SPECIATION AND SEQUESTRATION OF MANGANESE IN ORGANIC WETLAND SUBSTRATES

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WHY MANGANESE?

- Manganese (Mn) is nearly ubiquitous, but environments can easily reach toxic manganese concentrations
- Mn can end up in waterways as a result of pollution from mining wastes
- Accommodating for Mn in polluted environments complicated by lack of understanding of Mn speciation

HOW DO WE GET RID OF IT?

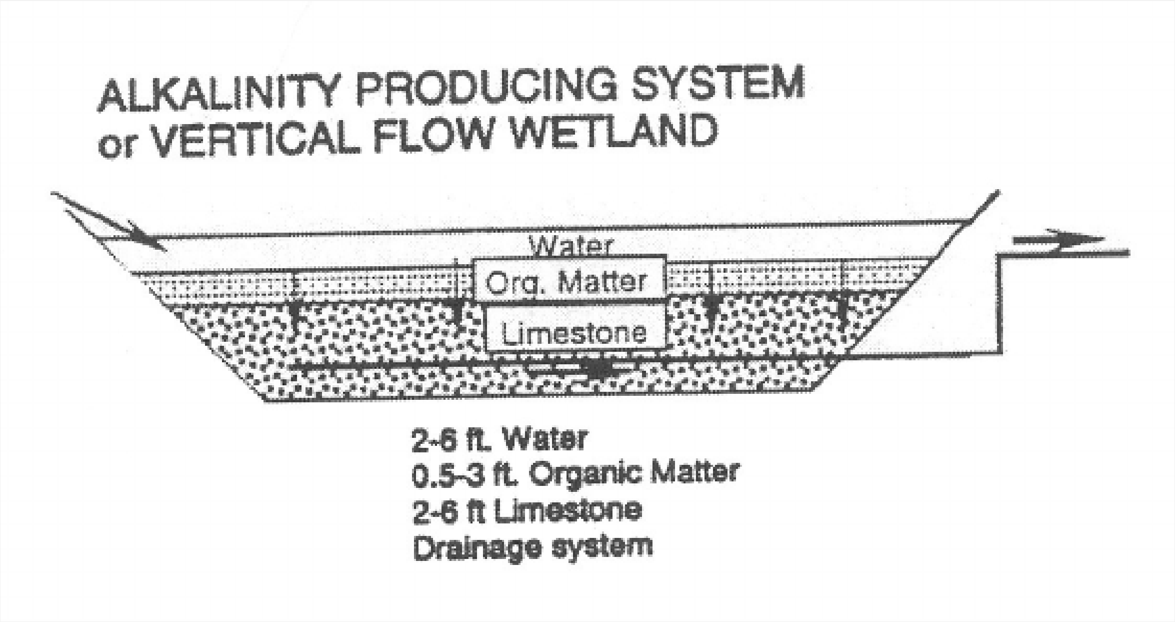
One way we treat contaminated waterways (often containing Mn), is through passive treatment systems

VFBR

Mayer Ranch Passive Treatment System – Google Earth 2026

VERTICAL FLOW BIOREACTOR (VFBR)

Organic-matter rich and **anaerobic**, like wetlands



Rose, 2010

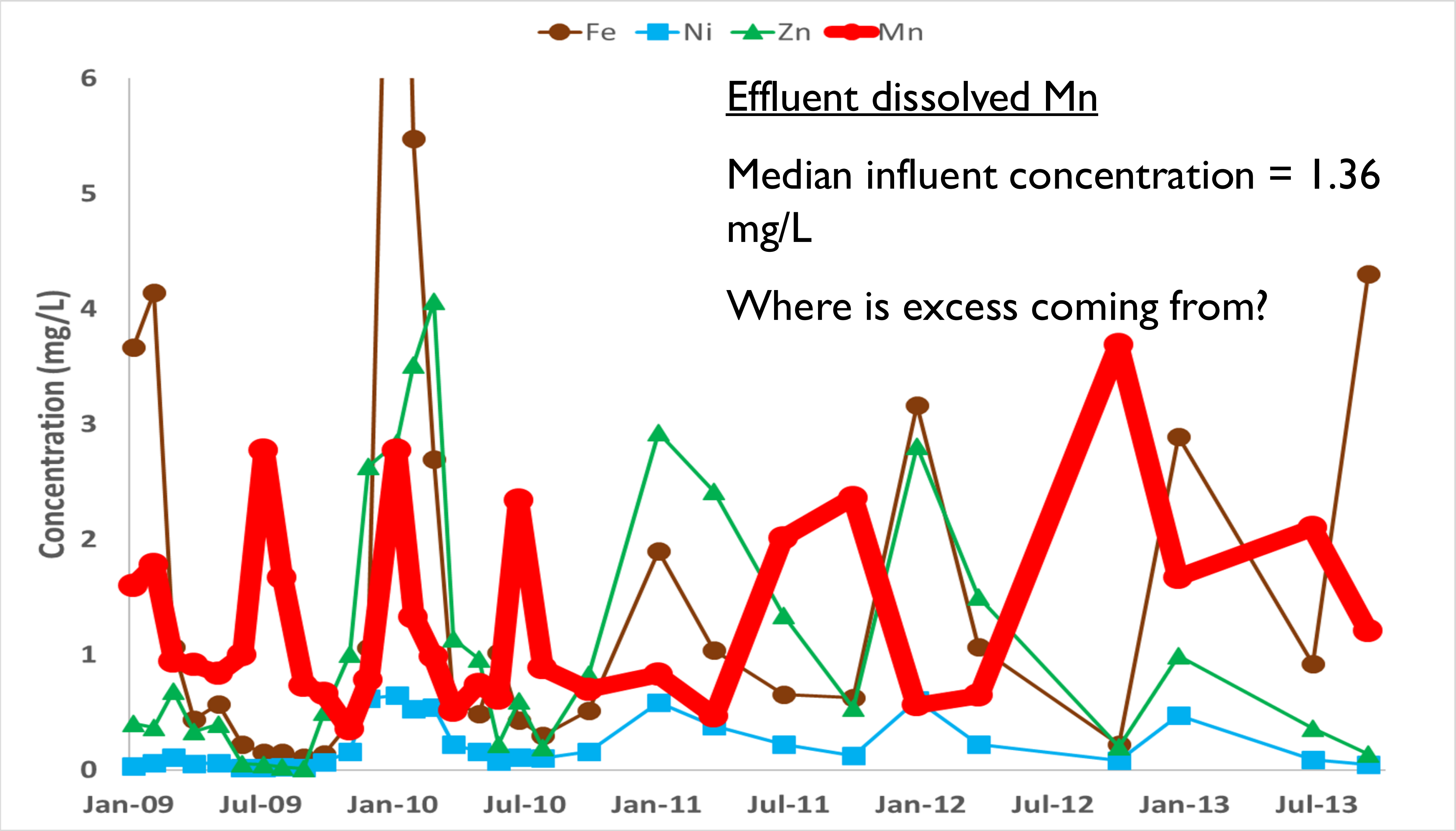
- Typically used to promote alkalinity
- Can also remove trace metals:
  - **Predominantly as sulfides**
  - Or as carbonates and oxides
  - Or through sorption or complexation

Mn not retained as sulfide because it is highly soluble, so what are we seeing?

Table 2
Combined median and first and third quartile concentrations in the influent, effluent, and porewater of MRPTS VFBR.

		Influent (Jan 2009–Jan 2015)				Porewater (July 2014)				Effluent (Jan 2009-Jan 2015)			
		N	Q1	Median	Q3	N	Q1	Median	Q3	N	Q1	Median	Q3
Flow (L/min)		5	289	309	325	–	–	–	–	–	–	–	–
T (°C)		66	9.10	19.1	25.9	14	27.2	28.3	28.6	66	6.76	17.8	23.8
pH (s.u.)		66	6.24	6.39	6.69	14	6.68	6.75	6.79	66	6.67	6.79	6.88
Cond (mS/cm)		66	2.27	2.80	3.18	14	3.42	3.50	3.57	66	2.16	2.60	3.10
DO (mg/L)		66	6.30	8.55	10.8	14	1.17	1.34	1.50	66	0.210	0.750	1.89
ORP (mV)		66	105	180	279	14	−124	−82.3	−13.0	66	−204	−90.5	41.3
Alk. (mg/L as $CaCO_3$)		66	134	145	160	14	139	160	171	66	179	220	273
Sulfate (mg/L)		52	2110	2250	2390	14	2030	2080	2100	52	2040	2140	2280
Sulfide (mg/L)		0	–	–	–	14	0.298	0.715	0.996	6	1.27	3.21	9.25
Ca (mg/L)	**Tot**	66	698	720	748	14	701	709	718	66	705	749	774
	Diss	36	685	699	760	14	717	721	725	36	689	716	783
Mg (mg/L)	**Tot**	66	178	192	200	14	167	170	173	66	175	193	203
	Diss	36	175	183	191	14	169	170	173	36	172	183	190
Na (mg/L)	**Tot**	66	93.1	100	108	14	90.5	91.0	91.2	66	92.3	101	109
	Diss	36	91.7	102	106	14	90.7	91.3	91.7	36	89.8	102	107
Fe (mg/L)	**Tot**	66	2.19	3.51	7.54	14	1.12	1.55	2.10	66	0.313	0.725	1.91
	Diss	35	0.060	0.310	6.02	14	0.494	1.29	2.12	34	0.113	0.418	1.23
Cd (mg/L)	**Tot**	26	0.001	0.001	0.002	6	0.001	0.001	0.001	10	0.001	0.001	0.001
	Diss	10	0.001	0.002	0.003	5	0.001	0.001	0.001	6	0.001	0.001	0.001
Co (mg/L)	**Tot**	66	0.038	0.056	0.065	10	0.02	0.008	0.023	38	0.003	0.008	0.020
	Diss	36	0.032	0.051	0.067	10	0.002	0.006	0.022	17	0.003	0.009	0.012
Mn (mg/L)	**Tot**	66	1.20	1.44	1.61	14	1.39	1.81	2.69	66	0.740	1.03	1.59
	Diss	36	1.10	1.36	1.75	14	1.35	1.80	2.68	36	0.669	1.21	2.10
Ni (mg/L)	**Tot**	66	0.709	0.790	0.831	14	0.100	0.161	0.296	66	0.039	0.113	0.289
	Diss	36	0.716	0.758	0.804	14	0.094	0.152	0.286	35	0.043	0.097	0.266
Pb (mg/L)	**Tot**	5	0.026	0.029	0.031	0	–	–	–	1	0.029	0.029	0.029
	Diss	6	0.026	0.027	0.029	0	–	–	–	3	0.025	0.030	0.028
Zn (mg/L)	**Tot**	66	4.24	5.26	6.51	14	0.060	0.525	1.27	66	0.139	0.577	1.686
	Diss	36	3.82	4.83	5.42	14	0.046	0.162	1.15	35	0.009	0.019	0.177

Labar and Nairn, 2018



Effluent dissolved Mn

Median influent concentration = 1.36 mg/L

Where is excess coming from?

[LaBar and Nairn, 2018](#)

Unpredictable Mn behavior in VFBR

Why is this happening?

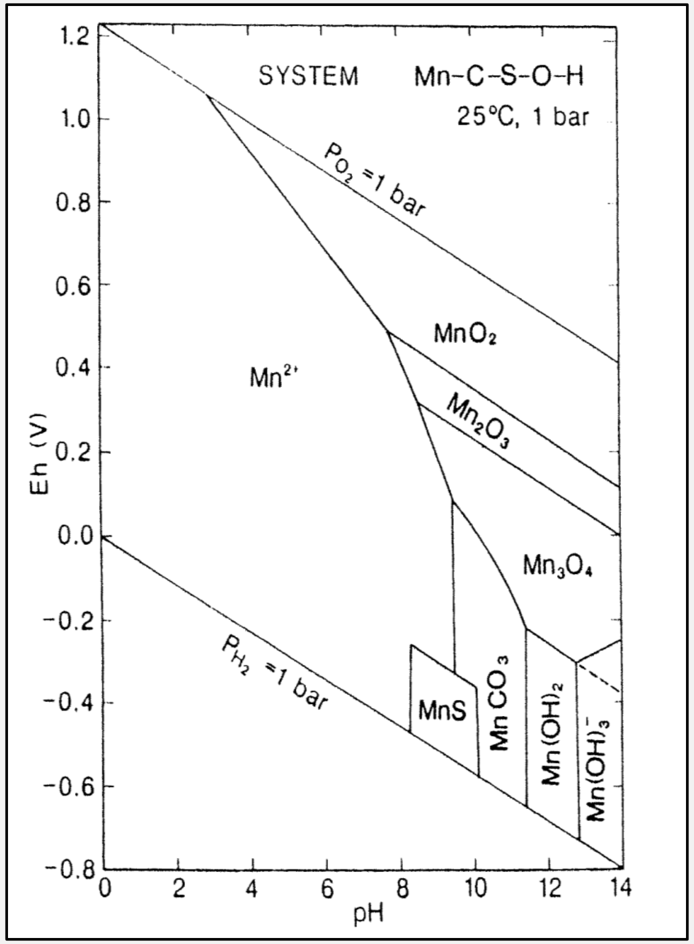
GOALS

- Study behavior and sequestration of Mn in these kinds of environments
- Proof of concept study – can we implement speciation?

- How?
  - Analyze for patterns in speciation for Mn(IV), (II), and (III) over time
  - Study Mn sequestration in the substrate itself

WHY ARE WE WORRIED ABOUT SPECIATION?

- Mn can exist as many different species, at least up to seven different oxidation states
- Mn can be readily removed through **aerobic** means



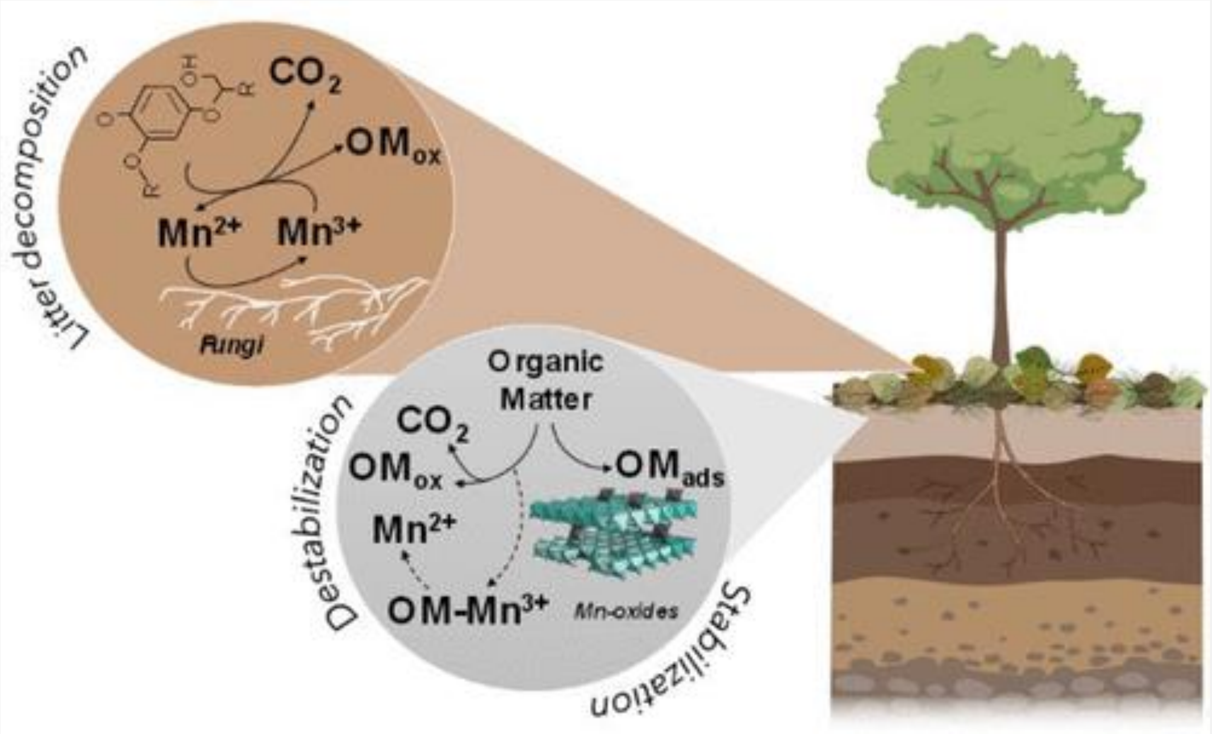
Langmuir, et al., 2004

MN (III)

- Previously, only Mn(II) considered dominant for **soluble** Mn fractions
- Re-evaluated to include Mn(III) bound to ligands
- Mn(III)-ligands can transfer electrons and therefore have a potential impact on redox chemistry
- Evidence also supports presence of Mn(III) in suboxic environments

Mn negatively associated with carbon storage in humus layers in forests

- Part of long-term decomposition, regulated by Mn peroxidase
- Mn(III) plays a role!
  - Litter-decomposing fungi oxidize Mn(II) into Mn(III)
  - OM decomposition when Mn(III) binds with organic ligands



Li, et al., 2021

METHODS

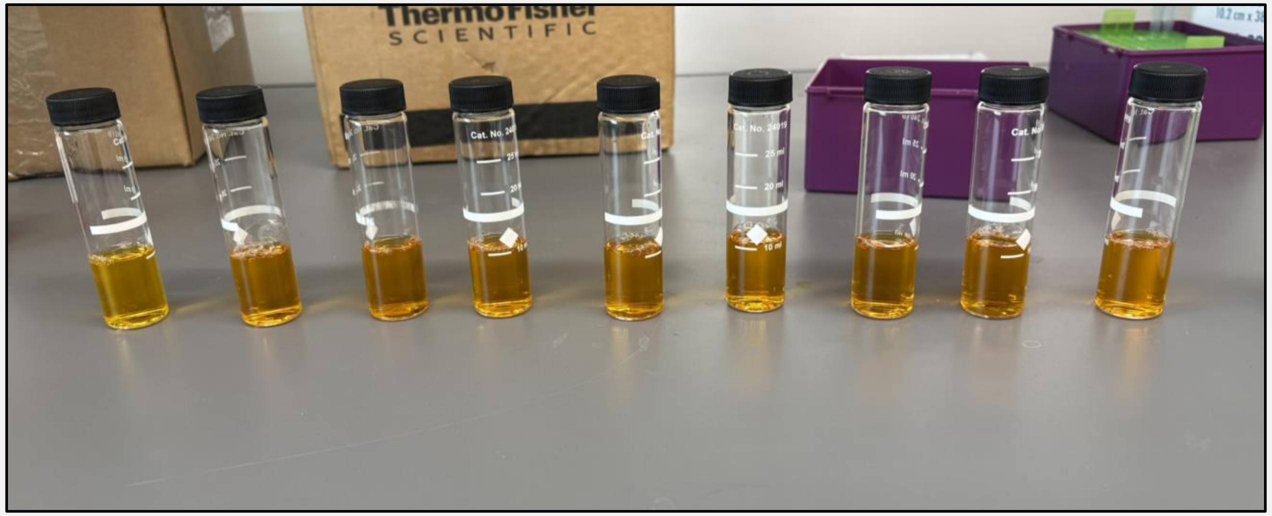
1. Recreate organic, anaerobic environment

- cubitainers filled with spent mushroom compost and ~0.5 mg/L Mn water at 12.5:1 ratio

2. Measure twice weekly for:

- pH
- Temperature
- Redox potential (ORP)
- Conductivity
- Dissolved oxygen (DO)
- Total Mn
- Mn(II)
- Mn(III)

MANGANESE



Known under anaerobic conditions: **Soluble Mn(II)/(III)** and **insoluble Mn(IV)**

1. Total Mn from 1 mL unfiltered sample
2. 3 mL soluble Mn samples filtered through 0.45 µm

   ↓

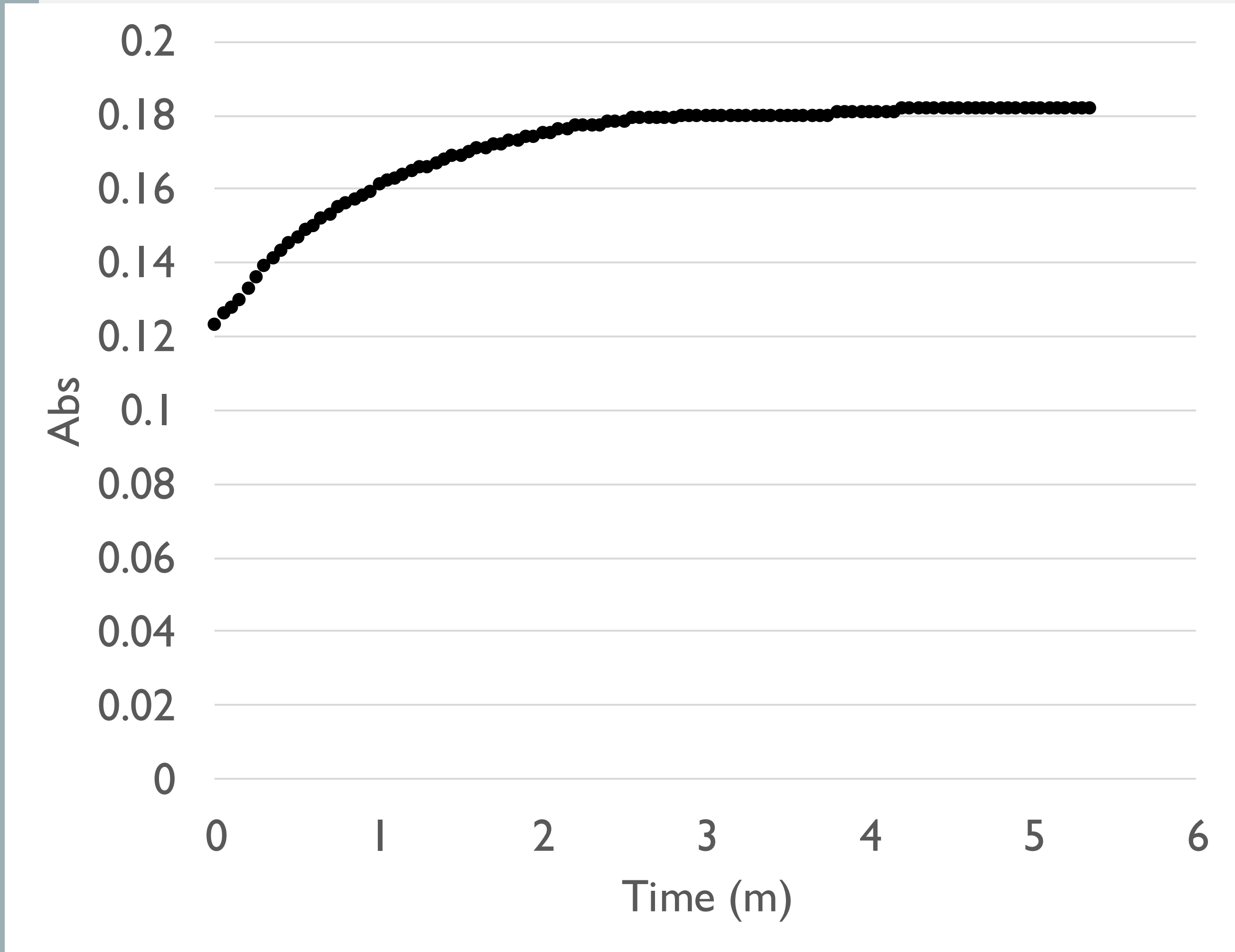
   Mn(II) and (III) evaluated by process described in Oldham et al. (2016)

PROCESS FOR SOLUBLE MN
as described in Oldham, et al., (2016)

Determination of soluble Mn concentrations through addition of a soluble porphyrin ligand:

- α,β,γ,δ-tetrakis(4-carboxyphenyl)porphine [T(4-CP)P]

1. Rapid Mn(II) oxidization into Mn(III)-Porphyrin complex (initial rise of curve!)
2. Mn(III) undergoes ligand substitution to form Mn(III)-porphyrin complex
3. Complex can be measured by UV-Vis spectrophotometry at 468nm



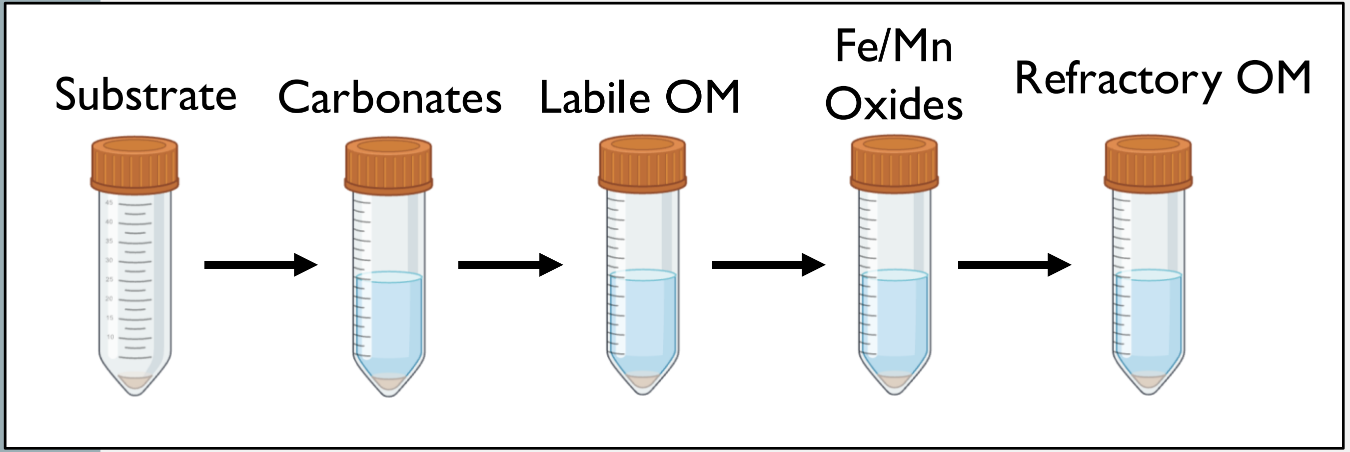
SEQUENTIAL EXTRACTIONS

Performed on substrate to analyze for Mn bound to:

- Carbonates
- Labile OM
- Fe/Mn Oxides
- Refractory OM

Labile OM: bound to humic and fulvic acids

Refractory OM: decay-resistant with low solubility



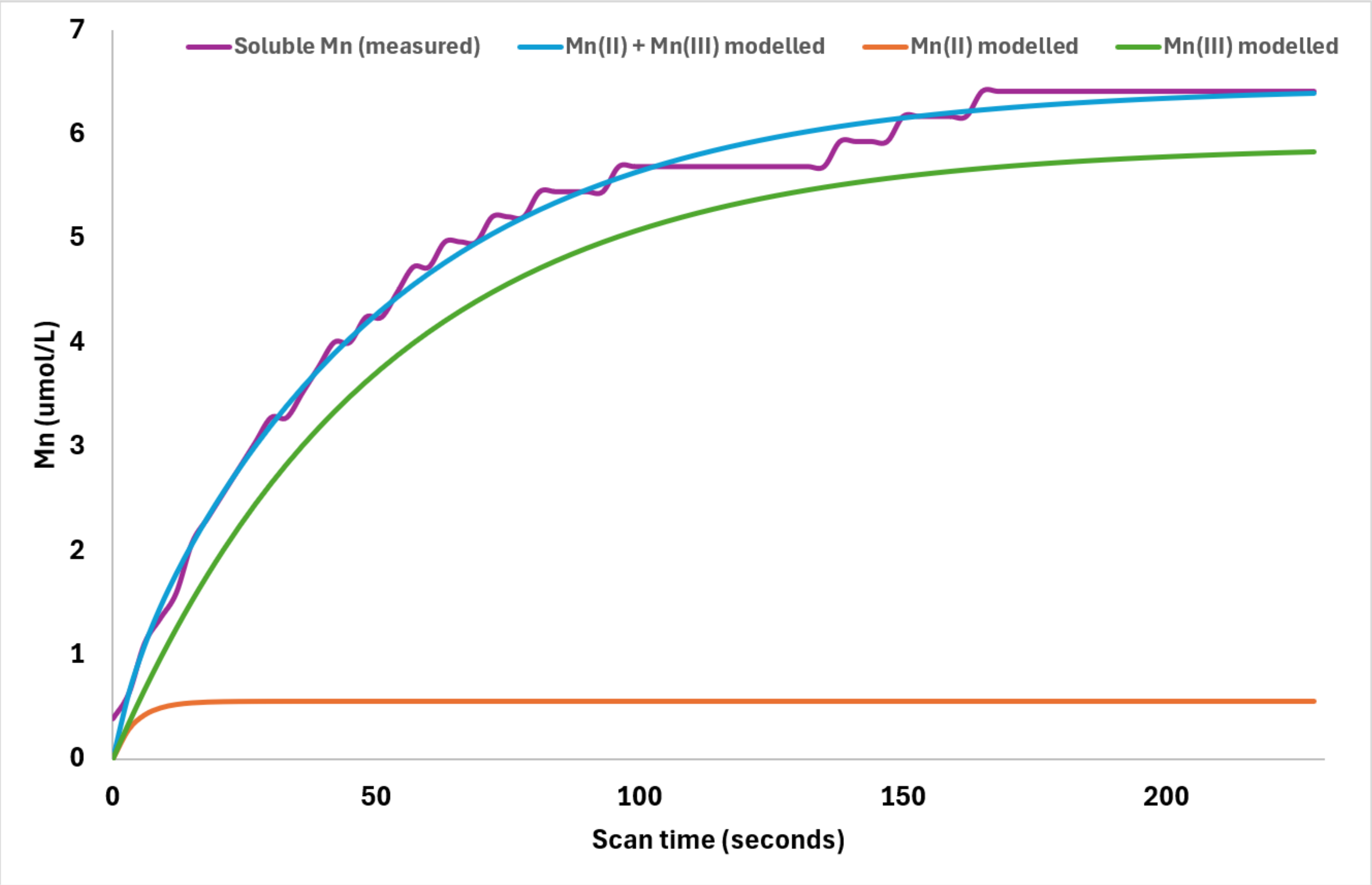
RESULTS

	pH	Cond (mS/cm)	DO (mg/L)	ORP (mV)	Temp (°C)	Mn(IV) (mg/L)	Soluble Mn (mg/L)
Ctrl	7.32±0.07	4.758±0.140	0.06±0.01	-70.5±59.8	22.0±0.2	0.915±0.080	0.050±0.002
Treatment	7.26±0.09	4.715±0.234	0.05±0.01	-103.8±60.7	22.1±0.2	0.914±0.114	0.050±0.002

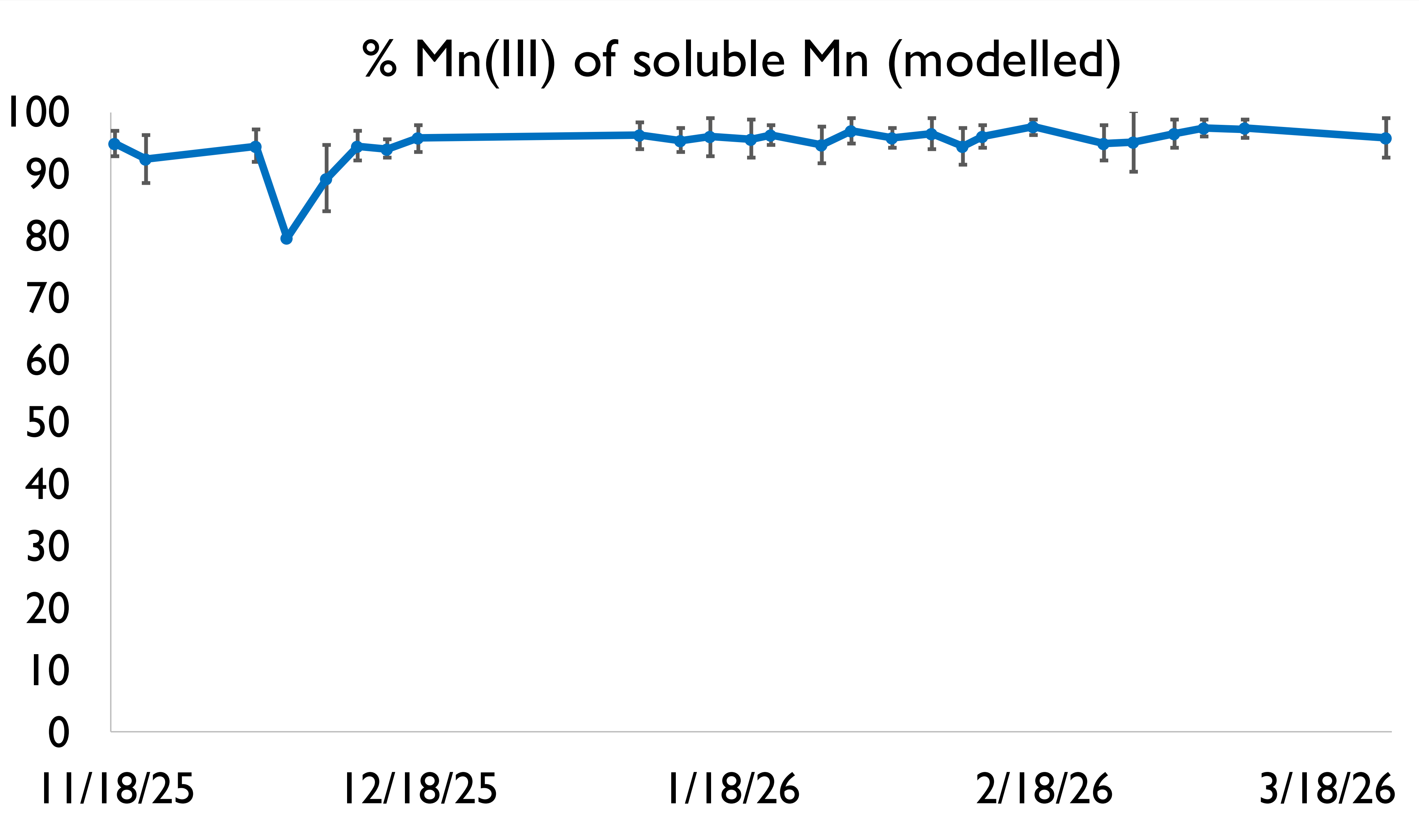
Table 1. Average conditions in cubitainers over 19 weeks

For solution in reactors:

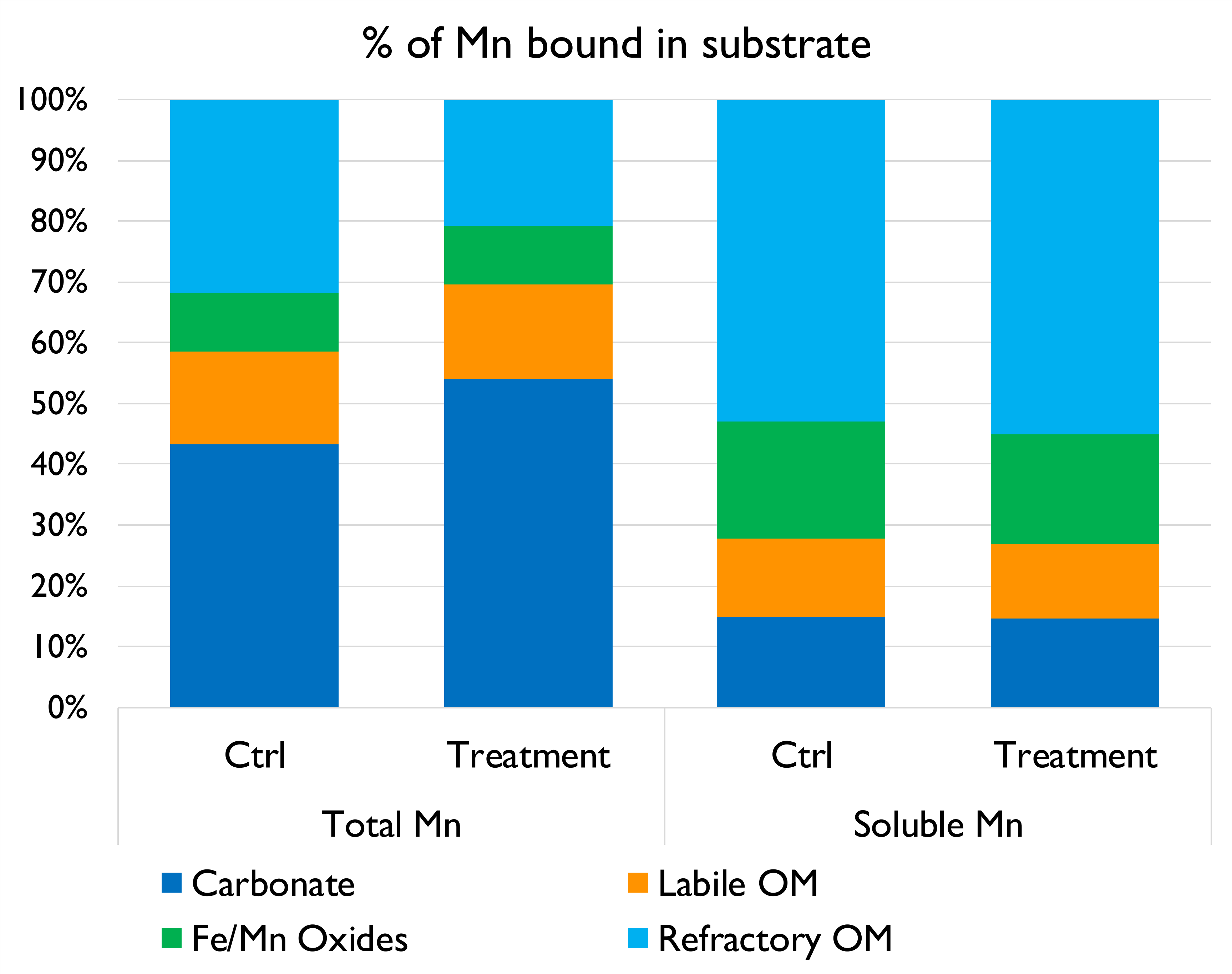
- Greater proportion of Mn present as Mn(IV) (insoluble) than soluble Mn



- Example of graphed output for Mn(II)/(III)



- On average ~95% of soluble Mn is present as Mn(III)



Changes in Mn storage in substrate with different speciation:

- Total Mn: greatest amount of Mn stored in carbonates
- Dissolved Mn: greatest amount stored in refractory OM

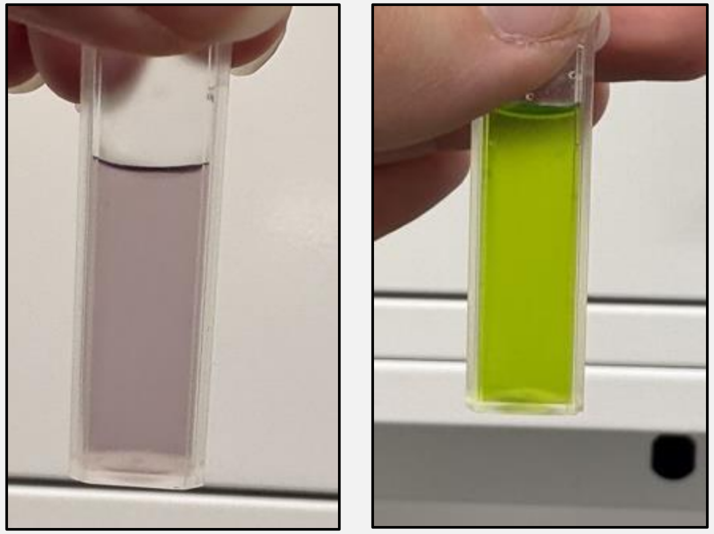
DISCUSSION

Proof of concept study: could the Oldham et al. method work for speciation of Mn?

- Mn(II)/(III) process could work, but took time to get consistent results
- Sequential extractions had matrix effects

1.

2.



1. Color difference for Labile OM extraction solution
2. Color change after addition of T(4-CP)P solution during Refractory OM extraction

DISCUSSION

- Growing concern over Mn impacts to the environment and human health
- Use data to understand where and how Mn is stored in wetland environments
- Apply new understandings to treatment systems to effectively reduce Mn concentrations

CONCLUSION

- Studied Mn speciation and sequestration under conditions observed in VFBRs
- Environment recreated and analyzed over time, then sacrificed for sequential extractions
- Results show patterns for speciation and indicate strong Mn(III) presence complexed to organic lipids
- Results can be used to adapt treatment systems to accommodate for Mn

FUTURE STUDIES

- Remove matrix effects for sequential extractions
- Geochemical modeling for Mn(II)/(III)
- Modifications to processes used:
  - Run longer study
  - Spectrophotometer: shorter increments than 3 seconds

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