Simultaneous prediction of trihalomethanes, haloacetic acids, haloacetonitriles and haloacetamides using simulated distribution system tests

Chrysoula Sfynia [a*,] Tom Bond [b], Rakesh Kanda [c], Michael R. Templeton [a]

a. Department of Civil and Environmental Engineering, Imperial College London, London SW7 2AZ, UK.
b. Department of Civil and Environmental Engineering, University of Surrey, Guildford GU2 7XH, UK.
c. Institute of Environment, Health and Societies, Brunel University London, Uxbridge UB8 3PH, UK.
∗   Corresponding author
E-mail address: c.sfynia13@imperial.ac.uk

Telephone/Fax: +44(0)20 7594 6120

Abstract

This study analysed the spatial and temporal occurrence of 29 disinfection by-products (DBPs) formed by chlorination and chloramination. Four full-scale treatment works, and distribution system locations were sampled, and results compared with laboratory-based Simulated Distribution System (SDS) tests. The DBPs monitored incorporated 4 trihalomethanes (THMs), 9 haloacetic acids (HAAs), 7 haloacetonitriles (HANs) and 9 haloacetamides (HAcAms). For the first time, SDS tests were shown to successfully simulate the levels and speciation of HANs and HAcAms in both chlorinated and chloraminated systems. While THM and HAA concentrations generally increased with water age, HAN and HAcAm concentrations fluctuated and resulted in less pronounced overall increases. To explore the impact of switching the disinfectant in distribution, free chlorine and chloramines were applied in the SDS tests, which showed that chloramination not only reduces the yields of THMs (by 34%) and HAAs (by 49%), but also HANs (by 61%) and HAcAms (by 51%), although it shifts speciation towards more brominated HAAs, HANs and HAcAms species when compared against chlorination. Overall, the aim of the study was to demonstrate that SDS tests can be recommended for the simultaneous estimation of THM, HAA, HAN and HAcAm concentrations in distribution systems and to assess the effect of potential DBP minimisation strategies, such as switching the disinfectant in distribution.

Key words: Disinfection by-products, chlor(am)ination, haloacetonitriles, haloacetamides, simulated distribution system tests.

1. Introduction

Disinfection of drinking water in treatment and distribution aims to safeguard consumers against the occurrence of waterborne diseases related to microbial contaminants and has been characterised as 'one of the most significant public health advancements' of the last century (1). However, research has shown that disinfectants, such as chlorine, interact to varying degrees with natural organic matter (NOM), inorganic compounds and anthropogenic constituents present in drinking water supplies to form disinfection by-products (DBPs).

Disinfection by-products have been a significant area of investigation since the mid-1970s following two publications (2,3) that reported the relationship between chloroform formation and the reactions of natural organic matter (NOM) and chlorine. To-date, literature refers to more than 700 DBPs from the main disinfection methods currently implemented, as well as their combinations (4,5), while ~40% of the mass of organic halogens in water remains unknown (6,7). From this identified amount of DBPs, an even smaller percentage has been quantified in drinking waters and distribution systems (8). Due to their known or suspected health risks (6,9), a number of countries have published regulations and guidelines to control the formation of some species in drinking water (10–15). In England and Wales, the Drinking Water Inspectorate (DWI) in 2012 advised water companies to 'design, operate and maintain the disinfection process so as to keep DBPs as low as possible, without compromising the effectiveness of disinfection (16). As of January 2021, the revised Drinking Water Directive entered in force maintaining a maximum regulatory level for THMs at 100 µg/L and introduced for the first time a regulatory limit for HAA5 at 60 µg/L (17).

To comply and control the formation of regulated THMs and HAAs, water utilities may consider switching from chlorination to chloramination, since it has been widely reported to minimise DBP formation (18–21). Despite the observed positive effects of chloramines, many studies report that the implementation of chloramines may encourage the formation of certain nitrogenous DBPs (N-DBPs) (4) or induce other side effects (e.g., promote Br-HAAs) (21,22). In fact, further knowledge on occurrence and formation mechanisms of N-DBPs is needed since they are suspected to be more toxic than their non-nitrogenous counterparts (23,24).Furthermore, much of the published research has focused on regulated and unregulated DBP formation within water treatment works, yet there is only sparse information about their ultimate fate in distribution systems, their typical concentrations in tap water and their most important formation factors (Table 1). Indeed, DBPs are known to exhibit significant spatial and temporal variability due to raw water quality fluctuations (e.g. NOM composition, bromide levels) and/or due to the conditions in the distribution networks (corrosion materials, biofilms, disinfectant residuals, pH, water age and temperature). The levels of the most abundant DBP class, THMs, are known to increase with

79   increasing water age and temperature in distribution, whereas some HAAs have been reported to chemically and

80   biologically degrade (25–27). On the contrary, HANs and HAcAms appear to be minimally affected by both water

81   age and temperature (28,29).

82   Water utilities and scientists require an evaluating tool to predict DBP occurrence and proactively adapt their

83   water supply processes. As such, the trihalomethane formation potential test (FP), which is a standardised method

84   (5710B) (30), was initially implemented to estimate the formation of THMs, and later of HAAs. However, FP

85   tests were mainly used for the purposes of evaluating the impact of precursors and efficiency of treatment

86   processes, rather than predicting the actual concentrations of DBPs in distribution systems, i.e., at consumer taps.

87   The FP test's characteristics - long incubation time (7 days), high incubation temperature ($25 \pm 2°C$) and excess

88   of chlorine residual (3-5 mg/L) - mean that it may overestimate actual DBP concentrations (31,32). Furthermore,

89   the relative formation of brominated species was reported to be lower in FP tests compared to reality, due to the

90   lower Br/Cl ratio in the excess chlorine conditions of the FP test (33). Therefore, in the early 1990s, Simulated

91   Distribution System tests (SDS) where developed and validated as the most appropriate method to realistically

92   predict the formation of trihalomethanes (THMs) in real distribution systems (25,30). In the first study by Koch

93   et al. (25), filtered effluent water samples from two different plants were collected, which were then dosed in the

94   lab with chlorine (representative of plant dosage) and incubated in typical distribution temperatures for up to 5

95   days (6 intermediates). Since then, these tests are recommended by the US EPA to American water utilities and

96   have been implemented in many US studies, and to a lesser extent in Europe, to collect abundant DBP information.

97   The SDS tests are implemented using a simple and inexpensive laboratory-based technique (batch incubation in

98   bottles), simulating three major parameters: water conditions (pH, temperature), disinfectant residuals and water

99   ages of a distribution system, allowing sampling at prescribed time intervals for analysis of temporal DBP

100   formation trends. Moreover, the SDS test provides key advantages over sampling programmes from real

101   distribution systems, namely (34):

102   ▪ It allows realistic DBP concentration assessment in site specific location, even before commissioning, so that

103   necessary operational adjustments can be done proactively.

104   ▪ It allows DBPs prediction that would result from proposed operational changes in distribution practices (e.g.,

105   switching from chlorination to chloramination)

106   ▪ It allows quantification of a range of different DBPs and other relevant water quality parameters (e.g., pH,

107   temperature, bromide, chlorine residual) in the same sample taken at the same time.

108   ▪ It gives an accurate knowledge of and control over water age when determining the DBPs.

109 ▪ It allows evaluation of the effect of booster chlor(am)ination on DBPs.

110 ▪ It is more cost-effective, less time intensive, and involves less manpower than extensive sampling from the
111   real distribution system.

112 However, information to-date argues that SDS tests do not account for all the *in-situ* conditions of a distribution

113 system, which may be relevant for some DBPs (35,36). Reducing agents present in pipe materials, such as iron

114 and/or sulphite, result in HAA degradation (37). In addition, degradation of halogenated compounds may be

115 triggered by biotic reactions, typically increased with the presence of bacteria found in biofilms (35,38). Metallic

116 pipe corrosion products and biofilm growth may also exert significant chlorine demand and thus leave less residual

117 disinfectant to react with NOM to form DBPs (39–41). Finally, bottle incubation may not fully represent mixing

118 and hydraulic conditions of a distribution and thus simulate the reaction rates (36). Nonetheless, Krasner et al.

119 (42) refers to SDS tests as a method that 'mimics' operations and water quality conditions in distribution systems,

120 with reported correlations against real water samples of 0.91, 0.81, 0.98 (R^2 value) for THMs, di-halogenated

121 HAAs and tri-halogenated HAAs, respectively. Previous studies have shown that SDS estimated the levels of

122 THMs, HAAs, 3 HANs, HKs and NDMA, either in chlorinated, chloraminated or UV/H_2O_2 systems (27,31,36,43–

123 47), but otherwise there is little information about whether SDS tests can be used as predictive tools for estimating

124 more N-DBP concentrations in distribution. AWWA studies, using nationally collected data, have reported that

125 the SDS method was a reasonably accurate method of also predicting intermediate fluctuations of THM and HAA

126 concentrations between the treatment plant and distribution system locations (27,48,49). Apart from these, SDS

127 test have also been used as evaluation tool to understand the impact of potential changes to distribution practices;

128 Andrews et al. (50) performed SDS tests by using real water matrices to investigate the changes in THMs and

129 HAAs concentrations when replacing chlorine with chlorine dioxide in selected water works.

130 To the authors' knowledge this study is the first time SDS tests are used to simultaneously predict the formation

131 of 9 HAcAms, 7 HANs, THMs and HAAs in both chlorinated and chloraminated systems. This resulted in one of

132 the most comprehensive databases in Europe of DBP occurrence and behaviour in distribution systems of the

133 commonly regulated trihalomethanes (THMs), the just regulated in EU - haloacetic acids (HAAs), as well as the

134 unregulated haloacetonitriles (HANs) and haloacetamides (HAcAms) of potential health significance, and their

135 individual species. Therefore, the overall aim of the study is to provide a comprehensive insight into the

136 monitoring, prediction and control of these DBPs in distribution systems.

137 **2. Materials and Methods**

2.1 Selection & sampling of water works and downstream locations

To validate the performance of SDS tests and address the spatial/seasonal variation of DBPs in distribution systems, four water treatment works in England and 12 downstream locations were sampled in four seasonal rounds over a period of one year. The criteria by which the four lowland reservoir water supply systems (Table 2) were selected to obtain fundamental knowledge for the fate of DBPs were the following; i) Frequent reported formation of 'moderate to high' levels of total THMs (>30 μg/L), from the assessment of historical data (2007-2015) in final waters and at storage points, ii) data availability to run a distribution system hydraulic model to determine water age variations in distribution, iii) inclusion of both chlorinated and chloraminated systems, iv) variation of geographical locations (varying bromide levels and NOM patterns), v) presence of storage locations (reservoirs, water towers etc.) equipped with sampling taps, vi) no evidence of system nitrification, vii) absence final water blending and absence of booster chlorination in distribution.

During each seasonal sampling round, two sets of samples were taken from each WTW; water from the treatment works (SDS tests) and from actual distribution locations to compare against the SDS predictions. In the chlorinated WTW, approximately 15 litres of filtered non-disinfected water were collected and preserved until their spiking and incubation as SDS tests. However, in-line chloramination was unable to be simulated in the lab due to health and safety limitations, and therefore the anticipated mimicking of the process was achieved by sampling the final disinfected water. Thus, in chloraminated WTW, SDS tests would initiate at the ammonisation step in the treatment works (contact time was monitored with online telemetry) and quenched at the pre-determined water age intervals during their transport. Following the sampling in the works, water samples were collected and quenched in duplicate from 3 selected downstream locations in each distribution system. All samples were collected in 1-5 L amber glass bottles with PBT (Polybutylene Terephthalate) screw caps with PTFE (Teflon) protected seal and stored in coolers with ice packs for transportation to the laboratory.

2.2 Water age modelling

The water age in the distribution systems at the sampling locations was modelled for each WTW separately. The software package used was SynerGEE v4.6.0 (DNV GL,Norway). The models were built from the water utility GIS data, which were then calibrated against real time telemetry data and field pressure logging to build a representative simulation of the water distribution systems, with all details of pumps, storage (towers and reservoirs), pressure regulators and mains. The hydraulic simulations were solved using the Darcy-Weisbach equations. The prediction of water age required the continuous input of real time pressures throughout the model

167 run time (> 10 days) until stable water age values were calculated, which led to the generation of maps of the

168 water ages ranges (between 6 and 144 hours) across the distribution systems (Figure 1).

169 **2.3 Experimental design of SDS tests**

170 The SDS test is a bench scale technique that involves incubating water samples at simulated distribution conditions

171 (i.e., disinfectant residuals, temperatures, water ages) [5710 C](30). Prior to disinfectant dosing and preparation,

172 the collected water was incubated to reach the in-situ temperature of the sampling date. On the day of the

173 disinfectant spiking, fresh chlorine and monochloramine solutions (N/Cl molar ratio: 1.4/1) were prepared from

174 stock solutions, with concentrations of these oxidants determined and monitored by DPD-FAS titration [4500-Cl

175 F] (30). The chlorine/ chloramine demand during each round was evaluated with trial-and-error titration

176 experiments on the day of the spiking, to ensure residual disinfectant concentration of 1.0 ± 0.2 mg/L. Since the

177 results of the SDS tests were to be compared against those of the real distribution system sampling locations,

178 representative water ages ranges in distribution were simulated as exact time intervals (6, 12, 24, 48, 72 and 106

179 hours) in SDS tests in duplicate.

180 The preparation of the SDS tests is summarised in the following steps:

181 a. The water sample was spiked with pre-determined volume of chlorine or chloramine solution (magnet stir

182   plate), to achieve the in-situ residual disinfectant concentration.

183 b. The SDS bottle was filled up to the top (avoid overflowing) until the water-air interface became convex.

184 c. The bottles were capped headspace free, inverted to mix and checked for trapped air bubbles. If air bubbles

185   were present, the bottle was refilled until no air was observed, to ensure the detection of volatile DBPs.

186 d. Finally, the SDS bottles were stored in the incubator at the on-site measured temperature and selected contact

187   time to simulate the water ages in distribution.

188 After the completion of the pre-determined incubation times (6, 12, 24, 48, 72, 106 hours), the samples were

189 quenched with 100 mg/L of ammonium chloride (chlorinated samples) and 50 mg/L of ascorbic acid

190 (chloraminated samples), to preserve the individual analytes (51–55). Prior to their quenching, residual

191 disinfectant, pH (Metler-Toledo, UK), UV absorbance at 254 nm (Camspec M550/1 double beam scanning, UK),

192 non-purgeable organic carbon (NPOC) (Shimadzu TOC-V, Japan) were measured and SUVA was calculated (S4).

193 It has to be noted that if a SDS sample post-incubation had a residual concentration of <0.2 mg/L of chlor(am)ine,

194 it was disposed and excluded from further assessment.

195 **2.4 DBP analyses**

196   The determination of all target DBPs in this study was performed by liquid-liquid extraction and gas

197   chromatography – electron capture detector (GC-ECD) (Perkin Elmer Clarus 500), using two separate methods;

198   a modified EPA Method 551.1 (for THMs, HANs and HAcAms) with a fused silica capillary column (RXi 5Sil

199   MS, 30m·0.25mm ID, 0.25 μm film thickness, Restek, USA) and added temperature increase rates up to 280°C

200   (Table S1), and EPA Method 552.3 (for HAAs) (Table S2) (51,52). With the analytical methods selected six

201   HANs (MBAN, DCAN, TCAN, BCAN, DBAN, DBCAN) and eight HAcAms (MBAcAm, DCAcAm, TCAcAm,

202   BCAcAm, DBAcAm, BDCAcAm, DBCAcAm, TBAcAm) were able to be quantified in water. For supplementary

203   information on the standards, analytes method detection limits, recovery rates and median values, the reader is

204   referred to Table S3.

205   For the purposes of this study, > 500 L of water were collected from water treatment works and downstream

206   locations. In total 480 bottles were filled headspace-free for incubation and approximately 1000 extraction vials

207   were taken for solvent extraction and GC-ECD analysis for DBP quantification.

2.5 Data analysis

209   The data analysis and correlations were performed in Excel and SPSS Statistics 25 (IBM, UK), with the

210   implementation of t-tests and ANOVA packages. The specific tests and Pearson product moment correlation

211   coefficient (r), with 95% confidence interval, were used to assess the statistical relation between the individual

212   DBP yields in SDS tests, actual distribution systems and water quality variables, in chlorinated and chloraminated

213   systems, separately and combined.

3.   Results and Discussion

3.1 Occurrence of regulated and unregulated DBPs in SDS tests

3.1.1   In chlorinated water supply systems

3.1.1.1 Occurrence of THMs and HAAs

218   In general, it was observed that SDS tests predicted to a high extent the formation patterns and speciation of THMs

219   (r=0.97) and HAAs (r=0.95) in the chlorinated systems (A & B WTW), while illustrating the various spatial and

220   seasonal trends. THM concentrations increased linearly with the increase of water age and decrease of chlorine

221   residual (from 1.0±0.2 to 0.2 mg/L Cl_2) in the incubation bottles. This trend was consistent with the results

222   obtained from the distribution locations (Figure 2a, S1a) and with literature (25,36,56). More specifically, the

223   lowest THM concentrations were observed after 6 hours (minimum incubation time), while the highest were

224   identified after 106 hours (maximum incubation time), during all four seasonal samplings. Between 6 and 106

225 hours, the THM increases were significant, averaging 60 % in the SDS tests (avg. 50 % in distribution system).

226 Generally, the concentration of the distribution samples would fall between the concentrations of the simulated

227 samples of the exact minimum and maximum hours of each range. However, in several cases in WTW B,

228 particularly in low water ages (6-12 hours), it was observed that the THMs from the distribution locations

229 exceeded those from the SDS tests of 6 and 12 hours. This was possibly related more to the complex hydraulic

230 conditions that enhanced chlorine reactions in the actual network than in the bottles. It is noteworthy that

231 concentrations increased more rapidly in lower (6-24 hours) than in higher water ages (48-106), which indicated

232 rapid THM generation in the early stages of distribution, possibly even immediately after the disinfection step

233 (57). Even though the increased rates had minimal correlation with water temperature or TOC fluctuation, this

234 was not the case with total mass concentrations in both WTWs, since THM yields varied between the seasonal

235 rounds. In fact, the highest THM concentration reported was 75.4 ± 1.2 µg/L after 106 hours during summer (22°),

236 while the concentration of the relative distribution system at 72-106 hours was 71.0 ± 3.2 µg/L (Fig.2 a). Likewise,

237 during the winter sampling round (8ºC) simulated tests presented the lowest total concentrations, ranging from

238 17.0 ($\pm$1.4) - 45 ($\pm$3.6) µg/L (21.0 ($\pm$0.2) - 42.0 ($\pm$0.2) µg/L in distribution system). In addition, SDS tests

239 simulated the formation pattern of the individual THM species of chloroform and brominated THMs in the

240 chlorinated systems (25). Similarly, to the distribution locations, brominated species, and predominantly

241 dibromochloromethane (DBCM), represented the majority of THM occurrence. This indicated that bromine

242 incorporation in the incubation bottles occurred in similar levels as in the actual networks; while bromide levels

243 were approx. 12 µg/L, chloroform and bromine containing THMs represented 15 and 85 % of TTHM, respectively

244 (16 and 84 % in distribution system, respectively).

245 Furthermore, as seen in Fig. 2b and S1b, SDS tests also simulated HAAs in chlorinated systems during the four

246 seasonal samplings. Overall, it can be noted that the concentrations generated at 6 hours were statistically similar

247 or slightly higher than those occurred in the highest incubation time (106 hours), regardless of the intermediate

248 variations. In any case, the magnitude of HAA yields increase during chlorination (avg. 9%, from 6 to106 hours)

249 was lower than that observed for THMs (avg. 60%). In the SDS tests of WTW A, total HAAs presented an increase

250 from 6 to 24 hours (avg. 15 %), where they peaked. After 24 hours, HAAs presented a decrease until 48 hours

251 (avg. 18%), and a subsequent increase until 72 and 106 hours (avg. 5%). The increases were associated with

252 continuous oxidation reactions in the presence of chlorine residual, in low water ages, or the accumulative effect

253 of other DBPs decomposition, in higher water ages (58). On the other hand, the hydrolysis of tri-HAA to their

254 corresponding THMs at the pH reported (pH range: 7.2-7.9) (59) functioned as the primary HAA degeneration

255 mechanism. Also, abiotic degradation might have occurred in the SDS samples; hydrolysis or reductive

256 dehalogenation of HAAs (37,58) induced with the pH increases observed in two rounds. The likelihood of

257 microbial carry over in the SDS tests was high, due to the sampling of pre-disinfected water, which may also be

258 responsible for biodegradation (38). Additionally, the formation of total HAAs in SDS samples had a strong

259 correlation with water temperature, since significantly lower concentrations were reported when the chlorinated

260 samples were incubated at 8°C; mean HAA levels were approximately 80%, 71% and 78% greater in summer

261 (22°C), autumn (14°C) and spring (17°C), respectively, than this of winter (8ºC) (downstream location presenting

262 75%, 67% and 76% greater levels, respectively). These percentages between seasonal samplings are consistent

263 will previous HAAs occurrence studies in the UK (44), but not as dramatic as these reported in Canada (60), that

264 saw four fold lower concentrations during winter. Concerning HAA speciation, the dominant species was DCAA,

265 followed by DBAA, same as those reported in the selected distribution locations. In the selected chlorinated

266 systems, the most prevalent HAAs species are regulated as HAA5. In general, the weight ratios of bromine

267 containing HAAs species identified were higher than that of the chlorinated ones, averaging 60% (58% in

268 downstream locations) (Table S5). In addition, the weight ratios of regulated (HAA$_5$) to total HAAs were similar

269 in both free chlorinated systems investigated, averaging 69% (68% in downstream locations). This suggested that

270 the non-regulated HAAs comprise just over 1/3 of the HAAs in the selected systems, regardless of the low bromide

271 levels.

272 **3.1.1.2 Occurrence of N-DBPs**

273 The accurate simulation of the trends and speciation of the THMs and HAAs described above, already known to

274 be well-predicted by SDS tests, validated the performance of the tests in our laboratory. Therefore, the same

275 samples were further assessed to investigate their potential in predicting the occurrence and speciation of

276 nitrogenous DBPs; HANs and HAcAms, for which there was uncertainty about whether the SDS test would be a

277 good predictor. Figures 2c (A WTW) and S1c (B WTW) demonstrate that most of total HAN concentrations

278 identified in actual systems were found to be between the concentrations identified in the lower and upper limits

279 of their water age ranges (r=0.83). However, few exceptions were observed especially in low water ages, where

280 total HANs levels in simulated samples were 2.5-20% lower (max mass difference 2.5 µg/L) than those in the

281 actual networks. From a practical viewpoint these deviations were minimal, when taking in account the order of

282 magnitude for the WHO guideline values for DCAN and DBAN, 20 and 70 µg/L, respectively (14), which are

283 significantly higher than the variations observed here. In this case, the underestimation was not linked to

284 determining factors, such as pH (r=-0.05) and chlorine residual (r=-0.41), since these were not statistically

285 different between the two set of samples and was more likely to occur due to the low circulation and mixing

286 conditions in the bottles that may have limited reactions. Total HANs reported by chlorinated SDS tests and

287 downstream locations were always < 9 µg/L, with mean values of 4.8 (±1.7) and 4.9 (±1.5) µg/L, respectively.

288 Generally, HANs increased between 6 hours and 106 hours, in both chlorinated SDS tests, with varying increase

289 rates; by on average 35%. This has been previously reported by Bond et al. (61) and Weinberg et al. (8) in

290 nationwide occurrence studies where HAN levels presented increases (by 7-50%) within the initial and final

291 location of real and simulated distribution networks. Regardless of the overall mass increases, decays were also

292 observed in intermediate incubation times. However, these decays were not significant enough to reset the total

293 HAN concentrations to their minimum levels, which were reported only in 6 hours during all four sampling

294 rounds. Even though clear formation/degradation patterns could not be extracted, the simulations data analysis

295 indicated that HANs presented an increase trend until 24 and 48 hours, then decreased at 48 and 72 hours

296 respectively, followed by another increase thereafter. The decreases observed are related to HANs hydrolysis to

297 form their HAcAms counterparts (only chlorinated species), confirmed in correlation analysis (r=0.74). The above

298 trend is in agreement with Koch et al. (25) in chlorinated SDS tests that reported the same water age trend, with

299 HAN levels increased until 24 hours, decreased until 72 hours and then increased back again to be very similar to

300 the initial concentrations of 3 hours. HAN occurrence was not characterised by any seasonal variability, since

301 similar levels were identified in low and high water temperature incubations. This observation suggested that

302 HANs formation was mainly affected by the constituents of the water matrix, rather than the environmental

303 conditions, of each sampling round (28,29,62). Similar to what was observed in distribution, the most predominant

304 HAN species in SDS tests were DBAN, followed by BCAN (brominated species represented 60-100%). An

305 exception was observed in summer, especially during low water ages; chlorine-containing species, and

306 particularly TCAN, were abundant, representing a mean weight fraction of 67%. This was possibly due to the

307 algal blooms and high water temperatures during that period that led to increased chlorine demand (63), thus

308 shifted the chlorine to bromine ratio in the water samples.

309 Apart from the HAN simulation, SDS tests acted as an equally accurate prediction tool for HAcAms (r=0.83) in

310 chlorinated systems (Figures 2-d and S1-d). However, several downstream location samples reported higher

311 HAcAm yields than the SDS bottles over the same amount of time (24-106 hours). This was potentially due to

312 the presence of reservoirs of organic materials associated with pipe walls in distribution, which may have acted

313 as supplementary HAcAm precursors at high water ages. The statistically significant deviations between the SDS

314 and distribution samples ranged between 0.5-2.5 µg/L (avg. 1.1µg/L), therefore Total HAcAms in SDS were

315 always <10 µg/L in both chlorinated systems, with mean values of 3.6 µg/L (3.4 µg/L in distribution samples).

316 From the results there was no consistent relationship between HAcAms occurrence and/or the magnitude of

317 intermediate increases/decays, and water age in both chlorinated systems. There was an overall pattern, though,

318 for HAcAms to degrade between 12 and 24 hours, likely linked to HAcAm hydrolysis and subsequent formation

319 of the relative HAAs, confirmed from HAAs levels in the same incubation time during all sampling rounds for

320 WTW A. Then, average concentrations would either increase, partially related to HAN hydrolysis, or would

321 continue to degrade until 106 hours. It is noteworthy that the HAcAm increases in WTW B did not necessarily

322 coincide with the hydrolysis of HANs (r=0.54), highlighting the potential independent formation of HAcAms

323 from separate precursors (20,64). These different patterns within the same system during the various sampling

324 rounds were not influenced by water temperature (r=0.2), or any other measured water quality parameter [e.g., pH

325 (r=-0.04), TOC (r=0.09)], but were more related to the nature of HAcAms precursors of the water matrix. NOM

326 quality is characterised by seasonal variations and therefore changes in molecular weight, solubility and functional

327 group composition (65,66). Concerning HAcAm speciation, the weight ratios of bromine containing HAcAm

328 species were similar, averaging 68% (64% in distribution) and 61% (55% in distribution) during the various

329 incubation times, in A and B WTW SDS samples, respectively (Table S5). Similar to distribution systems, the

330 most dominant HAcAm species in chlorinated SDS samples was BCAcAm, followed by TCAcAm and DCAcAm.

331 Overall, it was observed that SDS test encompassed the ranges of HANs and HAcAms concentrations and

332 speciation expected to be identified during the different water ages within the chlorinated distribution systems.

333 SDS tests predicted, even conservatively, the total HAcAms levels to be expected in the given water ages.

3.1.2   In chloraminated water supply systems

3.1.2.1 Occurrence of THMs and HAAs

336 Similarly, to the chlorinated systems, THM concentrations increased linearly as water age increased and chlorine

337 residual decreased (Table S4); a trend that was observed during all seasonal sampling rounds at both

338 chloraminated systems (Fig. 3-a and S2-a). Total THMs varied between the seasonal sampling rounds, though not

339 as much as in the chlorinated systems, and presented the same seasonal and temporal dependency as their relative

340 distribution samples (r=0.96). In the chloraminated systems THMs were always <40 µg/L even at 106 h, where

341 concentrations were expected to be found in their peak. The increases were noteworthy between 6 and 106 hours,

342 averaging 52% during the four sampling rounds (avg. 51% in distribution system). It has to be noted that unlike

343 the chlorinated samples, the yields here followed higher increase patterns between 48 and 106 hours, than between

344 6 and 24 hours. This is possibly related to the fact that chloramines are weaker oxidants than free chlorine and

therefore initially promote substitution and then oxidation reactions, with increasing formation rates as water age progressed (27). As seen in Figure S2-a during the autumn tests of D WTW, THMs presented an unexpected decrease (by approx. 23%) at the incubation time of 72 hours, while chloramine residual was < 0.5 mg/L. This was attributable to the decrease of THM species containing chlorine molecules and has been previously observed in SDS tests (27), where anoxic conditions occurring in high water ages were responsible (67). In addition, THM biodegradation may have occurred from the combining effect of nitrifying bacteria and disinfectant decrease (68). In the case of chloraminated supply systems, THM speciation was also predicted; in WTW C was characterised mainly by brominated THM species (i.e., DBCM and BDCM), whereas SDS samples of WTW D were dominated by BDCM and chloroform. In fact, bromide levels in WTW C (avg. 82 µg/L) were approximately four times higher than those of WTW D (avg. 20 µg/L) (Table 2), thus it was expected that the fraction of brominated species would be significantly higher than that of chloroform. Indeed, in WTW C the bromide-containing species constituted 82-94% of the total THMs (76-94 % in distribution network). On the other hand, in WTW D the weight fraction ratio of chloroform and bromide-containing was similar (48:52), as bromide incorporation was reduced due to relatively low bromide levels (avg. 20 µg/L). The data agreements between the two set of samples indicated that SDS tests simulated bromine incorporation to a high extent.

As far as the HAAs were concerned, similarly to the actual chloraminated systems (r=0.91), yields followed both overall increases (~25%) and decreases (~60%) trends from 6 to 106 hours amongst the seasonal sampling events, regardless of the intermediate fluctuations, which is consistent with previous studies (19,26,69,70). These trends are related to the pronounced HAA degradation in high temperatures, and the high disinfectant residuals and SUVA (approx. 2.8) found in the systems (18). Other parameters, pH, HAcAms hydrolysis or NOM nature may have acted as equally important triggers for HAA behaviour (27). Overall, it was expected that the yields of the chloraminated downstream locations would fall into the extremities of those identified by the relative SDS tests (r=0.91). In the few cases that there were statistical deviations between the two set of samples, the average overestimation and underestimation in SDS tests was 8% (max deviation: 6 µg/L) and 35% (max deviation:15 µg/L), respectively. The uncertainty of the exact water ages in distribution and inability of SDS to mimic the exact mixing and hydraulic conditions of the water pipes, may have acted as limiting factors in the enhanced prediction of the formation/ decay of HAAs. As in actual chloraminated distribution systems, the dominant HAA species was the currently unregulated TBAA, followed by DBAA and DCAA. Unlike in the chlorinated systems, other unregulated species, such as DBCAA and DBCAA were also present in relative high levels in the chloraminated systems. In general, the weight ratios of bromine containing HAAs species identified were significantly higher

than that of the chlorinated ones, averaging 62% (60% in downstream locations) and 59% (57% in downstream

locations) in WTW C and WTW D, respectively. In addition, the SDS results predicted with precision the weight

ratios of regulated (HAA$_5$) to total HAAs, averaging 28% (33% in downstream locations) and 40% (40% in

downstream locations), for C and D WTW, respectively. Greater bromide concentrations, as in WTW C, lead to

even lower HAA$_5$-to-HAA$_9$ mass ratios, as the bromine-containing species are not adequately represented by

HAA$_5$. These results highlighted the regulatory deficiency to cover the health hazard profile of these

chloraminated systems, since the identification of HAA$_5$ is only representative of one third of the total HAAs.

From a practical standpoint, the implementation of SDS tests by water utilities will provide a useful insight on the

expected HAA levels and speciation in chloraminated systems if further optimised, since contrary to THMs the

prediction of HAAs was more water-specific and water age-dependent.

3.1.2.2 Occurrence of N-DBPs

Overall, it was observed that SDS test encompassed the ranges of HAN (r=0.74) and HAcAm (r=0.73)

concentrations and speciation expected to be identified within the chloraminated distribution systems. Total HANs

were lower than those generated in chlorinated systems (28,71) and the levels predicted to generate in the early

stages of distribution were similar or slightly higher (by 0.1- 1.7 µg/L) at the final stages, thus increasing with

time. In more detail, total HANs were < 4 µg/L with mean yields of 1.7 µg/L (avg. in distr.: 1.9 µg/L) (Fig. 3-c

and S2-c). Unlike in chlorinated samples, several chloraminated SDS samples overestimated the occurrence of

HANs; especially in low and medium water ages. Nonetheless, these deviations were minimal from a practical

viewpoint; maximum deviation reported was just 0.8 µg/L (WTW C-Winter). This overestimation was likely due

to the different circulation conditions in the bottles that may have enhanced formation and/or delayed hydrolysis.

The potential impact of other parameters for this overestimation was possible but not wholly confirmed by the

data; low pH (<7) has been reported to enhance HANs stability (72), and lower disinfectant residual in distribution

enhances HANs hydrolysis (42). This tendency has been previously reported in chloraminated SDS tests, and SDS

bottles characterised by nitrification phenomena (8). Same as in chlorinated SDS tests, HANs increased between

6 and 106 hours in all chloraminated SDS samples, with varying increase rates; 6-52%. This agreed with

chloramination experiments by Yang et al. (62), where the effect of contact time was investigated and concluded

that HANs increased between 0 and 170 hours of incubation. Regardless of the overall increases in the current

study, HAN levels presented decays during the intermediate incubation times. These decays were mainly

identified around 48-72 hours, due to hydrolysis (61,73), and were not significant to influence the overall

occurrence. The same pattern was observed by Chen et al. (74), where HAN levels (3 species) were reported to

405 increase until 24 hours, with a subsequent decrease until 72 hours. Also, HAN occurrence was not characterised

406 by any seasonal variability upon chloramination, since similar levels were identified amongst the seasonal

407 samplings. Concerning HANs speciation, the most predominant species were DBAN, followed by DCAN and

408 BCAN. During the four sampling rounds the brominated species represented in average 53% and 16% of the total

409 HANs, in WTW C and D water samples, respectively.

410 Furthermore, Fig. 3-d and S2-d illustrate that chloraminated SDS tests succeeded in representing well the different

411 scenarios over the same amount of time and temperature in the case of HAcAms (r=0.73). If an exception was to

412 be noted, would be the tendency of some SDS samples to minimally overestimate the levels of HAcAms, with

413 deviations ranging 0.2-2 µg/L between the different sample sets. Even though literature does not provide any

414 explanation to this tendency, and the incubation bottles were isolated from the known HAcAms triggering factors

415 of distribution pipes, it was possible that inorganic nitrogen incorporation was enhanced during the mixing in

416 confined bottles (75). This assumption was not evaluated during this study since isotopically labelled

417 monochloramine was exempted from the experiments. Total HAcAms in SDS samples were always <7 µg/L in

418 both chloraminated systems, with mean values of 4.0 µg/L (3.9 µg/L in distribution) and 3.6 µg/L (3.7 µg/L in

419 distribution), in WTW C and D, respectively. Generally, HAcAm concentrations increased between 6 and 106

420 hours, in three of four sampling rounds (winter, spring, summer) by rates that were inversely proportional to water

421 temperature; partially confirmed from distribution samples. More specifically, in WTW C the increase rate

422 (between 6-106 hours) was significantly higher (73%) in winter, against those in spring (43%) and summer (20%).

423 From the average reported levels in each water age during all sampling rounds, it was observed that total HAcAms

424 followed an increase until 48 hours, with a subsequent degradation around 72 hours followed by a final increase

425 until 106 hours. This HAcAms degradation, though, was not necessarily linked with consequent formation of their

426 relative HAAs, while HAcAms increase was partially linked with HAN hydrolysis. Since this was observed in

427 both chlorinated and chloraminated systems, it indicated that the formation of HAcAms was associated with both

428 nitrogen and non-nitrogen organic precursors found in the samples water matrices (75–77), and could form

429 independently from HANs (64). Furthermore, HAcAm formation in chloraminated waters was not characterised

430 by any seasonal pattern, since the occurrence in 8°C was similar with that observed in 22°C (28,72). The weight

431 ratios of bromine containing HAcAms species (Table S5) were also similar, averaging 81% (86% in distribution)

432 and 66% (70% in distribution) during the various incubation times, in WTW C and D SDS samples, respectively.

433 The above percentages highlighted once more the importance of bromide, even in low concentrations as found in

434 WTW D, in the preponderance of brominated HAcAms in distribution systems. Same as in downstream samples,

435 the most abundant HAcAms species were DBAcAm, DCAcAm and BCAcAm. Finally, Krasner et al. (4) had

436 reported that upon chloramination DCAcAm and DCAN usually occur in similar levels. It was noteworthy that

437 observation was reported in this study in both chloraminated systems; DCAcAm and DCAN were on average 0.7

438 µg/L and 0.6 µg/L (WTW C), and 1.1 µg/L and 1.3 µg/L (WTW D), respectively.

3.2 The impact of switching from chlorine to chloramines

440 A fundamental question posed by this research was the simultaneous impact assessment of a potential disinfection

441 process alteration on the formation and fate of the selected DBPs in distribution which was allowed through the

442 SDS validation. Therefore, water samples from WTW A and B, usually chlorinated by the water utility, were also

443 chloraminated (with pre-formed chloramines) and incubated in the laboratory under the same conditions and water

444 ages as the initial SDS tests. Overall, switching from chlorine to chloramines in both systems, formed lower

445 THMs, HAAs, HANs and HAcAms levels during all the seasonal sampling rounds (Fig.4). Chloramination is

446 known to control THM and HAA formation when compared with chlorination (20,70,78). The novelty of our

447 findings lay in the fact that chloramination was proven to also limit the formation of both HANs and HAcAms.

448 Therefore, this was an indication that the nitrogen atom in N-DBPs came primarily from the organic nitrogen

449 present in the water matrices, rather than from the ammonia added during chloramination. In more detail,

450 switching from chlorine to chloramines in WTW A, reported average decreases of 30% in THMs, 47% in HAAs,

451 72% in HANs and 55% in HAcAms. Switching from chlorine to chloramines in WTW B, reported average

452 decreases of 36% in THM, 50% in HAAs, 50% in HANs and 47% in HAcAms. When chlorine was used as the

453 disinfectant, considerable variation was observed between the increase levels of THMs during each water age;

454 with mean yield 45 µg/L (range: 20-75 µg/L) between 6 to 106 hours during all sampling rounds. Whilst when

455 chloramines were applied to the same water matrix mean THMs were 30 µg/L and ranged between 16-55 µg/L.

456 Practically, this means that a potential switch to chloramines will not only decrease the total THMs in specific

457 water ages but also delay their formation; crucial to achieve regulatory compliance in large water networks with

458 water ages > 106 hours. Furthermore, the percentage of incorporated bromide in THMs was similar during both

459 chlorination (avg: 86%) and chloramination (avg 87%) of the selected water matrices. The minimisation

460 percentage in total HAAs upon shifting to chloramines was more significant (avg. reduction: 49%) than that of

461 THMs (avg. reduction: 34%). Namely, mean HAA levels during chlorination were 41 µg/L and 28 µg/L in WTW

462 A and B, respectively, whereas during chloramination were 14.5 µg/L and 13 µg/L (Fig.4 b). The impact on HAA

463 speciation during chloramination has been widely studied with researchers suggesting that switching from

464 chlorine to chloramines will be followed by a switch in speciation towards dihalogenated HAAs (22,79). The data

obtained in this study agreed partially with literature since, especially in WTW A samples, tri-HAAs became the major species in two of the three sampling rounds. This unusual behaviour may be attributable to the ability of ozonation in the treatment works to have efficiently removed important di-HAA precursors (78), mainly of non humic and hydrophilic character (80). Even so, di-HAAs formed during chlorination were substantially higher than those formed during chloramination, by approximately 57%, in line with a similar study by Hua et al. (78) where this difference was calculated to be 30%. In addition, the percentage of brominated HAAs was more elevated in chloraminated samples than in chlorinated by 10%, which indicated that the implementation of chloramines enhanced bromide incorporation in total HAAs.

The effect of applying chloramines as a disinfectant was similarly pronounced for HANs (Fig. 4 c) and HAcAms (Fig.4 d), and all N-DBP levels were lower than those identified with chlorination during all sampling events. In WTW A, mean HAN yields changed from 4.1 µg/L upon chlorination to 1.1 µg/L when applying chloramines, whereas mean HAcAms yields changed from 4.1 µg/L to 1.6 µg/L. The maximum total HANs observed during chloramination (4.1 µg/L) was approximately two times less than the maximum identified during chlorination (8.7 µg/L), both identified in summer at 72 hours. Likewise, in WTW B the average concentration of HANs changed from 4.3 µg/L in chlorinated to 1.8 µg/L when using chloramines, whereas mean concentration of HAcAms changed from 4.1 µg/L to 2.5 µg/L. Dominant species quantified during chlorination, such as DCAN and DBAN, were below the detection limits in several water ages during chloramination, which explained the low occurrence of N-DBPs. Overall, the results were comparable to the English nationwide occurrence survey where chloramines were reported to limit N-DBPs formation with similar values of 1.5 µg/L for HAN and 3.8 µg/L for HAcAm (28). A study by a different research group in the UK by Goslan et al. (70) reported HANs mean levels of 1.3 µg/L in chloraminated waters. Furthermore, knowledge on the impact of HANs and HAcAms speciation during chlorination is sparse (61) and during chloramination is even more limited. In this study the speciation leaned towards the di-HANs and di-HAcAms during both chlorination and chloramination, whereas tri-N-DBPs always occurred in lower levels. Thus, switching from chlorine to chloramines is expected to form less N-DBPs but without any considerable alteration in halogenation levels. In any case, the occurrence of HANs was in fact low and safely below the recommended guidelines values for DBAN (70 µg/L), and DCAN (20 µg/L) (14) during both disinfection processes. The percentage of bromine-containing HAcAms species was higher than that of chlorine-containing species during all water ages, with minimal variances between the two disinfection practices but with a tendency of higher bromide incorporation during chloramination. In more detail, bromine containing HAcAms represented approx. 50% of total HAcAms yields in chlorination and 62% in chloramination.

17

4. Conclusions

The key conclusions of this study are:

- Simulated distribution system tests are able to accurately and simultaneously predicted the occurrence and speciation of THMs, HAAs, HANs and HAcAms in both chlorinated (r=0.97, 0.95, 0.87 and 0.83) and chloraminated systems (r=0.96, 0.87, 0.74 and 0.73).

- SDS tests are recommended to water utilities not only to estimate the levels of the regulated and unregulated DBPs in distribution systems, but also to proactively design and adjust operational distribution disinfection practices.

- Whereas THM concentrations significantly increase with water age in both chlorinated and chloraminated systems, generally, HAA, HAN, and HAcAm concentrations increase to a lesser extent, with levels identified in the early stages of distribution either similar or only slightly higher at the final stages, and with intermediate fluctuations observed. Upon chlorination THMs, HAAs, HANs and HAcAms increased by 62%, 13%, 35% and 3% by mass between the treatment works and the final distribution sampling point, respectively. Upon chloramination THMs, HAAs, HANs and HAcAms increased by 48%, 5%, 43% and 20%, respectively.

- THMs and HAAs showed high seasonal dependence whereas HANs and HAcAms were relatively unaffected by the range of water temperatures tested.

- Switching from chlorine to chloramines resulted in average decreases of 34% in THMs, 49% in HAAs, 61% in HANs and 51% in HAcAms by mass.

- Switching to chloramines highlighted a tendency for higher bromide incorporation into HAAs, HANs and HAcAms.

Author contributions

CS, TB and MT contributed to the conceptualization and methodology of the study. CS then conducted the investigation, formal analysis, data curation and visualisation, while RK provided the validation and resources. The original draft was written by CS, whereas TB, RK and MT contributed further to the writing, reviewing and editing the manuscript.

Acknowledgements

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685

Table 1. Main formation factors of DBPs of water utilities interest and their expected corresponding occurrence trends (adapted from Chen and Weisel 1998b; Krasner et al. 2006; Yang et al. 2007; Sadiq and Rodriguez 2004; Hrudey and Charrois 2012; Templeton et al. 2012; UK WIR 2014).

DBPs Formation Factors	THMs	HAAs	N-DBPs	HANs	HAcAms
Concentration of disinfectant	↑	↑	~	❖	~
Disinfectant contact time	↑	↑↓ [a]	~	~	~
Concentration of organic/ inorganic matter	↑	↑	↑[b]	↑	↑
Bromide ions (Br⁻)	↑	↑	~	↑	↑
Water temperature	↑	↑	~	~	~
pH	↑	↓	↑↓	↑↓[c]	↑↓[d]
Water age (Distribution size)	↑	↑↓ [a]	~	~	~

↑ : Increase   ↓ : Decrease   ❖ : No effect   ~: Sparse evidence

a. Biodegradation (Zhang et al., 2009; Bayless et al., 2008).
b. Depends on the NOM content (algae, blended with treated wastewater effluent) (Bond et al., 2012).
c. Decreases at higher pH *(>7)* / Less stable at lower pH (Templeton et al., 2012; UWIR, 2013).
d. Decreases at lower pH *(<5)*/ Less stable at higher pH (Templeton et al., 2012; UWIR, 2013).

Table 2: Specifications of selected water treatment works for simulation distribution system monitoring.

Water Works (WTW)	Pre-oxidant	Treatment processes	Final disinfectant	Bromide [a] [µg/L] – *avg.*	Non-purgeable Organic carbon[a] [mg/L C] – *avg.*	pH[b] *avg.*	Total THMs [c] [µg/L] – *avg.*	Network size [m]	Water Age [hours]
A	Ozone	DAF Clarification, Rapid gravity filtration, GAC adsorption	Chlorine	[10-45] – *21.2*	[3.1-3.7] – *3.3*	*7.3*	[6-82] – *27.6*	1,150,800	6 →144
B	Ozone	DAF Clarification, Rapid gravity filtration, GAC adsorption	Chlorine	[9.4-48.1] – *25.85*	[2.9-4.2] – *3.5*	*7.3*	[5-72] – *26.6*	698,700	6 →106
C	Ozone	Clarification, Rapid gravity filtration, GAC adsorption	Chloramines	[75.7-135] – *97.05*	[2.1-4.0] – *3.1*	*7.4*	[5-75] – *32.5*	6,140,000	6 →144
D	n/a	Rapid gravity filtration (GAC), Slow sand filtration, aeration	Chloramines	[14.5-40.6] – *23.4*	[1.8-3.4] – *2.6*	*7.3*	[14-45] – *26.4*	264,000	6 →72

a.   Historical data from 2007-2018 (final water).
b.   In-situ measurement.
c.   Historical data of distribution network from 2007-2018.

Average Water age [hours] (n° node points)

- Not Applicable (6868)
- < 24.00 (1599)
- 24.00 - 48.00 (1349)
- 48.00 - 72.00 (5068)
- 72.00 - 96.00 (3704)
- 96.00 - 120.00 (1763)
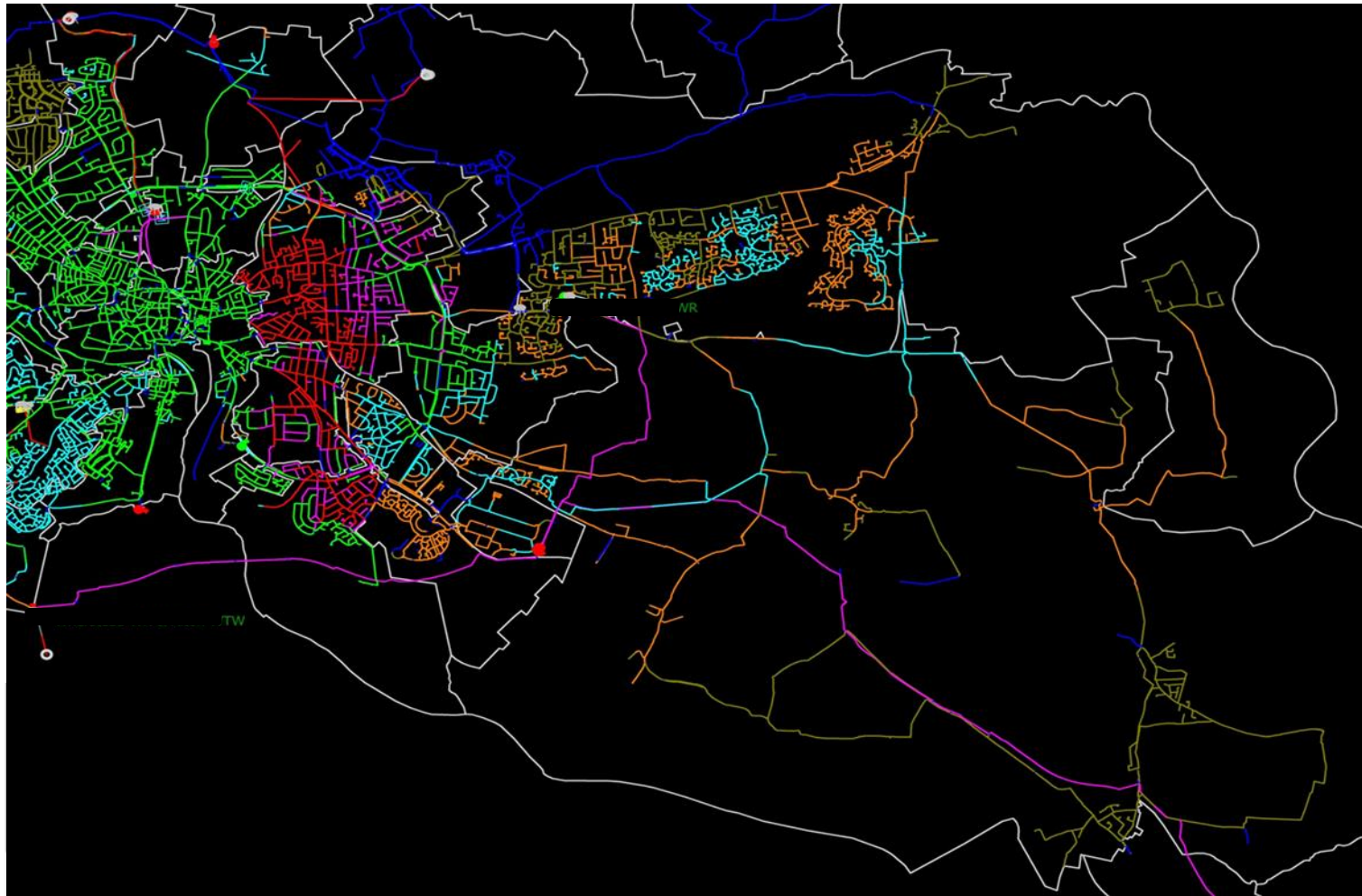- 120.00 - 144.00 (2021)
- > 144.00 (2792)

Figure 1: Water age map designed via SynerGEE v4.6.0 for the selection of water ages in distribution (WTW A).
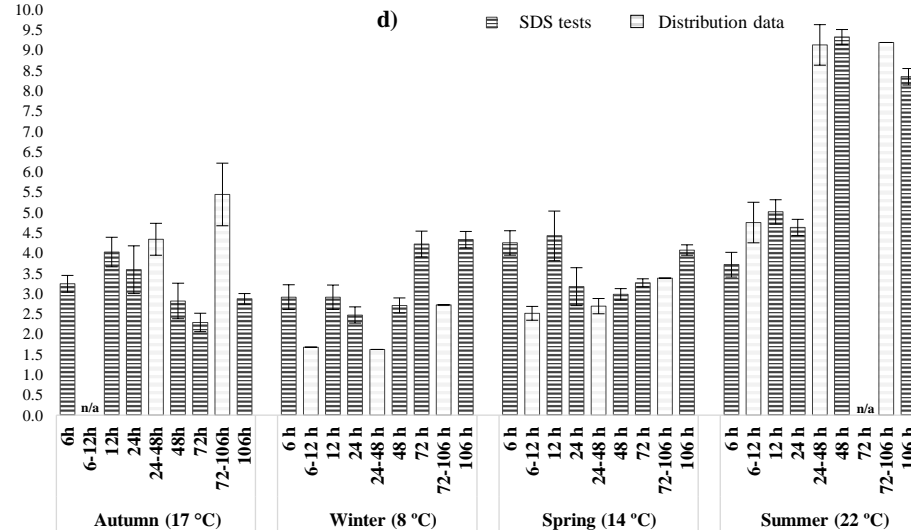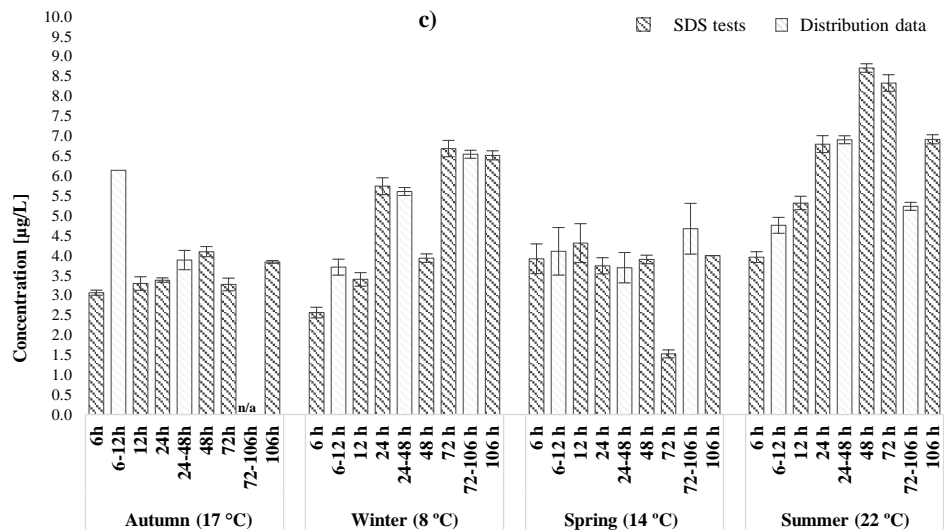
Figure 2: DBP occurrence of **a)** THMs, **b)** HAAs, **c)** HANs and **d)** HAcAms from SDS tests (*6, 12, 24, 48, 72, 106 hours*) and actual distribution samples (*6-12, 24-48, 72-106 hours*) in **chlorinated** water treatment works **A** (*4 seasonal rounds*).
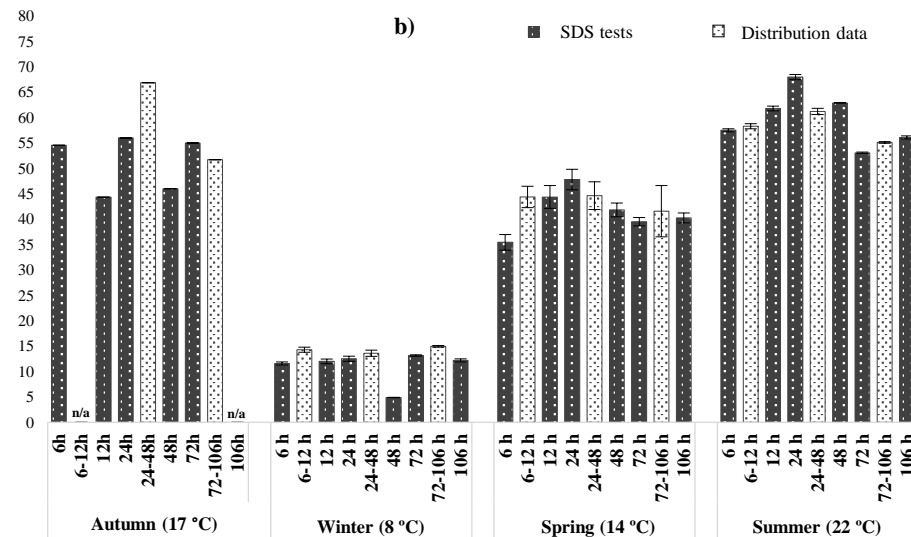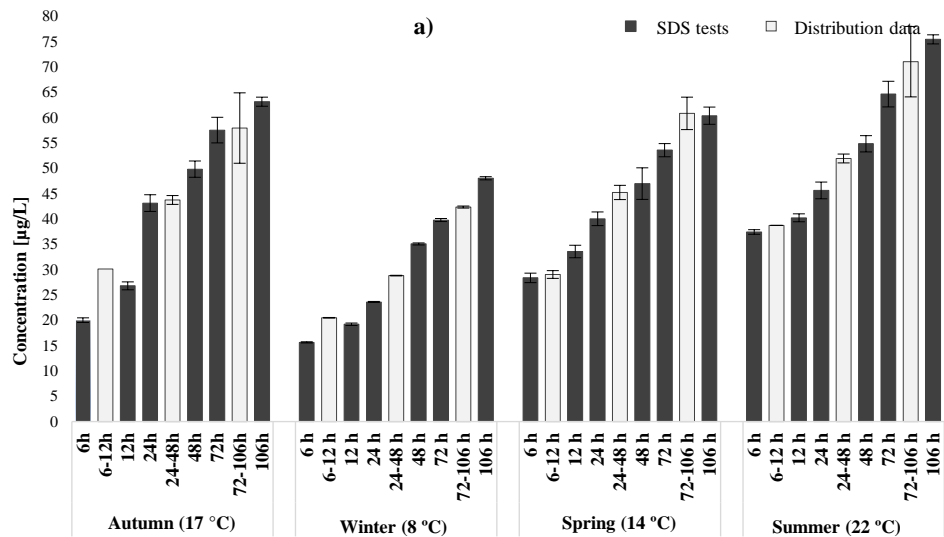
Figure 3: DBP occurrence of **a)** THMs, **b)** HAAs, **c)** HANs and **d)** HAcAms from SDS tests (*6, 12, 24, 48, 72, 106 hours*) and actual distribution samples (*6-12, 24-48, 72-106 hours*) in **chloraminated** water treatment works **C** (*4 seasonal rounds*).
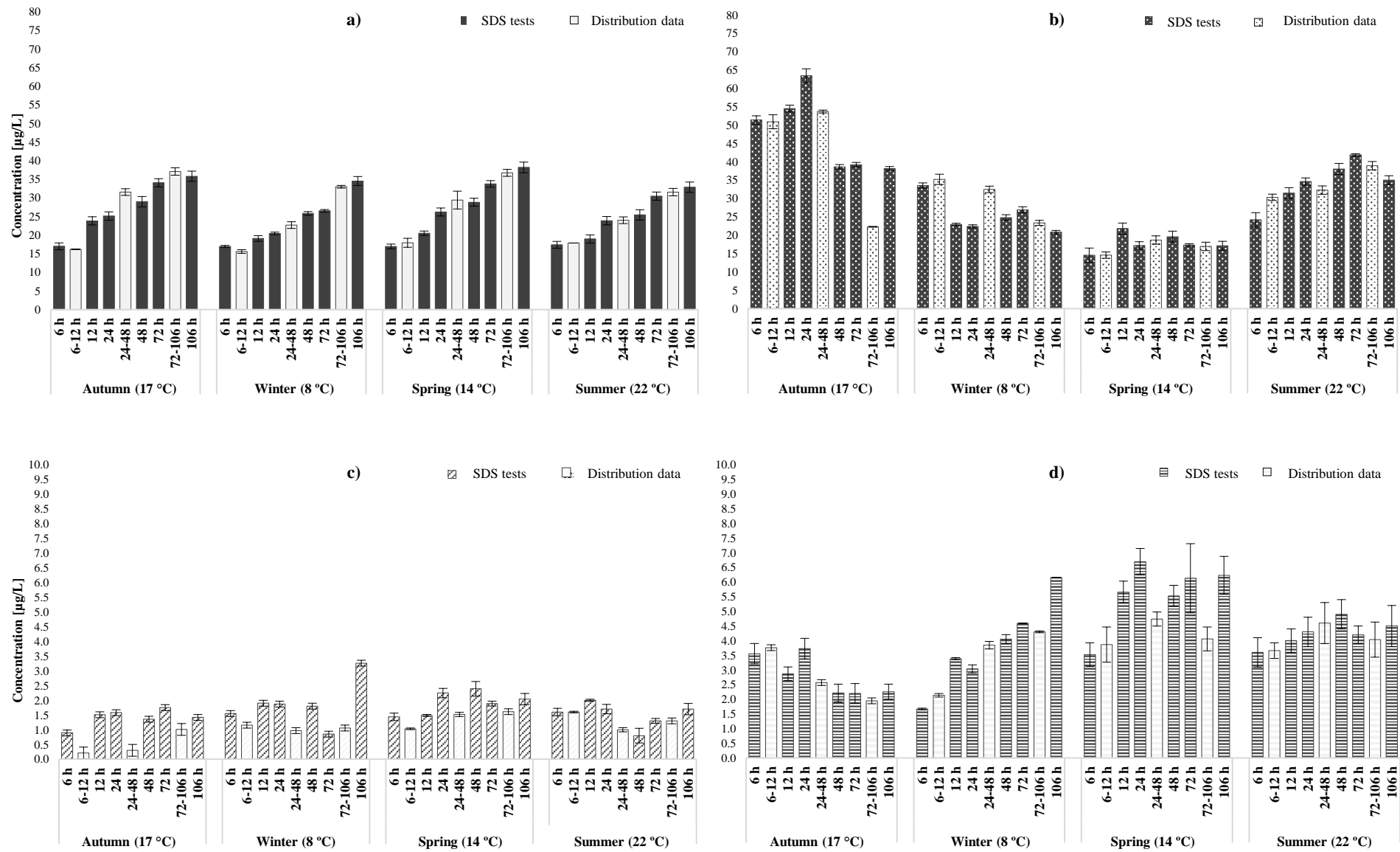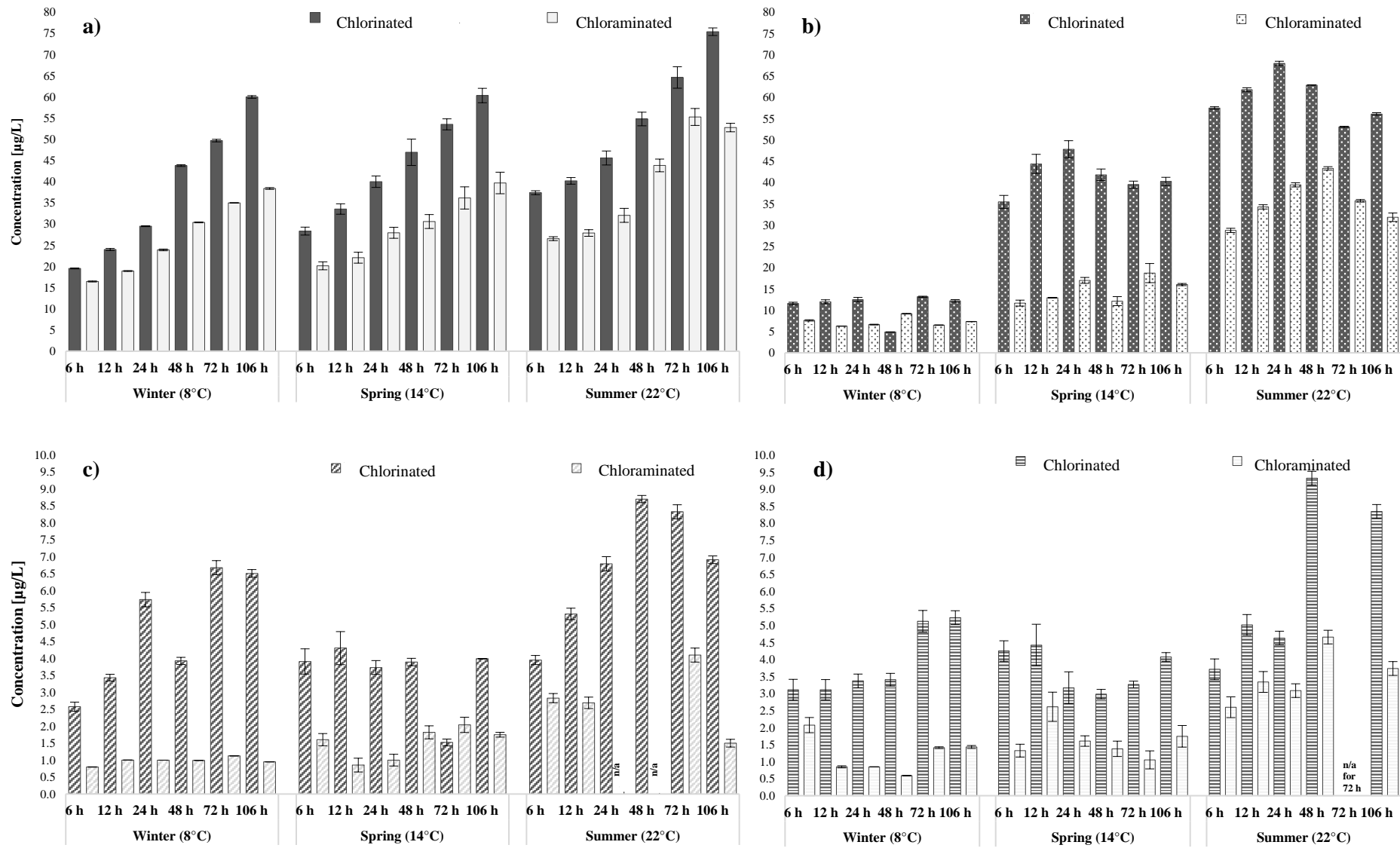
Figure 4: Comparison of total DBP concentrations in chlorination and chloramination of **a)** THMs, **b)** HAAs, **c)** HANs and **d)** HAcAms in WTW A.

Supporting Information

Simultaneous prediction of trihalomethanes, haloacetic acids, haloacetonitriles and haloacetamides using simulated distribution system tests

Chrysoula Sfynia [a*,] Tom Bond [b], Rakesh Kanda [c], Michael R. Templeton [a]

a. Department of Civil and Environmental Engineering, Imperial College London, London SW7 2AZ, UK.
b. Department of Civil and Environmental Engineering, University of Surrey, Guildford GU2 7XH, UK.
c. Institute of Environment, Health and Societies, Brunel University London, Uxbridge UB8 3PH, UK.

Table S1: Extraction and gas chromatography specifications and operational conditions in modified EPA Method 551.1, for THMs, HANs and HAcAms.

Extraction:	Liquid-liquid extraction (LLE) with MTBE Internal standard: bromofluorobenzene [1 µg/ml]
Primary Column:	RXi 5Sil MS, 30m · 0.25mm ID, 0.25 µm film thickness
Injector:	Injector temperature –170 °C; 2 mm straight quartz liner; injection volume 1 µL; splitless injection hold for 45 seconds then purge at 30 mL/min.
Carrier Gas:	Helium (*set at constant pressure*), velocity 33 cm/sec.
GC program:	▪ HOLD at 35°C for 22 minutes. ▪ INCREASE to 145°C at 10°C/min and hold at 145°C for 2 minutes. ▪ INCREASE to 225°C at 20°C/min and hold at 225°C for 15 minutes. ▪ INCREASE to 260°C at 10°C/min and hold at 260°C for 30 minutes.

Total time: 90 min/ sample

Detector:	Agilent Micro ECD (150 µL); Detector temperature: 290 °C; Make up gas: 99.9% nitrogen at 30 mL/min.

Table S2: Extraction and gas chromatography specifications, and operational conditions in EPA Method 552.3 for HAAs.

Extraction:	Liquid-liquid extraction (LLE) with MTBE, and derivatization via methylation Internal standard: 1,2,3-trichloropropane [1 µg/ml]
Primary column:	DB-1701, 30m · 0.25mm ID, 0.25 µm firm thickness.
Injector:	Injector temperature – 210°C; 2 mm straight quartz liner; injection volume 1 µL; splitless injection hold for 45 seconds then purge at 30 mL/min.
Carrier Gas:	Helium (set at constant pressure), velocity 33 cm/sec.
GC program:	▪ HOLD at 40°C for 10 minutes. ▪ INCREASE to 65°C at 2.5°C/min. ▪ INCREASE to 85°C at 10°C/min. ▪ INCREASE to 205°C at 20°C/min, and hold at 205°C for 7 minutes.

Total time: 35 min/ sample

Detector:	Agilent Micro ECD (150 µL); detector temperature: 290 °C; Make up gas: 99.9% nitrogen at 20 mL/min.

Table S3: DBP monitoring in numbers (MDL, recovery rate, n° of samples, median concentrations).

Target Analyte		MDL [µg/L]	Recovery rate [%]	Total samples [n°]	Samples >MDL [n°]	Median concentration [µg/L]
THMs	Chloroform	0.4	108	384	384	4.8
	Bromodichloromethane	0.3	110	384	384	6.8
	Dibromochloromethane	0.2	110	384	384	10.8
	Bromoform	0.4	98	384	376	7.7
HAAs	Monochloroacetic acid	0.2	95.8	374	320	3.3
	Monobromoacetic acid	0.5	92.2	374	358	1.4
	Dichloroacetic acid	0.2	93.8	374	324	4.4
	Trichloroacetic acid	0.2	105	374	364	0.9
	Bromochloroacetic acid	0.1	98	374	96	2.6
	Bromodichloroacetic acid	0.1	101	374	340	1.7
	Dibromoacetic acid	0.7	110	374	338	2.5
	Dibromochloroacetic acid	1	108	374	338	3.2
	Tribromoacetic acid	1	90.6	374	320	2.9
HANs	Dichloroacetonitrile	0.1	90	380	308	0.6
	Trichloroacetonitrile	0.1	95	380	302	0.7
	Dibromoacetonitrile	0.2	95	380	266	0.8
	Bromochloroacetonitrile	0.2	110	380	312	0.6
	Monochloroacetonitrile	-	n/a	380	n/a	n/a
	Monobromoacetonitrile	0.1	90	380	82	0.1
	Dibromochlroacetonitrile	0.5	95	380	0	n/a
HAcAms	Monochloroacetamide	-	n/a	372	n/a	n/a
	Monobromoacetamide	0.1	70	372	244	0.6
	Dichloroacetamide	0.1	85	372	368	0.8
	Trichloroacetamide	0.1	80	372	260	0.3
	Dibromoacetamide	0.1	88	372	350	0.6
	Bromochloroacetamide	0.1	73	372	326	0.8
	Bromodichloroacetamide	0.1	70	372	306	0.3
	Dibromochlroacetamide	0.1	71	372	190	0.3
	Tribromoacetamide	0.1	70	372	280	0.3

Table S4: Summary of water quality characteristics range of the chlorinated and chloraminated SDS tests (between 6-106 hours) during the seasonal samplings.

WTW	Units	A				B				C				D			
Sampling rounds		Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer
Disinfectant type	-	Chlorination				Chlorination				Chloramination				Chloramination			
Disinf. residual	mg/L Cl$_2$	0.9-0.2	0.7-0.2	1.0-0.2	1.1-0.3	0.6-0.2	0.6-0.3	0.6-0.4	1.1-0.4	1.2-0.9	1.0-0.3	0.9-0.5	1.0-0.5	0.6-0.2	0.8-0.6	1.0-0.2	1.0-0.2
Water temperature	°C	17.0	8.0	14.0	20.0	17.0	8.0	14.0	20.0	14.0	8.0	17.0	20.0	14.0	8.0	17.0	20.0
TOC	mg/L C	3.1-3.7	3.1-3.6	3.3-3.5	2.9-3.9	3.8	3.2-3.6	3.5-4.1	3.7-3.5	3.1-4.0	3.3-3.4	3.2-3.4	2.1-3.0	2.8-3.3	2.5-2.8	1.8-1.9	2.7-3.0
pH	-	7.2	7.5-7.9	7.0-7.5	7.0-7.1	n/a	7.2-7.7	7.0-7.7	7.2	6.9-7.3	7.6-7.7	7.4-7.6	7.4-7.5	6.5-7.3	7.3-7.5	7.3-7.5	7.5
Bromide	µg/L	<12.0	<12.0	<12.0	<12.0	<12.0	18.3	<12.0	12.0	82	85.1	76	80.0	13.2	19.9	26.4	<12.0
UV$_{abs}$	1/M·cm	n/a	0.04-0.06	0.06	n/a	n/a	0.04-0.06	0.04-0.07	n/a	n/a	0.06	0.04	0.05-0.06	0.03-0.05	0.06	0.04	0.05
SUVA	-	n/a	1.2-1.6	1.8	n/a	n/a	1.2-1.9	1.1-1.6	n/a	n/a	1.7	1.4	2.3-2.6	1.0-1.7	2.1-2.3	2.2-2.3	1.9

Table S5: Key concept and equation of the weight ratios [%].

The weight ratios [%], also referred as mass percent composition, can be abbreviated as w/w %. This is a type of generic calculation that enables us to assess the ratio of specific species/sub-species against the sum of a category. In DBP analysis, the weight ratio term is usually calculated to assess the contribution of brominated species of a specific class to the sum of species (total). Also, this calculation was used to calculate the contribution of HAA5 against HAA9. In this study the following equation was used to calculate the weight ratios:

Weight-Ratio [%] = Concentration of sub-category [mg/L] / Concentration of category (*total*) [mg/L] × 100
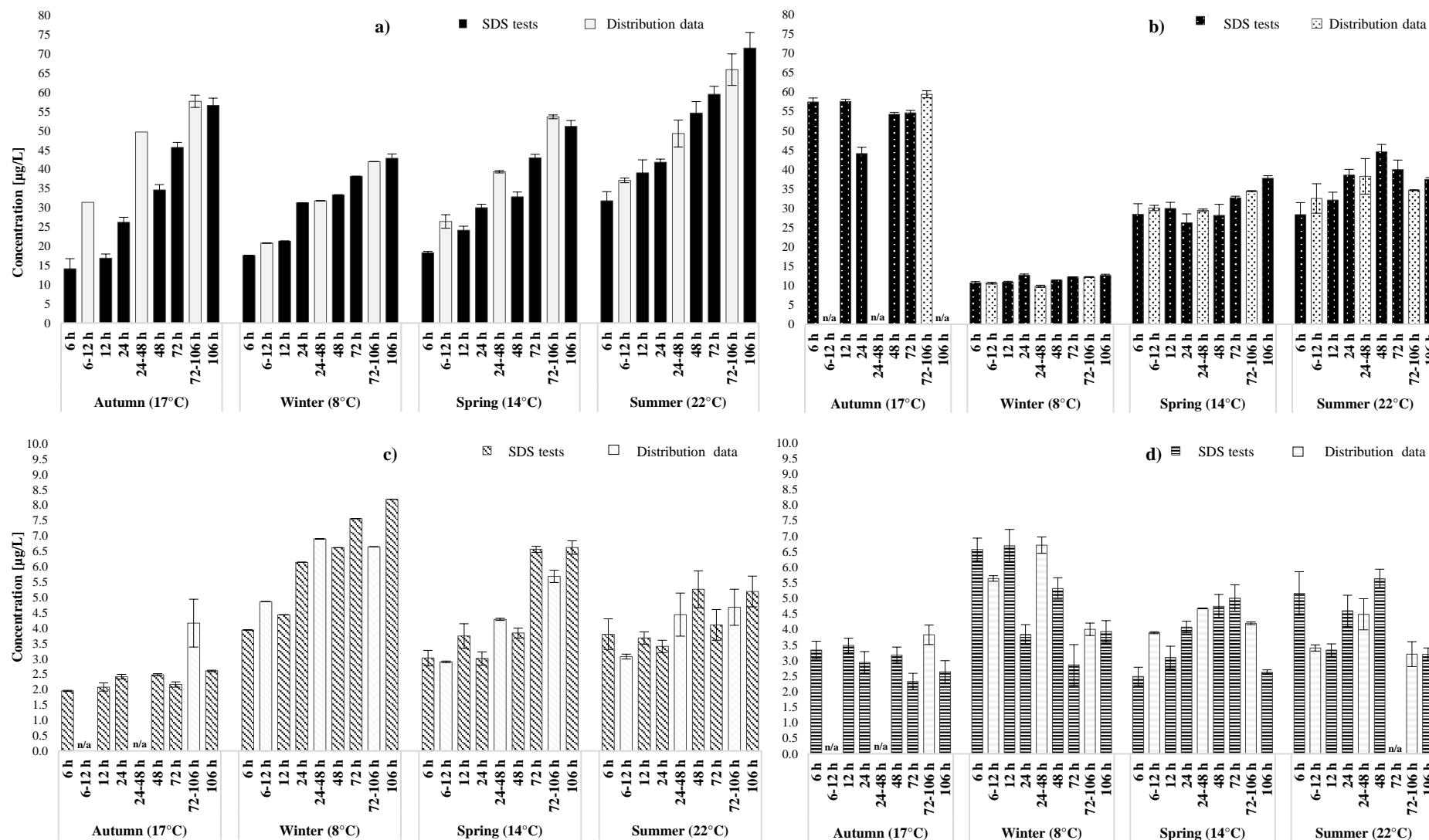
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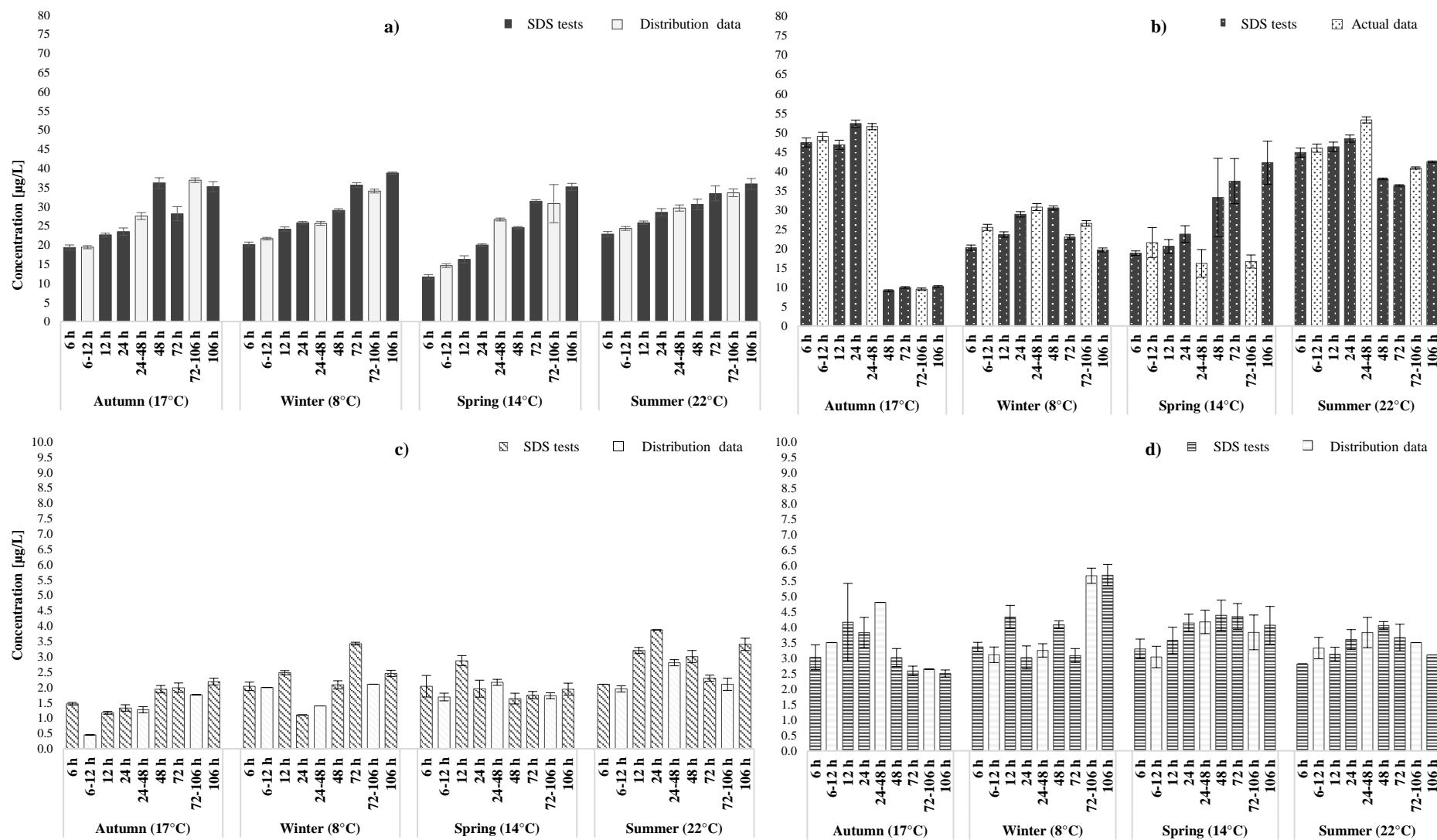
Figure S2: DBP occurrence of **a)** THMs, **b)** HAAs, **c)** HANs and **d)** HAcAms from SDS tests (*6, 12, 24, 48, 72, 106 hours*) and actual distribution samples (*6-12, 24-48, 72-106 hours*) in **chloraminated** water treatment works **D** (*4 seasonal rounds*).