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Volatile Halocarbons in Water

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Volatile halocarbons in drinking water have attracted increasing attention during recent years (Rook 1974; Symons et al. 1975; US EPA 1975; Eklund et al. 1978; Kroneld et al. 1978; Johnson et al. 1982; Skvortsov et al. 1983).

These substances are also found in body fluids (Dowty et al. 1975; Kroneld and Reunanen 1980; Pfaffenberger and Peoples 1982; Kroneld and Reunanen 1983).

All disinfectant chemicals used in water treatment seem to produce by-products. Of particular concern are the following substances from the use of various disinfectants according to US EPA (1975).

From chlorine: volatile halocarbons such as trihalomethanes, trichloroacetone and other largely uncharacterized chlorinated and oxidized intermediates formed from the complex set of precursors in natural water; chloramines; chlorophenols; and the largely unknown products of dechlorination.

From bromine and iodine: volatile halocarbons such as trihalomethanes, other bromine and iodine analogues of chlorinated species, bromophenols, bromoindoles and bromoanisoles are formed and the halogens themselves, which may remain in drinking water.

From chlorine dioxide: chlorinated aromatic compounds; chlorate and chlorite, which are often present as by-products of unreacted starting material from the production of chlorine dioxide; and chlorine dioxide itself.

The aim of the present study was to follow the formation and occurrence of volatile halocarbons in different types of water.

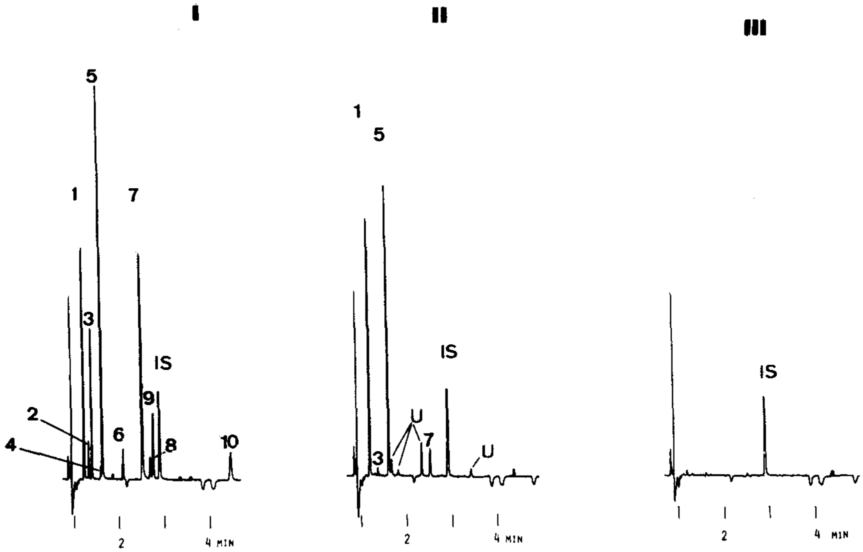

Figure 1. Chromatogram of calibration solution (I), and extract of chlorinated drinking water (II), and well-water (III). 1 = $CHCl_3$, 2 = $CHCCl_3$, 3 = CCl_4, 4 = $ChCl = CCl_2$, 5 = $CHBrCl_2$, 6 = $CBrCl_3$, 7 = $CHBr_2Cl$, 8 = $BrCH_2CH_2Br$, 9 = $Cl_2C = CCl_2$, 10 = $CHBr_3$, IS = international standard, U = unidentified. Column: SE-52, 20-m x 0.3-mm i.d.; temperature: 40 ^{o}C; carrier gas: 1.7 ml hydrogen/min.

MATERIALS AND METHODS

The volatile halocarbons were analyzed through elution with n-pentane (Kroneld and Reunanen 1983). The actual determinations were carried out by extracting 100 ml (22^{o}C) of water or of laboratory or hospital solutions or dialysis fluid made with water, with 5 ml of n-pentane containing an internal standard (400 ng/ml) for 5 min, and then injecting a 2 ul aliquot of the pentane phase into the gas chromatograph (GC) equipped with a split injector and an ^{63}Ni electron capture detector (ECD). A Schimadzu C-R1B calculating integrator calculated the concentrations of identified compounds according to the sorted calibration data (figures 1-2).

Samples of raw water, disinfected water and water from the distribution net of Turku were taken monthly during 1981-84. The effect of different chlorine doses on the formation of volatile halocarbons or especially total trihalomethane concentration (TTHM) at pH 7.5 and 25 ^{o}C was studied as well as the effect of ammonium with a chlorine dose of 1.0 g/l. The results of active charcoal filtering, of distillation and of serial resin ion-changing were also compared with the

Table 1. Concentrations of volatile halocarbons as monthly values in raw water, chlorinated and non-chlorinated water. *** = $p < 0.001$ for TTHM horizontally compared (each category of water source).

raw water	month											
n=12	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
µg/l												
$CHCl_3$	0.3±0.05	0.2±0.08	0.08±0.01	0.1±0.04	0.3±0.08	0.3±0.09	0.7±0.1	1.2±0.2	1.3±0.1	0.6±0.06	0.5±0.04	0.2±0.03
$CHBrCl_2$	0.03±0.01	0.03±0.01	0.02±0.01	0.04±0.01	0.04±0.02	0.06±0.02	0.09±0.02	0.2±0.02	0.08±0.03	0.02±0.08	0.04±0.01	0.04±0.01
$CHBr_2Cl$	0.02±0.01	0.02±0.02	0.02±0.01	0.03±0.01	0.03±0.02	0.04±0.02	0.04±0.03	0.08±0.02	0.05±0.01	0.07±0.01	0.04±0.02	0.03±0.01
$CHBr_3$	+	-	-	-	+	+	0.02±0.01	0.04±0.06	0.08±0.03	0.03±0.09	0.4±0.1	-
$Cl_2C=CCl_2$	-	-	+	+	-	-	0.10±0.04	0.03±0.01	+	+	+	-
CCl_4	+	0.02±0.01	+	+	-	0.02±0.01	0.02±0.01	0.05±0.02	0.02±0.01	+	-	-
TTHM	0.35±0.07	0.25±0.11	0.12±0.03	0.17±0.06	0.37±0.12	0.4±0.13	$0.90\pm0.16^{*}$	$1.72\pm0.36^{*}$	$1.57\pm0.17^{*}$	$1.27\pm0.24^{*}$	$0.98\pm0.17^{*}$	0.27±0.05
chlorinated water												
- after desinfection												
$CHCl_3$	10.1±0.4	18.2±0.6	17.5±0.6	32.3±0.6	44.1±0.7	46.1±0.5	67.2±0.9	68.5±0.4	80.1±0.8	99.2±1.2	101.2±1.3	52.1±1.3
$CHBrCl_2$	0.4±0.1	2.3±0.2	4.8±0.2	11.3±0.2	8.5±0.2	7.3±0.3	7.7±0.3	9.8±0.4	12.2±0.3	17.6±0.5	11.7±0.6	11.9±0.3
$CHBr_2Cl$	0.2±0.06	0.6±0.07	0.3±0.1	0.4±0.1	0.4±0.1	2.4±0.4	2.6±0.5	3.9±0.3	4.8±0.4	5.6±0.4	2.4±0.3	1.1±0.2
$CHBr_3$	-	-	+	-	-	-	+	+	+	-	-	-
$Cl_2C=CCl_2$	-	-	+	-	-	-	-	-	0.02±0.01	-	-	-
CCl_4	-	-	-	-	-	-	-	+	0.05±0.02	-	-	-
$CBrCl_3$	-	-	-	-	-	-	-	0.02±0.01	+	-	-	-
TTHM	10.7±0.56	$21.1\pm0.87^{***}$	$22.7\pm0.9^{***}$	$44.4\pm0.9^{***}$	$53.0\pm1.0^{***}$	$55.8\pm1.2^{***}$	$77.5\pm1.6^{***}$	$82.2\pm1.1^{***}$	$97.3\pm1.5^{***}$	$122.4\pm2.1^{***}$	$115.3\pm2.2^{***}$	$65.1\pm1.8^{***}$
	$p<0.001$	$p<0.001$	$p<0.001$	$p<0.001$	$p<0.001$	$p<0.001$	$p<0.001$	$p<0.001$	$p<0.001$	$p<0.001$	$p<0.001$	$p<0.001$
- distribution net												
$CHCl_3$	11.7±0.3	19.1±0.2	18.2±0.3	34.2±0.4	47.1±0.4	50.2±0.4	69.8±0.6	72.4±0.7	91.8±0.6	103.3±1.7	106.2±1.2	58.4±1.0
$CHBrCl_2$	0.6±0.1	2.7±0.1	5.8±0.3	13.8±0.4	13.8±0.4	8.4±0.3	8.9±0.3	10.9±0.6	14.8±0.8	19.8±0.6	13.4±0.8	14.2±0.6
$CHBr_2Cl$	0.4±0.06	0.8±0.03	0.5±0.08	0.6±0.07	0.6±0.07	3.4±0.2	3.1±0.3	5.2±0.5	5.4±0.6	6.4±0.5	4.4±0.2	1.8±0.2
$CHBr_3$	-	-	-	-	-	-	-	-	-	-	-	-
$Cl_2C=CCl_2$	-	-	-	-	-	-	-	0.02±0.01	0.03±0.01	0.05±0.02	0.03±0.02	-
CCl_4	-	-	-	-	-	-	-	0.02±0.01	0.05±0.02	0.02±0.01	0.02±0.01	-
$CBrCl_3$	-	-	-	-	-	-	-	-	0.14±0.08	0.12±0.02	0.16±0.04	-
TTHM	12.7±0.46	$22.6\pm0.33^{***}$	$24.5\pm0.68^{***}$	$48.6\pm0.87^{***}$	$50.9\pm0.64^{***}$	$62.0\pm0.9^{***}$	$81.8\pm1.2^{***}$	$88.5\pm1.8^{***}$	$113.0\pm2.0^{***}$	$129.5\pm2.8^{***}$	$124.0\pm2.2^{***}$	$74.4\pm1.8^{***}$
	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.	N.S.
nonchlorinated water												
- well water												
$CHCl_3$	-	-	-	-	-	-	-	-	-	-	-	-
$CHBrCl_2$	-	-	-	-	-	-	-	-	-	-	-	-
$CHBr_2Cl$	-	-	-	-	-	-	-	-	-	-	-	-
$CHBr_3$	-	-	-	-	-	-	-	-	-	-	-	-
$Cl_2C=CCl_2$	-	-	-	-	-	-	-	-	-	-	-	-
CCl_4	-	-	-	-	-	-	-	-	-	-	-	-
$CBrCl_3$	-	-	-	-	-	-	-	-	-	-	-	-
TTHM	-	-	-	-	-	-	-	-	-	-	-	-

+ = traces, - = not detected.
P values given. N.S. = not significant

concentrations of trihalomethanes in the drinking water. Volatile halocarbons in hospital and laboratory solutions from the medical industry in Turku that had been bottled at two different seasons of the year, were also analyzed. Analyses were also made in 1981-84 of the tap water of the Turku University Central Hospital, at different stages of its purification and of dialysis fluid. Nonchlorinated well-water was used as a control. The Student's t-test was used to analyze significance differences.

RESULTS AND DISCUSSION

The concentrations of the volatile halocarbons found in the raw and purified water samples are shown in table 1.

In the Aura river, i.e. raw water, only small concentrations of volatile halocarbons were found. The TTHM concentrations determined from the beginning of July to the end of November were significantly higher ($n = 12$) compared with the minimum value found during March. A maximum concentration for TTHM was found in August each year.

The total concentrations of trihalomethanes increased markedly and in a highly significant way after disinfection ($n = 12$) of the raw water. The maximum concentration for TTHM appeared in October and all the monthly values were significantly higher ($p < 0.001$) compared to the minimum value analyzed for January.

The total trihalomethane concentrations continued to increase in the distribution net ($n = 12$), with higher mean values compared to the mean values after disinfection. This increase was, however, not statistically significant.

Seasonal changes of volatile halocarbons in the different categories of water were registered with maximum concentrations of approximately 100-130 ug/l during autumn. Bromoform was found in the raw water and traces found in the samples from the distribution net. Tetrachloroethene, tetrachloromethane and bromotrichloromethane appeared in small concentrations or as traces in the different water categories analyzed.

The nonchlorinated well water was never found to contain volatile halocarbons ($n = 12$) during the study period.

The TTHM concentration increased with the dosage of chlorine (table 2), a phenomenon that also could be shown in studies at the water works of Turku by

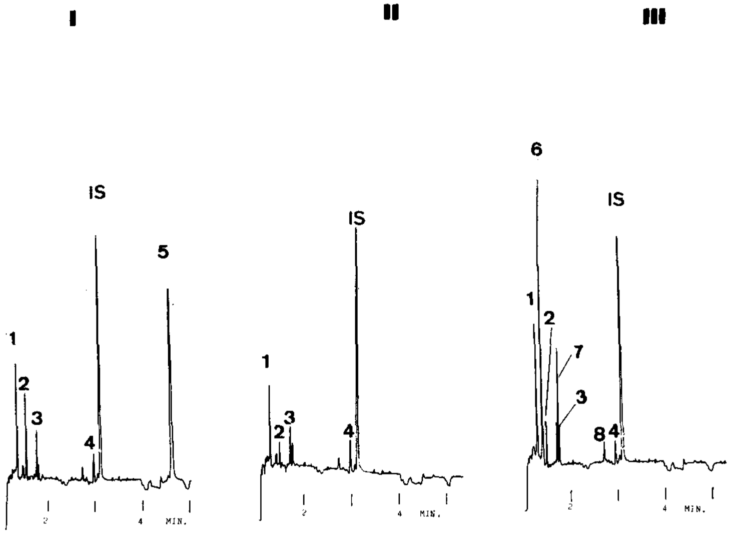

Figure 2. Gas chromatograms registered with electron-capture detection from a sodium citrate rinse solution (I), a sodium chloride infusion solution (II) and in a sample of a sodium chloride infusion solution passed through an infusion tube to a patient (III).
1 = $CHCl_3$, 2 = CCl_4, 3 = $CHCl = CCl_2$, 4 = $Cl_2C = CCl_2$, 5 = $CHBr_3$, 6 = $CHCl = CHCl$, 7 = $CHBrCl_2$, 8 = $CHBr_2Cl$, IS = internal standard. Chromatographic conditions the same as in Fig. 1.

Table 2. TTHM formation at different chlorine concentrations

Cl_2 g/l	0.5	1.0	2.0	3.0	4.0	5.0
n = 15						
TTHM µg/l	5.3±0.5	30.6±1.1 $p<0.001$	71.5±1.0 $p<0.001$	87.9±0.8 $p<0.001$	98.8±0.7 $p<0.001$	99.6±1.1 $p<0.001$

$p < 0.001$ by comparing with the initial values

following TTHM, chlorine and ammonium concentrations. The increase in the TTHM concentration was statistically highly significant.

Ammonium, on the other hand, which appears in the water in large quantities during seasonal run-off periods, binds chlorine (table 3).

Table 3. TTHM formation at different ammonium concentrations

NH_4^+ mg/l	0.1	0.2	0.4	0.6	0.8	1.0
n = 18						
TTHM µg/l	17.7±0.7	10.2±0.6 $p<0.001$	7.9±0.5 $p<0.001$	5.5±0.5 $p<0.001$	2.9±1.0 $p<0.001$	1.4±0.9 $p<0.001$

$p < 0.001$ by comparing with the initial value

As a result, both the possibility of chlorine reacting with organic material to produce trihalomethanes and the trihalomethane concentration then decrease. The decrease in TTHM concentration was statistically significant as ammonium ion content of the water increased.

Filtering with active charcoal or distillation seem to have no effect on the TTHM concentration (table 4). The small molecular size and the evaporation of the compounds may explain the results. The increase registered after distillation was significant (n=18).

The difficulty of eliminating volatile halocarbons may also explain why small amounts of these substances were found in the investigated hospital and laboratory solutions (table 5).

Table 4. Effects of distillation and active charcoal filtering on TTHM concentration

n=18	distribution net	after distillation	after charcoal filtering
TTHM µg/l	43.5±0.4	46.9±0.9 $p<0.01$	45.9±0.7 N.S.

p values given by comparing with the initial value.
N.S. = not significant

Hospital and laboratory solutions bottled during the autumn contained significantly higher concentrations of chloroform ($p < 0.001$), compared to solutions bottled during the spring (n=23). Statistical significance could not be found in this respect for other volatile halocarbons analyzed. Small amounts or traces of these compounds appeared, however, in all the solutions. Bromoform, which may be found in river water and the environment and in ozonated tap water, was found in two solutions.

Table 5. Volatile halocarbons in hospital and laboratory solutions made with water from the distribution net in Turku during autumn and spring.

Substance n = 23	Sodium chlor. isot. rinse solution		Sodium bicarb. 7.5 % solution		Sodium citr. rinse solution		Sodium chlor. physiol.inf. solution		Aqua sterilisata	
months	IX-XI	I-III	IX-XI	I-III	IX-XI	I-III	IX-XI	I-III	IX-XI	I-III
µg/l										
$CHCl_3$	4.4±0.3	2.2±0.1 p<0.001	2.4±0.2	0.3±0.01 p<0.001	2.1±0.1	0.6±0.03 p<0.001	1.7±0.08	0.4±0.06 p<0.001	5.3±3.7	0.2±0.1 p<0.001
$CHBrCl_2$	0.07±0.02	0.02±0.01 N.S.	0.04±0.01	+	0.05±0.01	0.02±0.01 N.S.	0.04±0.02	-	0.03±0.01	-
$CHBr_2Cl$	+	-	+	-	+	-	-	-	-	-
$CHBr_3$	-	-	0.11±0.08	-	0.05±0.1	-	-	-	-	-
CCl_4	0.02±0.01	-	0.02±0.01	-	0.03±0.01	-	-	0.02±0.01	0.01±0.01	+
$Cl_2C=CCl_2$	0.02±0.01	-	+	-	-	+	+	0.03±0.01	0.06±0.02	-
CHCl=CHCl	-	-	0.02±0.01	-	-	-	-	+	0.02±0.01	-

+ = traces, - = not detected

$p<0.001$, N.S. = not significant by comparing with the initial values

Table 6. Concentrations of volatile halocarbons in tap water and after each stage of water treatment.

Substance n = 20 µg/l	tap water	after water softening	after active charcoal filtering	after reverse osmosis	after paper filtering	used dialysis fluid
$CHCl_3$	67.9±0.6	43.9±0.5 p<0.001	44.9±0.6 p<0.001	37.9±1.7 p<0.001	37.6±0.5 p<0.001	33.6±0.4 p<0.001
$CHBrCl_2$	10.9±0.5	9.5±0.5 N.S.	9.7±0.5 N.S.	7.7±0.4" p<0.001	7.9±0.4 p<0.001	6.4±0.3 p<0.001
$CHBr_2Cl$	2.4±0.3	1.5±0.3 p<0.05	1.6±0.2 p<0.05	1.2±0.2 p<0.001	1.2±0.1 p<0.001	1.1±0.1 p<0.001

P values given by comparing with the initial values. N.S. = not significant

Table 6 shows the most prominent volatile halocarbons in tap water and after different treatment.

There was a highly significant decrease in the chloroform concentration and an almost significant decrease in dibromochloromethane after water softening and a highly significant decrease for all compounds analyzed after reverse osmosis. The substances were all reduced during the treatment, but not eliminated.

During autumn, when the volatile halocarbons were highest, approximately 100 to 130 ug/l, the use of chlorine is at its maximum. To reduce the concentrations of volatile halocarbons, primarily the TTHM concentration, it is suggested that the amount of precursors in the raw water should be lowered by more active prehandling and that chlorination should be optimized. The occurrence of volatile halocarbons could also indicate the occurrence of other, possibly even more hazardous, compounds produced through chlorination. Because analytical investigations have limitations in determining compounds with possible health risks in tap water, biological tests should be used to guarantee the highest quality of tap water in view of its importance for public health.

The difference in the concentrations of volatile halocarbons in the analyzed hospital and laboratory solutions was significant for chloroform according to seasonal changes in concentrations in tap water. The concentrations of volatile halocarbons generally might be explained by the fact that the medical industry uses water of different quality in their solutions. There was also a significant correlation between the concentrations in tap water and dialysis fluid according to seasonal changes.

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REFERENCES

Dowty B, Carlisle D and Laseter JL (1975) Halogenated hydrocarbons in New Orleans drinking water and blood plasma. Science 187:75-77.

Eklund G, Josefsson B and Roos C (1978) Trace analysis of volatile organic substances in Göteborg municipal drinking water. Vatten n:r 3:195-206.

Johnson JD, Christman RF, Norwood DL and Millington DS (1982) Reaction products of aquatic humic substances with chlorine. Environ Health Perspect 46:63-71.

Kroneld R and Reunanen M (1980) Volatile halocarbons in drinking water and serum (translated from Finnish). Finnish Med J N:o 13:1117-1121.

Kroneld R and Reunanen M (1983) Volatile halocarbons in tap water as a problem in haemodialysis therapy. Clinica Chimica Acta 129:141-149.

Kroneld R, Reunanen M and Wahlroos G (1981) Volatile halocarbons in Turku raw and drinking water (translated from Finnish). Finnish Chemistry n:o 3:141-144.

Pfaffenberger CD and Peoples AJ (1982) Long-term variation study of blood plasma levels of chloroform and related purgeable compounds. J Chromatogr 239: 217-226.

Rook JJ (1974) Formation of haloforms during chlorination of natural waters. Water Treatment Exam 23: 234-243.

Skvortsov AF, Sergeev EP, Elakhovskaia NP, Bonashevskaia TL and Mamulashivili NI (1983) Hygienic assessment of the chloroform content of the drinking water. Gig Sanit 3:10-13.

Symons JM, Bellar TA, Carswell JK, Demarco J, Kropp KL, Robeck GG, Seeger DR, Slocum CJ, Smith BL and Stevens AA (1975) National organic recoinnaissance survey for halogenated organics (NORS). J AWWA 67: 634-647.

US EPA (1975) Report to US Congress on suspect carcinogens in water supplies. U.S. EPA, Washington DC June 17.

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