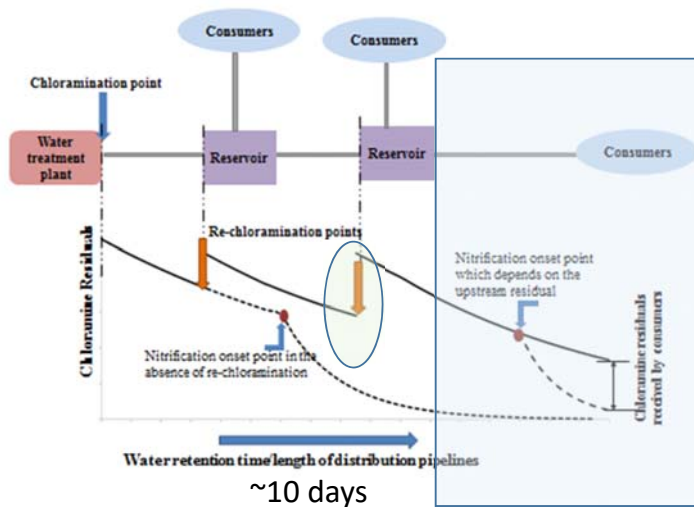


# Achieving disinfection in engineered systems with minimal side effects

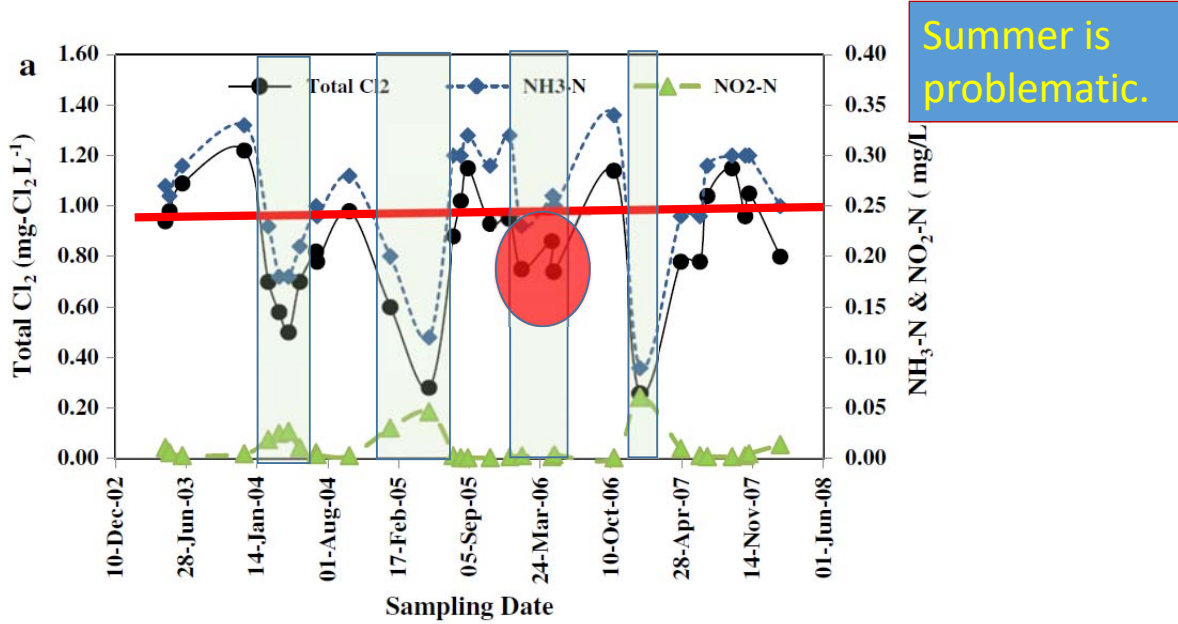
(Sathaa) Arumugam Sathasivan  
School of Engineering;  
Western Sydney University  
s.sathasivan@westernsydney.edu.au



## Chloramine profile along the system



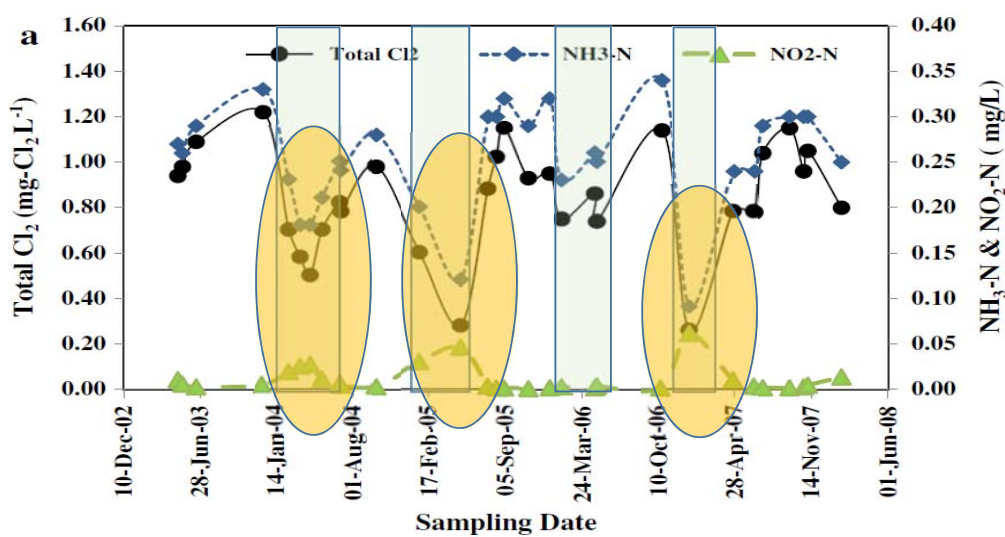
# Current status in many reservoirs



Chlorine addition does not always help or it cannot always be added.



# Traditional approach



Monitor parameters associated with nitrification, study and research solely about nitrifiers and their control for the last 100 years!!

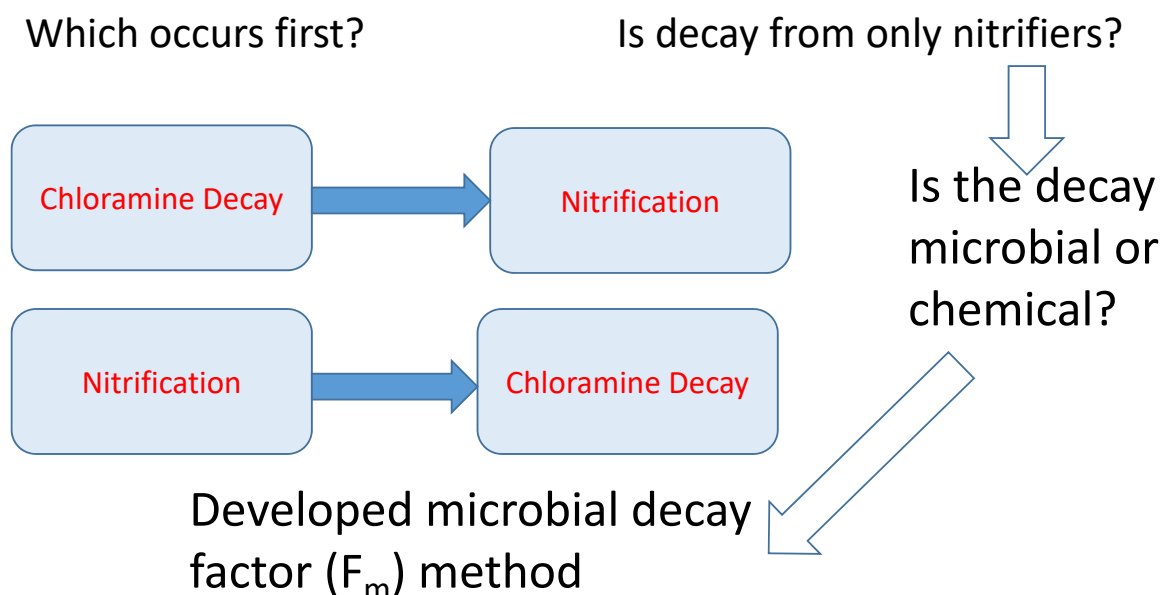


# Problem of traditional method

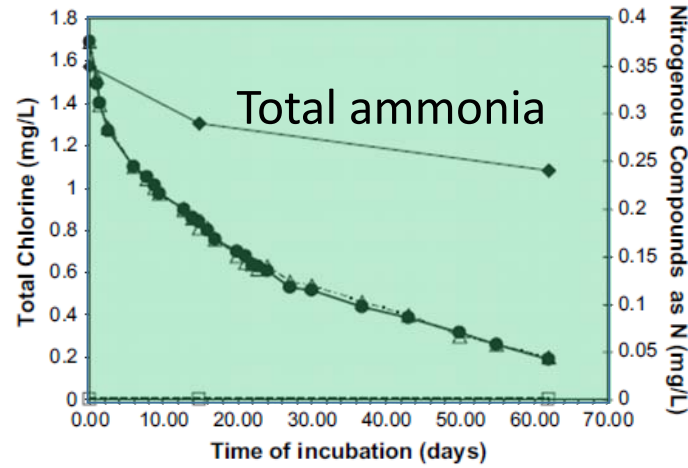
- No quantification, no prediction and hence no warning!!
- Always do their best to control the food to near zero level (Cl<sub>2</sub>/NH<sub>3</sub> ratio close to 4 – if we go more than that chlorine chemically disintegrate)!! OVER/UNDER REACTION ???



## Is traditional approach right?



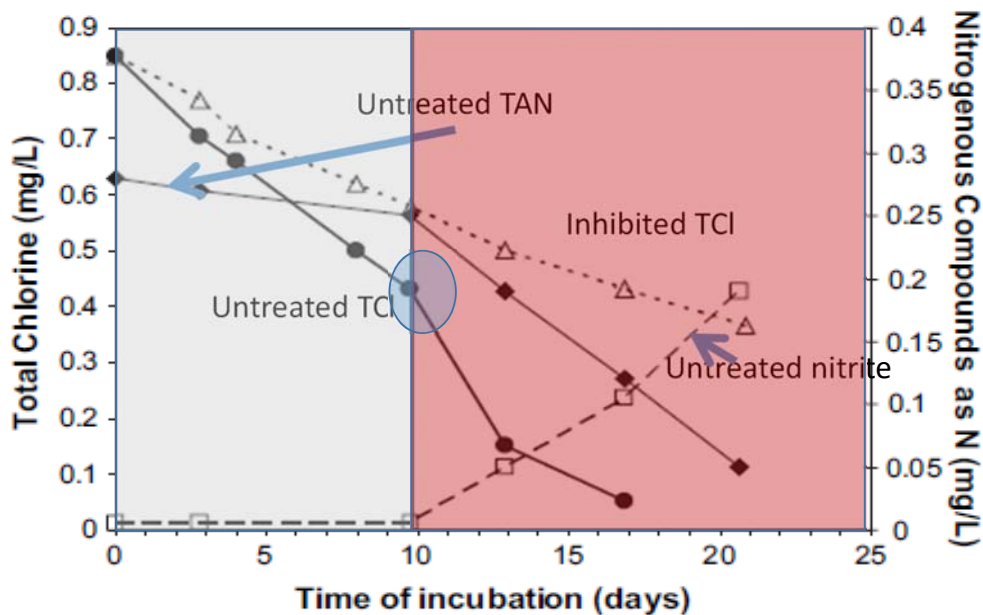
# Water from filtration plant (all chemical decay)



Sathasivan, Fisher, Tam (2008)  
Water research 42 (14), 3623-3632



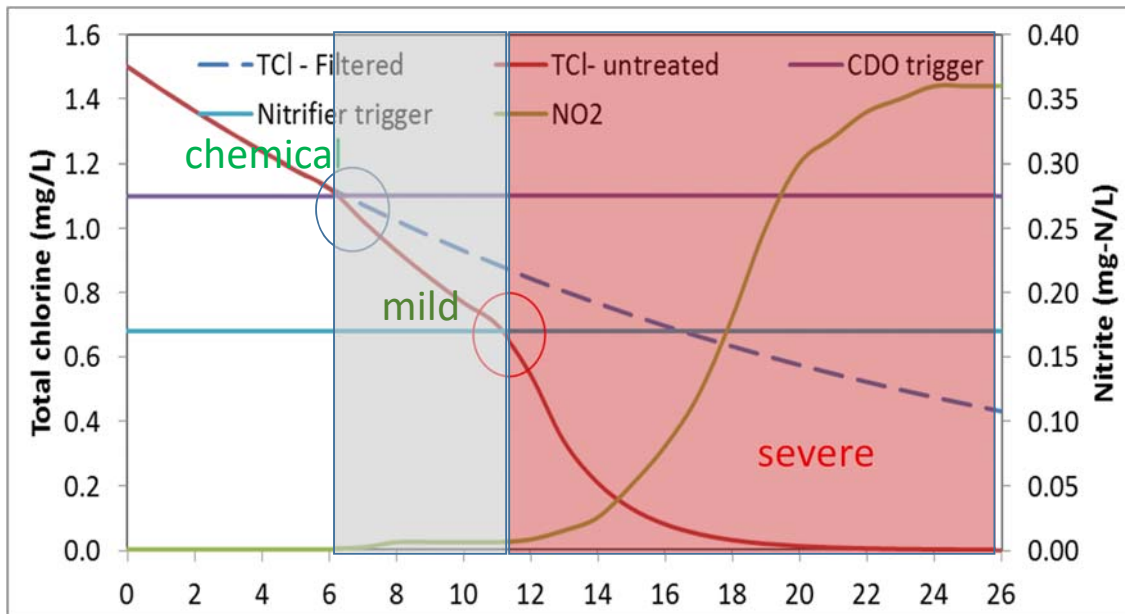
# Water from retic system (mild and severe)



Sathasivan, Fisher, Tam (2008)  
Water research 42 (14), 3623-3632



# What did $F_m$ method reveal?



## Biostable residual concentration (BRC) concept?

- Disinfectant (Chlorine) tries to kill
  - Kill rate  $\propto$  disinfectant concentration
  - Kill rate  $r_d = k \cdot Cl$
- Growth rate,  $r_g = \mu_m \frac{S}{K_S + S}$
- If  $r_g = r_d$ , bacterial number remains constant
- If  $r_g > r_d$ , bacterial number increases
- If  $r_g < r_d$ , bacterial number decreases
- A chlorine concentration at which  $r_g = r_d$  is called BRC

# In a chloraminated system

- For nitrifiers, free ammonia is the substrate

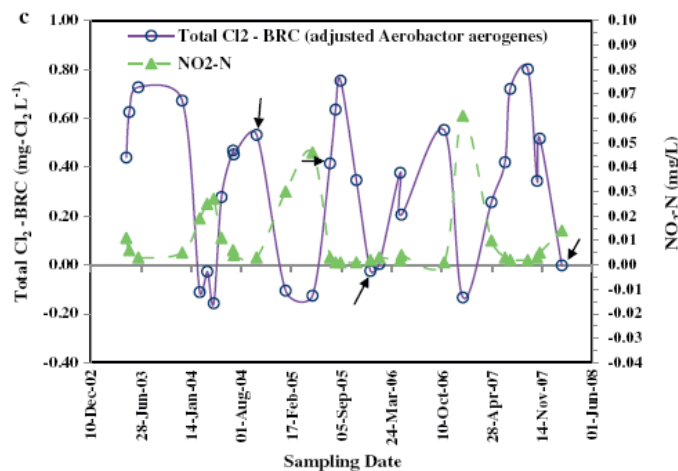
$$\frac{\mu_m (\text{free ammonia})}{(K_s + \text{free ammonia})} = k_d \times \text{BRC}$$

TCl > BRC killing  
TCl < BRC growth

Sathasivan, Fisher, Tam (2008)  
Water research 42 (14), 3623-3632

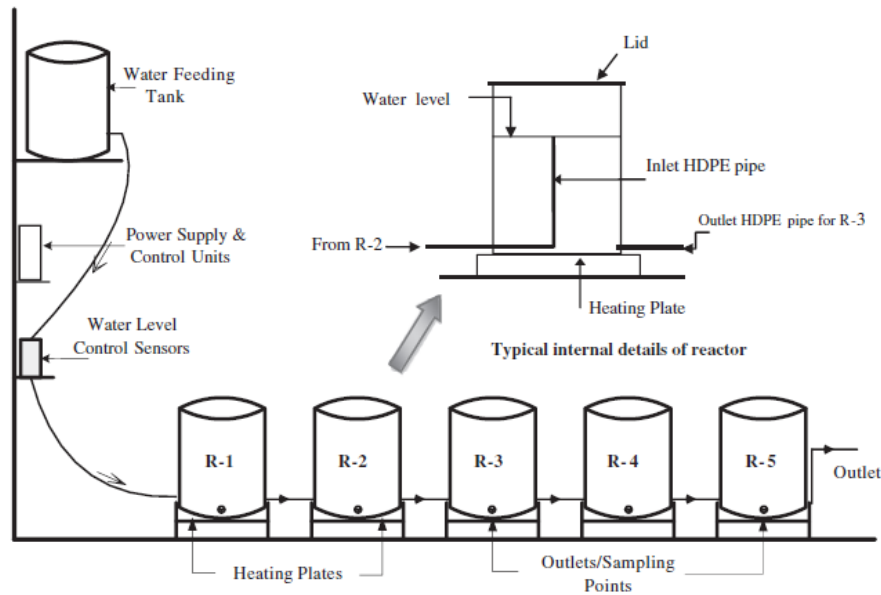
$\mu_m$ ,  $k_d$  are functions of temperature

## The model predicts the problems of growth



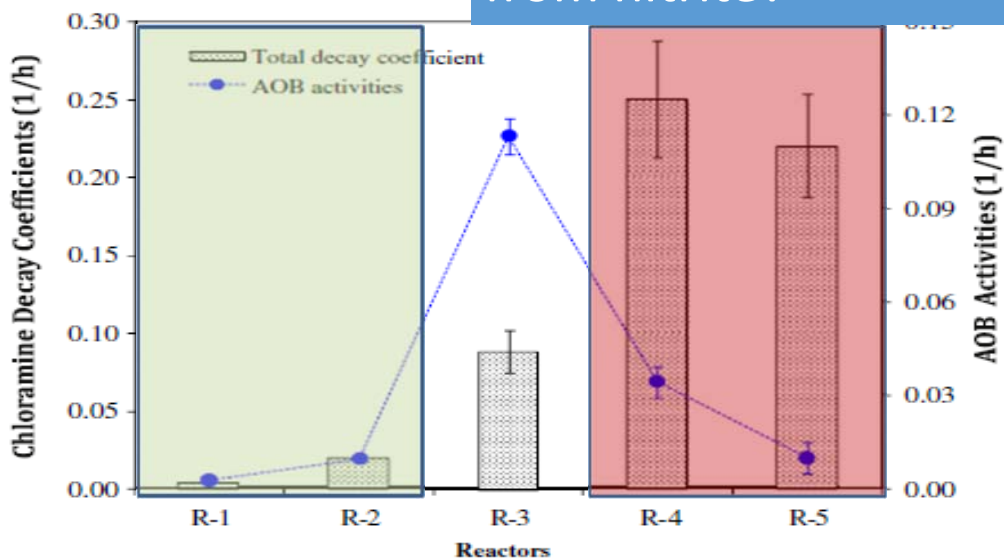
DC Sarker, A Sathasivan, CA Joll, A Heitz  
Science of the Total Environment 454, 88-98

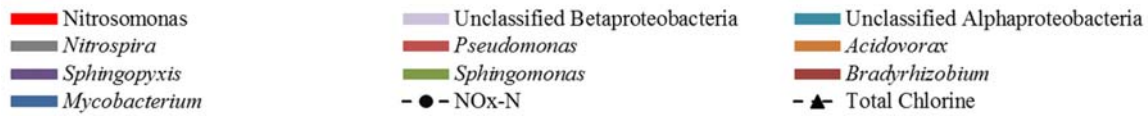
# Reactors simulating various phases



Initially NO<sub>x</sub> production correlates decay, but later it d

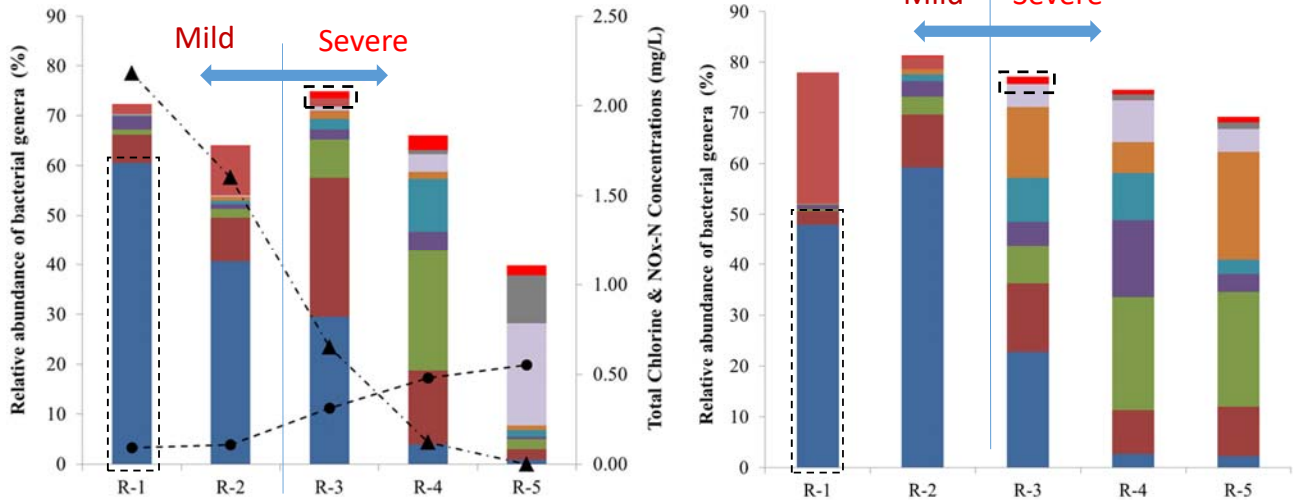
Is that chemical decay from nitrite?





[A] Bulk water

[B] Biofilm

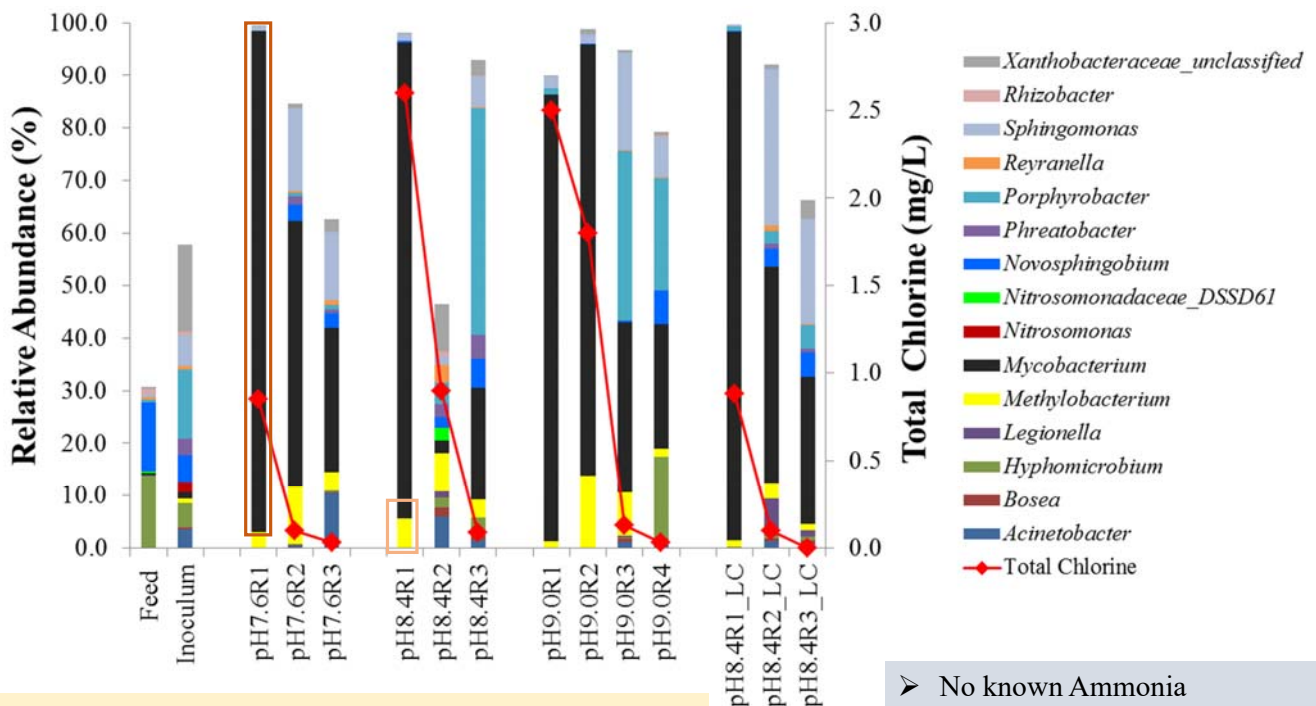


Origin of Samples

KCB Krishna, A Sathasivan, MP Ginige  
 Water research 47 (13), 4666-4679



## Bacterial Community Composition: Bulk Water

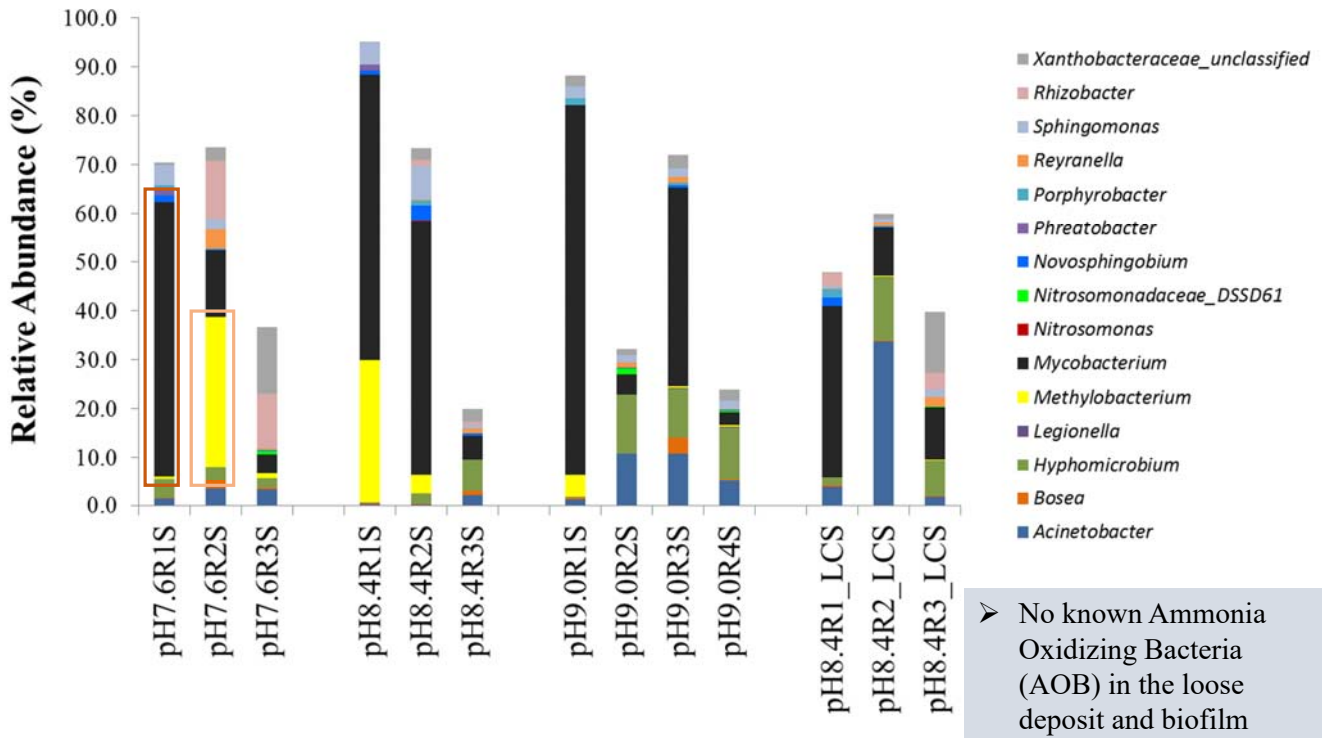


LC: Feed water chloramine residuals of 2.6 mg/L and others: 3.8 mg/L

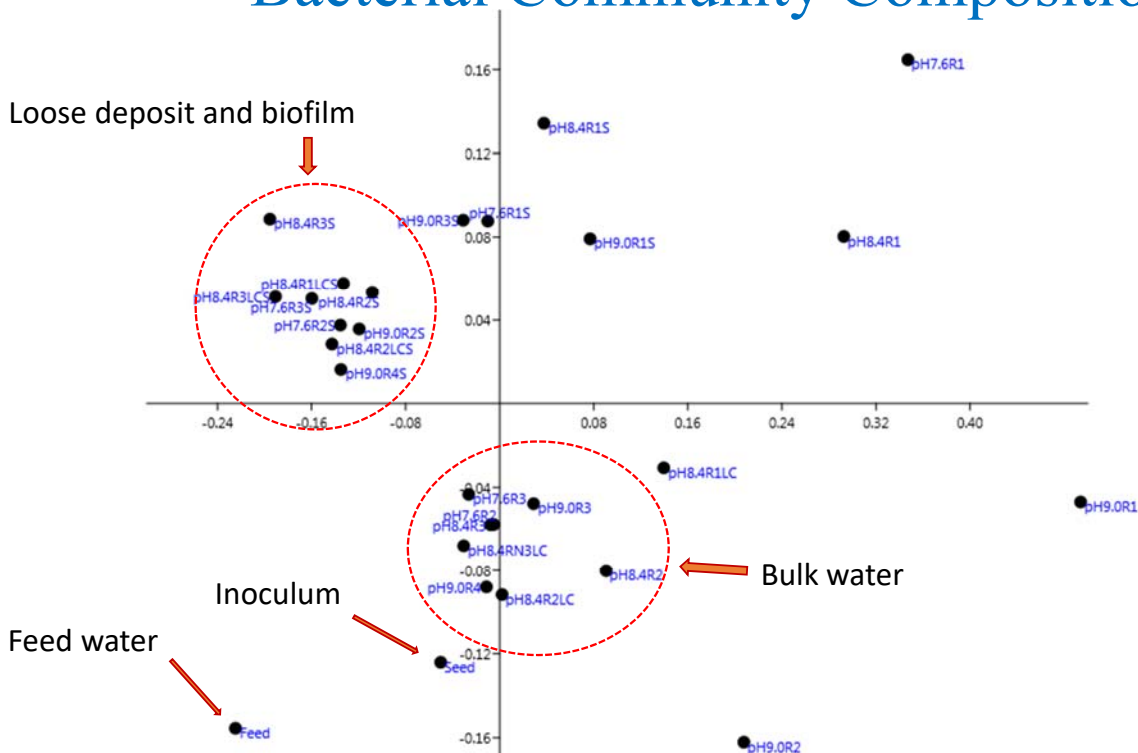
➤ No known Ammonia Oxidizing Bacteria (AOB) in the bulk waters



# Bacterial Community Composition: Loose deposit & Biofilm



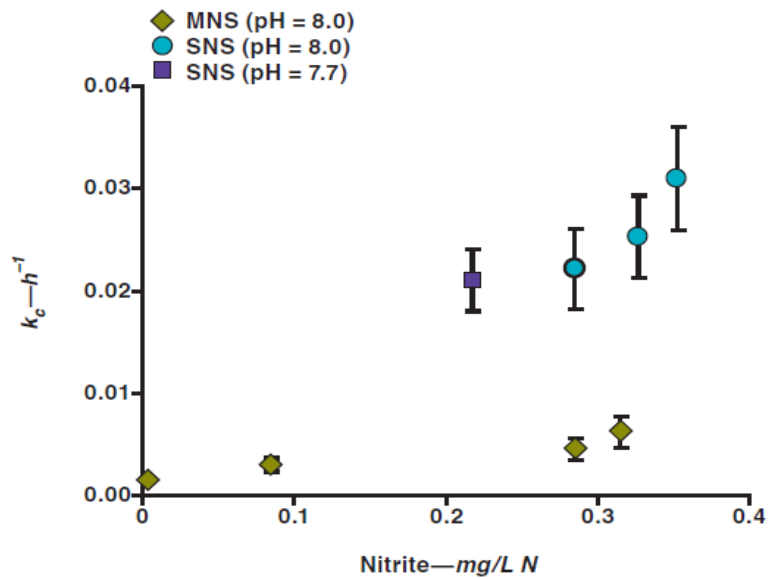
# Bacterial Community Composition



LC: Feed water chloramine residuals of 2.6 mg/L and others: 3.8 mg/L

S= Loose deposit and biofilm

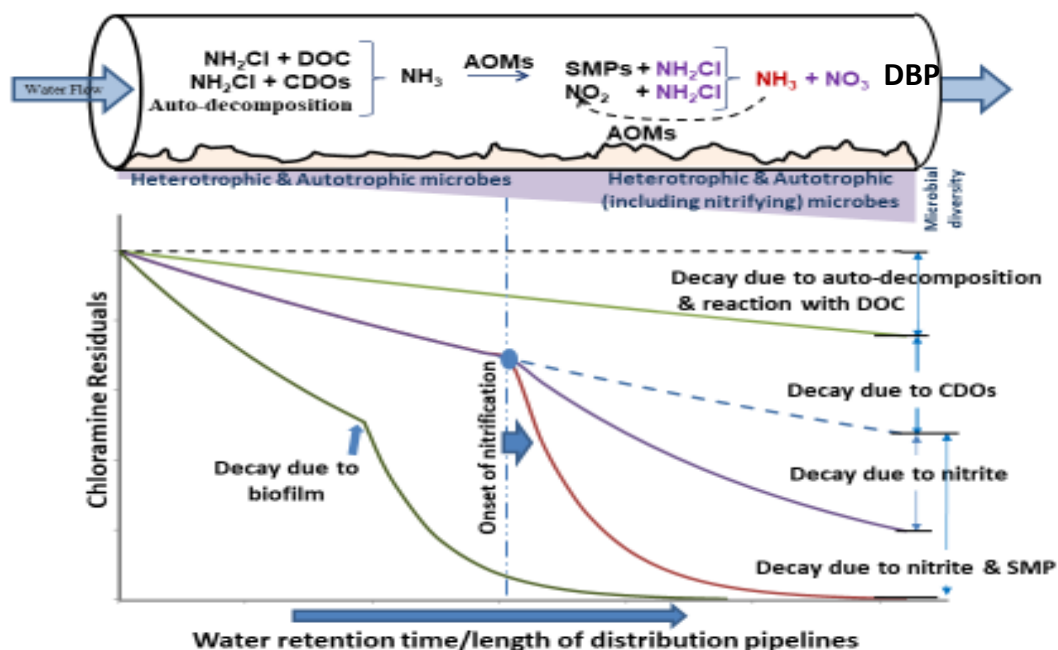
# Mild vs severe nitrifying filtered samples



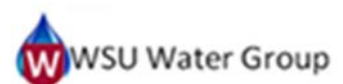
KC Bal Krishna, A Sathasivan, S Garbin  
 Water Science and Technology: Water  
 Supply 13 (4), 1090-1098



# Actual situation is much more complex

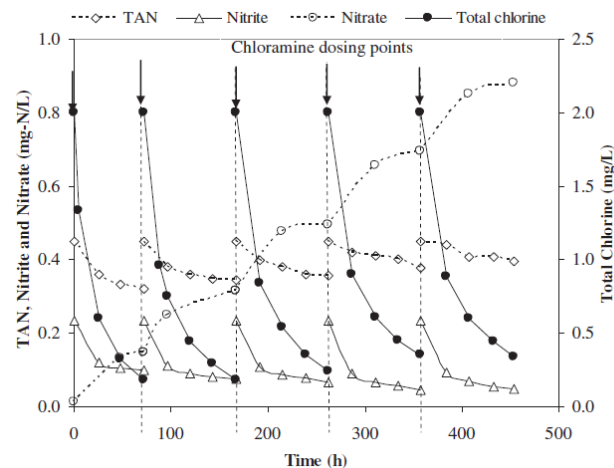


Sathasivan et al., 2016 :



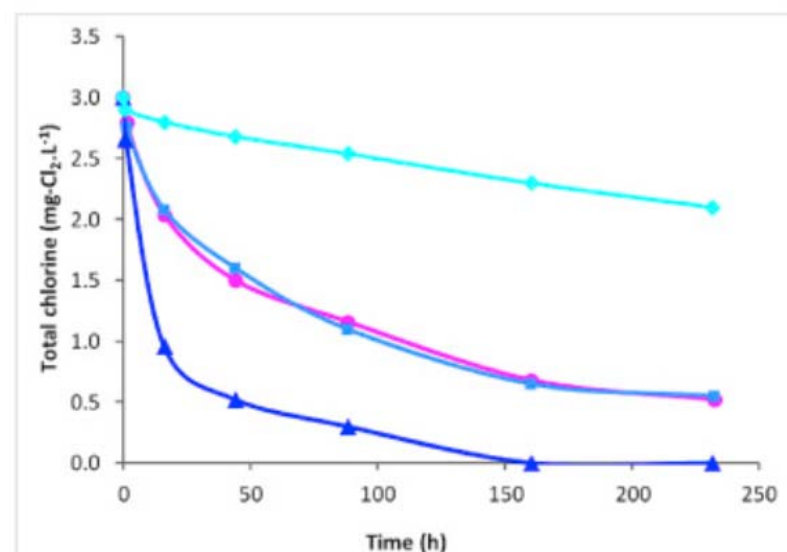
# Some interesting facts about SMP

- They are proteins of molecular weight 30-50 KDa
- They catalyse the disinfectant decay

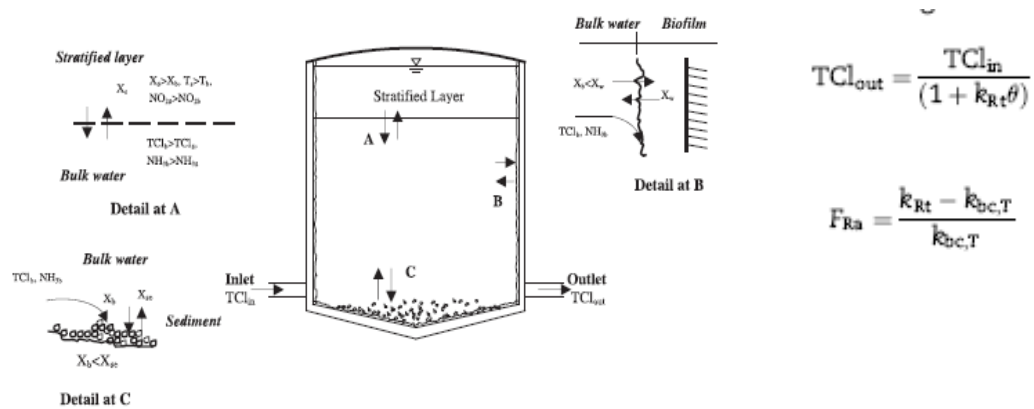


BS Herath, A Torres, A Sathasivan (2018) Chemosphere 212, 744-754  
KCB Krishna, A Sathasivan, DC Sarker (2012) Water research 46 (13), 3977-3988

CDPs are formed as a stress response



# Things at play in a service reservoir



$$\text{TCl}_{out} = \frac{\text{TCl}_{in}}{(1 + k_{Rt}\theta)}$$

$$F_{Ra} = \frac{k_{Rt} - k_{bc,T}}{k_{bc,T}}$$

Fig. 1 – Conceptual representation of factors affecting chloramine residual.  $X$  is the bacterial number and subscripts b, w, s and se represented bulk water, biofilm (wall), stratification and sediment, respectively.

A Sathasivan, KCB Krishna, I Fisher  
Water research 44 (15), 4463-4472

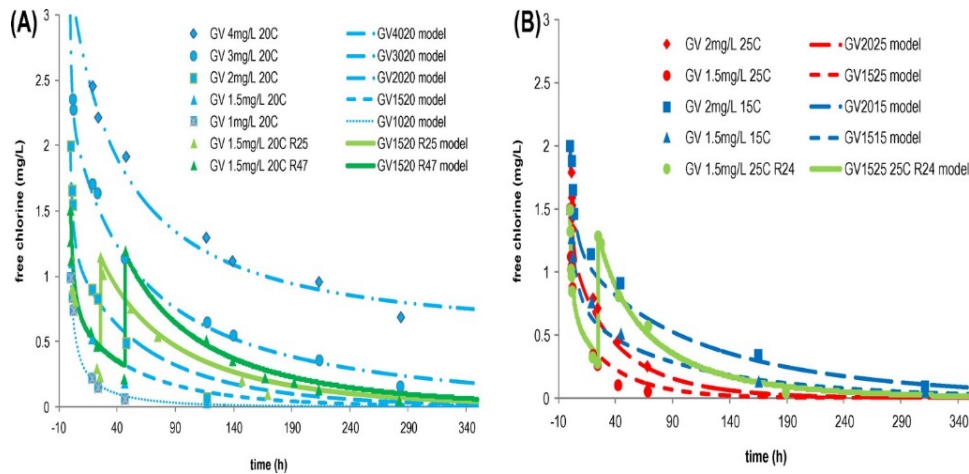
## Chlorination

- 2R model - Fast reacting and slow reacting agents (Fisher et al., 2016; 2017)
- $\frac{dCl}{dt} = (k_f \cdot FRA + k_s \cdot SRA) \cdot Cl$
- $k_T = k_{20} \cdot \exp\left(-\frac{E}{R} \cdot \left(\frac{1}{273+T} - \frac{1}{293}\right)\right)$
- Analytical solution (Kohpae and Sathasivan, 2011)

$$C_{Cl}(t) = \frac{C_{cl_{FRA}}(t) - c}{1 - \frac{c}{C_{cl_{FRA}}(t)} e^{-(C_{cl_{FRA}}(t) - c)k_{SRA}t}} \quad (37)$$

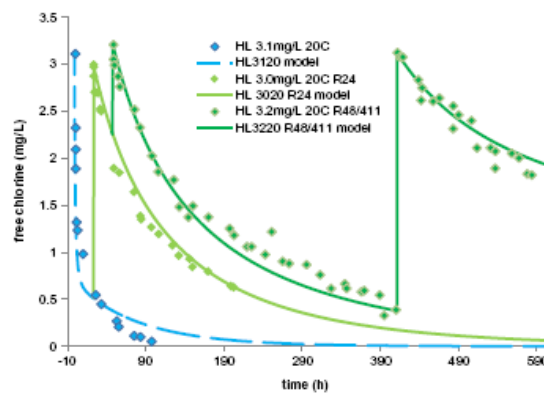
# Application

- With one set of parameters
  - different dosing,
  - different temperature,
  - rechlorination



I Fisher, G Kastl, A Sathasivan  
 Urban Water Journal 14 (4), 361-368

## Can apply for successive rechlorination



**Figure 2.** Chlorine concentrations from 2R model of Harsh Lake 2 water, calibrated against data set comprising a single ID and successive rechlorinations to 3 mg/L after 24, 48 and 411h (data from Boccelli *et al.* 2003). Markers, curves and legend are as defined in Figure 1.

I Fisher, G Kastl, A Sathasivan  
 Urban Water Journal 14 (4), 361-368

# Can apply for bend of two sources

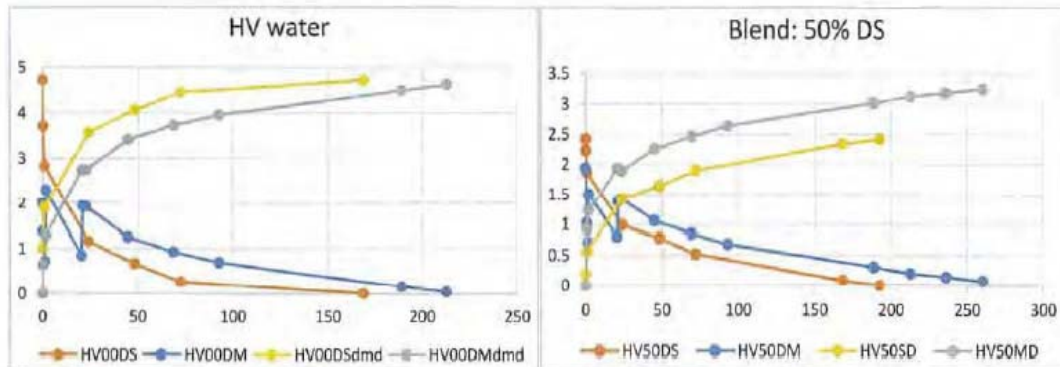


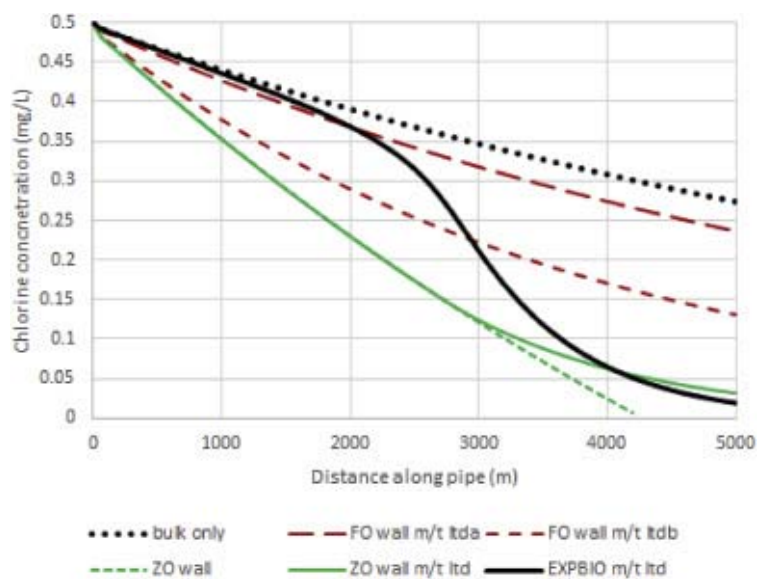
Figure 2. Single- (brown) and multiple-dose (blue) decay test data for: A – HV water alone; and B – HV blended with 50% DS water. Data source: Byrne et al. (2013). Corresponding demand curves (yellow and grey respectively) were constructed as shown in Figure 1.

I Fisher, G Kastl, F Shang, A Sathasivan (2018) Journal American Water Works Association 110 (11)

I Fisher, G Kastl, A Sathasivan, D Cook, L Seneverathne (2015) Journal of Environmental Engineering 141 (12), 04015039

I Fisher, G Kastl, A Sathasivan (2014) Water: Journal of the Australian Water Association 41 (8), 32

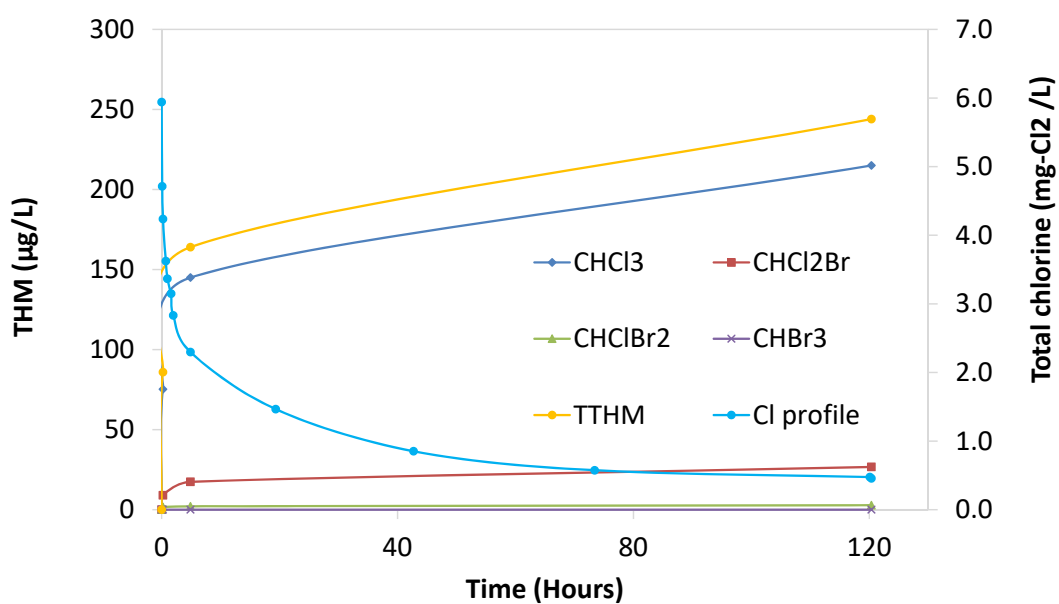
# Full scale application – evidence of microbial chlorine decay



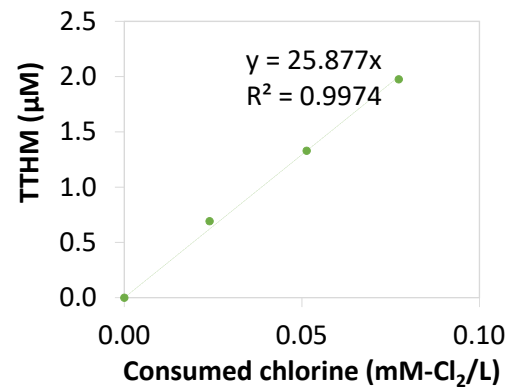
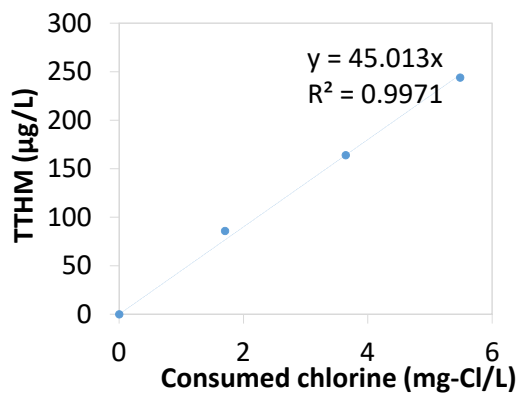
I Fisher, G Kastl, A Sathasivan Water research 125, 427-437

# How about THM?

## Behaviour during chlorine decay (Nepean Dam water, Australia)



# Yield calculation (Nepean Dam water, Australia)



This implies that if we know what chlorine we dosed and the concentration at a given point (predicted or measured), we can calculate the TTHM confidently

Sathasivan et al., 2019; NOM 7 conference proceedings



## Comparison

| Raw water or treatment details              | DOC (mg/L) | UV <sub>254</sub> (/cm) | SUVA | Br (µg/L)         | pH  | Cl <sub>2</sub> dose mg-Cl <sub>2</sub> /L | TTHM mass yield (mg TTHM / mg-Cl <sub>2</sub> consumed) (R <sup>2</sup> ) | TTHM molar yield (µmol TTHM / mmol Cl <sub>2</sub> consumed) (R <sup>2</sup> ) |
|---|------------|-------------------------|------|-------------------|-----|--|---|--|
| Nepean , Aus                                | 5.44       | 0.0828                  | 1.52 | 43                | 7.4 | 5.9  | 45.0 (0.997)  | 25.9(0.997)  |
| Wyong, Aus                                  | 8.99       | 0.3154                  | 3.51 | 187-159           | 7.3 | 6.9  | 40.9(0.980)   | 22.5(0.976)  |
| Petrie, Aus                                 | 9.88       | 0.3408                  | 3.45 | 48                | 7.3 | 8.3  | 43.7 (0.999)  | 25.4 (0.999)   |
| North Pine, Aus                             | 6.58       | 0.1418                  | 2.15 | 81                | 7.6 | 4.9  | 45.0 (0.963)  | 25.0 (0.964)   |
| Lake Gaillard WTP, USA <sup>1</sup>         | 1.91       | 0.03                    | 1.57 | 30-50             | 7.3 | 2.5<br>4.0                                 | 28.8 (0.988)<br>29.6 (0.982)  | 15.9 (0.964)<br>16.2 (0.97)  |
| Lime softened Lake Gaillard(?) <sup>1</sup> | -          | -                       | -    | 30-50 (?)<br>+100 | 7.5 | 2.5  | 44.7 (0.992)  | 16.5 (0.990)   |

<sup>1</sup>McClellan, 2000 PhD Thesis

Gallard & Gunten, 2002 - molar yield  $19.6 \pm 4.9 \mu\text{M TTHM}/\text{mM of Cl}_2$  reacted  $R^2 > 0.92$  in eight different raw water samples with SUVA 0.6-2.1

Sathasivan et al., 2019; NOM 7 conference proceedings





# Molar fractions

$$n_{CHCl_3} = \frac{C_{CHCl_3}}{MW_{CHCl_3}}$$

$$n_T = n_{CHCl_3} + n_{CHCl_2Br} + n_{CHClBr_2} + n_{CHBr_3}$$

$$f_{CHCl_3} = \frac{n_{CHCl_3}}{n_T}$$

Sathasivan et al., 2019; NOM 7 conference proceedings

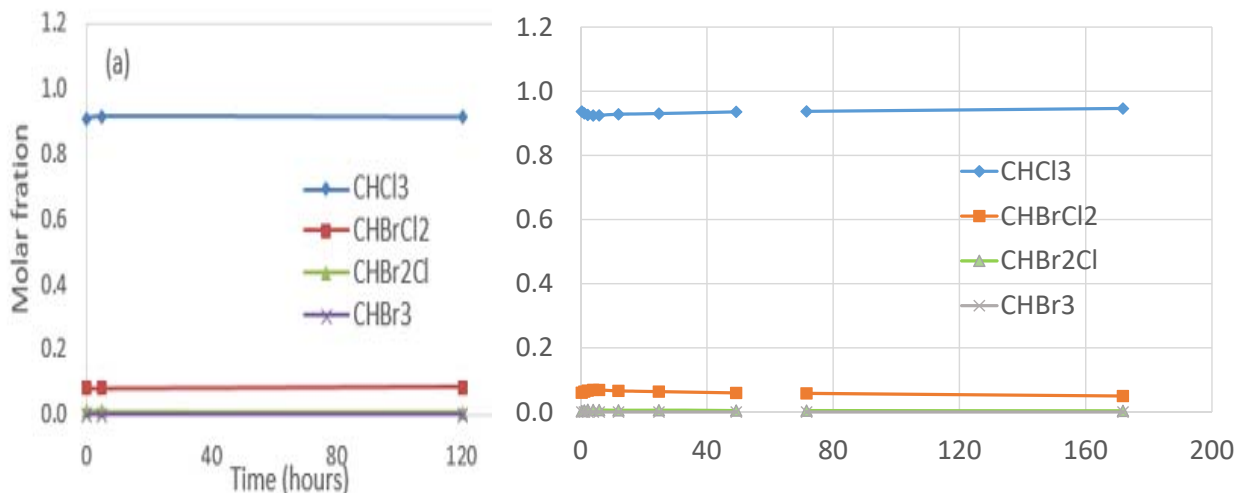


## Molar fractions of THM species in low Br waters

Nepean water (~40 µg-Br/L)

Lake Gaillard WTP (30-50 µg-Br/L),

McClellan, 2000 PhD Thesis



Sathasivan et al., 2019; NOM 7 conference proceedings



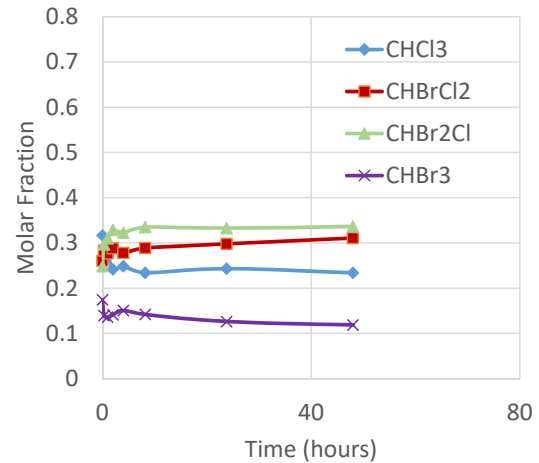
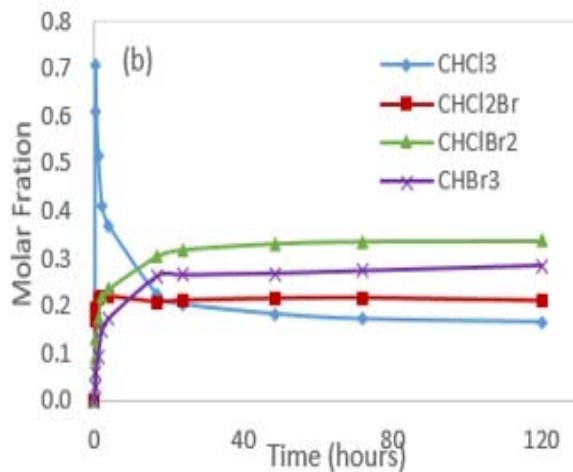
# Molar fraction of THM species in high Br waters

DOC = 2.22 mg/L; 159  $\mu\text{g-Br/L}$

Lime softened water, US

DOC ?, >100  $\mu\text{g-Br/L}$

McClellan, 2000 PhD Thesis



Sathasivan et al., 2019; NOM 7 conference proceedings



## Model of THM species

- Now chlorine decay can be described for a given water
- Yield (mass as well as molar) remains relatively constant
- Molar (mass) fraction of each species remains relatively constant for ret time,  $t > 24$  h in raw waters
- In treated water, constancy  $t > 4$  h

Sathasivan et al., 2019; NOM 7 conference proceedings

# Model

$$\frac{dTTHM}{dt} = \alpha_{mass}(k_f \cdot FRA + k_s \cdot SRA) \cdot Cl$$

$$\frac{dC_{CHCl_3}}{dt} = \alpha_{mol} \cdot f_{CHCl_3}(k_f \cdot FRA + k_s \cdot SRA) \cdot Cl \cdot MW_{CHCl_3}$$

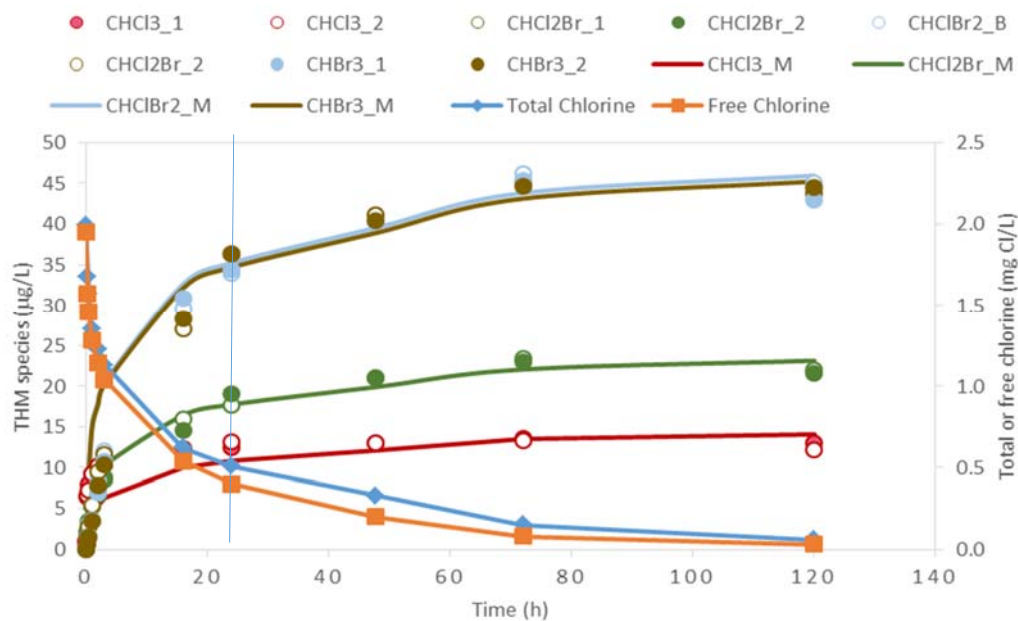
Or simply

$$C_{CHCl_3} = \alpha_{mol} \cdot (Cl_o - Cl_t) \cdot f_{CHCl_3} \cdot MW_{CHCl_3}$$

Sathasivan et al., 2019; NOM 7 conference proceedings



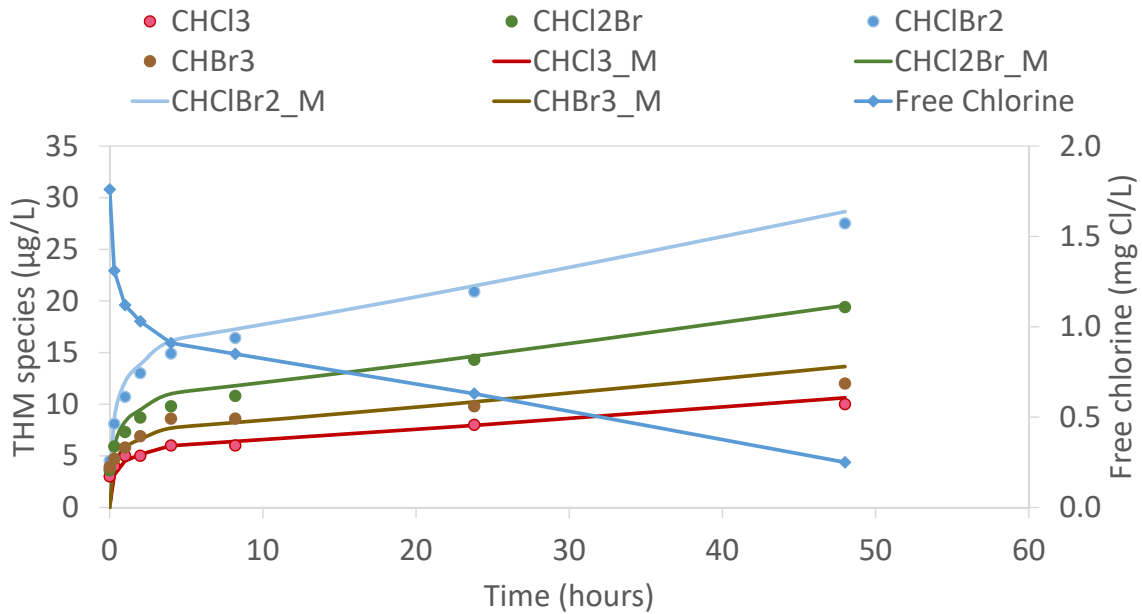
# Model agreement, our data



Sathasivan et al., 2019; NOM 7 conference proceedings



# Model agreement, US lime softened water<sup>1</sup>



<sup>1</sup> >100 µg-Br/L ; McClellan, 2000 PhD Thesis

Sathasivan et al., 2019; NOM 7 conference proceedings



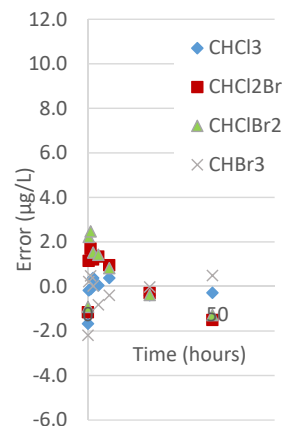
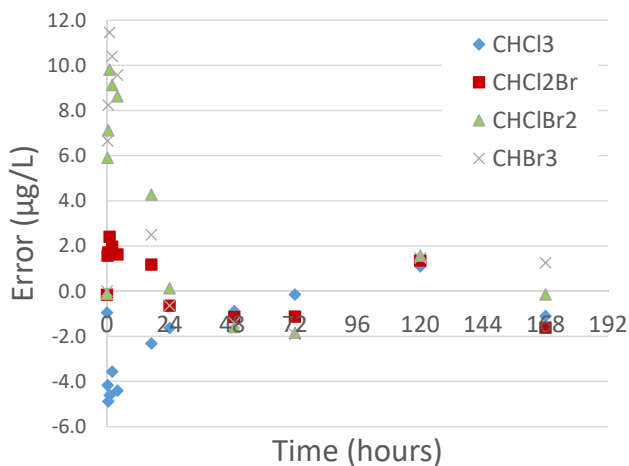
## Error in prediction

DOC = 2.22 mg/L; 159 µg-Br/L

Lime softened water, US

DOC ?, >100 µg-Br/L

McClellan, 2000 PhD Thesis




Sathasivan et al., 2019; NOM 7 conference proceedings



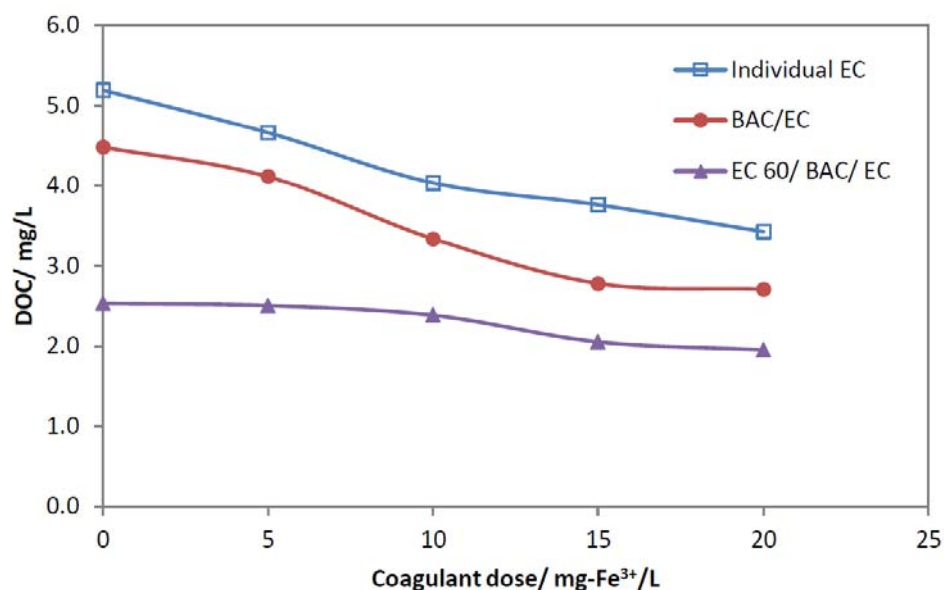
# Comparison of best models with the developed model

|                          | Standard error of best models ( $\mu\text{g/L}$ ) | Max error, raw water $t > 24$ h ( $\mu\text{g/L}$ ) | Max error Lime softened water, $t > 0$ h |
|--------------------------|---|---|--|
| $\text{CHCl}_3$          | 14.4  | <2  | <2                                       |
| $\text{CHCl}_2\text{Br}$ | 8.7   | <2  | <2                                       |
| $\text{CHBr}_3$          | 4.1   | <2  | <2                                       |
| $\text{CHClBr}_2$        | >35   | <2  | <2                                       |
| TTHM                     | 68.8 – 76.8                                       | <5  | <5                                       |

Yield & fixed molar fraction approach minimizes the error to below measurement error.

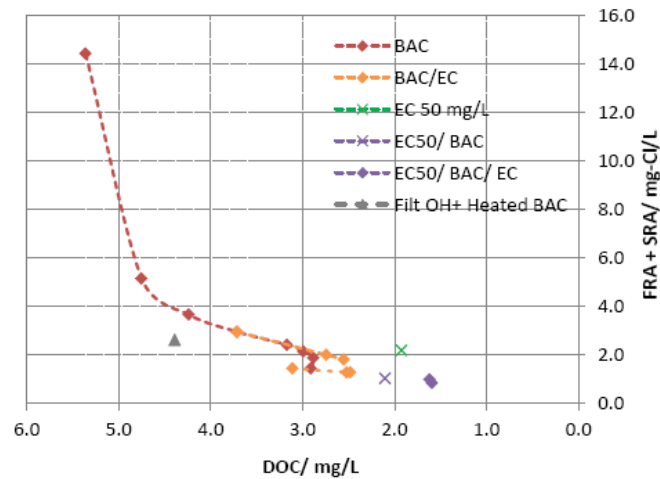
Sathasivan et al., 2019; NOM 7 conference proceedings; Water Research under review  SU Water Group

## BAC/Coagulation



Shashika Krotta Gamage (2019) PhD Thesis

# Is DOC good predictor of chlorine decay?



Shashika Krotta Gamage (2019) PhD Thesis

Thank you

Any questions??