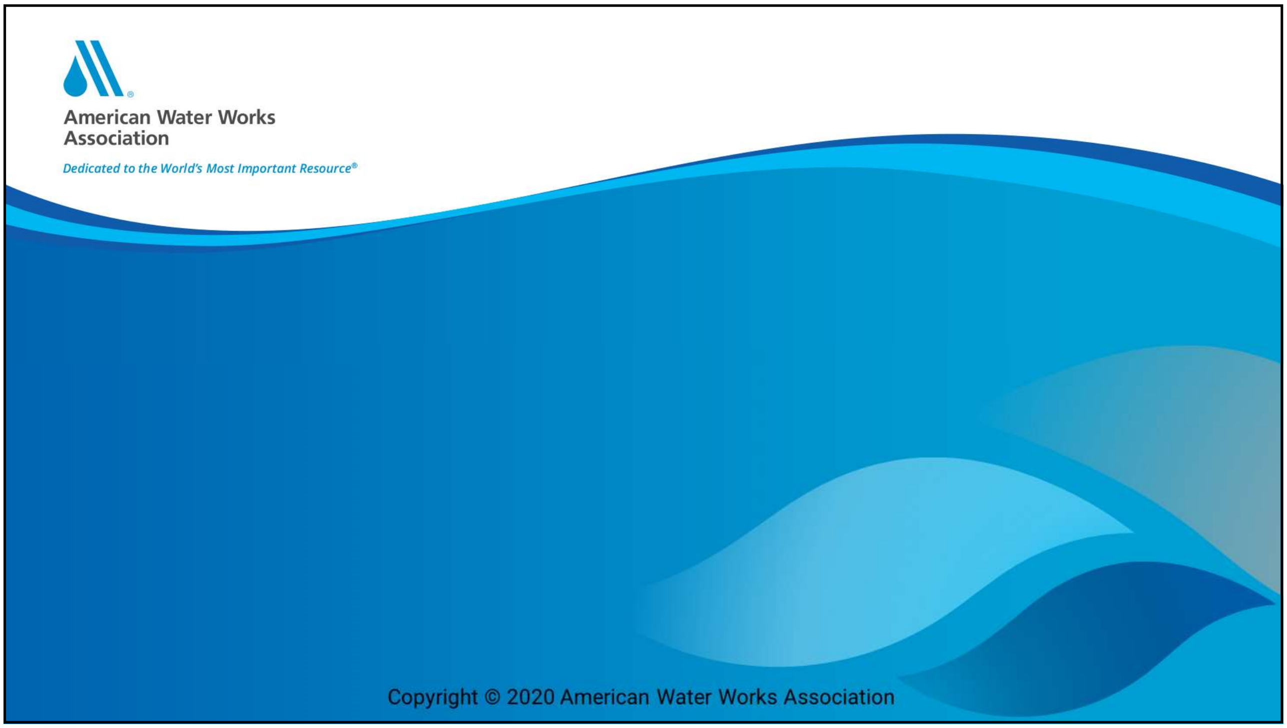
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WEBINAR MODERATOR

Milt Larsen

Project manager and Process Engineer

Kennedy/Jenks Consultants

Milt Larsen has a BS and MS in civil engineering from Kansas State University and is a licensed professional engineer in Washington, Oregon, and Hawaii. He is a project manager and process engineer for Kennedy/Jenks Consultants. Milt has conducted manganese treatment evaluations and designed manganese treatment facilities for over 30 years. Milt is a member of the AWWA Inorganic Contaminants Research Committee, Corrosion Control Committee, and chairs AWWA's Scale and Corrosion Control Chemicals Standards Committee. Milt participated in preparing AWWA Manual of Practice M58 Internal Corrosion Control and M64 Aeration and Air Stripping. Locally Milt is a member of the PNWS-AWWA Water Treatment Committee.

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PANEL OF EXPERTS

Phil Brandhuber
Chair of the AWWA Inorganics Committee

Milt Larsen
Project Manager and Process Engineer
Kennedy/Jenks Consultants

John Tobiason
Professor and Department Head of Civil and Environmental Engineering
University of Massachusetts at Amherst

7

7

AGENDA

A Review of Manganese in Drinking Water: Chemistry, Treatment, and Impact on Distribution Systems
Phil Brandhuber

Renton's Maplewood Well Field Water Quality Improvements
Milton Larson

Creative Process Combinations for Simultaneous Control of Mn, Fe and DBPs
John Tobiason

Time permitting – Q&A

Enter your **question** into the **question pane** at the lower right hand side of the screen.

Please specify to whom you are addressing the question.

8

8

A REVIEW OF MANGANESE IN DRINKING WATER: CHEMISTRY, TREATMENT, AND IMPACT ON DISTRIBUTION SYSTEMS

Phil Brandhuber PhD
BWQT LLC
PhilBWater@gmail.com

9

9

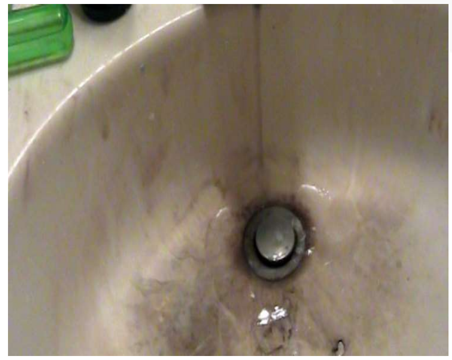
LEARNING OBJECTIVES

1. Review options available for the treatment of manganese (Mn)
   - Many effective methods for managing Mn
2. Appreciate issues caused by accumulated Mn in distribution systems
   - Aesthetic, operational and possibly health problems
3. Understand the inadequacy of Mn's current regulatory guidance
   - Mn should be managed to levels lower than the SMCL

10

10

Manganese can be beautiful



But not like this!

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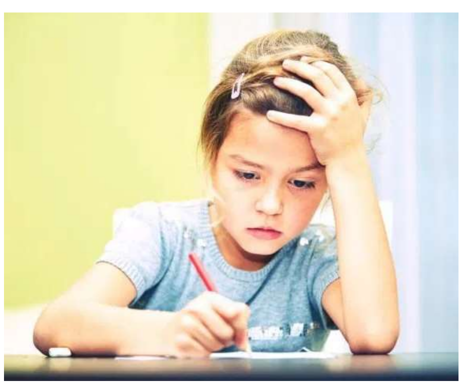
RESEARCH IS DOCUMENTING MORE SERIOUS PROBLEMS WITH MANGANESE



Reduced IQ

Behavior Problems

12

12

Mn CHEMISTRY – KEY FEATURES

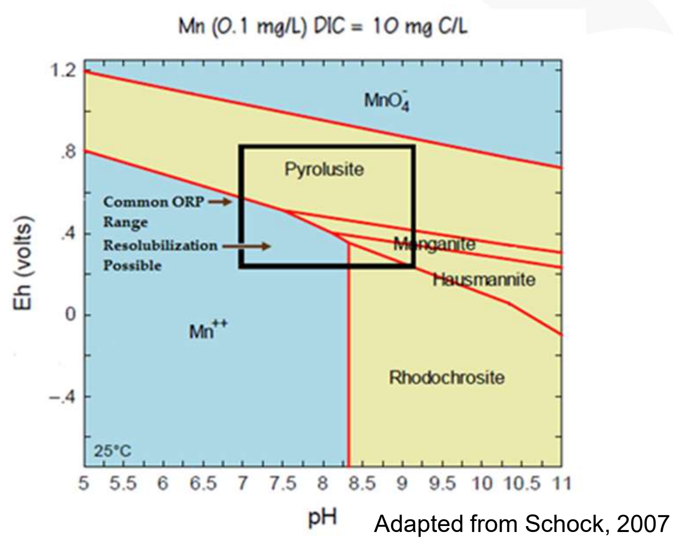
As a Contaminant		
Mn^{2+}	Manganous ion	• + II valance state • High solubility • Clear in water
MnO_x(s)	Manganese (di)oxide	• Combination of +III and + IV valance states • Low solubility • Discolors water - black or brown • Stains surfaces
As a Treatment Chemical		
$KMnO_4$ $NaMnO_4$	Potassium or sodium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

13

13

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 manipulating Eh and pH



Adapted from Schock, 2007

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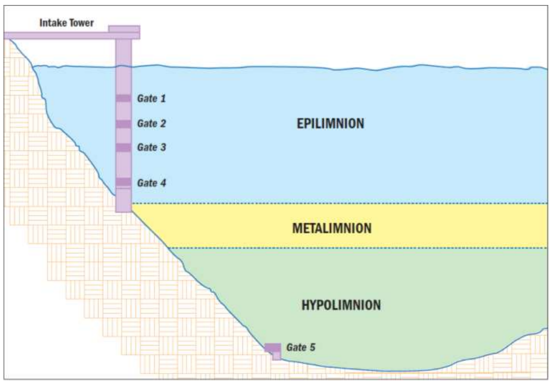
14

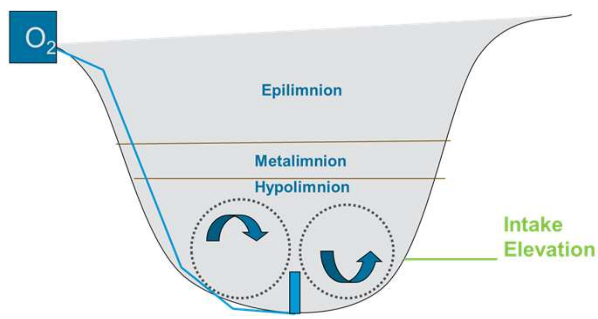
Mn CONTROL AT THE SOURCE – LAKES AND RESERVOIRS

Multiple intakes



Withdrawal at elevation with acceptable Mn levels

Reservoir aeration



Injection of O_2 controls soluble Mn by preventing its release from sediments into the hypolimnion

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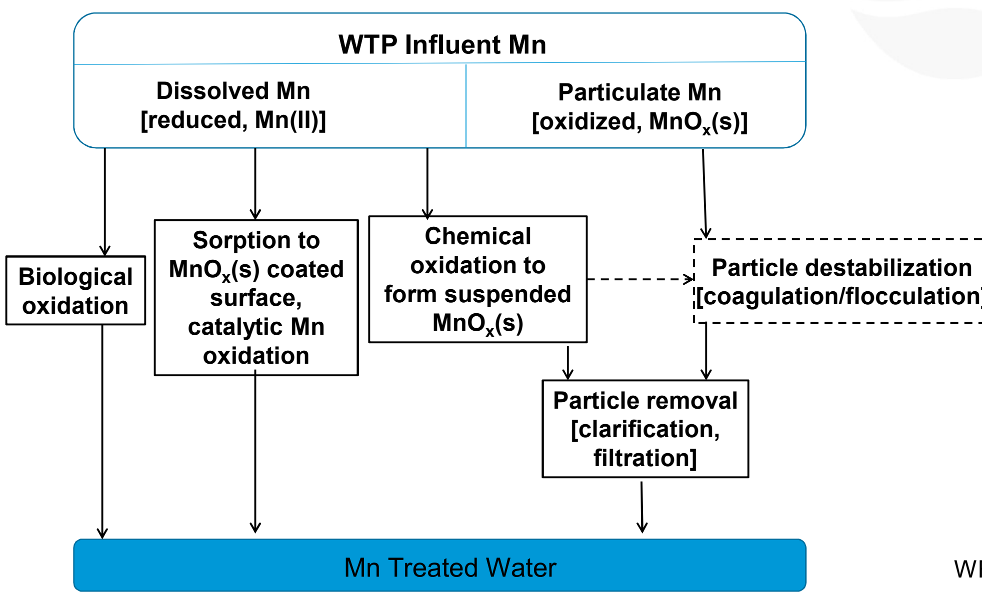
15

Mn PLANT TREATMENT OPTIONS



WRF4373

16

16

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

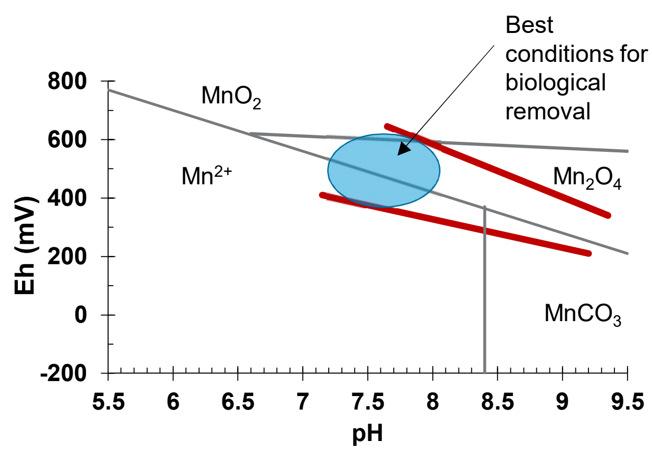
The rate of Mn(II) oxidation by chlorine is too slow at moderate pH to form filterable MnO_x(s) particles

17

17

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

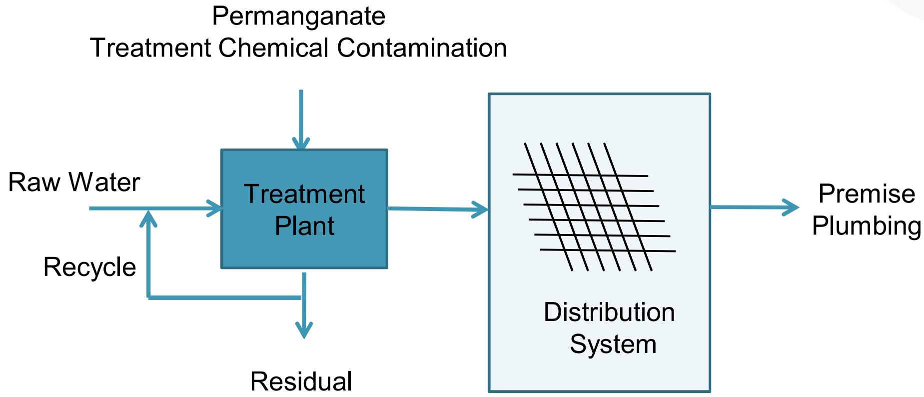


Adapted from Mouchet et al

18

18

SOURCES AND FATE OF MANGANESE



Accumulated manganese = Manganese in - Manganese out

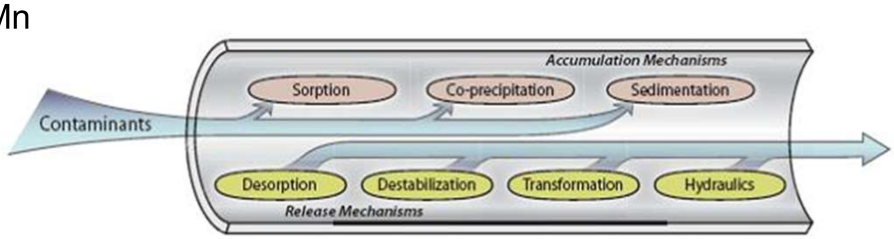
WRF 4314

19

19

LEGACY Mn IN THE DISTRIBUTION SYSTEM

- Large amount of Mn can accumulate in distribution system
- Impacts stability of corrosion scales in distribution system and premise plumbing
- Release can cause (focus of WRF 4314)
  - Colored water events
  - Customer exposure to regulated metals that were associated with Mn



Source: Hill et al., *JAWWA*, 2010

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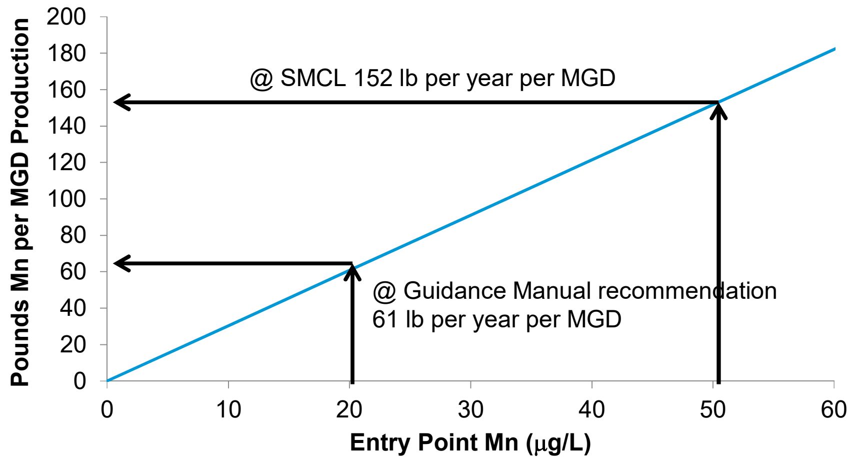
YEARLY Mn LOADING INTO DISTRIBUTION SYSTEM PER MGD PRODUCTION



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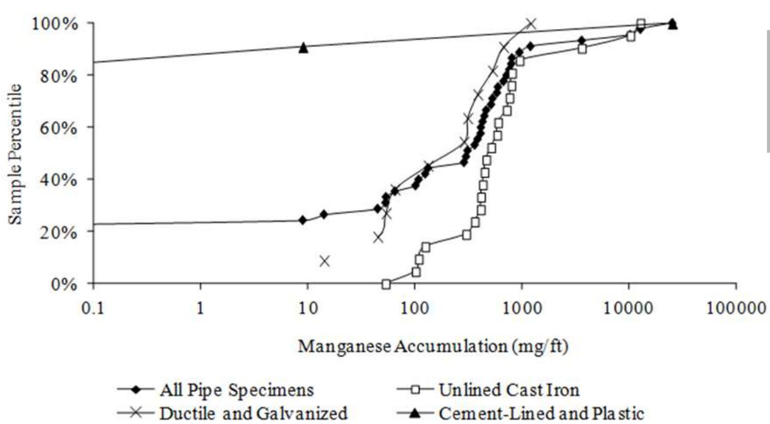
LEGACY Mn ACCUMULATES IN THE DISTRIBUTION SYSTEM



Median inventory (all pipes) of 300 mg/ft
- 3.8 lb/mile for 6-inch pipe
- 7.7 lb/mile for 12-inch pipe

Analysis by WRF 4314 of data collected by WRF 3118

22

22

IMPACTS OF Mn ON LEAD CORROSION AND RELEASE

Observation	Impact	Reference
Promotes formation amorphous lead scale	Weakens scale increasing risk of lead release	Schock et al. 2014
Interferes with formation of lead phosphate scales	Reduces effectiveness of orthophosphate as lead corrosion inhibitor	Schock 2017
Acts as lead scavenger	Vector for movement of particulate lead	Dong et al. 2000
Mn(IV) acts as electron acceptor for during lead oxidation	Release soluble lead	Trueman et al. 2019
Mn(II) catalyzes Pb(II) oxidation to Pb(IV) in presence of Cl_2	Possible benefit(!) of Mn by promoting formation of PbO_2	Pan et al. 2019
Use of polyphosphate to sequester Mn	Causes destabilization of lead scales and lead release	McNeill and Edwards 2004

23

23

CURRENT Mn REGULATORY ENVIRONMENT

Agency	Type	Level (mg/L)
USEPA	Maximum Contaminant Level (MCL)	None
	Secondary Maximum Contaminant Level (SMCL)	0.05
	Life-time Health Advisory (HA) Adult	0.3
	1- and 10-Day HA Adult	1.0
	10-Day HA Child	0.3
Health Canada	Maximum Acceptable Concentration (MAC)	0.12
	Aesthetic Objective Level	0.02
World Health Organization	Aesthetic Guideline	0.05
European Union	Indicator Parameter	0.05

Mn Treatment Guidance Manual (WRF4373) recommendation - 0.015 to 0.02 mg/L

24

24

INADEQUACY OF CURRENT Mn SMCL

- EPA rational for Mn SMCL is based on aesthetic effects
  - “Black to brown color; black staining; bitter metallic taste”
- Research does not support aesthetic effects at 0.05 mg/L
  - Mn (IV) color can occur at 10x < SMCL (Sain et.al.)
  - Mn(II) is transparent at many times > SMCL
  - Taste threshold is at least 50x > SMCL (Sain et.al.)
- Current SMCL is counterproductive
  - Technically wrong
  - May be misleading – Mn exposure is not ‘self protective’

25

25

EPA HEALTH ADVISORY VS. CANADIAN MAC

- EPA Health Advisory (2004)
  - Based on nutritional studies completed between 1966 – 1989
- Health Canada’s Maximum Acceptable Concentration (2019)
  - Based on health effects studies completed between 2007 – 2014
    - Arrested intellectual development, increase in hyperactivity decrease in IQ, decreases in memory and motor function performance
- Neurological impacts of Mn on childhood development well documented
  - > 30 papers published between 2002 - 2016 (Coetzee et al. 2016)
- In future
  - Health Advisory may not be considered protective of health

26

26

LEARNING OBJECTIVES

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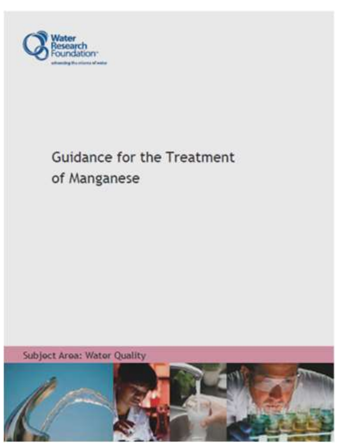
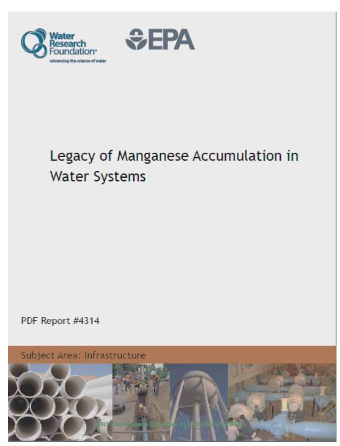
27

27

RESOURCES FOR Mn AVAILABLE FROM WRF WEBSITE (FREE!)



Collaborators
Bill Knocke
John Tobiason
Sarah Clark



Collaborators
Melinda Friedman
Andy Hill

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28

KJ
Kennedy Jenks

RENTON'S MAPLEWOOD WELLFIELD WATER QUALITY IMPROVEMENTS

Milt Larsen, PE
Kennedy/Jenks Consultants, Inc.

29

29

OBJECTIVES

- Increase understanding of water quality issues caused by manganese and other contaminants often found with manganese
- Treatment options one utility used to improve water quality and customer satisfaction that are applicable to other systems with similar issues

30

30

AGENDA

- Renton Maplewood Wellfield background and water quality issues
- What did not work
- Pilot testing program
- Improvements that increased customer satisfaction
- Lessons learned

31

31

MAPLEWOOD WELLFIELD

- Developed in response to a series of UGST leaks, pipeline leak, & overturned fuel truck near their major wellfield
- Located in a golf course
- 3 wells – 5,500 gpm
- Water treatment plant
- Booster pump station

32

32

Maplewood Water Quality

- Manganese 0.07 to 0.12 mg/L
- Sulfides 0.12 to 0.20 mg/L
- Ammonia 0.4 to 0.5 mg/L
- Organic Nitrogen ?
- Iron 0.04 mg/L
- Elevated pH 8.1 to 8.4
- High chlorine demand

33

33

Previous Water Treatment Work

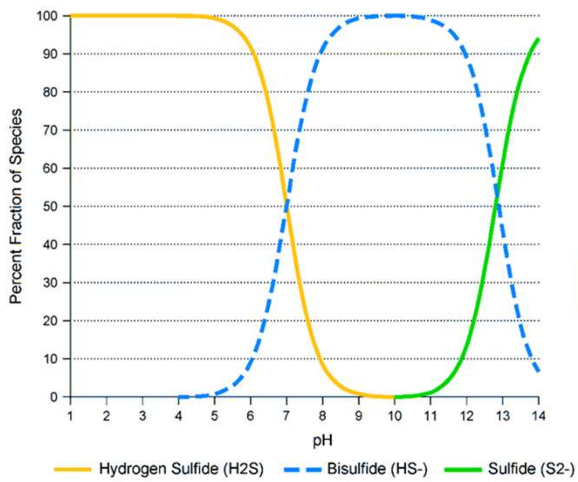
- Water Treatment Facility
  - H_2SO_4
  - Air Stripping of H_2S
  - Caustic Soda
  - Mn Sequestering
  - Chloramination

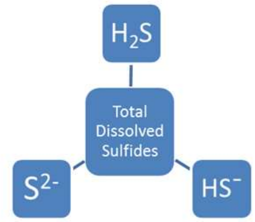
34

34

Sulfide Treatment Issues

- High H_2SO_4 required to convert HS^- to H_2S
- High NaOH dose
- DI corrosion failure at H_2SO_4 injection point
- Odors on golf course
- Corrosion inside water treatment facility
  - Hardware
  - Electrical panels
- Taste & odor complaints





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Ammonia & Mn Issues

- Missing Cl_2 residual
- Segregated distribution system - chloraminated & free chlorine
- Poor Mn sequestering

36

36

Goals

- Eliminate complaints due to Mn staining
- Eliminate sulfide odors at the golf course
- Improve the taste & odor of the water
- Produce water with a free chlorine residual for systemwide use
- Continued Pb & Cu Rule compliance

37

Water Treatment Evaluation

- Manganese
  - Adsorption/catalytic oxidation
- Sulfide
  - Oxidation
  - GAC
- Ammonia
  - Clinoptilolite
  - Breakpoint chlorination
- Taste & flavor evaluation

38

38

Pilot Testing

39

39

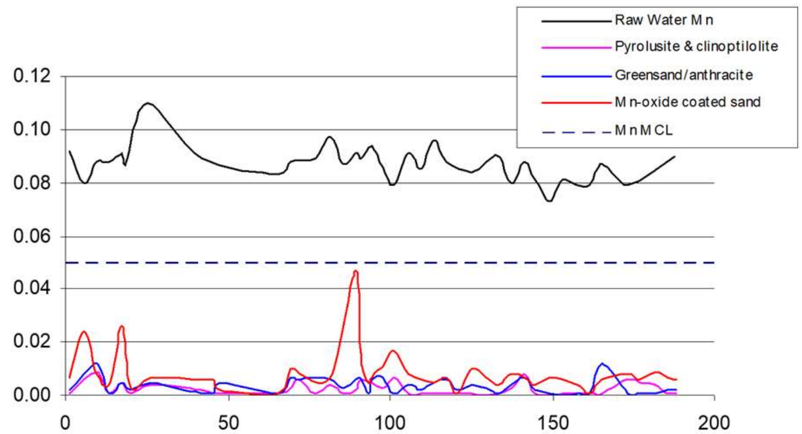
Manganese Removal

- Adsorption/catalytic oxidation
  - Pyrolusite (36”)
  - Greensand (15”) & anthracite (21”)
  - Mn-oxide coated silica sand (15”) & anthracite (21”)
- Oxidant - sodium hypochlorite
- Piloted at 4 to 12 gpm/SF
- All filter media performed well

40

40

Mn Removal – Media Comparison



41

41

Mn Removal Run 5

- Target filter loading rate – 12 gpm/SF
- Filter Run – 7.7 days
- UFRV – 108,000 to 120,000 gal/SF
- Cl_2 Dose – 5 mg/L

	Clino + Pyro	Greensand	Silica Sand
Mn	0.001	0.003	0.007
Sulfide	0.001	0.002	0.002
Free Cl_2	1.02	0.75	1.22
Total Cl_2	2.14	>2.2	>2.2

42

42

Clinoptilolite Ammonia Adsorption

- High cation exchange natural zeolite
- Preferentially adsorbs ammonia
- Uses
  - Water & wastewater treatment
  - Swimming pool filters
  - Livestock feed additive
  - Nuclear & mine waste treatment
  - Soap & detergent
  - Turf grass & athletic fields
  - Pet & stable litter

43

43

Ammonia – Clinoptilolite Adsorption

- Upstream of Mn removal
- Regenerate
  - 4 lb NaCl/ lb NH_3
  - 20 days per run
- EBCT – 12.5 minutes
- Good NH_3 removal at 3 gpm/SF
- Performance deteriorated at higher loading rates

44

44

Ammonia - Breakpoint Chlorination

- High & variable chlorine demand
- Theoretical Cl_2:NH_3 7.6:1
- Bench study Cl_2:NH_3 >10:1
- Post Mn filter contact time
- Initially targeted 0.5 to 1.0 mg/L free Cl_2 in Mn filter effluent
- No or very low Cl_2 residual in the morning
- Breakpoint reaction incomplete in the Mn filter
- Increased treated water Cl_2 residual target

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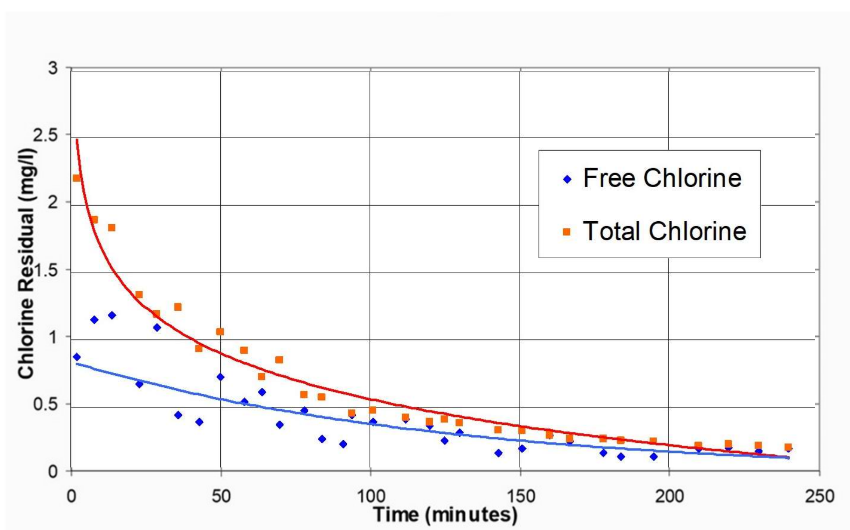
Chlorine Decay Curve



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46

Sulfide Removal Options

- Aeration
- Oxidation
  - Cl_2 2.1 to 8.3 mg/mg sulfide
  - Yields sulfur, polysulfides, sulfites, and sulfate
  - Polysulfide formation requires thiosulfate addition followed by rechlorination
- Oxidation/Filtration
- Catalytic GAC

47

47

GAC Adsorption & Catalytic Oxidation of Sulfide

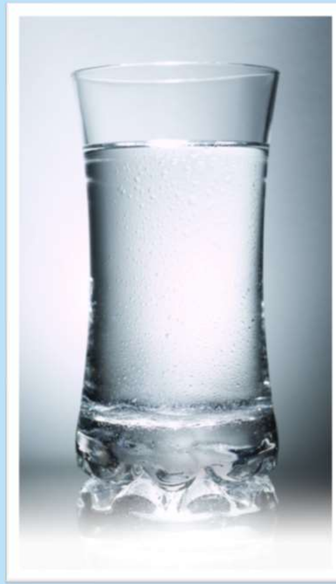
- Precede chlorination
- Adsorbs sulfides
- Catalyzes oxidation of sulfides to sulfate
- Dissolved O_2 required
- Excess dissolved O_2 to maintain aerobic conditions
- 3 to 5 minute EBCT
- Reduced sulfide from 0.12 to 0.002 mg/L
- Backwash 8 to 10 gpm/SF
- Bacterial growth

48

48

Taste & Flavor Evaluation

- Panel of City personnel & Maplewood customers
- Taste Ranking
    1. Awful
    2. Poor
    3. Mediocre
    4. Good
    5. Very Good
- Identified flavors for low rated water (<4)



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Taste & Flavor Testing

- Control – Bottled water
- City Hall – Downtown wells (gold standard)
- Maplewood Zone (City Shops)
- Clinoptilolite treated
- Clino + adsorption/catalytic filtration
- Clino + adsorption/catalytic filtration + bisulfite + Cl_2
- GAC + adsorption/catalytic filtration + breakpoint Cl_2

50

50

Taste & Flavor Test Scores

Water	Same Day	Next Day
Bottled Water	3.9	
City Hall	4.1	
Maplewood (shops)	3.3	
Pyrolusite	2.1	2.9
Greensand	2.7	2.9
Silica Sand	2.6	3.1
Clino + Pyro + Bisulfite +Cl_2	1.9	3.8
GAC + Greensand	3.5	3.9

51

51

Recommended Improvements

- Sidestream aeration
- Catalytic GAC
  - Sulfide oxidation to SO_4^{2-}
- Chlorination
- Adsorption/Catalytic Oxidation
  - Fe and Mn removal
- Breakpoint Chlorination
  - 90 minute contact basin
- Rechlorination

52

52

Lessons Learned

- Mn sequestering performed poorly
- High Mn filter loading rates possible with multiple media
- Biological growth in the GAC
  - Replaced upper 12 inches of GAC
  - Increased backwash frequency to weekly
- Including customers from the area receiving Maplewood water in the taste & odor panel was considered beneficial

53

53

Acknowledgements

JD Wilson

Ray Sled

Greg Pierson

54

54

Creative Process Combinations for Simultaneous Control of Mn, Fe and DBPs

John E. Tobiason, PhD, PE (NH), BCEE
(tobiason@umass.edu)
Professor and Head, Department of Civil & Environmental Engineering
University of Massachusetts at Amherst

AWWA Webinar
"Manganese: Exploring Treatment Technologies"

May 14, 2020

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Overview Comments

- "ironandmanganese" is NOT a word, or an element!
  - Manganese (Mn) Iron (Fe)
  - Separate, and different – understand that!
- Mn and/or Fe removal is a very common need, but complexities often ignored, "myths" perpetuated
- *Lack of characterization of <u>forms</u> of Mn/Fe in water (dissolved to aggregate continuum) can lead to problems, but characterization often not done, may not be inexpensive or easy.*
- Creative approaches can result from knowledge of transport & reaction fundamentals combined with data-based assessment for the source water

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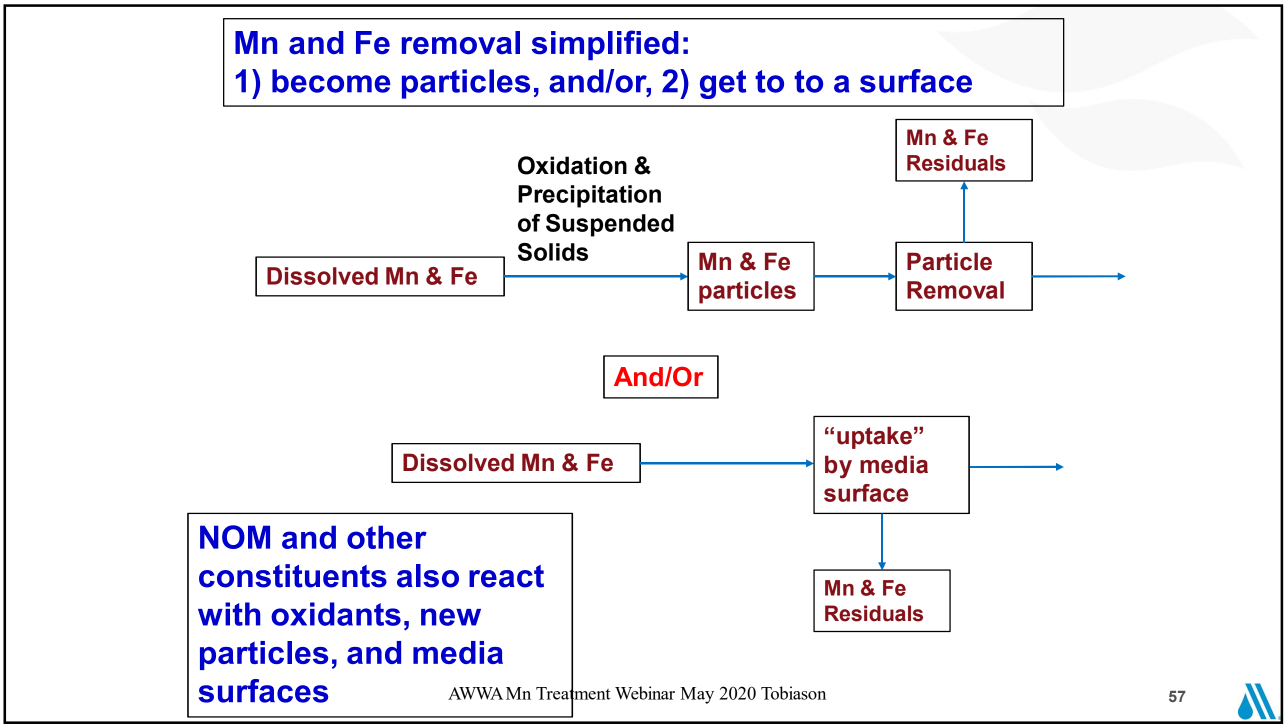
Mn and Fe removal simplified:
1) become particles, and/or, 2) get to to a surface
Dissolved Mn & Fe
Oxidation & Precipitation of Suspended Solids
Mn & Fe particles
Particle Removal
Mn & Fe Residuals
And/Or
Dissolved Mn & Fe
"uptake" by media surface
Mn & Fe Residuals
NOM and other constituents also react with oxidants, new particles, and media surfaces
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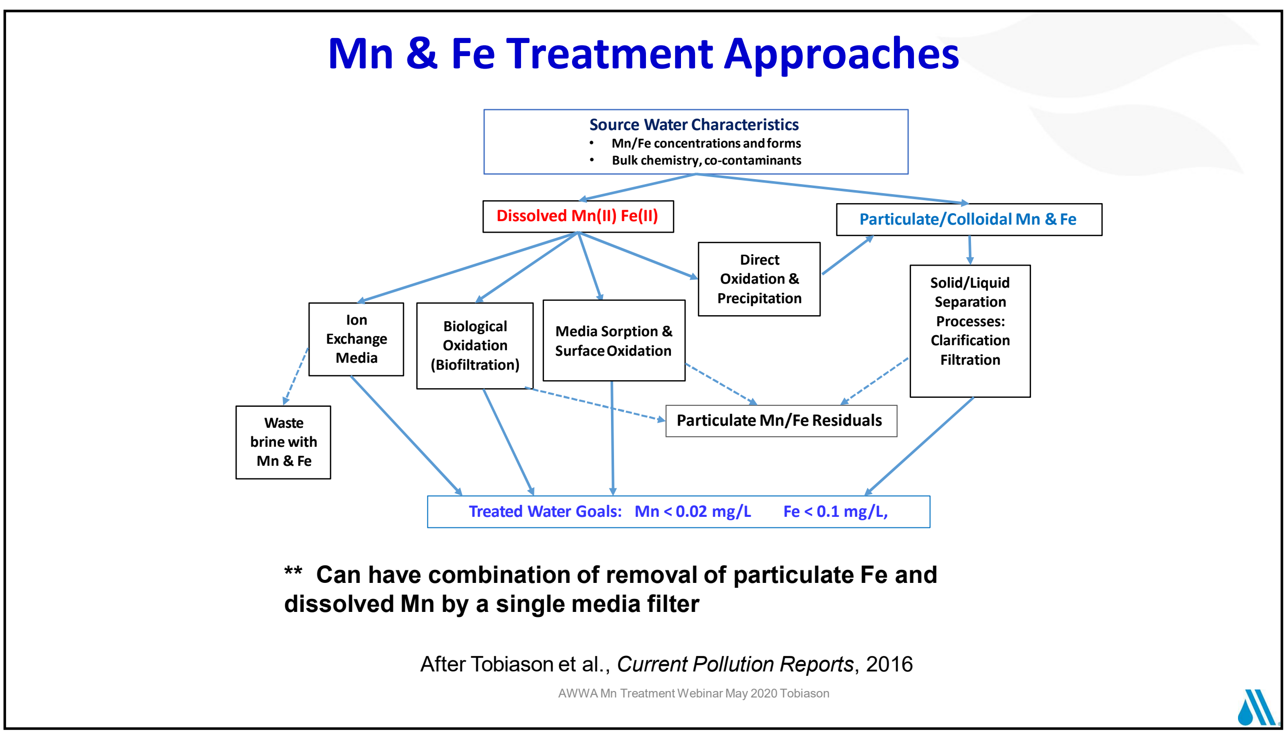
57

57


Mn & Fe Treatment Approaches
Source Water Characteristics
Mn/Fe concentrations and forms
Bulk chemistry, co-contaminants
Dissolved Mn(II) Fe(II)
Particulate/Colloidal Mn & Fe
Direct Oxidation & Precipitation
Solid/Liquid Separation Processes: Clarification Filtration
Ion Exchange Media
Biological Oxidation (Biofiltration)
Media Sorption & Surface Oxidation
Waste brine with Mn & Fe
Particulate Mn/Fe Residuals
Treated Water Goals: Mn < 0.02 mg/L Fe < 0.1 mg/L,
** Can have combination of removal of particulate Fe and dissolved Mn by a single media filter
After Tobiason et al., Current Pollution Reports, 2016
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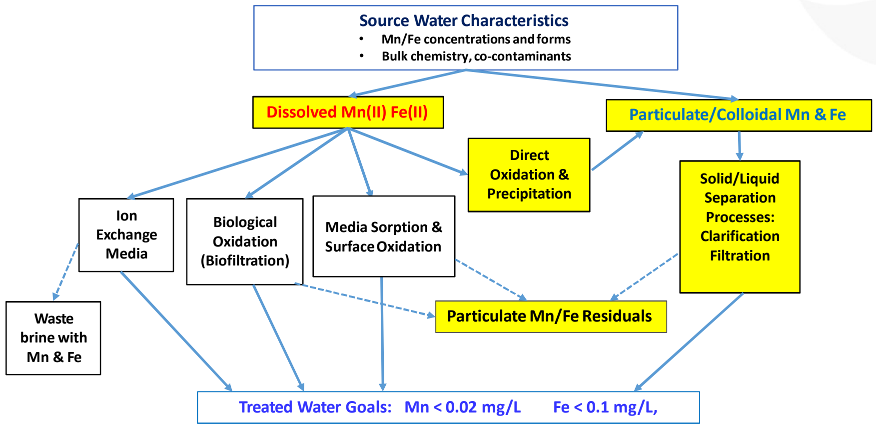
58

Mn & Fe Treatment Approaches



**** Can have combination of removal of particulate Fe and dissolved Mn by a single media filter**

After Tobiason et al., *Current Pollution Reports*, 2016

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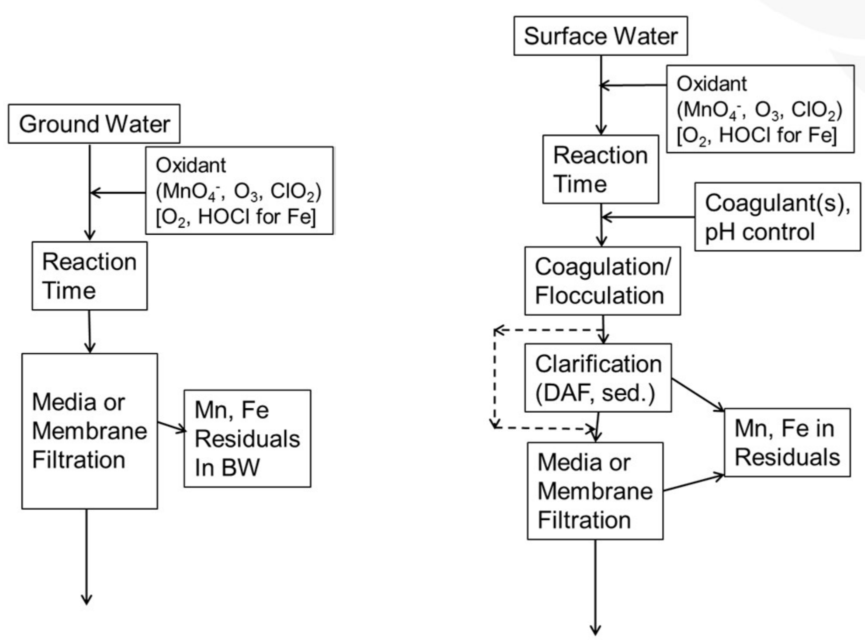
Chemical Oxidation and Particle Removal Process Schematics



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Forms of Mn and Fe in Water

- **Critical to know form of metal to design/operate treatment**
  - **Forms in raw water: select/design processes, operate well**
  - **Forms after any "chemical" addition: oxidant, pH control, coagulants (controls performance of subsequent process)**
- **Particulate, Colloidal, Dissolved: Operational Definitions**
  - **Field or laboratory filtration of samples**

↓

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

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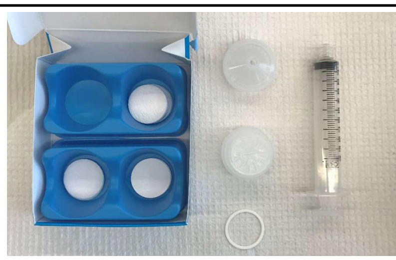

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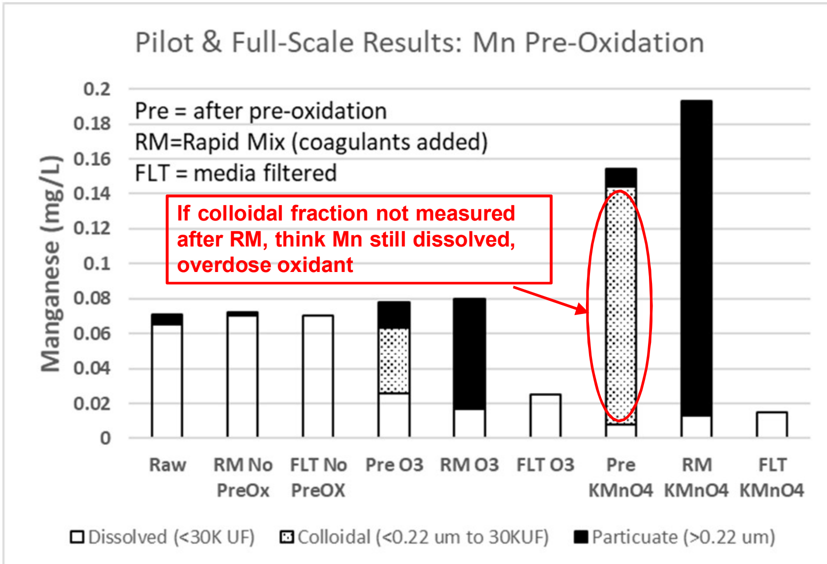
62

- $KMnO_4$ & O_3 make colloids; coagulation destabilizes/aggregates; media filters remove



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63

Chemical Oxidation & Particle Removal (1)

- ***Stoichiometry: add the right amount of oxidant***
  - ~ twice as much oxidant per mg of Mn as needed per mg of Fe (2 (Mn(II) to Mn(IV)) versus 1 (Fe(II) to Fe(III)) electron transfer per mole; similar atomic wgts: Mn (55) Fe (55.9))
  - must also satisfy competing oxidant demand (NOM, other reactive reduced species), so usually add in excess of stoichiometric amount (varies with oxidant and water quality, needs experimental assessment)
  - creation of particles may result in unexpected dosing impacts, especially in waters with both Mn & Fe

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64

Chemical Oxidation & Particle Removal (2)

- ***Reaction kinetics: have enough time***
  - **rate is typically affected by oxidant, pH, temperature, competing demands**
  - **Because Fe oxidation rate so fast relative to Mn, can add just enough oxidant (especially chlorine) to only oxidize Fe, but not Mn**
  - **And, Fe oxidized faster than DBP formation from HOCl + NOM reactions, so can target Fe oxidation only in raw water with NOM, but must NOT have a chlorine residual**

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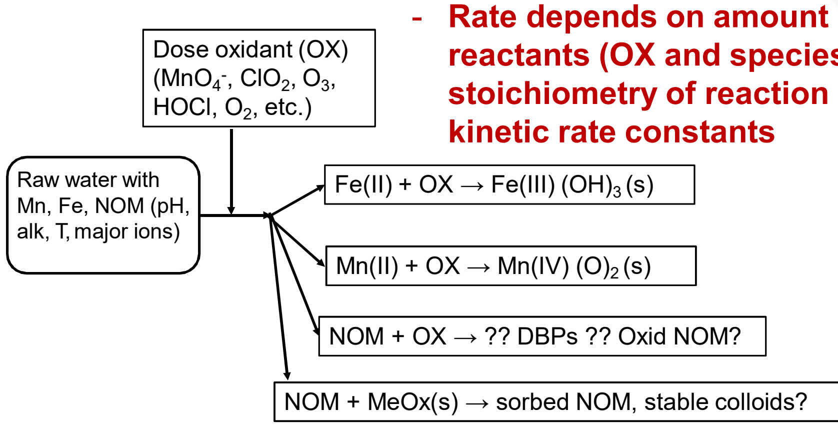
65

Treatment of waters with Mn and Fe and NOM

Multiple parallel reactions
- **Fastest reaction wins!**
- **Rate depends on amount of reactants (OX and species), stoichiometry of reaction and kinetic rate constants**



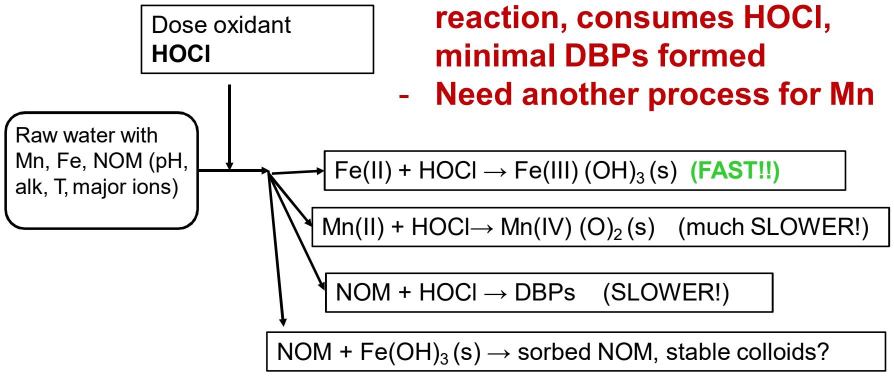
We do not get to choose the reactions we want versus those we do not want – need to carefully engineer & operate for the outcome we want!

66

Example: Waters with Mn and Fe and NOM, pre-oxidation with free chlorine

Chlorine: inexpensive, convenient, but leads to DBPs

- **Dose only enough HOCl to oxidize the Fe(II). Fast reaction, consumes HOCl, minimal DBPs formed**
- **Need another process for Mn**



By dosing design and operation, we get the desired result (oxidation of Fe with HOCl) without undesired DBP formation, then need separate approach for Mn

67

Dissolved Mn & Fe Removal by Media Surfaces
Fundamental (simplified) concept

Water with dissolved Mn(II), Fe(II)

↓

Possible oxidant, acid/base dosing →

↓

Tank/bed of granular media.
(pressure or gravity)
Metal cation uptake on media surface
(metal oxide, IX, biofilm)
[*and/or combined particle deposition*]

↓

Water with low [Mn] , [Fe]

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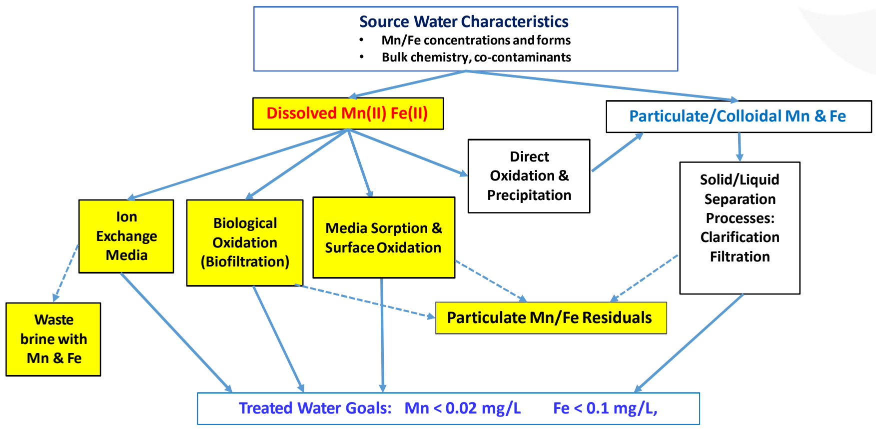
68

Mn & Fe Treatment Approaches



** Can have combination of removal of particulate Fe and dissolved Mn by a single media filter

After Tobiason et al., *Current Pollution Reports*, 2016

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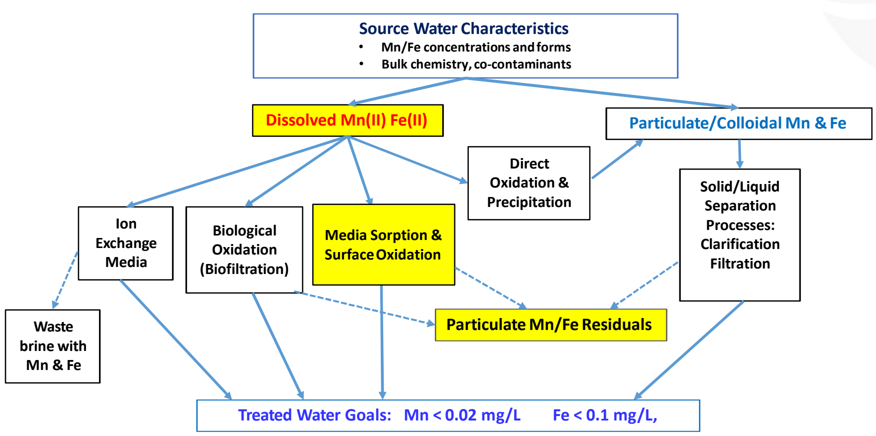
69

Mn & Fe Treatment Approaches



** Can have combination of removal of particulate Fe and dissolved Mn by a single media filter

After Tobiason et al., *Current Pollution Reports*, 2016

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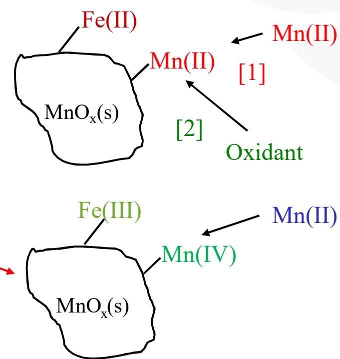
70

Sorption and Surface Oxidation

Two step process:

1) **Sorption of reduced Mn(II) (or Fe(II))**
   Removes dissolved Mn(II), Fe(II)
2) **Oxidation at surface**
   Regenerates media surface
   New sorption sites created



Oxidation

- **Continuous Regeneration (CR)**
  Oxidant always in media influent
  If get direct oxidation, then need particle removal (destabilization too maybe)
  For Mn & oxide surface, HOCl works well, O_2 not effective, strong oxidants make colloids & risk of undesired oxidant residual in effluent
  Fe removal typically/mostly by particle formation & deposition in CR case
- **Intermittent Regeneration (IR)**
  Sorbed metals & metal oxide surface oxidized by oxidant in backwash, $KMnO_4$ most commonly used (only clear situation for Fe(II) sorption)

71

Sorption and Surface Oxidation: Metal Oxide Surfaces

Three general "classes" of Applications
Typically Mn-Oxide media surface, catalyzes Mn oxidation by free chlorine

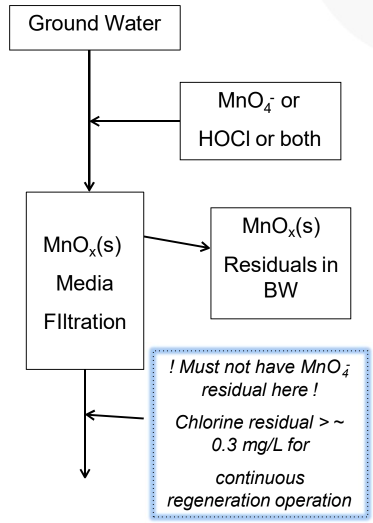
- **"greensand filtration" approach (often GW) (smaller media, pressure filters)**
  - **Mn & Fe; intermittent or continuous regeneration**
  - **Often combined Fe-particle removal & Mn sorption/surface oxidation**
- **oxide-coated media filtration (often SW) (typical particle removal media)**
  - **Primary media role is particle removal**
  - **Mn removal by Mn-oxide on media surface**
- **second stage (post-filter) contactor (coarse media, high HLR)**
  - **Primary media role is removal of dissolved Mn by sorption and surface oxidation; no particle removal expected**

72

1) Typical “Greensand” Approach (A)

Pre-Oxidant Addition

- Pre-oxidant may oxidize reduced Mn(II) prior to filter; now have particle filtration, NOT sorption! Particle stability (charge) may affect subsequent removal.
- Often the case for MnO_4^- (or ClO_2 or O_3) but rarely for HOCl
- If present, Fe(II) usually oxidized to particles, much faster than Mn(II), and by all oxidants (except O_2 sometimes)



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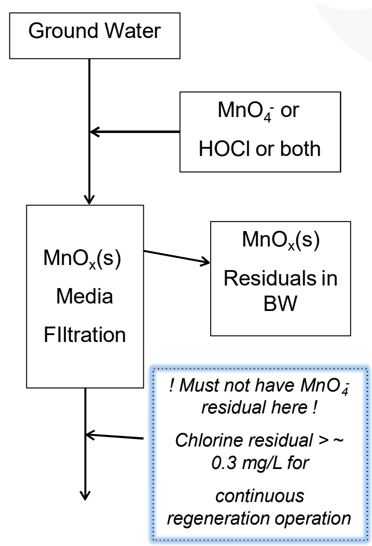
73

Typical “Greensand” Approach – (B)

Media Regeneration

- Continuous with HOCl effective, robust.
- Continuous with MnO_4^- challenging, risky. MnO_4^- arriving at media must be reduced to MnO_x(s) by serving as oxidant or it exits as “pink water”. MnO_x(s) created within media may not deposit
- Continuous MnO_4^- & HOCl
- <u>Intermittent regeneration</u> provides sorption sites, but sorption capacity is finite (breakthrough concerns).



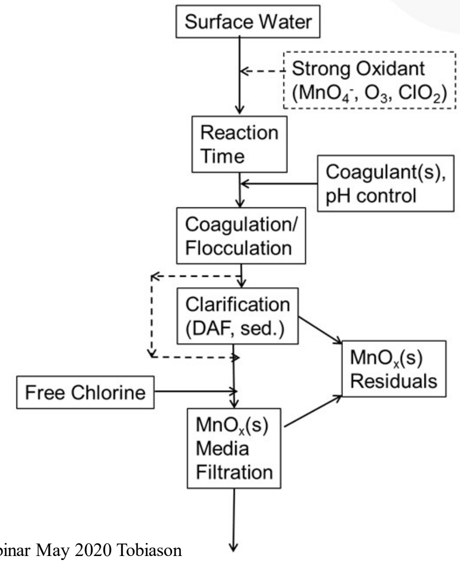
74

2) Mn via oxide-coated media filters used for particle removal

Key: adsorption & oxidation of soluble Mn^{2+}

- media coated with Mn oxide, naturally or intentionally (in-situ or as purchased)
- Mn^{2+} forms surface complex and is then rapidly oxidized by free chlorine from solution
- Regenerates oxidized MnO_x (s) coating for additional uptake of reduced Mn (so, autocatalytic)

- Some Mn-oxide coating removed with backwashing, but process very stable, slow or no net accumulation
- Easy to operate, robust
- Possible DBP concerns



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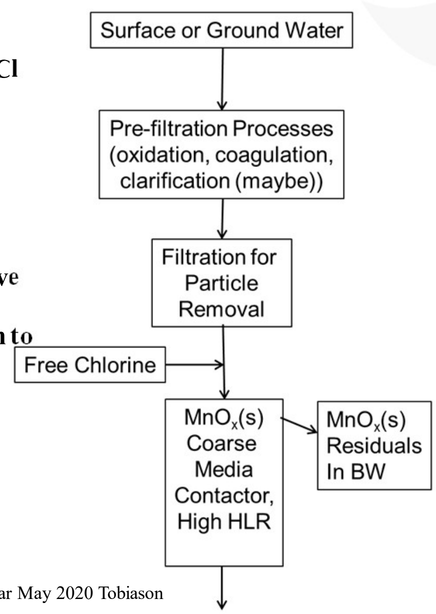
75

3) Mn removal via Post-filter Contactor

- **Concerns for prior approaches:**
  - Increase in DBPs due to pre-filter HOCl
  - Possible release of Mn if intermittent HOCl application
- **The "opportunity" for control w/ HOCl:**
  - First use a media filter for particle removal only – no HOCl. May also have pre-oxidation by strong oxidant for conversion of Fe and some (most?) Mn to particles.
  - Then use a media "contactor" with continuous HOCl addition for Mn uptake



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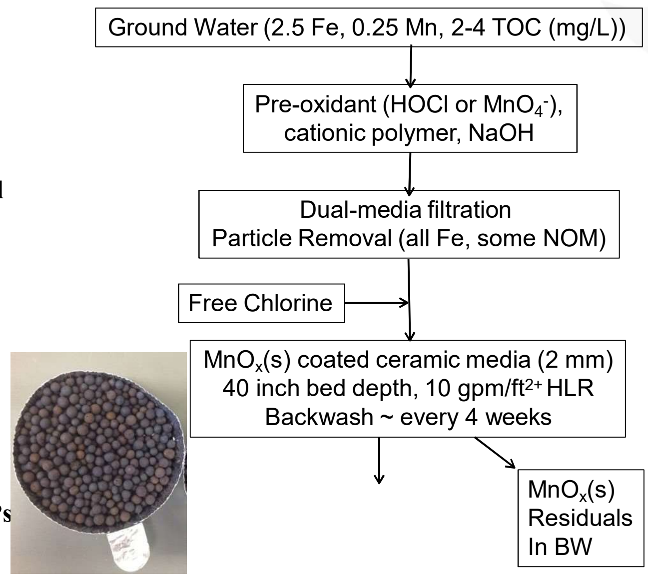
76

Fe, Mn and NOM by Two-Stage Process (particles & sorption) (Lantern Hill WTP, Aquarion Water Company of CT)

- **Prior to 2013**
  - Single stage filtration, pre-HOCl, $KMnO_4$, NaOH, polymer
  - Significant HOCl filter effluent residual required to avoid Mn release
  - High DBPs
- **July 2013**
  - New two stage process implemented
  - Much lower DBPs



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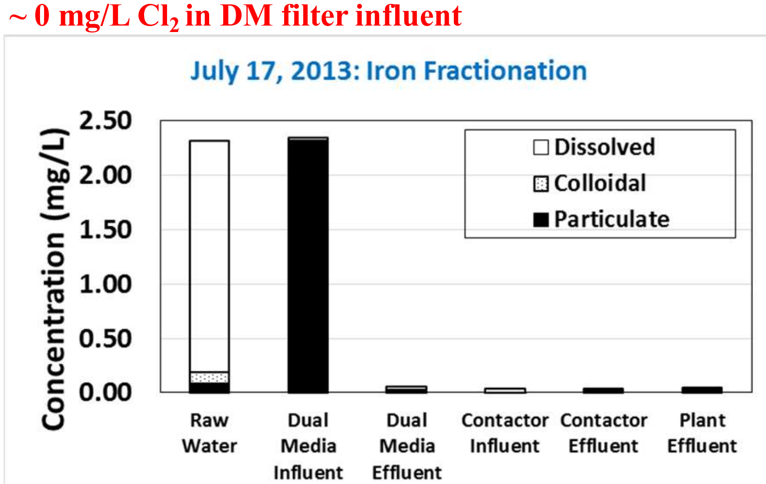
77

Fe Across the AWC LH Plant

- Raw water: nearly all Fe dissolved (Fe(II))
- 3 mg/L NaOCl dose to raw water converts all Fe to particulate form (Fe(III), $Fe(OH)_3$), removed by DM filter
- ~ 0 mg/L Cl_2 in DM filter influent



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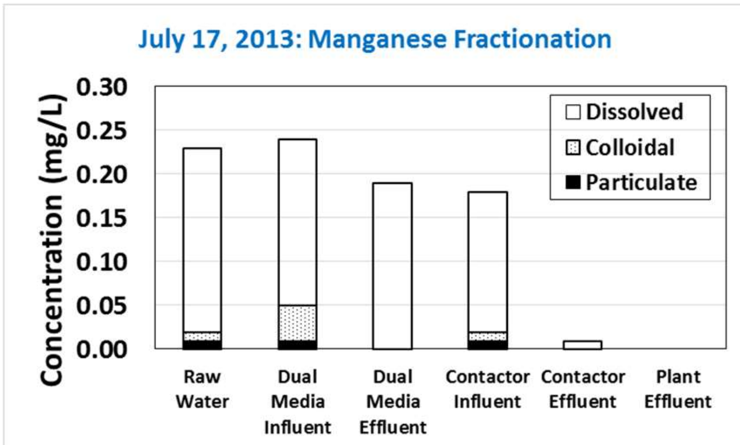
78

Mn Across the AWC LH Plant

- Raw water: nearly all dissolved (Mn(II)
- Pre-NaOCl does not oxidize much Mn, minor removal by DM filter
- Contactor influent has ~ 1.3 - 1.6 mg/L Cl_2, Mn mostly dissolved, removed across contactor



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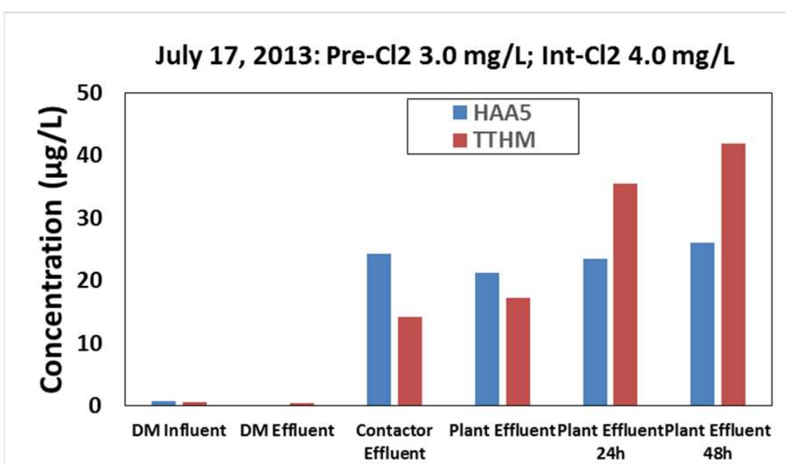
79

DBPs Across The AWC Lantern Hill Plant

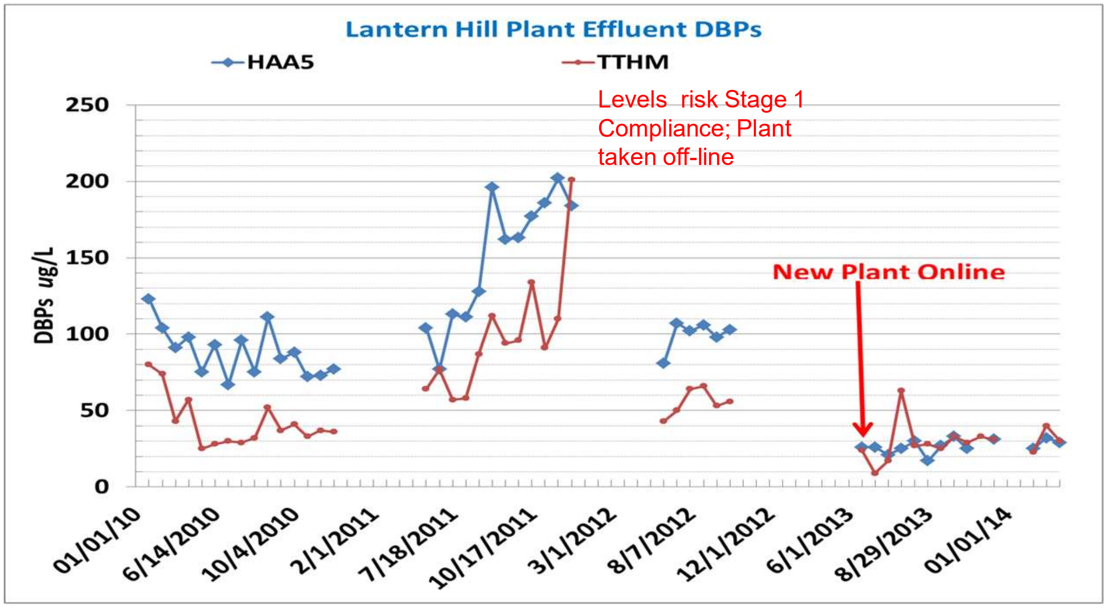
- Pre-chlorine: oxidizes Fe(II), does not form significant DBPs (as long as dose only for Fe(II) oxidation!)
- Removal of 1 to 2 mg/L TOC by DM filter; intermediate chlorine yields acceptable DBP levels



80

80

Historical Plant Effluent DBPs



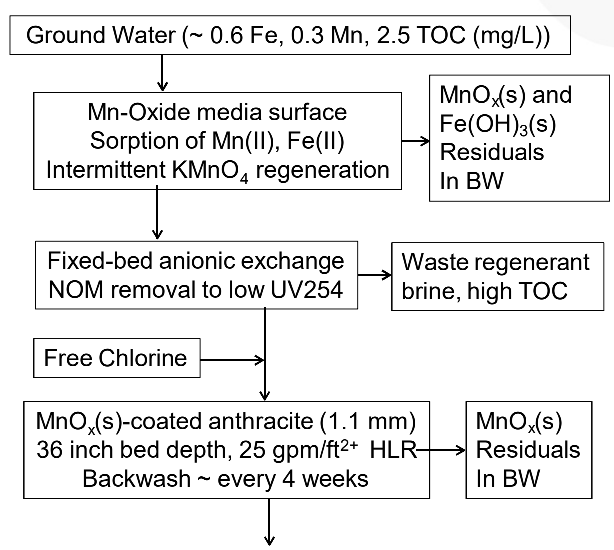
81

81

Fe, Mn and NOM by Three-Stage Process (3 different media!)

Brunswick Topsham Water District (ME) Jackson Station

- **Current Process**
  - **Single stage intermittently regenerated MnOx media, no NOM removal**
- **New facility (2021)**
  - **Extensive piloting led to selection of robust 3-stage process for Mn & DBP control**
  - **4 MGD Q_{design}**
  - **Free Cl_2 in DS**
  - **BTWD has other source using IX for Mn(II) and Fe(II) removal**



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82

Mn/Fe Control: Co-Constituent Issues - 1

Mn (II)/Fe(II) and ?	Related Issues/Constraints
Mn or Fe only	Many options available, few constraints; metal level main factor in option selection
Mn(II) and Fe(II)	Oxidant demands; Fe(II) oxidized first/faster than Mn(II); additional solids; two electron acceptors for microbial oxidation; O_2 & HOCl effective Fe(II) oxidants, but not for Mn(II)
NOM	Oxidant demand; impacts size & stability of ppt'd metal particles; may constrain how or if free chlorine is used in removal processes due to Cl-DBPs

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83

Mn/Fe Control: Co-Constituent Issues - 2

Mn (II)/Fe(II) and ?	Related Issues/Constraints
Arsenic (As)	As(III) to As(V) by oxidant; As removal often by Fe-oxides; As usually an oxy-anion, not cation
Radionuclides	Sorption or IX processes may be affected by Mn(II) or Fe(II) presence
Hardness (Ca^{2+}, Mg^{2+})	Controls IX processes; ppt at high pH; sequestering chemical demand;
Multiple!	Complicated parallel oxidation/reduction, precipitation, and sorption processes! Have fun!

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84

Impact of Other Treatment Objectives on Mn/Fe Control - 1

Objective	Constraints & Opportunities Related to Mn/Fe
Primary Disinfection	-Ozone and chlorine dioxide also effective dissolved Mn(II) oxidants; not true for free chlorine without an MnO_x(s) surface also. If free chlorine used, rational to combine with sorption & catalytic oxidation. - UV: dissolved Fe/Mn potential sleeve foulants
Coagulation	Opportunity to destabilize & aggregate MnO_x(s) and $Fe(OH)_3$(s) particles created prior to coagulation. pH control objectives may enhance or hinder metal oxidation relative to raw water conditions. ~ no removal of dissolved Mn(II) or Fe(II)

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85

Impact of Other Treatment Objectives on Mn/Fe Control - 2

Objective	Constraints & Opportunities Related to Mn/Fe
Intermediate Ozonation	Ozone after coag/floc/clarification great for decreased ozone demand. May have oxidation of Mn(II) to colloids, or even to Mn(VII) (pink water). Likely to require coagulant addition prior to media filtration.
Particle Removal	Method selection influences location and oxidant selection for creation of MnO_x(s) and $Fe(OH)_3$(s) .
Non-Mn biofiltration	Essentially eliminates sorption and catalytic oxidation with free chlorine on biofilter media for Mn(II) removal

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86

Acknowledgments

- Professor William Knocke, VA Tech (got me into this topic ~ 33 years ago!)
- Students (many!)
- Water utilities (especially Aquarion Water Company and Brunswick Topsham Water District) and funding agencies
- UMass colleagues Dave Reckhow & Jim Edzwald

87

Stoichiometry of Oxidation – Mn (atomic mass = 54.94 g/mole)

Oxidant	Reaction for Oxidation of Mn(II) to Mn(IV)	Stoichiometry (mg ox/mg Mn)
O_2 (aq)	$Mn^{2+} + ½ O_2 + H_2O \rightarrow MnO_2(s) + 2H^+$	0.29
$O_3 \rightarrow O_2$ (aq)	$Mn^{2+} + O_3 + H_2O \rightarrow MnO_2(s) + O_2 + 2H^+$	0.88
Cl_2 (HOCl)	$Mn^{2+} + HOCl + H_2O \rightarrow MnO_2(s) + Cl^- + 3H^+$	1.30
$ClO_2 \rightarrow ClO_2^-$	$Mn^{2+} + 2ClO_2 + 2H_2O \rightarrow MnO_2(s) + 2ClO_2^- + 4H^+$	2.45
MnO_4^-	$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2(s) + 4H^+$	1.44
$KMnO_4$ $NaMnO_4$	As above for MnO_4^- As above for MnO_4^-	1.92 1.72
FeO_4^{2-} ferrate, Fe(VI)	$3Mn^{2+} + 2FeO_4^{2-} + 4H_2O \rightarrow 3MnO_2(s) + 2Fe(OH)_3(s) + 2H^+$	1.45

88

Stoichiometry of Oxidation – Fe (atomic mass = 55.85 g/mole)

Oxidant	Reaction for Oxidation of Fe(II) to Fe(III)	Stoichiometry (mg ox/mg Fe)
O_2 (aq)	$2Fe^{2+} + ½ O_2 + 5H_2O \rightarrow 2Fe(OH)_3(s) + 4H^+$	0.14
$O_3 \rightarrow O_2$ (aq)	$2Fe^{2+} + O_3 + 5H_2O \rightarrow 2Fe(OH)_3(s) + O_2 + 4H^+$	0.43
Cl_2 (HOCl)	$2Fe^{2+} + HOCl + 5H_2O \rightarrow 2Fe(OH)_3(s) + Cl^- + 5H^+$	0.64
$ClO_2 \rightarrow ClO_2^-$	$Fe^{2+} + ClO_2 + 3H_2O \rightarrow Fe(OH)_3(s) + ClO_2^- + 3H^+$	1.20
MnO_4^-	$3Fe^{2+} + MnO_4^- + 7H_2O \rightarrow 3Fe(OH)_3(s) + MnO_2(s) + 5H^+$	0.71
$KMnO_4$ $NaMnO_4$	As above for MnO_4^- As above for MnO_4^-	0.94 0.85
FeO_4^{2-} ferrate, Fe(VI)	$3Fe^{2+} + FeO_4^{2-} + 8H_2O \rightarrow 4Fe(OH)_3(s) + 4H^+$	0.71

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89

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Phil Brandhuber

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90

90

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91

91

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92

92

PRESENTER BIOGRAPHY INFORMATION

Phil Brandhuber - *Phil specializes in drinking water quality and treatment. His work has involved inorganic contaminants, disinfection byproducts, potable reuse and brine management. Phil received his PhD from the University of Colorado Boulder, and has been the principal or co-principal investigator for ten research projects sponsored by the Water Research Foundation and other agencies. He is the current chair of the AWWA Inorganics Committee and past chair of the AWWA Emerging Water Quality Issues Committee. Phil has 20 years' experience as a consultant, working for McGuire Environmental and HDR. When not working on water quality issues, he can be found hiking and biking in the Colorado mountains.*

Milt Larsen - Milt Larsen has a BS and MS in civil engineering from Kansas State University and is a licensed professional engineer in Washington, Oregon, and Hawaii. He is a project manager and process engineer for Kennedy/Jenks Consultants. Milt has conducted manganese treatment evaluations and designed manganese treatment facilities for over 30 years. Milt is a member of the AWWA Inorganic Contaminants Research Committee, Corrosion Control Committee, and chairs AWWA's Scale and Corrosion Control Chemicals Standards Committee. Milt participated in preparing AWWA Manual of Practice M58 Internal Corrosion Control and M64 Aeration and Air Stripping. Locally Milt is a member of the PNWS-AWWA Water Treatment Committee.

John Tobiason - *John E. Tobiason is Professor and Department Head of Civil and Environmental Engineering at the University of Massachusetts at Amherst. BS in Civil Engineering University of New Hampshire (1976), MS in Environmental Engineering University of North Carolina at Chapel Hill (1979), PhD in Environmental Engineering Johns Hopkins University (1987). Past President of AEESP and past Chair of the AWWA Water Science Research Division Board of Trustees. He is a registered Professional Engineer (NH), and a Board Certified Environmental Engineer by the AAEES.*

93

93

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