WQTC 2017

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American Water Works Association

WATER QUALITY Technology Conference

Evidence for an additional NDMA formation pathway

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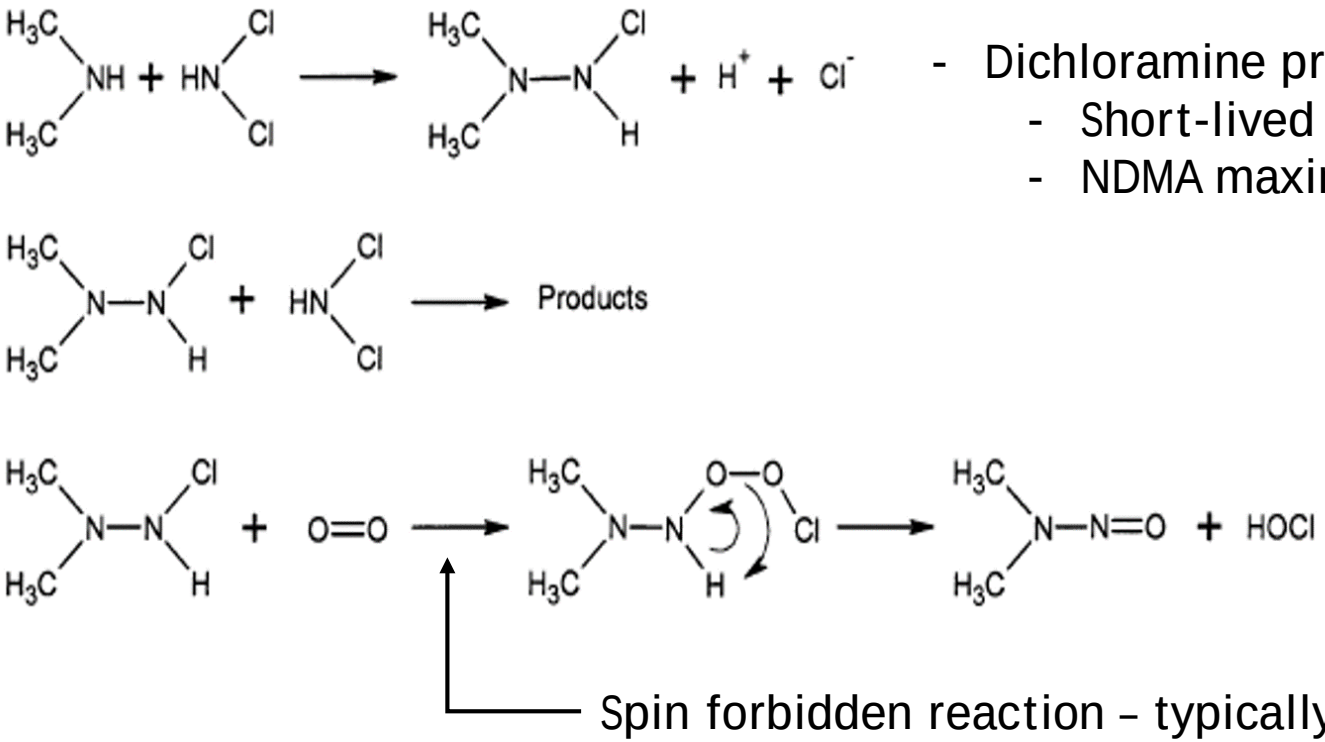
N-Nitrosodimethylamine (NDMA) Occurrence

- Elevated NDMA in ground water near rocket testing facilities
- Associated with chlorine and chloramine disinfection of water and wastewater
- Enhanced NDMA in storage and distribution systems with presence of nitrifying bacteria

N-Nitrosodimethylamine (NDMA) Occurrence

- NDMA is most commonly detected *N*-nitrosamine species in drinking water systems
- Toxicologically relevant at low ng/L levels
- Byproduct of meat preservation, industrial processes, and drinking water disinfection (i.e., DBP primarily associated with chloramines)

GENERALLY ACCEPTED NDMA FORMATION PATHWAY

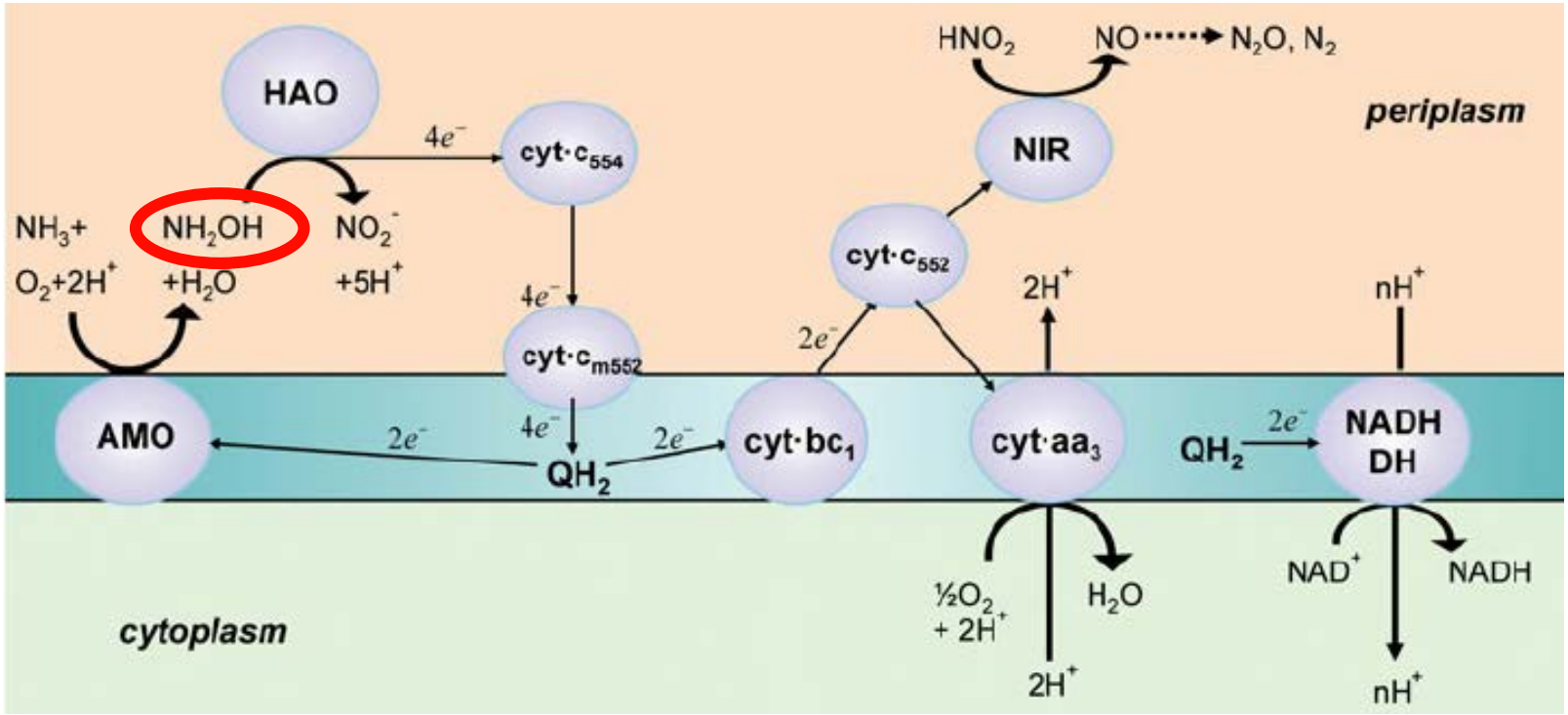


- Dichloramine proper
  - Short-lived at pH 9
  - NDMA maximal at pH 9

Additional pathway???

- Schreiber and Mitch (2006), ES&T

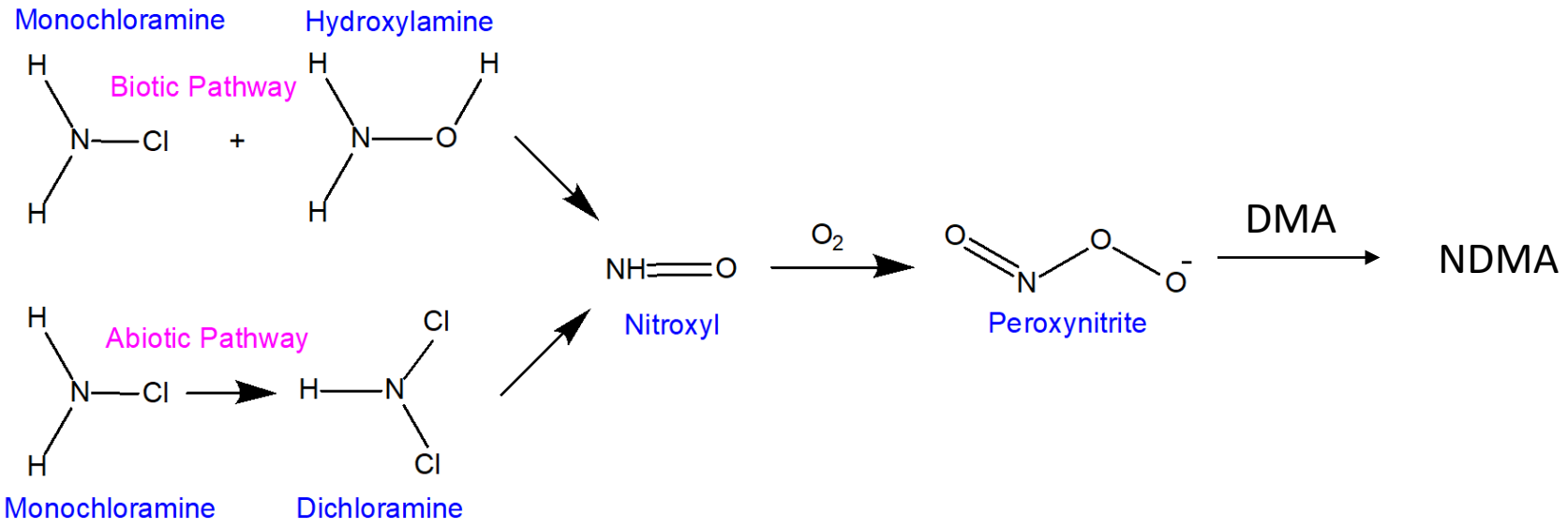
NITRIFICATION INTERMEDIATE – NH_2OH



Metabolic mechanism and electron transfer pathway of ammonia oxidation by AOB

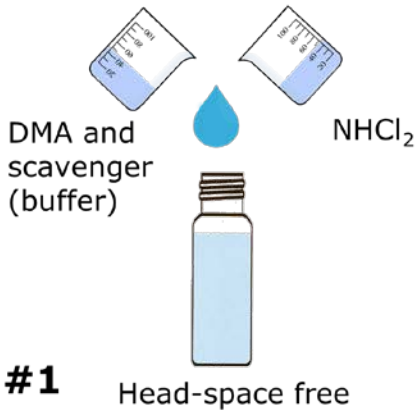
- Jianhua Guo et al. (2013)

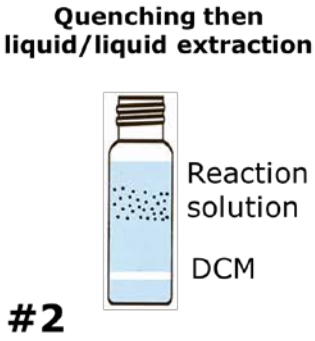
PROPOSED NDMA FORMATION PATHWAY



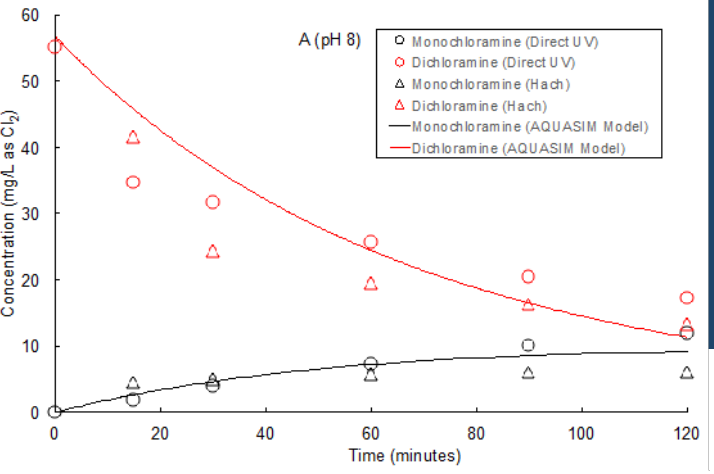
METHODS AND APPROACH

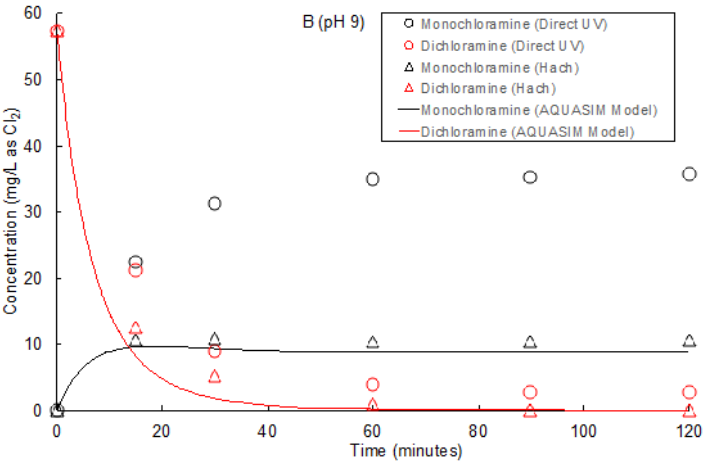
- Chloramine species: Colorimetric measurement of Total Chlorine and Monochloramine (Hach Method)
  - Calculate dichloramine by difference
- Unified chloramine model (Jafvert and Valentine 1992; Vikesland 2001) implemented in AQUASIM (Wahman and Speitel 2012) used to simulate monochloramine and dichloroamine kinetics
- NDMA: LLE into dichloromethane followed by GC-MS

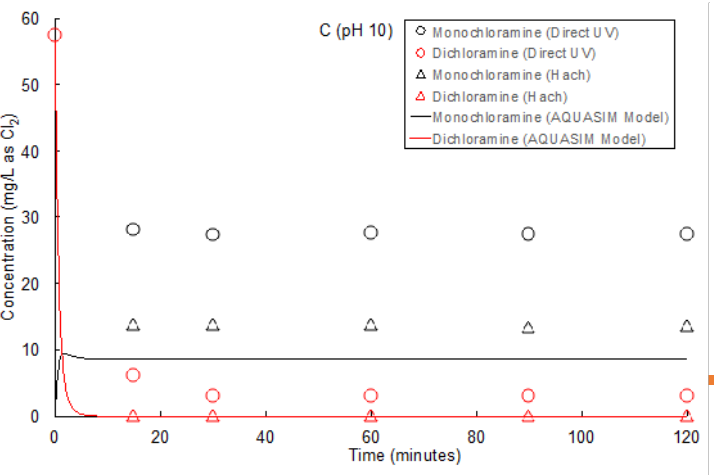




DICHLORAMINE DECAY

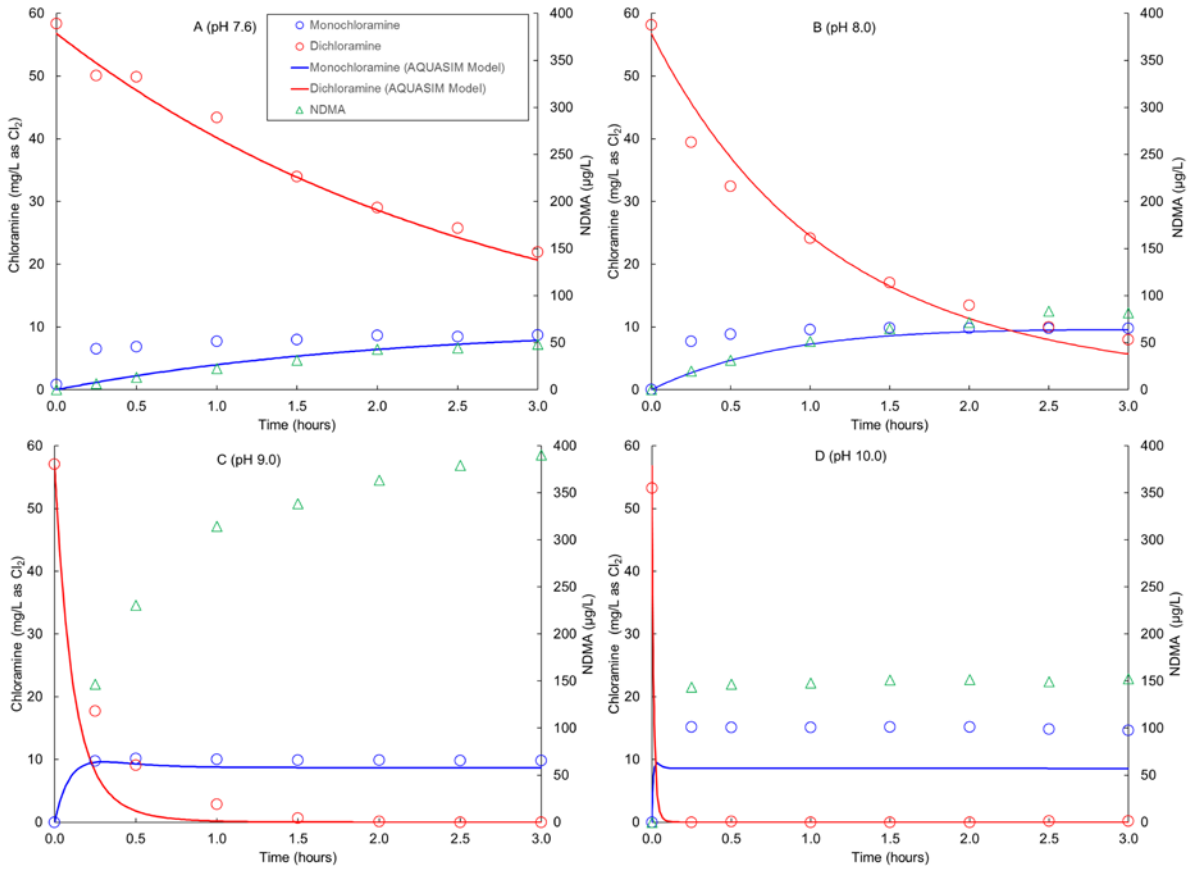






- Dichloramine decayed more rapidly as pH increased (pH 8, 9, 10)
- The Unified Chloramine model adequately captured dichloramine decay at pH 8-10 and formation of monochloramine at pH 8 and 9 but underestimated monochloramine at pH 10
- Unidentified compound of dichloramine decay (UC1) interfered with the Direct UV method at pH 9 and 10, and possibly Hach method at pH 10.

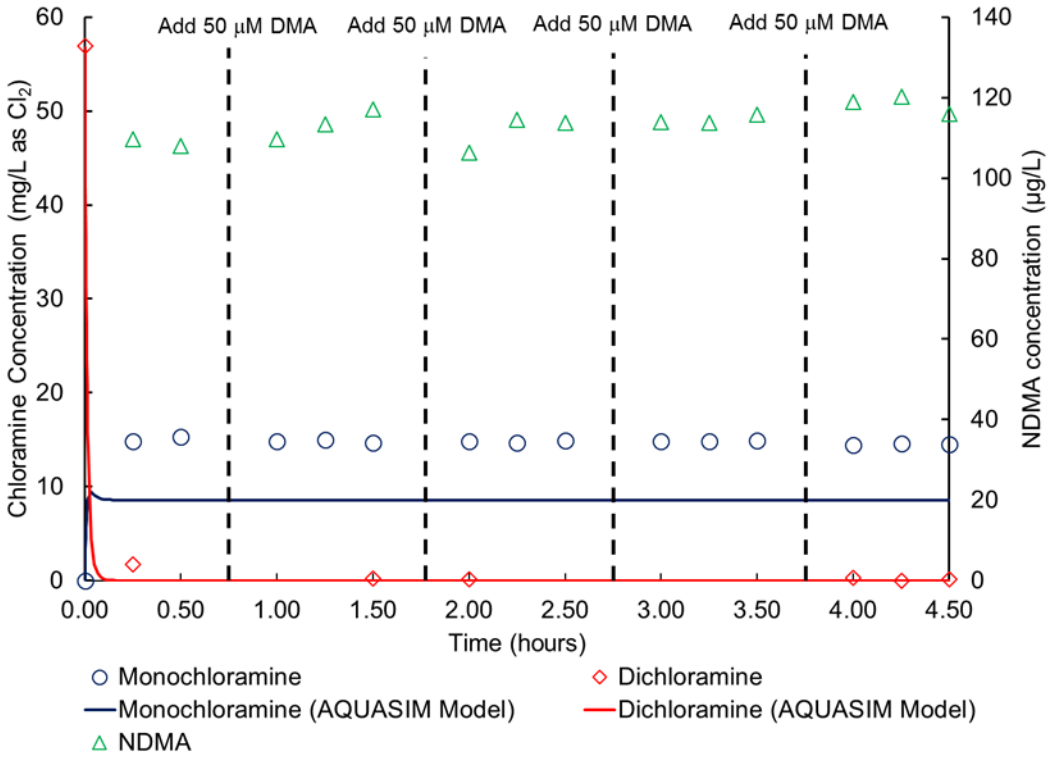
NDMA FORMATION: $NHCl_2$ and DMA



- NDMA yields pH dependent
  - Highest at pH 9.0
  - Same as Schreiber and Mitch (2006)
- At pH 9, NDMA formation continued after $NHCl_2$ completely decayed
  - Decay product of $NHCl_2$ rather than $NHCl_2$ proper
  - Could this decay product also form from monochloramine?

THE ROLE OF UC1 IN NDMA FORMATION

- $NHCl_2$ and DMA at pH 10
  - Forces formation of UC1
  - Measured NH_2Cl > Predicted by model
- No increase in NDMA formation upon DMA addition → UC1 is not a primary reactant in NDMA formation
- NDMA formation may involve an unstable intermediate
  - Nitroxyl, HNO
  - Need to test with HNO donors and scavengers



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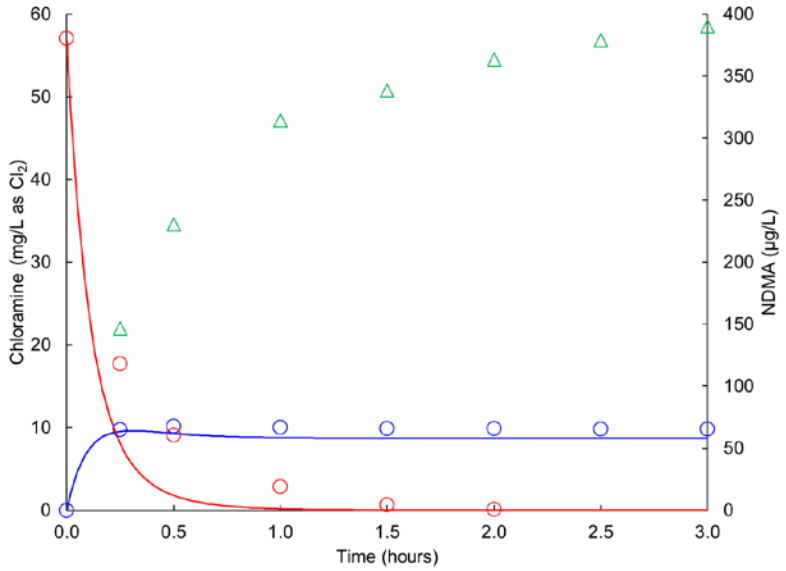
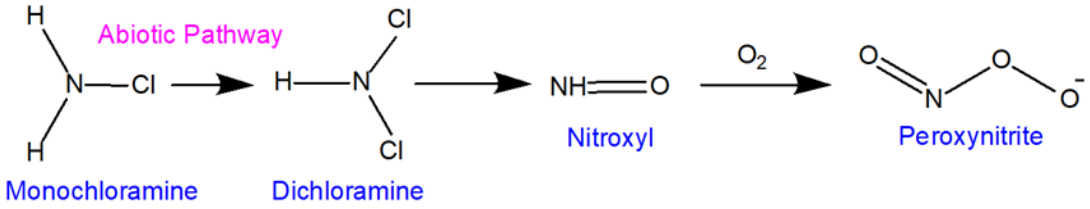
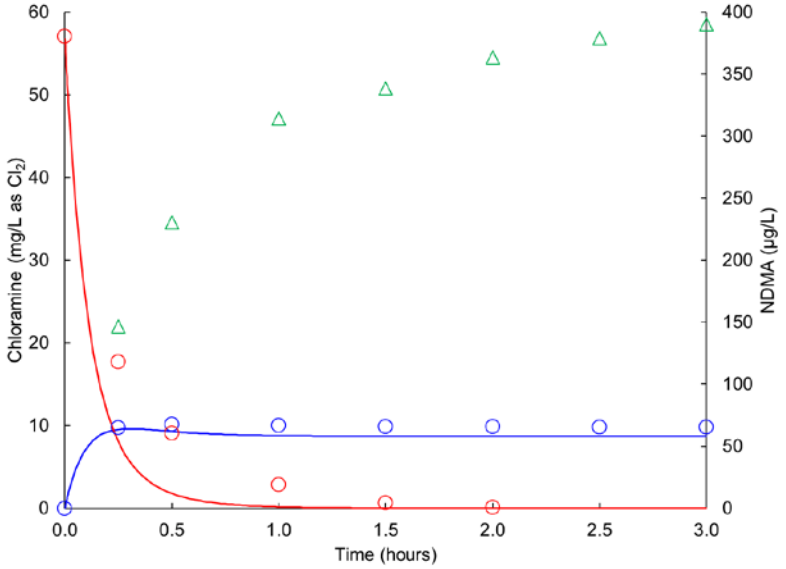


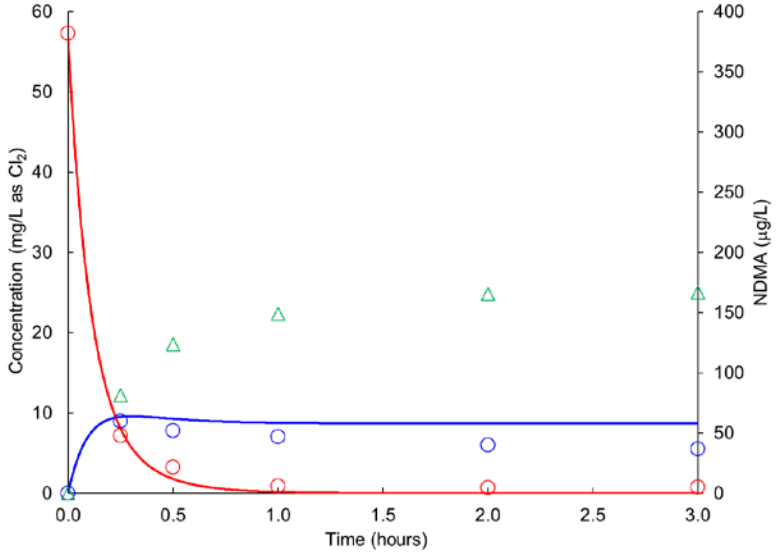


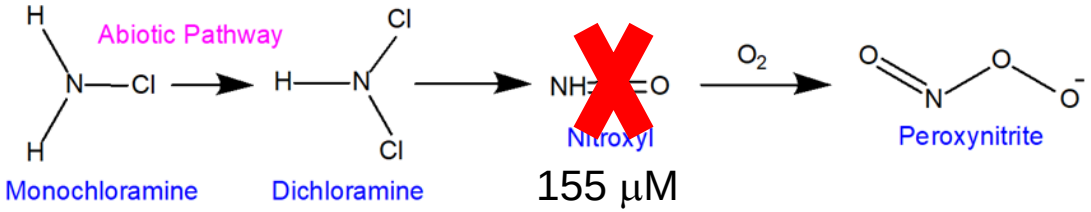
NDMA FORMATION: $NHCl_2$ and DMA

No Glutathione



155 µM Glutathione

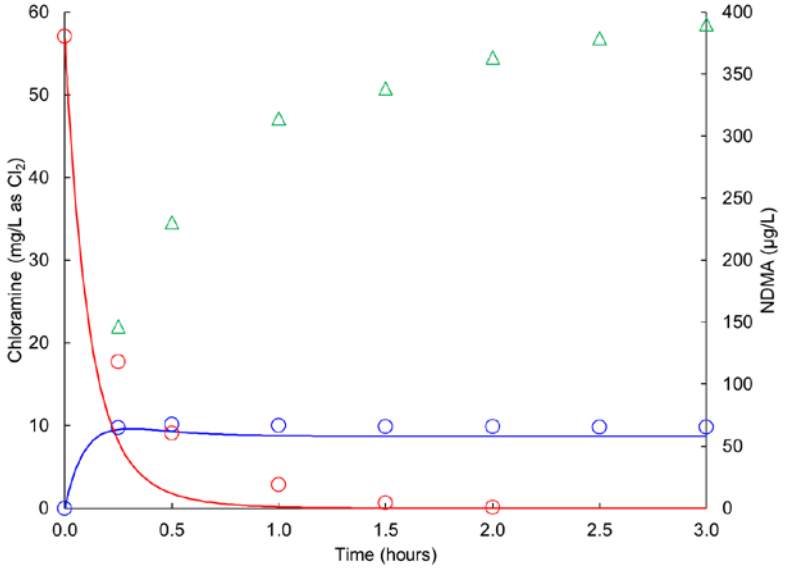




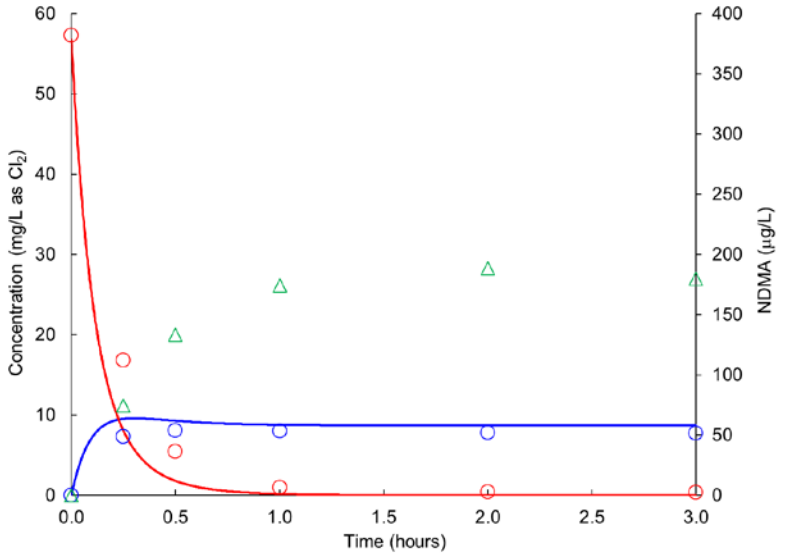
155 µM Glutathione

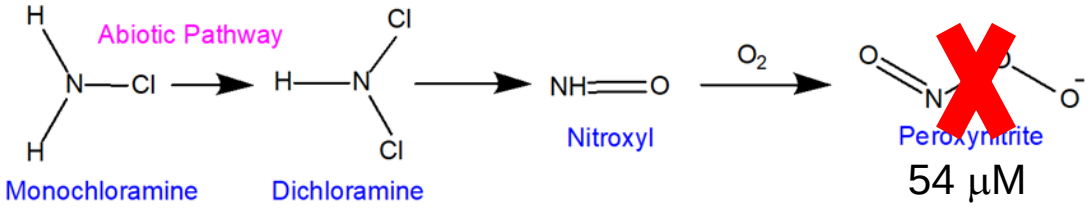
NDMA FORMATION: $NHCl_2$ and DMA

No Uric Acid



54 µM Uric Acid





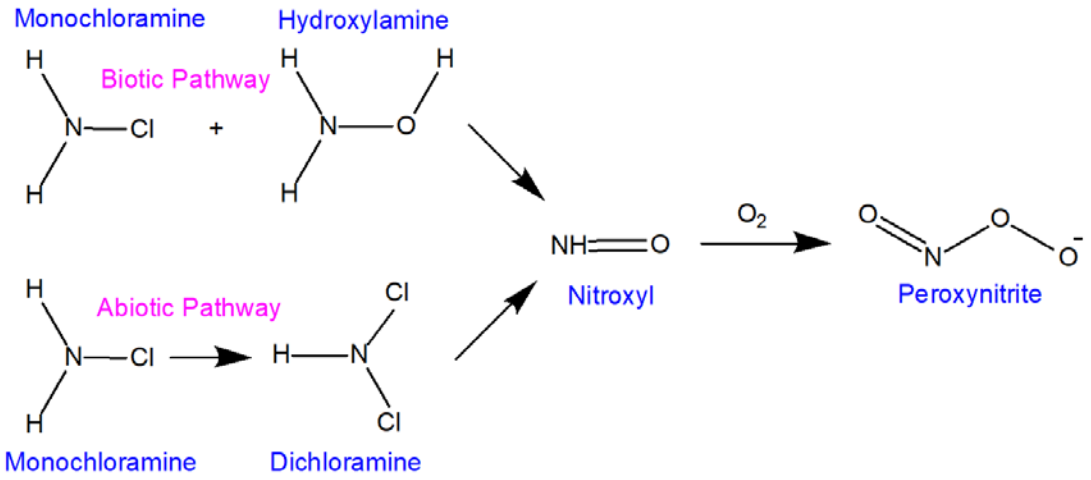
54 µM Uric Acid

NDMA FORMATION: $NHCl_2$ and DMA

- Increasing uric acid or glutathione addition resulted in decreased NDMA formation
- Nitroxyl and peroxynitrite likely play a role in NDMA formation under realistic chloramination conditions

Scavenger	Concentration (μM)	NDMA (μg/L)	Fraction
None	NA	363.7	1.00
Uric Acid	17	233.8	0.64
	54	188.7	0.52
	120	132.3	0.36
Glutathione	60	275.3	0.76
	155	165.4	0.45
	280	17.4	0.05
	560	ND	ND

IMPLICATIONS AND FUTURE WORK



- The presence of peroxynitrite and nitroxyl scavengers decrease NDMA formation
  - Suggest a role for nitroxyl (dichloramine decay product)
  - Nitroxyl can also be formed abiotically by reaction with hydroxylamine (nitrification)
- Batch kinetics experiments with DMA, chloramines and scavengers over range of pH and dissolved oxygen conditions

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