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Trihalomethane Levels in Municipal Drinking Water of Madrid (Spain) and Health Risk Assessment for Oral Exposure

Mª Concepción Almonacid Garrido[1] · Mª José Villanueva-Suárez[1] · Alberto Álamo Gómez[2] ·
Alejandra Garcia-Alonso[1] · Mª Dolores Tenorio Sanz[1]

Abstract

Trihalomethanes (THMs) are generated in the drinking water treatment plant, due to the reaction of the halogenated disinfection compounds with the natural organic matter (NOM). They are related to health problems both from the point of view of cancer development and other important diseases. This study aimed to assess the quality of tap water in Madrid in terms of prevention and control of THMs risks in the supply water treated by Canal de Isabel II (CYII) in a total of 108 samples throughout 2015 to 2020, to distinguish the problems of the different 21 districts or types of buildings, the seasonality and to estimate the risk of exposure to THMs from tap water in the population of Madrid. The variables considered include year, seasonality, district of Madrid and sampling point. The concentrations of THMs detected in all samples were within the current legal limit (100 µg/l). Chloroform was the compound with the highest contribution to the sum of THMs. A decreasing trend in THMs concentrations was observed over the years of the study related to the removal of NOM and the use of chloramines. THM levels were higher in the central area than in the peripheral districts and the lowest concentrations were detected in summer. Regarding risk assessment, the results of the non-carcinogenic risk indicate that there is no potential risk from tap water consumption for the adult population. For the carcinogenic risk, only water samples with THM concentrations between 50 and 75 µg/l could constitute a risk for high consumers.

Keywords Disinfection by-products · Trihalomethanes · Tap water · Regulatory compliance · Exposure assessment

Introduction

In the drinking water treatment process, chlorine and its derivatives are widely used in the disinfection step of tap water due to their low cost and high efficiency in reducing the presence of microbiological contaminants. These agents, in addition to eliminating pathogenic micro-organisms, are essential for the prevention of waterborne diseases and the protection of consumer health. However, they have the disadvantage of generating several disinfection by-products (DBPs), amongst which the halogenated organic compounds known as trihalomethanes (THMs) stand out for their higher concentration, this must be considered because of their impact on public health due to their carcinogenic potential (Villanueva et al. 2003, 2015). The four major THMs are chloroform or trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform or tribromomethane (TBM), with TCM being the most abundant in chlorinated drinking water (Palacios et al. 2000; Pérez-Pavón et al. 2008).

THMs are generated in the drinking water treatment plant in the pre-oxidation-pre-chlorination stage, due to the reaction of the disinfecting agent, mainly chlorine, chlorine dioxide or hypochlorite or other halogenated agents, with the natural organic matter (NOM) that exists in the water at source and which is mainly composed of humic and fulvic acids. They are also produced in the final disinfection stage by the application of chlorine or chloramines (Bracho et al. 2009; Fuentes Rivas et al. 2015).

The re-chlorination of the water supplied along the distribution network, in the different intermediate or regulating reservoirs, aimed at guaranteeing the quality of the water

✉ Mª Dolores Tenorio Sanz
dtenorio@ucm.es

1 Department of Nutrition and Food Science, Facultad de Farmacia, Universidad Complutense de Madrid, Plaza de Ramón y Cajal s/n, 28040 Madrid, Spain

2 Laboratory of Public Health, Madrid Salud, Calle Emigrantes, 22, 28043 Madrid, Spain

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throughout its journey through the distribution network to the consumer's tap, could as well lead to a further increase in THMs (Calderón et al. 2002; Olmedo-Sánchez 2008; Bracho et al. 2009; Salazar Serna and Peñuela 2016). This often occurs when the networks are very long, as the residual disinfectant needs to be maintained over many kilometres and for a long time (Liew et al. 2016).

On the other hand, regarding the type and amount of THMs generated, it will depend on several factors such as the origin of the water (Parvez et al. 2017; Pérez-Pavón et al. 2008), the nature of the precursors present in the water (Gallard and Gunten 2002; Dong et al. 2021), the variations in pH (Yu et al. 2019) and temperature (Toroz and Uyak 2005; Nuñez-Cerrato 2022; Stanhope et al. 2020; Mosaferi et al. 2021), the type and level of disinfectant (Olmedo-Sanchez 2008; Hernández Sánchez et al. 2011; Marchesi et al. 2020), the contact time between disinfectant and NOM (Fantuzzi et al. 2007; Yu et al. 2019) or the type and material of the distribution net (Nuñez-Cerrato 2022; Zhang et al. 2018; Ahmed et al. 2019). In the case of surface waters, pH, followed by reaction time and temperature, is the most significant factor affecting the formation of THMs during chlorination (Rodríguez et al. 2007; Yu et al. 2019).

Several epidemiological studies have found a clear association between chlorinated water consumption and an increase in cancer in the population. According to IARC (1999a, 1999b), TCM and BDCM are classified as possible carcinogens in humans (2B) mainly linked to bladder cancer (Villanueva et al. 2017, 2021), although they have also been linked to stomach and colon cancer (Richardson et al. 2007; Genisoglu et al. 2019). In Europe, 5% of bladder tumours are associated with THMs in water (Evlampidou et al. 2020). Another one of the most reported toxic effects of these compounds is liver damage (Summerhayes et al. 2021). Besides, reproductive and foetal developmental alterations have also been reported, mainly associated with BDCM (Jeong et al. 2012; Villanueva et al. 2015). Therefore, THMs should be at the lowest possible levels in drinking water without compromising disinfection efficacy at any time (Liu et al. 2019).

The European Directive 2020/2184 on sanitary criteria for drinking water quality, transposed into Spanish legislation by RD 3/2023, sets a parametric value (PV) of total THMs (sum of TCM, BDCM, DBCM and TBM concentrations) of 100 µg/l giving a risk-based approach to reduce potential morbidity and mortality from exposure to drinking water contamination and to ensure drinking water quality without risk to human health. Whenever possible and without affecting disinfection, EU Member States shall aim for the lowest PV. In the same way, to avoid the formation of THMs, but ensuring water disinfection, the maximum concentration of residual combined chlorine is also regulated, which cannot exceed 2.0 mg/l, nor that of residual free chlorine > 1 mg/l (RD 140/2003). No limit is set for chloramines,

although the WHO recommends a maximum concentration of 3 mg/l in water (WHO 2017).

According to the surveys carried out in the health study of the city of Madrid, in the population there is a high consumption of tap water, 73.6%, compared to only 12.5% of bottled mineral water (Díaz-Olalla et al. 2020). This fact makes it essential to control THMs in consumer tap water to avoid an increase in their levels that would have negative health repercussions on a large part of the population (Morales-Alonso et al. 2019).

The aim of this study was to assess the quality of Madrid tap water in terms of prevention and control of THMs risks over a period of 6 years by distinguish the problematic of different districts or building types, seasonality and estimating the risk of THMs exposure from tap water in the population of Madrid. Such information is essential to provide adequate health protection and potentially develop effective control strategies.

Materials and Methods

Sampling Location

Prospective sampling of Madrid water supply treated by Canal de Isabel II (CYII) was carried out to analyse THMs in a total of 108 samples over a period of 6 years: 2015 to 2020 in the 21 different districts of Madrid (Fig. 1). Critical sampling points have been established for each facility at the locations with the highest risk of THMs production. Most of the sampling was carried out at Official Sampling Stations (OSS), followed by drinking fountains in parks, schools and sports centres. In private buildings and other locations, such

1. Centro
2. Arganzuela
3. Retiro
4. Salamanca
5. Chamartín
6. Tetuán
7. Chamberí
8. Fuencarral-El Pardo
9. Moncloa-Aravaca
10. Latina
11. Carabanchel
12. Usera
13. Puente de Vallecas
14. Moratalaz
15. Ciudad Lineal
16. Hortaleza
17. Villaverde
18. Villa de Vallecas
19. Vicálvaro
20. San Blas
21. Barajas

Fig. 1 Districts of the city of Madrid

as public organisms, sampling was very low. Sampling took place in most cases in zone (D1–D7) that group together the largest number of homes according to the census: Centro, Arganzuela, Retiro, Salamanca, Chamartín, Tetuán and Chamberí and other adjacent districts.

Sample Collection

Samples were collected at the different locations mentioned above in 250-ml polyethylene containers, clean, hermetically sealed to avoid evaporation of THMs and easy to open. They were quickly transferred to the laboratory under refrigerated conditions (4 °C).

Analytical Methods

Determination of THMs by GC–MS

The determination of THMs was performed at the Public Health Laboratory of the Madrid City Council accredited by ENAC (n° 215/LE 406 and n° 215/LE 1915). The analysis of THMs was carried out using the headspace technique in a gas chromatograph (GC) (Agilent 7890, Palo Alto, CA, USA) coupled to a triple-quadrupole mass spectrometer (GC–MS) (Agilent 7000C, Palo Alto, CA, USA) that allows the quantification of volatile compounds.

The samples were received in airtight containers, to which sodium thiosulphate has been previously added to neutralise free chlorine and stop the formation of chlorination by-products. To encourage the THMs to pass into the gas phase, 2 g of sodium chloride was added to each vial to increase the ionic strength of the solution. 10 ml of each sample was taken in a headspace vial (20 ml) and 25 μl of a chlorobenzene-d5 solution (20 μg/ml) was added as internal standard and 25 μl of fluorobenzene (20 μg/ml) as surrogate standard to ensure the performance of the method. At the same time, one vial was left open to control possible environmental contamination in the laboratory. Incubation and simultaneous shaking at 70 °C were carried out for 20 min in a Combipal GC80. In the chromatograph 250 μl of gas phase, for their separation, two HP-5MS (Agilent Technologies) capillary columns (15 m long × 0.25 mm internal diameter and 0.25 μm thick) were used, placed one after the other, in an oven at an initial temperature of 40 °C (3 min), increasing to 90 °C at a rate of 10 °C/min until reaching 200 °C at a rate of 25 °C/min, for a total test time of 12.4 min. The carrier gas was helium with a constant flow rate of 1.2 ml/min in the first column and a further 0.2 ml/min in the second column. The concentration of chloroform, bromodichloromethane, dibromochloromethane and bromoform was obtained using the calibration line prepared from a standard solution of a THMs mixture 5000 μg/ml (LGC).

The working range extends from 2.5 to 150 μg/l ($r^2 > 0.98$). The validation parameters of the official method such as linearity, precision, accuracy, recovery, limit of detection (LOD) and limit of quantification (LOQ) were optimal, always in accordance with the standard (ISO 10301:1997; RD 140/2003).

THMs detection by mass spectrometry was performed after GC separation. Ionisation of the analytes was carried out by electron impact (EI) at 70 eV, and the transfer line and ionisation source temperatures were 280 °C and 230 °C, respectively. The SIM (selected ion monitoring) acquisition method acquires the ions contained in Table 1. The evaluation of the data was carried out using Mass Hunter software (Agilent Technologies). The analytes were initially identified by individual injection and comparison of the spectra obtained with those contained in the NIST library. From these data, in subsequent tests the identification is carried out by retention time and compliance with the ionic ratios, between the qualifiers and quantifiers of the samples and the value obtained for the same transitions calculated as the average of the values of the standards that constitute the calibration line.

Risk Assessment

Estimation of Exposure to THMs from Regulatory Sampling

The exposure assessment to THMs in water in this study was performed based on a deterministic approach. The exposure risk was estimated by considering the carcinogenic and non-carcinogenic risk from chronic ingestion in adult individuals. For the estimation of exposure to THMs through drinking water ingestion, as the present study is limited to Madrid population, drinking water intake data estimated by National Food Survey on adults, the elderly and pregnant women (ENALIA2) related to the Spanish adult population have been considered as a criterion for risk assessment and the case of an adult male has been used as an example. These

Table 1 Trihalomethanes: retention times, target and qualifier ions

Compound	RT (min)	Target ions	Qualifier ions
Trichloromethane	1.91	83	85, 47, 87
Fluorobenzene	2.40	96	70
Dichlorobromomethane	2.77	83	85, 129, 127
Chlorodibromomethane	4.34	129	127, 131, 210
Tribromomethane	6.17	173	171, 175, 254
Chlorobenzene-D5	5.35	117	119, 82

figures ranged from 1.9 l for the average consumer (P50) to 3.5 l for the extreme consumer (P95) (AECOSAN 2016).

Dietary exposure was calculated from both the concentration of each species and the sum of THMs in water, considering water consumption and according to the average standard body weight of 70 kg (Lee et al. 2004; Radwan et al. 2021). A lifetime chronic exposure (365 days/year for 70 years) was considered (Radwan et al. 2021). The following equation was used for the calculation:

$$DE = (C \times DI \times EF) / BW,$$

where DE is the dietary exposure (µg/kg/day), C is the concentration of THMs found in tap water (mg/l), DI corresponds to the average daily water intake rate (l/day), EF is the exposure factor: frequency and duration of exposure (in our study, a lifetime chronic exposure has been considered, so FE = 1) (Djam et al. 2020) and BW is the body weight (kg).

Risk Characterisation

The carcinogenic risk was calculated from the estimated chronic oral intake of tap water according to the following equation:

$$Cancer\ risk = CSF \times DE,$$

where CSF is the cancer slope factor or carcinogenic potency corresponding to the risk/unit dose (mg/kg/day) and takes the following values for each of the species: 0.031 (TCM); 0.0079 (TBM); 0.062 (BDCM); and 0.084 (DBCM) included in the EPA IRIS (Integrated Risk Information System) database and described by Pardakhti et al. (2011) and Amjad et al. (2013). If the risk index is lower than 10^{-6}, exposure is acceptable according to the general assumption of the different International Organisations. When it is between 10^{-6} and 10^{-4} the values are considered acceptable, but if they exceed 10^{-4} then there is a probable additional carcinogenic risk to the population.

To assess the non-carcinogenic risk, the hazard quotient (HQ) of the different species of THMs for the oral exposure route has been calculated from tap water intake according to the following equation:

$$HQ = DE / RfD,$$

where RfD is the reference dose defined as the daily exposure level that a person can receive over a lifetime without, with a degree of certainty, causing an adverse health effect, including the most vulnerable groups. The RfD expressed in mg/kg/day takes the following values for the different THM species: 0.01 (TCM), 0.02 (BDCM), 0.02 (DBCM) and 0.02 (TBM) reflected in the same IRIS database mentioned above and by Amjad et al. (2013). The hazard index (HI) of the total THMs is calculated by the sum of the HQs of each individual compound.

When the HQ ratio is < 1, the likelihood of adverse effects can be said to be minimal, and the risk can be considered negligible. Conversely, if the HQ ratio is > 1 and therefore the safe exposure threshold is exceeded, the likelihood of an adverse effect should be considered (Djam et al. 2020; Saradhi et al. 2015).

Results and Discussion

Concentration and Distribution of the Different THMs Species

The average THMs concentration of the 108 samples analysed over the period 2015–2020 was 33.1 µg/l, with a wide range of values from 4.5 to 74.2 µg/l (Table 2). The values detected in all the samples were in accordance with the limit in force in the current legislation: 100 µg/l.

Of the four species identified and quantified, TCM was the most abundant in the whole sampling, with a mean value of 25 µg/l, representing a percentage of 75.5% of THMs. The remaining detected compounds were in the minority, with DBCM and TBM standing out with mean levels of 3.8 and 2.8 µg/l, respectively. BDCM was the one that contributed the lowest values, even in some samples the results were considered equal to 0, a fact that can be appreciated by

Table 2 Levels of different species of trihalomethanes (THMs)

THMs (µg/l)	Mean ± SD	Min	Quartile 25	Quartile 75	Max	Median
TCM	25 ± 10.1	0	20	32.5	48	25.4
TBM	2.8 ± 4.8	0	0	5.2	26	0
BDCM	1.2 ± 2.8	0	0	2.8	23	0
DBCM	3.8 ± 3.6	0	0	6.5	14	0
Total	33.1 ± 21.3	4.5	23.5	40.4	74.2	23.5

TCM trichloromethane, *TBM* tribromomethane, *BDCM* bromodichloromethane, *DBCM* dibromochloromethane

the median value. The content of brominated trihalomethanes was generally low since the water supply of Madrid is mainly of surface origin from the rivers of the Guadarrama mountain range (Lozoya, Jarama, Guadalix, Manzanares, Guadarrama and Alberche), and bromine is a natural constituent of groundwater.

The concentration of THMs found in the water depends largely on the type of disinfection used. In fact, since the most widespread method in CAM is chloramination which prevents the formation of THMs, the concentrations of THMs in the samples analysed from Madrid were lower than if hypochlorite or chlorine gas with more possibilities of THMs formation had been applied.

However, the drinking water distribution network in Madrid is a very complex and extensive system, so that re-chlorination with different chlorine derivatives, mainly sodium hypochlorite, often occur at different points along the network and in intermediate reservoirs before reaching the final consumer. These re-chlorinations favour the formation of DBPs and could therefore be the reason for the variability of the THMs levels found in our research. This is consistent with the studies by Santa-Marina et al. (2010) on THMs in 25 municipalities in Guipuzcoa, where higher levels were found if chlorine is dosed in the traditional way (hypochlorite) or by eliminating pre-chlorination, than when only post-chlorination is used as an alternative.

Most of the distribution networks located in the municipality of Madrid are urban-meshed networks (85%), which have fewer problems with the presence of DBPs; however, there are also mixed (9%), non-meshed (5%), or unknown (2%) networks, which could have a greater possibility of water stagnation and in these cases higher concentrations of DBPs can be generated. This could also be the cause of the variability in THMs levels in the samples under study.

Palacios et al. (2000) carried out one of the first studies in Spain on THMs and found levels of organohalogen compounds in chlorinated drinking water in the order of 77.7 µg/l. On the other hand, Villanueva et al. (2003) carried out DBPs studies in drinking water samples from four Spanish regions, Alicante, Asturias, Barcelona and the Canary Islands, detecting THMs levels in the order of 35 µg/l in Alicante and Barcelona, close to the levels found in our work and lower values in Asturias or the Canary Islands (5–6 µg/l). In addition, different profiles of THMs constituent species were observed: in three of the four regions evaluated, BDCM predominated, whilst in Asturias, the most significant species was TCM, in agreement with the data found in Madrid in the present work. Similarly, Freire et al. (2008) determined THMs values in drinking water in the province of Granada, obtaining maximum values of 31.87 µg/l, identifying TCM as the main compound, which coincides with our data. They also investigated the impact of the origin of surface or groundwater on the level of THMs, concluding that the highest levels of these by-products were associated with treated surface water.

In the present study, the number of water samples falling into each THMs concentration range is shown in Table 3. It can be noted that the highest number of both THMs and TCM samples was found in the 30–40 µg/l range, followed by the 20–30 µg/l range. For TBM and DBCM species, the most representative value was < 2.5 µg/l. BDCM had maximum values between 2.5 and 10 µg/l.

Evlampidou et al. (2020) carried out a study of THMs levels between 2005 and 2018 in different European countries with a mean value of 11.7 µg/l, although the maximum levels did exceed the limits. Within our country, only in the 90th percentile of the samples from Cataluña did they detect a level of 197 µg/l above the VP. In general, the concentrations found in the other Spanish regions agreed with those obtained for other European countries (Italy, Lithuania or the UK) and also in the same order as those obtained in the present investigation. The use of ozone in the Netherlands, Germany and France, ultraviolet radiation in the case of Austria or the application of chloramines in countries, such as Finland or Sweden, explain the low concentration of THMs detected. In their study in the 100 administrative districts of France, Corso et al. (2018) observed large variations in THMs concentrations attributable to the different

Table 3 Distribution of the water samples in concentration ranges for trihalomethanes (THMs) and their different species

Range (µg/l)	TCM (N)	TBM (N)	DBCM (N)	BDCM (N)	THMs (N)	THMs (%)
0 < 2,5	8	72	78	32	0	2.78
2, 5–10	0	26	29	66	3	12.04
> 10 < 20	25	8	0	10	12	25.93
> 20–30	40	2	1	0	29	34.26
> 30–40	32	0	0	0	37	16.67
> 40–50	3	0	0	0	18	5.56
> 50–100	0	0	0	0	9	2.78

TCM trichloromethane, *TBM* tribromomethane, *BDCM* bromodichloromethane, *DBCM* dibromochloromethane

origin of the water: surface or groundwater. On the other hand, in Italy, the widespread use of chlorine dioxide instead of chloramines resulted in low levels of THMs. Disinfection by-products were found in 77% of all samples, in a range of concentrations with mean values ranging from 0.01 to 54 µg/l, but with a very low median value of 1.12 µg/l (Fantuzzi et al. 2007).

Sinha et al. (2021) in a comprehensive international review study indicates that research studies in the USA, Canada and Brazil had quantified concentrations of THMs higher than those recommended in some water samples and their decrease would be necessary to reduce the health risks associated with these compounds.

Distribution of THMs Species According to the Sampling Year

The results of THMs by year of study are shown in Table 4. The sampling frequency was not homogeneous over the study period, ranging from 48% in 2016 to 27.8% in 2015 of the total sampling.

Regarding the levels of THMs in this study, the highest average concentration was 43.1 µg/l (2015) and the lowest 24.2 µg/l (2019). Table 4 shows higher levels of THMs in the period 2015–17. The component with the highest relevance in relation to the total THMs was TCM, which represents a percentage of the total between 60.7% in 2015 and 92.7% in 2018. The higher content of this halogenated compound is due, as previously mentioned, to the fact that Madrid's water supply is mainly of surface origin. THMs arise from oxidation and substitution reactions of NOM with chlorine and other disinfectants. Therefore, filtering is very important to discharge NOM from the water to be treated and to maintain the low levels reflected in this study over time. Within the other species, BDCM was the brominated compound with the highest contribution to total THMs, with percentages between 14 and 19.5% (2015–2017) and between 4.5 and 7.3% (2018–2020). TBM was detected with maximum contributions to total THMs in 2015 (13%) and null in 2018. Finally, DBCM was found in negligible concentrations.

In the last 3 years of the study, there has been a clear decrease in the levels of THMs of around 33%. This could be due to the implementation by CYII of new technologies in drinking water treatment plants in recent years, in accordance with the 2030 AGENDA, achieving a higher degree of removal of NOM through oxidation processes with ozone and filtration through activated carbon to reduce the generation of by-products, such as trihalomethanes.

At the national level, as shown in Fig. 2, higher concentrations of THMs are found in supply areas with larger populations and samples taken at indoor facilities or at the consumer's tap, and although the average values, as highlighted in the national drinking water quality report, are

Table 4 Trihalomethanes (THMs) species levels by sampling year

| Year	Specie	Mean ± SD	Min	Median	Max
2015	TCM	26.1 ± 1.36	24	26	28
N = 7	TBM	5.59 ± 1.01	3.7	5.6	6.6
	DBCM	2.97 ± 0.3	2.6	2.8	3.4
	BDCM	8.43 ± 0.85	7.2	8.7	9.2
	THMs	43.09 ± 2.96	39.3	44.5	46
2016	TCM	24.5 ± 6.45	14	24	37
N = 30	TBM	4.35 ± 6.43	0	0	26
	DBCM	1.36 ± 2.18	0	0	6.7
	BDCM	5.14 ± 3.86	0	3.7	12
	THMs	35.34 ± 13.13	17	33.6	74.2
2017	TCM	32.45 ± 8.42	15	34	48
N = 20	TBM	1.92 ± 2.89	0	0	8.4
	DBCM	1.26 ± 2.02	0	0	5.1
	BDCM	5.78 ± 3.89	0	3.9	14
	THMs	41.41 ± 14.85	15	40.4	73.6
2018	TCM	26.14 ± 5.4	18	26	34
N = 14	TBM	0	0	0	0
	DBCM	0	0	0	0
	BDCM	2.07 ± 1.63	0	2.9	3.7
	THMs	28.21 ± 6.88	18	28.9	37.7
2019	TCM	19.94 ± 13.65	0	22	37
N = 17	TBM	2.61 ± 5.64	0	0	20
	DBCM	0.62 ± 1.43	0	0	4.8
	BDCM	1.09 ± 1.56	0	0	4.2
	THMs	24.25 ± 10.61	4.5	24.8	41.2
2020	TCM	21.3 ± 12.67	0	22.5	40
N = 20	TBM	2.29 ± 4.44	0	0	15
	DBCM	1.87 ± 5.19	0	0	23
	BDCM	1.77 ± 2.05	0	1.3	7.4
	THMs	27.22 ± 9.58	6.5	28.5	46

TCM trichloromethane, *TBM* tribromomethane, *BDCM* bromodichloromethane, *DBCM* dibromochloromethane, *N* sample number

discrete, both in 2017 and 2020 peak values of 346 and 464 µg/l, respectively, were recorded (MS 2018, 2021). Whereas in the present study, much lower maximum peaks were recorded with values of 74.2 µg/l and 73.6 µg/l in 2016 and 2017, respectively.

Distribution of THMs According to City Districts

Throughout the study period, sampling was carried out in all 21 districts of Madrid (Fig. 1). Sampling was not homogeneous in all of them. The highest percentage of sampling was in district 3 with 12% of samples, followed by districts D1, D2, D4, D5, D10, D11 and D17 with between 5 and 10% of the total sampling. The frequency in the remaining districts was low (<5%).

**Fig. 2** Comparative annual evolution of THMs levels in tap water in Spain vs. the city of Madrid
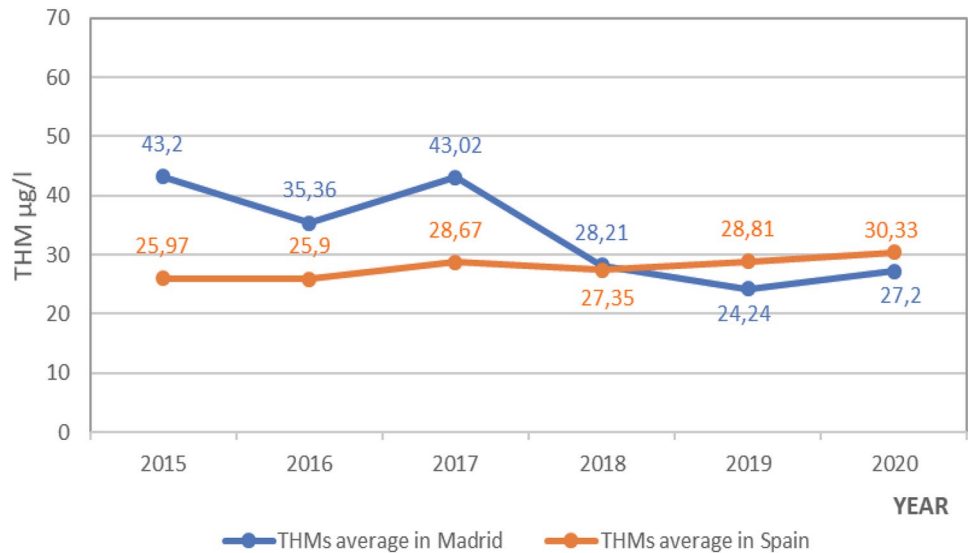
The highest level of THMs was detected in district D9 with mean values of 54.1 µg/l, whilst samples from district D2 had the lowest mean concentrations of 20.7 µg/l (Fig. 3). Within the THMs, TCM was the dominant structure, although very different ranges were found between 43.7 and 100% contribution depending on the district, as shown in Fig. 2, where districts D7, D9 and D14 had contributions close to 50% and in contrast districts 18 and 20 with 100% contribution. The districts with the highest TCM levels, above 30 µg/l, are D6, D12, D16, D17 and D21.

In the samples from districts D1-D4, D6-D8, D11 and D14 a decreasing order of magnitude sequence of the different species is observed: TCM > BDCM > TBM > DBCM. However, the THMs profile of the samples from districts D5, D9 and D10 was TCM > TBM > BDCM ≥ DBCM. In the samples from districts D12, D13, D15, D16, D 17, D19

and D21 neither TBM nor DBCM species were detected and in the samples from districts D18 and D20 no brominated species were quantified. On the other hand, the district D9, with the highest medium levels of the three brominated compounds (30.4 µg/l) are located above groundwater aquifers whose composition depends on the soil through which the water infiltrates and the presence of bromine which favours the formation of TBMs, BDCMs and DBCMs during the chlorination stage.

A comparison between the districts in the central area (D1-D7) and the periphery (D8-D21) showed a higher concentration of THMs in the central area (36.7 µg/l) compared to the levels in the other districts (31.5 µg/l), whose differences could be attributed to their different population densities. Thus, those located in the centre, with an average population density of 154,000 inhabitants, had the highest

Fig. 3 Levels of each species of THMs by sampling district
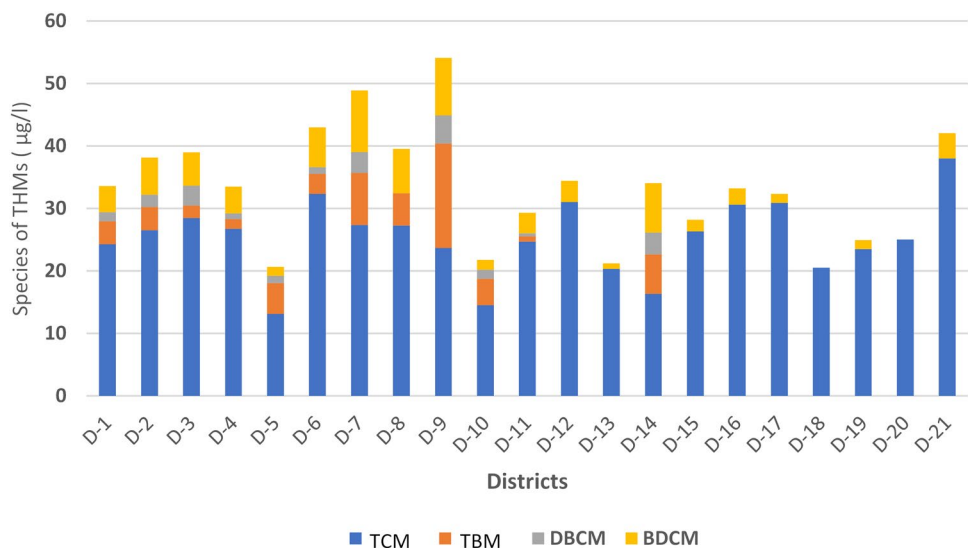
average THMs compared to the peripheral districts, with a higher population (around 200,000 inhabitants in D10, D11, D13, D15), whose average concentration was lower. The per capita water consumption in the most populated districts results in a shorter residence time of the water in the network and a lower formation of THMs. Exceptionally, the less populated district (D21) corresponding to Barajas with 50,010 inhabitants showed a higher average THMs (42 µg/l), possibly because it is a district in growth, with a more disaggregated population, with more extensive distribution networks and some still without netting with the consequent stagnation of water (INE 2020).

Analysis of THMs Concentration According to the Sampling Point

The results are shown in Fig. 4. In the study, most of the samples were taken at distribution network OSSs (83%), followed by fountains (5.6%), educational establishments (4.6%), public institutions (3.7%), sports centres (1.9%) and street public fountains (0.9%).

The results were uniform with mean values of THMs in the range of 30–40 µg/l. If a comparison is made between the values sampled in the OSSs and those from other sampling areas, no significant differences can be detected ($p \geq 0.05$).

In sports centres, an increase in THMs on tap was noted. This could be attributed to the fact that the indoor tanks in these facilities are located after the mains tap of the general supply network of CYII and are usually re-chlorinated, and on the other hand, the existence of long indoor distribution networks causes permanence and stagnation of water in these facilities.

Regarding the profile of the different species of THMs studied, in sport centres, TCM was the majority, but it only contributed 45.24% to the total THM value and both TBM and BDCM were very notable species with average levels

of 9 µg/l and a contribution of 21% to the totals THM. This could be because in periods of drought the general supply system of the CAM integrates, together with the use of surface water, groundwater, which is richer in bromine, as a source of supply, constituting a strategic resource for emergency situations and prolonged drought.

In the OSSs that constituted the bulk of the sampling, the contribution of the average TCM values to the total THMs was 74.6%, with BDCM standing out amongst the remaining compounds. Furthermore, within this sampling point, the highest maximum value of THMs (74.2 µg/l) was detected with respect to the other types.

The absence of TBM and DBCM was found in the samples from water connexions, schools and public institutions and therefore the highest contribution of TCM to THMs (92–100%).

Analysis of THMs According to Seasonality

In this study, sampling was carried out in the four seasons: spring, summer, autumn and winter. The highest volume of sampling occurred in autumn with 52.8% of the total samples, followed by winter with 25.9%, whilst the spring and summer seasons are less represented with sampling percentages of 11.1% and 10.2%, respectively.

As it is known, DBPs, including THMs, increase in concentration throughout the distribution network, since the residual disinfectant continues to react with organic matter over time and with greater emphasis in the hot seasons.

Brominated DBPs (DBCM) were found in higher concentrations in spring ($p > 0.05$), given the higher concentration of bromides present in this season, possibly attributable to the higher amount of organic materials due to the eutrophication of reservoirs with the consequent proliferation of algae, concurrent with the higher ambient temperature.

Fig. 4 Individual trihalomethanes (THMs) levels of as a function by sampling location
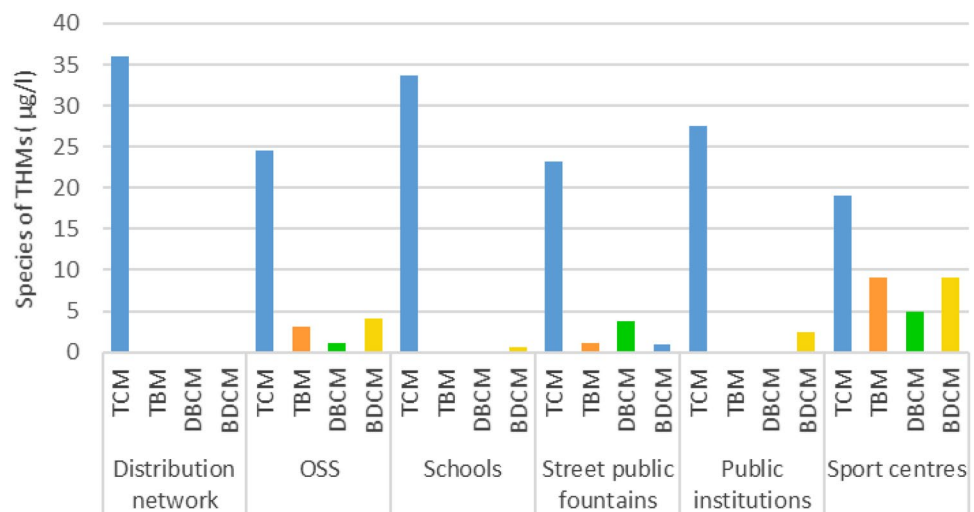
As it can be seen in Fig. 5, the highest mean values were detected in the winter and spring (41.25 µg/l and 39.56 µg/l, respectively) compared to those obtained during the autumn and summer periods (29.34 µg/l and 21.76 µg/l, respectively).

The main compound found was TCM, a similar trend is observed in the seasons. In the winter campaign the mean values were the highest (29.68 µg/l), whilst the summer sampling was notable for the lowest mean concentrations (16.27 µg/l).

THMs results reflect a weak but significant seasonal variability ($p < 0.05$), partly due to the low levels detected in most of the cases and partly due to the differences in the total volume of samples in the different seasons, especially lower in spring and summer. Although the low water level in summer should favour a higher rate of DBPs formation due to higher water temperature and higher chlorine dosage, in this case, the results indicate the opposite. This could be attributed to the high volatility of these compounds, since according to García-Villanova et al. (2010) at relatively high temperatures in the distribution network (20 °C), simple aeration of the water after chlorination is able to reduce the concentration of THMs.

Studies of seasonal variation of THMs in different Spanish cities show contradictory data. Freire et al. (2008) in a study carried out in the city of Granada found higher levels of THMs in the summer (0.01–31.87 µg/l) compared to those found in winter (0.14–18.75 µg/l), also highlighting the difference according to the origin of the water, with higher levels in surface water compared to groundwater. However, another study by Fraile et al. (2005) carried out in the period 2001–2003 in Navarra reported higher THMs values in winter. Jiménez-Restrepo et al. (2011) in their study

in 49 Spanish cities did not find that different climatic zones had any influence on THMs levels.

On the other hand, the studies by Villanueva et al. (2003, 2012) conclude that there is a clear increase in summer, due to the eutrophication of surface water supply reservoirs and therefore to the increase in re-chlorination to avoid this problem, with the consequence of a proportional increase in chlorinated by-products, especially THMs.

The studies by Hernández Sánchez et al. (2011) compile bibliographic information on THMs in drinking water from different areas and countries in the world: America, China, Greece, Turkey and Spain, including the comparative seasonal variation. In this research Spanish samples show levels ranging from > 90 µg/l in spring to 70–75 µg/l in summer, autumn and winter, the values were higher than in other countries, except for Greece which exceeds the limit of the level 100 µg/l.

Existing literature on THMs in different countries reveals the high incidence of these DBPs in drinking water distribution systems with highly variable percentages that vary widely between different seasons and according to the place of origin of sampling. Golfinopoulos (2000), in research carried out in Greece, highlights higher levels of THMs in summer-autumn compared to spring-winter.

Regarding the American continent, in Canada Chowdhury (2013) and Guilherme and Rodriguez (2014) detected higher THMs values in the summer months compared to the winter months, all of them within the legal limits set by each province, below 80 or 100 µg/l of THMs. Rodriguez et al. (2003) comparing THMs levels in Quebec in the winter and summer seasons, observed concentrations 2.5 to 5 times higher in the summer season. Serodes et al. (2003) in the same city found a higher proportion of these by-products in

Fig. 5 Individual trihalomethanes (THMs) levels by seasonality
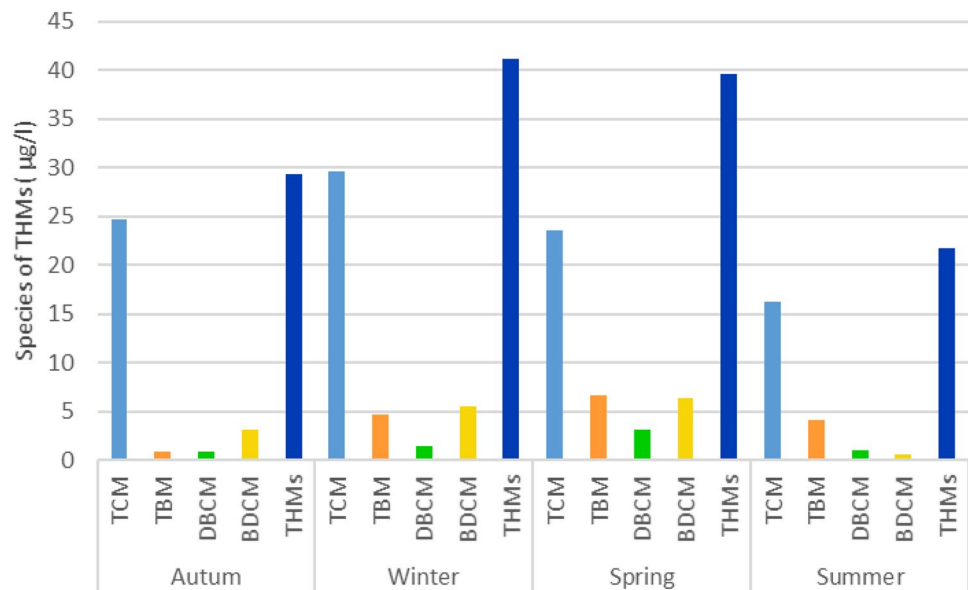
spring and this is in accordance with the research by Mosaferi et al. (2021) in Iranian waters, who found higher levels in the spring season than in the autumn. The studies Ahmed et al. (2019) in Bangladesh agree on the high concentrations detected in tap water, higher in summer.

It is clear from all these studies that there is enormous variability and that no single pattern of behaviour can be established based on this criterion alone.

Estimation of the Risk of Exposure to THMs

The risk assessment associated with the presence of contaminants in tap water is of great importance due to the high proportion of its intake to cover the water needs of the population. Madrid is the region with the lowest domestic consumption of bottled water, which makes the risk assessment of THMs in tap water even more relevant in the Madrid population (Díaz-Olalla et al. 2020).

In relation to THMs, as indicated above, two types of effects associated with this exposure have been demonstrated: carcinogenic effects that increase various types of cancer, mainly bladder cancer and colon cancer (Villanueva et al. 2017; Helte et al. 2022) and non-carcinogenic effects, including reproductive disorders and liver disorders and damage to the liver, kidneys and central nervous system amongst other toxic actions (Jeong et al. 2012; Villanueva et al. 2015; Summerhayes et al. 2021).

In this study, two critical effect endpoints were calculated: carcinogenic risk (CR) and non-carcinogenic risk (NCR) from tap water consumption by the population of Madrid. The exposure risk has been estimated considering the adult population, since the aim is to assess the risk of chronic exposure over the years. The DI calculation was estimated for average consumers (P50) and for high consumers (P95) and the samples were divided into 7 THMs concentration ranges between < 2.5 μg/l and 50–75 μg/l.

Table 5 shows the mean concentration of total THMs expressed in μg/l in the 7 ranges we have established, from 2.5 to 10 μg/l, up to the maximum range found of > 60–75 μg/l. The highest number of samples was found between the levels 30 and 40 μg/l (Table 2).

Carcinogenic Risk (CR)

The cancer risk has been estimated considering only the route of direct ingestion via the water supply, which is the most relevant. However, it is known that THMs can also enter the body, although to a lesser extent, via other potential routes, such as inhalation (showers) or dermal (bathing). According to the data found in the literature, ingestion would account for up to 80% compared to the other routes of exposure (Amjad et al. 2013).

Table 5 Distribution of samples according to concentration ranges of THMs species

THMs μg/l	Mean values (μg/l)				
	TCM	TBM	DBCM	BDCM	THMs
2.5–10	0.00	6.27	0.90	0.00	7.00
> 10 < 20	11.46	3.54	1.12	0.40	16.52
> 20–30	21.29	0.91	0.17	2.13	24.55
> 30–40	30.18	0.88	0.45	3.36	34.92
> 40–50	29.06	5.24	3.39	6.98	44.76
> 50–60	33.17	6.62	3.23	9.80	57.68
> 60–75	38.00	13.67	5.10	12.67	69.50

TCM trichloromethane, *TBM* tribromomethane, *BDCM* bromodichloromethane, *DBCM* dibromochloromethane

Amongst the different THMs, TCM has been reported to be the main THM causing cancer risk through both oral and dermal route of exposure, whilst in the case of inhalation it is mainly due to BDCM (EPA 2005).

The total cancer risk (TCR) for each rank has been obtained by summing the individual risk estimate for each of the four species (Table 6).

According to the results shown in the table, samples with THMs values in the range 2.5–10 μg/l had risk indexes in the order of 10^{-6} for both medium and high consumers, whilst ranges from > 10 to 50 μg/l reflect total cancer risk indexes in the order of 10^{-5} for both types of consumers, so that the values can be considered acceptable. Only in the total cancer risk assessment, the rates for high tap water consumers with total THM concentrations between 50 and 75 μg/l reach values in the order of 10^{-4} (0.98×10^{-4} and 1.2×10^{-4}) and a probable additional carcinogenic risk for the population could not be excluded. However, water samples in these ranges > 50 μg/l account for a low percentage of the total samples (8.34%).

Our estimate is in line with the three European case–control studies (France, Finland and Spain) carried out by Costet et al. (2011) that suggested a 47% increased likelihood of bladder cancer in men exposed to chlorination by-products corresponding to THMs concentrations above 50 μg/l.

In the estimation of the individual risk of each of the four THMs species, TCM was the one with the highest contribution to the total risk, followed by DBCM but always the cancer risk indices were in order of 10^{-6} or 10^{-5} and can be considered acceptable.

Non-carcinogenic Risk

The results of this non-carcinogenic risk characterisation shown in Table 7 would indicate that there is no potential risk of suffering any adverse effects from the ingestion of

Table 6 Carcinogenic risk ($\times 10^{-4}$) based on levels of THMs species in drinking water for adult population (medium and high consumer)

Carcinogenic risk ($\times 10^{-4}$)										
THMs µg/l	TCM		TBM		DBCM		BDCM		THMs	
	Medium	High	Medium	High	Medium	High	Medium	High	Medium	High
2.5–10	0.000	0.000	0.013	0.025	0.021	0.038	0.000	0.000	0.034	0.063
> 10 < 20	0.096	0.178	0.008	0.014	0.026	0.047	0.007	0.012	0.136	0.251
> 20–30	0.179	0.330	0.002	0.004	0.004	0.007	0.036	0.066	0.221	0.407
> 30–40	0.254	0.468	0.002	0.003	0.010	0.019	0.056	0.104	0.323	0.594
> 40–50	0.244	0.450	0.011	0.021	0.077	0.143	0.118	0.216	0.451	0.830
> 50–60	0.279	0.514	0.014	0.026	0.074	0.136	0.165	0.304	0.532	0.980
> 60–75	0.320	0.589	0.029	0.054	0.116	0.214	0.213	0.393	0.678	1.250

TCM trichloromethane, *TBM* tribromomethane, *BDCM* bromodichloromethane, *DBCM* dibromochloromethane

Table 7 Medium and high non-carcinogenic risk based on levels of THMs species in drinking water for adult population (medium and high consumer)

Non-carcinogenic risk										
THMs µg/l	TCM		TBM		DBCM		BDCM		THMs	
	Medium	High	Medium	High	Medium	High	Medium	High	Medium	High
2.5–10	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.01	0.02
> 10 < 20	0.03	0.06	0.00	0.01	0.00	0.00	0.00	0.00	0.04	0.07
> 20–30	0.06	0.11	0.00	0.00	0.00	0.00	0.00	0.01	0.06	0.11
> 30–40	0.08	0.15	0.00	0.00	0.00	0.00	0.00	0.01	0.09	0.16
> 40–50	0.07	0.15	0.01	0.01	0.00	0.01	0.01	0.02	0.10	0.18
> 50–60	0.09	0.17	0.01	0.02	0.00	0.01	0.01	0.02	0.12	0.21
> 60–75	0.10	0.19	0.02	0.03	0.01	0.01	0.02	0.03	0.15	0.27

TCM trichloromethane, *TBM* tribromomethane, *BDCM* bromodichloromethane, *DBCM* dibromochloromethane

tap water by the population of Madrid, since all the hazard quotients (HQ) that have been calculated are below unity.

Strategies to Reduce the Levels of THMs in Drinking Water

None of the samples in this study exceeded the VP of 100 µg/l established in the current legislation. However, as THMs are potentially carcinogenic compounds, strategies leading to their reduction or ideally their absence in tap water should be promoted without compromising the microbiological safety of the water by disinfection with chlorinated compounds.

The current levels of THMs have been reduced from the annual period 2015–17 to the period 2018–20 due to the improvements that have been applied in the treatment stages of pre-oxidation, coagulation-flocculation and filtration, disinfection and water distribution. Thus, in the pre-oxidation phase, most of the NOM has been removed from the water by ceasing chlorination at source (pre-chlorination) and using alternative oxidants to chlorine, such as ozone.

In the disinfection stage, the application of monochloramines is the treatment of choice in the disinfection of

drinking water in Madrid, which leads to a decrease in the formation of THMs. In addition, innovative studies are being carried out by the CYII that are reflected in the Strategic Plan 2018–2030 and include the modernisation of sustainable treatment technologies, reverse osmosis, UV radiation, ion exchange resins and others aimed at reducing THMs in Madrid's water (CYII 2018).

In the distribution network, due to its extension, it is necessary to carry out re-colorations, although the doses of chlorine have been optimised to maintain the residual chlorine at optimum levels with a minimum formation of SPD. In this way, current legislation regulates the maximum concentration of residual combined chlorine, which cannot exceed 2.0 mg/l, nor that of residual free chlorine > 1 mg/l (RD 3/2023). Regarding chloramines, no limit is set, although the WHO in the 2017 Guidelines recommends a maximum concentration of 3 mg/l in water.

In relation to the structure of distribution networks, although in Madrid there is a high percentage of meshed networks, it would be advisable to increase their percentage in the city as they generate fewer THMs than non-meshed networks, especially in the expansion areas and new urbanisations in the growing districts. If this is not

feasible, it is advisable to use specific filters in the connections, capable of retaining the organic matter that could penetrate the interior installation, which is already being applied in public buildings in Madrid.

In the domestic sphere, heating to boiling for a few minutes could be recommended to the population, which according to Krasner and Wright (2005), can cause the removal of between 68 and 98% of the total THMs, or also the application of domestic filters, which could reduce them by 43% or in the case of the application of active carbon filters up to 99% (Hernández Sánchez et al. 2011).

Conclusions

The concentrations of THMs detected in all samples were in accordance with the current legal limit. Chloroform was the compound with the highest contribution to the sum of THMs. A decreasing trend in THMs concentrations was observed over the years of the study related to the removal of NOM and the use of chloramines in the disinfection of water in Madrid. THMs levels were higher in the central area than in the peripheral districts and the lowest concentrations were detected in summer.

The results of the non-carcinogenic risk characterisation indicate that there is no potential risk from drinking tap water for Madrid adult population. Concerning the carcinogenic risk, only water samples with THMs concentrations between 50 and 75 µg/l could constitute a risk for high consumers.

Based on the results of this study it is confirmed that the Madrid tap water treatment strategy is positive for the control of THMs levels. Therefore, this strategy should be maintained in the future. On the other hand, as exposure to THMs can be increased by dermal or inhalation routes, it would be advisable to carry out future work to assess these routes of exposure.

Declarations

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