Occurrence of DBPs in Drinking Water of European Regions for Epidemiology Studies

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A three-year study was conducted on the occurrence of disinfection by-products (DBPs)—trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles—in drinking water of regions of Europe where epidemiology studies were being carried out. Thirteen systems in six countries (i.e., Italy, France, Greece, Lithuania, Spain, United Kingdom) were sampled. Typically chlorinated DBPs dominated. However, in most of Catalonia (Spain) and in Heraklion (Greece), brominated DBPs dominated. The degree of bromine incorporation into the DBP classes was in general similar among them. This is important, as brominated DBPs are a greater health concern. In parts of Catalonia, the reported levels of tribromoacetic acid were higher than in other parts of the world. In some regions, the levels of HAAs tended to be peaked in concentration in a different time period than when the levels of THMs peaked. In most epidemiology studies, THMs are used as a surrogate for other halogenated DBPs. This study provides exposure assessment information for epidemiology studies.

Keywords: disinfection by-products, drinking water, haloacetonitriles, occurrence, speciation

Water disinfection is one of the most important health advances, as millions of people worldwide receive quality drinking water every day from water systems (Calderon 2000). Chlorine, chloramines, chlorine dioxide, ozone, and ultraviolet irradiation are the most common disinfectants in use today; each produces its own suite of disinfection by-products (DBPs) in drinking water, with overlapping constituents, many of which are a health concern (Richardson et al. 2007).

A number of parameters during treatment and in distribution affect DBP concentrations in drinking water. Factors affecting DBP production in water include bromide content and the type and quantity of the natural organic matter (Krasner et al. 1996). During treatment, factors that affect the type and levels of DBPs formed include the treatment practices used, the water pH and temperature, the type and dose of disinfectants used, and the point in the treatment process at which the disinfectant is added (Krasner 2001). These all can have major effects on the formation of different DBP classes and their levels (Krasner et al. 2006, Richardson 2003).

DBP classes include trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones, halonitromethanes, haloamides, halogenated furanones, and nonhalogenated carbonyls; to date more than 600 DBPs have been reported in the literature for the major disinfectants used (Richardson et al. 2000, Richardson 1998). In the United States, extensive surveys have been carried out to assess the occurrence of a wide range of DBPs
In Europe, along with THMs, some HAAs have been investigated in finished drinking water (Malliarou et al. 2005, Villanueva et al. 2003, Palacios et al. 2000, Dojlido et al. 1999). Relatively few studies have been conducted in Europe on the occurrence of the nine HAAs and/or other haloegenated DBPs (e.g., haloacetonitriles, haloacetones, chloral hydrate, chloropicrin) in drinking water (Goslan et al. 2014, 2009; Jeong et al. 2012, Golfinopoulos & Nikolau 2005). For example, Palacios et al. (2000) found that THMs were the most abundant organohalogenated compounds present in treated drinking water, where current levels at study sites were below established guideline values.

THMs and HAAs are the DBP classes that have been intensively investigated. However, many studies in the United States measured only five of the nine HAAs, as four of the bromine-containing species are not regulated in the United States (McGuire et al. 2002). THMs and HAAs contribute to ~50–75% of the total haloegenated DBPs measured and only ~25–50% of the total organic halides measured (Krasner et al. 2006, 1989). Chloramines produce lower levels of THMs and trihalogenated HAAs (TXAAs) but may not adequately minimize the formation of dihalogenated HAAs (DXAAs) (Hong et al. 2007). Disinfection of waters high in bromide can form more brominated compounds, including THMs, HAAs, and other DBPs (Krasner et al. 2006).

Epidemiological studies have focused on the possible association between exposure to DBPs (typically based on total THMs) in chlorinated water and the incidence of human cancer (Rahman et al. 2010; Villanueva et al. 2007, 2004; Koivusalo et al. 1997; King & Marrett 1996) and potential adverse reproductive and developmental effects such as low birth weight, intrauterine growth retardation, and spontaneous abortion (Grellier et al. 2010, Savitz et al. 2005, Nieuwenhuijsen et al. 2000). Increased risk of various congenital anomalies has been reported to be associated with THM exposure in the water supply (Nieuwenhuijsen et al. 2008, Savitz et al. 1995). Recently Cantor et al. (2010) examined polymorphisms, DBPs, and the risk of bladder cancer in Spain. The results of this study strengthened the hypothesis that DBPs cause bladder cancer and suggested possible mechanisms, as well as the classes of compounds (e.g., bromine-containing DBPs) that were likely to be implicated.

Likewise, bromine-containing DBPs are believed to be of a higher health concern than the chlorine-containing analogues based on toxicology research (Plewia & Wagner 2009). Moreover, certain nitrogenous DBPs (e.g., HANs) are considered more cytotoxic and genotoxic than the regulated THMs and HAAs (Muellner et al. 2007), although nitrogenous DBPs are rarely examined in epidemiology studies.

In 2006, the European Commission established HIWATE (Health Impacts of Long-Term Exposure to Disinfection By-products in Drinking Water), a project to investigate potential human health risks associated with long-term exposure to DBPs (Nieuwenhuijsen et al. 2009). A three-year study (2007–2009) was conducted on the occurrence and speciation of DBPs in drinking water of different regions of Europe (in selected cities in Italy, France, Greece, Lithuania, Spain, and the United Kingdom). In many of the European regions selected, studies on the historical occurrence and levels of DBPs were limited. Moreover, these regions were selected because epidemiological studies were being conducted in each region to investigate potential human health risks associated with DBPs in water (Nieuwenhuijsen et al. 2009).

DBPs determined in this study included THMs, HANs, and HAAs. Note that because HAAs are not regulated in Europe, the occurrence of this class of DBPs is quite limited in most European countries (e.g., Toledano et al. 2005). Moreover, the occurrence of HANs in European drinking water has been rarely studied (e.g., Goslan et al. 2009). In the past, many epidemiology studies focused on the association between an adverse health effect and total THMs, sometimes considering bromine speciation. The aim of this study was to provide data on the occurrence (temporal and spatial variability) of THMs, HAAs, and HANs (including bromine-containing species), and to examine to what extent total THMs or individual THMs were surrogates for other DBPs. These data will provide exposure assessment information for epidemiology studies.

**EXPERIMENTAL SECTION**

**Sample sites and sample collection.** Drinking water samples (N) were collected from the distribution systems of 13 waterworks, which were in six countries: Northern Italy (147), France (64), Greece (108), Lithuania (85), Spain (322), and the United Kingdom (234) (Table 1). Five regions in Spain and four regions in the United Kingdom were studied, whereas for all of the other countries (except Italy) only one region was examined in each. Three regions in Northern Italy (i.e., Emilia–Romagna, Lombardia, Friuli) were studied. All together, the study sites represented a range of water qualities, treatment/disinfection practices, and DBP formation. In some of the European regions (e.g., Catalonia, Spain; Heraklion, Greece), the bromide content of the raw water was high (Table 2 or inferred from bromine incorporation into the DBPs in Table 3). Note that raw water bromide data were not available for many locations, as bromide was often sampled in the tap water, where chlorine would have transformed some of it to hypobromous acid. Nonetheless, the chlorine residuals in these study sites were in general quite low, so that the amount of bromide in the tap water was indicative of what was present in the raw water. Most of the plants in this study had conventional treatment and disinfection processes (e.g., coagulation, filtration, chlorination), whereas some also used granular activated carbon (GAC) adsorption and/or ozonation. Note that conventional treatment and GAC do not remove bromide (Summers et al. 1993). The water sources included surface water, groundwater, and/or blends of these two water types.

The sampling campaign was carried out over a three-year period (2007–2009), covering all seasons in most regions. Temperature, free chlorine residual, and pH were measured during sample collection. DBP samples were taken at different points of the distribution networks after treatment and final disinfection. Distribution system locations were selected to provide some indication of DBP exposure. For THM samples, ammonium chloride was added to the vials before sampling to eliminate any residual chlorine and additional formation of THMs. For HAN samples, a phosphate buffer (lowering the pH
to ~5.5) was added to inhibit base-catalyzed hydrolysis. For HAA samples, water samples were taken in vials that contained ammonium chloride. Samples were sent to the University of the Aegean in Greece, and care was taken to keep temperature ≤10°C during shipment. When sample deliveries were delayed, some samples were warm (>10°C). In such cases, THMs were not analyzed because of the potential loss of the more volatile DBPs. All samples were kept at 4°C until analysis, which was carried out within 14 days after sampling.

**DBP analysis.** Four THMs and four HANs were extracted and analyzed by gas chromatography with micro electron capture detection (GC-µECD) using a modification of US Environmental Protection Agency (USEPA) Method 551.1 (Nikolaou et al. 2005). This method included chloral hydrate and chloropicrin. However, there are nine haloacetaldehydes and nine halonitromethanes, so interpretation of the data for the latter two DBPs were not evaluated in this article because the brominated and dihalogenated analogues were not measured. On the other hand, the nine HAAs were derivatized and measured with GC-µECD using a modification of USEPA Method 552.3 (Nikolaou et al. 2005), so the impact of bromide on HAA formation could be addressed in this article. The limit of detection for each DBP analyzed was typically <1 µg/L. Over the study period, trichloroacetonitrile values were below the detection limit. Note that among the HAAs analyzed, monochloroacetic acid (MCAA) samples indicated interference problems; thus, MCAA was not reported. In other studies, the concentration of MCAA was substantially lower than that of the DXAAs or TXAAs (McGuire et al. 2002). Water quality parameters (total organic carbon [TOC], bromide, pH, temperature, residual chlorine) were measured by each of the

**TABLE 1**

<table>
<thead>
<tr>
<th>Waterworks Identification</th>
<th>Source</th>
<th>Treatment</th>
<th>Disinfectant</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spain</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalonia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>System 1</td>
<td>Surface and boreholes</td>
<td>Coagulation, sedimentation, filtration (granular media), GAC filtration</td>
<td>Ozone, chlorine dioxide, chlorine</td>
</tr>
<tr>
<td>System 2</td>
<td>Surface water</td>
<td>Coagulation, sedimentation, filtration (granular media), GAC filtration</td>
<td>Chlorine dioxide and chlorine</td>
</tr>
<tr>
<td>System 3</td>
<td>Surface water</td>
<td>Coagulation, sedimentation, filtration (granular media), GAC filtration</td>
<td>Chlorine dioxide and chlorine</td>
</tr>
<tr>
<td>System 4&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Surface water</td>
<td>Coagulation, sedimentation, filtration (granular media), GAC filtration</td>
<td>Chlorine dioxide and chlorine</td>
</tr>
<tr>
<td>Asturias</td>
<td>Surface water</td>
<td>Filtration</td>
<td>Chlorine</td>
</tr>
<tr>
<td>Basque Country</td>
<td>Surface water</td>
<td>Coagulation, sedimentation, filtration</td>
<td>Ozone and chlorine</td>
</tr>
<tr>
<td>Granada</td>
<td>Groundwater</td>
<td>Filtration</td>
<td>Chlorine</td>
</tr>
<tr>
<td>Valencia</td>
<td>Surface water (97%)</td>
<td>Coagulation, sedimentation, filtration</td>
<td>Ozone and chlorine</td>
</tr>
<tr>
<td></td>
<td>and groundwater</td>
<td>No treatment</td>
<td>Chlorine</td>
</tr>
<tr>
<td></td>
<td>Groundwater</td>
<td>No treatment</td>
<td>Chlorine</td>
</tr>
<tr>
<td><strong>United Kingdom</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bedford</td>
<td>Groundwater</td>
<td>Filtration</td>
<td>Chlorine</td>
</tr>
<tr>
<td>Bradford</td>
<td>Upland surface</td>
<td>Coagulation, sedimentation, filtration</td>
<td>Chlorine</td>
</tr>
<tr>
<td>Manchester</td>
<td>Upland surface</td>
<td>Coagulation, sedimentation, filtration</td>
<td>Chlorine</td>
</tr>
<tr>
<td>Nottingham</td>
<td>Lowland surface</td>
<td>Coagulation, sedimentation, filtration (granular media), GAC filtration</td>
<td>Chlorine</td>
</tr>
<tr>
<td>Rennes (France)</td>
<td>4% artificially recharged groundwater and 96% surface water</td>
<td>Coagulation, sedimentation, filtration (granular media), GAC</td>
<td>Ozone and chlorine</td>
</tr>
<tr>
<td>KAU1</td>
<td>Groundwater</td>
<td>Filtration</td>
<td>Chlorine</td>
</tr>
<tr>
<td>KAU2</td>
<td>Groundwater</td>
<td>No treatment</td>
<td>Chlorine</td>
</tr>
<tr>
<td>KAU3</td>
<td>Groundwater</td>
<td>No treatment</td>
<td>Chlorine</td>
</tr>
<tr>
<td>KAU4</td>
<td>Groundwater</td>
<td>No treatment</td>
<td>Chlorine</td>
</tr>
<tr>
<td>Heraklion (Greece)</td>
<td>Groundwater</td>
<td>No treatment</td>
<td>Chlorine</td>
</tr>
<tr>
<td>Northern Italy (three regions)</td>
<td>Groundwater or mixed</td>
<td>No treatment/filtration and GAC</td>
<td>Chlorine dioxide and chlorine</td>
</tr>
</tbody>
</table>

GAC—granular activated carbon

<sup>a</sup>System 4 receives water from systems 2 and 3.
local water companies (Table 2) using standard methods (e.g., 

**Statistical analysis.** Nonparametric statistics were used. In 
summarizing DBP occurrence (in a table), the range was reported 
as the 10th to 90th percentile so as to not include extreme outliers. 
Median values were also included. Seasonal and year-to-year 
variation in DBP occurrence was shown in figures (5–8, which will 
be discussed later in this article) with box-and-whisker plots. The 
box corresponds to the interquartile range (25th to 75th percentile), 
the line inside the box is the median, the whiskers are the 90th and 
10th percentiles, and points outside the whiskers are outliers.

**RESULTS AND DISCUSSION**

**Water quality.** The different waters studied represented a range 
of water qualities (TOC, bromide) (Table 2). In Catalonia and 
Asturias (Spain), the waterworks treated mainly surface water, 
whereas Basque Country, Granada, and Valencia (Spain) treated 
surface and groundwater (Table 1). In Catalonia, system 1 
downstream) and system 3 (upstream) both served some 
portion of Barcelona. The systems treated water mainly from 
the Llogregat River with high bromide content (≥0.9 mg/L) (GE 
2010) and moderately high TOC (≥4 mg/L). For system 1, the 
waterworks blended surface and borehole water (up to 40%) 
whenever surface water quality was poor. This river runs through a densely urbanized area and receives industrial 
wastewaters and surface runoff from agricultural areas, whereas 
high levels of bromide were reported as a result of salt mine 
activities (Huerta-Fontela et al. 2008; Kuster et al. 2008). System 
2, supplying water to some portions of Barcelona, treated water 
from the Ter River with a lower TOC content and no bromide 
content, whereas system 4 (Sabadell) received a blend of water 
from both systems 2 and 3.

<table>
<thead>
<tr>
<th>TABLE 2</th>
<th>Characteristics of water quality of raw water and drinking water (10th–90th percentile, median) in the studied regions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waterworks Identification</td>
<td>Raw Water</td>
</tr>
<tr>
<td></td>
<td>TOC mg/L</td>
</tr>
<tr>
<td>Spain</td>
<td></td>
</tr>
<tr>
<td>Catalonia</td>
<td></td>
</tr>
<tr>
<td>System 1</td>
<td>Surface &gt; 5</td>
</tr>
<tr>
<td></td>
<td>Borehole &lt; 2</td>
</tr>
<tr>
<td>System 2</td>
<td>-3</td>
</tr>
<tr>
<td>System 3</td>
<td>-4</td>
</tr>
<tr>
<td>System 4</td>
<td>(a)</td>
</tr>
<tr>
<td>Asturias</td>
<td>NA</td>
</tr>
<tr>
<td>Basque Country</td>
<td>0.4–2.3 (1.6)</td>
</tr>
<tr>
<td>Granada</td>
<td>Surface water &lt; 0.1</td>
</tr>
<tr>
<td></td>
<td>Groundwater (NA)</td>
</tr>
<tr>
<td>Valencia</td>
<td>Surface water &lt; 0.1</td>
</tr>
<tr>
<td></td>
<td>Groundwater (NA)</td>
</tr>
<tr>
<td>United Kingdom</td>
<td></td>
</tr>
<tr>
<td>Bedford</td>
<td>10</td>
</tr>
<tr>
<td>Bradford</td>
<td>NA</td>
</tr>
<tr>
<td>Nottingham</td>
<td>9.0</td>
</tr>
<tr>
<td>Manchester</td>
<td>14</td>
</tr>
<tr>
<td>Rennes (France)</td>
<td>1.7–2.6 (2.1)</td>
</tr>
<tr>
<td>Kaunas (Lithuania)</td>
<td></td>
</tr>
<tr>
<td>KAU1</td>
<td>2.3–3.2 (3.1)</td>
</tr>
<tr>
<td>KAU2</td>
<td>2.3–3.2 (3.1)</td>
</tr>
<tr>
<td>KAU3</td>
<td>2.3–3.2 (3.1)</td>
</tr>
<tr>
<td>KAU4</td>
<td>2.3–3.2 (3.1)</td>
</tr>
<tr>
<td>Heraklion (Crete, Greece)</td>
<td>NA</td>
</tr>
<tr>
<td>Northern Italy (three regions)</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

Br⁻—bromide, NA—data not available, TOC—total organic carbon
(a) System 4 treats a blend of water from systems 2 and 3.
Surface and groundwater plants in three of the studied regions of the United Kingdom had high levels of treated water TOC (medians of 5.6–7.5 mg/L), whereas Bradford had a low level (median = 1.6 mg/L). Bromide was low in three of the UK tap waters (90th percentiles = 0.02–0.06 mg/L), whereas it was sometimes high in Bedford tap water (median = 0.04 mg/L, 90th percentile = 0.51 mg/L). In Rennes (France), surface water blended with a small portion of artificially recharged groundwater was used, where the TOC was low (median = 1.7 mg/L). For all other regions studied—Kaunas, Lithuania; Heraklion, Greece; and Northern Italy—groundwater was used (or mixed in part of Northern Italy); however, the Bedford and Kaunas TOC were not that low for groundwater (10 mg/L and a median of 3.1 mg/L, respectively). In many European countries, low disinfectant doses were applied, which often resulted in low residuals in the distribution system (Table 2).

Overview of THM occurrence and associated epidemiology studies.

The occurrence and speciation of THMs in these finished drinking waters presented substantial differences between regions (Table 3). The median sum of the four regulated THMs (THM4) was the highest in Catalonia (77 µg/L), followed by Rennes (44 µg/L), Asturias (32 µg/L), Bradford (30 µg/L), and Manchester, U.K. (29 µg/L). The lowest THM occurrence (medians ≤20 µg/L) was in three other regions of Spain (the Basque Country, Granada, and Valencia), two other regions of the United Kingdom (Nottingham, Bedford), and in the studied regions of Kaunas, Heraklion, and Northern Italy.

In one epidemiology study from this project (Kogevinas et al. 2016), the association between exposure to THMs during pregnancy and birth outcomes in a European cohort study was conducted. Average levels of THMs in the study sites in France, Greece, Lithuania, Spain, and the United Kingdom ranged from around 10 µg/L to above the regulatory limit in the European Union of 100 µg/L. In this large European study, there was no association between birth outcomes and THM exposures (with total THMs or specific THM species) during pregnancy in the total population or in potentially genetically susceptible subgroups.

In Grazuleviciene et al. (2011), the relationship between internal dose of THMs and birth outcomes in Kaunas (Lithuania) was evaluated. The THM internal dose in pregnancy varied substantially across individuals (ranging from 0.0025 to 2.40 µg/day in this study), which depended on both water THM levels and water use habits. This study showed that internal dose may affect fetal growth. The reported epidemiology studies from this project to date investigated the association between total THMs and health

### Table 3

<table>
<thead>
<tr>
<th>Country</th>
<th>Spain</th>
<th>United Kingdom</th>
<th>France</th>
<th>Lithuania</th>
<th>Greece</th>
<th>Northern Italy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Asturias</td>
<td>Basque Country</td>
<td>Catalonia</td>
<td>Granada</td>
<td>Valencia</td>
<td>Bedford</td>
</tr>
<tr>
<td>(N)</td>
<td>30</td>
<td>39</td>
<td>147</td>
<td>30</td>
<td>76</td>
<td>36</td>
</tr>
<tr>
<td>THM4—µg/L</td>
<td>15–62</td>
<td>1.0–33</td>
<td>22–197</td>
<td>0.2–19</td>
<td>11</td>
<td>ND–72</td>
</tr>
<tr>
<td>THM/THM4—%</td>
<td>(76%)</td>
<td>(56%)</td>
<td>(44%)</td>
<td>(60%)</td>
<td>(38%)</td>
<td>(a)</td>
</tr>
<tr>
<td>DBAA—µg/L</td>
<td>5.1–42</td>
<td>(17)</td>
<td>1.0–7.6</td>
<td>2.4–27</td>
<td>(14)</td>
<td>2.9</td>
</tr>
<tr>
<td>TXAA—µg/L</td>
<td>14–48</td>
<td>(20)</td>
<td>1.3–8.1</td>
<td>5.9–36</td>
<td>(20)</td>
<td>3.2</td>
</tr>
<tr>
<td>HANs—µg/L</td>
<td>3.9–75</td>
<td>(5.7)</td>
<td>ND–4.0</td>
<td>ND–2.5</td>
<td>ND–2.6</td>
<td>NA</td>
</tr>
<tr>
<td>HAN/HANs—%</td>
<td>(HANs—%)</td>
<td>(DCAN—HANs)</td>
<td>(DCAN—HANs)</td>
<td>(DCAN—HANs)</td>
<td>(DCAN—HANs)</td>
<td>(DCAN—HANs)</td>
</tr>
</tbody>
</table>

NA—data not available; BDCM—bromodichloromethane, DBCM—dibromochloromethane, DBAA—dibromoacetic acid, DBAN—dibromonitrogenitile, DCAN—dichloroacetic acid, DCAA—dichloroacetate, DCAA—dichloroacetic acid, DXAA—dihaloacetic acid, DXAA—dihaloacetic acid, TXAA—trihalogenated acetic acid, TXAA—trihalogenated acetic acid, TXAAs—sum of trihalogenated acetic acids, HAN—haloacetic acid, HAN—sum of haloacetic acids, ND—not detected, TBAA—tribromoacetic acid, TBM—bromofrom, TCAA—trichloroacetic acid, TCM—chloroform, THM—trihalomethane, THM—sum of four THMs, TXAA—trihalogenated acetic acid, TXAAs—sum of trihalogenated acetic acids

(a)—ratio not applicable due to low values of analytes (<5 µg/L)
(b)—values correspond to BCAN and DBAN
effects. However, future studies will investigate the potential association between identified DBPs and epidemiology across the HWATE program.

**DBP formation in groundwaters.** DBP levels were the lowest or not detected in Northern Italy, Heraklion, Kaunas, and Bedford. Most groundwater plants typically produced very low amounts of DBPs as a result of the presence of low levels of DBP precursors. For example, in most of the regions studied in Northern Italy where the HWATE epidemiological studies were conducted, the drinking water was usually of high quality, was mostly groundwater, and low disinfectant doses were used; therefore, DBP formation was limited. Moreover, chlorine dioxide was usually adopted as the main disinfectant in the largest water distribution systems. The main DBP species in these regions were related to chlorinated medium—i.e., chlorite (median, 75th percentile, 90th percentile, and maximum were 0, 67, 119, and 523 µg/L, respectively) and chlorate (median, 75th percentile, 90th percentile, and maximum were 11, 23, 44, and 399 µg/L, respectively). In addition, bromate was sometimes detected (90th percentile was 0; when detected, the median and maximum were 4 and 14 µg/L, respectively). However, some groundwaters with substantial amounts of bromide, such as in Heraklion, were extracted from aquifers in nearby coastal areas. TOC was low (median = 0.5 mg/L; 90th percentile = 0.8 mg/L), whereas bromide was often high (median = 0.8 mg/L; 90th percentile = 3.5 mg/L), which suggests intrusion of seawater into these karstic aquifers (Kampioti & Stephanou 2002). Nonetheless, DBP formation was generally low (90th percentile THM4 = 5 µg/L).

Higher levels of THMs (median = 25 µg/L; 90th percentile = 32 µg/L) were produced in groundwater samples collected from the distribution network supplied by one waterworks in Kaunas (KAU1), whereas low THM levels (median = 1.1 µg/L; 90th percentile = 3.2 µg/L) were produced by the other waterworks serving this region. There was sufficient TOC to form THMs. However, THMs were not formed at KAU1 in one sample event. In the latter event, the chlorine dose was lowered from 0.9 to 0.3 mg/L, and the chlorine residual was reduced from 0.2 to 0 mg/L. Low chlorine doses (mostly <0.3 mg/L) and zero free-residual chlorine were typically associated with the other waterworks and their distribution networks in Kaunas. In addition to low chlorine dose issues in general, some water treatment plants treated groundwater with some ammonia in it. It takes 7.6 mg/L of chlorine (as Cl₂) to break out 1.0 mg/L of ammonia as N. So the chlorine dose during some sample events may have been too low to break out the ammonia and it did not result in a free chlorine residual (i.e., chloramines formed). Although free and total residuals were reported for most countries, only free chlorine residuals were reported in Lithuania. Also note that Heraklion and Bedford had little or no chlorine residuals in their distribution networks.

**Bromine speciation.** In this study, three types of bromine speciation patterns were present (Table 3), where most regions were dominated by chloride-containing DBP species. In certain regions in Spain (Granada, the Basque Country, Asturias, and in some areas of Catalonia), in three regions of the United Kingdom, and in the regions studied in Lithuania and Italy, chloroform (TCM) was the dominant THM species, bromodichloromethane was formed to a lesser extent, whereas usually little to none of the other bromine-containing species were detected, indicating the low-bromide content of these waters. In most of Catalonia, and in Heraklion, THMs were dominated by bromine-containing species, where bromoform (TBM) was the dominant THM species, the mixed bromochloro THMs were formed to a lesser extent, and TCM was present at a much lower level, indicating high-bromide waters or waters with a high ratio of bromide to TOC. Finally, in the regions of Valencia, Nottingham, and Rennes, the two mixed bromochloro THMs were the dominant THM species, being close to or >50% of the THM4 on a weight basis. TCM and TBM were detected at lower levels. This speciation pattern for the four THMs is characteristic of moderate-bromide waters or waters with a moderate ratio of bromide to TOC.

Among the studied regions in Spain, the United Kingdom, Kaunas, and Northern Italy that were dominated by chlorine-containing THMs, on a median basis, TCM in each region accounted for 56 to 80% (on a weight basis) of THM4. The major HAA species in these regions were dichloroacetic acid (DCAA), which accounted (on a median basis) for 65 to 92% of the DXAAs and, correspondingly, trichloroacetic acid (TCAA) accounted for 38 to 90% of the TXAAs. Likewise, dichloracetoneitrile (DCAN) was the most abundant HAN (where DCAN data were available) in Bradford and Asturia; on a median basis, DCAN accounted for 79 and 84%, respectively, of the HANs (on a weight basis). In the regions dominated by bromine-containing species, in Catalonia and Heraklion, TBM in each region (on a median basis) accounted for 44 and 58%, respectively, of THM4. On a median basis, the major HAA species were dibromoacetic acid (DBAA), where in Catalonia it accounted for 67% of the DXAAs, and tribromoacetic acid (TBA), which accounted for 42 and 50%, respectively, of the TXAAs. Note that, in most of the world, where all nine HAAs are measured, TBA is rarely detected and is usually a minor component of the TXAAs. Likewise in these two regions, dibromoacetoneitrile (DBAN) was the most abundant HAN; on a median basis, it accounted for 55 and 75%, respectively, of the HANs (on a weight basis).

The relative contributions of TCM or TBM, DCAA or DBAA, and TCAA or TBA to the respective DBP groups in the Spanish database are presented in Figures 1 and 2. In Spain there was a wide range of bromide and bromine-containing DBPs in the water, which was not the case for the other countries; thus, these two figures show only data from Spain. For the chlorine-containing DBPs, the linear regression trend lines had good correlations (R² = 0.85 and 0.87), and the slopes were 1.0 and 1.1, respectively. For the bromine-containing DBPs, the correlations were fair to good (R² = 0.80 and 0.66), and the slopes deviated somewhat from 1.0. For example, for TBA, the slope was 0.75, which suggested less bromine incorporation into TXAAs than into THMs. This could have been due to steric interferences from the carboxylic acid group or the instability of TBA.

Figure 3 shows the relative occurrence (on a weight basis) of DBAN and TBM in Catalonia, which had the highest occurrence of DBAN in this study. The weight ratio of DBAN to TBM ranged (25th to 75th percentile) from 14 to 28% (median = 21%). As shown in other studies, DCAN tended to form at approximately...
that of TCM (Krasner et al. 1989, Oliver 1983). In the present study, in Bradford and Manchester, the weight ratio of DCAN to TCM was ~10% on a median basis, but was as high as ~33%, which could be attributed to the presence of more amino acids from algae in these watersheds, which are a source of HAN precursors (Trehy et al. 1986). In terms of the higher ratio for DBAN to TBM, this may have reflected (in part) more bromine incorporation into HANs than into THMs (Obolensky & Singer 2005). Although bromine incorporation trends for the HAAs and HANs tended to track, in general, with those of the THMs, there were important deviations in which there tended to be less bromine incorporation into the TXAAs and more into the HANs.

Because most epidemiological studies on chlorinated drinking water have focused on THMs, it is important to not only examine THMs as a surrogate for the formation of other classes of DBPs, but to determine whether the impact of bromide on DBP speciation is similar, as the bromine-containing DBPs may be a higher health concern than the chlorine-containing species. Thus, certain parts of the different water systems at certain times of the year or in certain years were exposed to higher amounts of bromine-containing species, which may be a higher health concern than the chlorine-containing species.

**Formation of different DBP classes.** In addition to speciation, the relative formation of the different classes of DBPs is important, such as the HAN-to-THM ratio discussed earlier. For example, in Catalonia, DXAAs were sometimes inconsistently low in concentration when compared with the levels of THMs and

The equation for the linear regression line (not shown in the figure) is $y = 1.097x + 0.036$ ($R^2 = 0.87$) and $y = 1.039x + 0.027$ ($R^2 = 0.85$).
TXAAs. This could be attributed to the degradation of the DXAAs in water samples that were warm (median > 18°C) and were low in or absent of residual chlorine (<0.2 mg/L), which may have allowed for the biodegradation of these HAAs in the distribution system, whereas TXAAs are not biodegradable (Baribeau et al. 2005).

Temporal and spatial variability. In most of the countries studied, only one city or region was studied, which may not be representative of the different types of DBP profiles in that country. Alternatively, a wide range of systems were studied in Spain and the United Kingdom. Moreover, the study in Spain had a very wide range of DBP profiles (low versus high formation; dominated by chlorinated versus brominated species). Thus, there is more discussion about the data from the latter two countries.

Temporal (seasonal and year-to-year) and spatial (location in region) variability is important, especially when short-term exposure to DBPs may be of concern (e.g., possible associations with adverse reproductive or developmental effects) (Santa Marina et al. 2010). Data from a high-bromide-containing water (i.e., Catalonia) and from water low in bromine-containing DBPs (i.e., Bradford), which had sufficient occurrence of both HAAs and THMs, were examined for their variability over time and space.

In Bradford, THM4 was higher in summer and fall and lower in winter and spring, which is the typical seasonal variability for this class of DBPs (Figure 5). Tap water TOC was higher in the spring and fall (90th percentiles = 1.9–2.8 mg/L) than in the winter and spring (90th percentiles = 1.3–1.6 mg/L). Water temperature—which greatly affects THM formation—was notably higher in the summer (90th percentile = 19°C) than in the other seasons. In a year-to-year comparison, THM4 concentrations were similar on a central tendency basis in summer 2007 (median = 41 µg/L) and 2008 (median = 47 µg/L). However, THM4 concentrations were notably higher in fall 2007 (median = 71 µg/L) than in fall 2009 (median = 33 µg/L), indicating the importance of studying year-to-year variability. For HAAs, seasonal variability was not clearly demonstrated, as is shown in Figure 6. However, year-to-year HAA variability was more pronounced; there was substantially less HAA formation in summer and fall 2007 than in these two seasons in 2008. This is important because HAAs, the second major group of DBPs, may present different trends from those of THM4. In summer 2007, HAA concentrations were low (median = 12 µg/L) when compared with the THM4 formed (median = 41 µg/L), which could be attributed to the biodegradation of the HAAs, as these waters presented low chlorine residual (typically <0.1 mg/L as Cl₂) and high temperatures.

In Catalonia, the database showed considerable spatial variability. For the overall three-year study, median THM4 concentrations in drinking waters were higher for system 4 (Sabadell; 84 µg/L) and system 1 (portion of Barcelona; 77 µg/L) than for system 3 (50 µg/L) or system 2 (42 µg/L) (both supplying other portions of Barcelona). In the different portions of Catalonia, there were important spatial differences in the THM speciation as well as the sum of THMs.

For systems 1 and 2, more THM formation occurred in the summer than in the fall or spring (Figure 7; no data are...
available for the winter). In system 1, where bromine-containing species dominated, THM4 in summer was very high (median = 178 µg/L), whereas THM formation was lower and similar in the fall (median = 77 µg/L) and spring (median = 78 µg/L). Accordingly, in system 2, where chlorine-containing species dominated, THM4 concentrations were moderately high on a central tendency basis, whereas the interquartile range was high (median = 58 µg/L; 75th percentile = 166 µg/L) in summer 2008.

In system 2, HAA formation showed some seasonal variability (Figure 8); HAA concentrations (median = 14 µg/L) were lower in the fall than in the summer (median = 35 µg/L) or spring (median = 43 µg/L). In system 1, HAA formation showed a similar trend for the available data; HAA

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**FIGURE 5** Seasonal and year-to-year variation in occurrence of THMs in drinking water supplied by Bradford, United Kingdom, for the three-year study (2007–2009)

**FIGURE 6** Seasonal and year-to-year variation in occurrence of HAAs in drinking water supplied by Bradford, United Kingdom, for the three-year study (2007–2009)

**FIGURE 7** Seasonal variation in the occurrence of THM4 in drinking water supplied by systems 1 (S1) and 2 (S2) in Catalonia, Spain, for the three-year study (2007–2009)

**FIGURE 8** Seasonal variation in occurrence of HAAs in drinking water supplied by systems 1 (S1) and 2 (S2) in Catalonia, Spain, for the three-year study (2007–2009)

THM—trihalomethane, THM4—sum of four THMs

HAA9—sum of nine haloacetic acids

HAA9—sum of nine haloacetic acids

*a* HAAs for S1 not available for summer
concentrations were lower in the fall (median = 27 µg/L) than in the spring (median = 38 µg/L).

In this study, speciation patterns of THMs and HAAs were consistent in most portions of Catalonia; chlorine-containing DBPs typically dominated in waters distributed by system 2, whereas bromine-containing species were typically dominant in systems 1 and 3. However, for system 4, DBP speciation patterns were different throughout the study; in 2007, chlorine-containing species dominated, whereas in 2008 bromine-containing species were dominant. Moreover, in 2009, in certain sample events for system 4, TCM and TBM were the dominant species, accounting (on a median basis) for 18 and 45%, respectively, of THM4. For Valencia, speciation patterns presented a year-to-year variability. In 2007 the two mixed bromochloro species were the dominant THM species, whereas in 2009 bromine-containing species were the dominant species.

CONCLUSIONS

The occurrence of DBPs in drinking water presented great variability between and within the different European regions studied.

- THM concentrations were substantially higher for waterworks treating surface or blended water than those treating groundwater. HAA levels were typically lower than THMs. In some cases, DXAA concentrations were low when water temperature was warm and the chlorine residual was low, suggesting their biodegradation.

- There were three types of bromine speciation patterns, with most regions being dominated by chlorine-containing DBP species. In certain portions of Catalonia and Heraklion, bromine-containing species were the dominant species. In Valencia, Nottingham, and Rennes, the mixed bromochloro DBP species were the dominant species. These differences reflect differences in bromide levels and bromide/TOC ratios.

- Speciation patterns of THMs, DXAAs, and TXAAs were consistent, where chlorine-containing DBPs dominated over bromine-containing species and vice versa. However, in some portions of Catalonia, TCM and TBM dominated, with low formation of mixed bromochloro species. This type of speciation pattern has not been reported before. This likely reflected the blend of surface waters with different bromide contents, in which water dominated by bromine-containing species blended with water dominated by chlorine-containing species.

- The percentage of THM4 accounted for by TCM was similar to the percentage of DXAAs and TXAAs accounted for by DCAA and TCAA, respectively. However, TBM accounted for more THM4 than TBA accounted for TXAAs. This may reflect a lower formation of TBAA or formation followed by degradation. Nonetheless, levels of TBA in this study were far higher than elsewhere in the world.

- HAN speciation patterns were consistent with THM and HAA speciation patterns. DCAN tended to form in regions dominated by chlorine-containing DBP species, and DBAN in regions dominated by bromine-containing DBPs. However, the ratio of DBAN to TBM was higher than what has been reported for DCAN to TCM. This suggests that there was more bromine incorporation into the HANs than the THMs.

- DBP concentrations showed a temporal (seasonal and/or year-to-year) variability between and within regions treating surface or blended waters, whereas groundwater showed little or no variation. However, HAAs tended to be higher during a different period than were the THMs.

- Total THMs have been used as a surrogate for halogenated DBPs in most epidemiology studies. However, in this study, the occurrences of THMs and HAAs were found to vary from each other on either a seasonal or year-to-year basis. Despite the differences in the occurrence patterns of the THMs and HAAs, speciation of the THMs was a good surrogate, in general, for the speciation of the HAAs or HANs. Individual THM species were shown to be good indicators for the occurrence of other bromine-containing DBPs of health concern. This is important, because bromine-containing species are a greater health concern than chlorine-containing DBPs. This was especially important in Spain, where a recent bladder cancer study suggested the importance of bromine-containing THMs. The present study showed that some of the Spanish waters not only had a high concentration of brominated THMs, but also high levels of brominated HAAs and HANs, especially TBAA and DBAN, which are usually not detected at significant levels in other studies.

The results of this study indicate the importance of measuring other classes of DBPs for epidemiology studies. Not only should HAAs be considered but also HANs, which are substantially more toxic than THMs or HAAs. In this study, a method that measured both THMs and HANs was used, which allowed for the simultaneous investigation of both classes of DBPs. Moreover, epidemiologists should not rely only on compliance monitoring data, as that would miss four of the brominated HAAs in the United States. Again, a method that measures all nine species can be used.

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ENDNOTE

1Agilent 6890, Santa Clara, Calif.

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