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# CEE 697K

## ENVIRONMENTAL REACTION KINETICS

### Lecture #17

[Kinetic Modeling](#): Computer Models

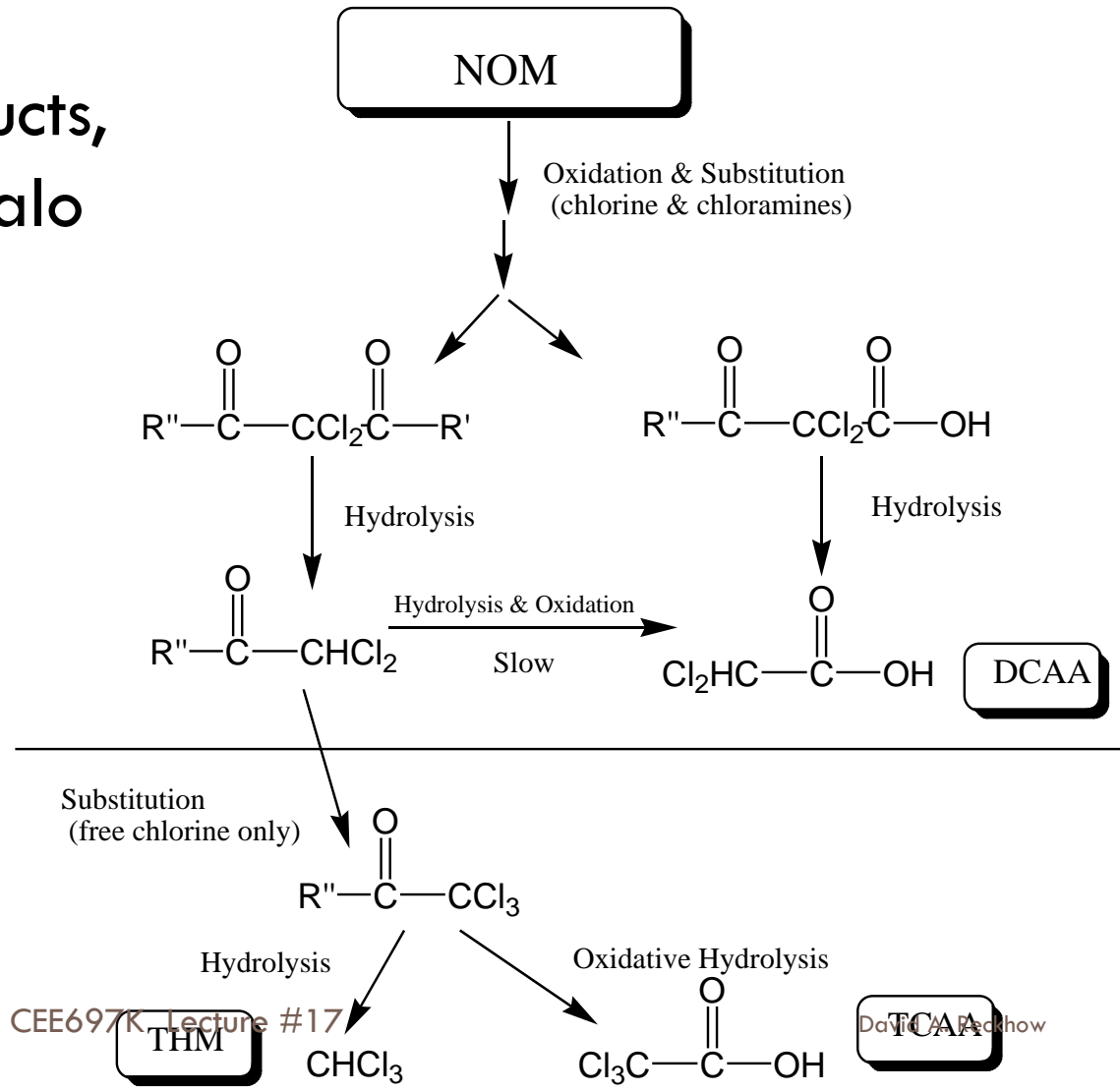
[Case Study](#): Chloramination II

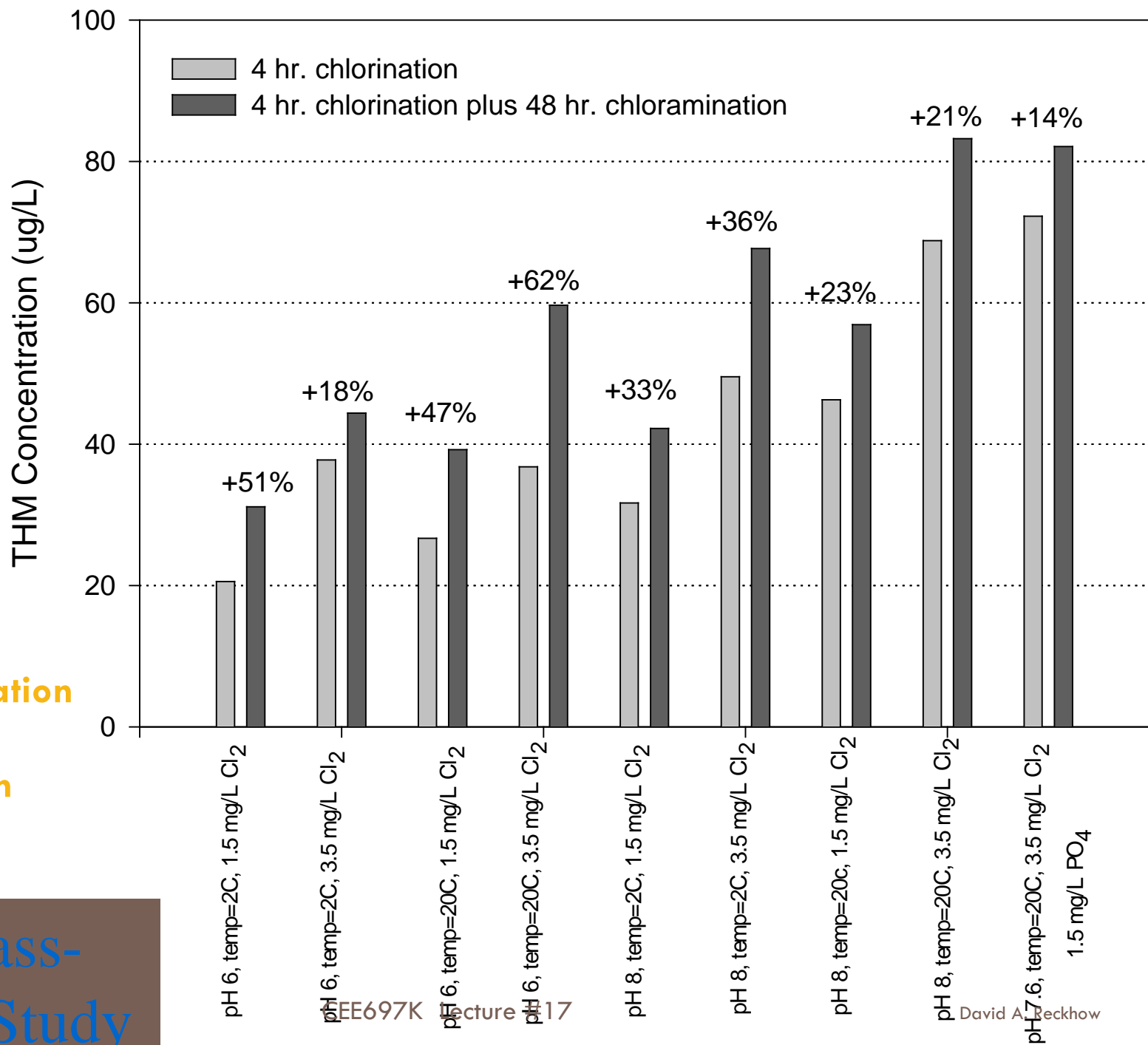
Brezonik, pp.

# HAAs: Chlorine vs Chloramine

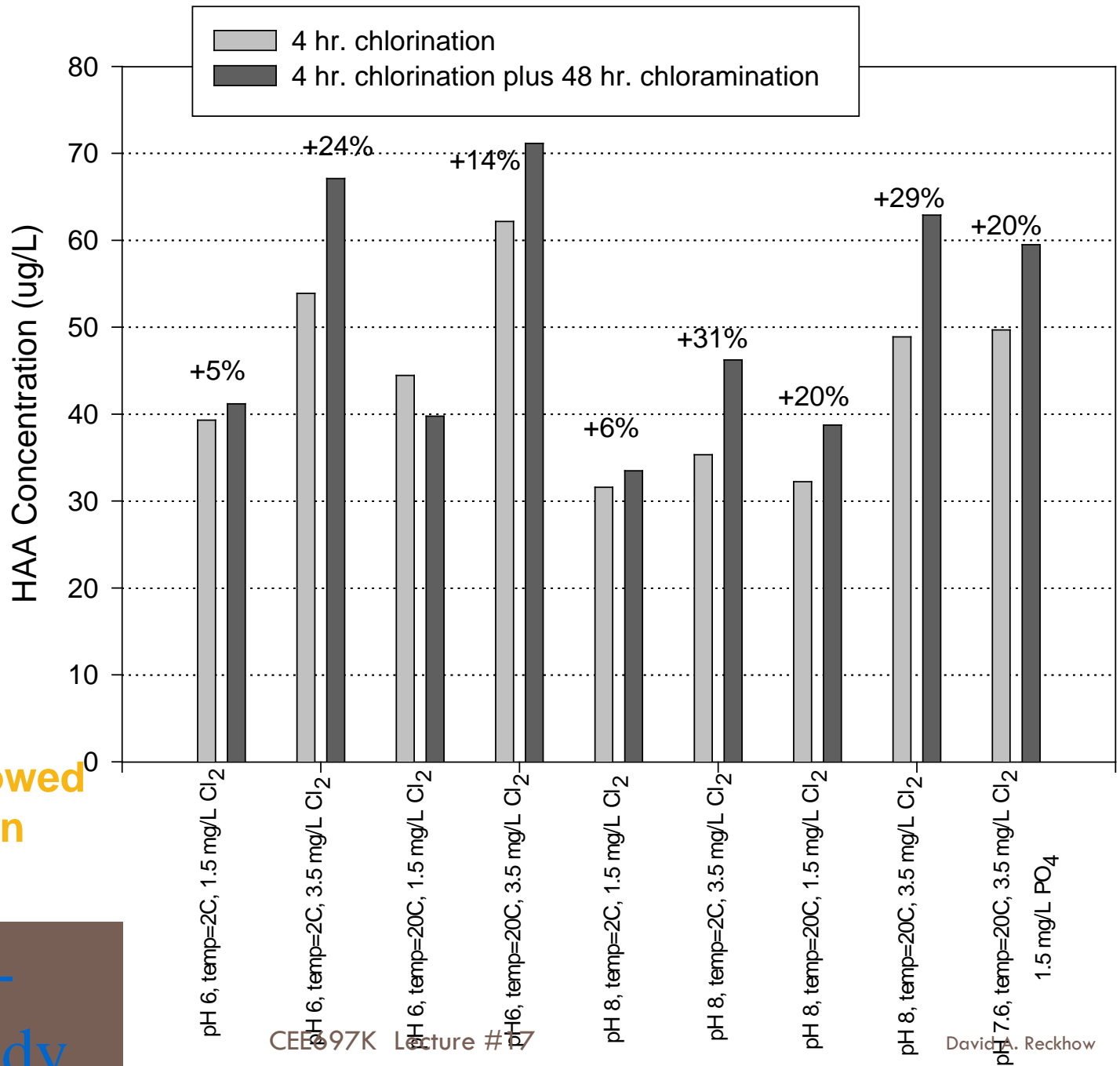
2

- Dihalo products, but little trihalo





THMs: Chlorination  
followed by  
Chloramination



HAA's:  
Chlorination followed  
by Chloramination

# Precursors & Behavior

General Trends

Mono & Dihalo-DBPs	Trihalo-DBPs	Precursor Origins	Removal by:	
			Coag. or Oxidation	Biodegrada-tion
Haloacids (DCAA)	THMs	General NOM	Average	Average
Aldehydes	Aldehydes (Chloral Hydrate)	Oxidized NOM (bacterial, solar, ozone)	Poor	Good
Ketones (Dichloropropanone)	Ketones (Trichloropropanone)			
Nitroalkanes	Nitroalkanes (Chloropicrin)	reactive Nitrogen species		
Nitriles (Dichloroacetonitrile)	Nitriles (Trichloroacetonitrile)	Algal (autochthonous)	Average	Average
Amides (Dichloroacetamide)	Amides (Trichloroacetamide)			
Cyanogen Halides (CNCl, CNBr)				
Halobenzoquinones?	Haloacids (TCAA)	Terrestrial - Lignin (allochthonous)	Good	Poor

# DBP control with DS management

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Parameter	THM	Tri-HAAs	Di-HAAs	HANs	TCP	DCP	CP	Iodo-DBPs
Time↓	↓	↓	↓	↑	↑	↑	↓	↑
Cl <sub>2</sub> Dose↓	↓	↓~	↓	↑	↑	↑↑	↓	↑
pH↓	↓	↑	~	↑	↑	↑		↑
Cl <sub>2</sub> to NH <sub>2</sub> Cl↑	↓	↓↓	↓~	~	~	↑	↑	↑
Temp↓	↓	~	↓	↑	↑	↑	↓	↑

Driven by Regulations



Notes:

- HANs: haloacetonitriles, including DCAN
- TCP: trichloropropanone, a haloketone
- DCP: dichloropropanone: a haloketone
- CP: chloropicrin: a halonitromethane
- Iodo-DBPs: include iodinated THMs, HAAs, etc

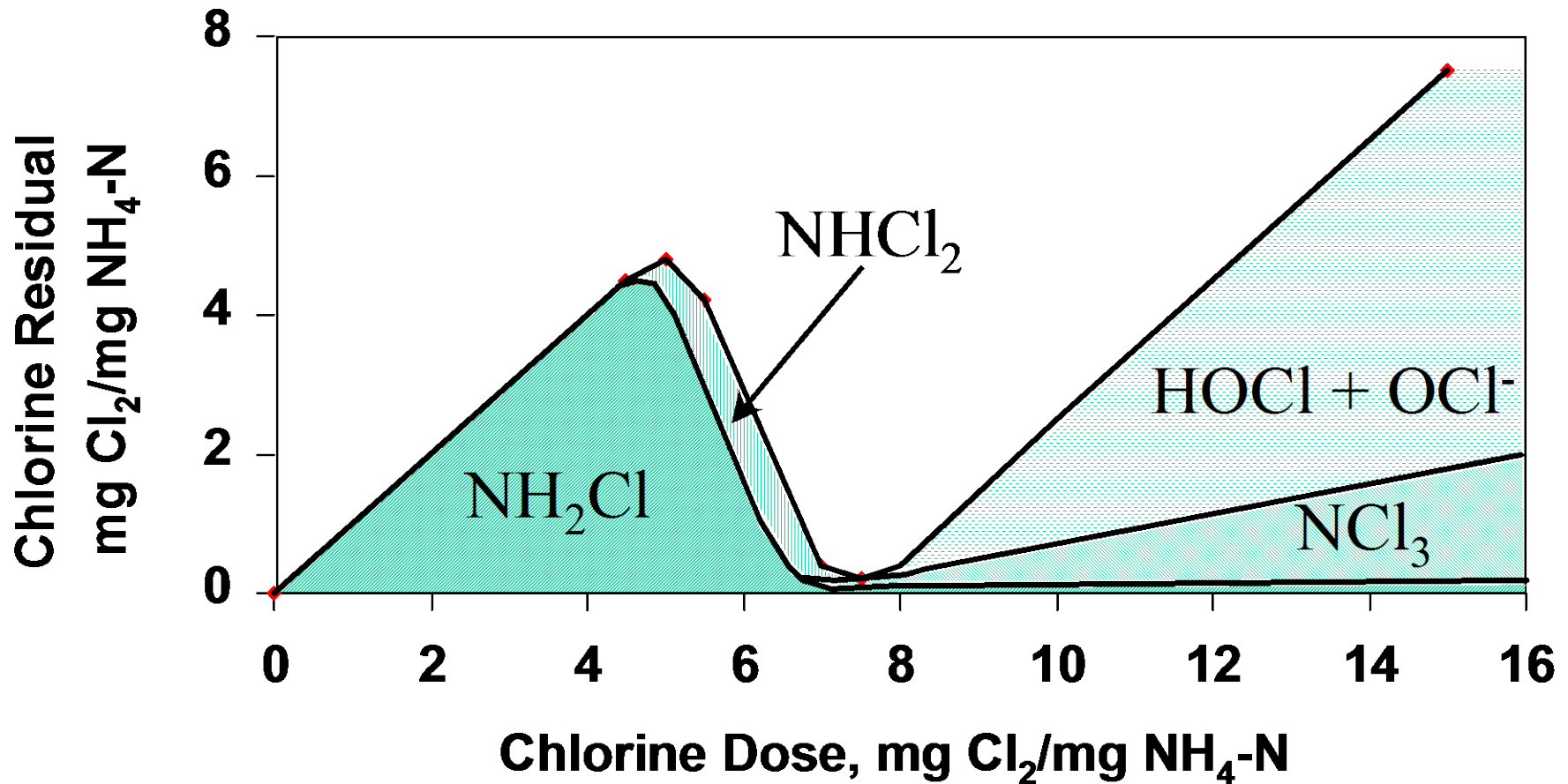
# Chloramines vs Free Chlorine

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- DBPs
  - ▣ Lower levels of trihalogenated byproducts
    - Easier to meet current DBP regulations
  - ▣ Less impact on dihalogenated compound
    - Some are higher with chloramines
  - ▣ More of some types of N-DBPs
    - Organic chloramines, nitriles, amides, nitro compds
- Other concerns
  - ▣ Growth of ammonia oxidizing bacteria
    - Loss of residual, formation of reactive intermediates
  - ▣ Reduction of Lead (IV)
  - ▣ Public perception & direct health effects

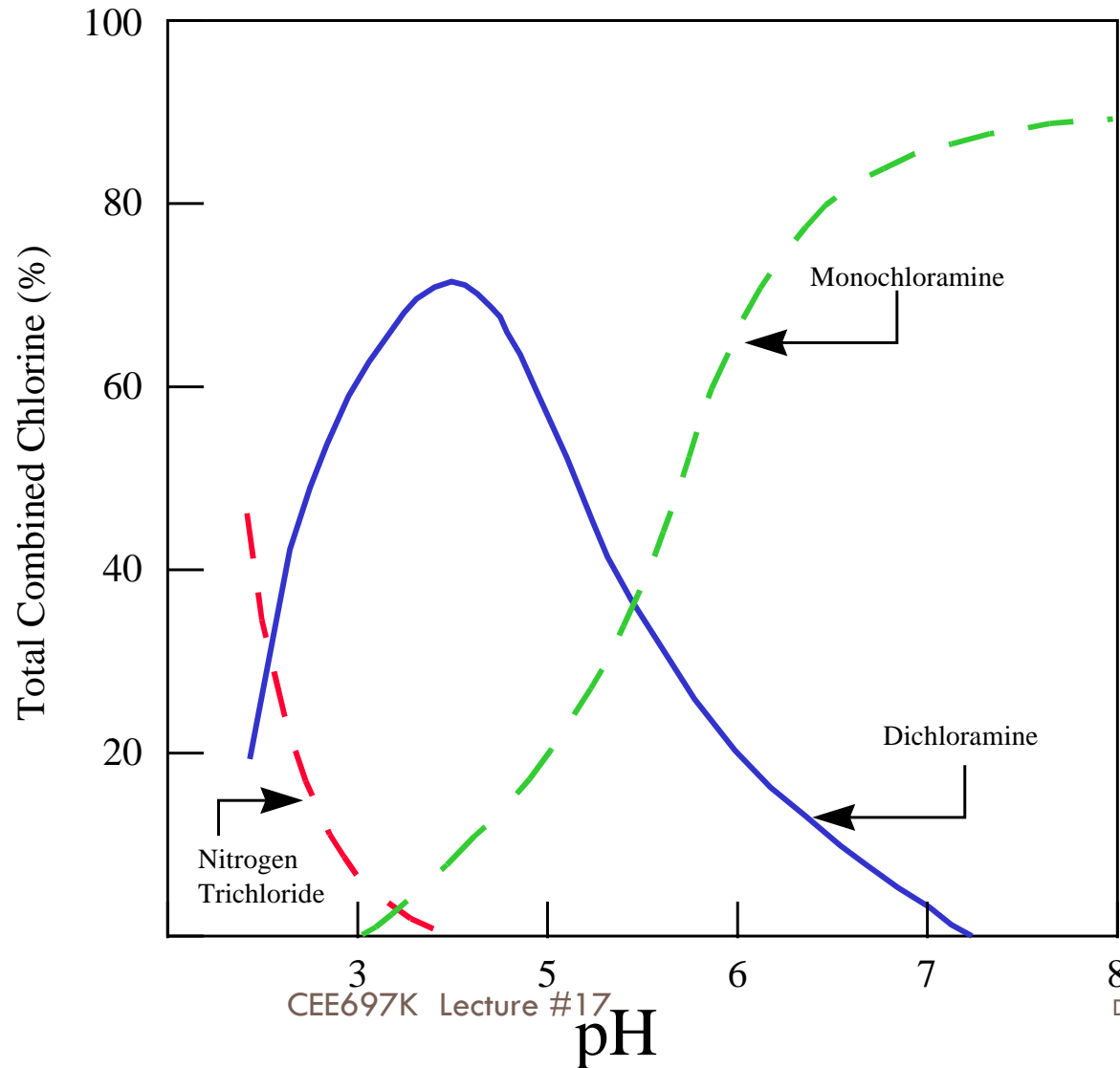
# Theoretical Breakpoint Curve

8





# Distribution Diagram for Chloramine Species with pH



# Jafvert & Valentine Model

Jafvert, C. T. and R. L. Valentine (1992). "[Reaction Scheme for the Chlorination of Ammoniacal Water.](#)" *Environmental Science & Technology* **26(3)**: 577-586.

Table I. Reactions and Associated Constants

reaction stoichiometry	rate expression	rate constant (25 °C)	ref
(1) HOCl + NH <sub>3</sub> → NH <sub>2</sub> Cl + H <sub>2</sub> O	$k_{am}[\text{HOCl}][\text{NH}_3]$	$k_{am} = 1.5 \times 10^{10} \text{ M}^{-1} \text{ h}^{-1}$	18
(2) NH <sub>2</sub> Cl + H <sub>2</sub> O → HOCl + NH <sub>3</sub>	$k_{ma}[\text{NH}_2\text{Cl}]$	$k_{ma} = 7.6 \times 10^{-2} \text{ h}^{-1}$	18
(3) HOCl + NH <sub>2</sub> Cl → NHCl <sub>2</sub> + H <sub>2</sub> O	$k_{md}[\text{HOCl}][\text{NH}_2\text{Cl}]$	$k_{md} = 1.0 \times 10^6 \text{ M}^{-1} \text{ h}^{-1}$	4, 17
(4) NHCl <sub>2</sub> + H <sub>2</sub> O → HOCl + NH <sub>2</sub> Cl	$k_{dm}[\text{NHCl}_2]$	$k_{dm} = 2.3 \times 10^{-3} \text{ h}^{-1}$	17
(5) NH <sub>2</sub> Cl + NH <sub>2</sub> Cl → NHCl <sub>2</sub> + NH <sub>3</sub>	$k_{mmd}[\text{NH}_2\text{Cl}]^2$	$k_{mmd}^a = k_H[\text{H}^+] + k_{\text{H}_2\text{P}}[\text{H}_2\text{PO}_4^-] + k_{\text{H}_3\text{P}}[\text{H}_3\text{PO}_4]$	20, 21
(6) NHCl <sub>2</sub> + NH <sub>3</sub> → NH <sub>2</sub> Cl + NH <sub>2</sub> Cl	$k_{dmm}[\text{NHCl}_2][\text{NH}_3][\text{H}^+]$	$k_{dmm} = 2.16 \times 10^8 \text{ M}^{-2} \text{ h}^{-1}$	9
(7) NHCl <sub>2</sub> + H <sub>2</sub> O → I	$k_{di}[\text{NHCl}_2][\text{OH}^-]$	$k_{di} = 4.0 \times 10^5 \text{ M}^{-1} \text{ h}^{-1}$	20, 28
(8) I + NHCl <sub>2</sub> → HOCl + products <sup>b</sup>	$k_{idp}[\text{I}][\text{NHCl}_2]$	$k_{idp} = 1.0 \times 10^8 \text{ M}^{-1} \text{ h}^{-1}$	6
(9) I + NH <sub>2</sub> Cl → products <sup>b</sup>	$k_{imp}[\text{I}][\text{NH}_2\text{Cl}]$	$k_{imp} = 3.0 \times 10^7 \text{ M}^{-1} \text{ h}^{-1}$	6
(10) NH <sub>2</sub> Cl + NHCl <sub>2</sub> → products <sup>b</sup>	$k_{mdp}[\text{NH}_2\text{Cl}][\text{NHCl}_2]$	$k_{mdp} = 55.0 \text{ M}^{-1} \text{ h}^{-1}$	6, 8
(11) HOCl + NHCl <sub>2</sub> → NCl <sub>3</sub> + H <sub>2</sub> O	$k_{dt}[\text{NHCl}_2][\text{HOCl}]$	$k_{dt}^c = k_{\text{HP}}[\text{HPO}_4^{2-}] + k_{\text{OCl}^-}[\text{OCl}^-] + k_{\text{OH}^-}[\text{OH}^-]$	9
(12) NHCl <sub>2</sub> + NCl <sub>3</sub> + 2H <sub>2</sub> O → 2HOCl + products <sup>b</sup>	$k_{dtp}[\text{NHCl}_2][\text{NCl}_3][\text{OH}^-]$	$k_{dtp} = 2.0 \times 10^{14} \text{ M}^{-2} \text{ h}^{-1}$	9, d
(13) NH <sub>2</sub> Cl + NCl <sub>3</sub> + H <sub>2</sub> O → HOCl + products <sup>b</sup>	$k_{mtp}[\text{NH}_2\text{Cl}][\text{NCl}_3][\text{OH}^-]$	$k_{mtp} = 5.0 \times 10^{12} \text{ M}^{-2} \text{ h}^{-1}$	d
(14) NHCl <sub>2</sub> + 2HOCl + H <sub>2</sub> O → NO <sub>3</sub> <sup>-</sup> + 5H <sup>+</sup> + 4Cl <sup>-</sup>	$k_{dhp}[\text{NHCl}_2][\text{OCl}^-]$	$k_{dhp} = 8.3 \times 10^5 \text{ M}^{-1} \text{ h}^{-1}$	d

<sup>a</sup>  $k_H = 2.5 \times 10^7 \text{ M}^{-2} \text{ h}^{-1}$ ;  $k_{\text{H}_2\text{P}} = 1.3 \times 10^3 \text{ M}^{-2} \text{ h}^{-1}$ ;  $k_{\text{H}_3\text{P}} = 3.2 \times 10^6 \text{ M}^{-2} \text{ h}^{-1}$ . In carbonate-buffered systems additional terms include  $k_{\text{H}_2\text{CO}_3}[\text{H}_2\text{CO}_3] + k_{\text{HCO}_3^-}[\text{HCO}_3^-]$ , where  $k_{\text{H}_2\text{CO}_3} = 2.7 \times 10^3 \text{ M}^{-2} \text{ h}^{-1}$  and  $k_{\text{HCO}_3^-} = 7.2 \text{ M}^{-2} \text{ h}^{-1}$  (21). <sup>b</sup> Products may include N<sub>2</sub>, H<sub>2</sub>O, Cl<sup>-</sup>, H<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and unidentified reaction products. For purposes of d[H<sup>+</sup>] calculation, products were assumed to contain 3H<sup>+</sup> for each reaction, consistent with N<sub>2</sub> formation. <sup>c</sup>  $k_{\text{HP}} = 5.72 \times 10^7 \text{ M}^{-2} \text{ h}^{-1}$ ;  $k_{\text{OCl}^-} = 3.24 \times 10^8 \text{ M}^{-2} \text{ h}^{-1}$ ;  $k_{\text{OH}^-} = 1.18 \times 10^{13} \text{ M}^{-2} \text{ h}^{-1}$ . In carbonate-buffered systems an additional term is  $k_{\text{CO}_3}[\text{CO}_3^{2-}]$ , where  $k_{\text{CO}_3} = 2.16 \times 10^{10} \text{ M}^{-2} \text{ h}^{-1}$  (9). <sup>d</sup> This work.

# Model Equations

Vikesland, P. J., K. Ozekin, et al. (2001).

"[Monochloramine decay in model and distribution system waters.](#)" *Water Research* **35(7)**: 1766-1776.

#	Reaction	Rate coefficient/equilibrium constant (25°C)	References
1.1	$\text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$	$k_{1.1} = 1.5 \times 10^{10} \text{ M}^{-1} \text{ h}^{-1}$	<a href="#">Morris and Isaac (1981)</a>
1.2	$\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_3$	$k_{1.2} = 7.6 \times 10^{-2} \text{ h}^{-1}$	<a href="#">Morris and Isaac (1981)</a>
1.3	$\text{HOCl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O}$	$k_{1.3} = 1.0 \times 10^6 \text{ M}^{-1} \text{ h}^{-1}$	<a href="#">Margerum et al. (1978)</a>
1.4	$\text{NHCl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_2\text{Cl}$	$k_{1.4} = 2.3 \times 10^{-3} \text{ h}^{-1}$	<a href="#">Margerum et al. (1978)</a>
1.5	$\text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{NH}_3$	$k_d^a$	Vikesland et al. (2001)
1.6	$\text{NHCl}_2 + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{NH}_2\text{Cl}$	$k_{1.6} = 2.2 \times 10^8 \text{ M}^{-2} \text{ h}^{-1}$	<a href="#">Hand and Margerum (1983)</a>
1.7	$\text{NHCl}_2 + \text{H}_2\text{O} \rightarrow \text{I}$	$k_{1.7} = 4.0 \times 10^5 \text{ M}^{-1} \text{ h}^{-1}$	<a href="#">Jafvert and Valentine (1987)</a>
1.8	$\text{I} + \text{NHCl}_2 \rightarrow \text{HOCl} + \text{products}$	$k_{1.8} = 1.0 \times 10^8 \text{ M}^{-1} \text{ h}^{-1}$	<a href="#">Leao (1981)</a>
1.9	$\text{I} + \text{NH}_2\text{Cl} \rightarrow \text{products}$	$k_{1.9} = 3.0 \times 10^7 \text{ M}^{-1} \text{ h}^{-1}$	<a href="#">Leao (1981)</a>
1.10	$\text{NH}_2\text{Cl} + \text{NHCl}_2 \rightarrow \text{products}$	$k_{1.10} = 55.0 \text{ M}^{-1} \text{ h}^{-1}$	<a href="#">Leao (1981)</a>
1.11	$\text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^-$	$\text{p}K_a = 7.5$	<a href="#">Snoeyink and Jenkins (1980)</a>
1.12	$\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$	$\text{p}K_a = 9.3$	<a href="#">Snoeyink and Jenkins (1980)</a>
1.13	$\text{H}_2\text{CO}_3 \rightarrow \text{HCO}_3^- + \text{H}^+$	$\text{p}K_a = 6.3$	<a href="#">Snoeyink and Jenkins (1980)</a>
1.14	$\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}^+$	$\text{p}K_a = 10.3$	<a href="#">Snoeyink and Jenkins (1980)</a>

# Vikesland modification

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□ Modified version of equation #5 for carbonate

$$\square k_d = k_H^+ [H^+] + k_{H_2CO_3} [H_2CO_3] + k_{HCO_3} [HCO_3]$$

□ Where

■  $k_H^+ = 2.5 \times 10^7 \text{ M}^{-2}\text{h}^{-1}$

■  $k_{H_2CO_3} = 4 \times 10^4 \text{ M}^{-2}\text{h}^{-1}$

■  $k_{HCO_3} = 800 \text{ M}^{-2}\text{h}^{-1}$

■ I is the unidentified monochloramine auto-decomposition intermediate

Vikesland, P. J., K. Ozekin, et al. (2001).

"Monochloramine decay in model and distribution system waters." *Water Research* 35(7): 1766-1776.

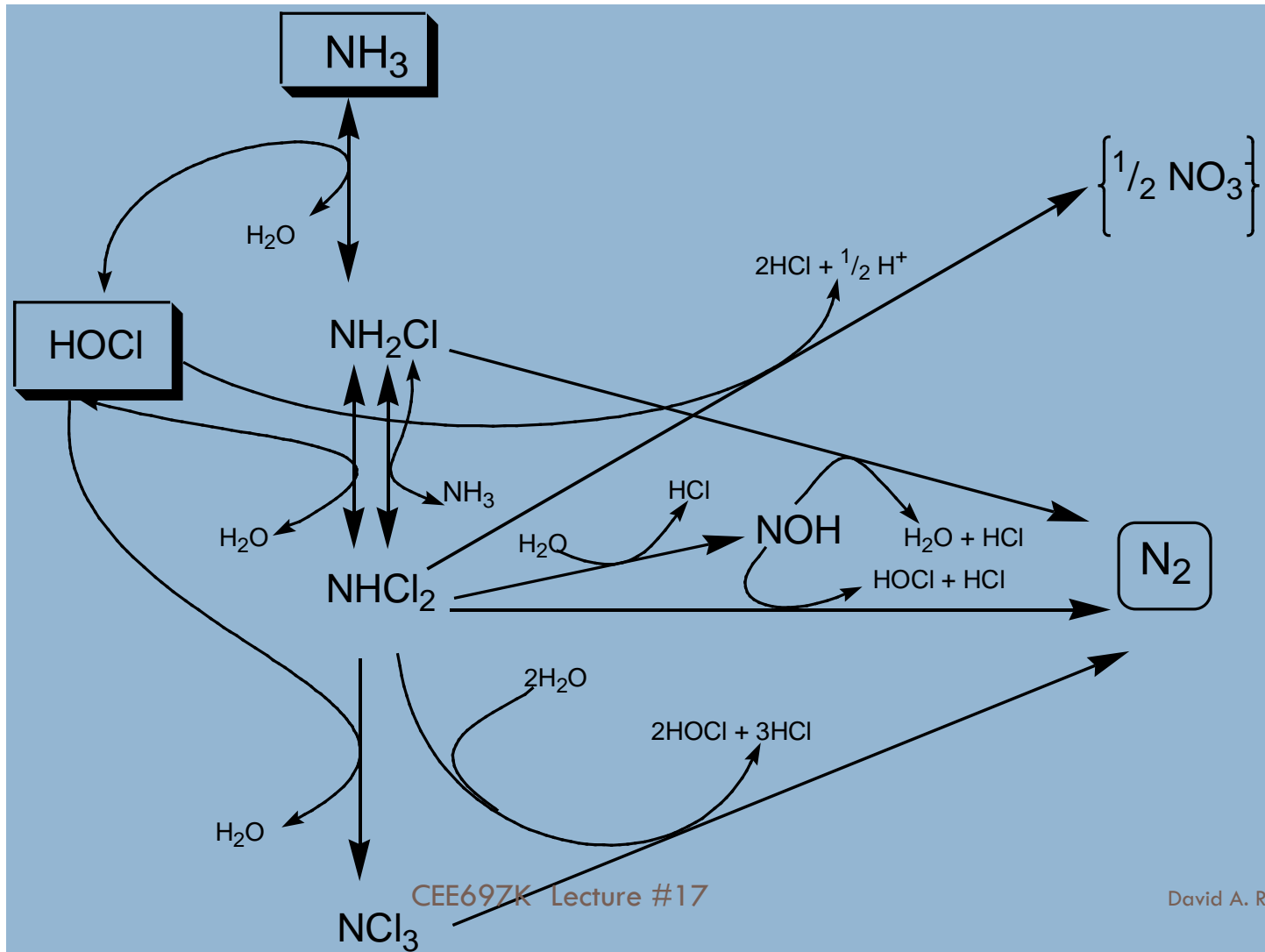
# Temperature Effects

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Reaction	Rate coefficient/equilibrium constant	References
$\text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$	$k_{1,1} = 2.37 \times 10^{12} \exp(-1510/T) \text{ M}^{-1} \text{ h}^{-1}$	<a href="#">Morris and Isaac (1981)</a>
$\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_3$	$k_{1,2} = 6.7 \times 10^{11} \exp(-8800/T) \text{ h}^{-1}$	<a href="#">Morris and Isaac (1981)</a>
$\text{HOCl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O}$	$k_{1,3} = 1.08 \times 10^9 \exp(-2010/T) \text{ M}^{-1} \text{ h}^{-1}$	<a href="#">Margerum et al. (1978)</a>
$\text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{NH}_3$	$k_{1,5} = k_{\text{H}^+}[\text{H}^+] + k_{\text{HCO}_3}[\text{HCO}_3^-] + k_{\text{H}_2\text{CO}_3}[\text{H}_2\text{CO}_3]$	
	$k_{\text{H}^+} = 3.78 \times 10^{10} \exp(-2169/T) \text{ M}^{-2} \text{ h}^{-1}$	<a href="#">Granstrom (1954)</a>
	$k_{\text{HCO}_3} = 1.5 \times 10^{35} \exp(-22144/T) \text{ M}^{-2} \text{ h}^{-1}$	Vikesland et al. (2001)
	$k_{\text{H}_2\text{CO}_3} = 2.95 \times 10^{10} \exp(-4026/T) \text{ M}^{-2} \text{ h}^{-1}$	Vikesland et al. (2001)
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	$\text{pka} = 1.48 \times 10^{-4} (T) - 9.39 \times 10^{-2} (T) + 21.2$	<a href="#">Snoeyink and Jenkins (1980)</a>
$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	$\text{pka} = 1.19 \times 10^{-4} (T) - 7.99 \times 10^{-2} (T) + 23.6$	<a href="#">Snoeyink and Jenkins (1980)</a>
$\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$	$\text{pka} = 1.03 \times 10^{-4} (T) - 9.21 \times 10^{-2} (T) + 27.6$	<a href="#">Bates and Pinching (1950)</a>
$\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+$	$\text{pka} = 1.18 \times 10^{-4} (T) - 7.86 \times 10^{-2} (T) + 20.5$	

# Chloramine Decay

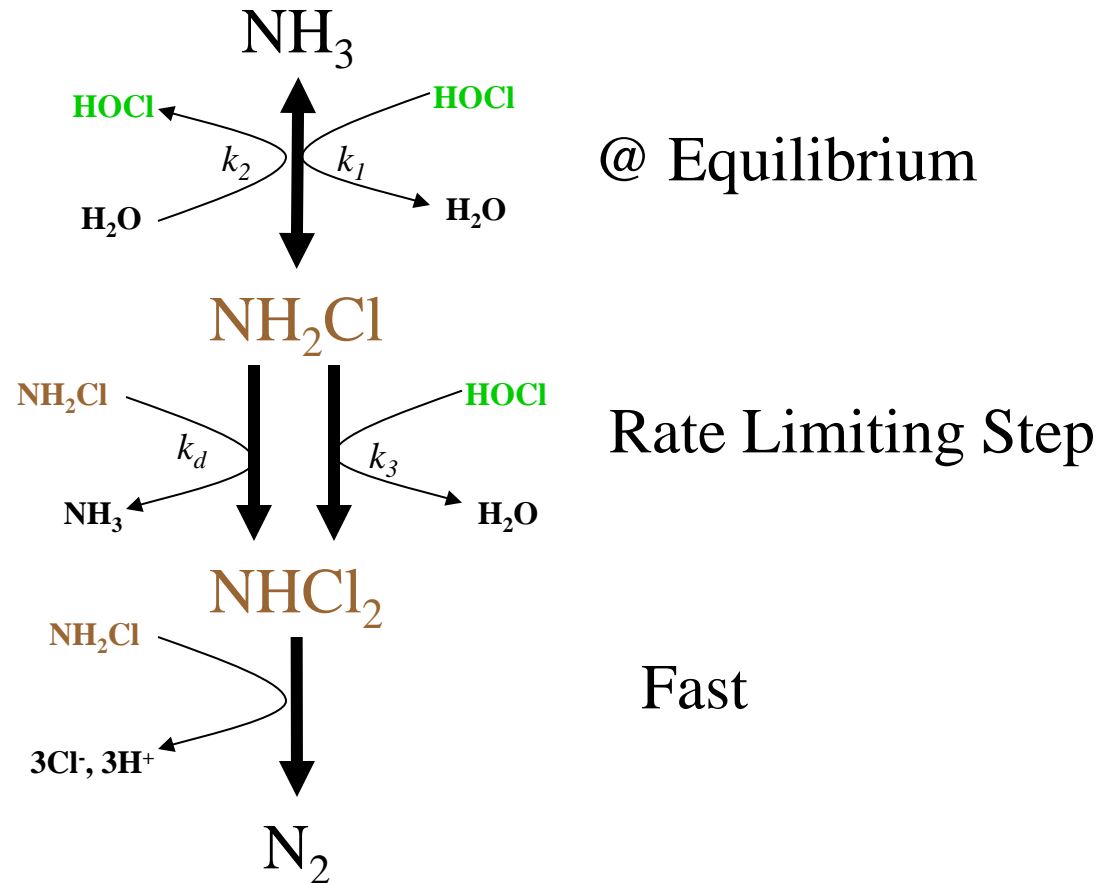
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# Valentine Model #1

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- Chloramine Formation and Decay pathway

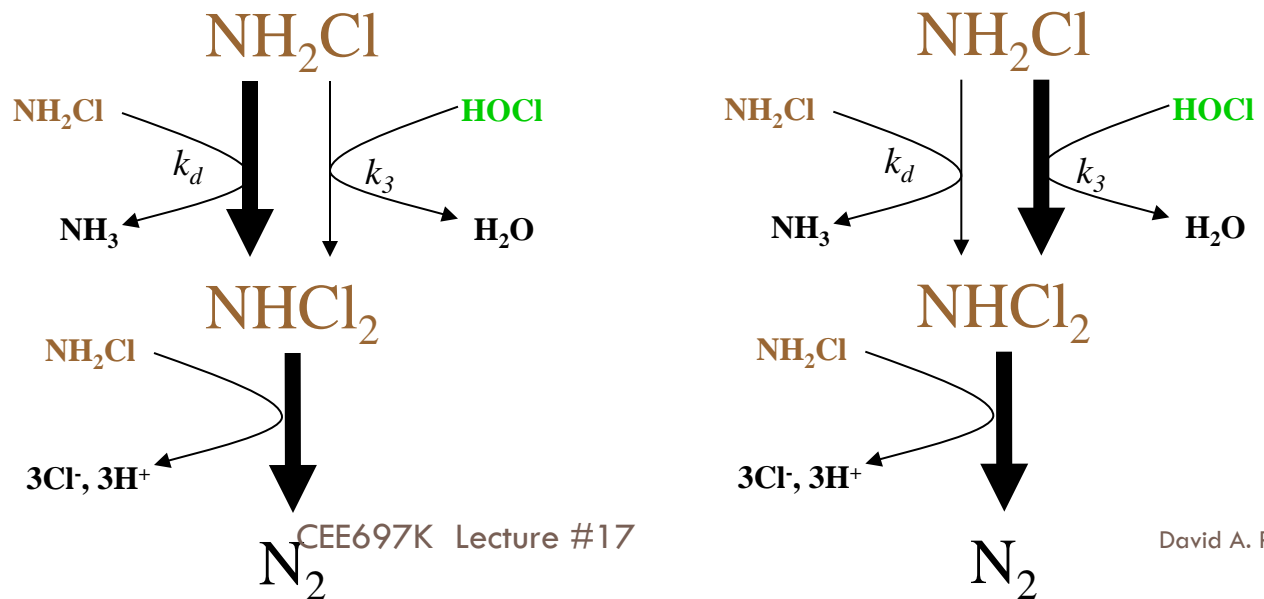


# Valentine Model #2

16

- Looking at the Rate Limiting Step

$$-\frac{d[NH_2Cl]}{dt} = \underbrace{3k_d[NH_2Cl][NH_2Cl]} + \underbrace{2k_3[NH_2Cl][HOCl]}$$





# Valentine Model #3

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□ Re-arranging:

$$-\frac{d[NH_2Cl]}{dt} = 3k_d[NH_2Cl][NH_2Cl] + 2k_3[NH_2Cl][HOCl]$$

$$-\frac{d[NH_2Cl]}{dt} = 3k_d[NH_2Cl]^2 + 2k_3[NH_2Cl][HOCl]$$

$$-\frac{d[NH_2Cl]}{dt} = \left( 3k_d + 2k_3 \frac{[HOCl]}{[NH_2Cl]} \right) [NH_2Cl]^2$$

# Valentine Model #4

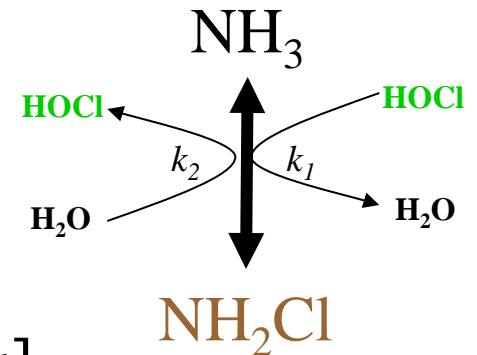
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- Looking at the first step
  - ▣ Forward reaction rate equals reverse rate
    - equilibrium

$$k_1[HOCl][NH_3] = k_2[NH_2Cl]$$

- ▣ Which leads to

$$\frac{[HOCl]}{[NH_2Cl]} = \frac{k_2}{k_1}$$



# Valentine Model #5

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## □ Combining

$$-\frac{d[NH_2Cl]}{dt} = \left( 3k_d + 2k_3 \frac{[HOCl]}{[NH_2Cl]} \right) [NH_2Cl]^2$$

$$\frac{[HOCl]}{[NH_2Cl]} = \frac{\left( \frac{k_2}{k_1} \right)}{[NH_3]}$$

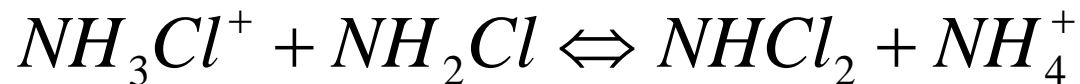
## □ We get:

$$-\frac{d[NH_2Cl]}{dt} = \left( 3k_d + \frac{2k_3 \left( \frac{k_2}{k_1} \right)}{[NH_3]} \right) [NH_2Cl]^2$$

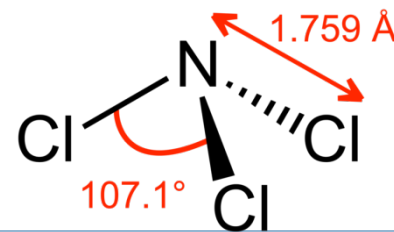
# pH effects

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- Ammonia and chloramine species are prone to protonation
- Dichloramine is more prevalent at low pH
  - ▣ Why?
    - The protonated form of monochloramine reacts more quickly than the neutral form or the reverse reaction is slower



# Nitrogen Trichloride



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## □ Acute Human toxicity ??

□ Drinking Water, showers and swimming pools

□ Blatchley's group:

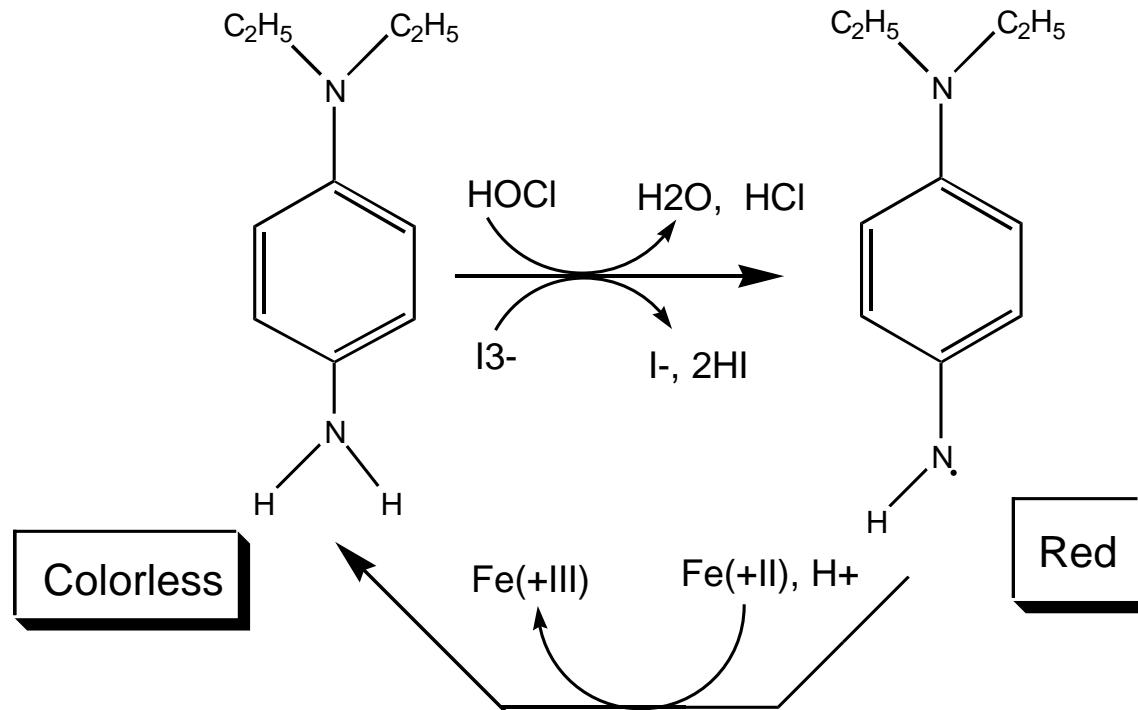
Weng, S.C., W.A. Weaver, M.Z. Afifi, T.N. Blatchley, J.S. Cramer, J. Chen, and E.R. Blatchley. 2011. Dynamics of gas-phase trichloramine (NCl<sub>3</sub>) in chlorinated, indoor swimming pool facilities. *Indoor Air* 21:391-399.

- “Trichloramine (NCl<sub>3</sub>), which is often associated with the ‘chlorine odor’ of swimming pools, has been identified as a common by-product of chlorination of many organic-N compounds that are common to swimming pools, including urea, creatinine, and amino acids.
- NCl<sub>3</sub> is a respiratory irritant to mice, and more recent studies have indicated NCl<sub>3</sub> to contribute to acute ocular and respiratory irritation symptoms in lifeguards and swimming pool workers.
- Retrospective studies have shown positive correlation between irritation symptoms among swimmers and patrons and high gas-phase NCl<sub>3</sub> concentration at indoor pool facilities.”

# Measuring chloramines

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## □ DPD titrimetric method



# Oxidation of DPD

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- Reaction with free chlorine or iodine

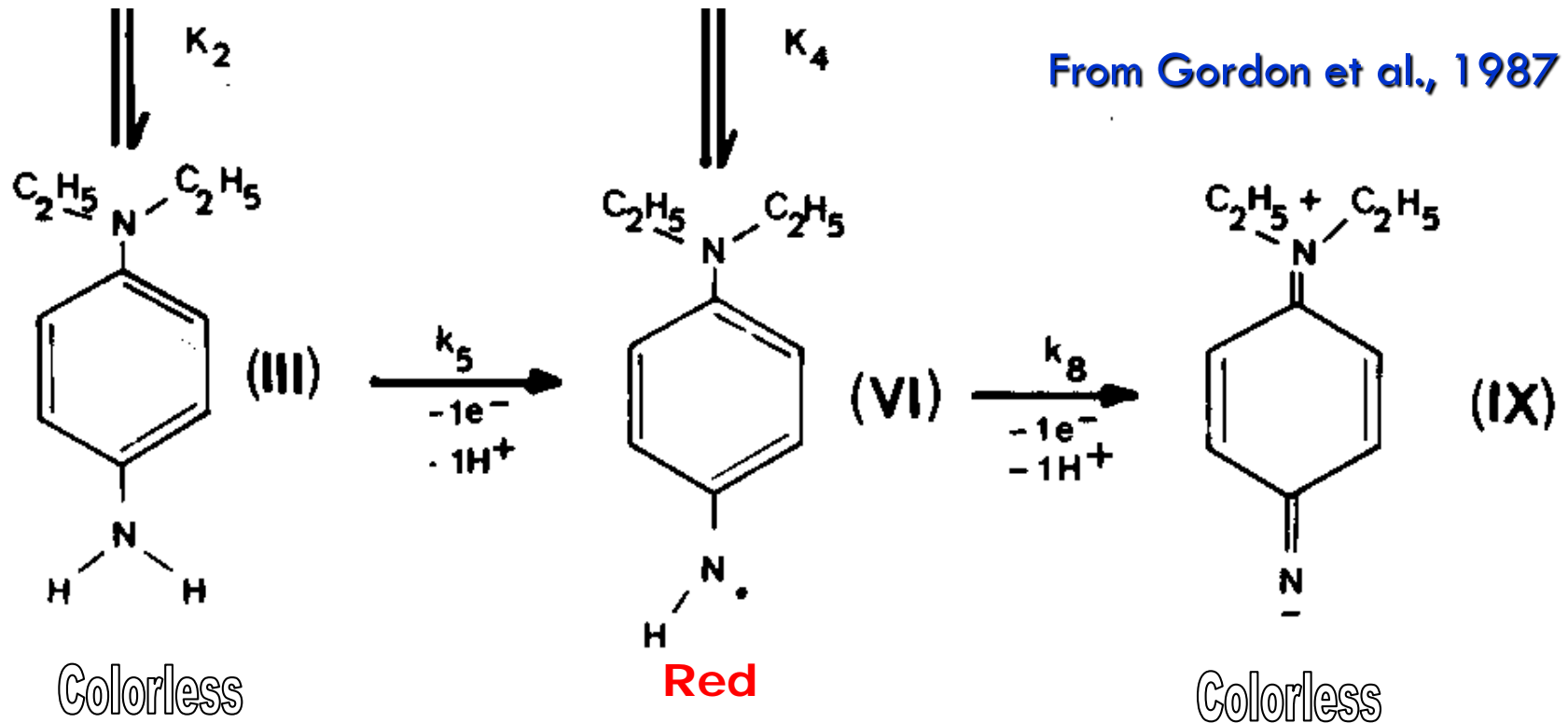


Figure 2.6 Oxidation-reduction/acid-base reaction of DPD

# Speciation with DPD

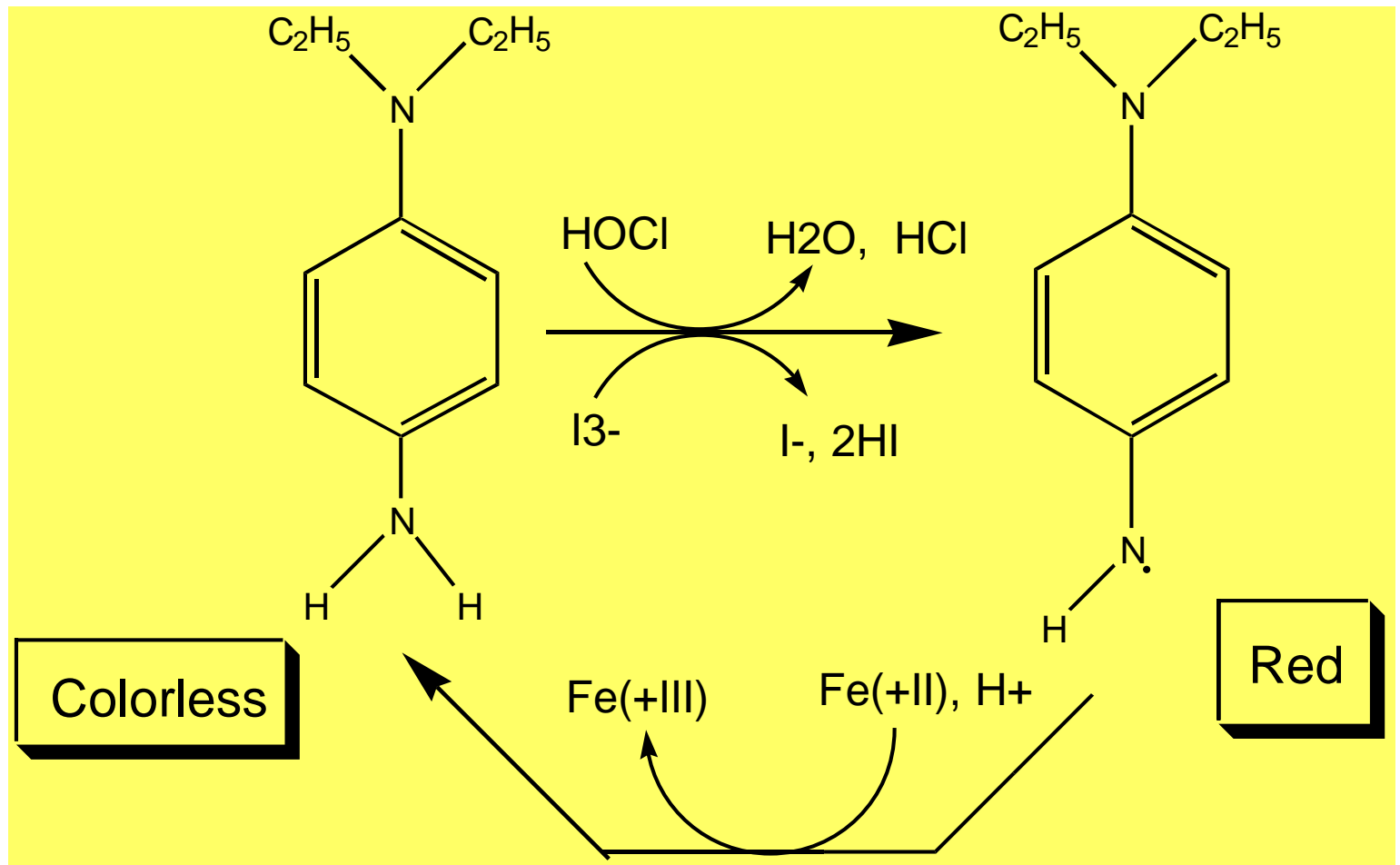
24

- FRC
  - ▣ Direct reaction of HOCl/OCl<sup>-</sup> with DPD
- Monochloramine
  - ▣ Oxidation of I<sup>-</sup> to I<sub>3</sub><sup>-</sup> by NH<sub>2</sub>Cl, and subsequent oxidation of DPD
    - Require only a small amount of iodide
- Dichloramine
  - ▣ Oxidation of I<sup>-</sup> to I<sub>3</sub><sup>-</sup> by NHCl<sub>2</sub>, and subsequent oxidation of DPD
    - Require a large amount of iodide and longer reaction time



# DPD titrimetric method

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# DPD titrimetric method

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- pH control
  - ▣ Low pH leads to protonated forms
  - ▣ High pH catalyzes DPD oxidation by atmospheric oxygen
- Potential interference
  - ▣ Any substance that can directly oxidize DPD
    - MCA can do this a bit, so we sometimes add  $\text{HgCl}_2$
  - ▣ Any substance that can oxidize iodide
    - Hydrogen peroxide, persulfate

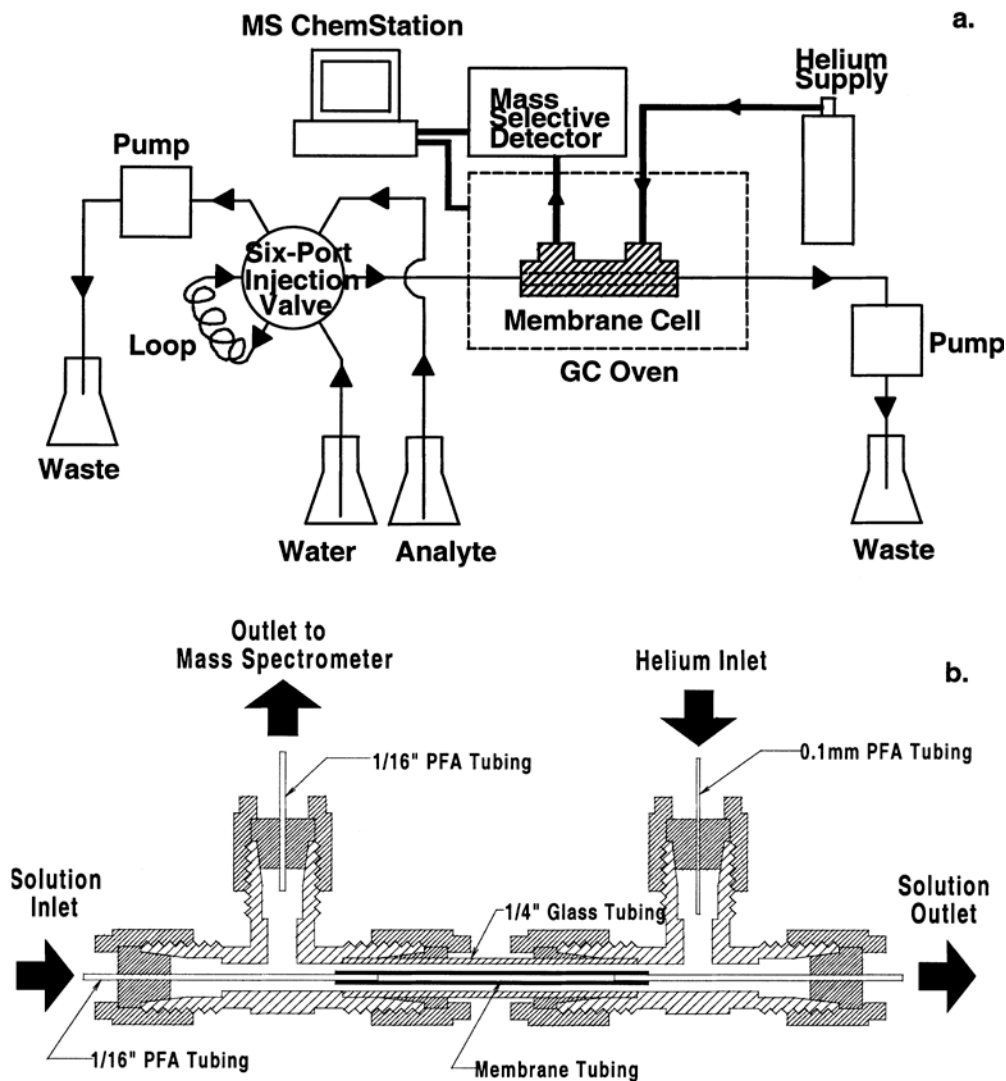


Figure 1 Schematic representation of the MIMS system (a) and configuration of the membrane cell (b).

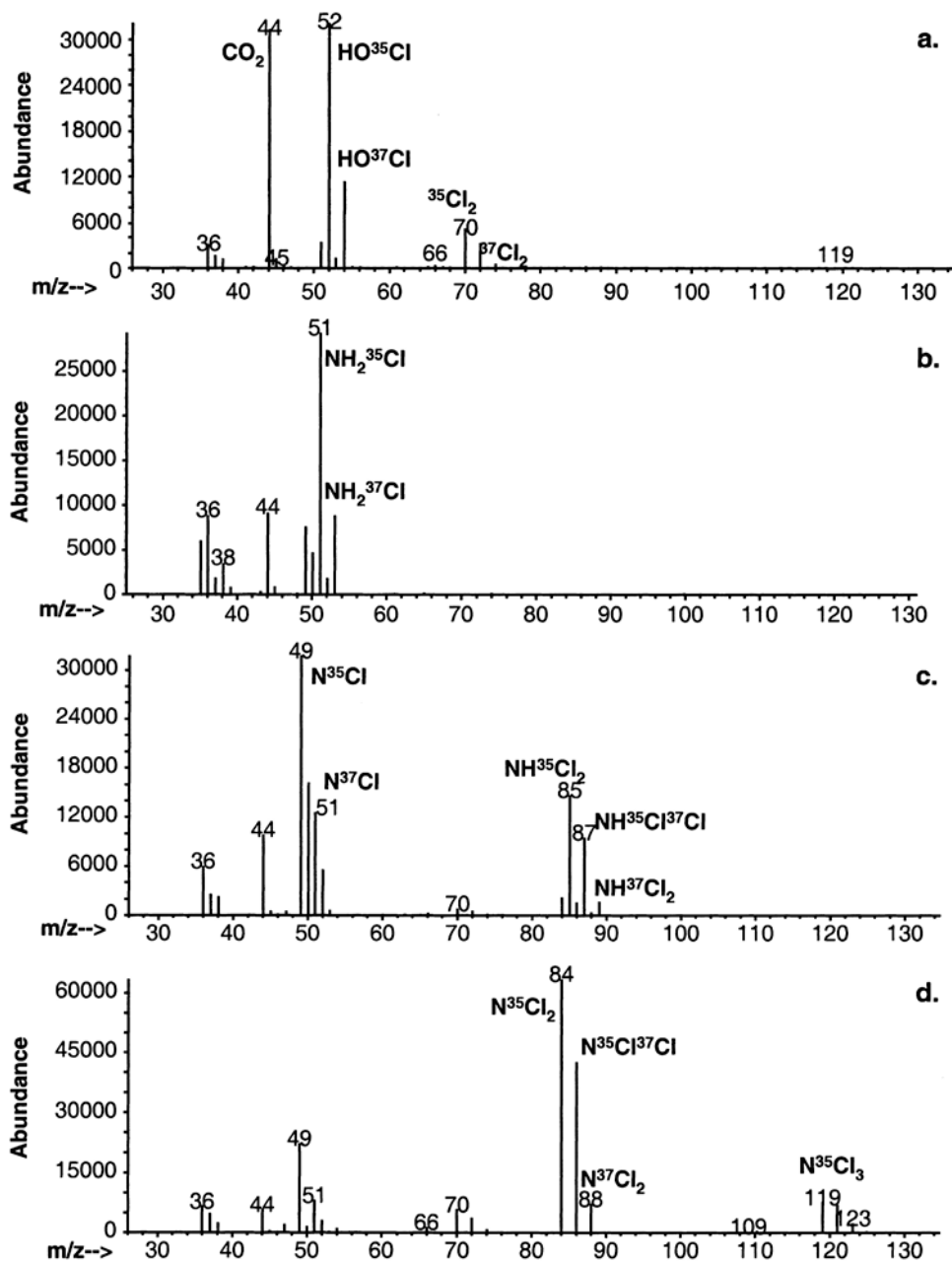


Figure 2 Representative EI mass spectra ( $35 \leq m/z \leq 125$ ) of:

- (a) free chlorine (2000 mg/L as  $Cl_2$ ),
- (b) monochloramine (40 mg/L as  $Cl_2$ ),
- (c) dichloramine (20 mg/L as  $Cl_2$ ), and
- (d) trichloramine (20 mg/L as  $Cl_2$ ).

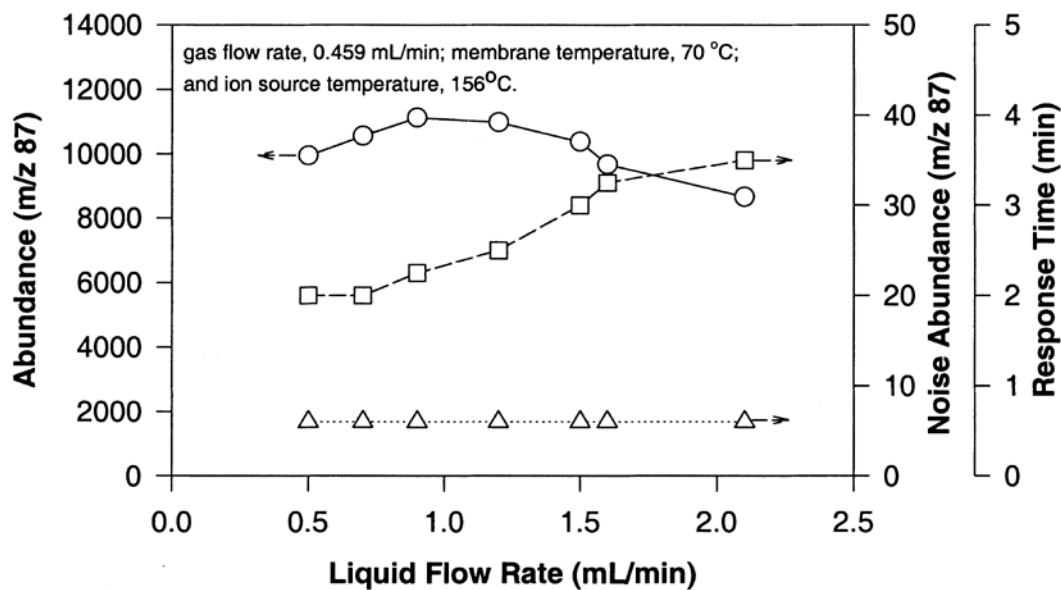
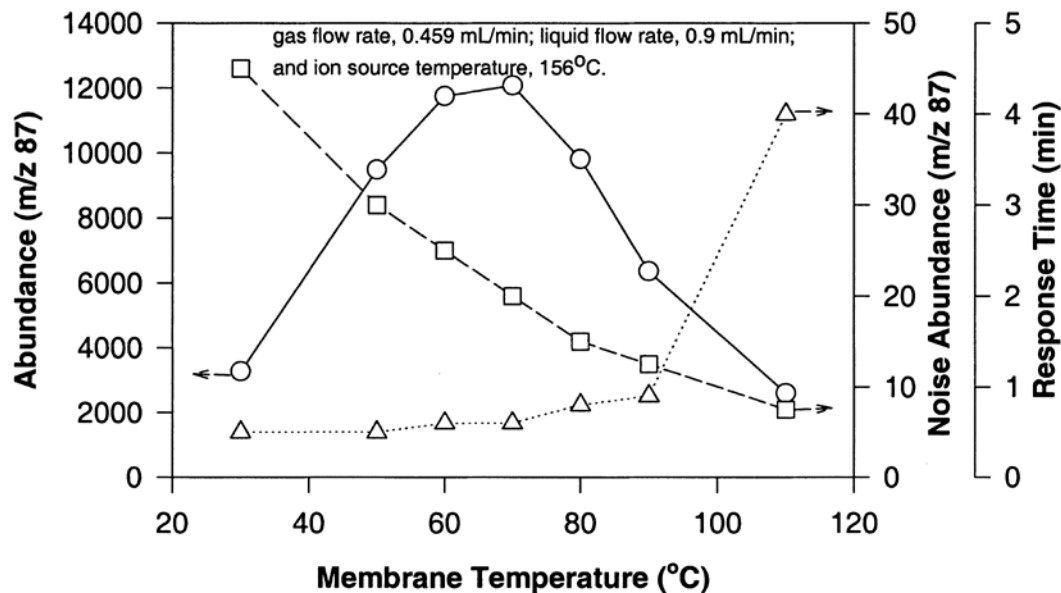


Figure 3 Effects of membrane temperature and liquid flow rate on the MIMS system performance (dichloramine at 9.2 and 8.5 mg/L as Cl<sub>2</sub>, respectively): ○, signal abundance; □, signal response time; △, signal noise.

$m/z$  53.00 (52.70 to 53.70)

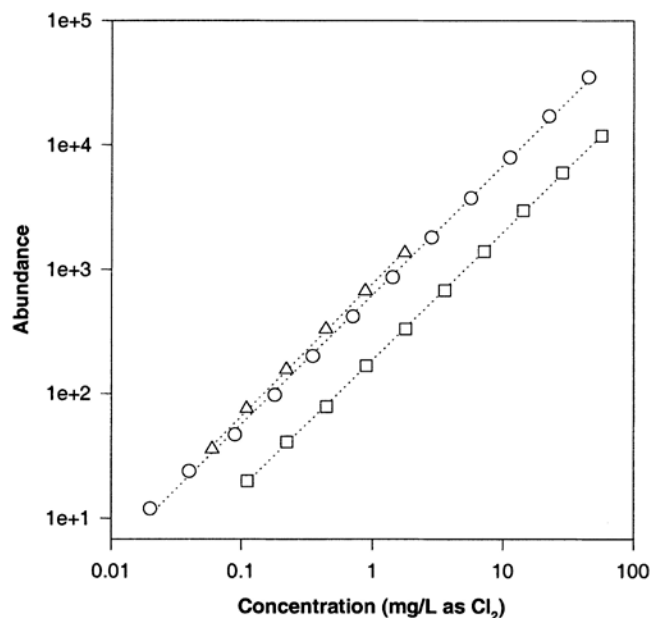
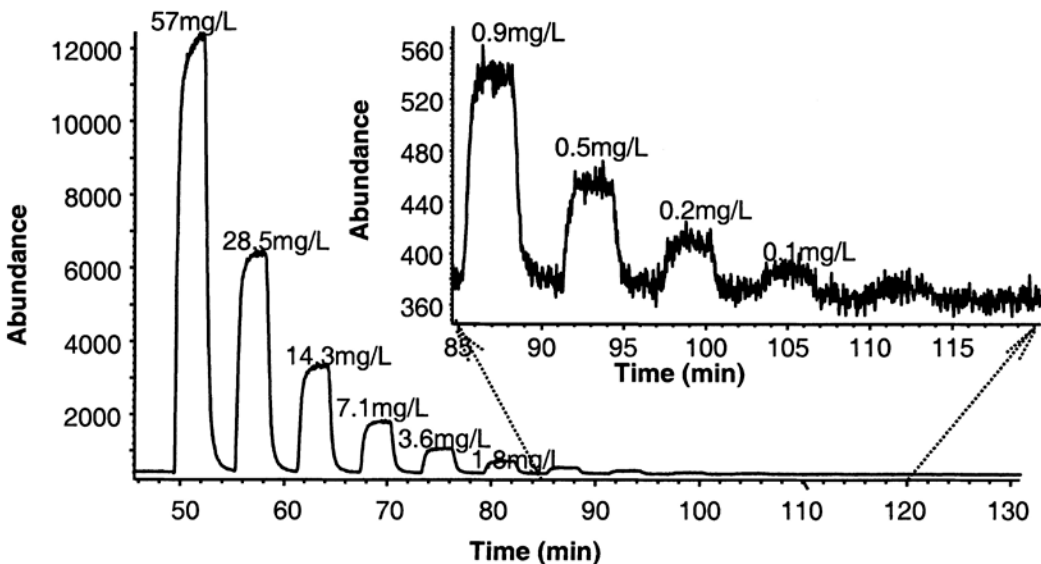


Figure 4 (a) Quantification of monochloramine by the MIMS method at  $m/z = 53$ : concentrations refer to titrimetrically determined values (as  $\text{Cl}_2$ ) up to the limit of detection (see insert). (b) Linear response curves of the MIMS method for chloramines:  $\square$ , monochloramine ( $m/z = 53$ );  $\circ$ , dichloramine ( $m/z = 87$ );  $\triangle$ , trichloramine ( $m/z = 119$ ).

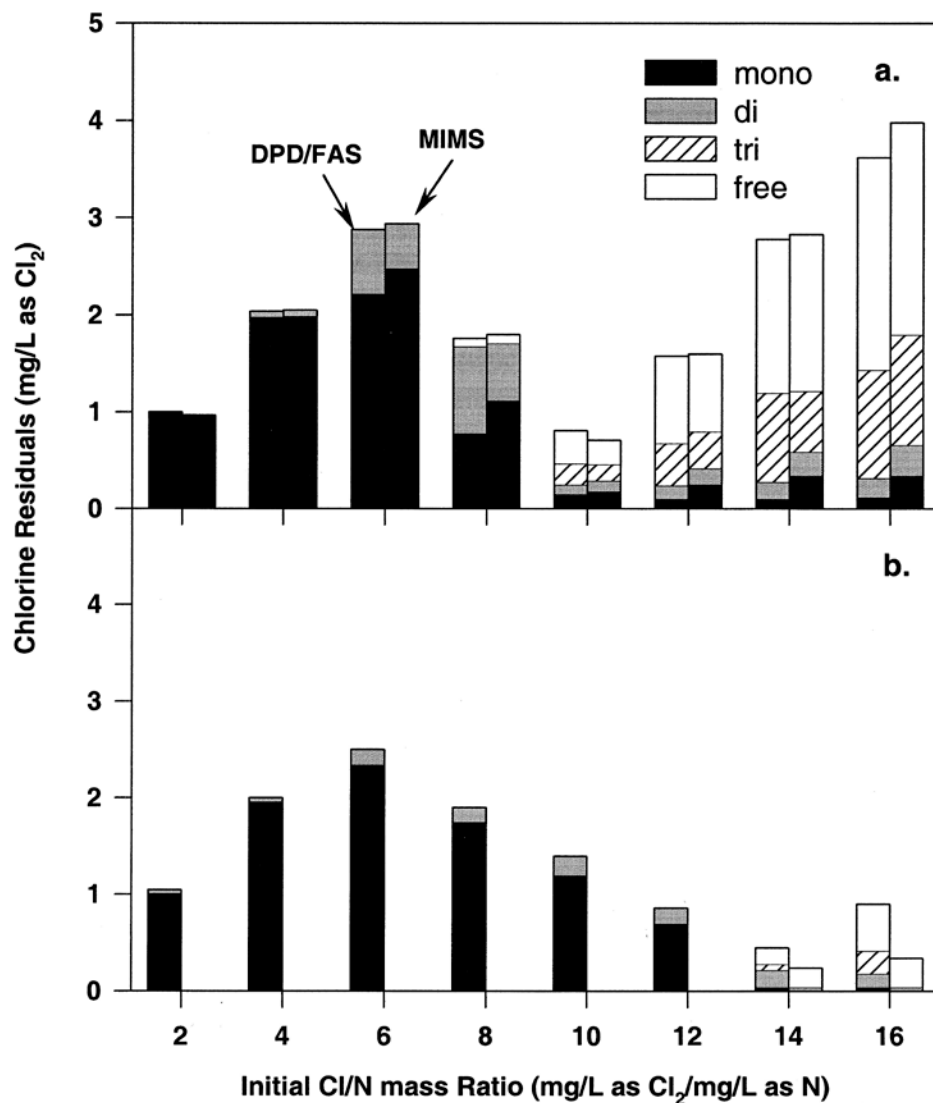


Figure 5 Residual chlorine concentrations as a function of Cl:N mass ratio after 30 min chlorination of an aqueous solution containing (a) ammonia and (b) glycine (0.5 mg/L as N) at pH 7. For each Cl:N ratio, residual chlorine was measured by DPD/FAS titration (left bar) and MIMS/EI (right bar).

Chlorine dose	species	DPD		MIMS		Lafayette wastewater (NH <sub>4</sub> <sup>+</sup> -N, 12.2 mg/L; org-N, 13.1 mg/L)		Purdue p otable wa ter (NH <sub>4</sub> <sup>+</sup> -N, 0.05 m g/L; org-N, 0.35 m g/L)
		mean	RSD <sup>b</sup> (%)	mean	RSD <sup>b</sup> (%)	DPD	MIMS	DPD
1.0	free	0		0		0	0	0.38
	mono	0.12	4 ( <i>n</i> = 6)	0		0.08	0.07	0.09
	di	0.05	12 ( <i>n</i> = 6)	0.03	2 ( <i>n</i> = 6)	0.04	0.02	0.02
	tri	0		0		0	0	0
5.0	free	0.16	14 ( <i>n</i> = 6)	0.17	5 ( <i>n</i> = 6)	0.16	0	4.28
	mono	0.15	17 ( <i>n</i> = 6)	0		1.94	2.05	0.14
	di	0.40	2 ( <i>n</i> = 6)	0.22	1 ( <i>n</i> = 6)	0.08	0.03	0
	tri	0		0		0	0	0.04
10.0	free	2.92	2 ( <i>n</i> = 3)	2.58	1 ( <i>n</i> = 3)	0.16	0	9.00
	mono	0.15	15 ( <i>n</i> = 3)	0.13	5 ( <i>n</i> = 3)	4.64	5.17	0.20
	di	0.77	8 ( <i>n</i> = 3)	0.37	0 ( <i>n</i> = 3)	0.40	0.24	0
	tri	0		0.08	3 ( <i>n</i> = 3)	0	0	0.04

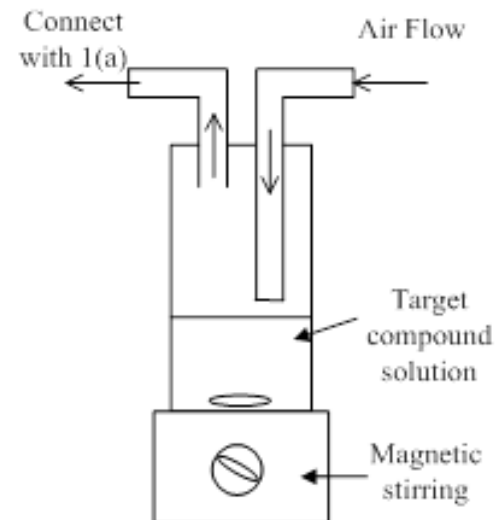
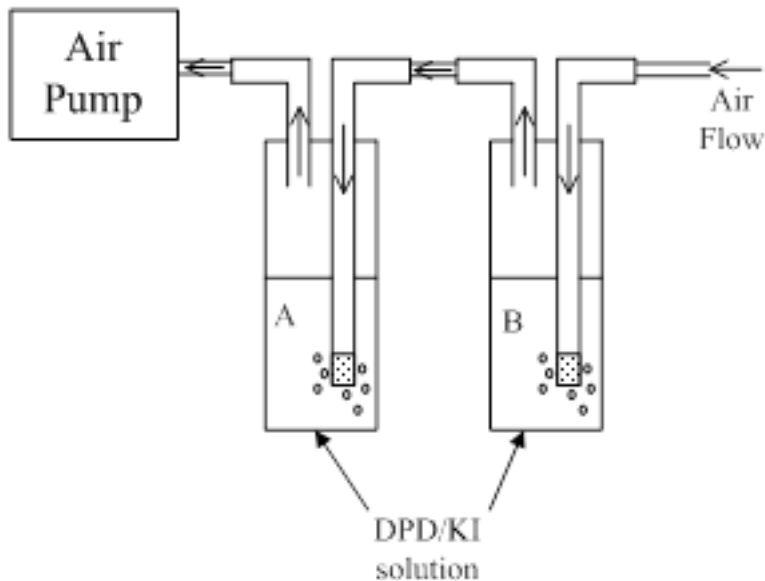


chlorine dose	species	DPD		MIMS		Lafayette waste-water (NH <sub>4</sub> <sup>+</sup> -N, 12.2 mg/L; org-N, 13.1 mg/L)		Purdue potable water (NH <sub>4</sub> <sup>+</sup> -N, 0.05 mg/L; org-N, 0.35 mg/L)	
		mean	RSD <sup>b</sup> (%)	mean	RSD <sup>b</sup> (%)	DPD	MIMS	DPD	MIMS
1.0	free	0		0		0	0	0.38	0.13
	mono	0.12	4 ( <i>n</i> = 6)	0		0.08	0.07	0.09	0
	di	0.05	12 ( <i>n</i> = 6)	0.03	2 ( <i>n</i> = 6)	0.04	0.02	0.02	0
	tri	0		0		0	0	0	0
5.0	free	0.16	14 ( <i>n</i> = 6)	0.17	5 ( <i>n</i> = 6)	0.16	0	4.28	3.22
	mono	0.15	17 ( <i>n</i> = 6)	0		1.94	2.05	0.14	0.26
	di	0.40	2 ( <i>n</i> = 6)	0.22	1 ( <i>n</i> = 6)	0.08	0.03	0	0.02
	tri	0		0		0	0	0.04	0
10.0	free	2.92	2 ( <i>n</i> = 3)	2.58	1 ( <i>n</i> = 3)	0.16	0	9.00	7.33
	mono	0.15	15 ( <i>n</i> = 3)	0.13	5 ( <i>n</i> = 3)	4.64	5.17	0.20	0.56
	di	0.77	8 ( <i>n</i> = 3)	0.37	0 ( <i>n</i> = 3)	0.40	0.24	0	0.05

# DPD based method for $\text{NCl}_3$

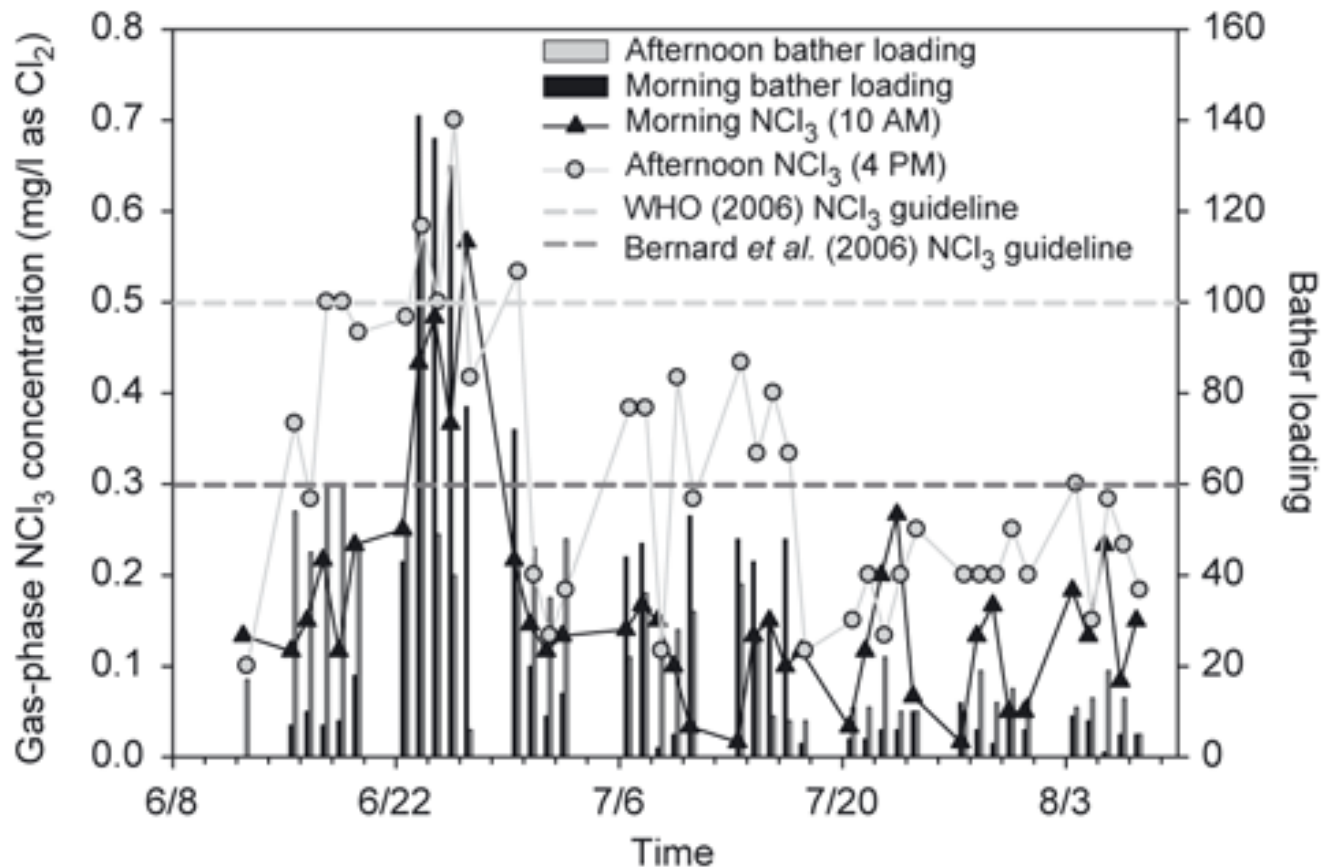
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- Schematic of impinger method for gas-phase  $\text{NCl}_3$  measurement. The arrows indicate the air flow pattern
- Validation experiment setup. A gas-washing bottle containing an aqueous solution of the target compound was prepared and connected to the air entrance of measuring impinger system



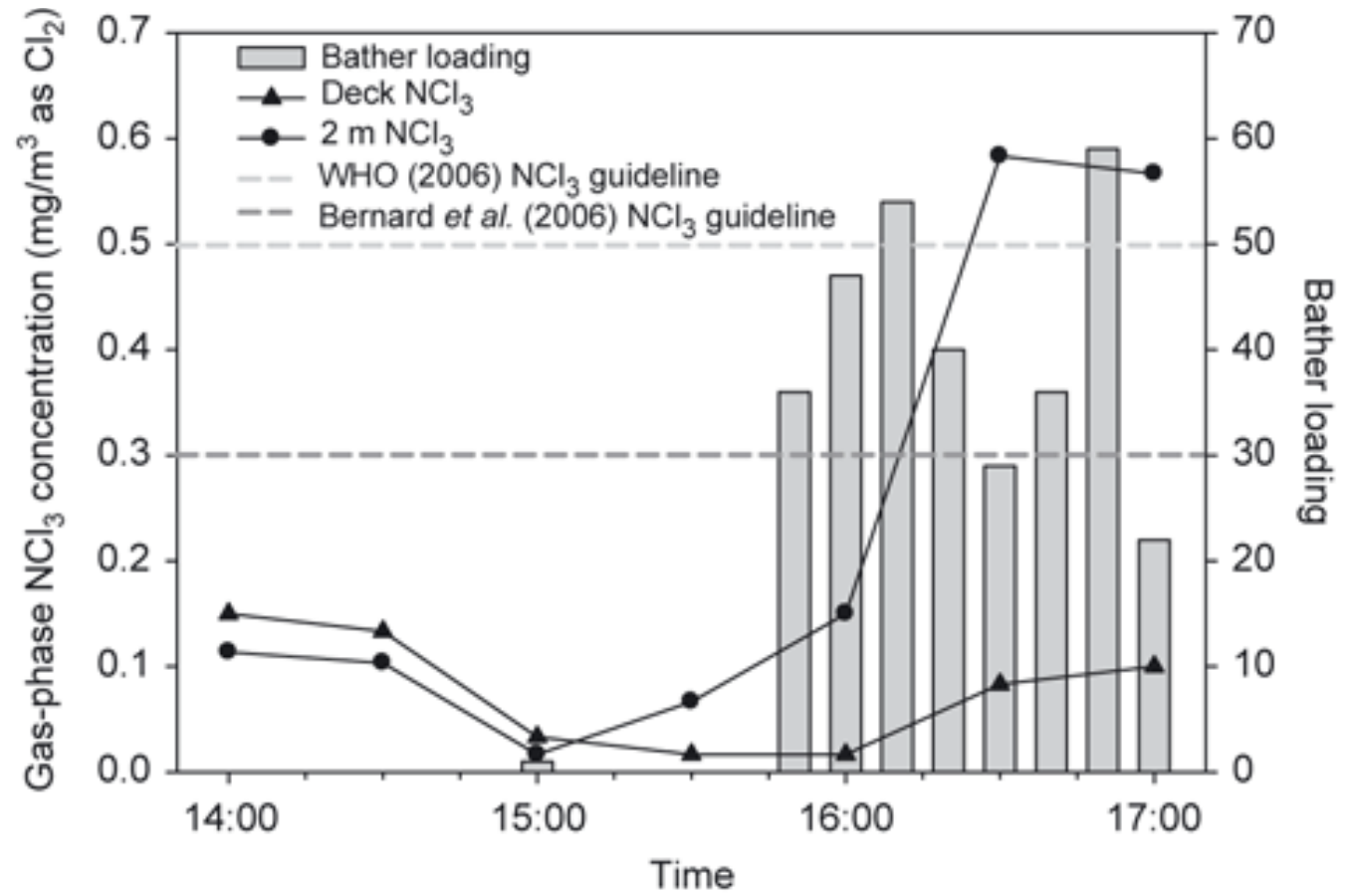
Compound	Typical liquid-phase concentration (mg/l) <sup>a</sup>	Henry's law constant (atm, 20°C) <sup>b</sup>	Equilibrium gas-phase Concentration (mg/m <sup>3</sup> )	Reported gas-phase concentration at pool area (mg/m <sup>3</sup> )
HOCl <sup>c</sup>	1.2	0.060	0.053	N.A
Cl <sub>2</sub> <sup>c</sup>	0.000012	767	0.0067	N.A
NH <sub>2</sub> Cl	0.30	0.45	0.10	N.A
NHCl <sub>2</sub>	0.10	1.52	0.11	N.A
NCl <sub>3</sub>	0.070	435	23	0.1–0.7 <sup>d</sup>
CHCl <sub>3</sub>	0.080	185	11	0.009–0.058 <sup>e</sup>
CHBr <sub>2</sub> Cl	0.0040	57.3	0.17	0.002–0.003 <sup>e</sup>
CHBr <sub>3</sub>	0.0010	21.5	0.016	0.0008 <sup>e</sup>
CNCl	0.0030	108	0.24	N.A
CNCHCl <sub>2</sub>	0.00080	0.21	0.00013	N.A
CH <sub>3</sub> NCl <sub>2</sub>	0.020	154	2.3	0.016–0.07 <sup>f</sup>

# Dynamics of gas-phase trichloramine ( $\text{NCl}_3$ ) in chlorinated, indoor swimming pool facilities



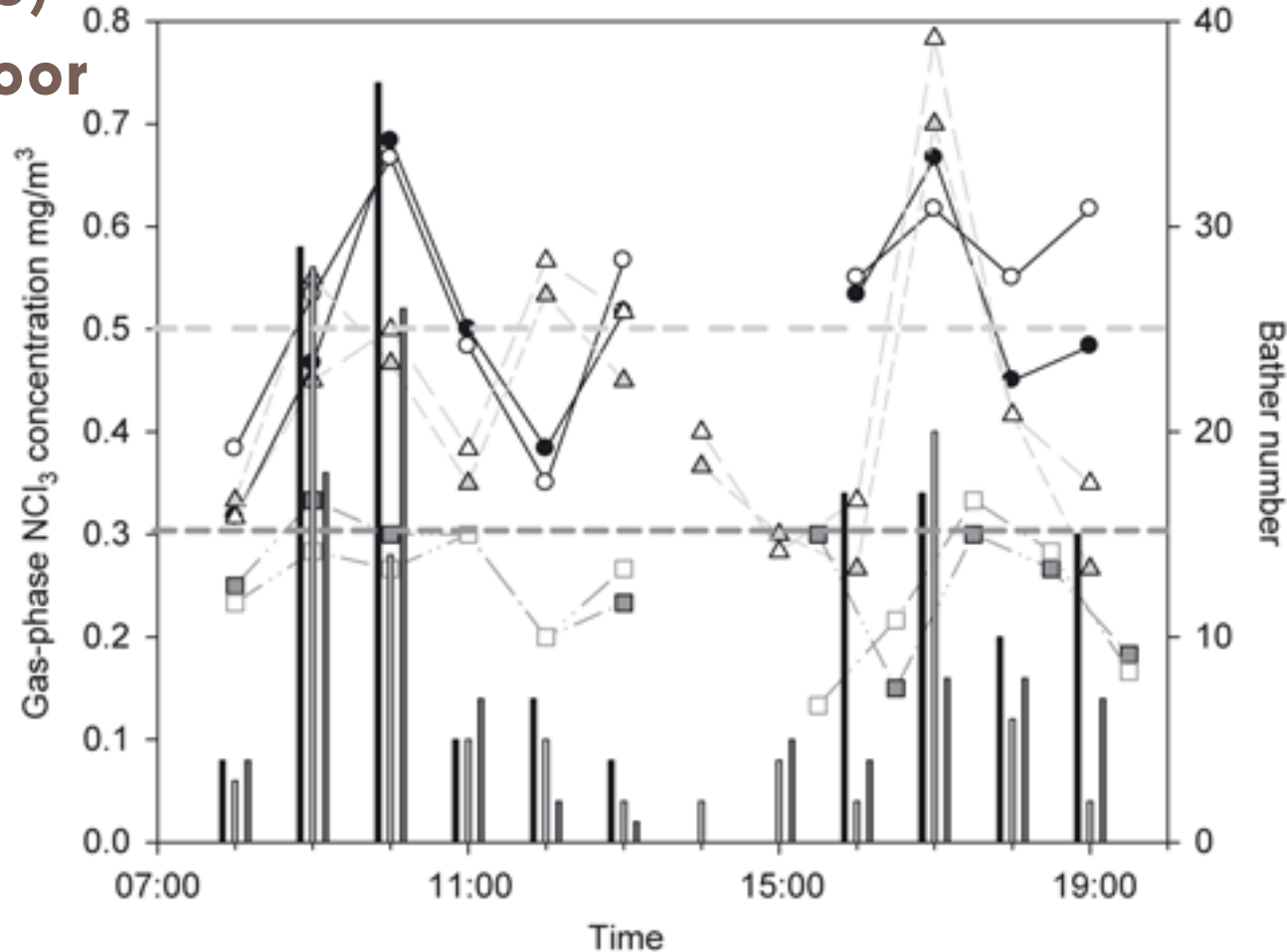
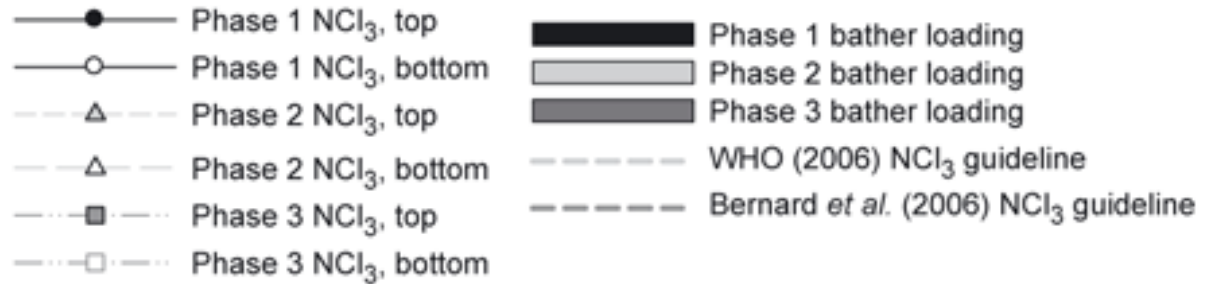
# Dynamics of gas-phase trichloramine ( $\text{NCl}_3$ ) in chlorinated, indoor swimming pool facilities

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# Dynamics of gas-phase trichloramine (NCl<sub>3</sub>) in chlorinated, indoor swimming pool facilities

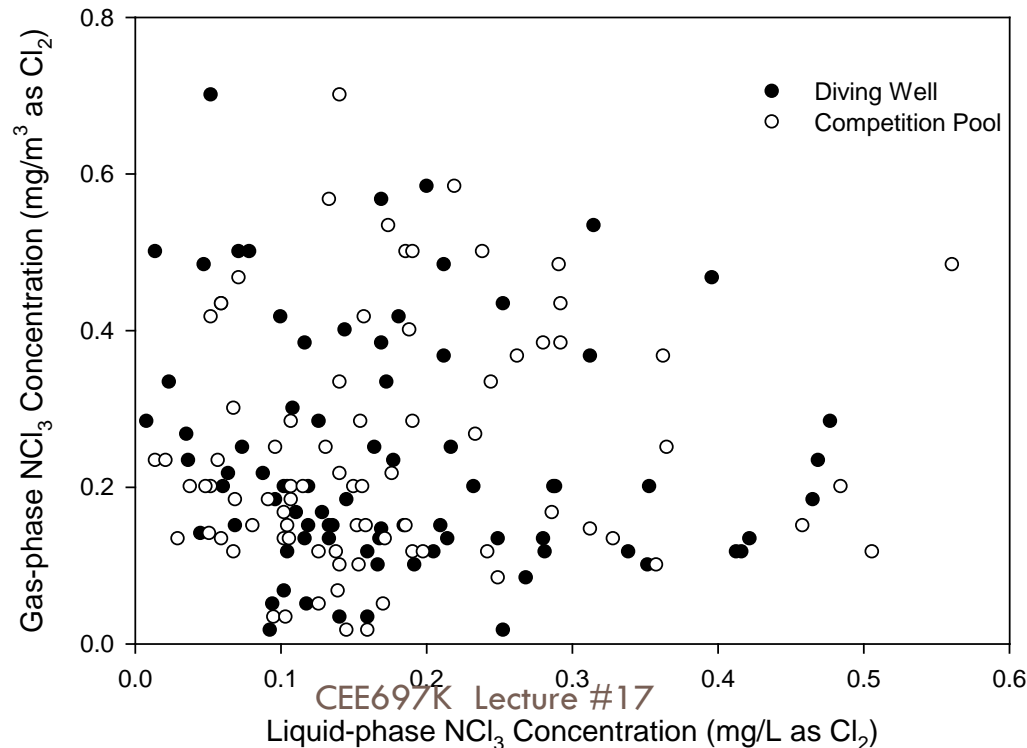
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# Liquid vs gas concentration

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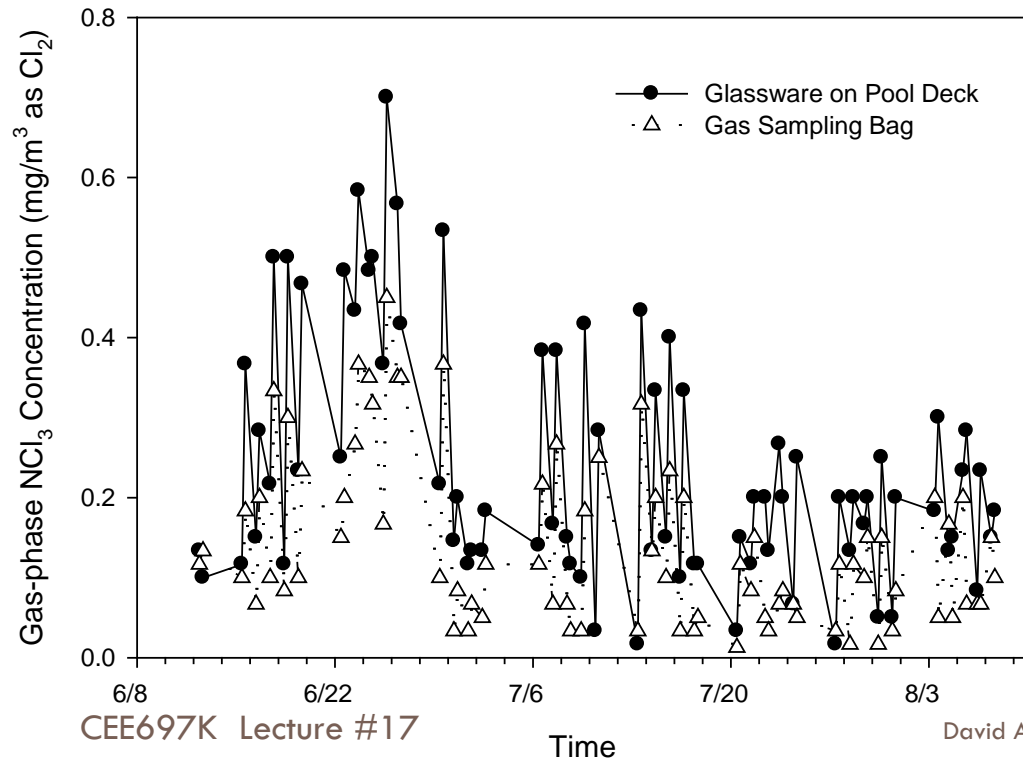
- Relationship between DPD-based liquid-phase  $\text{NCl}_3$  concentration and gas-phase  $\text{NCl}_3$  concentration in Pool A facility. The results showed no significant correlation between these two parameters for this facility. The correlation coefficients between liquid-phase and gas-phase  $\text{NCl}_3$  concentrations were -0.140 and 0.154 for the diving well and competition pool, respectively.



# Loss in Tedlar bag

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- Comparison of gas-phase  $\text{NCl}_3$  measurement at pool deck and in the laboratory with a Tedlar gas-sampling bag. The results showed apparent loss of  $\text{NCl}_3$  from the gas-sampling bag during transport





- To next lecture