



## Research article

## Swimming pool water disinfection by-products profiles and association patterns

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## ABSTRACT

The aim of this work was to determine and study the concentration of different groups of disinfection by-products (DBPs): trihalomethanes, haloacetic acids, haloacetonitriles, haloacetones and combined chlorine (as an indicator of chloramine levels), in the water of 175 public swimming pools in Gipuzkoa (Basque Country, Spain). The study included chlorinated and brominated pools, indoor and outdoor, used for recreational and sports purposes, and filled with water from calcareous and siliceous soils. The most abundant were haloacetic acids, followed by trihalomethanes, with chlorinated or brominated forms predominating depending on whether the pools were disinfected by chlorination or bromination, respectively. All the 75th percentiles of DBPs were below the limits established by the European Chemical Agency (ECHA), although the maximum values of trihalomethanes exceeded them. The same was true for dichloroacetonitrile in chlorinated pools and dibromoacetonitrile in brominated pools. All families of DBPs showed positive associations with each other, all being significant except for combined chlorine. Their mean levels were higher in outdoor pools than in indoor pools, significantly so in all except combined chlorine. Recreational pools showed higher levels of haloacetic acids and combined chlorine than sports pools. The concentrations of the different groups of DBPs were higher in the pools than in the mains water that fed them. This increase, especially that of the haloacetonitriles, as well as the high concentrations of brominated forms in the pools disinfected by bromination, make it necessary to focus on their toxicological implication. The differences in the DBP profiles of the filling network water were not transferred to the pool water.

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## 1. Introduction

Swimming is a popular physical activity among people of all ages and income group across the world [1–4], as it can provide health benefits [2,5–10]. In order to ensure that the health benefits are promoted without any collateral adverse health risks for individuals, it is important to ensure that this activity occurs in safe and healthy environments. During pool activities, human substances and personal care products can contaminate the swimming pool waters. For outdoor pools, additional pollutants come from leaves and dust in the surrounding environment or from the rainwater. These contaminants may carry pathogens, including bacteria, viruses and protozoa, which may result in some diseases or symptoms such as gastroenteritis and dermatitis [1,11]. So, adequate water disinfection practices are implemented in swimming pools to prevent microbial proliferation that might lead to serious infectious diseases [8].

Swimming pools are typically disinfected mostly with chlorine, and to a lesser extent with bromine, ozone, UV irradiation and electrochemically generated mixed oxidants (EGMO) [12]. The reaction of the oxidizing agents with the organic matter present in the filling water, or provided by bathers, generates a series of chemical substances known as disinfection by-products (DBPs). In drinking water, which is the area where most of the research on the formation of DBPs has been carried out, more than 600 DBPs have currently been identified [13–15]. At the same time, however, more than 50% of the total organic halogens formed during disinfection of drinking water remain unidentified [15,16]. In other major study in indoor swimming pools in Spain, in which either chlorination or bromination was used for disinfection, more than 100 different DBPs were identified [14]. Many of them were new and have not been reported previously in neither swimming pool nor drinking waters. Within DBPs we can find compounds such as trihalomethanes (THMs), haloacetic acids (HAAs), halo ketones (HKs), haloacetonitriles (HANs), as well as inorganic compounds such as chloramines (CAMs). The presence of these DBPs raises concern because of the nuisance they cause and because they are substances that can pose a risk to health and the environment [3,6,17–21], coming into conflict with the benefits that this physical activity provides, in addition to its recreational aspects.

Due to the continual input of organic matter via filling water and bather load (which may include human body excretions, personal care products, and pharmaceuticals), and continual availability of disinfectant, in terms of DBPs, swimming pools are a unique environment compared to other water matrices [22]. Besides, the concentrations of DBPs in swimming pool water often exceed those of drinking water [23]. Moreover, the effects of swimming pool operational parameters on the formation and speciation of DBPs in swimming pools have not been systematically investigated [24]. All these factors add an additional complication to the disinfection and toxicological safety of swimming pool water [2,4]. Despite this, public attention of DBPs in swimming pool waters is not as much as that in drinking waters according to the number of publications in the past years [1]. Moreover, as with other water types, many investigations of DBPs in swimming pool waters have focused on the occurrence and/or formation of trihalomethanes (THMs), haloacetic acids (HAAs), and chloramines (particularly trichloramine), with fewer studies including haloacetonitriles (HANs), or halo ketones (HKs) [25]. Carbonaceous and nitrogenous DBPs coexist in swimming pools, and the formation of nitrogenous DBPs may be promoted when the formation of THMs and HAAs are suppressed [26,27]. Accordingly, the formation of nitrogenous DBPs and carbonaceous DBPs during the disinfection process needs to be investigated simultaneously [28].

Although not exclusively, the use of chlorine based or bromine based disinfectants generally lead to the dominance of chlorinated and brominated DBPs, respectively [25]. With bromination the bromide ions increase in the pool water, which favours the formation of brominated species of DBPs [2,14,29,30]. Brominated DBPs are generally more toxic than their equivalent chlorinated DBPs [2,31]. However, while many of the existing studies primarily focus on chlorinated pools, less is known about DBPs in those treated with bromine [25].

The objective of this study is to identify and analyse the concentration of five different groups of DBPs: THMs, HAAs, HANs, HKs and combined chlorine (as an indicator of chloramines), in the water of swimming pools for public use in Gipuzkoa (Basque Country, Spain), and with disinfectant treatment using chlorinated or brominated products. Likewise, the relationship of these DBPs with each other have been analysed, as well as with variables related to the type of swimming pool, and with the physical-chemical parameters of the sanitary control of swimming pools.

## 2. Material and methods

### 2.1. Pool selection, sample collection and analysed compounds

A total of 175 different pools for public use from Gipuzkoa with a high influx of bathers were included in the study. Among the 155 chlorinated ones (mostly disinfected with hypochlorite); 86 were indoor pools and 69 outdoor pools, 98 had a recreational use, by either adults or children, and 57 had a sport use. The origin of the water was from calcareous terrains (limestone rock) in 80 and from siliceous terrains (granitic batholith) in 75 pools. Conversely, the pools treated by bromination (mostly disinfected with bromochlor-5,5-dimethylimidazolidine-2,4-dione) were 20; all of them outdoors, 18 for recreational use and 2 for sports, and 10 of them with water of calcareous origin and the other 10 of siliceous origin.

In each pool, water samples were collected in three containers: a 60 ml amber glass one for THMs, HANs and HKs, a 100 ml amber glass one for HAAs, and another 500 ml polypropylene one for pH, conductivity, turbidity, bromine, free chlorine and combined chlorine. Water was sampled in the middle of one long side of the pool, 1 m from the edge of the pool and at about 20 cm depth [32]. The samples were taken during 2017 and 2018; in the case of indoor pools throughout the year, and in the case of outdoor pools in the summer period, between June and August.

The DBPs analysed were: THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform), HAAs (monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid, dibromoacetic acid,

bromodichloroacetic acid, dibromochloroacetic acid, and tribromoacetic acid), HANs (trichloroacetonitrile, dichloroacetonitrile, bromochloroacetonitrile, and dibromoacetonitrile), HKs (1,1-dichloroacetone and 1,1,1-trichloroacetone), and combined chlorine, as an indicator of the chloramine content.

## 2.2. Chemical analysis

THMs, HANs, and HKs were analysed using a modified form of the Standard Method 6232B [33]: after being enriched with anhydrous sodium sulphate (40% w/v), water samples underwent liquid/liquid extraction with n-pentane. Quantification was conducted by gas chromatography with electron capture detection (GC-ECD) and 1,2-dibromopropane as internal standard. Chromatographic separation was accomplished on a 60 m × 0.25 mm I.D. × 1.00 μm film thickness DB-5MS UI column. Limit of quantification was 0.40 μg/l for THMs and 0.15 μg/l for HANs and HKs.

HAAs were determined using a modified form of USEPA Method 552.3 [34]: after being enriched with anhydrous sodium sulphate (45% w/v), water samples underwent liquid/liquid extraction with *tert*-butyl methyl ether at pH ≤ 0.5, followed by methyl derivatization with 10% sulphuric acid in methanol solution. Quantification was conducted by gas chromatography with mass spectrometry detector operated in negative chemical ionization and 2-bromobutanoic acid as internal standard. Chromatographic separation was accomplished on a 60 m × 0.25 mm I.D. × 1.00 μm film thickness DB-5MS UI column. Limit of quantification was 0.50 μg/l for monochloroacetic acid, 0.30 μg/l for tribromoacetic acid, 0.10 μg/l for monobromoacetic, dichloroacetic, bromochloroacetic, bromodichloroacetic and dibromochloroacetic acids, and 0.05 μg/l for trichloroacetic and dibromoacetic acids.

The pH was determined by potentiometry with a selective glass electrode. Turbidity by nephelometry (limit of quantification 0.25 NTU). Conductivity by direct measurement in a conductimeter. Free bromine, free chlorine and combined chlorine by reaction with *N,N*-diethyl-*p*-phenylenediamine (DPD) in a Nessler tube and subsequent spectrophotometric measurement at 515 nm (in the case of combined chlorine after addition of potassium iodide) [35]. Quantification limit for free bromine was 0.22 mg/l and for free chlorine and combined chlorine 0.05 mg/l.

The analysis were conducted in the Laboratory of Public Health of The Basque Government in Gipuzkoa. The laboratory is accredited (ISO/IEC 17025) to analyse THMs, pH, conductivity, turbidity, free bromine, free chlorine and combined chlorine in drinking water and swimming pools. The laboratory performs official control of these parameters for drinking water and swimming pools in Basque Country. All the methods are validated following the recommendations of the Eurachem guide [36], and fulfilling the trueness, precision, uncertainty and quantification limits established in the current EU drinking water legislation (EU 2020). For parameters not included in the EU drinking water legislation (e.g. HANs, HKs), the specifications of parameters with similar characteristics are followed (e.g. THMs, trichloroethene, tetrachloroethene). Quality control is based on the NORTEST report guide [37] and ISO/TS13530:2009 standard [38], and includes blanks, certified reference materials, additions, duplicates and control charts in each analytical batch. In addition, the laboratory regularly participates in inter-laboratory proficiency exercises of the LEAP Scheme of FAPAS. (<https://fapas.com>).

## 2.3. Toxicological evaluation

The limits set by the ECHA, in its Guide for the assessment of the risks that biocides can generate due to DBPs [15], were used as a reference with toxicological basis, for the interpretation of the results obtained in the water. It establishes the limit values for THMs, taking into account the three routes of exposure: inhalation, the dominant route, since it accounts for 80% of exposure in swimming pools [15], oral and dermal. For HAAs, given that they are low-volatile species and have little penetration through the skin, the ECHA considered that the limit established for drinking water would be overprotective, so specific values for swimming pool water were set in the guide. To set the limits of HANs in swimming pools, ECHA used the Tolerable Daily Intakes based on liver or growth effects.

## 2.4. Statistical method

The descriptive analysis summarized the information of the different DBPs analysed in the laboratory, including the descriptive parameters: minimum value, 25th, 50th (median) and 75th percentiles, maximum value observed, mean and standard deviation, together with the limits of quantification and the absolute and relative values observed below them. Half of the LOQ (limit of quantification) value was set for these non-quantifiable values. For a first analysis, the DBPs that included some bromine atom in their molecule were differentiated from those that did not have any, calling them, respectively, brominated and chlorinated.

For the bivariate analysis, however, only the sums ( $\Sigma$ ) of the different chemical species were analysed. The normal distribution was verified, by means of the Kolmogorov-Smirnov Z test, of the different sums of DBPs, as well as that of the pH, for homogeneous pools. Parametric statistical tests with these variables were used in the bivariate analysis; Student's *t*-test for comparisons of means, expressing its value and that of its standard error, and Pearson's correlation analysis, showing the correlation coefficient *r*. The correlation analysis between the DBPs and the indicator parameters of bathing water quality: conductivity, turbidity and free chlorine, was carried out using the Spearman's Rho test, since these variables did not fit the normal distribution.

The means of the DBPs of the filling water of the pools according to their origin (siliceous or calcareous), were compared using the Student *t*-test. Due to the poor adjustment to the normal distribution of some of the DBPs from the filling water to the pool (bromoform, dichloroacetone, bromochloroacetonitrile, dibromoacetonitrile, monochloroacetic, monobromoacetic, tribromoacetic acids, and sums of brominated HANs and chlorinated HHAs), the distribution of these variables was made using the Mann-Whitney test. No statistical treatment was made for trichloroacetonitrile because all its values were below the limit of quantification (Supplementary Table 2).

The differences observed in the levels of DBPs between parameters of chlorinated and brominated pools, as well as between indoor and outdoor pools, led us to perform a stratified analysis (Supplementary Tables 1 and 3). To compare the means of the groups of DBPs of swimming pools with chlorinated and brominated disinfection and, in order to neutralize the supplementary contribution in the weight/volume concentration derived from the higher atomic weight of bromine with respect to that of chlorine, a second analysis was carried out in molar units ( $\mu\text{mol/l}$ ) [25], restricting the calculation to indoor pools.

A multiple covariance model was used, including the families of DBPs, the bathing water quality variables, and the variables type of swimming pool (recreational or sports use) and type of filling water, in order to discover the underlying associations between these variables. The coefficient values and their standard error were expressed. For this statistical analysis, the physical-chemical parameters of bathing water quality, conductivity and free chlorine, were categorized into tertiles. The turbidity values were discretized into two categories, higher or lower than the LOQ, because the LOQ was only exceeded in 45 pools. The models initially included the variables that were related with the outcome at  $p < 0.20$  in the univariate analysis and excluding sequentially variables not related at  $p < 0.05$  in the adjusted model. The multivariate analysis of the brominated pools could not be carried out, as the sample only had 20 pools.

A value of  $p < 0.05$  was considered significant. For the statistical analysis, the statistical package SPSS (version 17.0) was used.

### 3. Results

Tables 1 and 2 show the descriptive parameters of the chlorinated and brominated pools, respectively. The maximum values of THMs and dichloroacetonitrile observed in the chlorinated pools exceeded the limit values established by the ECHA, although their 75th percentiles were below these limits, indicating that the majority of values were lower than those proposed by ECHA (Table 1). In the brominated pools (Table 2), the maximum values of THMs and dibromoacetonitrile exceeded the ECHA limit, whereas the rest of the values of the studied parameters were below the proposed limits.

In the chlorinated pools, the predominant DBPs were, from highest to lowest, trichloroacetic and dichloroacetic acids, chloroform, dichloroacetonitrile and trichloroacetone; and in brominated pools, dibromoacetic acid, bromoform, tribromoacetic acid, and dibromoacetonitrile (Tables 1 and 2).

Table 3 shows the mean levels of DBPs of the chlorinated pools, indoors and outdoors, and of the brominated ones, all of them indoors. Restricting the analysis to indoor pools, we observed that the DBPs with the presence of bromine were higher in the brominated pools than in the chlorinated pools. Conversely, the DBPs without presence of bromine in their molecule were higher in the chlorinated pools than in the brominated ones. The means in  $\mu\text{g/l}$  of the sum of THMs and HANs were significantly higher in the brominated pools, and the sum of HKs and HAAs showed higher values, although not significant, in the chlorinated indoor pools. However, when contrasting these means in molar units ( $\mu\text{mol/l}$ ), we observed that only HANs had significantly higher concentrations in the brominated pools, and with regard to HKs and HAAs, they appeared in greater amounts in the chlorinated pools. (Table 3).

Table 3 also compares the average levels of DBPs in chlorinated pools, depending on whether they are indoor or outdoor pools.

**Table 1**

Disinfection by-products analysed in chlorinated pools. Descriptive parameters ( $n = 155$ ;  $n = 154$  for combined chlorine).

DBPs ( $\mu\text{g/l}$ )	LOQ	<LOQ	<LOQ %	Mean	SD	Minimum	Median	Maximum
Chloroform	0.40	0	0.0	31.08	36.04	2.93	16.10	196.00
Bromodichloromethane	0.40	6	3.9	1.87	1.69	0.20	1.25	8.39
Dibromochloromethane	0.40	93	60.0	0.57	0.80	0.20	0.20	5.89
Bromoform	0.40	147	94.8	0.27	0.44	0.20	0.20	4.56
$\Sigma$ Brominated THMs	–	–	–	2.71	2.55	0.60	1.78	16.32
$\Sigma$ THMs	–	–	–	33.79	36.88	3.53	18.97	203.77
Trichloroacetonitrile	0.15	151	97.4	0.08	0.03	0.08	0.08	0.42
Dichloroacetonitrile	0.15	0	0.0	11.12	10.74	1.15	7.21	64.00
$\Sigma$ Chlorinated HANs	–	–	–	11.20	10.75	1.23	7.29	64.42
Bromochloroacetonitrile	0.15	40	25.8	0.64	0.84	0.08	0.49	7.21
Dibromoacetonitrile	0.15	135	87.1	0.14	0.44	0.08	0.08	5.30
$\Sigma$ Brominated HANs	–	–	–	0.78	1.19	0.15	0.58	12.51
$\Sigma$ HANs	–	–	–	11.98	10.87	1.45	8.33	65.20
Dichloroacetone	0.15	68	43.9	0.58	0.88	0.08	0.19	5.26
Trichloroacetone	0.15	1	0.6	10.43	16.61	0.08	2.36	91.60
$\Sigma$ Hks	–	–	–	11.01	17.34	0.15	2.46	95.86
Monochloroacetic acid	0.50	6	3.9	6.72	7.73	0.25	3.76	37.39
Dichloroacetic acid	0.10	0	0.0	147.99	202.17	9.34	69.60	1303.00
Trichloroacetic acid	0.05	0	0.0	165.00	201.67	8.90	98.00	1429.00
$\Sigma$ Chlorinated HAAs	–	–	–	319.71	370.25	22.93	171.79	2508.90
Monobromoacetic acid	0.10	45	29.0	0.37	1.60	0.05	0.19	20.00
Bromochloroacetic acid	0.05	0	0.0	4.26	2.99	0.59	3.27	13.30
Dibromoacetic acid	0.05	0	0.0	0.79	0.73	0.13	0.55	4.84
Bromodichloroacetic acid	0.05	0	0.0	3.73	1.74	0.62	3.36	11.30
Dibromochloroacetic acid	0.10	13	8.4	0.45	0.38	0.05	0.36	2.88
Tribromoacetic acid	0.30	144	92.9	0.18	0.12	0.15	0.15	1.11
$\Sigma$ Brominated HAAs	–	–	–	13.51	6.30	3.69	12.23	36.53
$\Sigma$ HAAs	–	–	–	329.48	371.90	28.46	182.15	2520.20
Combined chlorine (mg/l)	0.05	37	24.0	0.22	0.22	0.025	0.16	1.42

**Table 2**  
Disinfection by-products analysed in brominated pools. Descriptive parameters (n = 20).

DBPs (µg/l)	LOQ	<LOQ	<LOQ %	Mean	SD	Minimum	Median	Maximum
Chloroform	0.40	14	70.0	1.19	2.57	0.20	0.20	11.10
Bromodichloromethane	0.40	12	60.0	0.89	1.66	0.20	0.20	7.22
Dibromochloromethane	0.40	2	10.0	1.44	1.46	0.20	0.93	6.59
Bromoform	0.40	0	0.0	45.91	42.36	4.30	36.90	203.00
∑ Brominated THMs	–	–	–	48.24	42.69	4.70	38.43	204.09
∑ THMs	–	–	–	49.43	43.00	4.90	38.63	204.29
Trichloroacetonitrile	0.15	20	100	–	–	–	–	–
Dichloroacetonitrile	0.15	9	49.0	0.39	0.45	0.08	0.29	1.67
∑ Chlorinated HANs	–	–	–	0.46	0.45	0.15	0.37	1.75
Bromochloroacetonitrile	0.15	4	20.0	0.57	0.68	0.08	0.45	3.18
Dibromoacetonitrile	0.15	5	25.0	25.77	29.13	0.08	23.10	128.90
∑ Brominated HANs	–	–	–	26.34	29.20	0.15	23.78	129.27
∑ HANs	–	–	–	26.80	29.10	0.30	24.03	129.42
Dichloroacetone	0.15	19	95.5	0.08	0.03	0.08	0.08	0.20
Trichloroacetone	0.15	12	60.0	0.29	0.54	0.08	0.08	2.46
∑ Hks	–	–	–	0.37	0.54	0.15	0.15	2.54
Monochloroacetic acid	0.50	11	55.0	0.68	0.63	0.25	0.25	2.64
Dichloroacetic acid	0.10	0	0.0	7.79	5.11	0.98	8.21	19.30
Trichloroacetic acid	0.05	0	0.0	6.20	3.95	0.84	5.61	14.10
∑ Chlorinated HAAs	–	–	–	14.67	7.60	3.30	14.01	29.56
Monobromoacetic acid	0.10	0	0.0	6.35	6.20	1.26	3.97	26.10
Bromochloroacetic acid	0.05	0	0.0	7.48	4.74	2.01	6.01	21.80
Dibromoacetic acid	0.05	0	0.0	85.36	124.09	16.10	42.90	572.00
Bromodichloroacetic acid	0.05	0	0.0	3.42	1.23	1.48	3.22	6.17
Dibromochloroacetic acid	0.10	0	0.0	2.98	1.19	1.65	2.72	6.00
Tribromoacetic acid	0.30	0	0.0	38.83	36.27	10.80	29.80	175.00
∑ Brominated HAAs	–	–	–	147.83	167.08	45.97	105.88	802.85
∑ HAAs	–	–	–	159.08	163.24	64.14	117.47	801.36

**Table 3**

Mean value (standard error) of the mean of DBPs groups in relation to the disinfection system, using chlorinated or brominated products, differentiating within chlorinated pools, in turn, among indoor or outdoor ones. The families of DBPs in indoor pools are expressed in molar units, in addition to weight units.

Disinfection type	Chlorinated pools (n = 155)			Brominated pools (n = 20)	
	Indoor (n = 86)	Outdoor (n = 69)	p	Indoor (n = 20)	p <sup>a</sup>
Chloroform, µg/l	16.6 (2.2)	49.1 (5.2)	<0.001	1.2 (0.6)	0.001
∑ THMs Br, µg/l	2.4 (0.3)	3.1 (0.3)	0.096	48.2 (9.5)	<0.001
∑ THMs, µg/l	19.0 (2.2)	52.2 (5.3)	<0.001	49.4 (9.6)	<0.001
∑ THMs, µmol/l	0.15 (0.02)	–	–	0.20 (0.04)	0.229
∑ HANs Cl, µg/l	7.9 (0.8)	15.3 (1.5)	<0.001	0.5 (0.1)	<0.001
∑ HANs Br, µg/l	1.0 (0.2)	0.5 (0.1)	0.016	26.3 (6.5)	<0.001
∑ HANs, µg/l	8.9 (0.8)	15.8 (1.6)	<0.001	26.8 (6.5)	<0.001
∑ HANs, µmol/l	0.08 (0.01)	–	–	0.14 (0.03)	0.007
∑ Hks, µg/l	2.2 (0.5)	22.0 (2.5)	<0.001	0.4 (0.1)	0.079
∑ Hks, µmol/l	0.01 (0.003)	–	–	0.002 (0.001)	0.079
∑ HAAs Cl, µg/l	177.0 (18.4)	497.6 (56.0)	<0.001	14.7 (1.7)	<0.001
∑ HAAs Br, µg/l	11.9 (0.6)	15.4 (0.8)	<0.001	147.8 (37.4)	<0.001
∑ HAAs, µg/l	185.6 (18.5)	508.8 (56.2)	<0.001	159.1 (36.5)	0.532
∑ HAAs, µmol/l	1.28 (0.13)	–	–	0.75 (0.16)	0.065
Combined chlorine, mg/l	0.23 (0.02)	0.20 (0.02)	0.418	–	–

<sup>a</sup> Student t-test for brominated pools (all indoors) relative to indoor chlorinated pools.

Most mean values of DBPs were significantly higher in outdoor pools, except for brominated HANs, which were significantly higher in indoor pools, and brominated THMs and combined chlorine, in which no significant differences were found.

Pearson's correlation coefficients between the different families of DBPs analysed in chlorinated pools were positive and statistically significant, except for combined chlorine, an indicator of chloramine content, which was only positively and significantly correlated with HANs and HAAs (Table 4). In the chlorinated pools, the analysed DBPs without the presence of bromine, on the one hand, and those with bromine in their molecule, on the other hand, showed higher Pearson's correlation coefficients among them. Something similar occurred with the correlations between the DBPs in the brominated pools, with differentiated patterns of association between DBPs depending on the presence of bromine atoms in their molecule. The absence of statistical significance in some coefficients of the brominated pools may be due to the low number of brominated pools analysed (n = 20) (Table 4).

Table 4 shows Spearman's Rho coefficients for the DBPs in relation to the parameters of water quality, conductivity, turbidity and

**Table 4**

Pearson's correlation coefficients for DBPs and pH, and Spearman's Rho for conductivity, turbidity and residual free chlorine in chlorinated and brominated pools.

	Chloroform	∑ THMs Br	∑ THMs	∑ HANs Cl	∑ HANs Br	∑ HANs	∑ HKs	∑ HAAs Cl	∑ HAAs Br	∑ HAAs	Combined Cl
Chlorinated pools (n = 155)											
∑ THMs Br	0.299*	–									
∑ THMs	0.998*	0.361*	–								
∑ HANs Cl	0.525*	–0.072	0.508*	–							
∑ HANs Br	–0.103	0.400*	–0.073	0.050	–						
∑ HANs	0.507*	–0.027	0.494*	0.994*	0.159*	–					
∑ HKs	0.497*	0.009	0.487*	0.770*	–0.033	0.758*	–				
∑ HAAs Cl	0.442*	–0.162*	0.421*	0.693*	–0.106	0.674*	0.604*	–			
∑ HAAs Br	0.298*	0.399*	0.318*	0.186*	0.146	0.200*	0.345*	0.336*	–		
∑ HAAs	0.444*	–0.155	0.423*	0.693*	–0.104	0.673*	0.606*	0.999*	0.347*	–	
Combined chlorine	0.027	–0.094	0.020	0.212*	–0.031	0.206*	0.022	0.217*	0.152	0.218*	–
pH	–0.006	0.040	–0.003	–0.316*	–0.149	–0.328*	–0.304*	–0.005	–0.014	–0.005	–0.108
Conductivity <sup>a</sup>	0.437*	–0.247*	0.379*	0.491*	–0.201*	0.457*	0.512*	0.637*	–0.024	0.627*	–0.177*
Turbidity <sup>a</sup>	0.168*	–0.126	0.161*	0.324*	–0.033	0.315*	0.254*	0.263*	0.021	0.259*	0.275*
Free chlorine	0.035	0.121	0.050	–0.045	0.083	–0.037	–0.017	0.057	0.191*	0.060	0.191*
Brominated pools (n = 20)											
∑ THMs Br	0.092	–									
∑ THMs	0.151	0.998*	–								
∑ HANs Cl	0.693*	–0.078	–0.036	–							
∑ HANs Br	–0.312	0.645*	0.621*	–0.234	–						
∑ HANs	–0.302	0.646*	0.623*	–0.219	0.999*	–					
∑ HKs	0.902*	0.078	0.131	0.849*	–0.227	–0.215	–				
∑ HAAs Cl	0.483*	–0.350	–0.319	0.429	–0.383	–0.377	0.492*	–			
∑ HAAs Br	–0.217	0.756*	0.737*	–0.280	0.939*	0.938*	–0.204	–0.464	–		
∑ HAAs	–0.201	0.754*	0.736*	–0.269	0.940*	0.939*	–0.188	–0.431	0.999*	–	
pH	0.370	0.008	0.030	0.219	–0.347	–0.345	0.384	0.456	–0.355	–0.342	–
Conductivity	0.259	0.542*	0.546*	0.013	0.047	0.063	0.252	–0.055	0.137	0.108	–
Turbidity	–0.306	0.082	0.073	–0.253	0.500*	0.457	–0.296	–0.559*	0.536*	0.507*	–

\*: p &lt; 0.05.

<sup>a</sup> Spearman's Rho coefficients; remainder Pearson's correlation coefficients.

combined chlorine. The same table reports Pearson's correlation coefficients for the DBPs in relation to pH. In chlorinated pools, turbidity and conductivity presented a positive statistically significant association with all families of DBPs, whereas conductivity and combined chlorine correlated negatively with each other. The pH showed negative correlation coefficients with all DBPs, being statistically significant for HANs and HKs. For its part, residual free chlorine showed a positive and significant association only with combined chlorine. In the brominated pools, the pH did not reach any statistical significance; conductivity only showed a positive and significant correlation with the THMs; and turbidity showed a positive and significant correlation with the HAAs, and close to the limit of significance ( $p = 0.056$ ) with the HANs.

The analysis of the type of use, recreational or sports, within the chlorinated pools, showed that the pools for recreational use presented significantly higher mean levels of combined chlorine and HAAs (in this case due to the contribution of the chlorinated forms, that were predominant), while brominated THMs and brominated HANs were significantly higher in sports use. In brominated pools, chloroform and HKs were significantly higher in sports pools ( $n = 2$ ) (Supplementary Table 1).

Supplementary Table 2 shows that in the mains water used to fill the pools, the greatest contribution to the total content of DBPs corresponded to THMs and HAAs, with HANs and HKs contributing less. The overall levels of THMs, HANs, HKs and HAAs were significantly higher in the filling waters of calcareous origin than in those of siliceous origin, reaching in the latter, depending on the groups, between 45% and 70% of total amounts observed in those of calcareous origin. In addition, in the waters of calcareous origin, the percentage of compounds with only chlorine atoms in their molecules, reached in each group a considerably higher percentage than in the siliceous ones. In contrast, the sum of brominated forms reached higher percentages, within each group, in siliceous waters than in calcareous ones. Despite the fact that the total amount of DBPs in all groups was significantly higher in the calcareous ones than in the siliceous ones, for some brominated forms (bromochloroacetonitrile, dibromoacetonitrile and monobromo, dibromo and tri-bromoacetic acids) no significant differences were observed between both types of waters, or even the average was significantly higher in the siliceous ones (bromofrom). The filling waters of siliceous origin showed significantly lower levels of oxidability and conductivity than those of calcareous origin (Supplementary Table 2).

When comparing the values of the filling waters of the pools (Supplementary Table 2) with those of the pools (Tables 1 and 2), we observed that the values of all groups of DBPs were higher in the pools, although the HANs, HKs or HAAs largely than the THMs. Moreover, in the filling waters, THMs predominated or were at the same level as HAAs, while in the pools the predominance was clearly of HAAs (almost ten times more than THMs). If we exclude the pools disinfected with bromine, the percentage of brominated forms (specially brominated THMs) was more abundant in the filling water than in the pools.

Besides, neither the greater amount of DBPs in the filling waters of calcareous origin nor the greater relevance of the brominated species in the waters of siliceous origin, was later reflected in the DBPs content of the corresponding pools as it can be seen in Supplementary Table 3. This table describes the mean values of DBPs of the pools in relation to the type of mains water used for their renewal. In the subset of chlorinated pools, those using water of calcareous origin had significantly higher levels of brominated HAAs and HKs (in the latter case mainly due to the contribution of outdoor pools). In turn, those that used waters of siliceous origin had

**Table 5**

Regression coefficients (standard error) and statistical significance of the  $\sum$  DBPs in relation to the rest of the DBPs, the bathing water quality parameters and the type of water (siliceous vs. calcareous), type of pool (outdoor vs. indoor), and type of use of the pool (recreational vs. sports). Covariance analysis restricted to chlorinated pools.

	$\sum$ THMs ( $R^2 = 0.34$ )	$\sum$ HANs ( $R^2 = 0.70$ )	$\sum$ HKs ( $R^2 = 0.74$ )	$\sum$ HAAs ( $R^2 = 0.60$ )	Combined chlorine ( $R^2 = 0.11$ )
$\sum$ THMs	–	0.04 (0.02)	0.009	–	–
$\sum$ HANs	1.3 (0.2)	<0.001	–	1.0 (0.1)	<0.001
$\sum$ HKs	–	0.3 (0.04)	<0.001	–	–
$\sum$ HAAs	–	0.01 (0.002)	<0.001	–	0.0001 (0.00005)
Combined chlorine	–	5.0 (2.3)	0.032	–	193.4 (91.8)
pH	–	–7.6 (2.1)	<0.001	–7.6 (3.0)	0.011
Conductivity, 484–854 ( $n = 60$ )	–	–	–	–	66.3 (46.3)
Conductivity, >854 ( $n = 54$ )	–	–	–	–	246.6 (52.6)
Free chlorine (0.57–0.95; $n = 52$ )	–	–	–	–	–
Free chlorine (>0.95; $n = 51$ )	–	–	–	–	–
Turbidity (>0.125; $n = 57$ )	–	–	–	–	–
Type of pool, outdoor vs. indoor	24.0 (5.1)	<0.001	–	–	12.7 (1.6)
Type of use, recreational vs. sports	–	–	–	–	135.0 (44.1)
Type of water, calcareous vs. siliceous	–	–	–	–	105.3 (39.8)
			6.6 (1.5)	<0.001	–

significantly higher average contents of brominated HANs. In the subset of brominated pools, those that used water of calcareous origin had higher average contents of chlorinated HANs and chlorinated HAAs, than those that used water of siliceous origin. For the rest of the DBPs, no significant differences were found in relation to the origin of the filling water.

The statistical analysis of covariance (Table 5) was limited to the pools treated by chlorination, due to the limited number of brominated pools. Only the families of DPBs were analysed, including in the models the physical-chemical parameters of the pools, the type of pool (indoor or outdoor), the use of the pool (recreational or sports), and the type of filling water (calcareous or siliceous). THMs were found to be significantly associated with HANs, showing significantly higher concentrations in outdoor pools. The HANs, in turn, showed a significant positive association with the THMs, HKs, HAAs and with the combined chlorine, as well as, a negative association with the pH.

HKs were significantly associated with HANs, and negatively with pH, showing significantly higher levels in outdoor pools and with waters of calcareous origin. HAAs showed a significant association with HANs and with combined chlorine, and with conductivity. The levels were also significantly higher in outdoor pools compared to indoor pools, as well as in recreational pools compared to sports pools. Combined chlorine, finally, was significantly and positively associated with HAAs, residual free chlorine and turbidity. The observed determination coefficients were 34% for THMs, 70% for HANs, 74% for HKs, 60% for HAAs and 11% for combined chlorine (Table 5).

#### 4. Discussion

This study is based on the analysis of 175 different pools with moderate levels of DBPs, with their P75 below the limits established by the ECHA (2017) [15] in all cases. Among the DBPs studied, the predominant ones were HAAs, followed by THMs, which is also observed in other works [1,2,22,25,39,40].

The correlations observed between the DBPs, both in pools with brominated and chlorinated treatment, showed a differentiated pattern, with a high correlation between brominated species, as well as between non-brominated species, both in chlorinated and brominated pools. All families of DBPs were significantly and positively associated with each other, which highlights an association of all of them with the load of precursors accumulated in the pool. The exception to this generalized association was combined chlorine (chloramine level indicator), which was significantly associated only with HANs and HAAs. The association of combined chlorine with HANs may be because both are nitrogenous DBPs and, therefore, their respective levels in pool water are associated with the total level of nitrogenous precursors. Regarding the association of combined chlorine with HAAs, it can be attributed to the fact that, mono- and dichloramines and HAAs are less volatile than the rest of the DBPs studied [15,41] and, hence, tend to accumulate in the swimming pool water [1,2,12,14,39,40,42,43].

##### 4.1. Disinfectant type

Significantly higher mean levels of chlorinated THMs, HANs, HKs and HAAs were observed in pools with chlorination treatment. Same was observed for these DBPs in their brominated forms in pools with bromination treatment, in agreement with other studies [2, 25,42].

The statistical analysis of the DBPs in molar units shows that the HANs were found in significantly higher concentrations in the brominated pools, being not significant the differences between the rest of the means of the DBPs. Bromine is more active and faster than chlorine in forming DBPs [42,44,45]. However, once formed, Br–C bonded DBPs are generally more unstable than their respective Cl–C bonded DBPs [1,43]. The final result is the sum of both processes, which act in opposition. However, the degradation process is especially pronounced in trisubstituted HAAs that contain at least one bromine atom, compared to trichloroacetic acid, since they have a greater tendency to lose a CO<sub>2</sub> molecule to form the corresponding THM [1,2,43]. This explains the higher content of HAAs in chlorinated pools compared to brominated pools.

##### 4.2. Type of pool (indoor or outdoor) and use (sports or recreational)

In the chlorinated pools, in this study, the mean levels of the DBPs families were significantly higher in the outdoor pools for all groups of DBPs, except for combined chlorine, which did not show significant differences. The final concentration of DBPs in the water of a swimming pool is the result of the sum of different factors, which act concurrently and competitively, mainly: formation, transformation, evaporation, degradation and elimination by renewal. Various publications compare how these factors are affected by the type of pool, indoor vs. outdoor, and highlight the difficulty of predicting a trend, since the particular circumstances of each pool have a great influence [1,12,42,43].

Recreational pools showed higher levels of HAAs, and higher levels of combined chlorine. These pools are generally smaller in size and depth, with a greater influx of users and a high percentage of underage users, which translates into a higher organic load and, therefore, a higher concentration of DBPs [42]. However, the greater concurrence of users, which implies an increase in the agitation of the water in shallower vessels, or the higher temperature together with the injection of air in the case of SPAs, causes a greater elimination of volatile DBPs, due to evaporation [42]. This explains that only the less volatile DBPs, HAAs and combined chlorine [15, 41] accumulate in the pools.

#### 4.3. Origin of the filling water (siliceous or calcareous soils)

The observed global levels of THMs, HANs, HKs and HAAs, in this study, were higher in filling waters of calcareous origin than in those of siliceous origin. This could be explained by the fact that calcareous terrains in Gipuzkoa are limestone rock, very permeable to organic matter, whereas siliceous terrains are hard and compact granitic batholiths, chemically more inert, and younger in geological age. Therefore, siliceous terrains have a narrower stratum and contain less organic precursors and electrolytes than the former. Accordingly, water from siliceous soils has lower levels of oxidability and conductivity. On the other hand, the greater relevance of the brominated forms in the siliceous mains waters, compared to calcareous ones, could be explained by a higher content of bromide ions [22], since the reservoirs of the siliceous zones are closer to the coast and more exposed to the prevailing marine origin winds.

The levels of DBPs were higher in the pools than in the mains water that fed them, and the differences found in the DBP profiles of both types of mains water were not observed later in the water of the pools fed with one or the other. These two facts can be attributed to the strong transformations in the DBPs profile that undergoes the mains water, once in the pool, due to the continuous supply of disinfectant and precursors other than those originally contained [13,22,23,25]. Other authors [14] have also reported the higher content of HANs in swimming pools than in the fill water, whose toxicological importance is discussed later.

#### 4.4. Physical-chemical parameters

Several publications show variable and disparate associations of the different DBP families with pH, without reaching a consensus, with the exception of the negative and significant association between pH and mean levels of HANs, as was our case. It has been attributed to the chemical behaviour of the HANs, which degrade at  $\text{pH} > 7$  [2,40,42,43].

The conductivity in swimming pools is usually associated with the contaminant load increase and the lack of renewal of the water in the pool [2,43]. So, not surprisingly, it correlates with an increase in DBPs, especially with those that are more easily accumulated due to their low volatility, as is the case of HAAs [1,2,12,39,40,42,43]. Likewise, turbidity is also associated with an increase in the contaminant load and a lack of renewal of the water in the vessel [43], hence, a positive association with the mean levels of DBPs is also expected. Finally, other authors [2] have also found the association of residual free chlorine with combined chlorine.

#### 4.5. DBPs toxicity

DBPs have been shown to include hazardous substances that may pose a risk to human health or the environment. THMs have been linked with diseases such as bladder and colon cancer, asthma, irritation to the eyes and mucous membrane, and reproductive function [1,3,6,46,47]. Chloroform, bromodichloromethane, dichloroacetic acid, and trichloroacetic acid have been classified as contaminants possibly carcinogenic to humans (Group 2B) by International Agency for Research on Cancer [1,17–19,48]. Many DBPs have been demonstrated to be cytotoxic, neurotoxic, genotoxic, with several additionally demonstrating mutagenic, carcinogenic and/or teratogenic nature [13,25]. Dichloroacetonitrile in tap water is suspected of causing reduced fertility and decreases in litter size in a colony of laboratory rodents [23,49]. Chloramines may lead to eye and upper respiratory tract irritation, biomarker changes in the lung, and development of asthma [1,10]. In particular, trichloramine causes eye, skin, and respiratory tract irritation, has been associated with acute lung injuries, and has a suspected association to early-aged asthma [9,23]. Villanueva and Font-Ribera (2012) [21], and Font-Ribera et al. (2019) [3] described a higher prevalence of respiratory disorders such as asthma among pool workers and professional swimmers.

While toxicological studies in drinking water provide an insight to the health impact of DBPs, they are generally based on the risk associated with ingestion. As quantity and frequency of ingesting swimming pool water is significantly lower than that for drinking waters, and additional uptake mechanisms such as inhalation and dermal absorption are significant in pools [25,42], these health impact studies are therefore not directly applicable to assessing the risk associated with DBPs in the swimming pool environment. In comparison to their filling waters, pool waters have shown increased genomic DNA damage effects to CHO cells [25,50]. Links between exposure to swimming pool waters and several health issues, e.g. kidney and liver issues, as well as cancer of the bladder, have been suggested [21,25,47]. For some DBPs (e.g., chloroform), the dominant pathway for uptake during swimming is dermal absorption due to contact of large surface area of skin with water [23,51], which is particularly important because it provides direct access to the bloodstream, without going through the digestive system [23]. For other compounds (e.g., trichloramine), inhalation has been identified as an important route of exposure [4,23]. Inhalation and dermal absorption leads to higher blood levels for some DBPs than do oral exposures [14,52].

In swimming pool waters, nitrogenous DBPs have been shown to be generally more genotoxic (to Chinese hamster ovary cells) compared to most other DBPs [13,25], and greater toxicological effects were found to be associated with HANs than with THMs and HAAs [43,48,53,54]. Toxicological studies showed that HANs are more genotoxic and cytotoxic than THMs or HAAs [2,13,26,31]. Muellner et al. (2007) [31] indicated that dichloroacetonitrile is almost 300 times more cytotoxic than its haloacetic acid analogue (dichloroacetic acid).

#### 4.6. Strengths and weaknesses of this study

This study was carried out on a wide range of pools and with a moderate load in DBPs. A total of 21 chemical species of DBPs were studied, calculating the sums of the different species grouped in five families. Sampling method and collection of information regarding the pools were duly standardized, and chemical analyses of the water samples were carried out in a single accredited laboratory.

This work addresses the study of DBPs in swimming pools, which means providing information in a less common and less explored field than drinking water. In addition, it contemplates a considerable number of swimming pools of various characteristics: indoor and outdoor, for sports and recreational use, with different types of mains water used for filling, and with treatment by chlorination or bromination. It also includes, in addition to the most abundant and common DBPs (THMs and HAAs), some nitrogen-containing DBPs (HANs and combined chlorine as indicator of chloramines) and oxygen-containing DBPs (haloketones). It also includes several operational parameters of the swimming pools sanitary control: pH, conductivity, turbidity and disinfectant concentration.

Regarding the weaknesses, it is worth mentioning the low number of pools treated by bromination collected in this study, a consequence of the low use of this disinfection method, and which limited the information obtained from this type of pools. There are other types of DBPs, such as haloaldehydes, halobenzoquinones, halonitromethanes or haloacetamides, which have not been addressed in this work. Finally, it would be interesting for future studies to measure in the pools the load of nitrogenous precursors, for example as total organic nitrogen, to gain insight in the mechanisms involved in nitrogenous DBPs' formation.

## 5. Conclusions

This study shows that the predominant DBPs in swimming pool water are HAAs, followed by THMs. The DBPs with the presence of bromine atoms show a higher correlation with each other, as do the DBPs without the presence of these bromine atoms. The correlations between the families of DBPs were positive and significant, except for combined chlorine, which was only significantly associated with HANs and HAAs. The brominated pools showed levels of HANs in higher concentrations than in the chlorinated ones. Outdoor pools showed, except for combined chlorine, higher levels of DBPs than indoor pools. Likewise, those for recreational use showed higher levels of HAAs. The addition of disinfectants and organic matter, often nitrogenous, increases the concentration of the different families of DBPs, increasing their potential toxicity. In addition, the differences between the DBP profiles of the two types of mains water used for filling do not transfer to the pools.

The contrasted toxicity of these contaminants and, especially, that of the nitrogenous DBPs, leads us to encourage the establishment of strategies for their minimization, by improving hygiene and water renewal flows. This is particularly important in brominated pools, due to their greater capacity to generate compounds that are more toxic.

## Author contribution statement

Eunate Abilleira: analyzed and interpreted the data; wrote the paper. Fernando Goñi-Irigoyen: conceived and designed the experiments; performed the experiments; contributed reagents, materials, analysis tools or data; analyzed and interpreted the data; wrote the paper. Juan J. Aurrekoetxea: conceived and designed the experiments; analyzed and interpreted the data; wrote the paper. María A. Cortés: conceived and designed the experiments; contributed reagents, materials, analysis tools or data. Mikel Ayerdi: contributed reagents, materials, analysis tools or data. Jesús Ibarluzea: analyzed and interpreted the data; wrote the paper.

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## Data availability statement

Data will be made available on request.

## Declaration of interest's statement

The authors declare no conflict of interest.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2023.e13673>.

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