

*Ants TAMMEPUU**

CHLOROFORM CONTENT IN THE DRINKING WATER OF TALLINN

Abstract. Tallinn gets over 80% of its drinking water from Lake Ülemiste and its inflows. Free active chlorine is used for disinfection. Chlorination may give rise to the formation of halogenated organic compounds from organic matter and also from some algal components. The most common of these compounds is chloroform, which belongs to the trihalomethanes. Therefore, the chloroform content was measured in the water of Lake Ülemiste and in the drinking water of Tallinn. The results showed that the international maximum allowable concentration — $30 \mu\text{g} \cdot \text{l}^{-1}$ — was exceeded in most of the analysed samples of chlorinated water. The highest values were measured in the summer period, when the permitted level in drinking water was exceeded 2—3 times. The chloroform content correlated with pH, temperature, chlorine doses, turbidity, phytoplankton biomass, and colour. The chloroform content shows seasonal variation with maximum values measured in summer. Experimental heating of water to boiling decreased the chloroform concentration in most cases, but not always sufficiently to guarantee the quality required for drinking water.

Key words: water chlorination, chloroform precursors, chloroform content.

Introduction

Lake Ülemiste with its inflows is the main source of water supply of Tallinn, covering over 80% of the demand for drinking and industrial water of the town. As the inflow of biogens and organic substances is intensive, the lake has become sturdily eutrophic or even hypertrophic (Simm et al., 1980; Pork et al., 1980). For disinfection free active chlorine is used. The quality of raw water requires chlorination with moderate or large doses to produce water meeting drinking water standards.

The use of chlorine as a disinfectant has been implicated as contributing organic micropollutants to drinking water (Rook, 1976, 1977; Vogt and Regli, 1981). Several works have shown that under certain conditions chlorination causes the formation of halogenated organic compounds as a result of the reaction between free chlorine and the precursors contained in the natural water (Graun, 1985). A large number of chlorination by-products have been studied (Bedding et al., 1983; Красовский et al., 1987), the predominant of which are trihalomethanes (THM) (Babcock and Singer, 1979; Graun, 1985). Among the harmful substances identified, chlorinated phenols, benzoic acids, chlorinated methylbutane derivatives, chlorinated polynuclear aromatics, etc. occur in addition to the THMs (Cotruvo, 1981). Chloroform is considered to be the most widespread among all these compounds and is usually represented in the highest concentrations (Cotruvo, 1981; Vogt and Regli, 1981; Trussell and Umphres, 1978). The compound is usually measured in undetectable or low concentrations in raw waters but is always present in finished waters if chlorination has been used in the treatment process (Young and Singer, 1979).

THMs are formed by chemical interaction between chlorine and natural organic materials in water (Vogt and Regli, 1981). Various laboratory studies have proved that in principle several natural and synthetic organic

* Nooruse St. 7—208, EE-2400 Tartu, Estonia.

compounds can participate in haloform reaction (Stevens et al., 1976). The precursors of chloroform remain largely unknown, but humic and fulvic acids are considered to be the major ones (Bedding et al., 1983). Humic substances result from vegetative decay and make up a significant portion of the total organic carbon, forming ca 80% of all natural organic material (Babcock and Singer, 1979). It has been proved that the production of chloroform per unit mass of humic acids is bigger than its production per unit mass of fulvic acids (Peters et al., 1980; Babcock and Singer, 1979). Some researchers have detected that both green and blue-green algae produce cellular and extracellular substances which actively participate in the formation of haloforms (Hoehn et al., 1980). These substances can produce as much chloroform per unit of organic carbon as humic and fulvic acids (Hoehn et al., 1980). The mechanisms of chlorination reactions with cellular carbon compounds differ from those with humic substances (Oliver and Shindler, 1980).

The production of THM and chloroform depends on several properties of raw water and also on the treatment technology used. The THM and chloroform yields are influenced by the chlorination method, chlorine dose, and contact time (Bedding et al., 1983; Красовский et al., 1987). The most important among raw water quality properties from the aspect of chloroform yield are pH, temperature, and chemical composition (Peters et al., 1980; Young and Singer, 1979). One can notice a seasonal trend towards the highest concentrations occurring in the spring and summer months and the lowest concentrations in the winter months (Bedding et al., 1983).

Much attention has been paid to the anticipation of chloroform formation. Because of their resistance to biodegradation the THMs are very difficult to remove (Bedding et al., 1983). Therefore, the solution might be the prevention of THM production by the removal of precursors or by using alternative disinfection methods instead of chlorination. For example, coagulation before chlorination has been shown to be effective for precursor removal (Babcock and Singer, 1979).

The toxicity of chloroform has been studied quite thoroughly, but mostly acute toxicity has been dealt with. Chronic effect of toxic substances has not been studied very much yet (Руководство . . . , 1987). Information is available about the carcinogenicity of chloroform. In animal experiments where high doses were used, the compound has been proved to be a carcinogen (Руководство . . . , 1987). Harris was the first to show in 1974 that there was a connection between mortality from cancer and water chlorination (Красовский et al., 1987). Later studies have found associations between chlorinated surface water and either cancer incidence or mortality in nine cases out of ten (Graun, 1985). In 1979 Young and Singer reported an association between colon cancer mortality in Wisconsin and THM exposures in drinking water (Graun, 1985). Cantor et al. (1977) observed positive associations in several site-sex combinations with bladder, brain, lung, and colon cancer in both sexes.

Proceeding from the previous circumstances, the World Health Organization has established $30 \mu\text{g} \cdot \text{l}^{-1}$ as chloroform Maximum Allowable Concentration (MAC) in drinking water (Руководство . . . , 1987).

There is no information about the mutagenicity of chloroform. However, mutagenic effects of chlorination by-products, to whose presence chloroform indicates, have been detected (Onodera et al., 1986; Fielding and Horth, 1987; Holmbom and Kronberg, 1987).

Although the problem of toxic chlorination by-products has been studied quite well in the world practice, in Estonia no investigations of that kind have been carried out. Only some occasional water samples have been analysed by foreign researchers.

Materials and Methods

The study was carried out from April 1989 to June 1990 by the researchers of Tartu University. During that period, 32 samples of raw water and 128 samples of chlorinated water were analysed. In 1989 the samples were taken from raw water of Lake Ülemiste at the place of water intake, from the chlorine contact reservoir, from the water after sedimentation and flocculation processes, from the hydrant of Tallinn Water Treatment Plant, and from occasionally chosen points in Tallinn waterworks. In 1990 one more sampling point in the water distribution net was added. Unfortunately, the samples could not be taken with equal frequency.

The analyses of chloroform content were in general conducted using the methods recommended by Polish authors (Красовский et al., 1987). The analyses were performed with a GC Perkin-Elmer m. 3920 equipped with an electron capture detector. The glass column with the length of 2.0 m and with the diameter 2 mm was used. The column filling consisted of two phases. Chromosorb Q served as the solid phase and DC-200 as the liquid phase. Nitrogen (at $40 \text{ ml} \cdot \text{min}^{-1}$) was employed as the carrier gas. The temperature regime was the following: column — 30°C , injector — 100°C , interface — 300°C , and detector — 325°C . The samples were gathered into 100-ml glass bottles. The bottles were filled to the brim and closed hermetically; care was taken not to leave any bubbles in the samples. Up to 0.1 mg of ascorbic acid was put into the bottles meant for chlorinated water samples to exclude the influence of residual free chlorine.

Chloroform was extracted from the water samples with *n*-pentane previously controlled with regard to chloroform content. From the sample, 4 ml of water was put into the test-tube with a polished glass stopper. After that, 2 ml of *n*-pentane was added, the test-tube was firmly closed, and shaken for 30 sec. The chloroform concentration was ascertained with the help of a standard solution. In order to do that, $13 \mu\text{l}$ of chemically pure chloroform was dissolved in 50 ml of *n*-pentane. The solution was kept in a hermetically closed measuring flask in a refrigerator. A separate working solution was prepared for each measurement series by dissolving $10 \mu\text{l}$ of standard solution in 20 ml of *n*-pentane. For measuring, $0.8 \mu\text{l}$ of working solution was injected into the chromatograph and the same quantities of extracts from the samples were added. The chloroform concentrations were calculated by comparing the heights of the peaks of the working solution and those of the samples on the chromatogram.

As is generally known, consumers use an important part of their diurnal water demand in the form of thermally treated water. The vaporization of chloroform, however, takes place at a temperature below the boiling temperature of water. In order to observe what effect heating has on the chloroform content, the making of coffee was imitated. The samples taken from the water of the Tallinn water distribution net were heated to boiling and after that cooled to 60°C .

To find out the relations between the chloroform content in drinking water and the quality of raw water and chlorine doses, correlation analysis was carried out. Such indicators as temperature, pH, colour, turbidity, and phytoplankton biomass were studied. For each indicator 26 sample pairs were analysed. Data of the laboratories of the Tallinn Water Treatment Plant, having the same date as the chloroform analysis, were used for statistics.

As the frequency of sampling was unequal, weighted averages were calculated to complement the statistical characteristics (Table 1). The reciprocal values of the monthly absolute frequencies were used as weights.

Table 1

Chloroform content in the water of Lake Ülemiste, in the waters from treatment process in the Water Treatment Plant of Tallinn, and in the drinking water of the town, $\mu\text{g}\cdot\text{l}^{-1}$

Date	Place of sampling						
	Lake Ülemiste	Chlorine contact reservoir	Coagulated and deposited water	Hydrant of Tallinn Water Treatment Plant	Water distribution net (control point 1)	Water distribution net (control point 2)	Experimentally boiled water
05.04.89	0	12.8	—	12.9	—	—	—
10.04.89	0	22.1	—	28.0	—	—	—
19.04.89	0	—	—	36.6	—	—	—
25.04.89	0	30.4	27.8	30.4	34.0	—	—
04.05.89	0	34.3	37.3	38.6	—	—	—
10.05.89	0	44.1	40.5	45.8	54.3	—	—
16.05.89	0	41.0	47.5	51.2	53.1	—	—
26.05.89	0	45.9	45.6	46.7	—	—	—
09.06.89	0	40.9	45.2	43.2	48.6	—	—
15.06.89	0	41.2	46.0	45.6	42.9	—	—
06.07.89	0	42.3	61.3	59.8	65.6	—	—
07.07.89	0	49.3	50.8	59.7	—	—	—
25.07.89	0	97.8	72.9	63.6	76.8	—	—
03.08.89	0	45.2	59.4	64.7	66.4	—	—
08.08.89	0	34.6	43.1	48.5	—	—	—
16.08.89	0	46.9	55.0	67.7	67.3	—	—
22.08.89	0	96.3	53.1	71.5	72.9	—	—
31.08.89	0	40.2	42.7	44.2	50.2	—	—
06.09.89	0	44.2	39.5	43.6	—	—	—
14.11.89	0	22.4	24.9	24.4	31.2	—	—
10.01.90	0	11.8	11.9	14.6	15.1	15.0	—
24.01.90	0	12.3	19.2	25.3	24.6	34.3	26.0
01.02.90	0	18.6	20.3	23.9	27.7	25.0	18.2
06.02.90	0	11.9	18.0	20.2	24.4	26.4	23.4
21.03.90	0	18.9	19.3	22.1	23.4	27.0	22.3
10.04.90	0	23.0	23.9	23.0	27.0	27.0	29.2
18.04.90	0	54.8	40.5	47.3	43.0	43.1	19.6
25.04.90	0	32.0	34.5	40.3	53.3	45.4	36.6
08.05.90	0	43.6	47.8	49.6	54.9	56.4	38.4
16.05.90	0	36.1	44.0	48.1	60.1	54.1	45.1
22.05.90	0	36.1	40.0	38.1	38.8	30.9	32.9
06.06.90	0	33.8	37.9	42.2	52.5	50.5	20.7

Results and Discussion

The results of all the performed analyses are presented in Table 1. The analyses proved that the chloroform content in the water of Lake Ülemiste was, as presumed, far below the permissible level, being within the limits where the precision was too small for a trustworthy result. For this reason, the corresponding indicator was marked with zero in Table 1 and it served as the control sample, reflecting background.

The samples of chlorinated water showed the values of chloroform content ranging from $11.8 \mu\text{g}\cdot\text{l}^{-1}$ to $97.8 \mu\text{g}\cdot\text{l}^{-1}$ (Table 2). For unfinished waters from two stages of treatment process the chloroform content was from $11.8 \mu\text{g}\cdot\text{l}^{-1}$ to $97.8 \mu\text{g}\cdot\text{l}^{-1}$ (Figs. 1 and 2) and for drinking water from $12.9 \mu\text{g}\cdot\text{l}^{-1}$ to $76.8 \mu\text{g}\cdot\text{l}^{-1}$ (Figs. 3 and 4). The previous findings, together with the values of standard deviations (Table 2), indicated the chloroform content to be less steady in the samples of unfinished waters. During the research period the permitted level was exceeded in ca 70% of the samples of drinking water. Here it is necessary to take into account that in the summer period the samples were taken more frequently.

Table 2

Statistical characteristics of chloroform content, $\mu\text{g}\cdot\text{l}^{-1}$

Sampling place(s)	Number of samples	Average	Weighted averages	Median	Standard deviation	Minimum	Maximum
Chlorine contact reservoir	31	37.6 ± 3.6	34.2	36.1	20.0	11.8	97.8
Coagulated and deposited water	29	39.7 ± 2.7	36.0	40.5	14.5	11.9	72.9
Drinking water from hydrant	32	41.3 ± 2.8	38.0	43.4	15.6	12.9	71.5
Water distribution net 1	24	46.2 ± 3.6	41.6	49.4	17.4	15.1	76.8
All chlorinated water samples	128	40.5 ± 1.5	37.1	41.1	16.8	11.8	97.8
Water samples from treatment	60	38.6 ± 2.3	35.1	40.4	17.4	11.8	97.8
Drinking water samples	68	42.1 ± 2.0	38.8	43.2	16.1	12.9	76.8

Monthly averages were calculated to observe seasonal dynamics in chloroform concentrations. If only one analysis was performed a month, its result was presented instead of the average value (Figs. 5 and 6). The chloroform content starts increasing in April, reaching the maximum values in July-August (data for 1989), and then begins to fall, achieving the values below the internationally permitted level ($30 \mu\text{g}\cdot\text{l}^{-1}$) in September-October. Comparison of the chloroform contents in different sampling points shows the dynamics to be rather similar in all localities.

The average chloroform content was $40.0\pm 1.5 \mu\text{g}\cdot\text{l}^{-1}$ in all the chlorinated water samples, being $38.6\pm 2.3 \mu\text{g}\cdot\text{l}^{-1}$ in the water samples taken from the treatment process and $42.1\pm 2.0 \mu\text{g}\cdot\text{l}^{-1}$ in the samples of drinking water quality (Table 2). The weighted averages were respectively $37.1 \mu\text{g}\cdot\text{l}^{-1}$, $35.1 \mu\text{g}\cdot\text{l}^{-1}$, and $38.8 \mu\text{g}\cdot\text{l}^{-1}$. Thus it can be concluded that the average chloroform content exceeded the permitted level in all the sampling points where the water was chlorinated. At the same time the numbers characterizing the finished waters were bigger than those of the waters from the treatment process.

The comparison of statistical features of the sampling points (Fig. 7) showed that the chloroform content was increasing in the direction from the first contact with chlorine to the consumer. The values measured in the water samples after coagulation and deposition were on the average 3.7% higher than those of the chlorine contact reservoir. This means that even if coagulation had some positive effect on chloroform removal, it would be nullified by the simultaneously forming compound. The chloroform content in the hydrant of drinking water was on the average 7.7% higher than that in the coagulated and deposited water. The highest chloroform content was in the water distribution net, being on the average 9.0% higher than that in the hydrant of drinking water. Consequently, the chloroform formation was continuing in the water distribution net. This conclusion was confirmed by the results obtained from an additional point in the water distribution net added to the research project in 1990 (Table 1).

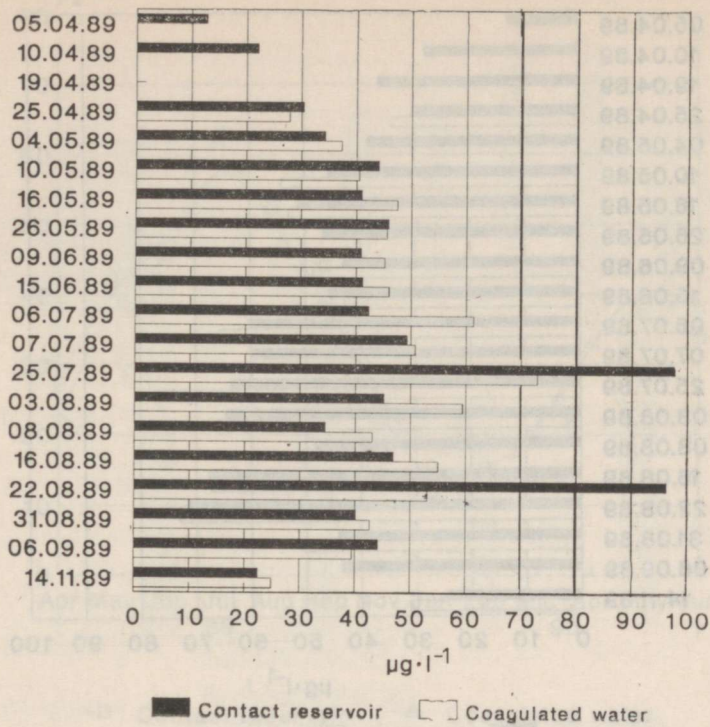


Fig. 1. Chloroform content in the water samples from treatment process in 1989.

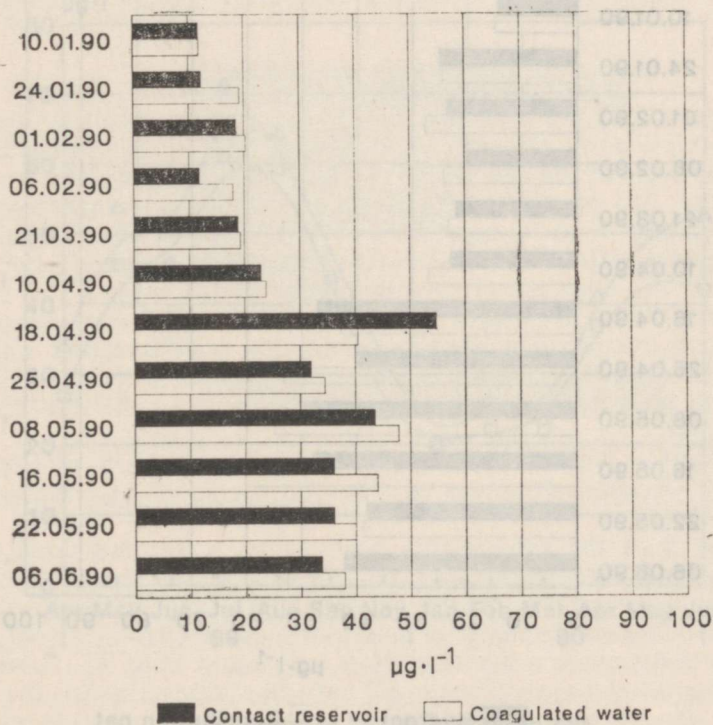


Fig. 2. Chloroform content in the water samples from treatment process in 1990.

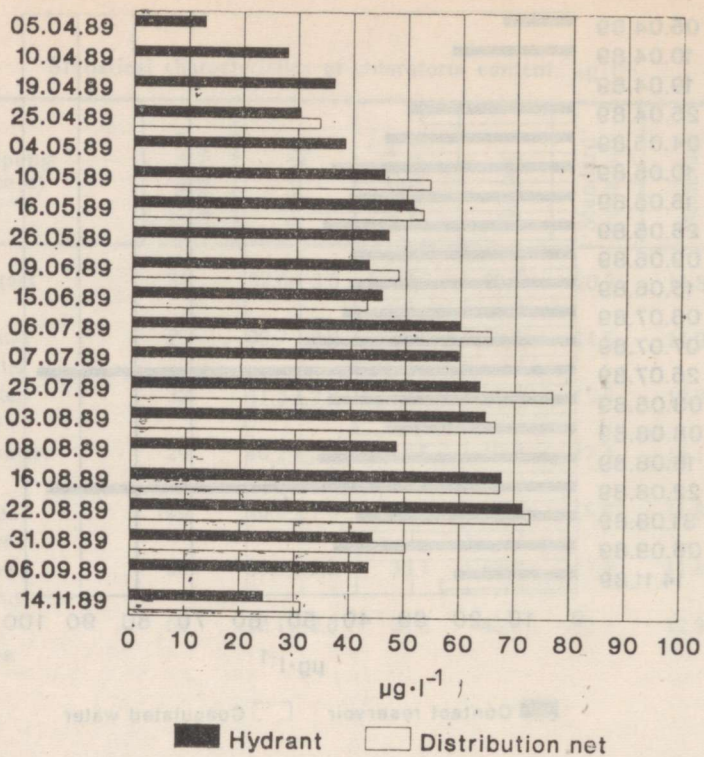


Fig. 3. Chloroform content in the samples of drinking water in 1989.

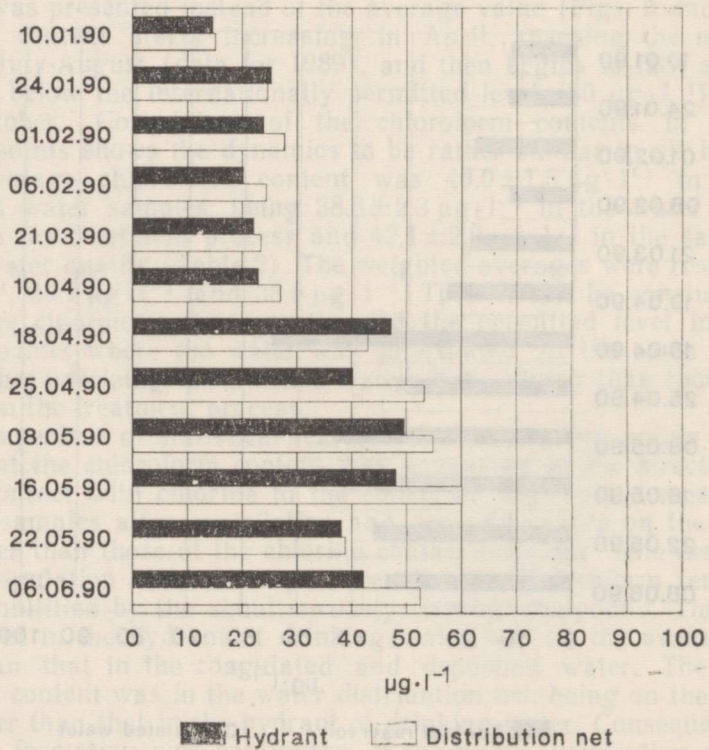


Fig. 4. Chloroform content in the samples of drinking water in 1990.

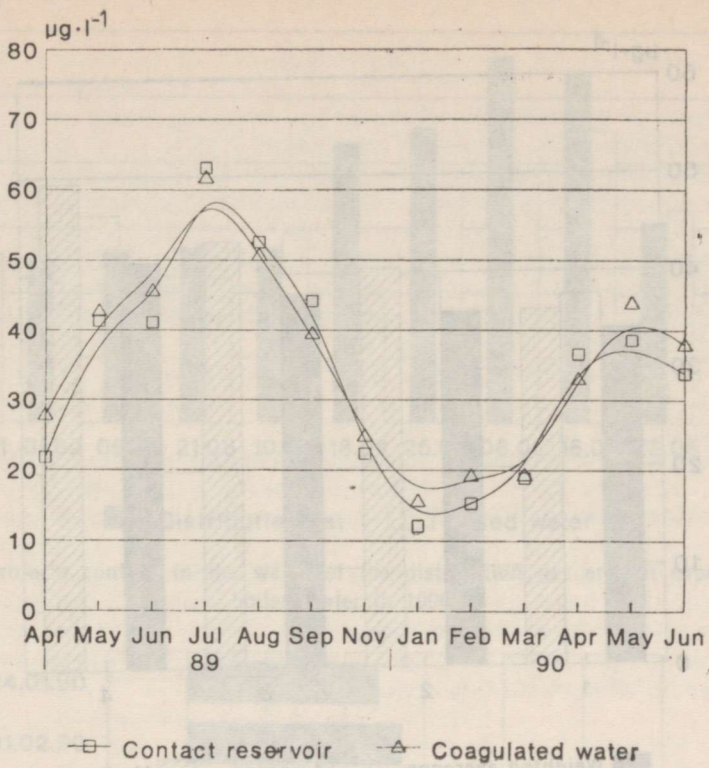


Fig. 5. Monthly average chloroform contents in the samples taken from the treatment process.

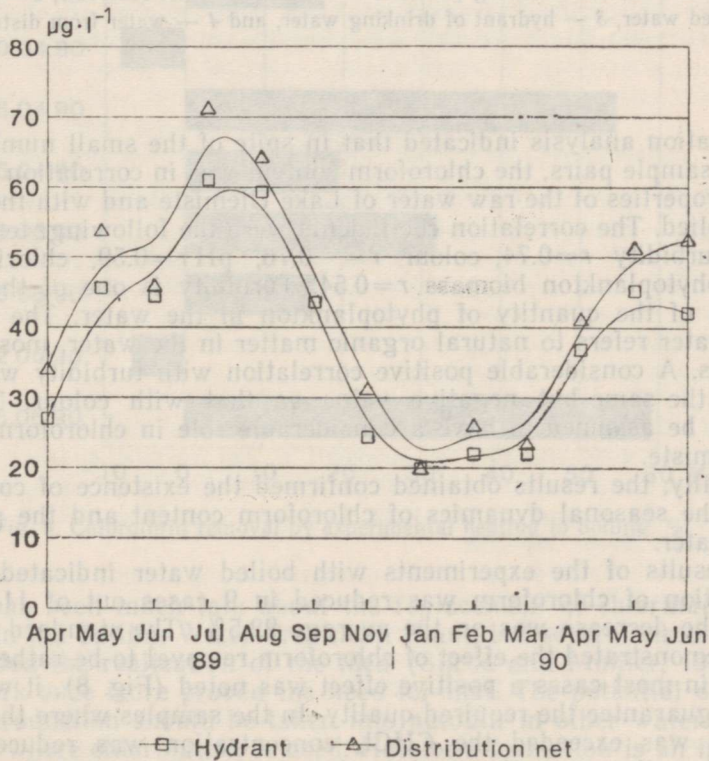


Fig. 6. Monthly average chloroform contents in the samples of drinking water.

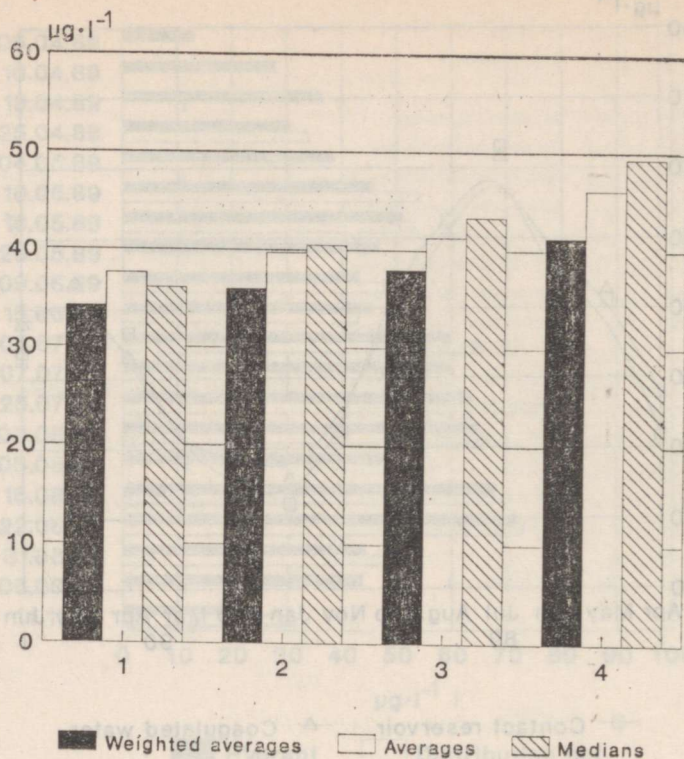


Fig. 7. Statistical characteristics of chloroform content in the period of researches in the water samples from the following points: 1 — chlorine contact reservoir, 2 — coagulated and deposited water, 3 — hydrant of drinking water, and 4 — water from distribution net.

Correlation analysis indicated that in spite of the small number of the observed sample pairs, the chloroform content was in correlation both with several properties of the raw water of Lake Ülemiste and with the chlorine doses applied. The correlation coefficients were the following: temperature $r=0.89$, turbidity $r=0.74$, colour $r=-0.76$, pH $r=0.59$, chlorine doses $r=0.70$, phytoplankton biomass $r=0.54$. Turbidity is one of the indirect indicators of the quantity of phytoplankton in the water. The colour of natural water refers to natural organic matter in the water, mostly humic substances. A considerable positive correlation with turbidity was found; it was of the same but negative value as that with colour. Therefore, algae can be assumed to have a considerable role in chloroform yield in Lake Ülemiste.

Generally, the results obtained confirmed the existence of connections between the seasonal dynamics of chloroform content and the properties of lake water.

The results of the experiments with boiled water indicated that the concentration of chloroform was reduced in 9 cases out of 11 (Figs. 8 and 9). The decrease was on the average 22.5%. The standard deviation of 30% demonstrated the effect of chloroform removal to be rather uneven. Although in most cases a positive effect was noted (Fig. 8), it was insufficient to guarantee the required quality. In the samples where the allowed normative was exceeded the CHCl_3 concentration was reduced to the values below the normative in less than half of the cases. The removal over 50% was achieved in only 2 samples.

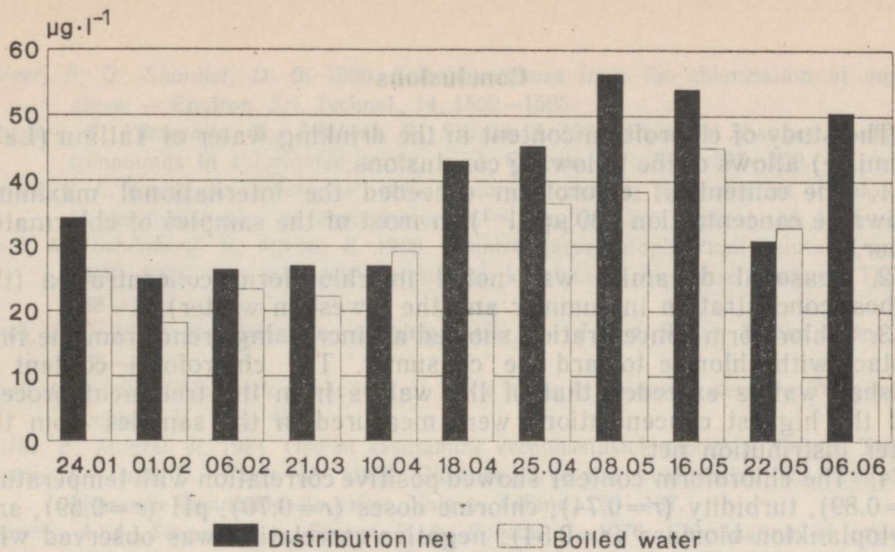


Fig. 8. Chloroform content in the water of the distribution net and in experimentally boiled water in 1990.

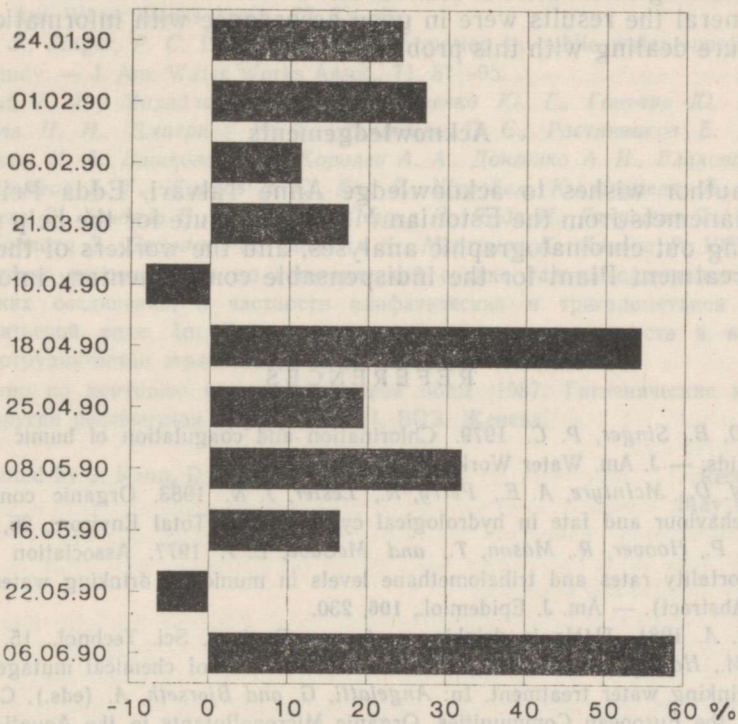


Fig. 9. Chloroform removal by experimental heating to boiling, %.

There has been much talk about the replacement of chlorination with ozonation in the Tallinn Water Treatment Plant, but several circumstances have impeded the realization of the idea (Siirde and Munter, 1984). The present work once more proved the need for that. The potential danger of haloform production should be taken into account in other water supplies in Estonia where chlorination is used. Haloform formation is an important factor to be considered also in exploiting new water supplies on the basis of surface waters in the future.

Conclusions

The study of chloroform content in the drinking water of Tallinn (Lake Ülemiste) allows of the following conclusions:

1. The content of chloroform exceeded the international maximum allowable concentration ($30 \mu\text{g} \cdot \text{l}^{-1}$) in most of the samples of chlorinated water.

2. Seasonal dynamics was noted in chloroform concentration (the highest concentration in summer and the lowest in winter).

3. Chloroform concentration showed an increasing trend from the first contact with chlorine toward the consumer. The chloroform content in finished waters exceeded that of the waters from the treatment process and the highest concentrations were measured in the samples from the water distribution net.

4. The chloroform content showed positive correlation with temperature ($r=0.89$), turbidity ($r=0.74$), chlorine doses ($r=0.70$), pH ($r=0.59$), and phytoplankton biomass ($r=0.54$); negative correlation was observed with colour ($r=-0.76$).

5. The experimental imitation of making coffee reduced chloroform concentration in most cases, but was not satisfactory to guarantee the content meeting international standards.

In general the results were in good accordance with information found in literature dealing with this problem.

Acknowledgements

The author wishes to acknowledge Anne Talvari, Edda Peikre, and Kadri Laanemets from the Estonian Marine Institute for the help rendered in carrying out chromatographic analyses, and the workers of the Tallinn Water Treatment Plant for the indispensable complementary information.

REFERENCES

- Babcock, D. B., Singer, P. C. 1979. Chlorination and coagulation of humic and fulvic acids. — J. Am. Water Works Assoc., 71, 149—152.
- Bedding, N. D., McIntyre, A. E., Perry, R., Lester, J. N. 1983. Organic contaminants. Behaviour and fate in hydrological cycle. — Sci. Total Environ., 26, 255—312.
- Cantor, K. P., Hoover, R., Mason, T., and McCabe, L. J. 1977. Association of cancer mortality rates and trihalomethane levels in municipal drinking water supplies. (Abstract). — Am. J. Epidemiol., 106, 230.
- Cotruvo, J. A. 1981. THMs in drinking water. — Environ. Sci. Technol., 15, 268—274.
- Fielding, M., Horth, H. 1987. The formation and removal of chemical mutagens during drinking water treatment. In: Angelatti, G. and Bjørseth, A. (eds.). Commission of the European Communities. Organic Micropollutants in the Aquatic Environment: Proceedings of the Fifth European Symposium Held in Rome, Italy, October 20—22, 284—298.
- Graun, G. F. 1985. Epidemiologic studies of organic micropollutants in drinking water. — Sci. Total Environ., 47, 461—472.
- Hoehn, R. C., Barnes, D. B., Thompson, B. C., Randall, C. W., Grizzard, T. J., Schaffner, P. T. B. 1980. Algae as sources of trihalomethane precursors. — J. Am. Water Works Assoc., 72, 344—350.
- Holmbom, B., Kronberg, L. 1987. Mutagenic compounds in chlorinated waters. In: Angelatti, G. and Bjørseth, A. (eds.). Commission of the European Communities. Organic Micropollutants in the Aquatic Environment: Proceedings of the Fifth European Symposium Held in Rome, Italy, October 20—22, 278—283.

- Oliver, B. G., Shindler, D. B. 1980. Trihalomethanes from the chlorination of aquatic algae. — *Environ. Sci. Technol.*, 14, 1502—1505.
- Onodera, S., Yamashita, M., Ishikura, S., Suzuki, S. 1986. Chemical changes of organic compounds in chlorinated water. — *J. Chromatogr.*, 360, 137—150.
- Peters, C. J., Young, R. J., Perry, R. 1980. Factors influencing the formation of haloforms in the chlorination of humic materials. — *Environ. Sci. Technol.*, 14, 1391—1395.
- Pork, M., Schönberg, N., Mirme, E. 1980. Ülemiste järve fütoplanktoni muutused aastail 1956—1976. In: *Eesti NSV pinnaveete kasutamine ja kaitse*. Valgus, Tallinn, 138—146.
- Rook, J. J. 1976. Haloforms in drinking water. — *J. Am. Water Works Assoc.*, 68, 168—172.
- Rook, J. J. 1977. Chlorination reactions of fulvic acids in natural waters. — *Environ. Sci. Technol.*, 11, 478—482.
- Siirde, E., Muntter, R. 1984. Osooni kasutamine veepuhastustehnoloogias. Valgus, Tallinn.
- Simm, H., Lokk, S., Parts, M. 1980. Ülemiste järve vee kvaliteedist. In: *Eesti NSV pinnaveete kasutamine ja kaitse*. Valgus, Tallinn, 125—137.
- Stevens, A. A., Slocum, C. I., Seeger, D. R., Robeck, G. 1976. Chlorination of organics in drinking water. — *J. Am. Water Works Assoc.*, 68, 615—620.
- Trussell, R. R., Umphres, M. D. 1978. The formation of trihalomethanes. — *J. Am. Water Works Assoc.*, 70, 604—612.
- Vogt, C., Règli, S. 1981. Controlling trihalomethanes while attaining disinfection. — *J. Am. Water Works Assoc.*, 73, 33—40.
- Young, J. S., Singer, P. C. 1979. Chloroform formation in public water supplies: A case study. — *J. Am. Water Works Assoc.*, 71, 87—95.
- Красовский Г. Н., Михайловский Н. Я., Марченко Ю. Г., Гонтарь Ю. В., Литвинов Н. Н., Дмитриев М. Т., Дергачева Т. С., Растянников Е. Г., Рахманина Н. А., Вашкова В. В., Королев А. А., Донченко А. И., Елаховская Н. П., Христов Х. Т., Журков В. С., Кох Р., Штробель К., Неуперт Л., Штоттмайстер Э., Хендель П., Гавлик Б., Халуца И., Янда И., Ганушева Я., Чанади М., Карпати З., Садовски С., Ваверня К., Мартинос К., Каньас Р. 1987. Методические рекомендации по гигиенической оценке галогенсодержащих органических соединений, в частности алифатических и тригалометанов (ТГМ), в питьевой воде. In: *Гигиеническая оценка вредных веществ в воде. Опыт сотрудничества стран-членов СЭВ*. Москва.
- Руководство по контролю качества питьевой воды. 1987. Гигиенические критерии и другая релевантная информация. II. ВОЗ. Женева.

Presented by J. Kann, D.Sc.

Received

May 4, 1992