THM formation in potable waters with reference to related variables and health data bases†

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Abstract

Drinking-water samples were selected country-wide over a period of 2 years and analysed for THM, pH, DOC, bromide and residual chlorine. The average THM concentration was 45 μg/ℓ. At 75 per cent of the sites chloroform was predominant. THM values were related to the measured variables. Standardised mortality rates were calculated for two causes of cancer deaths possibly related to water intake, i.e. carcinoma of the digestive organs and peritoneum and carcinoma of the genito-urinary organs. No relationship between THM levels and mortality from these 2 cancers was observed.

Introduction

Since the discovery by Rook (1974) and Bellar et al. (1974) that organohalogenated compounds are formed in drinking water as a result of its disinfection by chlorination, there has been a proliferation of publications on this topic, especially on the trihalomethanes (THMs). One of these compounds, namely chloroform, usually accounts for approximately 75 per cent of the total THMs and has been found to be an animal carcinogen (National Cancer Institute, 1976). In general, epidemiological investigations have not revealed any causative relationship between THMs and cancer. However, some investigators have suggested a relationship between these products and tumors of the bladder, large intestine and colon (KIWA, 1986). In spite of this, a lack of concensus on the associated health aspects still exists (Pieterse, 1988).

Several countries have introduced quality criteria for THMs, e.g. Canada 350 μg/ℓ, USA 100 μg/ℓ, Germany 25 μg/ℓ, The Netherlands 1 μg/ℓ, etc. (Pieterse, 1988; Gehr, 1989). South Africa has no official guidelines or regulations for THMs. The responsible authority is, however, contemplating the introduction of guidelines in this regard. In order to obtain more information in this connection, this study was undertaken over a period of 2 years to determine the occurrence and concentration of THMs in South African drinking waters and to relate the data to variables which could influence THM formation and to health data bases.

Methods

Forty sample sites were selected country-wide incorporating as large a portion of the domestic sector as possible. Tap waters from drinking-water reticulation systems were sampled twice a month over a period of 2 years (during 1986 to 1988).

The determinands for regular analysis were those which are directly related to the production of THMs in water, viz. pH, dissolved organic carbon (DOC), bromide and free residual chlorine (e.g. Johnson and Jensen, 1986; Fleischacker and Randtke, 1983). The terminology THMs represents the sum of the components chloroform, dichlorobromomethane, dibromochloromethane and bromoform.

The determination was done by gas chromatography according to the method described by Van Rensburg et al. (1978). Dissolved organic carbon analysis was based on photochemical oxidation (Van Steenderen and Lin, 1981).

Although all the water purification plants used chlorine disinfection as a final process, many tap-water samples did not contain free chlorine which indicated under-chlorination during the treatment process. For this reason it was decided to chlorinate one of the samples taken at each site to 1 mg/ℓ free chlorine residual which was left standing at room temperature for 2 d before THM analysis.

Results and discussion

The average THM concentrations are shown in Fig. 1. From this figure it follows that 4 out of 40 samples exceeded 100 μg/ℓ THMs. Upon chlorination to 1 mg/ℓ free chlorine residual, 8 of the 40 samples exceeded 100 μg/ℓ THMs. On average, water samples contained 45 μg/ℓ THMs. Upon chlorination to 1 mg/ℓ residual chlorine, this value rose to 74 μg/ℓ THMs. At 75 per cent of the sites chloroform was the predominant compound (>60 per cent). At the other 25 per cent of the sites all 4 THM compounds were evenly distributed.

A variety of chemicals were used in the treatment of the raw water sources. However, in all cases chlorine was used in the final stage. Forty five per cent of the treatment plants used aluminium sulphate while an equal amount used polyelectrolyte. The other 10 per cent represented ferric chloride, polyaluminium chloride, lime and combinations of various of the flocculants mentioned. No relationship between the chemical treatments and the THM concentrations could be established.

The highest THM concentrations occurred at sites where the raw water sources were known to be recipients of treated sewage effluents. The highest DOC values also occurred at these sites. Sites 29 and 40 drew from the same source, yet the THM and DOC values at site 29 were lower than at site 40. The difference in treatment was the use of powder activated carbon at site 29. The granular activated carbon used at site 40 was obviously exhausted in respect of THM removal. It is interesting to note that at the sites which were recognised recipients of secondary treated sewage, the 4 THM compounds were more evenly distributed.

The presence of algae in these eutrophied waters also plays an important role in the formation of THM precursors. *Microcystis aeruginosa* is one of the most common bloom formers in South

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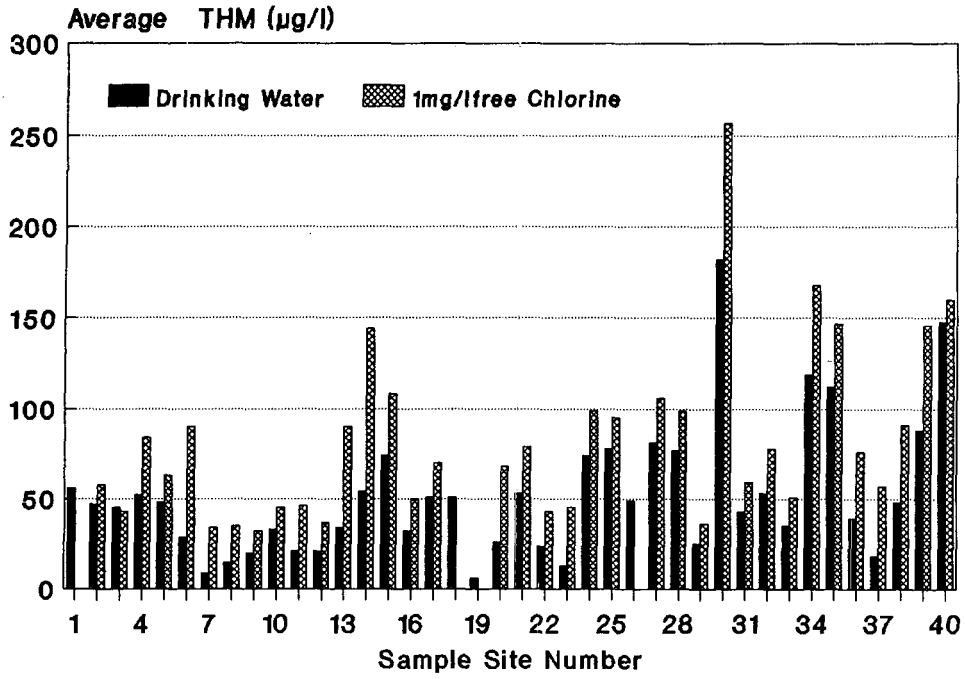

Figure 1
Average concentrations of THMs at sampling sites

Africa and is known to be a prolific organohalogen precursor (Van Steenderen et al., 1988). Upon death and lysis of these algae large amounts of extracellular products are released into the water which when chlorinated will produce THMs.

Simple and multivariate regression analysis was applied to determine whether any relationship existed between THM and the other measured determinands. Statistics did not accommodate factors such as seasonal influences, different sources of raw water, different chemical treatments or the final chlorination dosages. Box-and-whisker plots indicated a considerable skewness around the inter-quartile ranges for all determinands which can directly be attributed to the above-mentioned factors (Van Steenderen et al., 1989).

Although analysis of variance only indicates a 16,24 per cent THM dependence on DOC content, the probability level of this relationship is in the order of 90 per cent. The probability level of this relationship increases to 99,9 per cent under controlled chlorination conditions. One should, however, be very cautious in trying to find surrogate parameters for THM formation, although total organic carbon (TOC) has shown to be correlated with finished THM levels in national surveys (Batchelor et al., 1987).

The effect of chlorine on the formation of dibromochloromethane and bromoform in the presence of bromide was also demonstrated. Although r-squared only indicated a 5,57 per cent dependency on the formation of brominated compounds in the presence of bromide, the probability level of a relationship was 84 per cent and increased to 96 per cent under controlled chlorination conditions. This is in agreement with results by other researchers; Aiwaza et al. (1989) even stated that in the course of the THM formation reaction, bromination occurs preferentially, when chlorine and bromide react competitively. The formation of chloroform and dichlorobromomethane upon chlorination was not influenced by the presence of bromide.

Although pH is known to influence the formation of THM in the presence of dissolved organic material and free chlorine (Johnson and Jensen, 1986), this study was unable to confirm this phenomenon due to the small difference in pH found in the samples.

Based on data from this survey it appears that in general, South African drinking waters are within the USA THM criterion of 100 µg/ℓ.

Correlation of mortality with THM levels

To link the above data with health data, an abstract of all deaths registered among the westernised population of South Africa was obtained on computer tape from the Central Statistical Services for the period 1978 to 1982. (Although this period does not correspond directly with the period of the THM survey, there is no reason to believe that dramatic differences in the patterns would have taken place). The abstract contained details of the age, sex and cause of death of the deceased, coded to the international classification of diseases (ICD) (WHO, 1977). They were also coded spatially, according to the 284 magisterial districts into which the country is divided.

Two groups of carcinoma most possibly related to water were analysed, viz. cancer of the digestive organs and peritoneum (ICD codes 150-159) and cancer of the genito-urinary organs (ICD codes 179-189). Standardised mortality ratios (SMRs), an index of mortality which takes into account differences in population structure between areas, were calculated for each sex, for each of the magisterial districts in which THMs were sampled (Bourne, 1987). For those areas where more than one source of water was sampled, a mean value was used.

All the scattergrams of SMRs as a function of THM levels indicated no significant trend in mortality at the 5% level of significance using Spearman rank correlation tests (Examples appear in Figs. 2 and 3).

From this spatial analysis of mortality it follows that in the range of THM levels measured in South Africa, no relationship with mortality from these 2 groups of carcinoma was observed.

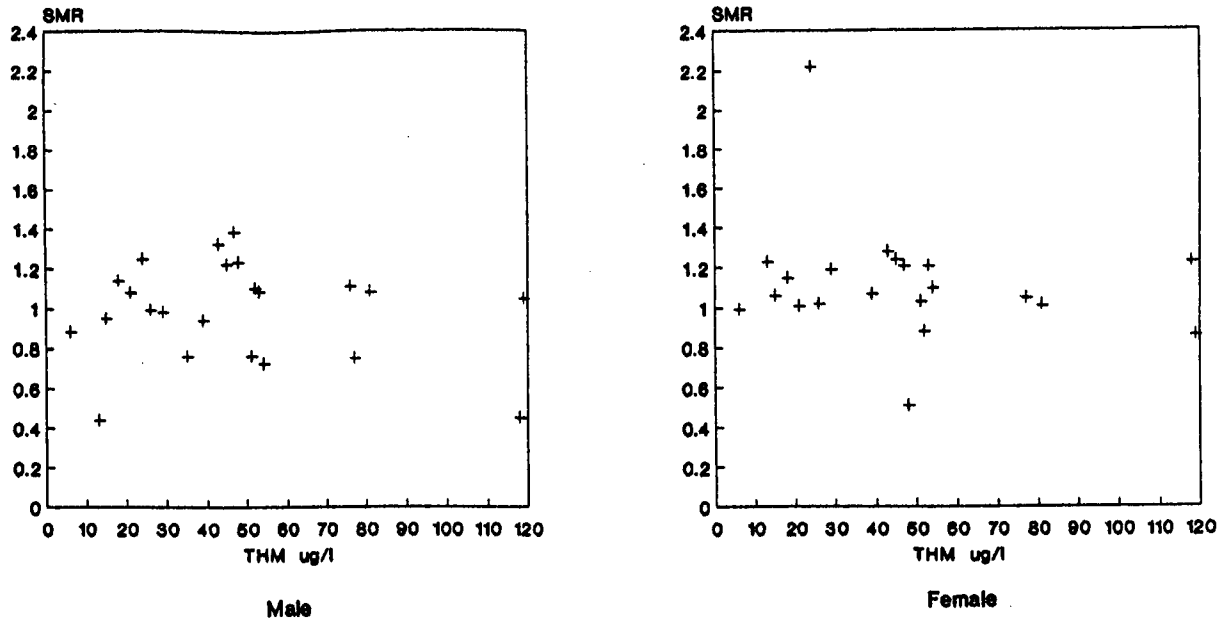

Figure 2
Standardised mortality ratio (SMR) for carcinoma of the digestive organs and peritoneum as a function of trihalomethane concentration

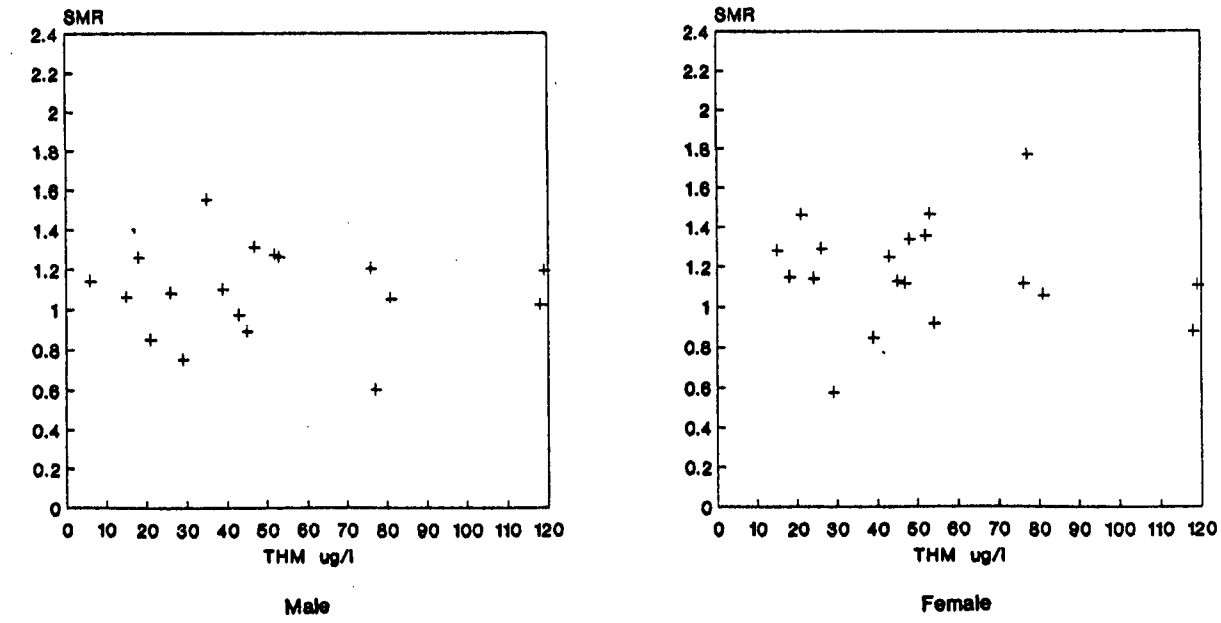

Figure 3
Standardised mortality ratio (SMR) for carcinoma of the genito-urinary organs as a function of trihalomethane concentration

References

AIWAZA, T, MAGARA, Y and MUSASHI, M (1989) Effect of bromide ions on trihalomethane (THM) formation in water. *Aqua* **38** 165-175.

BATCHELOR, B, FUSILIER, D and MURRAY, EH (1987) Developing haloform formation potential tests. *J. Am. Water Wks. Ass.* **79**(1) 50-55.

BELLAR, TA, LICHTENBURG, JJ and KRONER, RC (1974) The occurrence of organohalides in finished drinking waters. *J. Am. Water Wks. Ass.* **66** 703-706.

BOURNE, DE (1987) A mortality atlas of South Africa. *S. Afr. Med. J.* **72** 158.

FLEISCHACKER, SJ and RANDTKE, SJ (1983) Formation of organic chlorine in public water supplies. *J. Am. Water Wks. Ass.* **75**(3) 132-138.

GEHR, R (1989) Removal of trihalomethane precursors. Paper presented at Short Course on Algae in Water : Problems and Treatment. Pretoria, 14-15 August.

JOHNSON, JD and JENSEN JN (1986) THM and TOX formation: Routes, rates and precursors. *J. Am. Water Wks. Ass.* **78**(4) 156-162.

KIWA (1986) Chlorination by-products : Production and control. JC Kruithof (ed.) KIWA Communication No. 74, Nieuwegein, The Netherlands. Published by the AWWA Research Foundation.

NATIONAL CANCER INSTITUTE (1976) Report on the carcinogenesis bioassay of chloroform. National Cancer Institute, Carcinogenesis Program, Division of Cancer Cause and Prevention. Bethesda, Maryland.

PIETERSE, MJ (1988) The potential health risk of trihalomethanes in drinking water : A perspective. *S. Afr. J. Sci.* **84** 166-170.

ROOK, JJ (1974) Formation of haloforms during chlorination of natural waters. *J. Water Treat. Exam.* **23** 234-243.

VAN RENSBURG, JFJ, VAN HUYSSTEEN, JJ and HASSETT, AJ (1978) A semi-automated technique for the routine analysis of volatile organohalogens in water purification processes. *Water Res.* **12** 127-131.

VAN STEENDEREN, RA and LIN, JS (1981) Determination of dissolved organic carbon in water. *Anal. Chem.* **53** 2157-2158.

VAN STEENDEREN, RA, SCOTT, WE and WELCH, DI (1988) *Microcystis aeruginosa* as an organohalogen precursor. *Water SA* **14**(1) 59-62.

VAN STEENDEREN, RA, THERON, SJ and ENGELBRECHT, ACW (1989) An investigation into the occurrence and concentration of trihalomethanes and their precursors in South African drinking waters. WRC Report No. 194/1/89.

WHO (1977) *Manual of the International Statistical Classification of Diseases, Injuries and Causes of Death* - Ninth Revision. World Health Organisation, Geneva.