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Trihalomethanes in the Water Supplies of Sardinia, Italy

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There has been increasing uneasiness with the health authorities recently about the almost ubiquitous presence of organohalogenated compounds in drinking waters, as a consequence of their possible harmful effects on the consumers's health due to continous exposure. Although halogenated substances may already be present in untreated waters, the quantity and variety of synthetic organic compounds induced ex novo during potabilization treatment can significantly exceed those deriving from industrial and agricultural contamination. In particular, treatment for disinfection by chlorination of waters containing organic precursors (synthetic or natural) are to be considered the major source of organohalogenated compounds since they are present in many surface waters and some deep waters. In many cases dissolved humic substances in waters seem to be the main precursors of trihalomethanes (THMs), but other organic substances such as algae and their extracellular products can also assume a key role as precursors (Hoen et al. 1980).

The scientific interest in THMs has increased since their carcinogenic properties were ascertained (Symons et al. 1975; Young et al. 1987). For this reason several countries have set upper limits and guidelines for the total amount of THMs allowed in drinking waters which vary from country to country and fall into two main categories: a) effluent limits at treatment plant; b) limits at point of distribution. The reason for this difference is that formation of THMs continues as long as residual chlorine is present. Table 1 summarizes the limits for total trihalomethanes (TTHM) in drinking water adopted in the different countries. TTHM is defined as the sum of concentrations of chloroform, bromoform, dichlorobromomethane, and dibromochloromethane. The US Safe Drinking Water Committee, in reviewing the potential health effects of disinfection and disinfectant

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by-products, strongly recommends that the present limit of 100 µg/L of TTHM (NRC, 1987) should be lowered. The Italian law (DPR, May 1988) concerning the characteristics of waters for human comsumption follows the EEC Directive 80/778 of July 15, 1980. For halogenated compounds, including THMs, these rules fix a limit value of 30 µg/L (guideline: 1 µg/L) which will be in force in five years. This limit represents a caution value for habitual users of chlorine disinfected surface waters . Aiming at a better understanding of the maximum acceptable concentrations of THMs in drinking waters and considering the wide range of reported values in different countries, it has been considered useful to carry out a study on the presence of THMs in some Sardinian waters. This problem is of particular importance in that the water supplies are mainly derived from reservoirs affected by more or less heavy eutrophication phenomena that favour the formation of halogenated compounds (Sarritzu et al. 1983). This paper is an attempt at evaluating the THM concentration in the water distributed in the different villages; the final remarks will serve as premises for future studies both on the factors inducing such formation and on problems of risk for human health.

Table 1. TTHM limits in drinking water proposed in different countries

Country	µg/L	Source	Notes
Canada	350	WRC, 1980	Still accepted
EEC	1	EEC Directive, 1980	Guideline
Italy	30	DPR , 1988	Maximum value
Sweden	1	Ahl and Oden, 1975	Reccomended value
UK	no limit set	Zabel, 1980	No first priority
USA	100	EPA, 1979/1980	Users's tap
West Germany	25	WRC, 1980	Treatment effluent
WHO	30	WHO, 1984	Only chloroform

MATERIALS AND METHODS

The study area of concern is located in the province of Cagliari, in the South of Sardinia (Figure 1). The water supplies derive from three main systems:

A) Flumendosa-Mulargia. The main water source of this system is formed by two reservoirs; moreover there are 24 wells to integrate the water supply in times of low rainfall. The system serves a population of about 340,000 inhabitants.

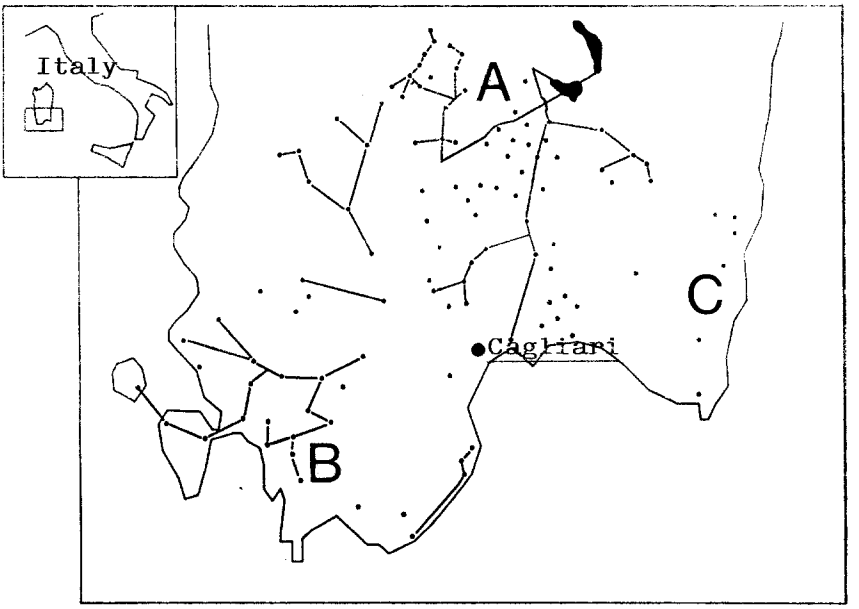

Figure 1. Sampling location in the three water systems in Sardinia (Italy).

B) Sulcis-Iglesiente. The system is constituted by the Bau Pressiu reservoir together with 10 additional wells and supplies water to about 140,000 consumers.
C) Sarrabus. This system, is only made up of wells and springs, and serves a population of 17,000 inhabitants. This system will be considered as a control area in this study.

During the period spring-autumn 1986, 113 water samples were collected along the three distribution networks (Fig.1). In order to evaluate the differences in THM content between superficial water and underground water, no mixed water sample was collected in the A and B systems. However , the consumers served by underground water or mixed-water only in these systems are about 10% of the total.
TTHM contents were determined according to Ziglio et al (1980) by the headspace analysis. A Varian Vista 6000 gas-chromatograph was equipped with a glass column (OD 1/4 ID 2 mm) packed with 10% DC 200 on Chromosorb 80-100 W-HP. The analyses were run isothermally at 70°C with an injection port temperature of 150 °C and a detector temperature of 250 °C. An Ni* 63 electron capture detector was employed . Nitrogen at 25 p.s.i. was used as the

Table 2. Mean concentration, geometric mean, range and standard deviation of residual chlorine (mg/L), TTHM (μg/L), and THMs (μg/L) in three water systems of Sardinia.

		Cl_2	TTHM	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$
A)Flumendosa-Mulargia							
	$\bar{x}$	0.4	53.4	18.1	17.7	15.3	3.1
Superficial	Gx	0.5	55.6	18.8	18.3	15.7	4.4
water (N=58)	Min	ND	32.5	4.2	9.8	8.3	1.3
	Max	1.9	73.3	27.9	27.6	23.2	20.4
	SD	0.3	9.6	4.5	3.7	2.9	3.1
	$\bar{x}$	0.6	10.8	1.2	1.5	3.1	4.6
Groundwater	Gx	0.8	14.8	1.4	2.4	4.7	6.3
(N=20)	Min	ND	1.9	0.3	0.2	0.1	0.4
	Max	2.2	35.5	2.7	6.4	11.9	16.0
	SD	0.6	9.5	0.7	1.8	3.5	4.2
B)Sulcis							
	$\bar{x}$	0.7	73.2	30.0	21.2	16.9	4.9
Superficial	Gx	0.8	77.3	33.5	22.8	17.6	8.7
water (N=17)	Min	ND	37.8	1.6	6.6	11.6	0.7
	Max	1.2	93.7	46.5	30.5	19.9	25.8
	SD	0.3	16.6	12.9	6.5	2.4	7.1
	$\bar{x}$	0.3	11.3	2.6	2.8	2.3	3.6
Groundwater	Gx	0.4	14.4	4.1	4.6	3.3	5.2
(N=10)	Min	ND	1.1	0.4	0.1	0.1	0.1
	Max	0.7	22.5	8.9	10.3	6.9	8.5
	SD	0.3	7.9	3.0	3.5	2.2	3.5
C) Sarrabus							
	$\bar{x}$	0.7	8.1	1.1	1.3	2.7	3.3
Groundwater	Gx	0.9	10.4	1.2	1.7	3.6	4.1
(N=5)	Min	0.3	3.0	0.7	0.3	1.0	1.6
	Max	1.0	14.7	1.3	2.4	4.8	6.4
	SD	0.3	5.1	0.2	1.0	1.9	2.0

carrier gas . To increase the partition coefficient 2 ml water samples were added in 5 ml vials with Teflon-faced septa to a saturated solution of MgSO4.7H20. The vials were then thermostated at 62°C in a water bath for 45 minutes .
The injections (100 μl) were made by using 100 μl Hamilton gas-tight syringes. Residual chlorine was determined by the DPD colorimetric method as described in Standard Methods (APHA et al.

1985) . To obtain information about the organic matter content, each sample was subjected to a potassium permanganate oxidation test (Rodier 1975).

RESULTS AND DISCUSSION

Table 2 presents data for residual chlorine, TTHM, and the most common forms of THMs. Table 3 reports the frequencies of water samples with TTHM concentrations of below, equal and above 30 µg/L for three levels of organic matter.

A) Flumendosa-Mulargia water system

Higher values of TTHM have been observed in lake water samples ($\bar{x}$= 54.3 µg/L) with respect to groundwater ($\bar{x}$= 10.8 µg/L). Among the different THMs the concentration of bromoform is higher in groundwater than in surface water. Dichlorobromomethane and dibromochloromethane present lower concentrations. A proportional increase of TTHM (above 30 µg/L) has been observed for

Table 3. Number of water samples with TTHM concentration below, equal and above 30 µg/L for three levels of organic matter

Water System	N	TTHM µg/L	Number of samples with organic matter content (mg/L) : ≤1	1-1.5	≥1.5	Users
A	78	≤30	15	3	2	99,000
		≥30	5	3	50	241,500
B	27	≤30	8	2	0	28,000
		≥30	2	0	15	112,000
C	6	≤30	5	0	0	15,000
		≥30	0	0	1	1,000

concentrations of organic substances higher than 1.5 mg/L in 50 out of 52 analyzed samples (Table 3).

B) Sulcis water system

All the 17 surface water samples present TTHM values higher than 30 µg/L, the mean value being equal to 73.3 µg/L , while the well water samples present values not exceeding 22.5 µg/L ($\bar{x}$= 11.3). Bromoform and chloroform are the two major compounds in the well water samples. The relationship between TTHM concentration and organic matter shows an increase in organohalogenated compounds when the concentrations of organic matter are higher (Table 3).

C) Sarrabus water system

TTHM levels are significantly lower than those measured in the two previous systems with the exception of some springs where bromide compounds reach maximum values of about 6.4 μg/L (Tab.2). The present results are of particular interest because:

i) They represent the first systematic survey carried out in Sardinia on the THMs in drinking waters.

ii)More than 70% of the users receive surface water from the reservoirs and since the quality of this water is classified as eutrophic (Gaggino et al 1985) it is clear that, following disinfection by chlorine or derivatives, the induced levels of THMs are such that according to the law in force by 1991, this water is to be considered non-drinkable .

iii) The hygienic and sanitary aspect is certainly the most worrying. As a matter of fact, the water supplied to 71% of the customers of Flumendosa-Mulargia water system and that supplied to 80% of the customers of the Sulcis system contains THMs concentrations higher than 30 μg/L (limit value of the italian law).

iv) On the basis of the proved carcinogenic effects of THMs, epidemiological studies are needed in order to have better predictions of the effects of these products on the resident population (over 30 years exposure), and on the 6 million tourists who visit the area every year.

The incidence of high concentrations of THMs in the water supplies of Sardinia requires an urgent evaluation of the possible methods of intervention at the different stages of production and distribution of drinking water. These include preventive and direct measures such as :

-reduction of organic precursors prior to the disinfection process which can be done by changing the order of the conventional treatment procedures. However a better approach is to improve specific conventional water treatment processes (in order to remove organic compounds) and to add others in order to minimize the organic precursors associated with THM production in chlorinated surface waters. The practice of aeration has been applied to remove volatile organic compounds from groundwater and surface water sources (Love et al. 1983).

-use of disinfectants other than chlorine that do not generate THM by-products. Altough chlorination continues to be the predominant method of drinking water disinfection, other alternatives, such as chlorine dioxide chlorination and ozonation, are being used increasingly in Europe and North America. The systems vary in cost, complexity and production of disinfectant residual, but careful design and operation can

produce satisfactory disinfection.
-establishment of reaction conditions that minimize THM formation.
-direct removal of THMs before distribution of finished waters to users by means of granular and powdered activated carbon, or synthetic resins.

In pointing out the risks of water disinfectants to human health, the epidemiological approach can contribute important insight for policy-makers on drinking water treatment strategies in Sardinia.

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