VOLATILE ORGANIC COMPOUNDS IN THE FINISHED WATER OF THE WATER TREATMENT PLANT IN THESSALONIKI, GREECE

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ABSTRACT

Chlorination has been the most widely used technology for the disinfection of drinking water around the world. The main purpose for the disinfection of drinking water is to protect it against microbial contamination in the distribution systems and to prevent or at least control re-growth of microorganisms in the pipelines.

A major disadvantage of chlorination is the formation of a wide variety of halogenated compounds from natural organic matter (Rook, 1974; Christman *et al.*, 1983). Some of these by-products, namely trihalomethanes, 1,2-dichloroethane, trichloro- and tetrachloro-ethene have diverse negative effects on human health, including toxicological, mutagenic and carcinogenic effects, as well as induction of congenital malformations and retarded fetal growth (Boorman *et al.*, 1999). Current regulations in Europe demand a target of 100 μg l^{-1} for trihalomethanes (THMs), 3 μg l^{-1} for 1,2-dichloroethane, 10 μg l^{-1} for the sum of trichloro- and tetrachloroethene, 1 μg l^{-1} for benzene and include all the prementioned compounds in the category of volatile organic compounds (VOCs).

Since September 2003, the city of Thessaloniki and its suburbs are partly supplied with drinking water from the Thessaloniki Water Treatment Plant (TWTP), which takes raw water from the river Aliakmonas. This study presents the regular monitoring results at the TWTP during the period February 2004 – February 2005 for THMs and VOCs included in the European guidelines. At the same time, parameters such as pH, temperature, chlorine demand, total organic carbon (TOC) and contact time (t_R) were monitored.

KEYWORDS: THMs, VOCs, drinking water, chlorination, disinfection by-products (DBPs)

1. INTRODUCTION

The main reason for drinking water disinfection is protection from microbial contamination in the pipelines along the distribution system, as well as prevention control of regrowth of microorganisms until the water safely reaches the consumers (Rook, 1974 / Christman *et al.*, 1983 / El-Shafy, Grűnwald, 2000).

Chlorine has been the most commonly used disinfectant in many water treatment plants. Its popularity arises from its high oxidation potential, low cost and prolonged disinfection effectiveness. The major disadvantage of using free chlorine as a disinfectant is its high and non-selective reactivity, which leads to the formation of disinfection by-products (DBPs) (Çapar, Yetiş, 2002). It rapidly reacts with natural organic matter (NOM),

principally humic and fulvic acids, by oxidation, addition and substitution reactions to form DBPs such as trihalomethanes (THMs), haloacetic acids (HAAs) and other halogenated volatile organic compounds (VOCs) (Villanueva *et al.*, 2003).

The presence of VOCs including THMs in the drinking water is the target of increasing regulation because these compounds are suspected for carcinogenicity and birth effects (Cantor, 1997; Nieuwenhuijsen *et al.* 2000).

Traditionally, THMs have been the most studied of the DBPs. Since the 1970's, several studies have evaluated their chemical properties, the kinetics of their formation reactions, their toxicology and human health effects (Villanueva *et al.*, 2003 / Cantor, 1997).

Apart from THMs, other VOCs are among the most commonly found contaminants in water. Several analytical methods were developed for the determination of these VOCs in water with the Purge & Trap / Gas Chromatography / Mass Spectrometry determination being the most sensitive and simplest one (Wang *et al.*, 1995; Golfinopoulos *et al.*, 2001). Numerous surveys were carried out evaluating THM content in water on the basis of regression models in order to pre-estimate their levels by monitoring other simple water parameters (Espigares, 2003; Golfinopoulos, 2002a; Golfinopoulos, 2002b).

In the present study, the levels of THMs and VOCs are determined as part of a routine monitoring program followed in the TWTP laboratory. These levels are correlated with temperature, pH, chlorine demand, TOC and contact time. VOCs and THMs levels are monitored during a year in order to determine the possible fluctuations throughout the four seasons.

2. MATERIALS AND METHODS

2.1 Sample collection

TWTP takes its raw water from the river Aliakmonas. The treatment applied in the plant consists of the following steps (Fig. 1): pre-ozonation / pH-adjustment / coagulation / flocculation / sedimentation / rapid sand filtration / ozonation / granulated active carbon (GAC) filtration / pH-adjustment to pHs / chlorination / storage. In TWTP, the ozonation process, which aims to break down organic compounds and facilitate their adsorption on the activated carbon, also serves as a first step disinfection. Final disinfection with chlorine is applied for its residual effectiveness. Samples were collected approximately 20 min after chlorination (sampling point A), as well as after the water had remained in the storage tank for several hours (sampling point B), just before it entered the distribution system.

These two different sampling points aimed to investigate the possible increase in the VOCs levels due to the contact time of water with chlorine in the storage tank. Duplicate samples were collected from the two prementioned sampling points (Fig. 1) in 40-ml amber glass vials, capped with PTFE-faced caps (EPA, Method 524.2, Revision 4.1, 1995). Ascorbic acid (Merck, pro analysi) was added in the vials as dechlorination agent. HCl (4 drops 6N/40ml, Carlo Erba, ISO-for analysis) was added to each sample to prevent biodegradation and dehydrohalogenation. The samples were analyzed immediately after sampling.

2.2 Method

The following VOCs were studied: chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), bromoform ($CHBr_3$), vinyl chloride ($CH_2=CHCl$), 1,2-dichloroethane ($ClCH_2CH_2Cl$), trichloroethene ($ClCH=CCl_2$), tetrachloroethene ($Cl_2C=CCl_2$), benzene (C_6H_6), 1,1-dichloroethene ($Cl_2C=CH_2$), *trans*-1,2-dichloroethene ($ClCH=CHCl$), *cis*-1,2-dichloroethene ($ClCH=CHCl$), 1,1,1-trichloroethane (Cl_3CCH_3), carbon tetrachloride (CCl_4), 1,2-dichloro-benzene ($C_6H_4Cl_2$), 1,2-dichloropropane ($ClCH_2CHClCH_3$), toluene ($C_6H_5CH_3$), ethyl-benzene ($C_6H_5C_2H_5$), p/m/o-xylene ($H_3CC_6H_4CH_3$), styrene ($C_6H_5CH=CH_2$), 1,4-dichloro-benzene (ClC_6H_4Cl). The prementioned VOCs were analyzed by the Purge and Trap method (EPA 524.2, Revision 4.1, 1995). In this method an inert gas is bubbled through 25 ml of water sample causing

the purgeable organics to migrate from the aqueous to the vapour phase. These organics are then adsorbed on a trap which, upon heating, desorbs the trapped organics onto the GC-MS system.

The prementioned VOCs were analyzed using a CDS 8000 Purge and Trap Sample Concentrator, fitted with a 25ml sample vessel, a 30cm Trap K (VOCARB 3000, Carbopack B / Carboxen 1000 & 1001) and a Perkin Elmer AutoSystem XL Chromatograph supported by Turbomass Gold Mass Spectrometer (Table 1).
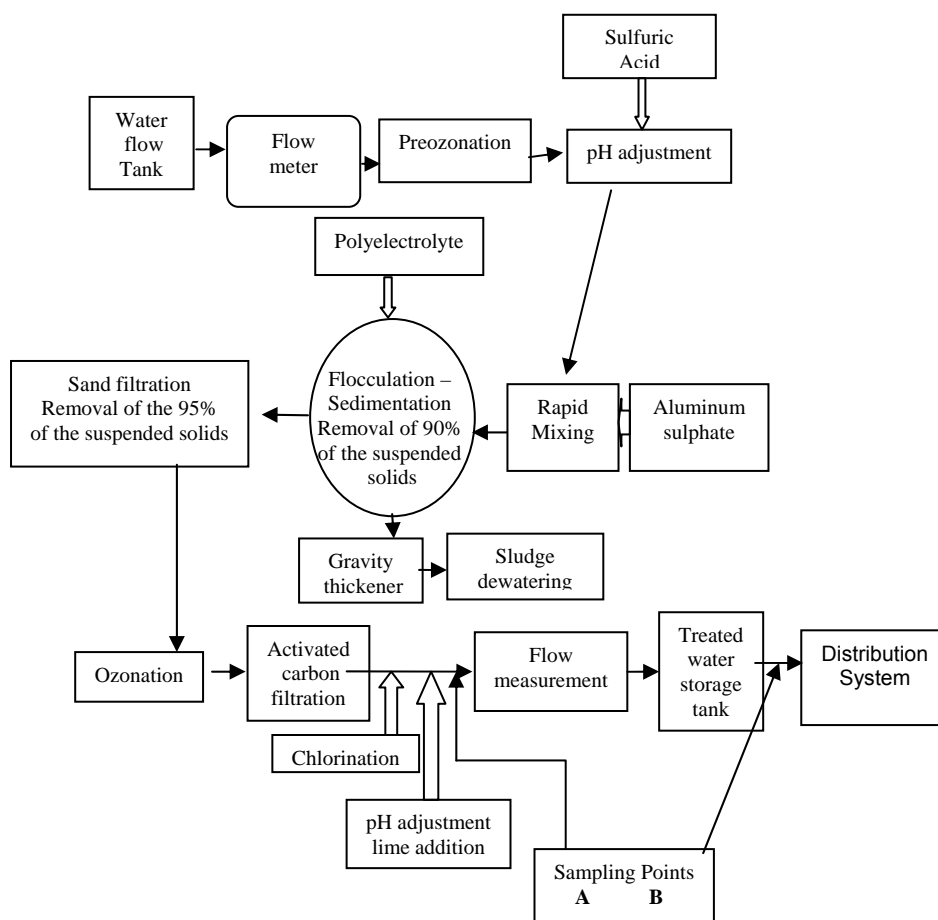
Figure 1: Thessaloniki Water Treatment Plant treatment process, sampling points A, B

The analytical quality control scheme included baseline controls, periodic analyses of certified VOCs and THM standard solutions (EPA 524.2 method, mixtures DW-VOC Mix #1A, #2A and THM, Restek) in methanol (Riedel de Haën, pestanal), fortified with internal standard (4-bromofluorobenzene, 524 Internal Standard/Surrogate Mix, Restek), blank water samples (ultrapure water, Easypure UV, TOC_{max}<2ppb, Mod. D7402-33) and laboratory fortified blank water samples (ultrapure water fortified with standard solutions). Standard solutions were prepared by injecting known volumes of the pre-mentioned mixtures to a 10-ml volumetric flask filled with methanol (Riedel de Häen, pestanal). Laboratory fortified blank water samples were prepared by adding known volumes of VOCs and THMs standards in 25-50 ml ultrapure water. Mixing was accomplished by inverting the volumetric flask three times.

Table 1. Purge and trap conditions

Vocarb 3000 trap	
Purge	40 ml/min He, 10 min, ambient temperature
Desorb	30 ml/min He, 250°C for 5 min (preheat 245°C)
Bake	260°C for 10 min
Temperatures	Line 150°C, Valve 150°C, Wettrap 200°C
GC parameters	
Oven Temperature	40°C for 4 min
First temperature ramp	From 40°C to 150°C at 6°C/min
Second temperature ramp	From 150°C to 180°C at 8°C/min for 1 min
Column	Rtx®-502.2, 40m x 0,18 mm i.d. x 1 µm film thickness, Restek
Injector	Split/Splitless, 200°C
Split ratio	30:1
Carrier	Helium, 1 ml/min (purity 99,9995%)
Mass spectrometer parameters	
Solvent delay	2 min
MS temperature	180°C
MS scan program	45-260
Scan/s	0,1

Table 2. Mean recovery (%), relative standard deviation (in parenthesis) of THMs and VOCs at five concentration levels and the MDL of these compounds

VOCs	Concentration levels ($\mu g\ l^{-1}$)					MDL ($\mu g\ l^{-1}$)
	0,1	0,5	1	2	5	
Chloroform	131 (14,3)	107 (4,2)	116 (9,3)	111 (9,5)	104 (6,3)	0,03
Bromodichloromethane	91 (10,2)	85 (11,6)	89,1 (13,7)	92 (12,4)	85 (8,9)	0,04
Chlorodibromomethane	72 (14,1)	67 (13,6)	66 (19,3)	61 (16,1)	63 (14,3)	0,04
Bromoform	47 (18,9)	50 (8,8)	48 (6,9)	45 (18,3)	43 (13,1)	0,06
Vinyl chloride	103 (13,4)	94 (13,9)	103 (10,8)	98 (11,2)	91 (7,1)	0,04
1,2-Dichloroethane	135 (11,5)	105 (8,1)	113 (4,3)	114 (11,5)	107 (6,5)	0,02
Trichloroethene	103 (14,1)	99 (10,5)	107 (2,5)	107 (14,6)	99 (7,3)	0,04
Tetrachloroethene	121 (10,3)	118 (6,6)	123 (3,2)	123 (12,5)	114 (8,3)	0,02
Benzene	134 (11,2)	107 (8,3)	116 (4,4)	117 (11,5)	110 (6,4)	0,02
1,1-Dichloroethene	78 (10,0)	91 (8,8)	95 (9,2)	99 (13,1)	85 (16,9)	0,04
Trans-1,2-dichloroethene	122 (14,8)	132 (14,0)	136 (3,2)	136 (11,2)	131 (6,8)	0,02
Cis-1,2-dichloroethene	118 (7,9)	116 (9,9)	122 (3,5)	123 (8,1)	115 (4,8)	0,03
1,1,1-Trichloroethane	98 (12,4)	90 (5,4)	94 (11,1)	108 (9,8)	96 (8,6)	0,06
Carbon tetrachloride	88 (15,1)	95 (14,3)	100 (11,8)	106 (12,7)	101 (8,1)	0,04
1,2-Dichlorobenzene	66 (9,4)	65 (16,4)	66 (13,0)	67 (6,1)	67 (8,6)	0,02
Dichloropropane	110 (15,5)	99 (9,7)	110 (9,6)	104 (8,7)	98 (5,5)	0,02
Toluene	110,2 (11,0)	118 (10,3)	122 (6,0)	121 (12,5)	114 (6,8)	0,02
Chlorobenzene	103 (7,1)	95 (12,4)	112 (7,5)	109 (10,1)	103 (5,9)	0,02
Ethyl-benzene	131 (6,4)	99 (18,9)	110 (10,8)	123 (13,1)	117 (8,9)	0,02
p-/m-xylene	113 (4,9)	84 (13,6)	94 (13,0)	121 (11,3)	117 (7,2)	0,03
o-xylene	109 (12,3)	92 (7,5)	102 (9,5)	91 (12,8)	100 (8,9)	0,04
Styrene	98 (8,5)	87 (10,1)	102 (9,5)	91 (12,8)	99 (8,9)	0,03
1,4-Dichlorobenzene	70 (14,0)	67 (12,3)	72 (11,1)	86 (6,5)	78 (7,3)	0,03

Preparation of vials included washing with detergent, rinsing with tap and ultrapure water, acetone (Riedel de Haën, puriss) and air drying.

The mean recoveries (Table 2) were estimated at five levels (0.1ppb – 5ppb) and ranged from 43% to 136%. Linearity was routinely evaluated between 0.1 to 100ppb for THMs, 0.1 to 10ppb for trichloroethene and tetrachloroethene according to the limit set by the European Guidelines and 0.1 to 5ppb for the rest of the compounds. Correlation coefficients (r^2) ranged from 0.983 – 0.999.

The method detection limit (MDL) was calculated as: MDL = SD*t where SD: standard deviation and t: 3.11 for 12-1 = 11 degrees of freedom at the 99% level from the one-sided t distribution table. The MDL for the majority of the compounds ranged from 0.02 to 0.04 ppb except for $CHBr_3$ and Cl_3CCH_3 for which it was 0.06 ppb. Calculated accuracy and precision of the method were within the limits required from European Guidelines (Table 3).

Table 3. Required characteristics according to European guidelines 98/83/EC

VOCs	Parametric value (ppb) according to 98/83/EC	Required Accuracy % of parametric value	Calculated Accuracy %	Required Precision % of parametric value	Calculated Precision %
Chloroform			10		3
Bromodichloromethane			2		3
Chlorodibromomethane	100	25	1	25	3
Bromoform			5		4
Vinyl chloride	-	-	24	-	5
1,2-Dichloroethane	3	25	14	25	3
Trichloroethene	10	25	15	25	3
Tetrachloroethene			10		2
Benzene	1	25	13	25	3
1,1-Dichloroethene	-	-	17	-	3
Trans-1,2-dichloroethene	-	-	9	-	1
Cis-1,2-dichloroethene	-	-	5	-	2
1,1,1-Trichloroethane	-	-	12	-	3
Carbon tetrachloride	-	-	13	-	2
1,2-Dichlorobenzene	-	-	4	-	4
Dichloropropane	-	-	7	-	1
Toluene	-	-	5	-	1
Chlorobenzene	-	-	9	-	1
Ethyl-benzene	-	-	4	-	2
p-/m-xylene	-	-	6	-	5
o-xylene	-	-	12	-	6
Styrene	-	-	2	-	6
1,4-Dichlorobenzene	-	-	6	-	4

Total organic carbon (TOC) was analyzed in a Shimadzu TOC Analyzer (TOC-V$_{CSH/CSN}$). Sample pH was measured with a portable HACH pH-meter fitted with thermometer and having temperature compensation.

3. RESULTS

The results of this study (Table 4) showed that THMs were present in all water samples analyzed. No sample exceeded the limit set by the European Guidelines (100 ppb). THM levels in all measured samples from sampling point A ranged from 0,16 to 2,47 ppb with

an average of 0,69 ppb, while samples from sampling point B ranged from 1,10 to 12,92 ppb with an average of 4,73 ppb. The maximum value in sampling point B (12,92 ppb) was measured in April 2004 and can be attributed to longer contact time (40h instead of 14-19h usually) of water with free chlorine in the storage tank. The lowest value (1,10 ppb) was observed in February 2005 and can be attributed to a combination of low temperature (4,4°C) and short contact time (t_R, 8h) in the storage tank. The rest of the VOCs monitored were never detected in any of the samples.

Table 4. Data for TTHMs and VOCs

Date of sampling	THMs (ppb) A	VOCs (ppb) A	THMs (ppb) B	VOCs (ppb) B	t_R (h)	TOC (ppm)	pH	T (°C)	Cl_2 demand (ppm), samp. point B
18/2/04			2,59	n.d.	19	0,772	7,26	5,6	0,38
25/2/04			3,42	n.d.	20	0,562	7,27	6,1	0,37
10/3/04			4,11	n.d.	20	1,012	7,49	7,6	0,54
31/3/04			5,46	n.d.	18	1,08	7,38	7,4	0,61
1/4/04	1,16	n.d.				1,096	7,32	7,3	0,61
5/4/04	**2,47**	n.d.	6,69	n.d.	16	0,955	7,33	13,2	0,64
13/4/04			**12,92**	n.d.	**40**	1,039	7,57	**16,6**	0,89
14/4/04			8,74	n.d.	21	1,176	7,55	15,6	0,81
19/4//04			5,42	n.d.	11	1,081	7,83	15,3	0,56
5/5/04			5,46	n.d.	18	1,221	7,58	17,9	0,49
12/5/04			4,99	n.d.	19	0,978	7,18	16,8	0,43
9/6/04			5,77	n.d.	24	0,96	7,13	19,3	0,43
22/6/04			7,82	n.d.	26	0,891	7,25	20,9	0,47
2/7/04			6,35	n.d.	19	0,972	7,28	23,1	0,35
29/7/04			4,23	n.d.	19	0,773	7,24	20,6	0,23
31/8/04			5,27	n.d.	18	0,863	7,21	21,2	0,17
8/9/04			4,01	n.d.	17	0,826	7,25	20,7	0,23
27/9/04			6,25	n.d.	25	0,822	7,17	21,2	0,25
5/10/04	0,61	n.d.	5,66	n.d.	27	0,842	7,18	20,2	0,24
22/10/04	0,65	n.d.	3,84	n.d.	7	0,949	7,36	18,4	0,47
9/11/04	0,52	n.d.	4,19	n.d.	19	0,884	7,53	15	0,24
19/11/04	0,42	n.d.	3,38	n.d.	15	0,917	7,39	11,9	0,38
22/11/04	0,91	n.d.	2,96	n.d.	11	0,889	7,43	9,7	0,43
8/12/04	0,67	n.d.	2,06	n.d.	13	1,23	7,44	12,7	0,41
23/12/04	**0,16**	n.d.	1,43	n.d.	14	1,095	7,27	7,9	0,45
5/1/05	0,18	n.d.	1,36	n.d.	10	0,916	7,39	7,5	0,3
25/1/05	0,24	n.d.	2,36	n.d.	17	1,018	7,03	7,3	0,2
2/2/05	0,25	n.d.	**1,10**	n.d.	**8**	1,074	7,44	**4,4**	0,28

4. DISCUSSION

Effect of contact time, t_R. It has long been recognized that the longer water contacts free chlorine the more abundant the THMs (Fleischacker, Randtke, 1983). This is confirmed in our study since THMs determined just after chlorination (sampling point A) were 3 to 10 times lower than those observed in the final reservoir (sampling point B) on the same days. As shown in Fig. 2, THM levels follow the variations of contact time. Nevertheless, there cannot be established a linear correlation between t_R – THMs, since other parameters also influence THM levels.

The large increase in THM levels after the initial contact time of 20 min (sampling point A), suggests that NOM of the treated water reacts at a relatively slow rate and therefore should be categorized as "slow former". The time needed for the formation of THMs depends on the composition of natural organic matter (NOM), which serves as precursor
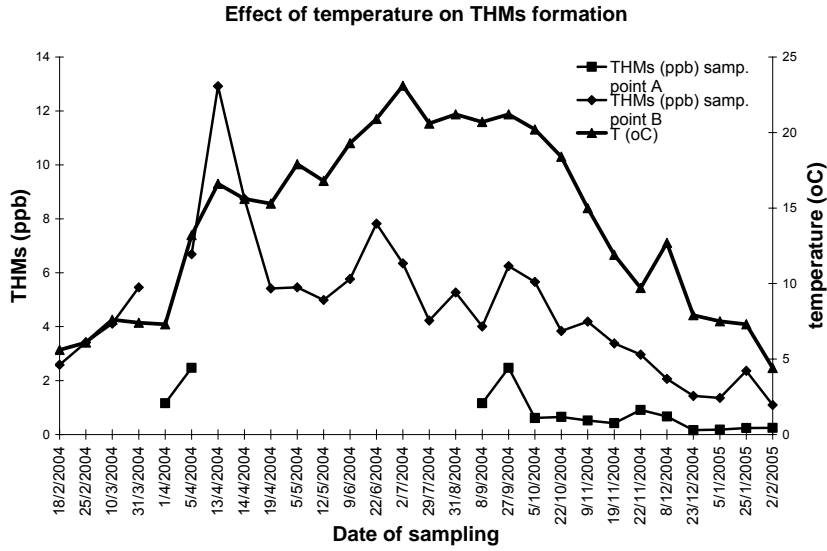
material. Certain NOM reacts quickly to form DBPs within the first 30 min of contact and is referred to as "quick formers", while NOM that needs more contact time to form DBPs, is referred to as "slow formers" (Carlson, Hardy, 1998).

Figure 2. Effect of contact time t_R on THMs formation

Effect of temperature. THM formation bears a strong correlation with temperature. The lower the temperature the lower the THM levels since the rate of reaction decreases. This is apparent in Fig. 3 since mostly low THM values are observed during winter.

Effect of TOC. TOC is directly correlated to NOM, the precursor for THM formation. In our case, TOC concentration is relatively stable at about 1 ppm and as a result, no correlation can be established with that parameter (Fig. 4). The low TOC concentration is responsible for low THM levels. Ensuring low TOC levels in the treated water (before chlorination) is one of the strong advantages of the combined ozonation-GAC adsorption process applied in the TWTP. The average TOC of untreated water is 1,95 ppm. The reduction of average TOC through the treatment train is shown below:

Untreated water → After flocculation/sedimentation/filtration → After O_3 → After GAC
    1,95 ppm   1,43 ppm   1,39 ppm   0,96 ppm

Distribution of THM species. The distribution of the individual THM species ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$) appears in Figure 5. The relatively lower concentrations of the brominated species offers an indication that bromide ion levels in the treated pre-chlorinated water are low (Symons *et al.*, 1993, Kampioti and Stephanou, 2002).

Effect of temperature on THMs formation

Figure 3. Effect of temperature (T) on THMs formation

Effect of TOC on THMs formation
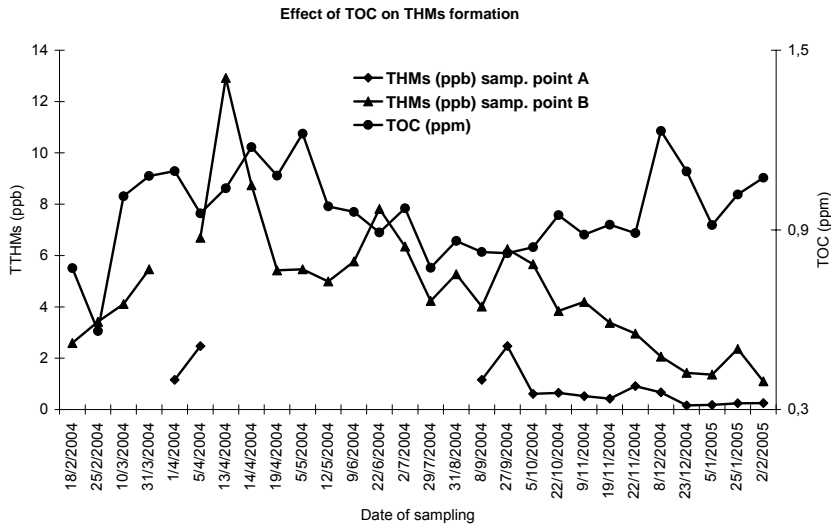

Figure 4. Effect of TOC on THMs formation

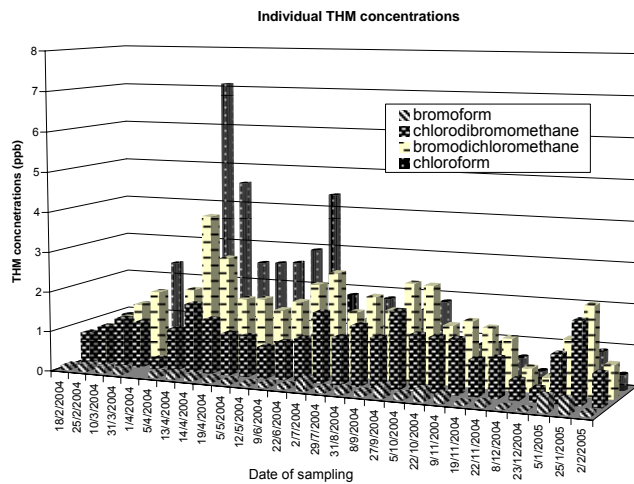**Individual THM concentrations**

Figure 5. Relative presence of individual THMs

5. CONCLUSIONS

Due to low TOC levels of the prechlorinated water and low chlorine dosage at the TWTP, THM levels of the finished drinking water are kept low. The advanced process design of the TWTP ensures maximum TOC removal through GAC adsorption and guaranteed low chlorine demand and dosage due to the preceding first disinfection step with ozonation.
Of the effects studied, free chlorine contact time (t_R) and temperature (T) appear to be the most evident regarding THM formation.
The monitoring program for the determination of VOCs in the finished drinking water of TWTP continues on a permanent basis so that consumers can freely enjoy the good quality of their water. The expansion of this program to THM formation further in the pipeline network and at the consumers' outlet is in our future plans.

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