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Survey of Saudi Arabian Drinking Water for Trihalomethanes

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Formation of trihalomethanes (THMs) as a result of drinking water chlorination is well documented (Rook 1974; Trussell and Umphres 1978; Allgeier et al. 1980). The presence of THMs in drinking water may adversely affect human health. Several studies have confirmed the carcinogenicity of chloroform to mammals (USEPA 1975; Velema 1987). Other brominated THMs were found to generate excessive tumors in tumor-induction tests with mice (USEPA 1978). Chlorination is the most widely used technique for water disinfection in Saudi Arabia. Information on THMs formation in the drinking water of Saudi Arabia has not yet been reported.

The major drinking water sources in the Kingdom are ground water and desalinated sea water. In most occasions, ground water is mixed with desalinated water before it is pumped into the water networks. This is due to the high concentration levels of total dissolved solids (TDS) in ground water in many areas of the Kingdom. However, in some areas where desalinated water is not available, ground water is still the major source of drinking water. Normally, ground water is mixed with desalinated water in the ratio of 1:4 to produce potable water. During the summer months, however, drinking water is blended at a higher proportion of ground water. This is mainly due to the increasing drinking water demands and the limited capacity of the desalination plants. As a result, the concentration levels of total organic carbon (TOC) and bromide ion (Br^-) in the blended water change accordingly. Moreover, water temperature, in some areas of Saudi Arabia, reaches 40°C during summer time. All these factors play an important role in THMs formation as it has been reported by several investigators (Rook 1978; Stevens and Symons 1980).

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The objectives of this study are to determine the concentration levels of THMs in drinking water of eight major cities in Saudi Arabia and to compare these concentrations with Saudi Arabian Water standards, as well as with THMs concentrations reported in drinking water in other parts of the world.

MATERIALS AND METHODS

Water samples were collected from eight cities in Saudi Arabia during the summer months of July to October 1989. Those cities are: Dammam, Riyadh, Buraydah, Hail, Madinah, Jeddah, Makkah and Abha. A location map of these cities is depicted in Figure 1. The number of samples collected from each city was determined according to its population. Sampling locations were selected in such a way as to represent the overall water quality in the distribution networks. Duplicate samples for THMs measurement were collected from each sampling location, without head space, in 40-mL glass vials capped with Teflon-faced rubber septa. Sodium sulfite (about 10 mg) was added to each sampling vial, in order to quench further formation of THMs after sampling. Sample temperature was maintained at 4°C, but allowed to equilibrate to room temperature immediately before analysis

Samples for non-volatile total organic carbon (NVTOC) measurements were collected in 15-mL glass bottles capped with Teflon-faced septa and acidified to pH 2 with concentrated phosphoric acid at the time of collection. Liquid-liquid extraction (USEPA 1978) was used for the concentration of THMs in water samples. The method involved extraction of 10-mL sample with 2 mL of pentane (glass-distilled, Burdick and Jackson).One uL of the pentane extract was then injected into a gas chromatograph (GC). A 30-m by 0.25 mm i.d. fused-silica capillary column coated with a 1.0 um film of the stationary phase, DB-5, was used for the chromatographic separation of THMs. The analysis was performed using a Varian 6000 gas chromatograph equipped with a Vista 401 data station and a ^{63}Ni electron capture detector. The GC oven temperature was programmed from 50 to 75°C at a ramp rate of 5°C/min. The initial and final hold times were 4 and 6 min, respectively. Nitrogen was used as the carrier gas. Flow rates were 1.5 mL/min through the column, 10 mL/min at the detector base 20 mL/min as makeup gas. The injection technique was splitless, with a split flow of 150 mL/min initiated automatically after 1 min and maintained for 5 min; the flow was then splitless during the remainder of the analysis time

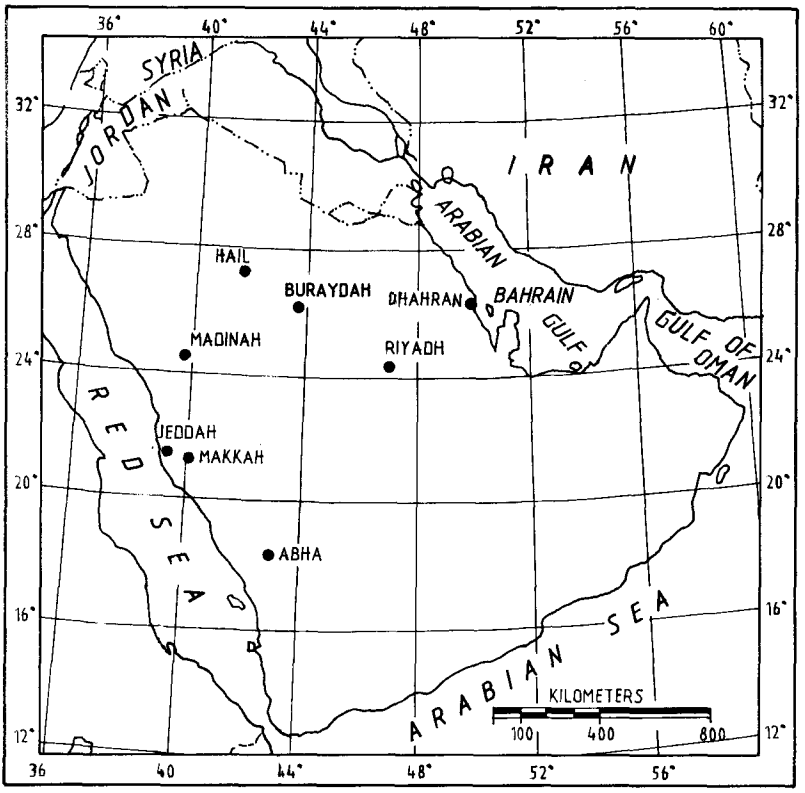

Figure 1. Location map showing the major cities in Saudi Arabia selected for this study.

The analytical quality control scheme applied included periodic analyses of certified THMs standards (Standard Reference Material 1639, National Bureau of Standards), distilled water and water samples fortified with known amounts of standards.

Non-volatile total organic carbon was determined using a Beckman Model 915-B TOC analyzer. Total residual chlorine was analyzed in-situ by DPD method using a Milton Roy Spectronic Mini 20 spectrophotometer. Water temperature and pH were also measured in the field.

RESULTS AND DISCUSSION

The results collected from the field survey of eight major cities in Saudi Arabia are summarized in Table 1. As shown in this table, three types of drinking water are used in Saudi Arabia. The majority of drinking water in the cities of Dammam, Riyadh, Madinah, Jeddah and Makkah is a blend of desalinated water and ground water. The desalinated water is produced from

desalination plants on the Arabian Gulf and the Red Sea coasts. On the other hand, the cities of Buraydah and Hail do not have a desalinated water source and use ground water from local wells. In Abha city, the main source of drinking water is desalinated water produced from a desalination plant at the Red Sea. This water is not blended with ground water.

Table 1 also shows that the levels of total residual chlorine found in drinking water in various cities range between 0.2 and 1.2 ppm. On several occasions, the residual chlorine levels in Hail, Dammam and Buraydah cities were high and exceeded the 0.5 ppm maximum recommended level for total residual chlorine set by the Saudi Arabia Standards Organization (SASO) (SASO 1984).

Table 1. Median values of field data collected for various cities in Saudi Arabia.

City	D. W. Source	No. of Samples	Cl_2 (ppm)	NVTOC (ppm)	Temp (^oC)	pH	$CHCl_3$ (ppb)	$CHCl_2Br$ (ppb)	$CHClBr_2$ (ppb)	$CHBr_3$ (ppb)
Dammam	G/D	35	0.7	<0.1	36	7.3	0.06	0.14	0.40	3.38
Riyadh	G/D	43	0.5	<0.1	40	8.3	0.08	0.26	1.15	3.84
Buraidah	G	27	0.6	<0.1	38	7.7	0.03	0.00	0.00	0.66
Hail	G	20	1.2	<0.1	30	7.5	0.00	0.06	0.24	1.11
Madinah	G/D	18	0.4	<0.1	37	7.8	0.24	0.48	1.04	4.80
Jeddah	G/D	45	0.3	<0.1	38	8.3	0.05	0.08	0.41	6.45
Makkah	G/D	23	0.4	<0.1	38	8.1	0.11	0.49	2.75	4.26
Abha	D	4	0.2	<0.1	36	8.3	0.29	0.55	0.55	0.23

D.W. = Drinking Water, G = Ground water, D = Desalinated Water, G/D = Blended Water.

The results of the survey have also shown that non-volatile total organic carbon (NVTOC) levels in most of the water samples were less than 0.1 ppm which is the detection limit of the TOC analyzer used in this study.

Median values of water temperatures measured in various distribution systems were found to range between 30 and 40^oC, while the median pH values range between 7.3 and 8.3.

Results obtained for the analysis of various trihalomethanes (THMs) have shown that brominated THMs dominate with bromoform ($CHBr_3$) as the most abundant THMs species in all samples. While chloroform ($CHCl_3$) was the least abundant THMs compound found throughout the whole survey areas. This is attributed to the high levels of the bromide ion (Br^-) in the water. As an

example, the concentration of bromide ion measured in the ground water of Dammam city was found to be approximately 8 ppm. This concentration is considerably higher than those reported in drinking water of several European countries which ranges between 0.01 and 2.5 ppm (Trussel et al. 1980). Although the bromide ion concentrations is reduced after blending with desalinated water, the resulting bromide ion concentration in the blended water remains high enough to contribute to the halogenation step of the THMs formation reaction. Several investigators have shown that the presence of bromide ions in chlorinated water results in a general increase in the total trihalomethane formed and a concomitant increase in the brominated species formed (Cooper et al. 1985). This behavior was attributed to the oxidation of the bromide ion present in the water to various species (hypobromous acid and hypobromite), which compete with chlorine for the active site of the precursor organic humic materials which naturally exist in the water. Rook et al. (1978) has shown that chlorine acts preferentially as an oxidant, whereas bromine is a more effective halogen substitution agent.

This explains the general trend of the high bromoform levels found in the water of various cities where ground water is mixed with desalinated water. It is also consistent with the low level of bromoform detected in drinking water of Abha city, where only pure desalinated water, characterized by very low levels of bromide, is used for drinking.

A comparison of the median levels of total THMs found in drinking water of various cities in Saudi Arabia is shown in Figure 2. It can be seen from this figure that the median concentration levels of THMs in all cities falls below 10 ppb. This value is far below the 250 ppb maximum allowable limit set by SASO (SASO 1984). It can also be seen that the maximum THMs levels were found in the cities of Jeddah and Dammam. The highest concentrations for the total THMs in Dammam city were found in those stations where the pH values of the water were higher than 8.5. Similar results were found in Jeddah city. Several investigators have shown that THMs formation increases as pH of the water increases (Rook 1976). Figure 2 also shows that the lowest median concentration levels of total THMs were found in Buraydah, Hail and Abha cities. It is worth mentioning that the sources of drinking water in the first two cities is ground water, while desalinated water is used in the third city. No mixing of desalinated water and ground water takes place in these cities. This may indicate that the THMs formed depend on the precursor

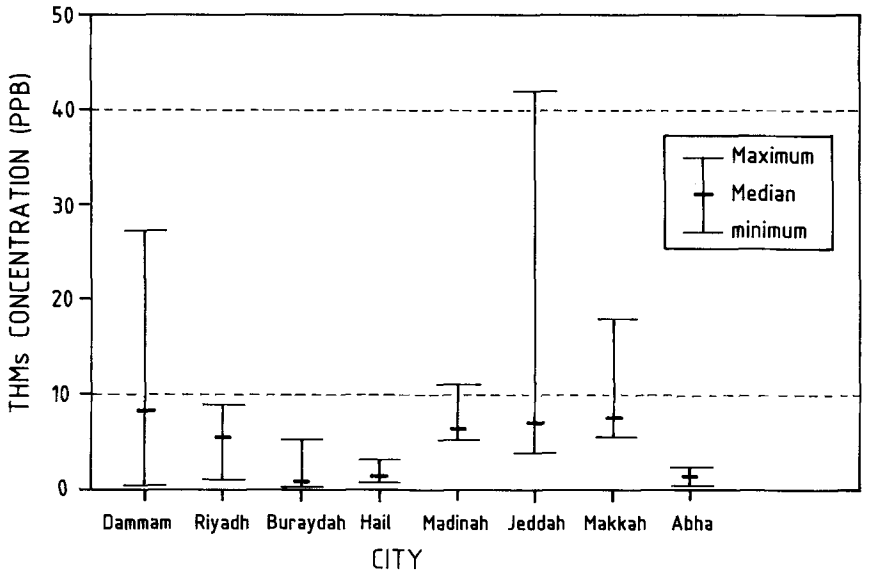

Figure 2. Minimum, maximum and median Concentration levels of total THMs found in drinking water of various cities in Saudi Arabia

Table 2. Trihalomethane concentrations (ppb) in drinking water of several countries

Country	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	TTHMs	Reference
Australia	11	4.1	0	0	15.1	[Trussell, 1980]
Brazil	17	4.4	0	0	21.4	[Trussell, 1980]
Canada	13	1.4	0.1	0	14.5	[Williams, 1980]
China	3.4	7.6	13	6.3	30.3	[Trussell, 1980]
Egypt	0	0	0	0	0	[Trussell, 1980]
England	5.8	6.4	2.3	0	14.5	[Trussell, 1980]
Indonesia	6.8	3.0	0.7	0	10.5	[Trussell, 1980]
Nicaragua	0.6	0	1.1	0	1.7	[Trussell, 1980]
Peru	6.4	5.7	2.7	0	14.8	[Trussell, 1980]
South Philipines	4.9	2.3	1.2	0	8.4	[Trussell, 1980]
North Philipines	1.8	1.7	1.5	0	5	[Trussell, 1980]
Taiwan	0.05	0	0	0	0.05	[Trussell, 1980]
United States	21	6.0	1.2	0	28.2	[Williams, 1980]
Japan (Osaka)	36.2	14	4.3	n.a	54.5	[Kajino, 1980]
Venezuela	57	10	0	0	67.0	[Trussell, 1980]
Wales	n.a	n.a	n.a.	n.a.	76.0	[Inverarity,1984]
Thiland(Bangkok)	53.3	8.3	0.47	n.d.	62.07	[Onodera, 1985]
Saudi Arabia	0.11	0.26	0.82	3.09	4.28	[*]

n.a. = not available, n.d. = not detected
* this study

compounds which exists in the mixed water, as it is the case in other cities. In a previous study performed in 1985 (Fayad and Iqbal 1985), the range and median levels for THMs in Dammam city were 1.6 - 40.3 and 12.4 ppb, respectively, while it has been found in this survey to be 0.04 - 26.9 and 9.1 ppb, respectively.

A survey of the literature for THMs in international drinking water is summarized in Table 2.Comparison of the concentration levels of THMs found in drinking water in various cities of Saudi Arabia with those reported in international drinking water reveals that Saudi Arabian levels are favorably comparable.

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