methods, unlike simple substitution methods, make use of the data above the detection limit to extrapolate below it. After the probability distributions have been obtained for the detected concentrations of each VOC, values were generated for the nondetected samples. These values lie between zero and the detection limit specific for each VOC and fit the probability distribution obtained for the VOC of concern. Generated concentrations were then used in exposure and risk calculations along with the measured concentrations.

The median, mean, and standard deviation of concentration data for each VOC is presented in Table 5.2 along with the minimum, maximum, 90th percentile, 95th percentile, and 99th percentile values. As seen in this table, the median concentrations calculated for BDCM, DBCM, bromoform, and benzene fell below the detection limits reported previously in Table 4.2 due to the generated concentration values for nondetected samples.

Table 5.2. Descriptive Statistics for VOC Concentrations in İzmir Drinking Water

VOC	Median	Mean	SD†	Min	Max	90th %ile*	95th %ile*	99th %ile*
Chloroform	0.04	4.41	9.36	3.84E-11	34.58	24.28	27.49	34.58
BDCM	0.02	3.73	7.78	1.58E-07	27.45	21.23	22.93	27.44
DBCM	0.03	2.61	5.20	4.09E-07	17.93	13.48	15.02	17.92
Bromoform	0.08	0.62	0.95	2.02E-04	4.19	2.12	2.57	4.19
Benzene	0.02	0.03	0.02	0.010	0.10	0.06	0.07	0.10
Toluene	0.05	0.09	0.18	0.007	1.60	0.16	0.43	1.59
p-Xylene	0.01	0.01	0.01	0.001	0.05	0.02	0.03	0.05
Naphthalene	0.03	0.06	0.13	0.004	0.90	0.11	0.20	0.90

N = 100 † Standard Deviation
All values are in µg/l. * Percentile

When these statistics were compared with those reported in studies previously summarized in Section 2.4, it was observed that the median, mean, and 90th percentile values listed in Table 5.2 were much smaller in almost all of the cases.

The exception for chloroform was the mean and 90th percentile concentrations reported by Sofuoglu et al. (2003) as part of the NHEXAS-Arizona study. The values calculated for Arizona and border populations for both tap and nontap water were less than those given above. For benzene, Robertson et al. (1999) have reported a median concentration below the detection limit of 0.03 µg/l and a 90th percentile concentration of 0.04 µg/l as part of the same study, both of which lie below the values calculated for benzene in this study.

The concentrations of THMs found in İzmir tap water (see Table 5.5) were much less than the concentrations reported by Tokmak et al. (2004). The relatively high concentrations detected in Ankara tap water is probably due to the characteristics of the raw water used in İvedik Water Treatment Plant. In addition to this, drinking water samples collected in our study included nontap waters which resulted in decreased values for THM concentration statistics. The difference between the VOC concentrations found in İzmir tap and nontap water samples were discussed in Section 5.1.1.2.

The final probability distributions were plotted for each VOC concentration as presented in Figures 5.2 through 5.9. Environmental data commonly exhibit probability distributions that are non-negative and skewed with heavy or long right tails (USEPA 2000a). Supporting this statement, all concentrations had right skewed distributions. The values in the x-axis are concentrations in µg/l while the y-axis indicates probability.

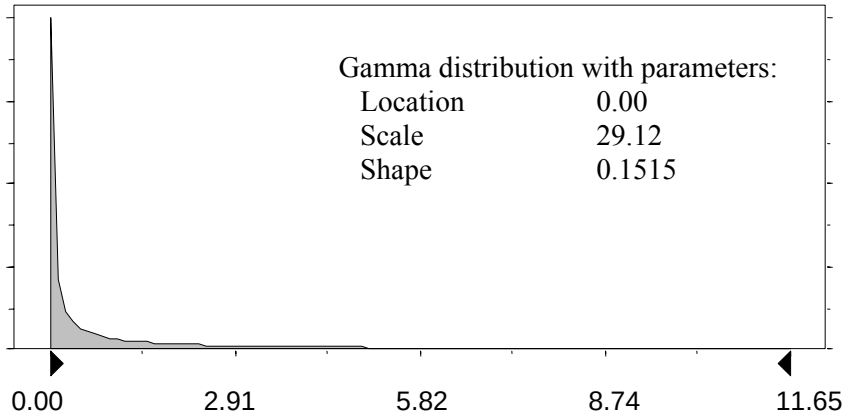

Figure 5.2. Probability Distribution for Chloroform Concentration

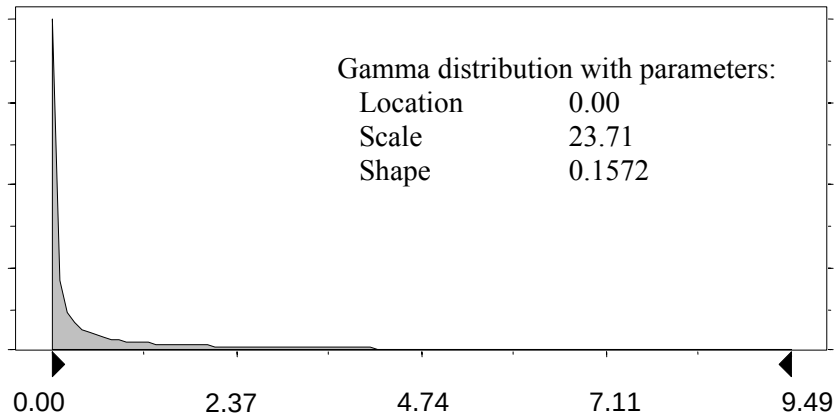

Figure 5.3. Probability Distribution for Bromodichloromethane Concentration

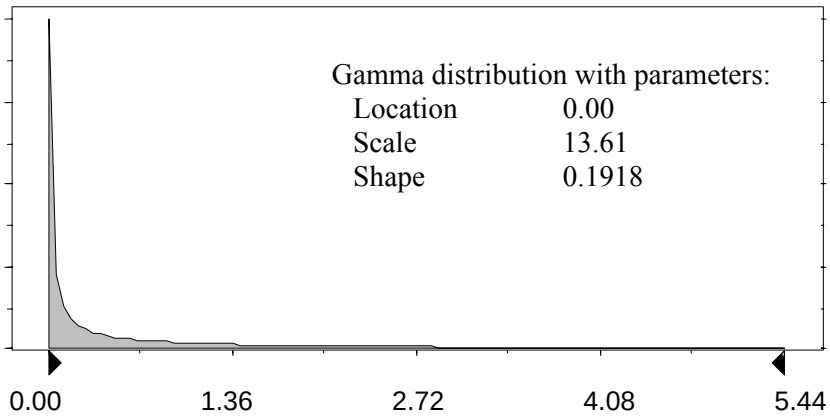

Figure 5.4. Probability Distribution for Dibromochloromethane Concentration

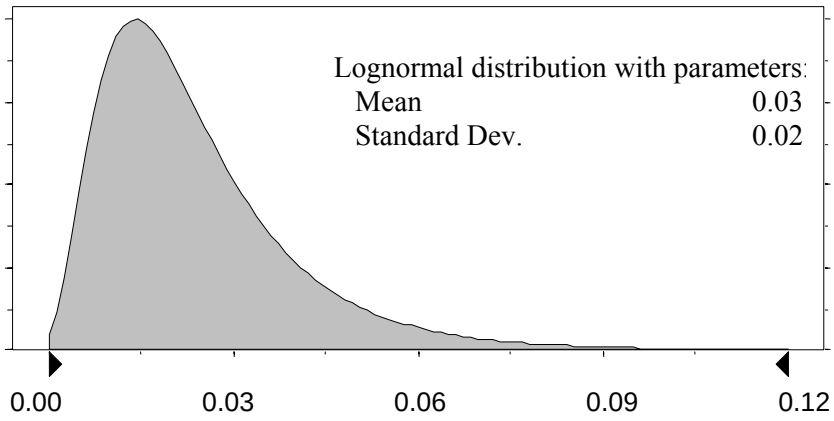

Figure 5.5. Probability Distribution for Benzene Concentration

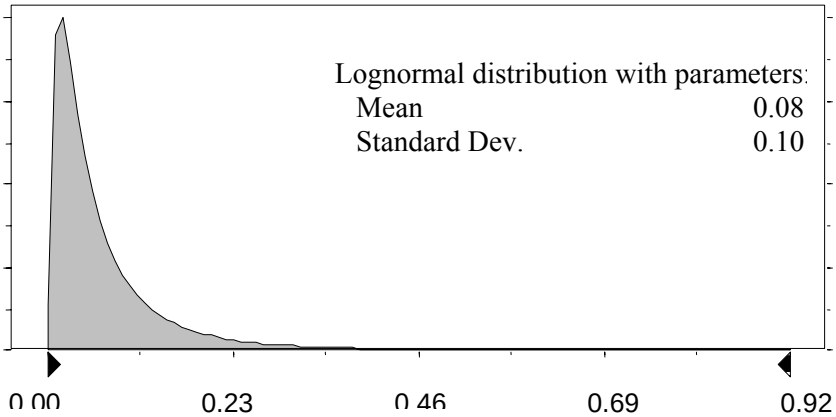

Figure 5.6. Probability Distribution for Toluene Concentration

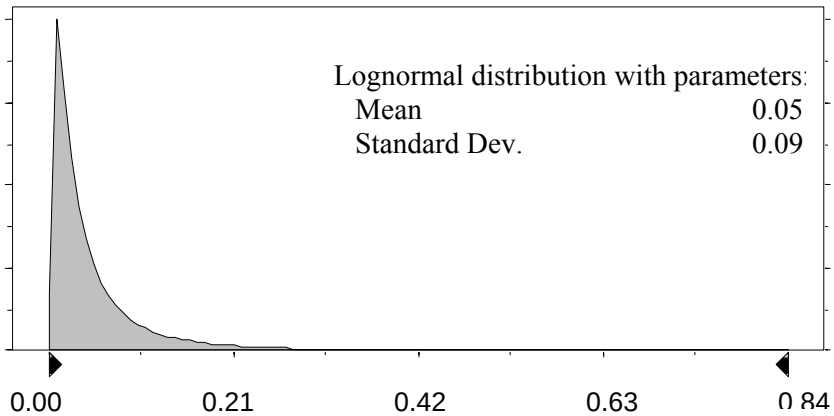

Figure 5.7. Probability Distribution for Naphthalene Concentration

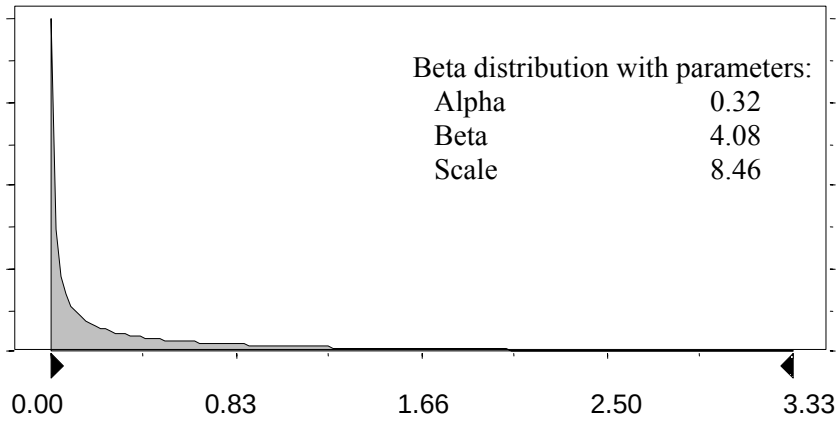

Figure 5.8. Probability Distribution for Bromoform Concentration

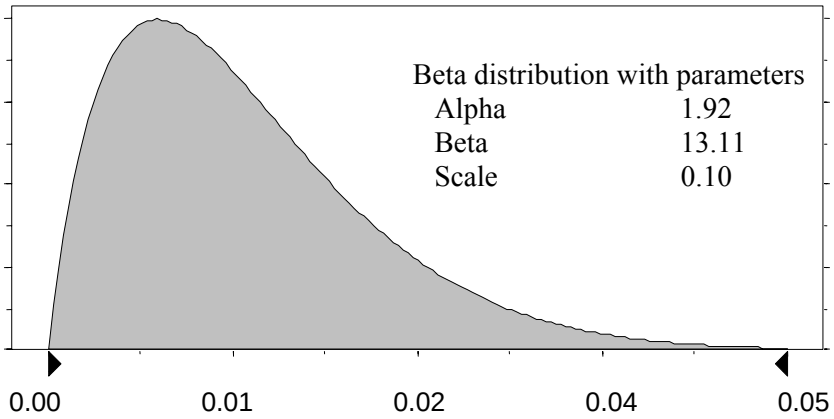

Figure 5.9. Probability Distribution for p-Xylene Concentration

Chloroform, BDCM, and DBCM were fit by gamma distributions each identified by individual location, scale, and shape parameters. Lognormal distribution best fit the concentration data for benzene, toluene, and naphthalene with the indicated mean and standard deviation values whereas bromoform and p-xylene concentration data were represented by beta distribution with alpha, beta, and scale parameters shown on each figure.

5.1.1.2. Differences across Subgroups

Statistical tests were used in order to determine whether VOC concentrations in drinking water samples differed across subgroups in İzmir population. Information gathered from questionnaires was examined and concentration data for each VOC were compared for subgroups for six categories; sex, area, water source, education level, homeland, and income level.

Mann-Whitney Test was applied to test the null hypothesis that the subgroups had identical distribution functions against the alternative hypothesis that the two distribution functions differed only with respect to location (median), if at all. Data were compared for sex, area, and water source using this statistical test.

Table 5.3. Results of Mann-Whitney Tests on Subgroups for VOC Concentrations

Category		Sex	Area	Water Source
Subgroups		Female/Male	Metropolitan/Other	Tap/Nontap
Sample sizes		60/40	67/33	65/35
p-values	Chloroform	0.714	*<0.001*	*<0.001*
	BDCM	0.822	*<0.001*	*<0.001*
	DBCM	0.888	*0.003*	*<0.001*
	Bromoform	0.696	0.101	*<0.001*
	Benzene	0.556	*<0.001*	0.736
	Toluene	0.840	*<0.001*	*0.001*
	p-Xylene	0.579	*<0.001*	*0.001*
	Naphthalene	0.234	*<0.001*	*<0.001*

p-values in *italics* indicate significant difference.

Mann-Whitney Test results revealed that the concentration of VOCs found in İzmir drinking water did not differ for sex category as indicated by high p-values in Table 5.3.

For the area category, each district of İzmir was placed in one of the following subgroups: (1) Metropolitan area in which tap water is served by İzmir Metropolitan Municipality (see Figure 4.1) and (2) Other districts. For all VOCs, the concentrations found in metropolitan area were greater than those in other districts as presented in Table 5.4. The difference was not significant at the presumed significance level for bromoform only, indicated by a p-value of 0.101.

Table 5.4. Statistics for VOC Concentrations across Area Subgroups

VOC	Area	Median	Mean	VOC	Area	Median	Mean
Chloroform	Metropolitan	0.110	6.172	Benzene	Metropolitan	0.030	0.033
	Other	0.007	0.833		Other	0.017	0.020
BDCM	Metropolitan	0.130	5.212	Toluene	Metropolitan	0.060	0.107
	Other	0.011	0.716		Other	0.020	0.051
DBCM	Metropolitan	0.280	3.626	p-Xylene	Metropolitan	0.010	0.014
	Other	0.009	0.548		Other	0.009	0.011
Bromoform	Metropolitan	0.180	0.767	Naphthalene	Metropolitan	0.040	0.084
	Other	0.068	0.331		Other	0.009	0.021

All values are in µg/l.

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 all other sources. All THM species were detected in higher concentrations in tap water whereas nontap water contained more benzene, toluene, p-xylene, and naphthalene as presented in Table 5.5. Mann-Whitney Test results suggested that the difference between tap and nontap water was significant for all VOCs except benzene which is indicated by a p-value of 0.736.

Table 5.5. Statistics for VOC Concentrations across Source Subgroups

VOC	Source	Median	Mean	VOC	Source	Median	Mean
Chloroform	tap	0.110	6.347	Benzene	tap	0.019	0.028
	nontap	0.020	0.812		nontap	0.020	0.029
BDCM	tap	0.130	5.384	Toluene	tap	0.030	0.088
	nontap	0.003	0.653		nontap	0.060	0.087
DBCM	tap	0.350	3.797	p-Xylene	tap	0.010	0.012
	nontap	0.006	0.408		nontap	0.010	0.015
Bromoform	tap	0.400	0.902	Naphthalene	tap	0.020	0.029
	nontap	0.057	0.104		nontap	0.060	0.126

All values are in µg/l.

Since education level, homeland, and income level included more than two subgroups, Kruskal-Wallis Test was applied to test the null hypothesis that all subgroups had identical distribution functions against the alternative hypothesis that at least two of the subgroups differed only with respect to location (median), if at all. In addition, Mann-Whitney Test was used to identify the differences between the subgroups when they were compared in groups of two.

Table 5.6. Results of Kruskal-Wallis Tests on Subgroups for VOC Concentrations

Category		Education Level	Homeland	Income Level
Subgroups		Up to high school/ High school grad/ Tech sch 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	Chloroform	0.334	*0.048*	0.217
	BDCM	0.096	0.062	0.065
	DBCM	0.201	*0.009*	0.375
	Bromoform	*0.026*	*0.034*	0.066
	Benzene	0.630	0.432	0.911
	Toluene	*0.005*	0.962	*0.004*
	p-Xylene	*0.006*	0.644	*0.013*
	Naphthalene	*<0.001*	0.643	*0.002*

p-values in *italics* indicate significant difference.

Education level was investigated in three subgroups; (1) up to high school, (2) high school graduate, and (3) technical school / college graduate. Bromoform concentration in the first subgroup was significantly higher than the other subgroups. For toluene, p-xylene, and naphthalene, concentrations increased with education level with significant differences especially between the first and third subgroups.

In the descriptive questionnaire, homeland category was divided into eight subgroups including all the regions in Turkey and a separate subgroup for foreigners. However, the sample sizes of most of these subgroups were not sufficient for effective statistical analyses. Therefore, Kruskal-Wallis Test was applied to only three of these subgroups, (1) Aegean Region, (2) Central Anatolia Region, and (3) Eastern Anatolia Region. Across these subgroups, the concentrations for benzene, toluene, p-xylene, and naphthalene were very close as indicated in Table 5.6 with high p-values. On the other hand, THM concentrations increased as: Eastern Anatolia Region > Central Anatolia Region > Aegean Region. The differences were significant especially between the Aegean Region and the Eastern Anatolia Region according to the Mann-Whitney Test results.

In order to determine the income level for each house, monthly income of every individual living in that house was summed up. The income level was examined in three subgroups; (1) Between 0 and 600 YTL, (2) Between 600 and 2,000 YTL, and (3) More than 2,000 YTL. For benzene and the four THM species, the concentrations did not differ across these subgroups. However, the concentrations for toluene, p-xylene, and

naphthalene increased as the income level increased. Mann-Whitney Test results revealed that the differences were significant between the subgroups 1& 2 and 1 & 3.

5.1.2. Average Daily Intake Rate of Drinking Water

The amount of drinking water consumed daily by each participant was found out by the help of the Descriptive Questionnaire. The number of standard (200-ml) glasses of water drunk per day for seven consecutive days in the week of sampling was reported, and then these values were converted to liters and the resultant frequency distribution for average daily intake rate of drinking water (DI) was plotted as shown in Figure 5.10.

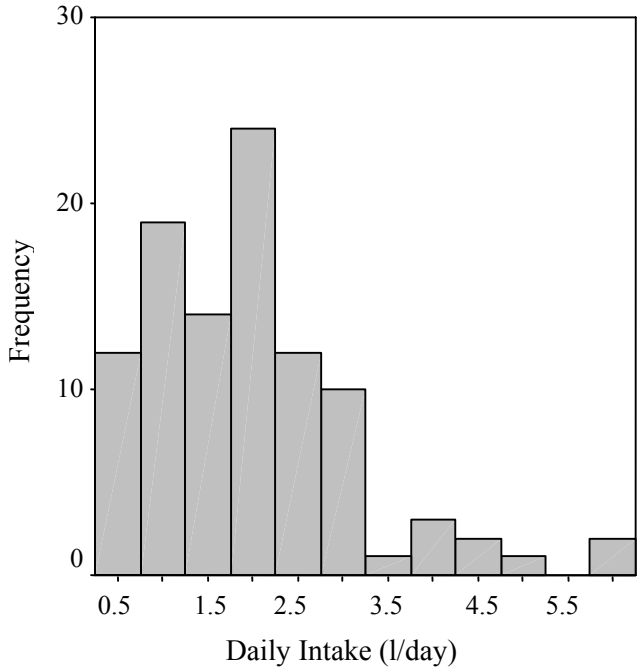

Figure 5.10. Frequency Distribution for Average Daily Intake Rate of Drinking Water

As demonstrated by the frequency distribution, most of the participants consumed drinking water in the range of 0.4-3.2 l/day. The percentage of people with an average daily intake rate of drinking water above 3.2 l/day was only 10%, which is indicated by the 90^{th} percentile value in Table 5.7.

Table 5.7. Descriptive Statistics for Average Daily Intake Rate of Drinking Water

Statistic	Daily Intake (l/day)
Median	1.80
Mean	1.95
Standard Deviation	1.15
Minimum	0.40
Maximum	6.00
90^{th} Percentile	3.20
95^{th} Percentile	4.38
99^{th} Percentile	6.00

N = 100

The mean DI value for İzmir population was found to be very close to the USEPA default value of 2 l/day and lie between the values reported in previous studies. Sofuoglu et al. (2003) have calculated mean drinking water consumption values of 0.92 and 0.95 l/day for Arizona and border populations respectively. However, these values were never used directly in exposure estimations. Making use of the NHEXAS-Arizona study questionnaires, exposure was estimated following the procedures explained for deterministic and probabilistic approaches previously in Chapter 3.

On the other hand, single DI values were used in other risk assessment studies which may have lead to over/underestimation of risk. Lee et al. (2004) used 4.48 l/day based on the Taiwan Recommended Value for Estimating Intake. Tokmak and co-workers (2004) preferred to make an assumption and inserted the USEPA value of 2 l/day into the exposure equation, which does not seem reasonable for Ankara population. It is obvious that DI varies according to climatical conditions; and 2 l/day is rather close to the mean DI value calculated for İzmir which has a hotter climate with high humidity compared to Ankara. When the median DI value of 1.8 is considered, the difference gets even greater. Our sampling campaign continued from September to December 2004, therefore we believe that our statistics are realistic estimations of annual values of the İzmir population.

In order to estimate exposure probabilistically, the probability distribution was fitted for average daily intake rate of drinking water to be used as an input distribution in Monte Carlo Simulation, which is presented in Figure 5.11. DI data follows a lognormal distribution, as the figure implies, with mean 1.99 and standard deviation 1.39.

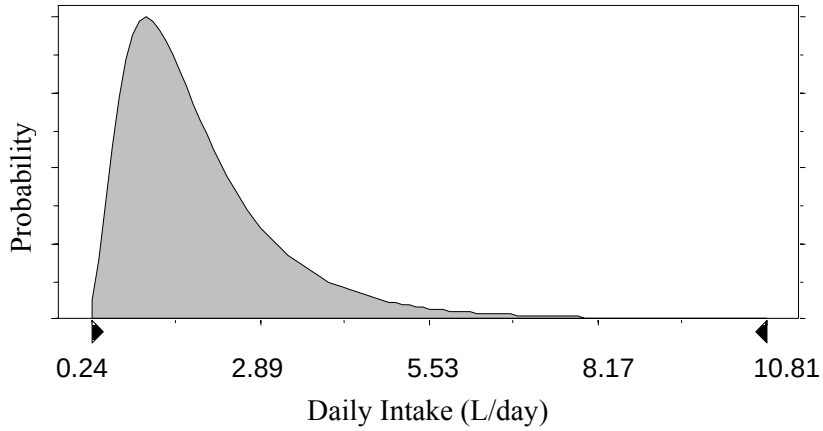

Figure 5.11. Probability Distribution for Average Daily Intake Rate of Drinking Water

5.1.3. Body Weight

The body weight of each participant was recorded during the administration of the Descriptive Questionnaire and the frequency distribution was constructed for our sample as presented in Figure 5.12.

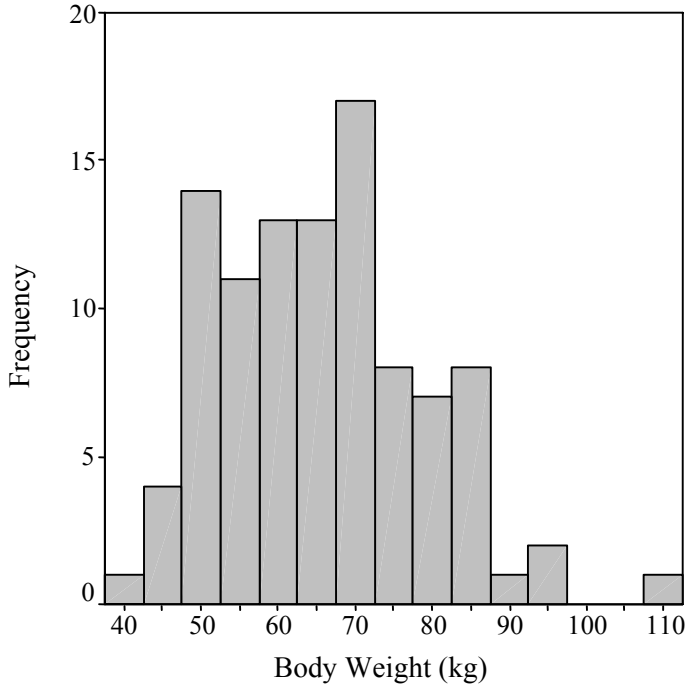

Figure 5.12. Frequency Distribution for Body Weight

62% of the participants had body weights between 50 and 70 kg while the percentage of people with a body weight between 70 and 90 kg was 23. The statistics calculated for body weight data are shown in Table 5.8.

Table 5.8. Descriptive Statistics for Body Weight

Statistic	Body Weight (kg)
Median	64.5
Mean	65.6
Standard Deviation	13.2
Minimum	38.0
Maximum	112.0
90th Percentile	85.0
95th Percentile	86.0
99th Percentile	111.8

N = 100

The median and mean body weights for İzmir population were found to be less than the value, 70 kg, suggested by the USEPA and used in many studies (Williams et al. 2002, Lee et al. 2004).

The mean body weights reported in the NHEXAS-Arizona study were 69.7 and 71.6 kg for Arizona and border subjects, respectively (Sofuoglu et al. 2003). For Ankara residents, Tokmak et al. (2004) used a constant body weight of 65 kg for females and 72 kg for males. In this study, the median and mean values were calculated as 58 kg and 60 kg for females and as 74.5 kg and 73.9 kg for males. If the body weight was assumed to be 70 kg for İzmir population, exposure and risk would have been underestimated for female participants and overestimated for male participants.

Body weight data was fit by a lognormal distribution, as shown in Figure 5.13, to be used as an input distribution in Monte Carlo Simulation. The parameters representing the probability distribution for body weight, i.e., mean and standard deviation, were calculated as 65.56 and 13.02, respectively.

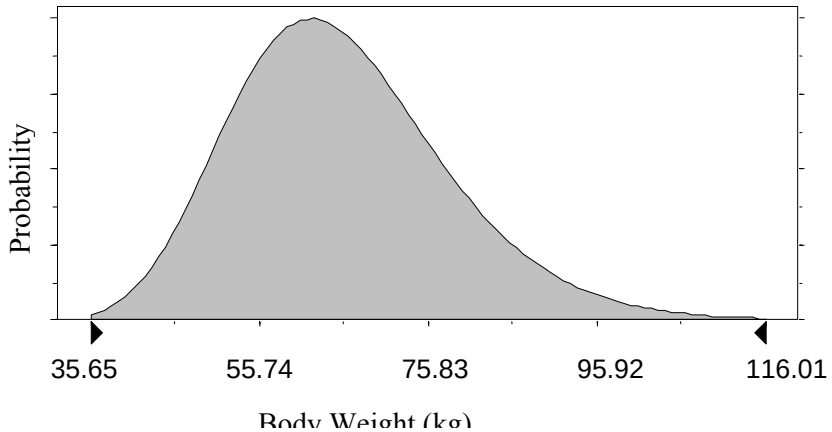

Figure 5.13. Probability Distribution for Body Weight

5.1.4. Exposure

5.1.4.1. Deterministic Exposure Assessment

Deterministic exposure assessment involved using Equation (3.1) to estimate individual exposures to each VOC. CDI values were calculated for each participant and the statistics are presented in Table 5.9.

Table 5.9. Descriptive Statistics for Deterministic Exposure Assessment

VOC	Median	Mean	SD†	Min	Max	90th %ile*	95th %ile*
Chloroform	0.0012	0.1280	0.3070	9.95E-13	1.301	0.582	0.986
BDCM	0.0006	0.1088	0.2666	5.17E-09	1.501	0.397	0.772
DBCM	0.0015	0.0769	0.1921	7.16E-09	1.233	0.331	0.522
Bromoform	0.0027	0.0184	0.0378	9.39E-06	0.264	0.066	0.084
Benzene	0.0006	0.0009	0.0008	7.84E-05	0.005	0.002	0.002
Toluene	0.0011	0.0028	0.0074	3.19E-05	0.069	0.005	0.010
p-Xylene	0.0003	0.0004	0.0003	1.76E-05	0.002	0.001	0.001
Naphthalene	0.0007	0.0022	0.0057	4.09E-05	0.039	0.003	0.006

N = 100 † Standard Deviation
All values are in µg/kg/d. * Percentile

The CDI statistics reported by Sofuoglu et al. (2003) using the deterministic approach were compared to the values calculated for chloroform and toluene in this study. The median, mean, and 90th percentile CDI values for chloroform listed above were greater than those calculated for NHEXAS Arizona and border populations. Toluene CDI statistics for İzmir and NHEXAS border populations were almost equal whereas the values calculated for the Arizona population were much greater.

The results of Mann-Whitney and Kruskal-Wallis Tests used to compare the CDI values across subgroups were in good agreement with the p-values reported for VOC concentrations. Significant differences discussed in Section 5.1.1.2 for all categories were valid for exposure. This indicates that the differences in exposure to VOCs 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 DI and BW values across subgroups also supported this inference pointing out significances only for the sex category.

5.1.4.2. Probabilistic Exposure Assessment

In order to estimate exposure probabilistically, Monte Carlo Simulation was run using the fitted probability distributions for VOC concentrations, body weight, and average daily intake rate of drinking water as the input variables. 10,000 trials were run for each VOC and resultant probability distributions were constructed. In Table 5.10, the statistics extracted from Monte Carlo Simulation run are shown.

Table 5.10. Descriptive Statistics for Probabilistic Exposure Assessment

VOC	Median	Mean	SD†	Min	Max	90th %ile*	95th %ile*
Chloroform	0.0050	0.1403	0.4801	1.78E-13	16.819	0.359	0.697
BDCM	0.0051	0.1120	0.3621	6.33E-10	7.885	0.312	0.624
DBCM	0.0060	0.0811	0.2665	2.09E-09	13.997	0.224	0.399
Bromoform	0.0047	0.0193	0.0393	4.59E-14	1.089	0.054	0.089
Benzene	0.0006	0.0009	0.0009	2.24E-05	0.020	0.002	0.002
Toluene	0.0012	0.0024	0.0040	9.94E-06	0.071	0.005	0.008
p-Xylene	0.0003	0.0004	0.0004	1.22E-06	0.008	0.001	0.001
Naphthalene	0.0008	0.0017	0.0033	1.06E-06	0.083	0.004	0.007

N = 10,000 † Standard Deviation
All values are in µg/kg/d. * Percentile

The median, mean, and 90th percentile CDI values for chloroform and toluene given above were compared to the values reported by Sofuoglu et al. (2003) using the probabilistic approach. Chloroform CDI statistics for the NHEXAS-Arizona study were less than the values obtained in this study while for toluene the opposite was observed.

Similar to the VOC concentrations, oral exposures to the investigated compounds had right skewed distributions as presented in Figures 5.14 through 5.21. Gamma was the best fitting distribution for the THM species whereas benzene, toluene, p-xylene, and naphthalene had lognormal distributions.

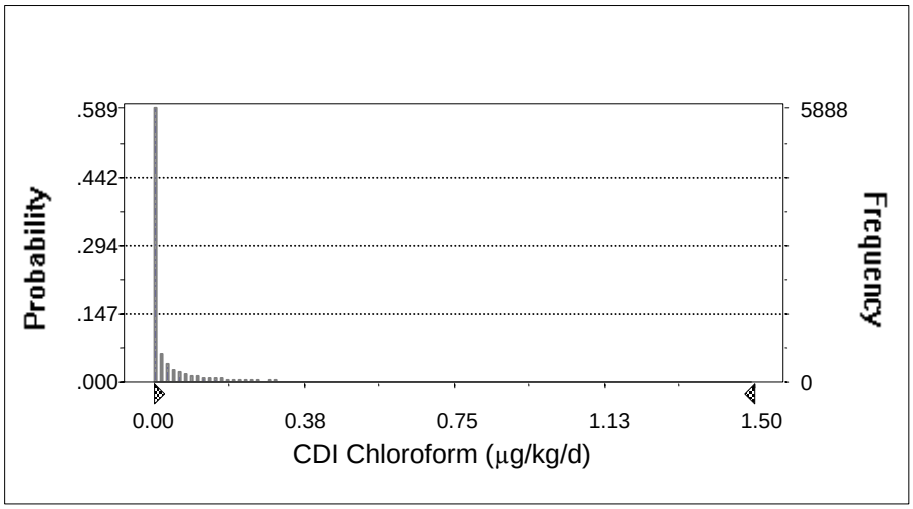

Figure 5.14. Probability Distribution for Chloroform Exposure

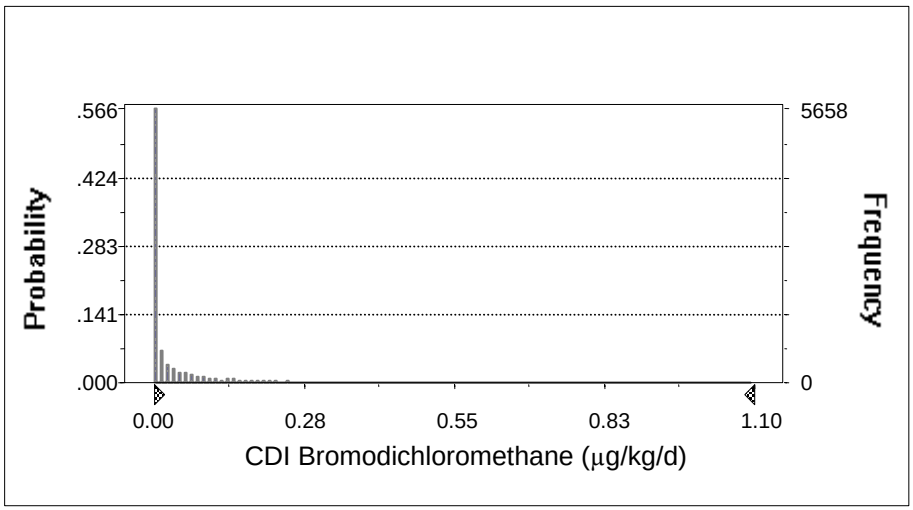

Figure 5.15. Probability Distribution for Bromodichloromethane Exposure

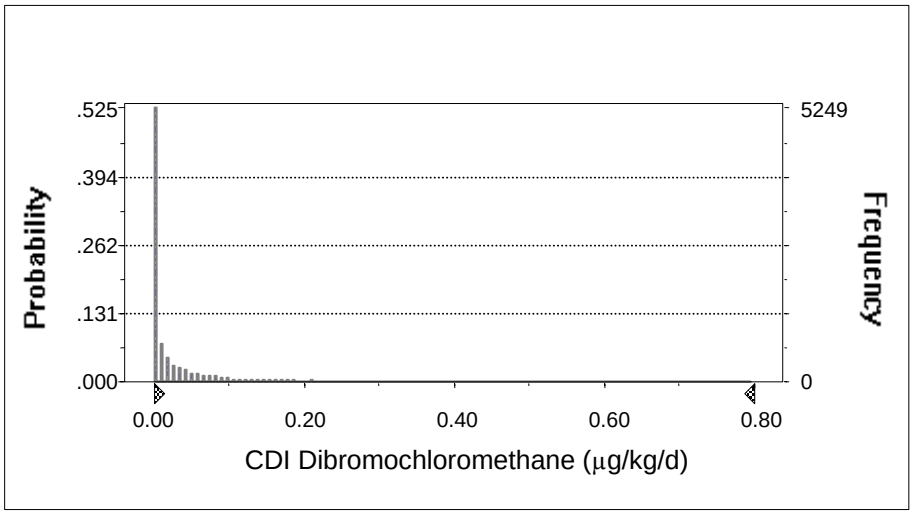

Figure 5.16. Probability Distribution for Dibromochloromethane Exposure

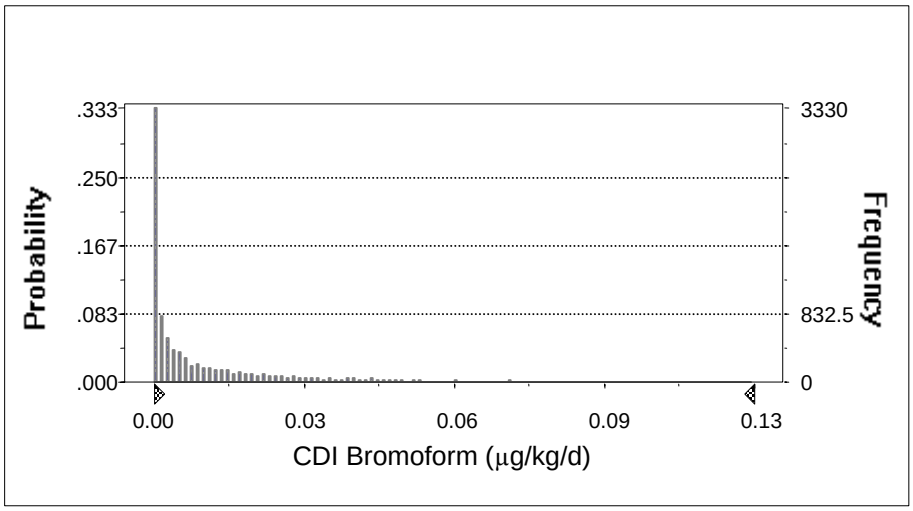

Figure 5.17. Probability Distribution for Bromoform Exposure

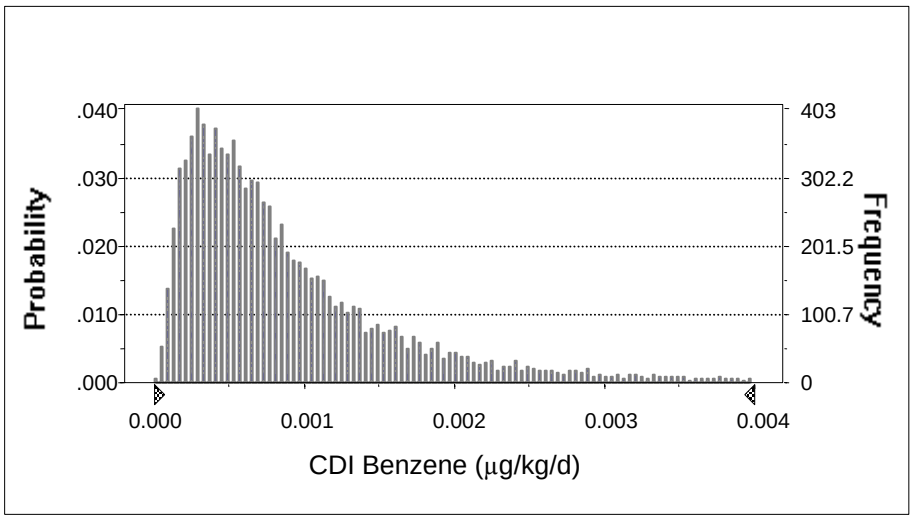

Figure 5.18. Probability Distribution for Benzene Exposure

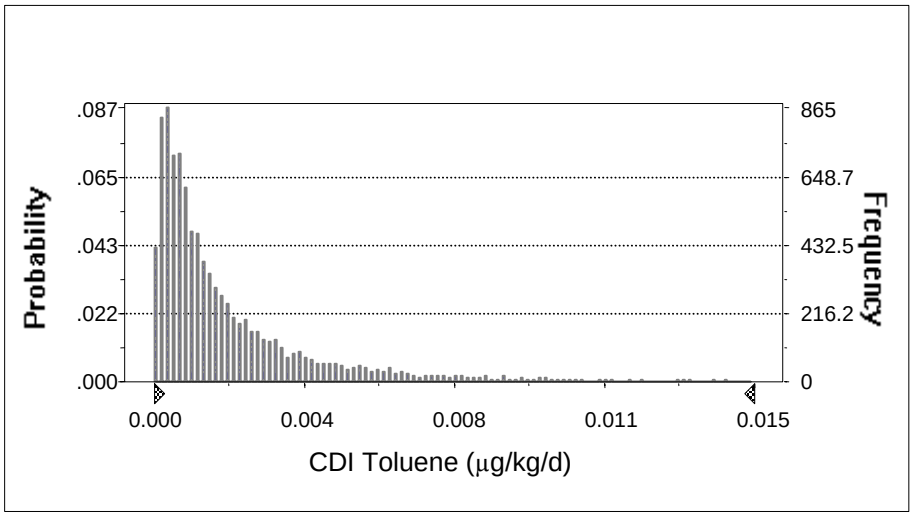

Figure 5.19. Probability Distribution for Toluene Exposure

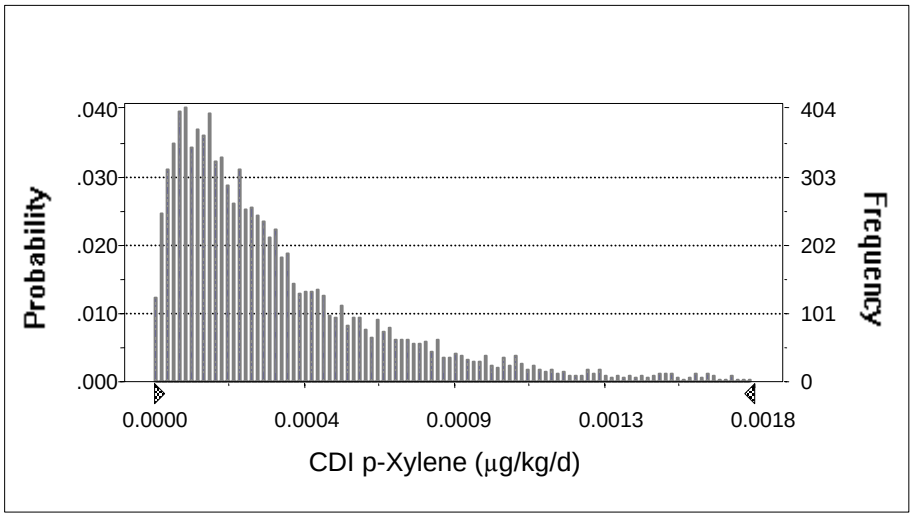

Figure 5.20. Probability Distribution for p-Xylene Exposure

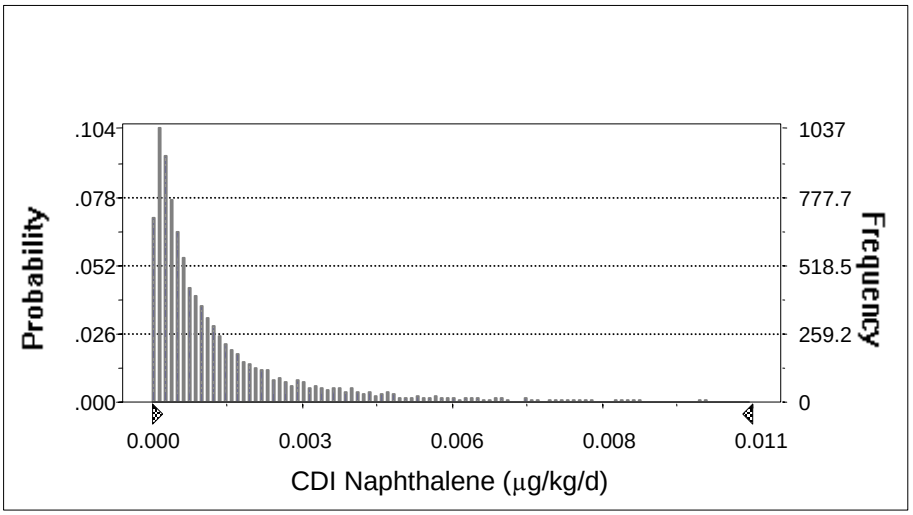

Figure 5.21. Probability Distribution for Naphthalene Exposure

When the results obtained from deterministic and probabilistic approaches were compared, they were in general agreement for exposure estimates. For benzene, toluene, p-xylene, and naphthalene, the median, mean, 90th percentile, and 95th percentile CDI values were almost equal. For the THMs, on the other hand, probabilistic approach resulted in slightly higher estimates for median and mean exposures; and slightly lower estimates for 90th and 95th percentiles.

5.2. Risk Assessment

In this section, carcinogenic and noncarcinogenic risks attributable to chloroform, bromodichloromethane, dibromochloromethane, bromoform, benzene, toluene, p-xylene, and naphthalene were assessed using both deterministic and probabilistic approaches. The estimated values for R and HQ were compared with the acceptable levels stated in Section 3.2.4 and with those reported in previous risk assessment studies.

5.2.1. Noncarcinogenic Risk

5.2.1.1. Deterministic Estimation of HQ

To estimate noncarcinogenic risk, the hazard quotient was calculated for each VOC using Equation (3.3). Individual exposures were divided by the corresponding reference doses and the statistics of the calculated HQ values were obtained as given in Table 5.11.

Table 5.11. Descriptive Statistics for Deterministic Noncarcinogenic Risk Assessment

VOC	Median	Mean	SD†	Min	Max	90th %ile*	95th %ile*
Chloroform	0.0001	0.0128	0.0307	9.95E-13	0.1301	0.0582	0.0986
BDCM	3.03E-05	0.0054	0.0133	2.59E-10	0.0750	0.0198	0.0386
DBCM	0.0001	0.0038	0.0096	3.58E-10	0.0616	0.0166	0.0261
Bromoform	0.0001	0.0009	0.0019	4.69E-07	0.0132	0.0033	0.0042
Benzene	0.0002	0.0002	0.0002	1.96E-05	0.0012	0.0004	0.0006
Toluene	5.53E-06	1.42E-05	3.69E-05	1.59E-07	0.0003	2.50E-05	0.0001
p-Xylene	1.57E-06	1.99E-06	1.72E-06	8.81E-08	8.18E-06	4.32E-06	6.15E-06
Naphthalene	3.59E-05	0.0001	0.0003	2.05E-06	0.0020	0.0002	0.0003

N = 100
† Standard Deviation
* Percentile

HQ values greater than 1 indicate a potential for an adverse effect to occur or the need for further study. For İzmir drinking water, however, the calculated HQ values pointed out negligible noncarcinogenic risks. Even the highest value, the maximum HQ

for chloroform, was far less than 1, similar to the case in NHEXAS-Arizona (Sofuoglu et al. 2003) given previously in Table 3.4.

Lee et al. (2004) have reported HQ values as high as 0.48 for chloroform and 0.52 for TTHMs. The reasons for these relatively high estimates are that the THM concentrations found in Hong Kong drinking water and the average daily intake rate used to estimate CDI values were greater than those found in İzmir and Arizona studies.

5.2.1.2. Probabilistic Estimation of HQ

Exposures estimated probabilistically by Monte Carlo Simulation were used in Equation (3.3) to calculate the HQ value for each compound. Probability distributions for noncarcinogenic risks were similar to those plotted for exposures given previously in Figures 5.14 through 5.21. Both noncarcinogenic risk and exposure plots were fit by the same distribution for each VOC since the only difference was the division by a constant, the RfD. For the same reason, the differences between population subgroups discussed for exposure are valid for noncarcinogenic risk also. Table 5.12 shows the statistics calculated for probabilistically estimated HQ values.

Table 5.12. Descriptive Statistics for Probabilistic Noncarcinogenic Risk Assessment

VOC	Median	Mean	SD†	Min	Max	90th %ile*	95th %ile*
Chloroform	0.0005	0.0140	0.0480	1.78E-14	1.6819	0.0359	0.0697
BDCM	0.0003	0.0060	0.0181	3.17E-11	0.3942	0.0156	0.0312
DBCM	0.0003	0.0041	0.0133	1.05E-10	0.6999	0.0112	0.0200
Bromoform	0.0002	0.0010	0.0020	2.29E-15	0.0545	0.0027	0.0044
Benzene	0.0002	0.0002	0.0002	5.59E-06	0.0049	0.0004	0.0006
Toluene	5.80E-06	1.19E-05	2.01E-05	4.97E-08	0.0004	2.68E-05	4.19E-05
p-Xylene	1.36E-06	2.03E-06	2.24E-06	6.11E-09	3.93E-05	4.39E-06	5.98E-06
Naphthalene	3.75E-05	0.0001	0.0002	5.29E-08	0.0041	0.0002	0.0003

N = 10,000
† Standard Deviation
* Percentile

Deterministic and probabilistic approaches resulted in almost equal HQ values as indicated by the statistics presented in Tables 5.11 and 5.12. The median, mean, 90th percentile, and 95th percentile HQ values were almost equal. Even though the differences were negligible, probabilistic approach resulted in slightly higher estimates

for median and mean HQs while 90th and 95th percentile values were slightly lower compared to those estimated deterministically.

5.2.2. Carcinogenic Risk

5.2.2.1. Deterministic Estimation of R

Lifetime cancer risk associated with exposure to the investigated VOCs via ingestion route was calculated for each participant using Equation (3.2). Individual exposures were multiplied by the SFs given for each VOC previously in Table 3.3. For benzene, the upper limit of the given range was used in calculations.

In Table 5.13, the statistics are presented for deterministically estimated R values. Cancer risks could not be calculated for chloroform, toluene, p-xylene, and naphthalene since SFs were not available for these VOCs as discussed in Section 3.2.2.

Table 5.13. Descriptive Statistics for Deterministic Carcinogenic Risk Assessment

VOC	Median	Mean	SD†	Min	Max	90th %ile*	95th %ile*
BDCM	3.75E-08	6.74E-06	1.65E-05	3.21E-13	9.31E-05	2.46E-05	4.78E-05
DBCM	1.24E-07	6.46E-06	1.61E-05	6.02E-13	1.04E-04	2.78E-05	4.38E-05
Bromoform	2.10E-08	1.46E-07	2.99E-07	7.42E-11	2.09E-06	5.18E-07	6.63E-07
Benzene	3.46E-08	4.69E-08	4.15E-08	4.31E-09	2.65E-07	9.42E-08	1.28E-07

N = 100
† Standard Deviation
* Percentile

Estimated individual lifetime cancer risks were compared to the acceptable risk level of 10^{-6} stated by the USEPA. The median, mean, 90th percentile, and 95th percentile cancer risks for benzene and bromoform, and the median cancer risks for BDCM and DBCM were below the stated level. The mean, 90th percentile, and 95th percentile cancer risks for BDCM and DBCM, however, exceeded this level. While all of the R values calculated for benzene were less than 10^{-6}; 23%, 29%, and 2% of individuals had lifetime cancer risks above this value for BDCM, DBCM, and bromoform, respectively.

The lifetime cancer risks for BDCM, DBCM, and bromoform reported by Hsu and co-workers (2001) for 2 l/day DI were greater than the median R values and less

than the mean R values given in Table 5.13. For Taiwan tap water, the acceptable risk level was exceeded for BDCM in all areas and for DBCM in two areas. In addition, Hsu et al. (2001) estimated increased cancer risks of up to 179 times the acceptable level for chloroform using a slope factor of $6.1x10^{-3}$ $(mg/kg/d)^{-1}$.

Lee et al. (2004) estimated lifetime cancer risks through ingestion of THMs in Hong Kong tap water and stated that the values calculated for chloroform, BDCM, and DBCM were greater than 10^{-6} in all districts. The highest estimates were obtained for BDCM and values as high as $6.82x10^{-5}$ were reported. In this study, however, higher risks were calculated for DBCM when compared to those for BDCM.

Tokmak et al. (2004) have pointed that the lifetime cancer risks associated with exposure to TTHMs found in Ankara tap water were above the acceptable risk level when all routes of exposure were taken into consideration. Although cancer risk estimates were not reported separately for the ingestion route, those should be higher than the values calculated for İzmir drinking water since (1) the concentrations of THMs found in Ankara drinking water were much greater than those found in İzmir drinking water, (2) the DI and BW constants they have used were not less than those given for the individuals investigated in this study.

5.2.2.2. Probabilistic Estimation of R

Lifetime cancer risks associated with ingestion of VOCs were estimated probabilistically by multiplying the exposures obtained from Monte Carlo Simulation by the SF of each compound as given in Equation (3.2). The resultant probability distributions were similar to those plotted for exposures given previously in Figures 5.14 through 5.21. Both carcinogenic risk and exposure plots were fit by the same distribution for each VOC since the only difference was the multiplication with a constant, the SF. Therefore, the differences between population subgroups and the discussion of significances for exposure data are valid for carcinogenic risk also.

Table 5.14. Descriptive Statistics for Probabilistic Carcinogenic Risk Assessment

VOC	Median	Mean	SD†	Min	Max	90th %ile*	95th %ile*
BDCM	3.18E-07	7.41E-06	2.25E-05	3.93E-14	4.89E-04	1.94E-05	3.87E-05
DBCM	5.07E-07	6.81E-06	2.24E-05	1.76E-13	1.18E-03	1.88E-05	3.35E-05
Bromoform	3.71E-08	1.53E-07	3.10E-07	3.62E-19	8.60E-06	4.27E-07	6.99E-07
Benzene	3.34E-08	4.73E-08	4.81E-08	1.23E-09	1.09E-06	9.65E-08	1.34E-07

N = 10,000
† Standard Deviation
* Percentile

The statistics calculated for probabilistically estimated R values are presented in Table 5.14 for BDCM, DBCM, bromoform, and benzene for which the SF values were available. When these statistics were compared to those given in Table 5.13, it was observed that the differences between the carcinogenic risks estimated by deterministic and probabilistic approaches were not as small as the differences between deterministically and probabilistically estimated noncarcinogenic risks. For BDCM, DBCM, and bromoform, probabilistic approach resulted in higher estimates for median and mean Rs while 90th and 95th percentile values were lower compared to those estimated deterministically. For benzene, however, the opposite was correct and the differences were relatively smaller.

Sofuoglu et al. (2003) have pointed out similar differences for carcinogenic risks estimated deterministically and probabilistically. According to the results of the NHEXAS-Arizona study, they have concluded that the deterministic approach should be preferred whenever data were available in order to prevent overestimation. However, the same conclusion could not be drawn swiftly in this study, because while in general median and mean levels estimated using deterministic approach were lower than those calculated by probabilistic approach, the opposite was true for the upper-end tail of the distributions. This is an indicator of close similarity between empirical distributions of individual exposures and risks, and the presumed population distributions; showing that semi-probabilistic sampling worked well to represent the İzmir population.

5.3. Uncertainty Analysis

After having estimated exposure to each VOC probabilistically using the Monte Carlo Simulation, bootstrapping was applied to the data set to analyze the uncertainties associated with the calculated statistics. Exposure estimates were used to generate 200 subsamples and the statistics were calculated repeatedly 1,000 times for each subsample in order to construct a distribution for each statistic previously presented in Table 5.10.

Probabilistic estimation of carcinogenic and noncarcinogenic risks involved multiplying and dividing, respectively, the exposure estimates by constant values (i.e., the slope factor and reference dose) for each VOC. Therefore, bootstrapping process resulted in similar distributions for the statistics of CDI, HQ, and R estimates of the same compound. For this reason, only the results for the distributions of exposure statistics are presented in Table 5.15.

Table 5.15. Uncertainty in Statistics of Simulated Exposure

VOC	Statistic	Median	Mean	SD†	Min	Max
Chloroform	Median	0.0046	0.0047	0.0010	0.0028	0.0079
	Mean	0.1355	0.1363	0.0137	0.0973	0.1746
	SD	0.4261	0.4341	0.0836	0.2765	0.9001
	90^{th} percentile	0.3553	0.3581	0.0392	0.2681	0.4672
	95^{th} percentile	0.7177	0.7143	0.0743	0.5239	0.9840
BDCM	Median	0.0045	0.0046	0.0009	0.0027	0.0082
	Mean	0.1169	0.1174	0.0126	0.0806	0.1505
	SD	0.3540	0.3699	0.0810	0.2125	0.7811
	90^{th} percentile	0.3001	0.3040	0.0353	0.2232	0.4391
	95^{th} percentile	0.5928	0.5990	0.0695	0.4277	0.8313
DBCM	Median	0.0058	0.0059	0.0010	0.0036	0.0088
	Mean	0.0821	0.0829	0.0078	0.0658	0.1138
	SD	0.2276	0.2397	0.0503	0.1637	0.5267
	90^{th} percentile	0.2160	0.2189	0.0223	0.1664	0.2872
	95^{th} percentile	0.4027	0.4102	0.0442	0.3067	0.5862
Bromoform	Median	0.0047	0.0047	0.0005	0.0035	0.0061
	Mean	0.0197	0.0196	0.0012	0.0165	0.0241
	SD	0.0392	0.0398	0.0044	0.0308	0.0547
	90^{th} percentile	0.0546	0.0545	0.0040	0.0441	0.0631
	95^{th} percentile	0.0877	0.0878	0.0070	0.0707	0.1058

(cont. on next page)

Table 5.15 (cont.). Uncertainty in Statistics of Simulated Exposure

VOC	Statistic	Median	Mean	SD†	Min	Max
Benzene	Median	0.0006	0.0006	0.00002	0.0005	0.0007
	Mean	0.0009	0.0009	0.00003	0.0008	0.0010
	SD	0.0010	0.0009	0.0001	0.0008	0.0014
	90^{th} percentile	0.0018	0.0018	0.0001	0.0016	0.0020
	95^{th} percentile	0.0025	0.0025	0.0001	0.0021	0.0029
Toluene	Median	0.0012	0.0012	0.0001	0.0010	0.0013
	Mean	0.0024	0.0024	0.0001	0.0021	0.0030
	SD	0.0041	0.0043	0.0011	0.0030	0.0140
	90^{th} percentile	0.0054	0.0054	0.0004	0.0047	0.0065
	95^{th} percentile	0.0083	0.0083	0.0006	0.0068	0.0100
p-Xylene	Median	0.0003	0.0003	0.00001	0.0002	0.0003
	Mean	0.0004	0.0004	0.00001	0.0004	0.0004
	SD	0.0004	0.0004	0.00004	0.0004	0.0005
	90^{th} percentile	0.0009	0.0009	0.00004	0.0007	0.0010
	95^{th} percentile	0.0012	0.0012	0.0001	0.0010	0.0014
Naphthalene	Median	0.0007	0.0007	0.00004	0.0006	0.0009
	Mean	0.0017	0.0017	0.0001	0.0015	0.0020
	SD	0.0032	0.0034	0.0007	0.0023	0.0067
	90^{th} percentile	0.0038	0.0039	0.0003	0.0032	0.0048
	95^{th} percentile	0.0061	0.0062	0.0005	0.0051	0.0077

Number of bootstrap samples = 200
Number of trials per sample = 1,000
All values are in µg/kg/d.
† Standard Deviation

The USEPA (2005) states that risk assessors should calculate, to the extent practicable, and present the central estimate and the corresponding upper and lower statistical bounds (such as confidence limits) to inform decision makers. The median, and mean carcinogenic risks estimates were given previously in Tables 5.13 and 5.14 along with the standard deviation, minimum, maximum, 90^{th} percentile, and 95^{th} percentile values computed using deterministic and probabilistic approaches. In deterministic approach, it was not possible to calculate uncertainties due to the reasons discussed in Section 3.3. For probabilistically estimated risks, on the other hand, it was possible to calculate the degree of confidence for each estimate, as required by the USEPA (1999b) in risk assessment studies, using bootstrapping.

90% and 95% confidence intervals for the median and mean carcinogenic risk estimates are presented in Table 5.16. The minimum and maximum values resulting from bootstrap analysis are also included, indicated by 100%, in the last row of each statistic. Taking the 95% confidence interval into consideration, for instance, decision

makers would be 95% certain that the given interval captures the unknown population statistic.

Table 5.16. Bootstrapping Results for the Estimation Intervals of Median and Mean Carcinogenic Risks

Statistic		Percent	Lower	Upper
BDCM Risk	Median	90	1.85E-07	3.80E-07
		95	1.76E-07	3.92E-07
		100	1.57E-07	4.08E-07
	Mean	90	6.24E-06	8.70E-06
		95	6.07E-06	8.89E-06
		100	5.28E-06	1.03E-05
DBCM Risk	Median	90	3.74E-07	6.18E-07
		95	3.63E-07	6.43E-07
		100	3.27E-07	7.20E-07
	Mean	90	5.97E-06	7.87E-06
		95	5.85E-06	8.48E-06
		100	5.31E-06	9.66E-06
Bromoform Risk	Median	90	3.17E-08	4.54E-08
		95	3.01E-08	4.61E-08
		100	2.79E-08	4.92E-08
	Mean	90	1.37E-07	1.75E-07
		95	1.33E-07	1.76E-07
		100	1.30E-07	1.90E-07
Benzene Risk	Median	90	3.18E-08	3.55E-08
		95	3.12E-08	3.56E-08
		100	3.09E-08	3.68E-08
	Mean	90	4.56E-08	5.05E-08
		95	4.50E-08	5.12E-08
		100	4.42E-08	5.34E-08

Number of bootstrap samples = 200
Number of trials per sample = 1,000

CHAPTER 6

CONCLUSIONS

The most frequently detected VOCs in İzmir drinking water were the four THM species (i.e., chloroform, BDCM, DBCM, and bromoform), benzene, toluene, p-xylene and naphthalene. The concentrations of these compounds ranged from below detection limit to 35 µg/l. None of the VOC concentrations found in drinking water samples exceeded the maximum contaminant levels stated in Turkish drinking water regulations, the European Communities drinking water regulations, the USEPA national primary drinking water regulations, and the WHO guidelines for drinking water quality.

The median and mean DI values (1.8 and 1.9 l/day, respectively) for İzmir population were found to be half a liter greater than the corresponding statistics of the American adults whereas the median and mean body weights were less than the value suggested by the USEPA, 70 kg. The data collected in this study showed that the characteristics of the Turkish people are different from the American counterparts, and that assumptions should be minimized in risk assessment studies in order to avoid under/overestimation of population risks.

Exposures and risks estimated using deterministic and probabilistic approaches were in general agreement for all VOCs. Exposure of İzmir residents to THMs and other VOCs via drinking water ingestion and the associated risk levels were found to be less than those reported for other Turkish cities.

Noncarcinogenic risks attributable to ingestion of VOCs in İzmir drinking water were negligible when the estimated HQ values were compared to the demarcation value of 1. Probabilistic approach resulted in slightly higher estimates for median and mean HQs while 90^{th} and 95^{th} percentile values were slightly lower compared to those estimated deterministically; however, none of these differences were statistically significant.

Considering the R values estimated both deterministically and probabilistically, the median, mean, 90^{th} percentile, and 95^{th} percentile carcinogenic risks for benzene and bromoform, and the median carcinogenic risks for BDCM and DBCM were below the acceptable level of one in a million (10^{-6}). The mean, 90^{th} percentile, and 95^{th} percentile carcinogenic risks for BDCM and DBCM, however, exceeded this level. While all of

the R values calculated for benzene were less than 10^{-6} in both approaches, deterministic calculations revealed that 23%, 29%, and 2% of individuals had lifetime cancer risks above the acceptable level for BDCM, DBCM, and bromoform, respectively. For BDCM, DBCM, and bromoform, probabilistic approach resulted in higher estimates for median and mean R values while 90^{th} and 95^{th} percentile carcinogenic risks were lower compared to those estimated deterministically. For benzene, however, the opposite was correct and the differences were relatively smaller.

Due to the fact that the median and mean exposure, carcinogenic risk, and noncarcinogenic risk levels estimated using deterministic approach were lower than those calculated by probabilistic approach and that the opposite was true for the upper-end tail of the distributions (i.e., 90^{th} and 95^{th} percentile values); it can be concluded that there is close similarity between empirical distributions of individual exposures and risks and the presumed population distributions; and therefore, that the semi-probabilistic sampling worked well to represent the İzmir population.

Mann-Whitney and Kruskal-Wallis Test results showed that the concentrations of VOCs found in drinking water and risk associated with exposure to these VOCs differed across population subgroups, the difference being considerably significant in some categories. For all VOCs, the concentrations found in metropolitan area and, therefore, carcinogenic and noncarcinogenic risks were greater than those in other districts.

All THM species were detected in higher concentrations in tap water whereas benzene, toluene, p-xylene, and naphthalene concentrations were higher in nontap water. As a result, the concentrations of benzene, toluene, p-xylene, and naphthalene increased with increasing income and education levels since bottled water was used as the main drinking water source in larger proportions within these subgroups. For the same reason, an increase in THM concentrations was observed in homeland category for Eastern Anatolia Region, Central Anatolia Region, and Aegean Region subgroups in decreasing order.

To conclude, the author would like to add that more studies regarding the contaminant levels in Turkish drinking waters are required to investigate the performance of drinking water treatment plants for compliance with the recently regulated Turkish drinking water standards and other international standards as well as the quality of bottled waters. Furthermore, more risk assessment studies concerning the Turkish population are necessary in order to improve the drinking water regulations

since the results of this study show that exposures to drinking water contaminants and associated risks may be higher than the acceptable levels, even if the concentrations fall below the stated standards.

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APPENDIX A

DESCRIPTIVE QUESTIONNAIRE

İzmir İli İçme Suyu Maruziyet Çalışması
Tanımlama Anketi

Uygulayan ☐ Kendisi ☐ Teknisyen HN ☐☐☐☐

Uygulanma Tarihi *gün* *ay* *yıl* ☐☐ / ☐☐ / ☐☐☐☐

Adres

Mahalle _____ Cadde/Sokak _____

Apt. No. _____ Daire No. _____ Semt _____

İlçe _____ Posta Kodu _____

Telefon No. _____

1. Uygulanan (Ad Soyad) _____

18 yaşından büyük olmalı

2. Burası sürekli yaşadığınız eviniz midir yoksa yılın yarısından azını geçirdiğiniz yazlık ya da ikinci eviniz midir? ☐ Sürekli *devam*

☐ Yazlık (ikinci ev) *dur,bu hane uygun değil*

3. Bu adreste kaç kişi yaşamaktadır? _____

4. Şimdi bu hanede sürekli (yıl boyu) yaşayanlar ile ilgili bazı bilgiler doldurulacaktır.

Aşağıdaki soruları bu hanede yaşayan herbir kişi için arka sayfalardaki tablolara yanıtlayınız.

a. İlk adı *Tablo 1*

b. Cinsiyeti *Tablo 1*

c. Doğum yılı *Tablo 1*

d. Memleketi *tablo E kolonu sonundaki seçeneklerden seçini* *Tablo 1*

e. Aylık gelir *tablo F kolonu sonundaki seçeneklerden seçiniz* *Tablo 1*

Gelir bilgileri, bilimsel araştırmalarda, benzer özelliklere sahip bireyleri gruplandırmak için sıkça kullanılır. Bu araştırma sonunda elde edilecek olan verilerin analizi sırasında gelir grupları da bir değişken olarak ele alınacaktır. Lütfen yanıtlarınızın gizli tutulacağını ve sadece bilimsel amaçlarla kullanılacağını unutmayınız.

Tanımlayıcı Anket
Tablo 1

A	B	C	D	E	F
Sakin No	İlk Adı	Cinsiyet	Doğum Yılı	Memleket	Aylık Gelir
a					
b					
c					
d					
e					
f					
g					
h					
i					
j					
k					
l					
m					
Uygun olanı seçiniz		**Cinsiyet:** Kız (1) Erkek (2) Cevap yok (55) Uygulanamaz (88)		**Memleket:** Ege (1) Marmara (2) Batı Karadeniz (3) Doğu Karadeniz (4) Doğu Anadolu (5) Güneydoğu Anadolu (6) Akdeniz (7) Yabancı (8) İç Anadolu (9) Cevap yok (55) Bilmiyorum (99)	**Aylık Gelir:** Çalışmıyorum (1) 0-300 milyon (2) 300-600 milyon (3) 600 milyon-1 milyar (4) 1-2 milyar (5) 2 milyardan fazla (6) Cevap yok (55) Bilmiyorum (99)

Demografik ve Kişisel Bilgiler

Bu bölümdeki sorular her hanedeki birincil katılımcı tarafından yanıtlanacaktır. Lütfen her soru için size uygun olan seçeneği yanındaki kutucuğu işaretleyerek belirtiniz. Seçenek sunulmamış olan soruları, kutucukların içine ya da ayrılmış olan boşluğa yazarak yanıtlayınız.

5. En son mezun olduğunuz okul

- ☐ a. Hiç okula gitmedim
- ☐ b. İlkokul
- ☐ c. Ortaokul
- ☐ d. Lise
- ☐ e. Meslek yüksek okulu
- ☐ f. Üniversite
- ☐ g. Lisansüstü

6. Cinsiyetiniz

☐ a. Kız ☐ b. Erkek

7. Doğum tarihiniz

gün *ay* *yıl*

☐☐ / ☐☐ / ☐☐☐☐

8. Kilonuz

☐☐☐ kg

9. Günde ne kadar zamanınızı evde geçiriyorsunuz? ☐☐ saat

10. Evde bulunduğunuz süre içinde ne kadar su tüketiyorsunuz? ☐☐ bardak

11. İşyerinizde veya okul/kurs gibi düzenli olarak bulunduğunuz yerlerde günde ne kadar zaman geçiriyorsunuz?

☐☐ saat

12. İşyeri/okul/kurs vb. yerlerde bulunduğunuz süre içinde ne kadar su tüketiyorsunuz?

☐☐ bardak

Bu bölümdeki sorular evinizle ilgilidir. Lütfen emin olmadığınız soruları ailenizin diğer bireylerine danışarak mümkün olduğunca doğru yanıtlar vermeye çalışınız.

13. Evinizin bulunduğu bina ne zaman inşa edilmiştir?

- ☐ a. 2000'den sonra
- ☐ b. 1990 – 1999
- ☐ c. 1980 – 1989
- ☐ d. 1970 – 1979
- ☐ e. 1960 – 1969
- ☐ f. 1960'dan önce
- ☐ g. Bilmiyorum

14. Siz bu eve ne zaman taşındınız?

- ☐ a. 2000'den sonra
- ☐ b. 1990 – 1999
- ☐ c. 1980 – 1989
- ☐ d. 1970 – 1979
- ☐ e. 1960 – 1969
- ☐ f. 1960'dan önce
- ☐ g. Bilmiyorum

15. Evinizin su tesisatında hangi tip borular kullanılmıştır?

- ☐ a. Metal
- ☐ b. Plastik
- ☐ c. Bilmiyorum

16. Bu evde yaşadığınız süre boyunca su borularınızda değişiklik yapıldı mı?

☐ a. Evet *lütfen belirtiniz* _____ ☐ b. Hayır

17. Evinizde musluk suyunuz var mı?

☐ a. Evet ☐ b. Hayır

18. Musluk suyunuzun kaynağı nedir?

- ☐ a. Şehir şebekesi
- ☐ b. Özel kuyu
- ☐ c. Su deposu
- ☐ d. Diğer *lütfen belirtiniz* _____
- ☐ e. Bilmiyorum

19. İçme suyu olarak hangi kaynağı kullanıyorsunuz?

- ☐ a. Musluk suyu
- ☐ b. Şişelenmiş su
- ☐ c. Kuyu suyu
- ☐ d. Diğer *lütfen belirtiniz* _____
- ☐ e. Bilmiyorum

20. İçme suyunuzu arıtmak için aşağıdaki yöntemlerden hangilerini kullanıyorsunuz?

	Evet	Hayır	Bilmiyorum
a. Kaynatmak	☐	☐	☐
b. Musluk tipi arıtma cihazı	☐	☐	☐
c. Apartman tipi arıtma cihazı	☐	☐	☐

d. Diğer *lütfen belirtiniz* _____

21. Evinizin yakınında benzin istasyonu var mı?

- ☐ a. Evet
- ☐ b. Hayır
- ☐ c. Bilmiyorum

22. Evinizin yakınında endüstri (fabrika, imalathane vb.) var mı?

- ☐ a. Evet *lütfen belirtiniz* _____
- ☐ b. Hayır
- ☐ c. Bilmiyorum

18. Isınmak için aşağıdakilerden hangilerini kullanıyorsunuz?

Birden fazla seçenek işaretleyebilirsiniz

- ☐ a. Merkezi sistem
- ☐ b. Kat kaloriferi
- ☐ c. Kömür sobası
- ☐ d. Elektrik sobası
- ☐ e. Gaz sobası
- ☐ f. Klima
- ☐ g. Şömine
- ☐ h. Diğer *lütfen belirtiniz* _____

19. Bulaşıklarınızı nasıl yıkıyorsunuz?

- ☐ a. Bulaşık makinası ile
- ☐ b. Elde
- ☐ c. Her ikisi

20. Çamaşırlarınızı nasıl yıkıyorsunuz?

- ☐ a. Çamaşır makinası ile
- ☐ b. Elde
- ☐ c. Her ikisi

23. Evinizde oda kokusu/spreyi, naftalin vb. kullanıyor musunuz?

- ☐ a. Evet
- ☐ b. Hayır
- ☐ c. Bilmiyorum

APPENDIX B

TIME – ACTIVITY QUESTIONNAIRE

Günlük Etkinlik Bilgileri

Uygulanan (Ad Soyad) HN ☐☐☐☐

☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐☐

Günlük Etkinlik Bilgileri Anketi'nde, bir gün içinde gerçekleştirdiğiniz bazı etkinliklerle ilgili sorular yer almaktadır. Bu çalışma 7 gün sürecektir. Her gün için 1 tablo ve 30 soru olmak üzere 2 sayfa hazırlanmış ve her sayfanın üst kısmında kaçıncı gün olduğu belirtilmiştir. Lütfen her akşam kısa bir sürenizi ayırarak size verilmiş olan soruları yanıtlayınız.

Birinci sayfadaki tabloda, gün içinde bulunabileceğiniz yerler listelenmiş ve günün 24 saati 24 ayrı kutucuk şeklinde gösterilmiştir. Her bir saat için, o süre içinde bulunduğunuz yerleri uygun kutucuğu doldurarak belirtiniz. Örneğin, üzerinde 7 sayısı bulunan kutucuk, sabah saat 07:00 ile 07:59 arasını temsil etmektedir. Eğer 07:00 ile 07:30 arasında evde, 07:30 ile 08:00 arasında otobüste bulunduysanız; tabloda hem ev (bina içi) hem de ulaşım satırında 7 sayısının altındaki kutucuğu doldurmalısınız. Lütfen günün her saati için en az bir yer işaretlediğinizden emin olunuz.

7. günün sonunda, Günlük Etkinlik Bilgileri Anketi'ni tamamladığınızda, anketinizi size verilmiş olan zarfa koyunuz. Bu zarfın üzerine adres bilgilerimiz yazılmış ve posta pulu yapıştırılmıştır. Zarfı, hiçbir ücret ödemeden, herhangi bir postaneye verebilirsiniz. "İzmir İlinde İçme Suyu Kaynaklı Maruziyet ve Risk Seviyelerinin Değerlendirilmesi" çalışmasına katkılarınızdan dolayı teşekkür ederiz.

1. GÜN

Bugünün Tarihi

gün *ay* *yıl*

☐☐ / ☐☐ / ☐☐☐☐

○ Pzt ○ Salı ○ Çar ○ Perş ○ Cum ○ Cmt ○ Pzr

Yer	Sabah						Öğleden Sonra						Akşam						Gece					
Ulaşım/Trafik	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	1	2	3	4	5
	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Ev (Bina İçi)	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	1	2	3	4	5
	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Okul/İş (Bina İçi)	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	1	2	3	4	5
	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Bar/Lokanta/Kahve	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	1	2	3	4	5
	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Diğer (Bina İçi)	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	1	2	3	4	5
	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Ev (Bina Dışı)	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	1	2	3	4	5
	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Okul/İş (Bina Dışı)	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	1	2	3	4	5
	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○
Diğer (Bina Dışı)	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	1	2	3	4	5
	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○	○

A. Bugün aşağıdakilerden hangilerini yaptığınızı her soru için evet ya da hayır kutucuğunu işaretleyerek belirtiniz.

1.	İçinde park edilmiş bir araç bulunan bir garajda 15 dakikadan fazla zaman geçirdiniz mi?	☐ a. Evet	☐ b. Hayır
2.	Benzin, gaz yağı vb. derinizle temas etti mi?	☐ a. Evet	☐ b. Hayır
3.	Toprak, yaprak,çim vb. derinizle temas etti mi?	☐ a. Evet	☐ b. Hayır
4.	Şömine ya da ocak temizlediniz mi?	☐ a. Evet	☐ b. Hayır
5.	Şömine ya da ocak yaktınız mı?	☐ a. Evet	☐ b. Hayır
6.	Mangal ya da yaprak, çöp vb. yaktınız mı?	☐ a. Evet	☐ b. Hayır
7.	Evinizin içinde tütün ürünleri içildi mi?	☐ a. Evet	☐ b. Hayır
8.	Duş aldınız mı?	☐ a. Evet	☐ b. Hayır
9.	Banyo yaptınız mı? (Küvete su doldurup içine girerek)	☐ a. Evet	☐ b. Hayır
10.	Zararlı bitki, haşere veya uçucu böcekleri önleyici bir madde kullandınız mı?	☐ a. Evet	☐ b. Hayır
11.	Zararlı bitki, haşere veya uçucu böcekleri önleyici bir madde hazırladınız mı?	☐ a. Evet	☐ b. Hayır

1. GÜN

12. Benzin, gaz yağı vb. pompaladınız ya da başka bir şekilde teneffüs ettiniz mi? ☐ a. Evet ☐ b. Hayır
13. Elde bulaşık yıkadınız mı? ☐ a. Evet ☐ b. Hayır

B. Bu bölümde, yanıtlarınızı kutucukların içine sayıyla yazınız.

14. Bugün kaç bardak su içtiniz? ☐☐ bardak
15. Bugün kaç tane sigara içtiniz? ☐☐ sigara
16. Bugün kaç tane pipo ya da puro içtiniz? ☐☐ pipo/puro
17. Bugün kaç kere ellerinizi yıkadınız? ☐☐ kere

C. Bu bölümdeki her soru için bugün geçirdiğiniz süreyi sayıyla kutucuğun içine yazınız ve yan tarafında saat mi dakika mı olduğunu belirtiniz.

18. Ulaşım amacıyla yolda geçirdiğiniz süre ☐☐ saat/dakika
19. Bina içinde sigara içen birisiye geçirdiğiniz süre ☐☐ saat/dakika
20. Araç içinde sigara içen birisiye geçirdiğiniz süre ☐☐ saat/dakika
21. Kapalı ya da açık yüzme havuzunda geçirdiğiniz süre ☐☐ saat/dakika
22. Temizlik ürünleri (deterjan, parlatıcı vb.) kullandığınız süre ☐☐ saat/dakika
23. Halı üzerinde oturduğunuz ya da uzandığınız süre ☐☐ saat/dakika
24. Garaj ya da atölye benzeri kapalı bir alanda geçirdiğiniz süre ☐☐ saat/dakika
25. Havalandırma amacıyla kapı veya camları açık tuttuğunuz süre ☐☐ saat/dakika
26. Toprak kazmak vb. ağır işler ile koşu, bisiklete binme, aerobik, basketbol, futbol vb. ağır egzersiz yaptığınız süre ☐☐ saat/dakika
27. Yürüyüş, bahçede çalışmak, ayakta iş yapmak, golf oynamak vb. hafif egzersiz yaptığınız süre ☐☐ saat/dakika
28. Elde bulaşık yıkadığınız süre ☐☐ saat/dakika
29. Duşta geçirdiğiniz süre ☐☐ saat/dakika
30. Banyoda (Küvete su doldurup içine girerek) geçirdiğiniz süre ☐☐ saat/dakika