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Disinfection byproduct formation in swimming pools

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Abstract

The fate of organic nitrogen and carbon introduced into a swimming pool by pool users has been studied using a 2.2 m^3 model pool. The study made use of a body fluid analogue, containing the primary endogenous organic amino compounds, and a soiling analogue represented by humic acid. The system was used to examine the effect of organic loading and organic carbon source (i.e. amino or humic acid) on the levels and speciation of the key chlorinated disinfection byproducts (DBPs) of trihalomethanes (THMs) and chloramines under operating conditions representative of those employed on a full-scale pool.

Results revealed organic carbon (OC), chloramines and THMs to all attain steady state levels after 200-500 hours of operation, reflecting mineralisation of the dosed OC. Steady state levels of OC were roughly linearly dependent on dose rate over the range of operational conditions investigated and, as with the chloramine levels recorded, were in reasonable agreement with those reported for full-scale pools. THM levels recorded were somewhat lower than those found in real pools, and were dependent on both on pH carbon source: the THM formation propensity for the soling analogue was around eight times than of the body fluid analogue. Of the assayed byproducts, only nitrate was found to accumulate, accounting for 4-28% of the dosed amino nitrogen. Contrary to previous postulations based on the application of Henry's Law, only insignificant amounts of the volatile byproducts were found to be lost to the atmosphere.

A mathematical model based on a consideration of equilibrium thermodynamics was shown to accurately predict the formation of chloramines and decay of chlorine for ex-situ closed-bottle experiments. Extension of the model to the pilot pool is problematic, however, since more empirical data from the chlorination of individual BFA constituents is required for this.

Keywords   Swimming pools, chlorination, disinfection by-products, trihalomethanes, chloramines, nitrate, humic acid, organic carbon.

1   Introduction

Two key disinfection by-products (DBPs) in swimming pools are trihalomethanes (THMs) and chloramines. Their health impacts have been subject to much study over the years (Table 1). No UK statutory regulations exist for levels of these DBPs in pools. Organisations such as the Pool Water Treatment Advisory Group (PWTAG) and the World Health Organisation (WHO) provide guidelines based on the precept of free chlorine levels being as low as possible whilst still providing adequate disinfection. Both the level itself and the chlorine demand required to maintain this level vary between pools due to the variation in the water treatment technology applied and the bather load with which it is challenged. Recommended levels in mg/l as Cl_2 are 1.5-2 in the UK, 1-3 in the USA, and 0.6-1.2 in Italy, (WHO 2000). However, pools run under the appropriate conditions can successfully and safely operate at a concentration of 0.5 mg/l or less, and the German DIN standard specifies that 0.2 mg/l can be used when dosing sodium or calcium hypochlorite at a pH of 6.9.

Table 1   DBP health effects

Reference	DBP	exposure route	type of danger investigated	subject	measured effect?	level needed to 'cause harm' or NOAEL level
Eaton *et al*, 1973	CA	blood/ dialysis	methaemo-globinaemia	human	yes	1 mg/l CA in blood
Daniel *et al* 1990, 1991	MCA	ingestion	toxicity	1)rats 2)mice	yes	NOAEL = 1)5.8 and 2) 8.6 mg/kg body weight
Robinson *et al*, 1986	MCA	dermal	hyperplasia (increased skin cell growth)	mice	no	No effect immersing in 1g/l for 10 minutes a day, for 4 days
Abdel-Rahman et al, 1982 and Carlton et al 1986	MCA	ingestion	reproductive or developmental toxicity	'lab animals'	no	No effect up to 15mg/kg body weight
NTP, 1992	CA	ingestion	carcinogenicity	mice	yes	>100 mg/l dose shows positive response
Keegan *et al* 1998	$CHCl_3$	ingestion	liver damage	mice	yes	>60g/kg body weight, NOAEL = 30g/kg
Templin *et al* 1996 (a) & (b)	$CHCl_3$	inhalation	hepatic (liver cell) growth	1) mice, 2) rats	no	1)<446mg/m^3 $CHCl_3$ for 6 hrs/7days a week. 2) NOAEL = 50mg/m^3
Jaimison *et al* 1996	$CHCl_3$	inhalation	hepatic (liver cell) growth	rats	yes	1490mg/m^3 for 90 days gave positive response

Since DBP levels in pool environments are strongly influenced by the treatment technology employed, it is of obvious interest to assess these technologies with specific regard to DBP formation on a common basis. No recognised protocol for testing these technologies currently exists, such that manufacturers' claims regarding the effectiveness of their products remain difficult to substantiate. Most evaluations are based on bench scale tests performed by the company and/or anecdotal evidence from pool operators. Such evidence is not always relevant or transferable due the varying requirements and operating parameters of different pools.

Results have recently been reported (Judd and Black, 2000) for a pilot-scale pool in which all operational parameters, including the dose of body fluids from bathers, were controlled. These data suggested that THM levels are:

- sensitive to the bromide concentration in make up water
- vary slightly with pH between ranges of 7.2-7.8
- vary greatly with the synthetic bather load, as provided by an analogue of key body fluid constituents, and
- sensitive to intermittent dosing

More significantly, a simple mass balance performed by the authors revealed that a large proportion of the carbon, nitrogen and chlorine was unaccounted for. It was speculated by the authors that, although steady-state levels of THMs were achieved within 3 days, accumulation of both chlorinated and unchlorinated organic matter may be taking place in the pool.

In the current study the same test pool as that of Judd and Black, which employs treatment processes applied in an average municipal swimming pool, has been used to conduct a more rigorous analysis in which additional wastewater quality determinants have been measured and a modified bather load analogue used. In addition to sampling for THMs and chloramine, the latest tests have included measurement of total organic carbon (TOC), total carbon (TC), nitrate (NO_3^-) and total nitrogen (TN). As with the previous study, the bather load was replicated using a body fluid analogue (BFA) to represent endogenous species in urine and sweat, but in this latest study humic acid was added to replicate soiling.

2 Experimental

2.1 Materials

The test pool has been described in detail by Judd and Black (2000). The pool is approximately $2.2m^3$ in volume and is a one-seventh linear scale model of the 25m installation at Cheltenham College, Cheltenham, UK. The treatment system includes in-line free chlorine measurement and hypochlorite addition, in-line pH adjustment, sand filtration, temperature control and air circulation. Design and operating parameters are included in Table 5.

2.1.1 Bather load

The BFA formulation was a modified version of that previously used (Judd and Black, 2000). Since the inorganic chemicals used in the original analogue were found to have no effect on DBP formation, they were omitted from the formulation used in the current study. Whilst the BFA formula (Table 2) does not contain *all* of the chemicals present in urine and sweat, the total absolute and relative concentrations of carbon and nitrogen are similar to those found in a 4:1 mixture of sweat and urine (Putnam, 1971). 200ml sweat and 50ml urine were assumed to be emitted from an average bather every hour (Judd and Black, 2000), and the bather loading rates were calculated based on an average pool volume of $500m^3$ and pool operation for 12 hours a day and 7 days a week. Organic soiling (dirt) from natural organic matter (NOM) was represented by humic acid (HA) which, along with fulvic acids, may constitute as much as 95% of the total dissolved NOM in aquatic systems (Stevenson, 1994). Of these two fractions, humic materials have the highest THM formation propensity (Trussel and Umphres, 1978; Krasner *et al,* 1996).

Table 2 BFA formulation, adapted from Judd and Black (2000)

Constituent	Concentration mg/l	Carbon[3], mg/l	Nitrogen mg/l	Grade and supplier
Ammonium Chloride	2000	-	520	BDH 'AnalaR'
Urea	14,800	2,960	6,900	BDH 'AnalaR'
L-Histidine	1,210	560	320	Aldrich 98%
Hippuric acid	1,710	1,040	134	Aldrich 98%
Uric acid	490	180	160	Aldrich 99+ %
Citric acid	640	240	-	Fisher 'SLR'
NaH_2PO_4	4,300	-	-	BDH 'AnalaR'
Creatinine[1]	1800	770	67	Aldrich 99%
TOTAL[2]	-	**4,980**	**7,890**	-

[1]run 6-9 only, [2]not including creatinine, [3]96-98% organic

2.1.2 Chemical dosing

Chlorine was dosed into the pool as sodium hypochlorite diluted to 24g/l as Cl_2. pH was regulated using 35% w/w hydrochloric acid (Table 3). The dosing of both the hypochlorite and hydrochloric acid was controlled using a *Dulcomarin* chemical dosing/regulating control panel (ProMinent Fluid Controls, Ashby), and pumped on a demand-only basis. The four *Gamma G4* self-metering chemical dosing pumps used were also supplied by ProMinent Fluid Controls. The humic acid (HA) was diluted to 0.39g/l and centrifuged at 7500 rpm for 5 minutes before being filtered using *Schleicher & Schuell* Grade 52 filter paper to remove suspended solids before dosing. All water used in dilutions and to fill the pool was deionised using standard twin bed ion exchange equipment.

Table 3   **Reagents used**

Chemical	Grade	Concentration	Supplier
Sodium hypochlorite	GPR grade	12% w/v as Cl_2	Merck Ltd. (Lutterworth, Leics.).
Hydrochloric acid	GPR Rectapur ™	35%	Merck
Humic acid (HA), disodium salt	99+%	around 39% C[1]	Sigma Aldrich Ltd (Poole, Dorset)
Methanol	AnalaR grade	99.8+%	Merck Ltd.
Sodium thiosulphate, anhydrous	GPR	97%	Merck Ltd.
Deionised water	Chiltern 'Hydrofine 200',		USF, Derbyshire

[1]approximately 96-98 % organic carbon

2.2   Methods

2.2.1   Air sampling

Trials were carried out both to test the efficiency of the sampling process adopted and to estimate pool atmosphere THM and chloramines levels. The sampling efficiency of the absorption system used was assessed by sparging a water sample containing a known quantity of THMs sample and passing the gas through two sequential absorption vessels, either at ambient temperature or at 5°C. Each vessel comprised a sintered glass aerator in a Dreschel bottle containing water or a water/methanol 50:50 mixture. The pool atmosphere was sampled at the same air flow rate as the control experiment. The absorbent was then assayed for THMs and/or chloramines.

2.2.2   Water sampling

Samples of water were extracted from 1cm below the pool surface for chloramine, nitrate, total nitrogen and TOC analysis. All were stored at 5°C for no more than 3 hours prior to analysis. Samples for THM analysis were obtained using a method adapted from that specified in standard methods 1060B(b) (APHA, 1998) for composite sampling. A 1L sample was taken directly from the pool, quenched with sodium thiosulphate, and then stirred for 5 minutes in a sealed container before apportioning into 3x15ml amber glass vials with PTFE-lined stoppers for storage.

Temporal analysis of the pool water revealed the original sampling method of taking single samples (Judd and Black, 2000) to be subject to wide standard deviation due to the intermittent dosing of chlorine and the volatility of THMs, and chloroform in particular. Spatial analysis of the pool water showed this variation was not simply due to variation in depth of sample extraction or proximity to inlet points. Recourse to composite sampling reduced the standard deviation to around 25%.

2.2.3   Analyses

Analytical methods and instrumentation are summarised in Table 4. Free and combined chlorine levels were assayed using the conventional DPD test (APHA 1998). THM concentration was measured using a purge-and-trap gas chromatograph fitted with a 0.53 mm diameter, 15m long column, and an electron capture detector. All samples were quenched before analysis using sodium thiosulphate, and stored in a refrigerator.

Table 4   **Water quality determinant measurement: instrumentation**

Determinant	Instrument	Range/LoD	Supplier
Nitrate	Nitrate Chromotropic Acid test kit	0-30 mg/l	*Camlab*, Over, Cambs.
Total Nitrogen (reading of above tests)	TNT test kit	0-150	*Camlab*, Over, Cambs.
	Hach 2010 portable datalogging spectrophotometer		*Camlab*, Over, Cambs.
THMs	purge-and-trap GC	0.5-100μg/l	*Interscience*, Dublin
TOC & TIC	TOC 5000A Shimadzu	0-500mg/l	*Shimadzu*, Milton Keynes

2.2.4   Test pool operation

Operating parameter values for the test pool are summarised in Table 5, and specific conditions appropriate to each run stipulated in Table 6. Carbon dose rates were calculated from TOC measurements of both the BFA and the HA solutions. Dose rates of N were calculated from the BFA chemical formulation. The contribution to the N balance from the humic acid was assumed to be insignificant at the doses applied.

Table 5   **Test pool design and operating parameter values**

Parameter	Value
Volume of pool (head space), m^3	2.2, 12
Circulation, m^3/hr	0.85
Water turnover time, hrs	2.5
Air flow, m^3/hr	72
Air turnover time, hrs	0.17
Temperature of water (air), ^oC	29 (30)
pH (limits)	a) 7.8 (7.7-7.9), b) 7.2 (7.1-7.3)
Free chlorine, mg/l	a)1.8 (1.7-1.9), b) 0.5 (0.45-0.55)
Air sampling rate, l/min.	*0.1-0.4*
Air sampling time, mins.	*5-120*
Validation experiment flow rate, l/min	*0.13*
Validation experiment time, mins.	*3-45*

Table 6   **Test pool operating conditions**

Run no.	pH	Free Cl_2 level mg/l	Bather dose (bathers/m^3/hr)	Carbon dose, g/hr C (from BFA)	Nitrogen dose, g/hr N (from BFA)	Carbon dose, from humic acid, g/hr C
1	7.8	1.8	0.06	0.082	0.1305	-
2	7.8	1.8	0.12	0.164	0.261	-
3	7.8	1.8	0.12	0.164	0.261	0.009
4	7.8	1.8	0.12	0.164	0.261	0.019
5	7.8	1.8	0.15	0.210	0.333	-
6[1]	7.8	1.8	0.1	0.137	0.217	-
7[1]	7.8	1.8	0.3	0.411	0.651	-
8[1]	7.8	1.8	0.1	0.137	0.217	-
9[1]	7.8	1.8	0.1	0.137	0.217	-
10	7.2	0.5	0.12	0.164	0.261	0.019

[1]with creatinine

3   Results

3.1   *Physical model*

Results (Tables 7-9) show that the levels of chloramines recorded were similar to those reported in the previous study by Judd and Black (2000). The THM levels, however, were much higher than those recorded previously and closer to, though still significantly lower than, those encountered in real pools (Table 7). Research into chlorination of other potential bather load constituents has shown that saliva and beauty products such as moisturising lotion are significant precursors for THMs as well as other DBPs such as dichloroacetonitrile (Kim *et al*, 2002). Quantification of specific precursors using such proprietary products is however, not possible, as formulations vary considerably between products.

Table 7   Comparison of pool data to that found in the literature

Parameter	Concentrations measured in the literature		Current study
	Concentration	*Reference*	
Total THM, ppb	43 – 543	Chambon et al (1983)	**5-65**
	19.5 – 31.1	Jo (1994)	
	9 –179	Aggazzotti et al (1995)	
Monochloramine, mg/l as Cl_2	0.06 - 0.8	Lomas (1967)	**0.05-0.4**
Dichloramine, mg/l as Cl_2	0.18 - 2.58	Lomas (1967)	**0.25-5**
Nitrate, mg/l	0-20	Beech (1980)	**0-22**
TOC, mg/l	3.8 –20.4	WRC/ DoE (priv. comm.)	**6.5-28**

3.1.1   *Chloramines*

In all runs, both mono- and di-chloramine (NH_2Cl and $NHCl_2$) concentrations reached a steady-state level. In the case of NH_2Cl, steady state was achieved after around 100 hrs of operation. In the absence of humic acid dosing the NH_2Cl and $NHCl_2$ equilibrium levels increased with increasing bather load. Dosing with HA at the lowest rate of 9 mg/hr (Run 3) had no significant effect on chloramine formation, whilst doubling the HA dose rate almost doubled the equilibrium concentration (0.9-1 mg/l compared to 0.5-0.6 mg/l). This would appear to corroborate research by Vikesland *et al* (1998) which has shown that addition of NOM, in the form of humic acid, facilitates the breakdown of NH_2Cl which may go on to form $NHCl_2$.

The addition of creatinine to the BFA formula significantly increased the $NHCl_2$ reading (up to 5mg/l), although it is known that when using the DPD/FAS titration method, a satisfactory endpoint cannot be reached during titration due to chlorocreatinine formation producing a false positive (Stottmeister, 1998). As expected from literature studies (McKee *et al*, 1960; Jafvert and Valentine, 1992), an increase in chloramine levels resulted from higher BFA dose rates (Run 1 vs Run 2) and $NHCl_2$ levels at lower pH values (Run10).

Table 8 **Results**

Run number	NH$_2$Cl equilib. level, mg/l as Cl$_2$	NHCl$_2$ equilib. level, mg/l as Cl$_2$	Average tTHM after equilib. (µg/l)	% equilib. THM as CHCl$_3$	% equilib.THM as CHCl$_2$Br	TOC accum. rate, mg/hr	TIC accum. rate, mg/hr	TOC equilib. level, mg/l	TOC equilib. time, hrs	alkalinity accum. rate, mg/hr as C	NO$_3$–N accum rate mg/hr	TN accum rate, mg/hr	Cl used, mg hr as Cl$_2$)	Actual chloride accum. rate[1], mg/hr
1	0.05	0.25	5-24	90-95	0-10	83		6.5	200	3-9	10, 17.6	4	370	1455
2	0.1-0.15	0.5	16	65	5-10	57	~50	14		23	21		1310	1168
3	0.15	0.5-0.6	20	63	8-20					40	45	63	2440	886
4	0.15-0.2	0.9-1	20-41	71	8-20	122	~50	13	600	39	74	74	3700	3137
5	0.1-0.15	>0.6	35-59	72-78	0-10		20	14	200	19	23-27		2000	
6	0.15	>1	5	66	0-10	100		>12	160	59	24		1220	
7	> 0.4	>5	51	72	0-10			28	250				6140	
8	0.15-0.2	1.1				123		7.5	150		9.2			
9	0.1-0.15	0.85				132		7.8	150		22			
10	> 0.2	0.45	35-65	75-85	15-20	146	16	16	500	12	40	132	1700	1321

[1] measured chloride accumulation rate minus the rate of addition from chloride in stock chlorine and BFA.

Table 9 **Elemental mass balance**

run	Init. TOC accum. in pool, % of dose	Initial TC accum. in pool, % of dose	%OC accounted for by init. THM accumulation	% N accounted for by NO$_3^-$	% N accounted for by init.chloramine accumulation	% N accounted for by TN	% N unaccounted for, total	% Chlorine accounted for[2]	% chlorine accounted for by NO$_3^-$ formation[3]
1	~100	~100	0.27	7.7-13.5	0.14		92[1]		
2	35	65	0.1	8	0.37		92[1]	91	6.4
3				17.2	0.26	24	76	37	7.4
4	74	105	0.06-0.15	28.4	0.20	28	72	71	7.9-10
5			0.30	6.9-8.1	0.12		93[1]	84	8.4
6	72			11.1	1.50		87[1]		
7				28.3	3.30		68[1]		
8	89			4.2	2.40		93[1]		
9	96		0.02	10.1	1.60		88[1]		
10	89	99	0.13	15.3	0.30	50	50	79	6.4

[1] Using nitrate and chloramines measurements. [2] Including chloramines measured in water (initial accum.), and chloride accumulation.
[3] Based on stoichiometry of $NH_3 + 4HOCl = 4HCl + 3H_2O$

3.1.2 THMs

Interpretation of the THM readings is influenced by the scatter in the data, which appears to be strongly influenced by the sampling method, and results quoted (Table 7) refer only to those of aggregated samples. At the lowest dose rates (Run 3) HA addition appears to have little effect. Doubling this rate, however, increased the tTHM concentration by around 150%, though the THM generation did not increase by more than 10% on doubling the dose further. Dosing with HA also resulted in a small increase in $CHCl_2Br$ generation: in Runs 3, 4 and 10 the $CHCl_2Br$ was always between 8-20% of the total THMs whilst in all other runs it never exceeded 10 %. Comparison of data from runs involving combined BFA/HA dosing with those of BFA alone reveals that carbon sourced from the humic acid has a THM formation propensity at least 8 times higher that of BFA carbon (Fig. 1). A decrease in both pH level and chlorine residual (Run 10 vs. Run 4) increases the tTHM concentration by a factor of 1.7 (Table 7), from a mean of around 30μg/l.
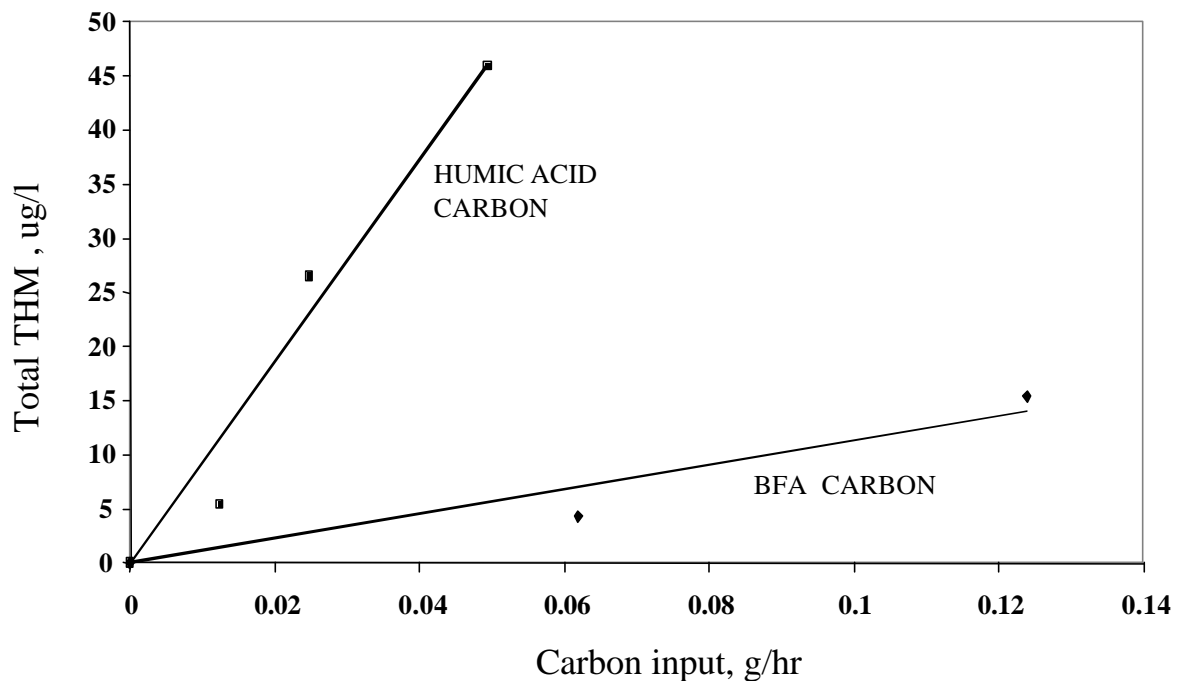
Fig. 1 Effect of humic acid on THM generation: total THM generated per g of carbon

pH influences not only the chlorine speciation but also that of humic acid, whose dissociation is also pH dependent. Experiments conducted at varying pH levels by Jiminez *et al* (1993) revealed that lower pH levels promote THM formation from NOM. Other research, however, reports the opposite effect of pH on THM levels (Singer, 1999), possibly due to differences in the experimental set-up of each study or variation in the precursors used.

3.1.3 Nitrate

Nitrate accumulation followed a linear trend, the rate depending on both the BFA and HA dose rates (Fig. 2). For Run 1 (0.06 bathers/m³.hr) a nitrate accumulation rate of 10-17mg/hr was recorded. Doubling this rate (Run 2), increased the rate to 21 mg/hr, and increasing the rate

further to 0.15 increased the rate to 23-27 mg/hr, and accumulation increased still further with dosing of humic acid (Fig. 3).
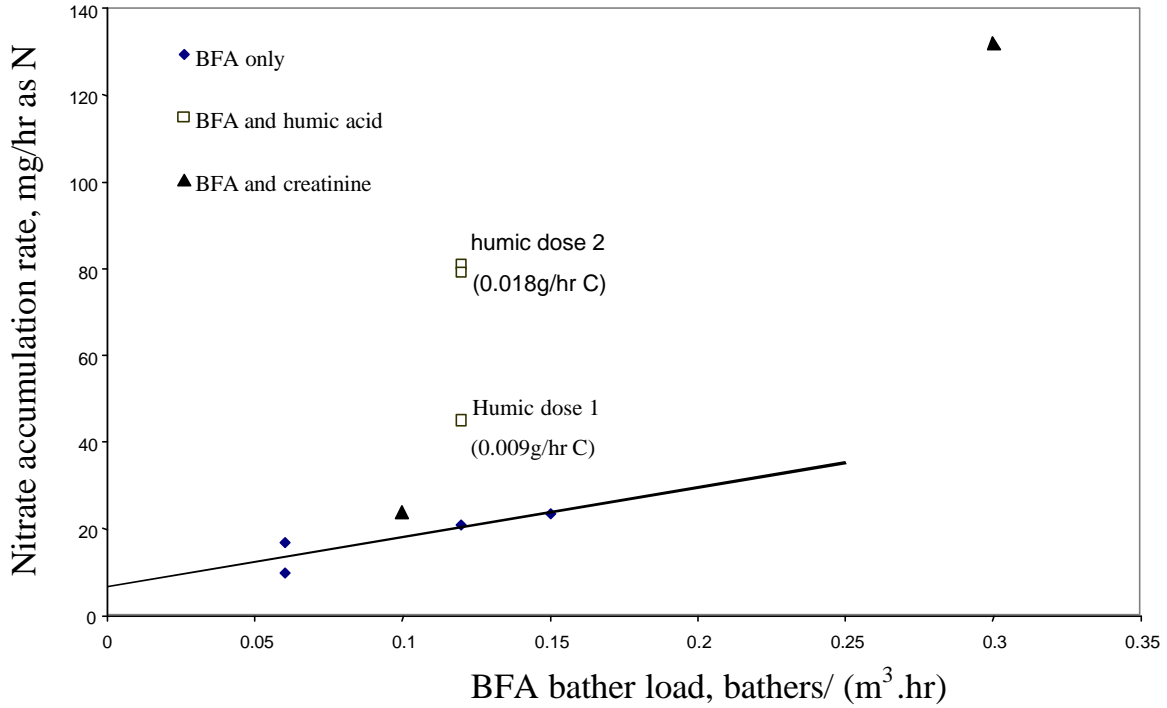

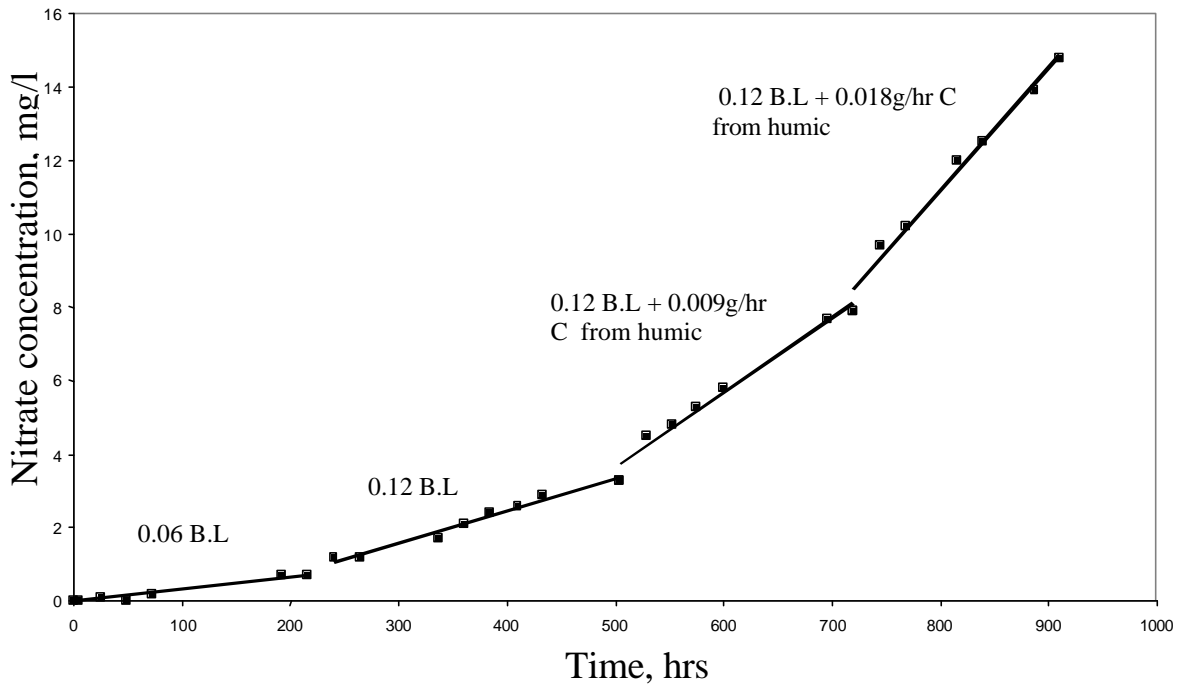Fig. 2 *Effect of humic acid, creatinine and bather load on nitrate accumulation rate*

Fig. 3 *Effect of adding humic acid to nitrate accumulation rate*

The increased nitrate accumulation rate on HA dosing (Fig 3) would appear to be contrary to the notion that HA competes with ammoniacal species for the chlorine. However, this effect of HA was also noted by Vikesland et al (1998). When decomposition of NH_2Cl takes place in the absence of NOM the expected primary decay products are NH_3, N_2 and some NO_3^-. When NOM is present, however, the proportion of N_2 produced decreases and that of NH_3 and NO_3^- increases. Vikesland et al noted that only a small percentage of the NH_2Cl broken down in the presence of NOM could be accounted for by measuring the halogenated DBPs. This suggested another route for NH_2Cl decay, and it was postulated that NOM could also increase NH_2Cl decay without the formation of halogenated products. Humic substances can act as general acid catalysts, and as other studies have shown (McKee, 1960; Valentine and Jafvert, 1998), the disproportionation of NH_2Cl molecules to form dichloramine is acid-catalysed, such that this represents a possible decomposition route. The measured increase in nitrate production and the increase in the dichloramine equilibrium level in these experiments support both these hypotheses.
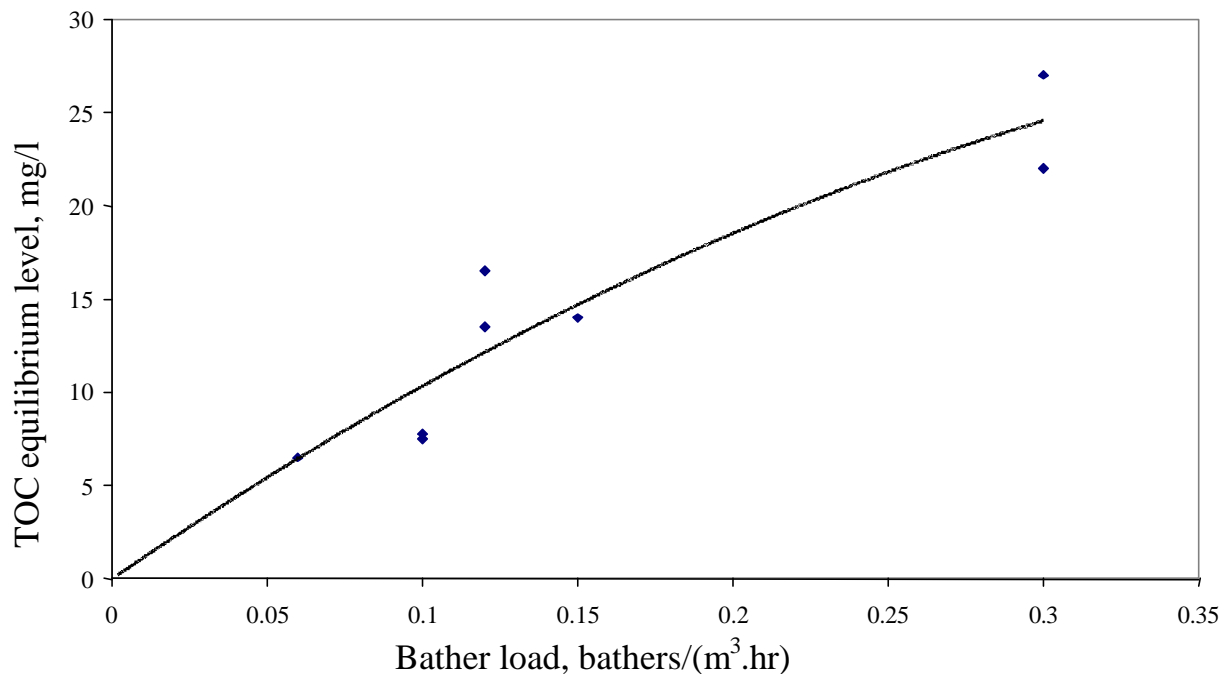

Fig. 4 Influence of bather load on TOC equilibrium level

Since, as a stable end product, nitrate accumulates continuously, dilution of pool water represents the only means of limiting nitrate concentration (as well as that of chloride). Results suggest that a high nitrate reading does not necessarily reflect a temporary overloading of a pool, for example after heavy use, but relates both to excessive bather loading combined with extended operation with insufficient dilution with fresh water. Simple dilution of water after backwashing once a week, as is normal practice, may not be sufficient to dilute those pools with higher bather loads.

3.1.4   Carbon
The OC was found to equilibrate after 150 to 600 hrs of operation. Both the equilibrium level (Fig. 4) and the accumulation rate appear to be roughly linearly related to dose rate. Decreasing the pH and/or chlorine level resulted in a rise in both the accumulation rate and equilibrium level

of the TOC (Fig.5). The inorganic carbon level (i.e. alkalinity) also decreased with decreasing pH, presumably because of the increasing CO_2:HCO_3^- ratio at lower pH levels. The OC concentration seemed to correlate with that of THMs: steady-state THM levels were achieved at around the same time as steady-state TOC levels.
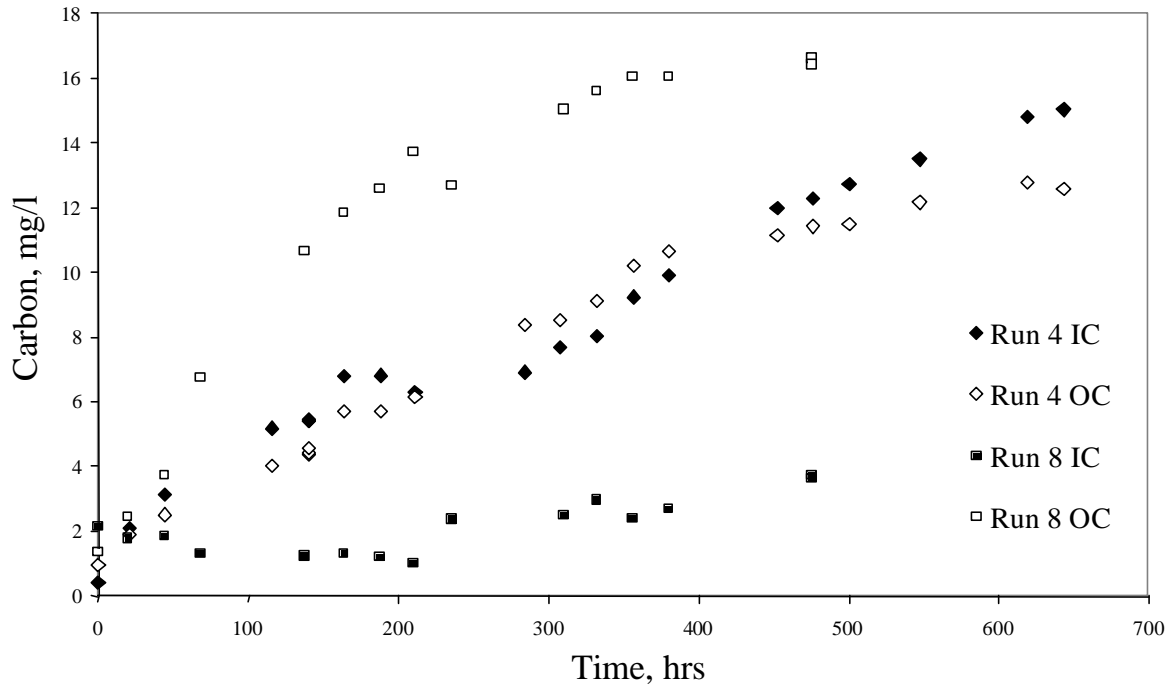

Fig. 5 Effect of differing pH on TC and IC equilibrium level and accumulation rate

3.1.5 Atmospheric discharges

The chloramine and THM concentrations measured in the absorbate were frequently close to or below the level of detection using the DPD/FAS titration method. However, the validation experiment showed the efficiency of the process to vary between 5-100 % and was not consistent under any condition. The LoD for the method (175 $\mu g/m^3$ in air, based on the GC limit LoD of 0.5 $\mu g/l$) was also too high to be able to effectively quantify the concentration measured in the pool air.

Assuming Henry's law constant applies (H = 0.00114 for $NHCl_2$ according to Holzwarth *et al,* 1984), the atmospheric concentration of $NHCl_2$ at a pool water concentration of ~0.7mg/l as Cl_2 would be predicted to be 0.8 mg/m^3. Hery (1995), using on an adsorptive air sampling method based on diarsenic trioxide, measured NCl_3 levels of 0.15 to 0.42 mg/m^3 as NCl_3 across six swimming pools, concentrations which are somewhat lower (on a stoichiometric basis) than the Henry's Law-based concentrations.

A 'zero ventilation' run was conducted to investigate whether the relatively low concentration of DBPs in the pool atmosphere (when compared to that calculated using Henry's law constant) was due to the high turnover rate employed. Results showed that concentrations of THMs and chloramines in the pool did not significantly increase as a result of reducing the air flow. This implies that equilibration of DBPs between the pool water and the atmosphere does not take

place and that that Henry's Law greatly overestimates atmospheric levels of THMs and chloramines.

3.2 Mathematical model

Each of the five BFA constituents were individually chlorinated at various Cl:C ratios in closed bottles, and the chloramines and free chlorine evaluated so as to formulate possible reaction mechanisms based on those of the Jafvert model (Jafvert and Valentine, 1992). Sample chloramine experimental and model data for the whole BFA are shown in Figure 6. Both the monochloramine and dichloramine levels predicted are within experimental errors of the empirical data. The concentration of chlorine dropped to approximately zero almost immediately which was also observed in the model predictions.
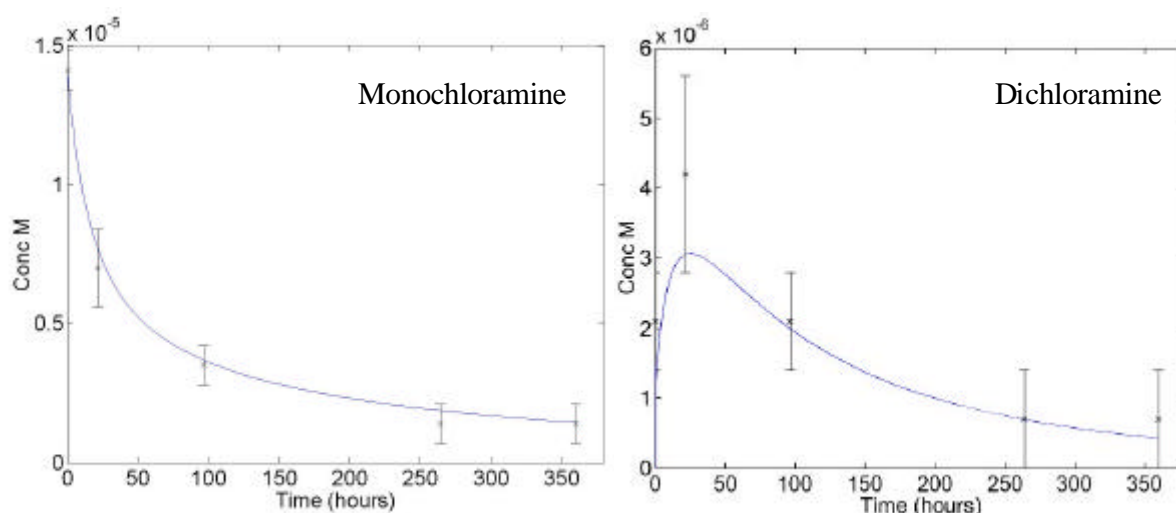

Fig. 6 Concentration transient for mono- and dichloramine for ex-situ tests

4   Mass balance

Mass balance calculations of carbon, nitrogen and chlorine were carried out (Table 9) in a similar way to that described by Judd and Black (2000), with the loss to the atmosphere being ignored.

4.1   Carbon

For the majority of runs the initial rate of accumulation of carbon in the pool has been measured and compared with that dosed into it. In most cases, the combination of the TOC and TIC accounts for 99-105% of the organic carbon dosed (Table 9), with the TIC being represented by alkalinity. Prior to equilibrium, it appears that little carbon is lost from the system and most of it remains as organic carbon, although alkalinity steadily increases throughout the run. At equilibrium 100% of the added OC and is lost from the system. Given that the THMs do not accumulate in the pool following the equilibration period, carbon must be either adsorbed or oxidised under steady-state conditions. There is no evidence for adsorption in the system, since (a) the concentration profile for the TOC does not resemble a typical sigma breakthrough curve, and (b) measurements of TOC in the filter backwash water at the end of each run, the sand filter

presenting the largest surface area available for adsorption loss, revealed only insignificant quantities of organic carbon. It must therefore be concluded that, contrary to the postulation of Judd and Black (2000), all organic carbon is mineralised following equilibration. Establishment of mineralisation is extremely important, since incomplete mineralisation would lead to intolerably high levels of chlorinated organic material.

Minerlisation at the operational pH would be expected to produce primarily bicarbonate (HCO_3^-). It appears, however, that the carbon is largely lost from the system as carbon dioxide (CO_2), since the increase in alkalinity (i.e. HCO_3^- and CO_3^{2-}) is minor and there was no evidence of scale formation in the system. At the lower pH used (Run 10), around 11% of the carbon in the pool is present as inorganic carbon, compared to 50% at a higher pH, reflecting the $HCO_3^- \leftrightarrow CO_2$ equilibrium.

4.2 Nitrogen

Only 4-28 % of the amino nitrogen added is accounted for by nitrate accumulation within the pool, with a maximum of 50% being accounted for in those runs employing TN measurement (Table 9). This is indicative of breakpoint chlorination, with most of the N being lost as nitrogen gas, N_2 (Vikesland *et al*, 1996) and smaller amounts arising as nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_3) and nitrous oxide (N_2O). Since there is a constant free chlorine residual maintained in the pool, nitrite would presumably not be present at measurable levels, being instantaneously and quantitatively converted to nitrate.

It is also possible that a steady-state concentration of slow reacting organic ammoniacal species remain in the pool. The total N measurement (which includes nitrate, ammoniacal and organic nitrogen) indicates that under selected conditions there are certain nitrogenous species that take longer to react than others. Measurements made at the end of Run 4 and Run 10 run show that the organic nitrogen concentration in the pool water does not exceed 3mg/l. This suggests that there is a significant concentration of ammoniacal nitrogen in the pool water (which must account for the rest of the Total Nitrogen measurement) which is not as rapidly breakpointed in the same way as ammonia. Other research has shown that some of the other constituents of the BFA will take much longer to react (due to the more complex nature of their structure), resulting in an extended time required for complete breakpointing to occur (Lomas 1967, Chambon 1983, Ueno, 1995). Ammoniacal species may also arise from decomposition of organic chloramines (Vikesland *et al*, 1998):

$$4NHRCl + 3H_2O \rightarrow 4Cl^- + 3NH_2R + NO_2 + 5H^+$$

An unidentified monochloramine decay product, as noted by several authors such a Leung and Valentine (1994) and Vikesland *et al* (1998), may account for a small fraction of nitrogen not recovered after breakpointing. Vikesland *et al* (1998) found that when chlorinating a monochloramine solution at a pH of 7.5 in a closed system, decay products of NH_3, NO_3^- and N_2 were measured after 15 minutes with around one third of the N being unaccounted for. When the experiment was performed with NOM under the same conditions, less of this unidentified product was formed, and higher levels of NH_3 were generated. It is likely, however, that this product, if present in the pool water, would be an intermediate in the breakpoint reaction and not a stable end product, and so would not accumulate within the pool.

4.3 Chlorine

Chloride, formed as a result of oxidation of ammoniacal species and chloramines, for example (Jafvert and Valentine, 1992):

$$NHCl_2 + 2HOCl + H_2O \rightarrow NO_3^- + 5H^+ + 4Cl^-$$

accounts for 37-91% of the dosed chlorine (Table 9). It must be assumed that the remainder of the chlorine is lost by volatilisation, since the experimental error in the chloride measurement is small.

There are many other DBPs that have been measured in pools that occur at levels which may be of concern to swimmers due to their carcinogenicity. For example, Christman (1983) identified dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) as the major non volatile DBPs of chlorination of humic acid. Stottmeister and Naglitsch (1996), measured a mean of 26mg/l of monochloroacetic acid (MCAA) and 23 mg/l dichloroacetic acid (DCAA) in municipal pools. Haloacetonitriles are also likely to be present in pools and are more inclined to accumulate in pool water that THMs as they are less volatile. Stottmeister (1998) measured 0.13 –148ug/l dichloroacetonitrile (DCAN) and 0.01-24 μg/l dibromoacetonitrile (DBAN) in a survey of indoor pools. Ueno *et al* (1995) chlorinated histidine, and measured both monochloroacetonitrile (MCAN) and trichloroacetonitrile (TCAN). Most of these, however, occur at relatively low levels cannot significantly contribute to the mass balance since they can be assumed to attain steady-state levels in the same way as the THMs and the TOC.

5 Conclusions

Trends recorded for DBP formation in a model swimming pool were as follows:
1. TOC, THM and chloramine levels all stabilised beyond a certain development time, the organic carbon being mineralised beyond following 150-500 hours of operation.
2. 4-28% of the organic ammoniacal nitrogen dosed into the pool was converted to nitrate, the conversion increasing with increasing dose rate, with the remainder presumed to form predominantly molecular nitrogen.
3. The equilibrium TOC level followed a roughly linear trend with OC dose rate, as did the THM concentration.
4. THM levels attained depended upon the nature of the carbon source, with humic materials (representing soiling) having around 8 times the THM formation propensity than that of the body fluid analogue containing all principal endogenous organic constituents.
5. The loss of carbon and nitrogen to the atmosphere, as a proportion of the total loaded into the pool, was negligible.
6. Measured steady-state concentrations of TOC, THMs and chloramines were in reasonable agreement with those encountered in real pools.
7. THM generation increased significantly, by almost a factor of two, on decreasing the pH from 7.8 to 7.2, despite decreasing the free chlorine level from 1.8 to 0.5 mg/l.
8. During the initial unsteady state period when TOC and organic ammino nitrogen were accumulating in the pool, the respective accumulation rates of OC as THMs and N as chloramines were 0.02-0.3% and 0.14-3.3% of the dosed OC and N.

It can be concluded that no nett accumulation of carbon takes place in a swimming pool, and that nitrogen accumulates only as nitrate. Steady state THM levels attained are more dependent on carbon source and operating pH than on organic carbon loading rate, such that a reduction of humic materials (soling) by pre-washing of bathers would have a more significant effect than reducing the bather load *per se*. A reduction in pH, whilst improving bacteridical potency of the chlorine disinfectant and thus allowing a lower chlorine dose, none-the-less promotes THM formation and would also be expected to increase levels of trichloramine (Jafvert and Valentine, 1992).

Acknowledgements

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