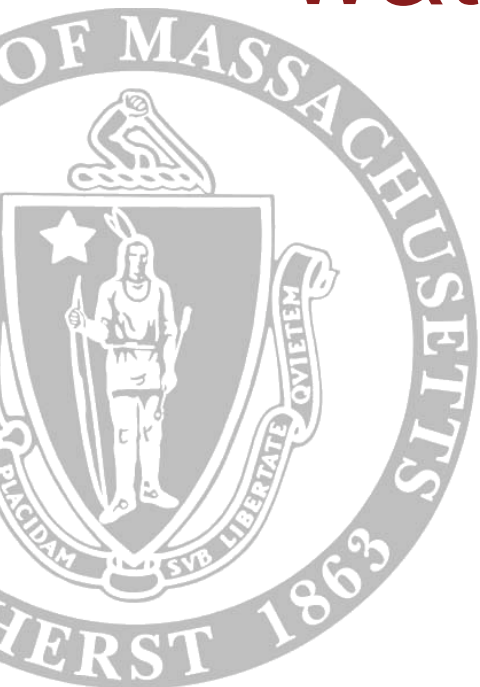


US EPA ARCHIVE DOCUMENT

Use of ferrate in small drinking water treatment systems



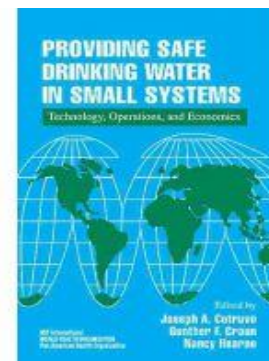
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Amherst, MA



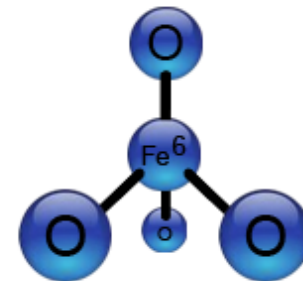
Background

Many small drinking water systems are at a comparative disadvantage due to their size (e.g., limited financial and human resources), and sometimes due to their remote location.



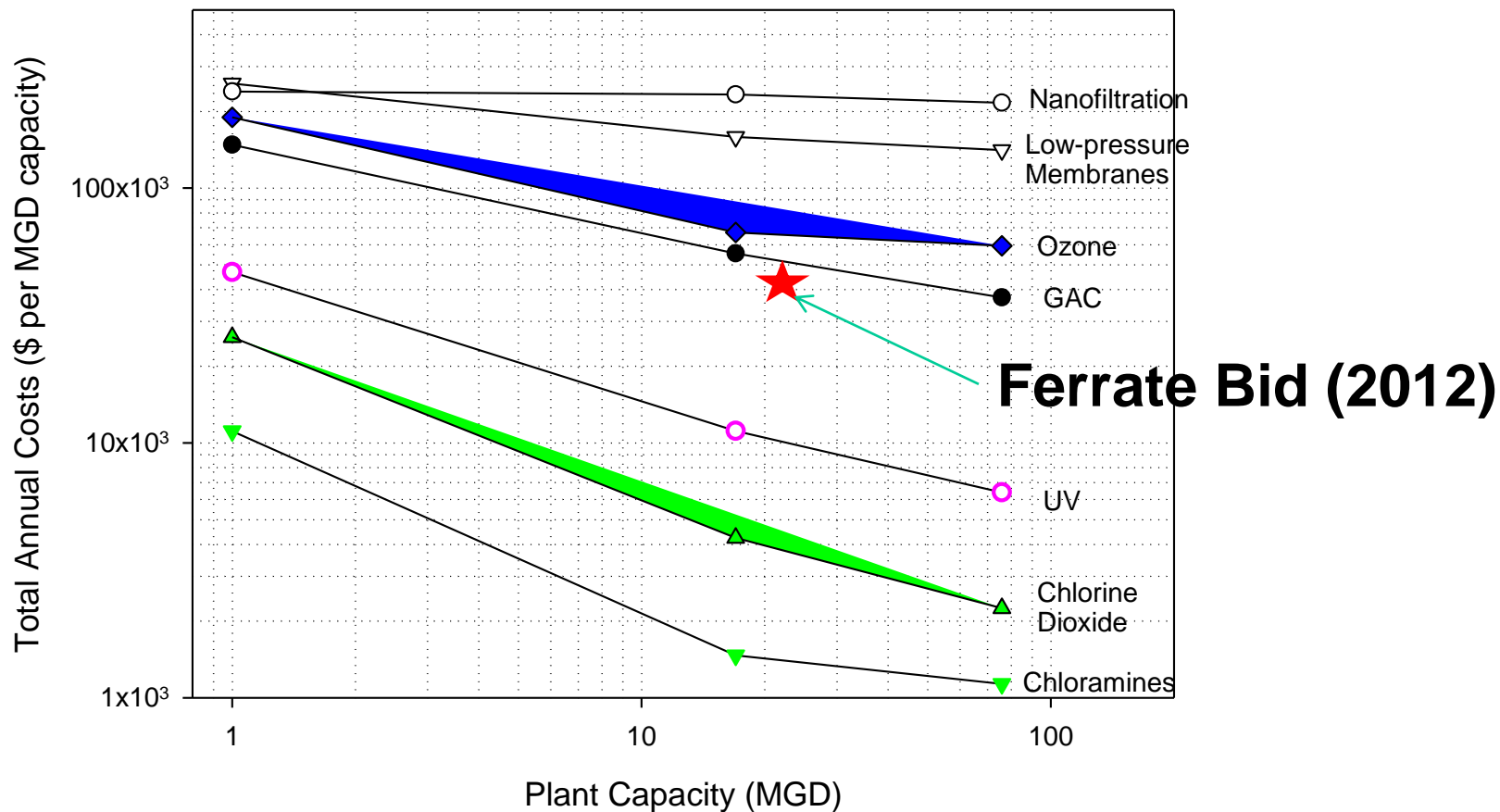
Ferrate (VI) basics:

- Highly selective oxidant
 - No any known hazardous byproducts (e.g., no brominated or chlorinated DBPs, no bromate or chlorite).
- Disinfectant
- Coagulant: Fe^{3+} and $\text{Fe}(\text{OH})_3$



Becoming Cost Competitive

- Comparison from Roy, 2010 [JAWWA 102(3)44-51]



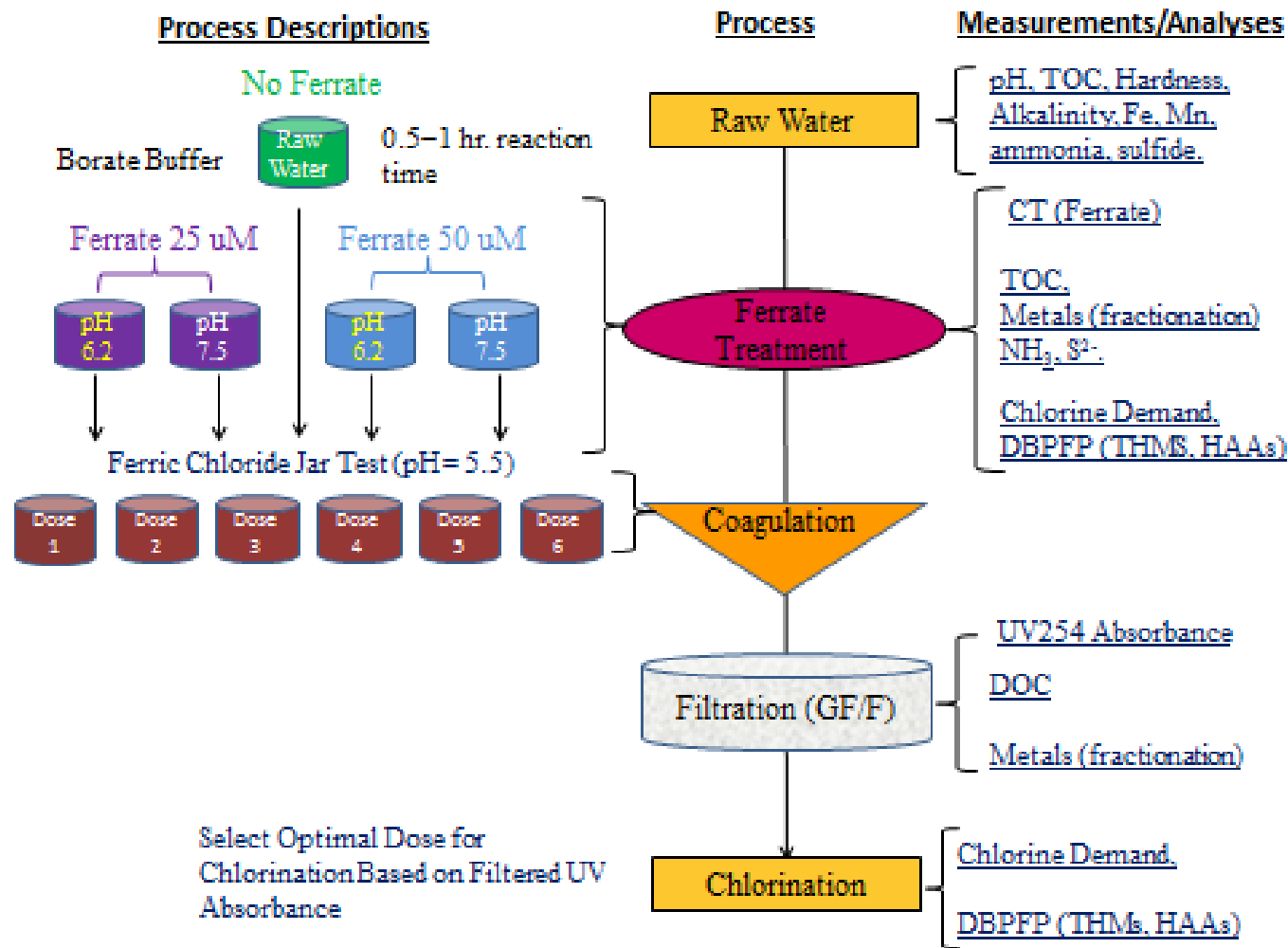
Project Objectives

The objective of this project is to test the ability of ferrate oxidation to solve a wide range of water quality and treatment problems faced by small systems.

Working Hypothesis

- Ferrate is more effective and less detrimental than conventional oxidative technologies such as chlorination, chloramination, and permanganate oxidation.
- Ferrate is comparable in performance to alternative oxidants such as ozone or chlorine dioxide, which are more costly, more hazardous or require specialized expertise to operate.

Bench-scale tests



Outline



1. Ferrate decomposition and lifetime in natural waters

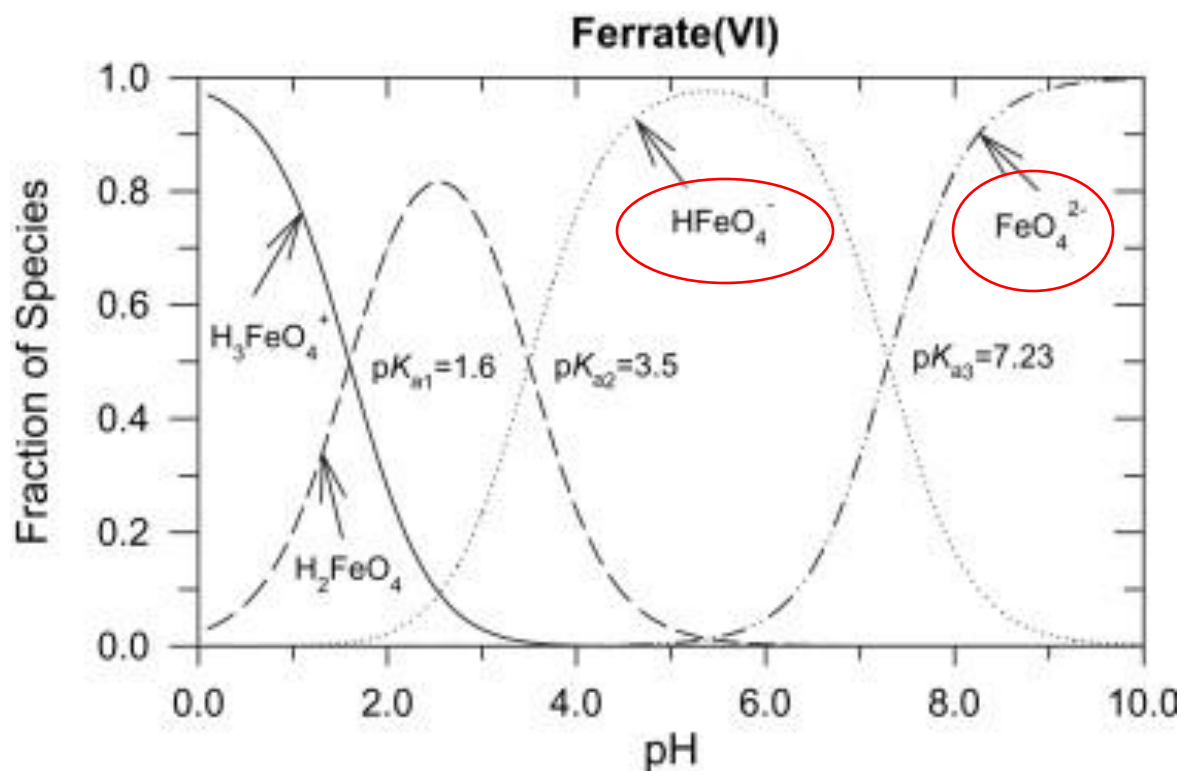
2. Direct Ferrate impacts on NOM and precursors

3. Direct ferrate impacts on Fe/Mn

4. Conclusions

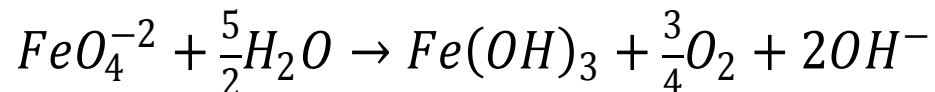
Ferrate proton speciation

Monoprotonated and unprotonated anions are dominant at most pHs.



Decomposition kinetics

- Ferrate decomposes in water.



- Carr model (2008)

- ❖ Overall mixed order

$$-\frac{d[Fe(VI)]}{dt} = k_1[Fe(VI)] + k_2[Fe(VI)]^2$$

- First order term

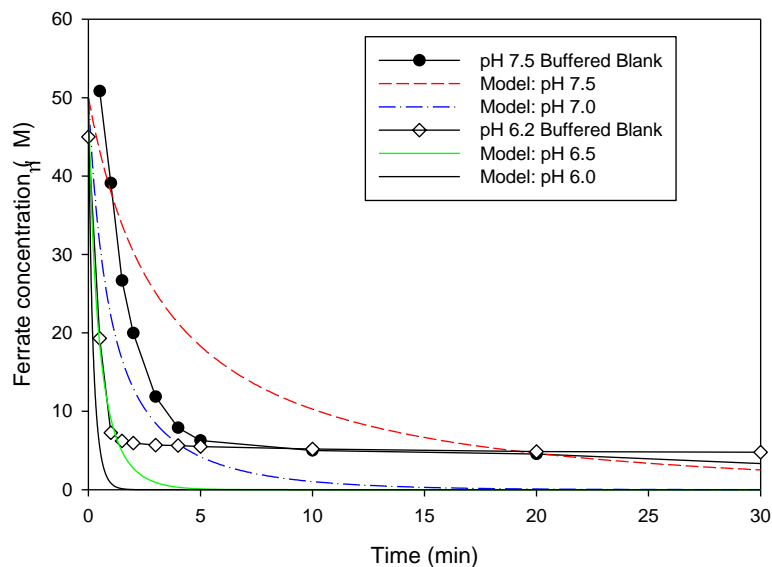
$$k_1[Fe(VI)] = k_{H_2FeO_4}[H_2FeO_4] + k_{HFeO_4}[HFeO_4^-] + k_{FeO_4}[FeO_4^{-2}]$$

- Includes phosphate catalysis

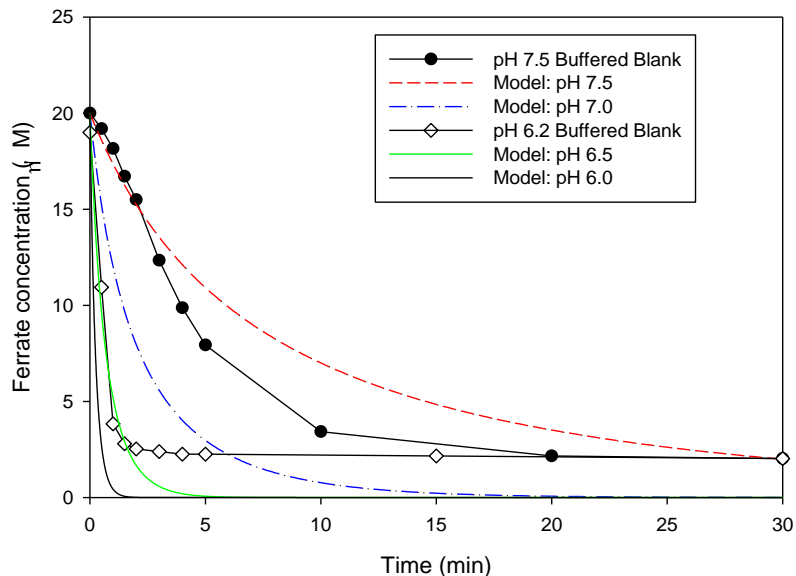
$$k_{HFeO_4}[HFeO_4^-] = k_{HFeO_4}[HFeO_4^-] + k_{HFeO_4}^c[H_2FeO_4^-][H_2PO_4^-]$$

Decomposition in pure water

High dose blank test vs model

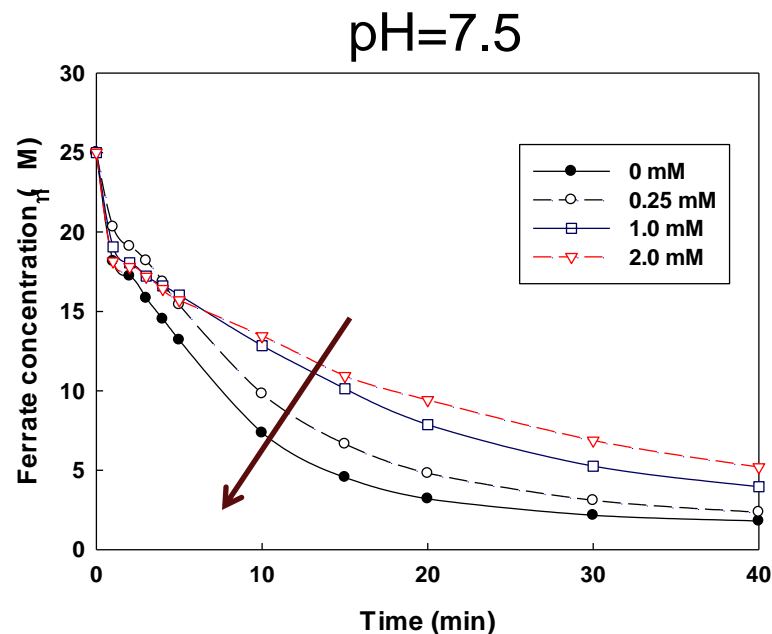
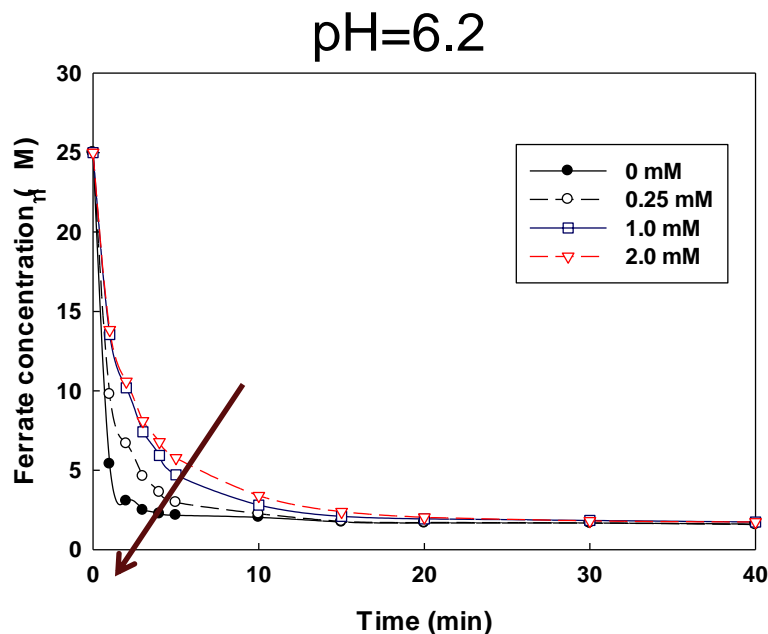


Low dose blank test vs model



- The Carr model does a good job of describing ferrate decomposition in pure waters containing borate.
- Borate buffer may slightly increase the rate of ferrate loss.

Effect of carbonate on ferrate decay

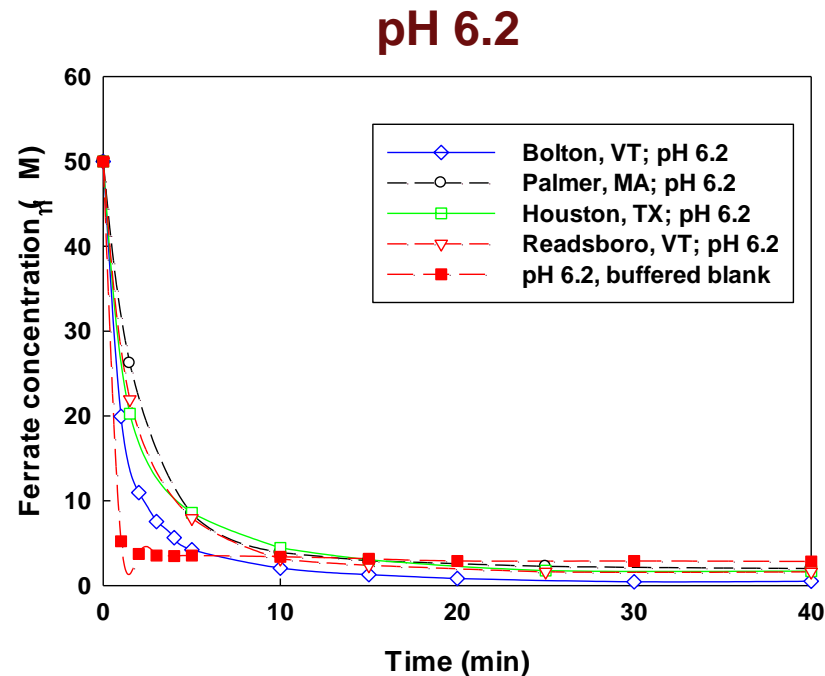
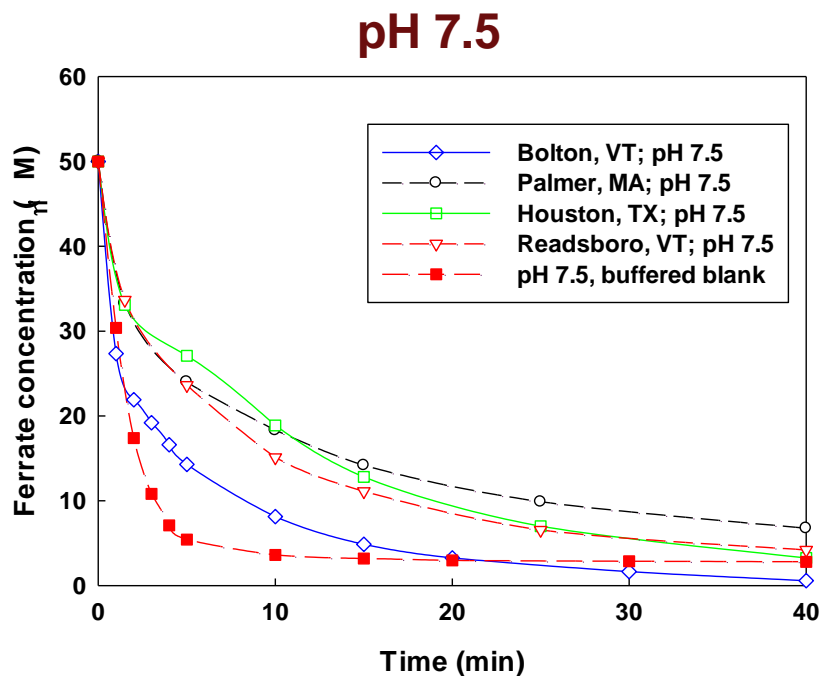


Carbonate concentration increases, ferrate decay rate decreases.

Carbonate slowed ferrate decay. This might be attributed to radical reactions that accelerate ferrate decomposition but are partly quenched by carbonate scavengers.

Raw Water Quality

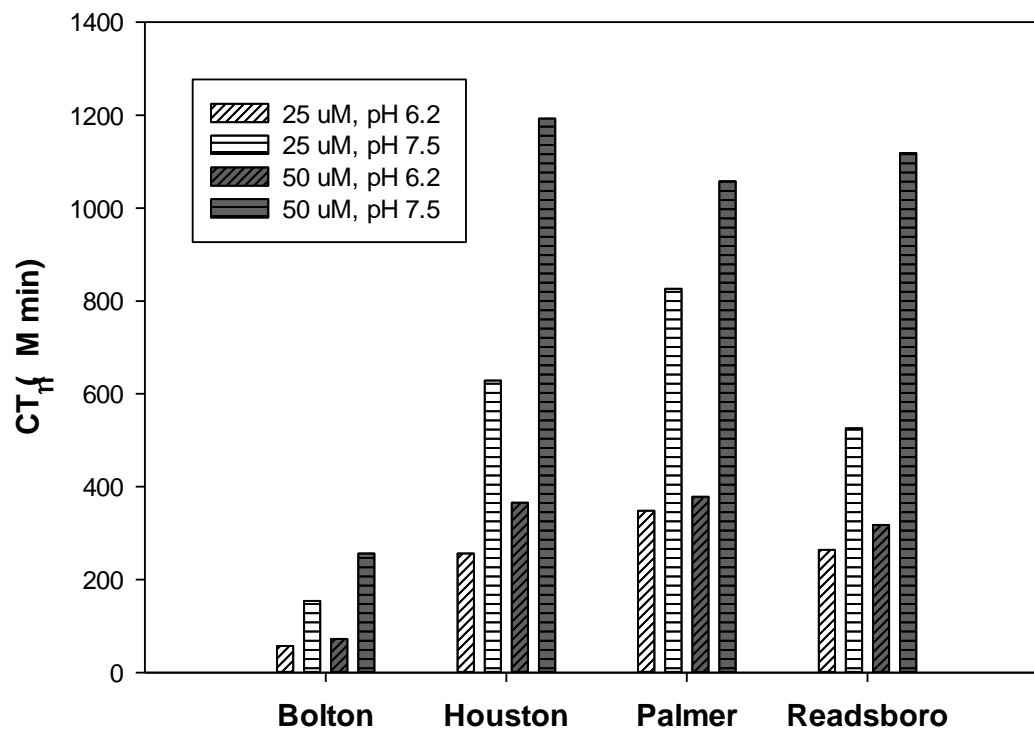
	TOC (mg/L)	DOC (mg/L)	UV ₂₅₄ (cm ⁻¹)	SUVA (L/mg/m)	pH
Amherst, MA	2.40	2.39	0.065	2.7	7.1
Houston TX	6.64	6.53	0.221	3.4	7.3
Palmer, MA	2.03	2.01	0.092	4.6	6.5
Readsboro, VT	2.03	2.03	0.119	5.9	6.0
Bolton, VT	5.86	5.18	0.215	4.2	6.6
Holton, KS	6.38	5.79	0.107	1.8	7.0
Stockbridge, MA	2.88	2.87	0.078	2.7	6.6
Lantern Hill, CT	3.48	3.40	0.153	4.4	6.5

Ferrate Decay, 50 μM 

Natural waters have a stabilizing effect on ferrate compared to similarly-buffered lab grade water.

- Slower decomposition of ferrate (e.g., carbonate effect), or
- Formation of other secondary oxidants also capable of oxidizing ABTS.

Ferrate exposure (CT product)



CT values at pH 6.2 are much lower than those at pH 7.5, pH had a great effect on CT values.

Outline

1. Ferrate decomposition and lifetime in natural waters

→ 2. Direct Ferrate impacts on NOM and DBP precursors

3. Direct ferrate impacts on Fe/Mn

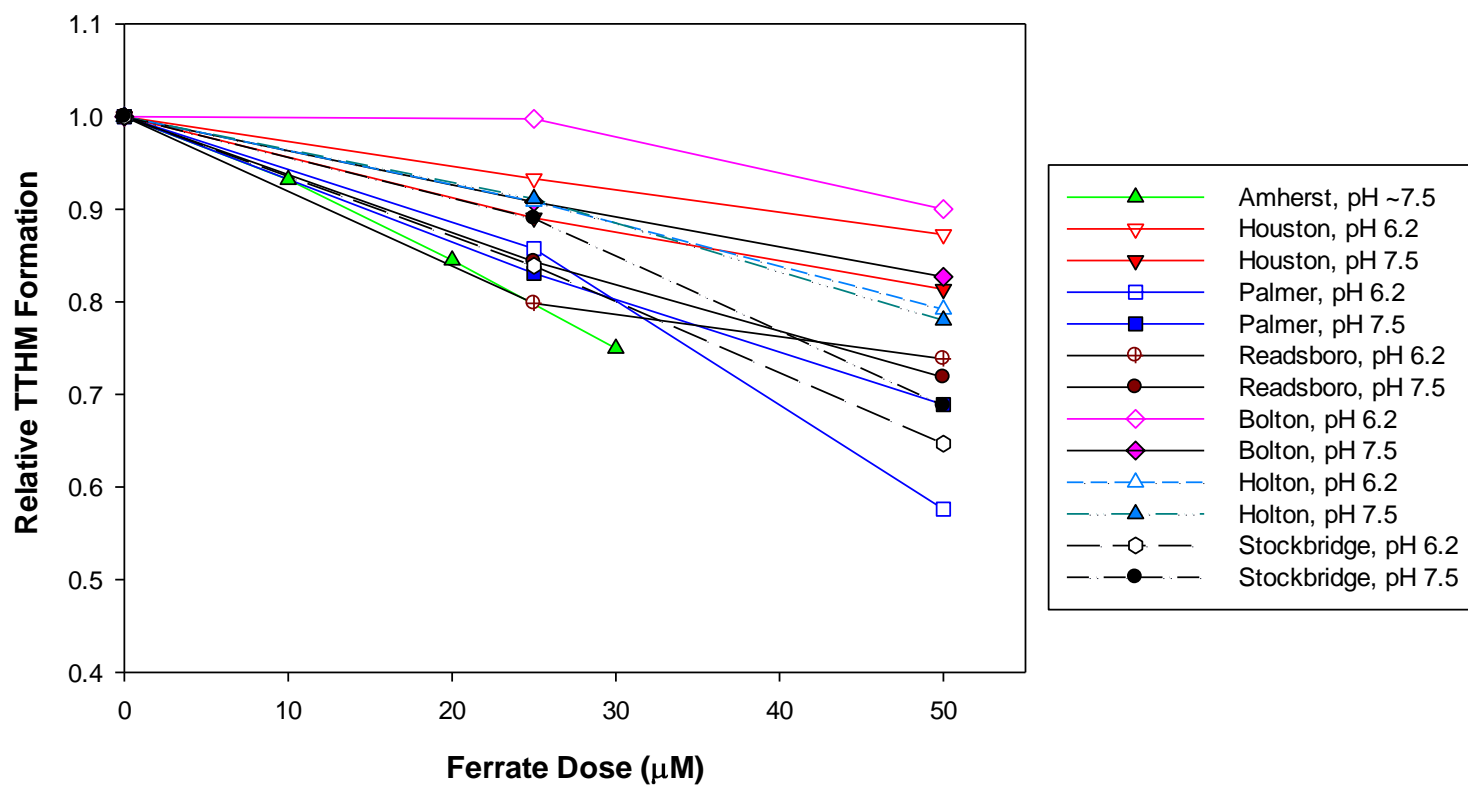
4. Conclusions

Precursor Testing

- Treat samples with ferrate
- Allow ferrate to dissipate (<60 min)
- Chlorinate in the lab
 - pH 7.0
 - Dose required for 3–5 mg/L residual after 72 hrs
 - 20°C
- Measure DBPs
 - Neutral Extractables (including THMs)
 - Haloacetic Acids (9 total)

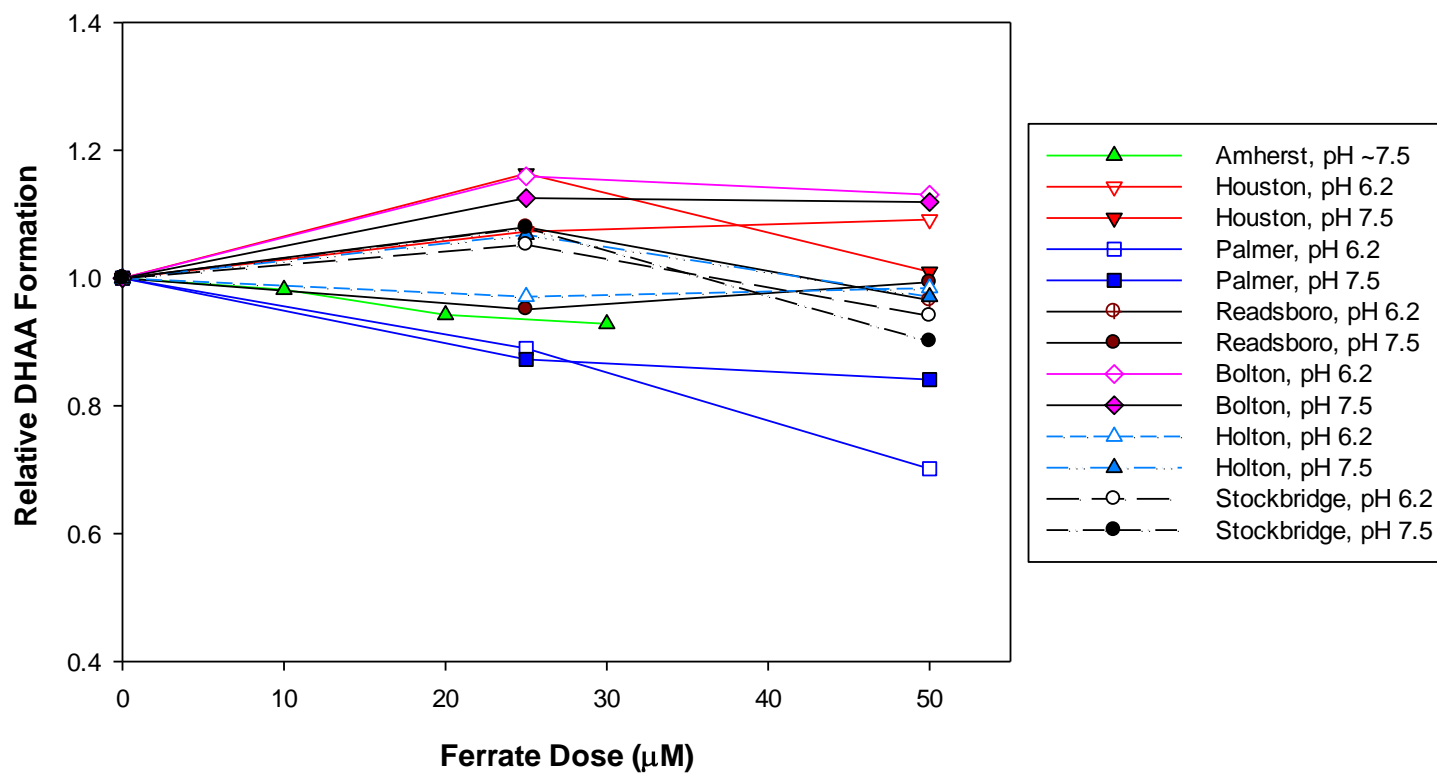
Trihalomethanes (THM)

Substantial decrease; little pH effect



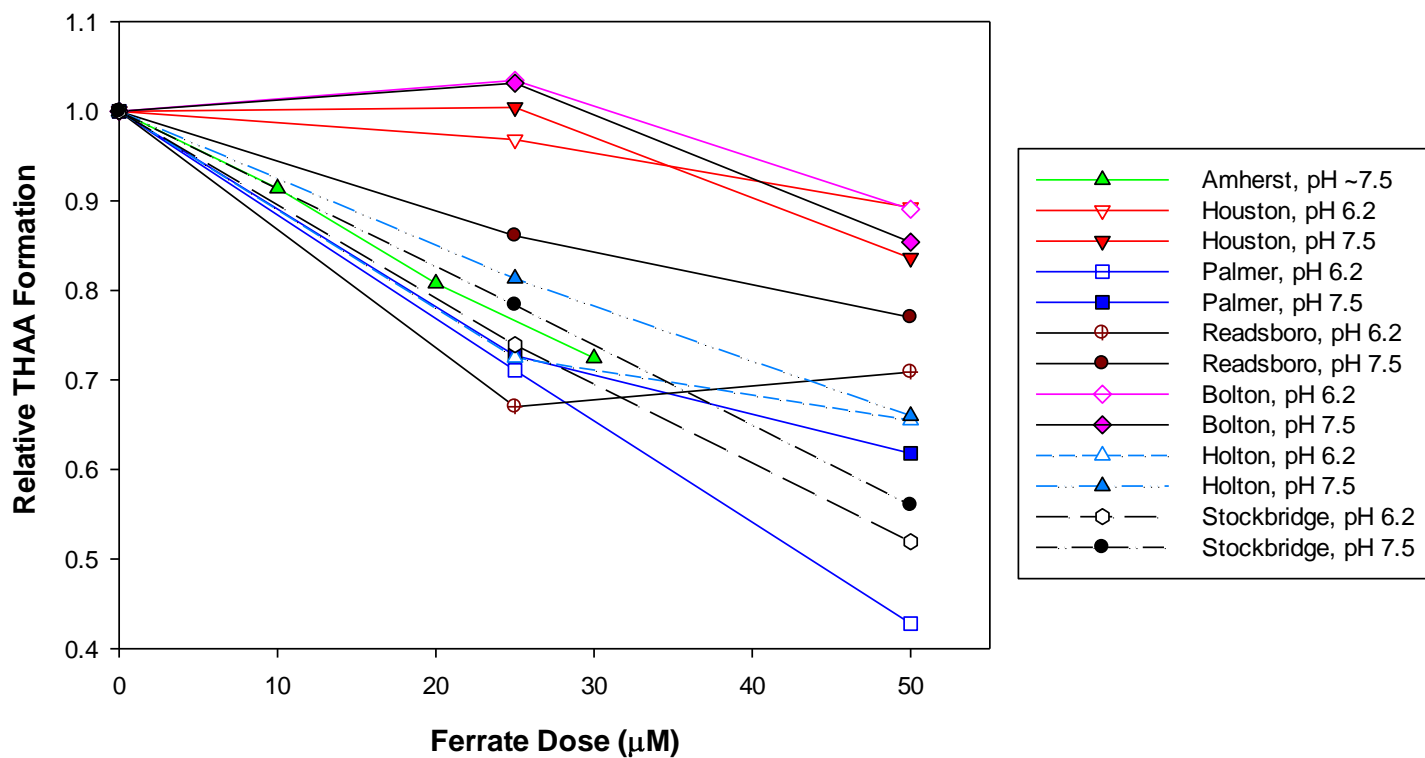
Dihaloacetic Acids (DHAA)

Less degradation than THMs



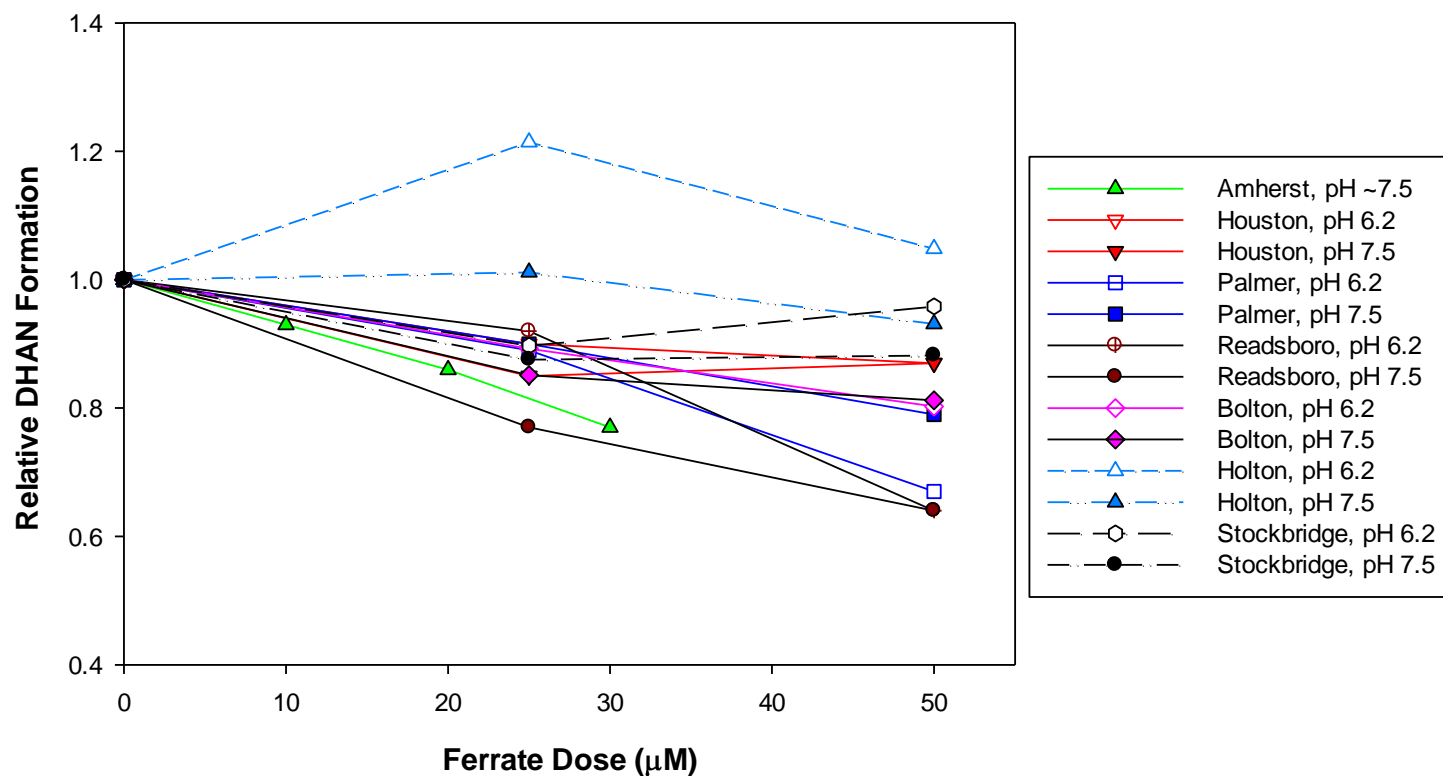
Trihaloacetic Acids (THAA)

More loss than THMs

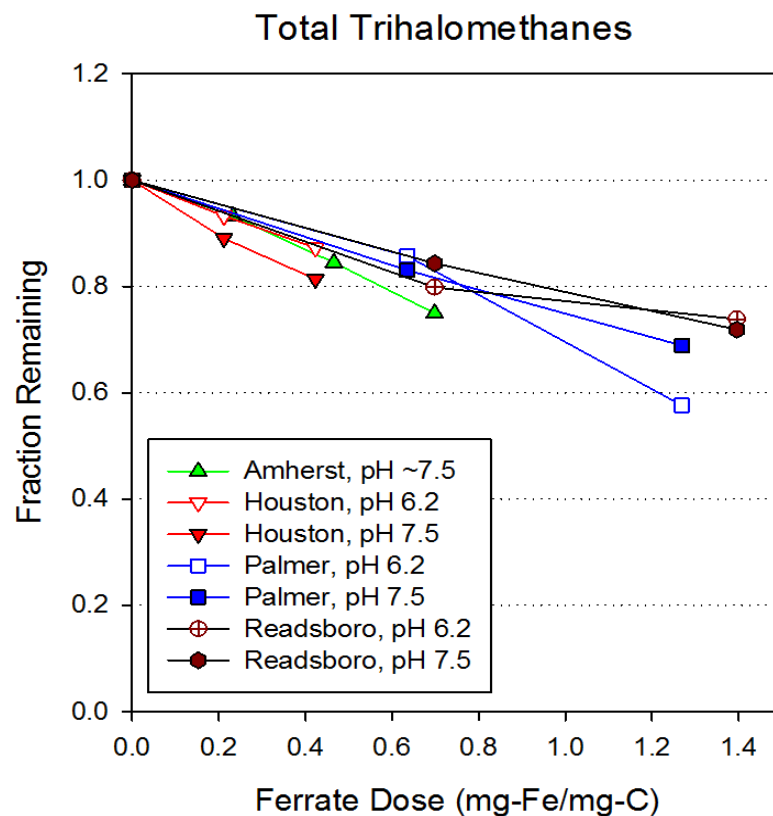
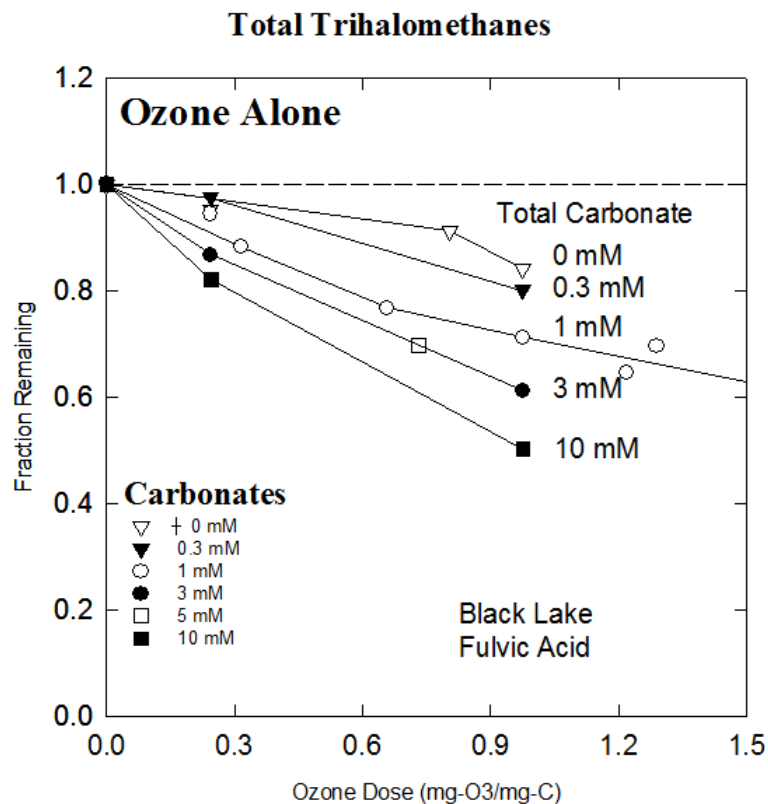


Dihaloacetonitrile (DHAN)

Substantial decrease



Comparison with ozone



Data from: Reckhow et al., 1986

Data from: current study

Lessons from Precursor Data

- Ferrate will directly destroy THM precursors by 25-40% at doses of 1.4 mg-Fe/mg-C.
 - THAA precursors are slightly better oxidized (25–55%);
 - DHAA precursors are less well oxidized (-10–30%);
 - DHAN precursors are similarly reduced by 21–36%.
- Precursor oxidation by ferrate is similar to that observed for ozone at equivalent doses
- Precursor destruction does not seem to diminish at lower pH where exposure (CT) is much lower
 - Precursor destruction is either faster when the reactants are more protonated, or ferrate decomposition products play an important role.

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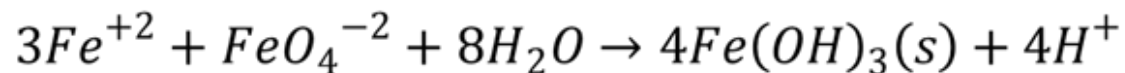
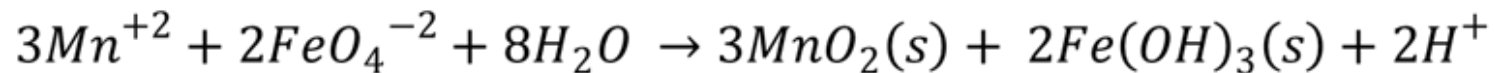
Metals Oxidation – Lantern Hill, CT

0.02

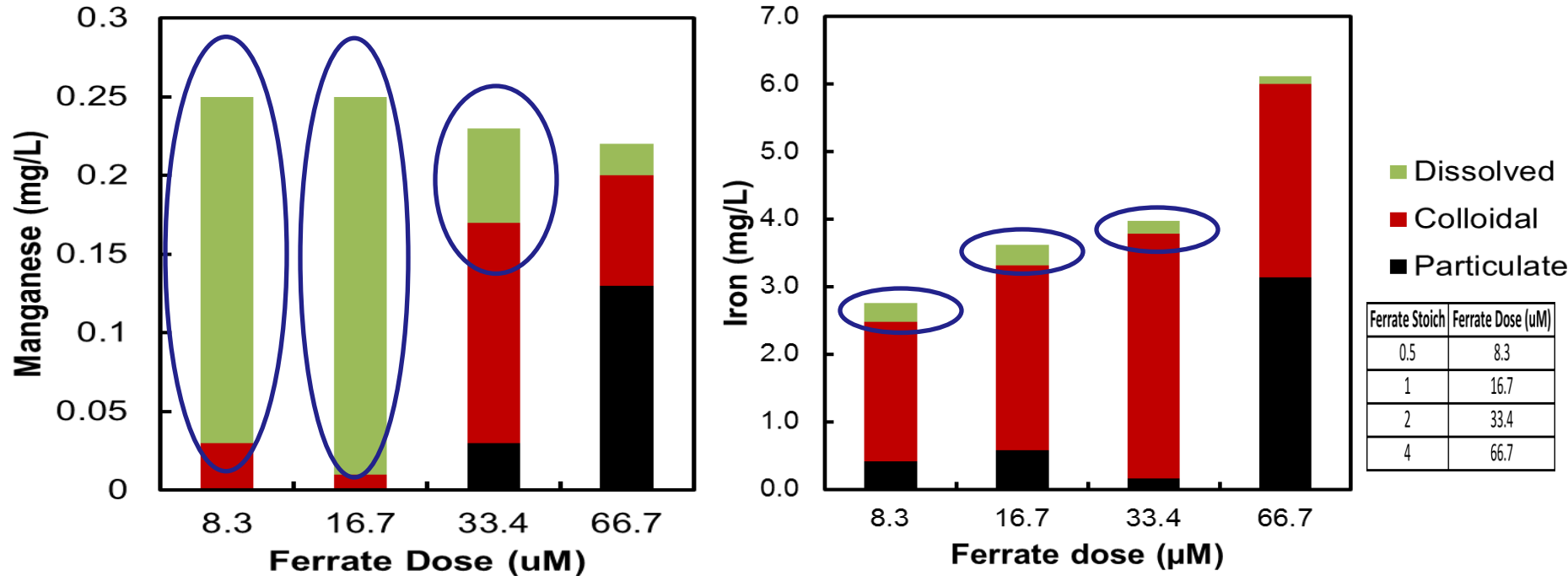
Raw Water Quality (Challenges)

0.3

	Total Mn (mg/L)	Dissolved Mn (mg/L)	Total Fe (mg/L)	Dissolved Fe (mg/L)	pH	UV ₂₅₄ (cm ⁻¹)	TOC (mg/L)
Average	0.17	0.17	1.85	1.69	6.51	0.153	3.48
Range	0.14-0.22	0.12-0.22	1.16-2.39	1.03-2.34	6.35-6.67	0.128-0.165	3.03-4.30

Mn²⁺ and Fe²⁺ Oxidation with Ferrate:

Metals Oxidation Lantern Hill – Mn & Fe



- Reaction kinetics favor Fe oxidation over manganese.
- The incomplete oxidation of Mn was also likely caused by competition by other oxidant demands, like NOM.
- Both Mn and Fe indicated the overwhelming majority of the oxidized metals exist in the colloidal phase.

Outline

1. Ferrate decomposition and lifetime in natural waters

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→ 4. Conclusions

Conclusions so far

- Ferrate is capable of oxidizing regulated DBP precursors, as well as Fe & Mn with an effectiveness similar to ozone.
 - Cost may be similar as well.
 - No apparent issues with DBP formation.
- Depending on EPA action regarding CT credit, ferrate may be an attractive option for meeting DBP regulations.
 - Perhaps especially well suited for small utilities

Future work

- Bench-scale work will continue to test waters with different properties and chemical contaminants (e.g., pesticides, sulfide, arsenic, PPCPs).
- Pilot-scale work will allow us to collect data on aspects that cannot be readily investigated at the bench scale such as biological removal, sludge production, and build-up of filter headloss.

Acknowledgements

- US EPA STAR program
- Dave Reckhow, John Tobiason, Joe Goodwill.
- UMass water research group
 - Sherrie Webb-Yagodzinski, Yun Yu, Arianne Bazilio, John Martin
- Participating Utility Personnel
 - Amherst, Houston, Palmer, Readsboro, Bolton
- Shankar Chellam (U of Houston)
- Carole Tomlinson (Haskell Indian Nations Univ).

THANK YOU!