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Behavior of Halogenated Disinfection By-Products in the Water Treatment Plant of Barcelona, Spain

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Chlorine is the most widely used disinfectant in drinking water disinfection. Despite the benefits of chlorine, halogenated disinfection by-products (DBPs) are formed due to the interaction of aqueous free chlorine with natural organic matter present in water. Trihalomethanes (THMs) were identified as the main DBPs as early as 1974 (Rook 1974; Bellar et al. 1974). Later, other DBPs such as haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), haloaldehydes, chlorinated phenols, chloropicrin (CP), cyanogen halides (XCN) and chloral hydrate (CH) were also reported (Krasner et al. 1989; Stevens et al. 1989; Peters et al. 1991).

The presence of DBPs in drinking water is a matter of concern for human health and may also cause an unpleasant organoleptic taste. For this reason, the occurrence of these DBPs in USA and Canadian water treatment plants (Lebel et al. 1997; Williams et al. 1997) has been studied and legislation has been established. Under Stage I of the D/DBP Rule, the USEPA sets maximum contaminant levels (MCLs) for total trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform) at 80 µg/L, for a total of five haloacetic acids (monochloroacetic, dichloroacetic, trichloroacetic, monobromoacetic and dibromoacetic acids) at 60 µg/L, for bromate at 10 µg/L and for chlorite at 1.0 mg/L (Fair 1992). In Europe, the 98/83/EU Directive is less restrictive than the USA legislation. The only DBPs to be controlled are the four trihalomethanes, with a proposed maximum of 100 µg/L. However , the World Health Organization has published drinking water guidelines for chloroform (200 µg/L), bromodichloromethane (60 µg/L), chlorodibromomethane (100 µg/L) and bromoform (100 µg/L) and provisional guideline values for dichloroacetic acid (50 µg/L), trichloroacetic acid (100 µg/L), chloral hydrate (10 µg/L), dichloroacetonitrile (90 µg/L), dibromoacetonitrile (100 µg/L) and trichloroacetonitrile (1 µg/L). It has been proved that the main DBPs (chloroform, bromodichloromethane and bromoform) cause cancer in laboratory animals; dichloroacetic and trichloroacetic acids induce liver tumors in mice at high doses. In addition, dichloroacetonitrile is a weak bacterial mutagen, trichloroacetonitrile is a teratogen in rats, and chloral hydrate is a weak bacterial mutagen and causes liver tumors in mice (Bull et al. 1991).

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The Llobregat river supplies drinking water to Barcelona and its area (3 million inhabitants). Barcelona's drinking water is characterized by the presence of brominated and chlorobrominated THMs as a major species (Ventura and Rivera, 1985). This shift to more brominated species is due to the high bromide levels in the raw water whose origin is the salt mines located in the upper course of the river. Several years ago a brine collector was built to discharge salt from the mines into the sea thus diminishing bromide levels (average of 7 mg/L in 1985) and consequently the potential formation of DBPs in the water treatment plant. The average levels of TOC and bromide in raw water entering the water treatment plant were 5.9 mg/L and 0.7 mg/L, respectively, in 1998. Thus, the aims of this paper are to provide current data on the levels of DBPs in the water treatment plant of Barcelona and extrapolate the results to the other main DBPs.

MATERIALS AND METHODS

The water treatment plant of the Llobregat river carries out a conventional treatment consisting of prechlorination (to break-point), flocculation (settling), sand filtration, ozonization, granular activated carbon (GAC) filtration and postchlorination (with a lower dosage of chlorine, to guarantee a 0.5-l ppm concentration of chlorine in the distribution system). Samples from the different stages of the treatment process plant were collected in 100-mL glass bottles with teflon-faced septa and polypropylene screw caps, filled without overflow. 0.1 mL of a freshly prepared 0.142 M ascorbic acid solution was added to each glass bottle for preservation, except for samples for HAA analyses because destruction of mixed haloacetic acids was observed.

Trihalomethanes were analyzed by headspace (HS). Samples (8 mL) were placed in 10 mL glass vials containing 4 µL of a methanolic solution of bromochloromethane and 1,4-dichlorobutane (50 mg/L and 500 mg/L, respectively) as internal standards. The vials were capped with teflon-faced septa and metallic seals and incubated at 70 °C for 15 minutes. An aliquot (0.5 mL) of the gas phase was automatically injected into the GC/ECD.

Acidic methanol esterification (AME) was used to analyze haloacetic acids in order to avoid the use of diazomethane that had proved unsuitable for the deriving mixed haloacetic acids (i.e. bromodichloro-, dibromochloroacetic). The reproducibility of the AME method was similar to that of the diazomethane method for brominated and chlorinated acids. Samples (30 mL) were placed in 40 mL EPA glass vials. To each sample, a surrogate standard (5 µL of an ether solution of 2-bromopropionic acid 60 mg/L); 3 mL of concentrated sulfuric acid (in order to obtain $pH<0.5$); 12 g of anhydrous sodium sulfate; 3 g of copper (II) sulfate pentahydrate and 2 mL of glass-bidistilled methyl *tert*-butyl ether (MtBE) were added. The vials were then sealed with teflon-faced septa, shaken for 2 minutes, placed upright and allowed to stand for 5 minutes. 900 µL of the methyl *tert*-butyl extract was transferred into a 10-mL vial containing 2 mL methanol/sulfuric acid (10 %) and a second surrogate standard (1 µL of an ether solution of 2-3-dibromopropionic acid 110 mg/L) was added. The 10-mL vials were placed into a 50 °C water bath for one hour. The vials were removed and cooled to 4 °C for 10 minutes, and 5 mL of a $CuSO_4$(10 %)/Na_2SO_4(5 %) solution was added. The samples were shaken by hand for 2 minutes. An aliquot of 400 µL of MtBE extract was transferred to a 2 mL vial and an internal standard (4 µL of an mixed ether solution of bromochloromethane and 1,2-dibromopropane 10 mg/L) was added. 1 µL of the MtBE extract was then injected into the GC/ECD. Extracts were analyzed within 24 hours.

Haloacetonitriles, haloketones, chloropicrin and chloral hydrate were analyzed by a modified EPA Method 551.1.Water samples (35 mL) were placed in 40 mL EPA glass vials (Wheaton, USA). To each sample, a surrogate standard (5 µL of a methanolic solution of 1,2-dibromopropane 70 mg/L), 10 g of anhydrous sodium sulfate in order to increase the ionic strength of the aqueous matrix and 2 mL of glass-bidistilled methyl *tert*-butyl ether (MtBE) were added. The vials were then sealed with teflon-faced septa, shaken for 2 minutes, placed upright and allowed to stand for 3 minutes. 500 µL of the organic layer was transferred into a 2 mL vial containing an internal standard (5 µL of bromochloromethane 10 mg/L). 1 µL of the MtBE extract was injected into the GC/ECD. Extracts were always analyzed within 24 hours.

Instrumental conditions used in these methods are indicated in Table 1. The response factor for each compound, relative to bromochloromethane, was used for trihalomethane quantification. A calibration curve of compound area/bromochloromethane area vs. concentration of the standards µg/L) was generated with a correlation coefficient (R^2) of 0.999 for all the other compounds.

Table 1. Gas chromatographic Conditions and Parameters

	HS/GC/ECD	Micro-LLE/GC/ECD and AME/GC/ECD
Injection	autosampler Fisons HS8000	manual
Volume:	0.5 mL gas phase	1 µL MtBE extract
Model / T (°C)	split (1/20) / 225 °C	splitless (60 sec) / 175 °C
Analytical column	DB-624 fused silica (J&W)	DB-1 fused silica (J&W)
	30 m x 0.32 mm; 1.8 µm (film)	30 m x 0.25 mm; 1.0 µm (film)
Temperature program:	40 °C (10 min); 2.5 °C/min; 65 °C (0 min); 9.0 °C/min; 140 °C (0 . min); 15 °C/min; 220 °C (10 min)	35 °C (9 min); 1 °C/min; 40 °C (3 min); 6 °C/min; 220 °C (10 min)
Gases		
carrier gas:	Helium (85 kPa)	Helium (140 kPa)
make-up:	Nitrogen (100 kPa)	Nitrogen (110 kPa)
Detector		
type / T (°C):	ECD, ^{63}Ni / 300 °C	ECD, ^{63}Ni / 300 °C

Identification was performed by injection of pure standards in two columns and by GC/MS. THM and HAA standards were purchased from Supelco (Bellefonte, USA); haloacetonitrile standards from Pfaltz and Bauer (Waterbury, USA); haloketone and internal standards from Sigma-Aldrich (Milwaukee, USA);

chloropicrin from Chem-Service (West Chester, U .); and chloral hydrate from Fluka (Büchs, Switzerland). 1,1 -bromochloropropanone, and l,l-dibromopropanone were previously synthesized in our laboratory. Other reagents were methanol (purge and trape grade) from Sigma-Aldrich; methyl-t-butyl-ether (suprasolv grade) from Merck (Darmstadt, Germany); sodium sulfate, copper (II) sulfate pentahydrate (ACS-ISO for analysis) and concentrated sulfuric acid (IS0 for analysis) from Carlo Erba (Odano, Italy).

RESULTS AND DISCUSSION

The determination of trihalomethanes (THMs) in the water treatment plant of Barcelona started in 1977 using liquid-liquid extraction followed by GC/ECD and pentane as extraction solvent (Ventura et al. 1982). Since 1992, THMs have been determined by HS/GC/ECD once a week. THMs were generated in all stages of the process, and the concentration of brominated and mixed THMs was higher than chlorinated ones and accounted for 87% of the total THMs (see Table 2). The reason for this was the high bromide level in raw water. Total THM (TTHM) concentration obtained at the prechlorination step was lower than that determined after sand filtration and ozonation. This can be explained because brominated and mixed THMs were sampled several minutes after the addition of chlorine, whereas DBP generation continues for about three hours until the water reaches the sand filters. Bromide is oxidized to hypobromous acid and can react with the organic DBP precursors to form bromoform and mixed compounds. TTHM levels remained practically constant after sand filtration and ozonization. A decrease in TTHM concentration was observed after the water had passed through GAC filters; the efficiency of activated carbon is greater for compounds with a high number of bromine atoms in the molecule (Ventura et al. 1982). As can be seen from Table 2, the average concentration decreased by 6% for $CHCl_3$, 6% for $CHCl_2Br$, 20% for $CHClBr_2$, and 30% for $CHBr_3$, after GAC filtration. At the postchlorination stage THMs were again formed at similar concentrations to those found at the sand filtration step. The average THM level determined in tap water from November (1997) to March (1998) was 72 µg/L, which compares favorably to the average levels of more than 200 µg/L of THMs measured during the eighties (Ventura and Rivera 1985). Figure 1a shows the chromatographic profile of HS/GC/ECD analysis from the water collected in the prechlorination step. Levels of THMs at the water plant varied considerably during the year due to changes in temperature, volume of raw water and break-point conditions.

Haloacetic acids (HAAs), analyzed every two weeks, are the second major compounds determined. Due to the high bromide concentration in the water, all the nine possible combinations of haloacetic acids, containing chlorine and/or bromine, were found. Mixed and brominated acids constituted 80% of the total HAAs, as found for THMs (see Table 2). Several factors besides bromide concentration may also influence HAA speciation, such as chlorine dose, reaction time, and TOC concentration among others. The trihalogenated species constituted the greatest molar fraction of the total HAA concentration (55-60%), the dihalogenated species represented 35-40%, and the monohalogenated species were only 0-2%. The speciation percentages are consistent with the values obtained by Gretchen and Singer (1996). Bromodichloro- and chlorodibromoacetic acids were the two principal species formed. The low values for tribromoacetic acid can be explained because it decomposes spontaneously in aqueous solution at 25 °C to form bromoform (Heller-Grosman et al. 1993). The HAA formation and evolution at the different stages of the process differed from that of THM. Thus, at the prechlorination stage, the HAA were rapidly formed and their concentration did not increase either in the sand filtration or at the ozonation step. At these two stages, total HAA (THAA) concentration represented 60% of the TTHM level. An important decrease was observed in THAA concentration when ozonated water passed through GAC filters, but HAAs were formed again with the postchlorination dosage, though at lower concentrations than in the previous stages. Total HAAs were near 22 µg/L in tap water as average level. It must be pointed out that trichloroacetic acid (TCAA) was present in raw water. TCAA is still used in industry as etching or pickling agent for surface treatment of metals, as a swelling agent and solvent in the plastic industry and in textile finishing (Reiman et al. 1996; Müller et al. 1996). Industrial activity on the banks of the Llobregat river explains its presence. Figure 1b shows the chromatogram of AME/GC/ECD analysis of the water sample collected at the prechlorination stage.

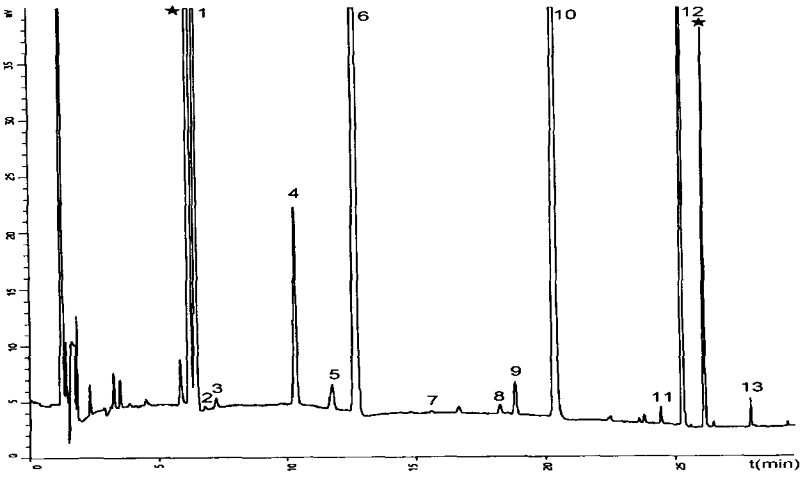

Figure 1a. GC/ECD chromatogram of HS extract from prechlorinated water.
1: chloroform, **2:** 1, 1, 1-trichloroethane, **3:** carbon tetrachloride, **4:** trichloroethylene, **5:** dibromomethane, **6:** bromodichloromethane, **7:** 1, 1-dichloropropanone, **8:** dichoroacetonitrile, **9:** perchloroethylene, **10:** dibromochloromethane, **11:** bromochloroacetonitrile, **12:** bromoform, **13:** dibromoacetonitrile. * denotes internal standards (bromochloromethane and 1,4-dichlorobutane).

An interfering peak appeared, which was identified by GC/MS as dimethyl sulfate $(CH_3)SO_4$ through library search. Its formation is due to the contact between the solvent and the acid when the methanol (10% H_2SO_4) is prepared. A further injection of the standard corroborated the identification. As the dimethyl sulfate peak does not overlap with either haloacetic ester or common disinfection by-products (see Figure 1b), the method can be used for HAA determination.

Table 2. DBP Average levels (µg/L) and (min – max) in Barcelona's water treatment plant (Nov'97- March'98). Results are in µg/L.

Compounds	Raw water	Pre chlor.	Sand filters	Ozone	GAC filters	Post chlor.
Chloroform	0.2 (nd-0.8)	8.0(2-17)	9.5(2-22)	8.0(2-16)	7.5(4-12)	7.0(4-13)
Bromodichloromethane	nd	13(6-28)	19(12-32)	18(11-28)	17(11-25)	17(11-25)
Chlorodibromomethane	nd	13(6-26)	30(22-52)	29(22-44)	23.5(18-31)	27(22-32)
Bromoform	nd	6.0(1.5-14)	22(15-31)	22(17-32)	15(13-20)	21(15-27)
TOTAL THMs	**0.2**(nd-2.4)	**40**(20-50)	**80.5**(56-102)	**77**(58-95)	**63**(47-80)	**72**(58-91)
Chloroacetic ac.	nd	nd	nd	Nd	nd	nd
Bromoacetic ac.	nd	1.3(nd-0.2)	0.3(nd-0.2)	1.0(nd-0.2)	nd	nd
Dichloroacetic ac.	nd	6.0(2.8-16)	5.8(2.8-14)	5.6(3.4-10)	0.4(nd-2.7)	0.9(nd-2.0)
Bromochloroacetic ac.	nd	8.8(6.4-15)	8.2(7.1-11)	9.1(8-11.4)	0.8(nd-3.2)	2.5(1-3.9)
Trichloroacetic ac.	1.0(0.3-1.6)	6.0(3.1-8.5)	4.8(3.5-4.5)	5.2(3.7-7.1)	1.5(nd-3)	1.5(0.3-2.5)
Dibromoacetic ac.	nd	5.6(3.1-10)	6.7(5-8.4)	7.7(5.2-10)	0.6(nd-3.1)	3.7(2.1-5.7)
Bromodichloroacetic ac.	nd	11(7.1-18)	9.4(7-12.5)	9.9(6.8-14)	2.4(nd-3.9)	4.2(1.1-7.6)
Chlorodibromoacetic ac.	nd	9.5(7.2-16)	8.3(4.7-11.5)	8.1(5.5-11)	2.3(nd-4.4)	4.8(3-7.2)
Tribromoacetic ac.	nd	5.1(2.3-10)	5.0(3-10)	5.5(3.1-10)	1.0(nd-1.7)	4.0(2.7-4.9)
TOTAL HAAs	**1.0**(0.8-1.6)	**53.4**(38-71)	**48.5**(42-76)	**52.1**(41-76)	**9.0**(nd-9)	**21.6**(11-32)
Trichloroacetonitrile	nd	nd	nd	Nd	nd	--
Dichloroacetonitrile	nd	1.1(0.6-1.6)	1.3(1-2)	1.2(0.9-1.6)	nd	0.4(0.2-1.0)
Bromochloroacetonitrile	nd	1.6(0.4-1.9)	3.2(1.3-4.3)	3.2(1.3-4.5)	nd	0.6(nd-0.7)
Dibromoacetonitrile	nd	2.5(0.6-7.6)	4.6(4.6-8.7)	7.0(5.5-9.9)	nd	1.5(0.6-3.1)
TOTAL HANs	nd	**5.2**(1.6-11)	**9.1**(6.9-14)	**11.4**(8.4-15)	nd	**2.5**
1,1-dichloroacetone	nd	0.4(0.1-0.2)	0.2(nd-0.5)	0.3(nd-0.4)	nd	0.1(nd-0.2)
1-bromo-1-chloroacetone	nd	0.3(0.1-0.3)	0.3(0.3-0.4)	0.3(0.3-0.4)	nd	nd
1,1,1-trichloroacetone	nd	0.4(0.2-1)	0.3(nd-0.5)	0.3(nd-0.5)	nd	nd
1,1-dibromoacetone	nd	0.6(0.2-2)	1.2(0.6-1.2)	1.2(0.6-2.1)	nd	0.3(0.1-0.7)
1,1-dibromobutanone	nd	nd	nd	Nd	nd	nd
TOTAL HKs	nd	**1.7**(0.9-2.8)	**0.5**(1.4-2.8)	**0.6**(0.5-2.1)	nd	**0.1**(0.1-0.8)
Chloropicrin	nd	nd	nd	Nd	nd	nd
Chloral hydrate	nd	**0.7**(0.6-1.1)	**1.1**(0.7-1.1)	**1.0**(0.7-1.4)	nd	**0.2**(nd-0.5)

-: below M.D.L. THMs (n=20, performed by HS/GC/ECD in DB-624 column). **HAAs** (n=10, performed by AME/GC/ECD in DB-1 column). **HANs, HKs, CH and CP** (n=10, performed by LLE/GC/ECD in DB-1 column).

Haloacetonitriles (HANs) formed in all stages of the process were analyzed every two weeks by micro-LLE/GC/ECD. The common HANs identified were dichloro-, bromochloro- and dibromoacetonitrile, the concentration of the last two accounting for 83% of the total HANs (THANs). Trichloroacetonitrile was identified only at concentrations lower than 0.5 µg/L when prechlorination conditions were higher than usual. THAN concentration was approximately 10% of the TTHM concentration for sand filtration and ozonated water samples.

Similar results were found by Xie et al. (1992). The formation and evolution of HANs in the different stages of the treatment plant was analogous to those explained above. The major concentrations determined were in sand filtered and ozonated waters. Unlike THMs, these compounds were completely adsorbed in GAC filters. HANs were again formed at the postchlorination stage; the average level in tap water was always lower than 5 µg/L.

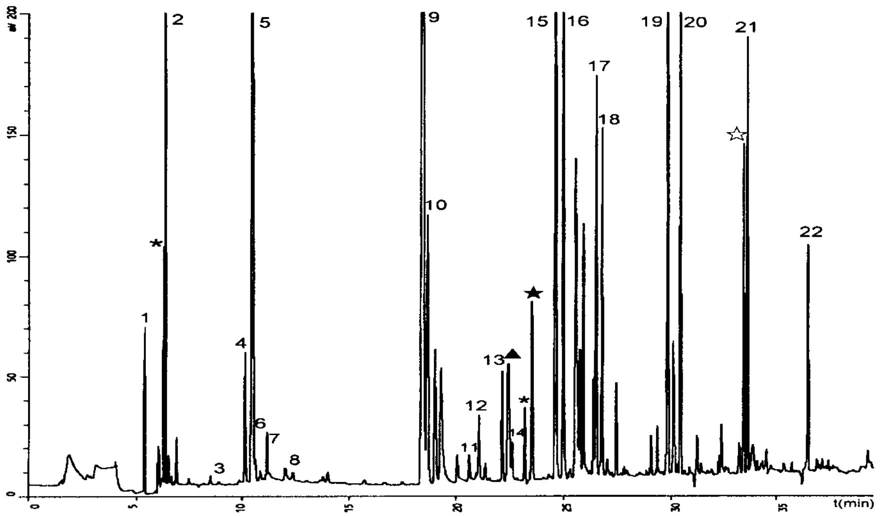

Figure 1b. GC/ECD chromatogram of AME extract from prechlorinated water. **1:** cyanogen bromide, 2: chloroform, 3: trichloroacetonitrile, 4: dichloroacetonitrile, 5: bromodichloromethane, **6:** trichloroethylene, **7:** chloral hydrate, **8:** 1,1 -dichloropropanone, **9:** dibromochloromethane, **10:** bromochloroacetonitrile, **11:** 1 -bromo- 1chloropropanone, **12:** bromoacetic acid, **13:** dichloroacetic acid, **14:** 1, 1, 1-trichloropropanone, **15:** bromoform, **16:** dibromoacetonitrile, 17: bromochloroacetic acid, **18:** trichloroacetic acid, **19:** dibromoacetic acid, **20:** bromodichloroacetic acid, **21:** dibromoacetic acid, **22:** tribromoacetic acid. * denotes internal standards (bromochloromethane, 1,2-dibromopropane), ★ denotes surrogate standard 1 (2-bromopropionic acid), ☆ denotes surrogate standard 2 (2,3-dibromopropionic acid) and ▲ dimethyl sulfate artifact.

Chloral hydrate (CH) and haloketones (HKs) formed the group of DBPs with lowest concentration. CH was always detected at prechlorinated, sand filtration and ozonization stages at an average level of i µg/L. Haloketones 1, 1 -dichloro-, 1 -bromo- 1 -chloro-, 1, 1 -dibromo- and 1,1,1 -trichloropropanone were also detected in the three stages by LLE/GC/ECD. CH and HKs were also completely adsorbed in the GAC filters; their concentrations in tap water were lower than 0.5 µg/L. Chloropicrin was not usually formed during the process. This compound has been described as a common DBP in water treatment plants where chloramines are the principal disinfectants used. In conclusion, the different DBP levels are within the European and American Directives. Other DBPs such as iodinated THMs, cyanogen halides and aldehydes formed at the water treatment plant are being studied.

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