Full scale test of UV-based water treatment technologies at Gladsaxe Sport Centre – with and without advanced oxidation mechanisms.

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Synopsis

A technology testing project is being undertaken for the Danish EPA with the objective to establish a solid knowledge basis regarding possibilities for improvement of pool water quality by application of four selected UV-based technologies. The tested technologies encompass: UV photolysis by low pressure UV and medium pressure UV - separately and in combination, low pressure UV in combination with a TiO_2 covered surface, UV in combination with ozone, and high pressure UV. This paper includes results from the three first mentioned technologies. All technologies were tested in full scale as side-stream treatment of the recirculation flow of a 50 m^3 warm water pool at Gladsaxe Sport Centre in Denmark. The main objective of the project was to study the impact from the technologies on the disinfection by-products: combined chlorine and total THM (TTHM) and to establish information regarding costs for investment and operation of the technologies. Besides combined chlorine and TTHM, the monitoring programme included monitoring of NVOC, AOX, THM-Formation Potential, and AOX-Formation Potential. TTHM was monitored on-line by application of MIMS – Membrane Inlet Mass Spectrometry. The on-line TTHM monitoring revealed that TTHM was a highly dynamic water quality parameter with significant variations over the day and over the week depending on bather load, pool activity, etc. The MIMS-data also revealed that salt addition to enhance the in-line-based chlorine electrolysis was followed by significant formation of brominated DBP's slowly returning to the usual low level after a couple of days. Medium pressure UV photolysis showed efficient for control of combined chlorine while low pressure UV photolysis was less efficient. When comparing the TTHM levels in the pool water during periods with UV treatment with reference periods with no UV treatment, no difference in TTHM level could be observed. Advanced oxidation with UV in combination with ozone was able to lower significantly the NVOC level, however, no similar effect on the TTHM level and the AOX level could be observed.

Background

Recreational industry is growing rapidly and it is expected that swimming pools and water theme parks, etc. are going to experience increased load from the bathers and more stringent demands from the users as regard to documentation and securing a satisfactory water quality so that the bathers can rely confidently on the facilities. Historically, chlorine has been the preferred disinfectant with reference to the protection of the hygienic water quality in swimming pools since the 20ies of last century. Chlorine has the advantage of being highly effective against most micro organisms. Chlorine acts quickly and when dosed sufficiently it secures a lasting disinfection effect in the water.

When adding free chlorine to swimming pool water, however, a large spectrum of unwanted chlorinated disinfection by-products (DBP) is formed during reactions between chlorine and contaminants from the filling water, the bathers and possibly from substances leaching from materials in contact with the pool water. There is considerable room for improvements regarding the nature and especially the amount of these contaminated substances. The best known disinfection by-products are chloramines (combined chlorine), trihalomethanes (THM), halogen acetic acid (HAA) and haloacetonitriles (HAN). Although “combined chlorine” has been used since long to describe a certain group of DBPs, there is insufficient knowledge about its composition and toxicological relevance. A large number of other chlorinated organic compounds are known to be formed, but these are not or only rarely analysed. The existence of such chlorinated disinfection by-products is a problem for both bathers and pool staff with regard to convenience as well as to health.

The accepted level of chlorine in public swimming pools varies significantly from country to country covering the range from 0.3 mg/l to 3 mg/l. Also the accepted level for combined chlorine varies considerably with the lowest values less than 0.2 mg/l – and the highest values less than 1.0 mg/l. The level of TTHM is regulated only in a limited number of countries with acceptable concentrations in the range 20-50 µg/l.

An analysis undertaken by the Danish EPA reveals that, the immediate perspective in Danish swimming pools is a continued use of chlorine as disinfectant, but with an improved control of DBP-formation induced by a decrease in the free chlorine concentration. Additionally, an improved water quality with reduced DBP-content can be achieved by using supplementary technology in the recycled water loop of the swimming pool as well as by optimization of existing water treatment steps. A number of relevant technologies are available, which can contribute to lower the DBP-content either by direct removal of the unwanted DBPs or by removal of precursors that are the prerequisite for the formation of the DBPs. However, there is a need for experimental work for establishing a qualified documentation to secure accurate design and maximal benefit of the investment in new water treatment technology – including estimation of the cost for investment and operation.

The objective for the present project is to investigate the impact and efficiency of selected UV-based technologies on pool water quality under real life conditions. Besides the contribution to cut down the level of DBP in the swimming pool water, these technologies may also support the disinfection process and improve disinfection of chlorine tolerant pathogens.

The test pool at Gladsaxe Sport Centre

The study was conducted in the warm water pool at Gladsaxe Sport Centre. The warm water pool at Gladsaxe Sport Centre consists of a traditional warm water basin connected to a small wading pool in parallel on the same water treatment plant. The basin is shown in Figure 1. The volume of the warm water basin represents the vast majority of the total basin volume.

Data for warm water pool are:

- Volume: 50 m³
- Turn over time: 30 minutes
- Temperature: 31-33 °C

The water treatment for the warm water pool consists of traditional coarse filtration, sand filtration, side stream activated carbon filtration and side stream UV treatment. Chlorine dosage is ensured with inline chlorine electrolysis for which reason sodium chloride is added to the pool water to maintain a chloride concentration around 0.4%. During the present experiments the activated carbon filter was not in operation.

Figure 1 Warm water pool - Gladsaxe Sport Centre

Experimental overview and monitoring programme

The objective of the project was to undertake performance tests and establish documentation for four UV-based technology concepts for treatment of swimming pool water aiming at improved water quality with respect to the disinfection by-products: combined chlorine and/or TTHM. Four technologies were included in this technology test including:

- Conventional UV-photolysis - 1200W Low Pressure lamps (LP) and 1200W Medium Pressure lamps (MP) to be tested separately and in combination
- Advanced oxidation based on UV/TiO_2 – 160W Low Pressure UV
- Combined ozone and UV – 2400W (LP and MP)
- Advanced photochemical reduction/oxidation based on high pressure UV

The test programme was initiated early 2008 and is expected to be finalised April 2009. This paper includes results from the first three technologies because the testing of the fourth technology is not finalised. An overview of the test programme is shown in Table 2.

The monitoring programme has encompassed both online and off-line measurements of several parameters. An overview of the monitoring parameters is shown in table 3.

The bather load was monitored by setting up a web-camera to take pictures of the pool each 15 minutes and transfer them through an internet connection to a central server from where the pictures were drawn for counting. The bather load was calculated by dividing the total sum of bathers per day from the pictures by 2 to estimate the half hourly daily bather load

Table 2 Overview of test programme for the project

Technology	Experimental Programme
UV Photolysis 1200W medium pressure 1200W low pressure Side-stream treatment ($25m^3/h$) Reactor volume – approx. 300 litres	Determination of capacity for removal of combined chlorine – without bather load – combined MP+LP, MP alone, LP alone. Determination of efficiency in the system for combined MP+LP, MP alone, LP alone. Operation for 12 weeks and comparison with reference period without UV-treatment.
UV/TiO_2 160W low pressure placed in tube sleeve coated with TiO_2. Side-stream treatment ($25m^3/h$) Reactor volume – (10-20 litres)	Determination of efficiency in the system. Operation for 8 weeks and comparison with reference periods without UV treatment.
UV/Ozone 1200W medium pressure 1200W low pressure Ozone generation 18-22 g ozone/h Side-stream treatment (7, 10 and $15m^3/h$) Reactor volume – approx. 300 litres Stripping of side-stream to avoid introduction of ozone to the pool – air/water ratio of 10-15.	Determination of efficiency in the system for three ozone concentration levels: 3 mg/l, 2 mg/l and 1.3 mg/l. On-line TTHM measurements before and after the AOP-treatment. Operation for 7 weeks and comparison with reference periods without UV-treatment.

Table 3 Overview of on-line and off-line monitoring parameters for the project

On-line	Off-line
Free chlorine (automated DPD)	Free chlorine (DPD)
pH	Combined chlorine (DPD)
Redox	NVOC
TTHM (MIMS)	TTHM
Bather Load (Automatic web cam photos each 15 minutes)	AOX
	THM-Formation potential
	AOX-Formation potential

On-line monitoring of total THM (TTHM) was conducted using membrane inlet mass spectrometry (MIMS). Membrane inlet mass spectrometry (MIMS) is a relatively new but well established technique for the direct analysis of volatile organic compounds in aqueous solution. It uses a thin polymer membrane as the only separation between the liquid sample and the vacuum of a mass spectrometer. Volatile organic compounds dissolve in the membrane, permeate through it and finally evaporate into the mass spectrometer, where they are ionised and analysed according to their m/z ratio. In this fashion the changing chemical environment in chemical and biological reactors can be monitored on-line. However, the method is limited because the sample is not separated into individual compounds before the analysis.

In this project the MIMS was set up to monitor characteristic target ions representing chloroform, bromdichlormethane, and dibromchlormethane at m/z ratios 83, 129 and 210 respectively. Neither dibromchlormethane nor bromoform was found at concentrations higher than the detection limit of around 1 µg/l at any instance in this pool. To calculate the chloroform concentration an algorithm was setup to subtract the contribution of bromdichlormethane on the chloroform signal at m/z 83. Total THM (TTHM) concentrations were calculated as the sum of the above compounds in $CHCl_3$ equivalents.

The MIMS signals were frequently calibrated against freshly prepared standards made from 0,1% stock solutions of chloroform, bromdichlormethane and dibromchlormethane in methanol for each set of filaments. The calibration curve was stable within a range of 5% throughout the life-time of the each set of filaments. During monitoring, concentrations of TTHM, chloroform and bromdichlormethane were measured every 5 minutes. A photo of the MIMS installation is shown in figure 2.

To avoid delay time in the TTHM measurements from the MIMS, a measurement-loop was set up from which the peristaltic pump on the MIMS instrument continuously drew sampling water. The delay time from the pool to the MIMS was calculated to be less than 2 minutes.

AOX was measured using a rapid analysis test kit from Hach-Lange (LCK391) which is based on the same pre-treatment principle as the standard method but with wet-oxidation of the carbon-disc and photometric determination of halogen ions (Cl^-). Formation potentials of AOX and TTHM were determined by reaction of 500 ml samples in the dark with an excess chlorine concentration of 3-5 mg/l for 48 hours. Results were given as the total AOX and TTHM concentration after reaction.

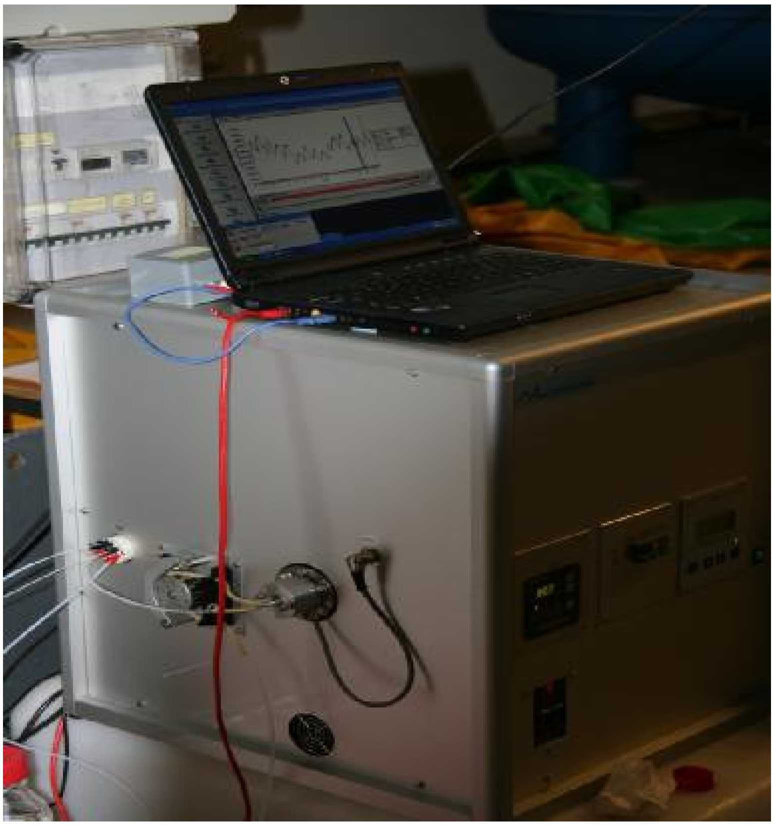

Figure 2 Pool-TTHM concentrations was monitored on-line using Membrane Inlet Mass Spectrometry (MIMS).

Results and discussion

Combined Chlorine (CC)

Conventional UV-photolysis is typically applied to lower the content of combined chlorine in pool water through well known photolysis of chloramines. To determine the CC removal capacity of the conventional UV-technology, dedicated degradation experiments were conducted. The UV-treatment was switched off during day time to build-up the CC concentration in pool water and switched on at pool closure to determine the removal rates during night time. The "CC removal rates" were determined for the LP, MP and combined MP+LP lamps respectively. Examples of degradation kinetics during night-time for the three combinations of lamps are shown in figure 3.

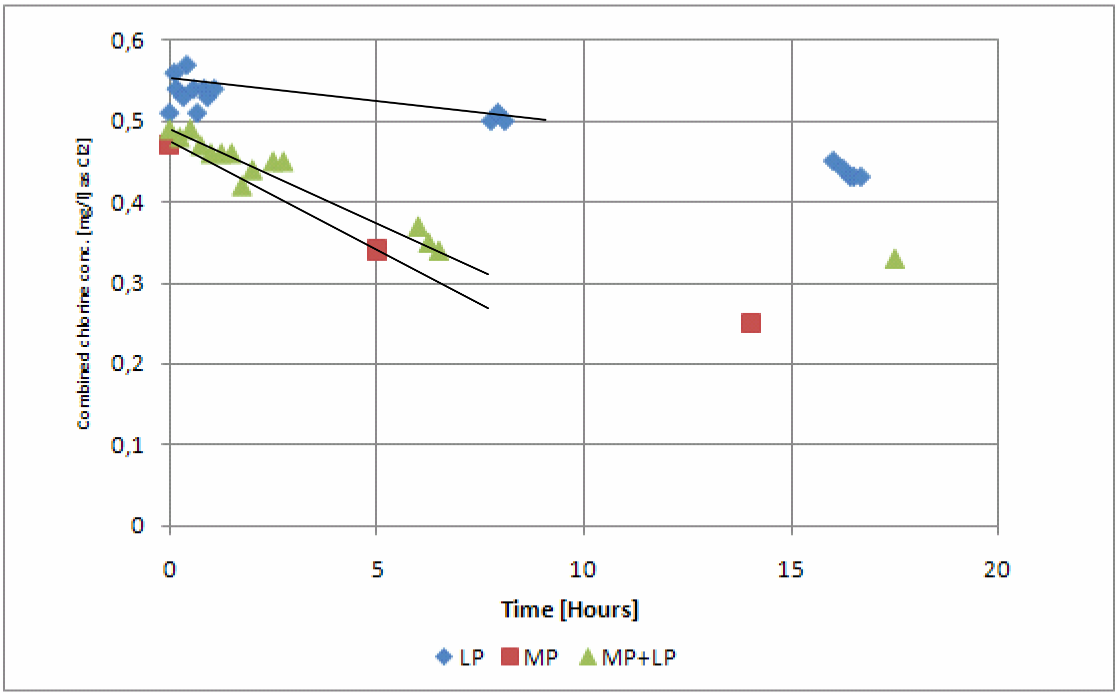

Figure 3 Removal of combined chlorine by UV treatment, 1200W MP and 1200W LP.

As seen from the figure the decay in CC concentration followed approximately zero order kinetics. In the actual system the removal of CC typically slowed down when reaching a level of around 0.3 mg/l. The results indicated that there was a pool of more slowly degradable CC compounds which could not be removed during short time photolysis (from one day to the next). In periods where the pool was closed for 1-2 days it was possible to further degrade these slowly degradable CC compounds and bring the CC concentration down to 0.1-0.15 mg/l. Due to the existence of these slowly degradable CC compounds, the CC removal capacities of the UV-technologies were determined only from the initial removal rates as showed in figure 3.

The CC removal rate for the LP lamps was found to be significantly lower than for the MP and combined lamps in all degradation experiments. This can be explained by a low quantum yield of the photolysis of monochloramine with LP-UV of only 0.4 mole Es^{-1} /1/ or a low concentration of monochloramine in the pool water as LP-UV primarily removes monochloramine due to an UV absorbance maximum by monochloramine near 254 nm where LP-lamps emit their UV light /1/. Recent studies on formation of DBP´s using MIMS indicate very low monochloramine concentration in pool water is very low /2/. The far higher degradation rate observed for the MP or combined lamps can be explained by the wider range of the UV-spectrum emitted by the MP lamp targeting other CC species with other UV absorbance maxima like dichloramine (207 and 297 nm) /3/ and trichloramine (225, 260, 343 nm) /4/ and possibly also some organic chloramine species.

Based on the data in figure 3, the CC removal capacities were estimated to 0.24 g/h, 1.3 g/h and 1.3 g/h for the LP, MP and combined MP+LP lamps respectively. However, removal capacities were concentration dependant and maximum capacities ranged from 1.3 and up to 3 g/h.

The level of CC in the pool during long-term operation of UV-photolysis with the different lamp combinations is shown in figure 4 and compared to a reference period (no UV-treatment).

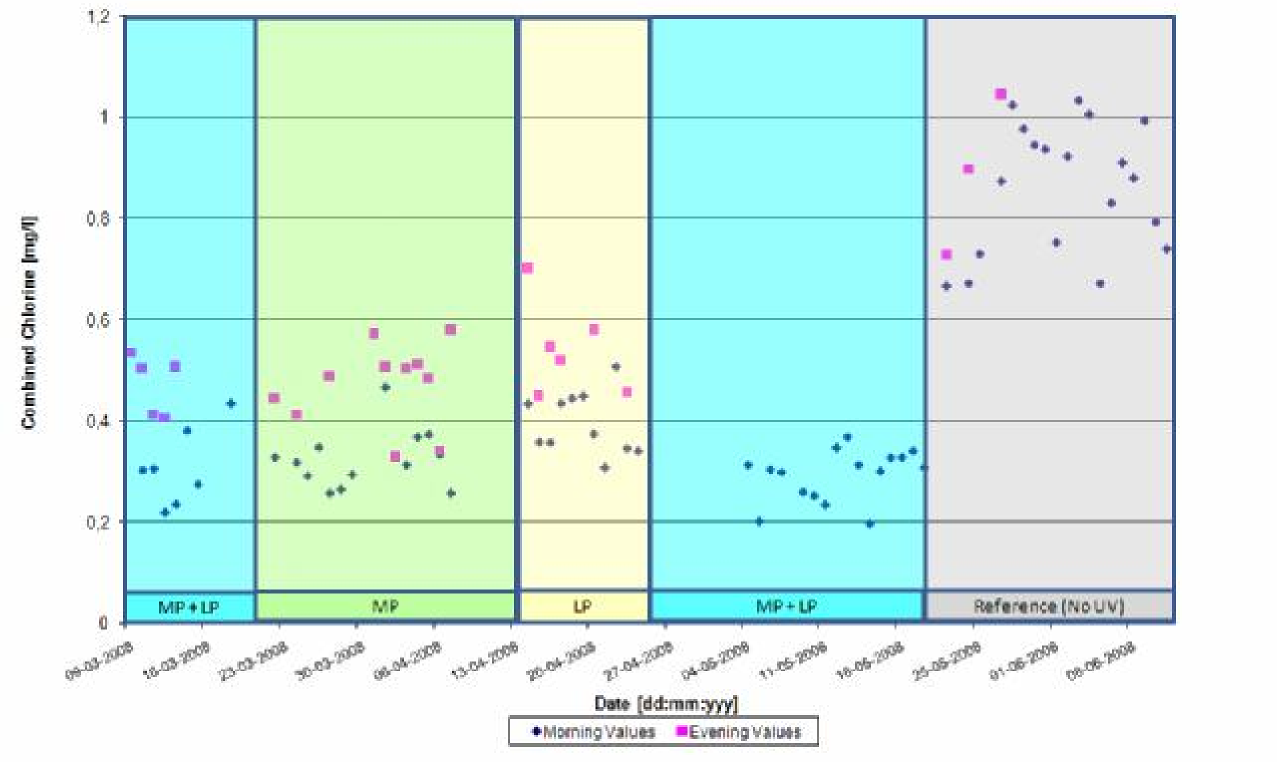

Figure 4 Combined chlorine in the pool for the various UV-technologies and without removal.

Despite the continuous removal of CC by the UV-treatment, a build-up in the CC concentration is observed during day-time peaking at pool closure. This shows that during opening hours the formation of CC is faster than removal by the UV-treatment. However, average CC concentration during irradiation is 0.3-0.4 mg/l compared to an average of 0.9 mg/l during the reference period.

In table 4, minimum, maximum and average concentrations of morning values of CC is shown for the different combinations of lamps and reference period together with the average daily bather load in the corresponding periods.

Table 4 Data for morning concentrations of CC in the pool water

	MP+LP	MP	LP	Reference
Average	0.30	0.33	0.39	0.82
Mimimum	0.20	0.26	0.31	0.67
Maximum	0.43	0.47	0.51	1.03
Bather Load [Bather / day]	231	262	238	292

Despite the slower removal rate of combined chlorine of the LP-UV lamps only a slightly higher overall CC concentration is observed (0.4 mg/l) compared to the MP and combined MP+LP lamps (0.3 mg/l as Cl_2). Thus, the installed UV-technology has a significant excess capacity in terms of UV-energy and possibilities for energy savings in operation exist.

During testing of the UV/TiO_2 no differences in the CC content compared to the reference period was observed. For the testing of the UV/Ozone technology the same UV-technology as used for the direct photolysis experiments was used and the CC content during the testing of UV/Ozone was comparable to the level when testing the MP+LP lamps alone (Data not shown).

TTHM

Figure 5 shows a typical pattern for concentrations of bromdichlormethane, chloroform and TTHM as monitored by the MIMS over a 9 day period.

TTHM concentrations varied significantly within a day, from day-to-day and over the week showing that the TTHM concentration is a highly dynamic parameter which is influenced by range of parameters and processes. The variations within a day followed a typical pattern where the TTHM concentration declined from pool opening until closure and increased during night-time. The decline during daytime was caused stripping of chloroform from the pool surface due to activity in the pool. The build-up during night time may be explained by higher formation rates compared to the “passive stripping” rates without activity in the pool. The results illustrate that processes governing TTHM concentration in the water are complex /5/ and even small variations of chlorine concentration, bather load, pool activity, back-flush frequency of sand filters, etc. have significant influence on the actual TTHM level.

Our results indicate that interpretation of experimental results based on the analysis of low-frequent grab samples in pools with high temperature and high bather load may be misleading. Depending on the local situation analytical results of grab samples are of limited value and may cause errors regarding establishment of correlations between processes/technologies and pool water quality.

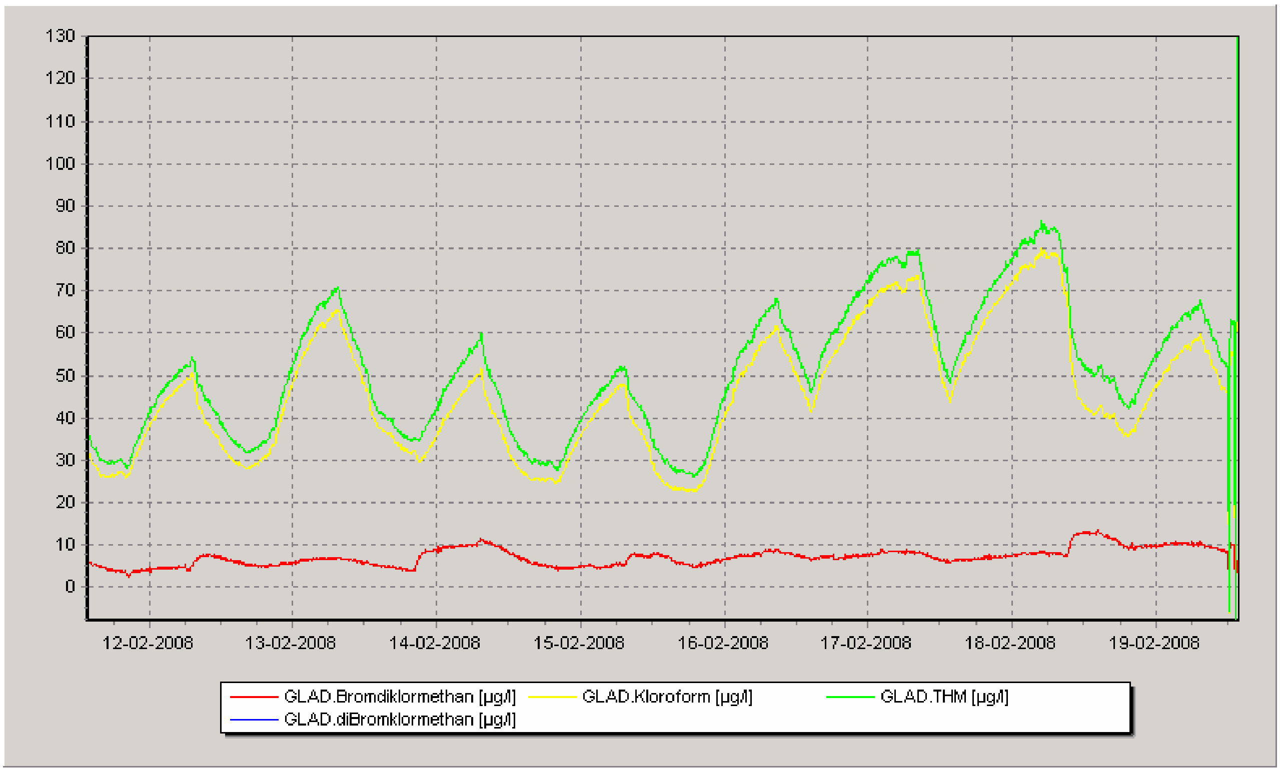

Figure 5 Typical daily variation pattern for TTHM in the pool.

In Gladsaxe, chlorine is produced by inline electrolysis of NaCl in the pool water. This process requires an increased concentration of sodium chloride in the pool water. Therefore, salt is added with varying frequency depending on the amount of freshwater make-up. TTHM monitoring results indicate that addition of salt had a visible influence on the composition and concentration of TTHM (Figure 6).

Figure 6 illustrates the increase of bromdichlormethane and total THMs immediately after addition of salt. The likely explanation is that the added salt contained trace amounts of bromide which upon oxidation with hypochlorite formed hypobromite reacting with organic compounds in the pool water and generating brominated THM´s. Brominous acid may form even higher concentrations of THM´s than chlorine /6/. The elevated level of bromdichlormethane was observed to remain in the pool water for 2-3 days after the addition of salt. This is probably caused by a lower stripping rate of bromdichlormethane due to a lower Henry´s constant and vapour pressure and a relatively low photolysis rate of bromdichlormethane in the UV-technologies. Although photolysis might be the major removal mechanism above, as brominated THM´s is fairly easily removed by UV-photolysis, the quantum yield of this process is fairly low, 0.43 mol Es^{-1}, for which reason the rate might be slow /7/.

In general, the elevated TTHM concentrations caused by salt addition complicated the interpretation of experimental results, although the influence from the salt addition was minimised during the project by changing the salt addition strategy from adding 100 kg at a time to adding 25 kg a day with a higher frequency.

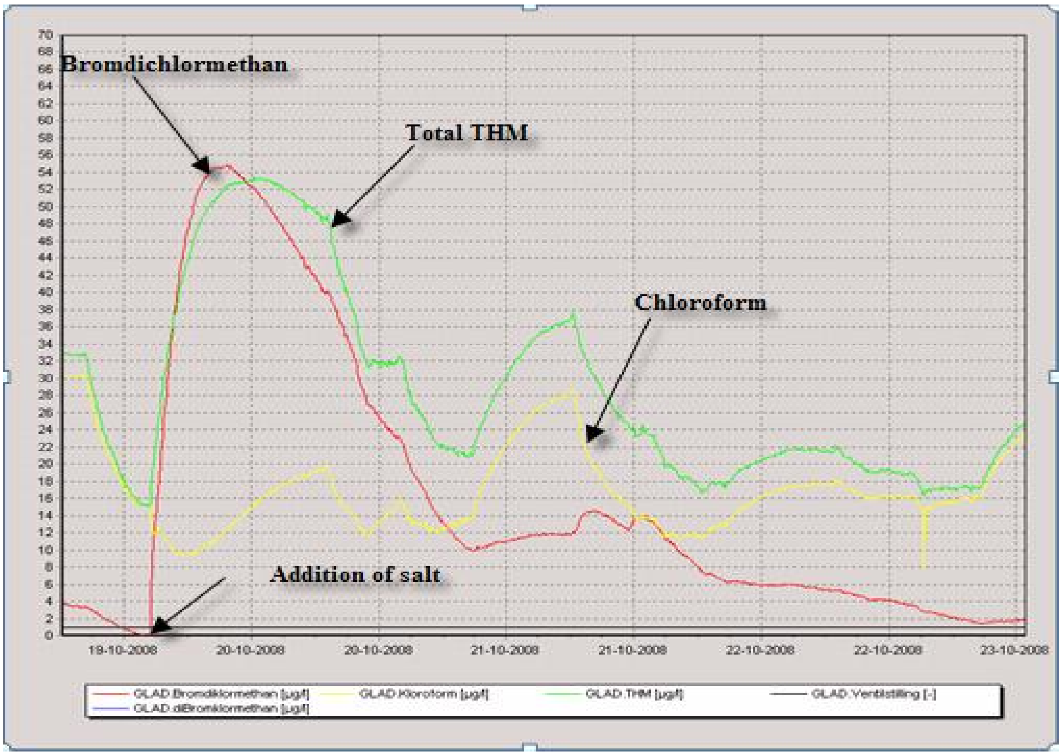

Figure 6 TTHM composition after addition of sodium chloride.

As shown in figure 5 the TTHM concentration peaked in the morning just before pool opening. To assess the influence of the UV-technologies on the TTHM concentration in the pool water, the daily peak values have been plotted as a time series and the periods with operation of different UV-technologies as well as reference periods have been marked on this plot as seen in figure 7.

Variations of the maximum daily TTHM values indicate that it is difficult to identify general trends comparing different technologies except for the period with UV/ozone, when a stripper was installed for ozone removal. This step significantly lowered the TTHM concentration moving the chloroform from the water- to the gas phase. Bather load monitoring also showed large variations and this may be another possible reason for the variations in maximum daily TTHM values. A correlation plot between peak TTHM values in the water and bather load is shown in figure 8.

Only a very weak correlation is measurable between bather load and maximum daily TTHM values, although the general trend shows increasing maximum daily TTHM values with increasing bather load. This may be taken as another argument for the complexity of TTHM formation in swimming pools, and that several parameters influence the actual concentration at any instance of time. The weak correlation to bather load may be caused by an influence from bather load on the TTHM formation on different time scales. There is an immediate and fast formation of TTHM probably from reactions of chlorine directly on the skin of the bathers, when the bathers enter the pool /5/. Secondly, there is a slower formation from larger organic macromolecules released from the skin that accumulates in the water and is more slowly converted to TTHM /8/. Thirdly, there is a TTHM formation from organic particles that accumulate in the sand filters in between filter back-wash.

Thus, the bather load will probably contribute to TTHM formation through both instant and accumulative mechanisms for which reasons a good correlation directly between bather load and TTHM concentration is not to be expected.

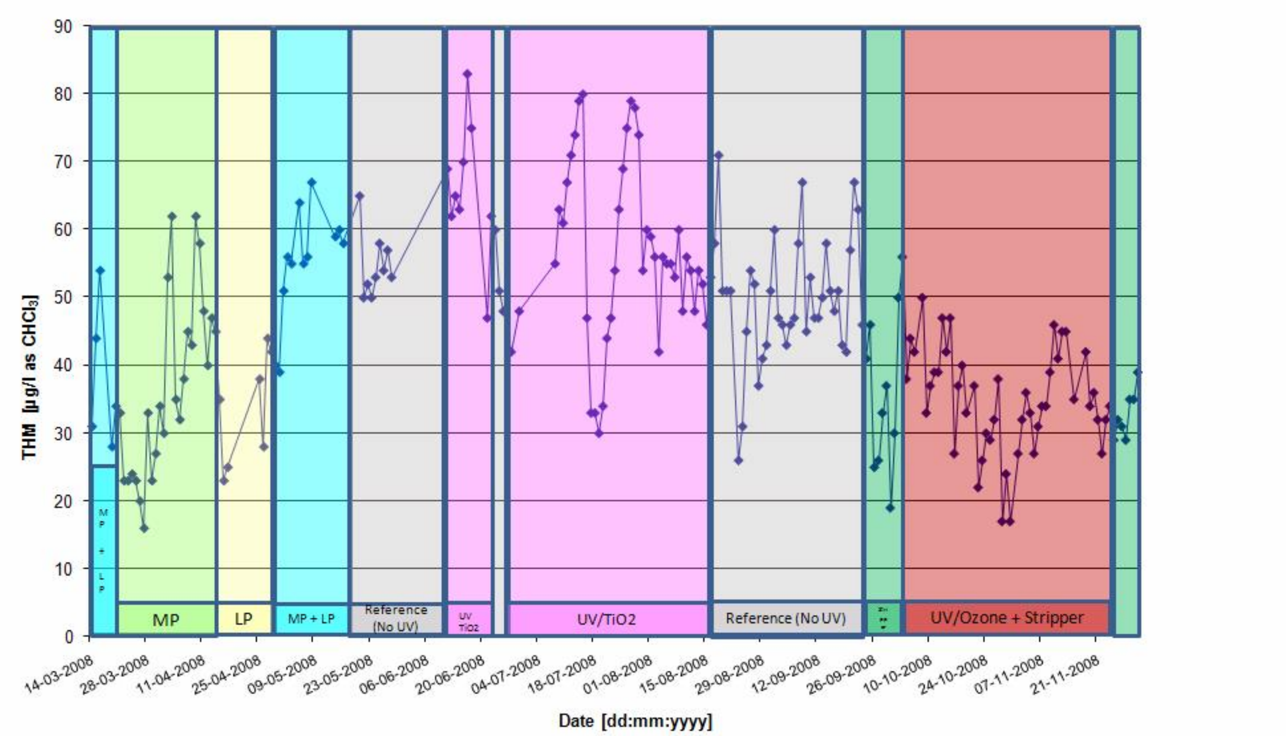

Figure 7 Daily peak TTHM in the pool water throughout the test period. .(MP=medium pressure UV lamp, LP=low pressure UV-lamp)

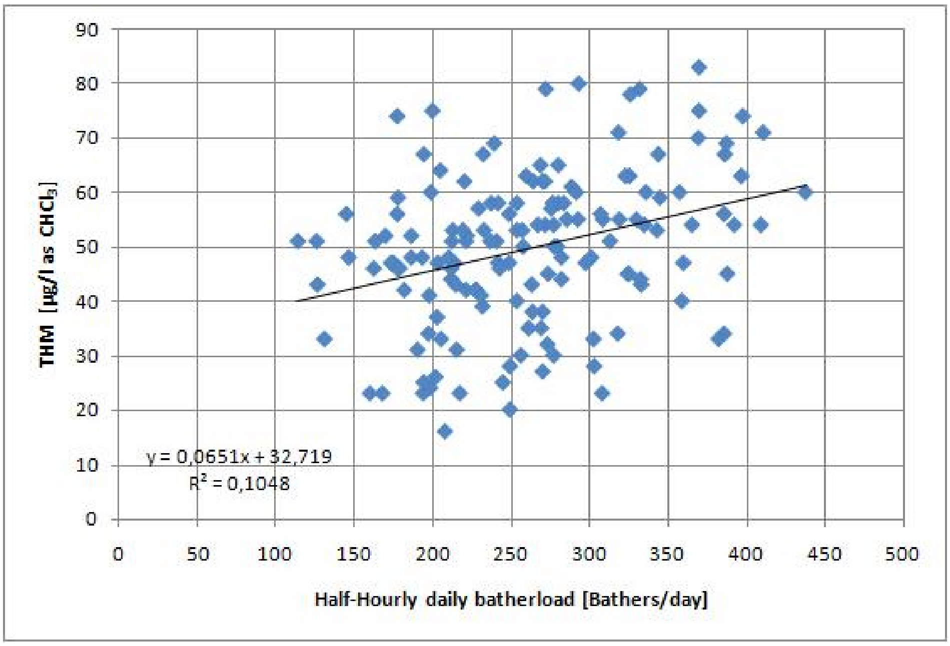

Figure 8 Maximum daily TTHM as a function of bather load.

In order to assess the influence of the different UV-technologies on the TTHM concentration in the pool water, the data for daily TTHM peak values were normalised to bather load, statistically processed and summed up in table 4.

Table 4 Daily peak TTHM values for various UV-treatments and reference data without UV

	Average peak TTHM [µg/l as $CHCl_3$]	Half-hourly daily bather load [Bathers/day]	Average peak TTHM normalised to bather load [µg/l·bather]
Combined MP+LP	53 ± 5.6	231 ± 25	0.22 ± 0.04
MP	37 ± 4.8	262 ± 23	0.14 ± 0.02
LP	34 ± 6.4	238 ± 15	0.14 ± 0.03
UV/TiO_2	59 ± 3.5	297 ± 21	0.19 ± 0.02
UV/Ozone + Stripper	35 ± 2.3	262 ± 17	0.13 ± 0.01
Reference	49 ± 2.3	233 ± 16	0.22 ± 0.02

During the various technology test periods, no significant increase in TTHM level could be observed when comparing the TTHM levels in the pool water during periods with UV treatment with reference periods with no UV treatment. This is contrary to results published so far, claiming that medium pressure UV-treatment may lead to elevated TTHM concentrations in pool water, e.g. /9/.

Delphine et al. /9/ suggested that increased TTHM concentration could be due to reactions with free chlorine radicals generated through the photolysis of free chlorine. However, the rate of formation of photo oxidants (i.e. hydroxyl radicals and chlorine radicals) from chlorine photolysis has been studied in detail in several recent studies /1, 10, 11/. From these studies it may be derived that the predominant photo oxidant produced during chlorine photolysis is OH radicals and that the rate of formation and reaction of the chlorine radical is negligible in the presence of organic compounds acting as radical scavengers /1,10,11/. Other authors /11,12/ further showed that UV photolysis of free chlorine in pre-chlorinated drinking water significantly decreases the TTHM formation due to both degradation of organics from the hydroxyl radicals and the lowered chlorine content to react with the organics. Thus, it seems unlikely that the increased TTHM concentrations observed during medium pressure UV treatment of swimming pool water is due to effects from the UV-treatment. More likely explanations for such observations might be dynamic variations taken into account or increased free chlorine concentration, which in the present study has been found to have a very significant influence on the TTHM level in the pool.

Conclusions

Three UV based technologies were tested in full scale at a 50 m^3 warm water pool at Gladsaxe Sport Centre in Denmark. Medium pressure UV photolysis (1200W) in a 25% side stream treatment loop showed efficient for control of combined chlorine while low pressure UV photolysis (1200W) was considerably less efficient. Even with this technology installed the lowest (morning) concentrations of CC observed were around 0.2-0.3 mg/l. This level of CC, was difficult to reduce by photolysis and could be decreased only after 1-2 days without any bathers using the pool. TTHM was monitored on-line by Membrane Inlet Mass Spectrometry. TTHM was a highly dynamic parameter with significant diurnal variations showing decreasing values during opening hours due to activity in the pool causing TTHM stripping and increasing values over the night when the TTHM formation was higher than the passive stripping. Also significant variations over the week were observed. Our results clearly indicate that monitoring of TTHM in relatively high loaded pools based on grab samples is of limited value and might cause serious misinterpretation regarding water quality. When comparing the TTHM levels in the pool water during periods with UV treatment with reference periods with no UV treatment, no difference in TTHM level could be observed. Advanced oxidation with UV in combination with ozone was able to lower significantly the NVOC level (Data not shown) without any similar effect on the TTHM level and the AOX level. The side-stream stripper applied to avoid any ozone from entering the pool area was, however, very efficient in bringing down the TTHM level in the pool water.

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