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Trihalomethanes in Water Supplies in the San Sebastian Area, Spain

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The disinfection of drinking water by chlorination produces a wide range of substances among which the trihalomethanes (THMs) play a relatively important role (Krasner et al. 1989). These substances constitute a potential risk factor to health. Several studies have confirmed the carcinogenicity of chloroform in mammals (Reuber 1979; Velema 1987). It is for this reason that upper limits for total trihalomethane concentrations (TTHM) in drinking water have been established. TTHM is defined as the sum of the respective concentrations of chloroform, bromoform, dichlorobromomethane, and dibromochloromethane. In the USA this limit has been established at 100 μg/L (USEPA 1979), though the US Drinking Water Committee has recommended that this be lowered (NCR, 1987). The quality of drinking water in EEC countries is covered by the 80/778 Directive, which dates from July 15th, 1980. This directive sets out a guideline of 1 μg/L for organohalogenated compounds which include THMs. No upper limit is, however, established.

Given the wide range of THM concentrations reported in different countries (McGuire and Meadow 1989; Contu et al. 1990; Fayad et al. 1991) and the lack of data concerning the contents of these substances in the Basque Country, it was considered appropriate that a study be carried out to determine the presence of THMs in drinking water according to supply sources. It was also considered convenient that trihalomethane formation potential (TTHMFP) be researched in order that the efficiency of the different treatment processes in the elimination of precursors might be evaluated. Moreover, different correlations and prediction models, both for instantaneous trihalomethanes (inst-THMs) as well as for the TTHMFPs with variables related to the quality of the raw water or treatment process, were analyzed. The results presented in this study concern the San Sebastian area, the Basque Country. It was envisaged as a pilot work which would lay the base for a further study covering the whole of the Basque Country supplied by treatment plants.

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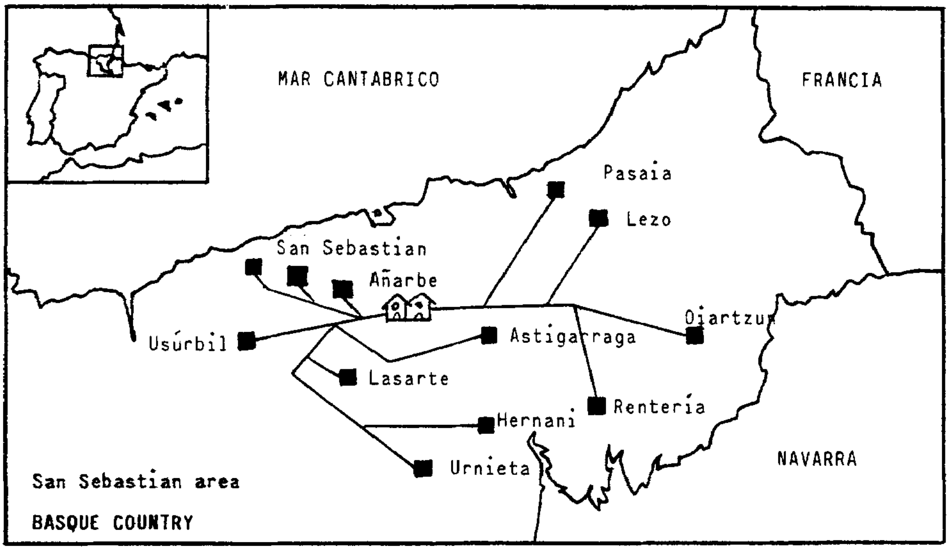

Figure 1. Location map showing the San Sebastian area.

MATERIALS AND METHODS

The San Sebastian area is mainly supplied by the Añarbe reservoir (Figure 1). The reservoir, which is protected, is characterized by its low concentrations of organic matter and color. The water from the reservoir is channelled to a treatment plant, which bears the same name, and, from there, distributed to the different municipalities in the area whose population totals approximately 275,000 inhabitants. The treatments to which the water is subjected are the following: ozonation, coagulation-flocculation, sedimentation, filtration and chlorination.

The sampling programme spanned one year from March 1991 to February 1992. Monthly samples were taken at both the treatment plant and from the supply network. The samples from the latter were taken at six final points in the main distribution areas and may therefore be considered representative of the worst quality conditions in terms of THM concentrations. Five sampling points were chosen in the treatment plant: raw, ozonized, sedimented, filtered and chlorinated water. The parameters determined were inst-TTHM, TTHMFP (only in those samples which corresponded to treatment), free residual chlorine (Cl_2), pH, temperature (Temp), and fluorescence (Flu).

Fluorescence intensity, used as index of the organic content of the water, was determined according to the methods described by Anderson et al (1981). The length of the excitation wavelength was of 340 nm and that of emission 440 nm. The relative fluorescence intensity was calculated against a standard of 50 μg/L of quinine sulfate in water. This standard was diluted 20 times more than in the original method given the low organic matter content the water studied presented. The fluorescent measurement was expressed as a percentage of the fluorescence intensity of the aforementioned standard. The detection limit was established at 0.8% of this intensity based on 3 times the background noise. The free residual chlorine (Cl_2) was determined using the DPD colorimetric method described in Standard Methods (APHA et al. 1989).

THM concentrations were determined by the liquid-liquid extraction technique with pentane as described in Standard Methods. Quantitation was carried out with a gas chromatograph with automatic injector and a ^{63}Ni electron capture detector. A capillary column of 5% phenyl-95% silica methyl was used; l=50 m, i.d.=0.32 mm and f.t.= 1 μm. The chromatographic conditions were: Temp.injector = 200°C, Temp.detector = 300°C, Temp.column = 40°C (5 min), 7°C/min to 180°C, 20°C/min to 240°C (7 min), in a total time of 35 min. Helium at 25 cm/sg was used as carrier gas and argon-methane (PR) at 50 mL/min used as support gas. 1 μl of the extract with a relation split of 1/25 was injected. The TTHMFP was determined using the 5710 B method of the referenced Standard Methods. A previously standardized solution of hypochlorite was added so as to obtain a free residual chlorine concentration of 15 ppm.

Each batch of samples was accompanied by a blank. Two independent aliquots were processed for each sample. The correlation of responses between aqueous standards and those prepared in pentane were lineal between 0.2 and 50 ppb ($r > 0.9999$). The detection limit based on three times the background noise was of 0.1 - 0.2 ppb. Given that the range of THM concentrations in the study (0.2 - 50 ppb) were too wide for a lineal result in the detector to be expected, multilevel calibrations with aqueous standards of 0.2, 0.5, 1, 2, 5, 10, 20 and 50 ppb were used. Two real samples with THM levels of approximately 1 and 10 ppb respectively were processed in duplicate by different operators on three different days (n = 6). A coefficient of variation inferior to 4% was obtained. The addition of different species of THMs at three levels (1, 5, and 25 ppb) gave rise to recoveries of 81-97% with an average of 90%.

Statistical treatment of the data was carried out using the Statistix 3.1 software package. Analyses of simple and multiple linear regressions were used to establish prediction equations among the dependent variables, different levels of trihalomethanes, and the indicator parameters. The statistical parameters taken into consideration were r^2, coefficient of determination; p, significance of the regression, and n, number of samples.

RESULTS AND DISCUSSION

Table 1 shows the average concentrations of THMs, of TTHMs and residual chlorine in drinking water on leaving the treatment plant and in the distribution network. In all of the latter the values of relative fluorescence intensity were inferior to the detection limit. The TTHM presented concentrations inferior to the 100 μg/L established as an upper limit by the USEPA, although the average levels of each of the THMs in the distribution network are above the guide level established by the EEC in most cases.

Table 1. Average values of THMs in drinking water in the San Sebastian area

Sampling point	n	residual chlorine (ppm)	$CHCl_3$ (µg/L)	$CHCl_2Br$ (µg/L)	$CHClBr_2$ (µg/L)	$CHBr_3$ (µg/L)	TTHM (µg/L)
Treatment point	12	0.91	0.59	0.80	1.45	0.72	3.56
Point 1	12	0.61	1.12	1.45	2.48	0.97	6.04
Point 2	12	0.70	1.03	1.45	2.45	0.96	5.90
Point 3	12	0.60	1.24	1.76	2.82	1.07	6.89
Point 4	12	0.65	1.08	1.55	2.53	0.95	6.12
Point 5	12	0.55	1.30	1.76	2.93	1.10	7.09
Point 6	12	0.72	1.28	1.94	3.05	1.10	7.38

1-6 are final sampling points in the distribution network

Dibromochloromethane is the THM that most contributes to the TTHMs, followed by dichlorobromomethane and chloroform. Despite the low levels detected, the reduced contribution of chloroform to the TTHMs (7.7% - 16.7%) warranted attention as it contrasted to the usually predominant role this species plays in surface water.

The increase in TTHMs from the point the water left the treatment plant to the point at which it reached the different points in the distribution network, while unimportant in absolute terms, presented increases that oscillated between 71% and 109%, the difference being significant in all cases ($p < 0.01$). This phenomenon is not uncommon and occurs as a result of the continuous formation of THMs in the distribution network until either chlorine or precursor is exhausted (Rook 1976).

The THM formation potential throughout the different treatment processes highlighted the efficiency of each and every one of the operations and of the process as a whole in the reduction of precursors of these compounds. In Table 2 the average values of the individual and total THMFPs may be observed.

Treatment reduced the TTHMFP of raw water in more than 50%. Ozonation and sedimentation proved the most effective operations. This reduction was achieved primarily at the expense of $CHCL_3FP$, which is the species that

Table 2. Summary of the characteristics of water in the different treatment processes. TTHMFP

Sampling point	Cl_2 (ppm)	pH	Temp (°C)	Flu (%)	$CHCl_3$ FP (μg/L)	$CHCl_2Br$ FP (μg/L)	$CHClBr_2$ FP (μg/L)	$CHBr_3$ FP (μg/L)	TTHM FP (μg/L)
Raw water	N.D.	6.93	11.8	35.7	37.38	12.69	2.30	0.04	52.42
Ozonized	N.D.	7.06	12.2	16.6	31.67	9.83	1.98	0.00	43.48
Sedimented	N.D.	7.14	11.3	8.6	22.12	7.53	1.89	0.17	31.72
Filtered	N.D.	7.19	10.4	5.6	17.95	6.19	1.70	0.21	26.06
Treated	0.91	7.28	11.3	0.9	18.56	4.83	1.47	0.22	25.09

12 samples were taken at each sampling point

contributes most in the determination of formation protentials. The change that the relative importance of the $CHCl_3$ experienced from the inst TTHM to the TTHMFP might have been due to a slow reaction between the chlorine and the precursors or, conversely, to a change in the reaction conditions in the determination of both parameters (Stevens and Symons 1977). The THMFP/TTHM relation was superior to 7 in treated water on leaving the plant. This highlighted the hypothetical concentrations that might have been observed in drinking water if retention time in the distribution network and reaction conditions had been similar to those of the formation potential test. The trihalomethane levels found at different stages in the distribution network were approximately double those in the treated water on leaving the plant and corresponded to retention times that oscillated between 17 and 36 hours.

Fluorescence has been correlated to the concentration of humic substances and to the precursors of trihalomethanes (Van Dongen; Unpub. Tech. Mem. CHR-TM77. Westvaco Charleston Res. Cntr, Charleston, S.C.). A significant relationship between the TTHM formation potential and fluorescence was also observed in raw water in this study. Table 3 shows the coefficient of determination and the predictive equation obtained in the simple lineal regression analysis. Other parameters such as total organic carbon and ultraviolet absorbance have been used mostly as indicator parameters of the TTHMFP in raw water with very good results (Singer et al 1989; Edzwald at al 1985). In these studies, however, highly colored or quite highly colored water was used whereas the water from the Añarbe reservoir, as stated earlier, is characterized by its low color and low organic matter content.

In order to predict the concentration of inst TTHM in the treated water numerous associations were examined between this dependent variable and the following: fluorescence, pH and temperature of the raw and treated water, the fluorescence removed in the desinfection process and the free residual chlorine. Table 3 shows the prediction models obtained for the TTHM and chloroform in the treated water through the multiple regression analyses. Both parameters can be predicted with a good level of signification according to the removal of fluorescence associated with desinfection, the pH of raw water and temperature of the treated water. Instantaneous chloroform can also be interpreted in terms of the quality of the raw water, fluorescence, pH and temperature and the residual chlorine in treated water. These regression models allow the possibility of the use of fluorescence as a quick, simple and inexpensive indicator in the control and monitorization of the treatment plant.

The limited number of samples used and the quality of the water from the Añarbe reservoir naturally advised caution regarding the models obtained and the use of fluorescence as an interest parameter. It will be necessary to use highly colored water with a greater content of organic matter in future studies. This will allow us to analyze if fluorescence really acts as a surrogate parameter.

Table 3. Summary of the analyses of simple and multiple regression for TTHMFP, inst-TTHM and inst $CHCl_3$

Dependent variables	Independent variables	r^2	p	n
TTHMFP(μg/L)	44.34(±3.16) + 0.22(±0.07)BFlu	0.49	0.011	12
Inst TTHM(μg/L)	-90.87(±19.11) + 0.09(±0.02)DFlu + 13.16(±2.73)BpH + 0.92(±0.20)TTemp - 8.61(±4.02)TCl	0.87	0.019	12
Inst TTHM(μg/L)	-88.49(±23.11) + 0.016(±0.012)BFlu + 12.21(±3.10)BpH + 0.56(±0.17)BT	0.79	0.019	12
Inst $CHCl_3$(μg/L)	-8.4(±3.4) + 0.02(±0.007)DFlu + 1.01(±0.45)BpH + 0.16(±0.04)TTemp	0.80	0.015	12
Inst $CHCl_3$(μg/L)	-10.8(±3.97) + 0.004(±0.002)BFlu + 1.16(±0.53)BpH + 0.12(±0.03)BTemp + 1.91(±0.84)TCl	0.82	0.040	12

B = raw water T = treated water DFlu = fluorescence removed in the disinfection

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