Evaluation of manganese oxide-modified activated carbon (MOMAC) for treatment of mercury contaminated sediments

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Manganese Oxide Affect the Fate of Contaminants

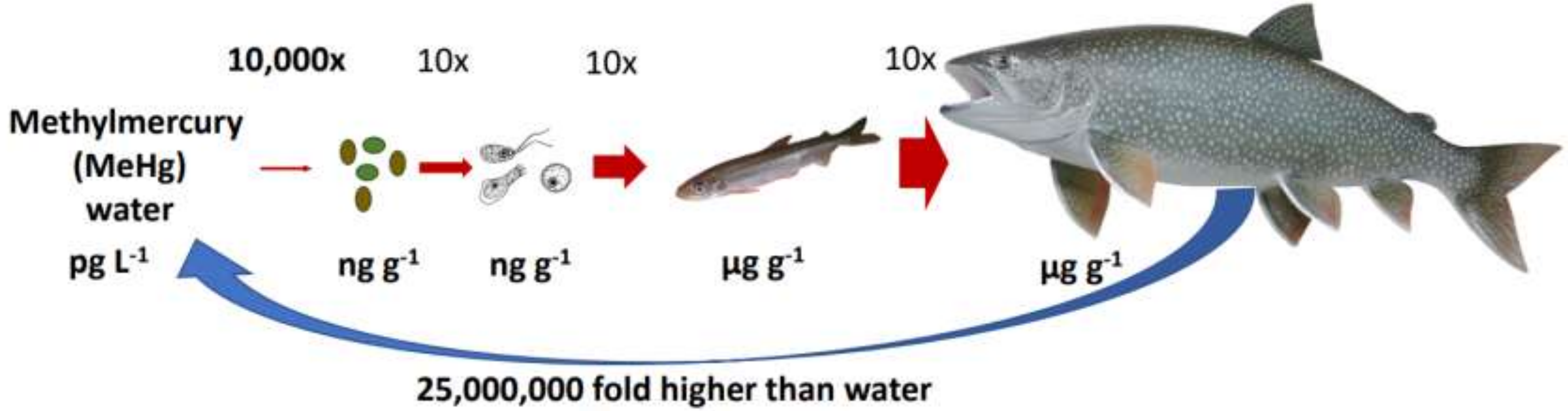
- Mn oxides ubiquitous in environmental systems
  - Present as Mn(II), (III), or (IV)
  - Different surface areas/ reactivities
- Strong oxidation and sorption properties influence fate of
  - Organic pollutants, As, Hg/ MeHg*, etc.

Table 1. Important Mn oxide minerals

Mineral	Chemical formula
Pyrolusite	MnO_2
Ramsdellite	MnO_2
Nsutite	$Mn(O,OH)_2$
Hollandite	$Ba_x(Mn^{4+},Mn^{3+})_8O_{16}$
Cryptomelane	$K_x(Mn^{4+},Mn^{3+})_8O_{16}$
Manjiroite	$Na_x(Mn^{4+},Mn^{3+})_8O_{16}$
Coronadite	$Pb_x(Mn^{4+},Mn^{3+})_8O_{16}$
Romanechite	$Ba_{.66}(Mn^{4+},Mn^{3+})_5O_{10}{\cdot}1.34H_2O$
Todorokite	$(Ca,Na,K)_x(Mn^{4+},Mn^{3+})_6O_{12}{\cdot}3.5H_2O$
Lithiophorite	$LiAl_2(Mn_2^{4+}Mn^{3+})O_6(OH)_6$
Chalcophanite	$ZnMn_3O_7{\cdot}3H_2O$
Birnessite	$(Na,Ca)Mn_7O_{14}{\cdot}2.8H_2O$
Vernadite	$MnO_2{\cdot}nH_2O$
Manganite	$MnOOH$
Groutite	$MnOOH$
Feitknechtite	$MnOOH$
Hausmannite	$Mn^{2+}Mn_2^{3+}O_4$
Bixbyite	Mn_2O_3
Pyrochroite	$Mn(OH)_2$
Manganosite	MnO

Post, 1999

Toxicity of Mercury and Methylmercury



Lepak et al. 2020

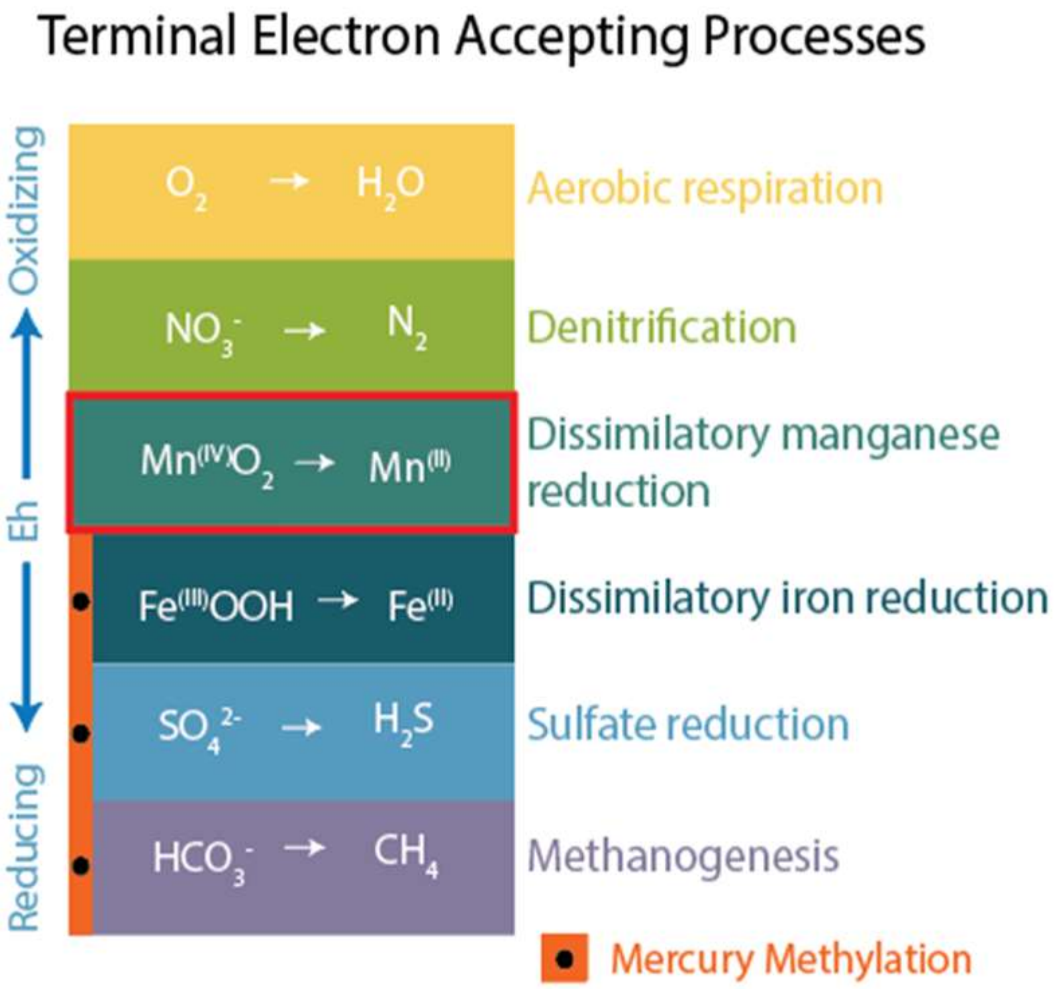
- Hg is a globally spread contaminant
- Hg(II) microbially converted to MeHg under *anaerobic*, *reducing* conditions
  - Sulfate-reducers, iron-reducers
- MeHg is a powerful neurotoxin that bioaccumulates and magnifies
- Low sediment/ water concentrations can lead to high fish concentrations

MnOx as a Sediment Amendment Technology

- Low-cost remediation strategy
- Targets source of MeHg production

For Hg-contaminated sediments

- MnOx acts as redox buffer to disfavor Hg-methylation pathways



Adapted from Dimitri Vlassopoulos

Activated Carbon as a Sediment Amendment Technology

- Thermal or chemical activation of C sources
- High surface area sorbent useful for:
  - Organic compounds
  - Metals and metalloids
- Variety of modifiable surfaces

Calgon Carbon

Combining Remediation Strategies

- MnOx disfavors MeHg production pathways through redox buffering
- Activated carbon (AC) serves as sorbent to bind Hg and MeHg to sediment

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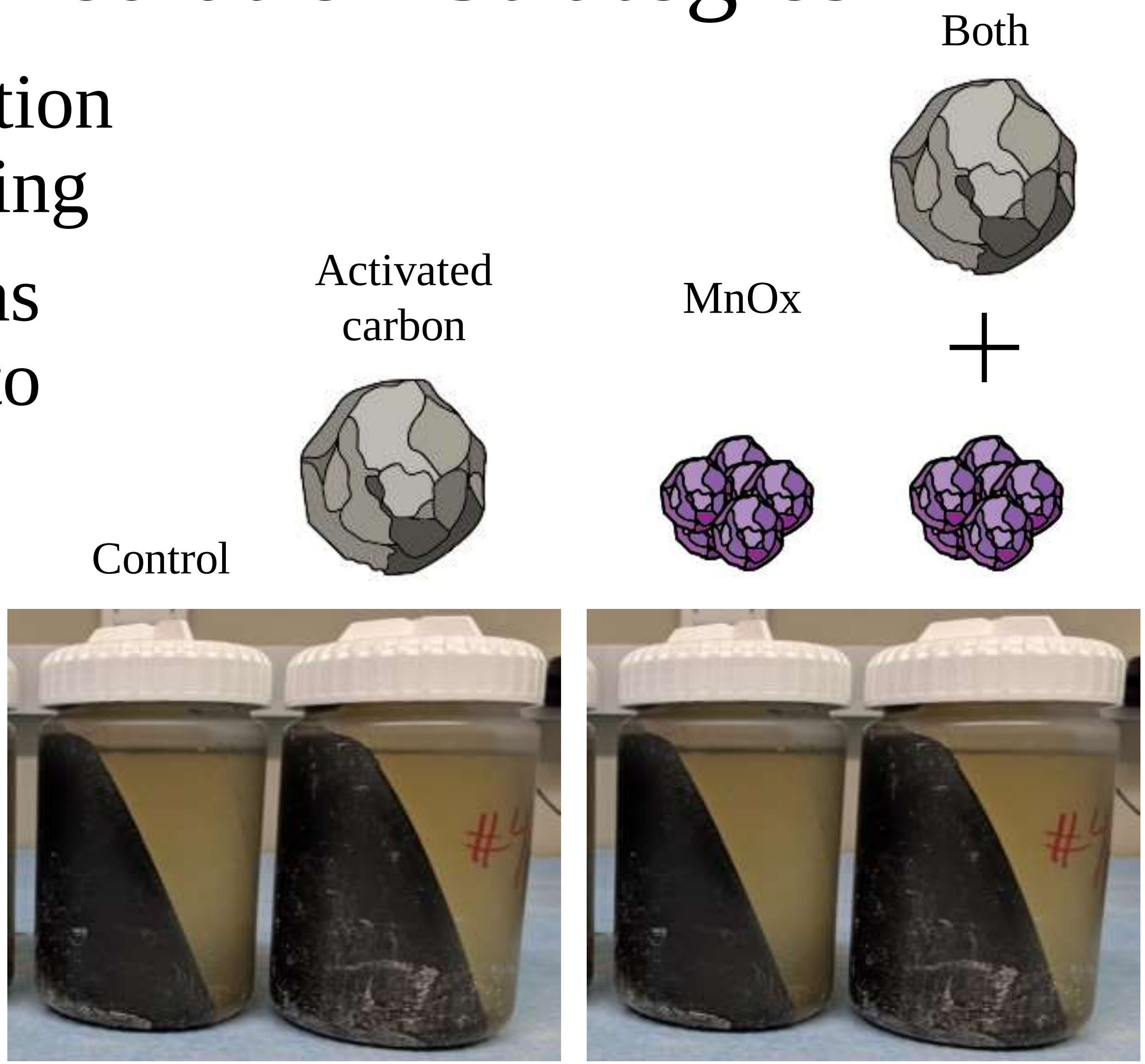
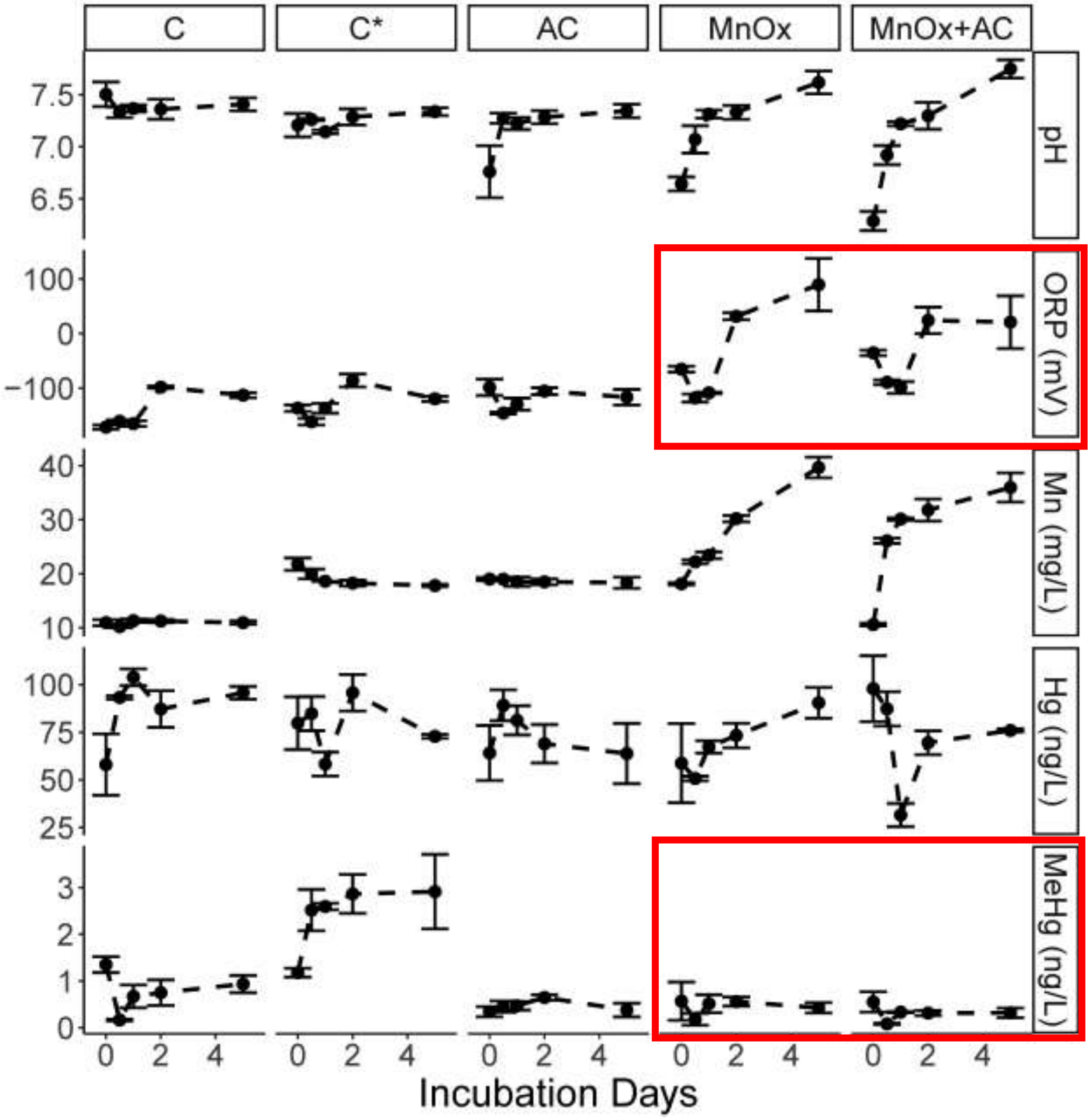


Sediment incubation experiments

- Guadalupe reservoir bottom sediment
- $5\%_{dry\ wt}$ Mn(IV)Ox amendment added
- $1\%_{dry\ wt}$ AC added
- $5_{Mn}:1_{AC}$ mix
- 0-20d and **0-5d**
- Methylation spike in 0-5d

Incubations with Physical Mixes

- MnOx buffered redox potential (ORP) and minimized porewater MeHg



Seelos, M. *et al.* **Evaluation of Manganese Oxide Amendments for Mercury Remediation in Contaminated Aquatic Sediments.** *ACS ES&T Eng* (2021) doi:10.1021/acsestengg.1c00267.

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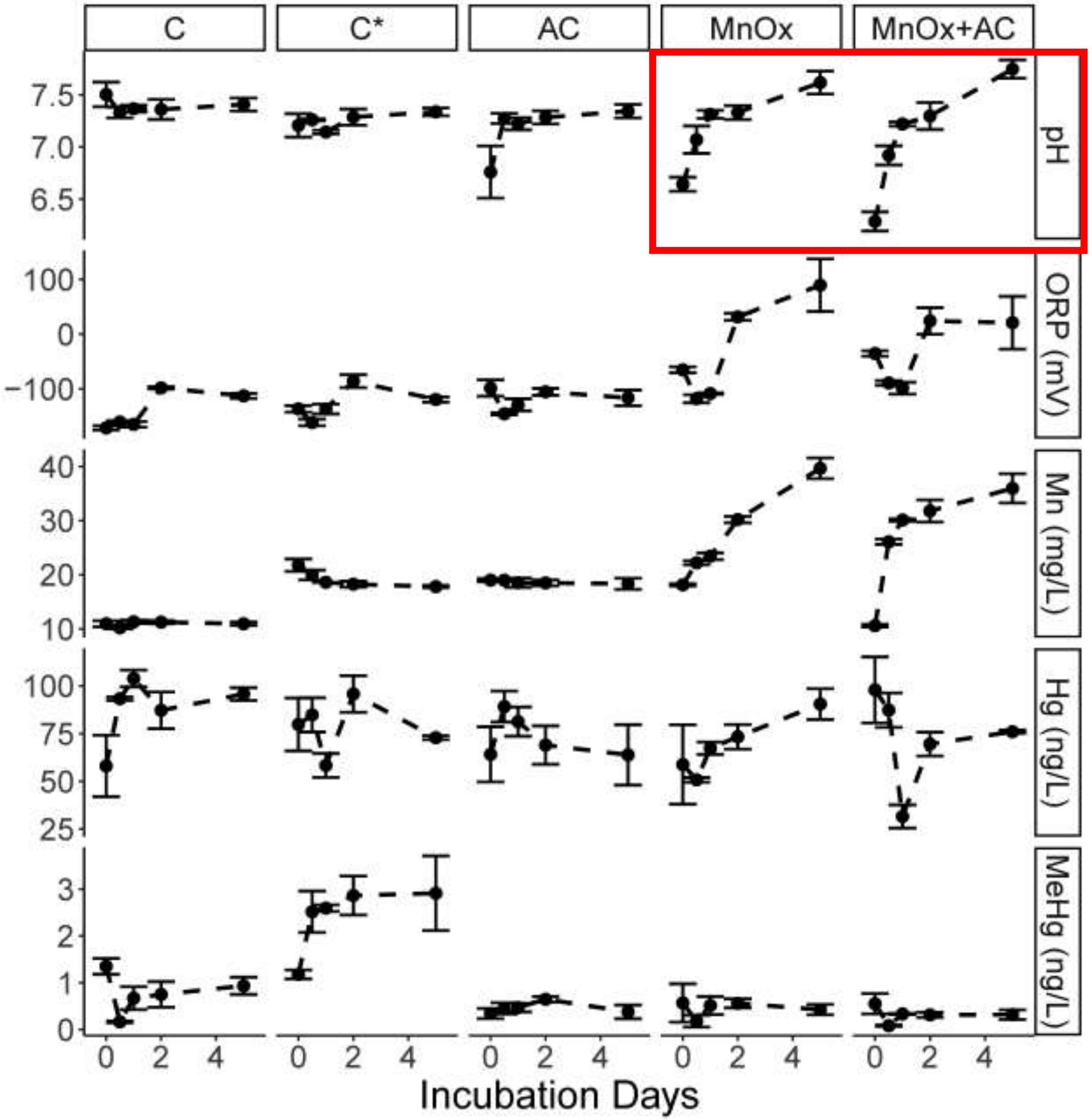
  - Oxidation of Fe(II)S to FeOOH



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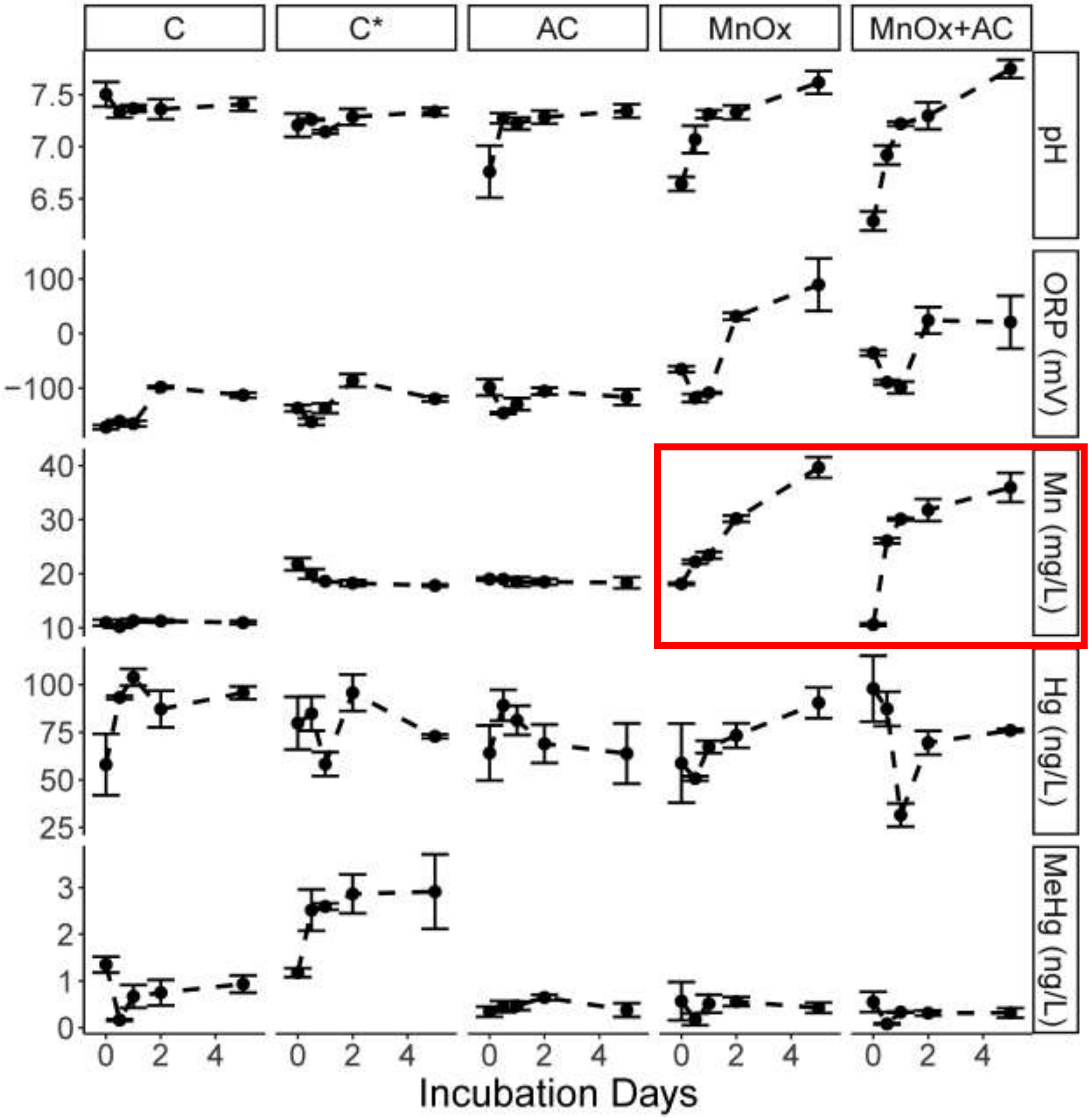
  - Oxidation of Fe(II)S to FeOOH
- Rapid reductive dissolution of Mn(IV)



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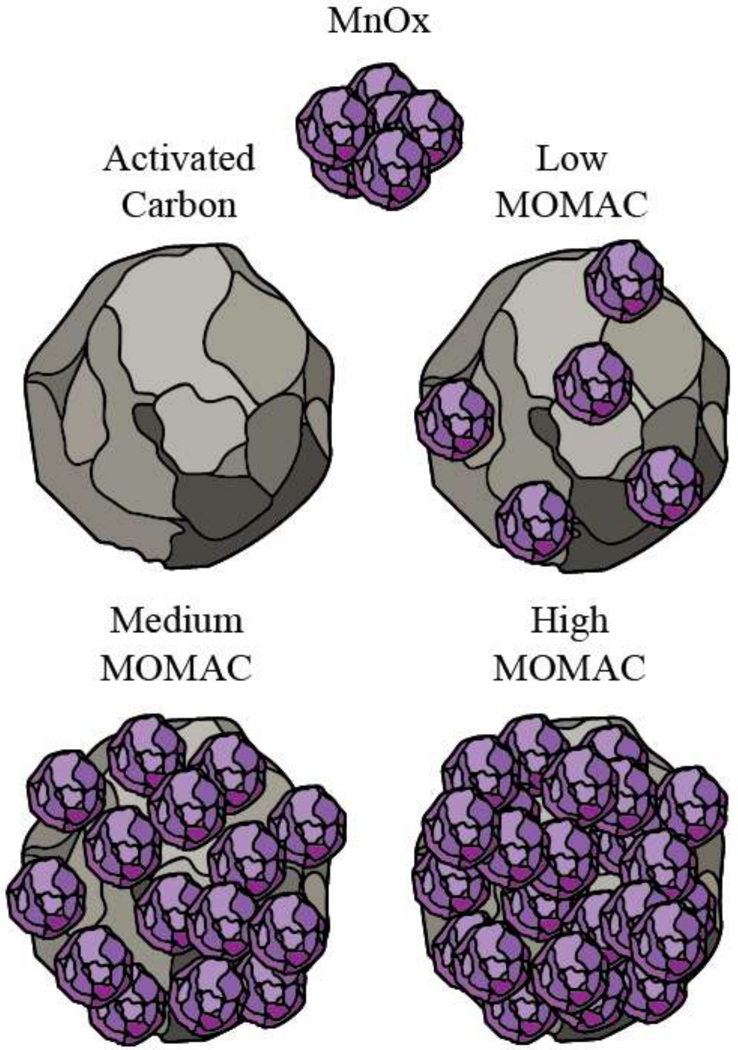
Manganese Oxide Modified Activated Carbon

- Adhering MnOx onto AC combines strategies
  - Practical implementation
  - Opens avenues to optimize
    - Redox buffering capacity
    - Reductive transformation
    - Longevity

Compare MOMAC against synthetic MnOx

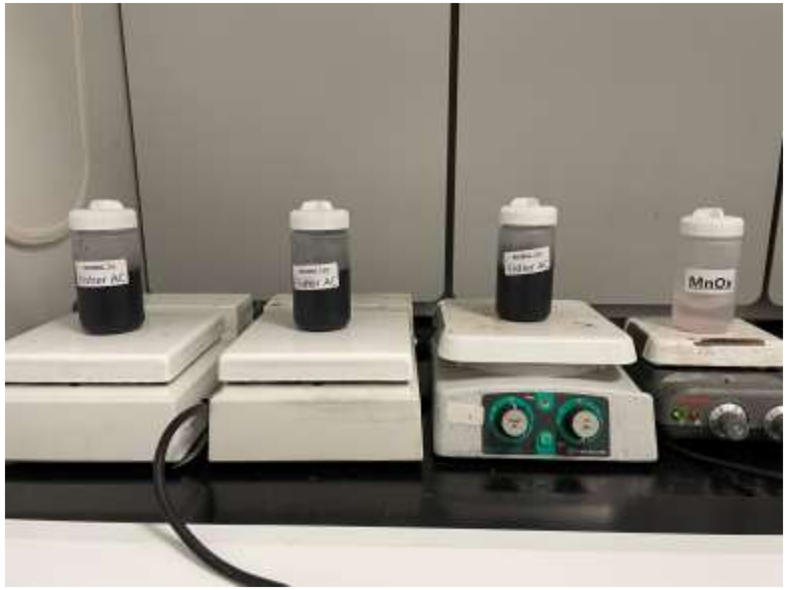


MOMAC Synthesis Overview

$$2\ KMnO_4 + 3\ MnCl_2{\cdot}4H_2O + 4\ NaOH \rightarrow 5\ MnO_2 + 2\ KCl + 4\ NaCl + 6\ H_2O$$

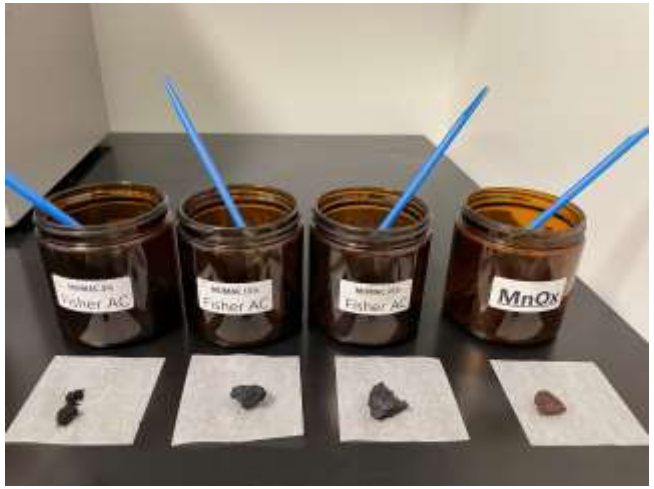
1. $MnCl_2{\cdot}4H_2O \pm AC$

$Mn^{II}(\pm AC) + KMn^{VII}O_4 + NaOH$



2. Wash 3X ($CaCl_2$) and rinse 3X (MQ water)

3. Dry at 55 °C



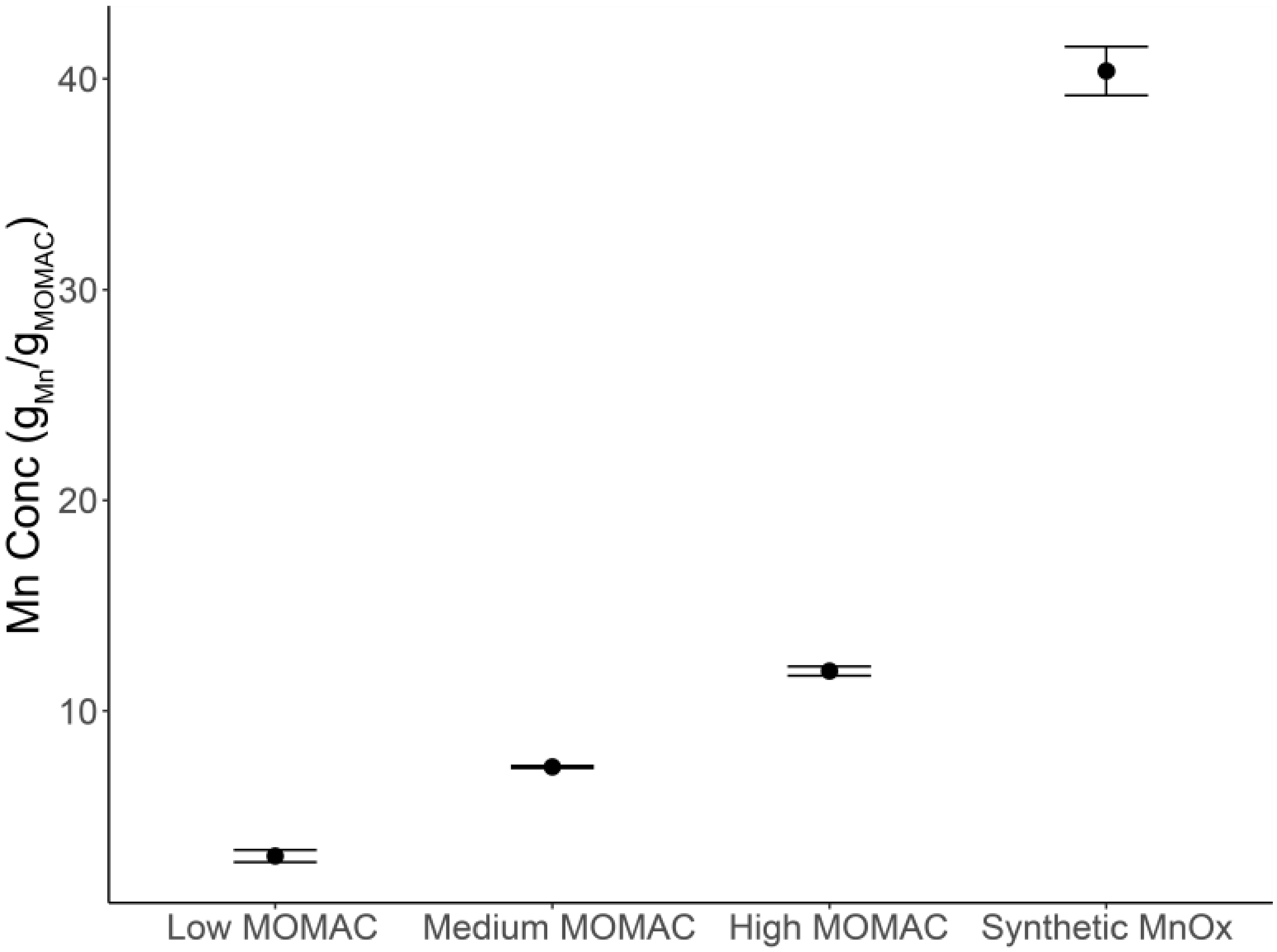
Evaluating MOMAC Products

- MOMAC products underwent characterization to determine
  - Total Mn in product (HHCl digestions)
  - Surface area (BET)
  - Dispersion of Mn (SEM/ STEM)
  - MnOx species (XAS)
  - Mn oxidation states (XPS)
- Assess performance through batch screening experiments

Characterization Method	**Purpose**
BET	Measure surface area of AC and compare to MOMAC treatments
EM-EDS	Capture images of individual AC and MOMAC grains and compare to verify presence of MnOx on AC surface
XPS	Determine average oxidation state of MnOx in sample Assess changes in AC functional groups (XPS)
XAS	Identify bulk MnOx oxidation state and chemical species
XRD	Identify distinct crystalline mineral phases
Acid digestions (HHCl)	Quantify mass of Mn on surface of AC

MOMAC Mn Content

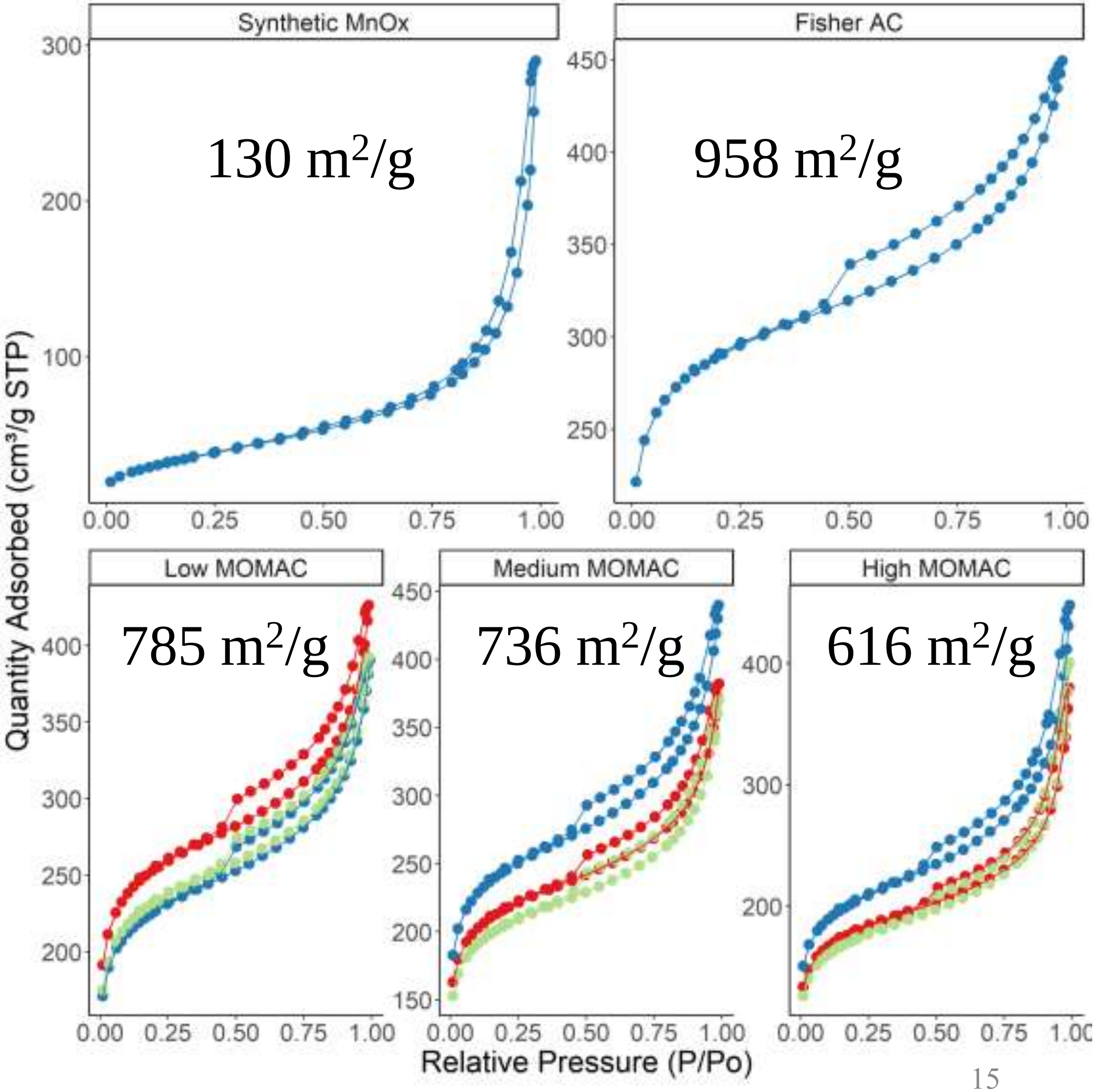
- MnOx and MOMAC digested in 0.1 M hydroxylamine hydrochloride in 0.01 HNO_3



Surface Area Analysis (BET)

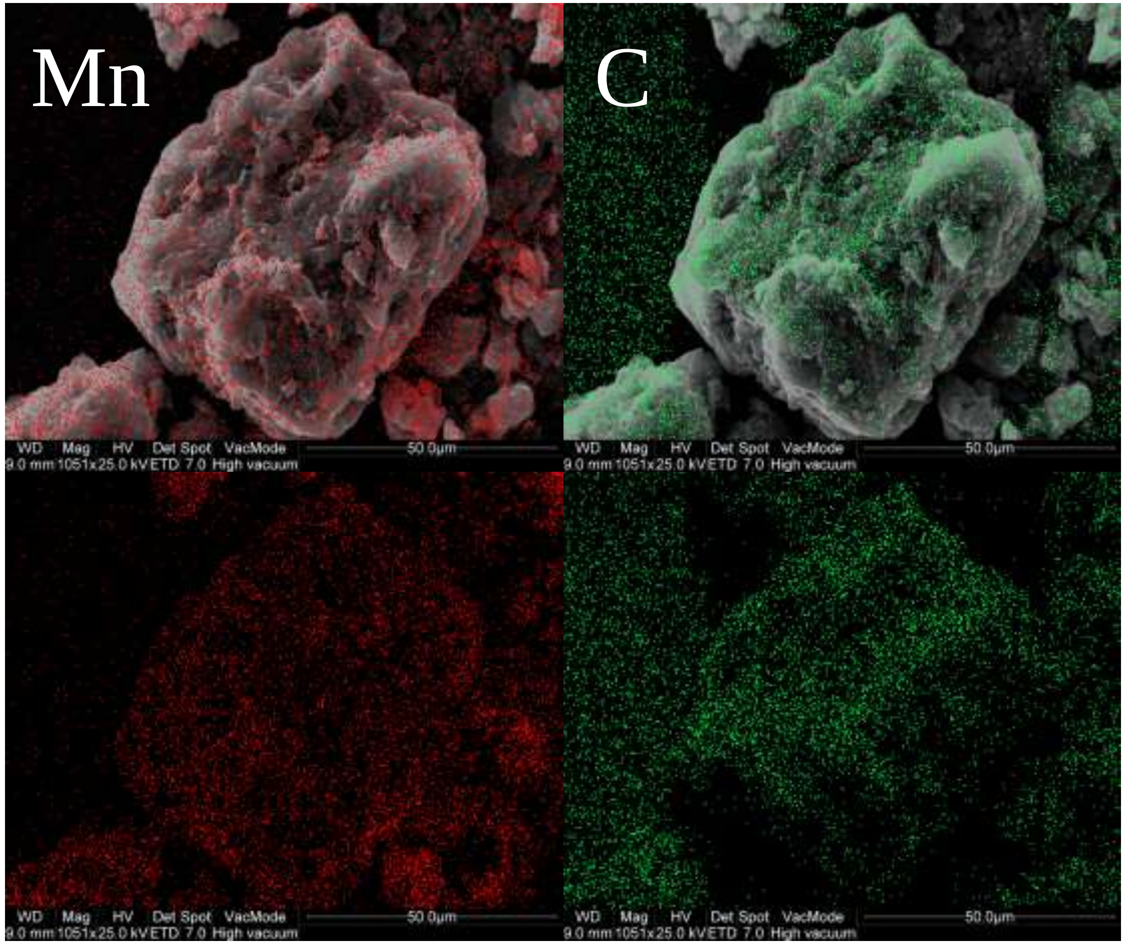
- Clean/ degas at 55 °C with N_2 overnight prior to analysis
- Surface area (SA) decreases with increasing loadings

Is the Mn adhered to AC surface or a separate phase?



Electron Microscopy

- Scanning and transmission electron microscopy (SEM/ STEM)
- Supplemented with energy dispersive X-ray spectroscopy (EDS)



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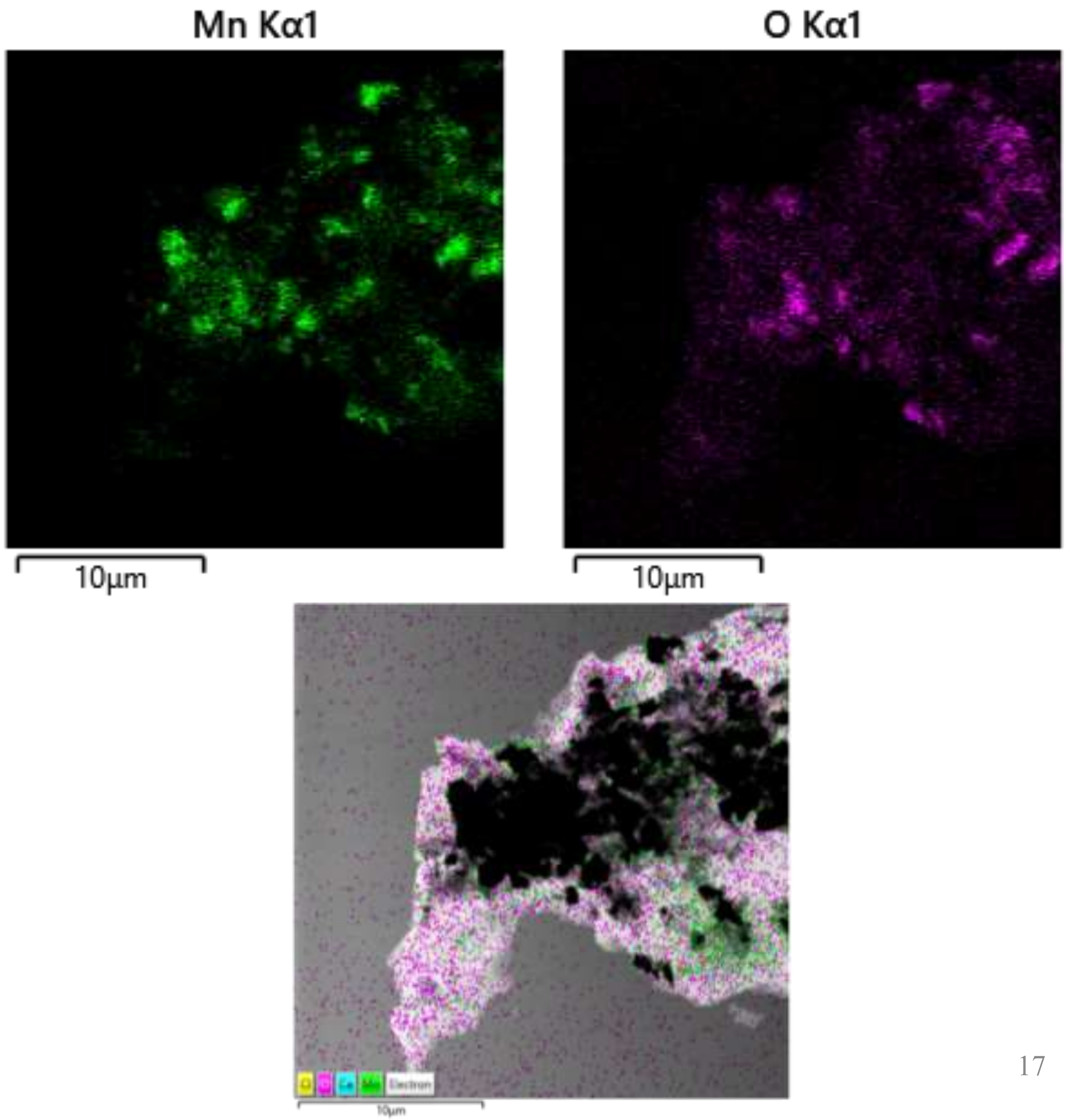
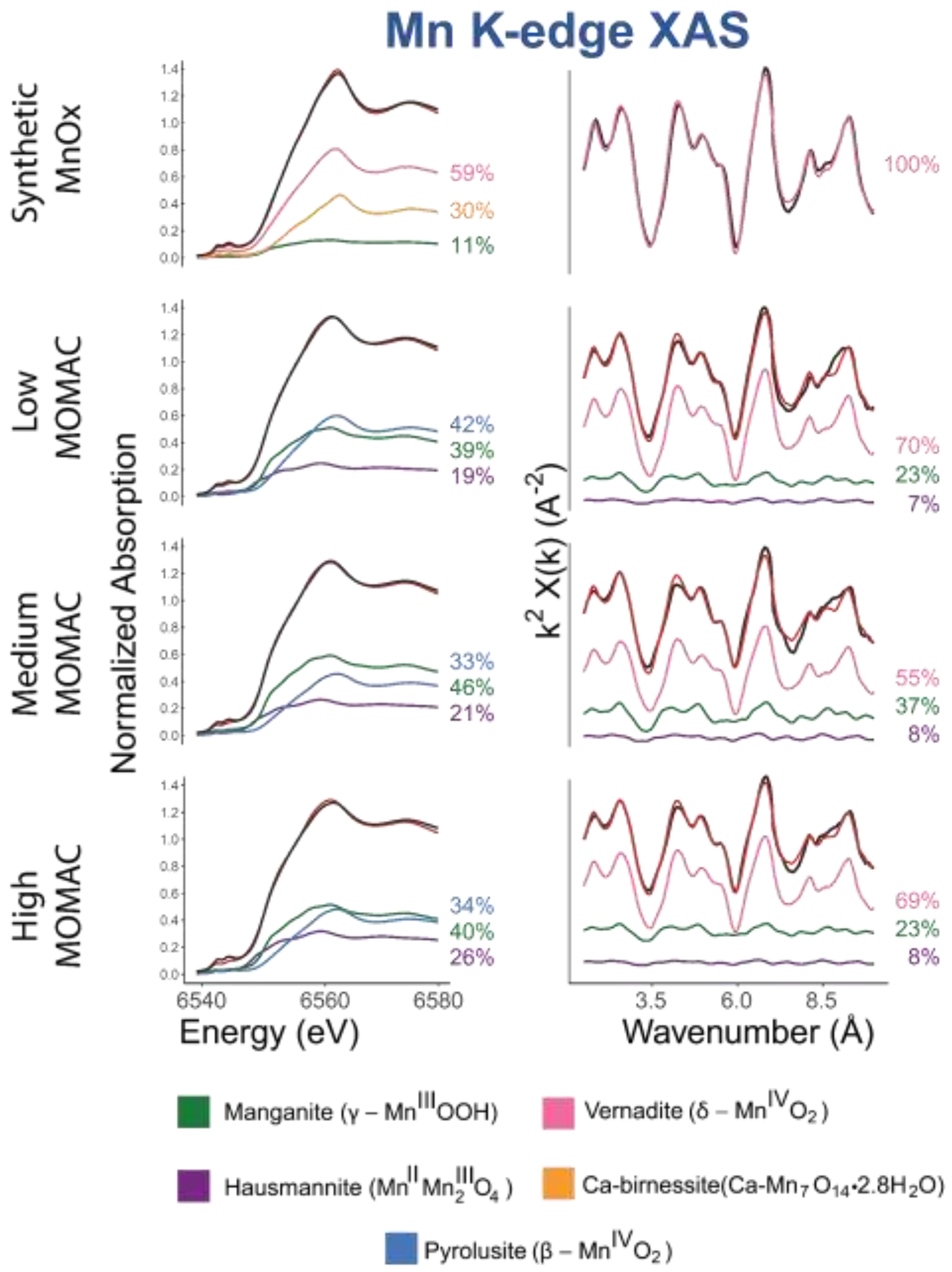
What Mn oxidation states and species are associated with MOMAC?



X-Ray Absorption Spectroscopy

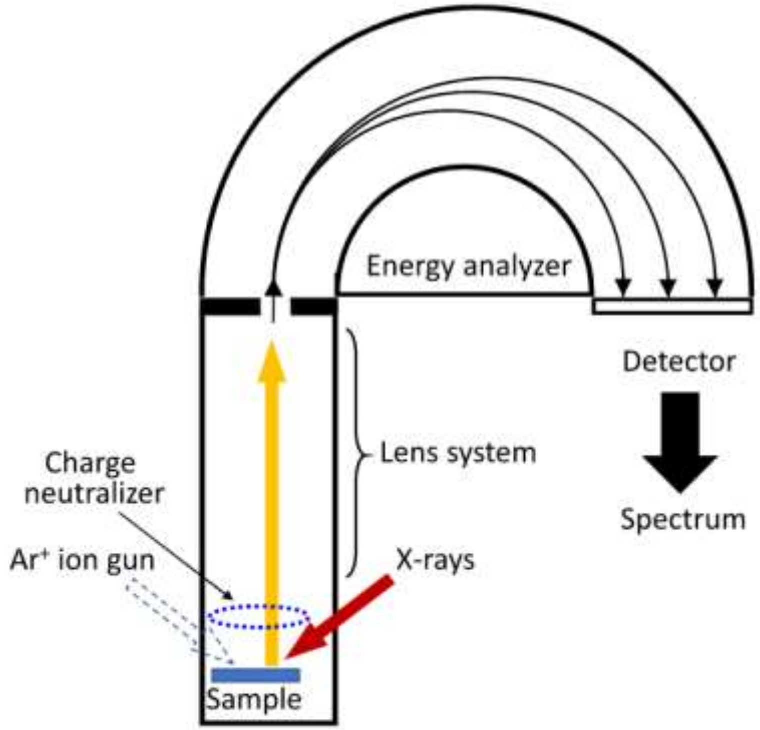
Bulk Mn species determined with linear combination fits using reference spectra

- Synthetic MnOx >80% Mn^{IV} and $Mn^{III, IV}$
- MOMAC consists of 39-45% manganite ($Mn^{III}OOH$) and 19-25% hausmannite ($Mn^{II},Mn^{III}_2O_4$)
- Similar distribution of Mn species among MOMAC samples

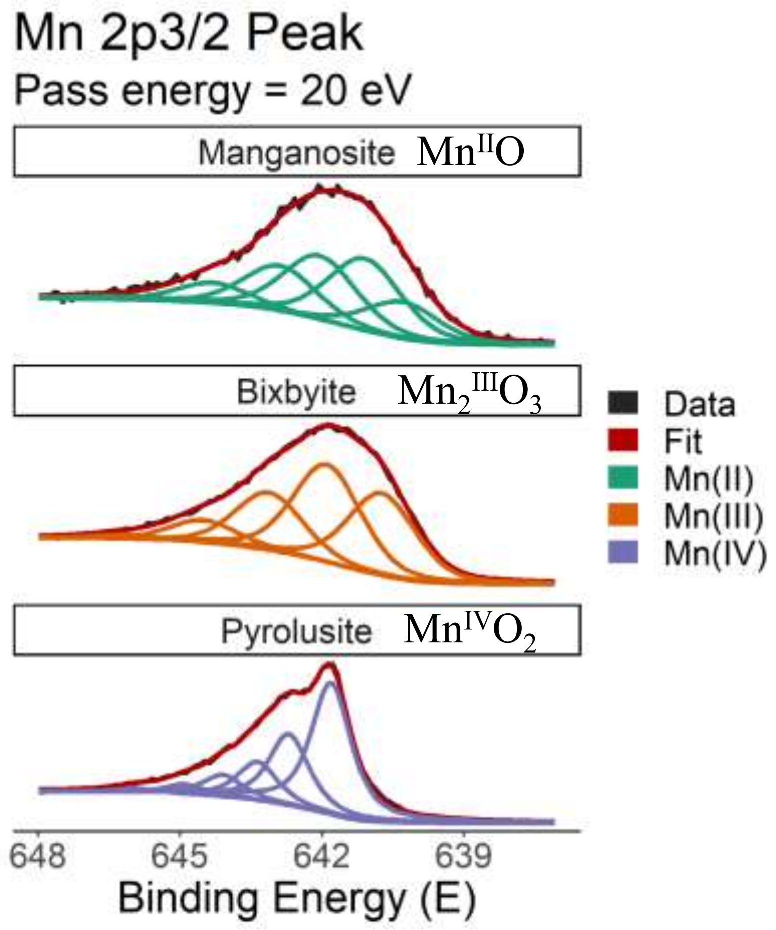


X-ray Photoelectron Spectroscopy (XPS)

- Quantify Mn *oxidation states* on surface (1-10 um)
- Fit with binding energies from literature (± 0.1 eV)

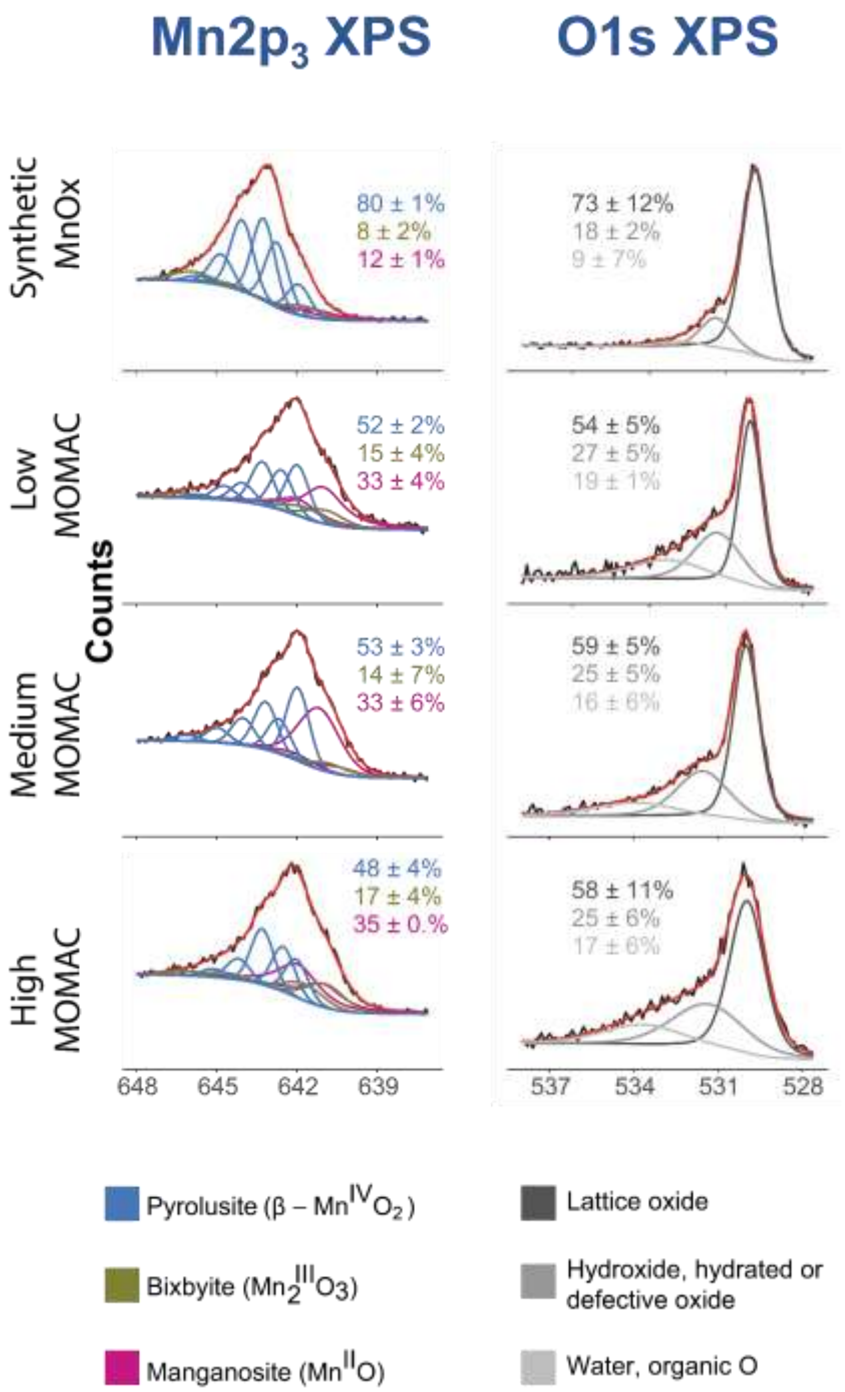


Greczynski & Hultman, 2019



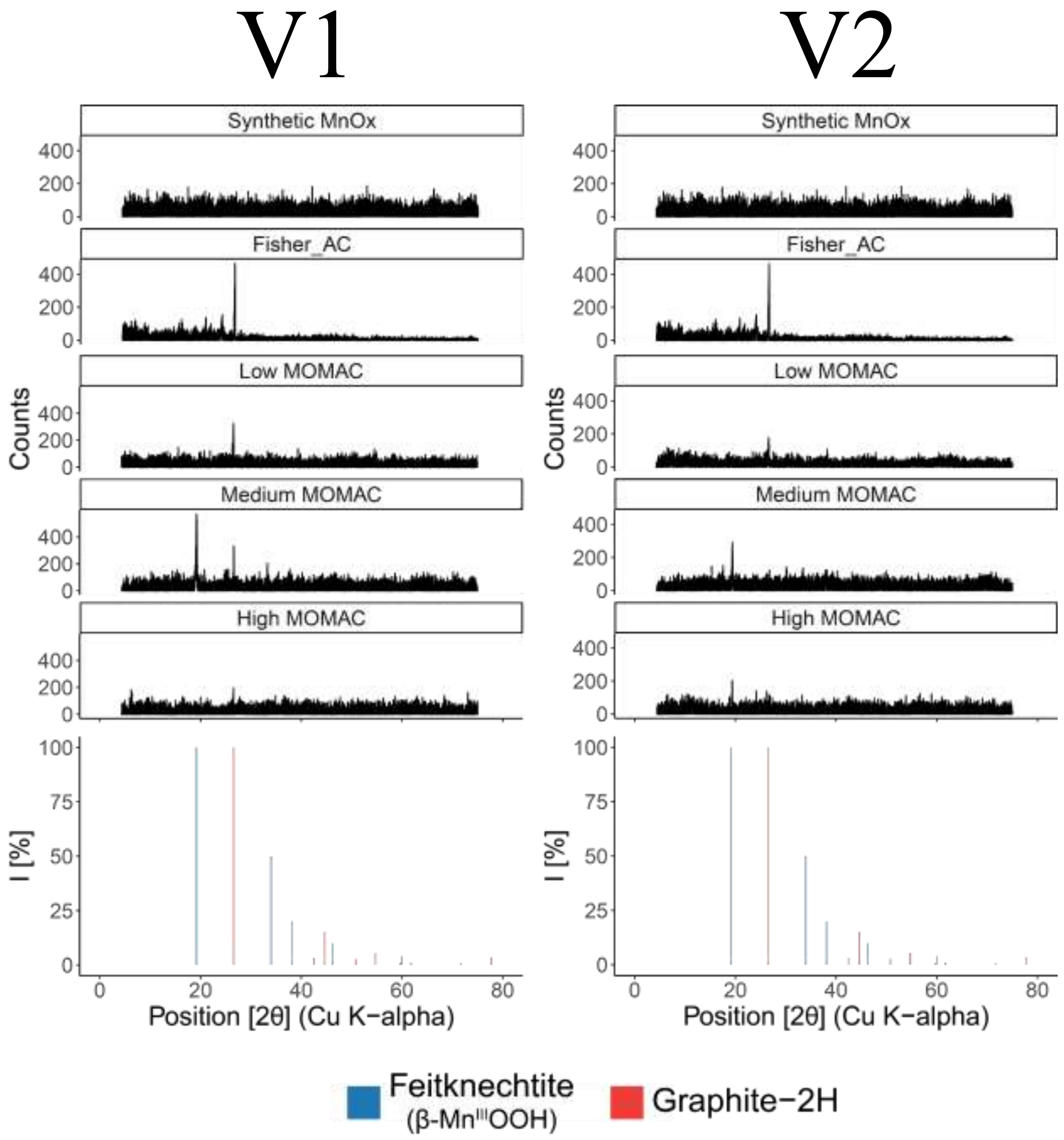
X-ray Photoelectron Spectroscopy

- Synthetic MnOx >80% Mn^{IV}
- MOMAC Mn2p3 XPS consisted of
  - 48-53% Mn(IV)
  - 14-17% Mn(III)
  - 33-35% Mn(II)
- O1s XPS showed higher OH^- fractions (25-27%) in MOMAC compared to MnOx (~18%)
- Similar distribution of Mn oxidation states among MOMAC samples



X-Ray Diffraction

- Synthetic MnOx is amorphous
- Presence of MnOOH (feitknechtite) in some MOMAC products
- Common C reflection from AC (graphite)



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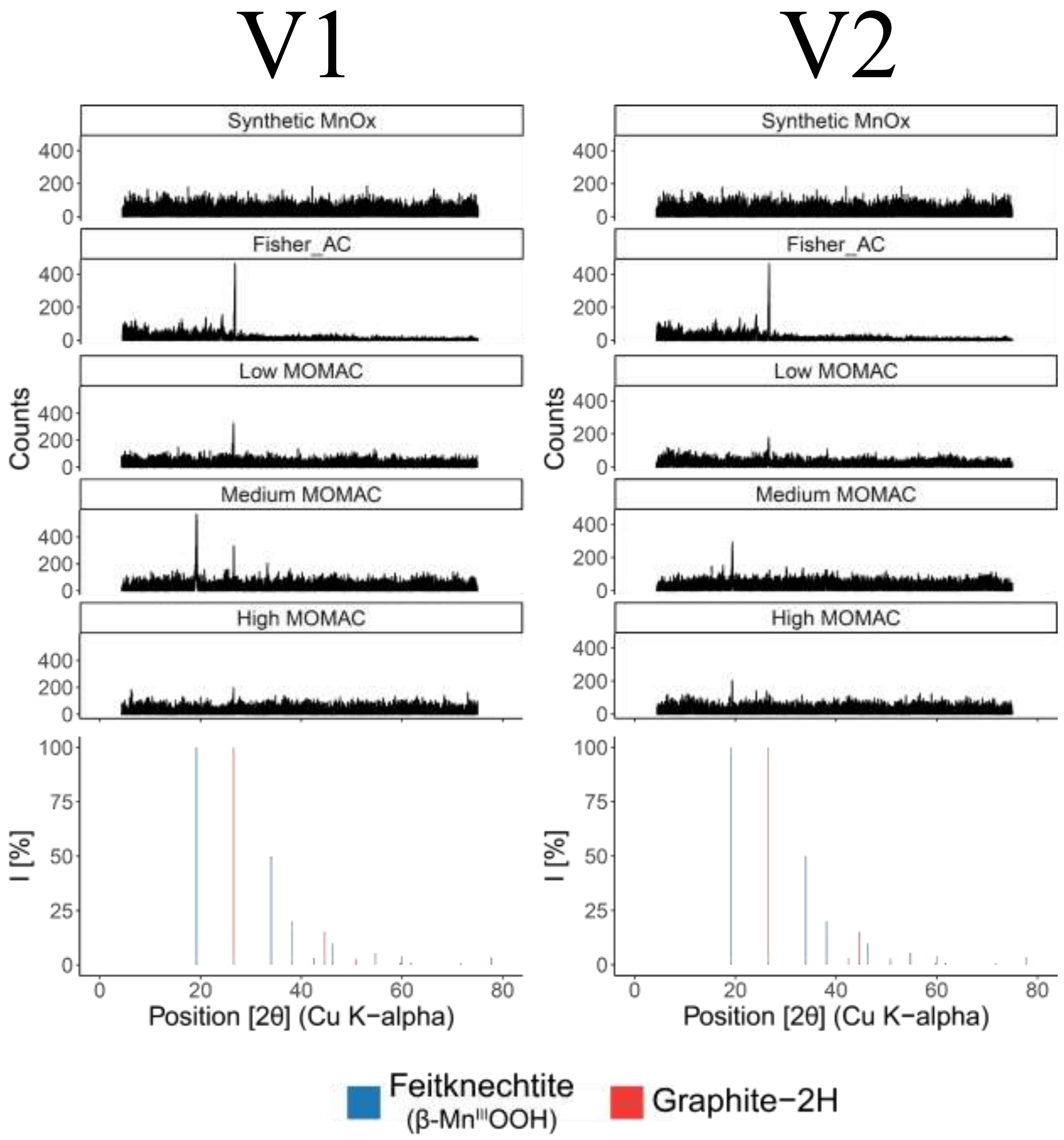
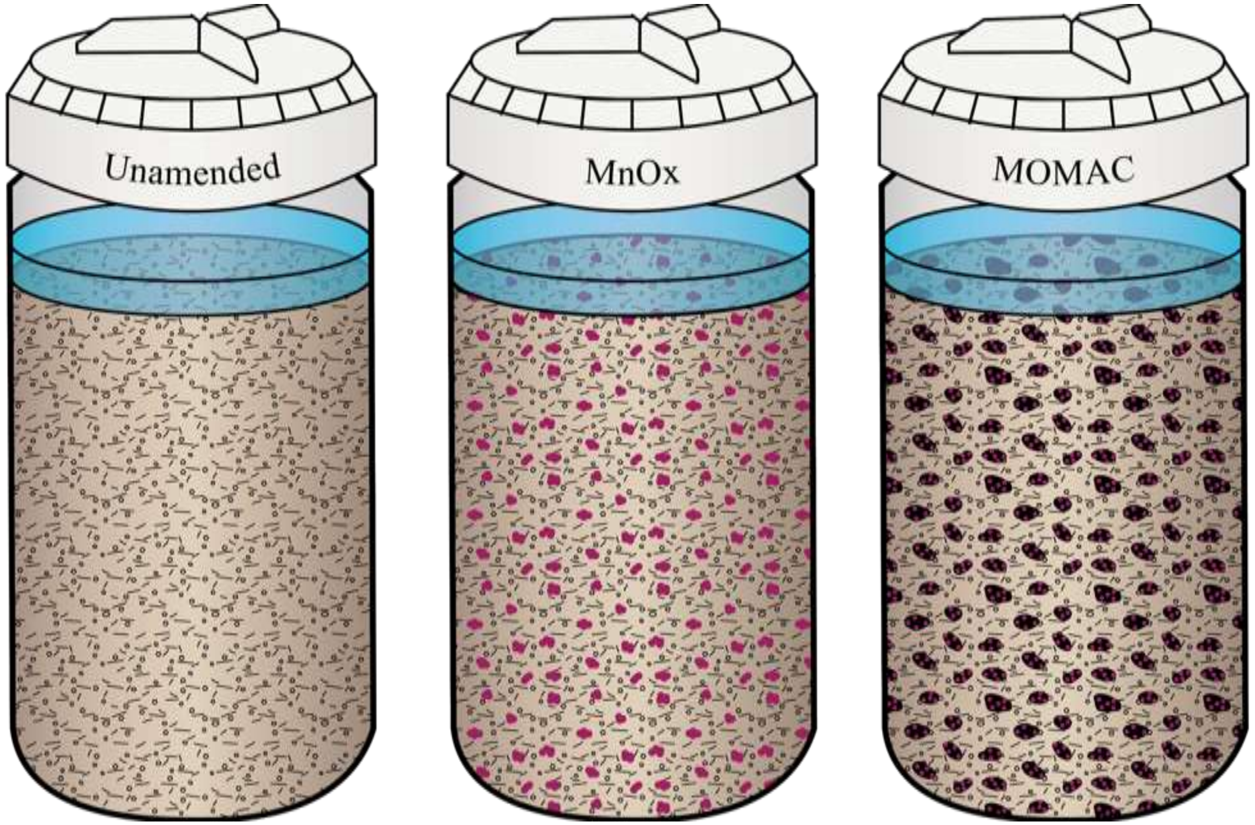
How does redox buffering compare between MOMAC and MnOx?



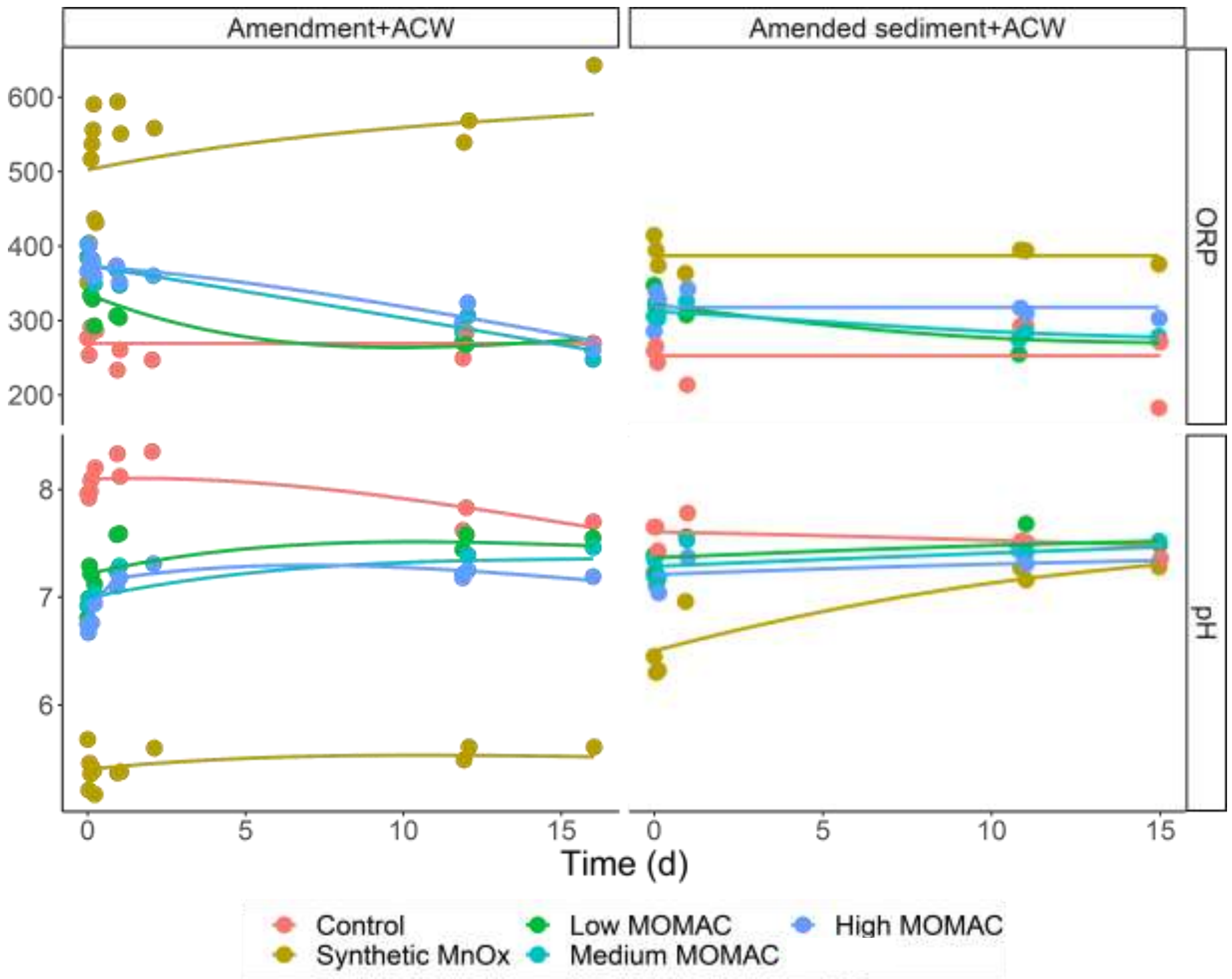
MOMAC pH and ORP Batch Screening

- Uncontaminated sediment from ORNL East Fork Poplar Creek streambed
- Artificial creek water (ACW) (~40 g)
- 5%$_{\text{dry wt}}$ amendment added (~0.3 g)
- With and without sediment
- Kept on rotator in N_2-filled glovebox
- Monitor change in pH and ORP over a 2-week period

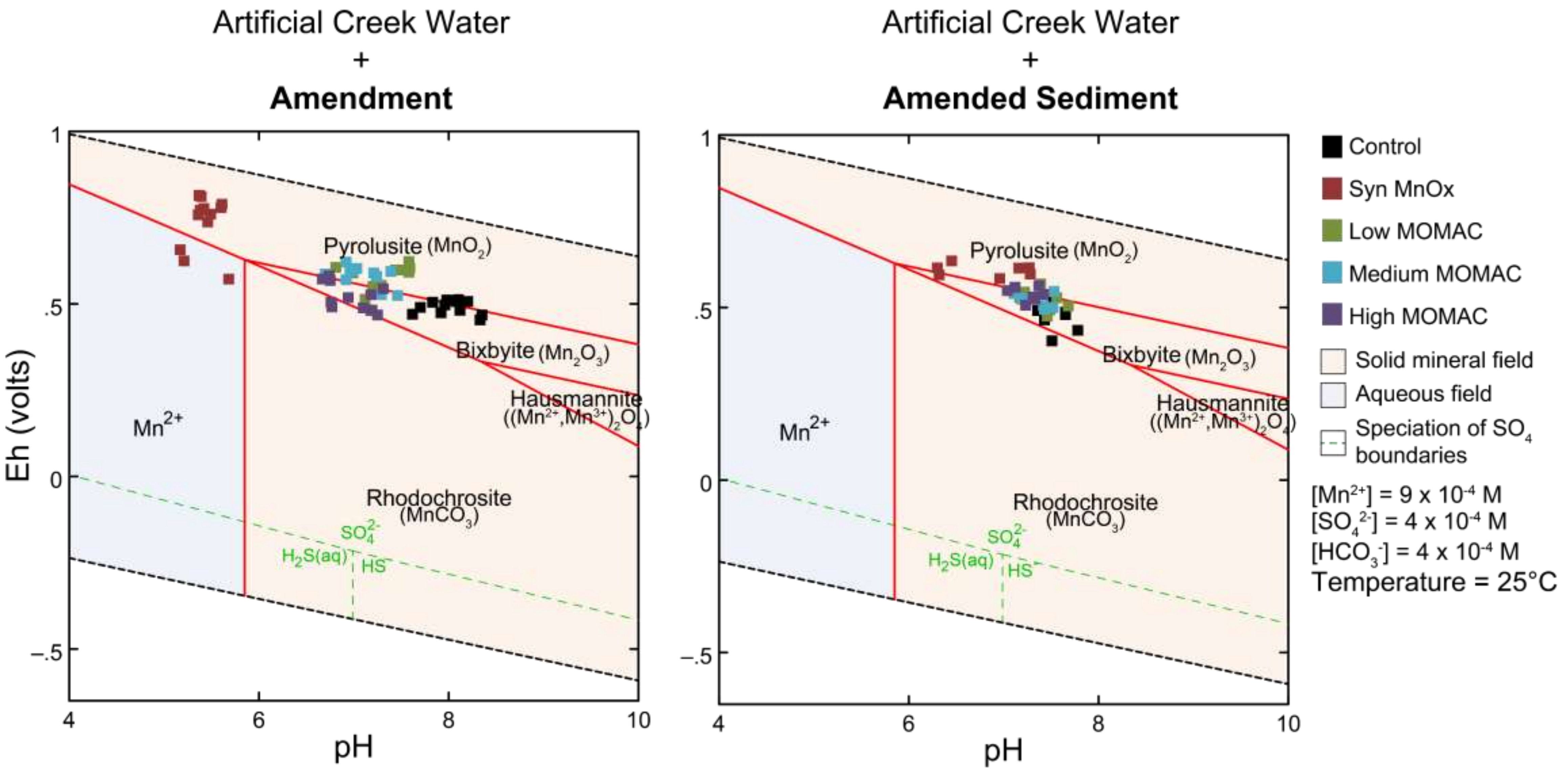


Screening Results

- Generalized additive model (GAM) fit used to observe trends
- **Not** normalized for mass of Mn
- ORP was higher in Mn-treated sediments compared to control
- Lower pH associated with MnOx
- Similar redox buffering among all MOMAC samples



Eh-pH Diagrams



MOMAC Evaluation Summary

- Characterization (XAS, XPS, XRD) show that
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  - MOMAC contains mixed-valent Mn phases
    - 39-53% Mn(IV)
    - 30-60% Mn(III) as $Mn^{III}OOH$ and $(Mn^{II},Mn_2^{III})O_4$ (hausmannite)
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- Mn species, oxidation state distribution, and redox buffering similar across MOMAC loadings (2-12 wt%)
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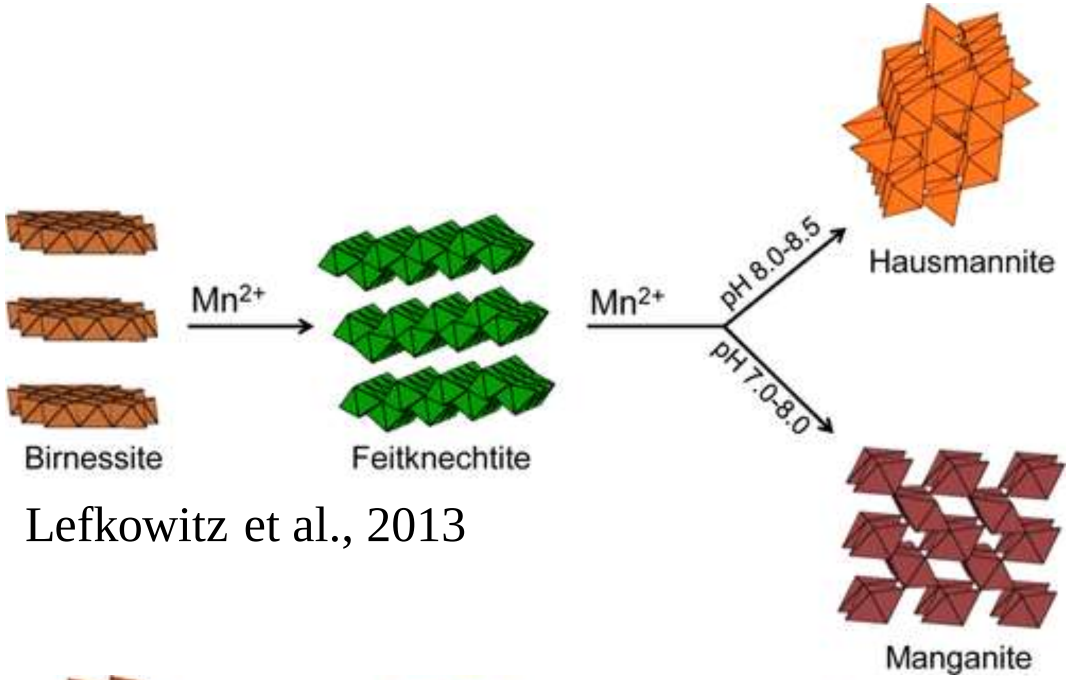
What causes the differences in the Mn species observed in synthetic MnOx compared with precipitation in the presence of AC?

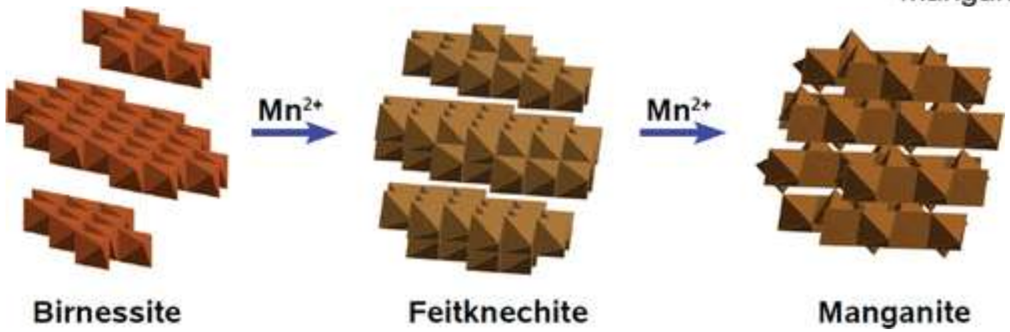
Mn(II) autocatalyzes reductive transformation

- Mn(II) adsorbed onto AC during synthesis may cause reductive transformation of Mn(IV)

How might the differences in Mn species influence longevity as a sediment amendment?



Lefkowitz et al., 2013



Elzinga, 2011

Implications for Hg Remediation and Future Steps

MOMAC may be favorable over MnOx when applied to sediments

- Formation of intermediate Mn phase, favored at higher pH, can improve longevity
- AC can sorb reduced Mn(II), slowing reduction of Mn(IV)

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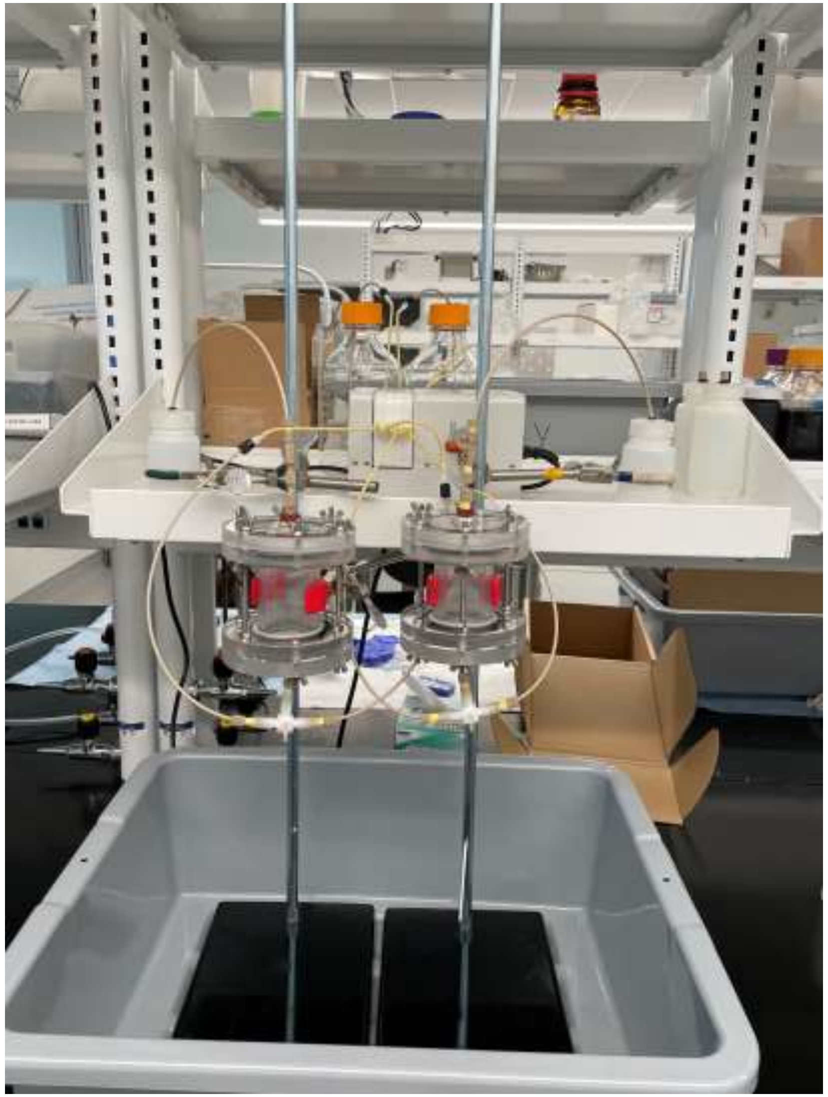
- Re-do screening normalized for mass of Mn
- Vary environmental system chemistry

Evaluate MOMAC in an environmentally representative experimental design



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Questions?