# Potential of the drinking water supplied to the city of Barcelona and its metropolitan area to form emerging disinfection byproducts

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**Abstract**

Chlorinated and brominated trihalomethanes (THM4) are the main disinfection by-products known to be formed in the water supplied to the city of Barcelona and its metropolitan area. Previous efforts and investment have forced the levels of THM4 below the current regulatory limits after the potabilization process and in the distribution system. The present work aims at generating new knowledge on the potential of this potable water to form additional (unregulated) disinfection by-products (DBPs) classes: iodinated trihalomethanes, trihalogenated haloacetaldehydes, halogenated acetonitriles, halogenated acetamides, and haloacetic acids. To study this, DBP formation potential tests were performed with different water matrices representative of the mixtures that commonly occur in the distribution system, at different temperatures, and residence times. Water matrices considered included the finished water of two drinking water treatment plants, Ter and Llobregat, and the finished water of a seawater reverse-osmosis desalination plant (SWRO), per se or in mixtures. As for the investigated emerging DBPs, dibrominated species of haloacetic acids were the most abundant compounds. Total unregulated DBP concentrations measured ranged between 82 and 105 µg/L in the investigated water matrices, except in the case of desalinated water, where almost no DBPs were detected. Formation of these unregulated DBPs was linked to the DBP precursors (e.g, natural organic matter and bromide content) present in the water.

**Keywords:** haloacetics acids, haloacetamides, haloacetonitriles, iodinated trihalomethanes, desalinated water, trihalogenated acetaldehydes, mass spectrometry, GC-MS analysis

## 1. Introduction

Chlorinated and brominated trihalomethanes (THM4) and bromate are the only disinfection by-products (DBPs) currently regulated in drinking water in Europe (Directive 98/83/EC), and consequently, in Spain (Real Decreto 140/2003), with maximum levels allowed in tap water of 100 µg/L for THM4, and 10 µg/L for bromate. Thus, many efforts have been directed to keep levels of THM4 and bromate in free chlorine-disinfected water below these limits in the last 15 years. This was the case also for ATLL CGSA, the water company that supplies potable water to more than 4.5 million people living in Barcelona and its metropolitan area. To date, the THM formation potential of their potable water is well investigated and documented, and despite the high bromide levels present naturally in one of the source water matrices they use to produce drinking water (Llobregat river water), the levels of these DBPs in their finished water and in their distribution system are always well below the regulatory limits.

In order to complement their THM4 records and to increase their knowledge on DBP formation, the present study aimed at assessing the potential of the water they supply to form several unregulated DBP classes: haloacetic acids (HAAs), haloacetaldehydes (HALs), haloacetamides (HAcAms), haloacetonitriles (HANs), and iodinated trihalomethanes (I-THMs). This was achieved through the performance of DBP formation potential tests with different water matrices at different temperatures and residence times.

## 2. Materials and methods

Target DBPs are summarized in Table 1.

DBP formation potential was investigated in the finished water produced by three different water treatment plants that use free chlorine as the final disinfectant: the Llobregat drinking water treatment plant (DWTP) that treats water from the Llobregat River, the Ter DWTP that treats water from the Ter River and a seawater reverse-osmosis (SWRO), and several mixtures of these water matrices. The mixtures performed were representative of the water supply system, and they were performed by combining equal volumes of the DWTP finished water matrices or by mixing one of the DWTP finished water matrices with SWRO desalinated water (80:20, v/v).

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**Table 1.**Target unregulated DBPs investigated in the water samples

| *DBP class* | *Analyte* | *CAS #* | *Molecular fórmula* |
|---|---|---|---|
| I-THMs | Dichloro-iodomethane | 594-04-7 | $Cl_2ICH$ |
| | Chloro-bromo-iodomethane | 34970-00-8 | BrClICH |
| | Dibromo-iodomethane | 593-94-2 | $Br_2ICH$ |
| | Chloro-diiodomethane | 638-73-3 | $ClI_2CH$ |
| | Bromo-diiodomethane | 557-95-9 | $BrI_2CH$ |
| | Triiodomethane (Iodoform) | 75-47-8 | $I_3CH$ |
| HALs | Trichloro acetaldehyde (Chloral) | 75-87-6 | $Cl_3C$-CHO |
| | Dichlorobromo acetaldehyde | 34619-29-9 | $BrCl_2C$-CHO |
| | Dibromochloro acetaldehyde | 64316-11-6 | $Br_2ClC$-CHO |
| | Tribromo acetaldehyde | 115-17-3 | $Br_3C$-CHO |
| HANs | Chloroacetonitrile | 107-14-2 | $ClCH_2$-CN |
| | Bromoacetonitrile | 590-17-0 | $BrCH_2$-CN |
| | IodoacetonitrilE | 624-75-9 | $ICH_2$-CN |
| | Dibromoacetonitrile | 3252-43-5 | $CHBr_2$-CN |
| | Dichloroacetonitrile | 3018-12-0 | $CHCl_2$-CN |
| | Bromodichloroacetonitrile | 60523-73-1 | $CBrCl_2$-CN |
| | Dibromochloroacetonitrile | 144772-39-4 | $CBr_2Cl$-CN |
| | Trichloroacetonitrile | 545-06-2 | $CCl_3$-CN |
| | Tribromoacetonitrile | 75519-19-6 | $CBr_3$-CN |
| HAAs | Chloroacetic acid | 79-11-8 | $ClCH_2$-COOH |
| | Bromoacetic acid | 79-08-3 | $BrCH_2$-COOH |
| | Iodo acetic acid | 64-69-7 | $ICH_2$-COOH |
| | Chlorobromo acetic acid | n/a | BrClCH-COOH |
| | Dichloroacetic acid | 79-53-6 | $Cl_2CH$-COOH |
| | Dibromoacetic acid | 631-64-1 | $Br_2CH$-COOH |
| | Chloroiodoacetic acid | 53715-09-6 | ClICH-COOH |
| | Bromoiodoacetic acid | 71815-43-5 | BrICH-COOH |
| | Diiodoacetic acid | 598-89-00 | $l_2CH$-COOH |
| | Trichloroacetic acid | 76-03-9 | $Cl_3C$-COOH |
| | Bromodichloroacetic acid | 71133-14-7 | $BrCl_2C$-COOH |
| | Dibromochloroacetic acid | 5278-95-5 | $Br_2ClC$-COOH |
| | Tribromoacetic acid | 75-96-7 | $Br_3C$-COOH |
| HAcAms | 2-Bromoacetamide | 683-57-8 | $BrCH_2$-$CONH_2$ |
| | 2-Chloroacetamide | 79-07-2 | $ClCH_2$-$CONH_2$ |
| | Iodoacetamide | 144-48-9 | $ICH_2$-$CONH_2$ |
| | Dibromoacetamide | 598-70-9 | $Br_2CH$-$CONH_2$ |
| | Dichloroacetamide | 683-72-7 | $Cl_2CH$-$CONH_2$ |
| | Diiodoacetamide | 5875-23-0 | $I_2CH$-$CONH_2$ |
| | Bromochloroacetamide | 62872-24-8 | BrClCH-$CONH_2$ |
| | Chloroiodoacetamide | 62872-35-9 | ClICH-$CONH_2$ |
| | Bromoiodoacetamide | 62872-36-0 | BrICH-$CONH_2$ |
| | Trichloroacetamide | 594-65-0 | $Cl_3C$-$CONH_2$ |

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|---|---|---|---|
| | Tribromoacetamide | 594-47-8 | $Br_3C\text{-}CONH_2$ |
| | Dibromochloroacetamide | 855878-13-6 | $ClBr_2C\text{-}CONH_2$ |
| | Bromodichloroacetamide | 98137-00-9 | $BrCl_2C\text{-}CONH_2$ |

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Each water matrix was placed in eight 500 mL amber glass bottles with no headspace. Four bottles were kept at 15 ºC and the remaining four were incubated at 30 ºC so that the temperature effect could be addressed. The effect of the water residence time was evaluated by sacrificing one bottle at 0, 24, 48 and 72 hours of incubation.

A variation of US EPA Method 551.1 for the determination of chlorination DBPs, chlorinated solvents and halogenated pesticides/herbicides in drinking water was applied to extract the target unregulated DBPs from the water samples, using methyl-tert-butyl ether (MTBE) as the extraction solvent. One-half of the MTBE extract was directly injected into the gas chromatography-mass spectrometry system (GC-MS) for the determination of all target DBPs but HAAs. The remaining half of the extract was derivatized with diazomethane so that HAAs were made amenable to GC-MS analysis.

In addition to the analysis of THM4 and unregulated DBPs, the inorganic ion content and physical-chemical properties of the water matrices tested were also investigated so that DBP precursors could be identified

## 3. Results and discussion

The THM4 concentration of the potable water leaving the Ter DWTP was 35 µg/L, and it was 50 µg/L in the case of the Llobregat DWTP. The total concentration of unregulated DBPs was very similar in both investigated DWTP finished water matrices: 85 µg/L in the case of the Llobregat DWTP finished water and 89 µg/L in the case of the Ter DWTP finished water. The most abundant class of unregulated DBPs in all water matrices was HAAs, whereas the least abundant class was iodinated THMs. Brominated species of DBPs, more toxic than their fully chlorinated counterparts (Plewa *et al.* 2008), were preferentially formed in the finished water of the Llobregat DWTP, due to the natural high bromide content of the raw water entering the DWTP (Llobregat River water). The formation of bromine-containing DBPs was also enhanced with the addition of desalinated water to the Ter DWTP finished water.

Overall, the potential of the water mixtures to form the investigated emerging DBP classes was lower than that of the DWTP finished waters. The SWRO finished water presented the lowest potential to form DBPs, due to its low concentration of organic matter. However, as aforementioned, and despite its low bromide levels, if this water matrix is mixed with a water of very low bromide content (i.e., the Ter DWTP finished water), it could contribute to increase the bromide concentration of the mixture and in consequence, enhance the formation of brominated DBP species.

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