

TRIHALOMETHANES IN LISBON INDOOR SWIMMING POOLS: OCCURRENCE AND DETERMINING FACTORS

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ABSTRACT

The main goal of this investigation project was to study the occurrence, distribution and determinants of THMs in indoor swimming pools. In order to achieve this goal the characterization of water quality from 30 Lisbon indoor swimming pools, using chorine based treatment techniques, was performed during a six month period. Because of laboratory working restrictions, chloroform (CF) concentration in pool air was studied only in 6 pools, at the same period. Several parameters such as total trihalomethane concentration (TTHMs), CF, other THMs concentration in water, free residual chlorine (FrCl), combined residual chlorine (CrCl), pH, water and air temperature (T_w and T_{air}), relative humidity (rel_Hum), chemical oxygen demand (COD), conductivity (Cond), turbidity (Turb) and chloride (Cl) were determined in each pool, once a month. The results herein presented refer to the first 3 month of the study, April to June.

CF was the THM obtained in higher concentrations: TTHMs water level ranged from 10 to 160 $\mu\text{g/L}$, while CF water level typically ranged from 5 to 150 $\mu\text{g/L}$. In air, CF level ranged from 40 to 200 $\mu\text{g/m}^3$, with occasional higher levels detected. T_w presented less variation (27 to 31 °C) than T_{air} (21 to 33 °C). FrCl and Cond presented higher values than the recommendations only in a small number of pools. Turb and COD values were also within portuguese guidelines. The pH varied from 7 to 8.5, with only a small number of pools having values higher than 7.8.

It was possible to obtain some interesting correlations. There was a clear positive correlation between CF_w and TTHMs ($R=0.986$; $p<0.001$), CF_w and CF_{air} ($R=0.640$; $p<0.05$), CF_w and FrCl ($R=0.225$; $p<0.05$), and CF_w and T_w ($R=0.284$; $p<0.05$). Other correlations TTHMs vs CF_{air} ($R=0.613$; $p<0.05$), TTHMs vs FrCl ($R=0.225$; $p<0.05$) and TTHMs vs T_w ($R=0.323$; $p<0.01$) were obtained.

Keywords	Indoor swimming pools, THMs, Water and air quality, Distribution and determinants, Correlations between variables
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INTRODUCTION

The presence of water disinfection by-products (DBPs) in swimming pools constitutes today a public health concern, particularly because swimming is an activity used by a high percentage of the population, namely elderly and young children. Moreover, several adverse short-term and long-term health effects have been associated with these compounds (Lakind et al., 2010; Zwiener et al., 2007).

Water disinfection methods are used in all swimming pools, namely in public pools, to ensure an adequate and effective protection of users against microbiological pathogens. Chlorination is the most common disinfection method used worldwide, because it is low cost, easy to use, efficient against a

broad spectrum of microorganisms, and enables the maintenance of a residual protection. The use of chlorine based treatment techniques has one strong drawback, which is the generation of several DBPs, potentially harmful products that can be absorbed by ingestion, inhalation and absorption through the skin (Lakind et al., 2010; Nieuwenhuijsen et al., 2009; Caro and Gallego, 2007).

DBPs comprise several compounds that are formed through the reaction of chlorine with organic matter present in water. Amongst DBPs, the most relevant and better characterized are THMs: CF, bromoform (BF), bromodichloromethane (BDCM), and chlorodibromomethane (DBCM). In most water samples CF is the prevalent compound, although, in the presence of bromine, brominated THMs can become more concentrated than CF (WHO, 2006). THMs are volatile compounds, slightly soluble in water, miscible with organic solvents, and with a structure similar to methane (CH₄), with three or four hydrogen atoms substituted by chlorine or bromine atoms (Figure 1).

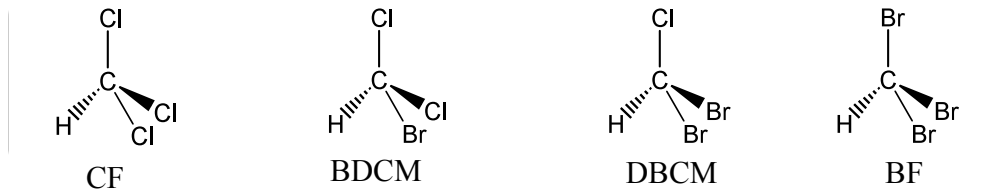


Figure 1 Chemical structure of THMs

Unlike drinking water, where the substrate for DBPs is the organic matter naturally present in the water, in pool water there are additionally other compounds that can act as precursors of DBPs and THMs. These compounds arise from human organic matter, such as sweat, urine, hair or chemical products applied by pool users, such as lotions, creams and hair sprays, and can influence the concentration of THMs in pool water. The presence of more reactive chlorinated species such as HOCl and OCl⁻ is dependent on T_w, pH and chlorine dose used in the pool, meaning that THMs concentration must be also dependent on these variables (Zwiener et al., 2007).

THMs have been associated with health effects such as respiratory, ocular and cutaneous symptoms and also with some long-term health effects such as cancer and adverse reproductive outcomes (Lee et al., 2009; Zwiener et al., 2007). Epidemiologic studies have suggested that drinking chlorinated water may be associated with increased incidences of bladder, rectal, and colon cancer and adverse reproductive effects, such as abortion, low birth weight, decline of semen quality (Lakind et al., 2010; Villanueva et al., 2007). Moreover, animal studies have suggested that high concentrations of some DBPs in drinking water may also cause an increased incidence of cancer and reproductive effects (Nieuwenhuijsen et al., 2009; Zwiener et al., 2007).

IARC (International Agency for the Research on Cancer) classifies CF and BDCM as being possible carcinogenic to humans (group 2B), and includes DBCM and BF in group 3, because there are no evidences of carcinogenic effects to humans (IARC, 1999).

Accurate exposure assessment of THMs in indoor pool environment is particularly difficult because their formation depends on many factors such as T_w and T_{air}, rel_Hum, pH, FrCl, total organic content and number of pool users (Lee et al., 2009). Drinking, bathing and showering are the main sources of exposure to DBPs from drinking water. Moreover, frequent indoor swimming pools users, such as professional swimmers, swimming trainers and people who practice indoor water sports (swimming, hydro gym) several hours per week are additionally exposed – by inhalation and dermal contact – to DBPs present in swimming pool water and indoor, making difficult the evaluation of the total exposure to DBPs and particularly to THMs (Weaver et al., 2009; Zwiener et al., 2007; Erdinger et al., 2004).

Exposure to THMs by inhalation depends on the physical activity intensity of the swimmers, the time spent in the pool and the amount of aerosols present in the air of the pool. The water turbulence gener-

ated by the practitioners, can influence the amount of aerosols present in the air. As a result, monitors and other pool workers can also be exposed to these compounds, as they spend several daily working hours in the pool environment (WHO, 2006).

Absorption of THMs through dermal contact is considered, by several authors, to be the most important route of exposure, depending on T_w and their concentration in the water (Lindstrom et al., 1997; Zwiener et al., 2007). Xu et al., (2002) developed an *in vitro* study with some DBPs and observed that THMs presented higher permeability coefficients through human skin than halo ketones or haloacetic acids.

In Portugal a specific legislation to assess the quality of swimming pool waters is inexistent. The guideline value used in this study for TTHMs is the one established in the Portuguese Law 306/2007, for drinking water quality - 100 $\mu\text{g/L}$ (Table 1). Some other water parameters determined in swimming pools such as T_w , Turb, pH, FrCl, total residual chlorine, Cond, COD and isocyanuric acid were assessed by Portuguese Law (DR) 5/97, regarding technical and safety conditions of closed environments with water diversions. WHO guidelines for safe recreational water environments (2006) were also used to assess some water and air parameters in pools. Standard 62.1 (2006) from American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) was also used to assess pool air parameters.

Table 1 present parametric values (PVs) for THMs from Portuguese Law 306/2007, and also guideline values (GVs) from World Health Organization (WHO, 2008) and Environmental Protection Agency from United States (US-EPA, 2003) for THMs in drinking water.

Table 1 Parametric and guideline values for THMs in drinking water.

THMs	Portugal (parametric value) ($\mu\text{g/L}$)	US-EPA (guideline value) ($\mu\text{g/L}$)	WHO (guideline values) ($\mu\text{g/L}$)
CF	-	-	200
BDCM	-	-	60
DBCM	-	-	100
BF	-	-	100
TTHMs	100	80	-

While WHO establishes guideline values for each THM, European Union (EU) and US-EPA define only one guideline value for TTHMs. EU values are now under revision, in order to consider both short term health effects and long term health effects. Although, WHO attributes individuals values to each THM, also establishes the following criteria:

$$\frac{C_{CF}}{300} + \frac{C_{BDCM}}{60} + \frac{C_{DBCM}}{100} + \frac{C_{BF}}{100} \leq 1 \quad (\text{eq. 1})$$

Being C the concentration of each compound in water.

At the present time, there are no studies on the total amount of THMs in Portuguese public indoor swimming pools. Therefore, it is of utmost interest to determine these compounds in the referred pools, as well as to study the factors that influence their formation, in order to provide better and safe water treatment conditions.

WORK DESCRIPTION

SAMPLING

30 indoor swimming pools, from Lisbon region, with similar characteristics regarding dimension and daily number of pool users, were chosen. Most of the pools are provided from public water supplying system, and use chlorine based disinfection methods: 17 pools use sodium hypochlorite (5 of which use UV radiation), 11 use chlorinated isocyanurates and 2 use both disinfection methods.

In the selected pools, water sampling was performed monthly, for a period of 6 month (April to June, September to November and few samples in December due some experimental problems). These samples were used to determine each THM concentration in water (CF_w , BDCM, DBCM and BF) and other chemical parameters, namely Cond, COD, Cl, Turb, Cianuric acid (Cian_ac). These parameters were determined in the Toxicology and Chemistry Laboratory of UAS of DSA/INSA. Herein only the results of the three month sampling are presented, because some confirmations regarding the last three month are still in progress.

In the sampling day, other determinations were made directly in the pool: pH, T_w and T_{air} , FrCl, CrCl and rel_Hum. These analyses were performed by specialized sampling technicians from Lisbon ACES (Health Centre Associations), responsible for all water and air sampling.

One of the goals of the participants in the study was to investigate whether a correlation between THMs concentration in water and air of the pool exists, although this was not the only purpose of the study. Some preliminary studies developed by the Air and Occupational Health Unit (UASO) of DSA, demonstrated that only CF is detected in the air of the chosen pools. Therefore, the quantification of CF in the air of the pool (CF_{air}) was included in the determined parameters. This parameter was determined by the UASO technicians in 6 swimming pools each month.

Water sampling, for the study of THMs, was performed in duplicate in two opposite spots of the pool tank, to allow some understanding of these compounds distribution in the pool tank. 15 ml vials were submerged about 20 cm depth, filled until the top and rapidly closed in order to prevent bubbles formation. In the case of water sampling for chemical analysis, the collection was performed only in one spot of the pool tank in 500 mL flasks. This spot was coincident with one of THMs collection spot. The sampling procedure was similar to THMs.

Air sampling was performed in two spots of the pool air environment, 30 cm of height from the water level, being one of the spots near the THMs collection spot. Sampling was done, during 2 hours, with two calibrated pumps, flow = 200 mL/min, using activated carbon tubes.

All water samples were carried to the laboratory in refrigerated bags, protected from sun light. Once having arrived to the laboratory, samples for THMs quantification, COD, and Cl, were stored at 4 °C, protected from light, until their analysis. Turb, Cond and Cian_ac were determined in the day of samples' arrival.

ANALYTICAL PROCEDURE

The pH was obtained with a portable potentiometer; FrCl and CrCl were determined by a colorimetric technique. Cond and Tub were analysed by electrometry and nefelometry. COD, a parameter which measures the total oxidizable matter present in the water, was determined by permanganate index (ISO 8467-1986). Cl was analysed by molecular absorption. CF_{air} was determined by gas chromatography (GC) with ionization flame detector (FID) – method number 1003 from NIOSH (National Institute for Occupational Safety and Health). For THMs quantification in water samples, a GC technique with electron capture detector (ECD) and headspace solid phase microextraction for sample preparation (HS-SPME) was used. The internal standard (IS) method (IS = 2-bromo-1-chloropropane) was used, in two different working ranges: – low range (CF 1.0–19.5 µg/L; BDCM and BF 0.50–3.04 µg/L and DBCM 0.41–2.48 µg/L); – high range (CF 19–160 µg/L; BDCM and BF 3–120 µg/L and DBCM 2.2–120 µg/L).

Chromatographic conditions used for both ranges are indicated in Table 2.

Table 2 Extraction and chromatographic conditions used in the determination of THMs in water samples – HS-SPME GC-ECD.

Sample preparation conditions (HS-SPME)	Extraction time: 10min (Room temperature: 20 ± 3°C)
Desorption time: 5min	
Flow gas	Helium: Flow- 0.9mL/min.
Make-up gas	Nitrogen: Flow – 30mL/min, Temperature – 290°C
Injector	Temperature: 250°C
Column programme	30°C (0min) 45°C – 20°C/min (1min) 51°C – 2°C/min (0min) 65°C – 5°C/min (0min) 230°C – 50°C/min (6min) Total time: 16.85min

STATISTICAL ANALYSIS

Descriptive analysis was applied to all variables in order to determine mean, median, standard deviation, minimum and maximum, and 1st and 3rd quartiles.

Kolmogorov-Smirnov statistic test was used to identify variables with a normal distribution. These variables were analysed using parametric tests and the remaining variables with non parametric tests. In order to investigate if a homogeneous distribution of THMs concentration in the two sampling spots

(water and air) exists, averages and medians obtained in the two sampling spots were compared using Paired t-Student or Wilcoxon tests, respectively.

Comparison of values obtained for each variable, during the three month study, was performed by ANOVA and Kruskal-Wallis tests. Possible correlation between the several parameters was also studied with Spearman test, using all the values obtained in that period.

Statistical significance were considered for differences with $p < 0.05$. The statistical analysis was performed with SPSS (Statistical Package for Social Sciences) software, version 18.0 and GraphPad Prim version 5.

DISCUSSION AND CONCLUSIONS

ANALYSIS OF CHEMICAL PARAMETERS

TTHMs water level ranged from 10 to 160 µg/L, while CF water level typically ranged from 5 to 150 µg/L, with occasional higher levels detected. Regarding other THMs levels in pool water, BDCM ranged from 0.5 to 15 µg/L, DBCM from 0.4 to 10 µg/L and BF was obtained in concentrations less than 2 µg/L. Moreover, in some pools, DBCM and BF were not detected. From these results, it can be concluded that there was a large variation in TTHMs and CF water levels between the pools and that CF was the THM obtained in higher concentrations. These results are in agreement with studies presented by other authors (Lee et al., 2009; Chu and Nieuwenhuijsen, 2002). Through out the three month CF and BDCM were always detected in pool water. DBCM was detected in 64% of the samples in April and May, and in 73% of the samples collected in June. BF was detected in less than 20% of the samples collected in each month.

In this study, in some pools, the concentration of CF was higher than the PV 100 µg/L, and as a result also TTHMs value. Nevertheless CF average or median was always inferior to the PV (Figure 2).

Comparison of each parameter average in pool water, through out the three month study, didn't show significant differences ($p > 0.05$). This comparison was not applied to BF, since few values were available. Comparing the experimental results with the ones obtained by other authors, similar variability was obtained (Lee et al., 2009; Mallika et al., 2008; Caro and Gallego, 2007).

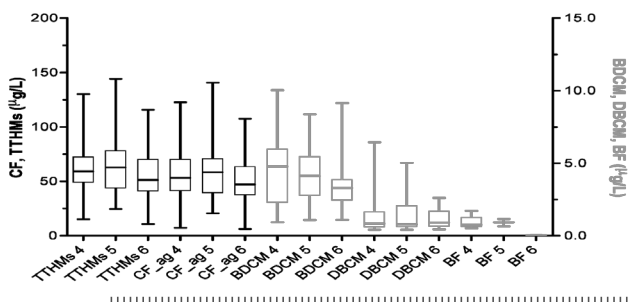


Figure 2 Medians, minimums, maximums and interquartile variation (1st quartile–3rd quartile) for TTHMs and each THM in April (4), May (5) and June (6) de 2010. The PV applied to drinking water is indicated (===).

CF is the compound detected in higher concentrations, followed by BDCM. DBCM and BF are obtained in very small concentrations or in values less than quantification (QL) limit of the method. The high concentration of CF can be explained due to the small bromine concentration present in the water supply, leading to a preferable formation of CF due to the reaction of the disinfectant with the organic matter present in the water (Chen and Weisel, 1998).

In air, CF level ranged from 40 to 200 $\mu\text{g}/\text{m}^3$, with occasional higher levels detected. Due to the small number of samples analysed, the Kolmogorov-Smirnov was not applied and this variable was considered not to have a normal distribution. Significant differences were not obtained ($p > 0.05$), when comparing the medians of CF_{air} obtained in the two sampling spots. This indicated that correlation between this value and CF_{w} can be performed in the first sampling spot.

As it happens with THMs concentration in pool water, THMs concentration in pool air is also not regulated by a specific legislation. Evaluation criteria used, were the ones established by Aguiar et al., (2009): 33, 36 and 136 $\mu\text{g}/\text{m}^3$ of THMs, for low, moderate and high exposition. Taking these values into account, it can be concluded that, in April, where CF_{air} concentration was higher than 136 $\mu\text{g}/\text{m}^3$, pool users were exposed to a high CF_{air} concentration, which can be associated to a high health risk. This high CF_{air} concentration can be related to a deficient ventilation system, collection procedures, high water turbulence and to the number of pool users present in the pool. The high variability associated with CF_{air} concentration has also been observed by other authors (Fantuzzi et al., 2010; Caro and Gallego, 2008; Erdinger et al., 2004).

Application of Kolmogorov-Smirnov statistical test to the other chemical determinations performed *in situ*, enabled the conclusion that all variables, with exception of Cl_{comb} , were considered normal variables ($p > 0.05$), during the three month.

The other chemical parameters such as COD, Cl, Cond e Cian_{ac} , were all subjected to Kolmogorov-Smirnov test, but COD was the only variable to present a normal distribution during the three month.

All these parameters were assessed by DR 5/97 or by WHO guidelines for Safe Recreational Water Environments, Volume 2: Swimming Pools and Similar Environments (2006).

T_{w} presented less variation (27 to 31 °C) than T_{air} (21 to 33 °C), although sporadic higher values were found. For T_{w} , higher values than the one indicated in the legislation (30 °C), were obtained, being 31.7 °C the highest value. Regarding T_{air} and rel_{Hum} , the DR 5/97 doesn't indicate anything and WHO guidelines (2006) only points out that these values must provide comfort to pool users. The standard ANSI/ASHRAE 1999b (*American National Standards Institute/American Society of Heating, Refrigerating and Air Conditioning Engineers*), recommends a rel_{Hum} of 50–60%, being T_{air} 2–5 °C above T_{w} . In this study some extreme values of rel_{Hum} were obtained in some pools, being the higher value of rel_{Hum} equal to 97.5%.

The pH was within the DR 5/97 recommendations (pH varied from 7.4 to 7.6 with 7 and 8 as extreme values) in most of the pools. Interquartile variation, between 7.4 and 7.6, indicates that 50% of the central results obtained in the three month, are within the recommended values. Only three pools in April,

two in May and one in June presented values higher than 8.0 (and <8.5). One of the pools presented always pH values higher than 8.0, in the three month study period. In this case, this swimming pool also presented FrCl always less than 1mg/L Cl₂, indicating that disinfectant levels are lower than the recommended values designated in the above legislation (0.5 to 1.2mg/L Cl₂ for pH between 7 and 7.4 and from 1 to 2mg/L Cl₂ for pH between 7.4 and 8). In the case of FrCl, some extreme situations were observed, not only of total absence of chlorine but also of high values like 5 mg/L. This situations were sporadic, although every month some pools with FrCl higher than 2 mg/L were detected, particularly two pools for the entire three month study.

Values for the other chemical parameters, such as COD, Cl, Cond and Cian_ac, were also subjected to Kolmogorov-Smirnov test. COD was the only variable to present a normal distribution through out the three month.

Turb presented, in most of the cases, values less than QL (<0,5 UNT). Being Turb an indicative parameter of the total organic matter in suspension, this result seems to indicate that filtration systems of the studied pools are efficient in the removal of these matters.

The values for COD, Cl, Cond and Cian_ac are presented in Table 2. Experimental quantification of the parameters in the 30 selected swimming pools was not always possible, due several sampling and experimental difficulties.

Table 2 COD, Cl, Cond e Cian_ac determined in indoor pools at Lisbon region, during a three month period – April until June.

April (N= 28)	COD (mg/L O ₂)	Cl (mg/L)	Cond (µS/cm; 20°C)	Cian_ac (mg/L)
N	26	26	26	8
Average	2.64	192	796	51.8
Median	2.49	104	527	53.5
1 st quartile	1.74	70,8	378	25.0
3 rd quartile	3.13	304	1216	73.8
min. – max.	1.02 – 5.44	30.2 – 562	203 – 2050	8.0 – 100
May(N= 28)	COD (mg/L O ₂)	Cl (mg/L)	Cond (µS/cm; 20°C)	Cian_ac (mg/L)
N	28	28	28	11
Average	2.84	215	867	31.4
Median	2.11	114	586	30.0
1 st quartile	1.70	76.2	363	7.0
3 rd quartile	3.70	393	1434	41.0
min. – max.	1.22 – 7.13	31.2 – 667	212 – 2300	5.0 – 81.0
June (N= 30)	COD (mg/L O ₂)	Cl (mg/L)	Cond (µS/cm; 20°C)	Ac_Cian (mg/L)
N	29	29	29	10
Average	2.69	225	892	24,0
Median	2.56	156	621	17.5
1 st quartile	1.75	72.5	344	6.75
3 rd quartile	3.41	380	1482	43.3
min. – max.	1.06 – 5.96	35.0 – 784	226 – 2670	6.0 – 52.0

COD quantifies the amount of oxygen necessary for the degradation of organic and some inorganic matter. Following DR 5/97 guidelines, a limit value of 4 mg/L is defined. If the legislation 306/2007 is considered for supply waters, the limit value is 5 mg/L. The average values varied from 2.64 to 2.84 mg/L de O₂, in the three month, although extreme values between 5.44 and 7.13 mg/L O₂ were obtained. Nevertheless the 3rd quartile was always inferior to values between 3.13 e 3.70 mg/L O₂, which indicates that 25% of the samples presented results higher than these values. This situation maybe associated with some contamination from pool users. Kim et al., (2002) indicated that organic matter from lotions, saliva, sweat, urine and hair can contribute to increase TOC concentration (total organic carbon).

For Cl, median values between 104 and 156mg/L, were obtained in the three months. This parameter is an indicator of the pool water quality, when compared with the value of Cl from the supply water. An increase of the value of Cl in the pool water may indicate a probable contamination of human origin, such as sweat, urine or dejects. Nevertheless the type of treatment used in the pool may also influence this value. For example the use of sodium hypochlorite may need an acidification with hydrogen chloride, which will also contribute to the increase of Cl. Legislation for drinking water 306/2007 indicates a guideline value of 250 mg/L for Cl. From table 2 values such as 784 mg/L, detected in a swimming pool in June, clearly indicate contamination. It would have been very useful to have COD and Cl values in the supplying system, which would enable evaluation of the level of contamination.

Cond medians presented lower values that the guidelines recommended in DR 5/97 (900 µS/cm; 20°C). However 3rd quartile was always higher than 900 µS/cm, indicating that more than 25% of the pools presented higher values than 1216, 1434 e 1482 µS/cm, in April, May and June, respectively. Nevertheless only very few pools presented Cond values higher than the limit value from DR 5/97 (1700 µS/cm). Being Cond a measure of the amount of salts present in the water, it can be used as an indirect evaluation of the amount of pollutants present in water (Esteves and Pacheco, 2009).

Cian_{ac}, determined only in the pools using isocianurates as disinfectants (N=33), was detected above 75mg/L (limit value from DR 5/97) only in four pools, in the three months. 3rd quartile was always inferior to this value.

Comparing the variability of all the parameters previously analysed, no significant differences were observed for the entire three month study ($p > 0.05$).

CORRELATIONS BETWEEN VARIABLES

The non parametric correlation Spearman test was applied to study possible associations between all variables, since not all variables had a normal distribution. This study was performed in all pools, through the three month period (N=86).

There was a clear positive linear correlation between CF_w and THMs water concentration ($R=0.986$, $p < 0.001$ – Figure 3), between CF_w and CF_{air} ($R= 0.640$; $p < 0.05$), CF_w and FrCl ($R= 0.225$; $p < 0.05$) and between CF_w and T_w ($R=0.284$; $p < 0.05$). Good correlations were also obtained between other THMs: there was a clear positive linear correlation between BDCM and DBCM water concentration ($R=0.560$, $p < 0.001$) and good correlation between BF and DBCM ($R=0.709$; $p < 0.05$).

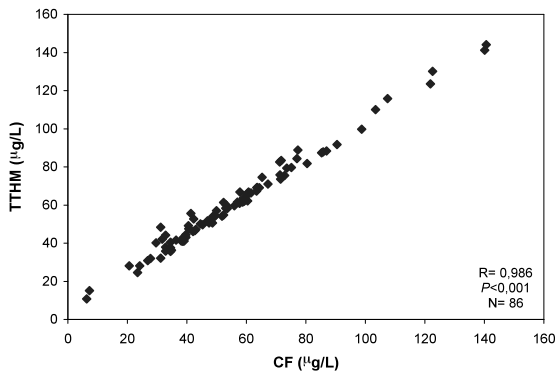


Figure 3 Spearman correlation between CFw and TTHMs.

The strong positive correlation obtained between CF_w and TTHMs was expected, since, usually, CF_w has the higher contribution to TTHMs concentration. CF_w is often considered as a good indicator of TTHMs concentration in water. Therefore some correlations between TTHMs and CF_{air} , FrCl, and T_w were expected and observed: TTHMs vs CF_{air} ($R = 0.613$; $p < 0.05$), TTHMs vs FrCl ($R = 0.225$; $p < 0.05$) and TTHMs vs T_w ($R = 0.323$; $p < 0.01$).

These results are in agreement with Chu and Nieuwenhuijsen (2002) which also obtained correlations between TTHMs water concentration and T_w . Keegan et al., (2001) also obtained correlations between TTHMs and CF_w , and between TTHMs and BDCM, but did not observe any relation between TTHMs and DBCM. Weaver et al., (2009) observed correlations between CF_w and DBCM, and between DBCM and BF.

As chlorine is added to water, the formation of species (FrCl) responsible for the disinfection increases, thus reacting with organic matter and leading to the formation of THMs in general, and CF in particular, because this is the most abundant THM in pool waters disinfected with chlorine (WHO, 2006). Since THMs formation depends on the T_w (Smith et al., 1980), an increase on that temperature will lead to the formation of more CF_w and as a result to more CF_{air} , due to evaporation.

Although Lee et al., (2009) obtained a positive linear correlation between CF_w and COD, in the present study, although expected, no correlation was obtained between these two variables, even though p was very close to the limit of significance ($R = 0.215$; $p = 0.051$). A possible explanation is that the method used for the determination of COD, oxidation with $KMnO_4$, quantifies the total reactive organic and inorganic matter, being difficult to obtain a correlation.

Xue et al., (2008) observed that, during the chlorination procedure of several fractions of dissolved organic matter (prepared in laboratory from water samples of secondary effluents), an increase of bromine originated a progressive change in the formation of THMs: at first the formation of chlorinated species was observed, followed by a mixture of bromochlorinated species and finally the formation of brominated species. This progressive change between chlorine and bromine atoms can be used to explain the correlations obtained in the present study: BDCM vs DBCM ($R = 0.560$; $p < 0.001$) and BF vs DBCM ($R = 0.709$; $p < 0.05$).

It was also observed a positive correlation between Cl and Cond ($R = 0.984$; $p < 0.001$), explained by the fact that Cond is a measure of the amount of ions in solution, therefore an increase of Cl^- water concentration will obviously lead to an increase of Cond.

As a conclusion, although the results presented herein refer only to 3 month of the study, they can give us an idea of the quality of Lisbon indoor swimming pools and of the main problems detected. Regarding general chemical parameters, the more concerning situations are related to the low values obtained for FrCl (or even inexistent) or extremely high values in some analysis, which can compromise the quality of pool water and the safety of pool users. Also some high values of COD, obtained in about 25% of the analysis, can indicate some water anthropogenic contamination, also compromising the

safety of pool users. The other chemical parameters indicate relative good water quality, although they should be regularly monitored.

TTHMs, presented a maximum value of 144 µg/L, with average values varying between 54.9 and 66.8 µg/L. Given that the 3rd quartile varied from 70.6 to 78.5 µg/L, it can be concluded that most pools presented acceptable TTHMs water values [less than 100 µg/L (Law 306/2007)]. Regarding CFair, although few pools were analysed, high values were obtained in April (median of 178 µg/m³) which indicates high exposition of pool users to this compound. In the other two months 70 and 56 µg/m³ were obtained, indicating moderate exposition to this compound. Therefore, it is of utmost interest to monitor regularly these and other DBPs in swimming pools, as well as to study the conditions that influence their formation, in order to provide better and safe water treatment conditions and to warrant the safety of swimming pool users.

ACKNOWLEDGMENTS

We would like to thank all sampling technicians, from ACES including Algueirão – Rio de Mouro, Sintra – Mafra, Oeiras, Amadora, Loures, Lisboa Oriental, Lisboa Central, Odivelas e Cacém – Queluz Health Centres, for their valuable collaboration in the sampling procedures.

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