Treatment of Groundwater for Iron and Manganese
While Avoiding Taste and Odor

Mark Carlson

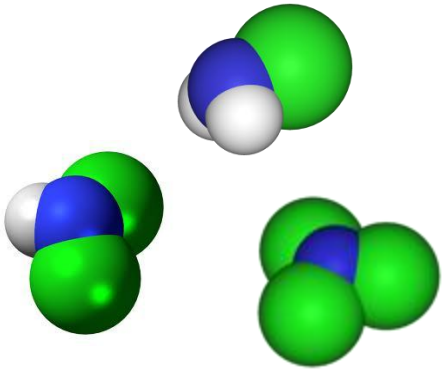
Introduction

- Statement of Problem
- Background Chemistry
- Two case studies

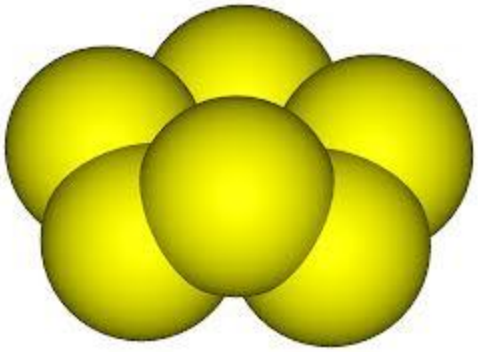
Statement of Problem

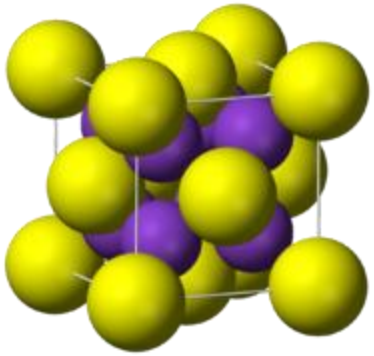
- Removal of iron or manganese requires an oxidant
- Chlorine is cheap, reliable and also disinfects
- However, side reactions do occur

Side Reactions



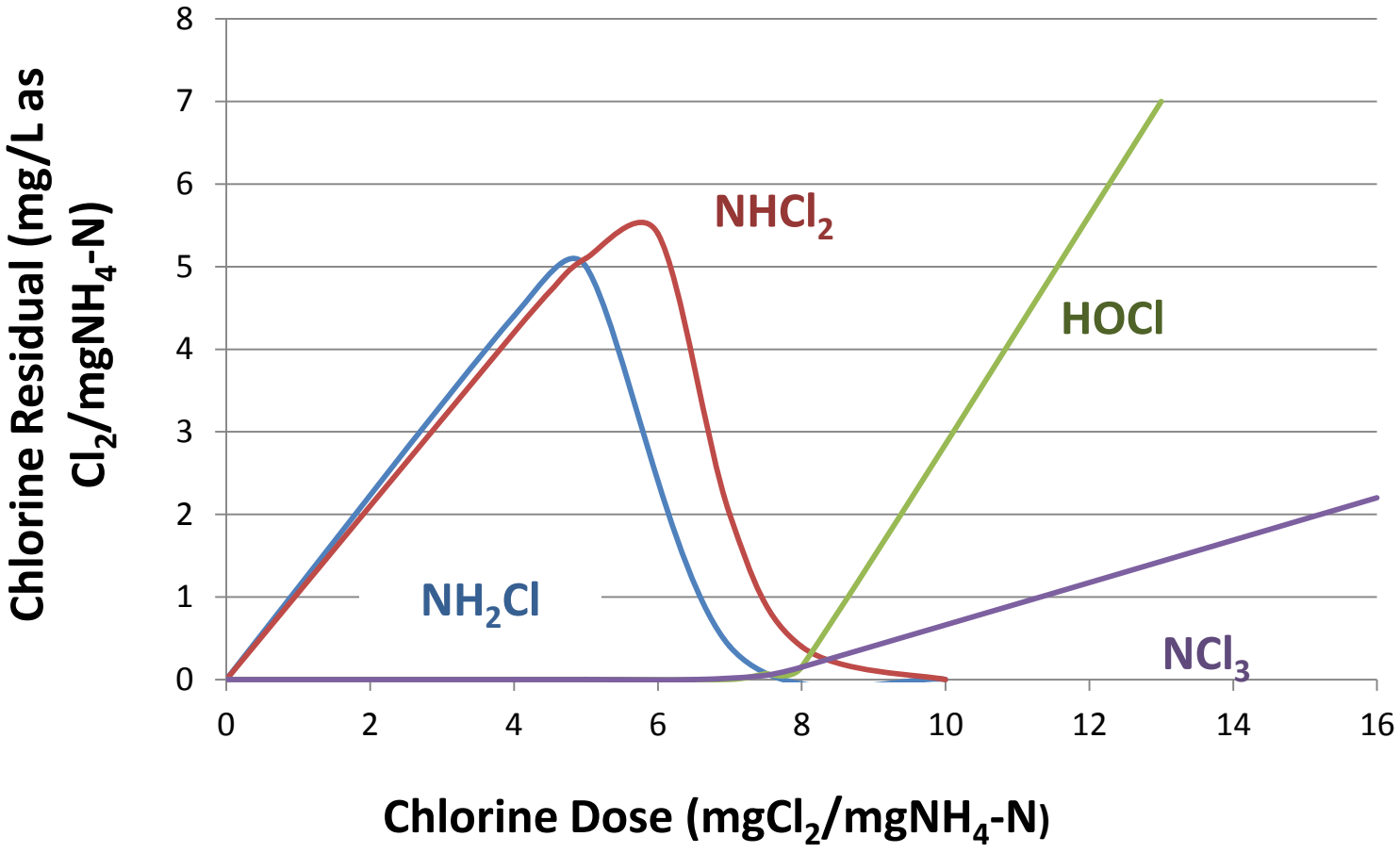
Chlorine +
Ammonia
=Chloramines





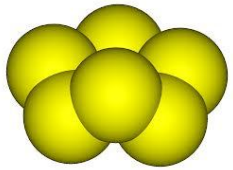
Chlorine +
Hydrogen Sulfide
= Sulfur and
Polysulfides

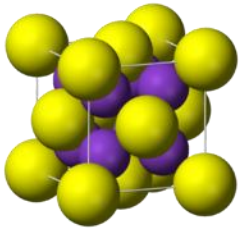
Chlorine Ammonia Reactions



Chlorine –Sulfide Reactions

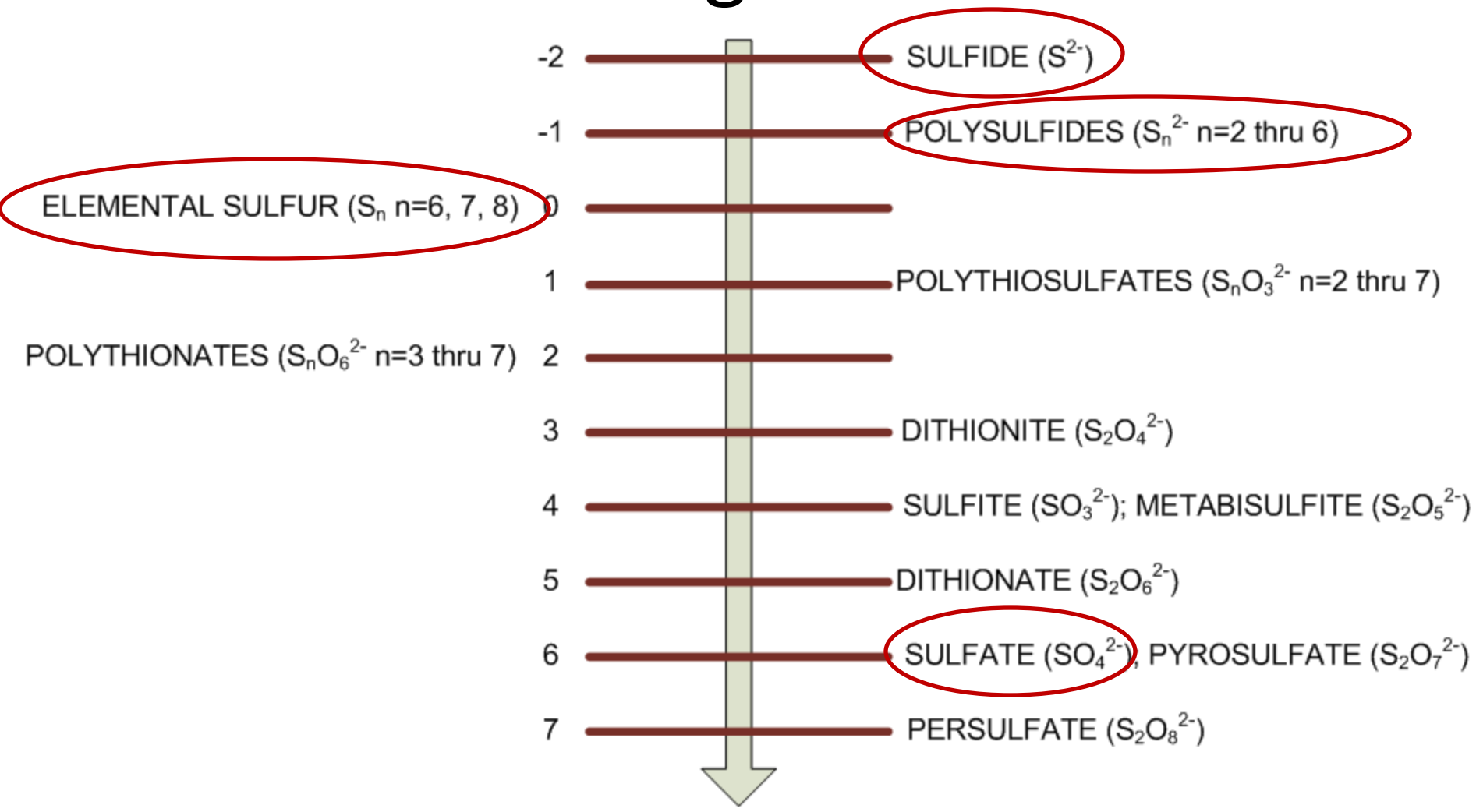
1. $H_2S + Cl_2 \longrightarrow 2HCl + S^0$

2. S^0 ⇉ S^0 (ppt) 

HS_n^- 

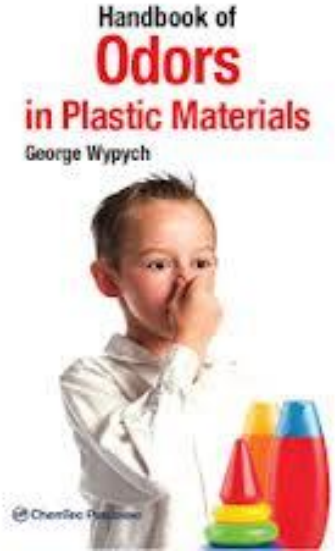
Note: These are reversible!

Increasing Oxidation

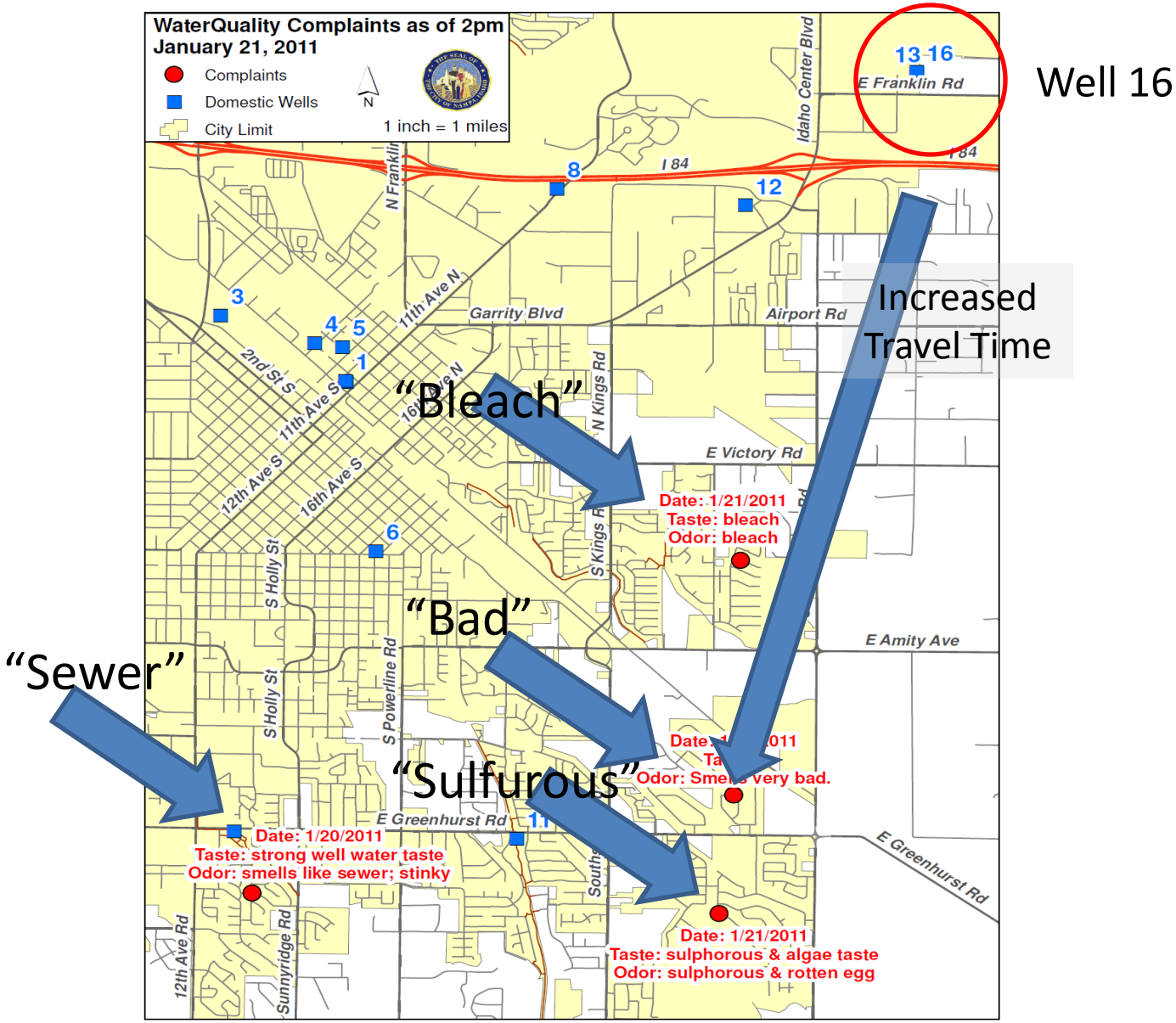


Polysulfide's Presents a Taste and Odor Concern

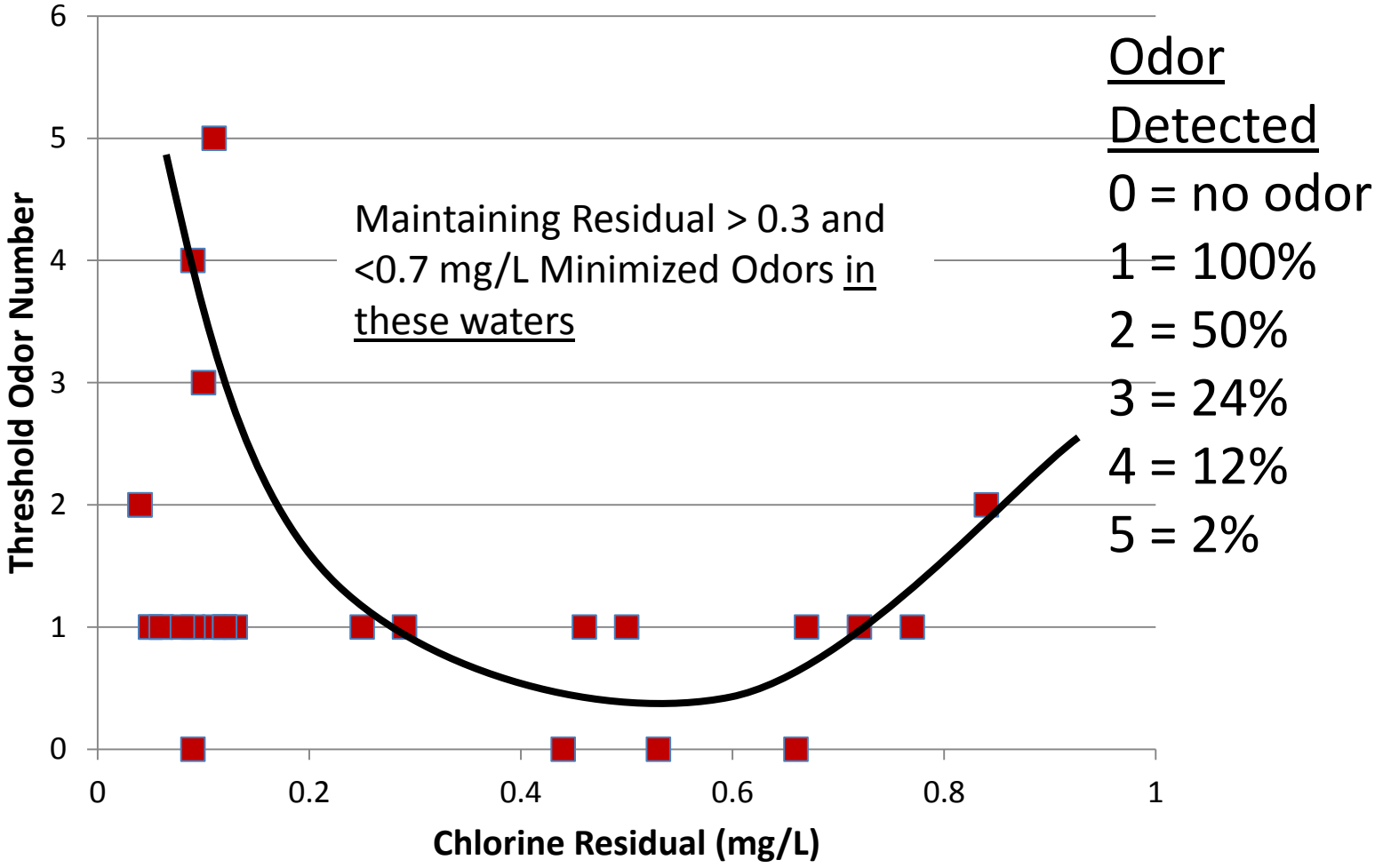
- Some have characteristic hydrogen sulfide odor
- Can have a metallic taste or bitter mouth feel



Travel Time Complications

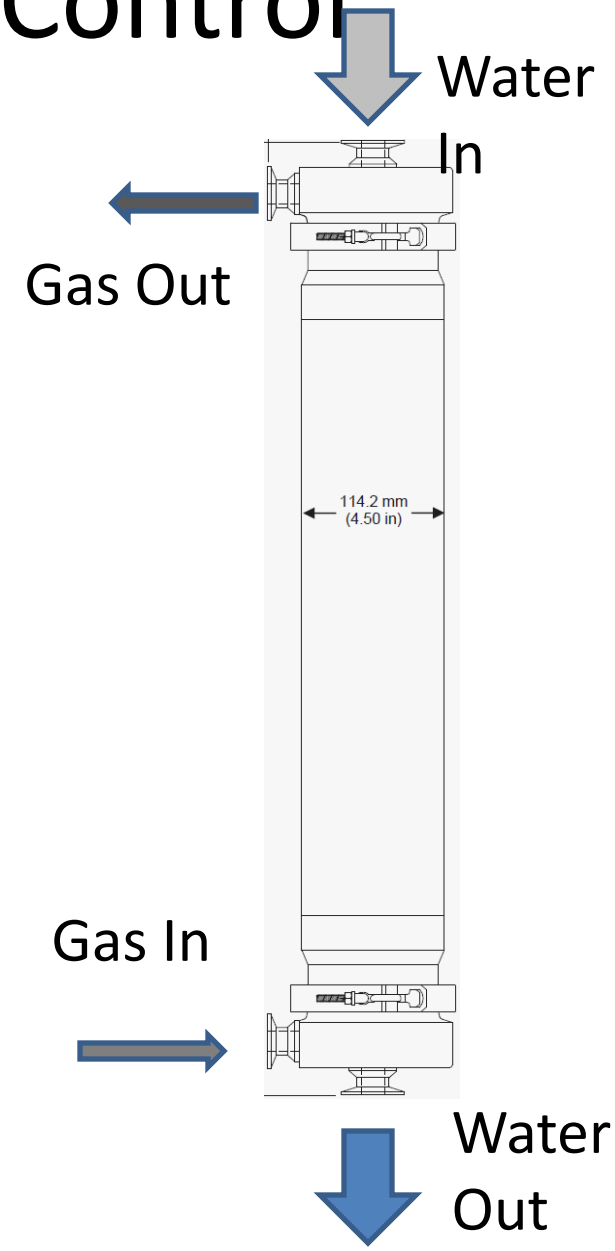


Careful Control of Chlorine Residual is Critical



Beyond Careful Chlorine Control

- Treatment
  - Catalytic Granular Activated Carbon
  - Membrane Degasser
  - Chloramines
- NonTreatment
  - Selective Aquifer Depths



Case Studies

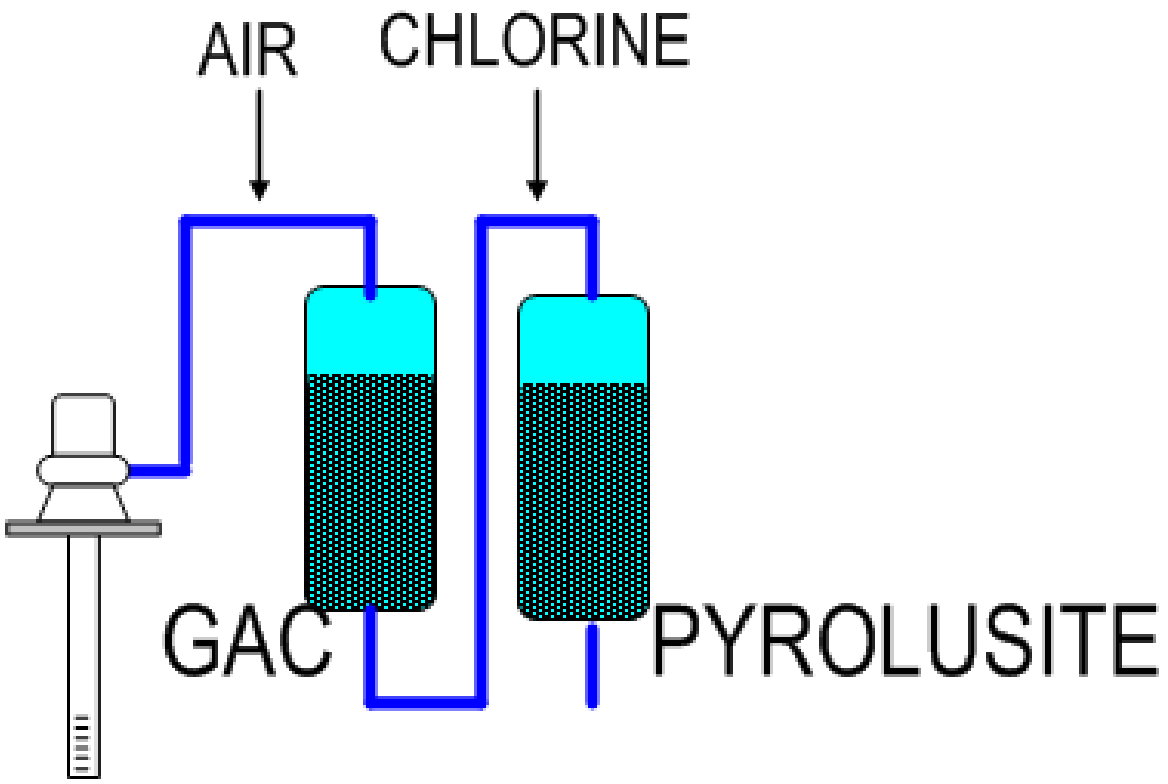
Well 16
Nampa, ID

Well 21
Meridian, ID

Nampa Water Quality

Parameter	Raw Well Water	Filtered
pH	9.2	9.0 to 9.2
H_2S (mg/L)	0.16	Below Detection
Mn (mg/L)	0.12	0.06
Fe (mg/L)	0.07	Below Detection
NH_4 (mg/L)	0.81	0.11
Threshold Odor Number	5	4

Granular Activated Carbon



Parameters Tested

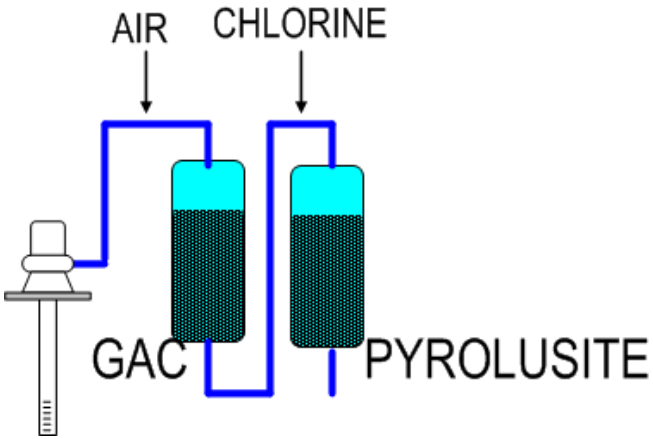
- Sulfide Concentration
- Threshold Odor Number

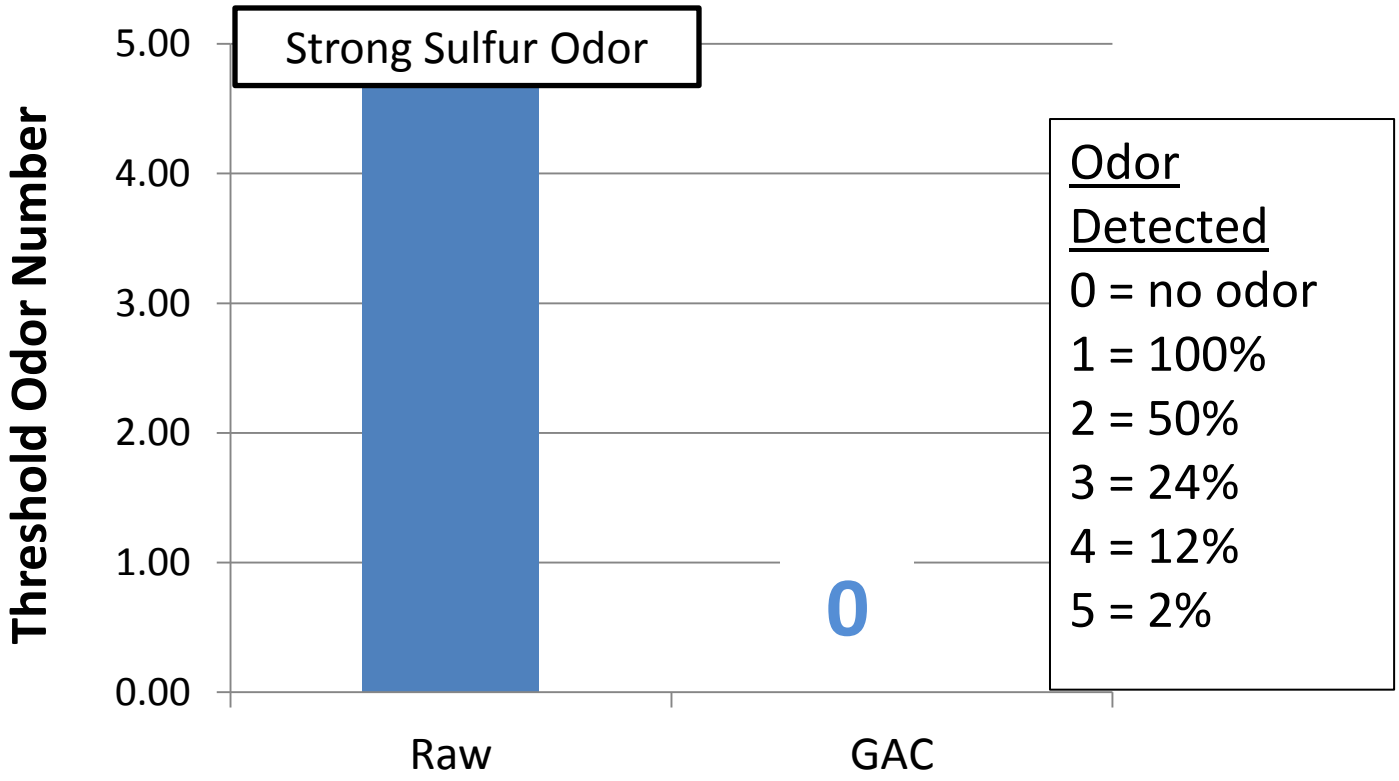
Odor Detected

0 = no odor
1 = 100%
2 = 50%
3 = 24%
4 = 12%
5 = 2%

- Chlorinous
- Sulfurous
- Metallic (polysulfides)

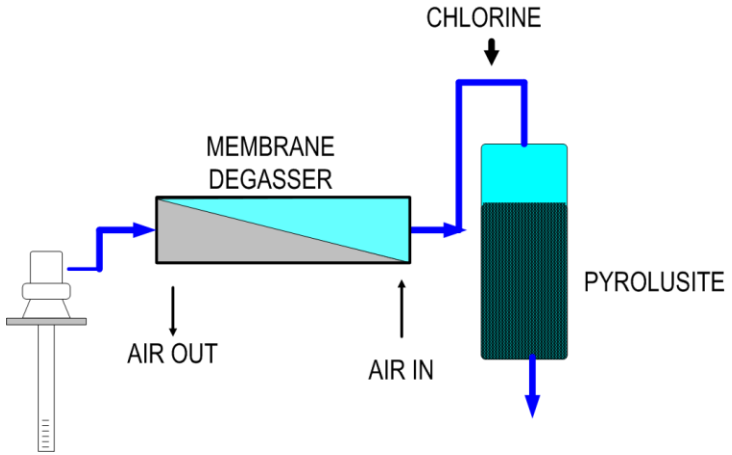
1. Catalytic GAC



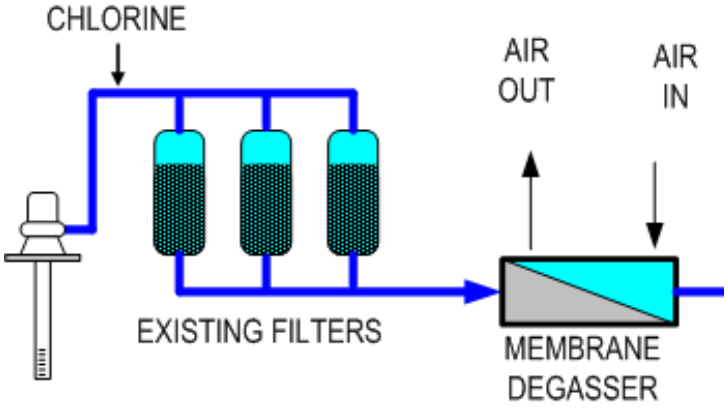


Two Tests of Membrane Degasser

2. Membrane Degasser Before Filters



3. Membrane Degasser After Filters



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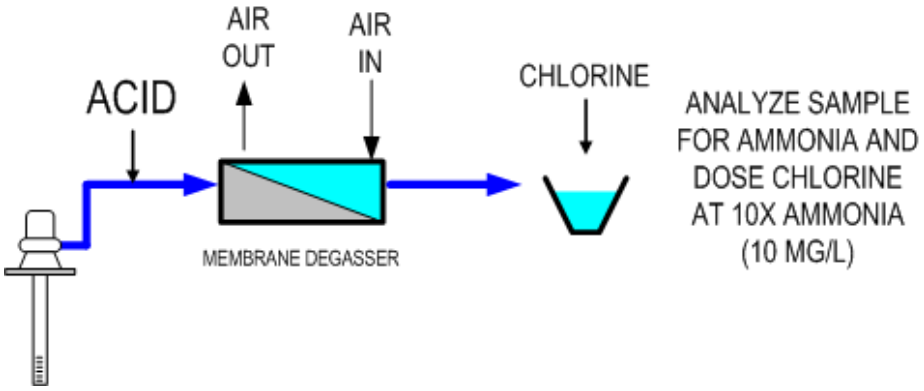
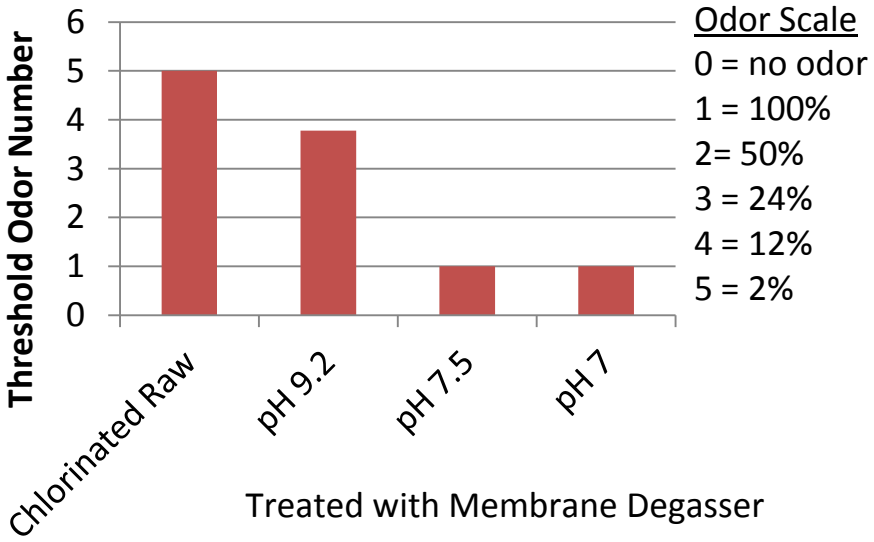
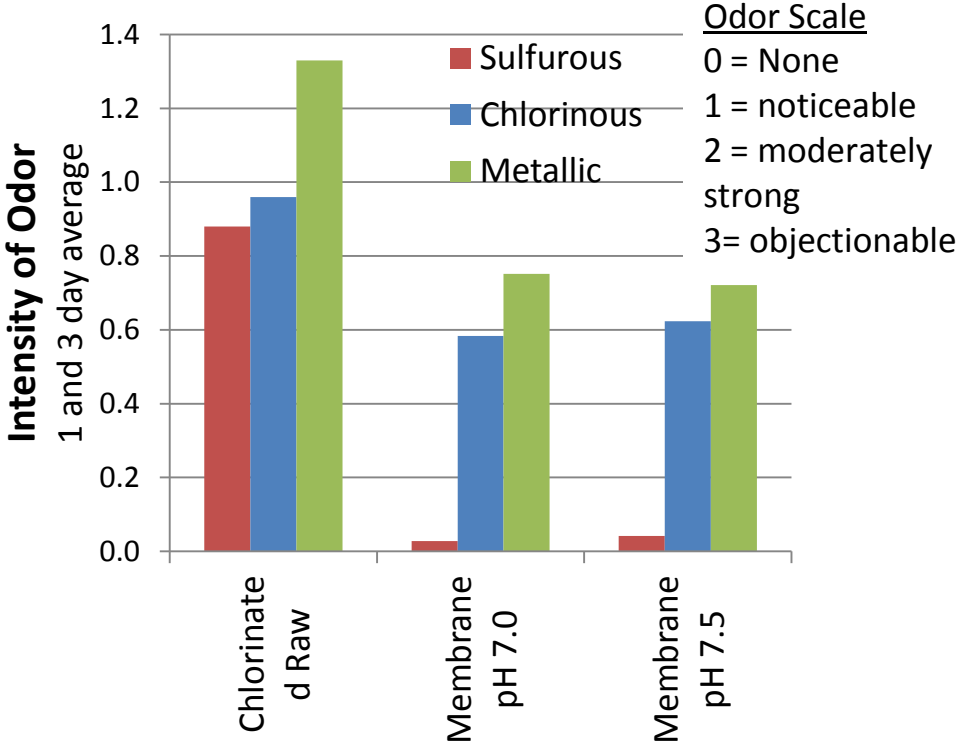


Threshold Odor Number



Nature of Taste and Odor



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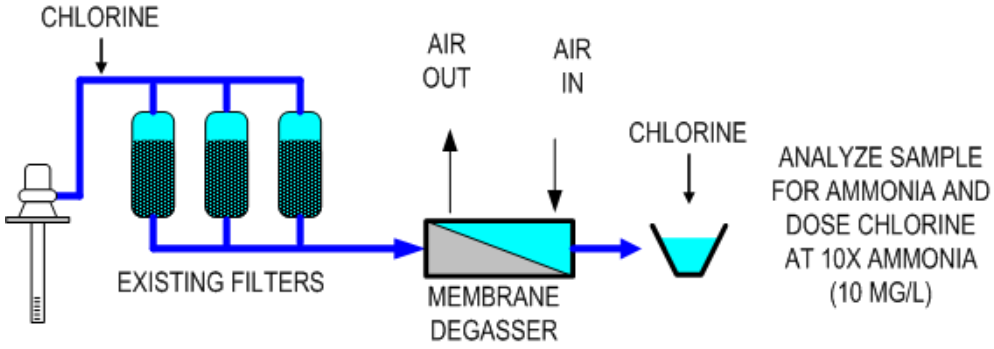
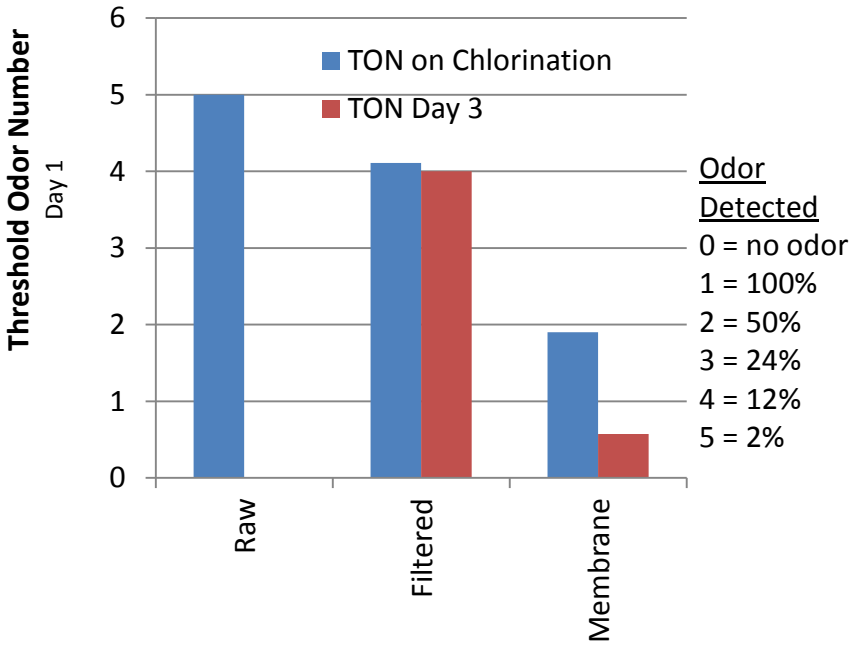


Threshold Odor Number



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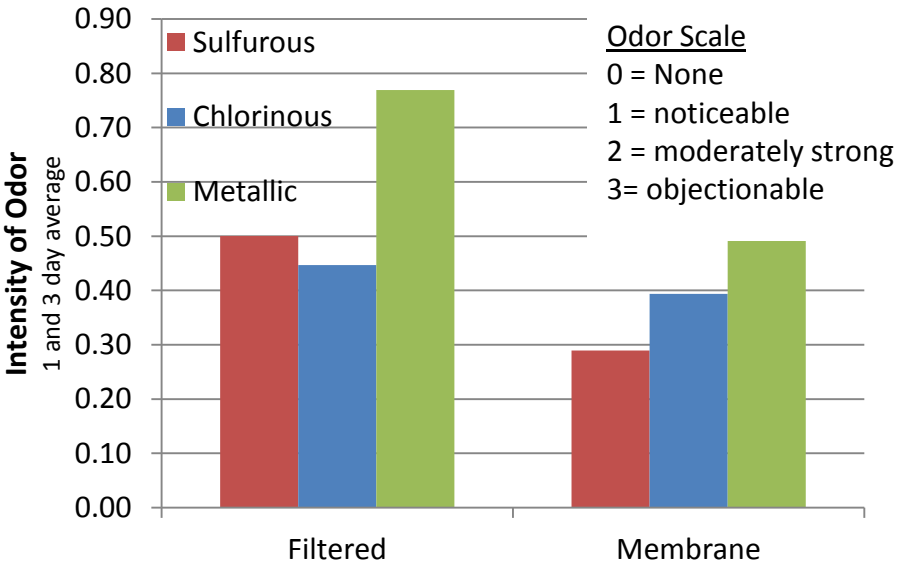


Well 16, Meridian - Approach

- Test Different Aquifer Depths
- Adjust Treatment to Minimize Tastes and Odors

Meridian Water Quality and Goals

Parameter	Raw Well Water	Goal
H_2S (mg/L)	Below Detection	Below Detection
Mn (mg/L)	0.30	<0.05
Fe (mg/L)	0.13	<0.3
NH_4 (mg/L)	0.73	No goal
pH	7.6	No goal

Minimize tastes and odors

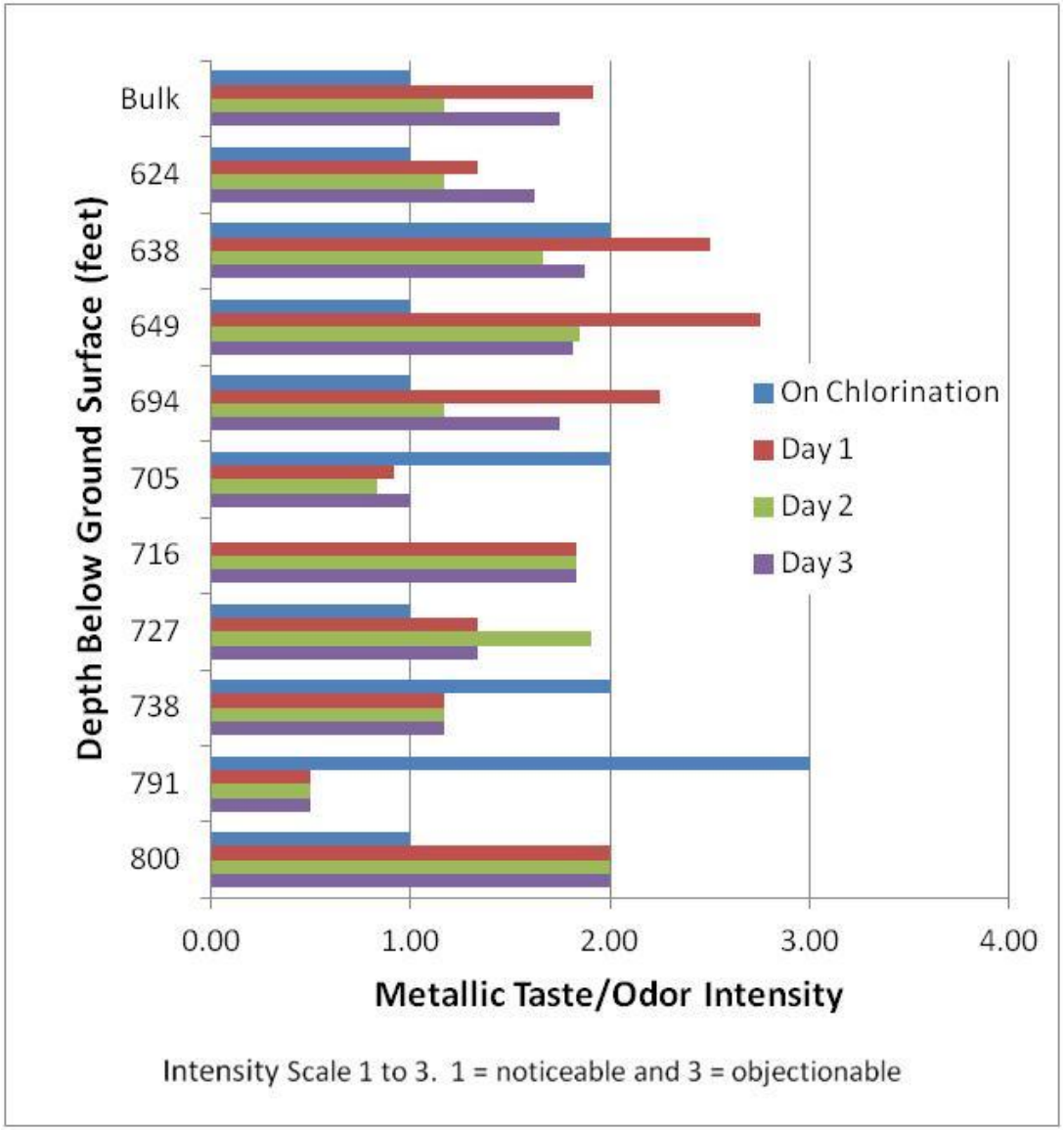
At each depth Below Ground Surface Water Chlorinated and Tested for Taste and Odors

- On collection water sample checked for ammonia
- Chlorine Dosed at 10x the ammonia concentration

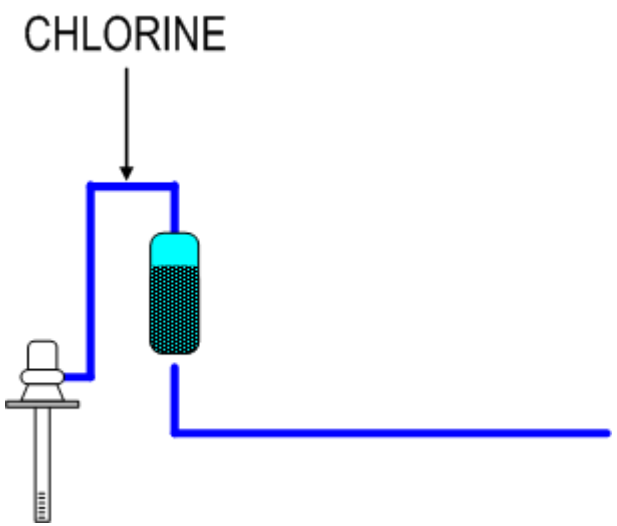
<u>Scale</u>

- 0 – no odor
- 1 – noticeable
- 2-moderately strong
- 3-objectionable

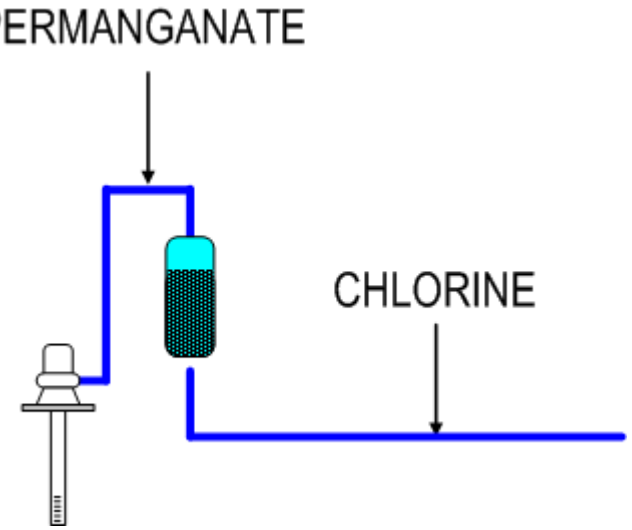
Metallic Taste Present at All Depths



Pilot Test Approach Chlorine vs. Permanganate



Dose chlorine at just enough to provide 0.5 mg/L residual (~10:1 Cl_2 to NH_3 Ratio)



Use Permanganate for Iron & Manganese and dose chlorine at 4:1 Cl_2 to NH_3 Ratio to maintain a residual

Taste and Odor Testing

Sample checked for tastes and odors

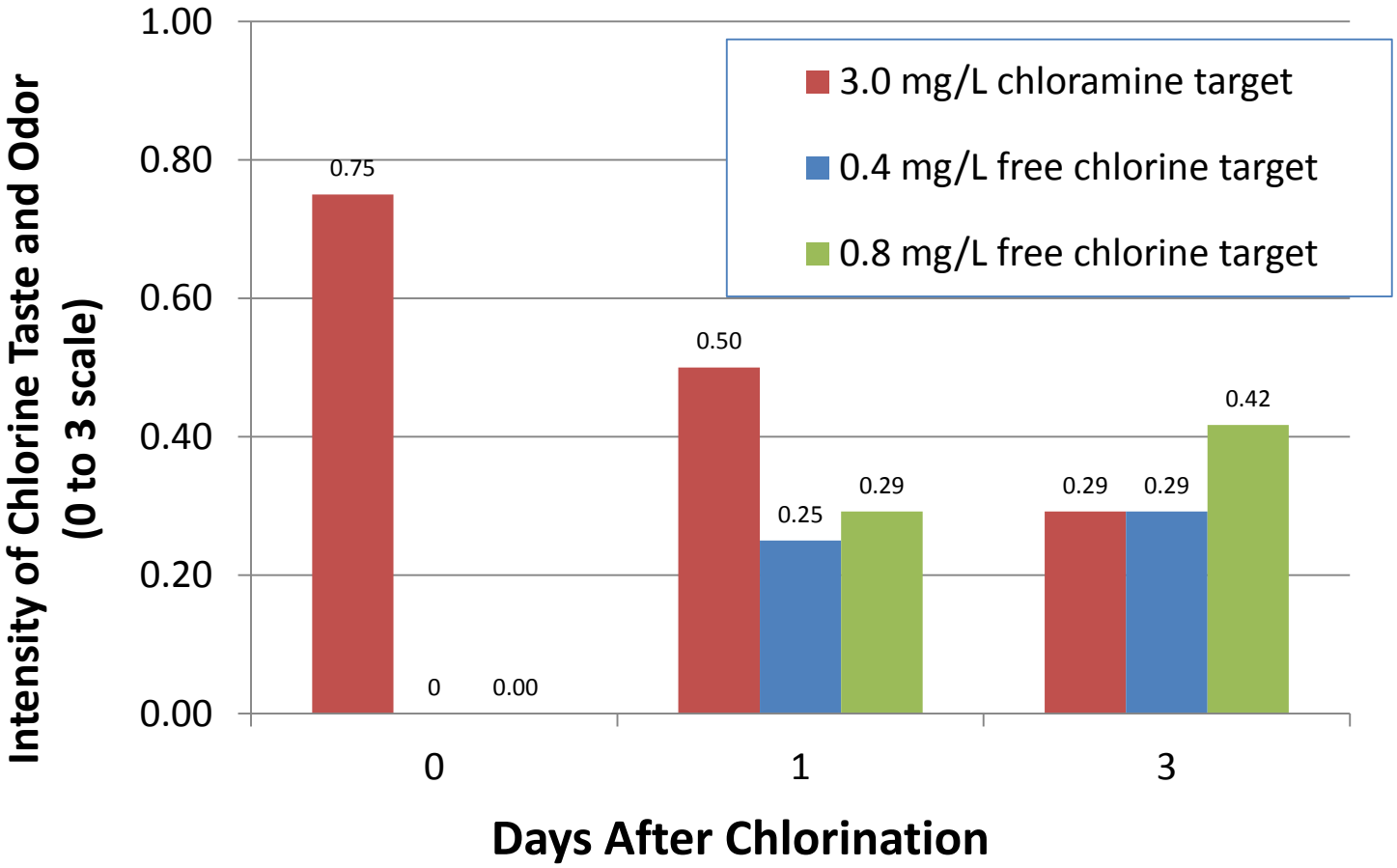
Scale

- 0 – no odor
- 1 – noticeable
- 2-moderately strong
- 3-objectionable

Results

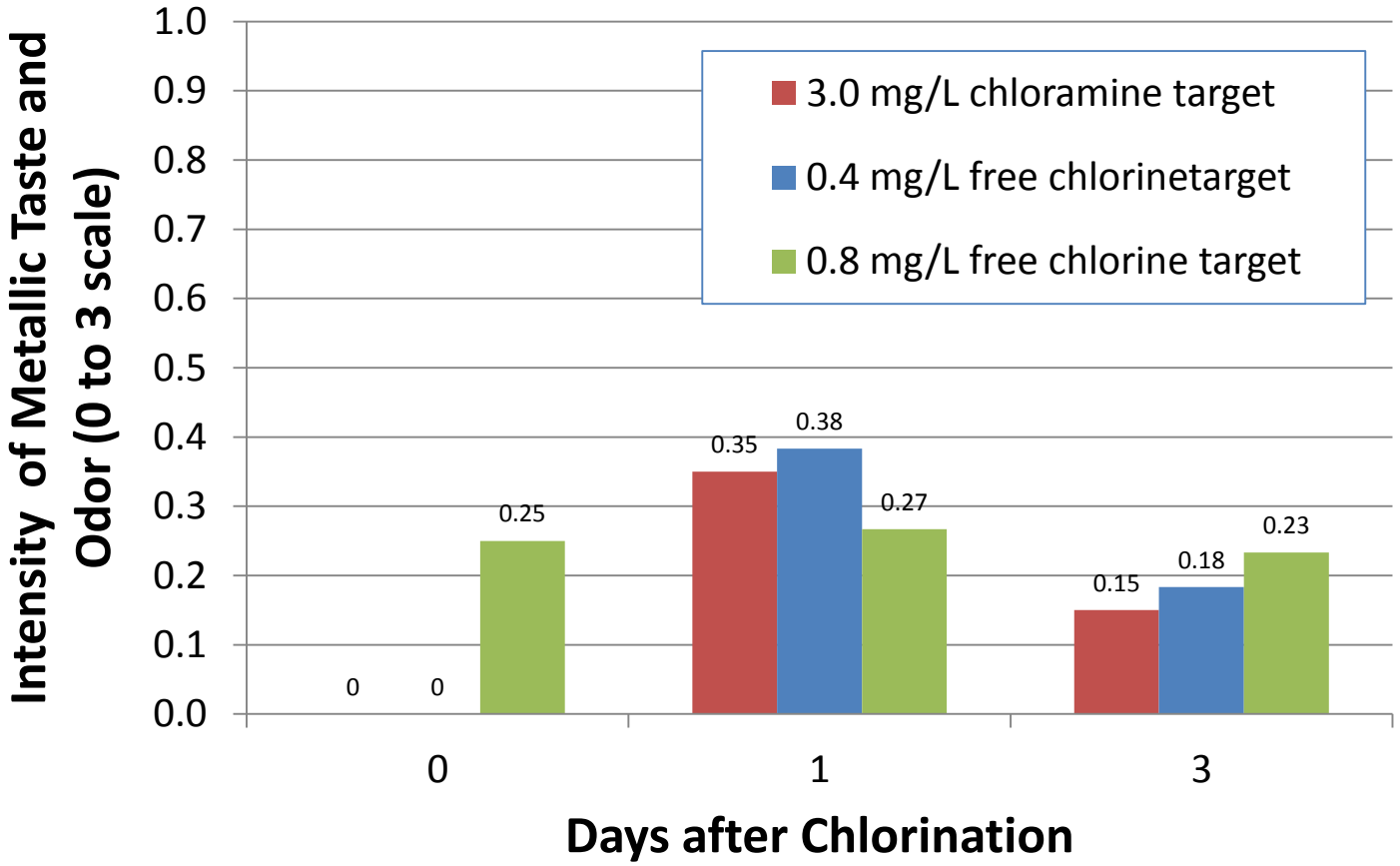
- Chlorine Filters: a dose of 8.4 mg/L Cl_2 needed
- Permanganate Filter: a dose of 0.7 mg/L $KMnO_4$ for oxidation and Cl_2 dose of 2.9 mg/L for residual maintenance

Chlorine Tastes and Odors



Remember a ranking of 1 = noticeable

Metallic Taste and Odor Results



Remember a ranking of 1 = noticeable

Conclusions

- Chlorine Dose and Residual Control Good First Step
- Catalytic GAC is Gold Standard for Hydrogen Sulfide Removal
- Membrane Degasser Has Promise – pH dependant
- Chloramine Residuals Minimized Metallic Taste and Reduced Dose

END

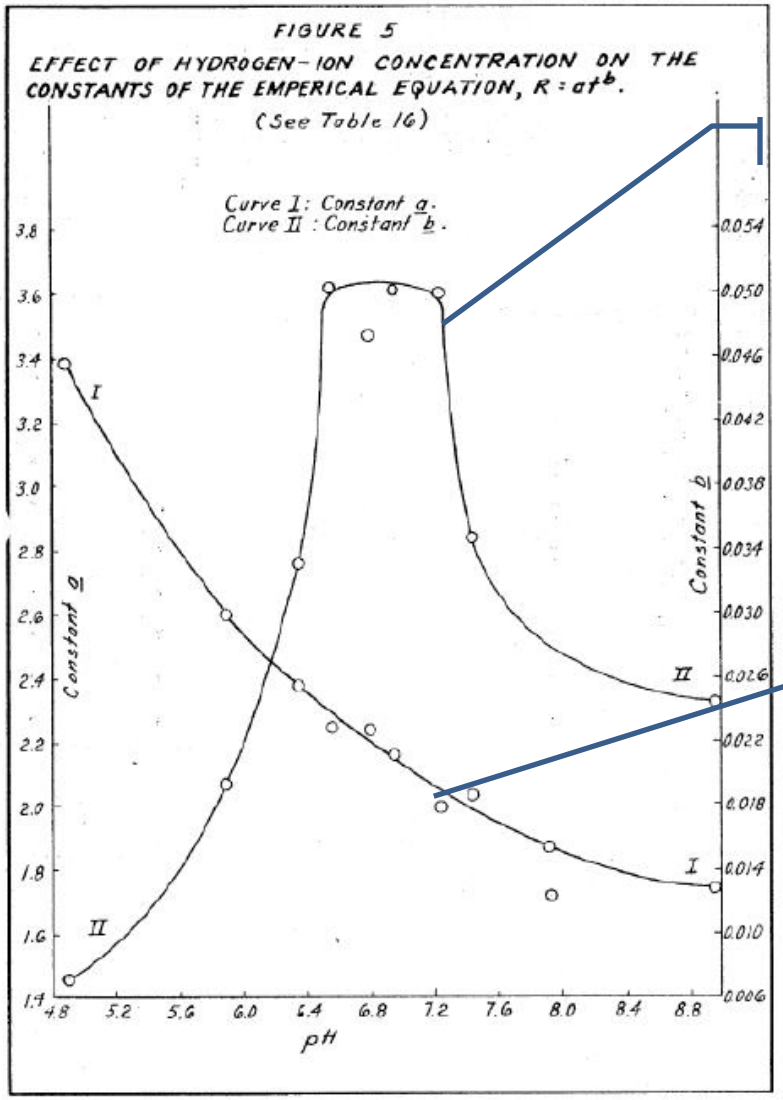
Comments and Questions

Extra Stuff

Chemical Doses

Chemical Treatment	Existing Well Water	Projections with Bottom of Well Packed off
Chlorine only	7.5 mg/L Cl_2	4 to 5 mg/L Cl_2
Permanganate for Fe & Mn Chlorine for residual	0.7 mg/L $KMnO_4$ 2.7 mg/L Cl_2	0.6 to 0.7 mg/L $KMnO_4$ 1.8 mg/L Cl_2

Chlorination pH impacts reaction



Extent of Reaction

- Extent of oxidation peaks between pH 6.5 and pH 7.2
- Sharply slows outside this range
- Rate of reaction slows as pH increases
- pH above 7.2 – partial oxidation and slower rate

Rate of Reaction

From: Goodson, James, The Oxidation of Sulfides by Chlorine in Dilute Aqueous Solutions, PhD Dissertation, University of Florida, 1950

Chlorine Sulfide Reactions

1. Chlorine reacts with hydrogen sulfide to form sulfur

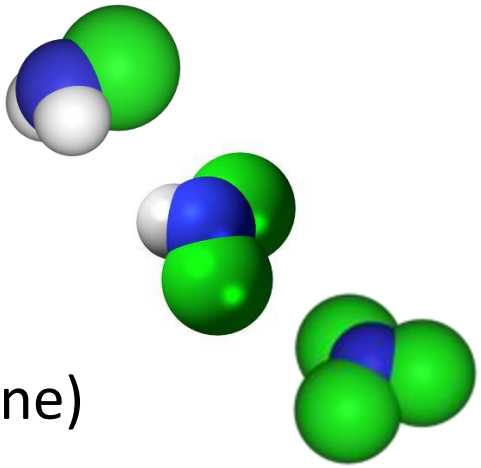
$$H_2S + Cl_2 \rightarrow 2HCl + S^0$$

2. Chlorine reacts with ammonia to form combined chlorine

$$Cl_2 + NH_4^+ \rightarrow NH_2Cl \text{ (monochloramine)}$$

$$\rightarrow NHCl_2 \text{ (dichloramine)}$$

$$\rightarrow NCl_3 \text{ (trichloramine)}$$



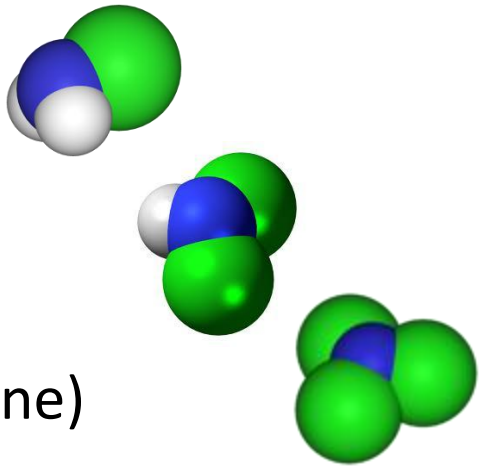
Chlorine Ammonia Reactions

Chlorine reacts with ammonia to form combined chlorine

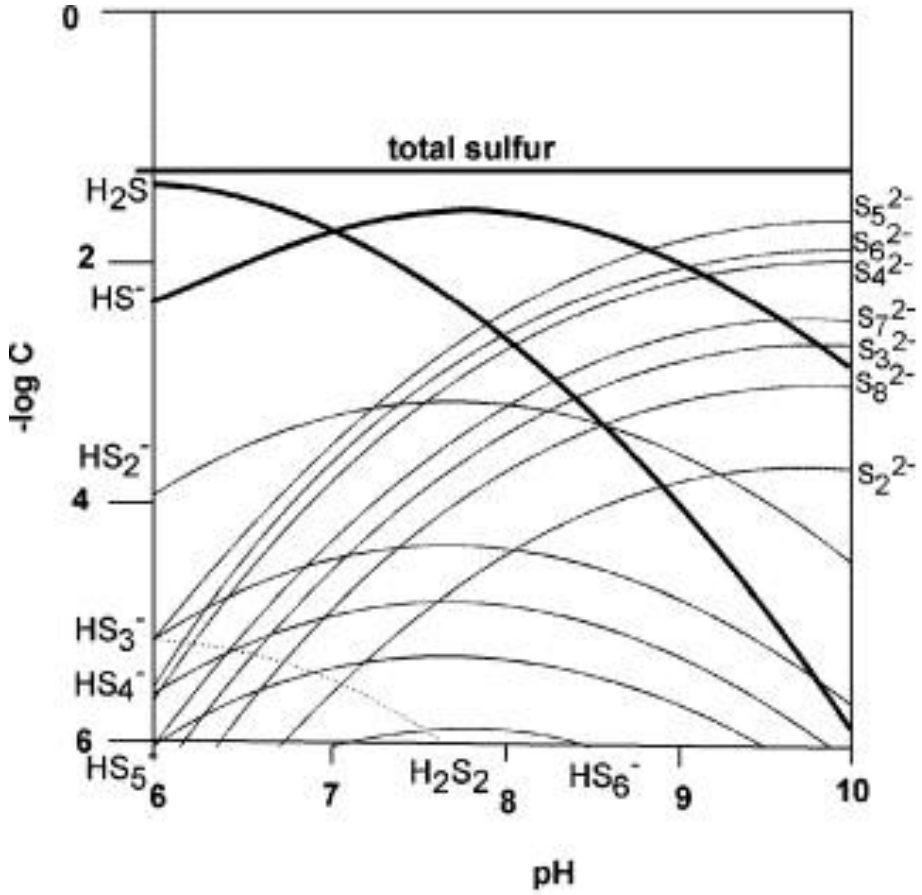
$Cl_2 + NH_4^+ \rightarrow NH_2Cl$ (monochloramine)

$\rightarrow NHCl_2$ (dichloramine)

$\rightarrow NCl_3$ (trichloramine)



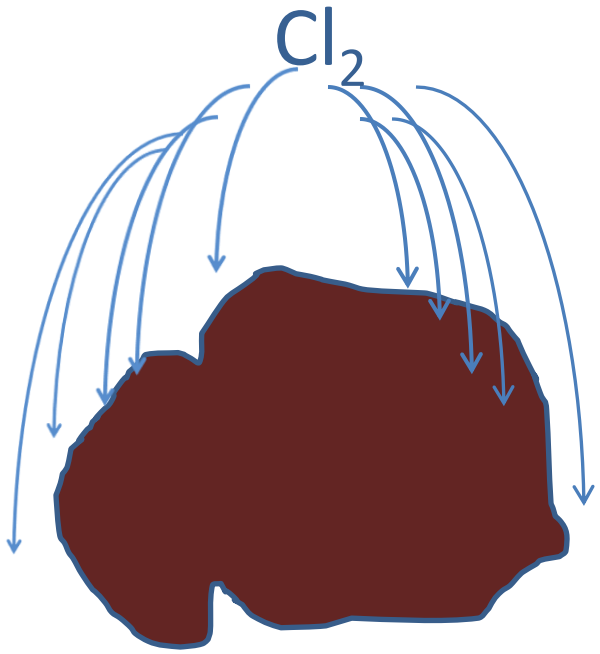
Polysulfide Chemistry is Complicated



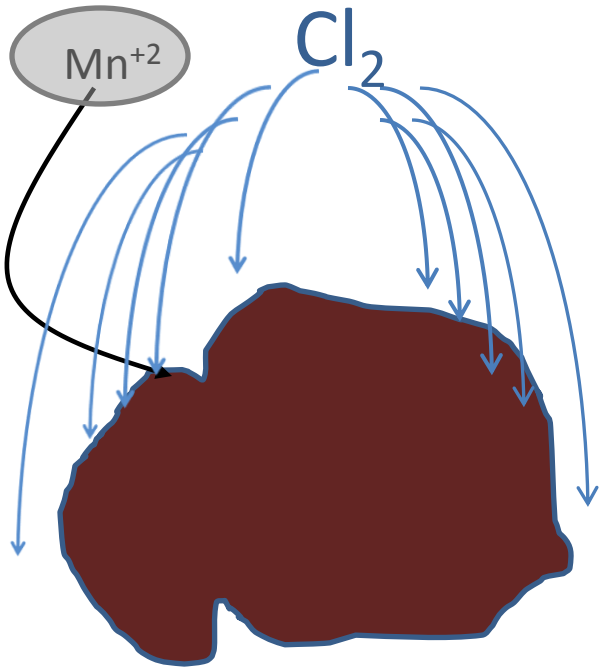
- An intermediate oxidation product
- Some peak between pH 7 and 8
- Others increase with pH
- Chemical analysis difficult to analyze
- Can be volatile

Iron and Manganese using a Sorbent Media

1. Sorbent Surface "Charged" with oxidant such as chlorine

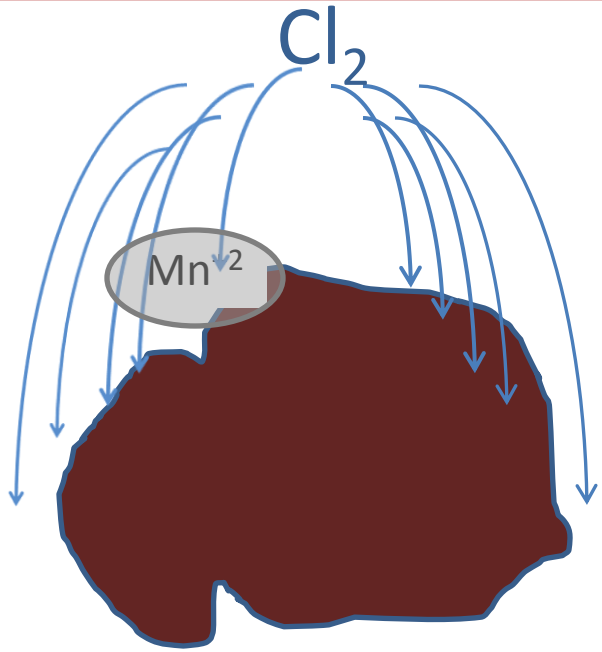


2. Dissolved Manganese is attracted to surface of sorbent

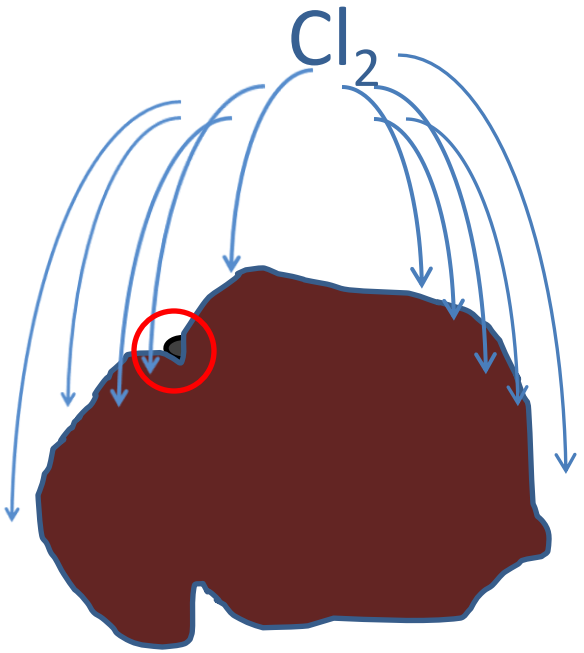


Iron and Manganese using a Sorbent Media

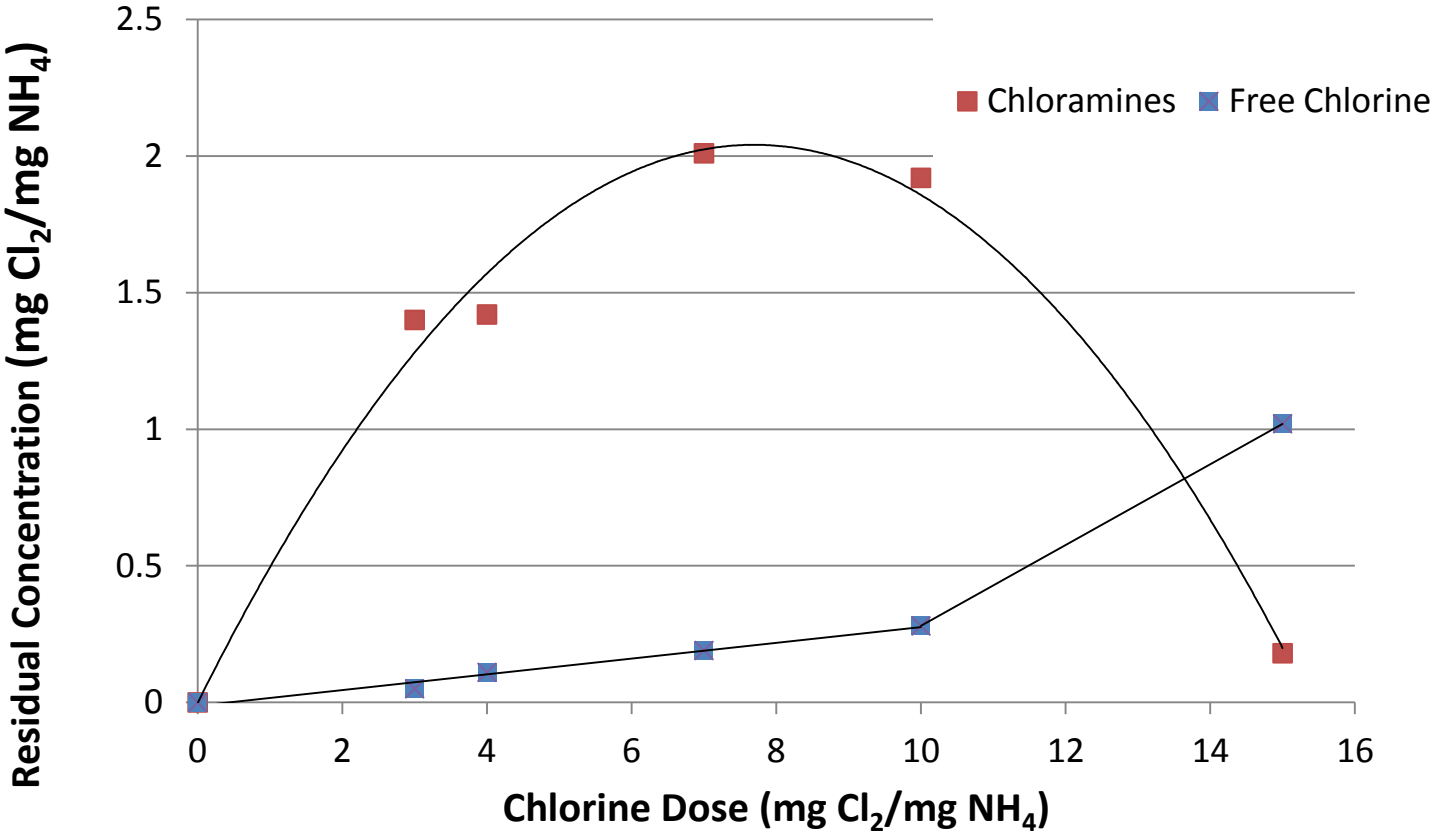
3. Dissolved Manganese is sorbs to surface of sorbent



4. Manganese oxidized - surface of sorbent acts as catalyst

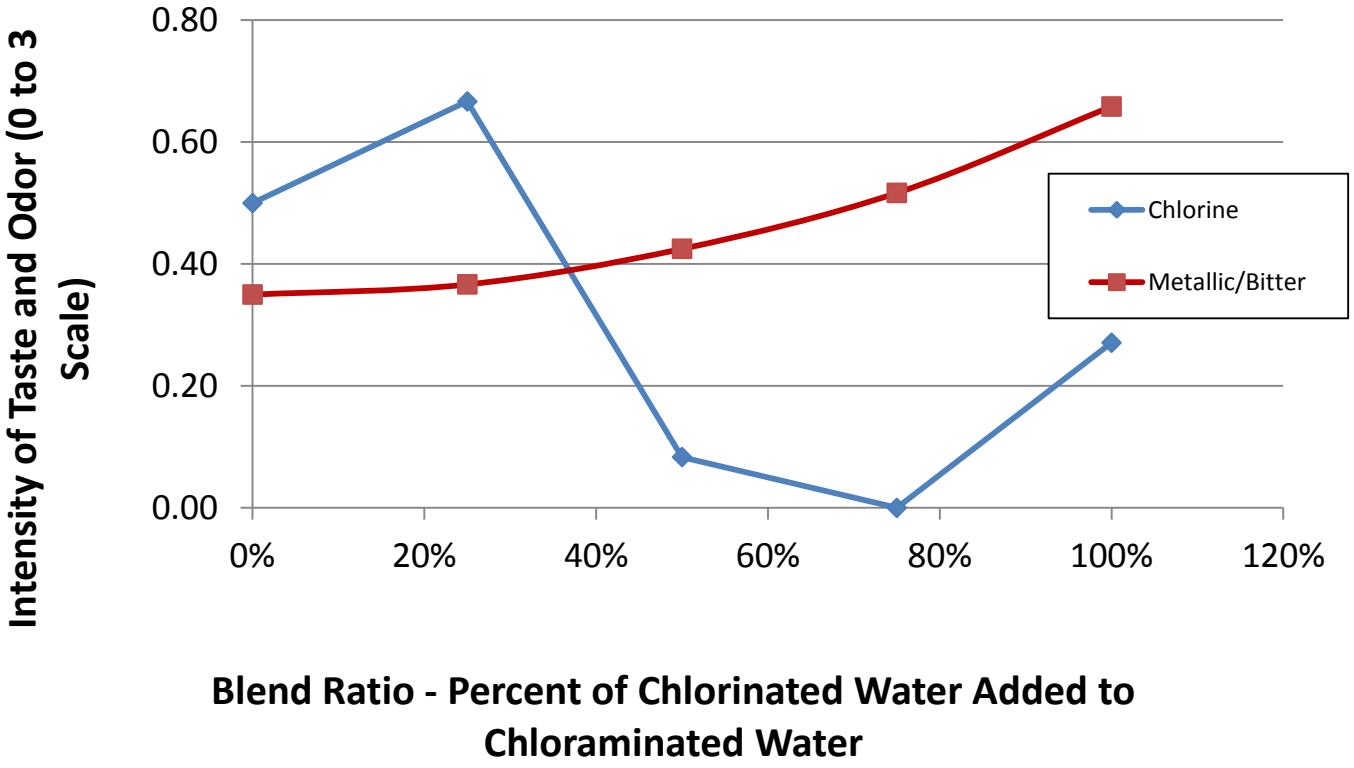


Meridian Chlorine Dose Response



0.73 mg/L NH_4

Impact of Blending Chlorine and Chloramines



Chlorine Ammonia Reactions