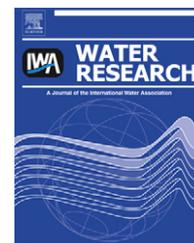


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# Disinfection by-product dynamics in a chlorinated, indoor swimming pool under conditions of heavy use: National swimming competition

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## ABSTRACT

Anecdotal evidence suggests that water quality in chlorinated, indoor pools deteriorates under conditions of heavy use. However, data to define these dynamics have not been reported. To address this issue, a study was performed in which water chemistry was monitored in a chlorinated, indoor pool before and during a national swimming competition, a period of heavy, intense use.  $\text{NCl}_3$  concentration was observed to double after the first day, and increased by a factor of 3–4 over the 4 days of competition.  $\text{CNCHCl}_2$  and  $\text{CH}_3\text{NCl}_2$  concentrations both increased by a factor of 2–3 during the course of the meet, while  $\text{CHCl}_3$  concentration showed only a modest increase during this same period. Diurnal patterns of  $\text{NCl}_3$ ,  $\text{CH}_3\text{NCl}_2$  and  $\text{CHCl}_3$  concentrations were observed, and these patterns appeared to depend on the Henry's law constant of the compound.

Urea concentration showed a diurnal pattern, superimposed on a trend of steady increase during each day of the competition; however, the diurnal pattern of urea behavior could not be explained by reactions with chlorine, as the urea-free chlorine reaction is relatively slow. It is more likely that the overnight decrease in urea concentration was attributable to mixing of surface water with water in the deeper parts of the pool. The findings of this study provide an indication of the changes in pool water chemistry that take place in a chlorinated, indoor pool under heavy use conditions.

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## 1. Introduction

Swimming is widely recognized as an activity that contributes to good health and competitive swimmers are generally viewed as being healthy people. However, swimmers and swimming activities adversely affect water and air quality in chlorinated, indoor pools, thereby introducing health risks to swimmers and pool employees (Weng et al., 2011). Chlorination of pool water is commonly practiced for control of microbial pathogens and oxidation of reduced compounds in

swimming pools. Chlorine also reacts with compounds “left behind” by swimmers (primarily the constituents of human urine and sweat) to yield a large number of disinfection by-products (DBPs). Richardson et al. (2010) identified more than 100 DBPs in pool water samples.

Two well-known DBP groups in chlorinated pool water are trihalomethanes (THMs) and chloramines. All four THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) have been shown to cause cancer in laboratory animals (Richardson et al., 2007), and they are regulated in the

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United States at a maximum contaminant level (MCL) of 80 µg/L (total THMs) in drinking water (U.S. EPA, 2006). THMs are common DBPs in pools. Weaver et al. (2009) observed TTHM concentrations in pools that ranged from (approximately) 4–400 µg/L. Lindstrom et al. (1997) estimated 80% of THM uptake for swimmers is via dermal absorption. Collectively, these factors indicate that THM exposure in pools can be more substantial than from drinking water.

On the other hand, trichloramine (NCl<sub>3</sub>), which is often identified as being responsible for the “chlorine odor” of swimming pools, has been identified as a byproduct of chlorination of many N-organics that are common to swimming pools, including: urea, creatinine, arginine, and histidine (Li and Blatchley, 2007; Blatchley and Cheng, 2010). Although there is uncertainty regarding the role of NCl<sub>3</sub> exposure in pools relative to childhood asthma (Weisel et al., 2009; Uyan et al., 2009), literature evidence indicates that NCl<sub>3</sub> is an irritant of several human tissues. Gagnaire et al. (1994) demonstrated NCl<sub>3</sub> to be a respiratory irritant to mice, and more recent studies have indicated NCl<sub>3</sub> to contribute to acute ocular and respiratory irritation symptoms in lifeguards, swimming pool workers, and competitive swimmers (Jacobs et al., 2007; Dang et al., 2010; Clearie et al., 2010). Previous retrospective studies have shown positive correlations between irritation symptoms among swimmers and patrons and high gas-phase NCl<sub>3</sub> concentration at indoor pool facilities (Kaydos-Daniels et al., 2008; Bowen et al., 2007).

Among the DBPs that are formed in pools, eleven volatile compounds have been identified that could adversely affect air quality in chlorinated, indoor pool facilities: monochloramine (NH<sub>2</sub>Cl), dichloramine (NHCl<sub>2</sub>), trichloramine (NCl<sub>3</sub>), cyanogen chloride (CNCl), cyanogen bromide (CNBr), chloroform (CHCl<sub>3</sub>), bromodichloromethane (CHBrCl<sub>2</sub>), dibromochloromethane (CHBr<sub>2</sub>Cl), bromoform (CHBr<sub>3</sub>), dichloromethylamine (CH<sub>3</sub>NCl<sub>2</sub>), and dichloroacetonitrile (CNCHCl<sub>2</sub>) (Li and Blatchley, 2007; Weaver et al., 2009). These compounds have the ability to adversely affect water and air quality, particularly within chlorinated, indoor swimming pools.

A recent study suggested that asthma is more likely to occur among elite swimmers than among other high-level athletes (Goodman and Hays, 2008). Moreover, anecdotal evidence suggests that water and air quality in a chlorinated, indoor pool both deteriorate under conditions of heavy use. Zwiener et al. (2007) demonstrated a positive relationship between THM concentrations in water and bather loading within several swimming pool facilities. However, relatively little information is available in the literature to characterize this behavior in terms of other DBPs or their precursors. To address this issue, an experiment was conducted to define changes in pool water chemistry that took place during a period of heavy use at a natatorium.

## 2. Methods

Water samples were collected without headspace from roughly 30 cm below the water surface of a chlorinated, indoor swimming pool facility before and during a national swimming competition in March 2010. The competition was

held at a natatorium facility that houses three pools: a competition pool (50 m long × 22.86 m wide × 1.22–3.66 m deep, 2790 m<sup>3</sup>); a diving well (19.20 m long × 22.86 m wide × 4.42 m deep, 1940 m<sup>3</sup>); and a spa (2.44 m long × 3.66 m wide × 0.91 m deep, 8.1 m<sup>3</sup>). The three pools are hydraulically independent, and have separate treatment/recirculation systems; however, the pools share a common air space. The target pool (competition pool) was operated to accomplish 4 turnovers per day, and the recirculation system for the pool includes a balance tank, filtration, and chlorination. The chlorine concentration of the pools was controlled by an automated chemical feed system. During the meet, the competition pool was configured into two zones: a warm-up zone and a competition zone (Fig. 1); these two zones were separated by a moveable bulkhead. Because the vast majority of swimming activity took place in the warm-up zone, samples were collected from there. The sample and event schedule is shown in Table 1.

Prior to the competition (March 11–12), samples were collected under conditions of normal use, where the typical bather load was 10–20 swimmers at any given time. The pre-competition sampling data were used to represent baseline conditions of water quality. After teams arrived (March 16), swimmer activity in the pool increased markedly; at times, as many as 200 swimmers were in the pool for practice or competition. In addition, the nature of the swimming activity during this period was generally more intense than the activity of recreational/lap swimmers that usually use this facility. Competition started on March 18, and most swimmers remained at the facility until the conclusion of competition on March 20. Measurements of water chemistry were monitored 3 or 4 times per day at 6:30 AM, 8:30 AM, 2:00 PM, and 9:30 PM. These sample times were selected to catch the impacts of intense use and to characterize the diurnal cycle of water quality.

Grab samples were collected from the warm-up zone, and were immediately transported (about 10 min) to the laboratory where they were analyzed for volatile DBPs by membrane introduction mass spectrometry (MIMS, Weaver et al., 2009), for urea by a colorimetric digestion method (Prescott and Jones, 1969), and for residual chlorine and inorganic chloramines by MIMS and the DPD/KI Colorimetric Method (APHA-AWWA-WEF, 1998).

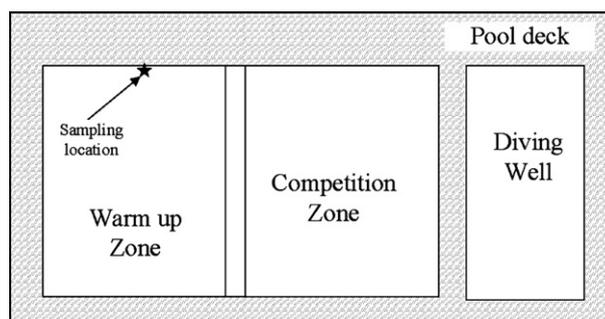


Fig. 1 – Scheme of swimming pool configuration and sample collection location.

**Table 1 – Sampling and event schedule during experiment period.**

Time	Date							
	3/11 (Thurs)	3/12 (Fri)	3/13–3/15	3/16 (Tue)	3/17 (Wed)	3/18 (Thurs)	3/19 (Fri)	3/20 (Sat)
06:30			Diving Competition		Sample	Sample	Sample	
06:30–08:30				Free practice	Free practice	Warm up	Warm up	Warm up
08:30	Sample	Sample		Sample	Sample	Sample	Sample	Sample
08:30–11:00				Free practice	Free practice	Warm up	Warm up	Warm up
11:30–13:30						Competition	Competition	Competition
14:00	Sample	Sample		Sample	Sample	Sample	Sample	Sample
14:00–19:00				Free practice	Free practice	Warm up	Warm up	Warm up
19:00–21:30						Competition	Competition	Competition
21:30	Sample	Sample		Sample	Sample	Sample	Sample	Sample
Note	Regular use, open for public		Natatorium closed to public; available to for competitors only			Competition Days		

### 3. Results and discussion

#### 3.1. Dynamic behavior of volatile DBPs in indoor, chlorinated swimming pools

Several processes are available that have the potential to influence the concentrations of chemicals in pool water samples collected from a near-surface location, including:

- Reactions that produce constituents,
- Reactions that consume constituents,
- Liquid-gas transfer,
- Mixing,
- Uptake by swimmers.

The results of previous experiments involving organic-N precursor chemicals that are common in human sweat and urine have demonstrated that some of these compounds (e.g., amino acids and creatinine) react rapidly with free chlorine (Li and Blatchley, 2007). These same reactions lead to formation of DBPs, including the volatile compounds that were the target of MIMS measurements. Among the DBPs that are formed in pools, some are chemically stable (e.g. THMs, CNCHCl<sub>2</sub>, NO<sub>3</sub>), while others may undergo additional reactions with chlorine, or other compounds, and therefore are unstable intermediates (e.g., CNCl, inorganic chloramines).

The MIMS configuration used in this research is selective for volatile chemicals. Specifically, the membrane interface is used to allow only those chemicals that are sufficiently volatile to pervaporate through the membrane to be introduced to the mass spectrometer. The ability to detect compounds in liquid water by MIMS is determined by the product of aqueous-phase concentration and Henry's law constant (i.e., escaping potential). Previous experiments have demonstrated that 11 volatile DBPs are consistently found in chlorinated pool water samples (Weaver et al., 2009); however, the Henry's law constants for these compounds vary by more than two orders of magnitude. Volatilization is a relevant process for only those DBPs with the highest Henry's law constants. Moreover, since volatilization will take place through an air:water interface, it is reasonable to expect that this process will lead to depletion of volatile chemicals from near-surface water.

Mixing processes will influence the distribution of chemicals in any body of water, including swimming pools. In a general sense, mixing within a pool may be attributed to recirculation of water from the pool through the treatment system, as well as mechanical mixing induced by swimmers themselves. Given the wide range of pool geometries and uses, it is difficult to generalize further.

The pool that was the target of this research is a tank with a rectangular plan and a sloped bottom (1.22–3.66 m depth). Water leaves the pool by gentle overflow into a gutter system that spans the entire perimeter of the pool. This water is then pumped through a surge tank and a treatment system. The treated water is re-introduced to the pool through a series of 56 10-cm diameter circular diffusers spaced in a uniform, staggered pattern across the bottom of the pool. This pattern of circulation within the pool is intended to yield gentle current within the pool that is essentially vertical (bottom to top).

The pool is used almost exclusively for lap swimming. During the course of this investigation, pool users were actively swimming while in the water. As such virtually all mechanical mixing and precursor introduction would have taken place in the near-surface area.

#### 3.2. Chlorine and chloramines

The competition brought intense use to the natatorium; bather loads were typically 150–200 swimmers during warm-up sessions, which is roughly 5–10 times the bather load that is normally present at this facility. A corresponding increase in chlorine demand was observed when the competition began. In order to maintain acceptable free chlorine concentration (NSPF (2006) have suggested a minimum chlorine concentration of 1 mg/L as Cl<sub>2</sub>), the operator of the swimming pool doubled the free chlorine application rate (in the form of calcium hypochlorite), relative to normal operating conditions. Figure S1 illustrates the mass of Ca(OCl)<sub>2</sub> added each day during the competition, as well as the free chlorine concentration measured at the chlorine controller by continuous titration.

Water losses from the pool by splashing and evaporation required replacement. Roughly 40,000 L (1.4% of total volume)

of water was added to the pool during the competition to maintain water level.

Fig. 2a illustrates the time-course behavior of residual chlorine measured by the DPD/KI colorimetric method. Free chlorine dropped rapidly after the competitors arrived, presumably because of introduction of reduced compounds that reacted with free chlorine. Note that the free chlorine concentration measured at the controller (Figure S1) was substantially higher than the corresponding free chlorine concentration measured in the pool water samples (Fig. 2a). It is likely that the difference in free chlorine concentrations between these two locations was attributable to chlorine demand that was expressed in the pool.

Measurements of the concentration of chloramines by the DPD/KI method did not change substantially over the sampling period. However, previous research has demonstrated that the DPD/KI method is susceptible to interference (Harp, 2002). Organic chloramines are believed to be largely responsible for this interference in pools (Weaver et al., 2009). In contrast, MIMS measurements demonstrated a rapid

increase in  $\text{NCl}_3$ , and a smaller increase in  $\text{NHCl}_2$ . DPD/KI measurements were consistently in excess of the MIMS measurements, presumably because of the presence of organic chloramines that interfere with the colorimetric method (Harp, 2002). MIMS has been demonstrated to provide an accurate measurement of inorganic chloramines (Shang and Blatchley, 1999). The MIMS data indicated that  $\text{NCl}_3$  concentration increased by a factor of 3–4 over the course of the event.

Aqueous  $\text{NCl}_3$  concentration displayed a consistent diurnal trend during the competition: decrease in the middle of the day and increase overnight. Three major mechanisms are believed to have influenced this diurnal pattern: loss by volatilization, formation by reactions between free chlorine and organic-N compounds, and mixing within the pool. The mid-day decrease was believed to be attributable to intense physical activity of the swimmers, which typically takes place at or near the surface of the pool. This activity has been demonstrated to promote liquid-gas transfer of volatile chemicals such as  $\text{NCl}_3$  (Weng et al., 2011). This “loss” of  $\text{NCl}_3$  would be expected to be most important for water located near the free surface, where all water samples were collected in this work. During the overnight hours, mechanical mixing of near-surface water would be substantially reduced, thereby reducing liquid-gas transfer. However, the general circulation pattern in the pool would have allowed for near-surface water to be removed, subjected to treatment (filtration and chlorination), and re-introduced to the pool through the diffusers located in the bottom of the pool. The 9 h (overnight) period between sampling events would also have allowed for DBP formation by reactions between chlorine and precursors.

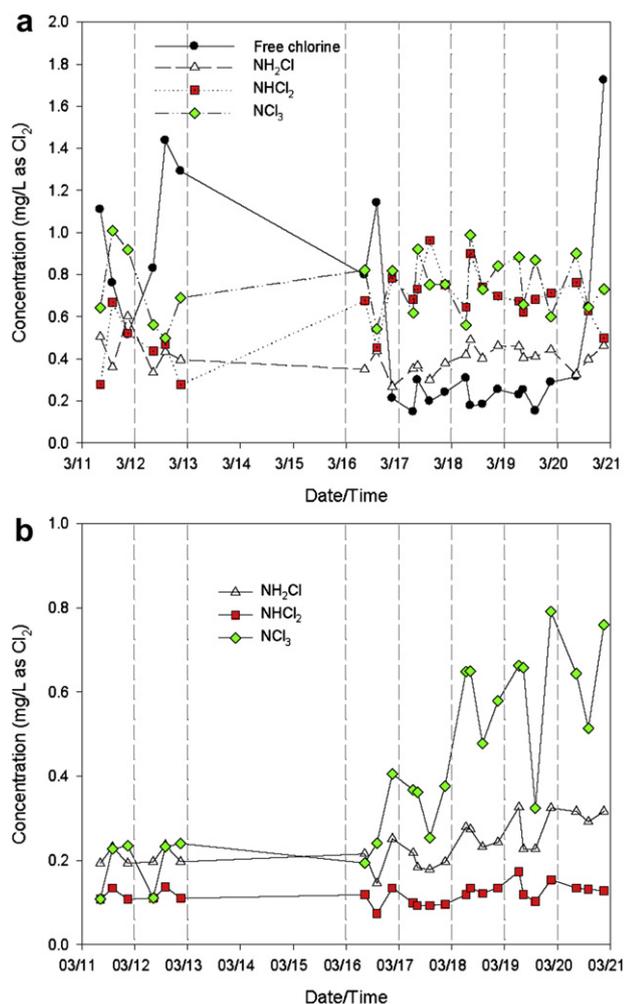
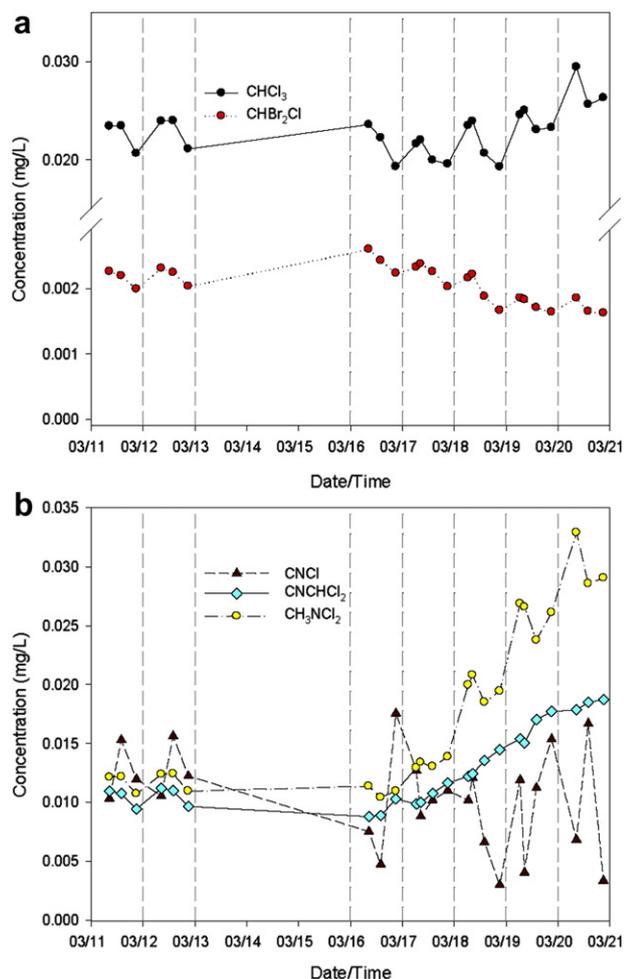


Fig. 2 – Dynamics of free chlorine and inorganic chloramine concentration measured by (a) DPD/KI method, and (b) MIMS. The vertical, dashed lines represent midnight of each day.

### 3.3. Volatile disinfection by-products

Volatile DBPs were analyzed by MIMS; Fig. 3 illustrates the results of these measurements.  $\text{CHCl}_3$  concentration trended upward during the competition and showed a consistent diurnal pattern: decrease in the daytime and increase overnight (see Fig. 3a). A similar diurnal pattern of  $\text{CHCl}_3$  concentration was reported by Kristensen et al. (2010). The loss during the day (while the pool was being used) is believed to be attributable to volatilization, which is known to be promoted by mixing associated with swimming activities (Weng et al., 2011). Losses due to volatilization would take place from near-surface locations, where samples were collected, and where competitive swimmers spend most of their time in the pool. As with  $\text{NCl}_3$ , the overnight increase is believed to be attributable to reactions that yield  $\text{CHCl}_3$ . A positive relationship between THM concentration and bather loading was proposed by Zwiener et al. (2007), suggesting that bathers may introduce precursors that react with chlorine to yield THMs. The diurnal pattern for  $\text{CHBr}_2\text{Cl}$  was less distinct than the pattern for  $\text{CHCl}_3$ ;  $\text{CHBr}_2\text{Cl}$  concentration generally decreased during the event. The overall decrease of  $\text{CHBr}_2\text{Cl}$  concentration suggests that the loss rate (e.g., volatilization) was higher than its formation rate. The concentrations of the other THMs were consistently low; in the case of  $\text{CHBrCl}_2$  and  $\text{CHBr}_3$ , concentrations were below the limit of detection for the MIMS instrument used in these experiments.

CNCHCl<sub>2</sub> and CH<sub>3</sub>NCl<sub>2</sub> concentrations both increased by a factor of 2–3 during the course of the meet. Li and Blatchley (2007) identified two constituents in human urine and sweat, creatinine and L-histidine, that function as precursors to formation of CH<sub>3</sub>NCl<sub>2</sub> and CNCHCl<sub>2</sub>, respectively, by chlorination. The data in Fig. 3b indicate a steady increase in the concentration of CNCHCl<sub>2</sub>, with no diurnal variations. On the other hand, time-course CH<sub>3</sub>NCl<sub>2</sub> concentration data showed a pattern that was similar to the behavior of CHCl<sub>3</sub>. Specifically, the CH<sub>3</sub>NCl<sub>2</sub> concentration data were characterized by a diurnal pattern with lowest daily concentrations being observed near mid-day and increases in concentration overnight, superimposed on a steady increase of concentration. No consistent trend for CNCl concentration was observed during the experiment period. Free chlorine is required for CNCl formation; however, Na and Olson (2004) demonstrated that CNCl is oxidized by an OCl<sup>-</sup>-catalyzed reaction. Therefore, the concentration of CNCl in pools will be strongly influenced by maintenance practices that influence residual (free) chlorine concentration in pools.



**Fig. 3** – The concentration of volatile DBPs sampling during sampling period, as analyzed by MIMS: (a) THMs (CHCl<sub>2</sub>Br and CHBr<sub>3</sub> are not shown because their concentrations were below the detection limits) (b) CNCl, CNCHCl<sub>2</sub> and CH<sub>3</sub>NCl<sub>2</sub>. The vertical, dashed lines represent midnight of each day.

### 3.4. Urea

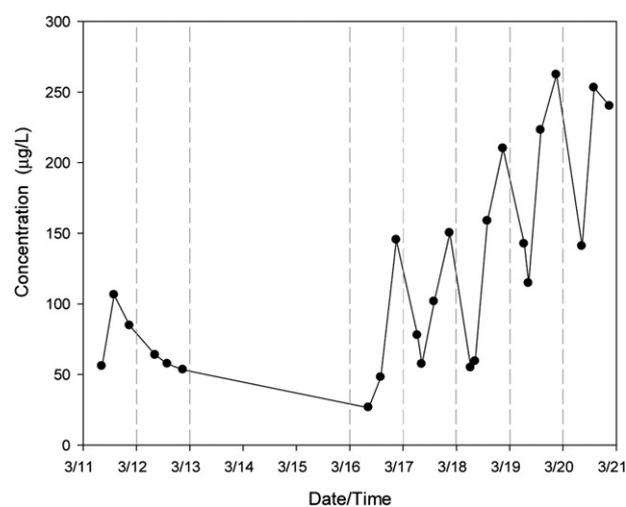
By mass, urea is likely to represent the greatest source of organic-N introduced to pools by swimmers. Urea is introduced to pools by swimmers via at least three sources: urine, sweat, and extraction of “natural moisturizing factor”, a group of chemicals that is produced in skin tissues to maintain skin moisture (Gunkel and Jessen, 1986; Erdinger et al., 1997; ISRM, 2009). De Laat et al. (2011) reported urea concentrations in swimming pools ranging from 0.12 mg/L to 3.6 mg/L. Urea concentrations measured in this study were at the low end of this range.

Fig. 4 illustrates the time-course pattern of urea concentration in the pool. During the competition, urea concentration in near-surface water showed a pattern of steady increase during each day of the competition, with a decrease at night. Superimposed on this diurnal pattern was an overall trend of increasing concentration during the entire event.

This diurnal pattern of urea behavior cannot be explained by reactions with chlorine, as the urea-free chlorine reaction is slow relative to the time-scale of sampling in this study (Blatchley and Cheng, 2010; De Laat et al., 2011). Given the lack of volatility of urea, it is more likely that the decrease in urea concentration for water samples collected at the surface was attributable to overnight mixing of surface water with water in the deeper parts of the pool.

Although urea is slow to react with free chlorine, it is an effective precursor to NCl<sub>3</sub> formation (Samples, 1959; Blatchley and Cheng, 2010). Among the inorganic chloramines, NCl<sub>3</sub> concentration doubled after the first day, and increased by a factor of 3–4 over the 4 days of competition, as shown in Fig. 2. The data illustrated in Fig. 4 indicate that a large mass of urea was introduced by competitors. In turn, this urea contributed to NCl<sub>3</sub> formation during the competition.

The data in Fig. 4 were used to estimate urea contributions per swimmer, based on the following assumptions:



**Fig. 4** – Time-course behavior of urea concentration during the sampling period. The vertical, dashed lines represent midnight of each day.

**Table 2 – Estimated contribution of urea from sweat and urine per swimmer.**

Date	Daily difference ( $\mu\text{g/L}$ ) <sup>a</sup>	Total urea introduction (g) <sup>b</sup>	Urea introduced per swimmer (g/person) <sup>c</sup>	Sweat introduced per swimmer (mL/swimmer) <sup>d</sup>	Urine introduced per swimmer (mL/swimmer)
3/16	117	138	0.92	1350	89.6
3/17	72.4	83.9	0.56	823	54.7
3/18	155	180	1.20	1760	117
3/19	120	139	0.93	1360	90.5
3/20	99.2	115	0.77	1130	74.9

a [urea concentration in the evening]-[urea concentration in the morning].

b Assume volume of top layer is half of the total volume in the pool ( $1.16 \times 10^6$  L) and was well-mixed.

c Assume there were 150 swimmers per day.

d 0.68 g urea/L of sweat and 10.245 g urea/L of urine (WHO, 2006).

- The pool was stratified into two layers during the daytime with equal depth where the top layer was well-mixed (because of the disturbance of swimmers).
- The urea measurements were representative of the top layer.
- No exchange (diffusion or recirculation effects) took place between the two layers while swimmers were in the pool.
- Consumption of urea by reaction with chlorine and uptake by swimmers was negligible.
- Bather loading was 150 persons each day during the competition.

The daily urea concentration increases ranged from 72.4  $\mu\text{g/L}$  to 155  $\mu\text{g/L}$  during the five-day period from March 16–20, as shown in Table 2. Based on the pool dimensions, the water volume in the pool was  $2.33 \times 10^6$  L, and the water volume of the top layer was equal to half of the total volume. Based on these assumptions, the total mass of urea introduced by swimmers was 83.9–180 g ( $1.16 \times 10^6$  L  $\times$  daily difference ( $\mu\text{g/L}$ )), which implies daily urea introduction ranged from 0.56 to 1.2 g/swimmer/day (total urea introduction (g)/150 swimmers/day).

Reported values of urea concentration in human sweat and urine are 0.68 g/L and 10.24 g/L, respectively (WHO, 2006). If all urea introduced to the pool is assumed to have originated from sweat, this implies a daily sweat introduction rate that ranged from 823 to 1760 mL/swimmer (urea introduced per person (g)/0.68 (g/L)). Similarly, if all urea is assumed to have

been introduced from urine, this implies a urine introduction rate that ranged from 54.7 to 117 mL/swimmer (urea introduced per person (g)/10.24 (g/L)). Previous studies have presented estimates of sweat introduction from 200 to 1000 mL/person; similarly, daily urine introduction estimates have ranged from 25 to 80 mL/person (Gunkel and Jessen, 1986; Erdinger et al., 1997; Seux et al., 1985). Although these calculations were based on several unvalidated assumptions, the results are consistent with previously published estimates of sweat and urine introduction rates. More generally, the data presented in Fig. 4 and Table 2 indicate that heavy use of a pool (such as a large competition) will result in substantial introduction of pollutants to a pool, and corresponding adverse effects on water quality.

## 2.5. Diurnal pattern of volatile DBPs and DBP precursors

Among DBPs, diurnal patterns of  $\text{NCl}_3$ ,  $\text{CH}_3\text{NCl}_2$ , and  $\text{CHCl}_3$  were evident, with concentration decreasing during the day, and increasing overnight, presumably due to the combined effects of swimmer-induced volatilization, DBP production, and mixing within the pool. As indicated by the Henry's law constants in Table 3, these chemicals are the most volatile DBPs detected in this study. This suggests that liquid-gas transfer contributes to diurnal behavior of these compounds in near-surface water.  $\text{CNCl}$  has the next highest Henry's law constant among those listed in Table 3.  $\text{CNCl}$  is a common byproduct from chlorination of amino acids (Lee et al., 2006).

**Table 3 – Henry's Law constants and liquid-phase behavior among volatile DBPs and urea.**

Compound	Henry's Law Constant (atm, 20 °C) <sup>a</sup>	Diurnal Pattern	Overall Concentration Changes	Description
$\text{NH}_2\text{Cl}$	0.45	No	–	–
$\text{NHCl}_2$	1.52	No	Slight Increase	–
$\text{NCl}_3$	432	Yes	Increase	Volatilization and formation
$\text{CHCl}_3$	185	Yes	Increase	Volatilization and formation
$\text{CHBr}_2\text{Cl}$	57.3	Yes	Decrease	Volatilization
$\text{CHBr}_3$ <sup>b</sup>	21.5	–	–	–
$\text{CNCl}$	108	No	–	Controlled by free chlorine
$\text{CNCHCl}_2$	0.21	No	–	Steady increase
$\text{CH}_3\text{NCl}_2$	154	Yes	Increase	Volatilization and formation
Urea	–	Yes	Increase	Mixing behavior between top and bottom layer

a Holzwarth et al. (1984); Krasner and Wright (2005); Cimetiere and De Laat (2009).

b Concentration of  $\text{CHBr}_3$  was close to detection limit.

CNCl is also known to be oxidized via an OCl<sup>-</sup>-catalyzed process (Na and Olson, 2004). The pattern of CNCl behavior observed over period of these experiments was erratic, possibly due to the combination of processes that are known to influence its behavior, and the fact that measured values of CNCl concentration were consistently near the limit of detection.

NH<sub>2</sub>Cl and NHCl<sub>2</sub> generally increased during the study, but trends in their behavior were less obvious. CNCHCl<sub>2</sub> increased steadily over the course of the competition. No pattern of diurnal behavior was evident for this compound, probably because of its relatively low volatility and stability in the presence of free chlorine.

The diurnal pattern of behavior for urea was essentially a mirror image of behavior observed with the volatile DBPs (CHCl<sub>3</sub>, NCl<sub>3</sub>, and CH<sub>3</sub>NCl<sub>2</sub>). Urea is slow to react with chlorine and is essentially non-volatile. The increases in urea concentration in near-surface samples that were observed during each day of competition were consistent with a pattern of steady urea input. The decrease that was observed overnight is believed to be attributable to mixing of near-surface water with water from other parts of the pool (i.e., deeper water), where urea input would be negligible, and daytime concentration was likely to be lower.

### 3. Conclusions

This study provided evidence of the influence of swimmers on swimming pool water quality in terms of free chlorine concentration, volatile DBPs, and urea. NCl<sub>3</sub> concentration increased by a factor of 3–4 during the competition; CHCl<sub>3</sub>, CNCHCl<sub>2</sub> and CH<sub>3</sub>NCl<sub>2</sub> concentrations increased during the competition, presumably due to introduction of precursor chemicals. Diurnal patterns of CHCl<sub>3</sub>, CH<sub>3</sub>NCl<sub>2</sub>, and NCl<sub>3</sub> were observed which were attributed to the combined effects of volatilization enhanced by aggressive swimmer activity, reactions to produce these DBPs, and mixing. Urea concentration increased at the water surface during the period of heavy use, and decreased overnight. A diurnal pattern in near-surface urea concentration was also observed.

Water quality deteriorated during the course of the competition, as represented by increases in the concentrations of volatile DBPs, thereby leading to enhanced DBP exposure by swimmers, pool employees, and spectators at the competition.

### Acknowledgments

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### Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.watres.2011.07.027.

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