EVOLUTION OF TRACE METAL REMOVAL PRODUCTS IN FIELD-SCALE VERTICAL FLOW BIOREACTORS

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Saint Francis University

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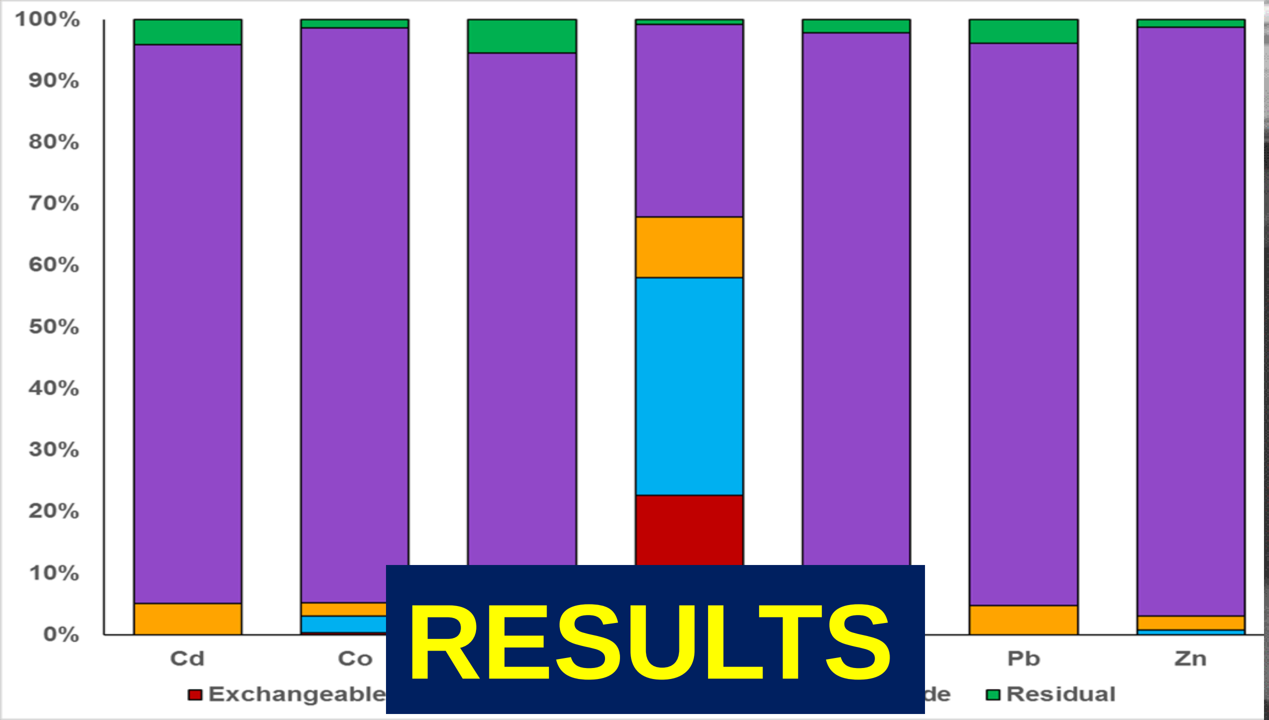
University of Oklahoma


BACKGROUND


METHODS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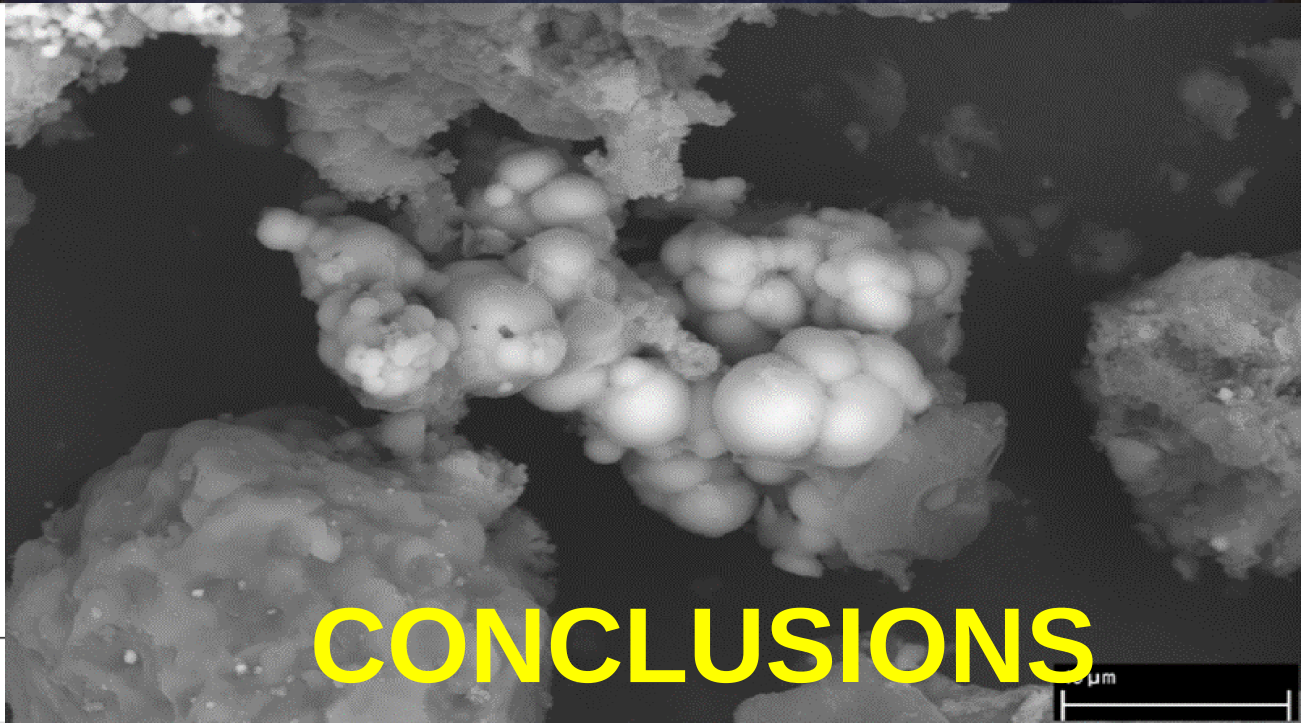
Exchangeable
Residual
RESULTS


CONCLUSIONS

BACKGROUND

MAYER RANCH PTS

- Constructed in 2008
- Treats water containing elevated metals, mineral acidity, and sulfate
- Water also contains elevated alkalinity
- Unit processes
  - Oxidation/settling pond
  - Settling wetlands
  - Vertical flow bioreactors
  - Reaeration ponds
  - Horizontal flow limestone beds
  - Polishing wetland

TRACE METAL REMOVAL

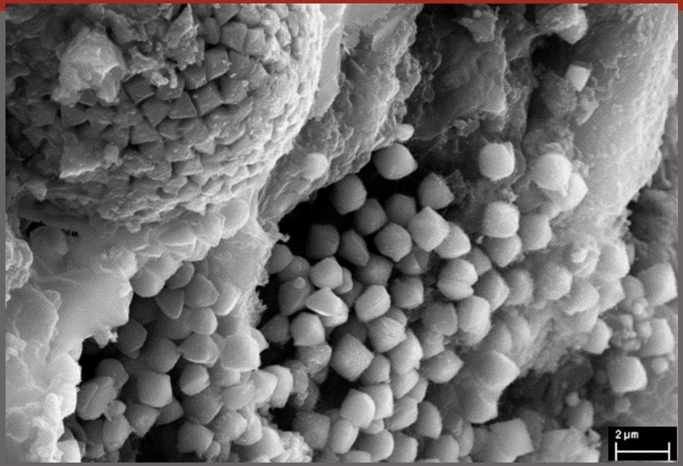
- Vertical flow bioreactors
  - 0.5 m organic substrate
    - 45:45:10 spent mushroom compost, wood chips, limestone sand
  - 0.5 m high-calcite limestone
- Water flows downward through organic substrate
  - Creates anoxic, reducing conditions
  - Promotes sulfate reduction by bacteria

TRACE METAL REMOVAL

- Goal of VFBR = remove trace metals via sulfide precipitation
  - Alkalinity generation in this system is a bonus

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

DETERMINING REMOVAL PRODUCTS



- Scanning or transmission electron microscopy (and XRD, XANES, SXRF)
  - Require high concentrations of crystalline products
  - Expensive and time-consuming
- Acid-volatile sulfides/simultaneously extracted metals
  - Preferred for amorphous precipitates
  - Some crystalline products will not be quantified
- Sequential extractions
  - Operationally-defined (e.g. acetic acid soluble)
  - Use specific reagents to extract targeted species

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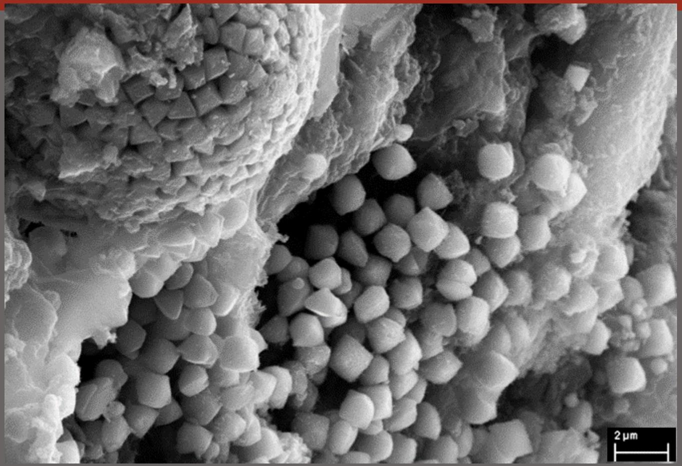

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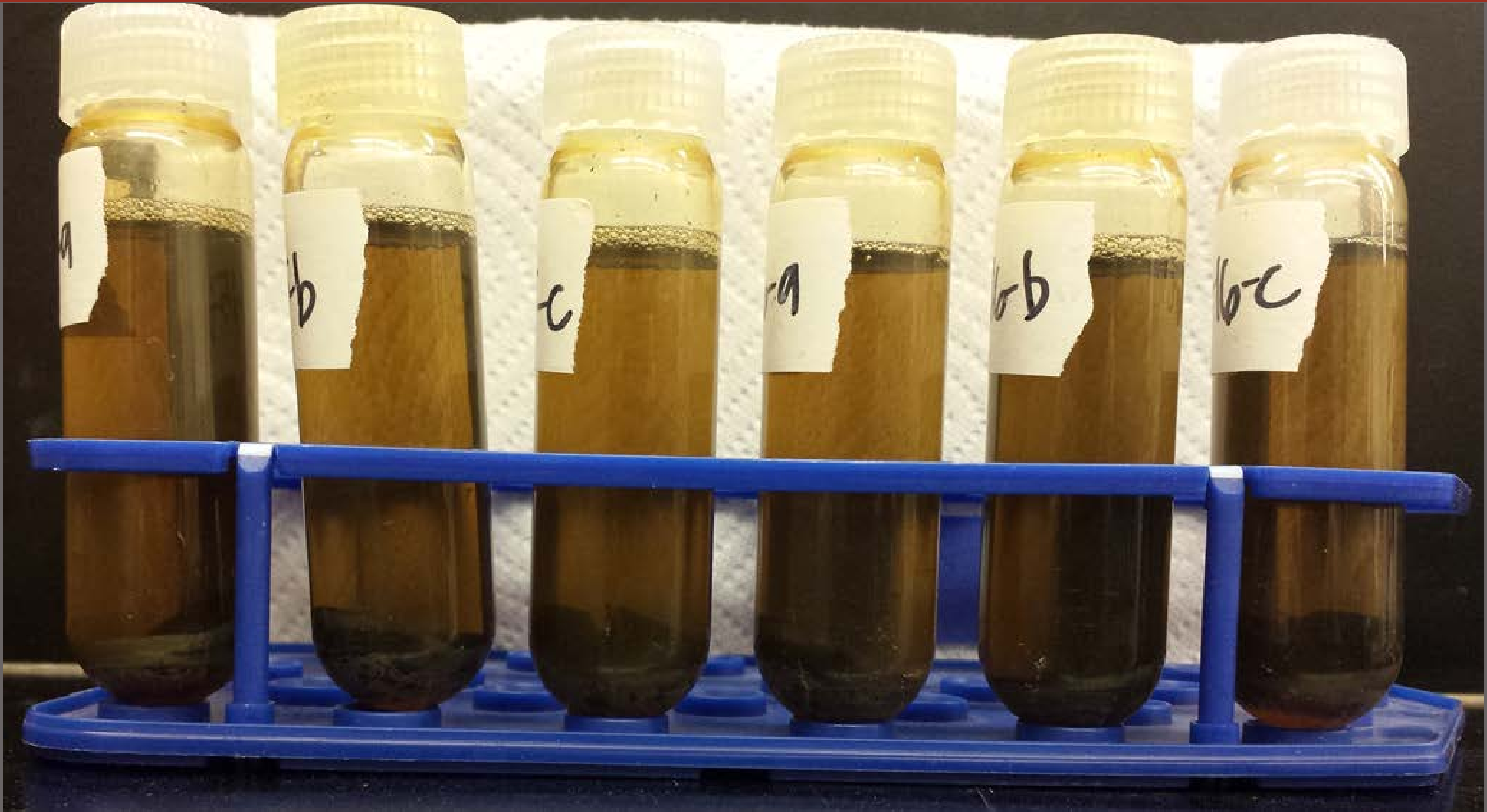
METHODS



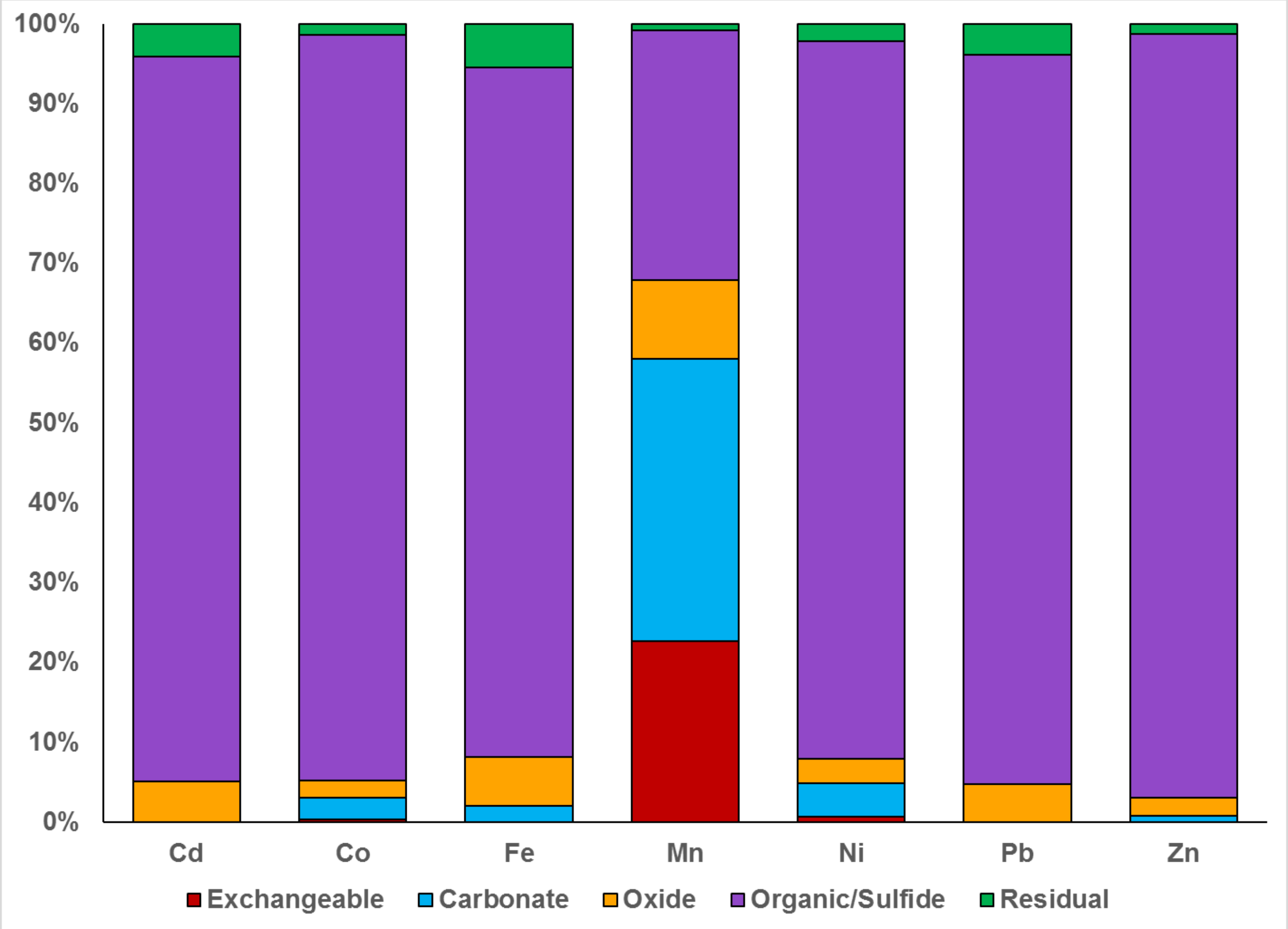
SUBSTRATE SAMPLING

- 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
- 2010 samples dried prior to analyses
  - Potential destruction of carbonate species
- 2014 samples never dried

SEQUENTIAL EXTRACTION SCHEME

Fraction	Target	Reagents	Procedure
Exchangeable (+ water soluble)	Metals that may be released through ion-exchange processes or are weakly adsorbed to the substrate surface	1 M $MgCl_2$ at pH 7	Agitate for 1 hour
Bound to carbonate	Metals that are precipitated or co-precipitated with carbonate and metals that are adsorbed to carbonate surfaces	1 M NaOAc adjusted to pH 5 with HOAc	Agitate for 1 hour and repeat
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

RESULTS



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Exchangeable
Carbonate
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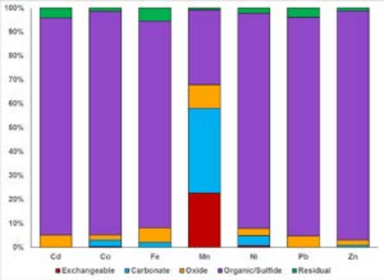
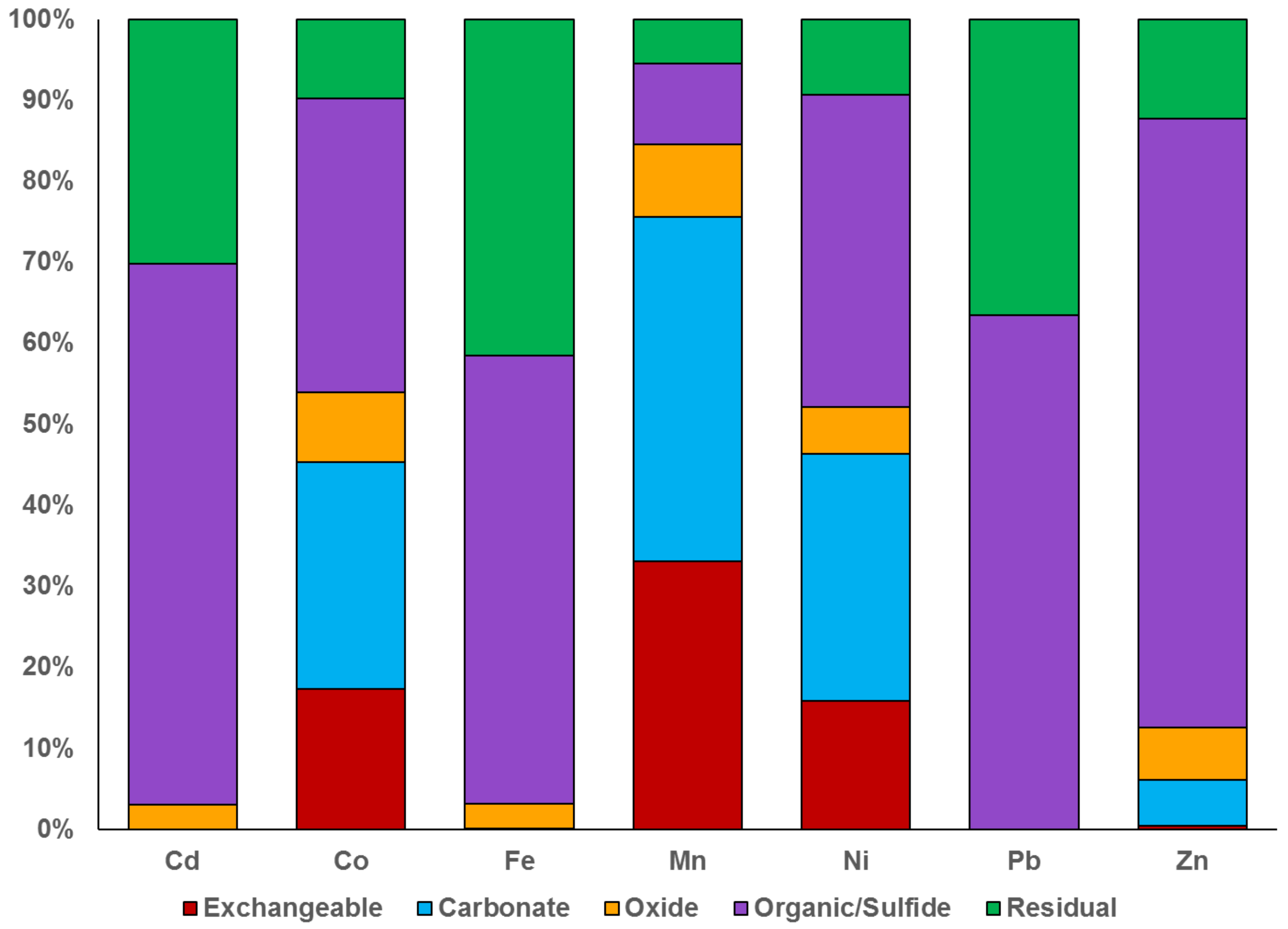
LOADING (11/2008 – 06/2010)



- 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
- 2010 sequential extractions:
  - Included water soluble fraction
  - Did not include labile organic fraction



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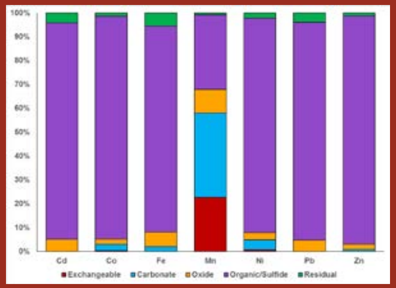
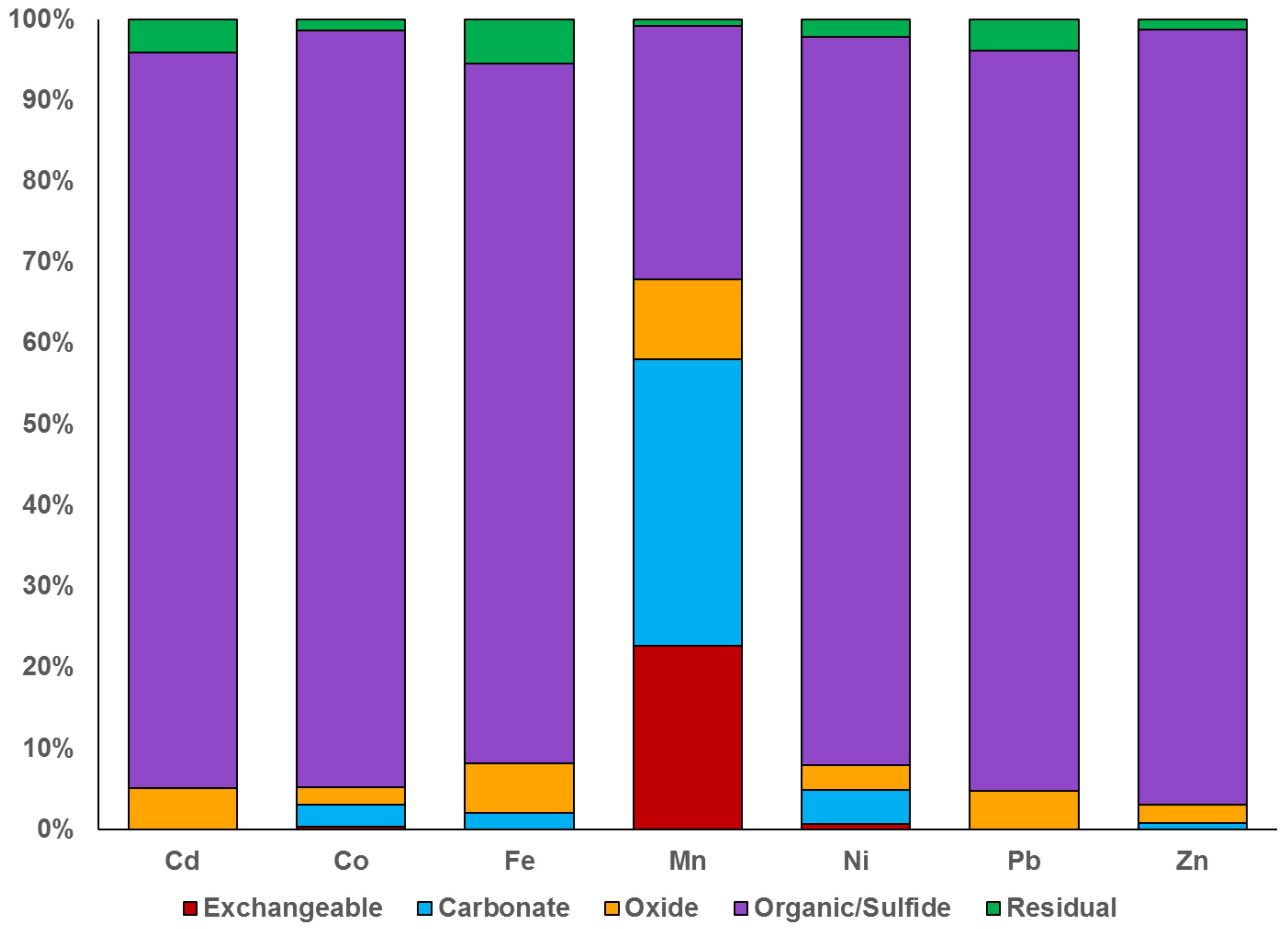
LOADING (11/2008 – 07/2014)



- 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
- 2014 sequential extractions
  - Did not include water soluble fraction
  - Did include labile organic fraction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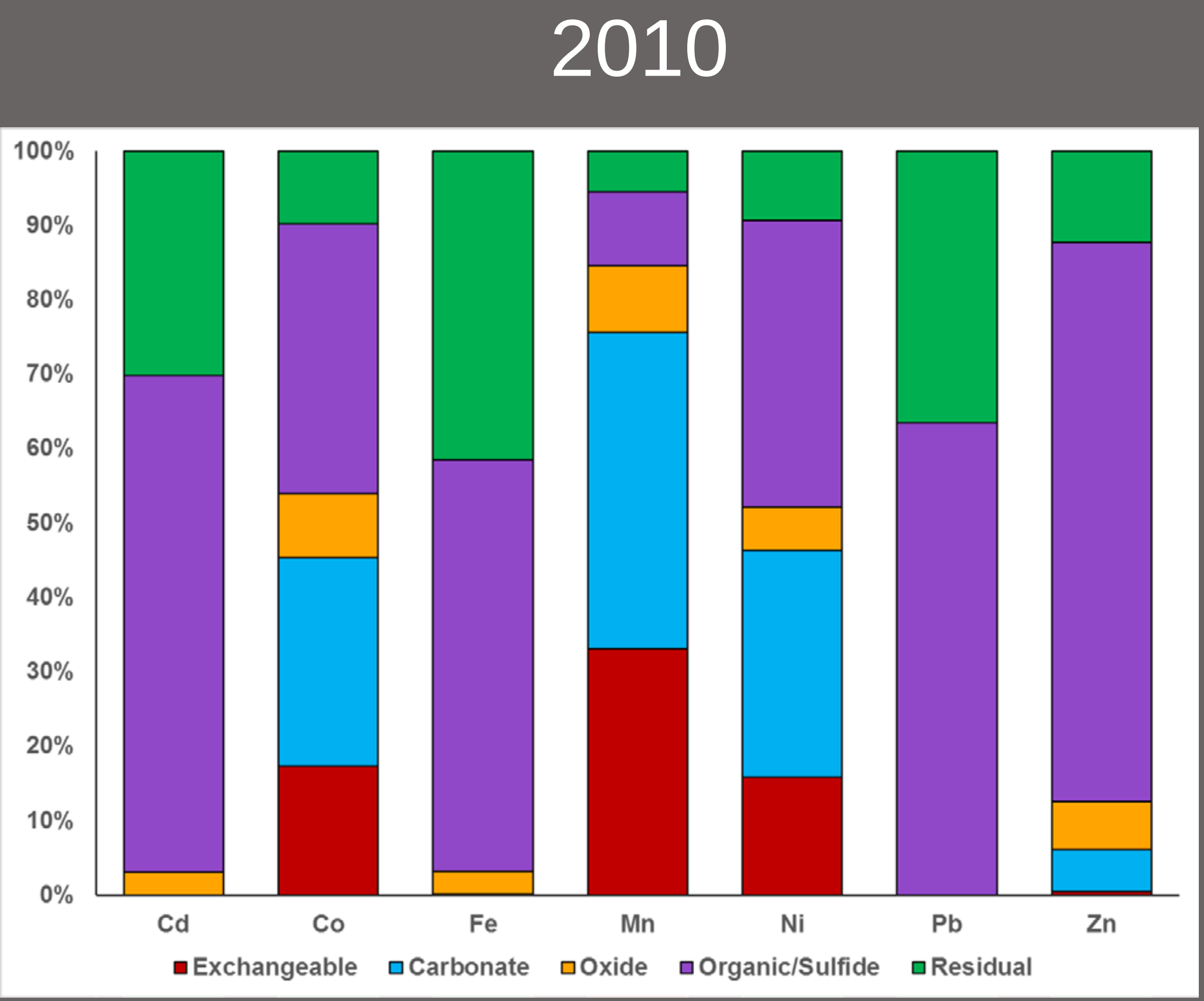
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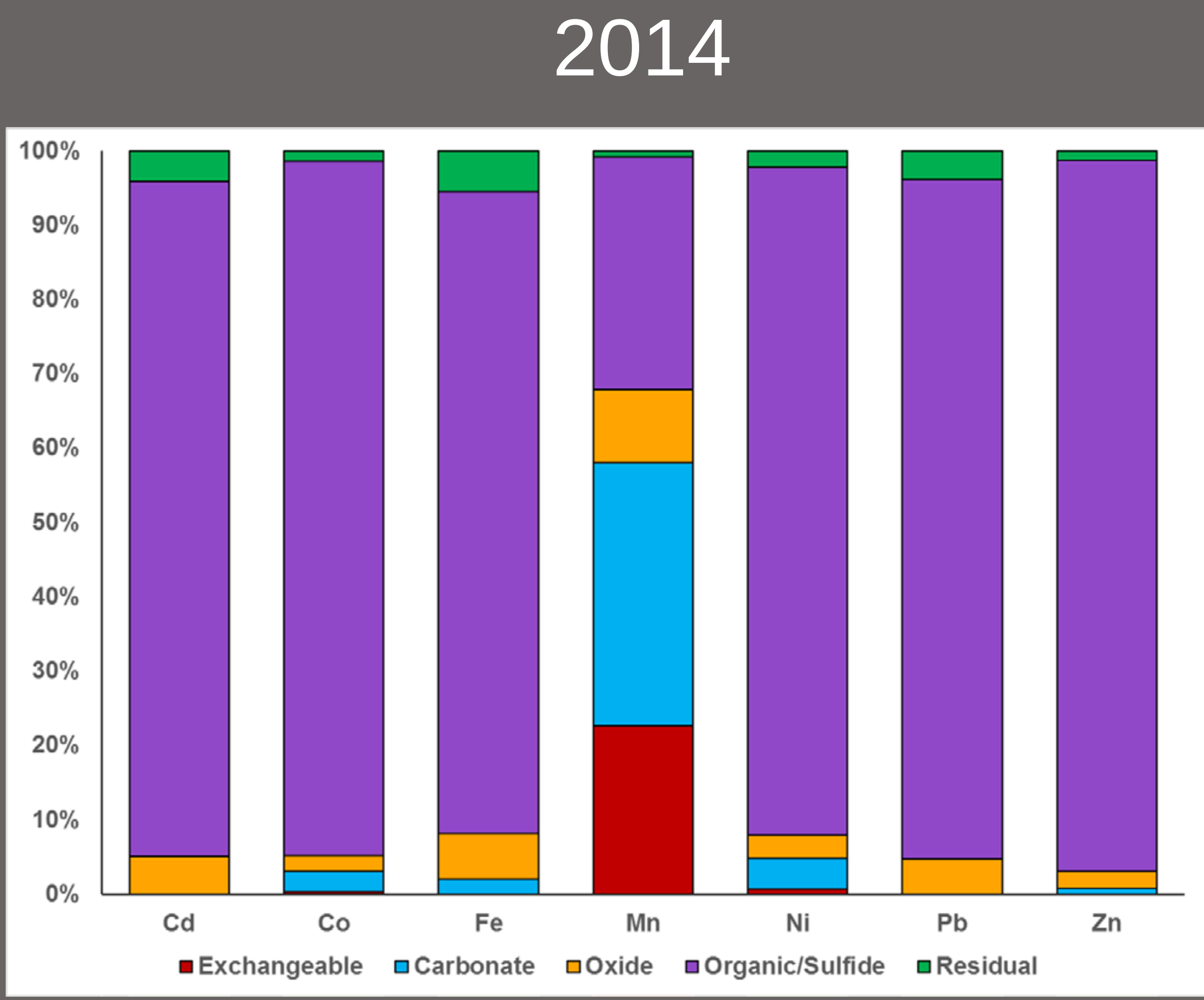
2014
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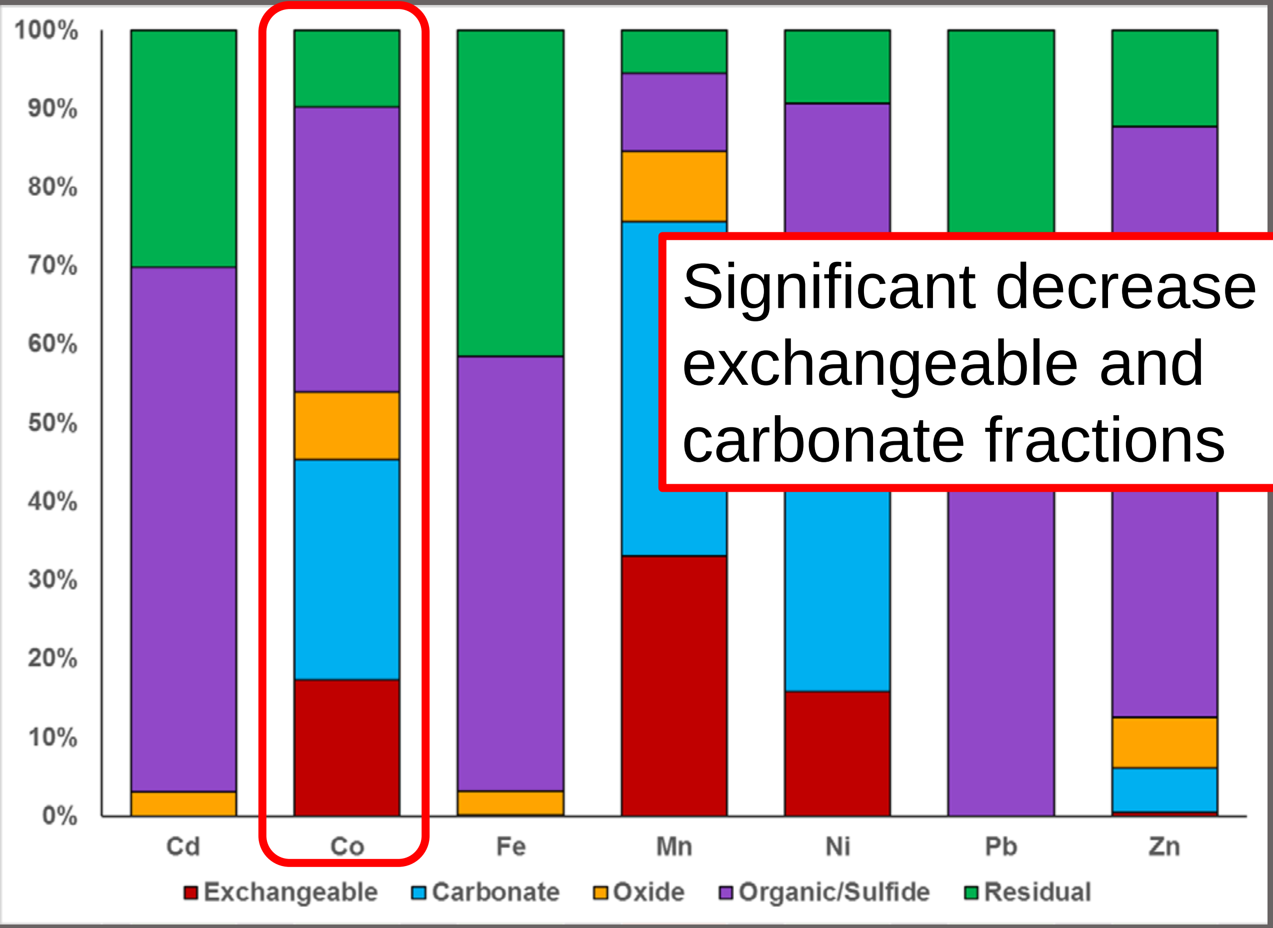
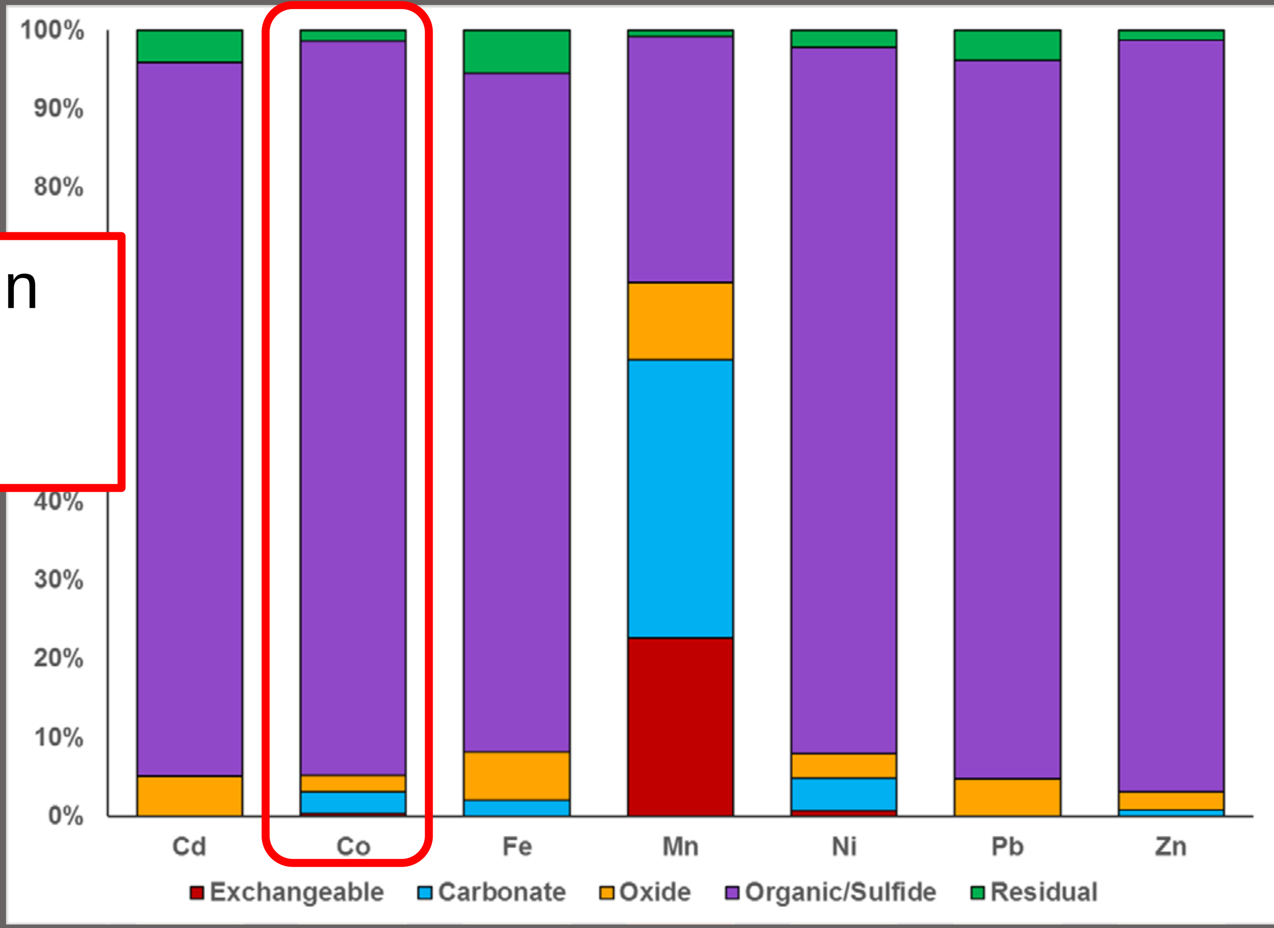
2010



2014



Significant decrease in exchangeable and carbonate fractions

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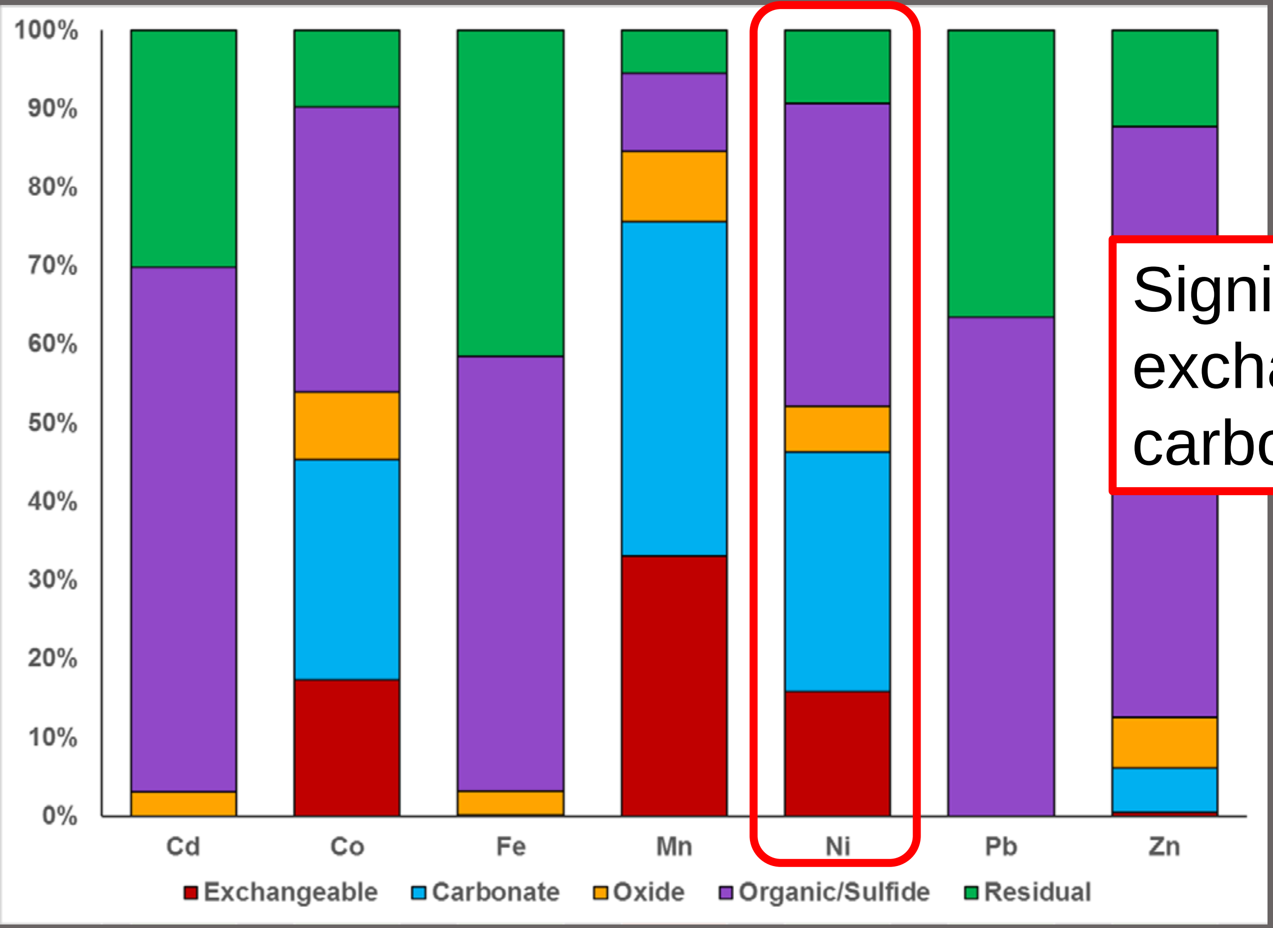
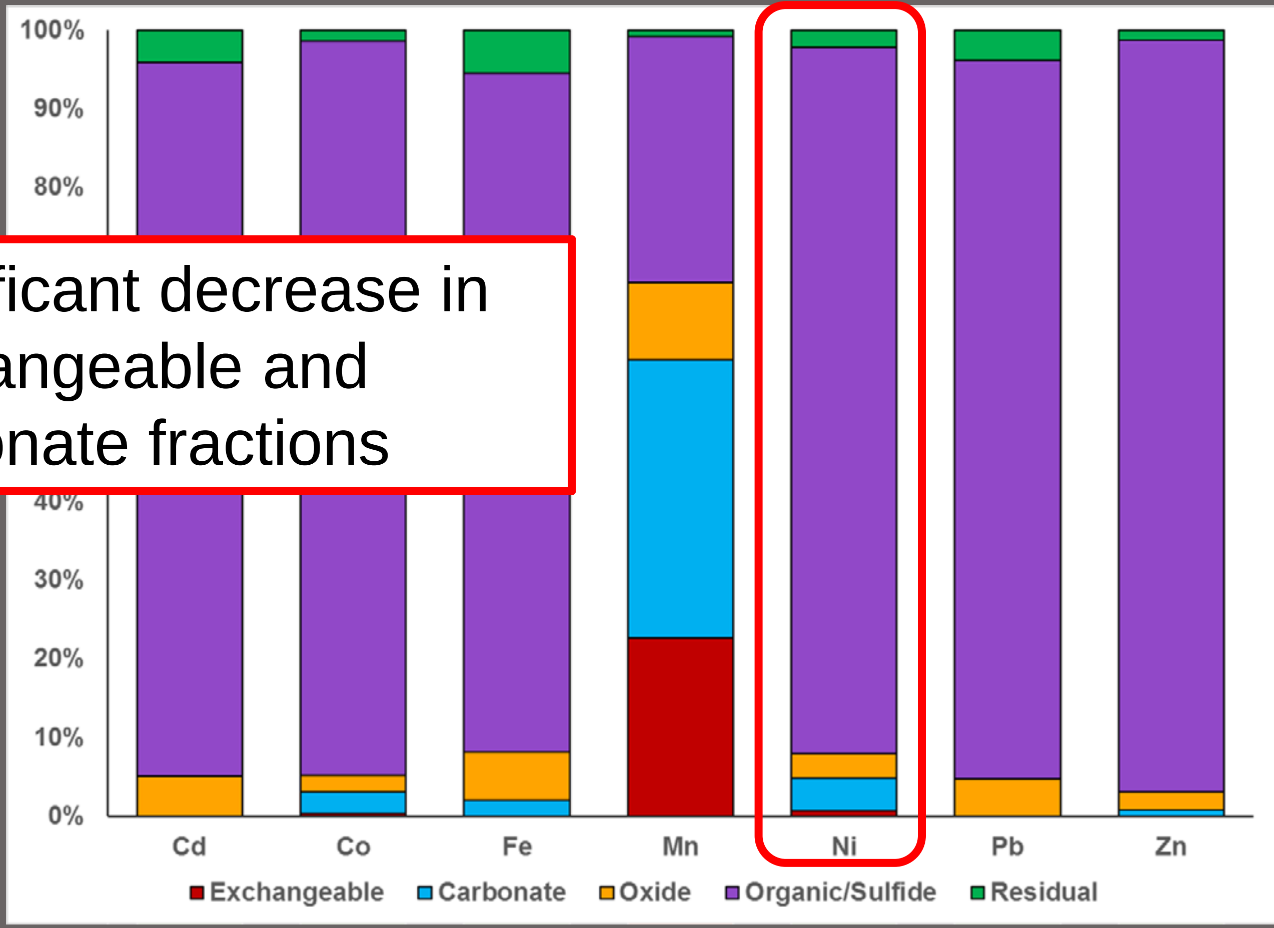


2014



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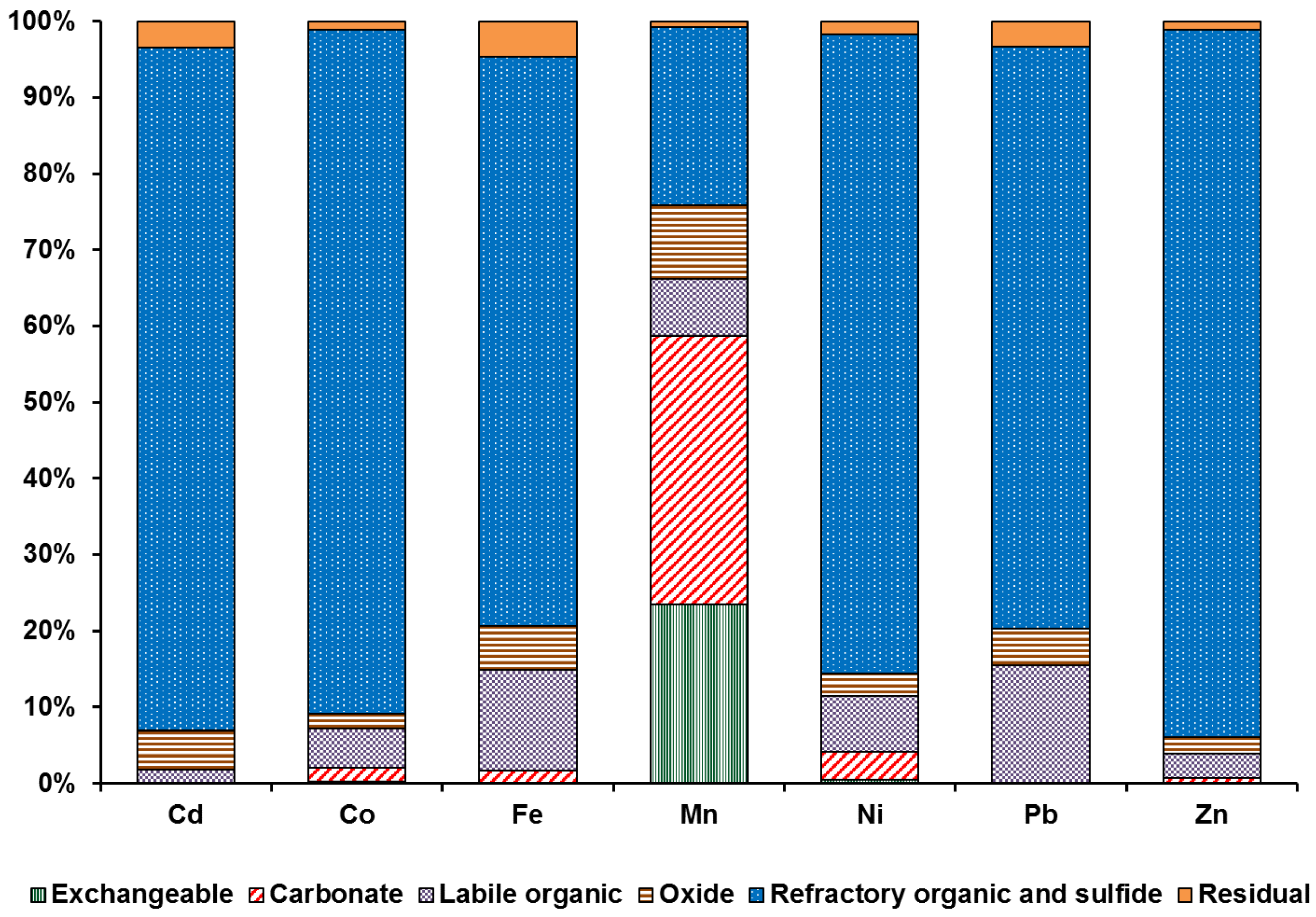
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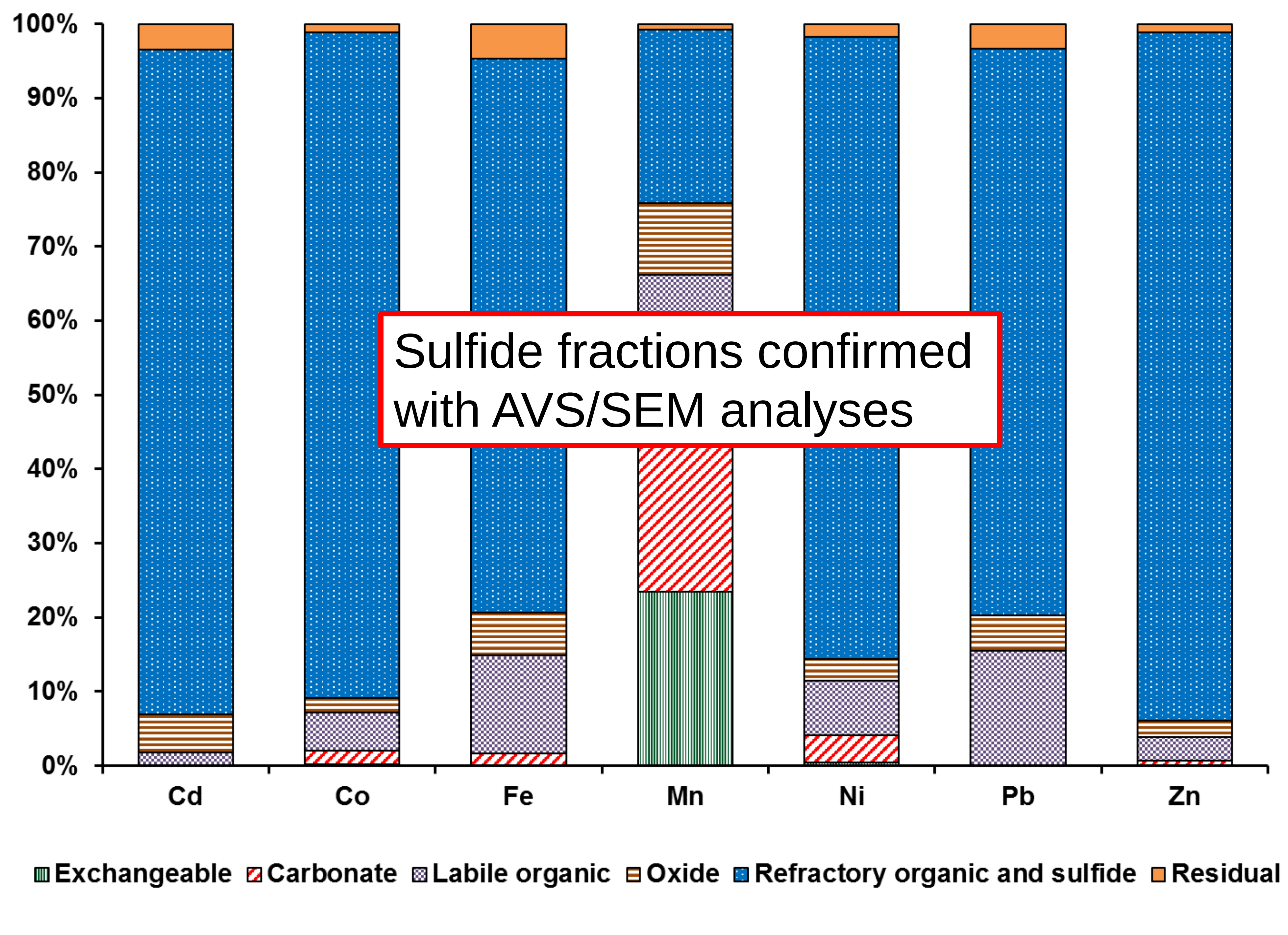
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Sulfide fractions confirmed with AVS/SEM analyses
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Metal	Fraction	PRE	2010	2014
Cd	Exchangeable	-	-	-
	Carbonate	0.04	-	-
	Oxide	**0.00**	**0.02**	**0.04**
	Organic/sulfide	**0.34**	**0.52**	**0.86**
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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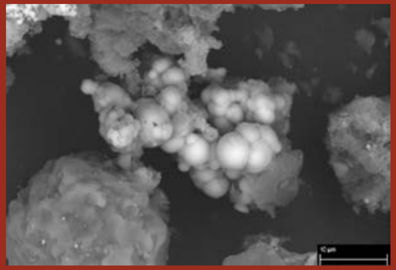
CONCLUSIONS



- 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

- Sulfide precipitation is the most important removal mechanism for trace metals (aside from Mn) at MRPTS

ACKNOWLEDGEMENTS

- Private Landowners
- USEPA Agreements FY04 104(b)(3) X7-97682001-0 and R-829423-01-0
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- Grand River Dam Authority Graduate Fellowship
- OU CREW
- Saint Francis University

QUESTIONS?