Comparing Manganese Treatment Technologies

Phil Brandhuber PhD

Brandhuber Water Quality and Treatment LLC

2023 PNWS Conference

Agenda

- Mn chemistry refresher
- Non-treatment source water management options
- Mn treatment options

Mn Chemistry Refresher

- Characteristics
- Contaminant vs. treatment chemical
- Eh/pH diagram
- Behavior in lakes and reservoirs

Characteristics of Mn

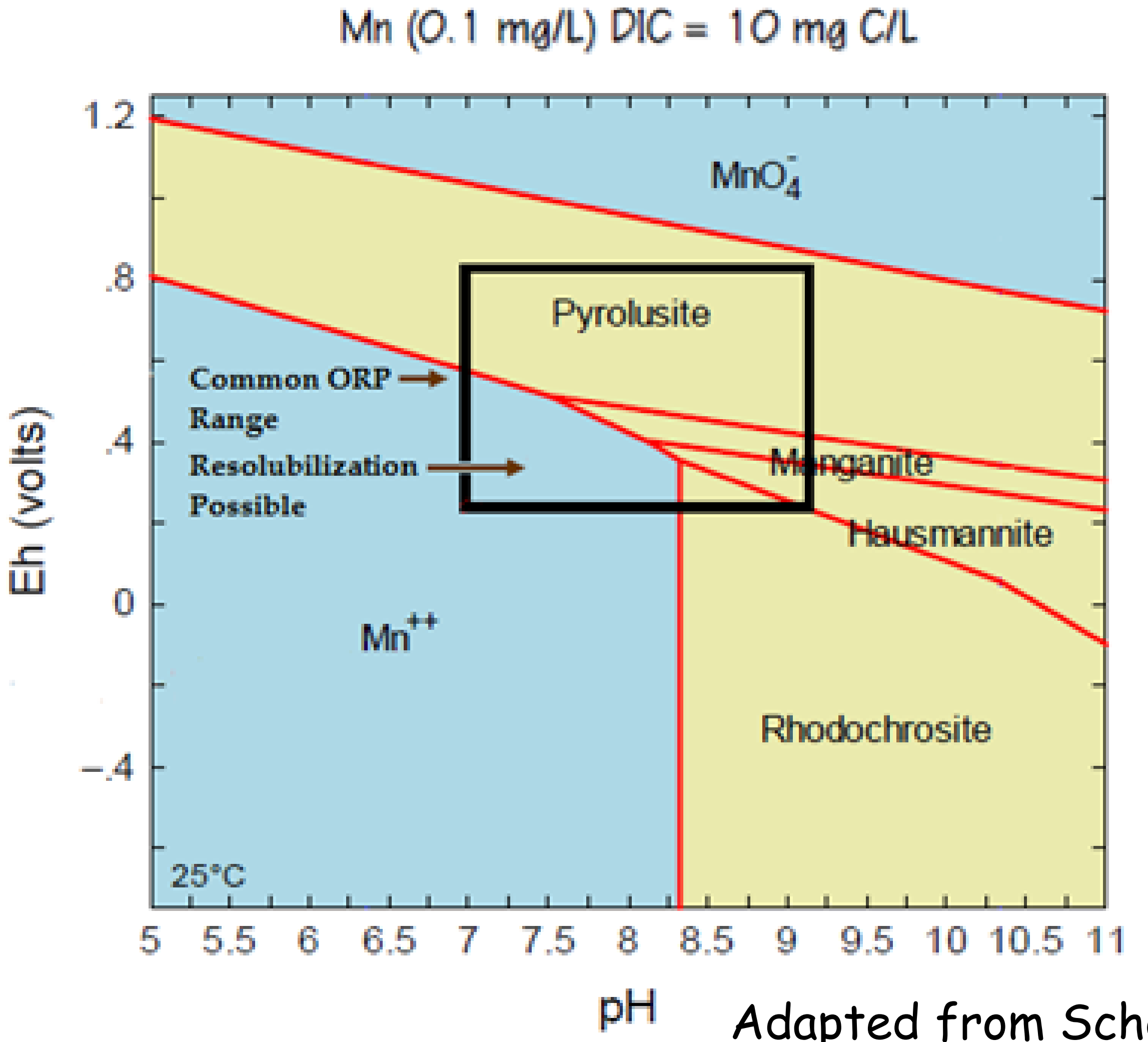
- Commonly present
  - Surface waters
  - Groundwaters
- Primary oxidation states
  - Mn(II) – Soluble; not visually detectable
  - Mn(III/IV) – Insoluble; visually detectable
- Important features
  - Oxidation state sensitive to pH and redox conditions
  - Rate of oxidation varies by oxidant
  - High capacity for sorption of inorganic species

Mn as Contaminant or Treatment Chemical

	As a Contaminant	
Mn^{2+}	Manganous ion	• + II valance state • High solubility • Clear in water
MnO_x(s)	Manganese (di)oxide	• Combination of +III and + IV valance states • Low solubility • Discolors water - black or brown • Stains surfaces
	As a Treatment Chemical	
$KMnO_4$ $NaMnO_4$	Potassium or sodium permanganate	• + VII valance state • High solubility • Strong oxidant • Discolors water - purple • Forms MnO_x(s) when reduced

Form of Mn Determined By Oxidation Reduction Potential and pH

- Particulate Mn
  - Oxidation potential (Eh) and/or pH is high
- Dissolved Mn
  - Eh and/or pH is low
- Mn treatment based on raising Eh or pH
- Mn release related to lower Eh or pH



Adapted from Schock, 2007

Mn in Lakes and Reservoirs

Spring

- Reservoir well mixed
- Temperature increases
- Biological activity increases
- Low Mn throughout reservoir

Summer

- Reservoir stratifies
- Oxygen depleted in hypolimnion
- Mn released from sediment into hypolimnion

Fall

- Turns over followed by mixing
- Mn distributes throughout reservoir
- Oxygen increases throughout reservoir
- Mn release from sediments stops

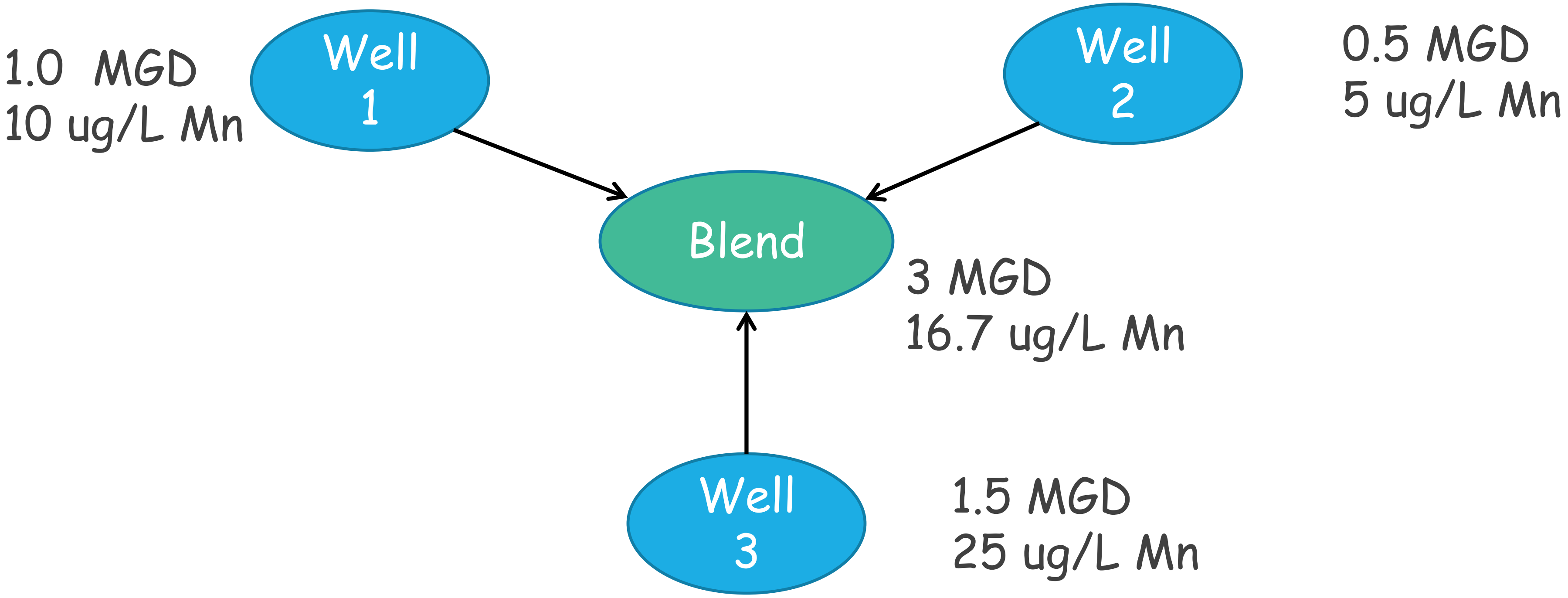
Winter

- High oxygen levels
- Mn returns to sediment

Non-treatment Source Water Management Options

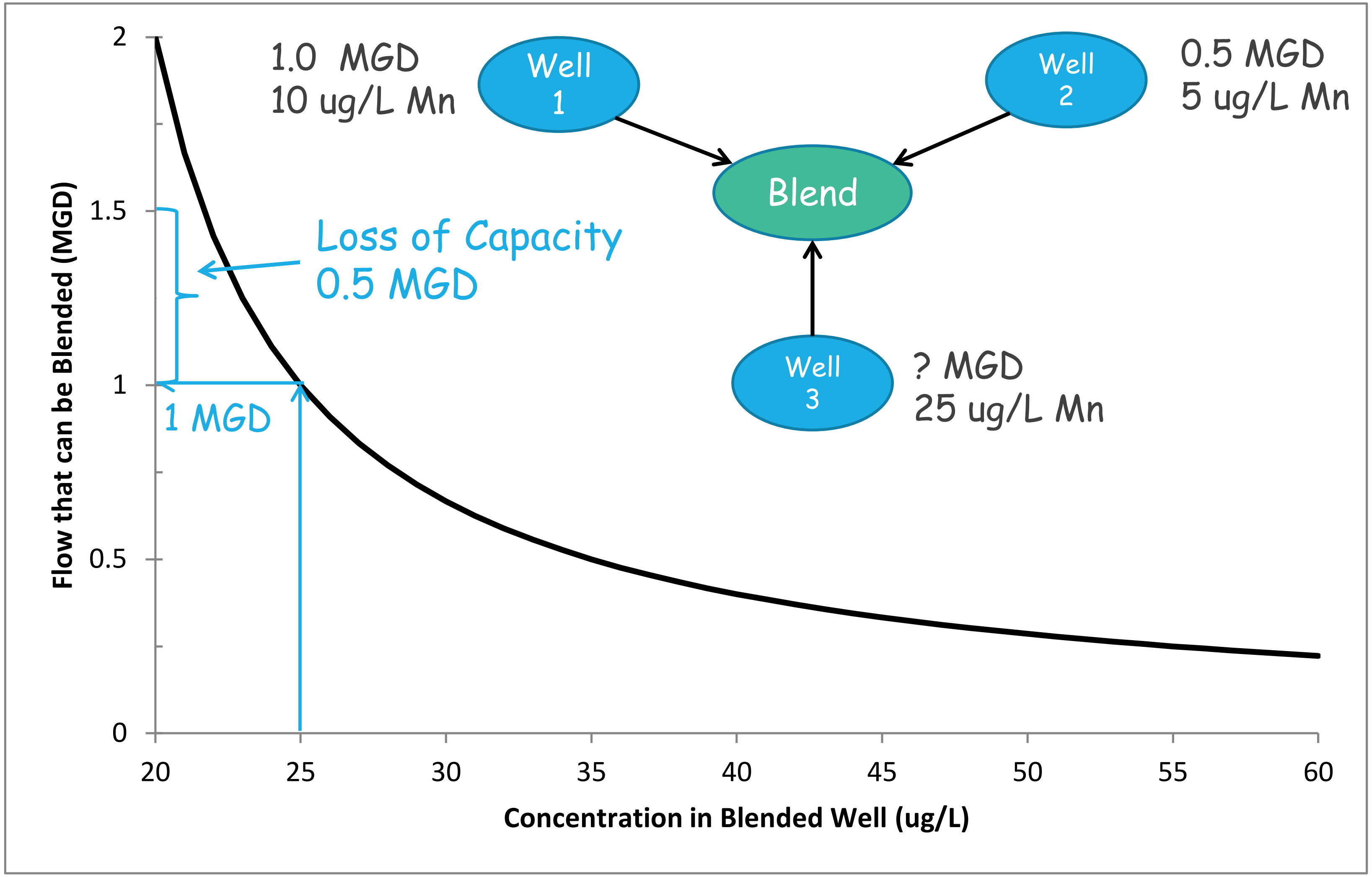
- Blending
- Selective withdrawal
- Lake/reservoir aeration

Managing Mn by Blending



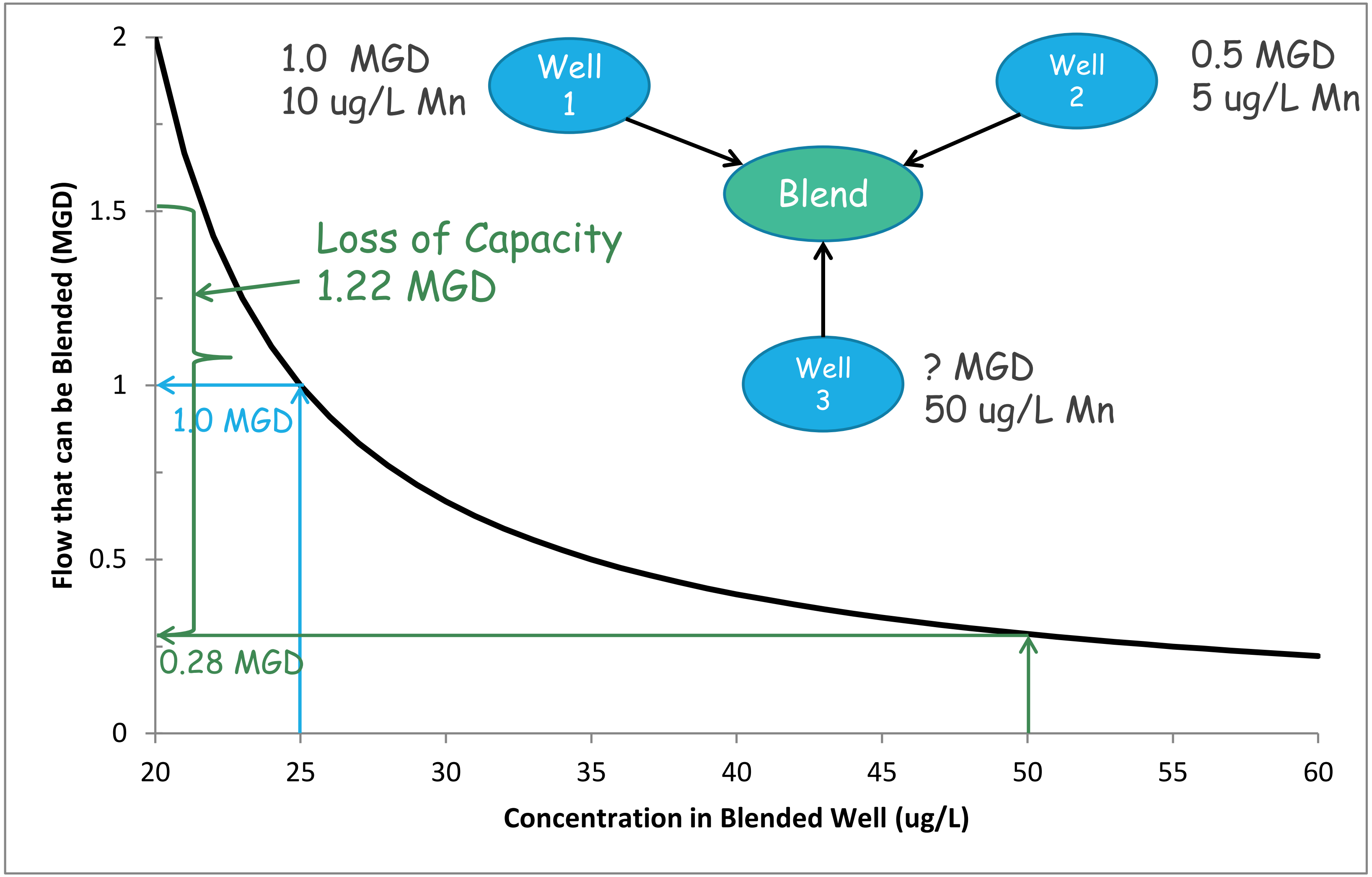
Blended Mn Concentration Goal ≤ 15 μg/L

Blending Example Well 3 = 25 μg/L



Blended Mn Concentration Goal ≤ 15 μg/L

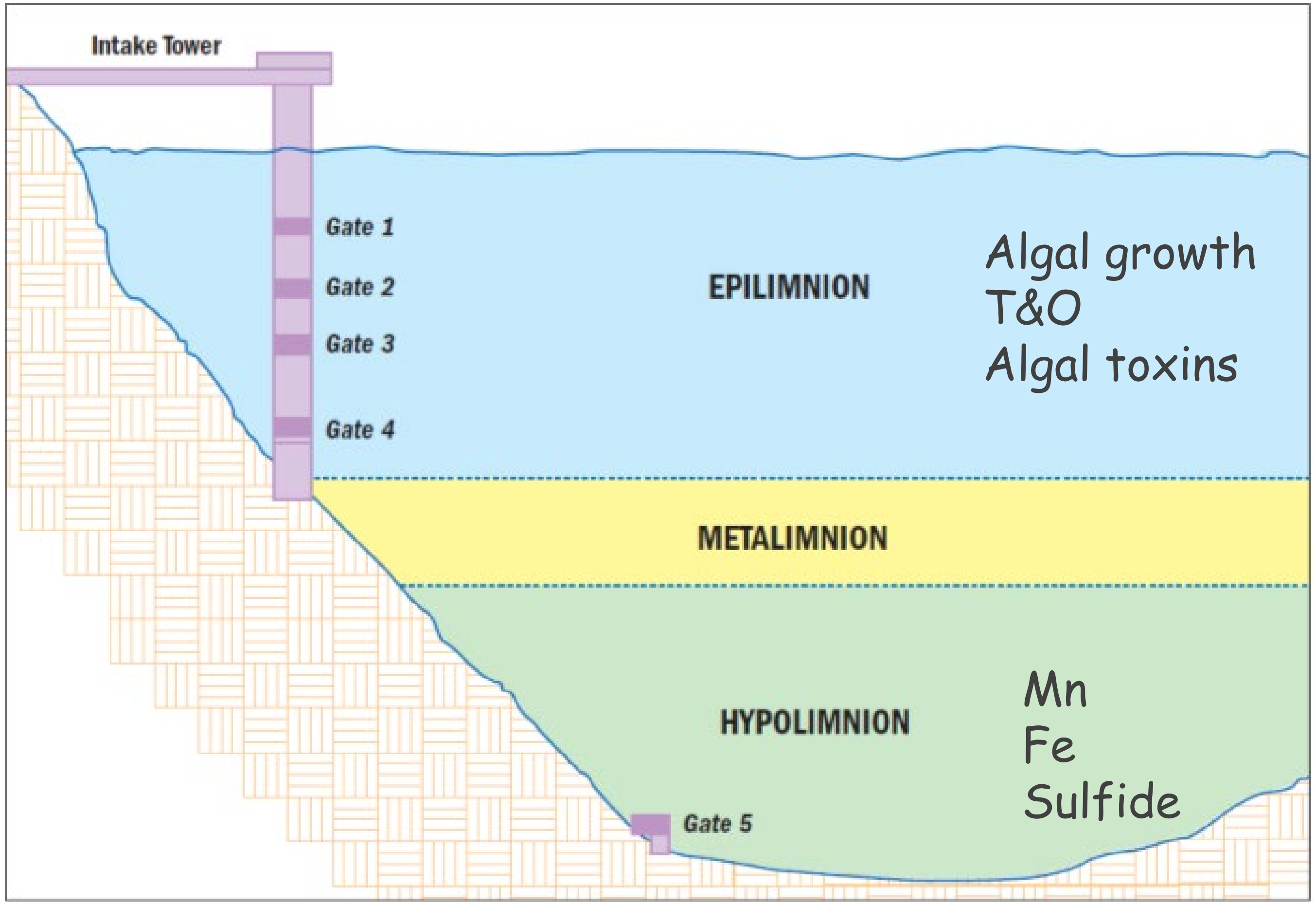
Blending Example Well 3 = 50 μg/L



Frequently blending results in an unacceptable loss of capacity

Blended Mn Concentration Goal ≤ 15 μg/L

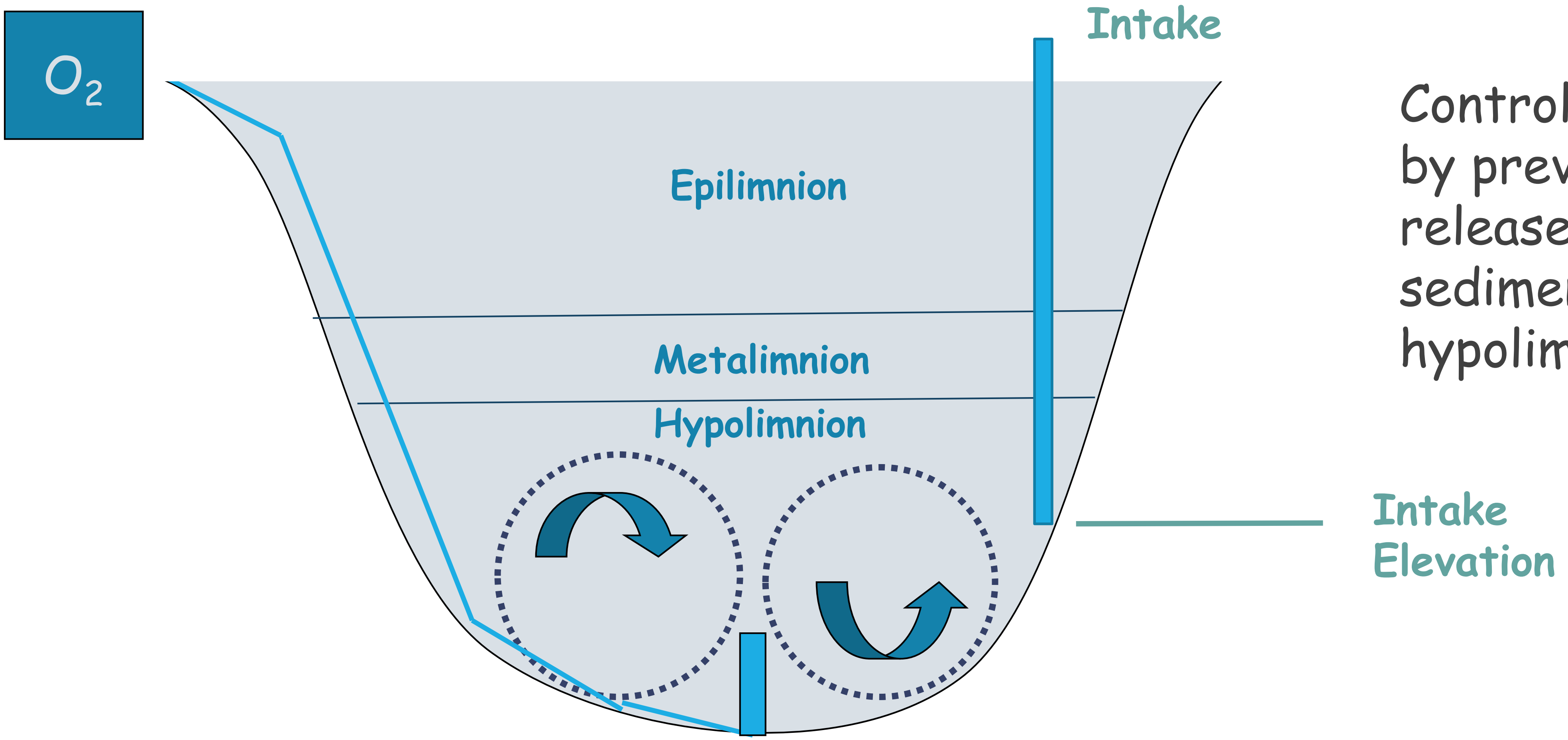
Mn Source Control by Selective Withdrawal



Withdrawal at elevation with acceptable Mn levels

- May trade one set of problems for another

Mn Source Control by Hypolimnic Aeration



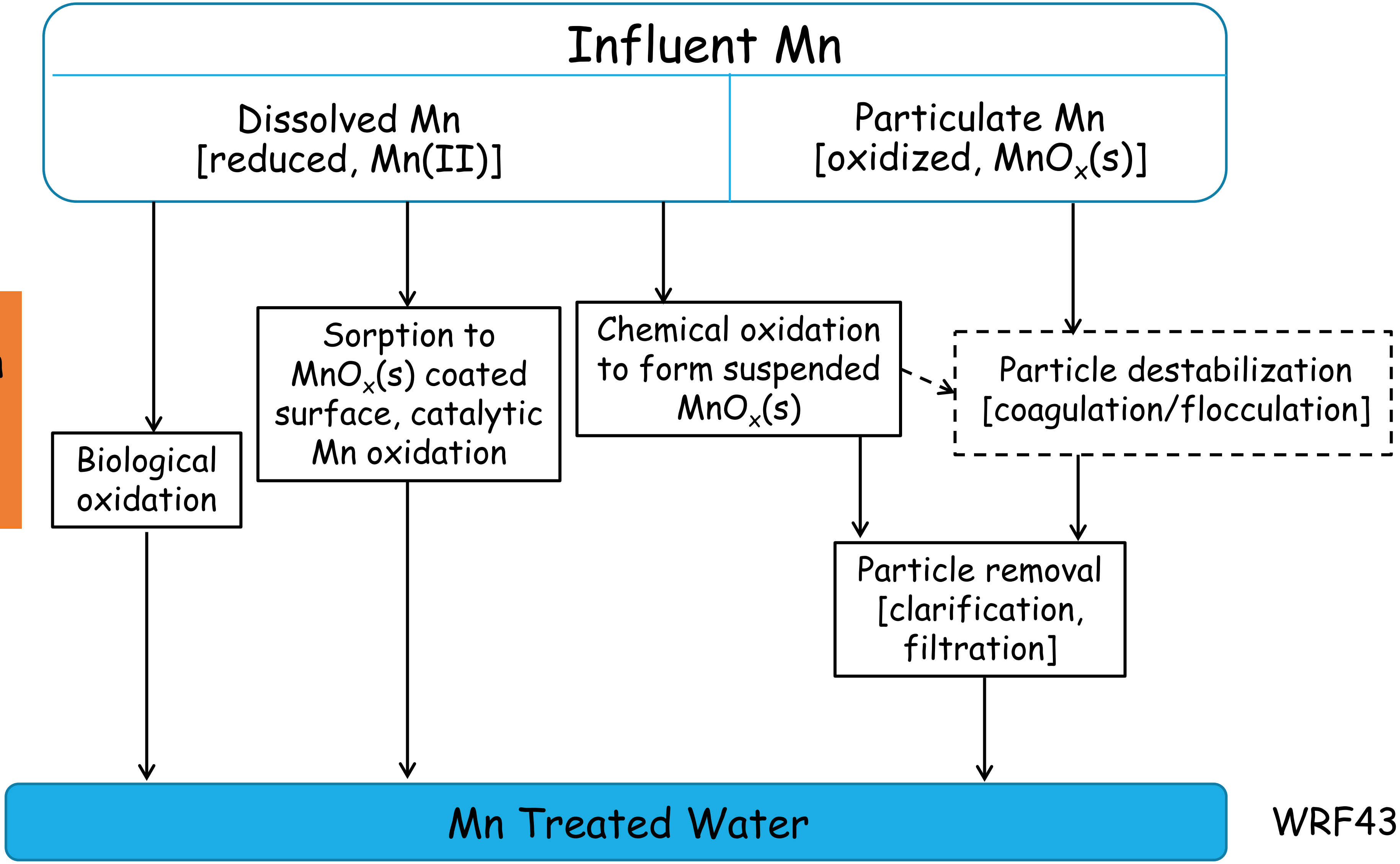
Controls soluble Mn by preventing release of Mn from sediment to hypolimnion

Treatment of Mn

- Treatment options
  - Oxidation/filtration
  - Oxidants
  - Sorption/catalytic oxidation on media
  - Biological oxidation

Several Mn Removal Options are Proven and Effective

Sequestration doesn't remove Mn but can prevent it from discoloring water



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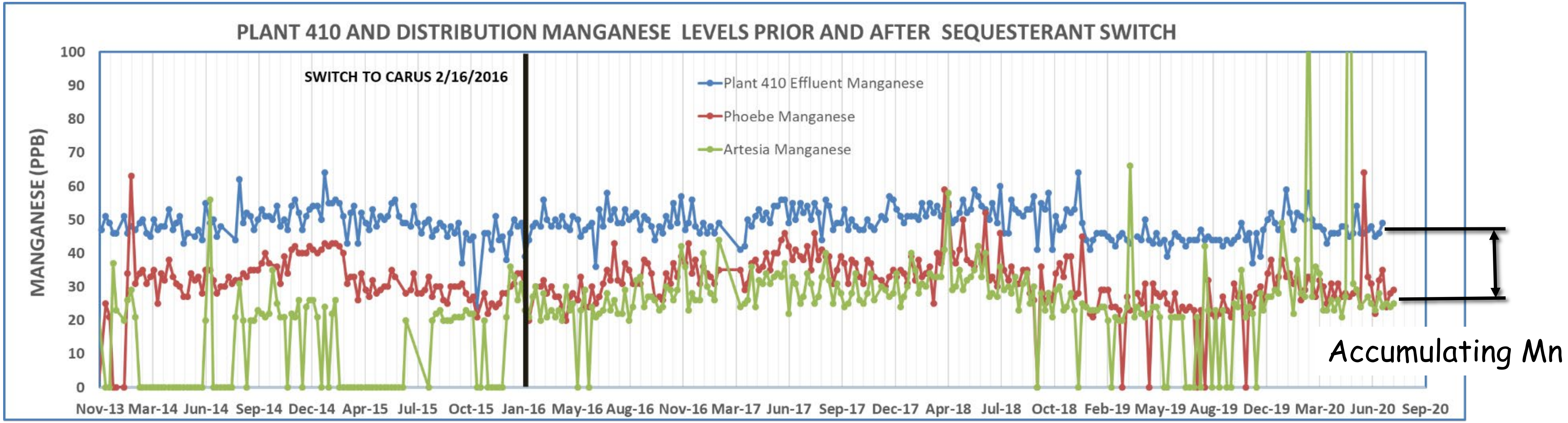
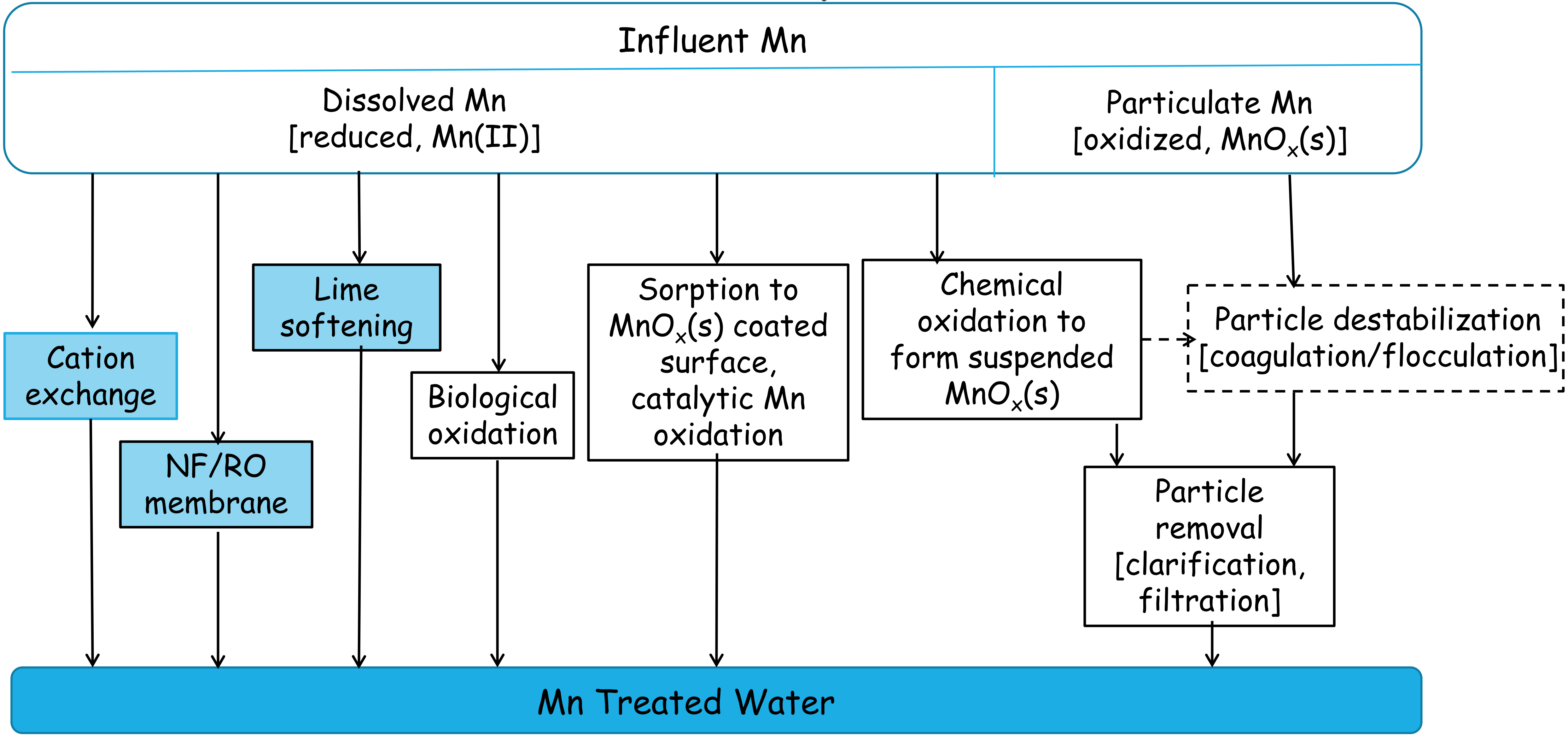
Considerations When Using a Sequestrant



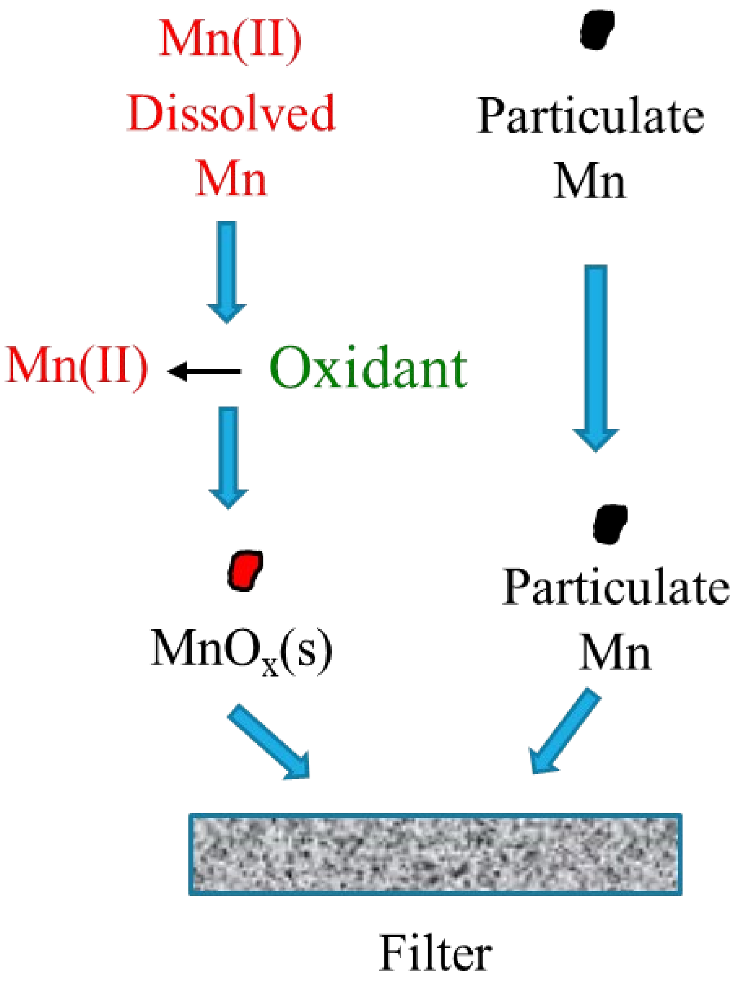
- Is all the Mn sequestered?
- How long does the Mn remain sequestered?
- Fate of Mn which is no longer sequestered?
- Are existing pipe scales being destabilized by sequestrant?

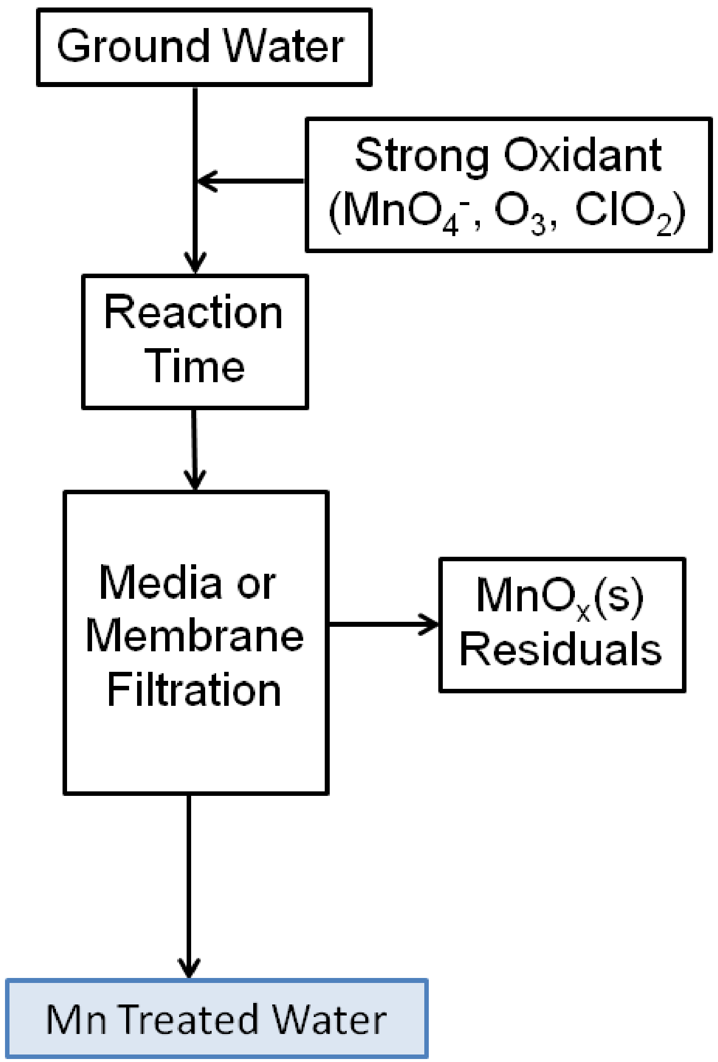
Suburban Water Systems, 2021

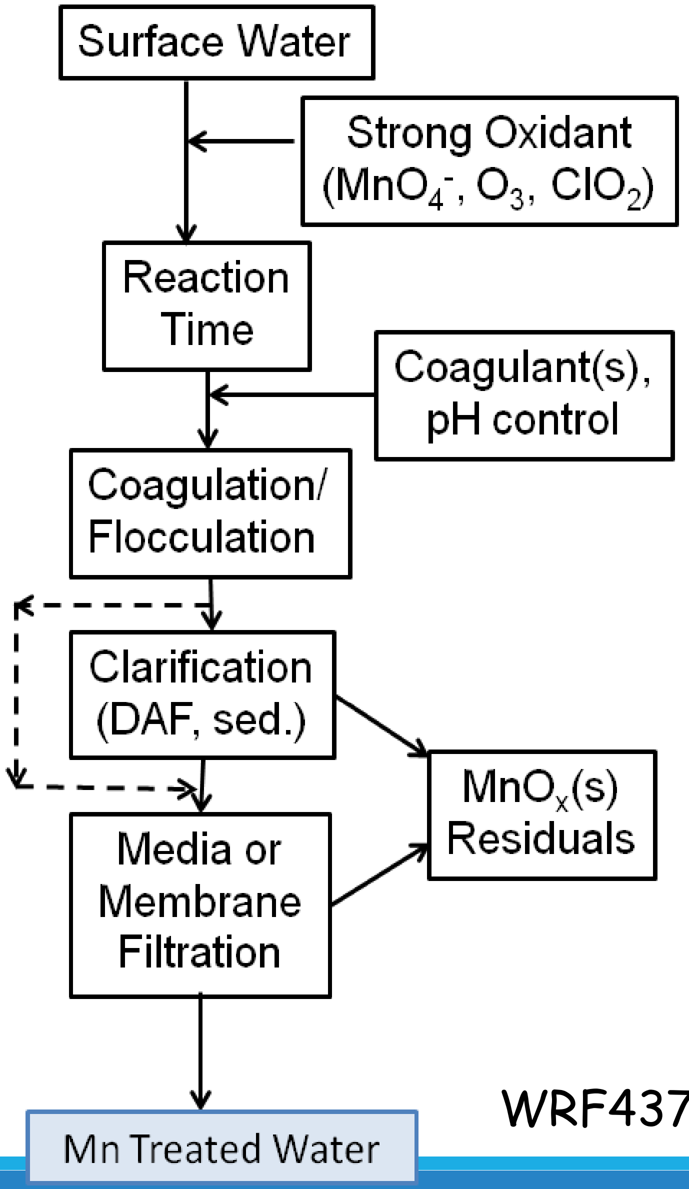
Full Suite of Mn Treatment Options



Removal by Chemical Oxidation Followed by Particle Filtration







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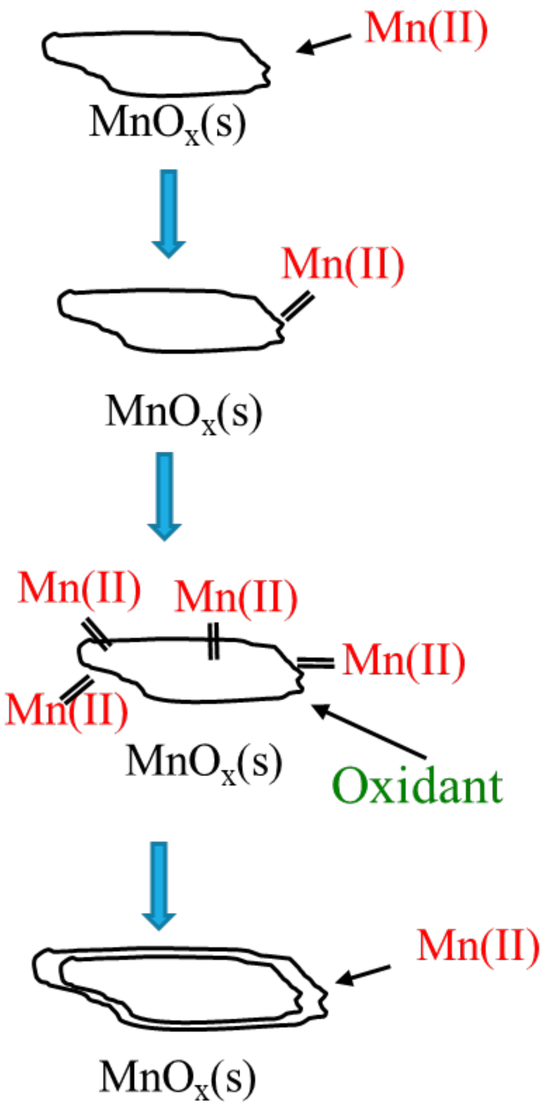
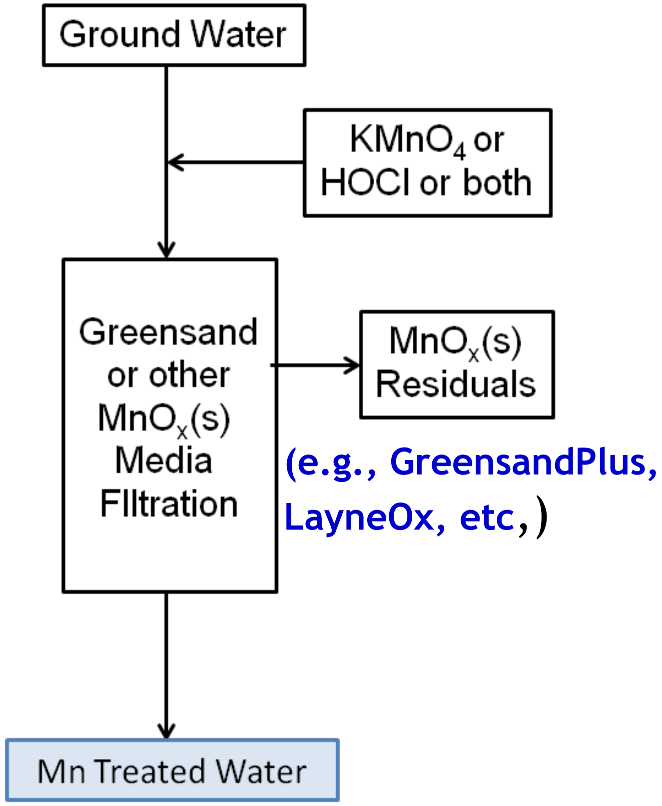
Comparison of Oxidants

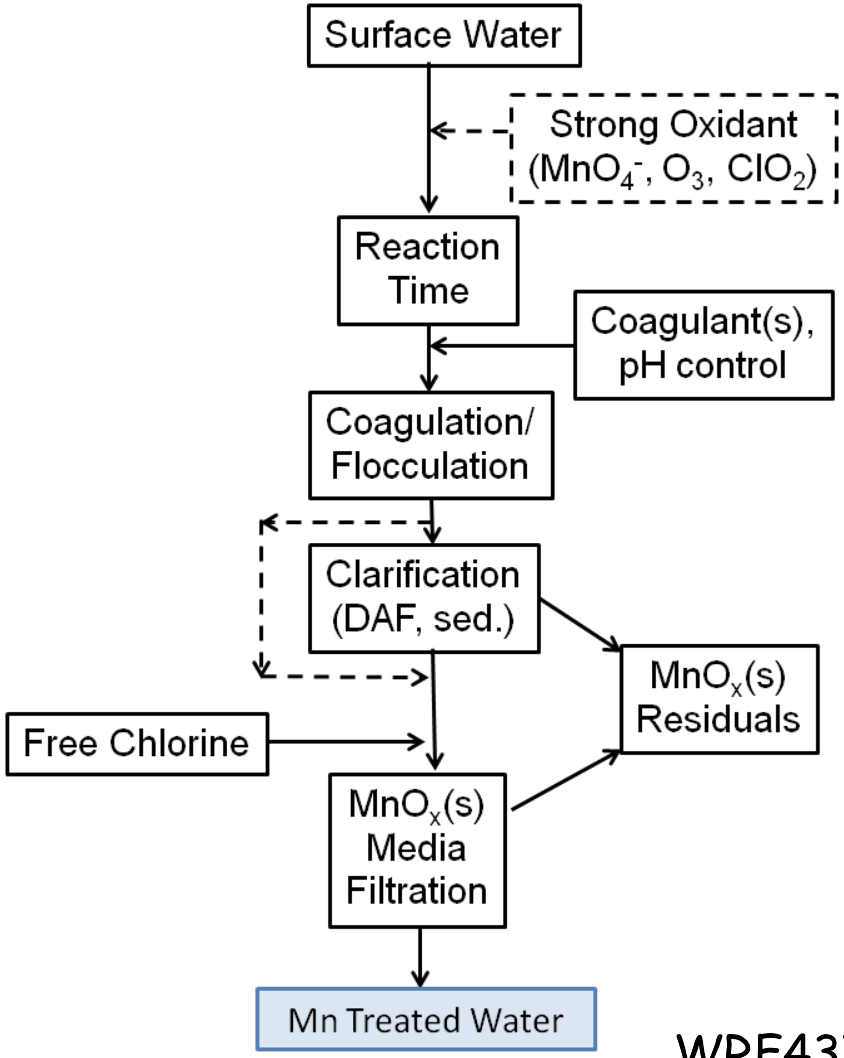
Strong Oxidant	Characteristics
Potassium Permanganate ($KMnO_4$) Sodium Permanganate ($NaMnO_4$)	• Easy to add • Overdose causes "pink" water • Adds Mn • Some T&O control
Chlorine Dioxide (ClO_2)	• Produce on-site • Limited by chlorite by-product MCL • Excellent disinfection, T&O control
Ozone (O_3)	• Produce on-site • Overdose may cause "pink" water • Bromate formation possible • Cannot reach very low Mn • Excellent disinfection, T&O control

The rate of Mn(II) oxidation by chlorine is too slow at moderate pH to form filterable MnO_x(s) particles – BUT sufficient to promote oxidation/deposition in distribution system

Removal by Sorption and Catalytic Oxidation on Media Surface







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Types of Media

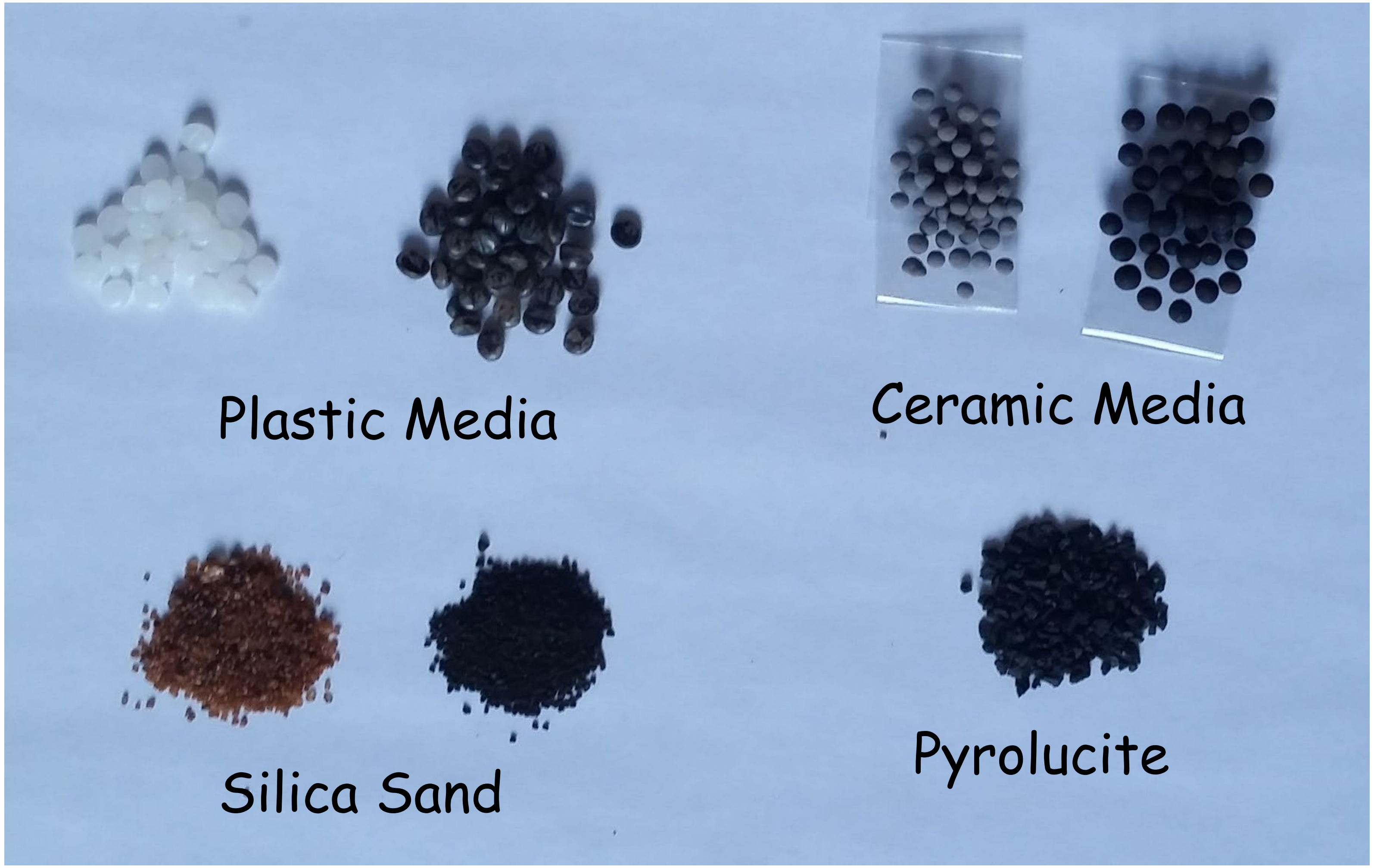


Photo J. Tobiason

Critical to Know Form of Mn

Form of Mn should be understood throughout Treatment process

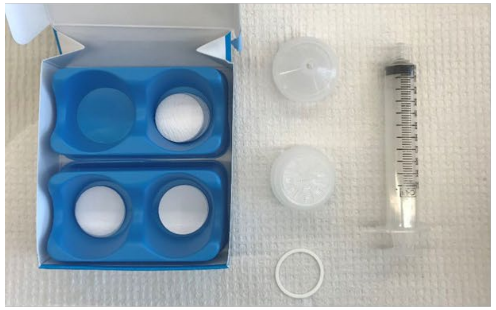
Particulate
= Total -[Colloidal +Dissolved]

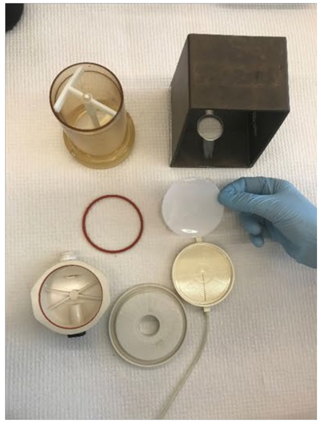
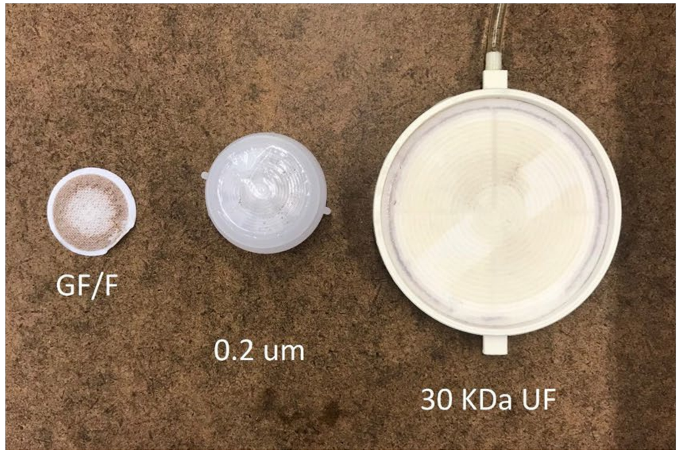
0.2 to 0.45 micron membrane filter

Colloidal
= (< 0.2 - 0.45 um) - (Dissolved)

30-100K molecular weight ultrafilter

Dissolved
= passing ultrafilter



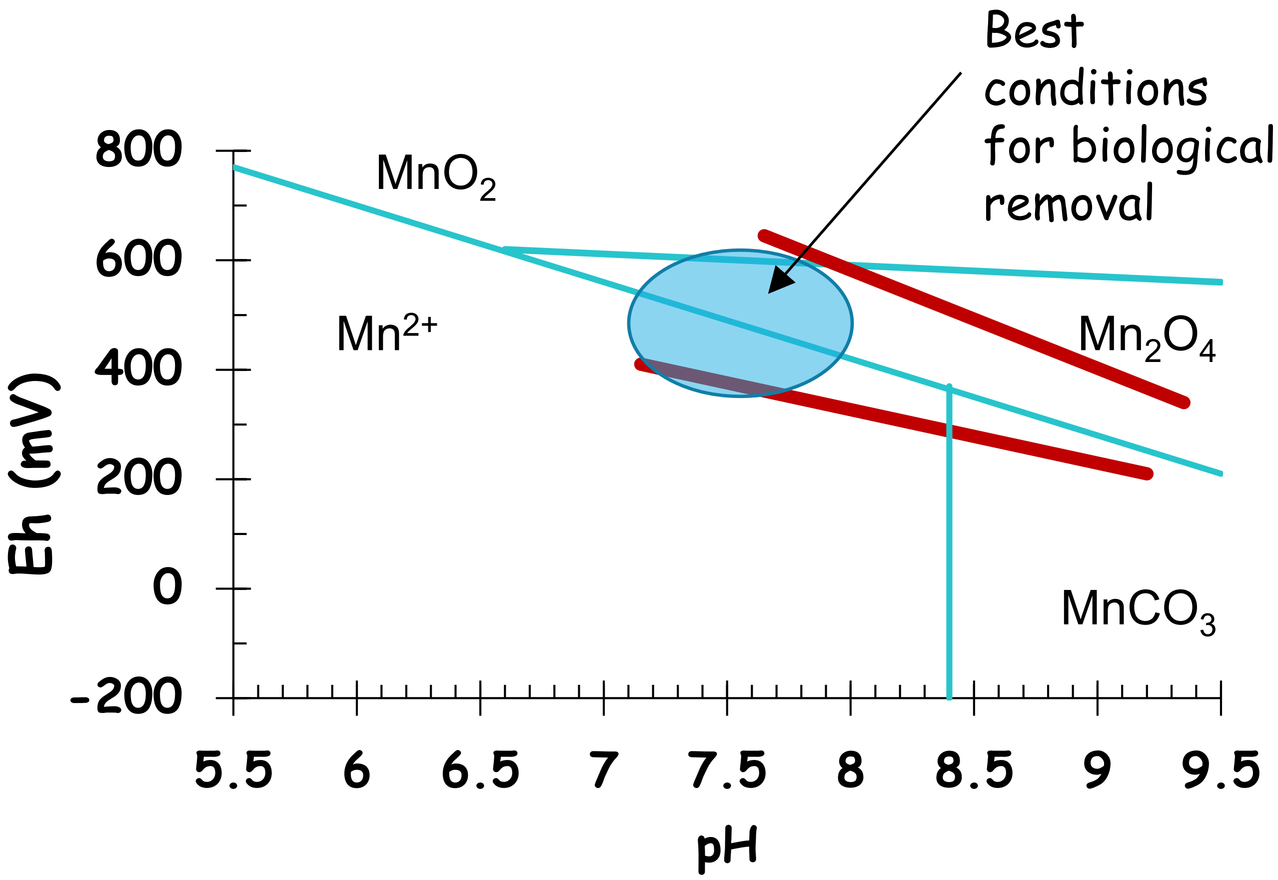



Courtesy J. Tobiason

Biological Treatment of Mn: Let Bugs do the Oxidizing

Unique considerations for each site

- Augmentation of nutrients to maximize removal
- Temperature dependence
- Head loss associated with biological activity
- Release of Mn if biological process interrupted
- Speed of restart after shutdown
- Media type/EBCT

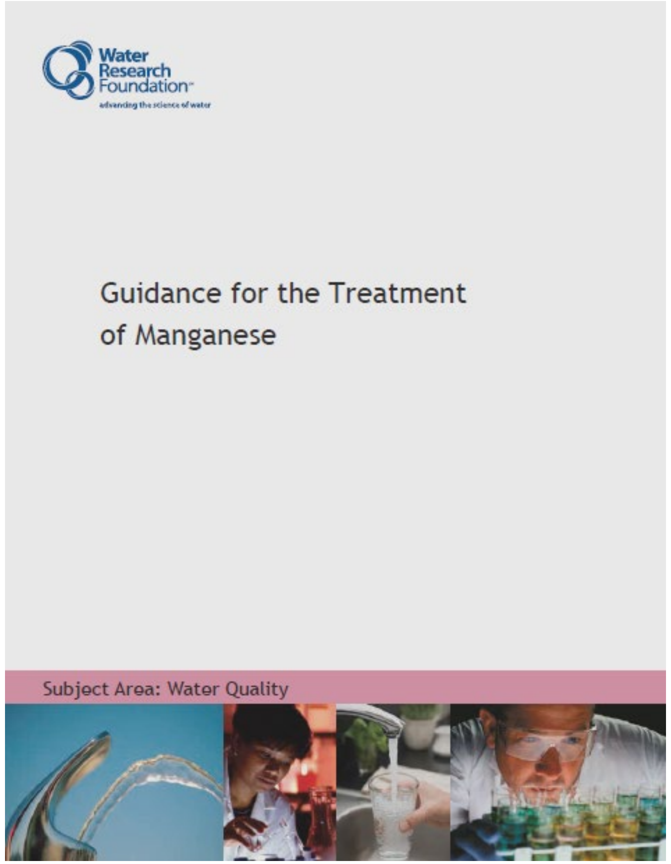


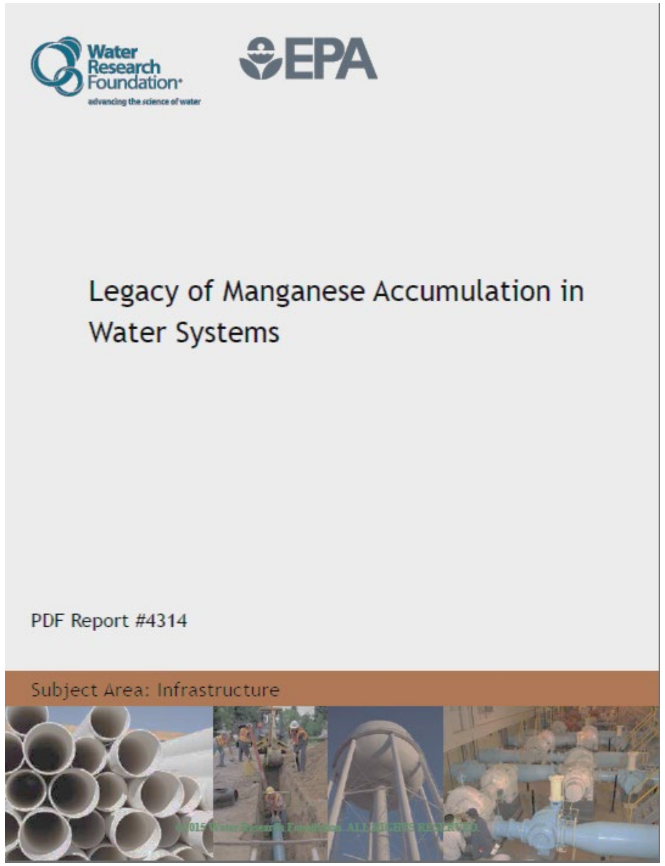
Adapted from Mouchet et al

Summing up

- Many mature technologies are capable of managing Mn to levels below 20 ug/L
  - Source water
  - Wellhead/plant
  - POU/POE
- Treatment choice/performance is function of Mn speciation and form
- Sequestration has significant drawbacks
  - May limit color issues
  - Does not mitigate other undesirable effects of Mn

Resources for Mn available from WRF Website





Collaborators
Bill Knocke
John Tobiason
Sarah Clark

Collaborators
Melinda Friedman
Andy Hill

Phil Brandhuber PhD
philbwater@gmail.com