

## HALOMETHANES AND ORGANIC POLLUTANTS IN DRINKING WATER AFTER DISINFECTION

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### S u m m a r y

Water supply of Riga City uses water from the river Daugava, lakes Baltezers as well as deep well groundwater as drinking water. Due to chlorination of drinking water before use, inhabitants health may be at risk due to trihalomethanes and some organic pollutants. The objective of this study was to determine the level of pollution of drinking water and possible health risk. Pollutants were determined with previous solid phase microextraction (on fibre coated with polydimethylsiloxane) or pentane extraction of chemical substances by use of gas chromatography and for benzo(a)pyrene by spectrofluorimetry. The summary concentration of trihalomethanes (bromoform, chloroform, bromodichloromethane, dibromochloromethane) ranged from 3.4  $\mu\text{g}/\text{dm}^3$  to 304.4  $\mu\text{g}/\text{dm}^3$  (maximum allowable concentration – MAC 100  $\mu\text{g}/\text{dm}^3$  according to water standards in Latvia), summary trichloroethene and tetrachloroethene occurred in the concentration from 1.0  $\mu\text{g}/\text{dm}^3$  to 13.4  $\mu\text{g}/\text{dm}^3$  (MAC = 10  $\mu\text{g}/\text{dm}^3$ ). The level of aromatic hydrocarbons benzene and toluene was below 0.2  $\mu\text{g}/\text{dm}^3$  (MAC = 1  $\mu\text{g}/\text{dm}^3$ ). The concentration of benzo(a)pyrene was below 0.002  $\mu\text{g}/\text{dm}^3$  (MAC = 0.01  $\mu\text{g}/\text{dm}^3$ ). Fluctuations of concentration were found to depend on the season and place of sampling. The results confirmed an occurrence of risk due to the impact of trihalomethanes to health. Therefore, water ozonation has been planned to replace chlorination with ozonation in Riga City.

### INTRODUCTION

Disinfection is usually a chemical process used in water systems to inactivate pathogens found in the source water. Disinfection through inactivation involves the use of disinfectants such as chlorine, ozone, chlorine dioxide and combination of chlorine and ammonia (chloramines). Chlorination processes are an important disinfection strategy in drinking water treatment to inactivate pathogens found in the surface water. Side reactions of chlorine species with naturally present organic matter, however, are known to produce toxic disinfection by-products (DBPs). One important class of DBPs is trihalomethanes (THM). Additionally haloacetic acids, haloacetonitrils, halogenated ketenes, bromate, chloral hydrate are reported as chlorination by-products [9, 14, 16, 18].

As a source of drinking water Riga City utilises surface water. Chlorination disinfection method had been used in drinking water supply system of Riga City as the only

method for inactivation of pathogens till last summer when ozonation was introduced. The level of THM as the most important pollutant can vary within wide range of different countries, but we have no information about by-products in drinking water of Riga City. [2, 5, 6, 12, 15].

Due to drinking water chlorination, inhabitants are exposed to trihalomethanes and some organic pollutants. [3, 4, 7, 8, 13, 21]. Main issues of interest so far have been low birth weight, preterm delivery, spontaneous abortions, stillbirth and birth defects – in particular central nervous, major cardiac defects, oral cleft, and respiratory defects. Various toxicological and epidemiological studies pointed towards an association between THM, one of the main DBPs, and low birth weight, although the evidence is not conclusive.

The objective of this study was to determine the level of pollution of drinking water and possible health risk.

## MATERIALS AND METHODS

Water samples were taken in the water supply system (7 points) and before intake (2 water intake places: Daugava and Baltezers) during summer and winter season. The samples were placed in a cooling bag, delivered to the laboratory and analysed at once. The following organic substances were determined according to standard method [17]: halogen hydrocarbons (dichloroethane, trichloroethene, tetrachloroethene, chloroform, bromoform, bromodichloromethane, dichlorobromomethane), aromatic hydrocarbons (benzene, toluene) and polycyclic aromatic hydrocarbon 3,4-benzo(a)pirene.

Table 1. Recovery and precision for chlorinated and aromatic hydrocarbons

Compound	Added amount $\mu\text{g}/\text{dm}^3$	Number of analyses	Amount recovered, $\mu\text{g}/\text{dm}^3$	Bias % recovery	RSD* %	Detection limit, $\mu\text{g}/\text{dm}^3$
1,2- Dichloroethane	10	5	$9.34 \pm 0.53$	93.4	5.67	0.3
Trichloroethene	10	5	$9.67 \pm 0.39$	96.7	4.03	0.5
Tetrachloroethene	150	5	$158.80 \pm 13.21$	105.9	8.31	0.5
Chloroform	150	5	$153.48 \pm 17.05$	102.3	11.11	0.4
Bromoform	5	5	$4.43 \pm 0.42$	88.6	9.48	2.4
Bromodichloro- methane	5	5	$4.88 \pm 0.33$	97.6	6.76	2.4
Dibromochloro- methane	5	5	$4.83 \pm 0.23$	96.7	4.76	2.4
Benzene	1	5	$1.07 \pm 0.04$	100.7	4.17	0.2
Toluene	1	5	$0.95 \pm 0.05$	95.2	3.78	0.2
Benzo(a)pirene	2	7	$1.84 \pm 0.09$	92	4.88	0.002

\* RSD – precision expressed as relative standard deviation; each analysis was made in duplicate

The pollutants were determined with previous pentane extraction of chemical substances or with solid phase microextraction (on fibre coated with polydimethylsiloxane) using gas chromatography (Varian 3800, with FID, capillary column 0.3 mm ID x 30 m, 0.14  $\mu\text{m}$  DB-1, linear velocity 40 cm/s and programmable temperature). For benzo(a)pyrene, spectrofluorimeter HITACHI-850 (initiation 299 nm, fluorescence

407 nm) was used. The precision of detection for individual substances varied from 3.8 to 11.1% (Tab. 1).

## RESULTS AND DISCUSSION

The total concentration of trihalomethanes (bromoform – TBM, chloroform – TCM, bromodichloromethane – BDCM, dibromochloromethane – DBCM) ranged from  $3.4 \mu\text{g}/\text{dm}^3$  to  $304.4 \mu\text{g}/\text{dm}^3$  (maximum allowable concentration – MAC  $100 \mu\text{g}/\text{dm}^3$  according to water standards in Latvia), summary trichloroethene – TCE and tetrachloroethene – PCE from  $1.0 \mu\text{g}/\text{dm}^3$  till  $13.4 \mu\text{g}/\text{dm}^3$  (MAC =  $10 \mu\text{g}/\text{dm}^3$ ). The level of aromatic hydrocarbons benzene and toluene were below  $0.2 \mu\text{g}/\text{dm}^3$  (MAC =  $1 \mu\text{g}/\text{dm}^3$ ). The concentration of benzo(a)pyrene was below  $0.002 \mu\text{g}/\text{dm}^3$  (MAC =  $0.01 \mu\text{g}/\text{dm}^3$ ). The determined concentrations of halogenated hydrocarbons are shown in Fig. 1.

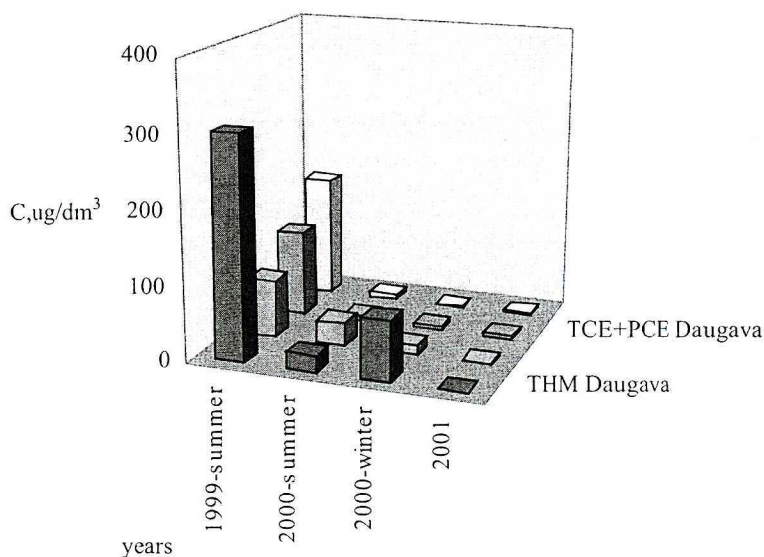


Figure 1. The concentration ( $\text{mg}/\text{dm}^3$ ) of trihalomethanes (THM) and trichloroethylene and perchloroethylene (TCE+PCE) in drinking water of two intake places (Daugava and Baltezers)

Fluctuations of THM concentration were determined according to the season and place of sampling (from water supply system or before intake). The THM concentration increased with distance from disinfecting place; increase was observed also in the summer time. The increase could be related to higher level of organic matter in water in summer time and to increase of contact time [10, 14, 19]. Chloroform was found to be the major THMs compound, which is consistent with results in majority of studies [6, 7, 10, 16]. However, other study reported the prevalence of brominated compounds [5].

Since June 2001 water ozonation with minimal chlorination was implemented in Riga City (20%  $\text{Cl}_2$  of the previous dose). The level of halogen hydrocarbons in drinking water decreased ten and more times before water intake in this case. Lykins and Koffskey [11] in

the case of using ozonation instead of chlorination found similar decrease of organic halide concentration, but other researchers determined bromate formation during ozonation [19].

Water treatment records and water consumption histories have typically reported exposure to disinfection by-products and health risk. However, other routes, such as dermal absorption and inhalation, may be important components of an individual's total exposure to DBPs through drinking, showering or bathing in tap water [1, 3, 12, 18, 20, 22]. It was concluded that breath measurements and whole blood THM levels are highly sensitive way to determine the routes of human exposure to these disinfection by-products and health risk.

## CONCLUSION

1. The results indicate an occurrence of health risk due to halogen hydrocarbons after chlorination of drinking water.
2. The ozonation of drinking water with minimal chlorination at the end excludes risk of halogen hydrocarbons to health.

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