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Factors Influencing the High Content of Brominated Trihalomethanes in Barcelona's Water Supply (Spain)

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Since Rook (1974) discovered that the chlorination of surface water produces brominated trihalomethanes (BrTHM's) when bromide is present in raw water, many authors have published their results showing how widespread these compounds are. It has been found that chloroform is a carcinogen in animals and probably BrTHM's may also be.

The U.S. Environmental Protection Agency included a final regulation controlling THM's in drinking water establishing a maximum contaminant level of 100 μg/l but in Europe, so far, most of the countries recommend to reduce THM levels as low as possible.

To acquire some knowledge about this problem, in view of future regulations in our country, we were interested in monitoring THM formation in Barcelona's drinking water. The aims of these studies were to analyze the quality of raw, filtered and finished water at the treatment plant and tap water with parameters influencing THM's formation.

Barcelona and its surroundings, with a population of 3.2 million inhabitants, is located in the N.E. of Spain. Llobregat and Ter rivers supply water to the city in a relationship of 35 and 55 percent respectively.

Llobregat River is a heavy polluted river bearing a lot of industries including textile, galvanic, coal and salt works, pulp mill, farms and domestic waste-waters. The water works plant is located 7 Km from the mouth and receives all these discharges. The plant is able to potabilize 5,3 m^3/s and employs prechlorination. coagulation with alum, settling, filtration (Pittsbourg F-200) and postchlorination.

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MATERIAL AND METHODS

Water samples were collected without space in 250 ml screw top bottles with PTFE coated silicona septa. Sodium thiosulfate was added to quench the chlorination reaction and the analyses were completed as soon as the samples were delivered to the laboratory, but never exceeding 4 hrs after the sampling.

The selected method was based on the extraction of THM's into pentane, Henderson et al. (1976), (ratio water/pentane 25:1) during 2 min and 1 μl of the extract was analyzed with a Konik-2000 gas chromatograph equipped with a Ni linearized electron capture detector Tracor 560. The chromatographic column was a 2 mm i.d. by 200 cm glass column containing 5% Carbowax 20M on Chromosorb W (60-80 mesh). The operating conditions were: injection temperature, 155ºC, detector temperature, 250ºC, column temperature 70ºC, and carrier gas Ar-CH_4 5% at 70 ml/min with a make-up of 20 ml/min.

To quantify THM contents we used the partition coefficients given by Hansch (1971) and the modifications proposed by Hu and Weiner (1980).

RESULTS AND DISCUSSION

Studies were carried out to determine a time vs rate formation potential curve on raw water of Llobregat river, with a bromide concentration of 0.63 mg/l, TOC 10.64 mg/l, and NH_3-N o.12 mg/l, and the corresponding finished water, Cl_2 dose was determined prior the test in order to have approximately less then 1 mg/l residual chlorine after 48 hr of contact time, as this is the maximum time for the water after leaving the treatment plant and prior to its use.

After intervals of 5 min, 30 min, 1,2,4,7,12,16,20,24, 28,32,51 and 73 hr the residual chlorine was neutralized with sodium thiosulfate. The studies showed a maximum THM formation for about 20 hr after the addition of Cl_2 to the raw water and these was supported by the results obtained with finished water. Some scattered results on the raw water samples are probably due to the turbidity of the sample (Lange and Kawczynski, 1978). The results of Cl_2 contact studies are tabulated in table 1.

Table 1. THM Formation Potential vs Chlorine Contact Time.

Water	Contact Time	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	THM µg/l
		THM µg/l				
	5'	25,5	19,5	30	16	91,5
	30'	28	26,5	41	22	117,5
	1 hr	30,5	32	47	24,5	134
	2 hr	41	42	59	29	171
	4 hr	49	49	67,5	37	202
Llobregat	7 hr	63	62,5	62,5	41,5	249,5
River	12,5 hr	92	83	113	62	350
	16 hr	102	100	134	66	402
raw water	20 hr	113	105,5	145,5	70,5	434,5
	24 hr	92	87,5	117,5	63	360
	28 hr	86,5	97,5	145,5	76,5	405,5
	32 hr	107	87,5	128	74,5	397
	51 hr	119,5	114	153,5	88,5	475,5
	73 hr	90,5	83,5	116	64	354
	2 hr	2	21	40,5	37	100,5
	6 hr	2	21	50	47,5	130,5
Finished	20 hr	23,5	41,5	90,5	241,5	397
	24 hr	19,5	37,5	83,5	241,5	382
	28 hr	19,5	28	57	272,5	377
	41 hr	19,5	37,5	86	275,5	418,5

The next test was performed to determine how much Cl_2 concentration affects the THM formation at different ammonia levels. The jar test was run with raw water using Cl_2 doses of 5,10,20,30 and 50 mg/l added directly to the settled water. Primary ammonia levels were 0,2 mg/l and enough NH_4Cl was added to another series of bottles to ensure the amount of 0.95 and 1.90 mg/l of NH_3-N, current levels found on Llobregat river. Water quality and results are shown graphycally in fig.1. Cl_2 contact time was established at 24 hr.

From this test it can be drawn the same effect noted by Lange and Kawczynski (1978): as the Cl_2 is increased, there is a shift towards more chlorinated compounds at the expense of the brominated ones. Nevertheless TTHM altogether of THM remain about the same for all samples. As seen in Table 2 dealing with raw waters with high contents of ammonia and bromide it is necessary to adjust with precission Cl_2 dosage at water works plant because a change of 1 mg/l of chloride can increase the THM content in more that 30% in some cases.

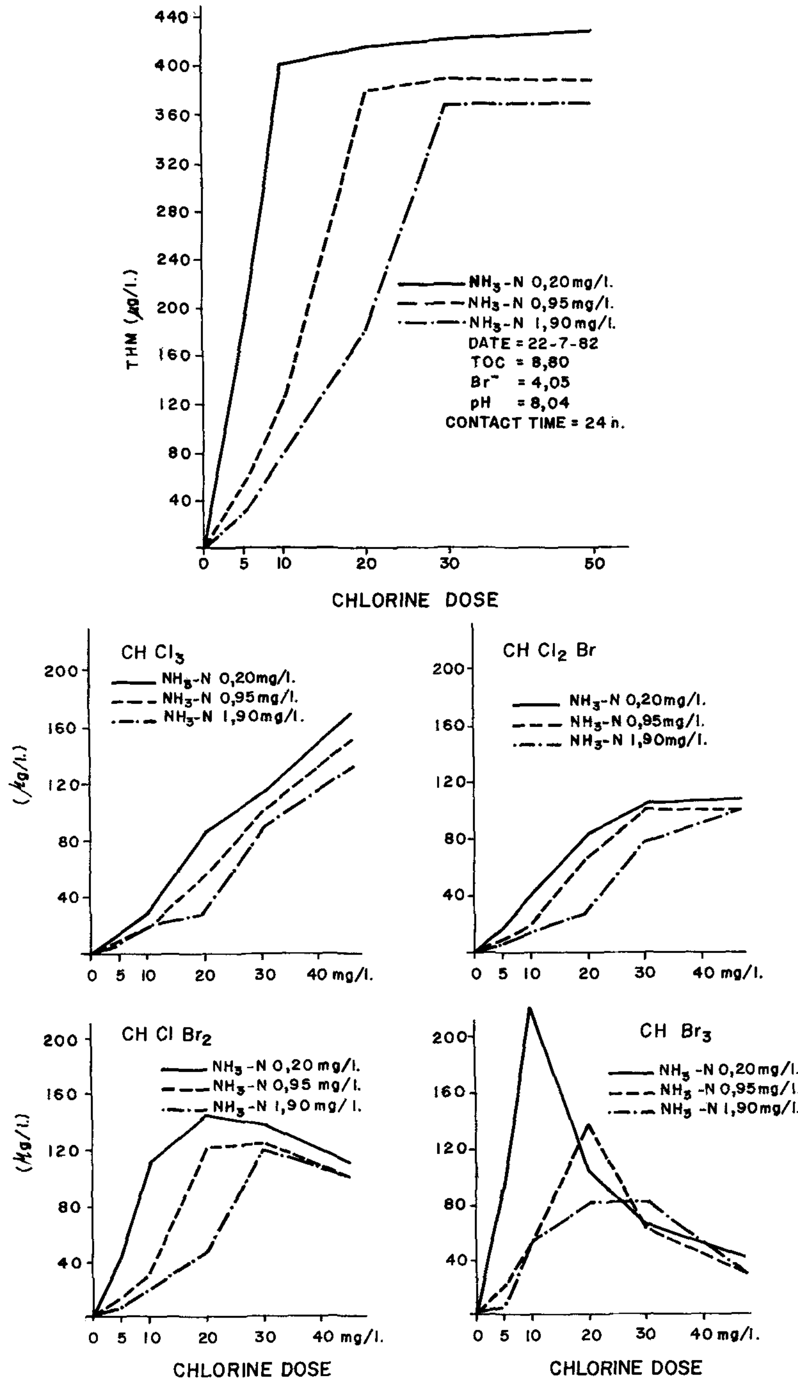

Figure 1. THM's formation at different chlorine and ammonia levels.

Table 2. Percent increase in THM Referred to 5 mg/l Cl_2 Dose.

Chlorine dose mg/l	NH_3-N (mg/l) 0.20	0.95
6	31	26.5
7	67	47
8	91	81
9	115	107
10	233	126

A prefixed Cl_2 dosage was added to a series of bottles containing raw water with an initial dose of 0.2 mg/l of NH_3-N. Enough amount of NH_4Cl was added for 0.6, 1.15, 3.5 and 5.0 mg/l of NH_3-N. The results measured after a contact time of 24 hr are shown graphycally in Figure 2 and shows the depression of brominated trihalomethanes. From it, can be understood that the production of chloroamines proceeds at a higher velocity than the synthesis of hipobromite (Johnson, 1977) and therefore probably bromoamines are produced at higher rates than BrTHM's and consequently low amounts of BrTHM's measured.

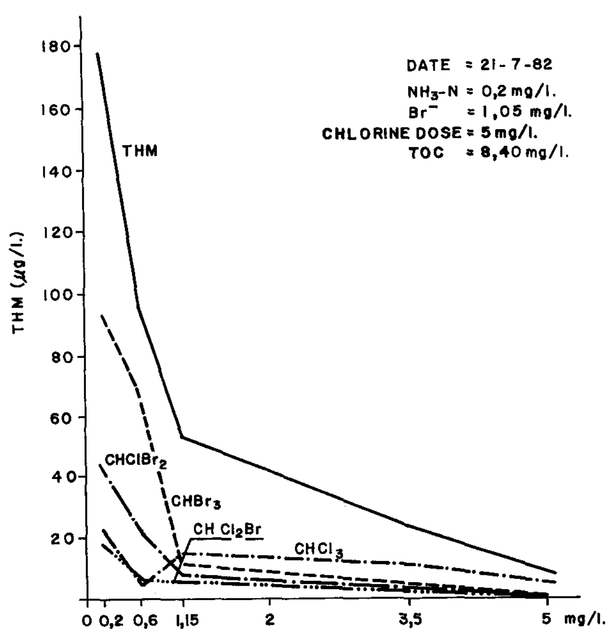

Figure 2. Influence of ammonia on THM's Formation

Granular activated carbon(GAC) installed on the water works was tested for efficiency on THM retention. Efficiency of GAC increases with increasing the number of bromine atoms in the molecule, but we observed a shorter life for THM's than in other cases reported elsewhere (De Marco et al, 1981) probably due to heavy organic pollution beared by this water. After six weeks the efficiency of GAC dropped down below 20% for THM, $CHCl_3$ was retained less than 20% at 3-4 weeks, 7-8 weeks for $CHCl_2Br$, 10 weeks for $CHClBr_2$ and more than 10 weeks for $CHBr_3$. A more detailed explanation is given elsewhere (Rivera and Ventura, 1982a).

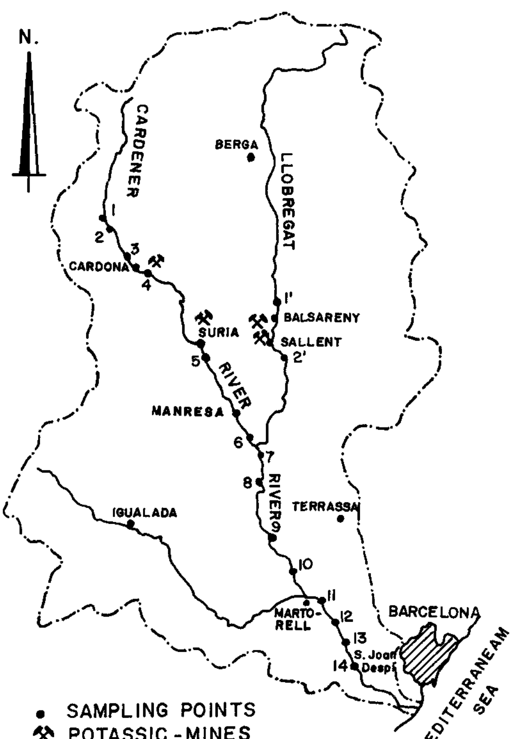

Figure 3. Sampling points along Llobregat and Cardoner rivers.

In order to evaluate the origin of BrTHM,it was proved that discharges of salt mines in Cardoner and Llobregat rivers increased the bromide content of raw water and that was the origin of BrTHM's at the water work plant.

Water samples of raw water were collected prior and after the mines, and chlorinated at 25 mg/l, except sample number 15 (Cl_2 dose 12 mg/l).

Contact time was 24 hr Sampling points are shown in fig. 3 and re sults are tabulated in tables 3 and 4.

Samples 4,5,6, and 2' also merge with of domestic wastewaters from Cardona, Súria and Sallent villages. It was also considered how different kind of discharges (domestic, industrial and agricultural) affect the quality of raw water for THM formation. Samples were collected the same day and from that results in a non homogeneous distribution of bromide. A discharge between points 3,4 and 1',2' flows to the river entering the water works plant in 5 or 6 days later depending on many parameters.

Table 3. Influence of Discharges from Salt Mines on Raw Water in BrTHM's Formation.

Water Source	Sample	Location	Br mg/l	NH_3-N mg/l	TOC mg/l	THM µg/l $CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	BrTHM µg/l	THM µg/l
	1	Sant Ponç	0.03	0.44	2.44	178	8	1	-	9	187
	2	After Sant Ponç	0.02	0.56	2.05	235	19.5	2	-	21.5	256.5
Cardoner	3	Before Cardona	0.01	0.56	2.44	286	39	2	-	41	327
River	4	After Cardona	1.98	0.60	5.08	36	55.5	122	115	292.5	328.5
	5	Antius	3.66	0.54	5.76	15	47	127.5	204.5	394	409
	6	Final Cardoner	2.16	2.20	7.61	196	55.5	144	284	483.5	679.5
Llobregat	1'	Balsareny	-	0.72	2.92	305	14	1	-	15	320
River	2'	Soler Vicens	3.95	0.60	4.49	72.5	39	116	204.5	359.5	432

Table 4. Factors Influencing THM Formation Along the River Course.

Water Source	Sample	Location	Br mg/l	NH_3-N mg/l	TOC mg/l	THM µg/l $CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	BrTHM µg/l	THM µg/l
	7	Can Burés	0.99	0.80	5.60	200	119.5	167	102	388.5	588.5
	8	Monistrol	1.95	0.72	6.24	168.5	139	253	258.5	650.5	819
	9	Salt Cairat	1.84	0.64	5.76	219.5	140	253	253	646	865.5
	10	Abrera	2.42	0.56	7.13	148	119.5	267	403	789.5	937.5
Llobregat	11	Presa Sedó	2.56	0.80	7.62	135	130.5	280	396.5	807	942
River	12	P. Capdevila	3.00	0.56	7.92	161	136	280	390	806	967
	13	P. Canal Dret	3.27	1.12	8.10	145	118	306	502	926	1071
	14	Water Works	3.53	0.44	7.03	148	125	295	469	889	1037
	15	Finished Water	0.95	-	7.13	41	69.5	160	444	673.5	714.5

THM levels in Barcelona's drinking water show strong differences due to the irregular discharges at the salt mines, industrial activity and extremely changing conditions of the regime of the river. Higher levels found in 1982 (714,5 μg/l) could be explained on the basis of higher contents of bromide in raw water (max 3.53 mg/l) than those of previous years, (Rivera et al. (1982b). Also, river flow should be taken into account. Comparing values for 1979-1982 period, BrTHM's reached values as high as 75,3% of THM's. An average value of different samples taken for each month is shown in Table 5. Maximum and minimum values may not correspond to the same day for different kinds of water, and that's the case for the maximum of 714 μg/l in finished water, not corresponding to the same day of the maximum of 335 μg/l for tap water.

Table 5: THM and BrTHM Levels during 1979-1982. Left: Minimum; Right: Maximum.

	THM μg/l					
	$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	BrTHM μg/l	THM μg/l
R.	0.5-17	nf-1.5	nf	nf	nf-1.5	0.5-17
F.	1-68.5	6-82	8.160	2.5-444	19-673.5	20-714.5
T.	2-155	10.5-59.5	9.5-129.5	nf-210	20-319	22-335.5

R = Raw; F = Finished; T = Tap.

One of the aims of this study was to asses the formation of trihalomethanes in Barcelona's drinking water, examing the main parameters that contribute to THM formation. Models with single independent variables were evaluated. The rehability of fit was evaluated for linear regressions using the Pearson correlation coefficient R and the F statistic, which measures the statistical significance of the regression (Singer et al, 1976). Many authors, (Symons et al, 1975, Quaghebeur et al, 1980) have tried to demonstrate that TOC is a good indicator of THM in drinking water but some others found no significant statistically correlation. Data from tables 3 and 4 indicated a statistically significant Pearson correlation coefficient r=0.73 for TTHM vs TOC beyond the 0.001 level, while studies performed during 1979-1982 gave no apparent correlation (r=0.35). Nevertheless, when we computed data from river sampling points for TTHM vs Br-/TOC, the correlation coefficient was r=0.95. Again no apparent correlation was found when values from

1979-1982 were tabulated from water works (r=0.43). The gap between both Pearson correlations coefficients could be explained on the basis of chlorine demand as during the four years chlorine demand ranged from 2.1 mg/l to 96.1 mg/l, while all samples taken along the river were chlorinated at 25 mg/l.

It seems reasonable to think that bromide, chlorine demand, and TOC play an important role on the THM formation of Barcelona's drinking water. High levels of BrTHM's will be dramatically reduced by fitting a pipeline for leading salted water from mines to the sea.

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