United States Environmental Protection Agency

Session 6: Iron and Manganese Control in Groundwater Systems

Asher Keithley
US EPA Office of Research and Development

EPA ORD-Region 4 Small Drinking Water Systems Meeting

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Fe and Mn in Drinking Water

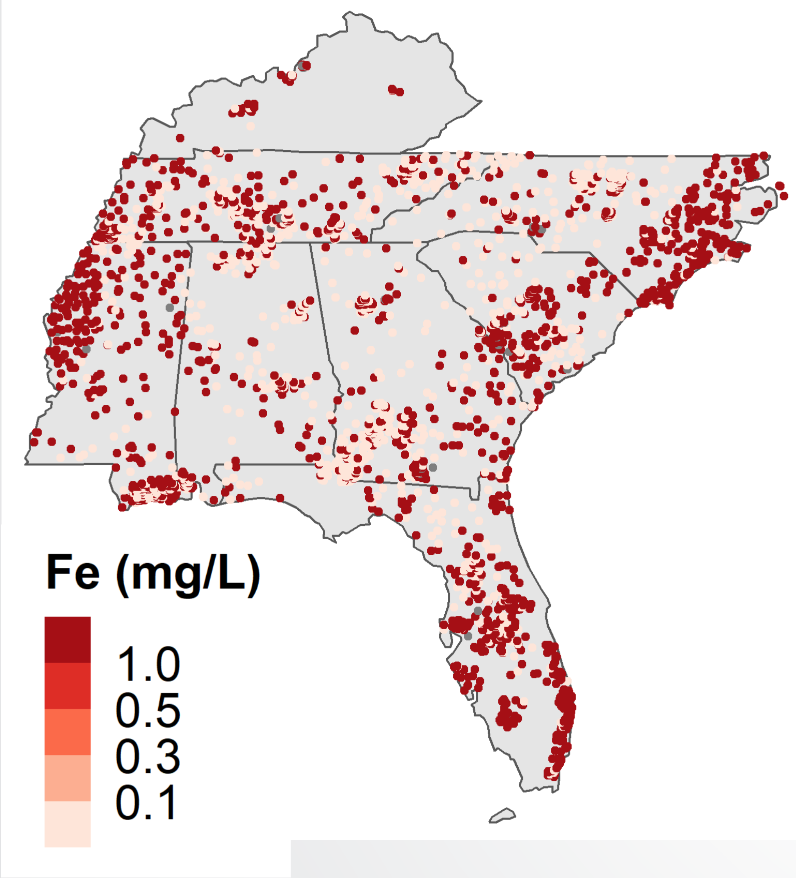
- Iron (Fe)
  - Secondary maximum contaminant level (SMCL) = 0.3 mg/L
  - Staining, red water, taste, accumulation in distribution system
- Manganese (Mn)
  - SMCL = 0.05 mg/L
    - Many systems target 0.01-0.02 mg/L
    - Staining, accumulation in distribution system
  - Health concerns
    - Neurotoxin
    - Lifetime Health Advisory Level (HAL) = 0.3 mg/L
    - Acute HAL = 1 mg/L
    - Health Canada – maximum allowable concentration = 0.12 mg/L
  - Included in Unregulated Contaminant Monitoring Rule (UCMR) 4

https://www.pbwatersoftening.com/5-harmful-effects-high-levels-iron-water/

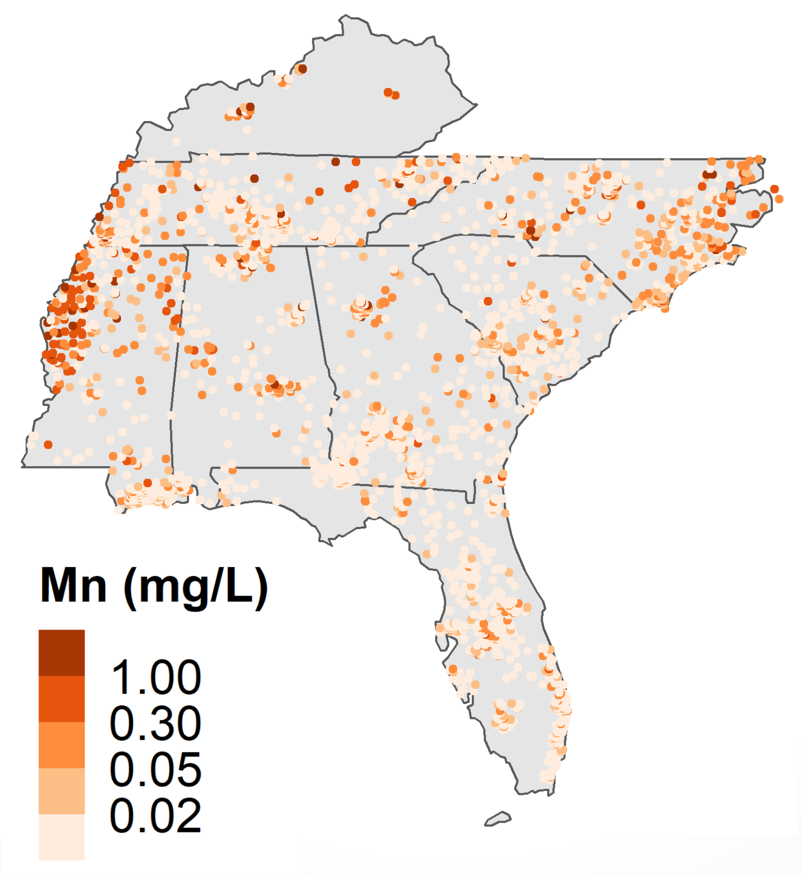
https://www.wachsws.com/using-unidirectional-flushing-programs-to-combat-tuberculation/

Occurrence in Groundwater

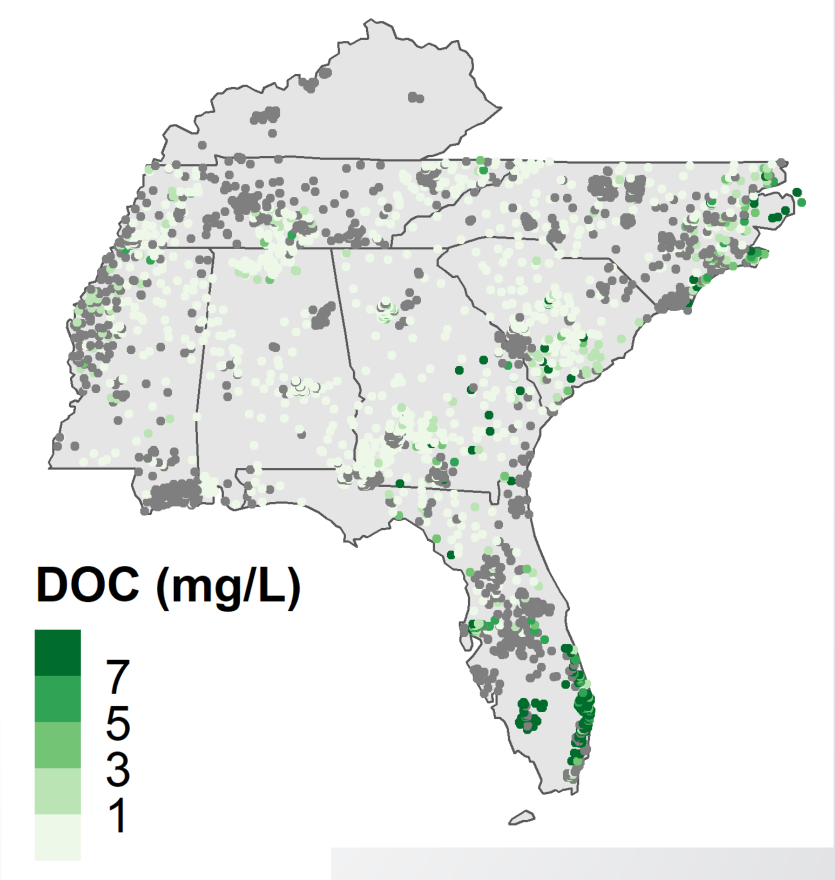
Iron



Manganese



Dissolved Organic Carbon



Data from USGS NWIS, McMahon et al. (2019)

Water Chemistry

- Mostly present in groundwater as Fe(II) (Fe^{2+}) and Mn(II) (Mn^{2+})
  - Soluble
- Oxidized forms Fe(III) (Fe^{3+}) and Mn(IV) (Mn^{4+}) are relatively insoluble (form a solid)
- Possible other reduced co-contaminants
  - Ammonia
  - Arsenic
  - Total organic carbon (TOC)

Sequestration does not remove Fe and Mn

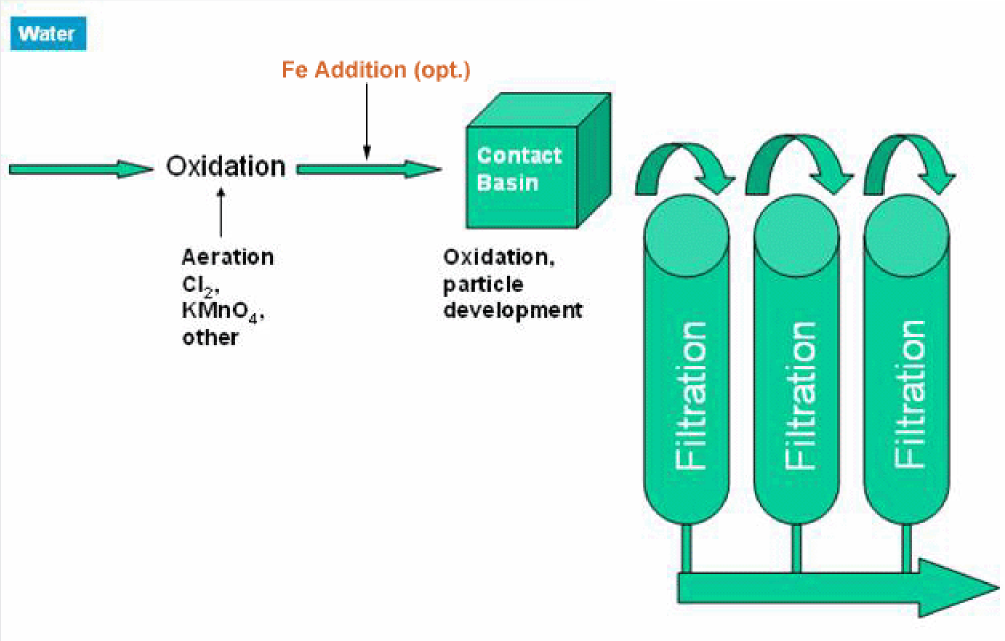
- Sequestration: add polyphosphate to disperse Fe^{3+} and Mn^{4+} colloidal particles
- Does not remove the Fe or Mn
  - Mn still poses a health concern
- Polyphosphates revert or breakdown over time
  - Reversion rate depends on chemical, water quality and temperature
  - Still get accumulation in the distribution system
  - Still get customer complaints
- Polyphosphate not recommended for corrosion control

Fe and Mn Treatment Techniques

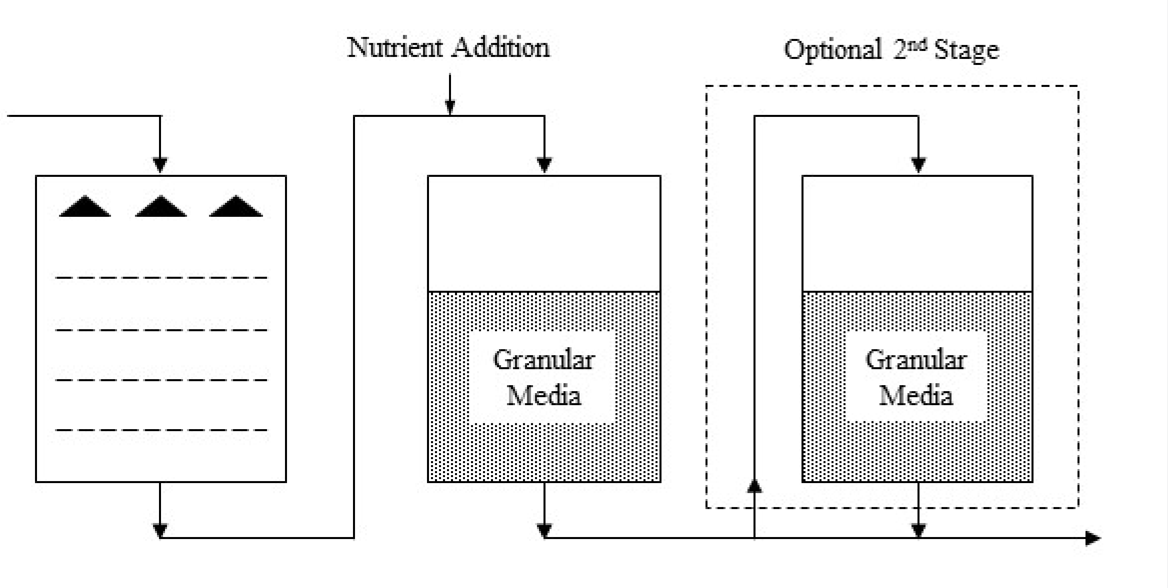
- Ion exchange
  - Maintain low Dissolved Oxygen (DO) and remove Fe^{2+} and Mn^{2+}
  - If bypass is used, some Fe and Mn would remain in the water
  - Generate waste brine
- Oxidation + physical separation
  - Chemical oxidation – Air, free chlorine (Cl_2), ozone (O_3), permanganate (MnO_4^-)
  - Biological oxidation – Bacteria naturally present in the groundwater can oxidize Fe and Mn
  - MnO_x – coated media can improve Mn removal
  - Generate residuals in backwash wastewater

Fe and Mn Treatment Schematics

Chemical Oxidation + Filtration



Biological Oxidation + Filtration



Fe and Mn Oxidant Comparison

Oxidant	Benefits	Drawbacks
Aeration	• Simple • Forms Fe particles that are easier to remove via filtration	• Not effective for Mn
Free Chlorine (Cl_2)	• Effective for Fe and Mn if filter media is coated with MnO_x	• Not effective if elevated NH_3 is present • Could form disinfection byproducts (DBPs) if TOC is elevated
Ozone (O_3)	• Rapid	• Forms colloidal Fe and Mn that are difficult to remove via filtration • Expensive
Permanganate (MnO_4^-)	• Effective for Fe and Mn even if NH_3 and TOC are elevated	• Overdosing problematic – pink water • Generate increased residuals
Biological	• Longer filter run times • Lower chemical cost • Can remove Fe, Mn and NH_3	• Mn-oxidizing bacteria have long acclimation time (3-6 months)

Process Selection Considerations

- Level of complexity and safety (strong chemical oxidants, backwash, etc.)
- Residual (e.g., backwash waste stream) disposal (acceptable route such as sanitary sewer)
- Water use restrictions (relatively frequent backwash necessary)
- Water chemistry
- Well understood process
- Operating costs
- Presence of co-occuring contaminants
- Potential unintended consequences

Case Studies

- Climax, MN
  - Cl_2 for Fe and Mn removal
  - Location also has arsenic (As)
- Waynesville, IL
  - MnO_4^- for Fe removal
  - Location also has As, NH_3, and TOC
- Gilbert, IA
  - Biological treatment for Fe and Mn removal
  - Location also has NH_3 and As

Climax, MN – Cl_2 and Filtration

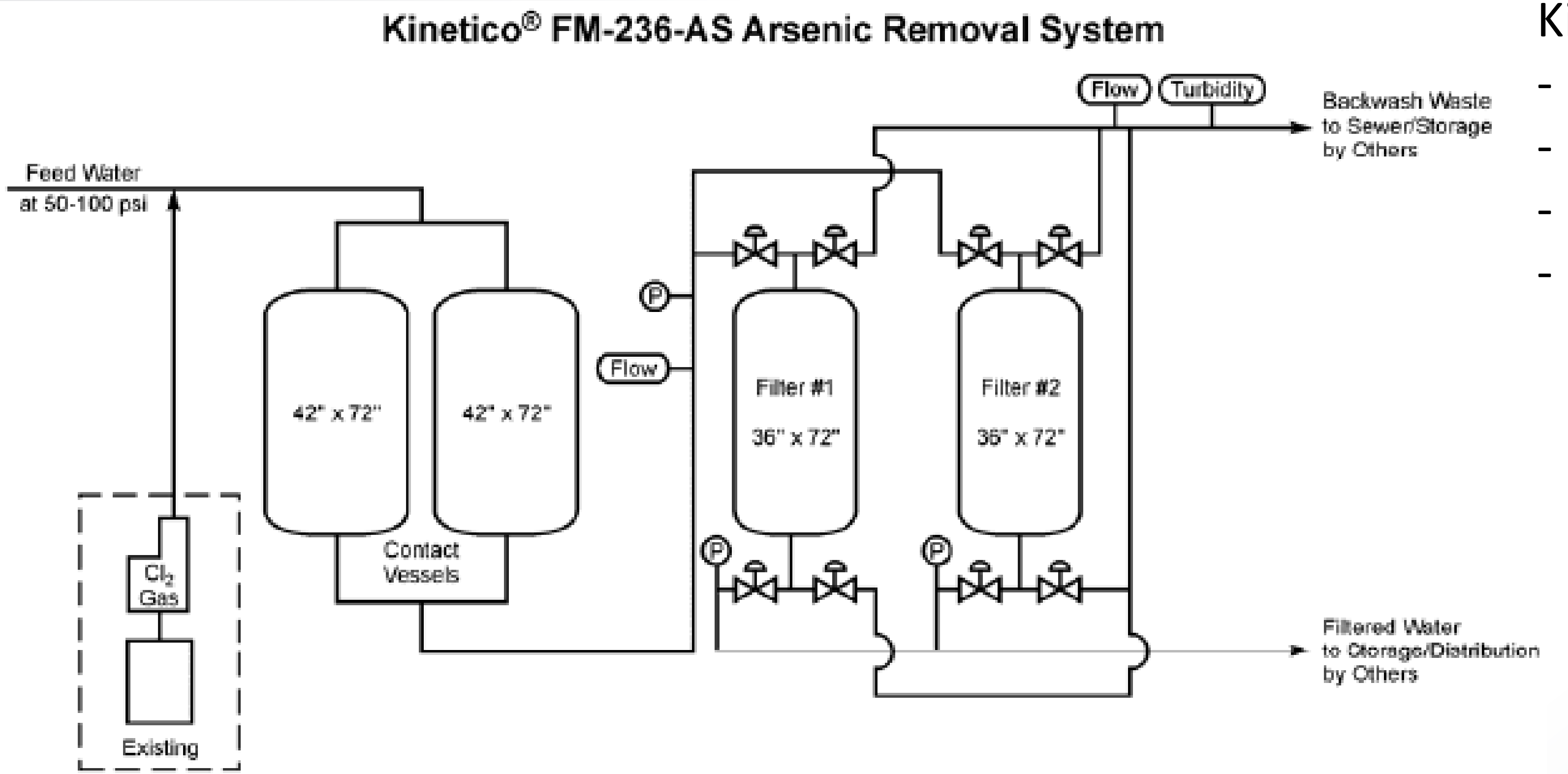
- Serves community of 264 people
- Supplied by 2 wells with combined capacity of 300 gallons per minute (gpm)

Raw Water Quality

Parameter	Unit	Concentration*
pH	--	7.5
Alkalinity	mg/L $CaCO_3$	319
Hardness	mg/L $CaCO_3$	270
Iron	mg/L	0.698
Manganese	mg/L	0.141
Arsenic	µg/L	37 [~95% as As(III)]
Chloride	mg/L	184
Sulfate	mg/L	114
Silica	mg/L	28

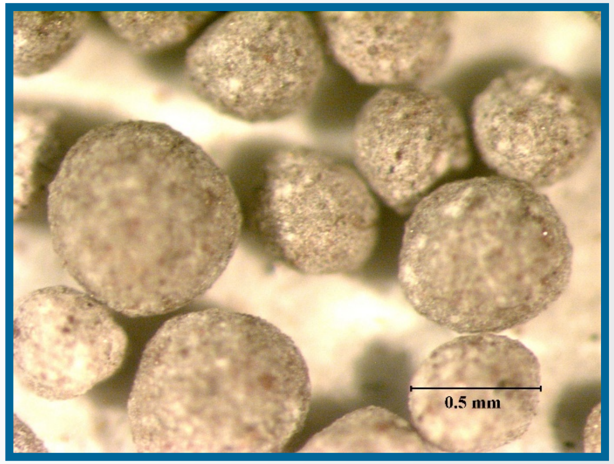
*Average concentration based on multiple samplings

Climax, MN – Treatment System



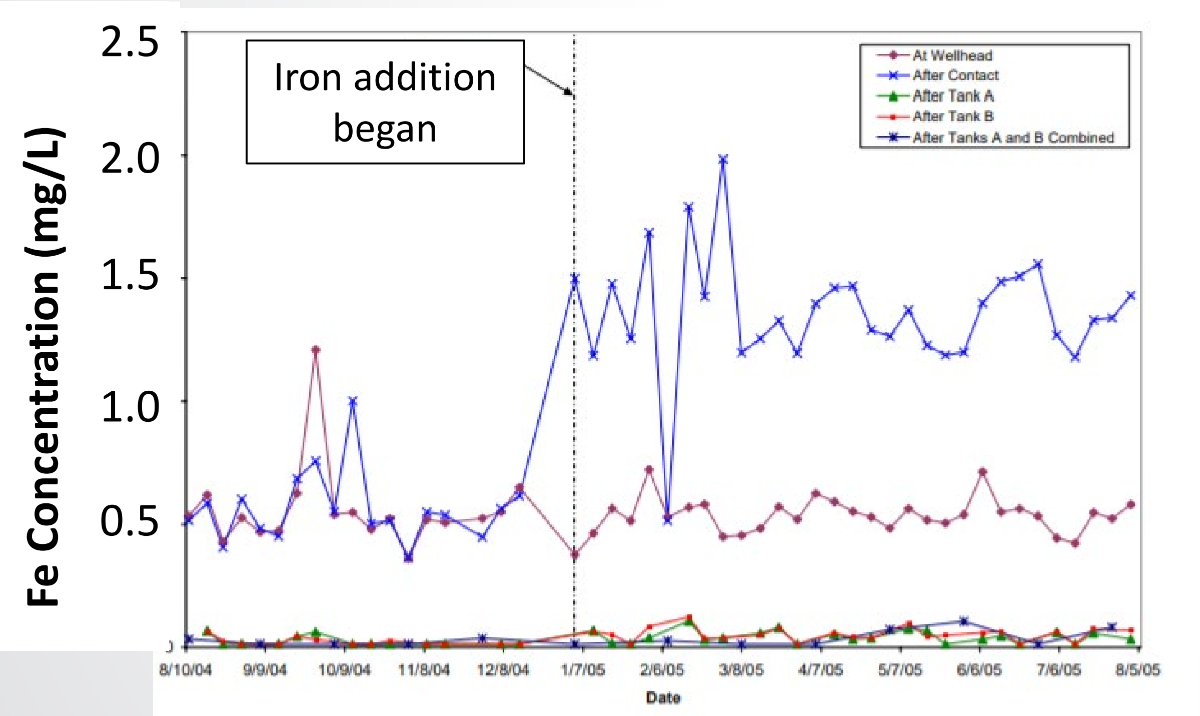
Kinetico® Mesh 40/60 Macrolite® Media

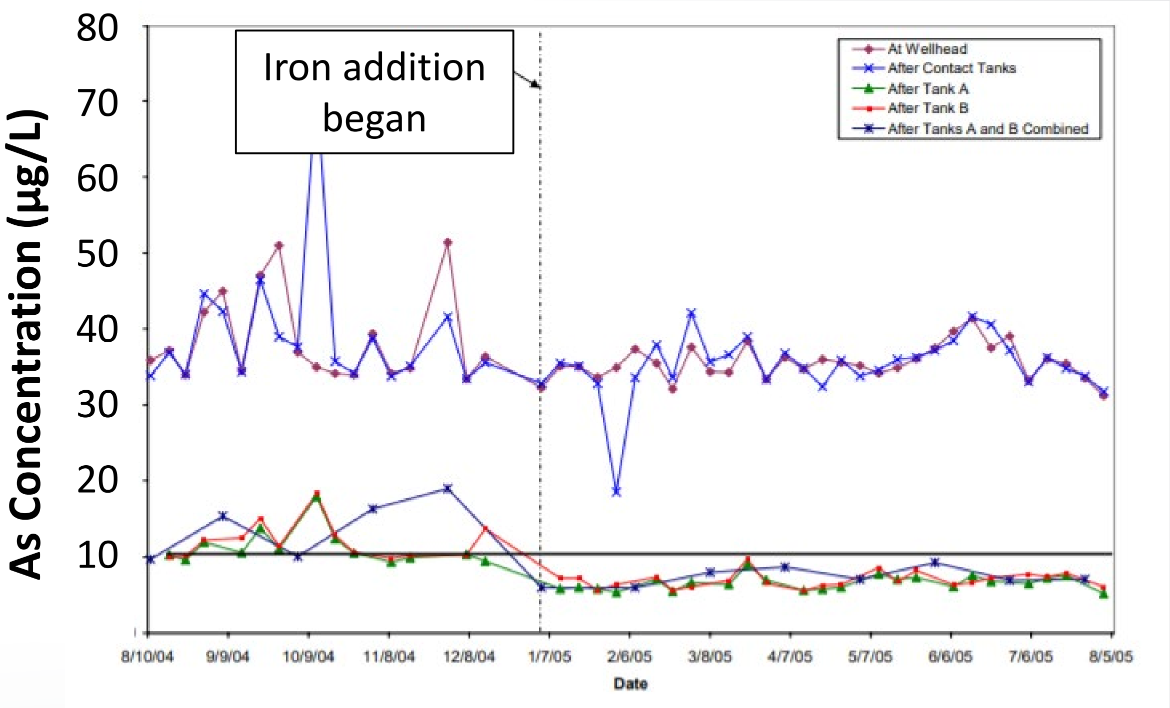
- Engineered ceramic filtration media
- Low density
- Spherical
- Up to 10 gpm/ft^2



Climax, MN – Fe and As removal

- Good Fe removal through the filters
- Supplement Fe to get better As removal
- Good As removal through the filters
- Effluent As concentration <10 µg/L (MCL) after Fe addition began





Climax, MN – Mn removal

- Mn removal not primary treatment objective
- Some Mn removal after chlorination in the contact tanks (~5 minutes)
- Macrolite® media not coated with $MnO_{x(s)}$
- Mn leaving the plant was still in soluble form
- Plant achieved some Mn removal, but still was above SMCL of 0.05 mg/L and optimized target of 0.02 mg/L

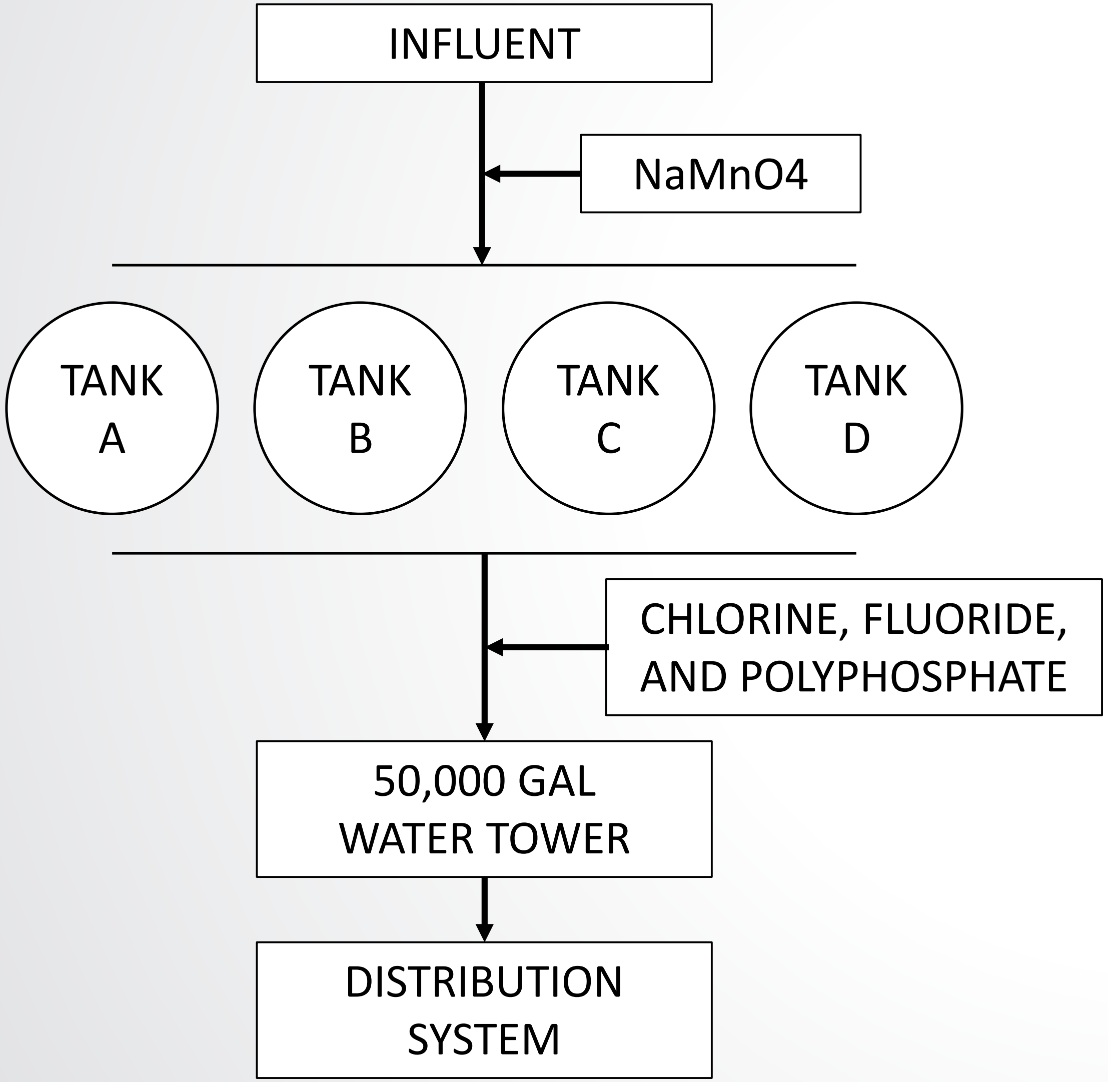
Location	Mn (mg/L)
Raw	0.112 - 0.218
After Contact Tanks	0.059 – 0.089
After Filters	0.055 – 0.092

Waynesville, IL – Background

- 452 residents
- Average daily demand = 29,000 gal
- 2 supply wells with combined capacity of 84 gpm
- Theoretical free chlorine dose = 30.6 mg/L
  - Very high
  - DBP concerns
- Selected $NaMnO_4$ as oxidant

Parameter	Units	Plant Influent Average (Range)
Arsenic	µg/L	33.1 (23.9 – 45.2)
Iron	mg/L	2.298 (1.939 – 2.720)
Manganese	mg/L	0.033 (0.021 – 0.108)
Ammonia	mg N/L	3.8 (3.4 – 4.2)
TOC	mg/L	7.9 (5.8 – 8.9)
pH	--	7.3 (6.9 – 8.0)
DO	mg/L	1.2 (0.6 – 2.5)
Alkalinity	mg/L as $CaCO_3$	599 (542 – 651)

Treatment Process



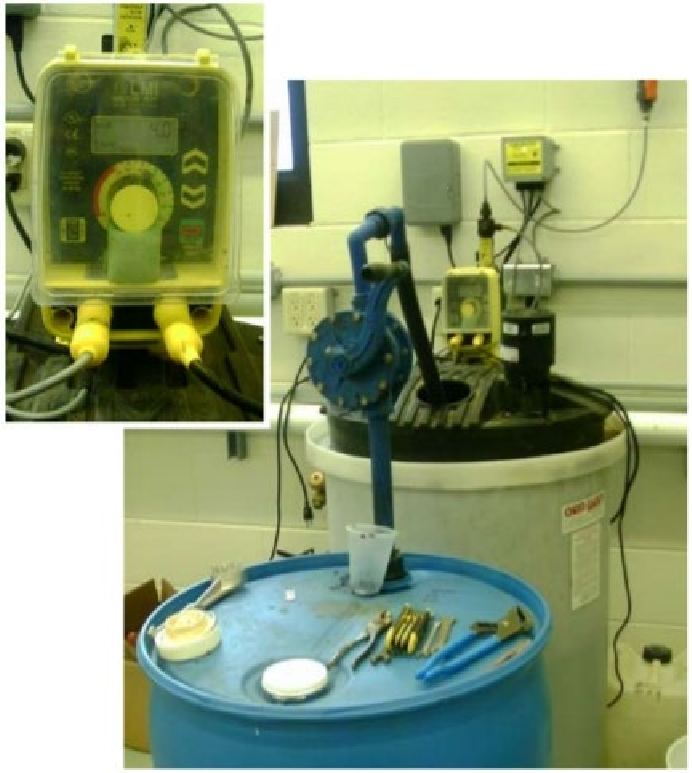
- Pressurized system to maintain low DO throughout
- (4) 3-ft diameter pressure vessels
    - 12 inches anthracite
    - 24 inches GreensandPlus™
- Design filtration rate 3.4 gpm/ft^2
- Backwash every 3 days
- Backwash wastewater discharged to sewer via (2) 2,000-gal tanks

Treatment Plant

Treatment Plant

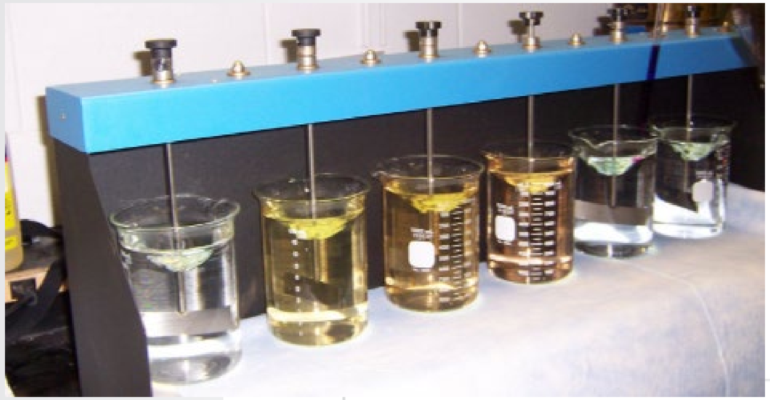
Operator onsite daily and spent ~20 min to perform visual inspections and record system operational parameters

$NaMnO_4$ Feed

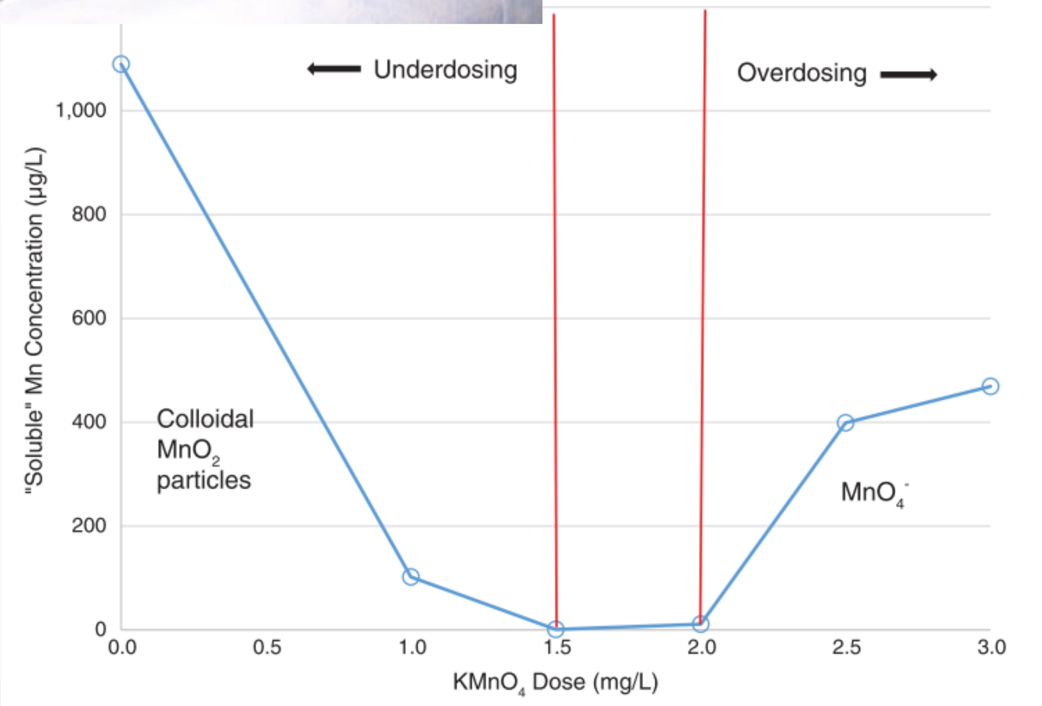


Pressure Vessels

MnO_4^- Dose Optimization



Jar tests performed at Sauk Centre, MN



- Underdosing
  - Incomplete oxidation
  - Form colloids
  - High Mn
- Overdosing
  - Pink water
  - High Mn
- Selected mass ratios
  - $KMnO_4$:Fe = 1.0 mg/mg
  - $KMnO_4$:Mn = 2.0 mg/mg
  - $KMnO_4$:As = 1.4 mg/mg
  - $KMnO_4$:TOC = 0.4 mg/mg

Finished Water Quality

Could improve Mn removal by:
1) Optimizing dose
2) Increasing contact time

Parameter	Units	Plant Influent Average (Range)	Filter Effluent Average (Range)	
Arsenic	µg/L	33.1 (23.9 – 45.2)	3.4 (2.5 – 4.6)	✓
Iron	mg/L	2.298 (1.939 – 2.720)	0.035 (<0.025 – 0.150)	✓
Manganese	mg/L	0.033 (0.021 – 0.108)	0.071 (0.038 – 0.119)	>50 µg/L SMCL
Ammonia	mg N/L	3.8 (3.4 – 4.2)	3.7 (3.5 – 4.0)	Unchanged
TOC	mg/L	7.9 (5.8 – 8.9)	7.4 (6.7 – 7.9)	Unchanged TTHM <4 µg/L. HAA5 <6 µg/L
pH	--	7.3 (6.9 – 8.0)	7.6 (6.7 – 8.2)	
DO	mg/L	1.2 (0.6 – 2.5)	0.9 (0.6 – 2.1)	Limits nitrification potential

Gilbert, IA – Biological Treatment

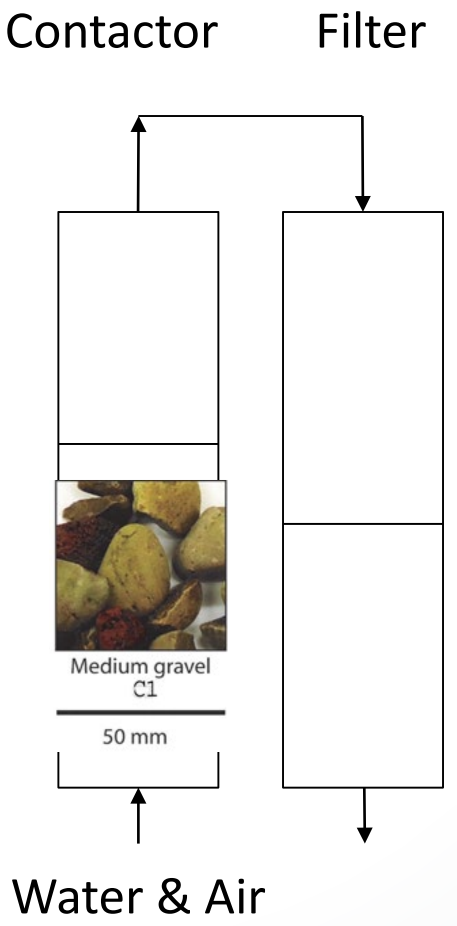
Parameter	Raw Water
Temperature	13.3 ^oC
pH	7.63
Alkalinity	410 mg $CaCO_3$/L
Hardness	280 mg $CaCO_3$/L
As	**23 µg/L**
Fe	**2.91 mg/L**
Mn	**0.08 mg/L**
NH_4	**2.91 mg N/L**
NO_2	0.01 mg N/L
NO_3	0.02 mg N/L
TOC	2.68 mg/L
DO	1.1 mg/L

- Population ~1,100
- High NH_3 can result in nitrification in the distribution system and NO_2 >1 mg N/L
- Pilot study leading to full-scale construction

https://cityofgilbertiowa.org/151/Water-Department

Pilot Reactor

- Contactor and filter are biologically active
  - Contactor is continuously aerated
  - Filter removes particles
- Nitrification requires 4.5 mg O_2/mg NH_3-N
- Fe oxidized by air and bacteria
- Bacteria oxidize As(III) → As(V), which then sorbs with Fe oxides
- Bacteria oxidize Mn



7 hours/day, 7 days/week

Contactor

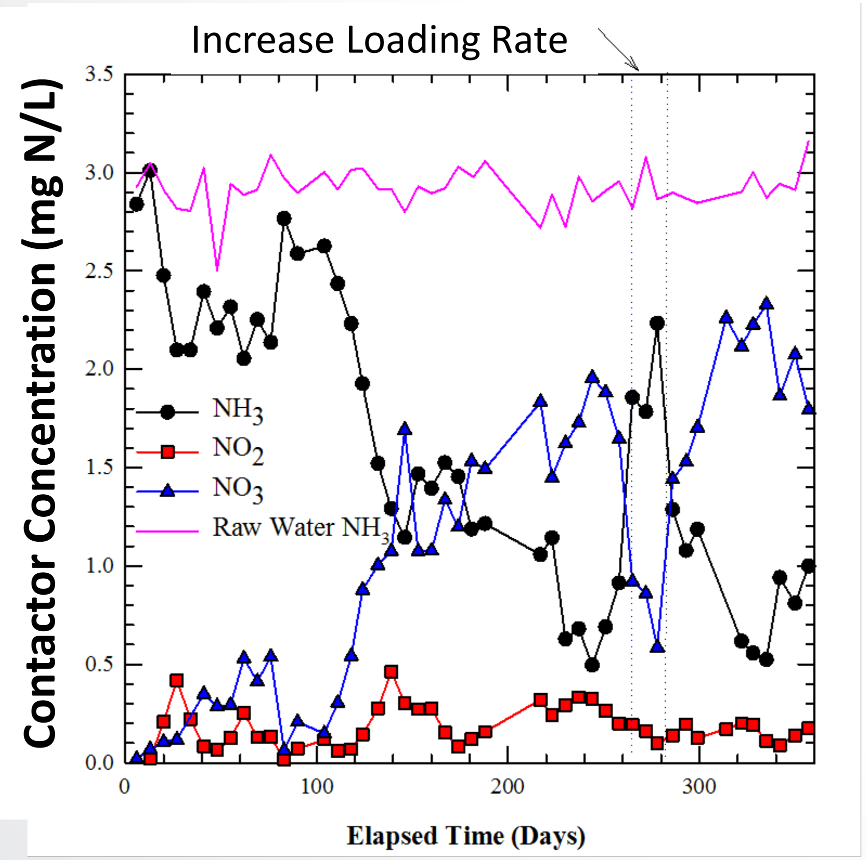
- 0.5 inch gravel
- Bed depth: 55 inches
- Air flow: 2.5 L/min
- Loading rate: 2.2 gpm/ft^2
- Backwash monthly

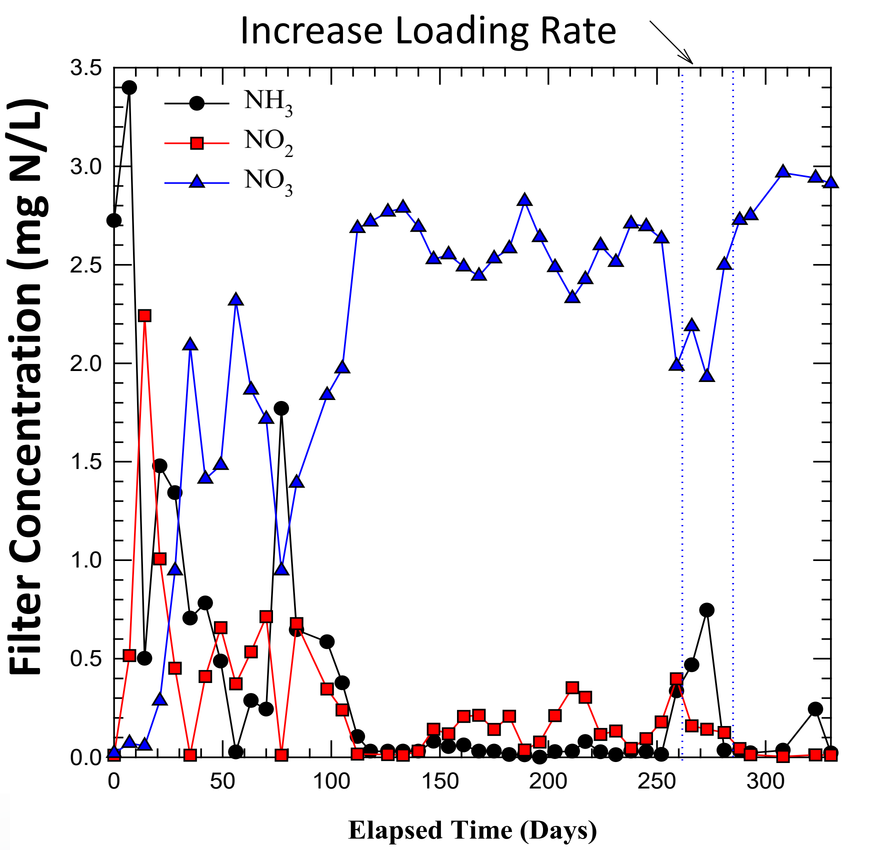
Filter

- Bed depth: 10 inches anthracite, 30 inches Mn-oxide coated sand
- Backwash every 24 h of operation

Complete Nitrification

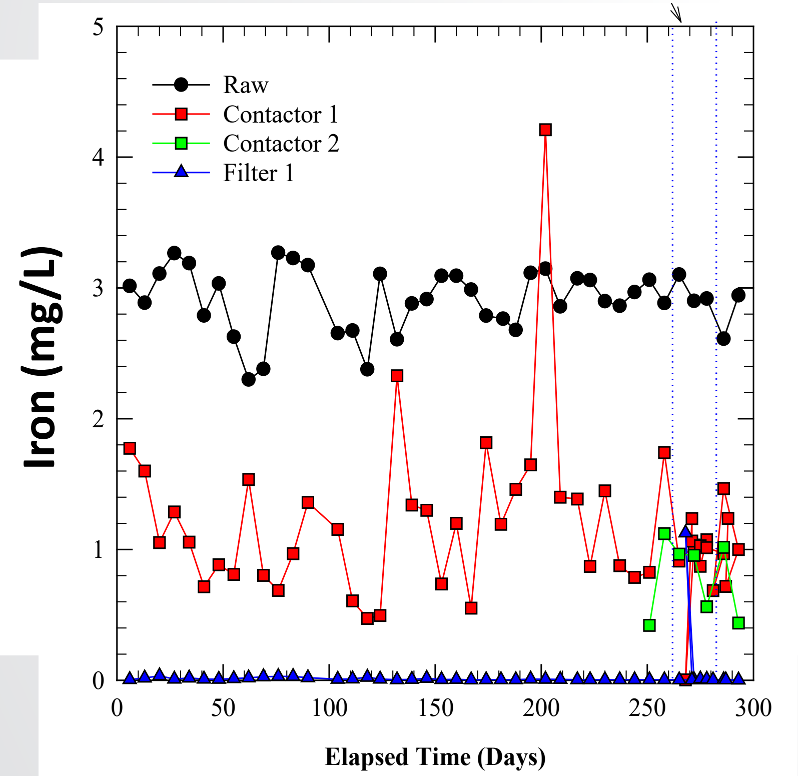
- Convert ~70% of NH_3 to NO_3 in the aerated contactor
- Polishing filter achieves finished water NH_3 <0.1 mg N/L
- Filter effluent NO_2 << MCL

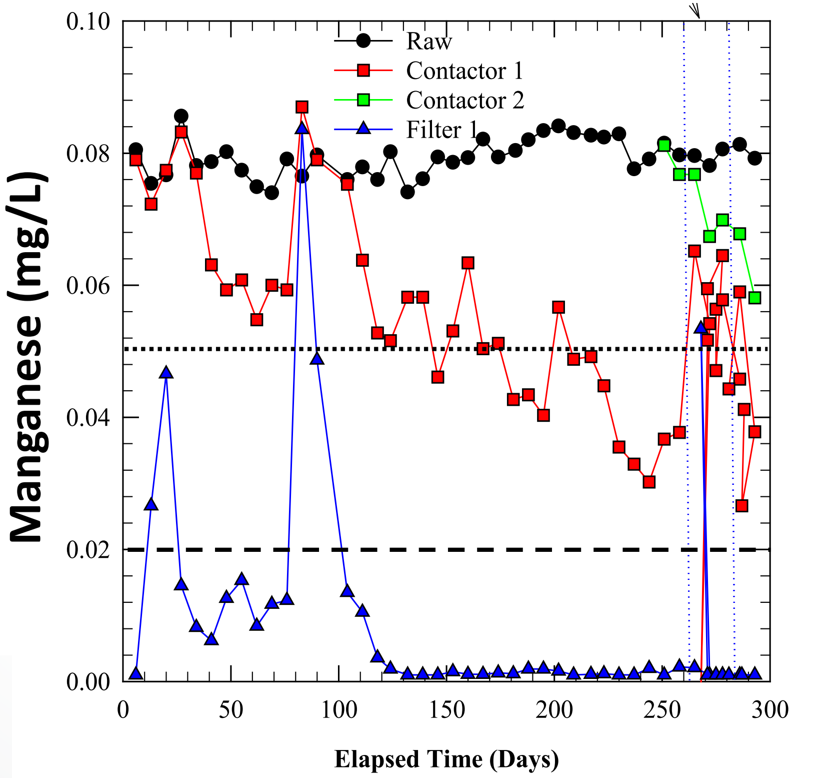


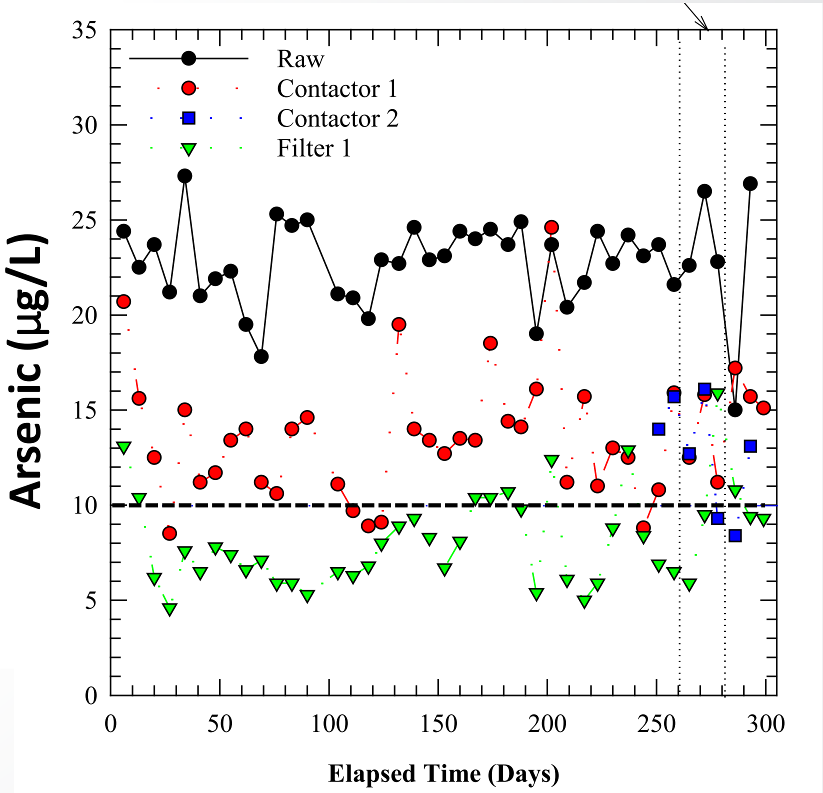


Good Fe, Mn, and As removal

- >50% removal of Fe, Mn, and As occurred in the contactor
- Filter effluent contained Fe < SMCL, Mn < target, and As < MCL







Summary

- Good to remove Fe and Mn at the treatment plant
- Sequestration is ineffective and does not protect human health when elevated Mn is present
- Chemical oxidation with Cl_2 or MnO_4^- effective for Fe and As removal
- Cl_2 + MnO_x-coated media effective for Mn removal
- Biological treatment can effectively remove Fe and Mn, as well as other co-occurring contaminants
- Choice of treatment technique driven by overall water quality

Contact

Asher Keithley, PhD
Postdoctoral Researcher
Drinking Water Management Branch
Center for Environmental Solutions and Emergency Response
US EPA Office of Research and Development
Keithley.Asher@epa.gov
513-569-7269

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Darren Lytle, PhD, PE, US EPA ORD
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