Chemical and Biological Hazard Prevention

Studies and Research Projects

REPORT **R-889**

The Impact of Four Swimming Pool Water Treatment Processes on Concentrations of Disinfection Byproducts

An Exploratory Study

Robert Tardif
Cyril Catto
Manuel Rodriguez

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Legal Deposit
Bibliothèque et Archives nationales du Québec
2015
ISBN: 978-2-89631-827-8 (PDF)
ISSN: 0820-8395

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This study was funded by the IRSST. The conclusions and recommendations are solely those of the authors.
This publication is a translation of the French original; only the original version (R-859) is authoritative.

ACKNOWLEDGMENTS

We sincerely thank Sylvie Desgagné, Yvon Brault, Stéphane Lafortune and Michel Pagé for their accessibility and for their valuable and indispensable assistance, which made the accomplishment of this original project possible. Additionally, we would like to thank all of the staff and the authorities who welcomed us to their facilities.

We also wish to acknowledge the members of the follow-up committee* who accompanied us as we conducted this research: Annie Boisclair, Ville de Montréal; Marie-France D'Amours, IRSST; Alain Desrosiers, SCFP, Ville de Montréal; Élaine Guénette, APSAM; Jean-Marc Lacroix, Ville de Gatineau and UMQ; Johane Lafleur, Canadian Red Cross; Marie-Josée Leblanc, ARAQ; Jocelyne Marquis, SFMM, Ville de Montréal; François Lépine, Lifesaving Society; Benoit Lévesque, INSPQ; François Proulx, Ville de Québec; Lorraine Vézina, Ville de Montréal.

We express our gratitude to Sabrina Simard (Université Laval) and Ginette Charest-Tardif (Université de Montréal) for their major and exceptional contributions, especially with regard to the planning and realization of the many laboratory analyses that were required for this project. Finally, we thank the Ville de Montréal, in particular, Lorraine Vézina, Josée Bisson, Daniel Sirois and Anne-Marie Bernier-Brière, as well as the laboratory staff of the Service de l'environnement, for their participation in the study.

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* Made up of stakeholders involved in the research, the follow-up committee provides its field expertise to the researchers during the definition, design and realization phases of the research, in the transfer and application of the results to the workplace and finally, in the assessment of the impact of this transfer. The composition of the committee is based on joint representation, the presence of organizations that can pass on information, and diverse points of view.

ABSTRACT

The public's exposure to disinfection byproducts (DBP) in swimming pools is of growing concern globally. DBPs are the inevitable result of chemical reactions between the disinfection agents added to swimming pool water and the organic or nitrogeneous matter that is naturally present or introduced by bathers. DBP formation and concentrations in pool water and the ambient air (for those that are volatile) vary according to the type of treatment used. However, no data are currently available to systematically compare these treatment approaches under controlled conditions in a single pool. This study aimed to provide such data. The objective was to explore the impact of various water treatment processes on DBP levels in swimming pool water and ambient air in order to determine the effectiveness of each and to help identify best practices to reduce exposure to them.

The swimming pool used for this research provided the possibility of putting the various procedures of its treatment system into operation for variable durations, both separately and simultaneously. Two campaigns (A and B) to measure DBP concentrations (in water and air) were carried out to understand the impact of four different changes made successively to the standard water treatment process, at different times of the year and under changing bather loads:

T1: additional activation of ultraviolet rays (UV);
T2: halt of air stripping with continuation of air extraction from the buffer tank;
T3: halt of air stripping and suppression of air extraction from the buffer tank;
T4: suppression of the polyaluminium silicate sulphate (PASS) flocculant.

The first stage in the analysis of results took into account the impact of every change in treatment for each class of DBP examined one-by-one over each of the two campaigns. UV rays have a marked impact, causing a potentially high increase of emerging DBPs, e.g., halonitromethanes (HNM), haloketones (HK), and trihalomethanes (THM), in the water and, subsequently, of THMs in the air. However, they also contribute to reducing the level of chloramines in the air and *N*-nitrosodimethylamine (NDMA) in the water. The results highlight the positive impact of air stripping in reducing volatile contaminants. The use of PASS does not appear to change the presence (quantity and speciation) of DBPs, except for the THMs, which appear to increase slightly with the use of this flocculant.

The second stage in the analysis of results details specific aspects related to variations in contamination levels between the various sampling points. In particular, it deals with: (i) increased contamination levels in pool water in relation to the potable water network that supplies the facility; (ii) the existence of seasonal variations in contamination levels (which basically doubled from one campaign to the other); (iii) the relationship between DBP levels measured at different times at a water intake situated between the end of the treatment process and the outlet into the pool with the levels measured directly in the pool; (iv) the existence of spatial variations in air contamination in the swimming pool area.

To the best of our knowledge, no other data using this original and systematic experimental approach exists. Clearly, this type of data is relevant to the desirable and strongly supported goal

of reducing exposure to DBPs in swimming pools and developing a better understanding of the dynamic of these contaminants. Managers are sure to find the information very useful in implementing more effective treatment processes and strategies (developing better practices), in particular, to better protect the health and well-being of swimming pool staff, given the concerns surrounding DBP exposure. In that sense, the investigation results will also raise awareness of the need to make choices in treatment procedures that take into account the specific context of each swimming pool and the related issues, in this case, DBP contamination.

As this is an exploratory study, the results cannot be generalized to validate (or invalidate) the use of different processes that have been considered in other contexts. For that, further study is required.

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LIST OF ACRONYMS AND ABBREVIATIONS

11DCPone	1,1-dichloro-2-propanone
111TCPone	1,1,1-trichloro-2-propanone
ANSES	Agence nationale de sécurité sanitaire de l’alimentation, de l’environnement et du travail (France)
BCA	Bromochloroacetic acid
BCAN	Bromochloroacetonitrile
CAM	Chloramine
CDBM	Chlorodibromomethane
CPK	Chloropicrin (trichloronitromethane)
DBA	Dibromoacetic acid
DBAN	Dibromoacetonitrile
DBP	Disinfection byproducts
DCA	Dichloroacetic acid
DCAM	Dichloramine
DCAN	Dichloroacetonitrile
DCBM	Dichlorobromomethane
eDBP	Emerging disinfection byproducts
HAA	Haloacetic acid
HAN	Haloacetonitriles
HK	Haloketones
HNM	Halonitromethanes
IRSST	Institut de recherche Robert-Sauvé en santé et en sécurité du travail
MBA	Monobromoacetic acid
MCA	Monochloroacetic acid
MCAM	Monochloramine
NDMA	*N*-nitrosodimethylamine
PASS	Polyaluminium silicate sulphate
TBM	Tribromomethane (bromoform)
TCA	Trichloroacetic acid
TCAM	Trichloramine
TCAN	Trichloroacetonitrile
TCM	Trichloromethane (chloroform)
THM	Trihalomethanes
TTHM	Total trihalomethanes (the four chief constituents together)
UV	Ultraviolet

1. INTRODUCTION

The evidence of potentially severe contamination of water and air at swimming pools by disinfection byproducts (DBP) raises concerns about the safety and comfort of employees, in terms of health (such as respiratory and eye irritation, bronchial hyperreactivity), in these environments. Also of concern are the suspected harmful effects associated with these pollutants and the particular conditions surrounding the exposure of pool employees in this context. Swimming pools are facilities with potentially high numbers of visitors, where exposure to DBPs could be much greater than exposure in domestic settings (such as by drinking water, or taking a bath/shower). Numerous factors (related to technical demands of maintenance and/or individual behaviour) may combine to facilitate (i) the formation and diffusion of large amounts of contaminants in environmental media (water, air), and (ii) people’s exposure to these contaminants. The recirculation of water, an unavoidable hydraulic practice to limit wastage, also contributes to increasing the concentrations of these pollutants in swimming pools.

Throughout Québec, a significant number of workers are affected by this problem. There are over 500 swimming pool employees in Québec City alone. According to the Lifesaving Society, in the province as a whole, there are more than 18,000 lifeguards and swimming instructors, etc., whose ages vary, for the most part, from between 16 to 24 years old, working in approximately 3300 aquatic facilities, including close to 850 indoor pools. This is a considerable population for which data on DBP exposure remain limited. This absence of data, which goes hand-in-hand with the absence of regulation in this area in Québec, is a shortcoming that should be remedied, at a time in which interest in the issue is growing worldwide, as well as being of concern to local governments.

It was in this context, and in response to the many expectations of various organizations (the Red Cross, the Lifeguard Society, unions, etc.), and the concerns expressed by workers themselves, that the Institut de recherche Robert-Sauvé en santé et en sécurité du travail (IRSST) financed an initial research project to assess workers’ exposure to disinfection byproducts in Québec swimming pools (Tardif et al., 2015). The project’s goal was to make a preliminary diagnosis of the situation by first providing an overview of environmental contamination (water and air) at 41 indoor pools, and then by measuring biological levels in samples of alveolar air and urine provided by swimming pool workers. There was so much interest in the study that volunteers had to be turned away in order not to exceed the analysis capacities. The results confirmed the scale and diversity of contamination and speciation of DBPs in swimming pools in Québec.

This study complements that initial research. In fact, the members of a follow-up committee expressed strong interest in a more in-depth diagnosis of the impacts of the water treatment processes in use and in conducting a study “[…] to appraise various solutions in order to better control exposure (in that the choice of the swimming pools studied would enable the impacts of various systems to be compared, i.e., before and after, at the same site).”[1] The research team thus seized the unique opportunity, provided by a single facility, to complete the initial work that is the subject of this report. Considering the diversity of the swimming pools highlighted by the committee and confirmed by the exploration of the environmental factors in the initial project,

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[1] Excerpt from the minutes of the first meeting of the follow-up committee.

with the changing configurations, practices and treatment procedures from one to another and over time, this additional research provides the opportunity to document some of the most relevant elements.

2. CURRENT SCIENTIFIC OR TECHNICAL KNOWLEDGE

2.1 The Issue of Exposure to DBPs: Classes of Compounds, Health Impacts and Regulations

A review of current knowledge on the issue was recently carried out, including, in particular, the various categories of DBPs, the health impacts associated with exposure to these contaminants, and an overview of the regulations (Tardif et al., 2015). It bears repeating that DBPs result from chemical reactions that occur among the disinfecting agents and the organic or nitrogeneous material naturally present in water or introduced by bathers.

Among these contaminants, we make a distinction between compounds that can be qualified as "traditional" and byproducts referred to as "emerging" (eDBP), i.e., that have been discovered more recently (Mercier Shanks et al., 2013; Richardson et al., 2007; Richardson et al., 2010; Weaver et al., 2009; Zwiener et al., 2007). In the category of traditional compounds, three classes are habitually identified: trihalomethanes (THM), including, in particular, chloroform (TCM), dichlorobromomethane (DCBM), chlorodibromomethane (CDBM) and bromoform (TBM); haloacetic acids (HAA), including, in particular, monochloroacetic acid (MCA), monobromoacetic acid (MBA), dichloroacetic acid (DCA), trichloroacetic acid (TCA), bromochloroacetic acid (BCA) and dibromoacetic acid (DBA); and chloramines (CAM), among which are monochloramine (MCAM), dichloramine (DCAM) and trichloramine (TCAM). The THMs, which are very volatile compounds, can disperse in the air, while the HAAs are mainly concentrated in the water. In the CAM group, we find mainly MCAM in water and TCAM in the air. The long list of eDBPs is made up of, in particular, haloacetonitriles (HAN), including trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), dibromoacetonitrile (DBAN) and bromochloroacetonitrile (BCAN); halonitromethanes (HNM), including chloropicrin or trichloronitromethane, as well as the haloketones (HK), including 1.1-Dichloro-2-propanone (11DCPone) or 1.1.1-trichloro-2-propanone (111TCPone); and *N*-nitrosodimethylamine (NDMA). This study will examine all these compounds.

2.2 The Impact of Treatment Processes on DBP Contamination

There is still very little scientific literature on the impact of swimming pool water treatment processes on DBP contamination. Most of the studies identified consist of laboratory experiments, and explore the mechanistic aspect of the formation of certain groups of DBPs by looking at the chemistry of the precursors and the adjustment of various operational parameters (Hansen et al., 2013a; Hansen et al., 2013b; Soltermann et al., 2013; Weng et al., 2012). A number of other studies have compared the contamination profiles (speciation) and levels observed in various swimming pools according to treatment type or various other characteristics (e.g., disinfectant type) (Lee et al., 2010; Righi et al., 2014). It is rare, and often impossible, to find case studies describing changes in contamination profiles and levels, under real conditions in a single swimming pool as the treatment processes are modified (Cassan et al., 2006).

The most relevant work with respect to the impact of the various procedures on the (types and levels) contamination portrait comes mainly from France, where the issue of reducing CAM exposure, recognized as a source of occupational asthma in lifeguards, has led to numerous studies. In particular, they have investigated the implementation of stripping procedures and UV ray systems. Stripping procedures act through aeration to promote the extraction of CAM by volatilization (Gérardin et al., 1999; Gérardin et al., 2001; Gérardin et al., 2005b). The action of UV ray systems, or dechloraminators, however, has not been as clear-cut as expected in terms of results and the advantages of these systems may be offset by an increased formation of THMs (Gérardin et al., 2005a). Hamel's thesis (2007) is also an important reference on this subject. It explored the impact of these means of reduction by enlarging the list of compounds studied to include CAMs and THMs in water and air, and enhanced the understanding of how operating conditions influence the formation of these DBPs. All these studies led ANSES (France's agency for food, environmental and occupational health and safety) to publish guidelines for authorization requests to implement treatment procedures, in particular, dechloraminators using UV rays, which must first undergo laboratory trials and experiments in a real environment (ANSES, 2011).

Weng et al. (2012) and Hansen et al. (2013b) remark that the impact of UV rays on THMs is a source of contradiction in the literature. While the study by Cassan et al. (2006) reported an increase in levels of THMs following the installation of a UV system at a swimming pool, Beyer et al. (2004) observed the opposite effect at a swimming pool that had switched to a similar system and, at a third swimming pool, Kristensen et al. (2009), did not see any notable difference in THM levels whether the UV rays were on or off. The impact of UV rays continues to be the subject of laboratory investigations, providing an exclusive perspective on DBP levels in the water. These studies broaden the sample of DBPs studied and underscore the various consequences of operating conditions. Weng et al. (2012) documented the impact of UV rays on nitrogenous DBPs and concluded that UV rays appear to increase concentrations of some and decrease concentrations of others. Hansen et al. (2013b) assessed the impact of UV rays on 12 different compounds and considered that UV application could help lower levels of brominated HANs and brominated THMs. Using water samples from a distribution network, Shah et al. (2011) highlighted the contrasting effects of different types of lamps on HANs and HNMs. Recently, Soltermann et al. (2013) documented the effects of UV rays on *N*-Nitrosamines, pointing out that the degradation of these compounds depends on the UV dosage applied and on the initial concentrations of these compounds and their precursors. They concluded that this type of swimming pool water treatment could lead to the formation of NDMA that counterbalances and surpasses the expected level of degradation.

Given the still limited and contradictory data, which do not systematically take into account all the DBPs in water and air, and which are very rarely generated under the conditions actually found in a swimming pool facility, this study is of undeniable interest.

3. RESEARCH OBJECTIVES

The general objective of this research is to provide data for an initial assessment of the impact of modifications to water treatment (disinfection, decontamination) and on levels of contamination of water and air by chlorination byproducts at a typical swimming pool.

Specifically, we will

- take a series of samples in order to document the levels before and after modifications to the water treatment process;
- compare the effectiveness of various water treatment processes with respect to the levels measured.

4. METHODOLOGY

The research is based on a case study of a swimming pool that provided the possibility of running the various procedures that constitute its water treatment process one at a time and simultaneously, over variable durations. Two campaigns (A and B) measuring DBP concentrations (in water and air) were conducted to study the impact of four different changes made successively to the baseline water treatment process, at different times of the year and under changing load conditions.

4.1 Presentation of the Host Facility (Case Study)

The host facility is an indoor swimming pool in the greater Montréal region, which was built in 1990. It underwent major renovations in 2010, including the introduction of a stripping system, which has greatly contributed to lowering the number of complaints regarding the irritating effects apparently associated with CAMs. The volume of the swimming pool is 875 m^3, with a 463 m^2 *L*-shaped basin of a maximum depth of 3.6 m. Water in the pool flows out through overflow gutters and skimmers and a drain in the bottom. The pool has not been completely drained since the renovation. Used air is exhausted through vents on the back wall near the diving boards. Fresh air is introduced near the skylights at deck level and at the top of the skylight. More air circulates from baffles located on the ceiling.

A total of 93 employees work at the facility, which receives approximately 2400 bathers per month (maximum bather load of 300 people). There are no restrictions regarding swimsuits, but bathing caps are mandatory. Soap is available in the change rooms to encourage bathers to take the normally compulsory shower.

The swimming pool's technical experts estimate that changes related to modifications made to the treatment process will occur within 48 hours. The water treatment process includes the following procedures:

i. Air stripping (SPENCER UB0055BZ-002 air booster with flow rate of 250 to 300 cubic feet per minute, in operation from 4:00 p.m. to 7:00 a.m. during the week and from 12:00 p.m. to 7:00 a.m. on the weekend, with ventilation 24 hours a day in the balancing tank); Stripping consists of removing the volatile compounds from the water through desorbing with air in the buffer tank.

ii. Flocculation (450 mL of polyaluminium silicate sulphate (PASS) per day, through four injections of 10 mL/min per day); flocculation causes agglomeration of colloidal particles through the addition of a polymer (flocculant).

iii. Filtration (two sand filters with a flow rate of 4608 m^3/day).

iv. UV dosing through medium pressure lamps (dose set at 61 mJ/cm^2, in operation 24 hours a day); recirculation of water at a flow rate varying from 3168 to 3632 L/minute.

v. Liquid chlorination (dose of 1 mg/L sodium hypochlorite).

Muriatic acid is occasionally injected to help regulate the pH.

4.2 Description of the Water Treatment Processes Under Study

The UV rays are normally de-activated during the summer months, but are active the rest of the year. For this study, de-activated UV rays were chosen in the reference situation that serves as the baseline for comparison.

During each campaign, the environmental concentrations of DBP in the swimming pool water and in the air around it were measured in order to successively and systematically address the impact of the following four treatment processes with respect to the baseline:

T1: activation of ultraviolet rays (UV);

T2: halt of air stripping with continuation of air extraction from the buffer tank;

T3: halt of air stripping and suppression of air extraction from the buffer tank;

T4: suppression of the polyaluminium silicate sulphate (PASS) flocculant.

The filtration and chlorination processes were not modified. The general ventilation conditions remained the same throughout each campaign, i.e., the addition of 4800 cubic feet (136 cubic metres) per minute of fresh outside air and the exhausting of 9775 cubic feet (277 cubic metres) per minute of indoor air.

4.3 List of Parameters Studied

Table 1 lists the parameters that were analyzed throughout each campaign and provides a short summary of the sampling techniques and analysis methods. These are more fully detailed in the previous report (Tardif et al., 2015). As during the previous investigation, the analyses of compounds in the water were the responsibility of the Chaire en eau potable at Université Laval in Québec City, which is accustomed to this type of analysis. The procedures to analyze levels of THM in the ambient air were set up in the laboratory at the Unité d’inhalation expérimentale of the Department of Environmental and Occupational Health of the Université de Montréal. The analyses of the CAM air samples were subcontracted to the laboratory of the environmental service of the City of Montréal. The water meters were read and the numbers of swimmers were counted during the sampling sessions.

Table 1 – Parameters quantified during campaigns A and B and measurement methods

Parameters	Measurement Methods
DBP in the air	
CAM (mainly TCAM)	- Suction of air at a flow rate of 1 L/min. for 120 min through filter cassettes - Analysis of desorbate using ionic chromatography
THM including TCM, DCBM, CDBM, TBM	- Suction of air at 165 mL/min for 95 min. through tubes filled with activated charcoal - Analysis by gas chromatography with electron capture detection
	-
DBP in the water	
THM including TCM, DCBM, CDBM, TBM	- 40 mL vials pretreated with ammonium chloride - Solid phase microextraction, headspace gas chromatography and mass spectrometric detection
HAA including MCA, MBA, DCA, TCA, BCA, and DBA	- Identical vials to those used for THM - Liquid-liquid extraction, gas chromatography with electron capture detection
HAN including TCAN, DCAN, BCAN and DBAN	- 60 mL amber vials, pretreated with ammonium chloride and phosphate buffer - Liquid-liquid extraction, gas chromatography with electron capture detection
HNM exclusively CPK	*Idem* HAN
HK including 11DCPone and 111TCPone	*Idem* HAN
NDMA	- 1 L bottle pretreated with sodium thiosulphate - Extraction followed by gas chromatography and detection with mass spectrometers
Physical-chemical parameters	
Free chlorine	Direct reading onsite with HACH colorimeter with DPD free chlorine reagent
Total chlorine	Direct reading onsite with HACH colorimeter with DPD total chlorine reagent
Monochloramine (MCAM)	Direct reading onsite with HACH colorimeter with Monochlor F reagent
pH	Direct reading onsite using a pH-meter with a gel probe
UV absorbance	Laboratory measurement with spectrophotometer using quartz cells
Conductivity	Laboratory measurement with Tetracon probe and handheld multimeter
Turbidity	Laboratory measurement with turbidimeter
Dissolved organic carbon	Laboratory measurement with carbon analyzer

4.4 Design of the Sampling Campaigns

The air and water samples were taken systematically before and after modifying the reference treatment process in each of the two campaigns (Table 2).

Campaign A, which consisted of the preliminary work, was carried out in the summer of 2013 and took advantage of the Saturday and Sunday closing of the swimming pool under study. This enabled us to study the short-term impact of changes in the environment with a minimal bather load. A first sampling series was carried out to get a baseline configuration on Friday mornings, just before the treatment process was modified. A second sampling series was taken 72 hours later, when the swimming pool reopened on the following Monday morning. The return to the baseline configuration took place after sampling on Monday morning, which thus enabled the initial situation to be re-established before the following Friday.

Campaign B was carried out in two phases (fall of 2013 and winter of 2014). It was designed to take into account the medium-term impact of treatment modifications with a high bather load. The first sampling took place on the Monday morning to get the baseline configuration, before modifying the treatment process the next day (Tuesday). Samples were gathered on Wednesday, 24 hours after modification. The team returned the following Monday to pick up the samples, six days after modification. The return to the baseline situation took place after sampling on that Monday. The process was repeated the following Monday, in order to study a new configuration and to re-establish a baseline.

In the scope of this campaign (B), two days of sampling were added (January 21 and March 12) to measure the levels of DBPs in the treatment configuration that would have normally been in operation if the interventions due to the project had not taken place, i.e., with all the treatment devices in operation (situation equivalent to the baseline situation with the UV rays activated). These two samplings would also take into account the “normal” contamination of the site during the week before starting the series of programmed modifications and one week after the re-establishment of the normal water treatment process used throughout the winter.

A series of major problems was noted by the maintenance crew two days before the last sampling (March 12): there was no air extraction from the buffering tank because of a breakdown in part of the ventilation duct, which caused the contaminants to outgas into the pool area while air stripping continued; there was no supply of PASS (empty barrel); free chlorine was at 0 because of a problem with the pumps, without anyone knowing when the outage began and how long it lasted. The situation gave us the opportunity, particularly relevant in the scope of the study, to document the repercussions on DBP contamination in the worst-case scenario (a breakdown of almost the entire water treatment process).

Table 2 –Calendar of Campaigns A and B.

Situation			**Campaign A Summer 2013**	**Campaign B Fall 2013/winter 2014**
T1	Activation of UV	Before (BL)	July 5	November 4
		After	July 8	November 6 and 12
T2	Deactivation of stripping	Before (BL)	July 12	February 24
		After	July 15	February 26 and March 4
T3	Deactivation of stripping and ventilation in the buffer tank	Before (BL)	July 19	February 10
		After	July 22	February 12 and 18
T4	Flocculation halted	Before (BL)	July 26	January 27
		After	July 29	January 29
NORMAL1	Normal treatment (complete)		-	January 21
NORMAL2	System failure		-	March 12

During each morning of sampling, the CAMs and THMs in the air were measured simultaneously at three points (A, B, C) around the pool, by taking samples of air at the breathing height of a man standing beside the pool (Figure 1). To do this, the pumps were positioned by the lifeguard chairs at approximately 150 cm above the surface of the water.

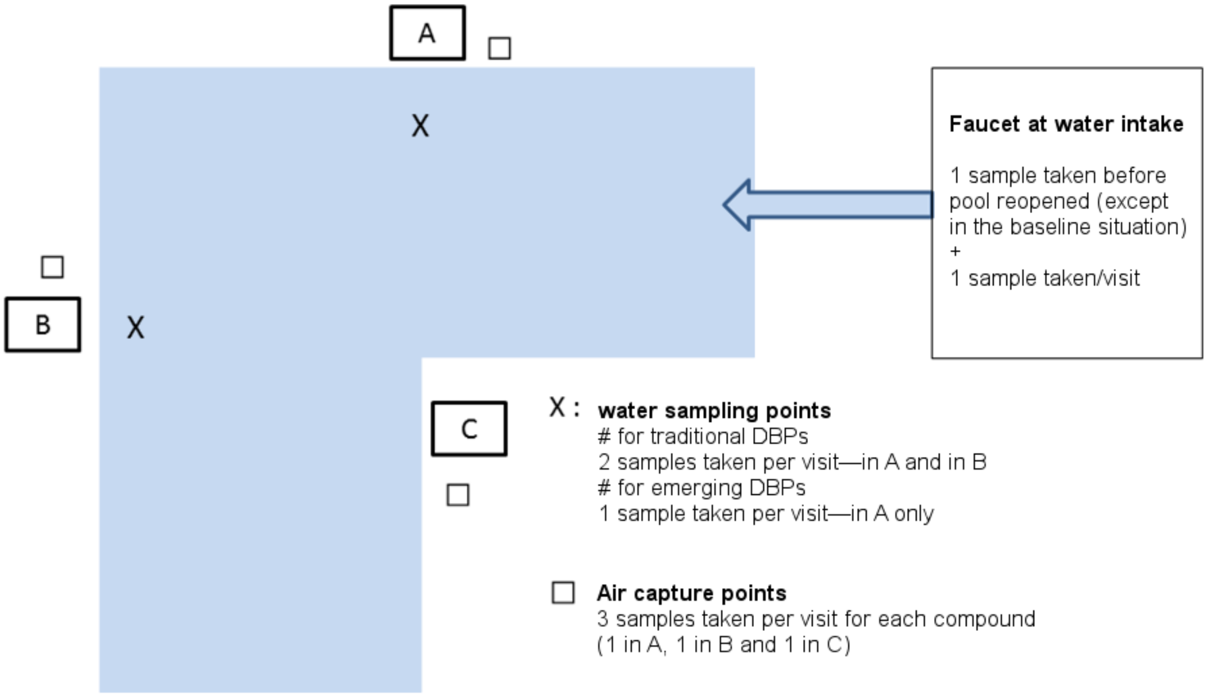


Figure 1 – Diagram of sampling plan

In the water, the traditional DBPs (i.e., THM, HAA) were systematically measured at two different points in the basin (A, B), in the middle of the visit. A few minutes before that, another sample for each of the two compounds was collected from a specially installed faucet at the end of the treatment process, just before the water inlet into the pool. During the days after modifications were made to the water treatment process, two samples (for each compound) were taken by the crew responsible for pool maintenance at the same point, before the facility opened. During campaign B, a sample was collected at the faucet to measure the concentration of traditional DBPs in the water distribution network supplying the swimming pool. With respect to eDBP, a single sample was taken in the basin, below the lifeguard chair corresponding to point A, in the middle of the visit. The physical and chemical parameters were measured at the same place.

4.5 Statistical Analyses

SAS (SAS Institute Inc.. 2009) software was used to verify the normality of distributions with the Shapiro-Wilk test and then proceeding, after controlling for the equality of variables, with a *t* test on two independent samples to compare the concentrations of THM and CAM measured at point C and those measured on average at points A and B. The threshold of statistical significance was set at 0.1.

5. RESULTS

Table 3 presents the averages of all the measurements of the various DBPs in the water in the pool and around it during the two campaigns, independently of modifications to the treatment processes. One can see that the DBP levels doubled between the first and second campaign, with concentrations of water and air contaminants being higher in the fall/winter. The results also showed typical contamination of predominantly chlorinated DBPs, with TCM representing more than 80% of total THMs and TCA and DCA representing around 70% and 20% of HAAs, respectively. Given this invariable profile of speciation, the following sections only take into account the results for the total quantity of each class of DBP, without detailing the specific results by compound for each one.

The first section (5.1), constituting the core of the results, takes into account the impact of each modification to treatment (T1, T2, T3, T4) for each class of DBP examined, throughout each of the two campaigns (A and B). Of note is that during campaign A, a power outage, which took place during the T1 case study, caused a temporary shutdown of the UV system from 3:00 p.m. on Sunday to 7:00 a.m. the next morning (on Monday, the day of the second sampling). Also during campaign A, another power outage affected all of the systems during the T3 case study (between 5:00 a.m. and 3:00 p.m. on Sunday, July 20). During campaign B, the very rapid deterioration in swimming pool water quality in the days following the PASS stoppage meant that it had to be re-injected before the targeted timeframe for the second sample taking could be reached (which is why there is a systemic absence of that data in the next figures). In the scope of campaign B, the results of the two additional days of sampling were reported with one completely functional treatment process (NORMAL1) and one almost completely dysfunctional treatment process (NORMAL2).

The second section (5.2) documents some specific aspects related to the variations in contamination levels between the different sampling points. The results of the physicochemical parameter analyses and the numbers of bathers are presented in the Appendix.

Table 3 – Mean concentrations of DBP in the water and air at the swimming pool studied during campaigns A and B

	Campaign A					**Campaign B**				
Variable	**n**[a]	**Me**[b]	**± e-t**[c]	**Min**	**Max**	**n**[a]	**Me**[b]	**± e-t**[c]	**Min**	**Max**
Air (µg/m^3)										
Total THM	**24**	121.0	47.2	62.5	210.1	**38**	241.1	85.0	128.9	491.4
TCM		101.6	37.3	55.5	185.0		230.9	81.2	123.3	470.1
DCBM		15.9	10.4	6.0	39.2		9.1	4.1	4.8	20.7
CDBM		3.3	2.7	1.0	9.6		1.0	0.5	0.3	2.0
TBM		0.3	0.2	<0.097	0.6		0.1	0.0	<0.097	0.2
Bromated THM		19.4	13.2	6.9	49.3		10.2	4.6	5.3	22.7
CAM (*mg/m^3*)	**24**	0.44	0.11	0.30	0.59	**40**	0.65	0.15	0.40	0.98
Water (µg/L)*										
Total THM	**16**	19.7	5.1	12.4	28.0	**26**	37.0	9.0	17.3	50.7
TCM		16.7	3.9	11.1	25.7		35.6	8.3	17.3	48.1
DCBM		2.6	1.5	0.8	5.5		1.9	0.6	<0.6	3.4
CDBM		1.3	0.3	<1.0	1.6		-	-	<1.0	<1.0
TBM		-	-	<0.8	<0.8		-	-	<1.0	<1.0
Bromated THM		3.0	2.0	0.8	7.1		1.4	1.0	<2.4	3.4
Total HAA	**16**	139.7	21.6	111.3	188.2	**26**	248.5	35.7	163.7	297.1
MCA		5.4	1.3	3.6	7.5		7.9	2.5	<1.0	12.3
MBA		-	-	<1.0	<1.0		1.2	0.2	<1.0	1.3
DCA		30.1	7.0	24.5	48.6		63.4	12.6	36.3	86.6
TCA		99.9	10.5	84.0	121.7		176.2	22.5	119.9	208.2
BCA		5.0	2.6	2.8	11.2		2.2	0.5	1.3	3.3
DBA		3.5	0.1	<1.0	3.6		-	-	<1.0	<1.0
Total HAN	**8**	12.22	4.13	8.76	21.11	**13**	26.14	4.54	21.21	34.98
TCAN		0.03	0.01	0.02	0.04		0.19	0.32	0.06	1.26
DCAN		8.74	2.40	6.30	13.55		24.32	4.38	19.67	32.97
BCAN		2.74	1.49	1.34	5.23		1.60	0.42	1.25	2.76
DBAN		0.71	0.73	0.15	2.29		0.04	0.04	0.01	0.15
HNM (CPK)	**8**	0.15	0.11	0.07	0.42	**13**	0.52	0.53	0.15	1.43
HK	**8**	2.11	0.64	1.38	3.30	**13**	3.12	1.62	1.83	6.50
11DCPone[d]		0.32	0.07	0.23	0.41		-	-	-	-
111TCPone		1.84	0.55	1.27	2.93		3.12	1.62	1.83	6.50
NDMA *	**8**	10.33	4.43	2.40	16.00	**13**	11.53	6.33	<1.6	25.40

[a] n indicates the number of samples analyzed

[b] mean

[c] ±standard deviation

[d] data unavailable for campaign B because of a quantification problem with the chromatographic analysis due to the presence of unknown contaminants in the swimming pool water

[*] the concentrations in the water are in µg/L, with the exception of the concentration of NDMA, expressed in ng/L

5.1 Impact of Treatment Processes on DBPs

5.1.1 Impact of Treatment Processes on CAMs in the Water

Figure 2 presents the average levels of CAM measured in the air around the pool before and after each modification to the treatment process during the two campaigns described in Table 2. A reduction in levels of CAM was observed in the air when the UV rays were operating, but only when there were bathers in the pool (campaign B). If stripping is halted (T2), maintaining air extraction from the buffer tank appears to delay the increase in air contamination, which reaches high levels after six days. Whether PASS is used or not does not appear to have any effect.

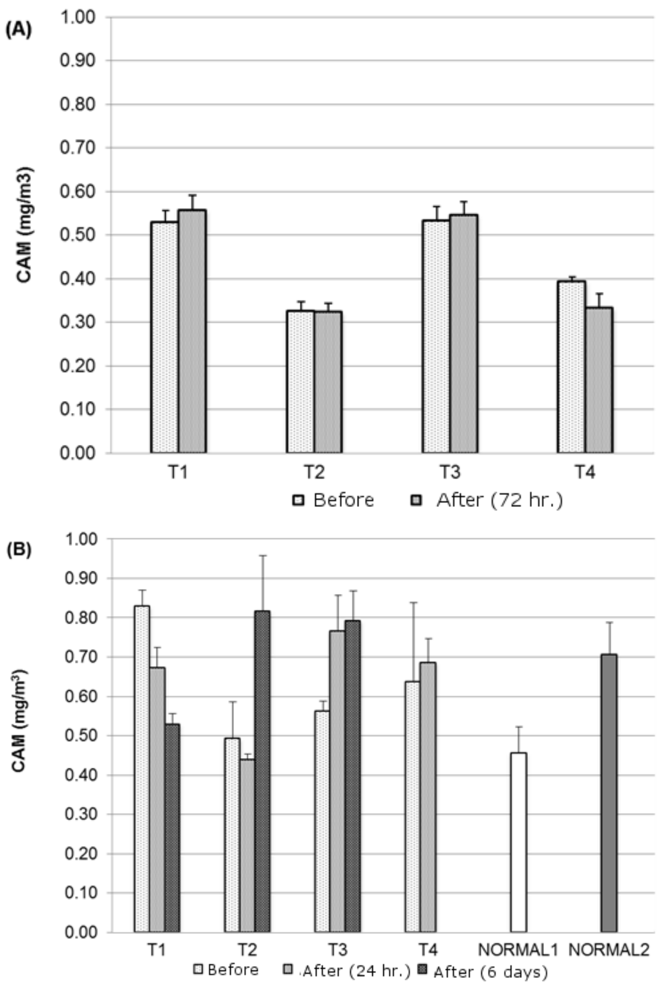


Figure 2 – Concentrations of CAM (mg/m^3) in the air around the pool before and after each modification to the water treatment process during campaigns A and B

5.1.2 Impact of Treatment Processes on THMs in the Air

Figure 3 presents the average levels of THM measured in the air around the pool before and after each modification to the treatment process during the two campaigns. Contrary to the case for CAMs, activation of UV rays led to an increase in THM levels in the air. On the other hand, as is the case for CAMs, maintaining air extraction from the buffer tank appears to delay the increase in levels of contaminants in the air around the main swimming basin when air stripping is halted. Suppression of PASS appears to result in a slight decrease in levels of THM contamination in the air.

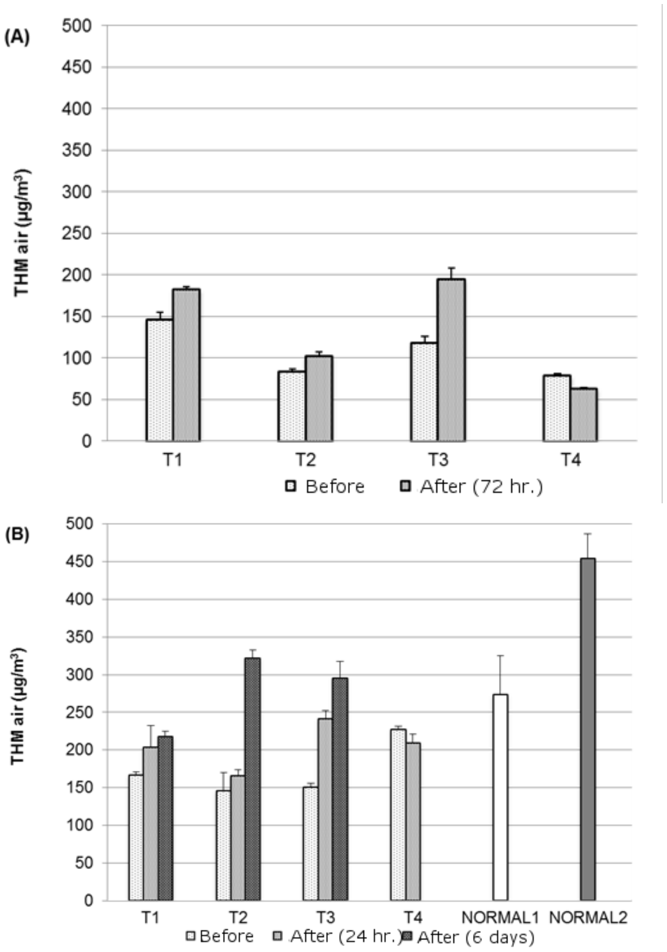


Figure 3 – Concentrations of THM (µg/m^3) in the air around the pool before and after each modification to the water treatment process during campaigns A and B

5.1.3 Impact of Treatment Processes on THMs in the Water

Figure 4 presents the average levels of THM measured in the pool water before and after each modification to the treatment process during the two campaigns. The same observations as those made for THMs in the air were made for THMs in the water, with, however, a more marked drop in levels when PASS is halted.

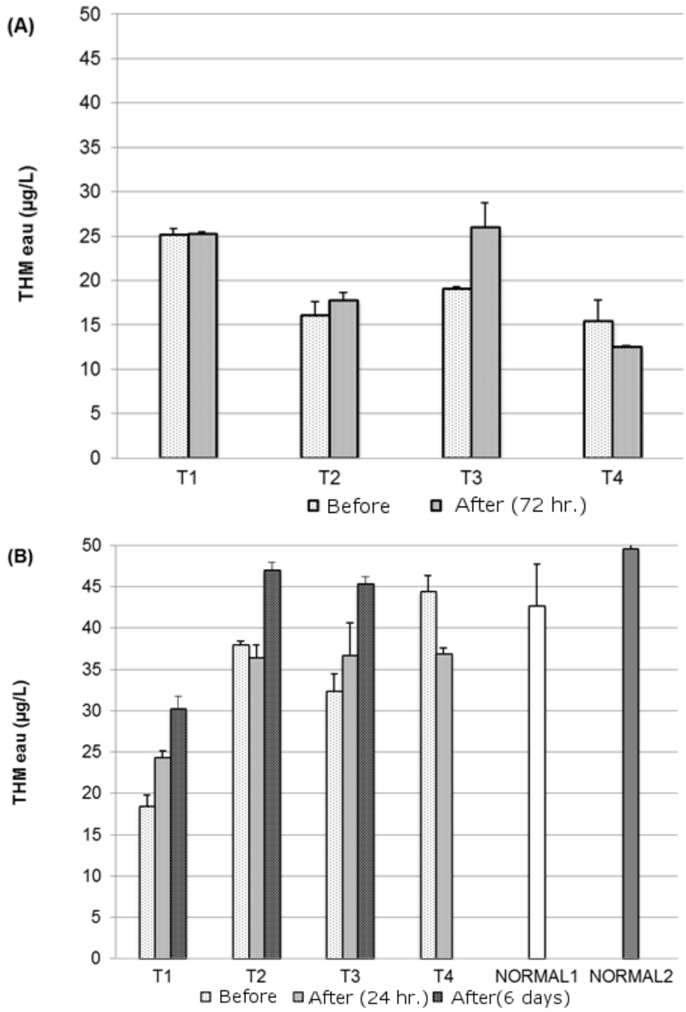


Figure 4 – Concentrations of THM (µg/L) in the pool water before and after each modification to the water treatment process during campaigns A and B

5.1.4 Impact of Treatment Processes on HAAs in the Water

Figure 5 presents the average levels of HAA measured in the pool water before and after each modification to the process during the two campaigns. No clear observations emerge from the comparison of different situations (with and without bathers during experimentation). In fact, the effect of UV rays (T1) is the opposite from one campaign to the other.

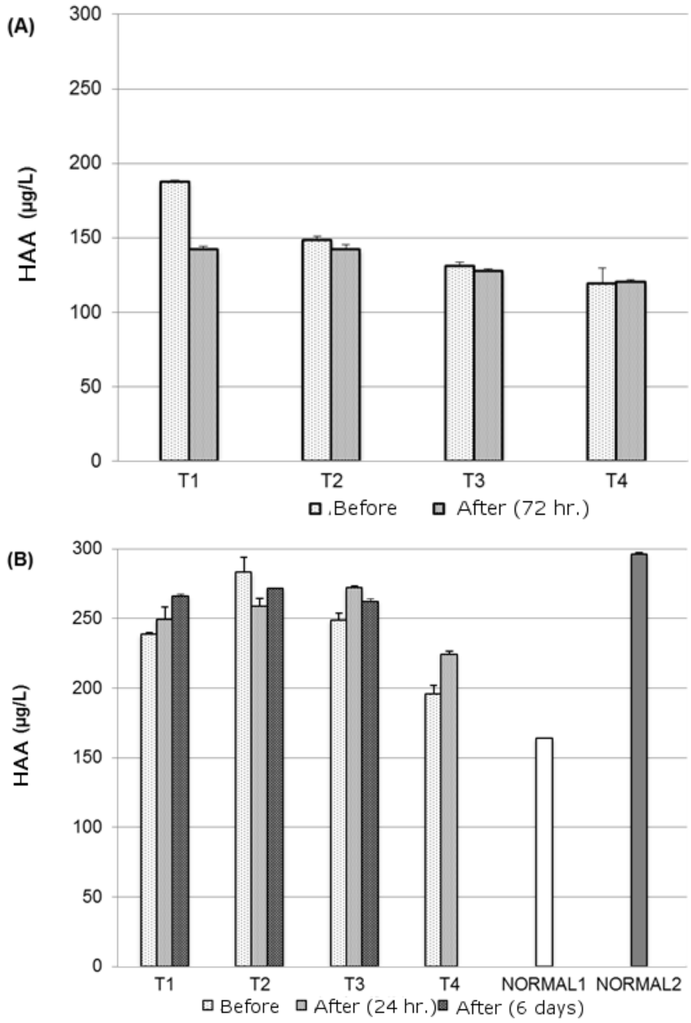


Figure 5 – Concentrations of HAA (µg/L) in the pool water before and after each modification to the water treatment process during campaigns A and B

5.1.5 Impact of Treatment Processes on HANs in the Water

Figure 6 presents the average levels of HAN measured in the pool water before and after each modification to the process during the two campaigns. As with the HAAs, we see no clear-cut impact with respect to HANs, specifically in terms of variability in the baseline measurements. Opposite effects are also observed from one campaign to the other.

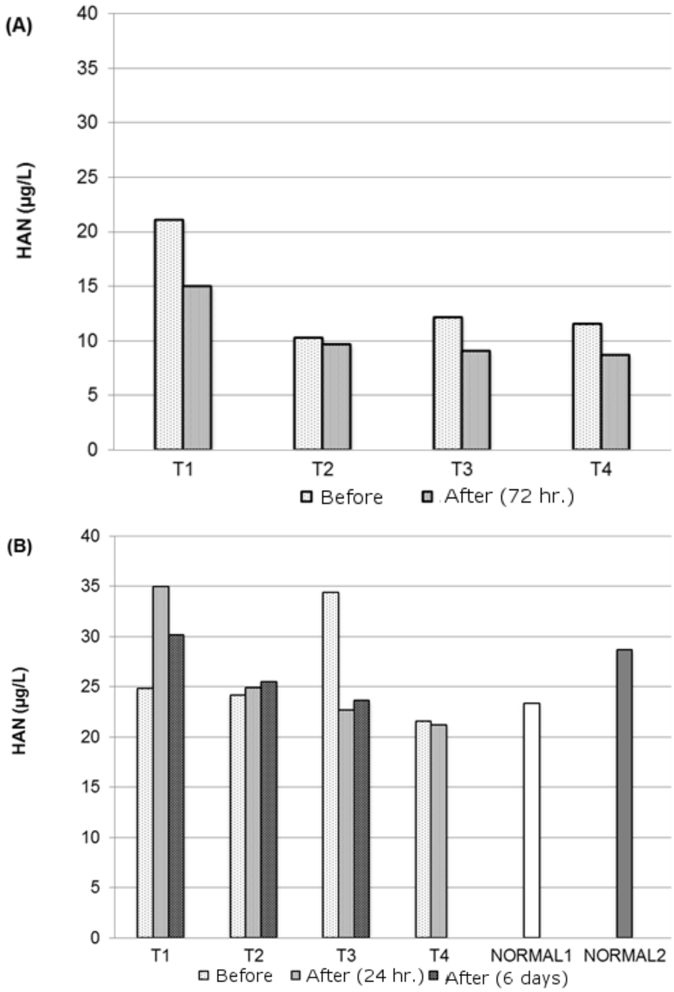


Figure 6 – Concentrations of HAN (µg/L) in the pool water before and after each modification to the treatment process during campaigns A and B

5.1.6 Impact of Treatment Processes on HNMs in the Water

Figure 7 presents the average levels of HNM, which consist exclusively of chloropicrin (CPK), measured in the pool water, before and after each modification to the treatment process during the two campaigns. UV activation appears to cause a significant increase in HNM levels. Other modifications to treatment have no effect.

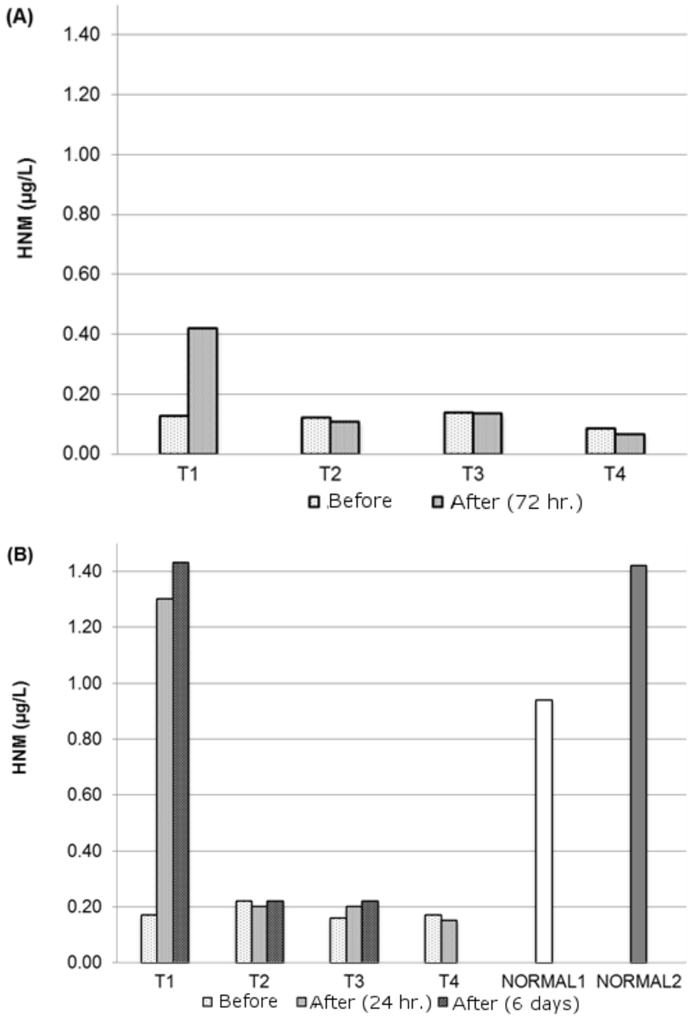


Figure 7 – Concentrations of HNM (µg/L) in the pool water before and after each modification to the treatment process during campaigns A and B

5.1.7 Impact of Treatment Processes on HKs in the Water

Figure 8 presents the average levels of HK measured in the swimming pool water before and after each modification to the treatment process during the two campaigns. As with the HNMs, UV rays appear to cause a marked increase in levels of HK when bathers are present (campaign B) while the other treatment processes do not appear to have notable effects on those levels.

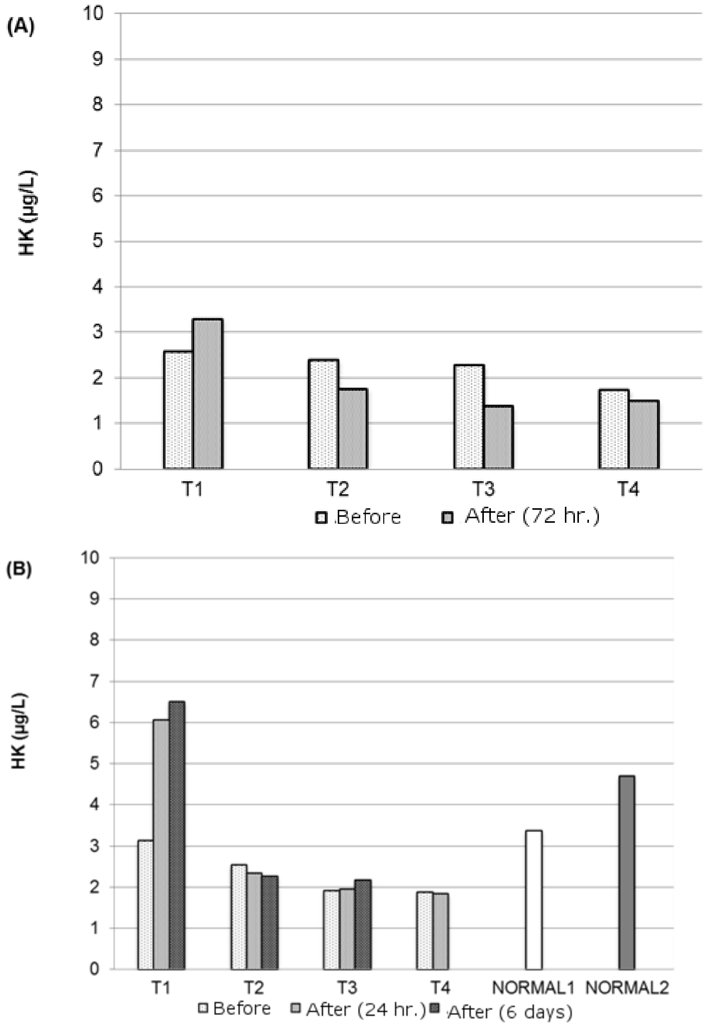
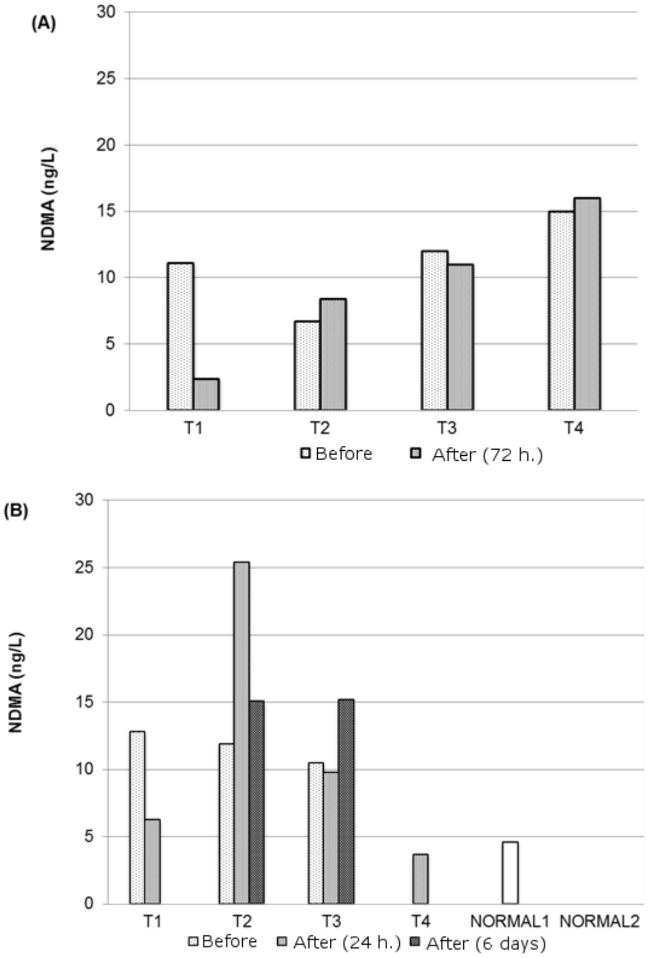


Figure 8 – Concentrations of HK (µg/L) in the pool water before and after each modification to the treatment process during campaigns A and B

5.1.8 Impact of Treatment Processes on NDMAs in the Water

Figure 9 presents the average levels of NDMA measured in the pool water, before and after each modification to the treatment process during the two campaigns. UV rays appear, in this case, to play a significant role in lowering levels of NDMA. The absence of stripping appears to increase concentrations of this compound in the water.



*with the exception of the case of "T4 after (6 days)," the missing values of NDMA concentrations correspond to values below the detection limit (1.6 ng/L)

Figure 9 – Concentrations of NDMA (ng/L) in the pool water before and after each modification to the treatment process during campaigns A and B.

5.2 Other General Considerations Regarding Spatial and Temporal Variations on Contamination Levels

5.2.1 Contamination of Water at the Source (Water Distribution System) Versus Contamination of Water in the Pool

During the second campaign (B), water samples were collected at one of the faucets at the facility to compare the THM and HAA levels originally present in the water in the distribution system supplying the facility with those measured in the swimming pool water. The results clearly showed a heightened presence of these contaminants in the swimming pool. In the water from the distribution system, we find constant concentrations of HAA throughout the duration of the campaign, averaging 16 (± 2.7) µg/L. During campaign B, the levels in the pool water reached values almost 20 times higher (Table 3) than those in the water distribution system. THM levels in the potable water distribution system are 18.5 (± 4.2) µg/L on average. There is, however, a difference between the average level in samples taken in the fall during that campaign (12.4 ± 0.6 µg/L, n=3) and those taken during the winter (20.3 ± 2.8 µg/L, n = 10). The THM levels are higher and more variable in the swimming pool water than in the distribution system water (campaign B), with an average concentration of 37.0 (± 9) µg/L. As well, in the swimming pool, an even greater difference is noted this time between the levels measured during the fall and those measured during the winter (24.3 ± 5.4 µg/L and 40.9 ± 5.7 µg/L). In that case, whatever the period, levels are only twice as high in the swimming pool water.

5.2.2 Contamination of Water Before It Enters the Pool (After Treatment) Versus Contamination of Water in the Pool

During each campaign, water samples (n=31) were taken at a water intake (point P) in the mechanical room, installed between the end of the water treatment process and the outlet into the pool, to compare levels of THM and HAA measured there with those measured in the pool. Out of all of these samples, 10 were taken on different days, before the pool opened to bathers. The other samples were taken during each of our visits, with bathers in the pool.

Figure 10 presents the correlations between levels of THM and HAA measured at point P before the pool opened, with no bathers, and those measured a few hours later. Comparable levels between the two samples were observed, with ratios between the second measurement and the first of between 0.86 and 1.12 for THMs and 0.84 and 1.05 for HAAs.

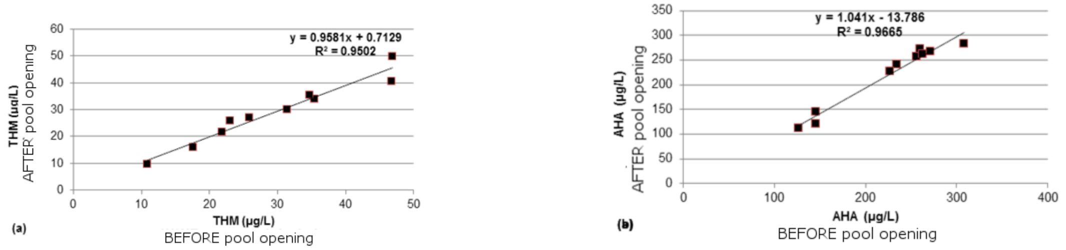


Figure 10 – Correlations (n=10) between THM (a) and HAA (b) levels measured at the water intake (point P) before the pool opened (without bathers) and a few hours later (with bathers present)

Figure 11 presents the correlations between the levels of THM and HAA measured at point P and those measured at the same time in the pool after it opened, with bathers present. Here again, there is no major difference between the measurements taken at these two sampling points, with ratios between measurement at the basin and measurement at point P alternating between 0.94 and 1.3 for the THMs and 0.93 and 1.17 for the HAAs.

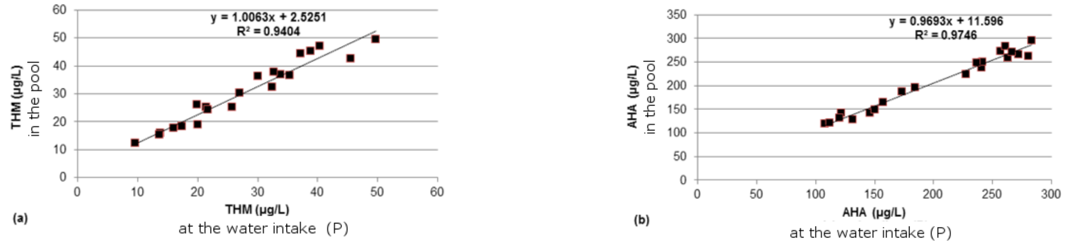


Figure 11 – Correlations (n=21) between THM (a) and HAA (b) levels measured at the water intake (point P) and those measured at the same time in the pool (average of the two sampling points).

5.2.3 Spatial Variations in Contamination Between Sampling Points

In the water, no major difference is observed between the THM and HAA measurements taken between the two sampling points, A and B. In the air, THM levels at sampling point C tend to be higher than the averages of levels measured at points A and B (in 15 points of comparison out of 19), but this result is not statistically significant (p=0.7). It is the same for measurements of CAM (21 points of comparison), but with a statistically significant difference of almost 0.10 (p=0.09), and a 17% increase, on average. The proximity of sampling point C to the buffer tank appears to explain the greater contamination level in that part of the pool area.

6. DISCUSSION

This study afforded an exceptional opportunity to gather data on the impact of various water treatment processes on water and air contamination by the main classes of DBPs, under controlled operational conditions and actual exposure at a single site. It is based on an original design comprising two successive campaigns, which provided insight into the impacts, not only during different seasons, but also of the absence (campaign A) or presence (campaign B) of bathers. Being able to investigate all these contexts within a single swimming pool facility minimized the variable environmental conditions that exist from one pool to another, which were broadly outlined in the previous report (Tardif et al., 2015). The access to treatment devices that are not currently widely used in Québec (air strippers, UV rays) at the swimming pool under study reinforces the value of this work. To our knowledge, data such as what we gathered, using an experimental systematic approach and covering a wide range of compounds, did not previously exist and are undeniably relevant in considering the highly desirable and strongly supported goal of reducing exposure levels to DBPs in swimming pools. However, it should be noted that the data generated in this report is exploratory and cannot be generalized or used to validate or invalidate the relevance and effectiveness of the various treatment processes at issue, without more extensive investigation.

6.1 Considerations Related to Levels of Contamination

It is important to note that the type of contamination found in the swimming pool studied in the scope of this project is typical, in that the predominant DBPs are chlorinated compounds (and not brominated compounds). Chloroform (TCM) thus makes up most of the THMs measured, and TCA (and to a much lesser extent, DCA) makes up most of the HAAs, as has often been reported in the literature (Bessonneau et al., 2011; Catto et al., 2012; Simard et al., 2013). In this configuration, the analyses of the results focus on the levels of each of the major classes of DBP, without looking closely at each individual compound.

The results detailed in subsection 5.2.1 confirm a significant increase in contamination levels in the pool water compared to levels at the source (up to 20 times more HAA and two times more THM). The substantial accumulation of non-volatile HAAs in the water and, conversely, the high volatility of THMs explain this difference.

The levels of the various contaminants measured in the swimming pool under study are consistent with those generally reported in similar environments in the literature, including those previously reported by our team (Catto et al., 2012; Simard et al., 2013; Tardif et al., 2015). With respect to these levels, we note that for the 64 measurements of CAM in the air, all are above or equal to the value of 0.3 mg/m^3 recommended by Parrat et al. (2012) to minimize the health impact of these compounds. The concentrations of THM in the water compare more favourably with the various baseline values in force internationally (20 µg/L in Germany, 30 µg/L in Switzerland, 100 µg/L in the United Kingdom, Finland and Denmark), notably during campaign A, but less so during campaign B. During that second campaign, there was an increase in levels of THM (and more broadly, in all of the DBPs), which appears to be associated with a seasonal impact that is especially reflected in increased levels at the source (water from the distribution system) (section 5.2.1) and a higher bather load. While, as has been widely observed at many other swimming pools, HAAs accumulate in the swimming pool water, where they reach levels that greatly exceed the standard set for drinking water in Québec (an annual average of 60 µg/L), it is worth noting that the average levels measured in this study remained below the median of the levels measured in a sample of 41 swimming pools during our previous investigation (Tardif et al., 2015). With respect to the levels of different eDBPs, they are situated around this same median. However, out of 21 samples of NDMA, although none surpass the maximum concentration level acceptable for drinking water recommended by Health Canada (40 ng/L), and the World Health Organization (100 ng/L), 12 exceed the standard in force for drinking water in Ontario (9 ng/L) (Soltermann et al., 2013).

Besides the seasonal variation in DBP levels described previously, if we compare the results obtained one-by-one following the baseline measurements, the figures in section 5.1 also underscore the weekly variations that are probably attributable to fluctuations in bather load. Generally, all the levels measured compare well with those estimated in a normal situation and even in the worst-case scenario. The levels measured at intake P, installed upstream from the pool's water inlet and downstream from treatment, appear to account for the equivalent levels of DBPs that can be measured in the pool. More thorough testing is required to better understand the impact of the presence of bathers over longer durations in the comparison of these two indicators. While the water contamination in the pool appears homogeneous with respect to the results of the analyses of typical DBPs at different sampling points, a ripple effect from the buffer tank appears to lead to increased air contamination, especially by CAMs, in the sampling area situated immediately beside the pool.

6.2 Considerations Related to the Compared Impact of Processes

In light of the overall results from section 5.1, it appears, unsurprisingly, that the various processes act differently on different categories of DBP, thus suggesting that the choice of the ideal water treatment process for a facility should be made by taking into account the types of issues encountered by the facility and the priorities that the manager intends to set to mitigate the identified issues.

UV rays (T1, NORMAL1, and NORMAL2) have a major impact. They seem to cause a potentially high increase in eDBPs, in particular, HNMs and HKs, as well as THMs, in the water. The increase of the latter, which are known to be quite volatile, appear to have subsequent repercussions on THM levels in the air. On the other hand, the activation of the UV ray device may, in this case, contribute to sharply decreasing the amount of CAM in the air and NDMA in the water. The positive impact of such devices, also called dechloraminators, on CAMs, and the opposite effect they appear to have in producing a surplus of THM, have already been demonstrated in previous investigations (Cassan et al., 2006; Gérardin et al., 2005a). In France, ANSES, the agency for food, environmental and occupational health and safety, set up guidelines for the implementation of such a process, in order to work out the best balance between CAMs and THMs (ANSES, 2011), among other things. With respect to NDMA, our empirical results should be compared with those of Soltermann et al. (2013), who stated that UV rays may cause an increase in levels of NDMA in swimming pool water.

As expected, the results underscore the positive impact of air stripping on reducing volatile contaminants in the air, while, unsurprisingly, halting mechanical mixing leads to increased levels of contaminants in the ambient air. The comparison of situations T2 and T3 (with and without air extraction in the buffer tank) reveals the buffering effect that the ventilation system could have in the event of failure of the stripping device, by, quite logically, temporarily slowing down an increase of air contamination by DBPs. The results in section 5.2.3, which pointed to an area of greater air contamination near the buffer tank, most likely related to the effect of outgassing, suggests that there could be a serious issue if the ventilation system failed but stripping continued.

The use of PASS does not appear to have an effect on the presence (quantity and speciation) of DBPs, except for THMs, which appear to increase slightly. However, to our knowledge, there is no sign in the literature of anything that could prove or refute that point. It should be remembered that there was a rapid impact in the hours and days following the suspension of PASS injection, and even after it was restarted, we were unable to collect all the data we needed (notably, after one week without flocculation).

7. CONCLUSION AND RECOMMENDATIONS

Based on a very original experimental design, and tested under real conditions, this project generated useful data to better understand the dynamic of DBP contamination in swimming pool water. Managers are sure to find the information very useful in implementing more effective treatment processes and strategies (developing better practices), in particular, to better protect the health and well-being of swimming pool staff, given the concerns surrounding DBP exposure.

This case study of the swimming pool visited revealed contamination by potentially high levels of CAM in the air, and to a lesser extent, of NDMA in the water. Our current knowledge indicates that these two contaminants may expose workers to major health risks. The use of UV rays is, therefore, a positive and indispensable step in reducing the quantities of these two contaminants, notwithstanding the increase in levels of eDBPs and THMs that this treatment seems to induce, albeit within reasonable limits. In addition to UV rays, air stripping appears to have a positive effect on reducing DBP levels. The isolated breakdown of one of the devices in the treatment system and the additional breakdowns of several others had an almost immediate impact.

More generally, the investigation results will also raise stakeholders’ awareness of the need to make choices about treatment processes that take into account the specific context of each swimming pool and the related issues, in this case, DBP contamination. As this was an exploratory study, the results cannot be used to validate (or invalidate) the various processes examined here in other contexts or to assess the health risks associated with DBP exposure. In fact, in the specific context of the swimming pool studied, the assessment of these impacts should be explored further with a more rigorous design and additional data in order to draw firmer conclusions. Studies of this type are undoubtedly extremely relevant with respect to the issue of DBP exposure and are to be recommended. Such studies could also widen the range of processes to be investigated and could include a cost/benefit analysis. Of course, the reality of the environment, which constitutes an extraordinarily vibrant microsystem, with a complex and unpredictable dynamic, makes this type of enterprise both delicate and ambitious, but very necessary.

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Appendix A – Results of physicochemical analyses and numbers of bathers on sampling days

Campaign	Treatment		Date	Laboratory measurements						Field measurements						Numbers of bathers counted during visits
				Conductivity	Turbidity	sorbance 254 nm		COD	pH	pH	Temperature	Free chlorine	Total chlorine	Combined chlorine	Monochloramine	
				µS/cm	NTU	5 cm cell	As per 1 cm	ppm			°C	mg/L Cl2	mg/L Cl2	mg/L Cl2	mg/L Cl2	
A	T1	before	July 5, 2013	1002	0,153	0,101	0,02	3,17	7,01	7,42	30,4	0,99	1,48	0,49	0,16	97
A	T1	after (72hr.)	July 8, 2013	1030	0,13	0,058	0,012	2,41	7,05	7,7	30,2	0,73	1,18	0,45	0,13	100
A	T2	before	July 12, 2013	1121	0,151	0,072	0,014	2,57	6,96	7,2	29	0,91	1,36	0,45	0,2	56
A	T2	after (72hr.)	July 15, 2013	1138	0,088	0,068	0,014	2,34	7,07	7,2	28,7	0,83	1,14	0,31	0,26	52
A	T3	before	July 19, 2013	1083	0,139	0,09	0,018	2,54	7,78	7,4	28,6	1	1,39	0,39	0,15	94
A	T3	after (72hr.)	July 22, 2013	1093	0,118	0,087	0,017	2,42	7,18	7,55	29,1	0,71	1,14	0,43	0,11	28
A	T4	before	July 26, 2013	1004	0,164	0,099	0,02	2,6	6,89	7,48	29,4	0,53	0,96	0,43	0,21	73
A	T4	after (72hr.)	July 29, 2013	1026	0,143	0,099	0,02	2,54	6,98	7,55	29,3	0,65	1,05	0,4	0,14	ND
B	T1	before	Nov. 4, 2013	1591	0,229	ND	0,0348	4,13	6,48	7,4	28,7	1,11	2,15	1,04	0,17	115
B	T1	after (24hr.)	Nov. 6, 2013	1473	0,196	ND	0,0238	4,07	6,78	7,48	28,7	1,38	2	0,62	0,14	81
B	T1	after (6days)	Nov. 12, 2013	1599	0,227	ND	0,017	3,86	6,77	7,67	29	1,48	2,2	0,72	0,25	97
B	NORMAL1		January 21, 2014	1612	0,225	ND	0,0132	2,72	6,95	7,57	26,7	1,5	1,85	0,35	0,22	104
B	T4	before	January 27, 2014	1626	0,575	ND	0,0264	3,4	7,14	7,57	28,1	1,13	1,79	0,66	0,31	82
B	T4	after (24hr.)	January 29, 2014	1613	0,532	ND	0,0276	3,42	6,91	7,65	27,2	1,24	1,87	0,63	0,14	122
B	T3	before	Feb. 10, 2014	1648	0,332	0,196	0,0392	4,03	7,16	7,62	28	1,23	1,98	0,75	0,11	97
B	T3	after (24hr.)	Feb. 12, 2014	1633	0,3	0,201	0,0402	7,03	7,03	7,62	27,5	1,79	2,1	0,31	0,13	80
B	T3	after (6days)	Feb. 18, 2014	1663	0,627	0,225	0,045	4,18	7,01	7,62	29,3	1,37	2,18	0,81	0,23	72
B	T2	before	Feb. 24, 2014	1684	0,388	0,235	0,047	4,28	7,06	7,56	29,1	1,33	2,28	0,95	0,3	101
B	T2	after (24hr.)	Feb. 26, 2014	1705	0,303	0,236	0,0472	4,36	7,05	7,62	29,1	1,31	2,54	1,23	0,33	84
B	T2	after (6days)	March 4, 2014	1743	0,484	0,257	0,0514	4,57	7,14	7,72	29,4	1,48	2,26	0,78	0,19	109
B	NORMAL2		March 12, 2014	1807	0,384	0,111	0,0222	4,48	7,28	7,83	28,2	1,79	2,44	0,65	0,25	88