Seasonal and spatial evolution of trihalomethanes in a drinking water distribution system according to the treatment process

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ABSTRACT

This paper comparatively shows the influence of four water treatment processes on the formation of trihalomethanes (THMs) in a water distribution system. The study was performed from February 2005 to January 2012 with analytical data of 600 samples taken in Aljaraque Water Treatment Plant (WTP) and 16 locations along the water distribution system (WDS) in the region of Andévalo and the coast of Huelva (southwest Spain), a region with significant seasonal and population changes. The comparison of results in the four different processes studied indicated a clear link of the treatment process with the formation of THM along the WDS. The most effective treatment process is preozonation and activated carbon filtration (P3), which is also the most stable under summer temperatures. Experiments also show low levels of THMs with the conventional process of preoxidation with potassium permanganate (P4), delaying the chlorination to the end of the WTP, however this simple and economical treatment process is less effective and less stable than P3. In this study, strong seasonal variations were obtained (increase of THM from winter- to summer of 1.17 to 1.85 times) and a strong spatial variation (1.1 to 1.7 times from WTP to end points of WDS) which largely depends on the treatment process applied. There was also a strong correlation between THMs levels and water temperature, contact time and pH. On the other hand, it was found that THM formation is not proportional to the applied chlorine dose in the treatment process, but there is a direct relationship with the accumulated dose of chlorine. Finally, predictive models based on multiple linear regressions are proposed for each treatment process.

KEYWORDS Trihalomethanes, water treatment process, distribution system, ozonation, permanganate, disinfection by-product.

1 Introduction

Chlorine and its compounds are the most commonly used disinfectants for water treatment and its popularity is due to its high oxidizing potential and its high permanence, which provides a minimum level of chlorine residual throughout the distribution system and protects against microbial recontamination (Sadiq and Rodriguez 2004). However, chlorine reacts with the natural organic matter (NOM) ubiquitous in water to form DBPs (Disinfection by-products) which are defined as compounds formed from reactions between organic and inorganic matter in water with chemical treatment agents during the water disinfection process. These compounds can take the form of trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), haloacetaldehydes (HAs), halonitromethanes (HNMs) and a host of other halogenated DBPs (Richardson et al. 2007). Trihalomethanes and haloacetic acids are the two most prevalent classes of DBPs in chlorinated drinking water (Krasner et al. 2006). Traditionally, trihalomethanes have been the most studied DBPs and have been frequently used as surrogates of these products (Mercier Shanks et al. 2013).

Many of these DBPs have been shown to be cytotoxic, genetoxic or cause cancer in laboratory animals, and for these reasons, they are considered to be of public health concern (Plewa et al. 2002). Some epidemiological studies have suggested a positive relationship between DBPs exposure and cancer in humans (bladder and colorectal cancers) at a trihalomethane concentration greater than 50 µg/L (Bove et al. 2007; Villanueva et al. 2007, Rahman et al. 2010, Lee et al. 2013) and adverse reproductive outcomes such as fetal growth retardation, spontaneous abortions, stillbirths, and birth defects, (Grazuleviciene et al., 2013, Grellier et al., 2010, Levallois et al., 2012, Summerhayes et al., 2012).

Identification of disinfection by-products and concern over the possible adverse health effects of these compounds have promoted considerable research activity in USA and Europe in order to minimize the risk of cancer. The United States Environmental Protection Agency (USEPA), World Health Organization (WHO) and the European Union (98/83/CE) introduced regulations for THMs in drinking water. In 1979 the USEPA established a maximum concentration of THMs in drinking water of 100 µg/L. In 1998 the USEPA issued the Stage 1 Disinfectants (D)/DBP Rule, which lowered permissible levels of THMs to 80 µg/L and regulated for the first time haloacetic acids (HAAs) to 60 µg/L, bromates to 10 µg/L and chlorite to 1000 µg/L. The European Union amended in 2009 the fixed limits for maximum THMs concentration from 150 to 100 µg/L (98/83/EC; RD140/2003).

With stricter regulations for THMs and HAAs, many drinking-water utilities have changed their disinfection practices to meet the new levels. Frequently, the primary disinfectant is changed from chlorine to the so-called alternative disinfectant, like ozone. In some cases, chlorine is used as a secondary disinfectant following primary treatment with an alternative disinfectant, particularly for ozone and chlorine dioxide (Richardson et al. 2007). Chlorine and chloramines have also been used in conjunction with ozone for this purpose (Badawy et al. 2012).

A basic strategy to minimize DPBs is to adapt the potable water treatment for removing organic precursor compounds. The removal of dissolved organic carbon (DOC) is important for maintaining water quality standards, minimizing concentrations of micropollutants and controlling bacterial regrowth within distribution systems, mainly due to the elimination of a subcomponent that can act as trihalomethane precursor (Gough et al. 2014; Wen-Hai et al. 2009).

On the other hand, THM concentrations can vary significantly throughout the water distribution system (WDS). Likewise, THM concentrations can be two or six fold higher in tap water than in the treatment plant (Rodríguez and Sérodes 2001), mainly depending on the reactivity of organic matter in the water, water treatment conditions and contact time in water mains (Smith et al. 1980). The reactivity of the organic matter changes throughout the year with the lowest reactivity in winter, increasing in spring and reaching a maximum in autumn (Uyak et al. 2008). Numerous studies have also demonstrated the influence of operational parameters and water quality in the evolution of THMs in the water distribution system (organic content, pH, water temperature, bromide ion concentrations, chlorine dose, reaction time, free residual chorine) (Chowdhury et al. 2009).

In Spain, a country with different climates and heterogeneous quality of water sources, the most used disinfectant is chlorine (Rodríguez and Sérodes 2004). The Andalusian health regulation (D70/2009) in southern Spain, requires the presence of free residual chlorine in tap water for consumers from 0.2 to 1 mg/L, to ensure the disinfection of drinking water, favoring the use of chlorine and training trihalomethanes.

In this work we have investigated the influence of four water treatment processes applied in the Aljaraque Water Treatment Plant (WTP), on the formation of THMs in the water distribution system of the coast of Huelva and "El Andévalo" area (southwest Spain), from February 2005 to January 2012. The treatment processes studied were: Conventional treatment with prechloration (P1), Preoxidation with potassium permanganate, Adsorption with activated carbon powder and intermediate chlorination (P2), Advanced treatment with preozonation and granular activated carbon (GAC) filtration (P3) and conventional treatment with potassium permanganate preoxidation (P4).

With each of the processes the influence of seasonal variables, operational and water quality, on the formation of THMs was analyzed, developing a predictive model for each treatment process considering seasonal variation; these models include the dose of chlorine as sum of dosages of chlorine added to the treated water and subsequent re-chlorinations. This study shows the great influence of the treatment process on the formation on THMs in water DS and its spatial and temporal variation.

2. Materials and methods

2.1. Description of the Water Treatment Plant and Distribution System.

The area of study is the distribution system located at "El Andévalo" on the coast of Huelva (southwest Spain) and the water treatment plant located at Aljaraque (Alj WTP), a village at 8.6 km from Huelva (Fig. 1). The area is subjected to important climatic variations during the year, with water temperatures in the range of 5-28 ºC. There is also a significant variation in population during the summer, under the influence of tourism in coastal areas, rising from 67,000 to 160,000 people.

Another feature of the distribution system is the long distance between the origin of the treated water (WTP) and the last point of consumption (86 Km), which causes high residence times in the supply networks and reservoirs, especially in winter when the consumption is lower. In the studied distribution system there are three sub-systems (areas supplied by the same water supply infrastructure) with corresponding re-chlorinations (Legay 2011). The combination of these characteristics constitutes an interesting and challenging aspect of this study.

The capacity of Alj WTP is 47,500 m^3/day of drinking water, which supplies sixteen townships of "El Andévalo" and Huelva coast. The plant was built in 1990 using a conventional treatment process: prechlorination, coagulation, flocculation, sedimentation (CFS), rapid sand filtration and post-chlorination. This conventional process plant was modified in 2008 in order to remove triazines and reduce THM levels in water including adsorption with activated carbon powder, preoxidation with potassium permanganate, CFS, sand filtration, and post-chlorination. In May 2009 Alj WTP was modified to adopt advanced treatment processes, which were more versatile allowing–different treatment options that include oxidation with potassium permanganate or ozone, powdered activated carbon, re-mineralization with carbon dioxide and calcium hydroxide, CFS, rapid sand filtration, intermediate ozonation and granular activated carbon (GAC).

In the present study the following treatment procedures were tested: (Fig. 2)

P1: February 2005 to July 2007 (Fig. 2.1): Prechlorination (22-45 mg/L NaClO), Coagulation (20-60 mg/L polyaluminium chloride 10 % Al_2O_3), Flocculation (0.1 mg/L anionic polyacrylamide), Sedimentation (Pulsator), Rapid Sand Filtration and disinfection (NaClO).

P2: March 2008 to April 2009 (Fig. 2.2): Preoxidation (0.3-0.7 mg/L $KMnO_4$), Adsorption (3-8 mg/L Powdered Activated Carbon), Coagulation (18-50 mg/L polyaluminium chloride 10 % Al_2O_3), Flocculation (0.6 mg/L polydadmac), Sedimentation (Pulsator), intermediate chlorination (NaClO), Rapid Sand Filtration and disinfection (NaClO). To prevent the formation of algae in tanks and filters, sodium hypochlorite was applied to the output of the clarifier until a concentration of 0.5 mg/L free chlorine

P3: May 2009 to April 2010 (Fig. 2.3): Pre-ozonation (1-2.5 mg/L O_3), Coagulation (15-45 mg/L polyaluminium chloride 18 % Al_2O_3), Flocculation (0.6 mg/L polydadmac), intermediate chlorination (NaClO), sedimentation (Pulsator), rapid and Filtration, Granular Activated Carbon (GAC) Filtration and disinfection (NaClO). To avoid the formation of algae at the Pulsator clarifier and filters intermediate chlorination is applied, maintaining 0.5 mg/L chlorine residual at the output of clarifier.

P4: February 2011 to January 2012 (Fig. 2.4): Preoxidation (0.3-0.7 mg/L $KMnO_4$), Coagulation (15-45 mg/L polyaluminium chloride 18 % Al_2O_3), Flocculation (0.6 mg/L polydadmac), Sedimentation (Pulsator), Rapid Sand Filtration and disinfection (NaClO).

Sodium hypochlorite was used as a disinfectant in the four treatment processes, applying a dose of 0.8 to 1.2 mg/L of free residual. The treated water was sent to the Alj WTP reservoir, afterwards the water was pumped to the reservoir tanks and the intermediate regulator deposits. The distribution system was divided into four sub-systems with intermediate and final reservoirs, all with rechlorination to maintain free residual chlorine at the tap water, within the range levels required by regulation (D70/2009).

2.2. Sampling campaign

Database 1: Consecutive monthly sampling campaigns were carried out between Feb 2005 and Jan 2012 in 16 locations along the distribution system (Fig1). The main objective of the use of this database was to investigate the spatial and seasonal variation of THMs in the water distribution system and its relation to the treatment process applied. For each treatment process 86 samples were taken (56 distribution system, 14 treated water, 14 raw water) from Feb 05 to Jul 07 with P1 treatment process, Mar 08 to Apr 09 with P2; May 09 to Apr 10 with P3 and Feb 11 to Jan 12 with P4 treatment process. In summary, a total of 336 samples were collected [(56+14+14) x4=336 samples].

The sample points were selected using the following criteria: The selected points should be uniformly distributed along the network to represent the entire range of residence times observed upstream from the reservoir; they should all be supplied by the same main pipe or by secondary pipes supplied by this main pipe; the points should be selected in the network sectors where hydraulic conditions were relatively stables. Moreover, these points must always be accessible during the same day of the week, approximately at the same time. These sample points should be supplied exclusively by the reservoir and to represent a short and a long residence time from the outlet of the reservoir (Chanks et al. 2013; Simard et al. 2011). In response to these different criteria 2-4 sampling points in each location were chosen along the distribution system (reservoirs and local networks). To minimize errors associated with the residence time variable, sampling points chosen corresponding to sectors where hydraulic conditions were relatively stable. Sampling was done on the same day of the week and at the same time of the day to minimize variations due to consumer demand for water.

Database 2: Similarly monthly sampling campaigns were carried out between Jan 2007 and Jul 2012 in 3 reservoirs and network points of the distribution system “San Bartolomé” (SB), “Tharsis” (TH) and “Cabezas Rubias” (CR), located at 34, 55 and 71 km respectively from Alj WTP (measured as real distance pipeline). In each sampling monthly campaign 11 samples were taken (2 samples of the treated water, and 3 samples of each reservoir SB, TH, CR). The samples taken were

1 from the exit pipe of the reservoir and 2 at sampling points along the network closest to the reservoir. Samples were collected for six months for each process. Therefore, a total of 264 samples were collected (6x11x4=264 samples).

The aim of this database 2 was to investigate the factors affecting THM formation and develop models in order to adequately consider the THMs variations within WDS. For the statistical analysis, samples were grouped considering the seasonality: 1) Higher Range Temperature (HRT) taken from May to October, with water temperature in the range of 19.3-28.7ºC and 2) Lower Range Temperature (LRT) taken during January to April, November and December with water temperature in the range of 9.1-19.3ºC.

All samples (database 1 and 2) were sampled following the same pattern: the samples were taken once a month, in the first week of each month, the same day each week, with the same sampling route and the same time assuring the stability of the hydraulic conditions and the representativeness of the samples in the studied system.

Samples were taken at the tap of each sample point after a flow of cold tap water for about 5 minutes to ensure the representativeness of the sample. Temperature, pH, turbidity, conductivity and residual chlorine, were measured "in situ" while dissolved organic carbon, and trihalomethanes species were determined in the laboratory.

For measuring THMs duplicate samples were collected in 125 mL amber glass bottles with teflon-lined screw caps. Bottles were filled completely leaving no headspace; 1.5 mL of a sodium thiosulfate solution 0.1 M was added to each bottle to eliminate any remaining residual chlorine and to stop further THM formation. The samples were stored at 4°C and analyzed within 2 days after collection. If the time between sample collection and analysis exceeded 2 days, samples were stored at –20 °C during a maximum period of 30 days. To ensure the accuracy associated with sample collection, preservation, transport to the laboratory and storage, as well as laboratory procedures were maintained throughout the study period.

During each campaign (database 1 and 2), the following operational parameters of the treatment plant and distribution system were collected: reagent doses applied in WTP, treatment flow, disinfectant dose in re-chlorination, flow rate, water consumption. These data were used to calculate the operational variables.

2.3. Analytical methods

Free residual chlorine concentrations were analyzed using DPD (N,N-diethyl-p-phenylenediamine) colorimetric method (Standard Method 4500-Cl-G) using a Hanna photometer HI-93711. Turbidity was measured with a HACH 2100P turbidimeter. Water pH was measured with a Metrohm 744 pH-meter equipped with a gel-filled electrode, and conductivity with a Crison CM35 conductivimeter. DOC concentration was determined using a TOC-5000 Shimadzu analyzer, according to the EPA Standard Method 5310C after filtering the samples through 2 µm glass microfiber filter.

2.3.1. Analysis of trihalomethanes

Headspace-solid-phase microextraction (HS-SPME) technique and Gas Chromatography-Mass Spectrometry (GC-MS) analysis has been successfully applied to the analysis of THMs in water (Lara-Gonzalo et al. 2008; Antoniou et al. 2006; San Juan et al. 2007; Stack et al. 2000; Valencia et al. 2013, Maia et al. 2014). The analytical method used in this work and the optimization of extraction conditions were based on a previous reported procedure with some modifications (Milton-Moreano et al. 2012; Cho, D.-H., et al. 2003). The extraction was carried out using a carboxen / polydimethylsiloxane fiber (CAR/PDMS 85 µm) purchased from Sigma Aldrich. Before use, each fiber was exposed to injector port of GC under a helium flow and conditioned at 250 ºC for 30 minutes to remove contaminants and to stabilize the solid phase. For HS-SPME extraction, 2 ml of sample was transferred to sample vials of 4 ml with a magnetic bar, 250 µl of saturated sodium chloride salt and internal standard (IS) solution. The samples were sealed using a screw cap, containing a PTFE-faced rubber septum. The analytes were extracted at 40 ºC for 30 minutes with stirring speed of 250 rpm. When the extraction was complete, the fiber was immediately introduced into the GC injection port to 270 ºC during 4 minutes for desorption.

The THMs were analyzed into a Varian CP-3800 gas chromatograph coupled to an ion trap mass spectrometer Varian Saturn 2000 MS (Varian, Sunnyvale, CA, USA). The analytical column was a DB-5ms 30 m x 0.25 mm x 0.25 µm (Agilent Technologies). The GC temperature program was 40 ºC for 4 minutes, 10 ºC/min to 120 ºC and hold for 1.5 min, 25 ºC/min to 250 ºC and hold for 5 min. The total run time was 23.7 min.

The injection was conducted in the split mode with a split ratio of 1:10 for 3 min at 220 ºC. Helium gas was used as carrier gas at a constant pressure of 29 kPa and constant flow rate of 1 ml / min. The source and transfer line temperatures at 250 ºC and 180 ºC respectively. Electron ionization mass spectra were recorded in scan mode using the m/z 29-300 at 3.5 scan per s. The ions selected (SIM mode) for identification and quantification of THMs were: $CHCl_3$: 47, 83, 85, $CHCl_2Br$: 83, 85, 129, $CHClBr_2$: 79, 127, 129, $CHBr_3$: 171, 173, 175 and IS 1,2-dibromopropane: 42, 121, 123 (SIM mode). Each compound was quantified by comparing the relative area of internal standard (IS) to the target ion.

Standard solution of THM mixture ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) containing each compound at 100 µg/µL MeOH were purchased from Sigma-Aldrich (Madrid Spain) Standard stock and Intermediate solutions at 20 µg/ml and 200 µg/L, respectively were obtained by the dilution of stock standard solution with methanol (Merk Darmstadt, Germany). Working solutions of THMs were diluted using ultrapure water (18 MΩcm) from a Milli-Q water-purification system (Millipore, Watford, UK). The internal standard (IS) solution (1,2-dibromopropane) was prepared in methanol at 5 mg/L to achieve a final concentration of 5 µg/L.

For validation of the method the linearity, limit of detection (LOD), limit of quantification (LOQ), repeatability, reproducibility and recovery extraction were determined. The linearity of the method was evaluated over standard solutions prepared with ultrapure water spiked with concentration range from 5 to 100 µg/L of each THMs. The linearity was examined by plotting calibration curves of the relative area (ratio of the peak areas of the THMs to the peak areas of the internal standard) versus the concentration of each analyte. Overall, linearity was very good along the whole evaluated range with (R^2) ranging from 0.990 to 0.999. The detection and quantification limits were calculated with the data generated in the linearity studies, as the analyte concentration that corresponds to a signal equal to "*a+3Sy*" and "*a+10Sy/x*" respectively where "*a*" is the origin ordinate, and "*Sy/x*" indicates the random error for the slops. The LOD were: 1.3, 0.8, 1.1 and 0.9 µg/L and LOQ: 4.2, 2.5, 3.6 and 3.0 µg/L for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ respectively.

The precision of the method was evaluated by determination of the repeatability and reproducibility analyzing ultrapure water samples spiked with 5 µg/L of each THMs and presented as relative standard deviations (RSDs). The repeatability was studied by analyzing seven water samples in one day. The values range of repeatability (RSD) were 6-9 %. The reproducibility refers to the analysis of 12 samples over 3 different days. The value range of reproductibility obtained was 7-12% (RSD%) The recoveries from spiked samples (% REC, n=5; THM of 5, 50, 100 and 150 µg/L) were 88.9, 91.7, 99.2 and 108.2 % respectively.

2.3.2. Quality assurance and quality control.

Before analyzing samples from each sampling campaign (monthly), the quality of the analytical method was controlled by introducing four external standards with different concentrations of THMs, verifying the consistency of the results obtained with the parameters of the analytical method validation (RSD<9 %) and the linearity (R^2>0.99). All THM concentrations were determined with two replicates samples, checking the precision of the measurements. Blanks were also used for background correction and checking of other sources of error. At each sampling campaign three white field and three white spiked with 20 µg/L of each THM were analyzed and were subtracted from the analytical results of THMs in water samples, to remove the contribution of contamination in laboratory and sampling process.

2.4. Statistical analyses

Analyses of variance (ANOVA) were carried out to determine whether the differences observed between the average concentrations of DBPs in the different sub-groups of samples, grouped by season, treatment process and spatial localization were statistically significant. Pearson correlation was conducted to evaluate the statistically significant variables of the system at the 95 % significance. In order to predict the formation of THMs according the treatment processes used, four statistical models were developed. For model development, multiple regression analysis was performed using Minitab 15 software (Minitab Inc., State College, PA, USA, 2007). The results from the experimental were compared with the predicted value for the model validation.

3. Results and discussion

3.1. THMs presence at WTP and Distribution Systems

Alj WTP treats the raw water of the Chanza Reservoir. Table 1 summarizes the chemical characteristics of this water. Raw water used in the treatment processes was taken from Piedras Canal, and comes from Chanza Reservoir. DOC level was 5.69 mg/L, (min/max: 2.15 to 12.2 mg/L), and the value of UV absorbance at 254 nm was 0.112 cm^{-1}. Specific UV absorbance (SUVA) was 1.58 L/m mg estimated by the ratio of UV absorbance relative to the concentration of DOC (UV254*100/DOC). Frequently bromide levels were moderately low (175.15 µg/L), although occasionally measured peak values in summer were higher than 315 µg/L. The total trihalomethanes formation potential was 145.52 µg/L (min/max: 127.26 to 158.3 µg/L).

Absorbance in the ultraviolet range is directly related to hydrophobic/aromatic content of natural organic matter (NOM) (Iriarte-Velasco et al. 2007). The SUVA was 1.59 and denotes medium aromatic of NOM contained in the raw water. The concentrations of THMs in the treated water in each process are shown in Table 2 and Fig. 3. THMs mean values in the distribution system are shown in Table 3 and Fig. 4. As we can see in Table 2, the lowest concentrations of THMs are obtained with the process P3 which ranged from 20.58 to 57.6 µg/L with a mean value of 40.94 µg/L. In this process, ozone oxidizes the organic matter contained in the raw water, removing most of the organic precursors and preventing their reaction in the subsequent treatment. Likewise, the addition of sodium hypochlorite during the sedimentation process does not affect significantly the formation of THMs. Finally, GAC stage helps the stability of the treatment, maintaining low THM values at WTP treated water.

With the treatment process P2, the raw water organic matter was oxidized with potassium permanganate, and activated carbon powder was applied as a coadjuvant of CFS. The use of powdered activated carbon as coadjuvant of CFS (dose: 10-50 mg/L) favors removal of organic matter, THM and allows coagulant dose reduction (Álvarez-Uriarte et al. 2010) $KMnO_4$ and PAC adsorption, can enhance the performance of conventional water treatment processes in removing DBP precursors (Wenhai Chu et al. 2012). Preoxidation with ozone or with potassium permanganate benefited the subsequent coagulation process. Their efficacies were influenced by the oxidant dosage and water quality (Chen et al. 2007). The results show that using P2 sedimentation process is improved due to the 12 % reduction of the coagulant. Also $CHCl_3$ (TCM) decreased using P2, favored by the application of activated carbon powder. However, the decrease of total

THM (TTHM) is not significant compared to P4, probably because the dosage of activated carbon is low, and the effect of chlorination intermediate, by the reaction of chlorine with organic precursors not oxidized in the preoxidation with permanganate.

The process P4 is the simplest and cheapest method, which is based on a preoxidation with potassium permanganate without using chlorine during the treatment process. The chlorine is applied to the treated water, for disinfection before distribution system. Despite its simplicity, this process has been successfully applied, with low values of THM at the effluent of the WTP and distribution system, but on the contrary, it has the disadvantage of a high dispersion thorough out the distribution system, especially in the summer, as well as an increased proliferation of algae at the Pulsator clarifier, requiring a periodic cleaning.

The conventional process P1, was used in Alj WTP prior to 2008, in this case THMs concentrations obtained were high (average and maximum values of 112.31 and 146 µg/L) due to the direct application of chlorine to the organic matter in raw water, where THMs are formed as soon as chlorine is added to water. During the subsequent processes of sedimentation, filtration, and disinfection, DBPs were formed through a reaction of residual chlorine with precursors in water. Under the conditions studied, the process P1 is not effective to meet the current regulatory requirements (<100 µg/L TTHM from 2009).

On the other hand, the formation of THM species is presented in Tables 2 and 3. In the treated waters outside the Alj WTP, before distribution, $CHCl_3$ (TCM) was the predominant THM compound, representing averaged percentages of 51.5 % (57.84 µg/L), 56.2 % (23.48 µg/L), 36.41 % (21.31 µg/L), and 35.27 % (14.44 µg/L) with processes P1, P4, P2, and P3 respectively. With all the treatment processes, $CHBrCl_2$ (BDCM) was found to be the most important brominated THM but the levels were lower than the maximum acceptable level recommended by the WHO (60 µg/L), mainly for P3 (12.6 µg/L) and P4 (11.7 µg/L). Lower average levels of $CHBr_2Cl$ (DBCM) were found at P1, P2, P3 and P4: 19.51 % (21.91 µg/L), 29.11 % (17.04 µg/L), 29.9 % (12.24 µg/L) and 12.66 % (5.29 µg/L) respectively. Therefore, $CHBr_3$ (TBM) was not found using the processes P1, P2 and P4.

During the chlorination process, bromine as well as chlorine tends to react with NOM to form organo-bromine by-products. This fact indicates that both bromine-NOM interactions during ozonation and bromine/chlorine-NOM interaction during chlorination play a very important role in controlling the formation of bromate or halogenated DBPs in water treatment (Teksoy et al. 2008).

The lowest values of TCM, BDCM and DBCM were determined with P3 (preozonation using GAC filtration), which appears to be the most effective process to remove brominated THM precursors. This fact is probably due to the adsorption capacity of GAC, which reduces the aliphatic groups responsible for the brominated THMs formation.

The distribution of THM species at the water supply was comparable to the treated water outside Alj WTP, but the levels are slightly higher. Table 3 and Fig. 4 show that the lowest average values of THM in the distribution system were obtained with the P4 (48.8 µg/L) but with higher dispersion (22.3-98.95 µg/L). The process with less variability was P3 (40.7-82.4 µg/L). Likewise, there was an increase of brominated species in the water supply. The greatest increase of brominated species was observed with P3 process (48.9 %); this may be due to increased pH and bromide in water, due to the dosage of sodium hypochlorite used for disinfection and subsequent re-chlorinations (Garcia-Villanova et al. 2010, Lin et al. 2014, Roccaro et al. 2014).

3.2. Seasonal Variations of THMs

High temperatures will generally increase the rate of reaction, so water temperature was significantly correlated with the ratio of THMs. In addition to the direct effects of temperature, seasonal variations in the characteristics and composition of organic precursors have also been found to be significant (Brown et al. 2011). The THM occurrence in urban distribution systems is highly variable with the ambient temperature, but also with the localization. THMs increase about 1.5 to 2 times from the effluent of the plant to the end. Moreover, when water temperature exceeds 15 ºC, spatial THM variations are particularly high (from 2 to 4 times higher). However, it is difficult to identify the effect of each operational and water quality parameter on THM occurrence in water utilities, due to the interaction between parameters (Rodriguez and Serodes 2001).

A previous study carried out at the Buyukcekmece water treatment plant in Istanbul City, which use conventional treatment, showed that THM concentrations vary significantly between finished waters and water at the distribution network. When water temperature exceeds 24 °C in summer, the THM levels are particularly 1.2 to 1.8 times higher than finished water, while when water temperature is below 15 °C in the spring and autumn, the measured THM concentrations at the distribution system were very rarely higher than 100 µg/L (Toroz and Uyack 2005). Equally, a study of Karoom River water, showed that THM formation potential (THMFP) levels vary significantly from one season to another; when water temperature exceeds 26 ºC in summer, THMFP levels are particularly 1.2 to 1.6 times higher than spring season. (Fooladvand et al. 2011). Most of the distribution systems studied showed THM seasonal variation between cold and warm months (Summerhayes et al. 2011, Lee et al. 2013, Charisiadis et al. 2015, Scheili et al. 2015, Uyak et al. 2014), but some papers did not find any correlation between water temperature and THMs content (El-Shahat et al. 1998; Gallard and Von-Gunten 2002).

In this study, as can be seen in Fig. 5, significant seasonal variations of THMs occurred in the finished water of Alj WTP with the four processes studied. Levels of THMs were higher during summer and lower in winter. Indeed, the average levels of THMs measured in the summer months at the distribution system were from 1.17 to 1.85 times higher than the average levels in the winter months, while the temperature varied from 24.7 °C in summer to 14.3 °C in winter. It was also observed that the seasonal variations of the water quality can be influenced by the treatment process. Likewise, while using the processes P1, P2 and P3, THM concentrations increased (1.21, 1.22 and 1.17 times, respectively) from winter to summer, the seasonal variation is higher with P4 (1.85 times higher in summer). As can be observed, the lowest seasonal variation occurred with the process P3, which can be related to the better efficiency of organic precursors removal (ozonation+GAC) of this process against that is used in P4. However, lower THMs concentrations were measured with the four treatment processes in winter than in summer.

On the other hand, we applied ANOVA to the TTHM levels measured during summer and winter and, the results indicated significant differences ($p<0.05$) between the means of TTHM in both seasonal periods.

3.3. Spatial Variations of THMs

In this study the influence of the distance (measured in kilometers of pipeline) from sampling points to the Alj. WTP on the formation of THMs were analyzed. As can be observed in Fig. 6 and Fig. 7 a positive correlation was been found between THMs concentration and distance to the Alj WTP, which depends on the treatment process. The results show that in all treatment processes studied, there are considerable differences between the concentration of THMs in the treatment plant and THMs at the ends of the distribution system. The formation of THMs in the WTP represents about 90.1

%, 65.5 %, 58.2 %, and 69.9 % (P1-P4 respectively) of the THMs found at the end of the distribution system, while the rest was formed in the pipelines and reservoirs.

Depending on the treatment process, average THM levels were from 1.1 to 1.7 times higher at the ends of the system than in the effluent of the WTP. The range of THMs (span between minimal and maximal values) was lower using P3. The highest range concentrations of THMs were found in the sampling points located at the ends (North And), in summer.

Applying ANOVA on the distribution of concentrations of TTHM in Coast and “North Andévalo” with the four processes studied (normal: $p=0.071>0.05$), the existence of significant differences were demonstrated ($p<0.005$) between the means of TTHM concentration of both groups.

The increase of the THMs concentration with the distance may be due to several factors, especially the contact time, which reaches high levels in the distribution system. It can also significantly affect the addition of hypochlorite in successive re-chlorination for water disinfection and to maintain the residual chlorine concentration required by regulations.

3.4. Factors affecting THM formation

3.4.1. Influence of chlorine dose used in the WTP

In this paper we have also analyzed the influence of chlorine dose applied in each treatment process concerning the formation of THMs in treated water. With conventional treatment process P1 the preoxidation was directly on the raw water using a high dose of chlorine to maintain 0.5 mg/L of residual chlorine in the decanter. Then in the second stage was dosed sodium hypochlorite for disinfecting the finished water prior to distribution. Mean total dose of chlorine applied P1 was 5.23 mg/L, resulting in high concentrations of THM (average of 112.31 µg/L). With the treatment process P2, organic matter was initially oxidized with KMnO4 avoiding chlorine dosage in the first treatment stage, chlorine was dosed into the decanter to prevent the formation of algae and in the treated water for disinfection prior to distribution. The average dose used in P2 was 4.66 mg/L. THMs concentrations obtained were lower than P1 (P2 average 58.53 µg/L). In the treatment process P3, organic matter was oxidized with ozone, chlorine was dosed into the decanter and at treated water for disinfection prior to distribution. The average total dose of chlorine applied in P3 was 4.63 mg/L and the lowest of THMs (40.94 µg/L) concentrations were obtained. Finally, in the process P4, organic matter is oxidized with $KMnO_4$ avoiding chlorine dosing during treatment until the final disinfecting before distribution reservoir. Finally, low THMs concentrations are also obtained with P4 (average: 41.78 µg/L) with an average chlorine dose 2.63 mg/L (Table 4). In the four treatment processes studied we obtained significant differences of THMs applying similar doses of chlorine. Thus we proved the nonexistence of correlation between the dose of chlorine in WTP and THMs formation. It was found that the dose of chlorine in the WTP has less influence on the formation of THMs that the type of oxidation process and chlorine dosing point.

Then, we can conclude that the most effective way to minimize DBP occurrence in drinking water distribution systems is to remove organic matter before the first chlorination point. This strategy has the advantage of favoring the control and effectiveness of disinfection downstream and reducing DBP formation, with the associated potential health risks. According to the above described results, we can suggest that preoxidation of organic matter with non-chlorine compounds may reduce the occurrence of THMs during the treatment process, as well as a delay of chlorine injection to the last stage would also contribute.

Then, the process P3 (ozonation + CAG) generates the lowest concentration of THMs due to its effective removal of the organic matter before chlorination, and good results are also obtained with P4 process ($KMnO_4$) in which chlorine injection is delayed.

3.4.2. Influence and correlation of temperature, pH, DOC and chlorine dose

Numerous studies based on field data have demonstrated the influence of operational parameters and water quality in the evolution of THMs concentration in the distribution system. Studies based on field data are more realistic, however have limitations due to the difficulty of measuring some parameters and the difficulty of analyzing simultaneously the changes in the water quality and operational variable occurring in the "real scenario" affected by the conditions of distribution systems and specially for the treatment processes. Due to the interaction of these and other factors, the results of studies based on field data do not always match well.

Most of studies reported a significant positive correlation of temperature and DOC in the formation of TTHM. Using Pearson correlation a moderate positive correlation (r: 0.520) and a strong positive correlation (r: 0.927) was reported by Toroz and Uyack et al (2005), respectively. In the same way Liu et al (2015) found higher variations of THMs in water at high temperature. Similarly, many studies establishes that water temperature can promote the reaction of trihalomethanes, although some authors have observed lower correlations with the temperature (r: 0.441) and DOC (r: 0.585), although a higher correlation was found between the residence time and the formation of THMs, especially TCM (r: 0.89) with a nonlinear relationship (El-Shafy and Grüenwald 2000).

It has been shown that increases in pH can increase the formation of THMs. Chowdhury and Champagne (2008) identified pH, temperature and reaction time as significant for THMs formation. Foolandvand et al. (2011) found a remarkable effect of alkaline pH on THMs formation. A positive correlation has also been found between chlorine dose and THMs formation. Abdullah M.P. et al (2009) found that a high pH value could increase the THM level. Using Pearson correlation, a low but significant relationship (r: 0.285) was found between pH and the formation of THM. High pH levels increase the hydrolysis rate of the THMs precursors and increase the rate of reaction with chlorine. Increasing pH from 6 to 8.5 promote significantly the formation of TTHM. On the other hand, it has also been found a high between pH and the dose of chlorine. TTHM concentration increases with increasing dose of chlorine, but the change is not directly proportional to the applied dose of chlorine. (Fooladvand et al.2011; El-Dib and Rizkak 1995).

Recently response surface methodology (RSM) has been employed in several studies at the laboratory scale to investigate the effect and the interaction between different parameters on THMs and other DBPs formation during water disinfection. Studies developed through laboratory experiments have been found to be more reliable than field-scale study because they employ controlled conditions where effects of a particular parameter can be determined by keeping the other parameter constants or by performing factorial analyses (Chowdhury et al. 2009, Bezerra et al. 2008). Studies based on laboratory have clear advantages but not always reflect the changes that occur in the "real scenario" of the WTP and its distribution system. Therefore both types of studies can be complementary to evaluate the factors affecting the formation of THMs.

Doederer K et al. (2014) applied RSM and concluded that increased temperatures led to higher formation of THMs, during chlorination, pH was identified as the major influencing factor for most DBP formation, except for TCM for which the reaction time was the most significant factor. Chlorination at elevated pH led to an increased formation of the four THMs. Watson K, et al. (2015) studied 18 synthetic waters of differing characteristics found that DOC was the predominant factor in the formation of TCM. Formation of fully chlorinated DBPs was highly dependent on DOC concentration at the point of disinfection, with high DOC levels being correlated to high chlorinated DBP formation. Molar yield of THM increased with DOC, bromide and chlorine concentration. Platikanov et al. (2010) found that higher DOM fraction concentration led to higher THM concentration, an increase of pH corresponding to higher concentration levels of chloroform and reduced bromoform, higher levels of chlorine dose and temperature produced a rise in the total THM formation, especially of the chlorinated THMs; higher bromide concentration generates higher concentrations of brominated THMs.

Our study was performed with field data. THM formation was evaluated at three distribution system reservoirs: San Bartolomé (SB), Tharsis (TH) and Cabezas Rubias (CR) located at 34, 55 and 71 km respectively from Alj WTP. The samples are grouped considering the seasonality: 1) HRT taken from May to October, with water temperature in the range of 19.3-28.7 °C and 2) LRT taken during January, February, March, April, November and December with water temperature in the range of 9.1-19.3 °C.

The flow diagram for the system studied was WTP ► SB Reservoir ► TH Reservoir ► CR Reservoir. There is automatic re-chlorination with automatic equipment for measuring residual chlorine and automatic dosing of sodium hypoclorite in each reservoir, which ensures the concentration of free residual chlorine in the water reservoir within the value range assigned (chlorine values of 1-1.2 mg/L maintaining chlorine range of 0.2-0.8 mg/L in the consumers tap, as required by regulation). Statistical analysis using Pearson correlation showed no correlation (r: 0.17-0.23) between chlorine dose applied to each rechlorination process and the presence of THMs in water distribution system; however a clear correlation with the total chlorine applied (sum of doses of chlorine added) was observed (r: 0.578-0.865).

After that, using Pearson correlation method we have assessed the influence and correlation of the accumulated dose (D) of disinfectant chlorine applied in treatment and re-chlorination (D = sum of doses of chlorine added output from the WTP and subsequent re-chlorinations to the sampling point), contact time in the distribution system (t) temperature (T), DOC and pH of the water on the formation of THMs in distribution system of Alj WTP in the samples collected at SB, TH and CR reservoirs, with the two groups of temperatures studied, HRT and LRT according to the water temperature. (Table 5 and 6). The statistical analysis showed a very good positive correlation between the temperature and TTHM with the highest incidence at high temperature range (HRT: 19.3 to 28.7°C). We have also found a direct positive relation between the water pH and the formation of THM with the four studied processes. On the other hand, re-chlorination favors the increase of water ph (r: 0.545-0.932) and finally, THM concentration was also found to be positively correlated with the accumulated dose of chlorine by successive re-chlorination effect.

By contrast, a moderate correlation of organic matter such as DOC with THM formation has been found, but there is a certain correlation between the decrease in DOC and the accumulated doses of chlorine, which is more important at higher temperature range (r: -0.577, -0.741, -0.666 and -0.703 in P1, P2, P3 and P4.).

3.4.3. Residence time

The residence time of water in reservoirs is calculated considering the flow of water supplied to each population nucleus by assuming complete mixing inside the reservoirs. In Alj WTP distribution system there was significant seasonal differences in water consumption of populations due to high summer temperatures and the increase in the population living in the tourist resorts of the coast. Increased water consumption in summer implies a reduction of average residence times in the water reservoirs located at “El Andévalo” and Cost of 30.3 % and 66 %, respectively over the winter. The reduction of the residence times in the reservoirs favors the reduction of chlorine dose and pH, and consequently the reduction of the

THMs levels. This effect is opposite to that occurring due to the increase of temperature in summer. In Alj WTP supply high residence times were measured in winter (13.7 days in the farthest reservoir).

Finally, according to the results obtained in the four treatment processes, using Pearson correlation a strong correlation between the residence time and THM in the two periods analyzed (r: 0.882-0.998) was found. The increase of THM concentrations was a nonlinear relationship which can be expressed as a potential function of residence time.

3.5. Modelling

Different modelling approaches have been used to establish relations between water quality and operational parameters with DBP concentrations in water. Most of the reported models have used DOC (or TOC), disinfectant dose, pH, temperature, and reaction time as the explanatory parameters. (Chowdhury et al. 2009; Uyak et al. 2005; Rodriguez et al. 2000; Serodes et al. 2003)

Using THMs occurrence data and operational data from Database 2 four models were investigated to predict THMs presence in the distribution system, according to the treatment process applied. To evaluate the statistical significant variables, multiple regression analysis was applied, using Minitab statistical software. Simple variables are selected that can be measured in the reservoirs with automatic instruments, directly or indirectly, in order to facilitate the implementation and practical application of the model to the control of water quality through supervisory control and data acquisition (SCADA) and remote control. The explanatory variables with high significance ($p<0.05$) considered in the model were temperature ºC (T), dissolved organic carbon mg/L (DOC), water pH (pH) and accumulated dose of chlorine, mg/L (D). In each treatment process, values have been divided into two seasonal groups (HRT and LRT) according to the water temperature. In this way it is possible to get better correlations and lower error with a single model for the entire period.

The model chosen was a logarithmic regression $y = K\,(x)^a\,(z)^b \ldots (m)^n$ where "y" denotes the variable to be modelled, in this case TTHM levels; "$x, z \ldots m$" denote the explanatory variables, $a, b, \ldots m$ represent the statistical coefficients to be estimated, and "K" is a constant term. The results of the regression analysis of the models are presented in Table 7 and it was found to be statistically significant for all variables ($p<0.05$). In general, the statistical determination coefficient of the models R^2 and the standard error of the estimates appeared satisfactory. In addition the comparison of measured and modeled THM values with R^2 value of 0.968 to 0.830 is satisfactory.

In full-scale study, the quantification of certain operational parameters suffers from uncertainties. A number of interventions have been implemented to reduce the effect of these uncertainties on the quality of the developed model.

During the study period, the CFS process was controlled. Each week Jar-Test was performed to adjust the dose of coagulant, flocculant and oxidant. Decanting process was controlled to prevent flocs leakage; during the study period the decanted water turbidity remained less than 0.7 NTU. Good practices on treatment processes were applied; involvement and experience of the management company was crucial. At all times stable process conditions were maintained, avoiding sampling during process occasional fluctuations.

Sodium hypochlorite was used in the disinfection process; the concentration of chlorine in the solution decreases with storage time and temperature, therefore it was taken into account the concentration of chlorine in sodium hypochlorite (150-123 gr/L) for calculating the accumulated dose of chlorine and chlorine dose. The residence time of water in reservoirs is calculated daily considering the flow of water supplied to each population nucleus by assuming complete mixing inside the reservoirs. The residence time was the weekly average, in stable conditions. The range of application of the model is determined by the characteristics of the study site T: (12.7-28.7); D: (2.48-9.7); pH: (6.87-8.08); COD: (2.13-3.58)

The developed model can be used as a basic tool to choose the water treatment process to apply, according to the explanatory variables and considering treatment cost. As an example, with the application of the P3 model to data collected in July, THMs values were 25.6, 45.1, 63.4 and 45.1 µg/L in WTP, SB, TH and CR, respectively. By applying the P4 model to the same data, THMs values were 57.5, 80.9, 105.6 and 89.1 µg/L. In relation to these results it can be predicted that the most appropriate treatment process applied in the month of July was P3 despite its higher cost (pre-ozonation: 4.70 €/1000m^3); the P4 process would not be appropriate in the month of July because Tharsis reservoir exceeds the legal limit of THM (100 µg/L). If the same comparative analysis was performed with data from the month of November, low levels of THMs were obtained with both processes with no significant differences between them. Therefore, in November the P4 process would be the most appropriate treatment for their lower cost (pre-$KMnO_4$: € 2.48/1000 m^3).

4. Conclusions

In this paper we investigated the influence of four different treatment processes on the seasonal and spatial occurrence of THMs in a water distribution system. The results can be summarized in the following items:

- Significant seasonal variations of THMs in the distribution system have been found; in this way THMs measured in summer were 1.17-1.85 times higher than that in winter.
- Significant spatial variations of THMs have also been found, ranging from 1.1 to 1.7 times higher at the end of distribution system than in WTP treated water.
- Both spatial and seasonal variations are strongly related to effectiveness of organic precursors removal process.
- The advanced process P3 (preozonation, CFS, Sand Filtration and GAC filtration) was the most effective and stable treatment process, getting the lowest values of THMs with less influence of seasonal and spatial variation. In conventional process P4 (pre-KMnO4, CFS, Sand Filtration) low concentrations of THMs were obtained in the distribution system. This process has advantages of simplicity and low cost, but has disadvantages associated to the high presence of THMs in summer and proliferation of algal blooms in the decanter. The keys for this process (P4) are the optimization of oxidation treatment and the delay of the chlorination. The treatment process P2 (pre-$KMnO_4$, PAC, CFS and Sand Filtration) improved the sedimentation, reducing the coagulant dose (12 %) and allowing a good removal of TCM , although the THM decreasing is not lower than that in conventional process P4 and P3. THMs values obtained with conventional treatment P1 were too high, due to the direct application of pre-chlorination on the organic matter in raw water; therefore the process P1 is not recommended.
- No correlation was found between the dose of chlorine applied in the water treatment plant and level of THMs in distribution system, however good correlation of the chlorine accumulated dose (D= sum of chlorine dose added in WTP and re-chlorinations along WDS) was found. This fact has not been reported previously.
- A direct relationship of the temperature and pH of the water with the level of THMs in the distribution system was found. In addition was checked that increasing the residence time increases concentration of THM.

- Predictive models were developed for each treatment process with simple variables that can be measured in the reservoirs with automatic instruments: accumulated dose of chlorine (D), temperature (T), pH and dissolved organic carbon (DOC). In each treatment process, values have been divided into two seasonal groups (HRT and LRT) according to the water temperature. The comparison of measured and modeled THM values (with R^2 value of 0.968 to 0.830) was satisfactory. This fact corroborates the seasonal influence in the occurrence of THMs.
- Based on the results obtained may be recommended the advanced treatment process P3 (Preozonation, CFS, Sand filtration and GAC) as the most effective and stable to maintain a controlled and lower formation of THMs in drinking water. A good practice to minimize the formation of THMs is the effective removal of organic matter before the first chlorination point. It is also advisable to use predictive models to select the suitable process according to the characteristics of the water distribution system and environmental conditions, in order to minimize THMs levels and treatment cost.

Ethical Statement

The authors manifest that manuscript has not been submitted to other journal and the results have not published previously. Consent to submit has been received explicitly from all co-authors and no have conflict of interest.

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FIGURE CAPTIONS

Figure 1. WTP Aljaraque supply zone

Figure 2. Aljaraque Water Treatment Plant

Figure 3. THMs in treated water according the treatment process
* Average value TTHM

Figure 4. THMs in Water Distribution Sytem according the treatment process
* Average value TTHM

Figure 5. Seasonal variation of THMs in Water Distribution System according the treatment process
Average temperature water ºC (standard deviation): 1. Spring 20.37 ºC (2.37), 2. Summer 24.7 ºC (1.67), 3. Fall 18.6 ºC (3.28), 4. Winter 14.3 ºC (2.22).
* Average value TTHM

Figure 6. Spatial variation of THMs in Distribution System according to the Treatment Process.
1.Coast r: 23km; 2.South And. r: 45km; 3.North And. r: 88km.
* Average value TTHM

Figure 7. Spatial evolution of THMs in Distribution System, according to distance from WTP.

TABLES

Table 1. Raw water quality parameters.

Parameters	Unit	Mean	Min-max
Turbidity	NTU	8.56 (6.42)	0.7-28.5
pH	---	7.01 (0.25)	6.5-7.56
TDS	mg/L	224 (32.22)	167-290
Conductivity	µs/cm	208.33 (30.41)	125-266
Temperature	ºC	18.39 (3.94)	8.6-25.5
Total Hardness	mg $CaCO_3$/L	112.02 (9.7)	88.5-134.75
Ca	mg/L	9.29 (2.21)	5.6-14.19
Mg	mg/L	6.78 (1.71)	5.3-9.65
DOC	mg/L	5.69 (2.7)	2.15-12.2
UV_{254}	cm^{-1}	0.112 (0.032)	0.069-0.190
Bromide	µg/L	175.15 (177)	<50-315
THMFP	µg/L	145.52 (11.86)	127.26-158.3

Standard deviation in parenthesis

Table 2. THM value at finished water in Water Aljaraque Treatment Plant

WTP		TTHM	TCM	BDCM	DBCM	TBM
	Mean (SD)	112.31 (19.74)	57.84 (21.48)	32.58 (11.74)	21.91 (8.23)	ND
P1	Median	108.55	60	34,2	18.2	ND
(N=14)	Min-max	69.00-146.00	17.00-91.1	9.00-52.00	11.6-41.00	ND
	% total THMs		51.5 %	29.01 %	19.51 %	
	Mean (SD)	58.53 (16.27)	21.31 (8.1)	20.19 (4.96)	17.04 (5.49)	ND
P2	Median	57	19.15	19.4	15.25	ND
(N=14)	Min-max	29.8-81.4	9.5-35.00	10.30-26.80	10.10-30.10	ND
	% total THMs		36.41 %	34.45 %	29.11 %	
	Mean (SD)	40.94 (12.10)	14.44 (9.04)	12.44 (4.69)	12.24 (4.92)	1.82(3.03)
P3	Median	44.15	14.75	12.6	12.2	ND
(N=14)	Min-max	20.28-57-6	ND-28.9	6.50-22.00	5.00-19.7	ND-7.8
	% total THMs		35.27 %	30.39 %	29.9 %	4.45 %
	Mean (SD)	41.78 (12.60)	23.48 (7.59)	13.01 (5.95)	5.29 (4.01)	ND
P4	Median	38.41	22.6	11.7	6.4	ND
(N=14)	Min-max	26.6-68.5	11.23-34.9	6.3-29.4	0-11.63	ND
	% total THMs		56.2 %	31.14 %	12.66 %	

Standard deviation in parenthesis

Table 3. THM value at supply water. Distribution System.

SUPPLY		TTHM	TCM	BDCM	DBCM	TBM
	Mean (SD)	115.21 (17.44)	63.78 (19.25)	33.20 (8.52)	18.45 (7.84)	ND
P1	Median	113.8	71	32.8	17.1	ND
(N=56)	Min-max	79-146	13-105.9	15-53	0-49	ND
	% total THMs		55.36 %	28.82 %	16.01 %	
	Mean (SD)	81.99 (16.38)	35.72 (11.06)	27.16 (5.15)	18.77 (5.46)	0.33 (1.46)
P2	Median	81.9	36.6	26.8	18.9	ND
(N=56)	Min-max	48.9-122	18.9-62.2	16.3-40.8	6.6-28.7	ND-7.9
	% total THMs		43.57 %	33.13 %	22.89 %	0.41 %
	Mean (SD)	64.42 (11.28)	25.35 (9.52)	21.02 (5.62)	14,96 (6.81)	3.48 (4.99)
P3	Median	66.3	25.2	21	13.8	<DL
(N=56)	Min-max	40.7-82.4	7.9-46.8	6.4-34.3	ND-27.5	ND-17.3
	% total THMs		39.35 %	32.63 %	23.22 %	5.4 %
	Mean (SD)	48.80 (18.05)	27.34 (12.29)	14.34 (8.48)	7.12 (6.92)	ND
P4	Median	45.7	22.7	12.35	6.75	ND
(N=56)	Min-max	22.3-98.95	ND-65.38	ND-34.2	ND-26.7	ND
	% total THMs		56.04 %	23.39 %	14.59 %	

Standard deviation in parenthesis

Table 4. Influence Dose chlorine in WTP.

WTP		Chlorine dose	DOC	TTHM	Oxidation
P1	Mean (SD)	5.23 (1.03)	3.78 (0.98)	112.31 (19.74)	Pre-chlorine
(N=28)	Min-max	3.09-4.2	2.3-5.8	69.00-146.00	
P2	Mean (SD)	4.66 (1.25)	3.75 (0.59)	58.53 (16.27)	Pre-$KMnO_4$
(N=28)	Min-max	2.97-6.54	2.7-4.5	29.8-81.40	Inter-chlor.
P3	Mean (SD)	4.63 (0.53)	2.93 (0.55)	40.94 (12.10)	Pre-Ozone
(N=28)	Min-max	3.40-5.57	2.2-3.7	20.28-57.6	Inter-chlor.
P4	Mean (SD)	2.63 (0.29)	3.98 (0.77)	41.78 (12.60)	Pre-$KMnO_4$
(N=28)	Min-max	2.11-3.25	2.0-4.9	26.6-68.5	

Standard deviation in parenthesis

Chlorine Dose: (mg/L) chlorine

DOC (mg/L): Dissolved organic carbon, in treated water

Table 5. Average Value TTHM, Temperature (T), pH, DOC, accumulate dose (D) and contact time (t)

		HRT							LRT					
		L *(Km)*	t *(day)*	T *ºC*	pH	DOC *mg/L*	D *mg/L*	TTHM *µg/L*	t *(day)*	T *ºC*	pH	DOC *mg/L*	D *mg/L*	TTHM *µg/L*
P1	Alj WTP	0	0.00	22.07	7.20	3.58	5.54	123.73	0.00	15.53	7.58	3.4	5.39	107.83
	SB	34	0.93	23.57	7.57	3.57	6.20	126.53	1.22	15.60	7.60	3.43	5.40	108.14
	TH	55	2.44	24.07	7.65	3.23	6.91	129.01	3.29	16.00	7.63	3.22	6.03	131.98
	CR	71	7.57	24.13	7.80	3.13	9.36	133.53	9.94	15.97	7.80	3.03	7.53	124.79
P2	Alj WTP	0	0.00	22.55	7.40	3.47	5.30	43.55	0.00	13.38	7.35	4.03	4.83	56.75
	SB	34	0.91	24.73	7.67	3.27	6.25	79.17	1.21	12.67	7.55	3.73	5.27	61.40
	TH	55	2.40	25.07	7.83	3.20	7.06	95.47	3.2	13.17	7.80	3.56	5.83	73.67
	CR	71	7.53	25.00	8.08	3.05	9.70	89.23	9.91	14.07	7.98	3.00	7.42	72.03
P3	Alj WTP	0	0.00	25.47	7.30	2,90	4.68	38.43	0.00	13.38	7.28	2.95	4.58	36.82
	SB	34	0.91	26.57	7.43	2,60	5.48	45.87	1.19	13.67	7.40	2.80	4.43	47.80
	TH	55	2.39	28.13	7.57	2,40	7.08	61.27	3.15	14.27	7.53	2.63	5.04	53.20
	CR	71	7.46	27.50	7.77	2,13	9.59	58.93	9.89	16.00	7.80	2.43	6.60	62.57
P4	Alj WTP	0	0.00	22.93	6.87	3.38	2.78	37.29	0.00	16.83	6.74	4.58	2.48	26.42
	SB	34	0.90	23.87	6.93	3.10	3.46	53.53	1.19	16.50	6.87	3.84	3.00	27.88
	TH	55	2.37	24.43	7.15	2.77	4.26	64.73	3.14	17.03	6.88	3.21	3.62	33.53
	CR	71	7.46	25.07	7.37	2.50	6.58	64.14	9.88	17.77	7.12	2.87	5.13	35.30

Alj WTP: Treated water WTP outside; SB: San Bartolomé Reservoir; TH: Tharsis Reservoir; CR: Cabezas Rubias Reservoir.

*HRT: Higher Range Temperature: (May,Jun,Jul,Aug,Sep,Oct).

*LRT: Lower Range Temperature: (Jan,Feb,Mar,Abr,Nov,Dec).

D: Dose chlorine: accumulate dose chlorine distribution system.

Table 6. Correlation Matrix.

		HRT				LRT			
		P1	P2	P3	P4	P1	P2	P3	P4
THM-T	r	0.649	0.732	0.817	0.861	0.927	0.751	0.705	0.642
	p	0.022	0.007	0.001	0.001	0.0001	0.005	0.001	0.024
THM-pH	r	0.880	0.805	0.871	0.815	0.618	0.862	0.871	0.746
	p	0.0001	0.002	0.0001	0.001	0.032	0.0001	0.0001	0.005
THM-DOC	r	-0.902	-0.626	-0.757	-0.656	0.704	-0.578	-0.584	-0.856
	p	0.0001	0.03	0.004	0.021	0.011	0.049	0.046	0.0001
THM-D	r	0.581	0.628	0.677	0.745	0.658	0.578	0.704	0.865
	p	0.047	0.029	0.016	0.005	0.021	0.049	0.011	0.0001
pH-D	r	0.545	0.916	0.925	0.932	0.586	0.891	0.757	0.764
	p	0.047	0.001	0.0001	0.001	0.023	0.0001	0.004	0.004
T-D	r	0.377	0.392	0.643	0.806	0.636	0.337	0.645	0.484
	p	0.226	0.208	0.024	0.002	0.026	0.284	0.023	0.111

r: correlation coephicent, p: pearson coephicent.

HRT: May,Jun,Jul,Aug,Sep,Oct; LRT: Jan,Feb,Mar,Apr,Nov,Dic.

D: Dose chlorine: accumulate dose chlorine distribution system.

Table 7. Model summary

	K	*a*	*b*	*c*	*d*	R^2	R^2adj	p	s	R^2*
P1; HRT	104.71	-0.118	-0.348	-0.0147	0.505	0.939	0.904	0.0001	0.0067	0.891
P2; HRT	$4.26x10^{-9}$	2.63	-1.98	-1.10	9.60	0.929	0.888	0.0001	0.0488	0.957
P3; HRT	$2.51x10^{-12}$	3.27	-0.555	-0.884	10.9	0.970	0.952	0.0001	0.0251	0.915
P4; HRT	$2.69x10^{-6}$	5.33	-0.193	-0.027	0.04	0.864	0.786	0.004	0.0534	0.892
P1; LRT	$9.12x10^{-5}$	4.95	-0.288	-0.045	0.413	0.894	0.833	0.002	0.0212	0.891
P2; LRT	$1.94x10^{-4}$	0.186	-0.146	-0.863	6.84	0.986	0.979	0.0001	0.0001	0.968
P3; LRT	$1.74x10^{-7}$	1.40	0.961	-0.385	7.65	0.804	0.748	0.007	0.0050	0.893
P4; LRT	12.59	0.624	-0.226	0.323	-0.51	0.835	0.741	0.007	0.0361	0.830

Model: $TTHM = K (T)^{a} (DOC)^{b} (D)^{c} (pH)^{d}$

R^2/R^2 adj: correlation coefficient model and adjusted.

p: level of significance

s: standard errors

R^2*: correlation coefficient between measured and predicted THMs.

Seasonal and spatial evolution of trihalomethanes in a drinking water distribution system according to the treatment process

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ABSTRACT

This paper comparatively shows the influence of four water treatment processes on the formation of trihalomethanes (THMs) in a water distribution system. The study was performed from February 2005 to January 2012 with analytical data of 600 samples taken in Aljaraque Water Treatment Plant (WTP) and 16 locations along the water distribution system (WDS) in the region of Andévalo and the coast of Huelva (southwest Spain), a region with significant seasonal and population changes. The comparison of results in the four different processes studied indicated a clear link of the treatment process with the formation of THM along the WDS. The most effective treatment process is preozonation and activated carbon filtration (P3), which is also the most stable under summer temperatures. Experiments also show low levels of THMs with the conventional process of preoxidation with potassium permanganate (P4), delaying the chlorination to the end of the WTP, however this simple and economical treatment process is less effective and less stable than P3. In this study, strong seasonal variations were obtained (increase of THM from winter- to summer of 1.17 to 1.85 times) and a strong spatial variation (1.1 to 1.7 times from WTP to end points of WDS) which largely depends on the treatment process applied. There was also a strong correlation between THMs levels and water temperature, contact time and pH. On the other hand, it was found that THM formation is not proportional to the applied chlorine dose in the treatment process, but there is a direct relationship with the accumulated dose of chlorine. Finally, predictive models based on multiple linear regressions are proposed for each treatment process.

KEYWORDS Trihalomethanes, water treatment process, distribution system, ozonation, permanganate, disinfection by-product.

1 Introduction

Chlorine and its compounds are the most commonly used disinfectants for water treatment and its popularity is due to its high oxidizing potential and its high permanence, which provides a minimum level of chlorine residual throughout the distribution system and protects against microbial recontamination (Sadiq and Rodriguez 2004). However, chlorine reacts with the natural organic matter (NOM) ubiquitous in water to form DBPs (Disinfection by-products) which are defined as compounds formed from reactions between organic and inorganic matter in water with chemical treatment agents during the water disinfection process. These compounds can take the form of trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), haloacetaldehydes (HAs), halonitromethanes (HNMs) and a host of other halogenated DBPs (Richardson et al. 2007). Trihalomethanes and haloacetic acids are the two most prevalent classes of DBPs in chlorinated drinking water (Krasner et al. 2006). Traditionally, trihalomethanes have been the most studied DBPs and have been frequently used as surrogates of these products (Mercier Shanks et al. 2013).

Many of these DBPs have been shown to be cytotoxic, genetoxic or cause cancer in laboratory animals, and for these reasons, they are considered to be of public health concern (Plewa et al. 2002). Some epidemiological studies have suggested a positive relationship between DBPs exposure and cancer in humans (bladder and colorectal cancers) at a trihalomethane concentration greater than 50 µg/L (Bove et al. 2007; Villanueva et al. 2007, Rahman et al. 2010, Lee et al. 2013) and adverse reproductive outcomes such as fetal growth retardation, spontaneous abortions, stillbirths, and birth defects, (Grazuleviciene et al., 2013, Grellier et al., 2010, Levallois et al., 2012, Summerhayes et al., 2012).

Identification of disinfection by-products and concern over the possible adverse health effects of these compounds have promoted considerable research activity in USA and Europe in order to minimize the risk of cancer. The United States Environmental Protection Agency (USEPA), World Health Organization (WHO) and the European Union (98/83/CE) introduced regulations for THMs in drinking water. In 1979 the USEPA established a maximum concentration of THMs in drinking water of 100 µg/L. In 1998 the USEPA issued the Stage 1 Disinfectants (D)/DBP Rule, which lowered permissible levels of THMs to 80 µg/L and regulated for the first time haloacetic acids (HAAs) to 60 µg/L, bromates to 10 µg/L and chlorite to 1000 µg/L. The European Union amended in 2009 the fixed limits for maximum THMs concentration from 150 to 100 µg/L (98/83/EC; RD140/2003).

With stricter regulations for THMs and HAAs, many drinking-water utilities have changed their disinfection practices to meet the new levels. Frequently, the primary disinfectant is changed from chlorine to the so-called alternative disinfectant, like ozone. In some cases, chlorine is used as a secondary disinfectant following primary treatment with an alternative disinfectant, particularly for ozone and chlorine dioxide (Richardson et al. 2007). Chlorine and chloramines have also been used in conjunction with ozone for this purpose (Badawy et al. 2012).

A basic strategy to minimize DPBs is to adapt the potable water treatment for removing organic precursor compounds. The removal of dissolved organic carbon (DOC) is important for maintaining water quality standards, minimizing concentrations of micropollutants and controlling bacterial regrowth within distribution systems, mainly due to the elimination of a subcomponent that can act as trihalomethane precursor (Gough et al. 2014; Wen-Hai et al. 2009).

On the other hand, THM concentrations can vary significantly throughout the water distribution system (WDS). Likewise, THM concentrations can be two or six fold higher in tap water than in the treatment plant (Rodríguez and Sérodes 2001), mainly depending on the reactivity of organic matter in the water, water treatment conditions and contact time in water mains (Smith et al. 1980). The reactivity of the organic matter changes throughout the year with the lowest reactivity in winter, increasing in spring and reaching a maximum in autumn (Uyak et al. 2008). Numerous studies have also demonstrated the influence of operational parameters and water quality in the evolution of THMs in the water distribution system (organic content, pH, water temperature, bromide ion concentrations, chlorine dose, reaction time, free residual chorine) (Chowdhury et al. 2009).

In Spain, a country with different climates and heterogeneous quality of water sources, the most used disinfectant is chlorine (Rodríguez and Sérodes 2004). The Andalusian health regulation (D70/2009) in southern Spain, requires the presence of free residual chlorine in tap water for consumers from 0.2 to 1 mg/L, to ensure the disinfection of drinking water, favoring the use of chlorine and training trihalomethanes.

In this work we have investigated the influence of four water treatment processes applied in the Aljaraque Water Treatment Plant (WTP), on the formation of THMs in the water distribution system of the coast of Huelva and "El Andévalo" area (southwest Spain), from February 2005 to January 2012. The treatment processes studied were: Conventional treatment with prechloration (P1), Preoxidation with potassium permanganate, Adsorption with activated carbon powder and intermediate chlorination (P2), Advanced treatment with preozonation and granular activated carbon (GAC) filtration (P3) and conventional treatment with potassium permanganate preoxidation (P4).

With each of the processes the influence of seasonal variables, operational and water quality, on the formation of THMs was analyzed, developing a predictive model for each treatment process considering seasonal variation; these models include the dose of chlorine as sum of dosages of chlorine added to the treated water and subsequent re-chlorinations. This study shows the great influence of the treatment process on the formation on THMs in water DS and its spatial and temporal variation.

2. Materials and methods

2.1. Description of the Water Treatment Plant and Distribution System.

The area of study is the distribution system located at "El Andévalo" on the coast of Huelva (southwest Spain) and the water treatment plant located at Aljaraque (Alj WTP), a village at 8.6 km from Huelva (Fig. 1). The area is subjected to important climatic variations during the year, with water temperatures in the range of 5-28 ºC. There is also a significant variation in population during the summer, under the influence of tourism in coastal areas, rising from 67,000 to 160,000 people.

Another feature of the distribution system is the long distance between the origin of the treated water (WTP) and the last point of consumption (86 Km), which causes high residence times in the supply networks and reservoirs, especially in winter when the consumption is lower. In the studied distribution system there are three sub-systems (areas supplied by the same water supply infrastructure) with corresponding re-chlorinations (Legay 2011). The combination of these characteristics constitutes an interesting and challenging aspect of this study.

The capacity of Alj WTP is 47,500 m^3/day of drinking water, which supplies sixteen townships of "El Andévalo" and Huelva coast. The plant was built in 1990 using a conventional treatment process: prechlorination, coagulation, flocculation, sedimentation (CFS), rapid sand filtration and post-chlorination. This conventional process plant was modified in 2008 in order to remove triazines and reduce THM levels in water including adsorption with activated carbon powder, preoxidation with potassium permanganate, CFS, sand filtration, and post-chlorination. In May 2009 Alj WTP was modified to adopt advanced treatment processes, which were more versatile allowing–different treatment options that include oxidation with potassium permanganate or ozone, powdered activated carbon, re-mineralization with carbon dioxide and calcium hydroxide, CFS, rapid sand filtration, intermediate ozonation and granular activated carbon (GAC).

In the present study the following treatment procedures were tested: (Fig. 2)

P1: February 2005 to July 2007 (Fig. 2.1): Prechlorination (22-45 mg/L NaClO), Coagulation (20-60 mg/L polyaluminium chloride 10 % Al_2O_3), Flocculation (0.1 mg/L anionic polyacrylamide), Sedimentation (Pulsator), Rapid Sand Filtration and disinfection (NaClO).

P2: March 2008 to April 2009 (Fig. 2.2): Preoxidation (0.3-0.7 mg/L $KMnO_4$), Adsorption (3-8 mg/L Powdered Activated Carbon), Coagulation (18-50 mg/L polyaluminium chloride 10 % Al_2O_3), Flocculation (0.6 mg/L polydadmac), Sedimentation (Pulsator), intermediate chlorination (NaClO), Rapid Sand Filtration and disinfection (NaClO). To prevent the formation of algae in tanks and filters, sodium hypochlorite was applied to the output of the clarifier until a concentration of 0.5 mg/L free chlorine

P3: May 2009 to April 2010 (Fig. 2.3): Pre-ozonation (1-2.5 mg/L O_3), Coagulation (15-45 mg/L polyaluminium chloride 18 % Al_2O_3), Flocculation (0.6 mg/L polydadmac), intermediate chlorination (NaClO), sedimentation (Pulsator), rapid and Filtration, Granular Activated Carbon (GAC) Filtration and disinfection (NaClO). To avoid the formation of algae at the Pulsator clarifier and filters intermediate chlorination is applied, maintaining 0.5 mg/L chlorine residual at the output of clarifier.

P4: February 2011 to January 2012 (Fig. 2.4): Preoxidation (0.3-0.7 mg/L $KMnO_4$), Coagulation (15-45 mg/L polyaluminium chloride 18 % Al_2O_3), Flocculation (0.6 mg/L polydadmac), Sedimentation (Pulsator), Rapid Sand Filtration and disinfection (NaClO).

Sodium hypochlorite was used as a disinfectant in the four treatment processes, applying a dose of 0.8 to 1.2 mg/L of free residual. The treated water was sent to the Alj WTP reservoir, afterwards the water was pumped to the reservoir tanks and the intermediate regulator deposits. The distribution system was divided into four sub-systems with intermediate and final reservoirs, all with rechlorination to maintain free residual chlorine at the tap water, within the range levels required by regulation (D70/2009).

2.2. Sampling campaign

Database 1: Consecutive monthly sampling campaigns were carried out between Feb 2005 and Jan 2012 in 16 locations along the distribution system (Fig1). The main objective of the use of this database was to investigate the spatial and seasonal variation of THMs in the water distribution system and its relation to the treatment process applied. For each treatment process 86 samples were taken (56 distribution system, 14 treated water, 14 raw water) from Feb 05 to Jul 07 with P1 treatment process, Mar 08 to Apr 09 with P2; May 09 to Apr 10 with P3 and Feb 11 to Jan 12 with P4 treatment process. In summary, a total of 336 samples were collected [(56+14+14) x4=336 samples].

The sample points were selected using the following criteria: The selected points should be uniformly distributed along the network to represent the entire range of residence times observed upstream from the reservoir; they should all be supplied by the same main pipe or by secondary pipes supplied by this main pipe; the points should be selected in the network sectors where hydraulic conditions were relatively stables. Moreover, these points must always be accessible during the same day of the week, approximately at the same time. These sample points should be supplied exclusively by the reservoir and to represent a short and a long residence time from the outlet of the reservoir (Chanks et al. 2013; Simard et al. 2011). In response to these different criteria 2-4 sampling points in each location were chosen along the distribution system (reservoirs and local networks). To minimize errors associated with the residence time variable, sampling points chosen corresponding to sectors where hydraulic conditions were relatively stable. Sampling was done on the same day of the week and at the same time of the day to minimize variations due to consumer demand for water.

Database 2: Similarly monthly sampling campaigns were carried out between Jan 2007 and Jul 2012 in 3 reservoirs and network points of the distribution system “San Bartolomé” (SB), “Tharsis” (TH) and “Cabezas Rubias” (CR), located at 34, 55 and 71 km respectively from Alj WTP (measured as real distance pipeline). In each sampling monthly campaign 11 samples were taken (2 samples of the treated water, and 3 samples of each reservoir SB, TH, CR). The samples taken were

1 from the exit pipe of the reservoir and 2 at sampling points along the network closest to the reservoir. Samples were collected for six months for each process. Therefore, a total of 264 samples were collected (6x11x4=264 samples).

The aim of this database 2 was to investigate the factors affecting THM formation and develop models in order to adequately consider the THMs variations within WDS. For the statistical analysis, samples were grouped considering the seasonality: 1) Higher Range Temperature (HRT) taken from May to October, with water temperature in the range of 19.3-28.7ºC and 2) Lower Range Temperature (LRT) taken during January to April, November and December with water temperature in the range of 9.1-19.3ºC.

All samples (database 1 and 2) were sampled following the same pattern: the samples were taken once a month, in the first week of each month, the same day each week, with the same sampling route and the same time assuring the stability of the hydraulic conditions and the representativeness of the samples in the studied system.

Samples were taken at the tap of each sample point after a flow of cold tap water for about 5 minutes to ensure the representativeness of the sample. Temperature, pH, turbidity, conductivity and residual chlorine, were measured "in situ" while dissolved organic carbon, and trihalomethanes species were determined in the laboratory.

For measuring THMs duplicate samples were collected in 125 mL amber glass bottles with teflon-lined screw caps. Bottles were filled completely leaving no headspace; 1.5 mL of a sodium thiosulfate solution 0.1 M was added to each bottle to eliminate any remaining residual chlorine and to stop further THM formation. The samples were stored at 4°C and analyzed within 2 days after collection. If the time between sample collection and analysis exceeded 2 days, samples were stored at –20 °C during a maximum period of 30 days. To ensure the accuracy associated with sample collection, preservation, transport to the laboratory and storage, as well as laboratory procedures were maintained throughout the study period.

During each campaign (database 1 and 2), the following operational parameters of the treatment plant and distribution system were collected: reagent doses applied in WTP, treatment flow, disinfectant dose in re-chlorination, flow rate, water consumption. These data were used to calculate the operational variables.

2.3. Analytical methods

Free residual chlorine concentrations were analyzed using DPD (N,N-diethyl-p-phenylenediamine) colorimetric method (Standard Method 4500-Cl-G) using a Hanna photometer HI-93711. Turbidity was measured with a HACH 2100P turbidimeter. Water pH was measured with a Metrohm 744 pH-meter equipped with a gel-filled electrode, and conductivity with a Crison CM35 conductivimeter. DOC concentration was determined using a TOC-5000 Shimadzu analyzer, according to the EPA Standard Method 5310C after filtering the samples through 2 µm glass microfiber filter.

2.3.1. Analysis of trihalomethanes

Headspace-solid-phase microextraction (HS-SPME) technique and Gas Chromatography-Mass Spectrometry (GC-MS) analysis has been successfully applied to the analysis of THMs in water (Lara-Gonzalo et al. 2008; Antoniou et al. 2006; San Juan et al. 2007; Stack et al. 2000; Valencia et al. 2013, Maia et al. 2014). The analytical method used in this work and the optimization of extraction conditions were based on a previous reported procedure with some modifications (Milton-Moreano et al. 2012; Cho, D.-H., et al. 2003). The extraction was carried out using a carboxen / polydimethylsiloxane fiber (CAR/PDMS 85 µm) purchased from Sigma Aldrich. Before use, each fiber was exposed to injector port of GC under a helium flow and conditioned at 250 ºC for 30 minutes to remove contaminants and to stabilize the solid phase. For HS-SPME extraction, 2 ml of sample was transferred to sample vials of 4 ml with a magnetic bar, 250 µl of saturated sodium chloride salt and internal standard (IS) solution. The samples were sealed using a screw cap, containing a PTFE-faced rubber septum. The analytes were extracted at 40 ºC for 30 minutes with stirring speed of 250 rpm. When the extraction was complete, the fiber was immediately introduced into the GC injection port to 270 ºC during 4 minutes for desorption.

The THMs were analyzed into a Varian CP-3800 gas chromatograph coupled to an ion trap mass spectrometer Varian Saturn 2000 MS (Varian, Sunnyvale, CA, USA). The analytical column was a DB-5ms 30 m x 0.25 mm x 0.25 µm (Agilent Technologies). The GC temperature program was 40 ºC for 4 minutes, 10 ºC/min to 120 ºC and hold for 1.5 min, 25 ºC/min to 250 ºC and hold for 5 min. The total run time was 23.7 min.

The injection was conducted in the split mode with a split ratio of 1:10 for 3 min at 220 ºC. Helium gas was used as carrier gas at a constant pressure of 29 kPa and constant flow rate of 1 ml / min. The source and transfer line temperatures at 250 ºC and 180 ºC respectively. Electron ionization mass spectra were recorded in scan mode using the m/z 29-300 at 3.5 scan per s. The ions selected (SIM mode) for identification and quantification of THMs were: $CHCl_3$: 47, 83, 85, $CHCl_2Br$: 83, 85, 129, $CHClBr_2$: 79, 127, 129, $CHBr_3$: 171, 173, 175 and IS 1,2-dibromopropane: 42, 121, 123 (SIM mode). Each compound was quantified by comparing the relative area of internal standard (IS) to the target ion.

Standard solution of THM mixture ($CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$) containing each compound at 100 µg/ µL MeOH were purchased from Sigma-Aldrich (Madrid Spain) Standard stock and Intermediate solutions at 20 µg/ml and 200 µg/L, respectively were obtained by the dilution of stock standard solution with methanol (Merk Darmstadt, Germany). Working solutions of THMs were diluted using ultrapure water (18 MΩcm) from a Milli-Q water-purification system (Millipore, Watford, UK). The internal standard (IS) solution (1,2-dibromopropane) was prepared in methanol at 5 mg/L to achieve a final concentration of 5 µg/L.

For validation of the method the linearity, limit of detection (LOD), limit of quantification (LOQ), repeatability, reproducibility and recovery extraction were determined. The linearity of the method was evaluated over standard solutions prepared with ultrapure water spiked with concentration range from 5 to 100 µg/L of each THMs. The linearity was examined by plotting calibration curves of the relative area (ratio of the peak areas of the THMs to the peak areas of the internal standard) versus the concentration of each analyte. Overall, linearity was very good along the whole evaluated range with (R^2) ranging from 0.990 to 0.999. The detection and quantification limits were calculated with the data generated in the linearity studies, as the analyte concentration that corresponds to a signal equal to "*a+3Sy*" and "*a+10Sy/x*" respectively where "*a*" is the origin ordinate, and "*Sy/x*" indicates the random error for the slops. The LOD were: 1.3, 0.8, 1.1 and 0.9 µg/L and LOQ: 4.2, 2.5, 3.6 and 3.0 µg/L for $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$ respectively.

The precision of the method was evaluated by determination of the repeatability and reproducibility analyzing ultrapure water samples spiked with 5 µg/L of each THMs and presented as relative standard deviations (RSDs). The repeatability was studied by analyzing seven water samples in one day. The values range of repeatability (RSD) were 6-9 %. The reproducibility refers to the analysis of 12 samples over 3 different days. The value range of reproductibility obtained was 7-12% (RSD%) The recoveries from spiked samples (% REC, n=5; THM of 5, 50, 100 and 150 µg/L) were 88.9, 91.7, 99.2 and 108.2 % respectively.

2.3.2. Quality assurance and quality control.

Before analyzing samples from each sampling campaign (monthly), the quality of the analytical method was controlled by introducing four external standards with different concentrations of THMs, verifying the consistency of the results obtained with the parameters of the analytical method validation (RSD<9 %) and the linearity (R^2>0.99). All THM concentrations were determined with two replicates samples, checking the precision of the measurements. Blanks were also used for background correction and checking of other sources of error. At each sampling campaign three white field and three white spiked with 20 µg/L of each THM were analyzed and were subtracted from the analytical results of THMs in water samples, to remove the contribution of contamination in laboratory and sampling process.

2.4. Statistical analyses

Analyses of variance (ANOVA) were carried out to determine whether the differences observed between the average concentrations of DBPs in the different sub-groups of samples, grouped by season, treatment process and spatial localization were statistically significant. Pearson correlation was conducted to evaluate the statistically significant variables of the system at the 95 % significance. In order to predict the formation of THMs according the treatment processes used, four statistical models were developed. For model development, multiple regression analysis was performed using Minitab 15 software (Minitab Inc., State College, PA, USA, 2007). The results from the experimental were compared with the predicted value for the model validation.

3. Results and discussion

3.1. THMs presence at WTP and Distribution Systems

Alj WTP treats the raw water of the Chanza Reservoir. Table 1 summarizes the chemical characteristics of this water. Raw water used in the treatment processes was taken from Piedras Canal, and comes from Chanza Reservoir. DOC level was 5.69 mg/L, (min/max: 2.15 to 12.2 mg/L), and the value of UV absorbance at 254 nm was 0.112 cm^{-1}. Specific UV absorbance (SUVA) was 1.58 L/m mg estimated by the ratio of UV absorbance relative to the concentration of DOC (UV254*100/DOC). Frequently bromide levels were moderately low (175.15 µg/L), although occasionally measured peak values in summer were higher than 315 µg/L. The total trihalomethanes formation potential was 145.52 µg/L (min/max: 127.26 to 158.3 µg/L).

Absorbance in the ultraviolet range is directly related to hydrophobic/aromatic content of natural organic matter (NOM) (Iriarte-Velasco et al. 2007). The SUVA was 1.59 and denotes medium aromatic of NOM contained in the raw water. The concentrations of THMs in the treated water in each process are shown in Table 2 and Fig. 3. THMs mean values in the distribution system are shown in Table 3 and Fig. 4. As we can see in Table 2, the lowest concentrations of THMs are obtained with the process P3 which ranged from 20.58 to 57.6 µg/L with a mean value of 40.94 µg/L. In this process, ozone oxidizes the organic matter contained in the raw water, removing most of the organic precursors and preventing their reaction in the subsequent treatment. Likewise, the addition of sodium hypochlorite during the sedimentation process does not affect significantly the formation of THMs. Finally, GAC stage helps the stability of the treatment, maintaining low THM values at WTP treated water.

With the treatment process P2, the raw water organic matter was oxidized with potassium permanganate, and activated carbon powder was applied as a coadjuvant of CFS. The use of powdered activated carbon as coadjuvant of CFS (dose: 10-50 mg/L) favors removal of organic matter, THM and allows coagulant dose reduction (Álvarez-Uriarte et al. 2010) $KMnO_4$ and PAC adsorption, can enhance the performance of conventional water treatment processes in removing DBP precursors (Wenhai Chu et al. 2012). Preoxidation with ozone or with potassium permanganate benefited the subsequent coagulation process. Their efficacies were influenced by the oxidant dosage and water quality (Chen et al. 2007). The results show that using P2 sedimentation process is improved due to the 12 % reduction of the coagulant. Also $CHCl_3$ (TCM) decreased using P2, favored by the application of activated carbon powder. However, the decrease of total

THM (TTHM) is not significant compared to P4, probably because the dosage of activated carbon is low, and the effect of chlorination intermediate, by the reaction of chlorine with organic precursors not oxidized in the preoxidation with permanganate.

The process P4 is the simplest and cheapest method, which is based on a preoxidation with potassium permanganate without using chlorine during the treatment process. The chlorine is applied to the treated water, for disinfection before distribution system. Despite its simplicity, this process has been successfully applied, with low values of THM at the effluent of the WTP and distribution system, but on the contrary, it has the disadvantage of a high dispersion thorough out the distribution system, especially in the summer, as well as an increased proliferation of algae at the Pulsator clarifier, requiring a periodic cleaning.

The conventional process P1, was used in Alj WTP prior to 2008, in this case THMs concentrations obtained were high (average and maximum values of 112.31 and 146 µg/L) due to the direct application of chlorine to the organic matter in raw water, where THMs are formed as soon as chlorine is added to water. During the subsequent processes of sedimentation, filtration, and disinfection, DBPs were formed through a reaction of residual chlorine with precursors in water. Under the conditions studied, the process P1 is not effective to meet the current regulatory requirements (<100 µg/L TTHM from 2009).

On the other hand, the formation of THM species is presented in Tables 2 and 3. In the treated waters outside the Alj WTP, before distribution, $CHCl_3$ (TCM) was the predominant THM compound, representing averaged percentages of 51.5 % (57.84 µg/L), 56.2 % (23.48 µg/L), 36.41 % (21.31 µg/L), and 35.27 % (14.44 µg/L) with processes P1, P4, P2, and P3 respectively. With all the treatment processes, $CHBrCl_2$ (BDCM) was found to be the most important brominated THM but the levels were lower than the maximum acceptable level recommended by the WHO (60 µg/L), mainly for P3 (12.6 µg/L) and P4 (11.7 µg/L). Lower average levels of $CHBr_2Cl$ (DBCM) were found at P1, P2, P3 and P4: 19.51 % (21.91 µg/L), 29.11 % (17.04 µg/L), 29.9 % (12.24 µg/L) and 12.66 % (5.29 µg/L) respectively. Therefore, $CHBr_3$ (TBM) was not found using the processes P1, P2 and P4.

During the chlorination process, bromine as well as chlorine tends to react with NOM to form organo-bromine by-products. This fact indicates that both bromine-NOM interactions during ozonation and bromine/chlorine-NOM interaction during chlorination play a very important role in controlling the formation of bromate or halogenated DBPs in water treatment (Teksoy et al. 2008).

The lowest values of TCM, BDCM and DBCM were determined with P3 (preozonation using GAC filtration), which appears to be the most effective process to remove brominated THM precursors. This fact is probably due to the adsorption capacity of GAC, which reduces the aliphatic groups responsible for the brominated THMs formation.

The distribution of THM species at the water supply was comparable to the treated water outside Alj WTP, but the levels are slightly higher. Table 3 and Fig. 4 show that the lowest average values of THM in the distribution system were obtained with the P4 (48.8 µg/L) but with higher dispersion (22.3-98.95 µg/L). The process with less variability was P3 (40.7-82.4 µg/L). Likewise, there was an increase of brominated species in the water supply. The greatest increase of brominated species was observed with P3 process (48.9 %); this may be due to increased pH and bromide in water, due to the dosage of sodium hypochlorite used for disinfection and subsequent re-chlorinations (Garcia-Villanova et al. 2010, Lin et al. 2014, Roccaro et al. 2014).

3.2. Seasonal Variations of THMs

High temperatures will generally increase the rate of reaction, so water temperature was significantly correlated with the ratio of THMs. In addition to the direct effects of temperature, seasonal variations in the characteristics and composition of organic precursors have also been found to be significant (Brown et al. 2011). The THM occurrence in urban distribution systems is highly variable with the ambient temperature, but also with the localization. THMs increase about 1.5 to 2 times from the effluent of the plant to the end. Moreover, when water temperature exceeds 15 ºC, spatial THM variations are particularly high (from 2 to 4 times higher). However, it is difficult to identify the effect of each operational and water quality parameter on THM occurrence in water utilities, due to the interaction between parameters (Rodriguez and Serodes 2001).

A previous study carried out at the Buyukcekmece water treatment plant in Istanbul City, which use conventional treatment, showed that THM concentrations vary significantly between finished waters and water at the distribution network. When water temperature exceeds 24 °C in summer, the THM levels are particularly 1.2 to 1.8 times higher than finished water, while when water temperature is below 15 °C in the spring and autumn, the measured THM concentrations at the distribution system were very rarely higher than 100 µg/L (Toroz and Uyack 2005). Equally, a study of Karoom River water, showed that THM formation potential (THMFP) levels vary significantly from one season to another; when water temperature exceeds 26 ºC in summer, THMFP levels are particularly 1.2 to 1.6 times higher than spring season. (Fooladvand et al. 2011). Most of the distribution systems studied showed THM seasonal variation between cold and warm months (Summerhayes et al. 2011, Lee et al. 2013, Charisiadis et al. 2015, Scheili et al. 2015, Uyak et al. 2014), but some papers did not find any correlation between water temperature and THMs content (El-Shahat et al. 1998; Gallard and Von-Gunten 2002).

In this study, as can be seen in Fig. 5, significant seasonal variations of THMs occurred in the finished water of Alj WTP with the four processes studied. Levels of THMs were higher during summer and lower in winter. Indeed, the average levels of THMs measured in the summer months at the distribution system were from 1.17 to 1.85 times higher than the average levels in the winter months, while the temperature varied from 24.7 °C in summer to 14.3 °C in winter. It was also observed that the seasonal variations of the water quality can be influenced by the treatment process. Likewise, while using the processes P1, P2 and P3, THM concentrations increased (1.21, 1.22 and 1.17 times, respectively) from winter to summer, the seasonal variation is higher with P4 (1.85 times higher in summer). As can be observed, the lowest seasonal variation occurred with the process P3, which can be related to the better efficiency of organic precursors removal (ozonation+GAC) of this process against that is used in P4. However, lower THMs concentrations were measured with the four treatment processes in winter than in summer.

On the other hand, we applied ANOVA to the TTHM levels measured during summer and winter and, the results indicated significant differences ($p<0.05$) between the means of TTHM in both seasonal periods.

3.3. Spatial Variations of THMs

In this study the influence of the distance (measured in kilometers of pipeline) from sampling points to the Alj. WTP on the formation of THMs were analyzed. As can be observed in Fig. 6 and Fig. 7 a positive correlation was been found between THMs concentration and distance to the Alj WTP, which depends on the treatment process. The results show that in all treatment processes studied, there are considerable differences between the concentration of THMs in the treatment plant and THMs at the ends of the distribution system. The formation of THMs in the WTP represents about 90.1

%, 65.5 %, 58.2 %, and 69.9 % (P1-P4 respectively) of the THMs found at the end of the distribution system, while the rest was formed in the pipelines and reservoirs.

Depending on the treatment process, average THM levels were from 1.1 to 1.7 times higher at the ends of the system than in the effluent of the WTP. The range of THMs (span between minimal and maximal values) was lower using P3. The highest range concentrations of THMs were found in the sampling points located at the ends (North And), in summer.

Applying ANOVA on the distribution of concentrations of TTHM in Coast and “North Andévalo” with the four processes studied (normal: $p=0.071>0.05$), the existence of significant differences were demonstrated ($p<0.005$) between the means of TTHM concentration of both groups.

The increase of the THMs concentration with the distance may be due to several factors, especially the contact time, which reaches high levels in the distribution system. It can also significantly affect the addition of hypochlorite in successive re-chlorination for water disinfection and to maintain the residual chlorine concentration required by regulations.

3.4. Factors affecting THM formation

3.4.1. Influence of chlorine dose used in the WTP

In this paper we have also analyzed the influence of chlorine dose applied in each treatment process concerning the formation of THMs in treated water. With conventional treatment process P1 the preoxidation was directly on the raw water using a high dose of chlorine to maintain 0.5 mg/L of residual chlorine in the decanter. Then in the second stage was dosed sodium hypochlorite for disinfecting the finished water prior to distribution. Mean total dose of chlorine applied P1 was 5.23 mg/L, resulting in high concentrations of THM (average of 112.31 µg/L). With the treatment process P2, organic matter was initially oxidized with KMnO4 avoiding chlorine dosage in the first treatment stage, chlorine was dosed into the decanter to prevent the formation of algae and in the treated water for disinfection prior to distribution. The average dose used in P2 was 4.66 mg/L. THMs concentrations obtained were lower than P1 (P2 average 58.53 µg/L). In the treatment process P3, organic matter was oxidized with ozone, chlorine was dosed into the decanter and at treated water for disinfection prior to distribution. The average total dose of chlorine applied in P3 was 4.63 mg/L and the lowest of THMs (40.94 µg/L) concentrations were obtained. Finally, in the process P4, organic matter is oxidized with $KMnO_4$ avoiding chlorine dosing during treatment until the final disinfecting before distribution reservoir. Finally, low THMs concentrations are also obtained with P4 (average: 41.78 µg/L) with an average chlorine dose 2.63 mg/L (Table 4). In the four treatment processes studied we obtained significant differences of THMs applying similar doses of chlorine. Thus we proved the nonexistence of correlation between the dose of chlorine in WTP and THMs formation. It was found that the dose of chlorine in the WTP has less influence on the formation of THMs that the type of oxidation process and chlorine dosing point.

Then, we can conclude that the most effective way to minimize DBP occurrence in drinking water distribution systems is to remove organic matter before the first chlorination point. This strategy has the advantage of favoring the control and effectiveness of disinfection downstream and reducing DBP formation, with the associated potential health risks. According to the above described results, we can suggest that preoxidation of organic matter with non-chlorine compounds may reduce the occurrence of THMs during the treatment process, as well as a delay of chlorine injection to the last stage would also contribute.

Then, the process P3 (ozonation + CAG) generates the lowest concentration of THMs due to its effective removal of the organic matter before chlorination, and good results are also obtained with P4 process ($KMnO_4$) in which chlorine injection is delayed.

3.4.2. Influence and correlation of temperature, pH, DOC and chlorine dose

Numerous studies based on field data have demonstrated the influence of operational parameters and water quality in the evolution of THMs concentration in the distribution system. Studies based on field data are more realistic, however have limitations due to the difficulty of measuring some parameters and the difficulty of analyzing simultaneously the changes in the water quality and operational variable occurring in the "real scenario" affected by the conditions of distribution systems and specially for the treatment processes. Due to the interaction of these and other factors, the results of studies based on field data do not always match well.

Most of studies reported a significant positive correlation of temperature and DOC in the formation of TTHM. Using Pearson correlation a moderate positive correlation (r: 0.520) and a strong positive correlation (r: 0.927) was reported by Toroz and Uyack et al (2005), respectively. In the same way Liu et al (2015) found higher variations of THMs in water at high temperature. Similarly, many studies establishes that water temperature can promote the reaction of trihalomethanes, although some authors have observed lower correlations with the temperature (r: 0.441) and DOC (r: 0.585), although a higher correlation was found between the residence time and the formation of THMs, especially TCM (r: 0.89) with a nonlinear relationship (El-Shafy and Grüenwald 2000).

It has been shown that increases in pH can increase the formation of THMs. Chowdhury and Champagne (2008) identified pH, temperature and reaction time as significant for THMs formation. Foolandvand et al. (2011) found a remarkable effect of alkaline pH on THMs formation. A positive correlation has also been found between chlorine dose and THMs formation. Abdullah M.P. et al (2009) found that a high pH value could increase the THM level. Using Pearson correlation, a low but significant relationship (r: 0.285) was found between pH and the formation of THM. High pH levels increase the hydrolysis rate of the THMs precursors and increase the rate of reaction with chlorine. Increasing pH from 6 to 8.5 promote significantly the formation of TTHM. On the other hand, it has also been found a high between pH and the dose of chlorine. TTHM concentration increases with increasing dose of chlorine, but the change is not directly proportional to the applied dose of chlorine. (Fooladvand et al.2011; El-Dib and Rizkak 1995).

Recently response surface methodology (RSM) has been employed in several studies at the laboratory scale to investigate the effect and the interaction between different parameters on THMs and other DBPs formation during water disinfection. Studies developed through laboratory experiments have been found to be more reliable than field-scale study because they employ controlled conditions where effects of a particular parameter can be determined by keeping the other parameter constants or by performing factorial analyses (Chowdhury et al. 2009, Bezerra et al. 2008). Studies based on laboratory have clear advantages but not always reflect the changes that occur in the "real scenario" of the WTP and its distribution system. Therefore both types of studies can be complementary to evaluate the factors affecting the formation of THMs.

Doederer K et al. (2014) applied RSM and concluded that increased temperatures led to higher formation of THMs, during chlorination, pH was identified as the major influencing factor for most DBP formation, except for TCM for which the reaction time was the most significant factor. Chlorination at elevated pH led to an increased formation of the four THMs. Watson K, et al. (2015) studied 18 synthetic waters of differing characteristics found that DOC was the predominant factor in the formation of TCM. Formation of fully chlorinated DBPs was highly dependent on DOC concentration at the point of disinfection, with high DOC levels being correlated to high chlorinated DBP formation. Molar yield of THM increased with DOC, bromide and chlorine concentration. Platikanov et al. (2010) found that higher DOM fraction concentration led to higher THM concentration, an increase of pH corresponding to higher concentration levels of chloroform and reduced bromoform, higher levels of chlorine dose and temperature produced a rise in the total THM formation, especially of the chlorinated THMs; higher bromide concentration generates higher concentrations of brominated THMs.

Our study was performed with field data. THM formation was evaluated at three distribution system reservoirs: San Bartolomé (SB), Tharsis (TH) and Cabezas Rubias (CR) located at 34, 55 and 71 km respectively from Alj WTP. The samples are grouped considering the seasonality: 1) HRT taken from May to October, with water temperature in the range of 19.3-28.7 °C and 2) LRT taken during January, February, March, April, November and December with water temperature in the range of 9.1-19.3 °C.

The flow diagram for the system studied was WTP ► SB Reservoir ► TH Reservoir ► CR Reservoir. There is automatic re-chlorination with automatic equipment for measuring residual chlorine and automatic dosing of sodium hypoclorite in each reservoir, which ensures the concentration of free residual chlorine in the water reservoir within the value range assigned (chlorine values of 1-1.2 mg/L maintaining chlorine range of 0.2-0.8 mg/L in the consumers tap, as required by regulation). Statistical analysis using Pearson correlation showed no correlation (r: 0.17-0.23) between chlorine dose applied to each rechlorination process and the presence of THMs in water distribution system; however a clear correlation with the total chlorine applied (sum of doses of chlorine added) was observed (r: 0.578-0.865).

After that, using Pearson correlation method we have assessed the influence and correlation of the accumulated dose (D) of disinfectant chlorine applied in treatment and re-chlorination (D = sum of doses of chlorine added output from the WTP and subsequent re-chlorinations to the sampling point), contact time in the distribution system (t) temperature (T), DOC and pH of the water on the formation of THMs in distribution system of Alj WTP in the samples collected at SB, TH and CR reservoirs, with the two groups of temperatures studied, HRT and LRT according to the water temperature. (Table 5 and 6). The statistical analysis showed a very good positive correlation between the temperature and TTHM with the highest incidence at high temperature range (HRT: 19.3 to 28.7°C). We have also found a direct positive relation between the water pH and the formation of THM with the four studied processes. On the other hand, re-chlorination favors the increase of water ph (r: 0.545-0.932) and finally, THM concentration was also found to be positively correlated with the accumulated dose of chlorine by successive re-chlorination effect.

By contrast, a moderate correlation of organic matter such as DOC with THM formation has been found, but there is a certain correlation between the decrease in DOC and the accumulated doses of chlorine, which is more important at higher temperature range (r: -0.577, -0.741, -0.666 and -0.703 in P1, P2, P3 and P4.).

3.4.3. Residence time

The residence time of water in reservoirs is calculated considering the flow of water supplied to each population nucleus by assuming complete mixing inside the reservoirs. In Alj WTP distribution system there was significant seasonal differences in water consumption of populations due to high summer temperatures and the increase in the population living in the tourist resorts of the coast. Increased water consumption in summer implies a reduction of average residence times in the water reservoirs located at “El Andévalo” and Cost of 30.3 % and 66 %, respectively over the winter. The reduction of the residence times in the reservoirs favors the reduction of chlorine dose and pH, and consequently the reduction of the

THMs levels. This effect is opposite to that occurring due to the increase of temperature in summer. In Alj WTP supply high residence times were measured in winter (13.7 days in the farthest reservoir).

Finally, according to the results obtained in the four treatment processes, using Pearson correlation a strong correlation between the residence time and THM in the two periods analyzed (r: 0.882-0.998) was found. The increase of THM concentrations was a nonlinear relationship which can be expressed as a potential function of residence time.

3.5. Modelling

Different modelling approaches have been used to establish relations between water quality and operational parameters with DBP concentrations in water. Most of the reported models have used DOC (or TOC), disinfectant dose, pH, temperature, and reaction time as the explanatory parameters. (Chowdhury et al. 2009; Uyak et al. 2005; Rodriguez et al. 2000; Serodes et al. 2003)

Using THMs occurrence data and operational data from Database 2 four models were investigated to predict THMs presence in the distribution system, according to the treatment process applied. To evaluate the statistical significant variables, multiple regression analysis was applied, using Minitab statistical software. Simple variables are selected that can be measured in the reservoirs with automatic instruments, directly or indirectly, in order to facilitate the implementation and practical application of the model to the control of water quality through supervisory control and data acquisition (SCADA) and remote control. The explanatory variables with high significance ($p<0.05$) considered in the model were temperature ºC (T), dissolved organic carbon mg/L (DOC), water pH (pH) and accumulated dose of chlorine, mg/L (D). In each treatment process, values have been divided into two seasonal groups (HRT and LRT) according to the water temperature. In this way it is possible to get better correlations and lower error with a single model for the entire period.

The model chosen was a logarithmic regression $y = K\,(x)^{a}\,(z)^{b} \ldots (m)^{n}$ where "y" denotes the variable to be modelled, in this case TTHM levels; "$x,z \ldots m$" denote the explanatory variables, $a,b,\ldots m$ represent the statistical coefficients to be estimated, and "K" is a constant term. The results of the regression analysis of the models are presented in Table 7 and it was found to be statistically significant for all variables ($p<0.05$). In general, the statistical determination coefficient of the models R^2 and the standard error of the estimates appeared satisfactory. In addition the comparison of measured and modeled THM values with R^2 value of 0.968 to 0.830 is satisfactory.

In full-scale study, the quantification of certain operational parameters suffers from uncertainties. A number of interventions have been implemented to reduce the effect of these uncertainties on the quality of the developed model.

During the study period, the CFS process was controlled. Each week Jar-Test was performed to adjust the dose of coagulant, flocculant and oxidant. Decanting process was controlled to prevent flocs leakage; during the study period the decanted water turbidity remained less than 0.7 NTU. Good practices on treatment processes were applied; involvement and experience of the management company was crucial. At all times stable process conditions were maintained, avoiding sampling during process occasional fluctuations.

Sodium hypochlorite was used in the disinfection process; the concentration of chlorine in the solution decreases with storage time and temperature, therefore it was taken into account the concentration of chlorine in sodium hypochlorite (150-123 gr/L) for calculating the accumulated dose of chlorine and chlorine dose. The residence time of water in reservoirs is calculated daily considering the flow of water supplied to each population nucleus by assuming complete mixing inside the reservoirs. The residence time was the weekly average, in stable conditions. The range of application of the model is determined by the characteristics of the study site T: (12.7-28.7); D: (2.48-9.7); pH: (6.87-8.08); COD: (2.13-3.58)

The developed model can be used as a basic tool to choose the water treatment process to apply, according to the explanatory variables and considering treatment cost. As an example, with the application of the P3 model to data collected in July, THMs values were 25.6, 45.1, 63.4 and 45.1 µg/L in WTP, SB, TH and CR, respectively. By applying the P4 model to the same data, THMs values were 57.5, 80.9, 105.6 and 89.1 µg/L. In relation to these results it can be predicted that the most appropriate treatment process applied in the month of July was P3 despite its higher cost (pre-ozonation: 4.70 €/1000m^3); the P4 process would not be appropriate in the month of July because Tharsis reservoir exceeds the legal limit of THM (100 µg/L). If the same comparative analysis was performed with data from the month of November, low levels of THMs were obtained with both processes with no significant differences between them. Therefore, in November the P4 process would be the most appropriate treatment for their lower cost (pre-$KMnO_4$: € 2.48/1000 m^3).

4. Conclusions

In this paper we investigated the influence of four different treatment processes on the seasonal and spatial occurrence of THMs in a water distribution system. The results can be summarized in the following items:

- Significant seasonal variations of THMs in the distribution system have been found; in this way THMs measured in summer were 1.17-1.85 times higher than that in winter.
- Significant spatial variations of THMs have also been found, ranging from 1.1 to 1.7 times higher at the end of distribution system than in WTP treated water.
- Both spatial and seasonal variations are strongly related to effectiveness of organic precursors removal process.
- The advanced process P3 (preozonation, CFS, Sand Filtration and GAC filtration) was the most effective and stable treatment process, getting the lowest values of THMs with less influence of seasonal and spatial variation. In conventional process P4 (pre-KMnO4, CFS, Sand Filtration) low concentrations of THMs were obtained in the distribution system. This process has advantages of simplicity and low cost, but has disadvantages associated to the high presence of THMs in summer and proliferation of algal blooms in the decanter. The keys for this process (P4) are the optimization of oxidation treatment and the delay of the chlorination. The treatment process P2 (pre-$KMnO_4$, PAC, CFS and Sand Filtration) improved the sedimentation, reducing the coagulant dose (12 %) and allowing a good removal of TCM , although the THM decreasing is not lower than that in conventional process P4 and P3. THMs values obtained with conventional treatment P1 were too high, due to the direct application of pre-chlorination on the organic matter in raw water; therefore the process P1 is not recommended.
- No correlation was found between the dose of chlorine applied in the water treatment plant and level of THMs in distribution system, however good correlation of the chlorine accumulated dose (D= sum of chlorine dose added in WTP and re-chlorinations along WDS) was found. This fact has not been reported previously.
- A direct relationship of the temperature and pH of the water with the level of THMs in the distribution system was found. In addition was checked that increasing the residence time increases concentration of THM.

- Predictive models were developed for each treatment process with simple variables that can be measured in the reservoirs with automatic instruments: accumulated dose of chlorine (D), temperature (T), pH and dissolved organic carbon (DOC). In each treatment process, values have been divided into two seasonal groups (HRT and LRT) according to the water temperature. The comparison of measured and modeled THM values (with R^2 value of 0.968 to 0.830) was satisfactory. This fact corroborates the seasonal influence in the occurrence of THMs.

- Based on the results obtained may be recommended the advanced treatment process P3 (Preozonation, CFS, Sand filtration and GAC) as the most effective and stable to maintain a controlled and lower formation of THMs in drinking water. A good practice to minimize the formation of THMs is the effective removal of organic matter before the first chlorination point. It is also advisable to use predictive models to select the suitable process according to the characteristics of the water distribution system and environmental conditions, in order to minimize THMs levels and treatment cost.

Ethical Statement

The authors manifest that manuscript has not been submitted to other journal and the results have not published previously. Consent to submit has been received explicitly from all co-authors and no have conflict of interest.

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FIGURE CAPTIONS

Figure 1. WTP Aljaraque supply zone

Figure 2. Aljaraque Water Treatment Plant

Figure 3. THMs in treated water according the treatment process
* Average value TTHM

Figure 4. THMs in Water Distribution Sytem according the treatment process
* Average value TTHM

Figure 5. Seasonal variation of THMs in Water Distribution System according the treatment process
Average temperature water ºC (standard deviation): 1. Spring 20.37 ºC (2.37), 2. Summer 24.7 ºC (1.67), 3. Fall 18.6 ºC (3.28), 4. Winter 14.3 ºC (2.22).
* Average value TTHM

Figure 6. Spatial variation of THMs in Distribution System according to the Treatment Process.
1.Coast r: 23km; 2.South And. r: 45km; 3.North And. r: 88km.
* Average value TTHM

Figure 7. Spatial evolution of THMs in Distribution System, according to distance from WTP.

TABLES

Table 1. Raw water quality parameters.

Parameters	Unit	Mean	Min-max
Turbidity	NTU	8.56 (6.42)	0.7-28.5
pH	---	7.01 (0.25)	6.5-7.56
TDS	mg/L	224 (32.22)	167-290
Conductivity	µs/cm	208.33 (30.41)	125-266
Temperature	ºC	18.39 (3.94)	8.6-25.5
Total Hardness	mg CaCO$_3$/L	112.02 (9.7)	88.5-134.75
Ca	mg/L	9.29 (2.21)	5.6-14.19
Mg	mg/L	6.78 (1.71)	5.3-9.65
DOC	mg/L	5.69 (2.7)	2.15-12.2
UV$_{254}$	cm^{-1}	0.112 (0.032)	0.069-0.190
Bromide	µg/L	175.15 (177)	<50-315
THMFP	µg/L	145.52 (11.86)	127.26-158.3

Standard deviation in parenthesis

Table 2. THM value at finished water in Water Aljaraque Treatment Plant

WTP		TTHM	TCM	BDCM	DBCM	TBM
	Mean (SD)	112.31 (19.74)	57.84 (21.48)	32.58 (11.74)	21.91 (8.23)	ND
P1	Median	108.55	60	34,2	18.2	ND
(N=14)	Min-max	69.00-146.00	17.00-91.1	9.00-52.00	11.6-41.00	ND
	% total THMs		51.5 %	29.01 %	19.51 %	
	Mean (SD)	58.53 (16.27)	21.31 (8.1)	20.19 (4.96)	17.04 (5.49)	ND
P2	Median	57	19.15	19.4	15.25	ND
(N=14)	Min-max	29.8-81.4	9.5-35.00	10.30-26.80	10.10-30.10	ND
	% total THMs		36.41 %	34.45 %	29.11 %	
	Mean (SD)	40.94 (12.10)	14.44 (9.04)	12.44 (4.69)	12.24 (4.92)	1.82(3.03)
P3	Median	44.15	14.75	12.6	12.2	ND
(N=14)	Min-max	20.28-57-6	ND-28.9	6.50-22.00	5.00-19.7	ND-7.8
	% total THMs		35.27 %	30.39 %	29.9 %	4.45 %
	Mean (SD)	41.78 (12.60)	23.48 (7.59)	13.01 (5.95)	5.29 (4.01)	ND
P4	Median	38.41	22.6	11.7	6.4	ND
(N=14)	Min-max	26.6-68.5	11.23-34.9	6.3-29.4	0-11.63	ND
	% total THMs		56.2 %	31.14 %	12.66 %	

Standard deviation in parenthesis

Table 3. THM value at supply water. Distribution System.

SUPPLY		TTHM	TCM	BDCM	DBCM	TBM
	Mean (SD)	115.21 (17.44)	63.78 (19.25)	33.20 (8.52)	18.45 (7.84)	ND
P1	Median	113.8	71	32.8	17.1	ND
(N=56)	Min-max	79-146	13-105.9	15-53	0-49	ND
	% total THMs		55.36 %	28.82 %	16.01 %	
	Mean (SD)	81.99 (16.38)	35.72 (11.06)	27.16 (5.15)	18.77 (5.46)	0.33 (1.46)
P2	Median	81.9	36.6	26.8	18.9	ND
(N=56)	Min-max	48.9-122	18.9-62.2	16.3-40.8	6.6-28.7	ND-7.9
	% total THMs		43.57 %	33.13 %	22.89 %	0.41 %
	Mean (SD)	64.42 (11.28)	25.35 (9.52)	21.02 (5.62)	14,96 (6.81)	3.48 (4.99)
P3	Median	66.3	25.2	21	13.8	<DL
(N=56)	Min-max	40.7-82.4	7.9-46.8	6.4-34.3	ND-27.5	ND-17.3
	% total THMs		39.35 %	32.63 %	23.22 %	5.4 %
	Mean (SD)	48.80 (18.05)	27.34 (12.29)	14.34 (8.48)	7.12 (6.92)	ND
P4	Median	45.7	22.7	12.35	6.75	ND
(N=56)	Min-max	22.3-98.95	ND-65.38	ND-34.2	ND-26.7	ND
	% total THMs		56.04 %	23.39 %	14.59 %	

Standard deviation in parenthesis

Table 4. Influence Dose chlorine in WTP.

WTP		Chlorine dose	DOC	TTHM	Oxidation
P1	Mean (SD)	5.23 (1.03)	3.78 (0.98)	112.31 (19.74)	Pre-chlorine
(N=28)	Min-max	3.09-4.2	2.3-5.8	69.00-146.00	
P2	Mean (SD)	4.66 (1.25)	3.75 (0.59)	58.53 (16.27)	Pre-KMnO$_4$
(N=28)	Min-max	2.97-6.54	2.7-4.5	29.8-81.40	Inter-chlor.
P3	Mean (SD)	4.63 (0.53)	2.93 (0.55)	40.94 (12.10)	Pre-Ozone
(N=28)	Min-max	3.40-5.57	2.2-3.7	20.28-57.6	Inter-chlor.
P4	Mean (SD)	2.63 (0.29)	3.98 (0.77)	41.78 (12.60)	Pre-KMnO$_4$
(N=28)	Min-max	2.11-3.25	2.0-4.9	26.6-68.5	

Standard deviation in parenthesis

Chlorine Dose: (mg/L) chlorine

DOC (mg/L): Dissolved organic carbon, in treated water

Table 5. Average Value TTHM, Temperature (T), pH, DOC, accumulate dose (D) and contact time (t)

		HRT							LRT					
		L *(Km)*	t *(day)*	T *ºC*	pH	DOC *mg/L*	D *mg/L*	TTHM *µg/L*	t *(day)*	T *ºC*	pH	DOC *mg/L*	D *mg/L*	TTHM *µg/L*
P1	Alj WTP	0	0.00	22.07	7.20	3.58	5.54	123.73	0.00	15.53	7.58	3.4	5.39	107.83
	SB	34	0.93	23.57	7.57	3.57	6.20	126.53	1.22	15.60	7.60	3.43	5.40	108.14
	TH	55	2.44	24.07	7.65	3.23	6.91	129.01	3.29	16.00	7.63	3.22	6.03	131.98
	CR	71	7.57	24.13	7.80	3.13	9.36	133.53	9.94	15.97	7.80	3.03	7.53	124.79
P2	Alj WTP	0	0.00	22.55	7.40	3.47	5.30	43.55	0.00	13.38	7.35	4.03	4.83	56.75
	SB	34	0.91	24.73	7.67	3.27	6.25	79.17	1.21	12.67	7.55	3.73	5.27	61.40
	TH	55	2.40	25.07	7.83	3.20	7.06	95.47	3.2	13.17	7.80	3.56	5.83	73.67
	CR	71	7.53	25.00	8.08	3.05	9.70	89.23	9.91	14.07	7.98	3.00	7.42	72.03
P3	Alj WTP	0	0.00	25.47	7.30	2,90	4.68	38.43	0.00	13.38	7.28	2.95	4.58	36.82
	SB	34	0.91	26.57	7.43	2,60	5.48	45.87	1.19	13.67	7.40	2.80	4.43	47.80
	TH	55	2.39	28.13	7.57	2,40	7.08	61.27	3.15	14.27	7.53	2.63	5.04	53.20
	CR	71	7.46	27.50	7.77	2,13	9.59	58.93	9.89	16.00	7.80	2.43	6.60	62.57
P4	Alj WTP	0	0.00	22.93	6.87	3.38	2.78	37.29	0.00	16.83	6.74	4.58	2.48	26.42
	SB	34	0.90	23.87	6.93	3.10	3.46	53.53	1.19	16.50	6.87	3.84	3.00	27.88
	TH	55	2.37	24.43	7.15	2.77	4.26	64.73	3.14	17.03	6.88	3.21	3.62	33.53
	CR	71	7.46	25.07	7.37	2.50	6.58	64.14	9.88	17.77	7.12	2.87	5.13	35.30

Alj WTP: Treated water WTP outside; SB: San Bartolomé Reservoir; TH: Tharsis Reservoir; CR: Cabezas Rubias Reservoir.

*HRT: Higher Range Temperature: (May,Jun,Jul,Aug,Sep,Oct).

*LRT: Lower Range Temperature: (Jan,Feb,Mar,Abr,Nov,Dec).

D: Dose chlorine: accumulate dose chlorine distribution system.

Table 6. Correlation Matrix.

		HRT				LRT			
		P1	P2	P3	P4	P1	P2	P3	P4
THM-T	r	0.649	0.732	0.817	0.861	0.927	0.751	0.705	0.642
	p	0.022	0.007	0.001	0.001	0.0001	0.005	0.001	0.024
THM-pH	r	0.880	0.805	0.871	0.815	0.618	0.862	0.871	0.746
	p	0.0001	0.002	0.0001	0.001	0.032	0.0001	0.0001	0.005
THM-DOC	r	-0.902	-0.626	-0.757	-0.656	0.704	-0.578	-0.584	-0.856
	p	0.0001	0.03	0.004	0.021	0.011	0.049	0.046	0.0001
THM-D	r	0.581	0.628	0.677	0.745	0.658	0.578	0.704	0.865
	p	0.047	0.029	0.016	0.005	0.021	0.049	0.011	0.0001
pH-D	r	0.545	0.916	0.925	0.932	0.586	0.891	0.757	0.764
	p	0.047	0.001	0.0001	0.001	0.023	0.0001	0.004	0.004
T-D	r	0.377	0.392	0.643	0.806	0.636	0.337	0.645	0.484
	p	0.226	0.208	0.024	0.002	0.026	0.284	0.023	0.111

r: correlation coephicent, p: pearson coephicent.

HRT: May,Jun,Jul,Aug,Sep,Oct; LRT: Jan,Feb,Mar,Apr,Nov,Dic.

D: Dose chlorine: accumulate dose chlorine distribution system.

Table 7. Model summary

	K	*a*	*b*	*c*	*d*	R^2	R^2adj	p	s	R^{2}*
P1; HRT	104.71	-0.118	-0.348	-0.0147	0.505	0.939	0.904	0.0001	0.0067	0.891
P2; HRT	4.26×10^{-9}	2.63	-1.98	-1.10	9.60	0.929	0.888	0.0001	0.0488	0.957
P3; HRT	2.51×10^{-12}	3.27	-0.555	-0.884	10.9	0.970	0.952	0.0001	0.0251	0.915
P4; HRT	2.69×10^{-6}	5.33	-0.193	-0.027	0.04	0.864	0.786	0.004	0.0534	0.892
P1; LRT	9.12×10^{-5}	4.95	-0.288	-0.045	0.413	0.894	0.833	0.002	0.0212	0.891
P2; LRT	1.94×10^{-4}	0.186	-0.146	-0.863	6.84	0.986	0.979	0.0001	0.0001	0.968
P3; LRT	1.74×10^{-7}	1.40	0.961	-0.385	7.65	0.804	0.748	0.007	0.0050	0.893
P4; LRT	12.59	0.624	-0.226	0.323	-0.51	0.835	0.741	0.007	0.0361	0.830

Model: $TTHM = K\,(T)^{a}\,(DOC)^{b}\,(D)^{c}\,(pH)^{d}$

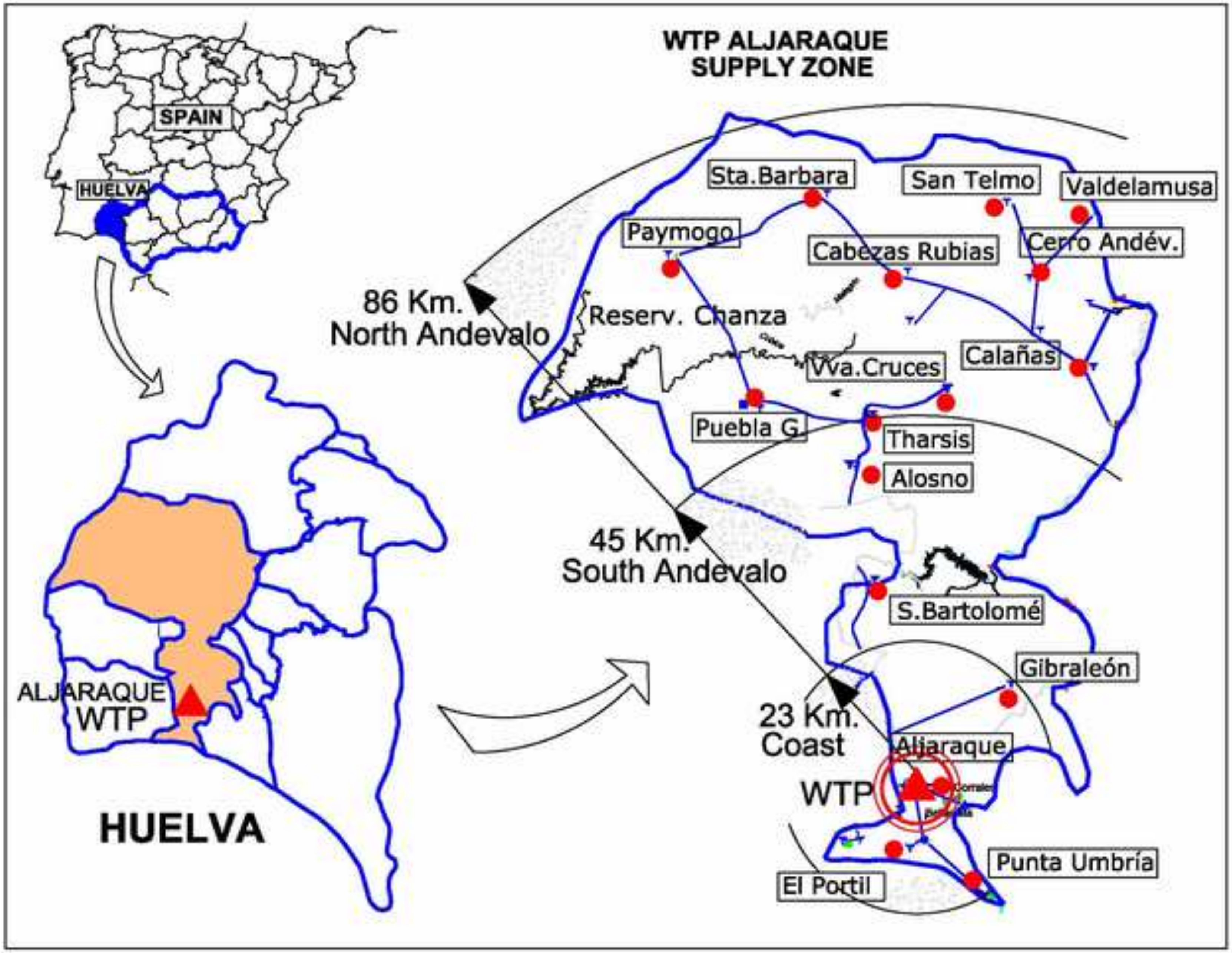
R^2/R^2 adj: correlation coefficient model and adjusted.

p: level of significance

s: standard errors

R^{2}*: correlation coefficient between measured and predicted THMs.

Figure 1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ALJARAQUE
WTP
HUELVA
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SUPPLY ZONE
Sta.Barbara
San Telmo
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Paymogo
Cabezas Rubias
Cerro Andév.
86 Km.
North Andevalo
Reserv. Chanza
Calañas
Vva.Cruces
Puebla G.
Tharsis
Alosno
45 Km.
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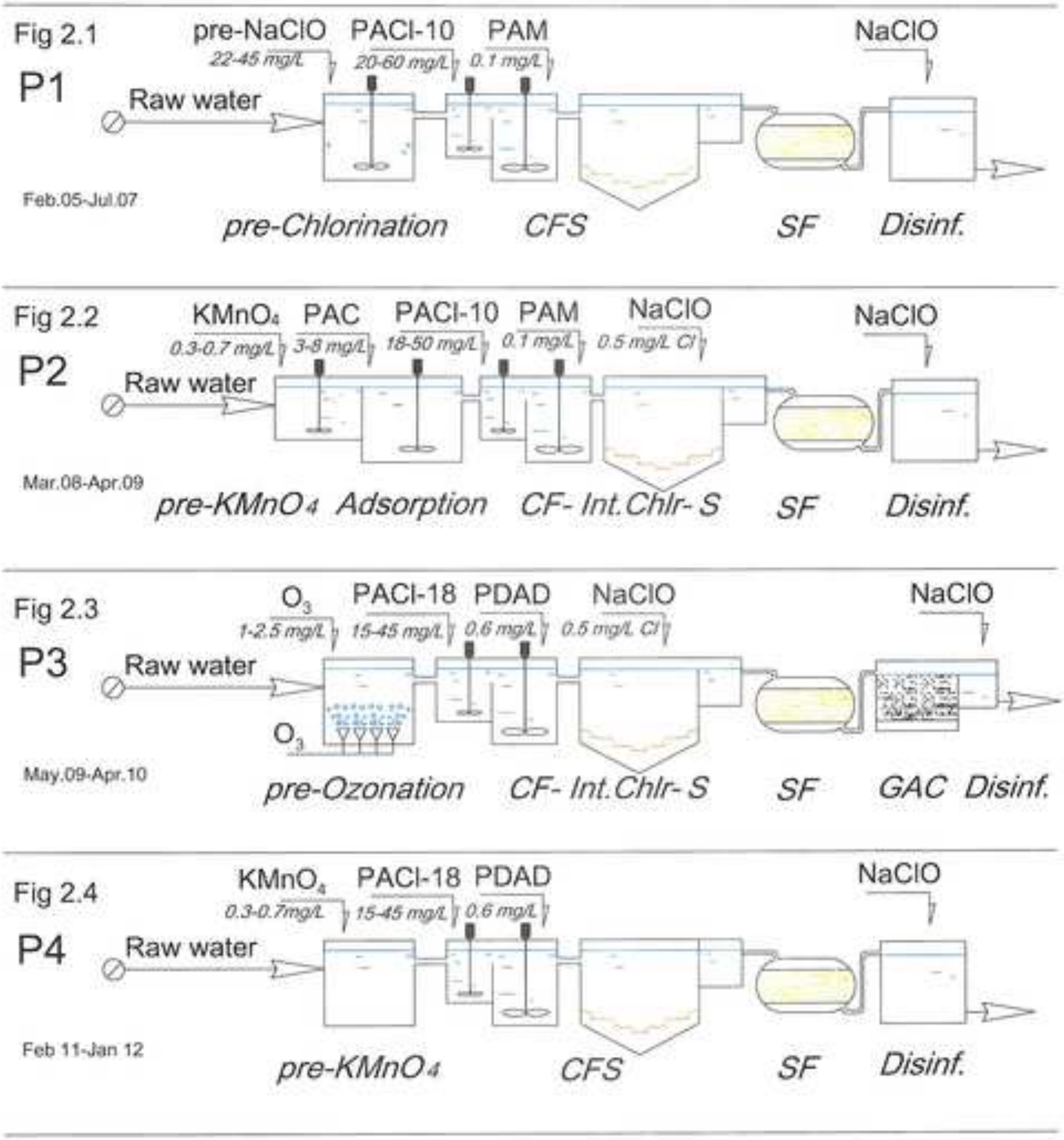
Coast
Aljaraque
WTP
Punta Umbría
El Portil

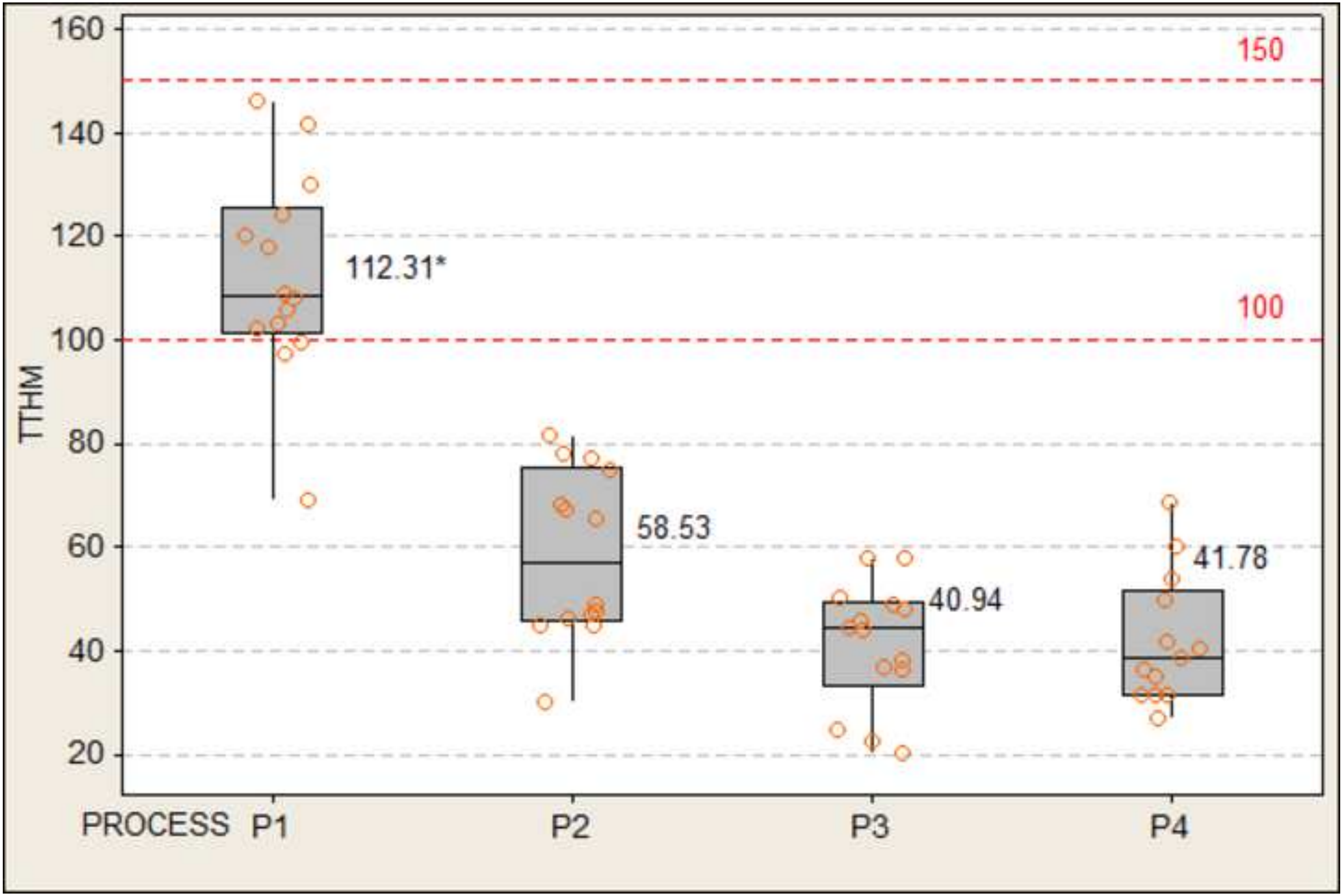
Figure 2



PACl-10 and PACl-18: Polyaluminium chloride 10% and 18%
PDAD: polydiallyldimethylammonium chloride PAM: polyacrylamide
CFS: Coagulation - Flocculation - Sedimentation
CF- Int.Chlr- S: Coagulation - Flocculation - Intermediate chlorination - Sedimentation
SF: Sable filtration *GAC:* Granular Activate Carbon *Disinf.:* Disinfection

Fig.2 Aljaraque Water Treatment Plant.

Figure 3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TTHM
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PROCESS
P1
P2
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P4

Figure 4

Click here to download Figure: Fig.4.tif

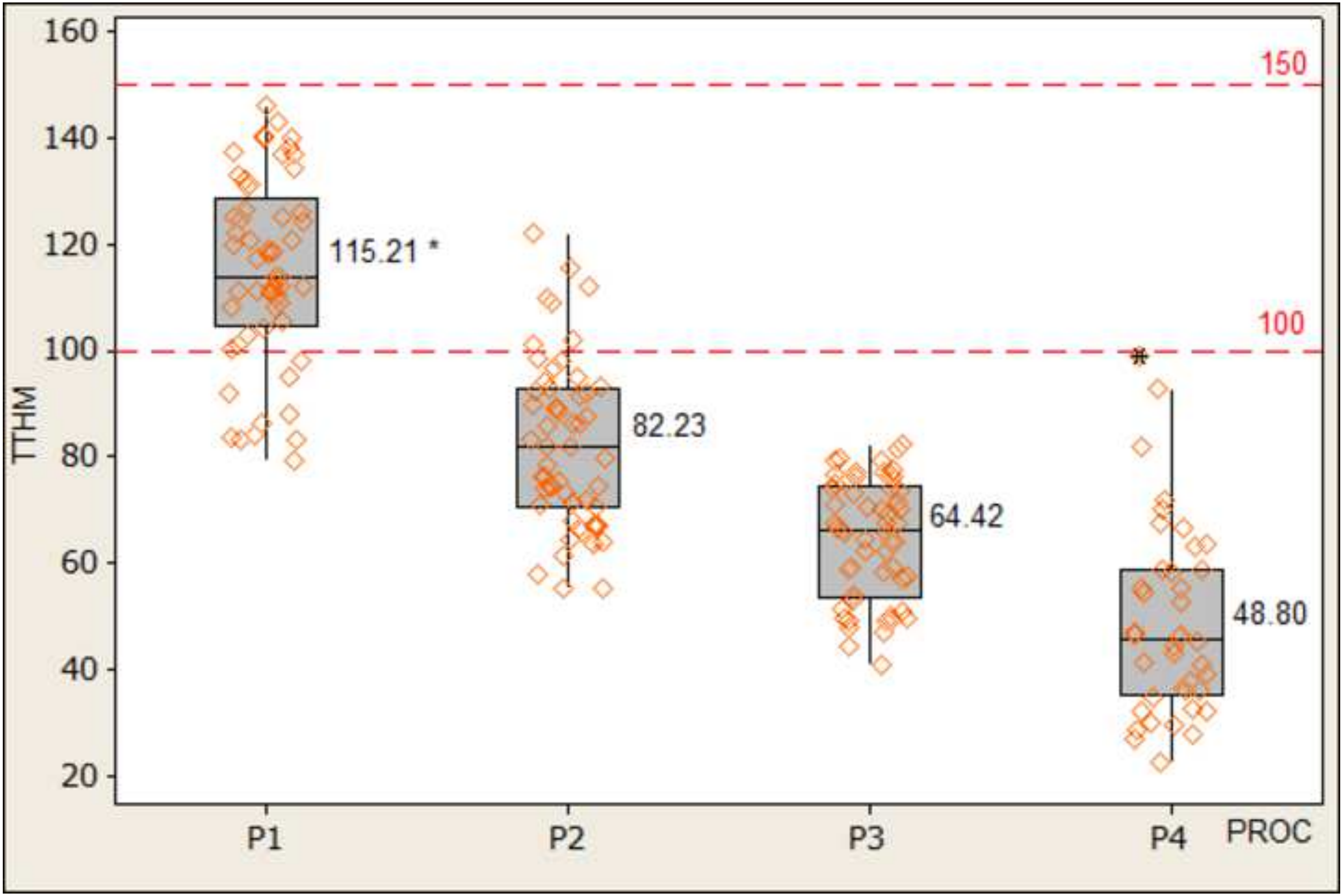

Figure 5

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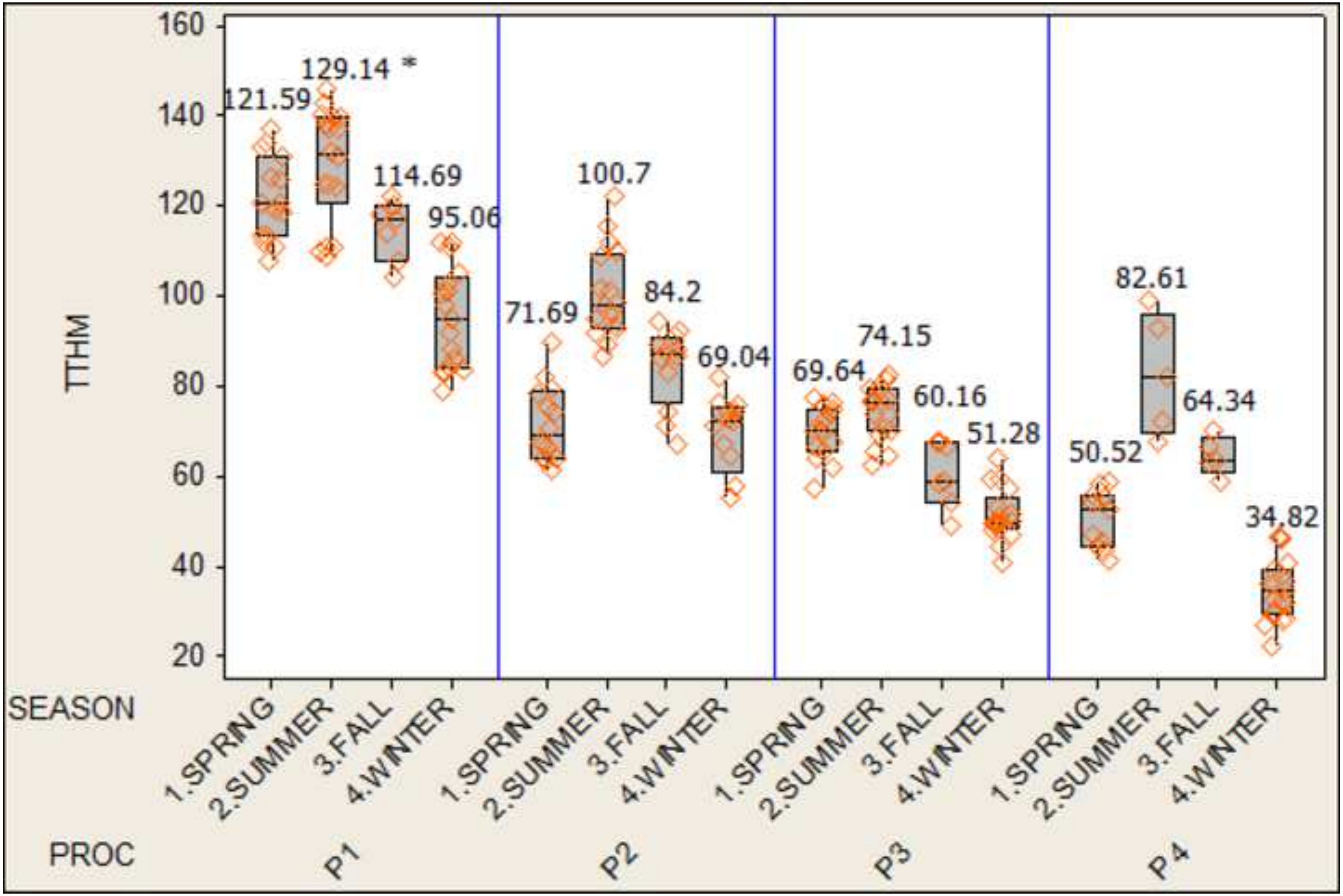
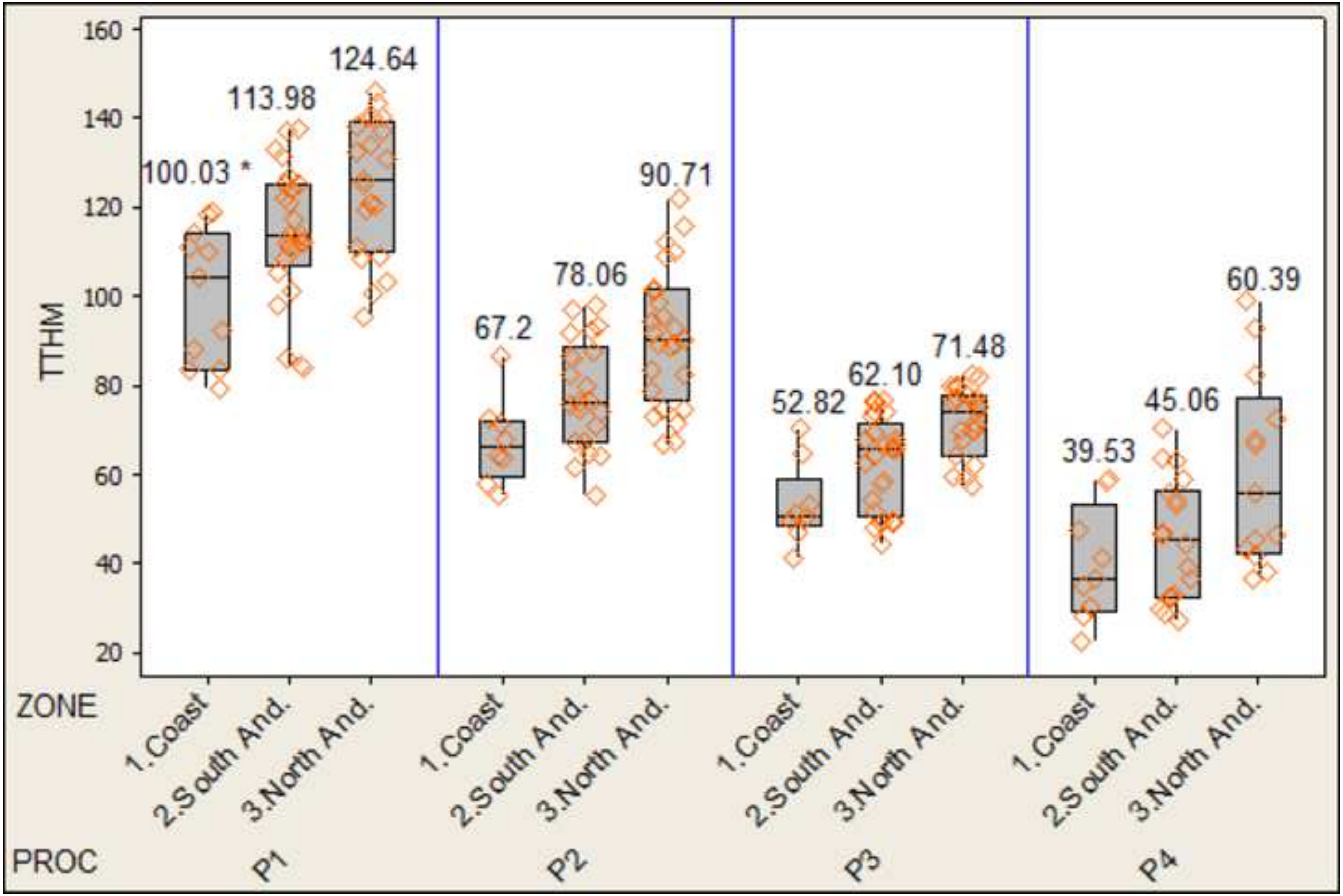


Figure 6


TTHM
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124.64
67.2
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ZONE
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3.North And.
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Figure 7

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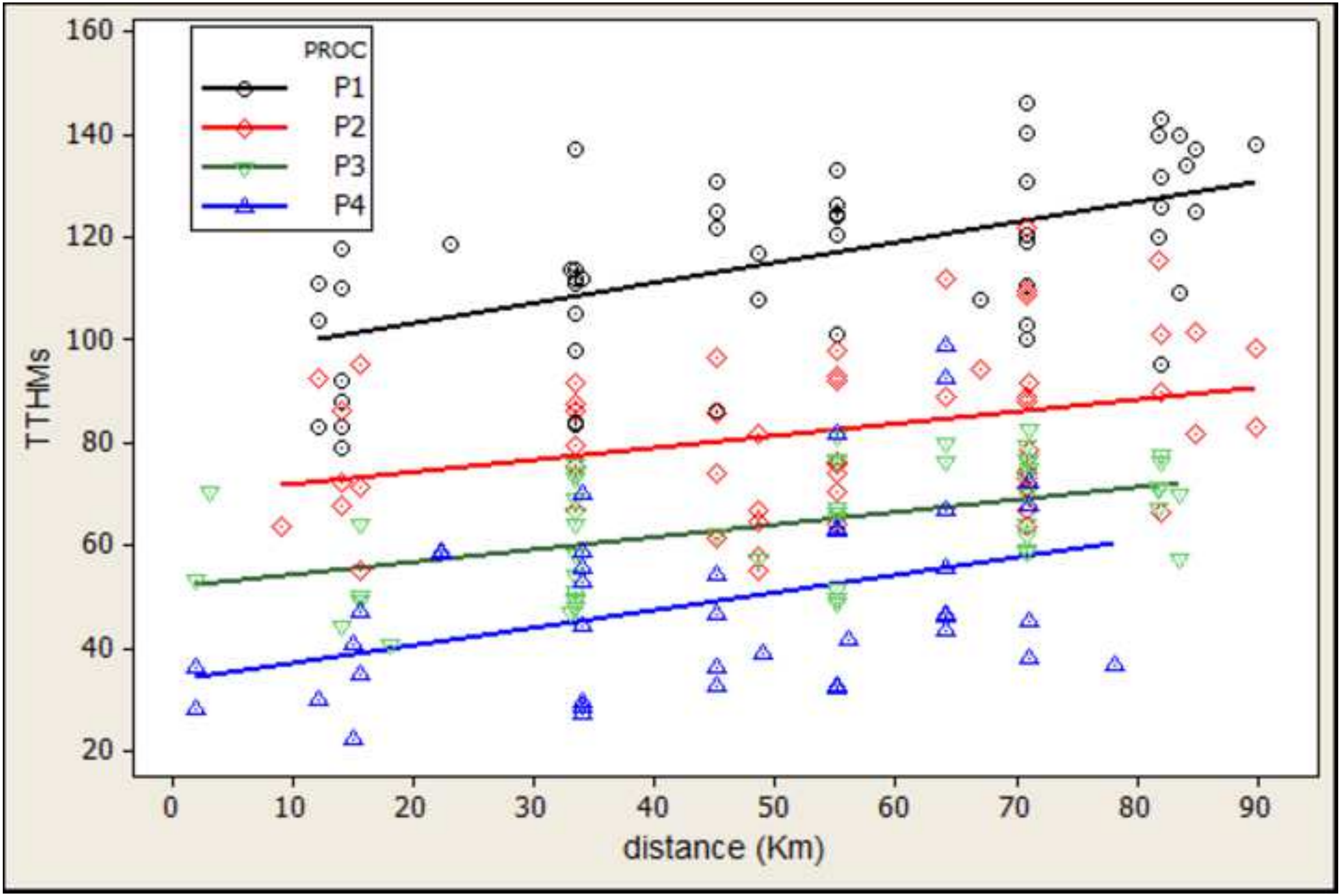

REVIEW OF ARTICLE:

“Seasonal and spatial evolution of trihalomethanes in a drinking water distribution system according to the treatment process”

- Internal standard should be used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component. Monitoring the IS response (peak area or peak height) of all samples during each analysis day is necessary.
  Internal Standard (IS) 1,2-dibromopropane was used as internal standard in the validation and sample analysis of trihalomethanes. The text of the work was modified in relation to this point, including the use of internal standard (IS). (lines 192, 203, 209, 214, 215).

- While sampling field duplicates should be collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.
  We modified the text 2.2. Sampling campaign to express more clearly the process of sampling and to show quality assurance sampling associated with the quality of analytical results. (lines 133-176)

- Limit of Quantification (LOQ) should be calculated along with LOD for the samples.
  The performance of the analytical method was included in the text (LOD, LOQ, repeatability, reproducibility and recovery extraction). (lines 211-220)

- To examine the factors affecting TTHMs formation potential different up-to-date models (Response Surface Methodology) should be used for better understanding of the viewers.
  We modified the text including recent works using RSM based on laboratory data to evaluate the factors affecting the TTHMs formation and their interactions. (lines 386-426).

- Different optimization studies (optimizing amounts of salt, sample volume, extraction time and temperature, desorption time and temperature etc.) should also be discussed to some extent.
  The extraction conditions of THMs with HS SPME are based on previous publications from other authors with some small changes performed in our laboratory (lines 186-188).

- Quality Control Sample (QCS) should be taken which contains method analytes in a solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.
  We have modified the text including quality control procedure followed during the study to monitor the quality of analytical results. (lines 227-234)

- Specific Gas Chromatography System, detector and column should also be mentioned with specifications.
  The text was modified. The analytical method was expressed in more detail (lines 195-204).

- Schematic Diagram showing different treatment process in the Water Treatment Plant (WTP) should be drawn for better understanding.

  Figure 2 have been modified in order a better understanding of Water Treatment Plant.

- Graphs showing comparison between TTHMs concentration and seasonal, spatial variation should be included to get a clear picture.

  Figs 5 and 6 in the manuscript intend to explain changes in concentration in the different treatment processes (P1, P2, P3 and P4) in relation to seasons and spatial location of Distribution systems, respectively, in order to establish the influence of these components in the formation of TTHM. However, to clarify the discussion an additional Fig. 7 has been added, which collects the TTHM variations in relation to the distance in Km.

- Recommendations should be given for further improvement of the Water Treatment Plant (WTP).

  We modified the text including recommendations based on the results. (lines 540-545)

- Comprehensive interventions should also be mentioned.
  We have included in the text comprehensive interventions. (484-495)