Temporal variability in trace metal removal in vertical flow bioreactors

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Outline

- Vertical flow bioreactors
- Study objectives and site
- Trace metal removal
  - Changes over time
- Products of removal
  - Changes over time
- Conclusions

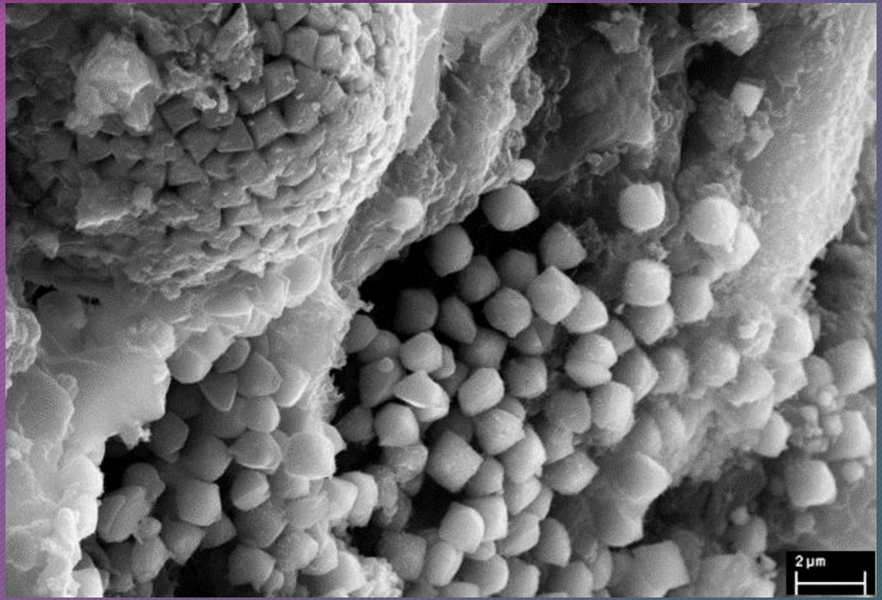
Vertical flow bioreactors (VFBR)

- May follow oxidation step
  - Net-alkaline
  - Low Fe
  - Circum-neutral pH

- Goals
  - Force water vertically through organic substrate
  - Create anoxic, reducing conditions
    - Promote bacterial sulfate reduction (BSR)
    - Generate alkalinity through BSR and limestone dissolution
  - Remove divalent trace metals as insoluble sulfides

Trace metal removal in VFBR

- Goals of VFBR
  - Generate alkalinity
  - Remove trace metals via sulfide precipitation



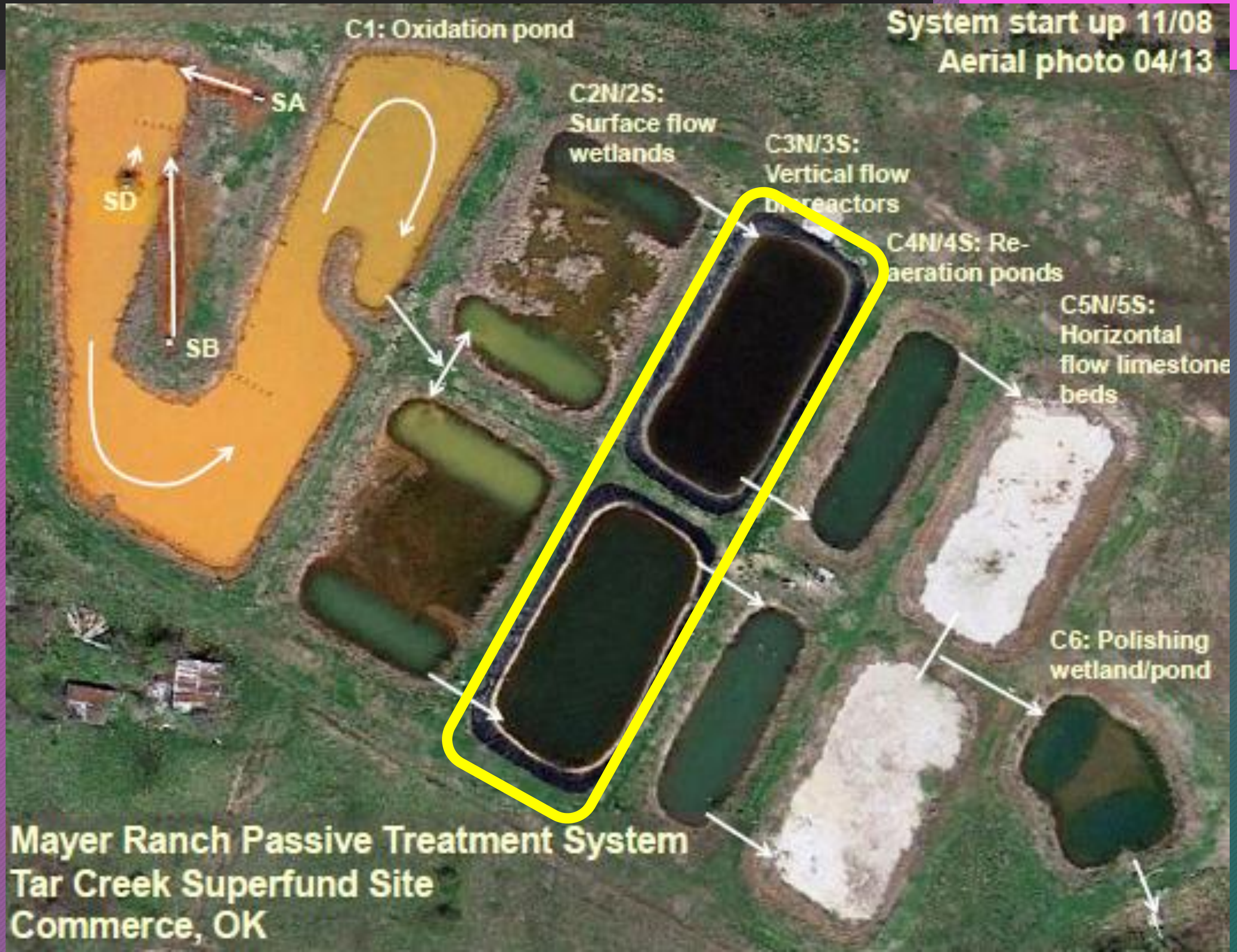
- Reality = remove trace metals via a variety of mechanisms
  - Adsorption, carbonate formation, complexation with HA/FA

Study objectives

- Proof of concept – field proof of trace metal removal and products
- Evaluate whether overall treatment effectiveness changes over the short term
- Determine if removal products change over time

Mayer Ranch Passive Treatment System

- First mine drainage treatment of any kind attempted in the Tri-State Mining District
  - Oxidation pond
  - Settling wetlands
  - Vertical flow bioreactors
  - Re-aeration ponds
  - Horizontal flow LS beds
  - Polishing wetland



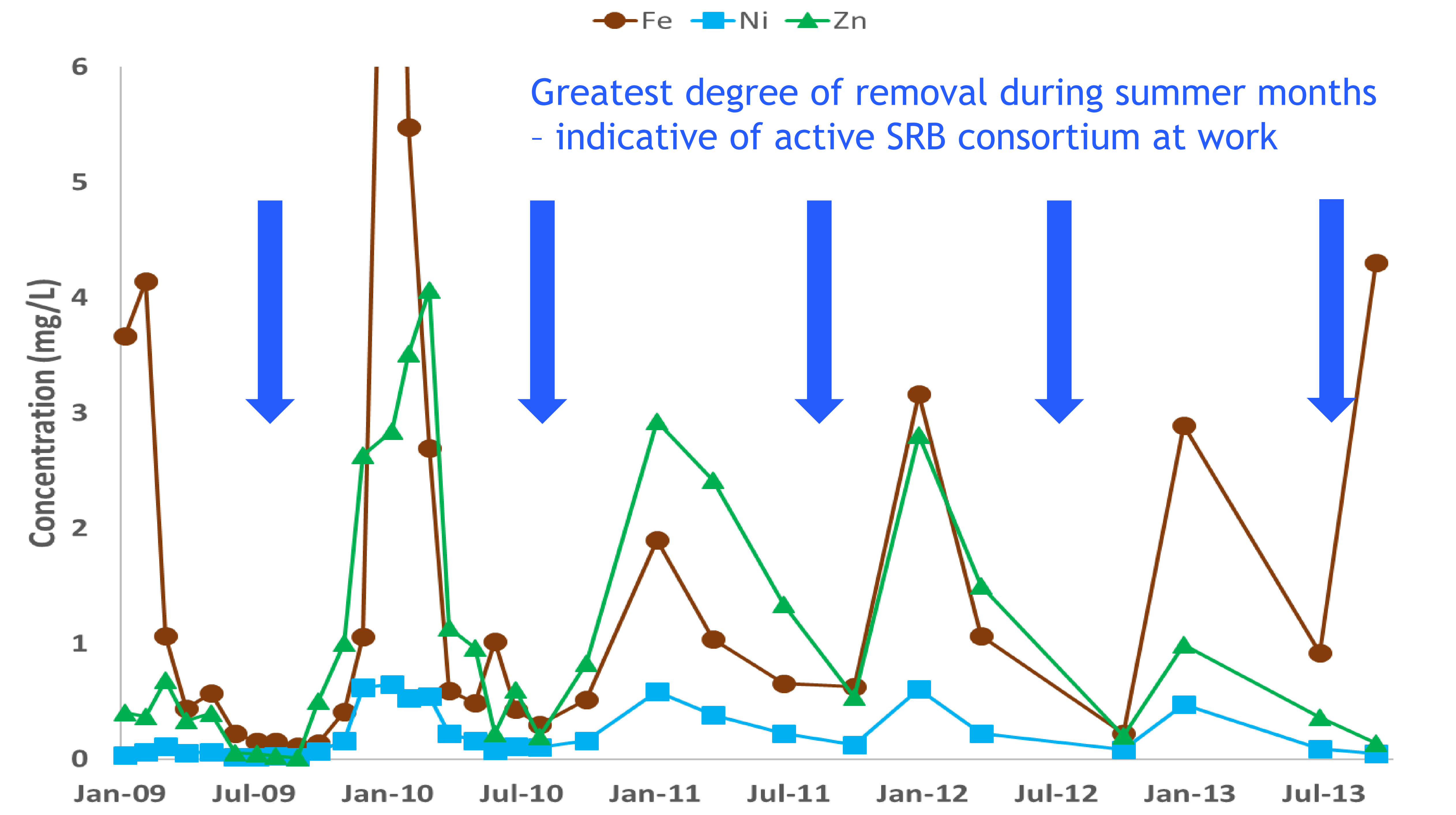
Mayer Ranch Passive Treatment System

- 2 VFBR in parallel
- 0.5 m organic substrate
  - 45:45:10 spent mushroom compost, wood chips, limestone sand
- 0.5 m high-calcite limestone
- Approximately 760 m^2

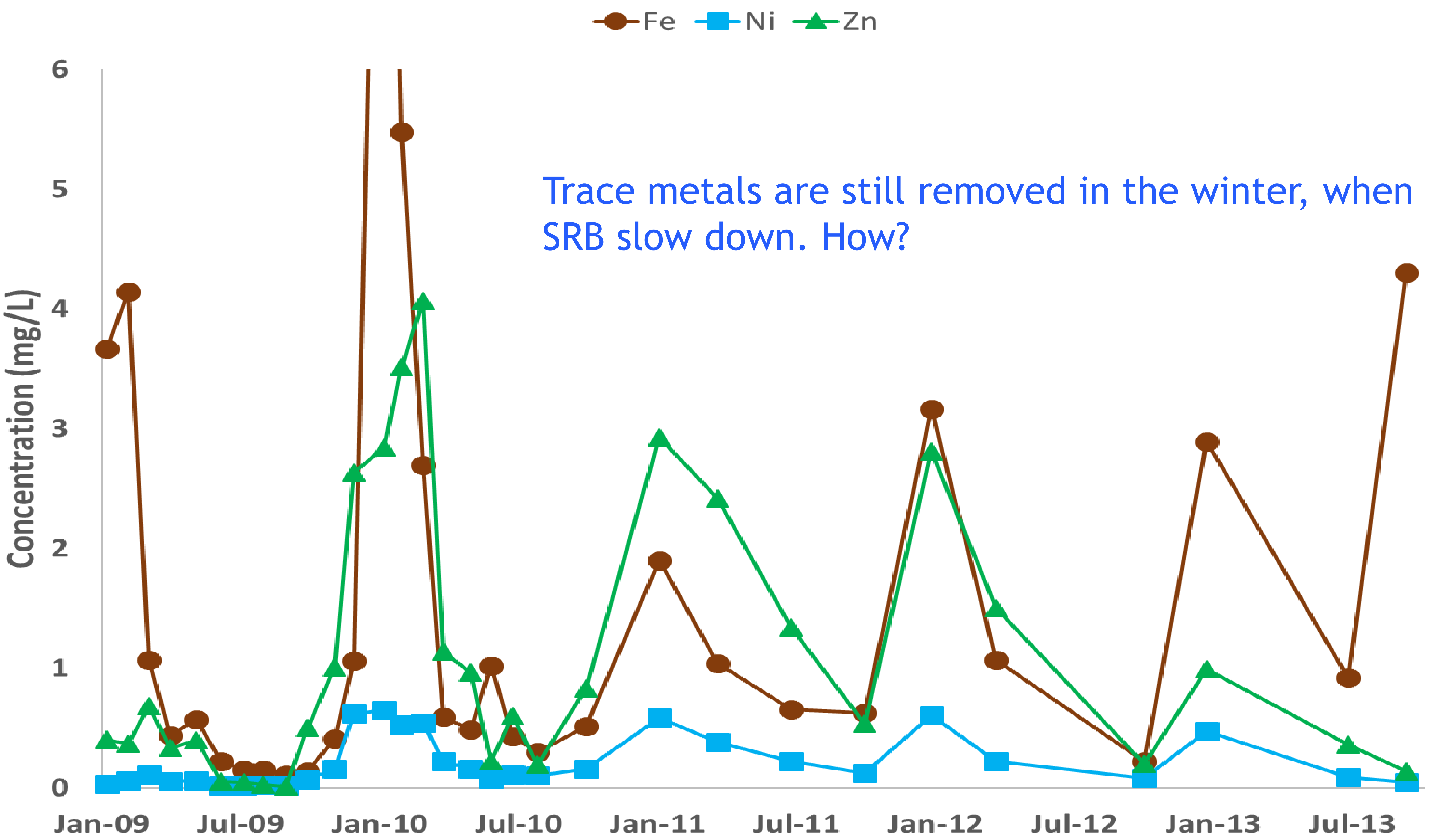
	In		Out	
	N	Median	N	Median
T (°C)	66	19.1	66	17.8
pH (s.u.)	66	6.39	66	6.79
Cond (mS/cm)	66	2.80	66	2.60
DO (mg/L)	66	8.55	66	0.750
ORP (mV)	66	180	66	-90.5
Alkalinity (mg/L as $CaCO_3$)	66	145	66	220
Sulfate (mg/L)	52	2250	52	2140
Sulfide (mg/L)	0	-	6	3.21
Fe (mg/L)	35	0.310	34	0.418
Cd (mg/L)	10	0.002	6	0.001
Co (mg/L)	36	0.051	17	0.009
Mn (mg/L)	36	1.36	36	1.21
Ni (mg/L)	36	0.758	35	0.097
Pb (mg/L)	6	0.027	3	0.030
Zn (mg/L)	36	4.83	35	0.019

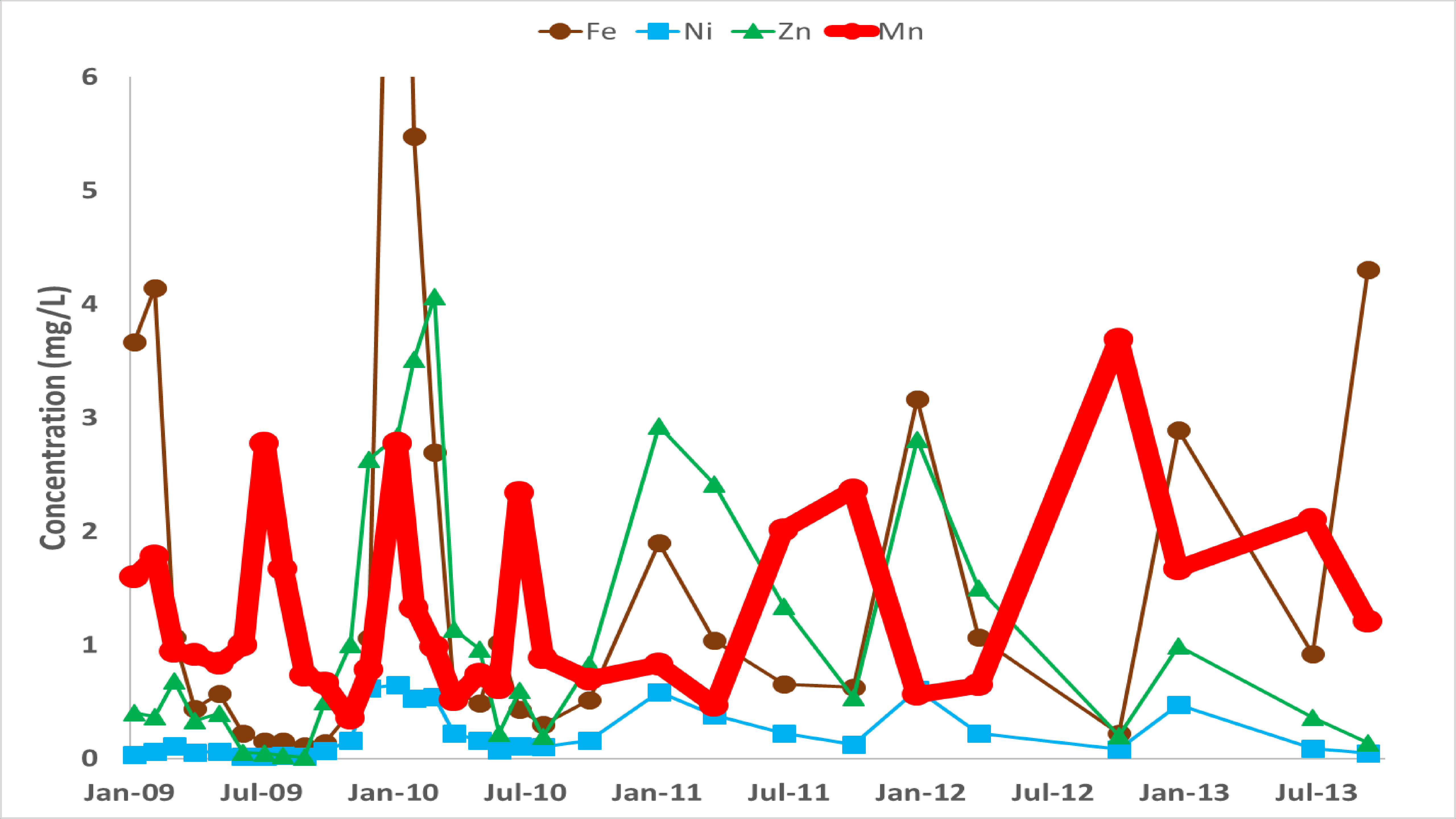
In general:

- Modest sulfate removal
- No apparent iron removal
- Removal of Co and Ni
- A lot of Zn removal



Fe
Ni
Zn
Greatest degree of removal during summer months
– indicative of active SRB consortium at work
Concentration (mg/L)
0
1
2
3
4
5
6
Jan-09
Jul-09
Jan-10
Jul-10
Jan-11
Jul-11
Jan-12
Jul-12
Jan-13
Jul-13


Fe
Ni
Zn
Concentration (mg/L)
6
5
4
3
2
1
0
Jan-09
Jul-09
Jan-10
Jul-10
Jan-11
Jul-11
Jan-12
Jul-12
Jan-13
Jul-13
Trace metals are still removed in the winter, when SRB slow down. How?



Fe
Ni
Zn
Mn
Concentration (mg/L)
0
1
2
3
4
5
6
Jan-09
Jul-09
Jan-10
Jul-10
Jan-11
Jul-11
Jan-12
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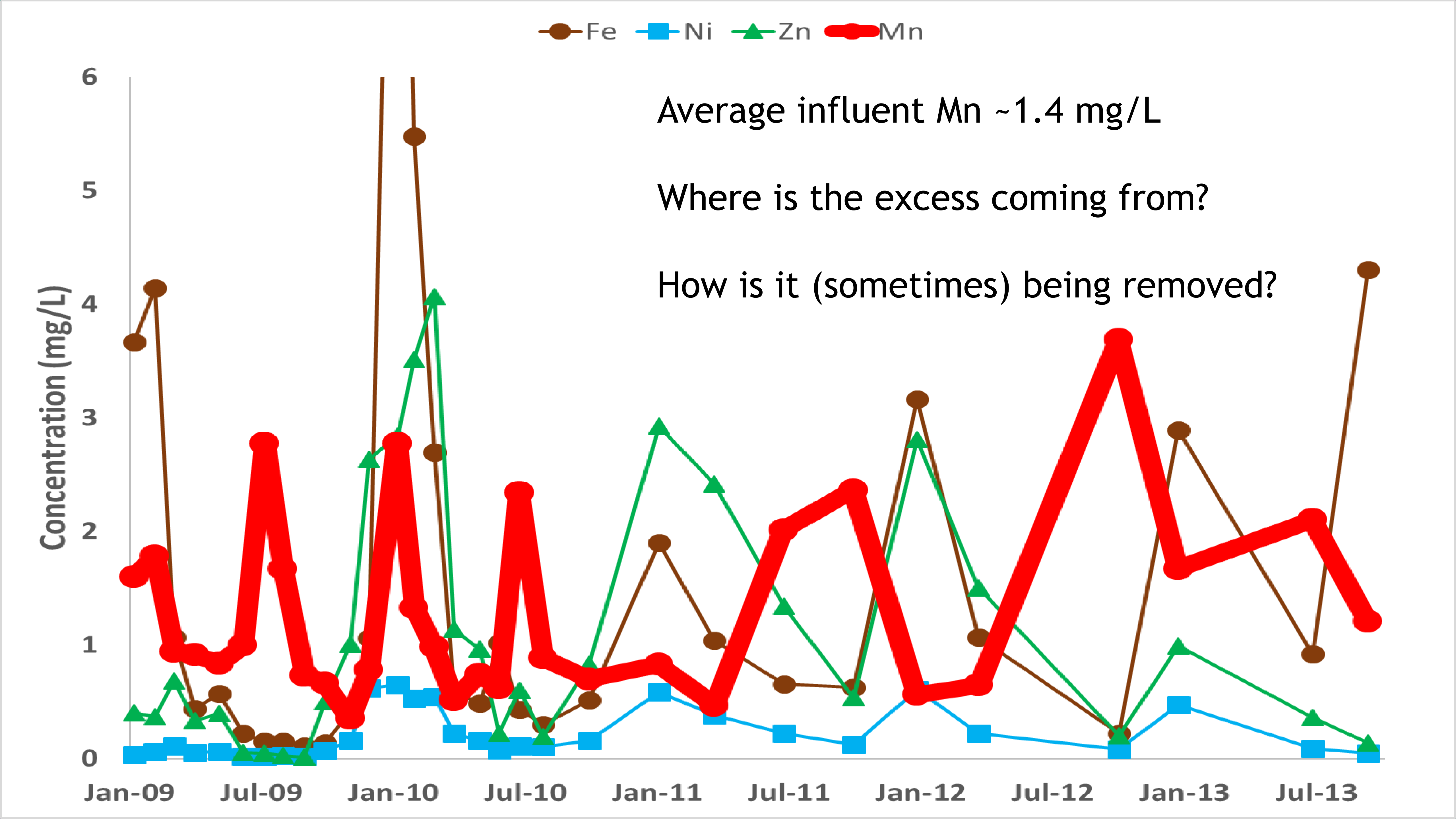
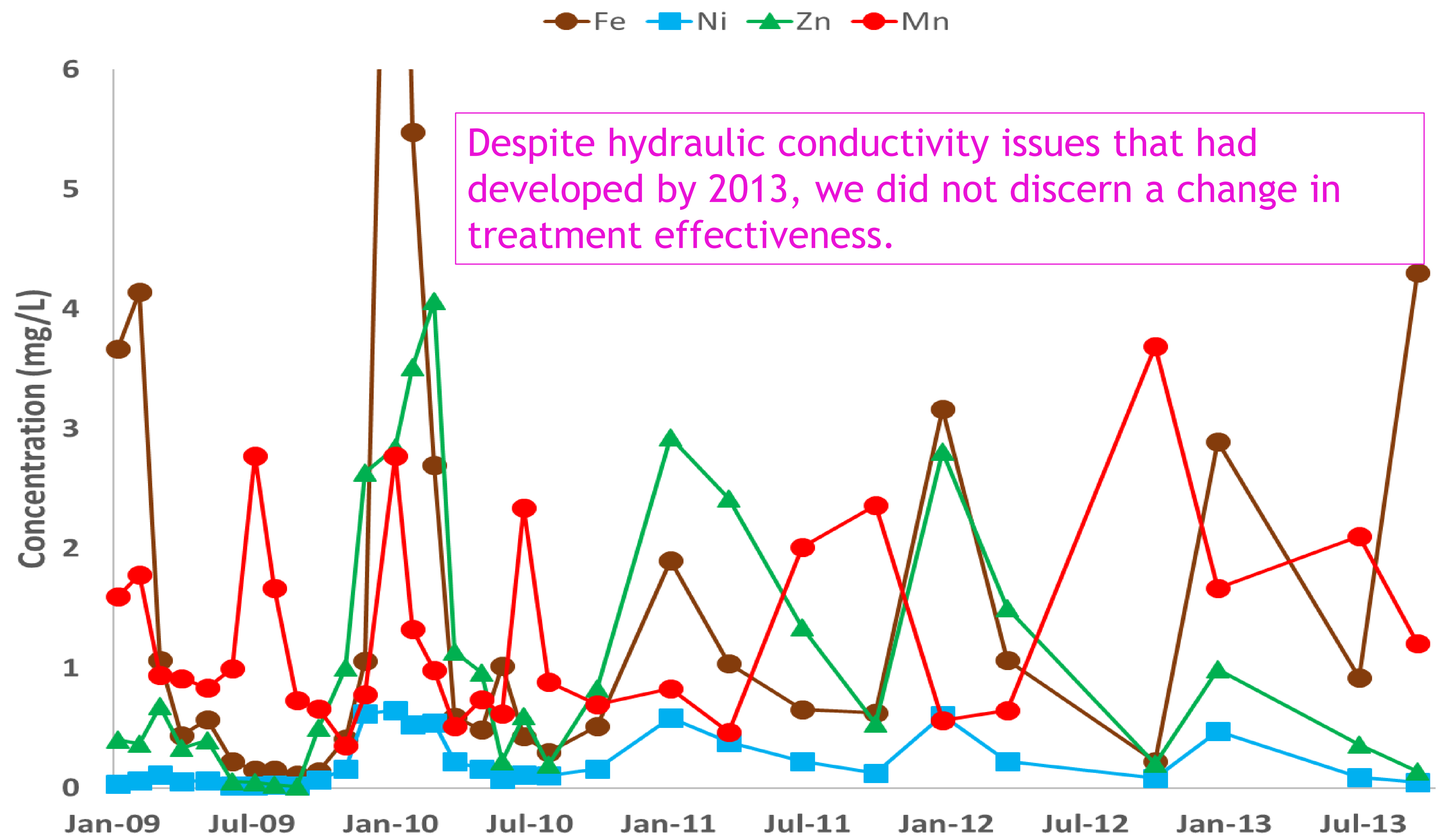
Jul-13


Fe
Ni
Zn
Mn
Average influent Mn ~1.4 mg/L
Where is the excess coming from?
How is it (sometimes) being removed?
Concentration (mg/L)
0
1
2
3
4
5
6
Jan-09
Jul-09
Jan-10
Jul-10
Jan-11
Jul-11
Jan-12
Jul-12
Jan-13
Jul-13


Fe
Ni
Zn
Mn
Concentration (mg/L)
6
5
4
3
2
1
0
Jan-09
Jul-09
Jan-10
Jul-10
Jan-11
Jul-11
Jan-12
Jul-12
Jan-13
Jul-13
Despite hydraulic conductivity issues that had developed by 2013, we did not discern a change in treatment effectiveness.

Total removal

- By June 2010, the VFBR had removed:
  - 770 g Cd
  - 30 kg Co
  - 1,750 kg Fe
  - 257 kg Mn
  - 428 kg Ni
  - 18 kg Pb
  - 2,950 kg Zn
- By July 2014, the VFBR had removed:
  - 3 kg Cd
  - 110 kg Co
  - 6,400 kg Fe
  - 937 kg Mn
  - 1,550 kg Ni
  - 66 kg Pb
  - 10,700 kg Zn

Substrate sampling

- Samples collected at equidistant points in each VFBR
  - 2010 – nine cores
  - 2014 – sixteen samples
- Immediately placed in air-tight plastic bags
- Stored at < 4°C (but above freezing)
- 2010 samples dried prior to analyses
  - Potential destruction of carbonate species
- 2014 samples never dried

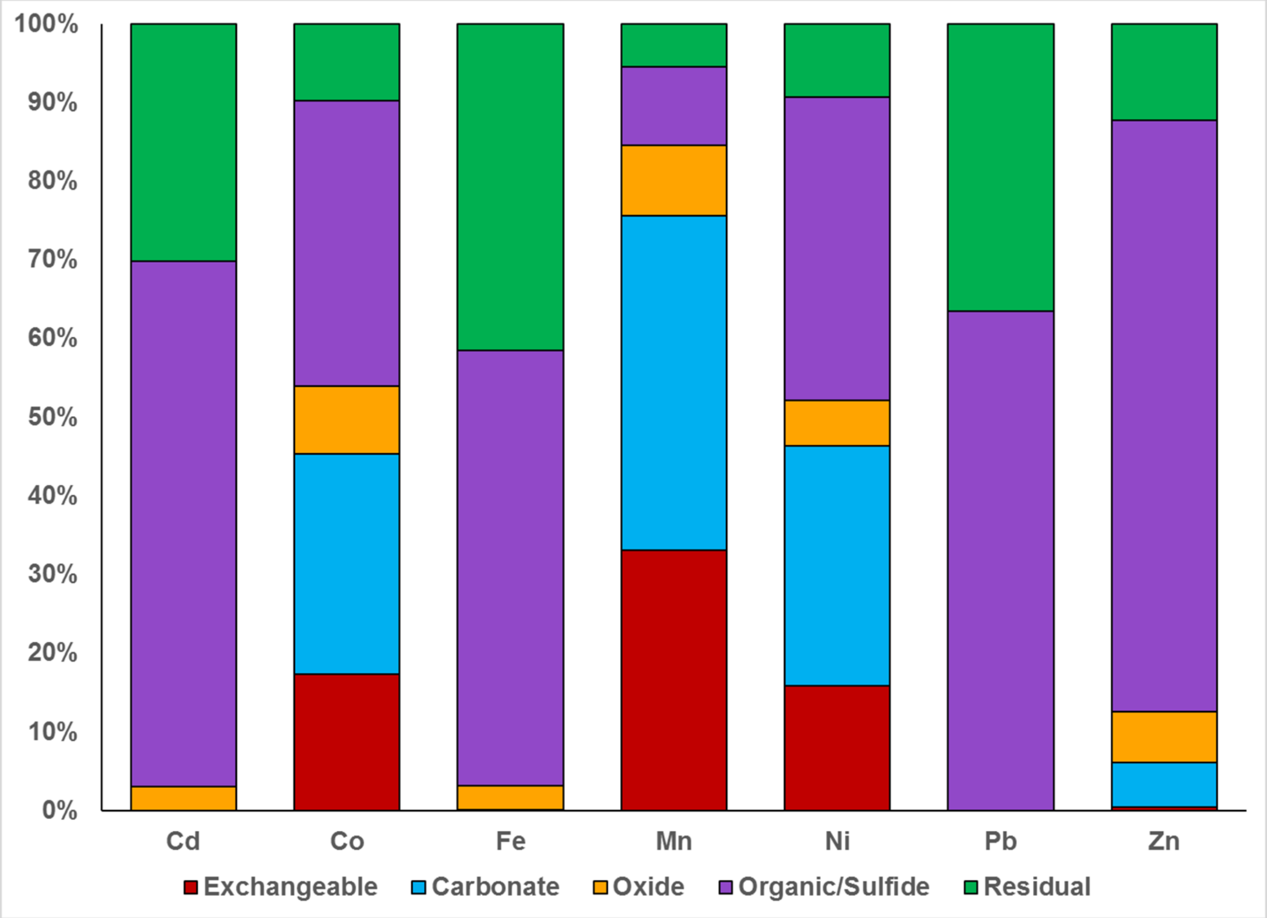
Sequential extraction scheme

2010 extractions included a water soluble fraction

2014 extractions included a labile organic matter fraction

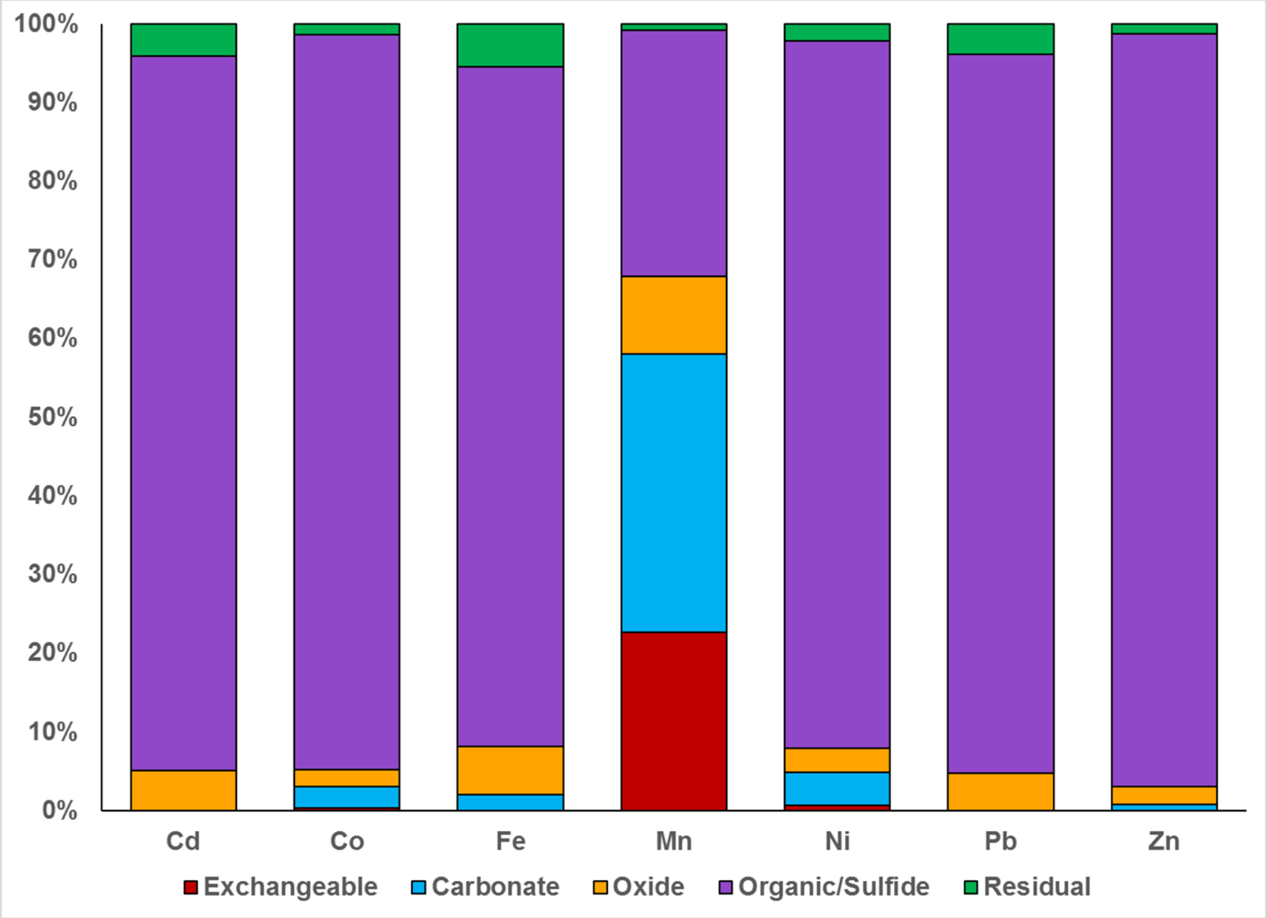
Fraction	Target	Reagents	Procedure
Exchangeable (+ water soluble)			
Bound to carbonate	that are adsorbed to carbonate surfaces		peat
Bound to labile organic matter	Metals that are bound in humic and fulvic acids through complexation	0.1 M $Na_4P_2O_7 \cdot 10H_2O$ at pH 10	Agitate for 1 hour and repeat
Bound to Fe/Mn oxides	Fe and Mn oxides and any metals that may be adsorbed to them	0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) HOAc	Agitate for 1 hour
Bound to refractory organic matter and sulfides	Metals that are bound to sulfides and decay-resistant organic matter with low solubility	3-mL of 0.02 M HNO_3 30% H_2O_2 adjusted to pH 2 with HNO_3 3.2 M NH_4OAc in 20% (v/v) HNO_3 and sparged ultrapure water	Heated to 85±2°C for 5 hours with occasional agitation Agitate for 30 minutes
Residual	Metals that are bound to primary and secondary minerals, particularly silicates, which typically enter the environment through weathering	Concentrated HNO_3	Microwave digestion

2010



Water soluble fraction has been added to exchangeable fraction to provide comparison to 2014 data

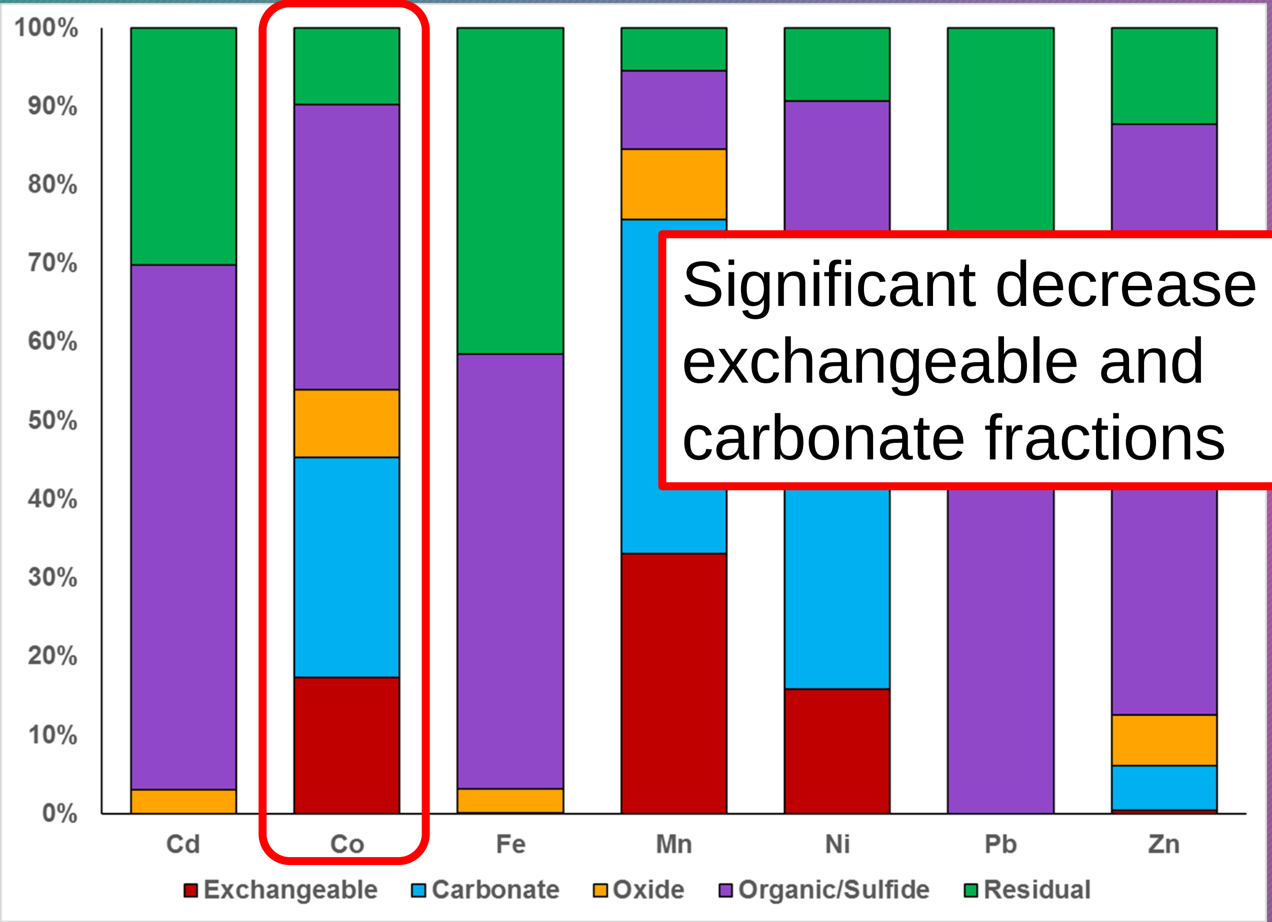
2014

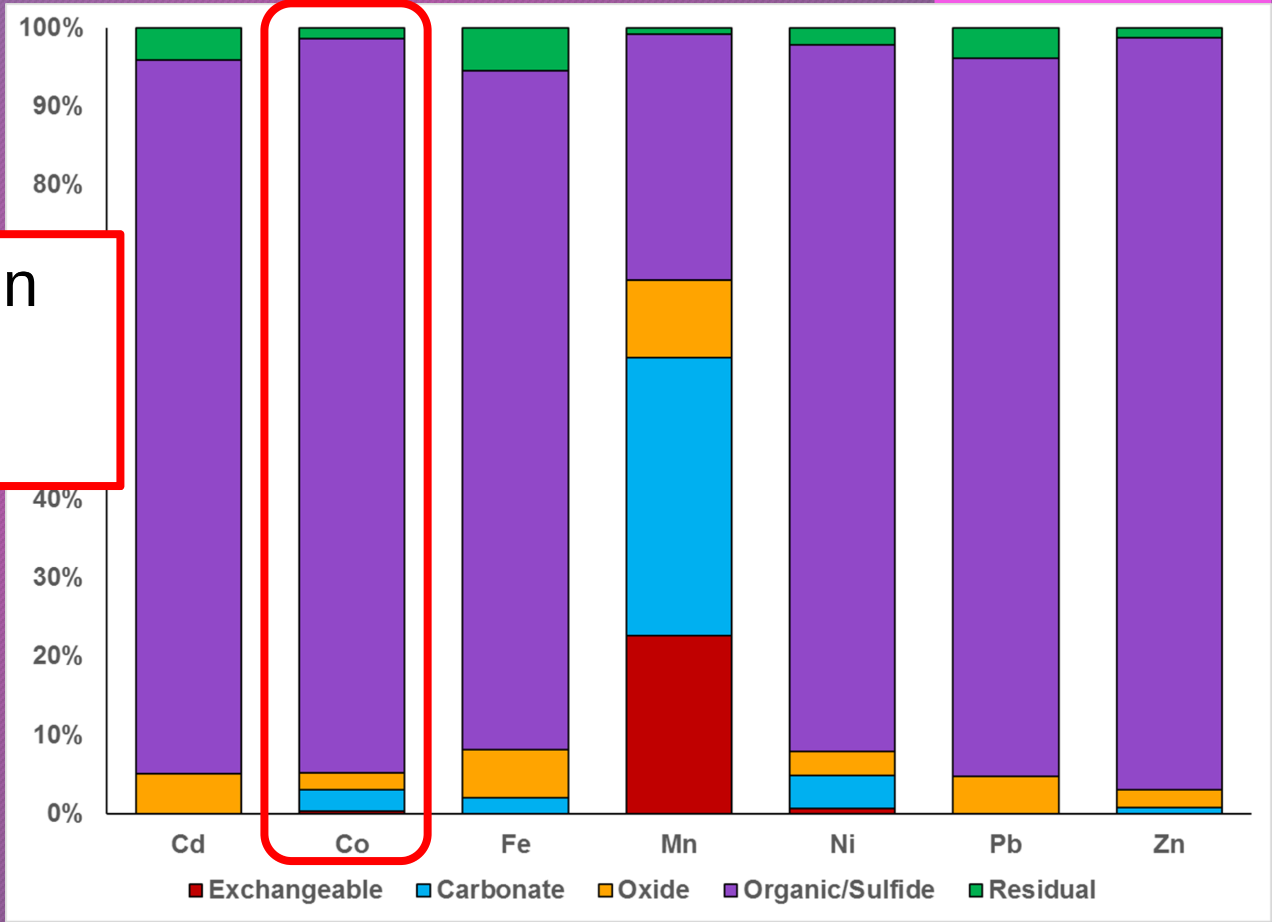


Labile organic fraction has been added to organic/sulfide fraction to provide comparison to 2010 data

2010

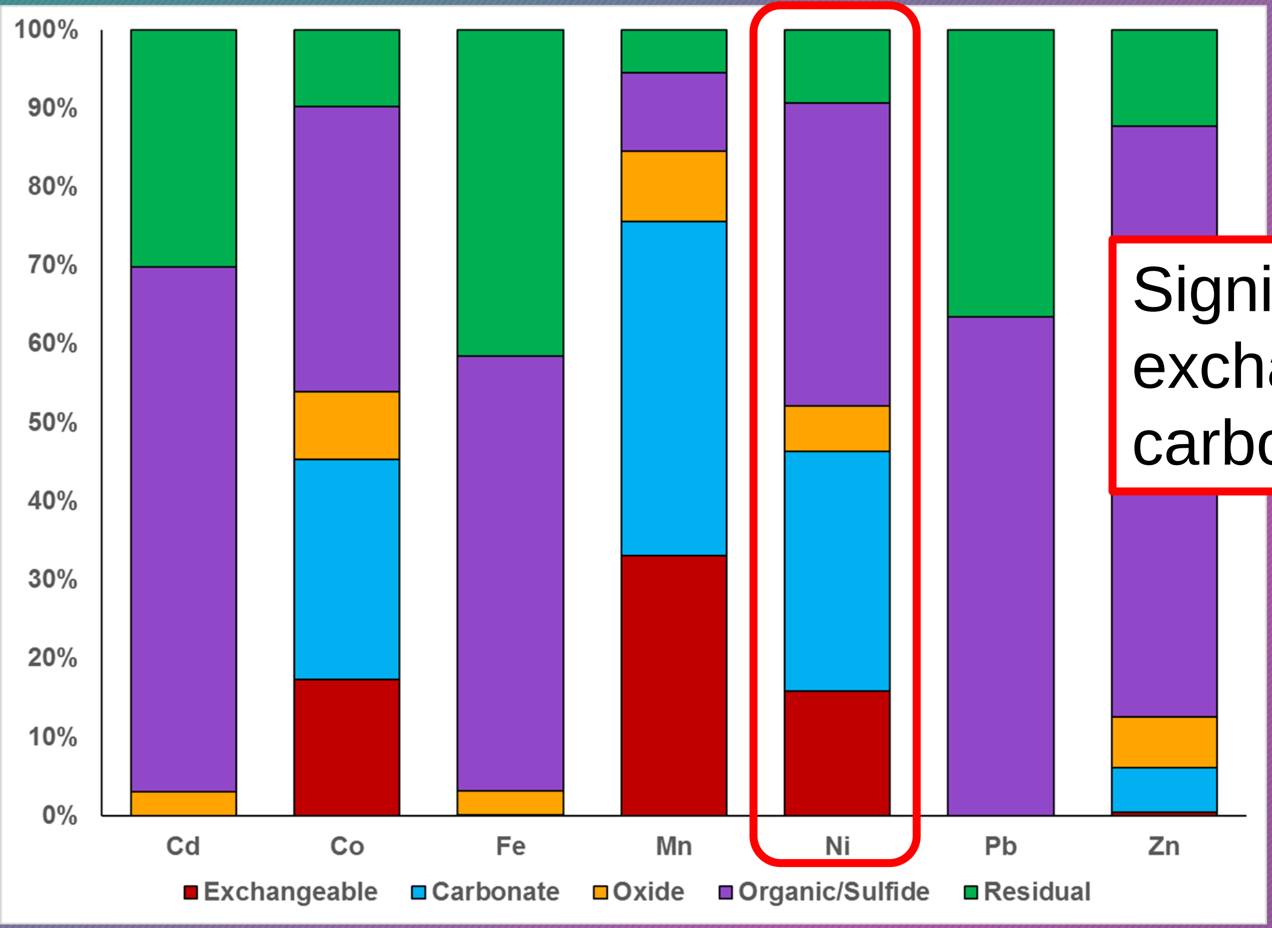
2014



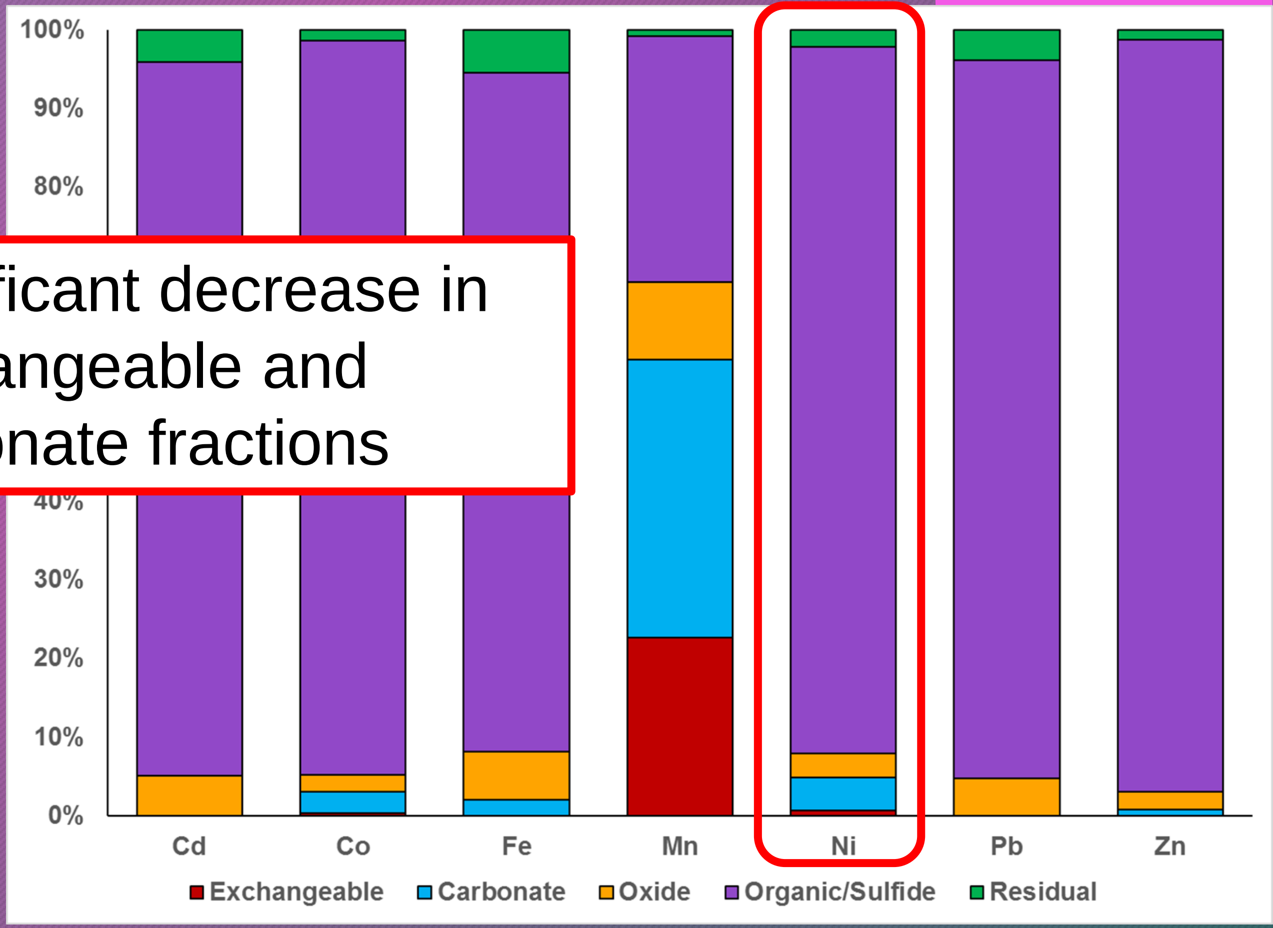


Significant decrease in exchangeable and carbonate fractions

2010



2014



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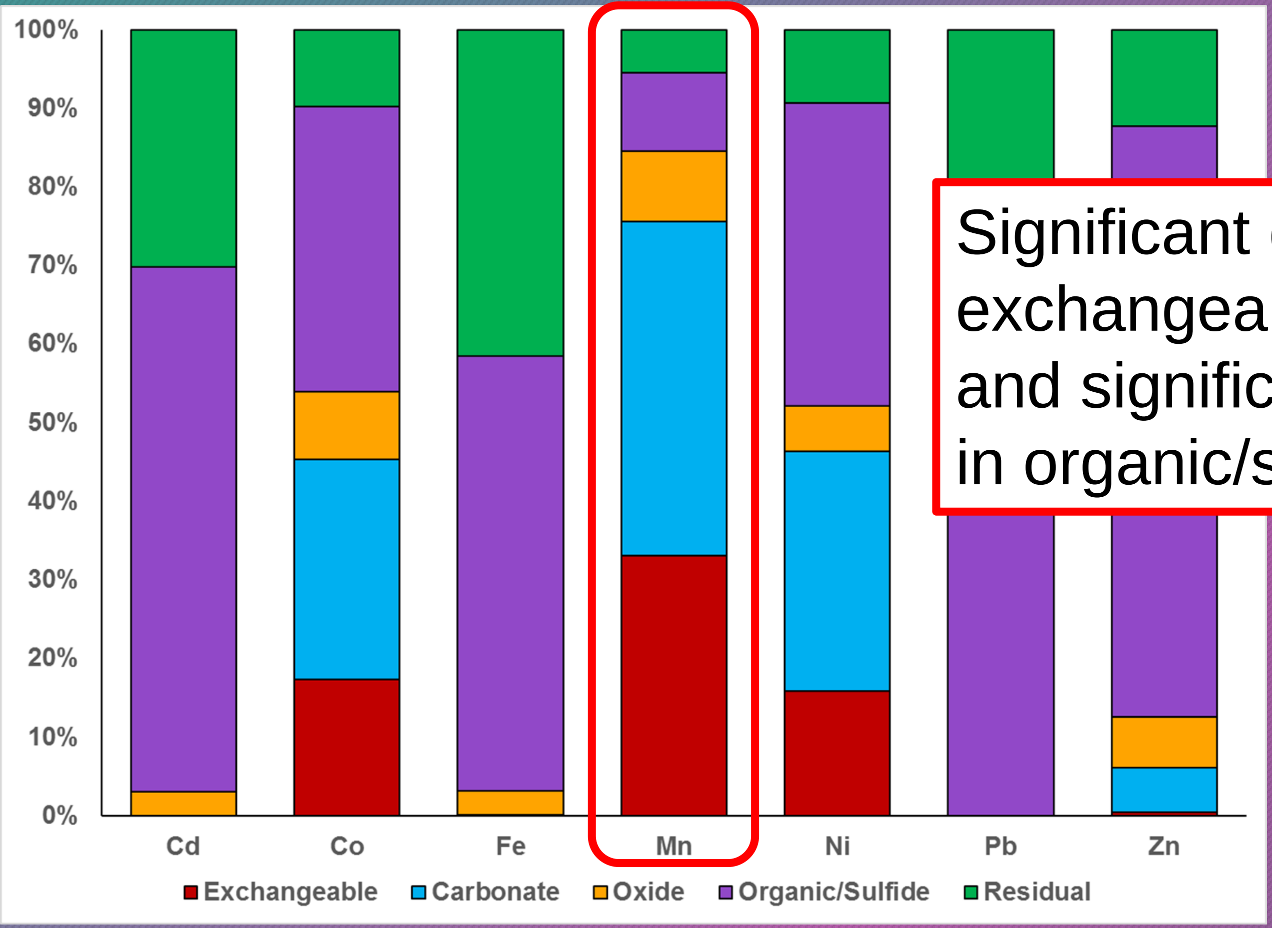
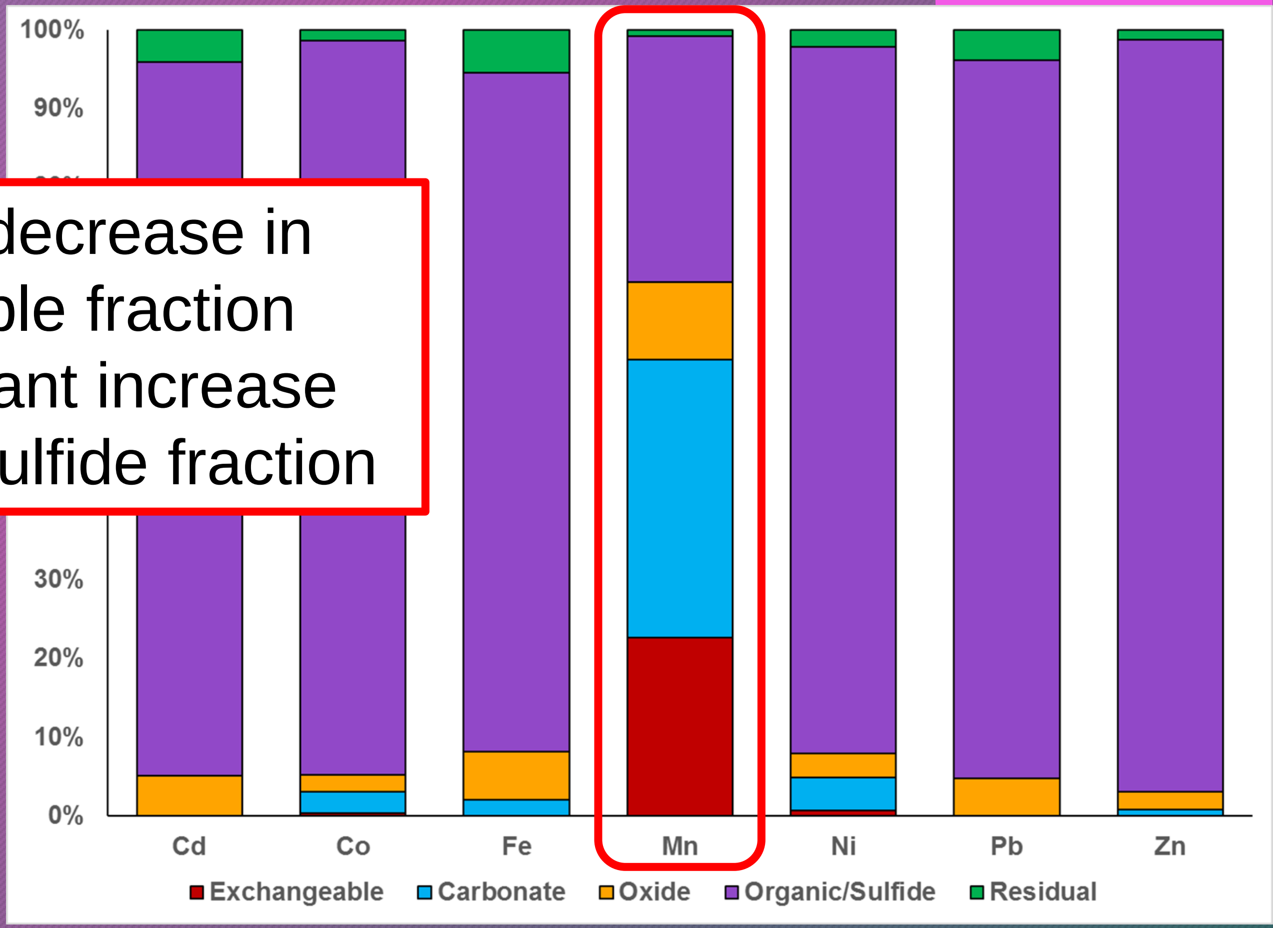
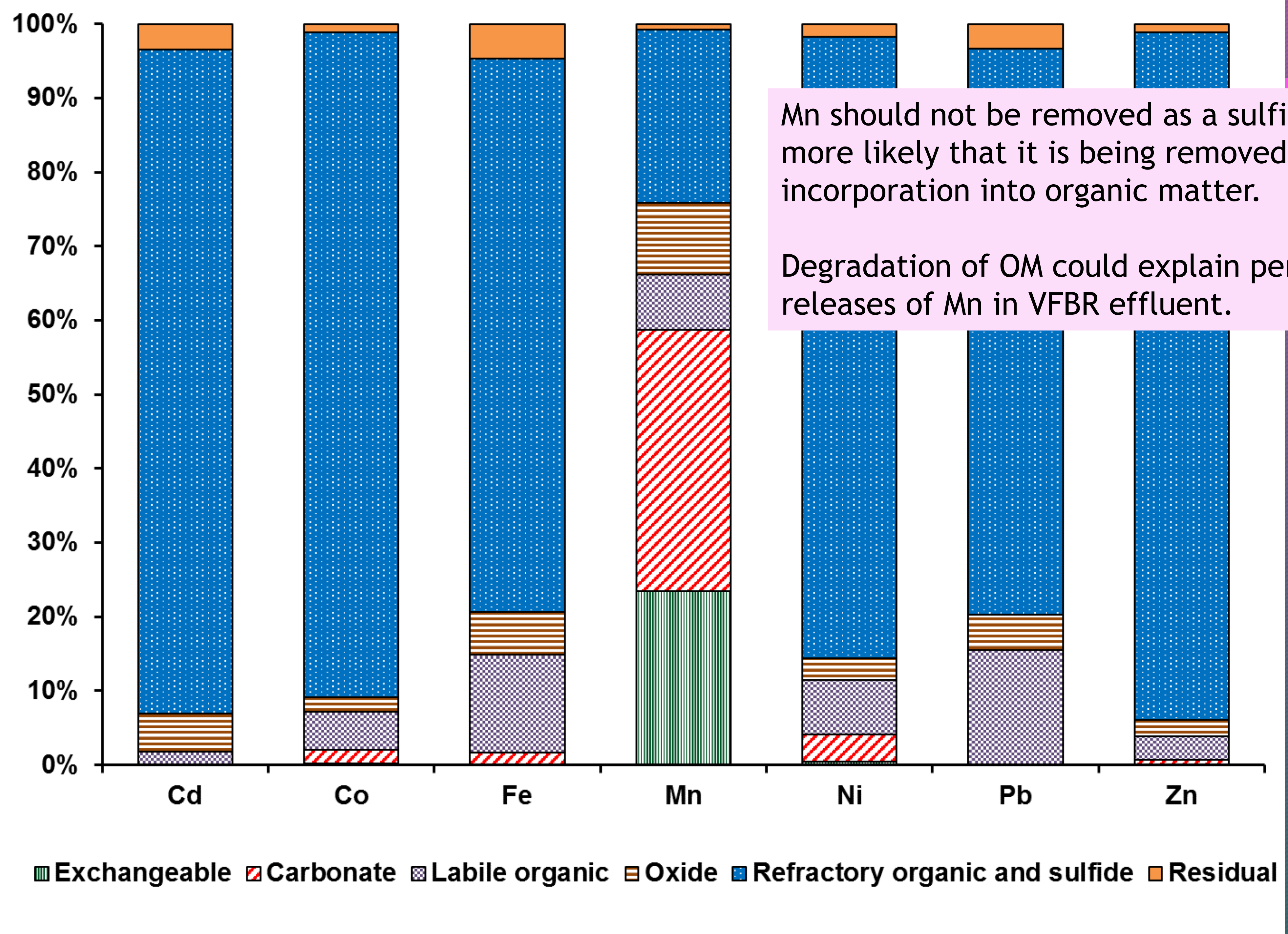


2014



Significant decrease in exchangeable fraction and significant increase in organic/sulfide fraction



Mn should not be removed as a sulfide; it is more likely that it is being removed via incorporation into organic matter.

Degradation of OM could explain periodic releases of Mn in VFBR effluent.

Metal	Fraction	PRE	2010	2014
Cd	Exchangeable	-	-	-
	Carbonate	0.04	-	-
	Oxide	**0.00**	**0.02**	**0.04**
	Organic/sulfide	**0.34**	**0.52**	**0.86**
Co	Exchangeable	**0.04**	**2.4**	**0.14**
	Carbonate	**0.03**	**3.4**	**1.5**
	Oxide	**0.05**	**1.0**	1.3
	Organic/sulfide	**0.79**	**4.0**	**69**
Fe	Exchangeable	**1.2**	**0.44**	-
	Carbonate	**111**	**1.5**	**130**
	Oxide	**25**	**104**	**410**
	Organic/sulfide	2040	**2100**	**6500**
Mn	Exchangeable	**27**	**45**	**61**
	Carbonate	76	**54**	**91**
	Oxide	**2.3**	**9.9**	**25**
	Organic/sulfide	**40**	**11**	**81**

Metal	Fraction	PRE	2010	2014
Ni	Exchangeable	**0.15**	**43**	**5.3**
	Carbonate	**0.03**	**86**	**48**
	Oxide	**0.02**	**16**	**47**
	Organic/sulfide	**3.4**	**103**	**1330**
Pb	Exchangeable	0.17	-	-
	Carbonate	0.46	-	-
	Oxide	**0.01**	-	**0.58**
	Organic/sulfide	5.1	**3.1**	**9.9**
Zn	Exchangeable	**0.33**	**16**	**3.1**
	Carbonate	**13**	**160**	140
	Oxide	**0.19**	**170**	**370**
	Organic/sulfide	**37**	**2230**	**13700**

Median concentrations (mg/kg)

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Median concentrations (mg/kg)

Conclusions

- As expected, adsorption played an important role in trace metal removal in system's youth
  - All metals but Mn were released to some extent between 2010 and 2014
  - Mn continued to be adsorbed between 2010 and 2014
- Carbonate precipitation and/or sorption plays an important role in Mn removal
  - Viable route for Fe and Zn removal, but less important than sulfide formation
- Metals removed as carbonates may be remobilized and removed via another pathway
- Being bound up in organic matter provides some removal, but is likely temporary

Acknowledgements

- Private Landowners
- USEPA Agreements FY04 104(b)(3) X7-97682001-0 and R-829423-01-0
- US Dept. of Education GAANN Program
- ASMR PhD Research Grant 2011
- ASMR Memorial Scholarship, PhD Level 2012
- Grand River Dam Authority Graduate Fellowship
- OU CREW
- Saint Francis University

Questions?