Manganese Treatment and Distribution System Management

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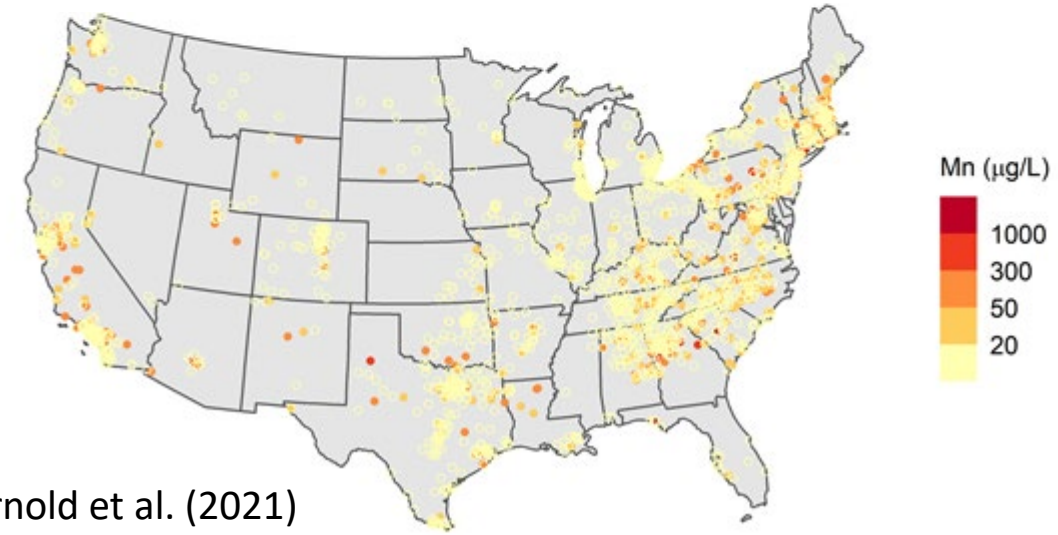
U.S. EPA, Office of Research and Development

Mn Occurrence and Regulatory Status

Groundwater

Surface Water

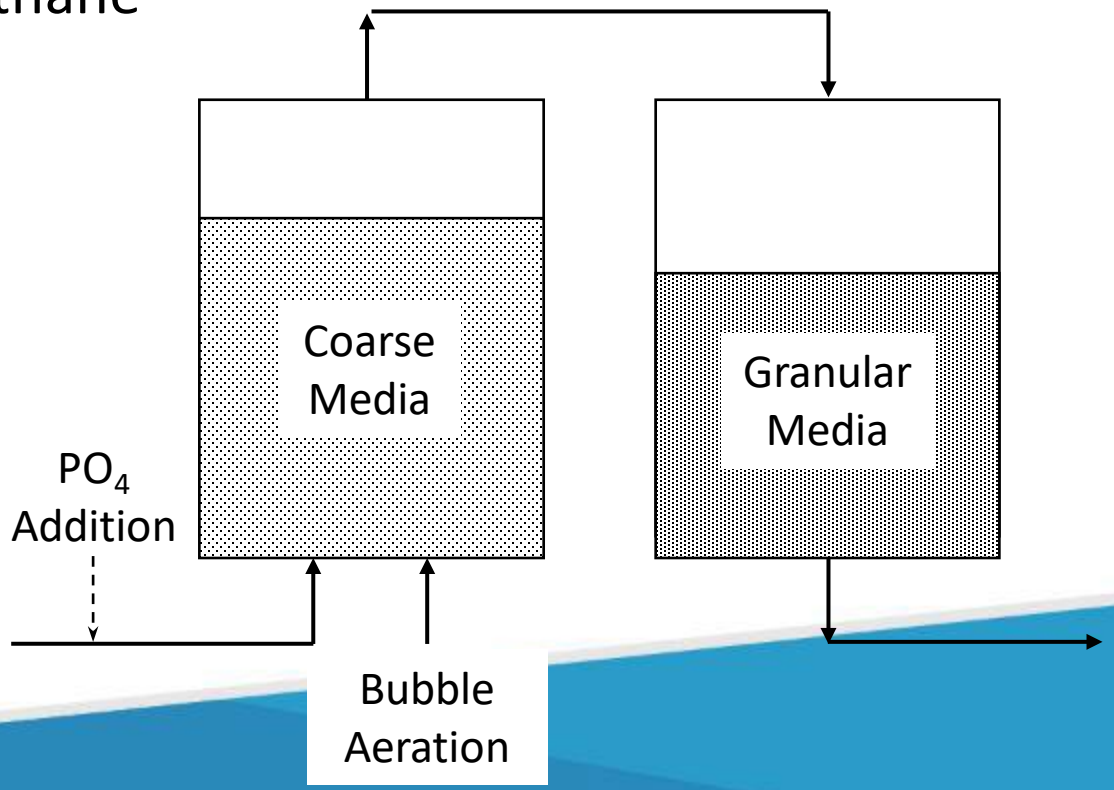


Arnold et al. (2021)

- Included in Unregulated Contaminant Monitoring Rule (UCMR) 4
  - Maps show maximum entry point concentration from UCMR 4 (2017-2021)
- Included on Contaminant Candidate List (CCL) 5
- Health Advisory Levels (HALs)
  - 0.3 mg/L for lifetime and infant acute
  - 1 mg/L for acute
- Secondary Maximum Contaminant Level (SMCL) = 0.05 mg/L

Biological Treatment of Groundwaters

- Reducing conditions (low dissolved oxygen) with multiple contaminants
  - Ammonia, iron, arsenic, manganese, methane
- Aerated contactor + filter bioreactor
  - Continuous air sparging satisfies O_2 demand for nitrification ~ 4.6 mg O_2/ mg NH_3-N
  - Most oxidation occurs in contactor
  - Filter provides particle removal and additional oxidation

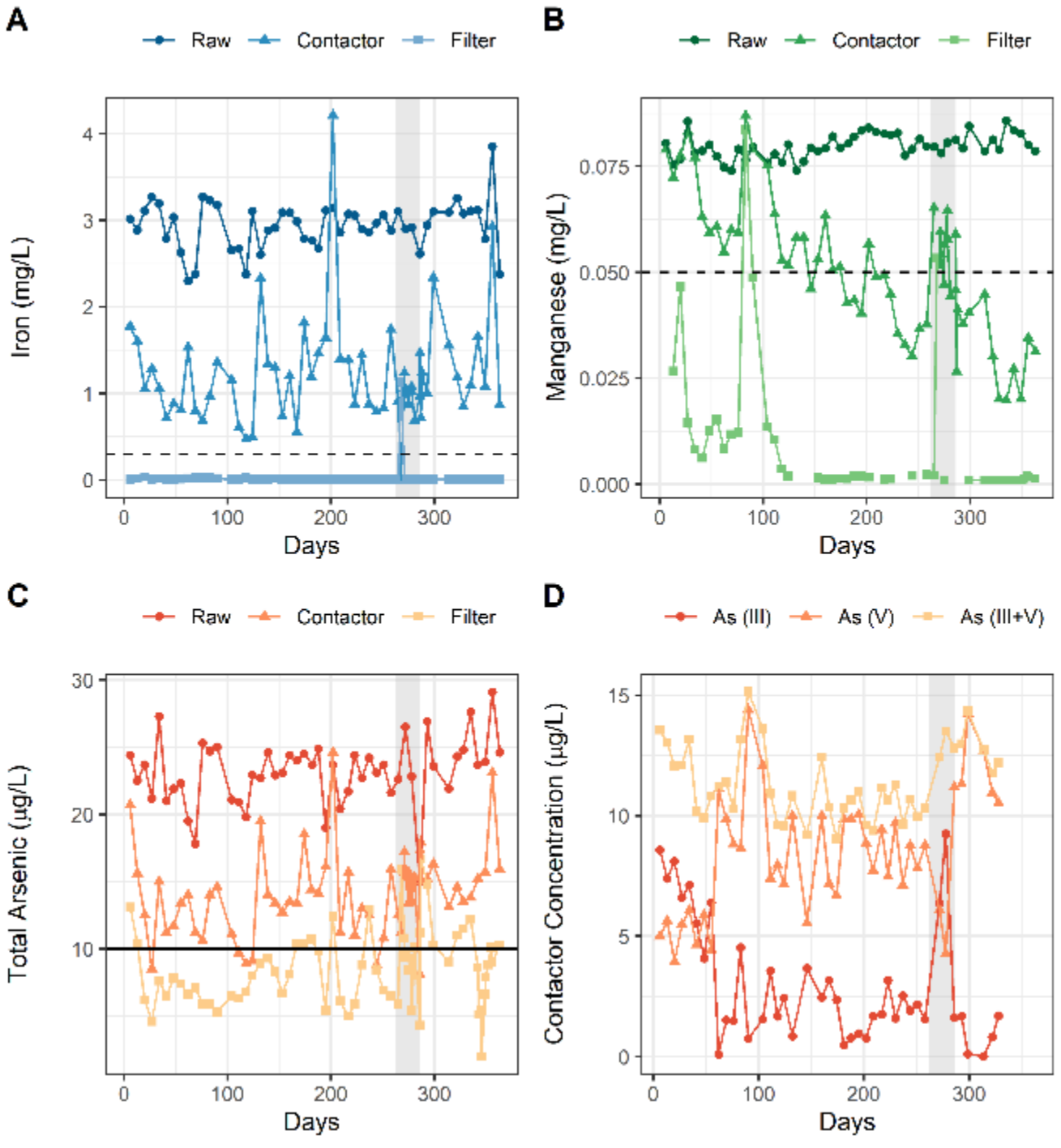


Pilot- and Full-Scale
Small System in Iowa

- Pilot study August 2016 – July 2017

Parameter	Well
Arsenic	27 µg/L
Iron	4.25 mg/L
Manganese	0.16 mg/L
Ammonia	3.0 mg N/L
TOC	3.0 mg/L
pH	7.55
Hardness	332 mg/L $CaCO_3$
Alkalinity	410 mg/L $CaCO_3$

Lytle et al. (2020)



Pilot- and Full-Scale Treatment at a Small System in Iowa

Full Scale Design

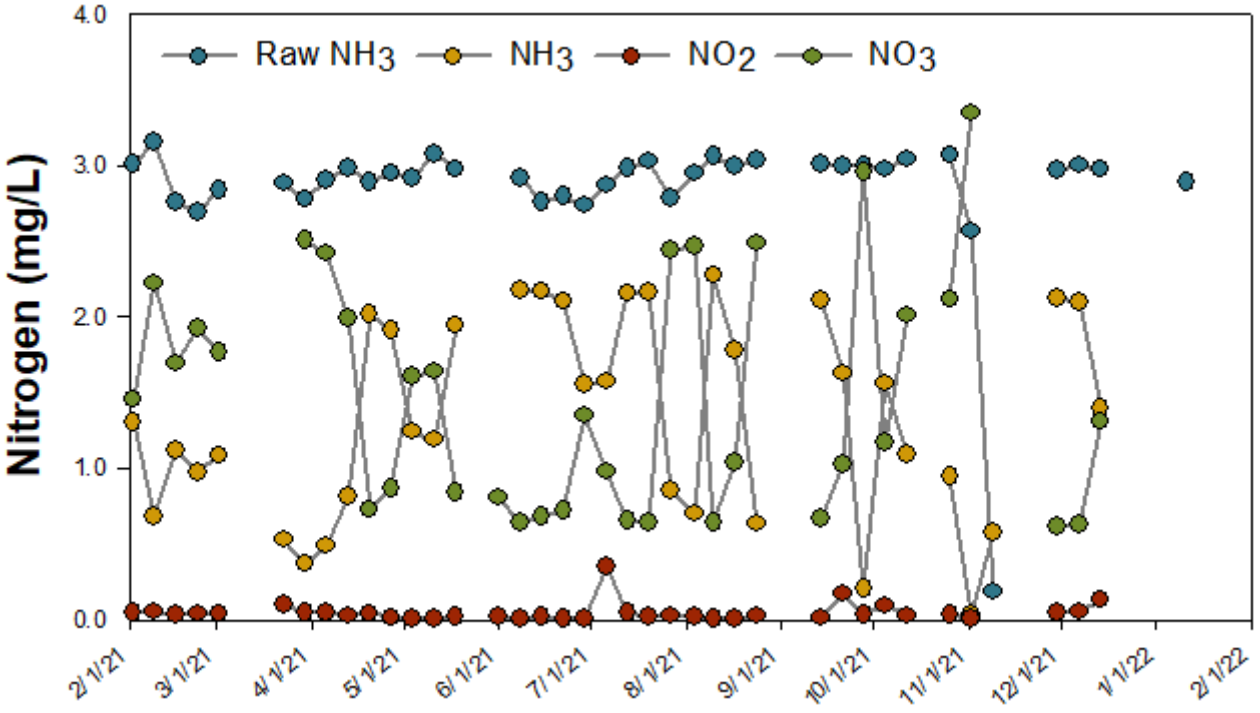
Parameter	Units	Value
Plant capacity	gpm	400
Average day flow	gpm	180
Number of contactors	--	2
Contactor diameter	ft	11
Contactor bed depth	ft	4.58
Contactor media type	--	Gravel
Contactor avg loading rate	gpm/ft^2	0.95
Contactor avg EBCT	min	36
Number of filters	--	4
Filter media type	--	Anthracite/ Sand

Start Up Schedule

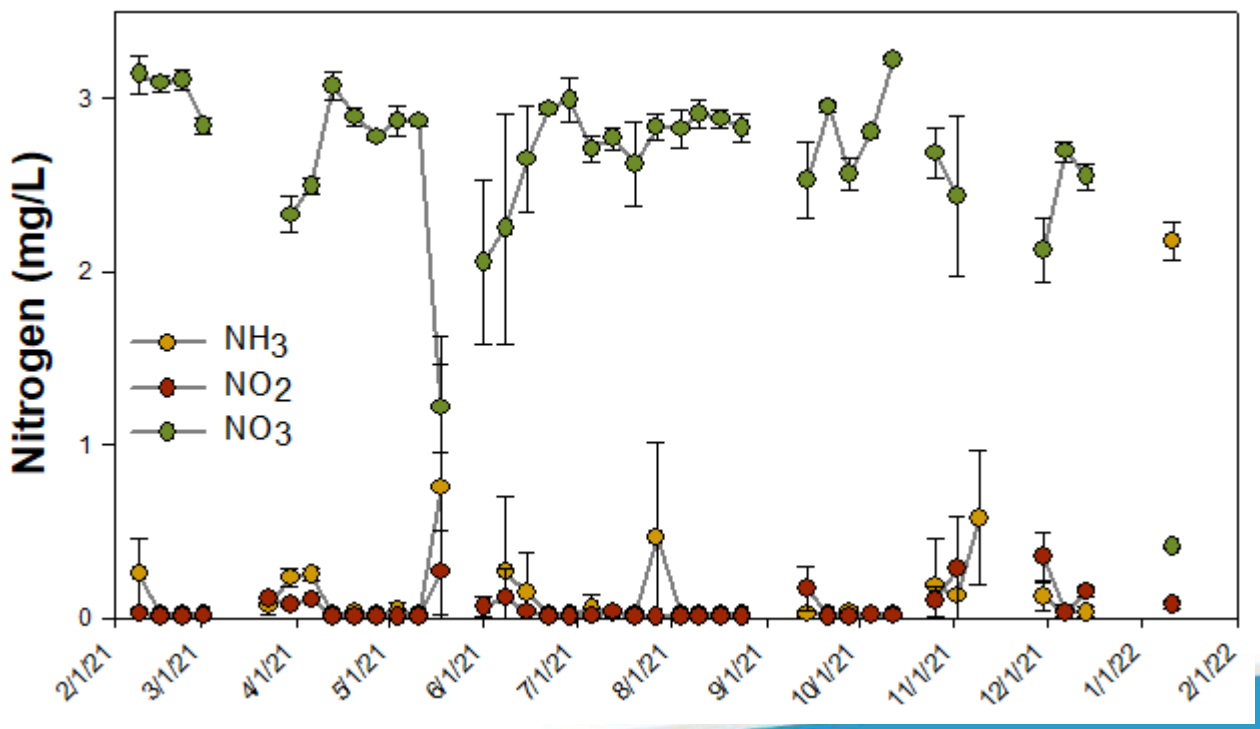
Date	Notes
November 2020	Started flow through contactors
February 2021	EPA-ORD sampling program started
February 2021	Started flow through filters
April 2021	Decreased PO_4 feed to improve arsenic removal
July 2021	Online and operating at full capacity
January 2022	EPA-ORD sampling program ended

Pilot- and Full-Scale Treatment at a Small System in Iowa

Incomplete nitrification in contactors

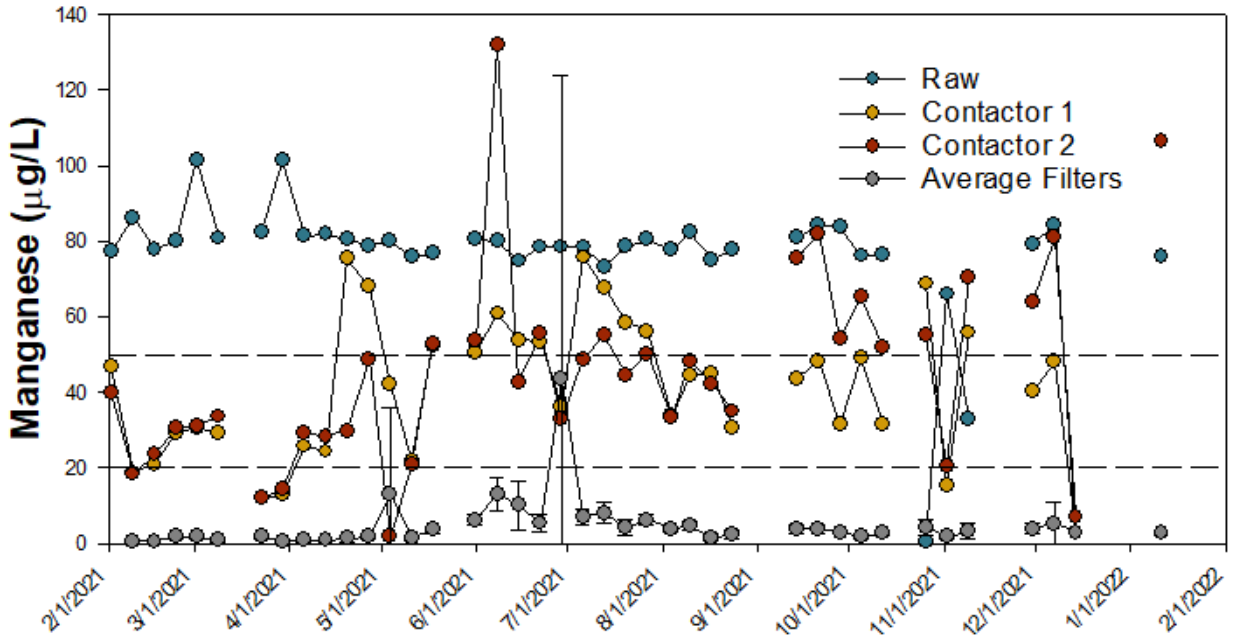


Typically complete nitrification in filters

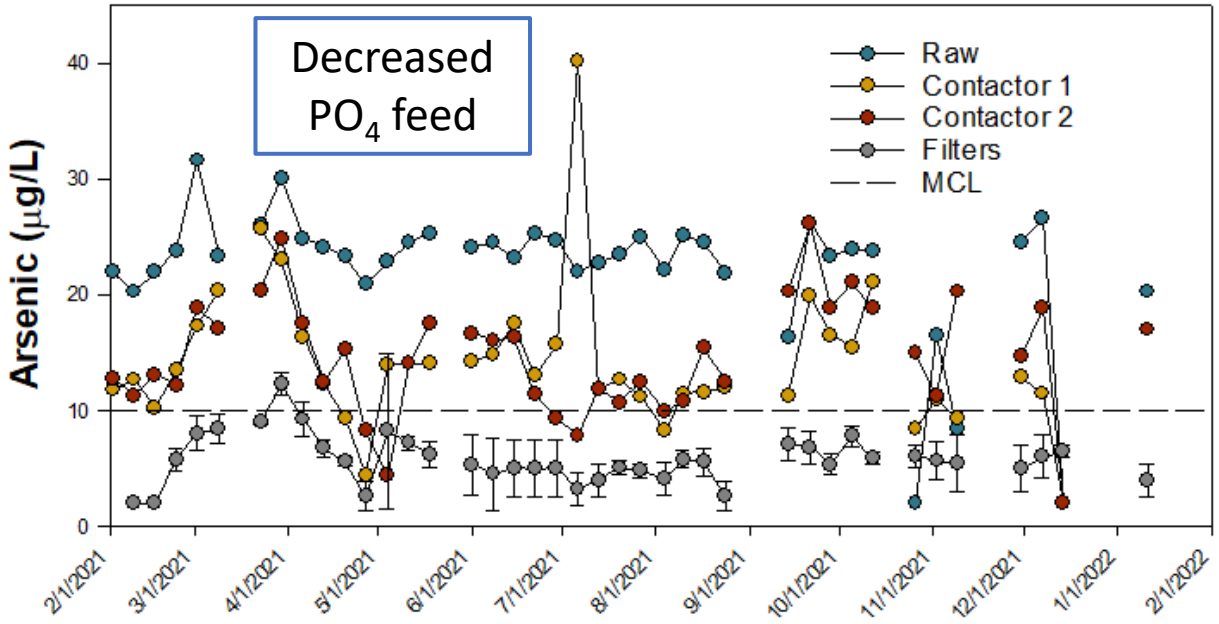


Pilot- and Full-Scale Treatment at a Small System in Iowa

Avg filter effluent Mn = 5 µg/L



Avg filter effluent As = 5.8 µg/L



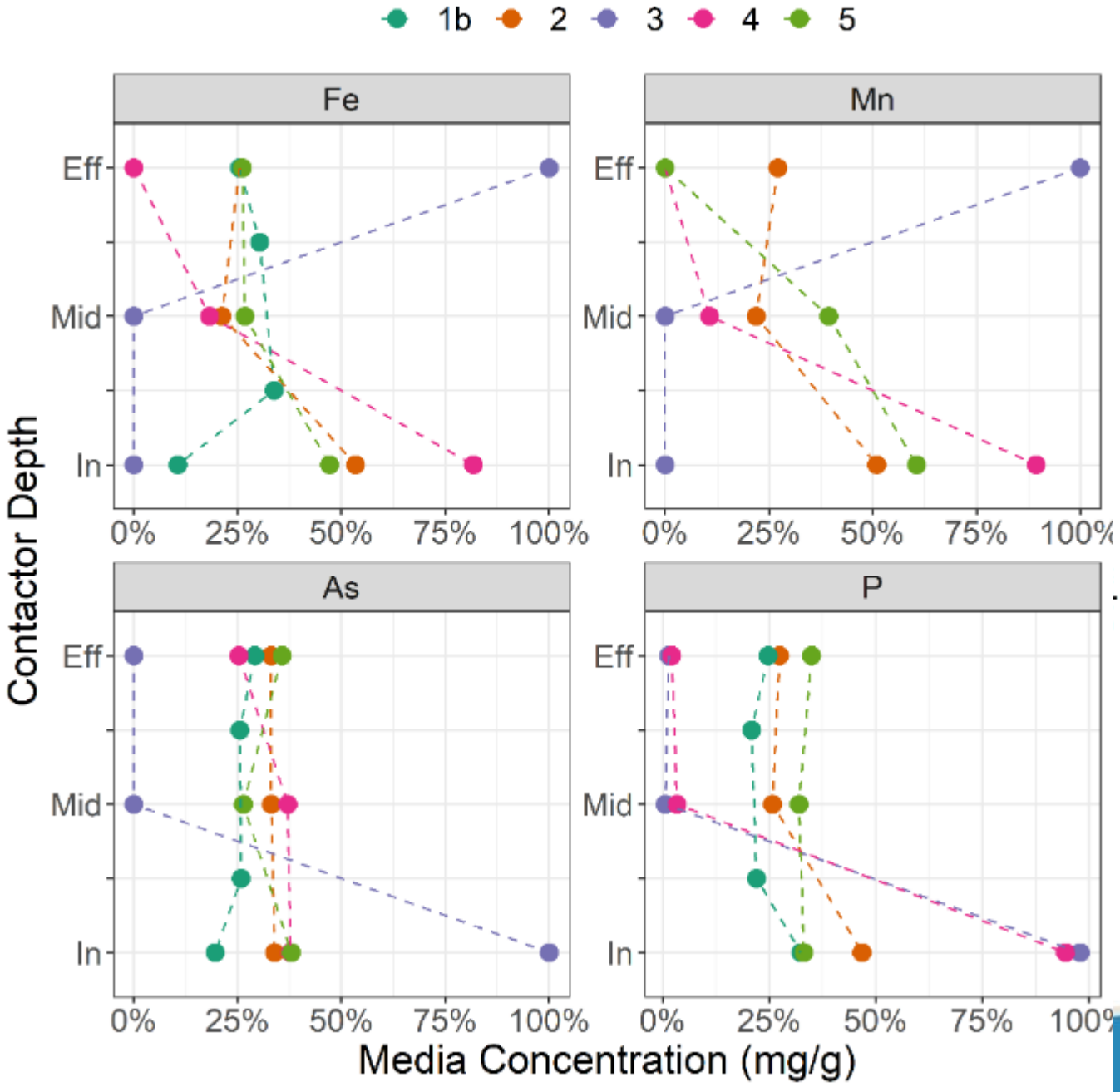
Key takeaway: Aerated contactor + filter biotreatment system effectively treated arsenic, iron, manganese, and ammonia

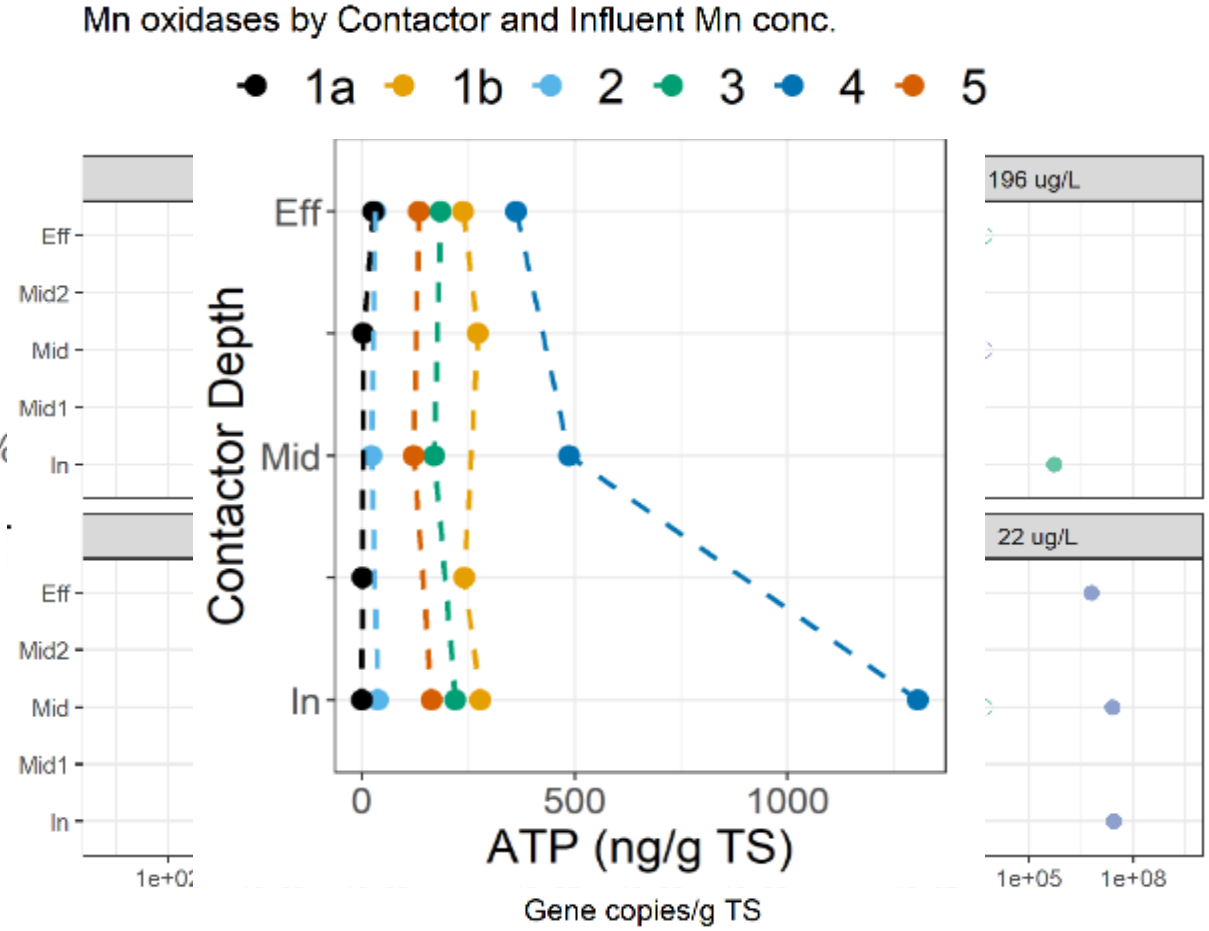
Mn Removal within Aerated Contactor

- Where does Mn removal occur within aerated contactors?
  - Different mixing and DO profiles than filters
- What is the relationship between media surface Mn and Mn oxidases concentrations?
- Collected media samples at influent end, middle, and effluent end of 6 pilot-scale aerated contactors

Parameter	Range
NH_3	2.3 - 3.4 mg N/L
Fe	0.1 - 3.95 mg/L
Mn	2 - 196 µg/L
As	< 4 - 23 µg/L
TOC	0.1 - 7.1 mg/L
pH	6.5 - 7.9
Hardness	215 - 374 mg/L $CaCO_3$

Parameter	Range
Media Type	Ceramic, GAC, Gravel
Loading Rate	3.1-7.3 m/h
EBCT	9-25 min
Air:Water Ratio	6-11 L/min:L/min


1b
2
3
4
5
Fe
Mn
As
P
Eff
Mid
In
0%
25%
50%
75%
100%
Contactor Depth
Media Concentration (mg/g)

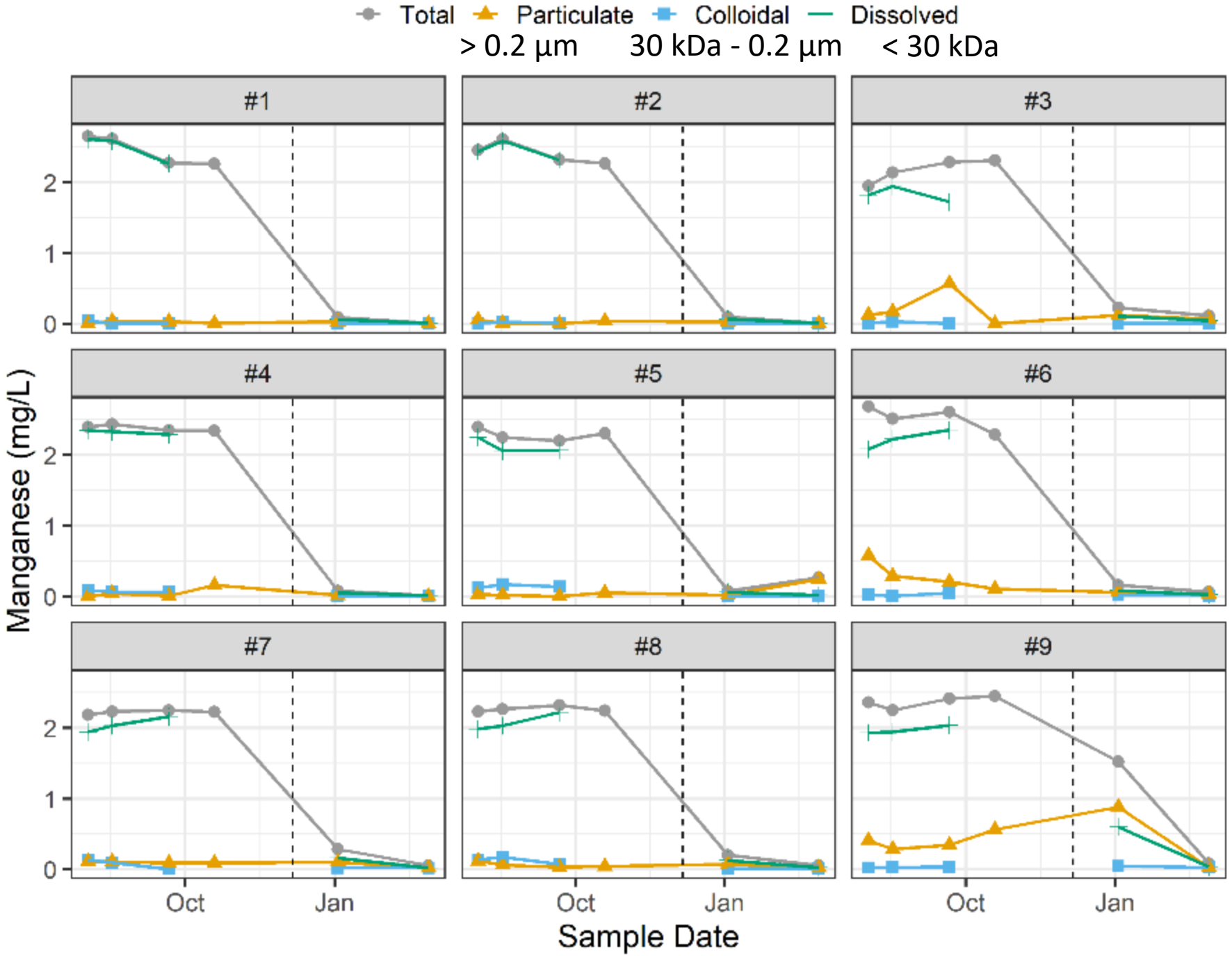

Mn oxidases by Contactor and Influent Mn conc.
1a
1b
2
3
4
5
Eff
Mid2
Mid
Mid1
In
1e+02
196 ug/L
22 ug/L
1e+05
1e+08
Contactor Depth
0
500
1000
ATP (ng/g TS)
Gene copies/g TS

Distribution System Mn after Switching Sources

- System had been operating with Mn > 2 mg/L for decades
- Recently switched sources to a source with low Mn
  - Otherwise similar water quality
- Chloramines for disinfectant residual
- Dose blended PO_4. Plan to slowly convert to ortho-PO_4 after system acclimates to new source
- Monthly sampling at entry point + 9 sites in the distribution system
  - 4 events before the switch
  - 3 events since the switch

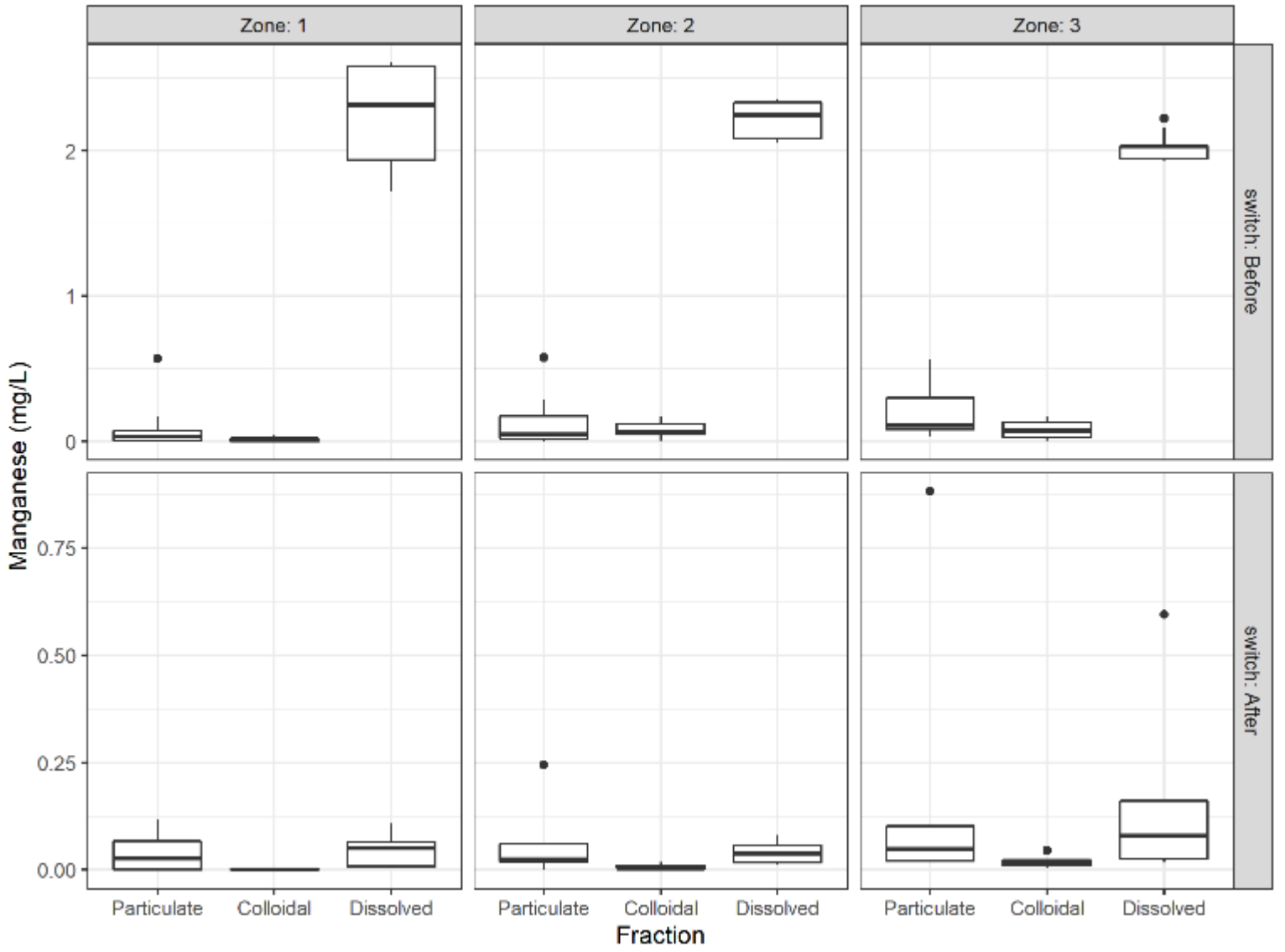
Water Quality – Entry Point

Parameter	Before Switch	After Switch
pH	7.60	8.30
Mn (mg/L)	2.29	0.021
Fe (mg/L)	0.122	0.012
Ca (mg/L)	72.7	55.7
Mg (mg/L)	28.6	26.0
Total Cl2 (mg/L)	1.30	2.29


Total
Particulate
Colloidal
Dissolved
> 0.2 µm
30 kDa - 0.2 µm
< 30 kDa
#1
#2
#3
#4
#5
#6
#7
#8
#9
Manganese (mg/L)
0
1
2
Oct
Jan
Sample Date

Mn Speciation

- Particulate > 0.2 µm
- Colloidal 30 kDa-0.2 µm
- Dissolved < 30 kDa



Summary

- Manganese is prevalent in regions throughout the U.S.
- A Mn regulation could necessitate systems to install treatment and manage legacy Mn in the distribution system
- Biological treatment of groundwaters with multiple contaminants via aerated contactor + filter consistently achieved Mn < 10 µg/L
- Mn surface concentrations greatest at influent end of contactor and not related to Mn oxidases concentrations
- Total Mn decreased substantially after switching sources, but evidence of some instability in Mn particulates farther out in DS

Acknowledgements

- EPA: Matt Noerpel
- Water systems operators
- WesTech: Eric Lawrence, Tom Dumbaugh

Questions?

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Notice

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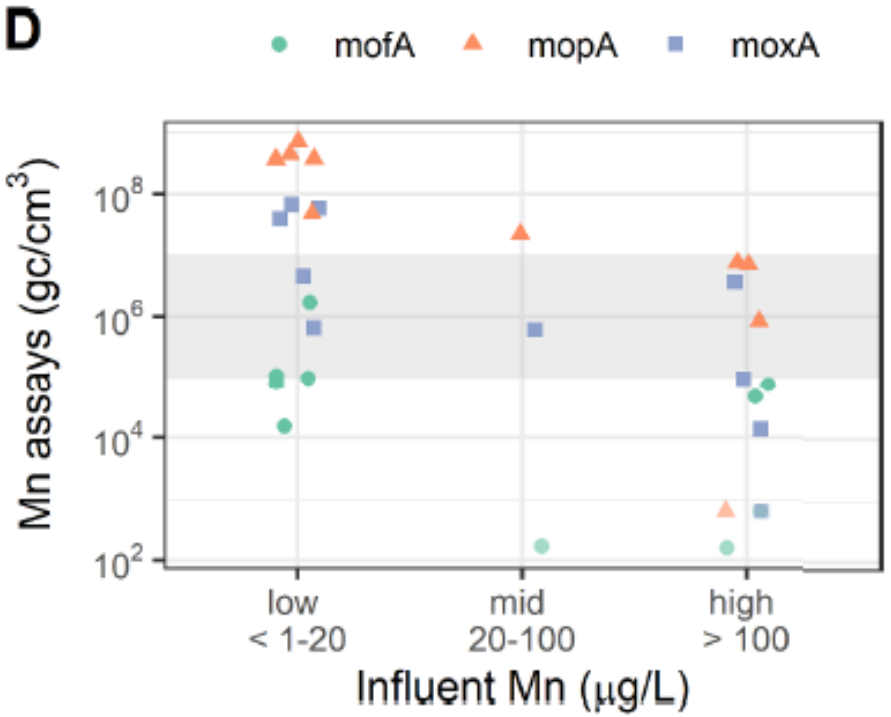
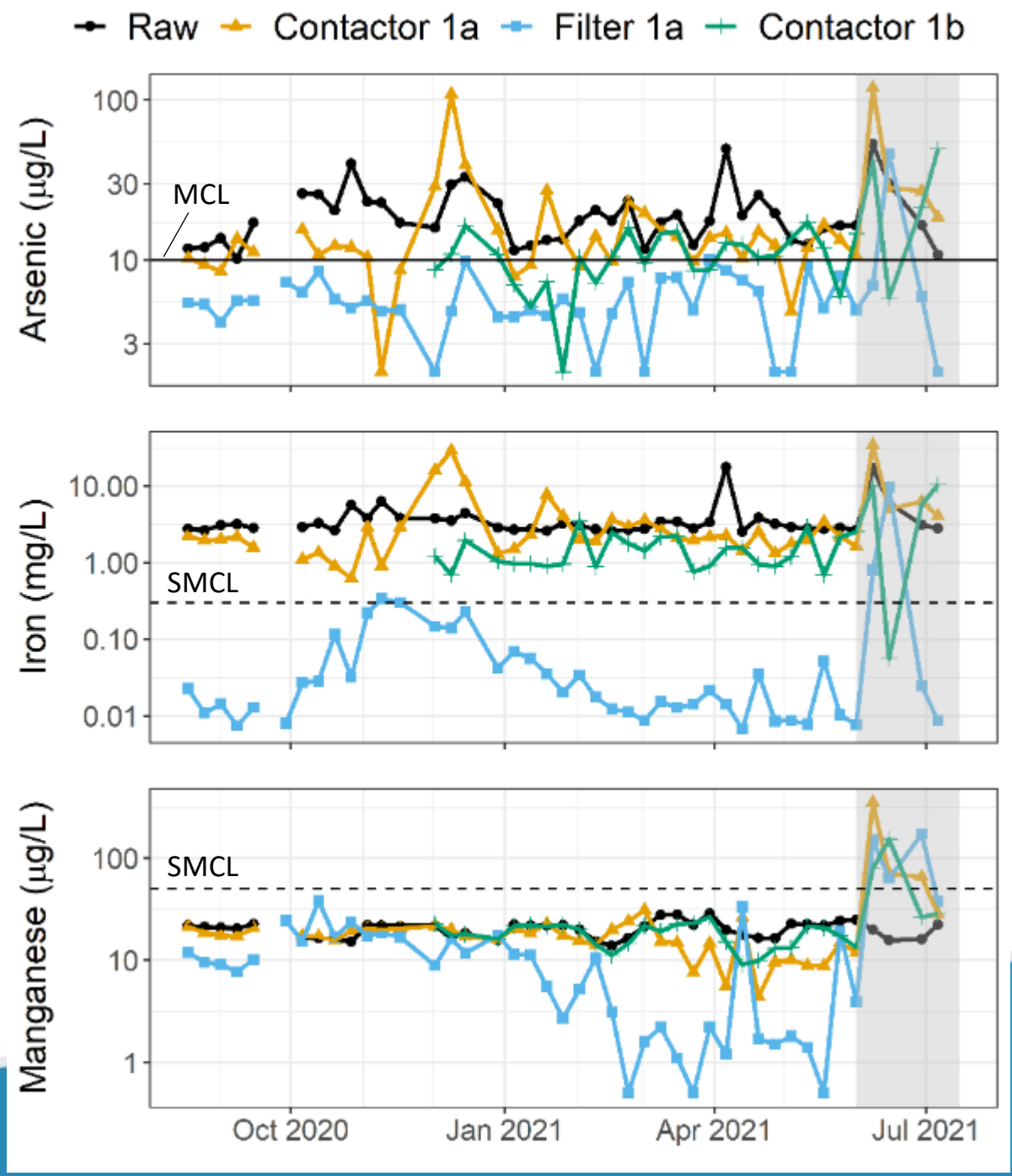
- Apparent slight negative relationship between influent Mn concentration and Mn oxidases concentrations
  - Importance of abiotic removal mechanisms



Site 1: Metals Removal

- Filter important for meeting treatment goals
- Arsenic
  - Oxidation + Fe particle removal
  - < MCL in filter effluent
  - 1-2-week acclimation time
- Iron
  - Oxidation + particle removal
  - 1-week acclimation time
- Manganese
  - Oxidation + surface coating
  - Improved in all 3 columns
  - 5-month acclimation time



Additional Pilot Contactors for Comparisons

Contactor	Media	EBCT (min)	NH_3 [mg N/L] (% Removal)	Fe [mg/L] (% Removal)	Mn [µg/L] (% Removal)	As [µg/L] (% Removal)
1a	12 mm Gravel	9 ± 2	3.5 ± 0.4 (93%)	3.3 ± 0.9 (48%)	20 ± 4 (40%)	20 ± 9 (34%)
1b	2.2 mm Ceramic	16 ± 6	3.5 ± 0.4 (68%)	3.3 ± 0.9 (63%)	20 ± 4 (21%)	20 ± 9 (38%)
2	2.2 mm GAC	16	2.1 (59%)	3.1 (22%)	196 (53%)	< 2
3	2.0 mm Ceramic	16	3.1 (100%)	0.1 (23%)	57 (92%)	< 2
4	1.6 mm Ceramic	25	3.1 (100%)	1.1 (-41%)	52 (28%)	23 (-24%)
5	1.6 mm Ceramic	25	2.1 (85%)	2.1 (62%)	22 (-5%)	< 2

All systems dosed orthophosphate