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Technical Note

Benefits of carbon dioxide as pH reducer in chlorinated indoor swimming pools

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ABSTRACT

Carbon dioxide is seldom used as pH reducer in swimming pools. Nevertheless it offers two interesting advantages. First, its use instead of the usual hydrochloric acid avoids the characteristic and serious accident of mixing the disinfectant with that strong acid, which forms a dangerous chlorine gas cloud and, second, it allows the facility to become slightly a depository of that greenhouse gas.

This work introduces the experience of using CO_2 as pH reducer in real working swimming pools, showing three more advantages: lower chlorine consumption, lower presence of oxidants in the air above the swimming pool and a diminished formation of trihalomethanes in the swimming pool water. Experiments lasted 4 years and they were run in three swimming pools in the Barcelona area, where the conventional system based upon HCl and a system based upon CO_2 were consecutively exchanged.

1. Introduction

Swimming pools and spas are associated to the idea of wellness and health. Nevertheless, these facilities require a considerable degree of disinfection to avoid microbiological pollution, being the formation of disinfection by-products (DPB) paradoxically a new health hazard (Caro and Gallego, 2007; Zwiener et al., 2007). Chlorine-based disinfectants, such as sodium hypochlorite, are the most frequently used in swimming pools. DPB such as chloramines or trihalomethanes (THM) are formed when chlorine reacts with the natural organic matter (NOM), a constituent ubiquitous in water supplies (Rook, 1974; Urano et al., 1983; Reckhow et al., 1990), or with nitrogenous substances coming from bathers' contribution (WHO, 2000; Kim et al., 2002; Judd and Bullock, 2003). Some of the formed DBP are highly volatile and they can be found in the atmosphere of indoor swimming pools (Li and Blatchley, 2007; Barrera et al., 2008; Cimetiere and De Laat, 2009; Weaver et al., 2009). The concentration of these pollutants in air is higher near the water surface, being maximal just where swimmers breathe (Lahl et al., 1981). Since some of these DBP can act as oxidants, their inhalation is the most likely responsible for some disorders observed in usual swimming pools visitors, particularly in child swimmers and competitive swimmers (Zwick et al., 1990; Thickett et al., 2002; Bernard et al., 2006; Nickmilder and Bernard, 2007). Finally, THM have received a lot of attention because of their carcinogenic (USEPA, 1999; Villanueva et al., 2007) and teratogenic character (Nieuwenhuijsen et al., 2000).

Reduction of DBP in water treatment is currently based on testing new disinfectants and/or limiting the presence of organic matter or pre-processing it. For instance, UV radiation lamps can reduce chloramines concentration, although formation of some THM is enhanced (Cassan et al., 2006). But there is a third actor in swimming pools, the pH reducer. This chemical agent is added because the continuous dosage of NaClO ($pK_a = 7.54$, at 25 °C) results in system basification. An acid compound is dosed to maintain pH at an appropriate value ($pH = 7.3$) for the effectiveness of the disinfectant and the safety of the bathers. The most common pH reducers are hydrochloric acid and sulphuric acid. Carbon dioxide is not usually considered as pH reducer, but it offers two major returns: (i) the suppression of the risk of accidental mixing of HCl and NaClO and thus, chlorine gas formation, and (ii) the reduction of the facility carbon footprint.

Particularly for the first reason, a few years ago CO_2 was chosen to substitute conventional HCl as pH reducer in three real indoor swimming pools. The subjective perception of maintenance personal and bathers that the typical smell of indoor swimming pool had been reduced was thought to be indicating a possible new way to reduce DBP, and it was actually the origin of this study.

Thus, this work aimed to analyse the effect of substituting the common pH reducer, HCl, for CO_2. For this purpose, different periods using alternatively HCl and CO_2 as pH reducer in those swimming pools were monitored along the last 4 years (2005–2009). The parameters chosen to assess the effects of the change were:

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total oxidants (TO) in the air just over the water surface, THM in water, disinfectant (chlorine) consumption and conductivity.

2. Materials and methods

2.1. Swimming pool facilities

Two swimming pools from Universitat Autònoma de Barcelona (UAB) from now on named SP_a and SP_b, were used to assess THM formation, chlorine consumption and conductivity. University students and children from neighbourhood schools are their users, which results in a very high occupancy and water stirring according a predictable timetable. Seasonal variations are also well defined; therefore periods without comparable conditions could be avoided.

Another swimming pool (SP_c) from Consell Català de l'Esport (CCE), placed in the Barcelona area, was also studied. It hosted only high level athletes, resulting in a very low and also foreseeable occupancy and limited water stirring. Experimental research on SP_c was used to determine variations of oxidants concentration in the air over the water surface since the air-conditioning unit with free-cooling could be operated to keep the same air-renewal ratio throughout the study. Indoor and outdoor environmental CO_2 was measured with a Testo 535 with infrared sensor to ensure constant ventilation conditions. In all the measurements, the differences between inside and outside were low (maximum: 398 mg m^{-3}; mean value: 221 mg m^{-3}) indicating an appropriate and constant ventilation level. At the same time, air velocity in the studied points was also measured in the zenith and azimuth planes with a Testo 405-V1 to ensure that the draught of air was not diminishing real values. In both cases, the air velocity was always lower than 0.06 m s^{-1}. Chlorine consumption was also studied in this facility.

Table 1 summarises the characteristics of the three swimming pools used in this study. Either swimming pool from UAB or from CCE used the same pH control structure with HCl or CO_2, therefore switching between both systems was simple. Before any experiment was conducted, at least one residence time after any change of the pH reducer had to elapse. Residence time was calculated as the swimming pool volume divided by the average flow of renewal water (Table 1).

The three studied swimming pools used exclusively the same commercial solution of sodium hypochlorite, 15% w/w, as disinfectant. The disinfectant daily dosage was recorded from 2003 for SP_a and SP_b and from 2006 for SP_c.

Water temperature and chlorine (free and total) conditions were controlled and they can be considered constant at their respective setpoints (see Table 1). Besides the on-line control, free and total chlorine in water were analysed twice a day.

Table 1
Summary of the physical characteristics of the studied swimming pools. Average instantaneous occupation was determined sampling the number of people in each swimming pool between twice and five times per hour during the opening time of the facility.

Parameter	SP_a	SP_b	SP_c
Volume (m^3)	119	884	625
Dimensions (length, width, height, in m)	7 × 17 × 1	25 × 17 × 2	25 × 10 × 2.5
Temperature (°C)	30	27	27.5
Renewal daily volume (%)	3	1	1
Residence time (d)	30	100	100
Free-chlorine set point (mg L^{-1})	1	1	0.9
pH set point	7.3	7.3	7.3
Average instantaneous occupation (people mean value ± standard deviation)	11.4 ± 3.5	17.3 ± 4.0	2.2 ± 0.5
Average instantaneous occupation per m^3	0.096	0.020	0.007
Water consumption (m^3 y^{-1})	1300	3100	2300

Fig. 1 shows the water flow scheme of the three swimming pools. A continuous water renewal is necessary to balance the water losses via evaporation and filter backwash among others. This water renewal comes from the network supply, which is fed via the buffer tank. Chlorine and pH are measured on-line before sand filters with an amperometric probe for free-chlorine and a pH electrode. They are controlled with an automatic dosage of the disinfectant and the pH reducer (HCl 25% w/w or pure CO_2), both commanded by their respective proportional-integral controllers. Both dosages are made as the last step of the treatment, after the filtration unit in the pipeline that takes water back to the swimming pool. Their respective dosing points are close (<2 m) in the three cases, as it is usual in swimming pools. Industrial dry CO_2 is provided in 35 kg gas-pressured bottles (Linde). The set points chosen were 1 mg L^{-1} and 0.9 mg L^{-1} free chlorine and pH = 7.3 in the three cases. Combined chlorine (i.e. total chlorine minus free chlorine) is limited by local rules to a maximum of 0.6 mg L^{-1}.

CO_2 is bubbled into the pipeline coming from the sand filter. The amount of CO_2 bubbled is controlled with the same device and criteria that controls the HCl injection pump. During the entire study, each pH-reducing system was kept for a minimum of 100 d in order to exceed the longest residence time.

2.2. Analytical measurements

Free and total chlorine in water were analysed with the N, N-diethyl-p-phenylenediamine colorimetric method (4500-C1-G) described elsewhere (APHA, 1998) using a commercial colorimeter (HACH, Düsseldorf, Germany).

TO in air were determined with a Dräger CMS (Drägerwerk AG & Co. KgaA, Lübeck, Germany) as chlorine with its own chips measuring in a range of 0.59–29 mg m^{-3}. They were measured in the worst air quality point of SP_c: one of the edges of the swimming pool and at 10 cm over its water surface.

To measure THM in water, weekly samples from SP_a and SP_b were withdrawn from a layer of 20 cm beneath the water surface. This operation was always conducted before 8 am, so that any sport activity had not started yet. For all samples, it was taken into account also the seasonal use of the facility, ruling school-holiday periods out and running the experiments in similar occupancy levels of the swimming pools. That led to the low standard deviation figures showed by the instantaneous occupancy parameter (Table 1). A Schott bottle (1 L) was filled with water from the swimming pool minimising the headspace. Samples were instantaneously stabilized with ascorbic acid in the moment of the collection, immediately refrigerated (5 °C) and analyzed in the next 24 h.

THM were determined by headspace (Agilent 7694, Agilent Technologies, Inc. Santa Clara, CA) gas chromatography (Agilent 6890) with electron capture detection. Analyte separation was carried out with a DB 624 capillary column (30.0 m × 320 μm id × 1.8 μm film thickness). Standards were prepared daily from a Sigma–Aldrich 47904 (Sigma–Aldrich, Inc. St. Louis, MO) calibration mix fresh vial. More than 20% of the samples were measured in duplicate in a different laboratory to validate the results obtained.

Conductivity was on-line measured in SP_a with a CRISON CM38P conductimeter (Alella, Spain) and recorded twice a day.

3. Results and discussion

Firstly, Fig. 2 shows the TO concentrations in air measured during either HCl or carbon dioxide periods in SP_c. TO exceeded only

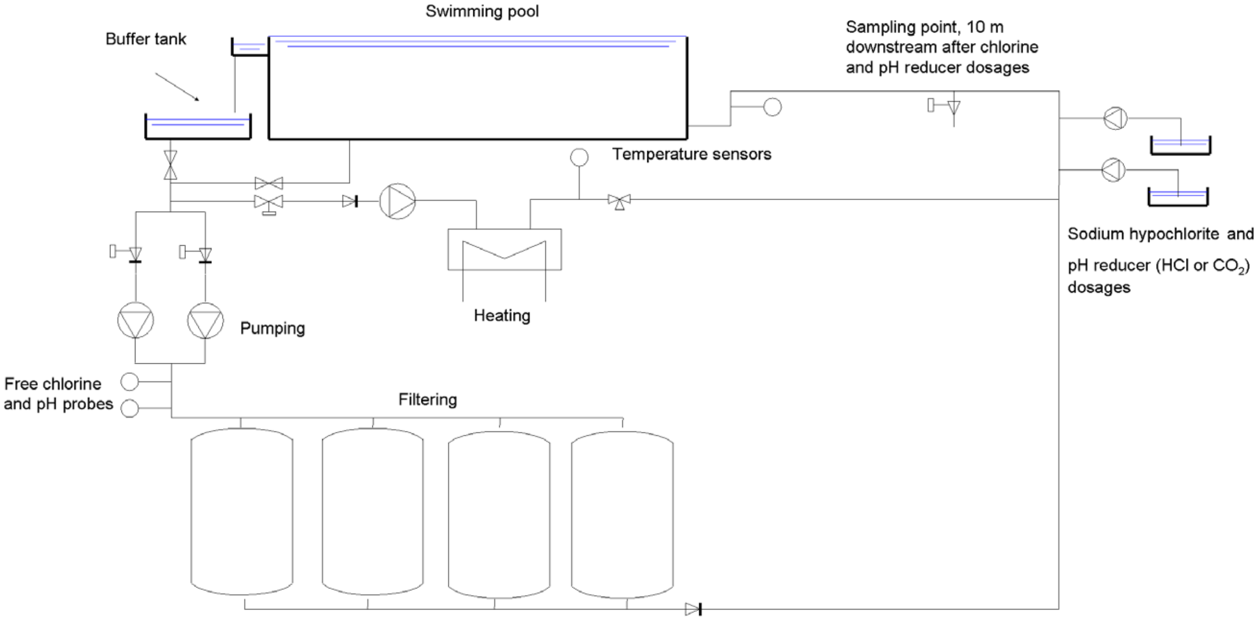

Fig. 1. Water flow scheme for any of the three studied swimming pools.

once the 0.59 mg m^{-3} threshold during the CO_2 phase while all the measurements exceeded that value during the HCl phase. Such results matched with the subjective perception of the maintenance personal and 40 bathers of less "typical smell" to swimming pool during the CO_2 period, according to two opinion polls conducted at UAB and CCE swimming pool halls.

Secondly, routine THM analysis showed unexpected results when comparing the operation with HCl or with CO_2 as pH reducers. The results indicated that the THM formation was significantly reduced during carbon dioxide periods. Some clarifications are required to understand this reduction. On the one hand, THM precursors coming from bathers' contribution could be considered constant since bathers' load was similar during the studied periods. Hence, the main variations in THM formation could come either from different treatment conditions or from different precursor concentrations coming from the supply network. For this reason, the THM concentration should be always related to the network concentration to assess the effects of treatment modifications. Both the supply network water and the swimming pool water share THM precursors coming from the supply network. According to that, THM in the UAB swimming pools were measured simultaneously to the THM in the water of the supply network.

Table 2 shows percentages of variation between THM concentrations in the swimming pools and those in the network. In the CO_2 periods, THM concentrations in our swimming pools were always lower than those in the supply network. This observation contrasted with the HCl periods, when THM concentrations were not so lower or they were even higher. pH was correctly held in all cases at the set point (7.3).

Only one similar result has been so far reported in the literature. Reckhow et al. (1986) analysed the effectiveness of mixing ozone with NaClO as disinfectant and observed a significant THM reduction when bicarbonate was present. They attributed this observation to a longer lifetime of ozone due to some effect of

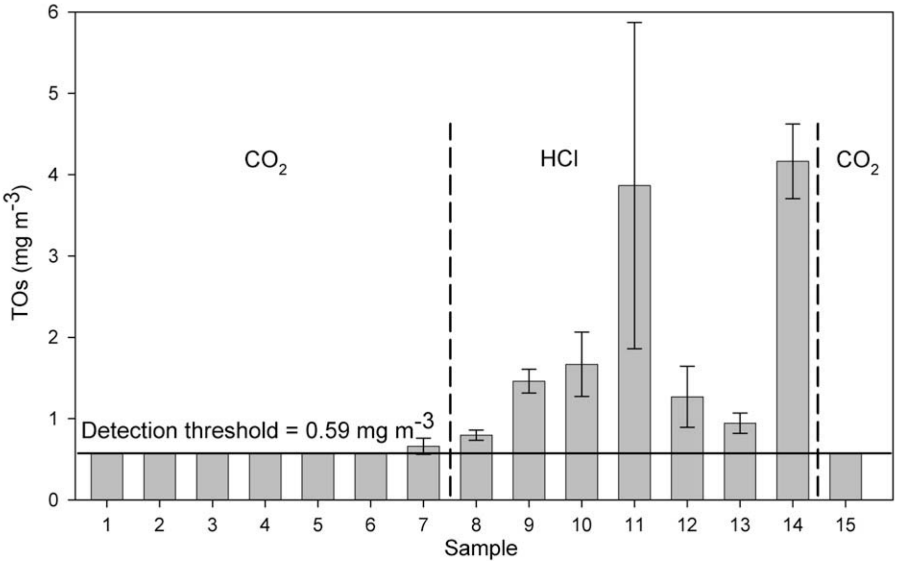

Fig. 2. Total oxidants in air at 10 cm over the water surface of the swimming pool SP_c.

Table 2
THM measurements during the different periods with HCl or CO_2 dosage as pH reducer in SP_a and SP_b. The last column includes the reduction in THM concentration with respect to the network supply when using CO_2. [THM] ± $I_{n-1}^{95\%}$ ($I_{n-1}^{95\%} = s_{n-1} \cdot t_{n-1}/n^{1/2}$; n = samples).

	HCl	CO_2	CO_2	HCl	CO_2	HCl	CO_2	
Duration of the period (months)	8	6	2	5	2	Mean	Mean	% THM formation reduction, CO_2 with respect to HCl
Samples	2	5	5	15	9			
THM mean value in network supply (μg L^{-1})	51 ± 13[a]	61 ± 17	44 ± 5	42 ± 2	78 ± 3			
THM mean value in SP_a (μg L^{-1})	55 ± 18[a]	47 ± 15	32 ± 4	46 ± 2	53 ± 3			
Mean variation with respect to network in SP_a%	9	−23	−34	13	−28	13	−28	41
THM mean value in SP_b (μg L^{-1})		37 ± 8	34 ± 7	38 ± 2	40 ± 4			
Mean variation with respect to network in SP_b%		−39	−29	−6	−45	−6	−39	33

[a] [THM] ± s_{n-1}.

Table 3
Daily consumption of disinfectant during different periods with HCl or CO_2 as pH reducer. Last columns are the time-weighted mean daily consumption and the mean reduction of consumption using CO_2 instead of HCl.

		HCl	HCl	CO_2	HCl	CO_2	CO_2	HCl	CO_2	HCl	CO_2	HCl	CO_2	CO_2	HCl	% Reduction
SP_a	Duration of the period (months)	12	13	7	1	5	5	2	16	5	10	4	2	Mean	Mean	
	Consumption (L d^{-1})	18.5	18.9	11.0	23.3	11.2	11.0	13.1	12.8	13.3	14.8	15.2	12.5	12.6	17.4	28%
SP_b	Duration of the period (months)	12	13	7	1	5	5	5	2	16	5	10				
	Consumption (L d^{-1})	7.2	7.5	6.2	12.7	6.4	3.7	4.1	5.8	7.4	7.4	8.3		5.9	7.9	19%
SP_c	Duration of the period (months)									11	9.5	5.5	2			
	Consumption (L d^{-1})									21.9	15.6	18.6	13	15.2	20.8	27%

bicarbonate. Nevertheless, this effect was not possible during our study because there was no ozonation, nor an activated carbon phase, in the swimming pools during the experimental period.

In third place, Table 3 shows the daily consumption of chlorine throughout the different periods (7 years for SP_a and SP_b and the last two and a half years for SP_c). A reduction of chlorine consumption was observed when CO_2 was used instead of HCl as pH reducer.

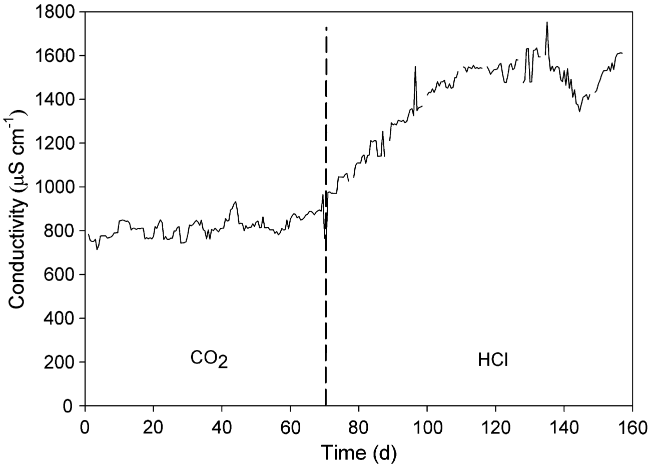

Fig. 3. Conductivity (25 °C) trend in SP_a during two and a half months with CO_2 and four months with HCl as pH reducer.

Despite this reduction, free-chlorine set points were kept correctly in the three cases, so the disinfection power was not lessened by the lower chlorine consumption. Moreover, combined chlorine level did not show any relationship with the pH reducer used. It remained between 0.4 and 0.6 mg L^{-1} in all cases.

Finally, Fig. 3 shows the conductivity trend for an 6-month period when CO_2 was used the first two and a half months and HCl was the pH reducer the rest of the time. The use of HCl as pH reducer resulted in a clear conductivity increase of almost 100% with respect to the use of CO_2 (from 800 to 1600 μS cm^{-1}). This result is noticeable from an environmental point of view, since waste from filter backwashing to sewerage will represent a lower impact with lower conductivity. For instance, outside the range of 150–500 μS cm^{-1} water could not be suitable for certain species of fish or macroinvertebrates (USEPA, 2006).

From the stand point of a simple mass balance, the lower presence of oxidants in the air during the periods of CO_2 treatment could explain the reduction in the chlorine consumption. And such reduction could be a reason for the other observed advantage of CO_2 utilisation versus HCl: the lower formation of THM in water. Reported models on THM formation in chlorinated waters (Sadiq and Rodriguez, 2004; Chowdhury et al., 2009), predict that THM

Table 4
Measures of free and total chlorine and pH in the pipeline of SP_a 10 m downstream the disinfectant and pH reducer injection points and in the on-line controller.

	pH in the pipeline	Free/Total chlorine (mg L^{-1}) in the pipeline	pH at the on-line controller	Free chlorine at the on-line controller (mg L^{-1})
After 5 min of constant HCl injection, without simultaneous disinfectant addition	6.7	1.2/1.8	7.2	1.1
After 5 min of constant CO_2 injection, without simultaneous disinfectant addition	7.2	1.0/1.6	7.3	1.1
After 5 min of constant NaClO injection, being HCl the pH reducer	7.4	2.2/2.8	7.2	1.2
After 5 min of constant NaClO injection, being CO_2 the pH reducer	7.4	2.2/2.8	7.3	1.1

formation is proportional to chlorine dose. Therefore, the observed reduction of chlorine consumption (28% in SP_a and 19% in SP_b) would be a candidate to explain the observed reduction in the formation of THM (41% and 33%, respectively).

During the CO_2 periods, a mean value of 137 ± 9 mg L^{-1} of HCO_3^- was measured, while it was reduced to 15 ± 1 mg L^{-1} when HCl was the pH reducer. Hence, different behaviour of the reactions taking place is expectable, since a more stable pH is achieved when using CO_2 because of the higher buffer capacity of the solution. Table 4 shows the measured effect of the different pH reducer in the pipeline of SP_a. It can be highlighted that lower pH values (6.7) are achieved in that point when HCl is used, while pH remains unaltered (7.2) with CO_2.

Finally, the consumption of CO_2 (mean value in 4 years of 4 kg m^{-3} of basin per year) slightly reduced the carbon footprint of the facility, what potentially converts every swimming pool in a depository of that greenhouse gas.

4. Conclusion

The use of CO_2 instead of HCl as pH reducer in three real working swimming pools resulted in a better performance of the water treatment in terms of less presence of TO in the air, less THM formation in the water and less chlorine consumption. Such results suggest that, besides acting on the disinfectant and/or avoiding or pre-processing NOM, acting on the pH reducer could also be a strategy for reducing DBP, at least in swimming pools.

Further research is needed to determine if the buffer effect that CO_2 addition provides is the main responsible for such behaviour.

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