

# **ESTIMATION OF TRIHALOMETHANES IN CHLORINATED DRINKING WATER FROM SEA WATER DESALINATION PLANTS IN AL-JUBAIL, AL-KHOBAR AND AL-KHAFJI.<sup>1</sup>**

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## **ABSTRACT**

Chlorination of drinking water from natural sources results in the formation of several organic compounds as disinfection by products. The most widely studied among them is a group of compounds collectively called trihalomethanes (THMs), some of which are reported to be toxic for human consumption. Consequently water supply authorities in some countries are forced to resort to costly corrective measures in order to reduce their levels below the maximum concentration limits (MCL) set by the environmental protection and health authorities. It is well established by now that the formation of such compounds is due to reactions between chlorine and some precursor organics originally present in raw water.

Many countries in the arid region are now meeting most of their drinking water requirements through sea water desalination. Sea water contains a variety of organic contaminants from several sources including industrial and municipal discharges, oil spills etc. A survey was therefore conducted to quantitatively estimate the levels of individual and total trihalomethanes in potable water supplies, originating from sea water desalination plants, in the Eastern Province and Riyadh areas of Saudi Arabia. Samples of both finished drinking water and brackish well water used for blending with the distillates from these plants and several towns and cities served by them were analysed for trihalomethane compounds. The results are presented in this report and compared with the concentrations reported to be found in some finished drinking water supplies from natural sources and with the MCL set by WHO and other organizations for these compounds in drinking water in order to minimize health effects.

## **INTRODUCTION**

The major source of drinking water in the Kingdom of Saudi Arabia originates from sea water desalination. Saline Water Conversion Corporation (SWCC), the Government Agency responsible for producing desalinated water in the Kingdom, has an installed capacity of around 550 MGD and uses both multistage flash distillation (MSF) and reverse osmosis (RO) techniques. MSF plants contribute the major share of the water being produced in the Kingdom.

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<sup>1</sup> Issued in December, 1989.

The distillates from MSF plants are normally blended with adequate amount of brackish water in order to enhance the mineral contents, followed by disinfection before sending to the distributing net works for domestic consumption.

Chlorination is the most widely used method employed in Saudi Arabia for the disinfection of the desalinated water both before and after blending. Concern has been raised about the possible formation of some toxic organic compounds in desalinated drinking water as a result of chlorination. During the past decade and a half investigators from several countries have reported the presence of a variety of organic substances in their chlorinated drinking water supplies originating from natural sources like rivers, lakes, etc. The most widely prevalent among them is a group of four halogenated hydrocarbon compounds, namely chloroform ( $\text{CHCl}_3$ ), dichlorobromomethane ( $\text{CHCl}_2\text{Br}$ ), chlorodibromomethane ( $\text{CHClBr}_2$ ) and bromoform ( $\text{CHBr}_3$ ) which are collectively known as trihalomethanes (THMs). Besides THMs, two other halogenated compounds which were reported to be found though rarely in finished water from natural sources are carbon tetrachloride ( $\text{CCl}_4$ ) and 1,2-dichloroethanes ( $\text{C}_2\text{H}_4\text{Cl}_2$ ). World attention on the presence of such compounds in chlorinated drinking water was first drawn by two pioneering studies reported in 1974 (1,2). Later, the US Environmental Protection Agency (USEPA) undertook a survey of 80 cities in US to measure the concentrations of these and other organic compounds in raw and finished water originated from natural sources (3). Other countries also conducted similar studies soon after and discovered that the presence of THMs in chlorinated drinking water is a global phenomena not confined to any specific geographical area alone.

Potential risk to human health from possible carcinogenic properties of the halogenated compounds found in chlorinated drinking water was also investigated. A report from National Cancer Institute, Washington in 1976 (4) and another from Theiss et al in 1977 (5) indicated that both chloroform and bromoform, respectively, are potential carcinogens. Subsequently, USEPA limited the maximum total concentration of THMs permissible in drinking water supply at 100  $\mu\text{g/L}$  (6). Considering a greater cancer risk from chloroform WHO in 1984 set a guideline value of 30  $\mu\text{g/L}$  for this compound in drinking water (7). There have been reports indicating that USEPA is currently considering to lower the maximum concentration limit of total THMs below 100  $\mu\text{g/L}$  (8). A limited number of field studies carried out in our laboratories previously (9) on some samples of desalinated drinking water in the Eastern Province of Saudi Arabia indicated the presence of THMs in trace concentrations. Though their presence was far below the maximum concentration limit (MCL) set by USEPA/WHO, it was decided to carry out further investigations to determine the levels of THMs in water supplies covering larger areas of the Kingdom. The present studies cover several towns and communities in the Eastern Province as well as the capital city, Riyadh. These areas are supplied with potable water originated from the desalination plants located at three places in the Eastern Province: (1) Al-Jubail (290 MGD), (2) Al-Khobar (60 MGD) and (3) Al-Khafji (6 MGD). Al-Jubail plant supplies water to SWCC housing compound, Naval Base and other areas of Al-Jubail town through three blending stations, BS #1, 2 and 3, respectively. Al-Jubail plant also supplies  $\text{CO}_2$ /lime-treated distillate to the Al-Jubail Industrial City located at about 40 Km and the Riyadh City located at 480 Km away from the plant site. In Riyadh, the treated distillate is received

at high point terminal (HPT) and blended with brackish water from Wasia well fields and distributed for domestic consumption after disinfection with chlorine gas. Al-Khobar plant serves several nearby areas such as SWCC housing compound, the towns of Al-Khobar, Dammam, Saihat, Qatif, Safwa and Rahima/Rastanura. Blending is carried out at separate blending stations located at each of these localities. Al-Khafji plant supplies water to SWCC housing compound and Al-Khafji town. At present there is no blending facilities in this area.

Replicate samples of blended and chlorinated potable water and brackish water from most of the wells used for blending were collected and analysed for the individual THMs and other volatile organic compounds using standard methods. Total THMs were computed from the concentrations of the individual compounds. The results are presented and compared with the maximum concentration levels set for these compounds by WHO, USEPA and the Saudi Arabian Standardization Organization (SASO).

## **ANALYTICAL METHODS**

### ***Sampling:***

Potable water samples were collected from blending stations at Al-Jubail, Al-Khobar, Dammam, Qatif, Rahima and Al-Khafji in the Eastern Province and from Al-Wasia potable water tanks serving the city of Riyadh. Brackish water from most of the wells used for blending the desalinated water in Eastern Province was also collected for analysis. There are around 60 wells in the Wasia well field serving the blending station at HPT. Water from several wells at a time are pumped to a common well water storage tank at Wasia and sent to the HPT blending station through a header pipe. Therefore, instead of collecting the samples from all the sixty wells individually, samples were only collected from two sampling points; one from the incoming well water header at HPT (HPT Composite) and the other from the well water storage tank (Wasia Composite)

All samples were collected in 250 ml amber coloured bottles, previously cleaned and dried at 350 C for 2 hours. A few mgs of sodium thiosulfate was added to the sample bottles before collecting the chlorinated water samples to destroy the residual chlorine. The bottles were preserved at 4 C in refrigerator, if not analysed immediately. Sodium thiosulfate was not added while collecting samples of unchlorinated well water. The latter samples were collected in glass bottles, chlorinated by adding standard sodium hypochlorite solution in the laboratory to obtain about 0.5 ppm residual chlorine and analysed after permitting an equilibration time of 24 hours under laboratory temperature (25°C)

### ***Analytical Procedure:***

Trihalomethanes and other volatile organics were analysed by purge and trap technique as described in USEPA method 624 (10). 5 ml water samples were purged with helium gas for 10 min. using Tekmar Model LSC2 Liquid Sample

Concentrator connected to the GC. Organics trapped on a Tenax Column were desorbed at 180 °C and injected directly into the gas chromatograph through a sample splitter.

Hewlett-Packard Model HP-5880 gas chromatograph with <sup>63</sup>Ni EC detector was used for separation and quantification of the individual THM compounds. Fused silica capillary column DB5, 30Mx0.5mm/id was used for the chromatographic separation of the individual THMs. Injector and detector temperatures were kept at 200 and 250° C, respectively. Oven temperature was programmed to remain constant at 40 °C for 3 min. and rise to 150 °C at a ramp rate of 8 C/min. Helium was used as carrier gas and nitrogen as make-up gas at a flow rate of 60 ml/min.

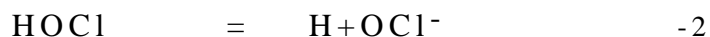
## RESULTS AND DISCUSSION

Concentrations of individual as well as total THMs found in several blended potable water samples collected from various areas covered in the present study are given in [Table 1](#). Presence of the other two chlorocompounds, i.e. carbon tetrachloride and 1,2-dichloroethane were below detection level in all samples analysed. It can be seen that, except at two locations, the total THM concentrations were less than 10 ug/L. Out of the four detected compounds, bromoform was found to dominate in all the samples tested while the presence of chloroform was the least. Concentrations of the individual trihalomethanes in all samples were found to increase as the number of substituted bromine atoms in them - i.e.  $\text{CHCl}_3 < \text{CHCl}_2\text{Br} < \text{CHClBr}_2 < \text{CHBr}_3$ . This is in contrast with the results obtained for well water samples as seen from [Table 2](#). In the latter case, though bromoform was again found to dominate, chloroform contents were slightly higher than the mono- and di-bromo derivatives. Out of several well water samples analysed only six samples registered total THM concentrations ranging between 10 - 20 ug/L, the rest of them contained 10 ug/L. Wells in Jubail and Qatif indicated much lower THM content than wells from other areas tested.

The total THMs detected in all samples of brackish and blended potable water samples were considerably lower than the MCL of 1000 ug/L set by both USEPA and WHO. Further, in comparison with the MCL of 2000 ug/L set by SASO and of 350 ug/L set by the Canadians the concentrations observed in both desalinated potable water and brackish water used for blending become much less significant.

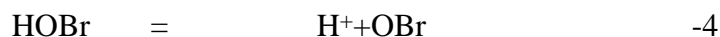
The composition of various trihalomethane compounds in chlorinated water depends on several factors such as the nature and concentration of organic precursors present in raw water, pH, temperature, contact time, concentrations of bromide ions and to some extent, residual chlorine, etc. While Rook (11), and Barry Oliver and John Lawrence (12) considered naturally occurring humic/fulvic materials to be the major precursors contributing to the formation of THMs on chlorination, Stevens et al (13) indicated that low molecular weight methyl ketones were also important haloform precursors. While these compounds together with chlorine determine the total concentration of THMs it has been well established that the presence of Br<sup>-</sup> ions in raw water has a significant role in determining the composition of the individual THM compounds (14).

In water, free chlorine exists as a mixture of hypochlorous acid (HOCl) and hypochlorite ions (OCl<sup>-</sup>):



The final concentrations of each of these species are pH dependent and at neutral pH they are found to be almost equal in concentrations.

Being a strong oxidising agent free chlorine rapidly oxidises bromide ions present in water to hypobromous acid (HOBr) and hypobromite ions (OBr<sup>-</sup>):



Both these reactions are again pH dependent, reaction rates decreasing linearly as pH increases (15). The reaction between bromine and precursor organics present in water was reported to be much more rapid than similar reactions between chlorine and the organics as reported by Stevens et al (14), resulting in high proportion of bromine - containing organic species in water containing traces of bromide. Stevens et al (14) have shown that the concentration of brominated species in the total trihalomethanes produced on chlorination of water containing as low as 0.5 ppm bromide is above 90%. Present data agrees well with these reported results. It may be noted that the blended water samples from Al-Khobar, Dammam, Qatif and Rahima contain slightly high total THMs than samples from other locations. All these water supplies originate from the distillates of the Al-Khobar MSF plant. The increase is mainly due to higher concentrations of bromoform in these samples as is evident from [table 1](#). Previous study in our laboratories (9) had indicated the presence of higher concentrations of bromoform in unchlorinated distillates from Al-Khobar plant, in comparison to the other two plants, probably due to carry over of bromoform from flash chambers.

Many well water samples were found to contain slightly higher concentrations of chloroform than the blended water samples, though bromoform constituted the major share of the THM total in well water samples as well. It appears from these results that chloroform - forming organic precursors are preferentially excluded from the desalted water during distillation process.

Drinking water supplies originating from natural sources from several parts of the world were reported to contain significant levels of THMs. For instance, the results of three major THM surveys carried out in U.S. during three different periods, as reported recently by MC Guire et al (16) indicate that the levels of THM are much higher in comparison with the concentrations in desalinated drinking water found during the present survey ([see table 3](#)). In U.S. there has been 40 - 50 percent reduction in THM content in drinking water from natural sources by 1984-86 (AWWARF survey) in comparison to the

previous years. MC Guire et al (16) reports that this reduction is the result of compliance by the water utilities with the regulation of 100 ug/L limit for THM in water promulgated by U.S. Environmental Protection Agency in 1979.

Frequency distribution of THM data obtained in the present study, as shown in [Figures 1 and 2](#), for blended water and well water samples respectively, indicates median concentrations of bromoform to be about 5 ug/L in both cases. Median concentrations of the other three compounds were close to or less than 1 ug/L in all the samples tested.

Several reasons could be attributed to the presence of THM in such low concentrations in drinking water supplies originating from sea water desalination. MSF distillation process is capable of producing nearly clean distillates, free from not only the dissolved inorganic salts, but also from trace organics which might be present in sea water. During the process of distillation most of the volatile organics might escape through vacuum vent system, while high boiling organics will be rejected along with the blow down brines. Our previous studies (9) indicated near absence of THMs in chlorinated product distillates from Al-Jubail Plant. However, some abnormal operating conditions might cause carry over of traces of THMs into the distillates from the flashing brine. Samples of chlorinated well water used for remineralization of the distillate contain traces of THM as discussed above though the concentrations are again much lower than those found in surface water samples. This is not surprising since the underground well water is expected to contain lower amounts of naturally occurring organic precursors in comparison to surface water sources, due to a variety of environmental and chemical factors. It is also obvious from the present studies that the traces of THM found in blended desalinated water samples derive mostly from chlorinated well water used for blending purpose.

## CONCLUSION

Samples of finished drinking water originating from the three sea water desalination plants in the Eastern Province of Saudi Arabia and supplied to the city of Riyadh and several other areas were analysed for trihalomethane contents. Chlorinated brackish well water used for blending with distillates from several wells in the respective areas were also tested for the same compounds. The results indicated that the trihalomethane content in the finished water as well as the chlorinated well water were significantly lower than the maximum contaminant levels set for these compounds in drinking water by WHO and various national organizations.

## REFERENCES

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**TABLE-1**  
**INDIVIDUAL AND TOTAL THMs IN BLENDED POTABLE**  
**WATER SAMPLES (ug/L)**

SL	CHCl <sub>3</sub>		CHBrCl <sub>2</sub>		CHBr <sub>2</sub> Cl		CHBr <sub>3</sub>		Tot. THM
	Avg	Range	Avg	Range	Avg	Range	Avg	Range	Avg
1.	0.02	0-0.07	0.36	0-0.5	0.76	.7-0.8	2.42	2.4-2.5	3.56
2.	0.03	0-0.06	0.31	.3-0.4	0.85	.8-0.9	1.89	1.8-2.	3.08
3.	0.01	0-0.01	0.36	0-0.48	0.86	0-1	4.66	0-5.9	5.89
4.	0.02	0-0.05	0.29	.2-0.3	0.99	.9-1.1	7.2	5.6-8.5	8.52
5.	0.02	0-0.04	0.35	.3-.47	1.4	1.-1.9	9.1	7.8-9.7	10.8
6.	0.01	0-0.03	0.25	.2-.28	1.07	.7-1.22	8.54	7.7-9.7	9.8
7.	0	-	0.29	.25-.3	1.32	1.1-1.5	10.67	9.-12.	12.3
8.	0.24	.060.92	0.41	.1-0.74	1	.8-1.14	1.69	1.5-1.7	3.3
9.	0.45	0-0.9	0.82	.75-0.9	0.9	.86-.92	1.77	1.6-2.	3.9
10	0	-	1.51	-	1.63	-	2.3	-	5.4
11	0.03	0-0.09	0.46	.4-0.5	1.31	1.2-1.4	2.31	2.-2.5	4.1
12	0.03	0-0.1	0.44	.39-.5	1.3	1.2-1.4	2.29	2.1-2.5	4.06
13	0.04	0-0.1	0.42	.34-0.5	1.28	1.2-1.4	2.42	2.3-2.7	4.16

SL= Sampling Locations - Avg: Average

1=Jubail BS#1, 2=Jubail #2, 3=Jubail BS#3, 4 = Khobar BS, 5 = Dammam BS  
6=Qatif BS, 7= Rahima, 8 = Khafji T#1, 9=Khafji#2, 10=Khafji City Tank  
11= Riyadh TG-1, 12= Riyadh TG-2, 13=Riyadh TG-3

**TABLE - 2**  
**INDIVIDUAL AND TOTAL THMs IN CHLORINATED WELL WATER**  
**USED FOR BLENDING (ug/L)**

Sampling Location	CHCl <sub>3</sub>	CHBrCl <sub>2</sub>	CHBr <sub>2</sub> Cl	CHBr <sub>3</sub>	Total THM
<u>Al-Jubail Area</u>					
BS#1 WWST (a)	0.91	0.15	0.11	0.77	1.94
BS#2 WWST	0.50	0.16	0.28	1.97	2.90
BS#3 Well #4	0.71	0.16	0.09	0.50	1.46
<u>Al Khobar Area</u>					
Fowzia	1.62	0.32	0.41	2.92	5.27
Aqrabia (W)	1.84	0.41	1.12	6.17	9.54
Aqrabia (E)	1.42	0.96	0.80	7.39	10.57
Tuqba (E)	1.27	0.34	0.40	5.60	7.61
Tuqba (W)	1.44	0.49	0.83	7.17	9.93
S.Pump Station	1.08	0.27	0.64	4.75	6.74
N.Pump Station	1.27	0.32	1.25	8.13	10.97
Bandaria	1.17	0.29	0.61	5.76	7.83
Green Belt	2.18	0.30	0.46	4.71	7.65
Al Khobar Tank	1.85	0.26	0.35	4.50	6.96
Oneza	1.94	0.18	0.76	16.41	19.29
Al-Saudia	1.28	0.26	0.19	3.74	5.47
Al Raka	1.54	0.15	0.31	8.59	10.59
<u>Dammam Area</u>					
Well No.78	4.66	0.0	0.33	3.27	8.26
Well No.37	2.40	0.0	0.21	1.44	4.05
Well No.76	2.84	0.0	0.93	5.22	8.99
Well No.91	3.51	0.0	0.07	2.65	6.23
Al-Jameen	4.55	0.16	4.16	13.60	22.47
Dammam WWST	0.00	1.02	3.51	11.10	15.62
Qatif WWST	0.0	0.0	0.02	0.18	0.20
Rahima	0.0	0.0	0.40	5.50	5.90
<u>Riyadh</u>					
HPT Composite	0.03	0.53	1.14	2.98	4.68
Wasia Composite	2.36	0.42	0.60	6.30	9.68

(a) WWST = Well Water Storage Tank

TABLE -3

COMPARISON OF RESULTS WITH SOME NATIONAL  
THM SURVEYS CARRIED OUT IN U.S.

Survey	Number of Cities	Mean	THMs ( ug/L)Rang
NORS (1)	80	68	ND* - 482
NOMS (2)	105/113	84	ND - 784
AWWARF (3)	727	42	ND - 360
s w c c (RDC) (4)	10	6	ND - 12.3

1. National Organics Reconnaissance Survey ( U.S.,1975)
2. National Organic Monitoring Survey, Average of 3 Phases (U.S.197677)
3. American Water Works Association Research Foundations (U.S.,1984-86)
4. Saline Water Conversion Corporation, Research and Development Center (Saudi Arabia, 1989 - Blended potable water - This study )

ND\* = None detected

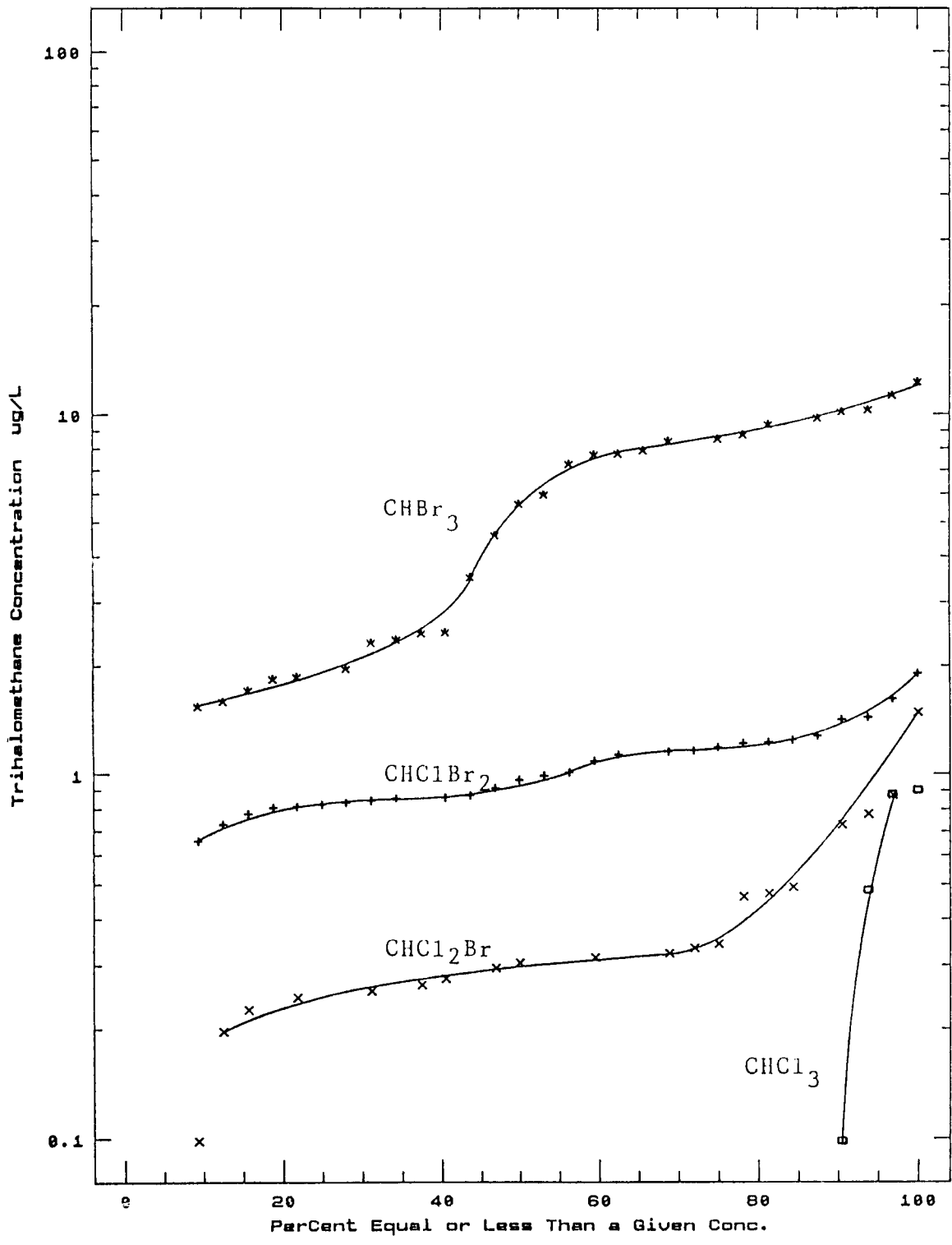


FIG.1 : Frequency distribution of THMs data in blended and chlorinated potable water.

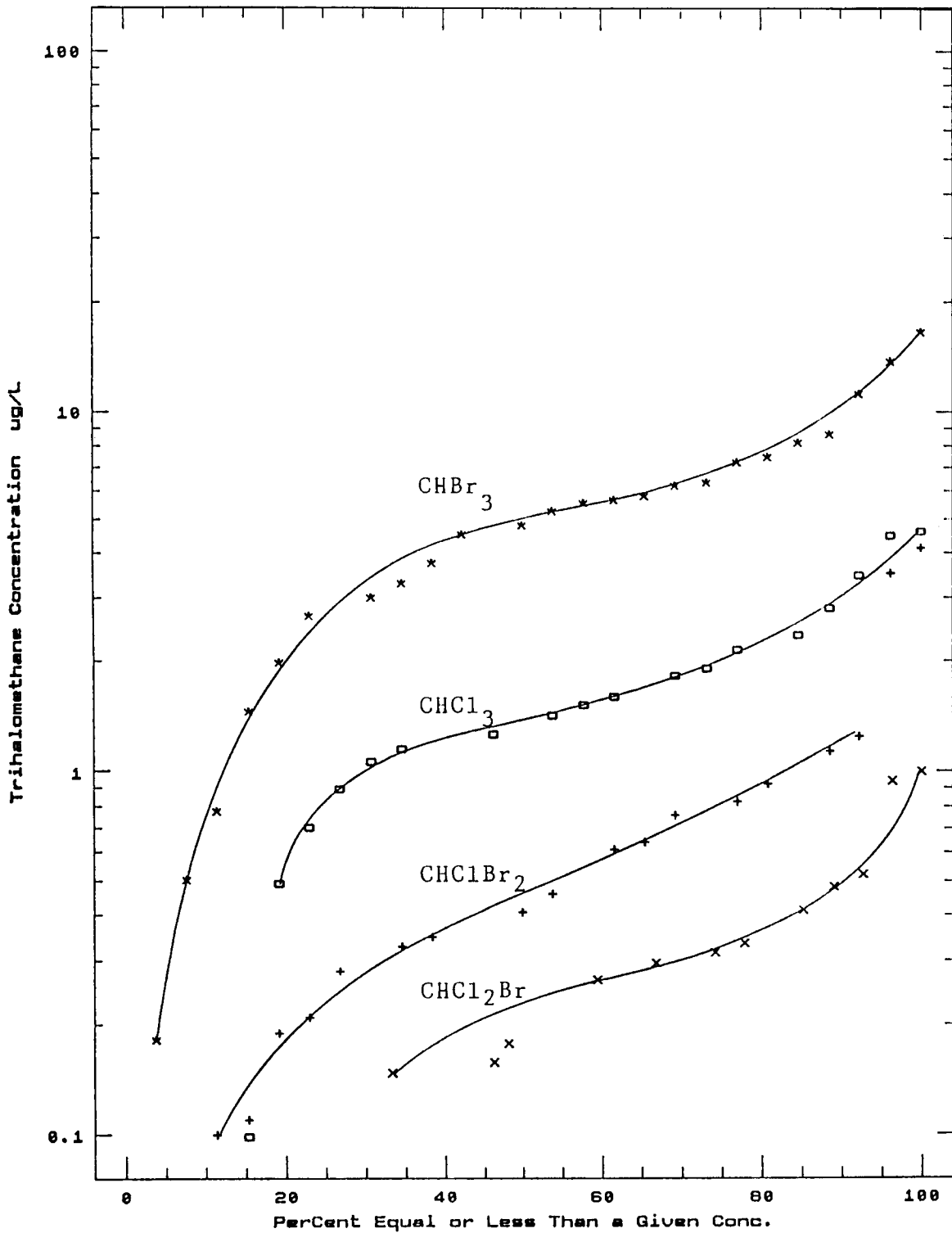


FIG. 2 : Frequency distribution of THMs data in chlorinated brackish well water.