A Summary of Work Undertaken at Bristol University

Prepared for PWTAG Steering Committee - 13 August 2002

Gareth Davis

Gillian Bullock

1 Verification of J & V Model

Jafvert and Valentine [1] produced a kinetic model for the chlorination of ammonia through empirical data and mechanistic considerations. In our subsequent modelling we use this scheme as a backbone to develop for the chlorination of swimming pools. To begin, we must verify (and adapt) the prosed reaction system before extending it.

1.1 Chlorine Loss

We undertook our experiments in a closed-bottle environment with no headspace. Despite this, we expect to observe chlorine decay (i.e. due to Cl^-/Cl_2 in solution) which is not accounted for in the original model. Taking only HOCl in a bottle and measuring the free chlorine levels at various time intervals, we achieve the concentration profile shown in figure 1.

We assume that a first order decay occurs [2] and hence we ammend the Jafvert model to include the following as a loss term for HOCl:

$$k_{loss}[\mathrm{HOCl}] \tag{1}$$

This agrees favourably as demonstrated in figure 2

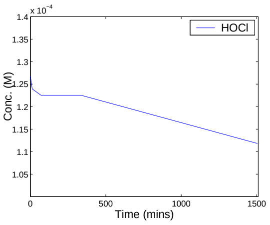


Figure 1: Decay of chlorine over time

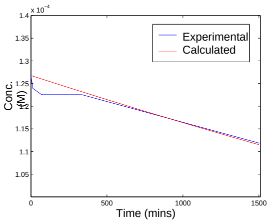
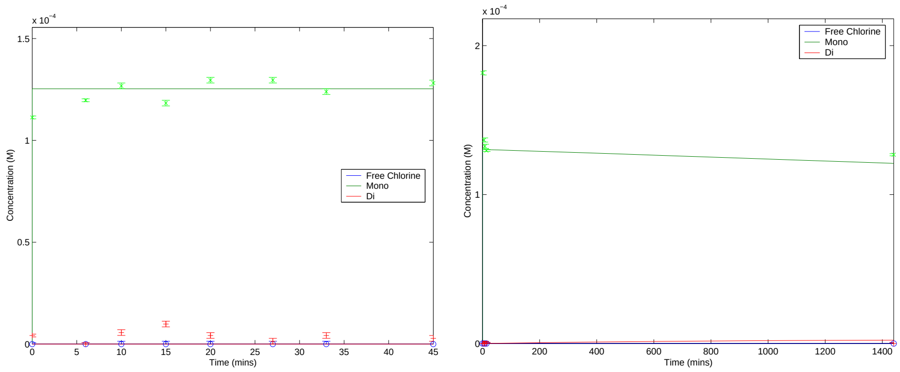


Figure 2: Comparison of empirical and numerical decay of chlorine over time

1.2 Comparison of Model with Empirical Data

We now react various concentrations of ammonia and HOCl together in closed vessels. Comparing our data with the model simulations (including the decay term from equation (1)) we see excellent correlation as shown in figures 3-4:

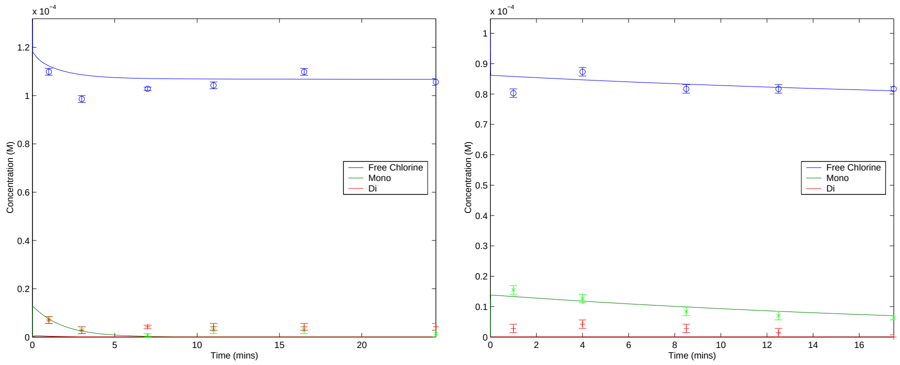
Note that no dichloramine is shown in the simulations, however a small amount is



(a) HOCl = $2.54 \, \mathrm{x} \, 10^{-4}$M, pH=9.7, $NH_3 = 1.03 \, \mathrm{x} \, 10^{-3}$M

(b) HOCl = $2.64 \, \mathrm{x} \, 10^{-4}$M, pH=10.7, $NH_3 = 12.5 \, \mathrm{x} \, 10^{-3}$M

Figure 3: Comparison of simulated and empirical data for initial Cl/N ratio<1



(a) HOCl = $2.64 \, \mathrm{x} \, 10^{-4}$M, pH=8, $NH_3 = 2.58 \, \mathrm{x} \, 10^{-5}$M

(b) HOCl = $2.11 \, \mathrm{x} \, 10^{-4}$M, pH=9.3, $NH_3 = 3.5 \, \mathrm{x} \, 10^{-5}$M

Figure 4: Comparison of simulated and empirical data for initial Cl/N ratio>1

produced in experiments 3(a), 4(a), 4(b). We observe this in future studies and hence suggest that there is a slight failing with the Jafvert model. It seems likely that the rate term for the reaction:

$$\mathrm{HOCl} + \mathrm{NHCl_2} \longrightarrow \mathrm{NCl_3} + \mathrm{H_2O} \tag{2}$$

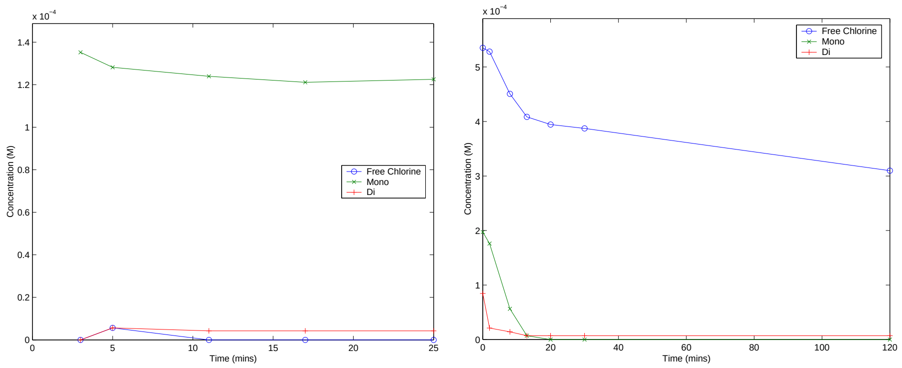
needs adapting, as we also observe moderately high concentrations of trichloramine at high pH's in the simulations. For now we ignore any production of trichloramine and note that the model cannot accurately predict dichloramine levels.

2 Chlorination of BFA Species

In order to model the chlorination of the BFA as a whole, we firstly observe each BFA species in isolation. Once again we chlorinate each component in a closed-bottle environment and note the production of CAs and decay of free chlorine.

2.1 Results

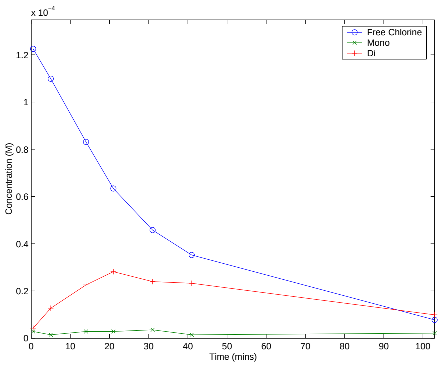
2.1.1 Ammonium Chloride



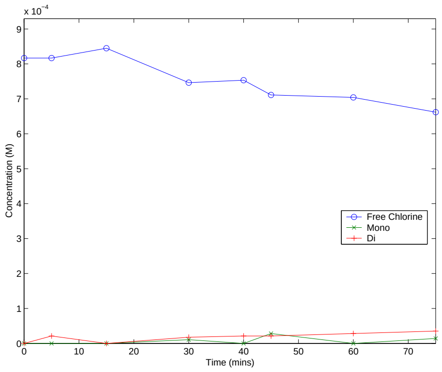
(a) $\mathrm{NH_4Cl} = 3.63\,\mathrm{x}\,10^{-4}\mathrm{M}$, $\mathrm{HOCl} = 1.39\,\mathrm{x}\,10^{-4}\mathrm{M}$

(b) $\mathrm{NH_4Cl} = 3.07\,\mathrm{x}\,10^{-4}\mathrm{M}$, $\mathrm{HOCl} = 8.17\,\mathrm{x}\,10^{-4}\mathrm{M}$

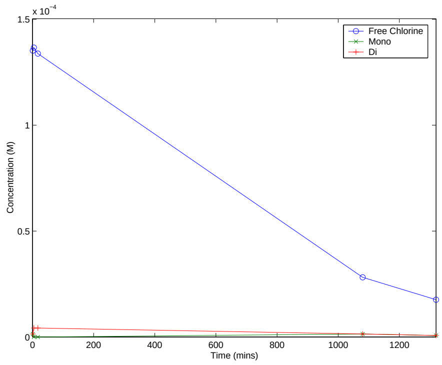
2.1.2 Urea



(a) Urea=3.425 x 10^{-3}M, HOCl = 1.3 x 10^{-4}M

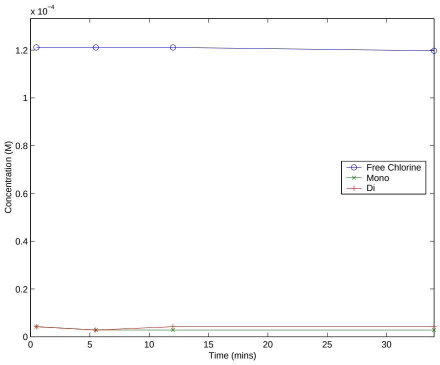


(b) Urea=7.2 x 10^{-4}M, HOCl = 8.45 x 10^{-4}M

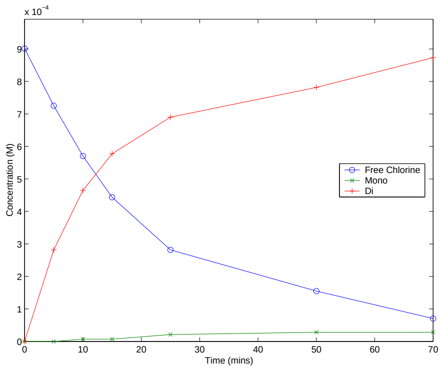


(c) Urea=3.58 x 10^{-4}M, HOCl = 1.41 x 10^{-4}M

2.1.3 Hippuric Acid

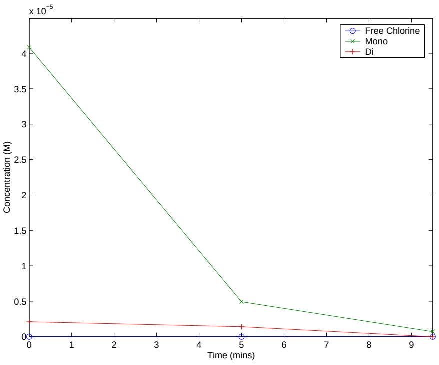


(a) Hipp=2.25×10^{-3}M, HOCl = 1.3×10^{-4}M

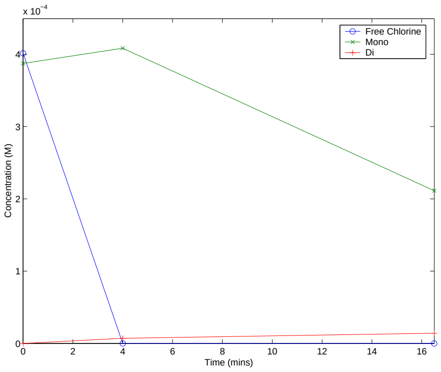


(b) Hipp=1.7×10^{-2}M, HOCl = 9.0×10^{-4}M

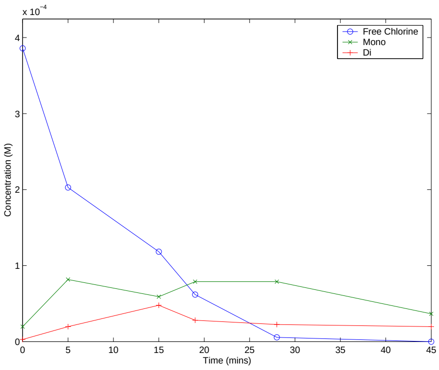
2.1.4 Histidine



(a) Hist=1.29×10^{-4}M,HOCl = 4.3×10^{-5}M

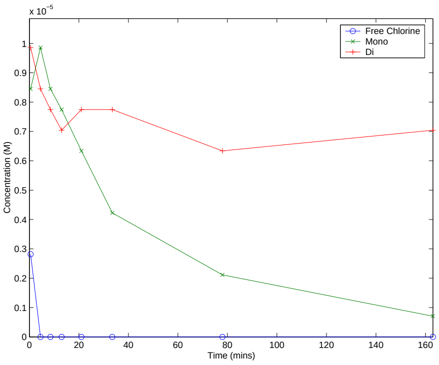


(b) Hist=1.29×10^{-3}M,HOCl = 7.9×10^{-4}M

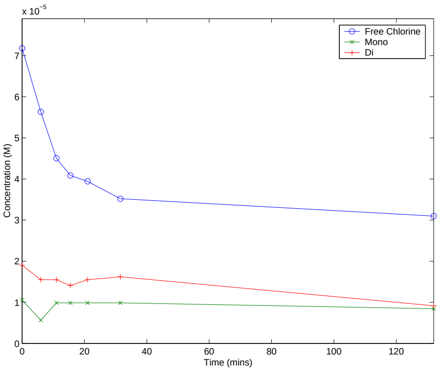


(c) Hist=4.7×10^{-4}M,HOCl = 4.1×10^{-4}M

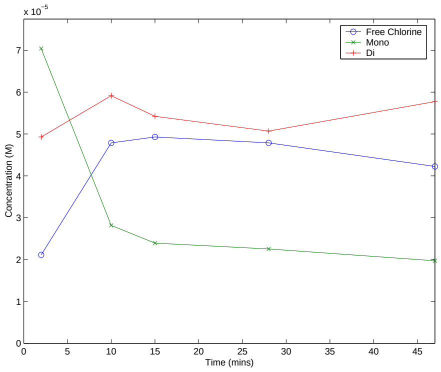
2.1.5 Uric Acid



(a) Uric=5.95×10^{-5}M, HOCl = 2.11×10^{-5}M



(b) Uric=5.95×10^{-5}M, HOCl = 1.01×10^{-4}M



(c) Uric=3.55×10^{-4}M, HOCl = 1.41×10^{-4}M

2.2 Modelling Individual BFA components

2.2.1 Ammonium Chloride

We can assume that ammonium chloride reacts as ammonia due to its dissociation:

$$\mathrm{NH_4Cl} \Longleftrightarrow \mathrm{NH_4^+} + \mathrm{Cl^-} \tag{3}$$

As the model accounts for the different ionic species in solution, we can therefore feed ammonium chloride into the system as if it was ammonia.

2.2.2 Urea

Given the results of section 2.1.2, we see that urea does not produce significant amounts of CAs (except for when urea is in excess when moderately high dichloramine levels are measured). However, we observe a considerable decay of chlorine. This is due to the formation of N-chlorourea and susequent chlorination to di/tri/tetra-chloro urea [3]. We can account for the loss of chlorine to these products by including the following term in the model:

$$k_{urea}[\mathrm{urea}][\mathrm{HOCl}], \qquad k_{urea} = 778.8\mathrm{M^{-1}h^{-1}} \tag{4}$$

For simplicity, we only account for the production of N-chlorourea as the rate terms for the other chlorinated urea products are small in comparison.

2.2.3 Hippuric Acid

We see in 2.1.3(a) that there is little activity between hippuric acid and HOCl over the time period examined. Comparing this with the 2.1.3(b) we hypothesise that a high concentration of HOCl is required to break certain bonds and form reaction products. In this second experiment we observe high levels of dichloramine and a corresponding decay of free chlorine. As we do not achieve a significant quantity of monochloramine it seems likely that the dichloramine reading is a false positive and that the products are in fact chlorinated organic compounds.

2.2.4 Histidine

Looking at the concentration graphs in 2.1.4, we see a large decay of free chlorine and mainly production of monochloramine. The monochloramine experiences a large decay, but not to dichloramine, perhaps suggesting that it is not in fact monochloramine that we have measured, but some chlorinated organic species. Even if we assume that the product is monochloramine, we see at most a 32% conversion of histidine to monochloramine.

2.2.5 Uric Acid

Here we observe production of monochloramine of at most 20% of the initial uric acid concentration. In all three experiments we see stable levels of dichloramine, although in experiments 2.1.5(b) and 2.1.5(c) we also observe free chlorine present. This suggests that this is not dichloramine which is recorded, as we would expect this to breakpoint. Note there does not seem to be a pattern between the levels of CAs recorded and the initial ratios of reactants.

3 Modelling the Complete BFA

3.1 Discussion

The typical BFA make-up used in the pool runs is shown in Table 1. We see that the most abundant species are ammonium chloride and urea. Table 2 shows the possible levels of CAs obtainable using information obtained from our experimental results. Given the concentrations of CAs produced (and free chlorine used) for histidine/hippuric acid/uric acid in our experiments and their abundance in the BFA,

BFA Component	Concentration (gl^{-1})
Urea	7.4
Ammonium Chloride	2
Hippuric Acid	0.85
Histidine	0.6
Uric Acid	0.245

Table 1: BFA composition

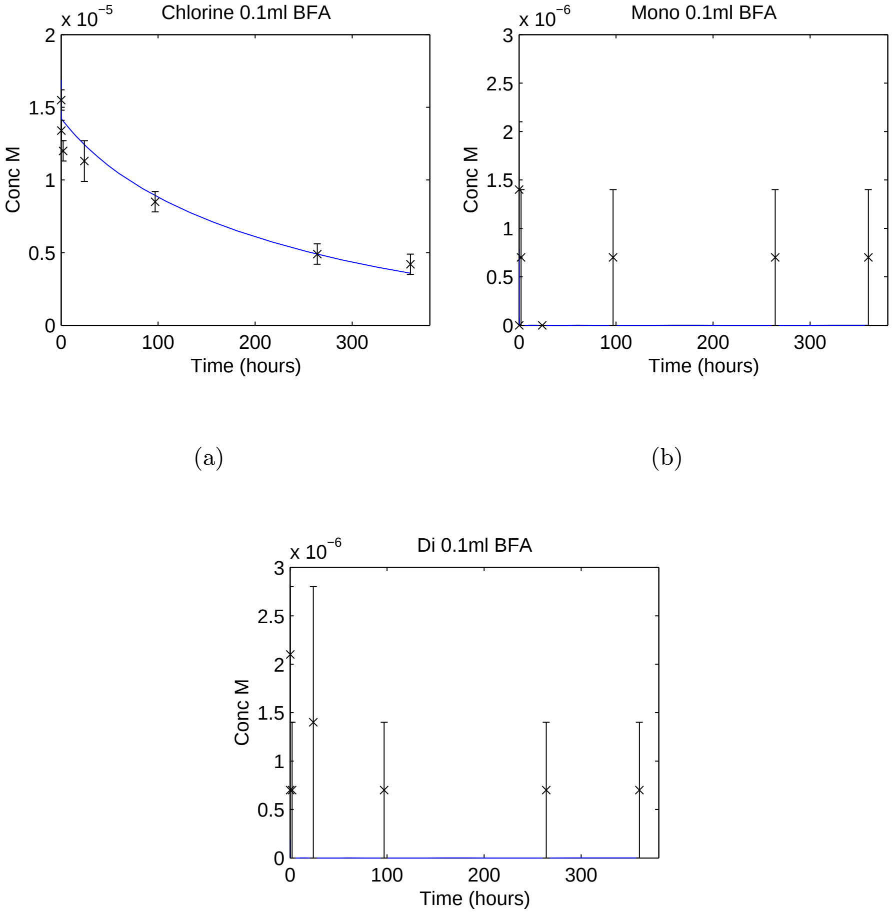
BFA component	Max % of BFA forming mono	Max conc of mono (gl^{-1})
Urea	4	0.296
Ammonium Chloride	65	1.3
Hippuric Acid	0.5	0.003
Histidine	32	0.192
Uric Acid	20	0.049

Table 2: Potential to form monochloramine

we omit these compounds from our simulated BFA make-up. By taking merely ammonium chloride and urea we find that the system dynamics are not significantly altered.

3.2 Full BFA results

By performing closed bottle experiments on the full BFA at two different concentrations, we find that the model does indeed replicate the behaviour of the system, despite ignoring three components. We see good agreement although we note that the model does not predict any production of monochloramine and dichloramine for the first experiment (however this is within our error bounds).

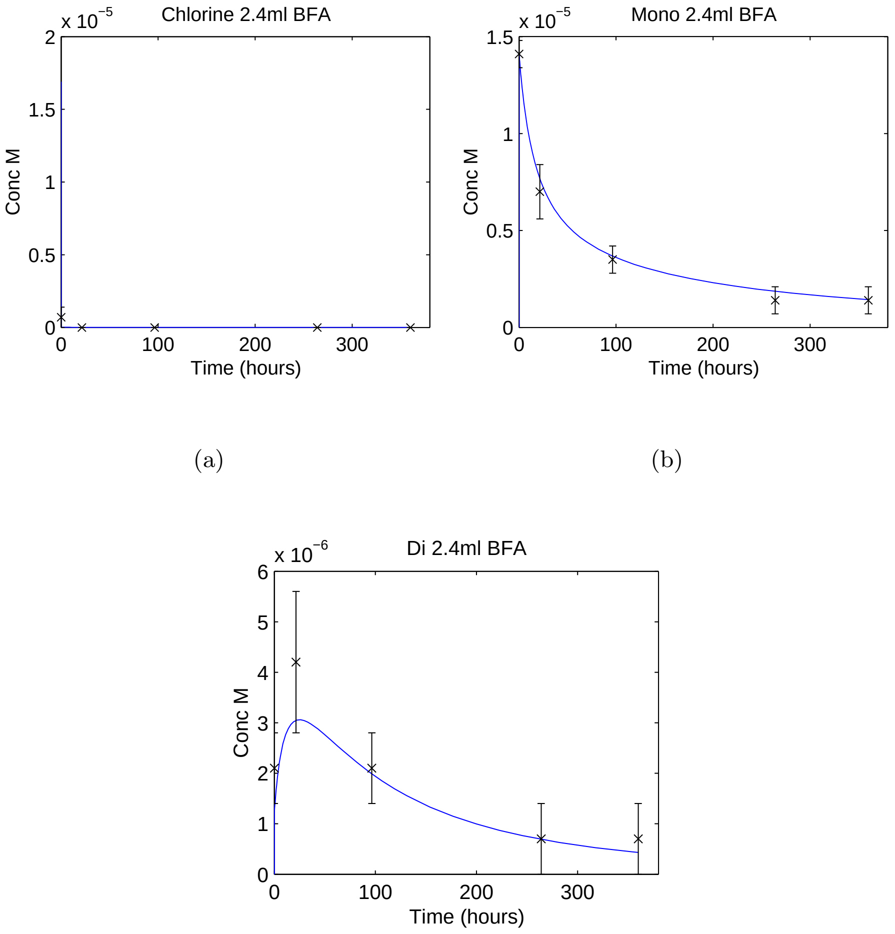


(a)

(b)

(c)

Figure 5: Chlorine and CA profiles over time for 0.1 ml BFA, 1.25 mgl^{-1} HOCl



(a)

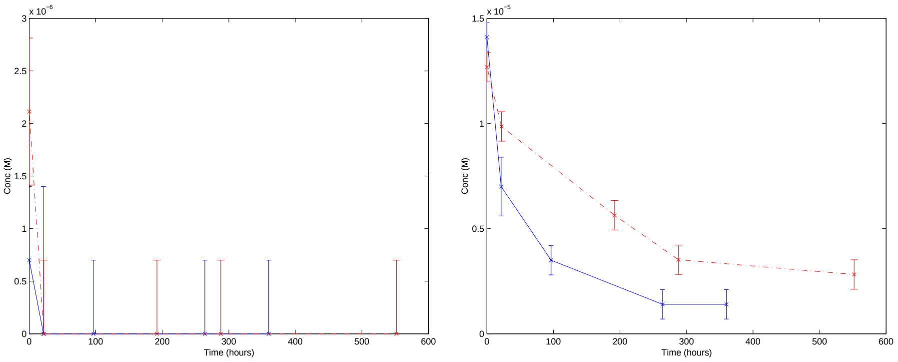
(b)

(c)

Figure 6: Chlorine and CA profiles over time for 2.4 ml BFA, 1.25 mgl^{-1} HOCl

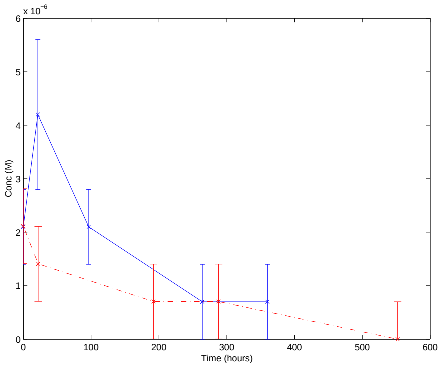
3.3 BFA and Humic Acid

To see the effect of humic acid on CA production, we repeated the experiment with 2.4 ml BFA, 1.25 mgl^{-1} HOCl, only this time we added 1 ml of $1/16^{\mathrm{th}}$ strength humic acid. We found that only low levels of THMs were produced (<1 ppb), however the decay of monochloramine seemed to be restricted. The following diagrams show the two sets of results (red=with humic acid, blue=without):



(a) Chlorine

(b) Monochloramine



(c) Dichloramine

Figure 7: Chlorine and CA profiles over time for 2.4 ml BFA, 1.25 mgl^{-1} HOCl, 1 ml humic acid

4 Modelling the Pool

In order to examine how relevant the model is to the overall pool dynamics, we will simulate the operating conditions set out in Gill's runs 10 and 11. Note that we do not have specific data available for small time-steps (i.e. for each hour) and the concentrations of rectants entering the pool may decay over the course of a run. Because of this we can only produce suitable limits on the concentration of reactants. We will not attempt to reproduce accurate concentration profiles, but strive to bound the concentrations.

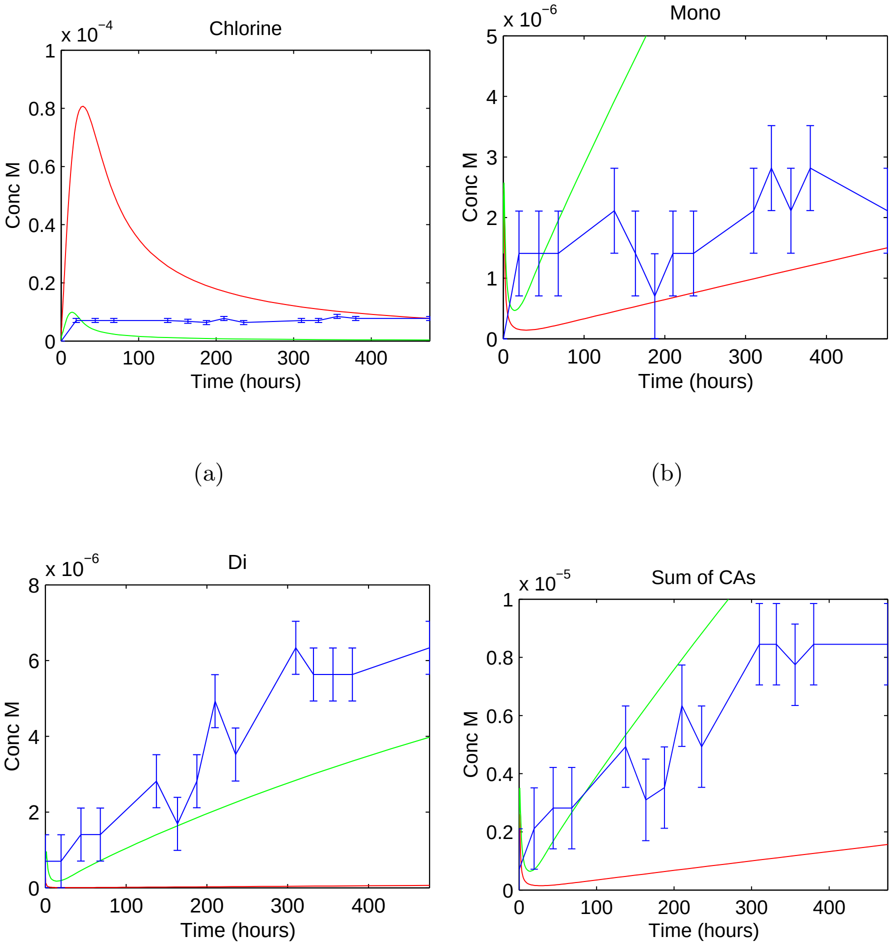
4.1 Assumptions

When modelling the pool, we must assume the following:

1. no spatial variation of concentration
2. BFA and HOCl pumped at approximately constant rate
3. assume closed system (ignore loss of Cl_2 to air)
4. assume constant pH and temperature

4.2 Preliminary Results

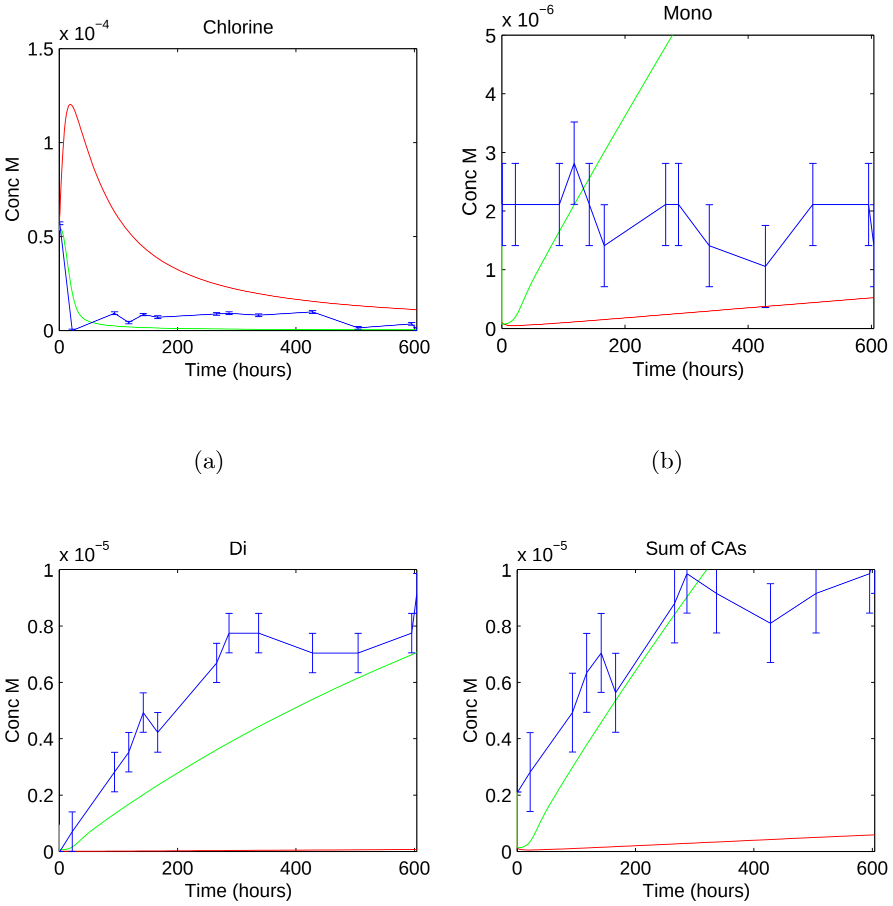
Given the prerequisites of section 4.1, we find that we can indeed produce sensible bounds for the concentration of free chlorine and monochloramine. We ignore the initial transient periods of around 100 hours in each case. Again we note difficulties when simulating dichloramine. Due to this we analyse total CAs produced to see that these values do lie within our bounds.



(a) (b)

(c) (d)

Figure 8: Chlorine and CA profiles over time for Run 10



(a)

(b)

(c)

(d)

Figure 9: Chlorine and CA profiles over time for Run 11

4.3 Discussion

This study represents a first-step into modelling a swimming pool environment mathematically. Our results show that it does seem possible to produce useful results from our adapted Jafvert model. Given more accurate input data, we should be able to reproduce concentration profiles for free chlorine and the CAs more precisely. Obviously more work needs to be undertaken to fully understand and hence adequately describe the system. Some points of note are:

- Jafvert model requires further analysis as a stand-alone chlorine-ammonia system
- DPD method is inappropriate as a measuring tool for CAs when chlorinating BFA components
- More individual BFA-chlorination experiments are needed on the bench scale (at various initial Cl/N ratios and pHs)
- Even using the model pool, stricter operating conditions need to be utilised in order to produce beneficial results

5 THM Production

In order to analyse THM production, we undertook bench-scale experiments on the chlorination of both citric acid and humic material. Throughout the course of the study it was evident that obtaining accurate THM measurements was extremely difficult given the volatility of THMs and the method of sampling. Despite this setback, we our results can be examined to show trends and general magnitudes of THM production. [1]

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[1] In the succeeding work we only analyse chloroform as levels of the other THMs were at most 7ppb

5.1 Results

5.1.1 Citric Acid

Time	Chloroform measured (ppb)			Free chlorine
(Hours)	min	max	average (of 3 results)	(mgl^{-1})
0	1.97	1.97	1.97	4.15
21.5	93.45	712.90	388.20	0.5
70	255.05	1245.26	601.70	0
334.5	82.65	397.55	283.12	0

Table 3: Chloroform production for 168.3 mgl^{-1} citric acid, 4.9 mgl^{-1} HOCl

5.1.2 Humic Acid

Time	Chloroform measured (ppb)			Free chlorine
(Hours)	min	max	average (of 2 results)	(mgl^{-1})
0	2.18	4.43	3.31	47
4.5	16.36	16.68	16.52	44
23.5	18.55	37.13	27.84	44
47.5	38.12	75.93	57.01	36
70	66.72	17.3	22.66	19.98
239	7.70	9.92	8.81	38.5
480	17.2	19.67	18.44	25.0

Table 4: Chloroform production for 0.5 mgl^{-1} humic acid, 49 mgl^{-1} HOCl

Time (Hours)	Chloroform measured (ppb)			Free chlorine (mgl^{-1})
	min	max	average (of 2 results)	
0	15.02	15.02	15.02	3.55
2.3	31.30	31.30	31.30	2.0
5	54.14	295.91	175.03	1.8
23.5	69.52	104.45	87.03	1.3
47.5	59.06	223.32	141.19	0.8
70	66.72	588.39	327.56	0.3
239	16.18	17.63	16.91	0
480	28.30	61.33	44.82	0

Table 5: Chloroform production for 5 mgl^{-1} humic acid, 4.9 mgl^{-1} HOCl

Time (Hours)	Chloroform measured (ppb)			Free chlorine (mgl^{-1})
	min	max	average (of 3 results)	
0	1.40	2.52	1.96	3.9
19	22.32	55.29	41.00	2.2
116.5	16.62	55.12	34.24	0.8

Table 6: Chloroform production for 5 mgl^{-1} humic acid, 4.9 mgl^{-1} HOCl

Time (Hours)	Chloroform measured (ppb)			Free chlorine (mgl^{-1})
	min	max	average (of 3 results)	
0	2.17	2.86	1.96	2.52
19.5	36.11	96.30	67.17	35.0
42.5	21.56	71.20	46.09	38.5
378.5	59.63	93.56	72.01	36.0

Table 7: Chloroform production for 5 mgl^{-1} humic acid, 49 mgl^{-1} HOCl

References

[1] R. L. Valentine C. T. Jafvert. Reaction scheme for the chlorination of ammoniacal water. *Environ. Sci. Technol.*, 26:577–586, 1992.

[2] J. C. Powell et al. Performance of various kinetic models for chlorine decay. *Journal of Water Resources, Planning and Management*, 2000.

[3] W. Samples. *A Study on the Chlorination of Urea.* PhD thesis, Harvard University, 1956.