Metals Release from Mining-Impacted Streambed Sediments: North Fork Clear Creek, Colorado

Presented by Barbara Butler

August 20, 2010

Presentation Outline

- Background
  - Acid Mine Drainage (AMD)
  - Metals Transport
  - North Fork Clear Creek (NFCC)
- Bed Sediment Metals Research
- Future Research

Background – AMD

- Prevalent in the western U.S.
  - Heavy metal mining
    - Gold, silver, copper, lead, zinc, uranium, molybdenum, etc.
- Prevalent in the eastern U.S.
  - Coal mining

Background – AMD

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- Prevalent in the eastern U.S.
  - Coal mining

Note: Affected streams may or may not be acidic

Background – AMD

- Acid-mine drainage (AMD)
  - Mining process
    - Exposes pyrite to the atmosphere
    - Grinding processes
      - Larger surface areas for exposure

Background – AMD

$$4FeS_{2(s)} + 15O_{2(g)} + 14H_2O \longrightarrow 4Fe(OH)_{3(s)} + 8SO_4{}^{2-}{}_{(aq)} + 16H^+{}_{(aq)}$$

Background – AMD

$$4FeS_{2(s)} + 15O_{2(g)} + 14H_2O \longrightarrow 4Fe(OH)_{3(s)} + 8SO_4{}^{2-}{}_{(aq)} + 16H^+{}_{(aq)}$$

Rapid formation in water column

Background – AMD

$$4FeS_{2(s)} + 15O_{2(g)} + 14H_2O \longrightarrow 4Fe(OH)_{3(s)} + 8SO_4{}^{2-}{}_{(aq)} + 16H^+{}_{(aq)}$$

Acid-Dissolution

Rocks $\longrightarrow$ Metals

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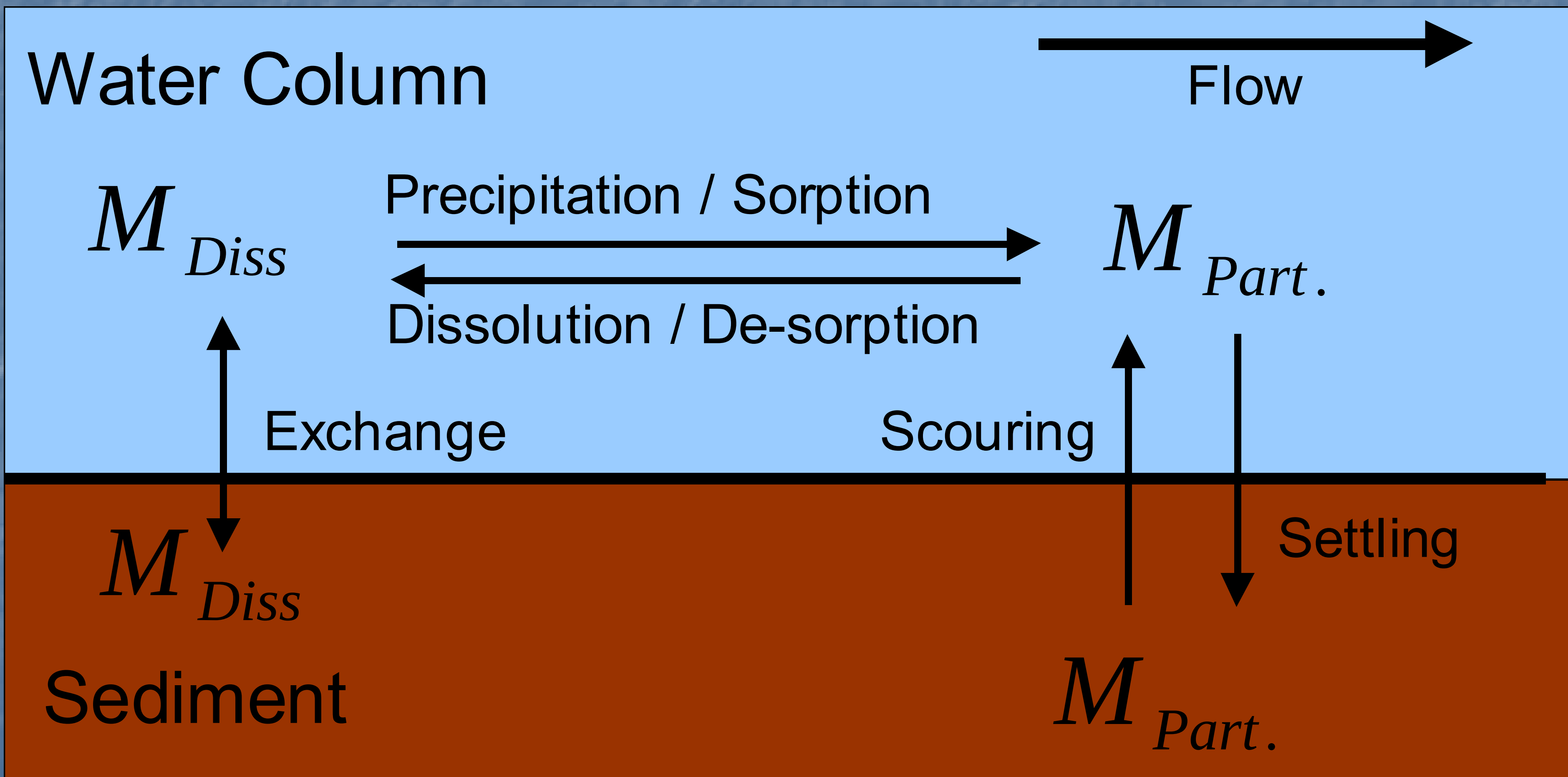
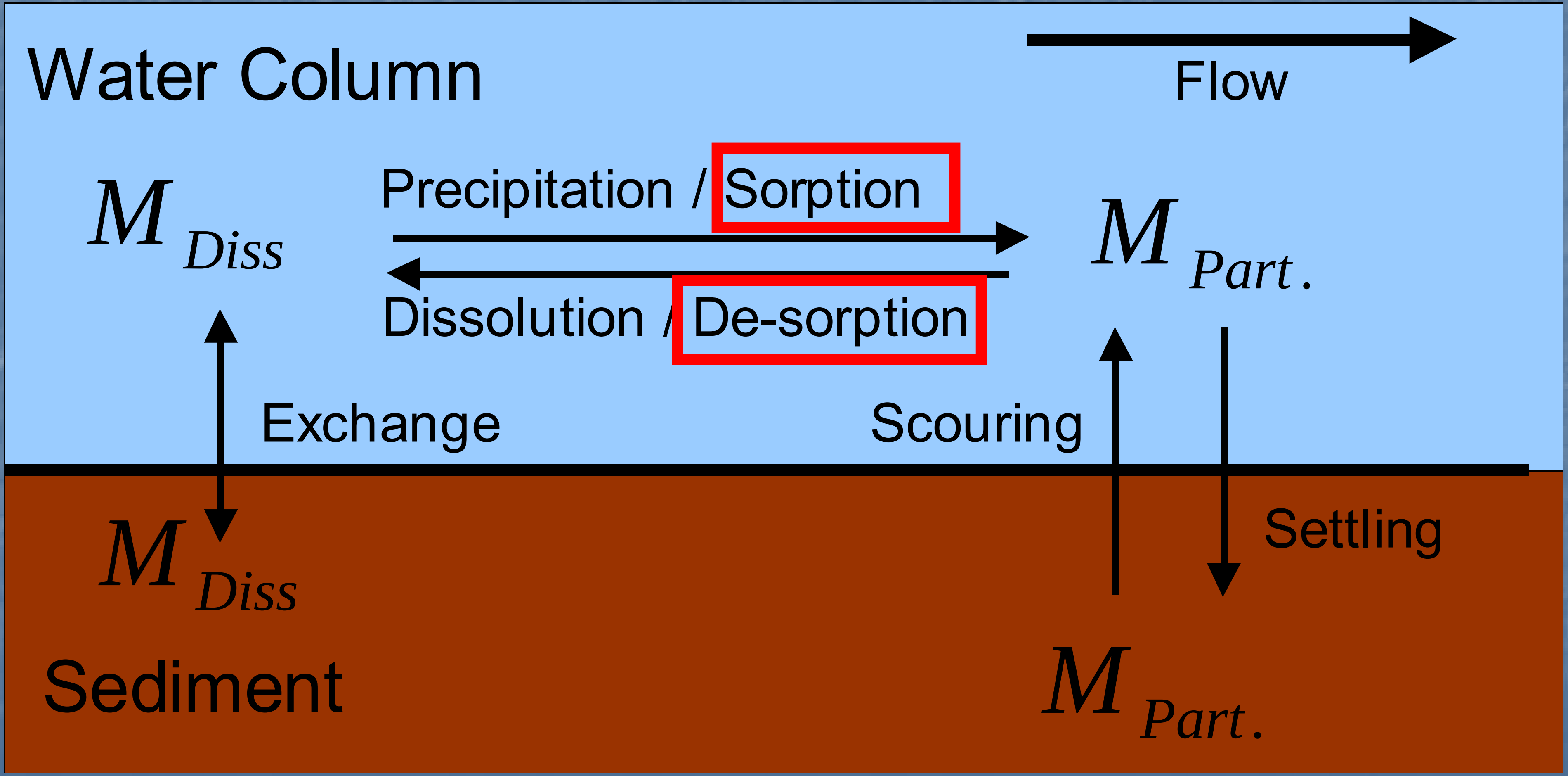
Background – Metals Transport



'M' = metal; 'Diss' = dissolved; 'Part' = particulate

Background – Metals Transport



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Background – Metals Transport

- Sorption
  - Surface complexation

Background – Metals Transport

- Sorption
  - Surface complexation
    - Analogous to aqueous complexation

$$M^{2+} + H_2O \longrightarrow MOH^{+} + H^{+}$$

Background – Metals Transport

- Sorption
  - Surface complexation
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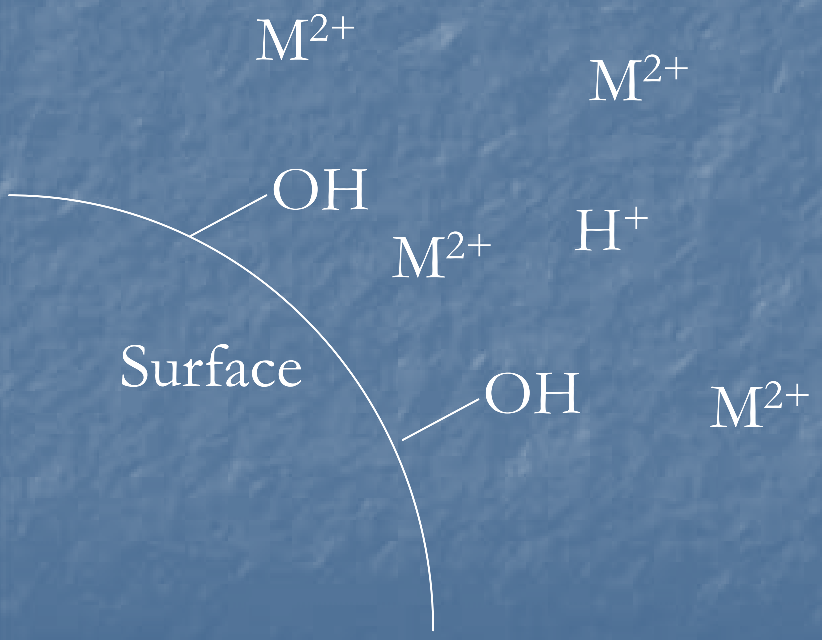

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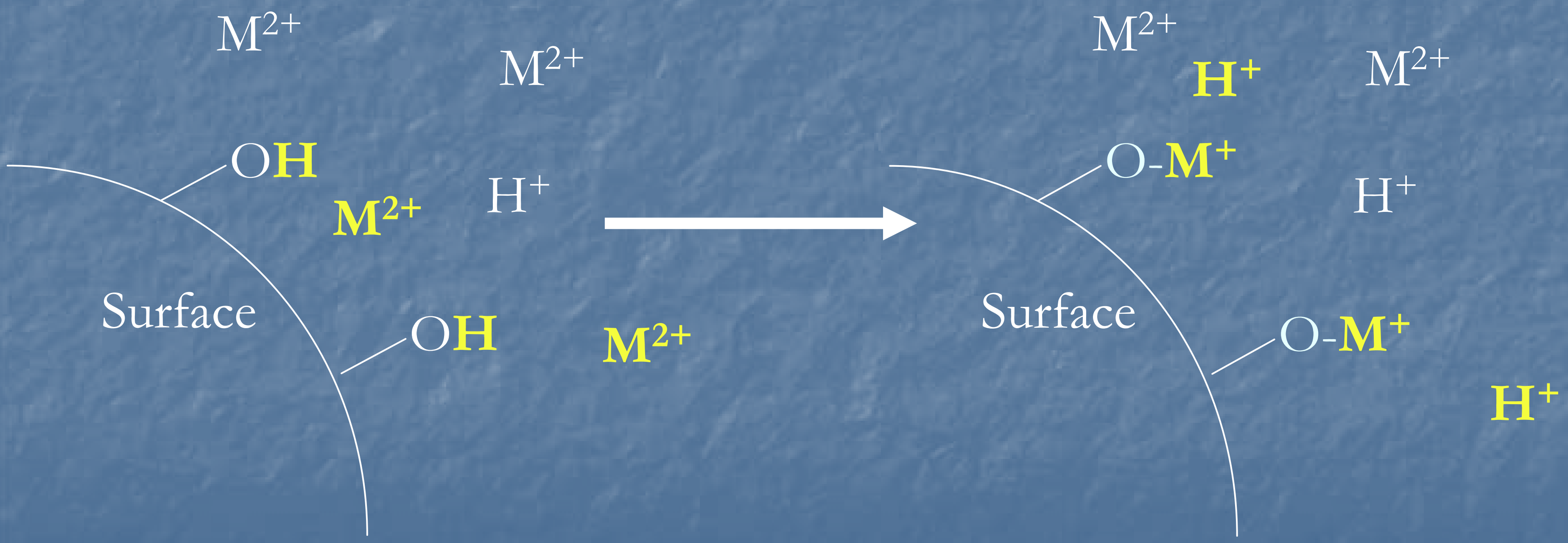


Background – Metals Transport

- Two main types of sorption
  - Outer-sphere
    - Weak ionic interaction
    - Affected by changes in ionic strength (I)
      - Higher I $\longrightarrow$ more metal in solution
      - Lower I $\longrightarrow$ more metal sorbed

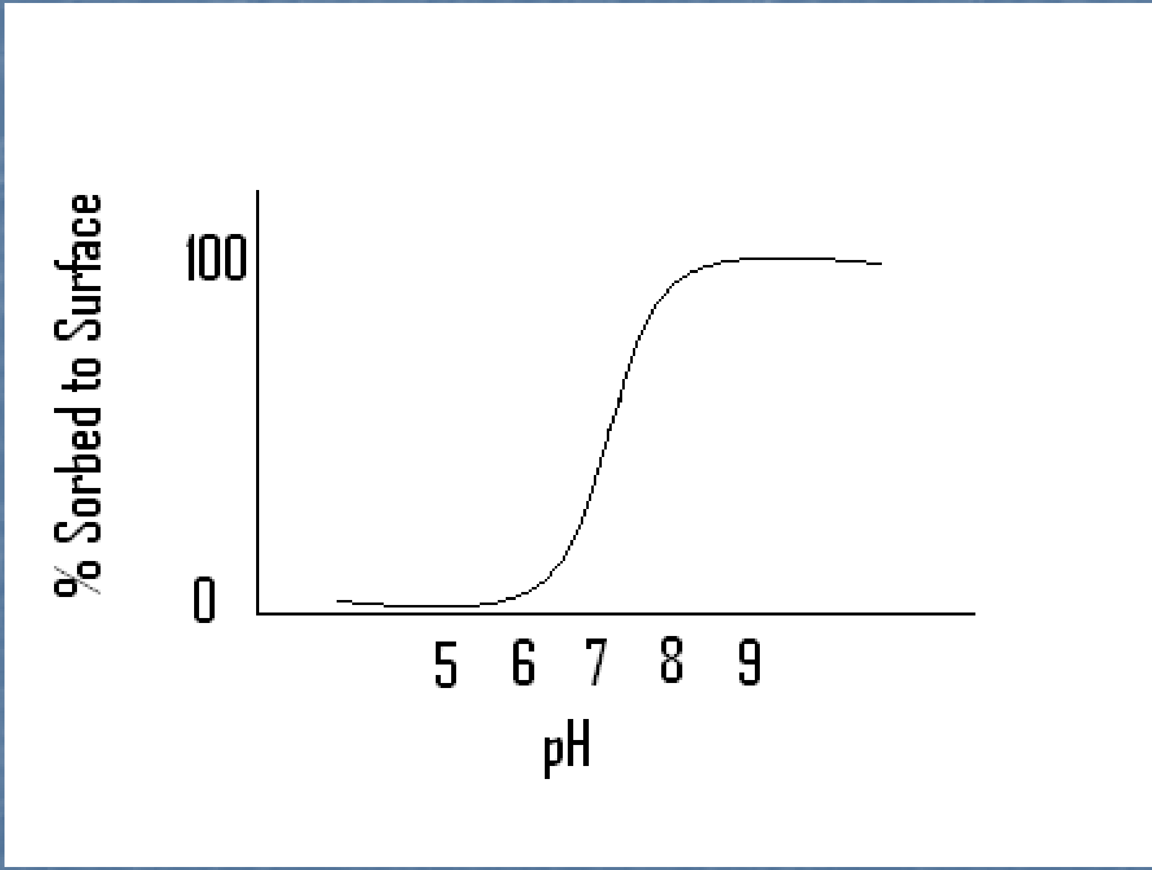
Background – Metals Transport

- Two main types of sorption
  - Outer-sphere
    - Weak ionic interaction
    - Affected by changes in ionic strength (I)
      - Higher I $\longrightarrow$ more metal in solution
      - Lower I $\longrightarrow$ more metal sorbed
    - Affected by changes in pH
      - Higher pH $\longrightarrow$ more metal sorbed

Background – Metals Transport

- Two main types of sorption
  - Inner-sphere
    - Strong chemical bond
      - Higher pH → more metal sorbed
      - Not (*strongly*) affected by changes in ionic strength

Background – Metals Transport

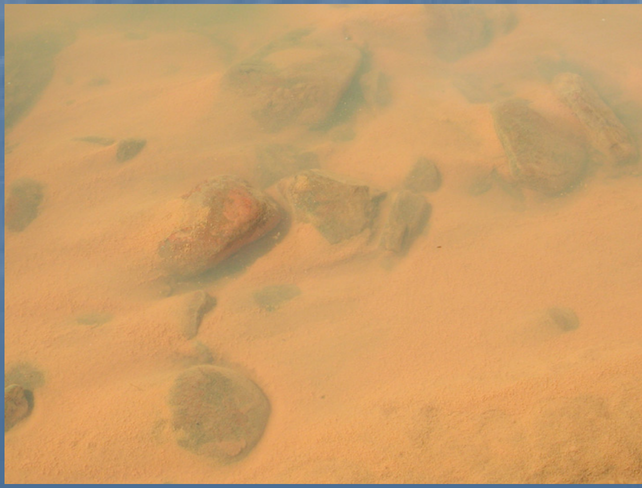


Background – Metals Transport

- Three common inorganic surfaces in AMD-impacted stream systems
  - Iron oxyhydroxide (HFO)
  - Aluminum oxyhydroxide (ALO)
  - Manganese oxyhydroxide (HMO)

Background – Metals Transport

- Iron oxyhydroxide (HFO)
  - Rapid formation in water column at pH > ~ 4
    - Oxidation of ferrous iron precedes precipitation



Background – Metals Transport

- Aluminum oxyhydroxide (ALO)
  - Rapid formation in water column at pH > ~ 5
    - No oxidation necessary

Background – Metals Transport

- Manganese oxyhydroxide (HMO)
  - Requires oxidation
  - Requires a surface for formation
  - Formation at pH > ~ 9

Background – Metals Transport

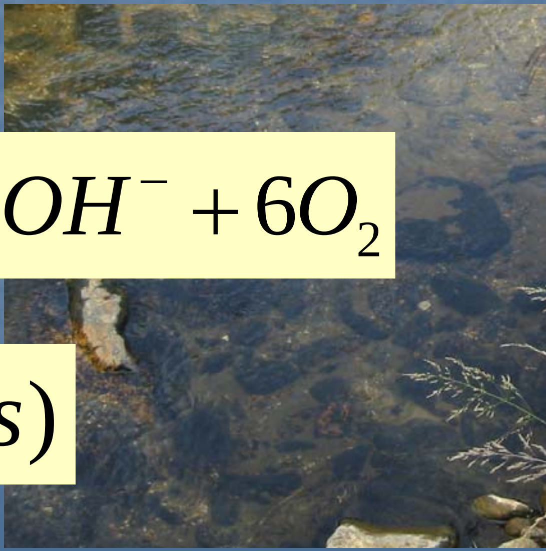
- Manganese oxyhydroxide (HMO)
  - Formation may be facilitated by periphyton

Background – Metals Transport

- Manganese oxyhydroxide (HMO)
  - Formation may be facilitated by periphyton
    - Algal photosynthesis

$$6HCO_3^{\,-} + 6H_2O \xrightarrow{h\upsilon} C_6H_{12}O_6 + 6OH^- + 6O_2$$

$$Mn^{2+} + O_2 \xrightarrow{high-ph} MnO_2(s)$$

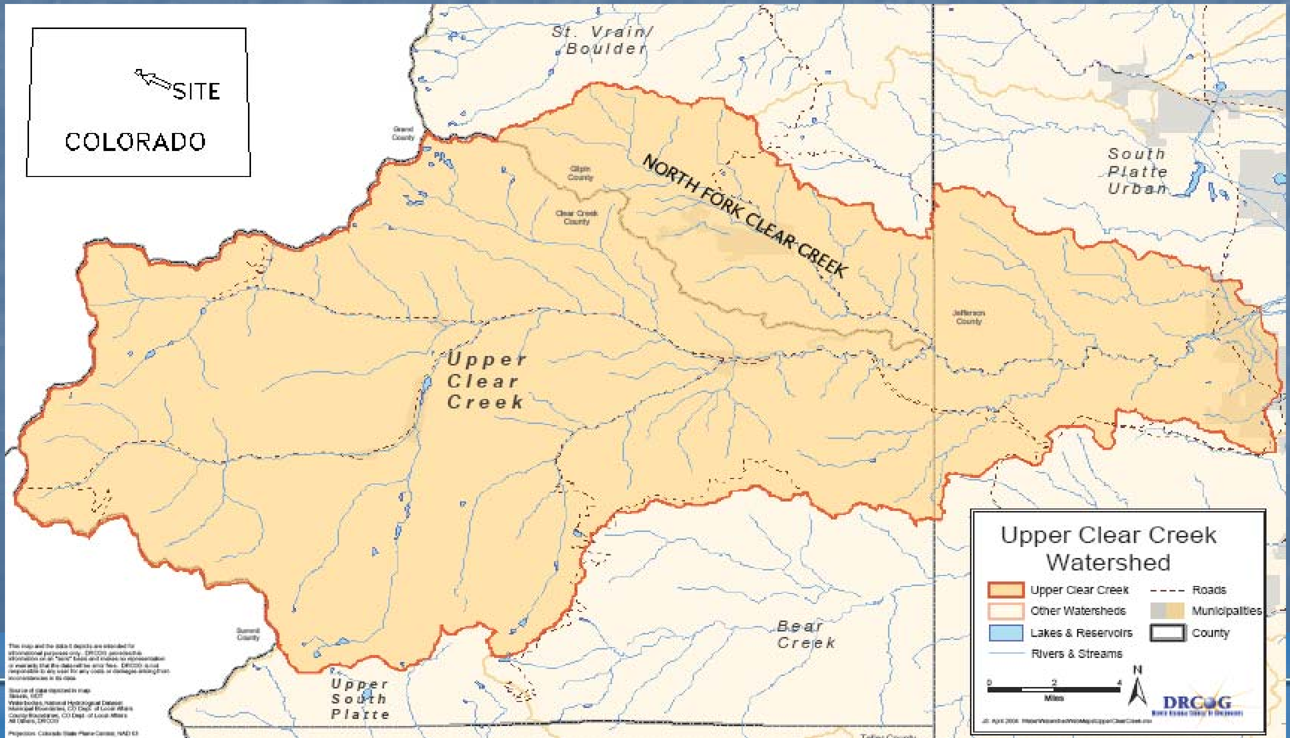


Presentation Outline

- Background
  - Acid Mine Drainage (AMD)
  - Metals Transport
  - **North Fork Clear Creek (NFCC)**
- Bed Sediment Metals Research
- Future Research

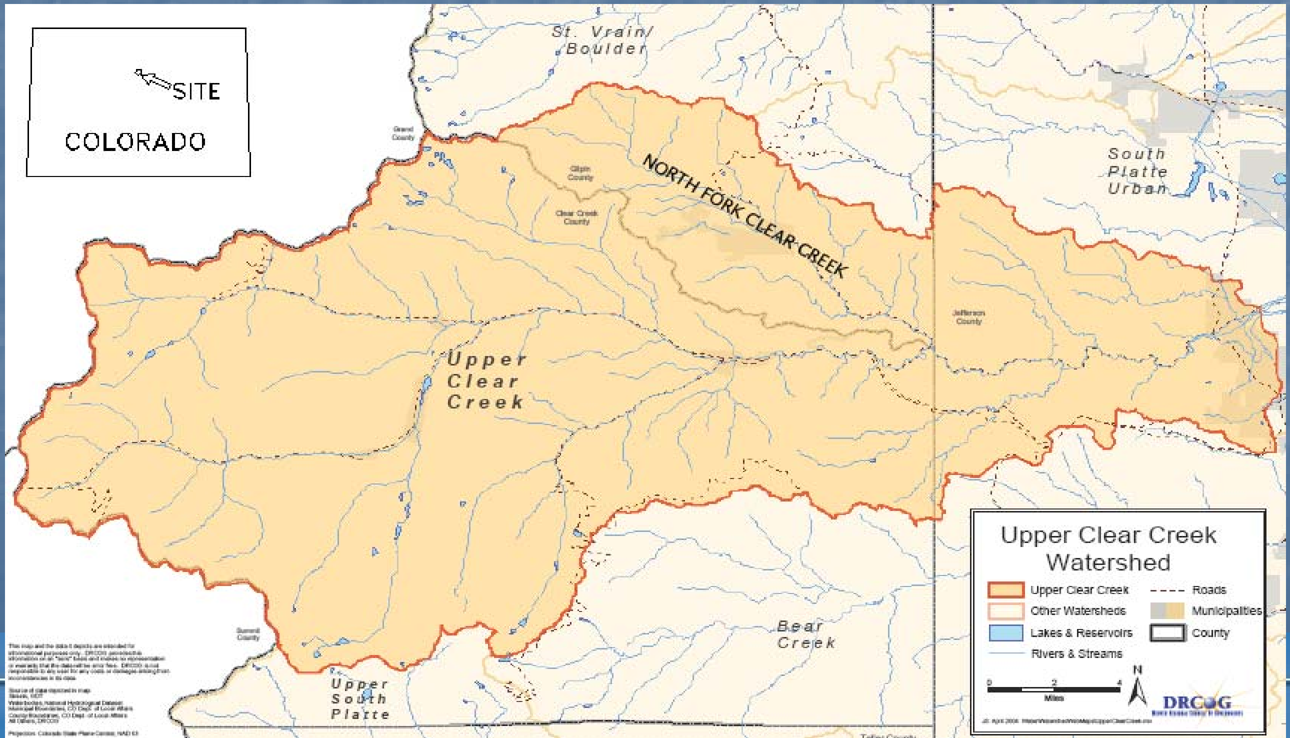
Background – NFCC

- Clear Creek Watershed (~ 400 sq. mi)
  - Rocky Mountains – west of Denver, CO



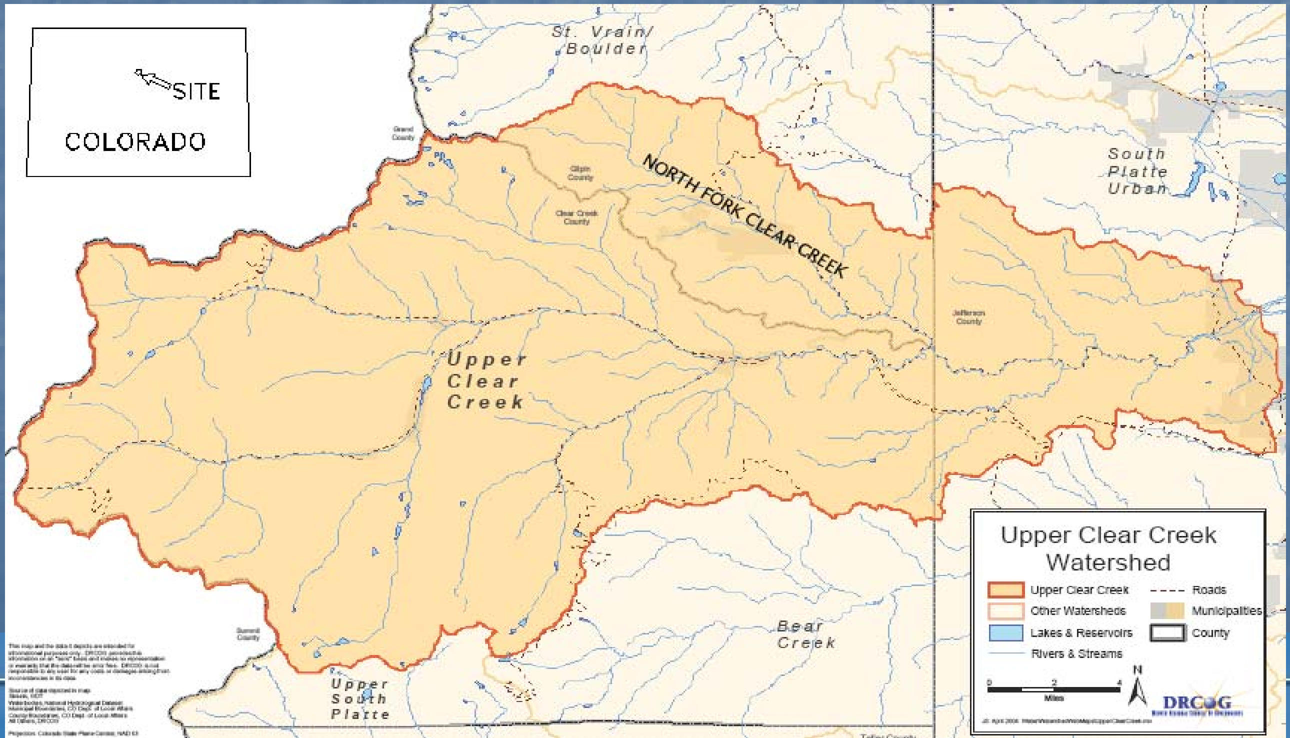
Background – NFCC

- Clear Creek Watershed (~ 400 sq. mi)
  - Colorado Mineral Belt (CMB)
    - Extensive mining for gold, silver, copper, lead and zinc in the late 1800's



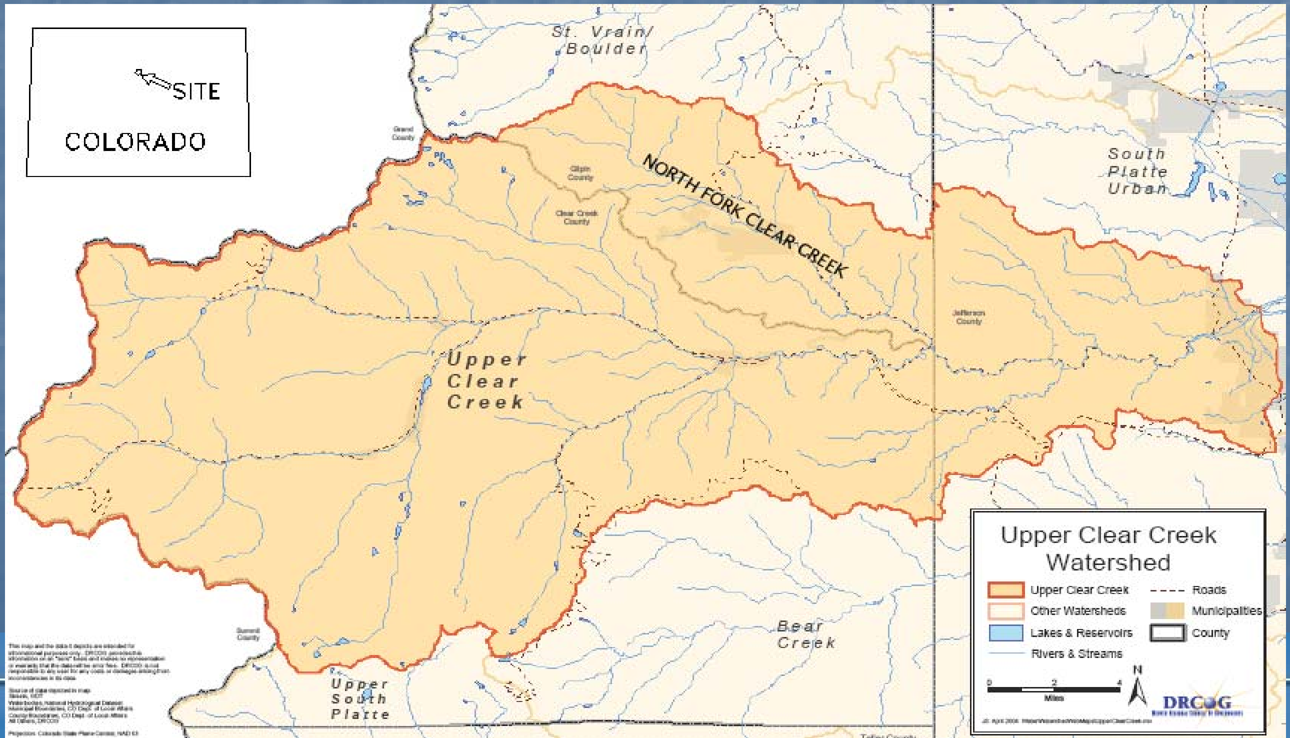
Background – NFCC

- Clear Creek Watershed (~ 400 sq. mi)
  - ~ 1,300 abandoned mines (USGS 1997 estimate)



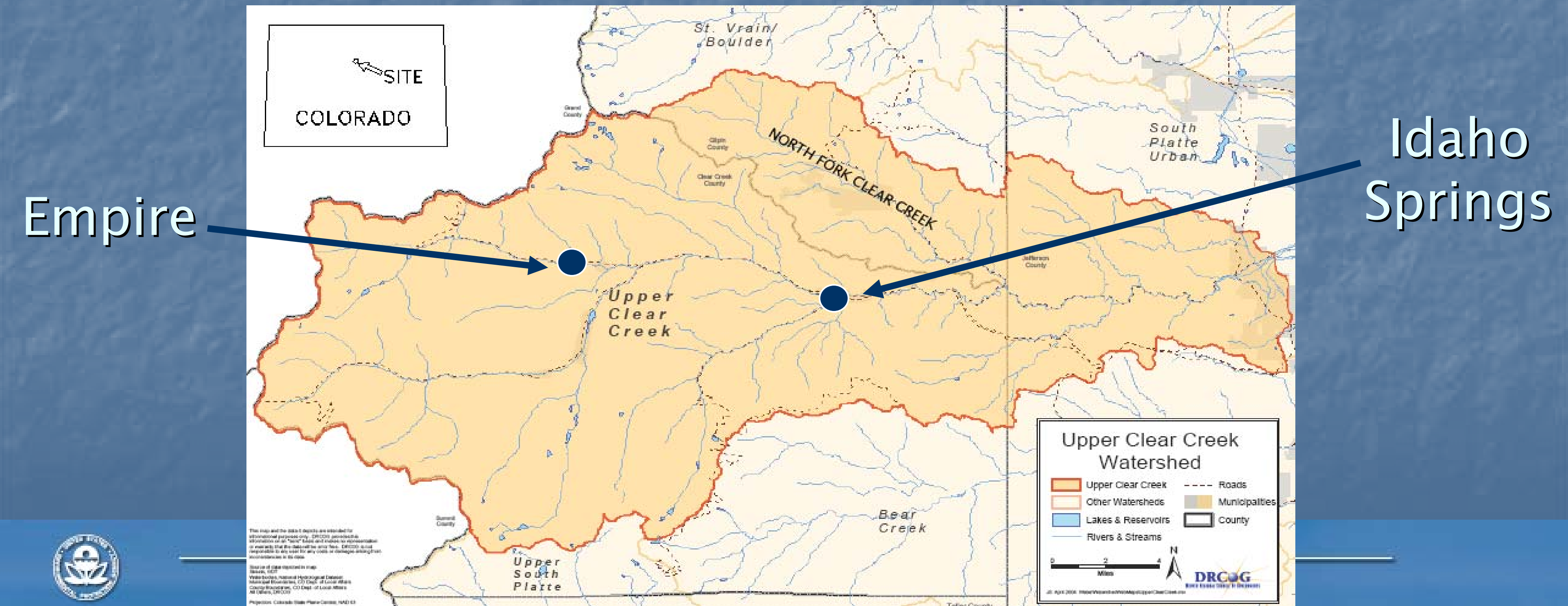
Background – NFCC

- Clear Creek Watershed (~ 400 sq. mi)
  - Superfund site
  - Listed on National Priorities List (NPL) in 1983

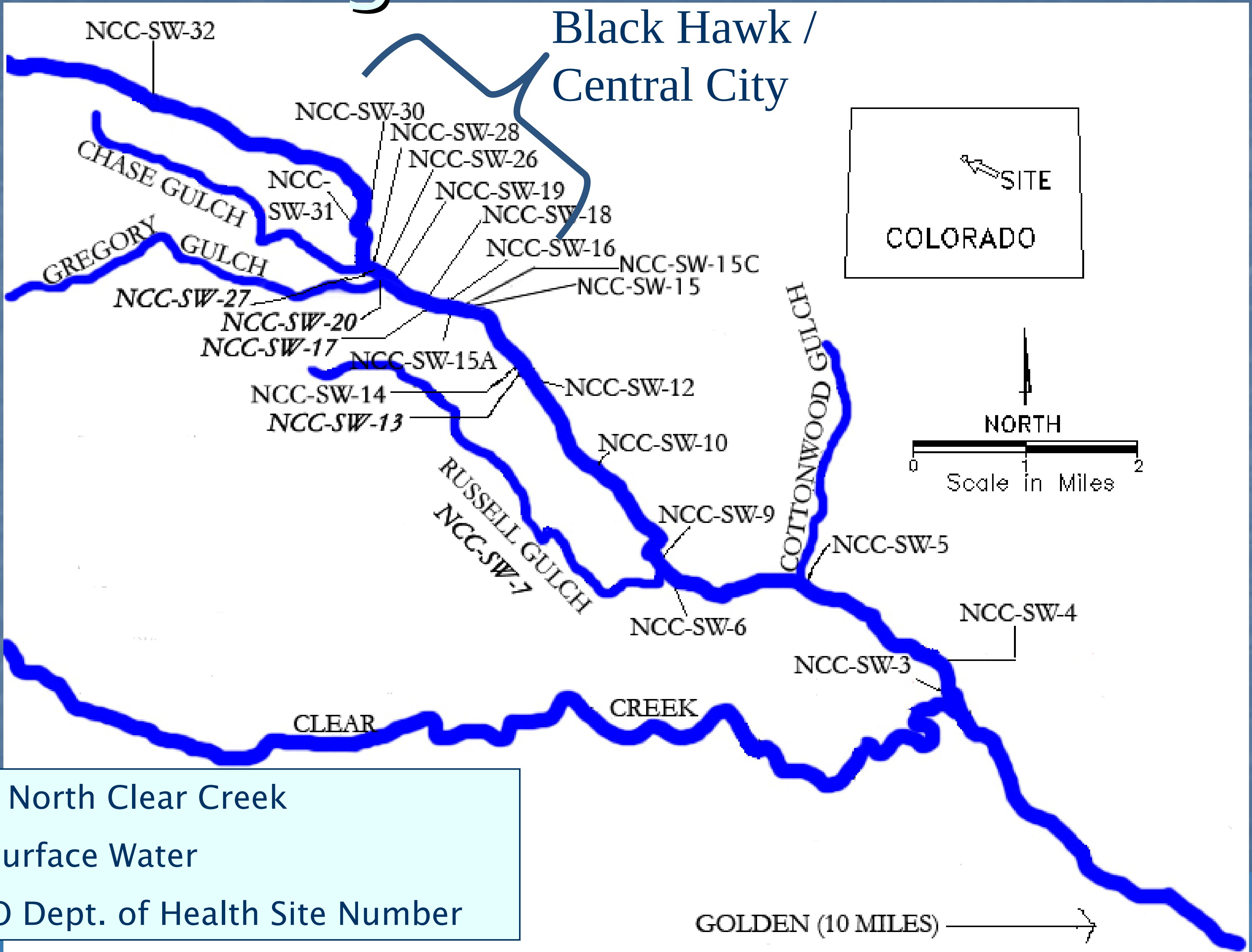


Background – NFCC

- Clear Creek Watershed (~ 400 sq. mi)
  - Improvement in water quality in the main stem of Clear Creek from 2 water treatment plants in 1997



Background – NFCC



NCC = North Clear Creek

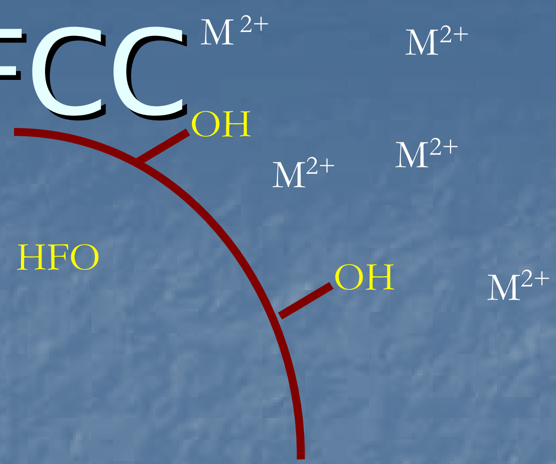
SW = Surface Water

is CO Dept. of Health Site Number

Background – NFCC

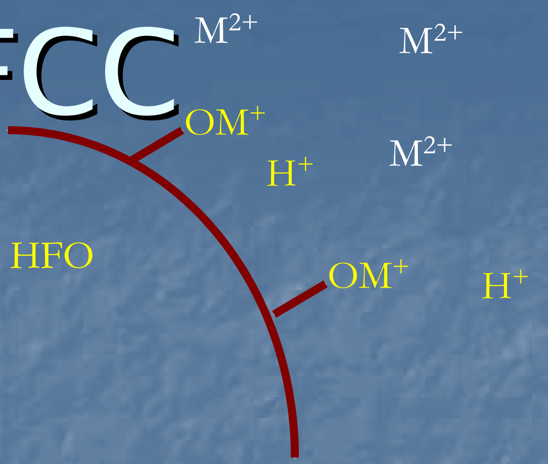
- North Fork Clear Creek
  - Dominant processes are:

Background – NFCC



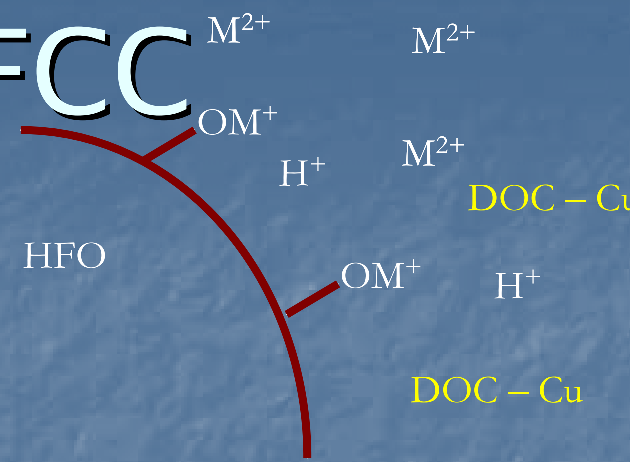
- North Fork Clear Creek
  - Dominant processes are:
    - Rapid oxidation and precipitation of iron as ferric oxyhydroxides (HFO)

Background – NFCC



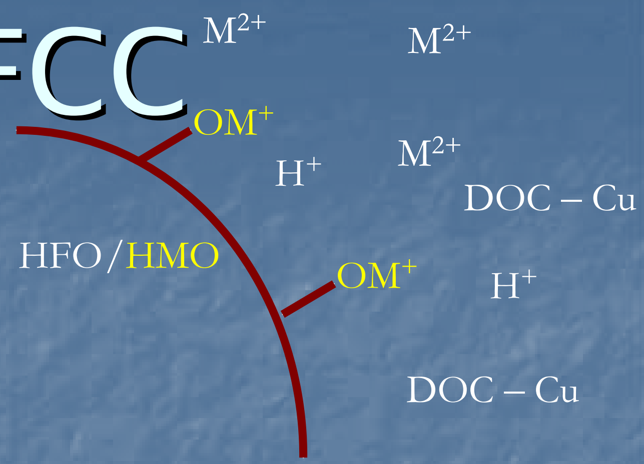
- North Fork Clear Creek
  - Dominant processes are:
    - Rapid oxidation and precipitation of iron as ferric oxyhydroxides (HFO)
    - Sorption and/or coprecipitation of metals with HFO

Background – NFCC



- North Fork Clear Creek
  - Dominant processes are:
    - Rapid oxidation and precipitation of iron as ferric oxyhydroxides (HFO)
    - Sorption and/or coprecipitation of metals with HFO
    - Complexation of copper with DOC

Background – NFCC



- North Fork Clear Creek
  - Dominant processes are:
    - Rapid oxidation and precipitation of iron as ferric oxyhydroxides (HFO)
    - Sorption and/or coprecipitation of metals with HFO
    - Complexation of copper with DOC
  - To a lesser extent
    - Hydrous manganese oxyhydroxide (HMO) precipitation onto rock surfaces with sorption and/or coprecipitation of metals

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  - Metals Transport
  - North Fork Clear Creek (NFCC)
- **Bed Sediment Metals Research**
  - Aerobic Study

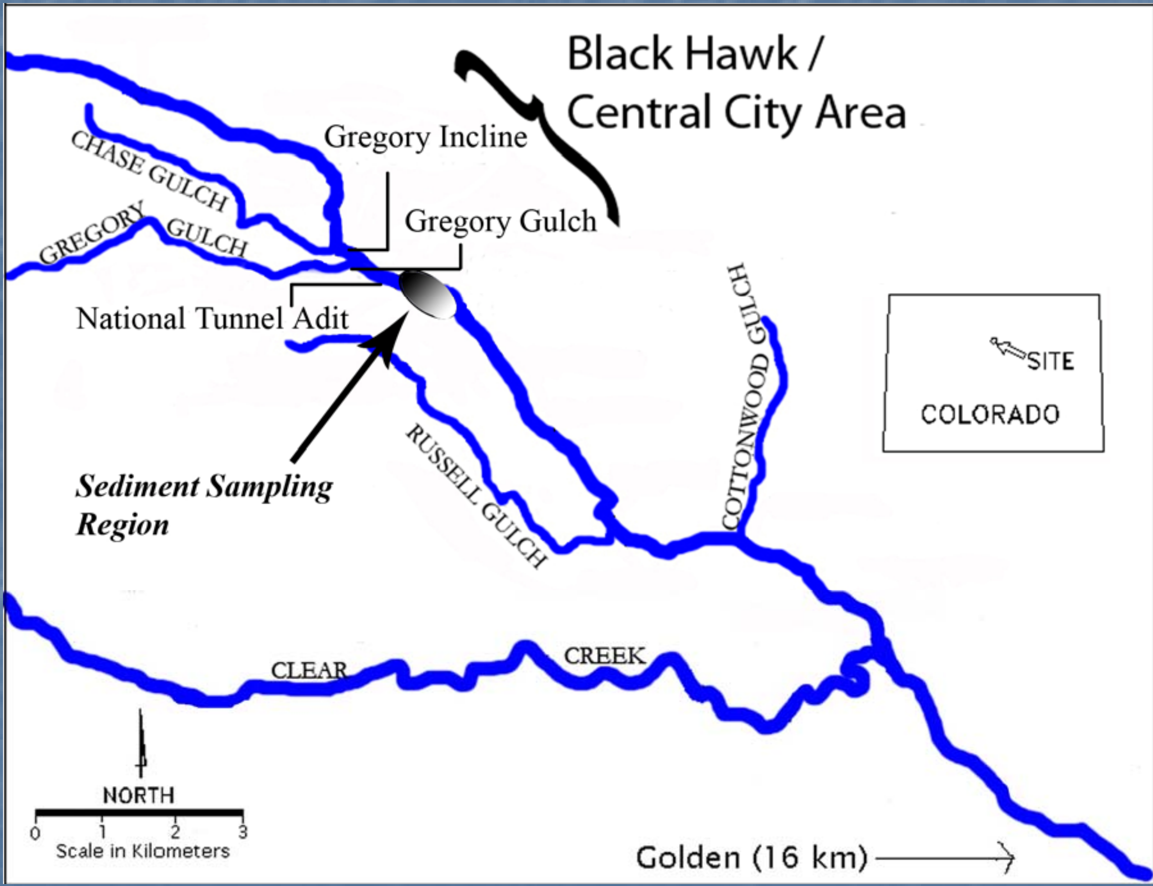
Bed Sediment Research






Bed Sediment Research

- NFCC Record of Decision (ROD)
  - Gregory Incline and Gregory Gulch – water treatment plant
  - National Tunnel diversion to downstream anaerobic treatment



Bed Sediment Research

- How will the existing sediments respond to the absence of mining-inputs?

Bed Sediment Research

- Expected changes
  - Decreased ionic strength
    - Important for outer-sphere sorption (increased sorption)
    - Increased colloidal stability (less/slower aggregation)

Bed Sediment Research

- Expected changes
  - Decreased ionic strength
    - Important for outer-sphere sorption (increased sorption)
    - Increased colloidal stability (less/slower aggregation)
  - Increased dissolved organic carbon
    - Important for dissolved metal complexation (increased dissolved metal)

Bed Sediment Research

- Expected changes
  - Increased pH
    - Important for inner- and outer-sphere sorption (increased sorption)

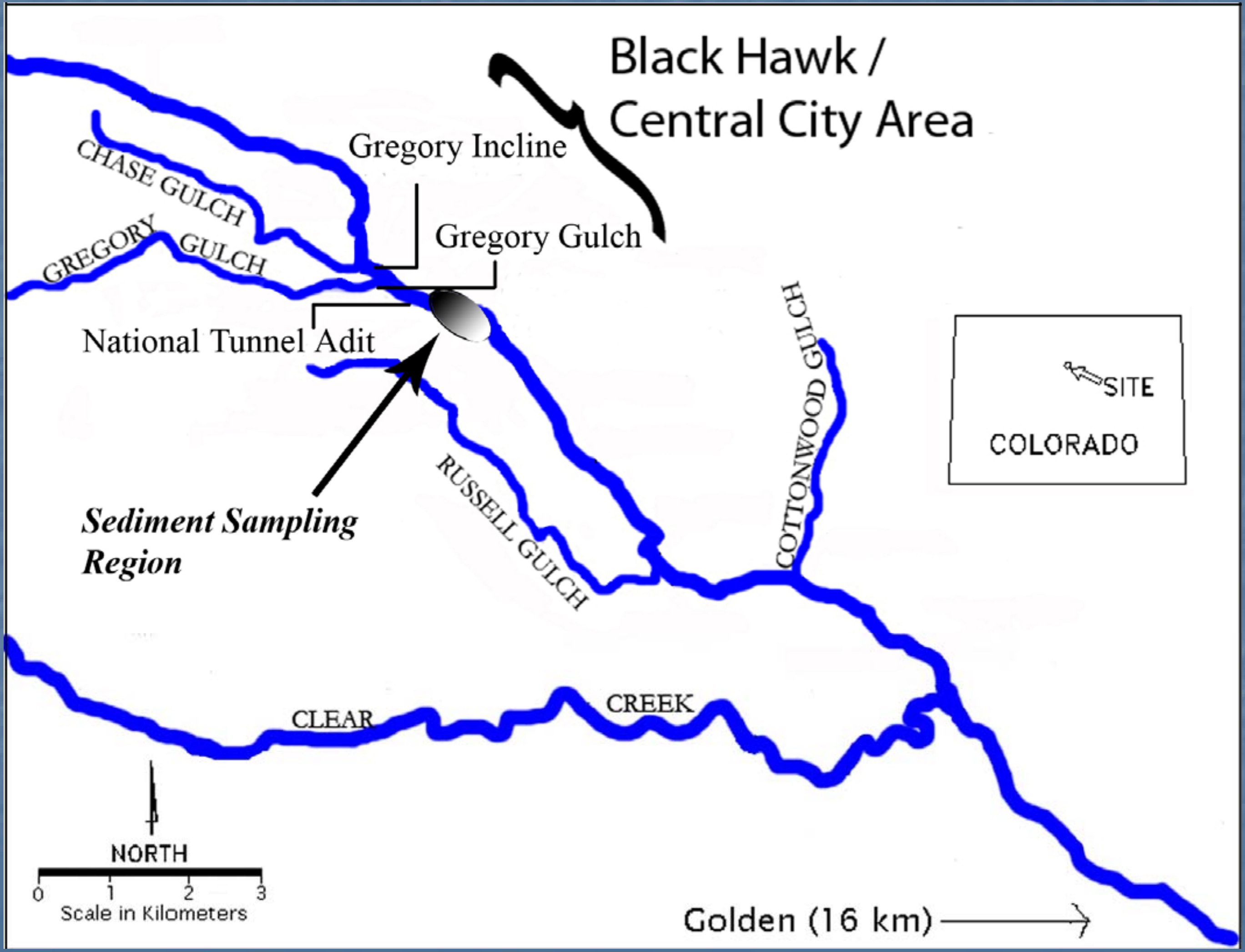
Bed Sediment Research

- Other parameters of importance
  - Sediment size – smaller particle sizes have a larger specific surface area for sorption

Bed Sediment Research

- Other parameters of importance
  - Sediment size – smaller particle sizes have a larger specific surface area for sorption
  - Kinetics
    - Equilibrium?

Bed Sediment Research



Bed Sediment Research

- Factorial design (2x2x2x2x10)

Bed Sediment Research

- Factorial design (2x2x2x2x10)
  - Particle size
    - 63-µm < x ≤ 2-mm and < 63-µm

Bed Sediment Research

- Factorial design (2x2x2x2x10)
  - Ionic strength
    - 40 and 80% less than ambient
      - = 2 and 0.7 mM
        - Na, Ca, CO_3, SO_4 salts

Bed Sediment Research

- Factorial design (2x2x2x2x10)
  - Ionic strength
    - 40 and 80% less than ambient
      - = 2 and 0.8 mM
        - Na, Ca, CO_3, SO_4 salts
  - pH
    - 6 and 8
      - ambient typically ranges from 5.5-8.5
        - NaOH or HNO_3

Bed Sediment Research

- Factorial design (2x2x2x2x10)
  - DOC
    - 1 and 3 mg/l higher than ambient
      - = 3 and 5 mg/l C
        - Citrate

Bed Sediment Research

- Factorial design (2x2x2x2x10)
  - DOC
    - 1 and 3 mg/l higher than ambient
      - = 3 and 5 mg/l C
        - Citrate
  - Time
    - 0, 1, 10, 30, and 60 min; 2, 5, 10, 24, and 48 hr
    - Individual units sacrificed over time

Bed Sediment Research

- Factorial design (2x2x2x2x10)
  - DOC
    - 1 and 3 mg/l higher than ambient
      - = 3 and 5 mg/l C
        - Citrate
  - Time
    - 0, 1, 10, 30, and 60 min; 2, 5, 10, 24, and 48 hr
    - Individual units sacrificed over time
  - Alkalinity
    - Ambient 15 mg/l as $CaCO_3$

Bed Sediment Research

- 8 different solutions prepared
- 160 individual experimental units

Bed Sediment Research

- ~ 5 g wet < 63-μm
- ~ 8 g dry 63-μm < x ≤ 2-mm
- 40 ml solution

Bed Sediment Research

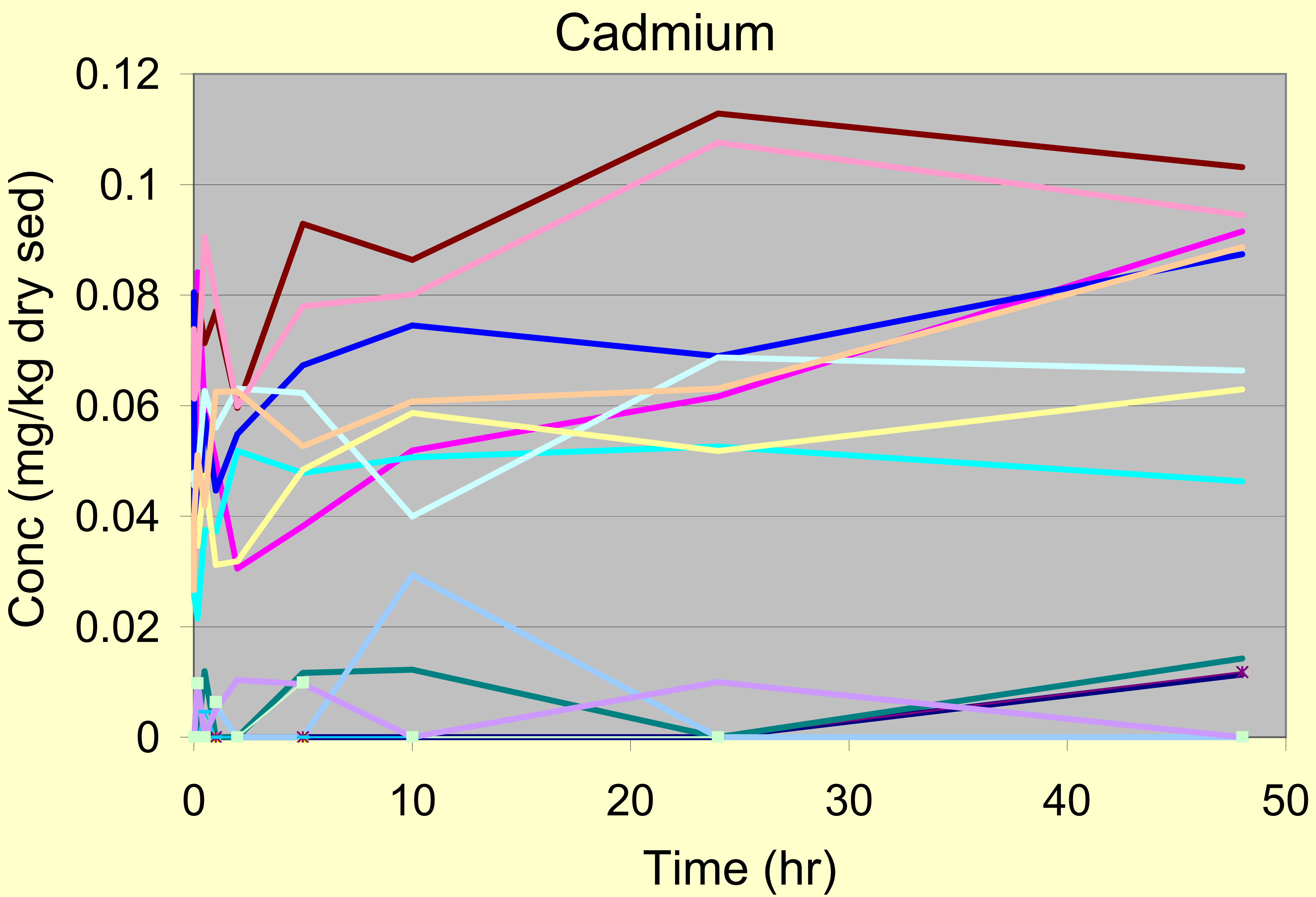
- Measured parameters at t = x
  - pH
  - Dissolved (< 0.45-μm) Cd, Cu, Fe, Mn, Zn
    - Inductively coupled plasma – atomic emission spectroscopy (ICP-AES)

Bed Sediment Research

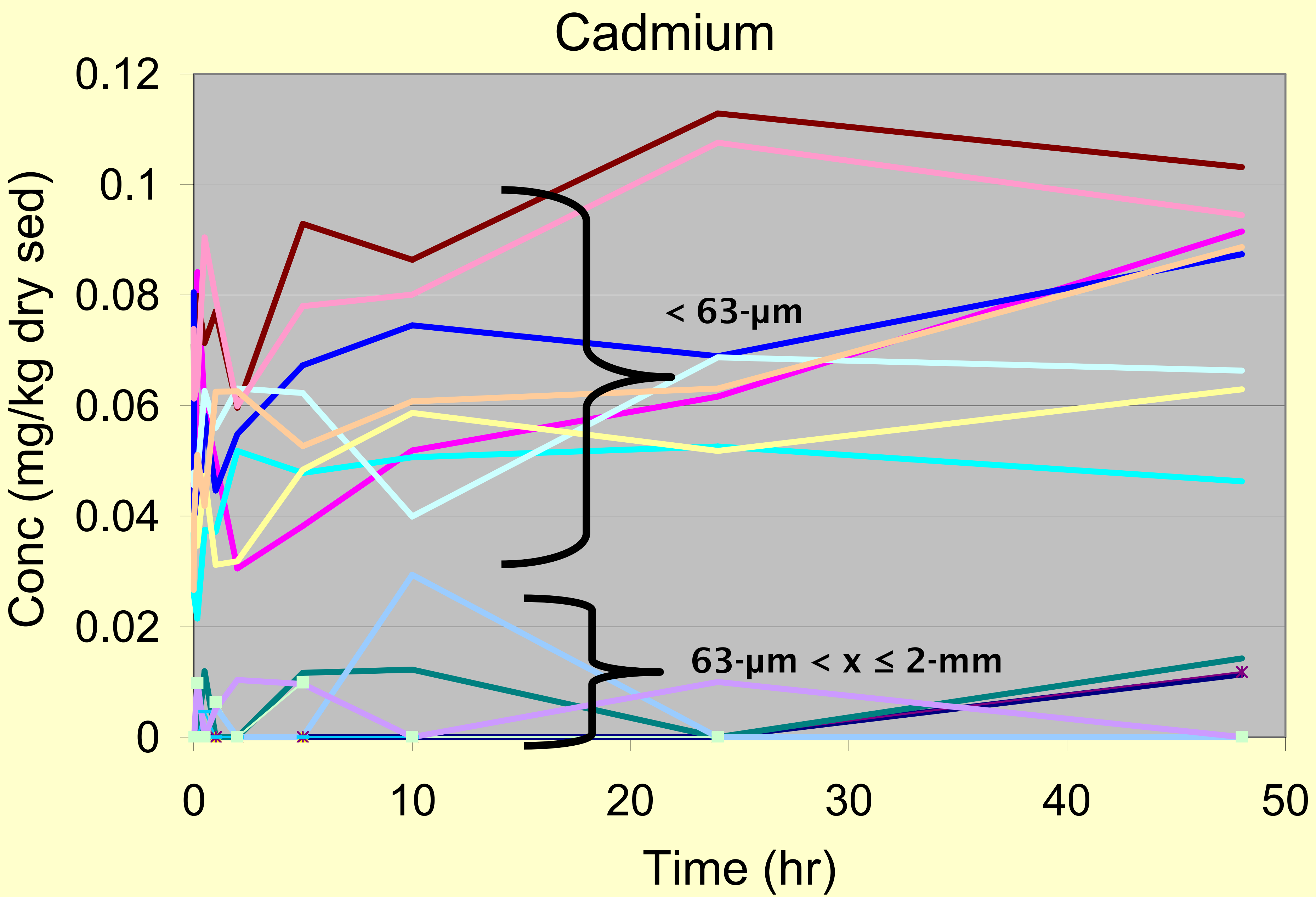
- General MANOVA results (2x2x2x2x10)
  - Data showed large differences between particle size fractions versus within each size fraction

Bed Sediment Research

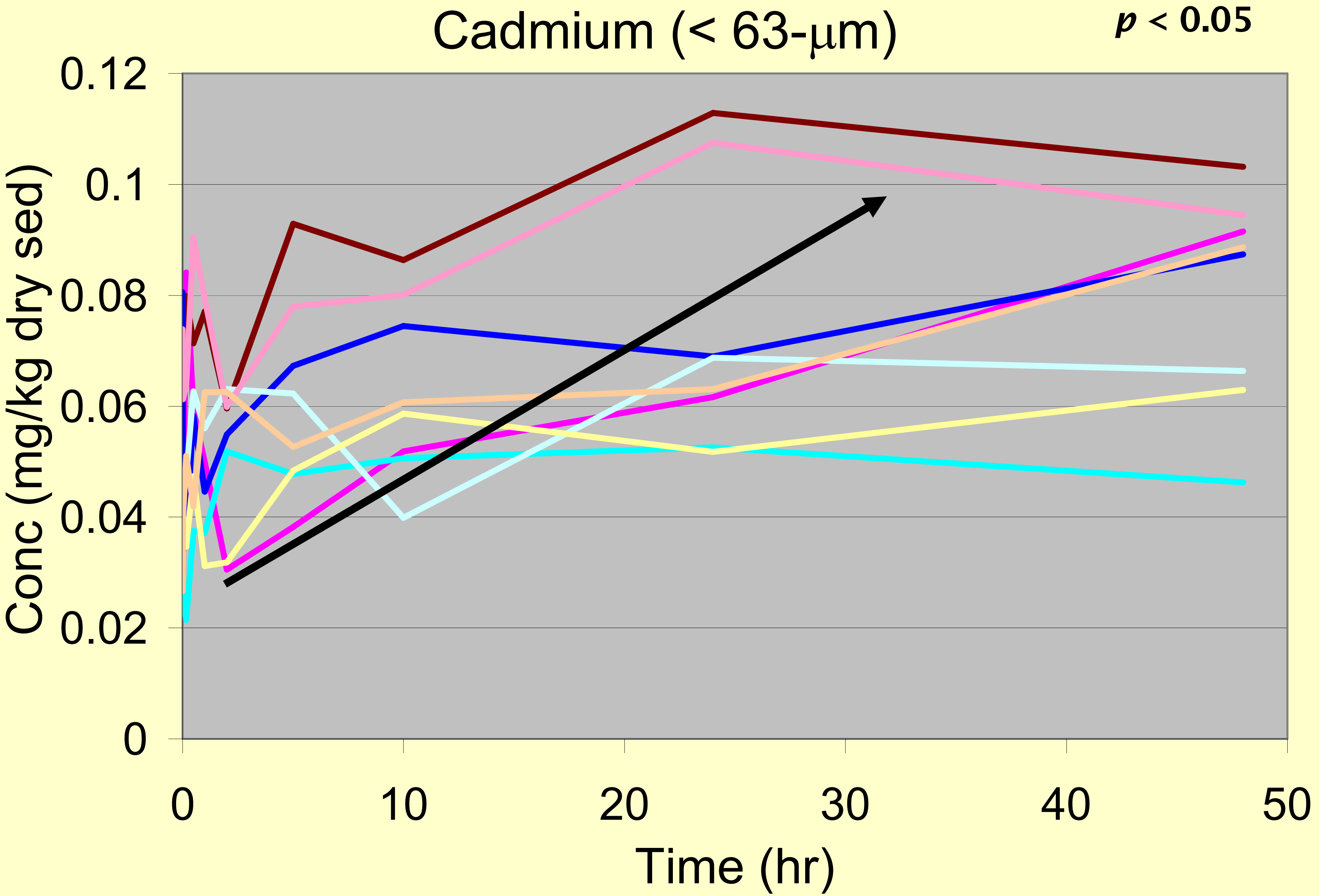
- General MANOVA results (2x2x2x2x10)
  - Data showed large differences between particle size fractions versus within each size fraction
    - Individual MANOVAs done to assess effects of chemistry within size fractions



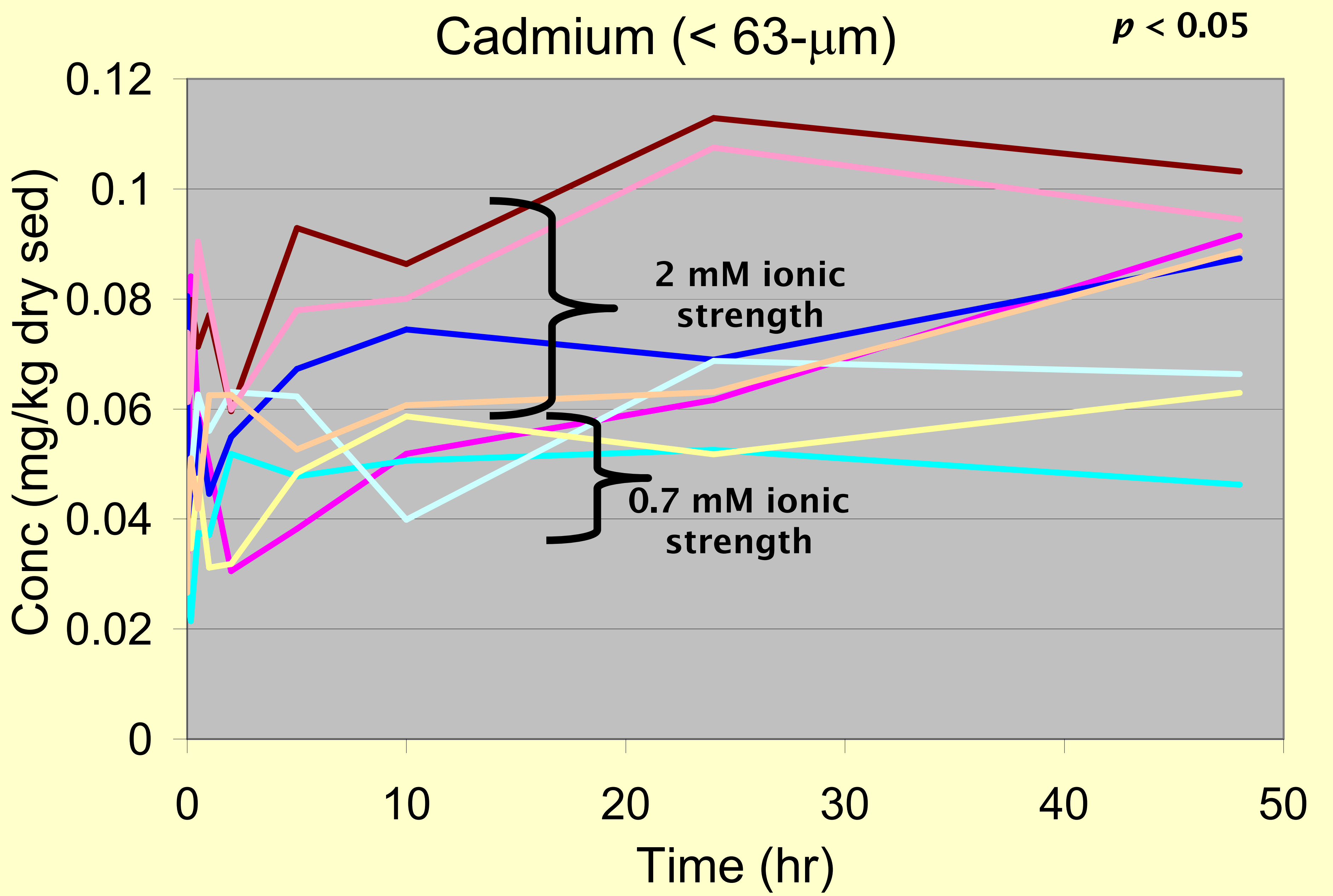
Cadmium
Conc (mg/kg dry sed)
0.12
0.1
0.08
0.06
0.04
0.02
0
0
10
20
30
40
50
Time (hr)



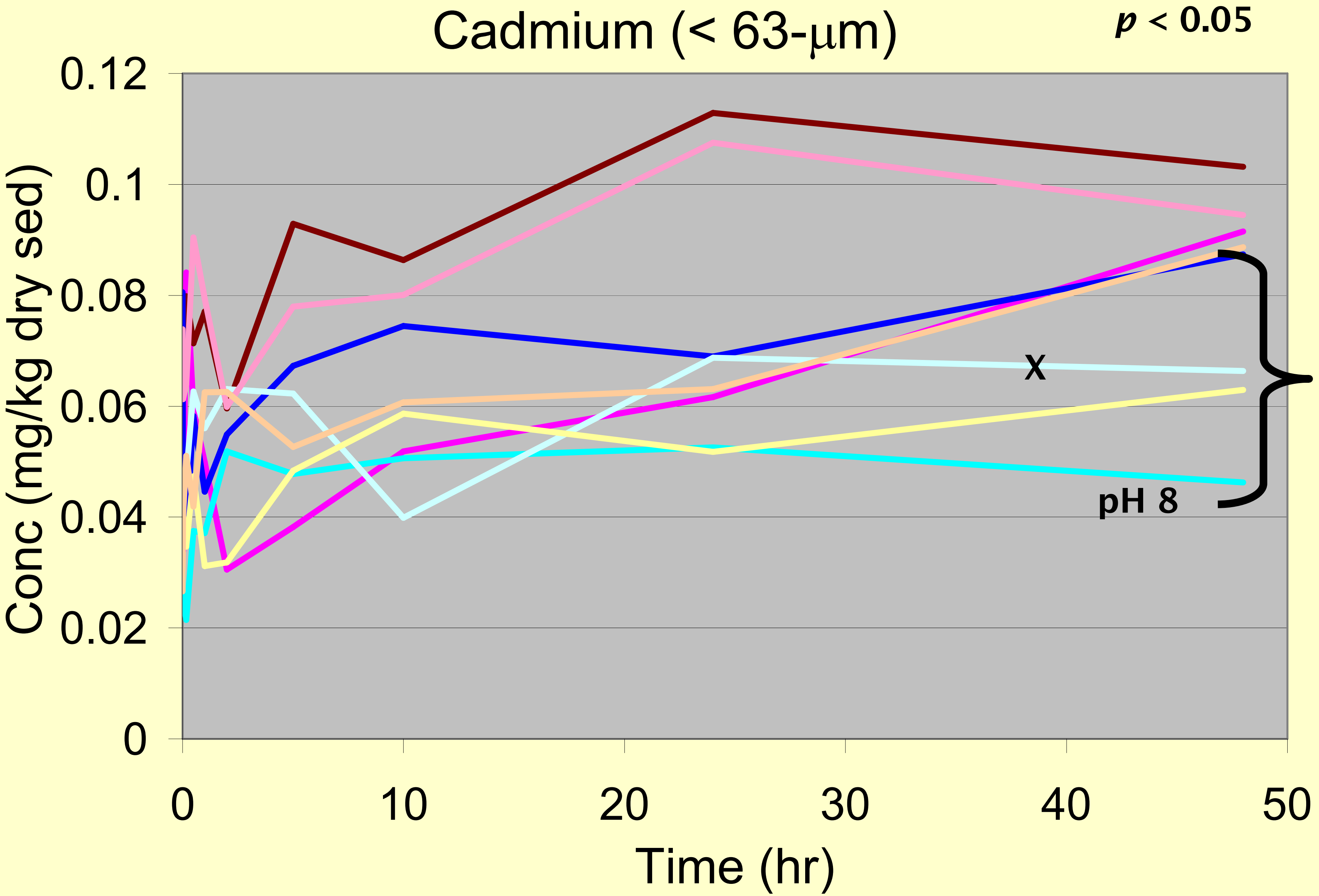
Cadmium
0.12
0.1
0.08
0.06
0.04
0.02
0
Conc (mg/kg dry sed)
0
10
20
30
40
50
Time (hr)
< 63-µm
63-µm < x ≤ 2-mm

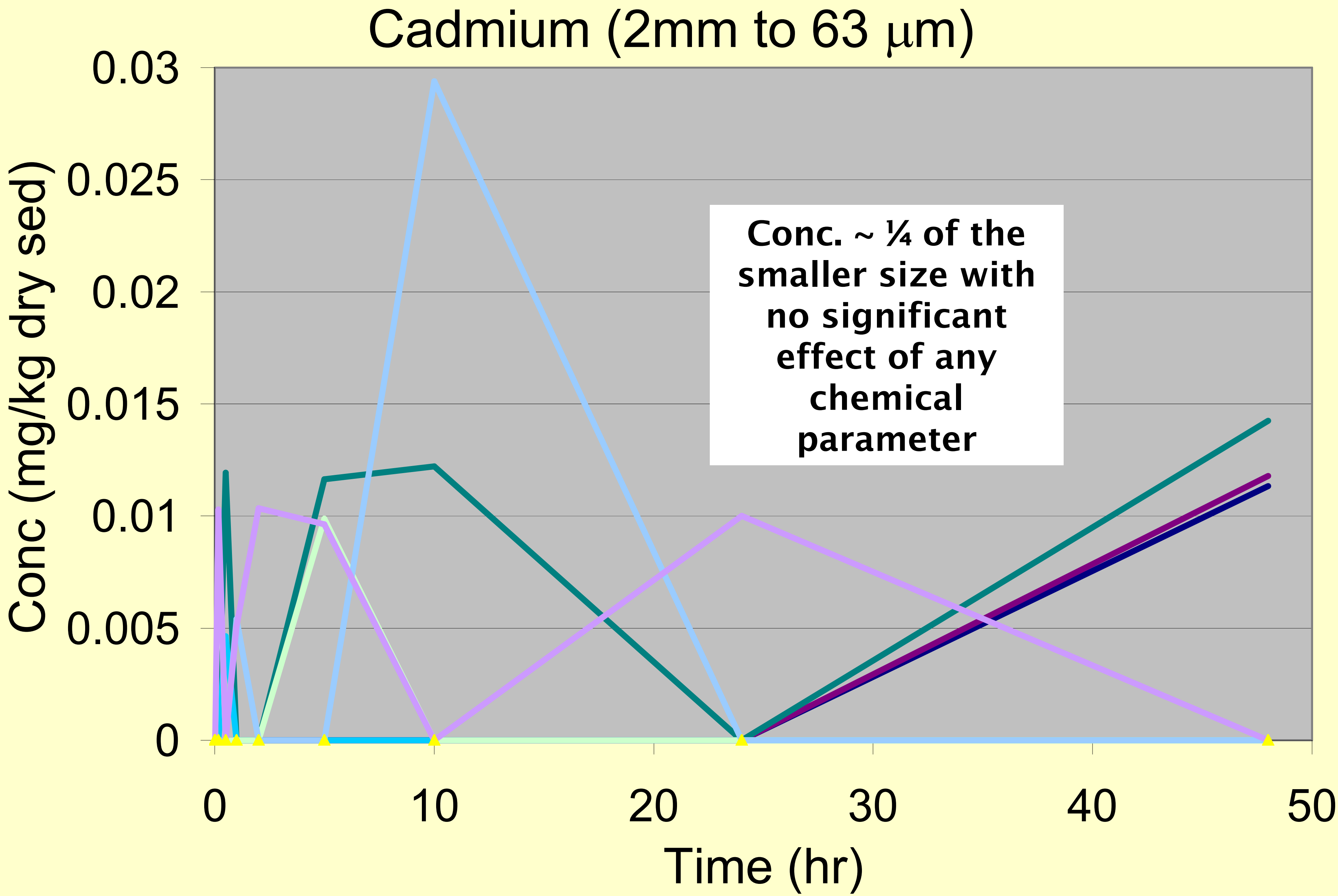


Cadmium (< 63-μm)
p < 0.05
0.12
0.1
0.08
0.06
0.04
0.02
0
Conc (mg/kg dry sed)
0
10
20
30
40
50
Time (hr)

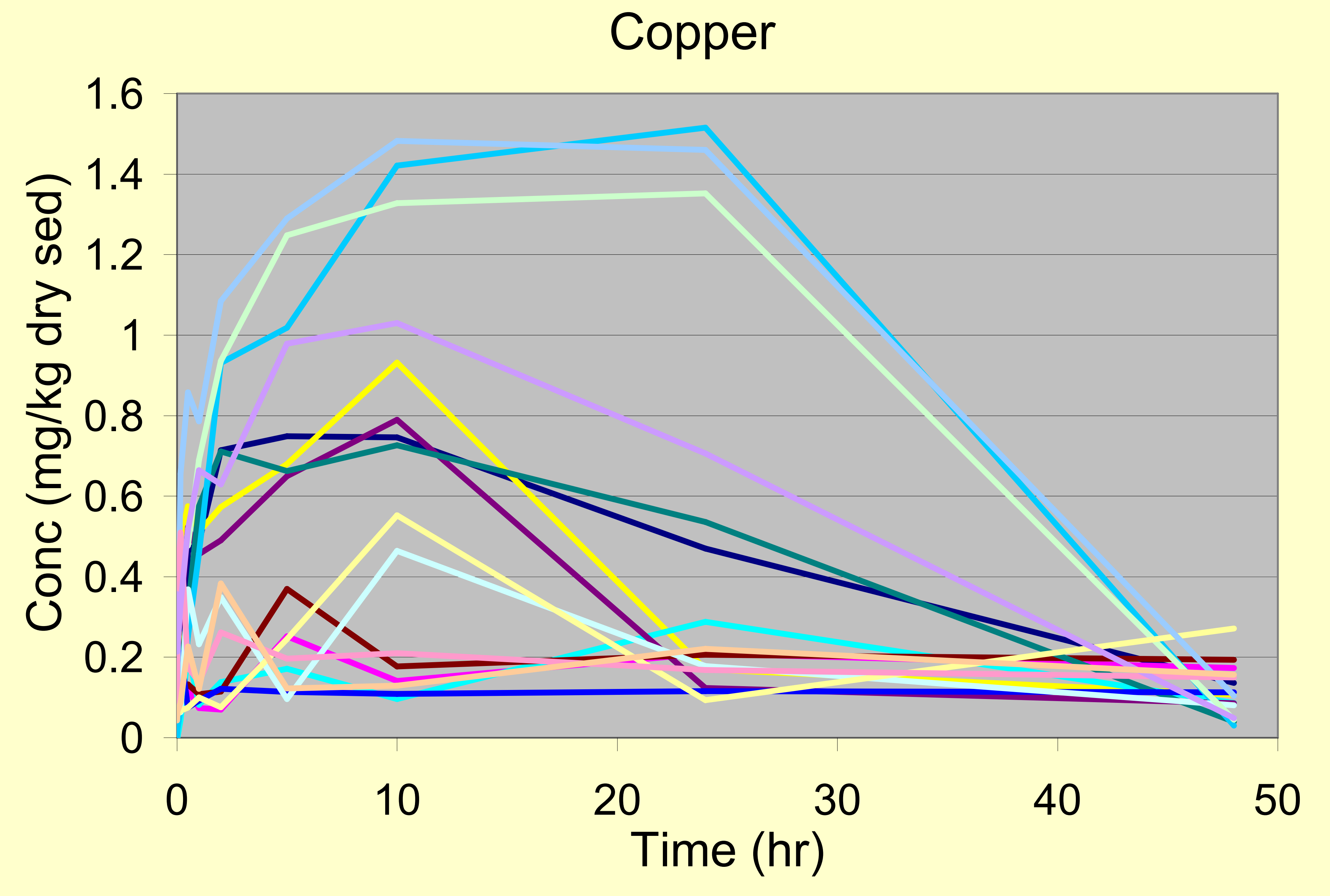


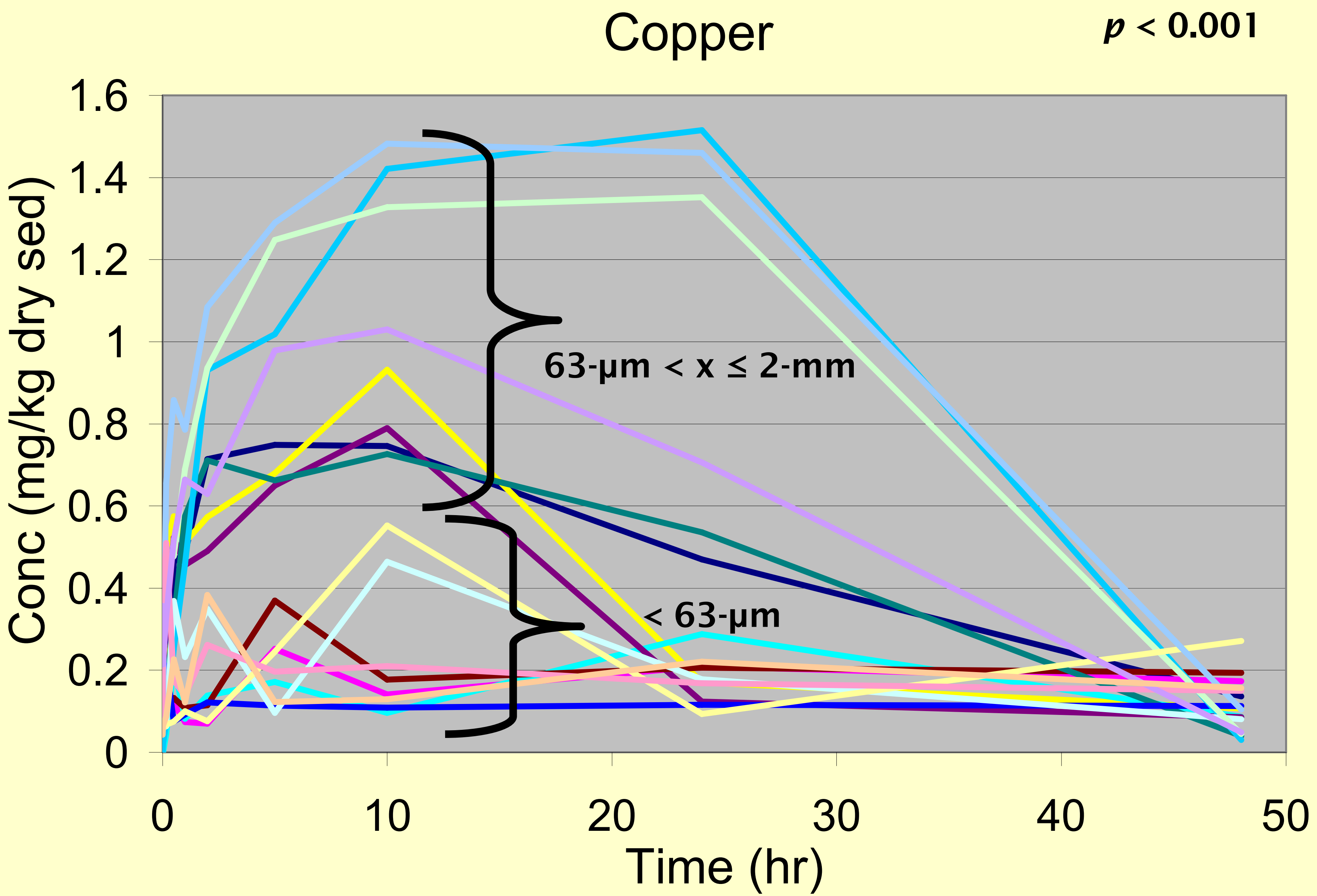
Cadmium (< 63-μm)
p < 0.05
0.12
0.1
0.08
0.06
0.04
0.02
0
Conc (mg/kg dry sed)
2 mM ionic strength
0.7 mM ionic strength
0
10
20
30
40
50
Time (hr)


Cadmium (< 63-μm)
p < 0.05
Conc (mg/kg dry sed)
0.12
0.1
0.08
0.06
0.04
0.02
0
0
10
20
30
40
50
Time (hr)
X
pH 8



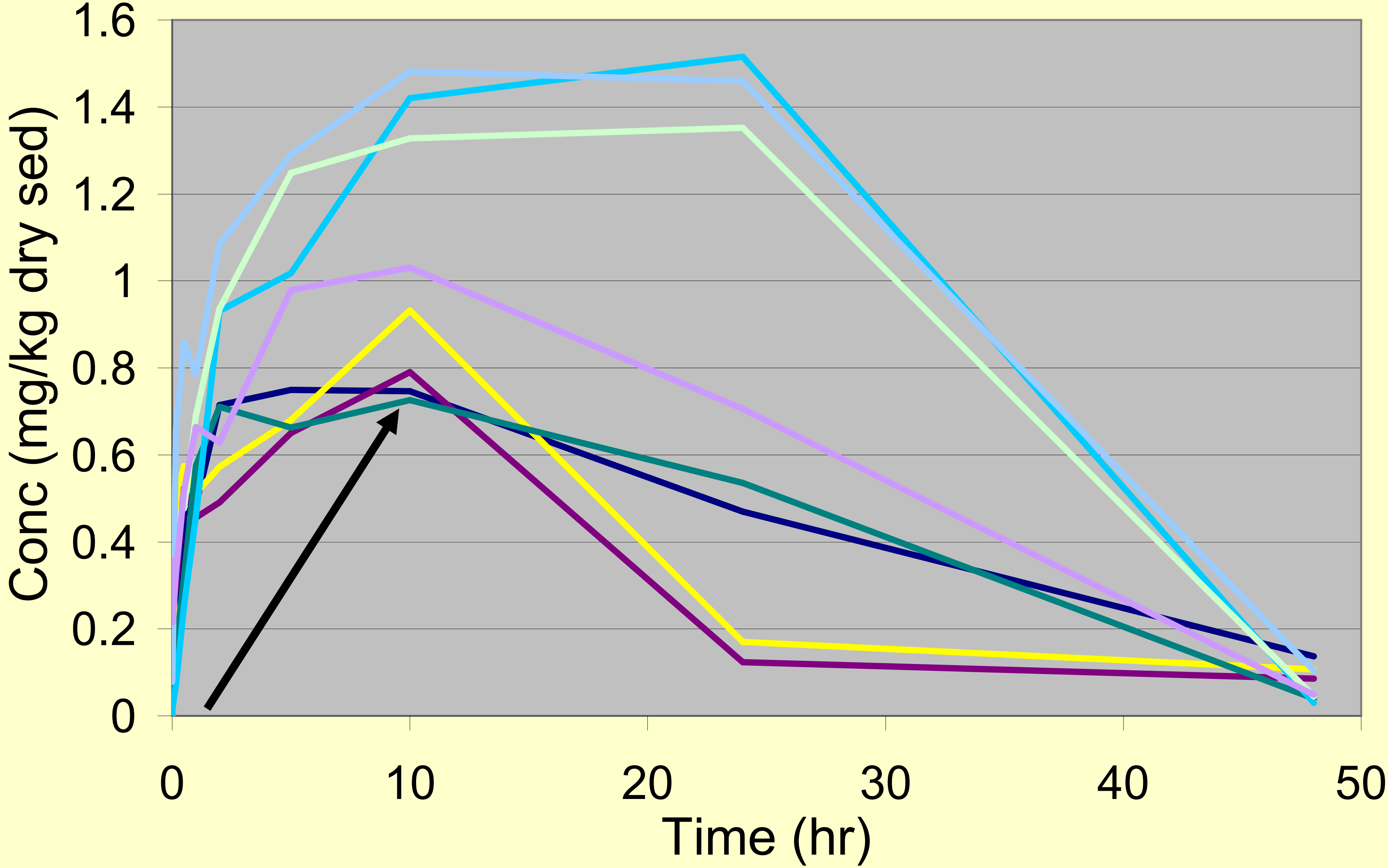
Cadmium (2mm to 63 μm)
Conc (mg/kg dry sed)
Time (hr)
0.03
0.025
0.02
0.015
0.01
0.005
0
0
10
20
30
40
50
Conc. ~ ¼ of the smaller size with no significant effect of any chemical parameter

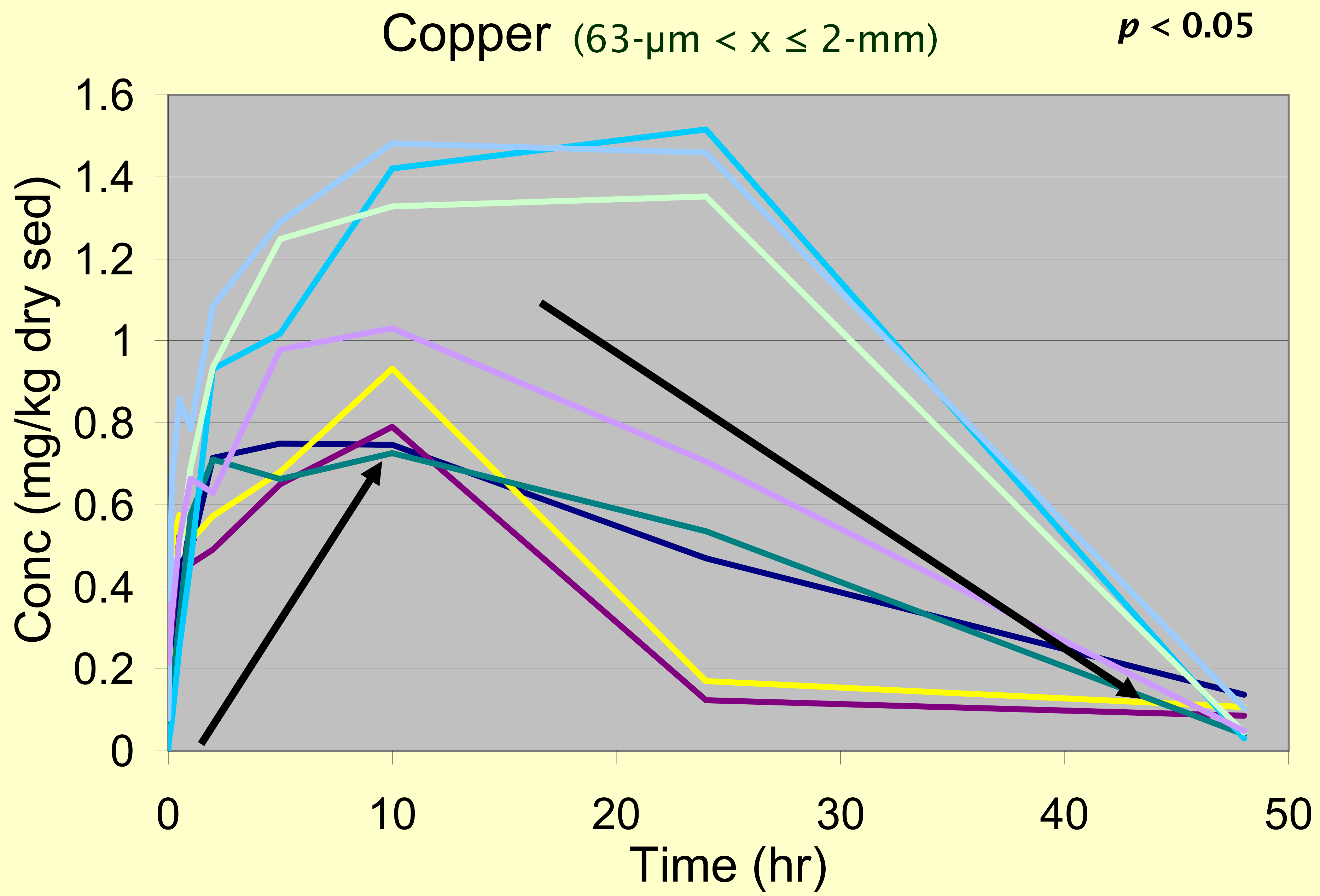

Copper
Conc (mg/kg dry sed)
Time (hr)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
10
20
30
40
50

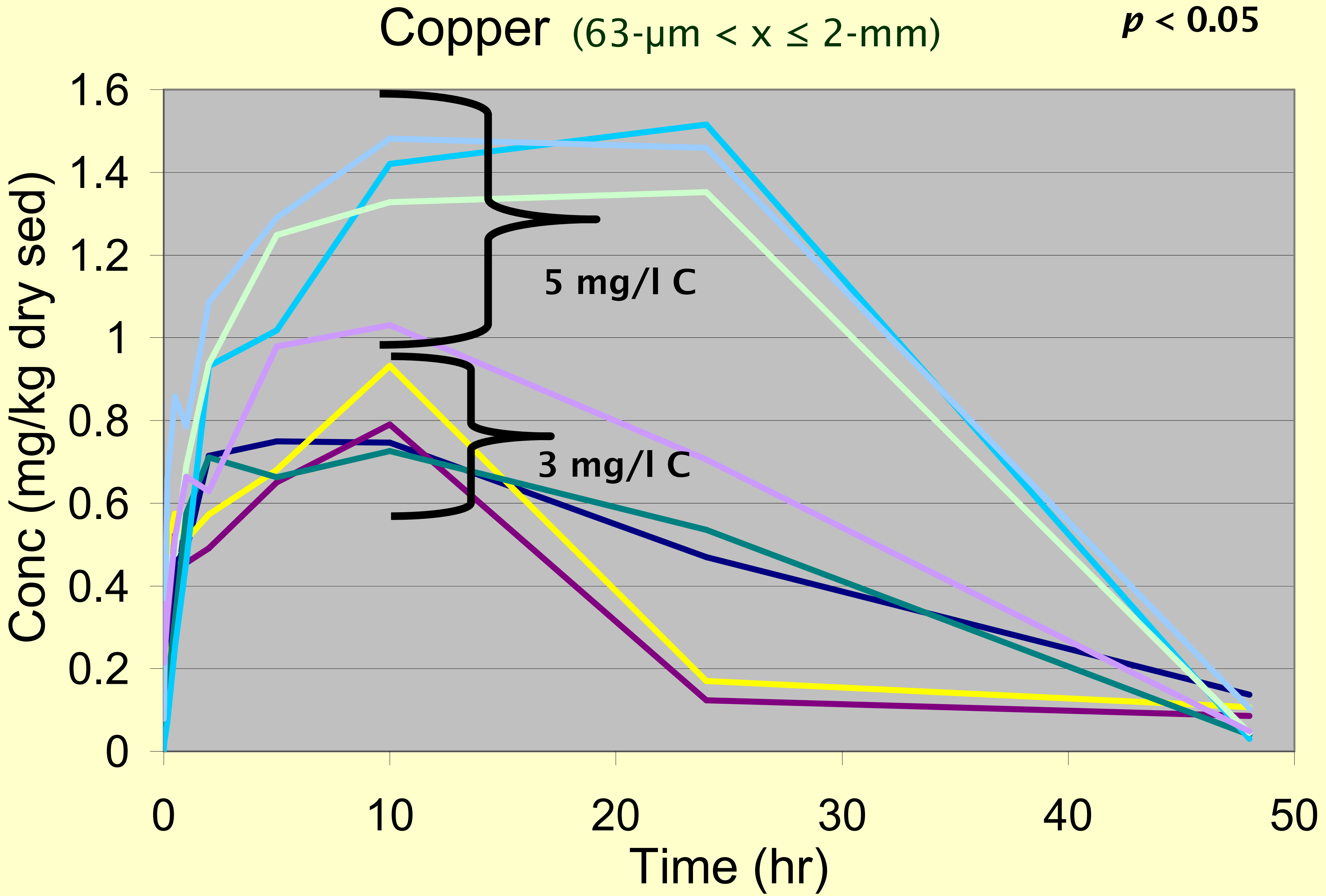

Copper
p < 0.001
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Conc (mg/kg dry sed)
63-µm < x ≤ 2-mm
< 63-µm
0
10
20
30
40
50
Time (hr)

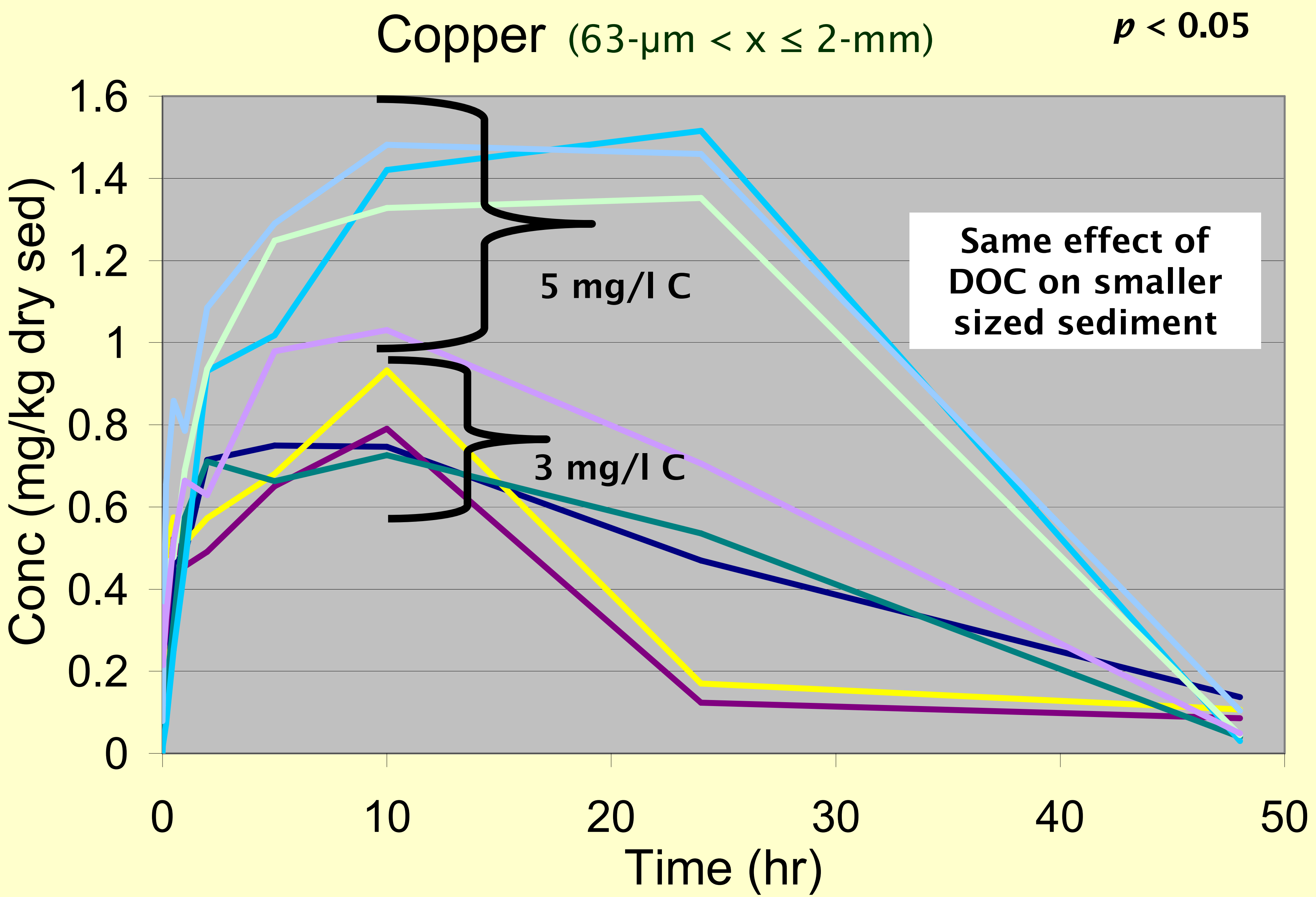
Copper (63-µm < x ≤ 2-mm)

$p < 0.05$

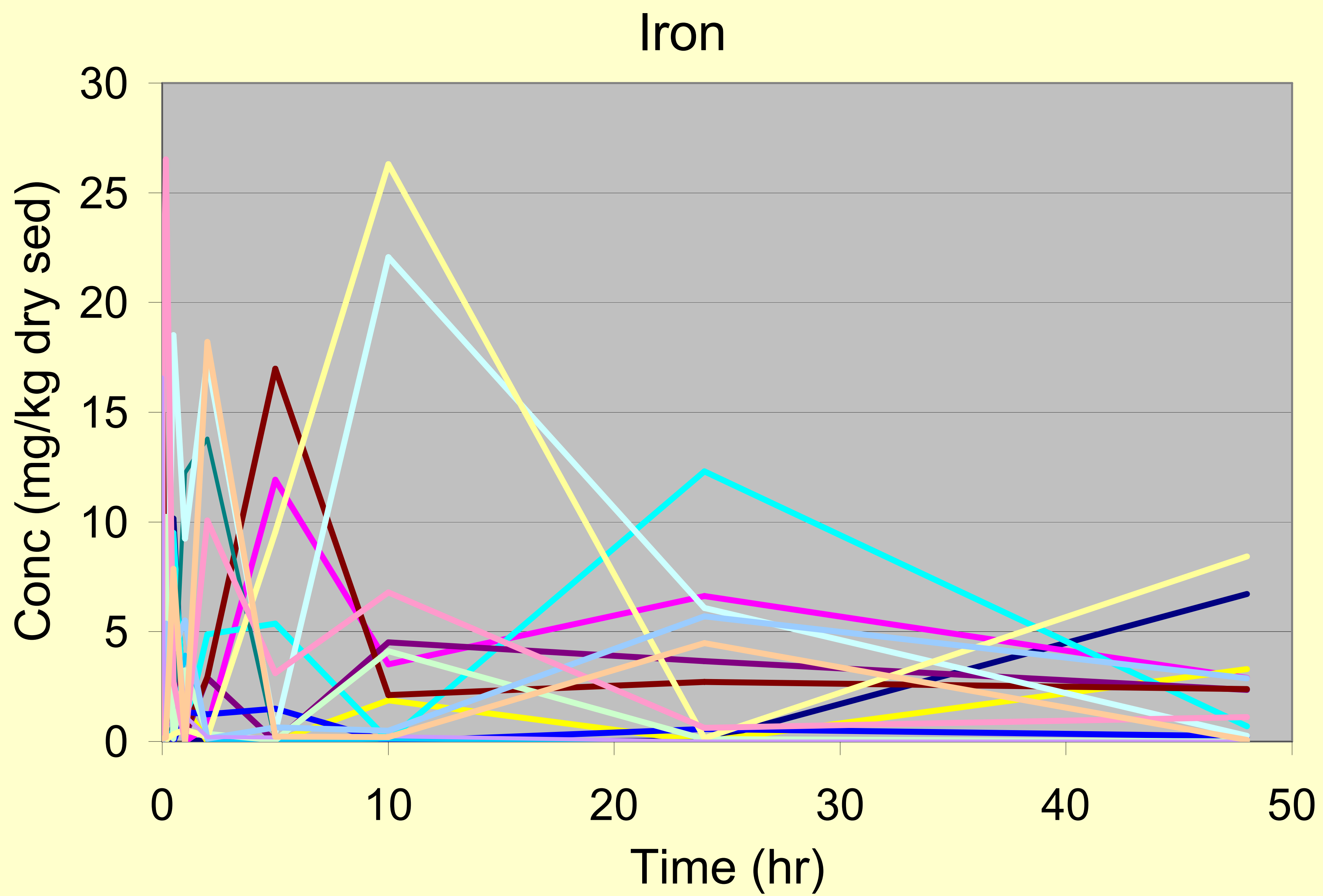


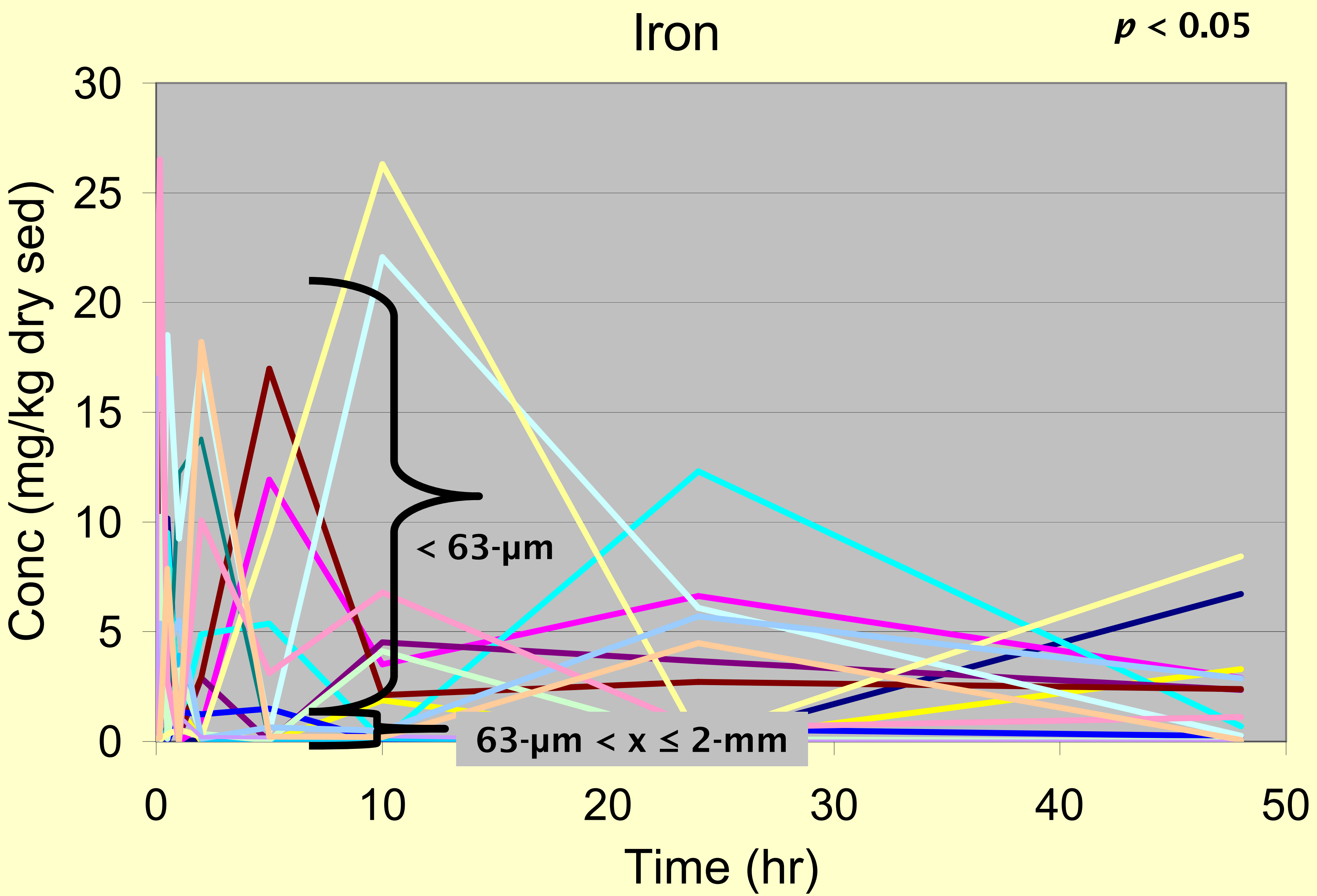

Copper (63-µm < x ≤ 2-mm)
p < 0.05
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Conc (mg/kg dry sed)
0
10
20
30
40
50
Time (hr)


Copper (63-µm < x ≤ 2-mm)
p < 0.05
5 mg/l C
3 mg/l C
Conc (mg/kg dry sed)
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
10
20
30
40
50
Time (hr)

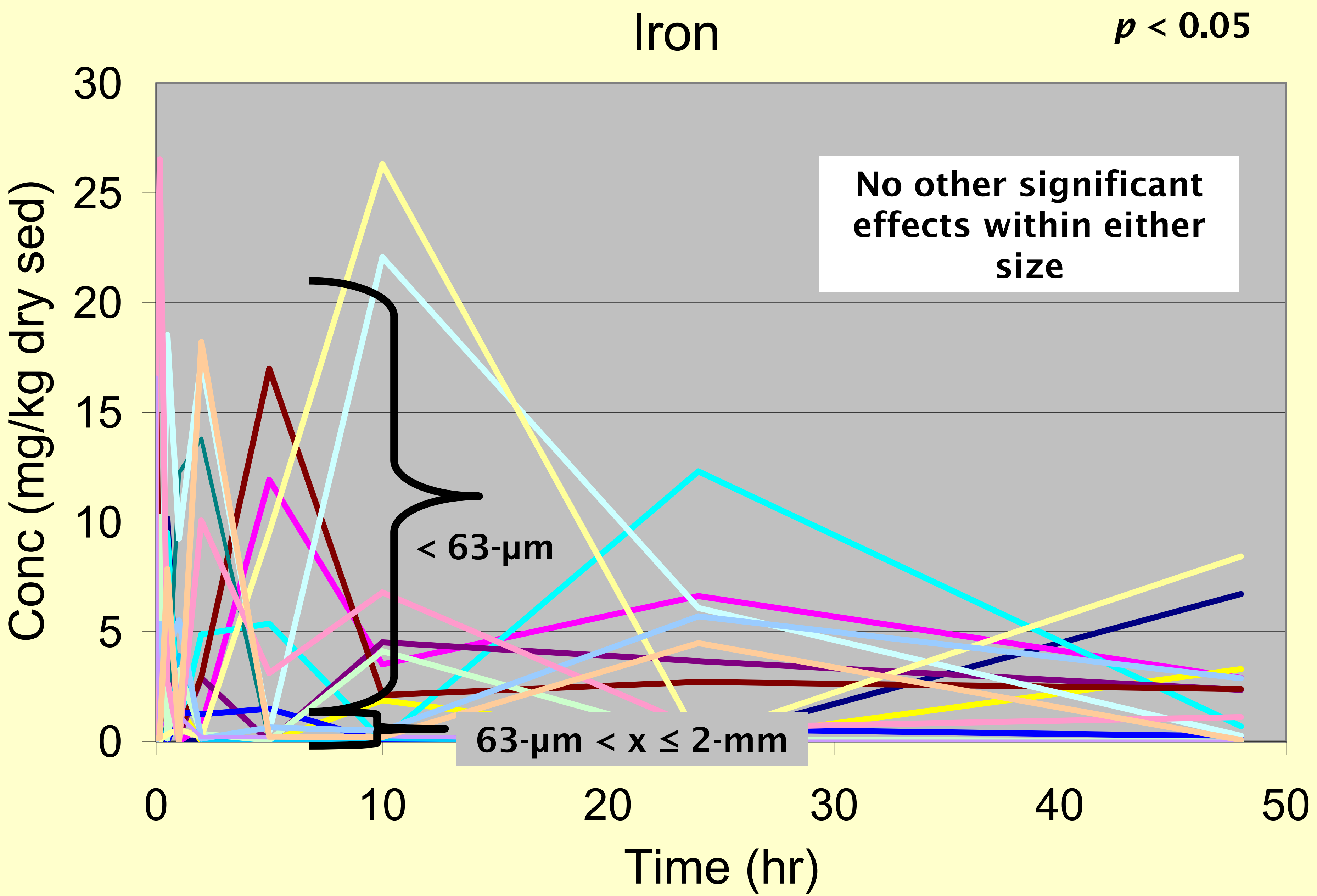


Copper (63-µm < x ≤ 2-mm)
p < 0.05
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Conc (mg/kg dry sed)
0
10
20
30
40
50
Time (hr)
5 mg/l C
3 mg/l C
Same effect of DOC on smaller sized sediment

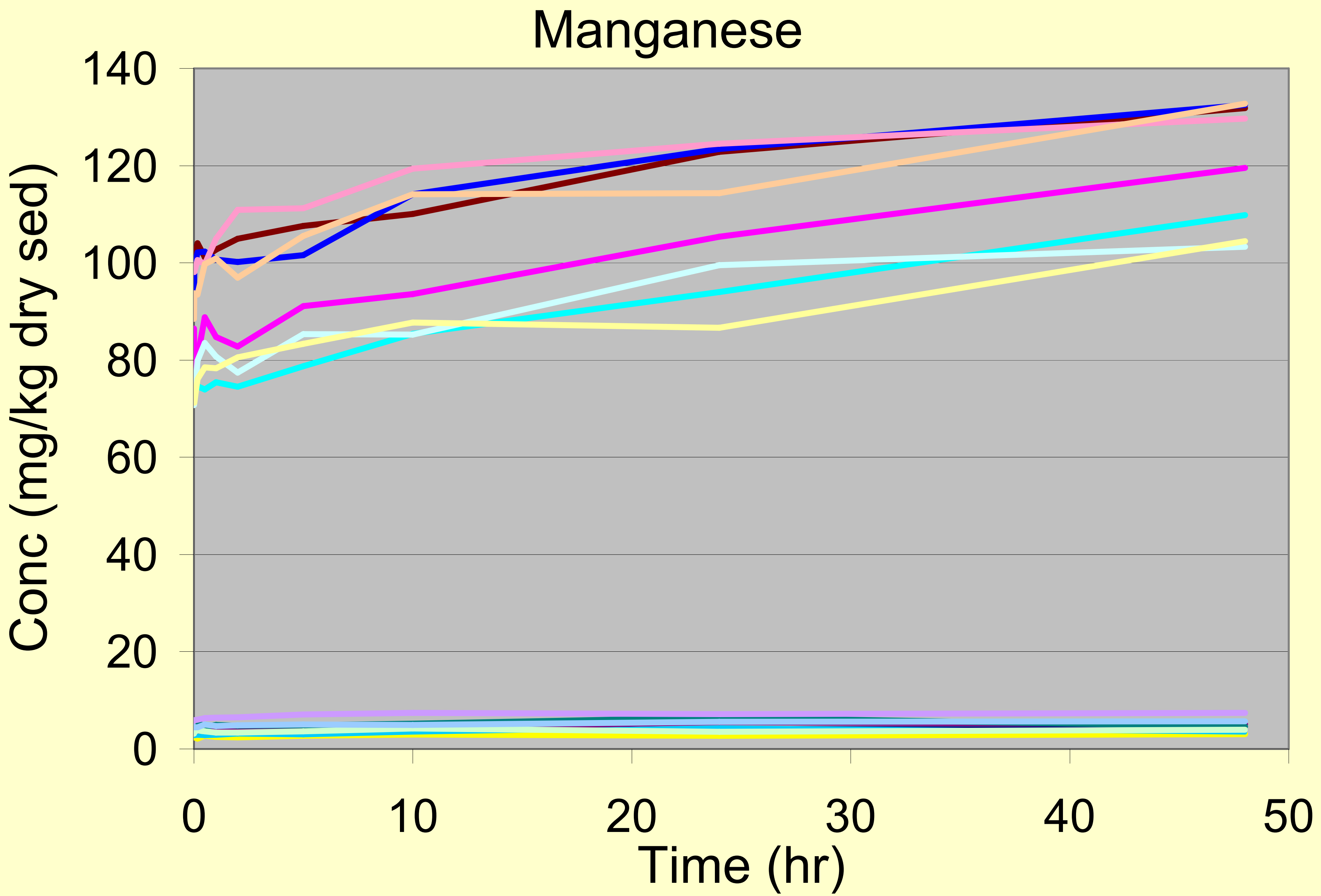

Iron
Conc (mg/kg dry sed)
30
25
20
15
10
5
0
0
10
20
30
40
50
Time (hr)



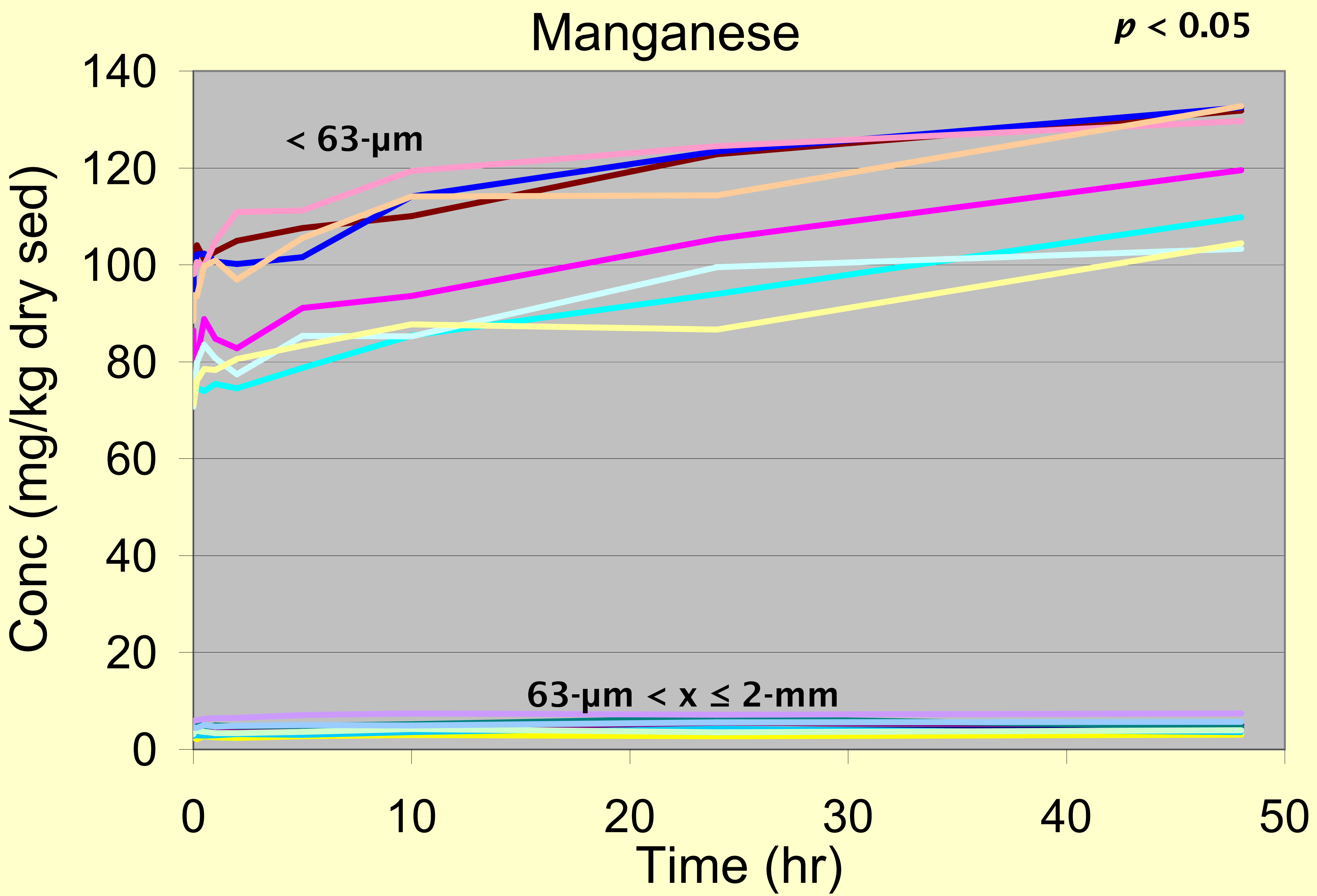
Iron
$p < 0.05$
Conc (mg/kg dry sed)
30
25
20
15
10
5
0
< 63-µm
63-µm < x ≤ 2-mm
0
10
20
30
40
50
Time (hr)



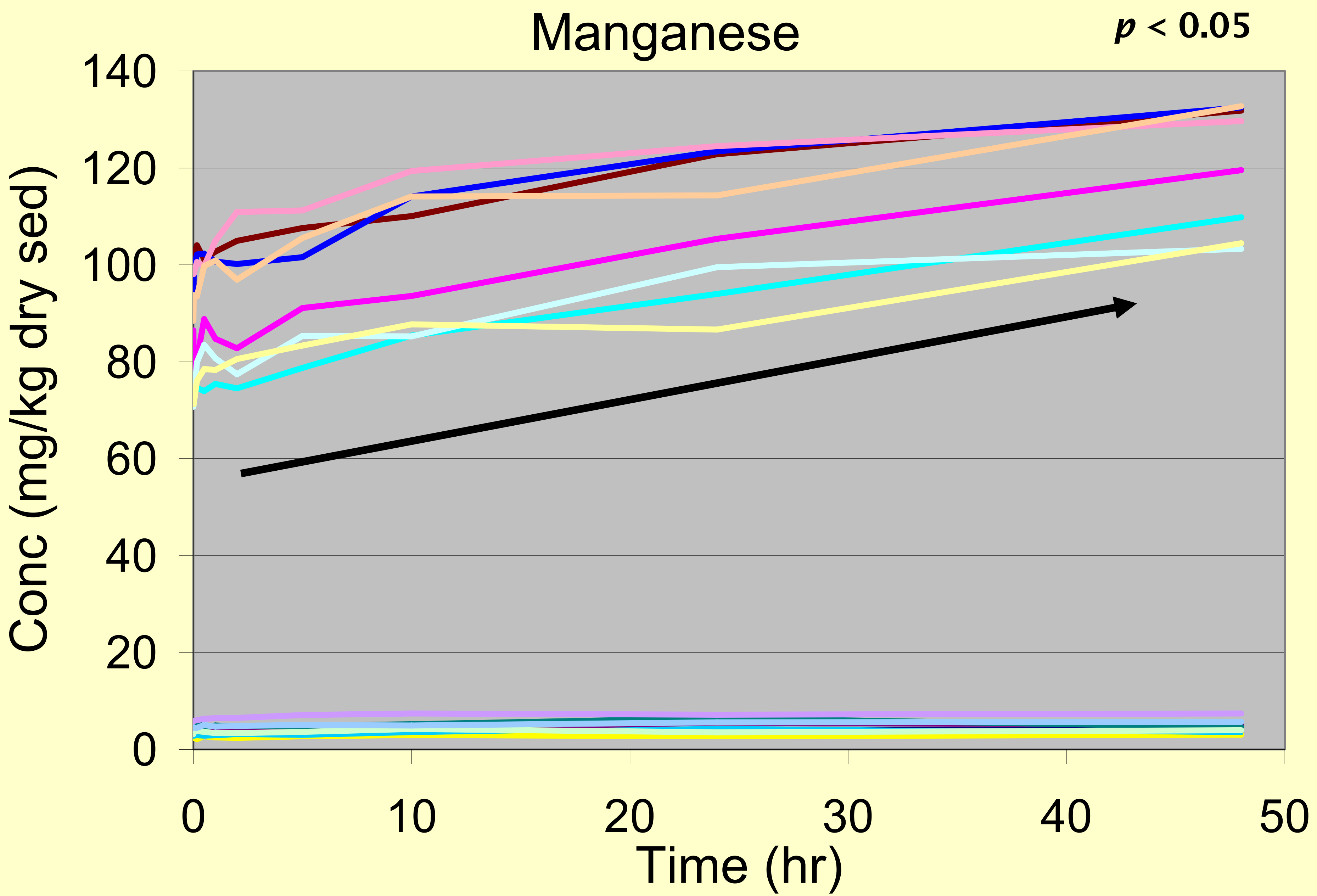
Iron
$p < 0.05$
No other significant effects within either size
< 63-µm
63-µm < x ≤ 2-mm
Conc (mg/kg dry sed)
Time (hr)
30
25
20
15
10
5
0
0
10
20
30
40
50

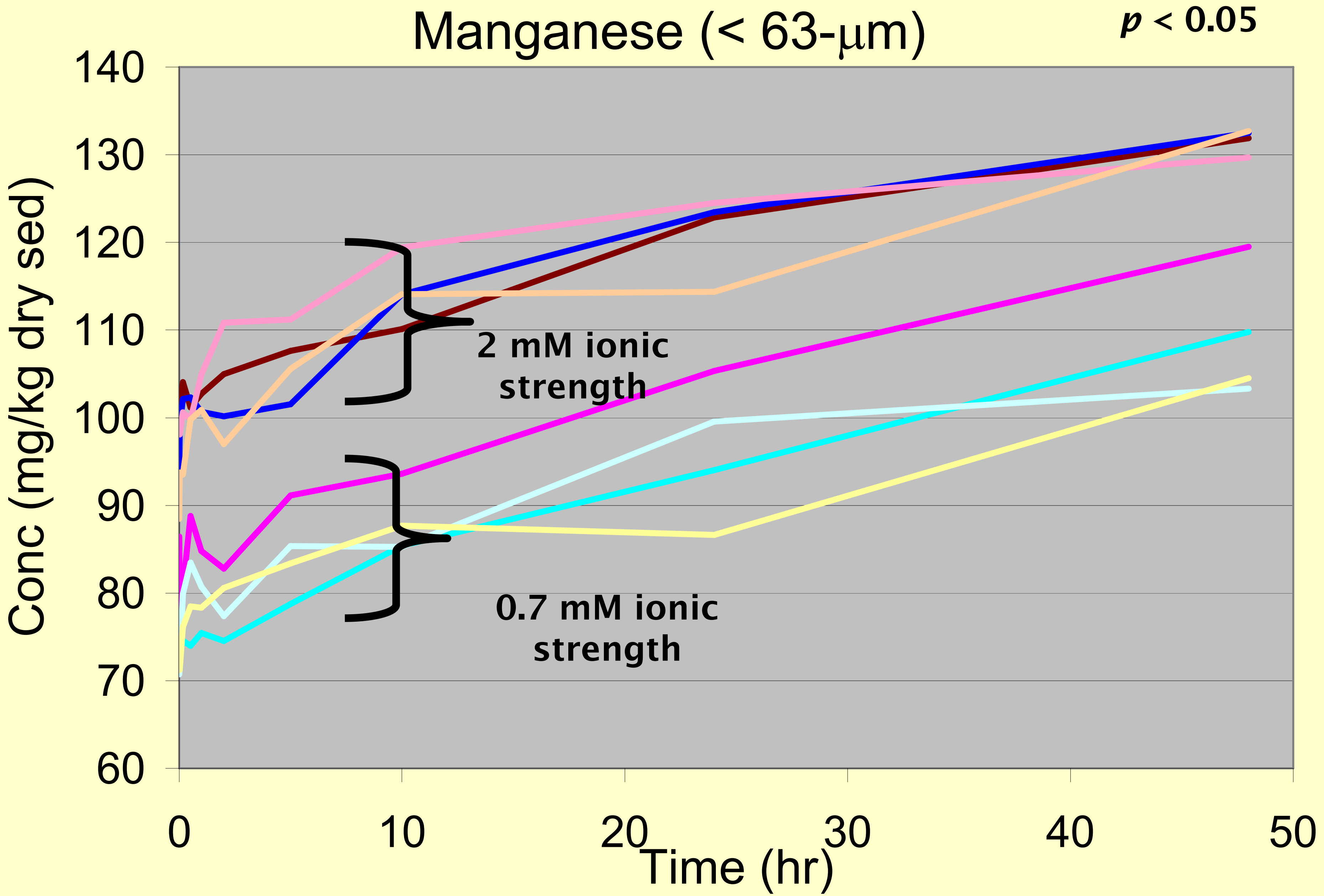


Manganese
Conc (mg/kg dry sed)
0
20
40
60
80
100
120
140
0
10
20
30
40
50
Time (hr)

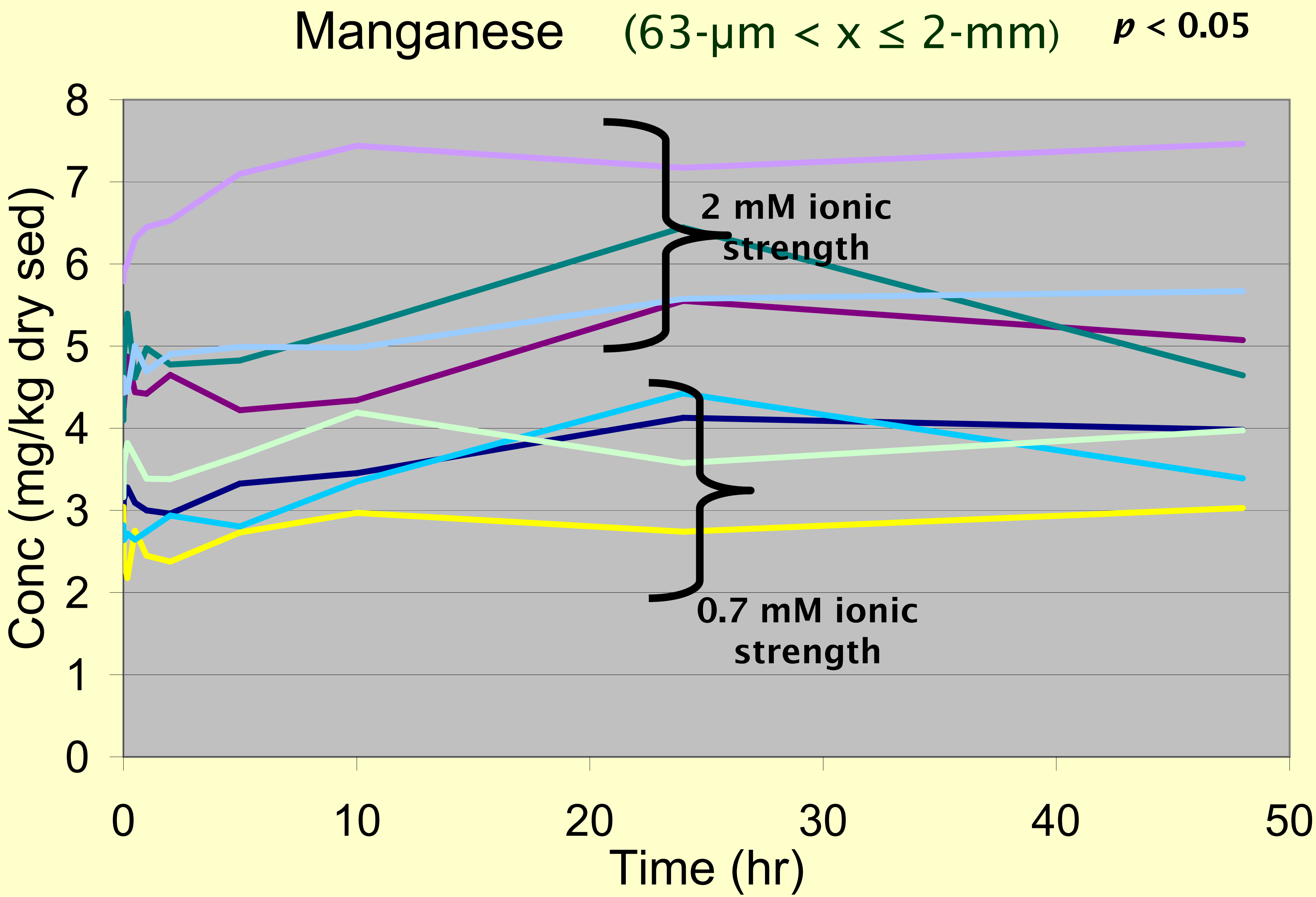


Manganese
p < 0.05
< 63-µm
63-µm < x ≤ 2-mm
Conc (mg/kg dry sed)
0
20
40
60
80
100
120
140
0
10
20
30
40
50
Time (hr)

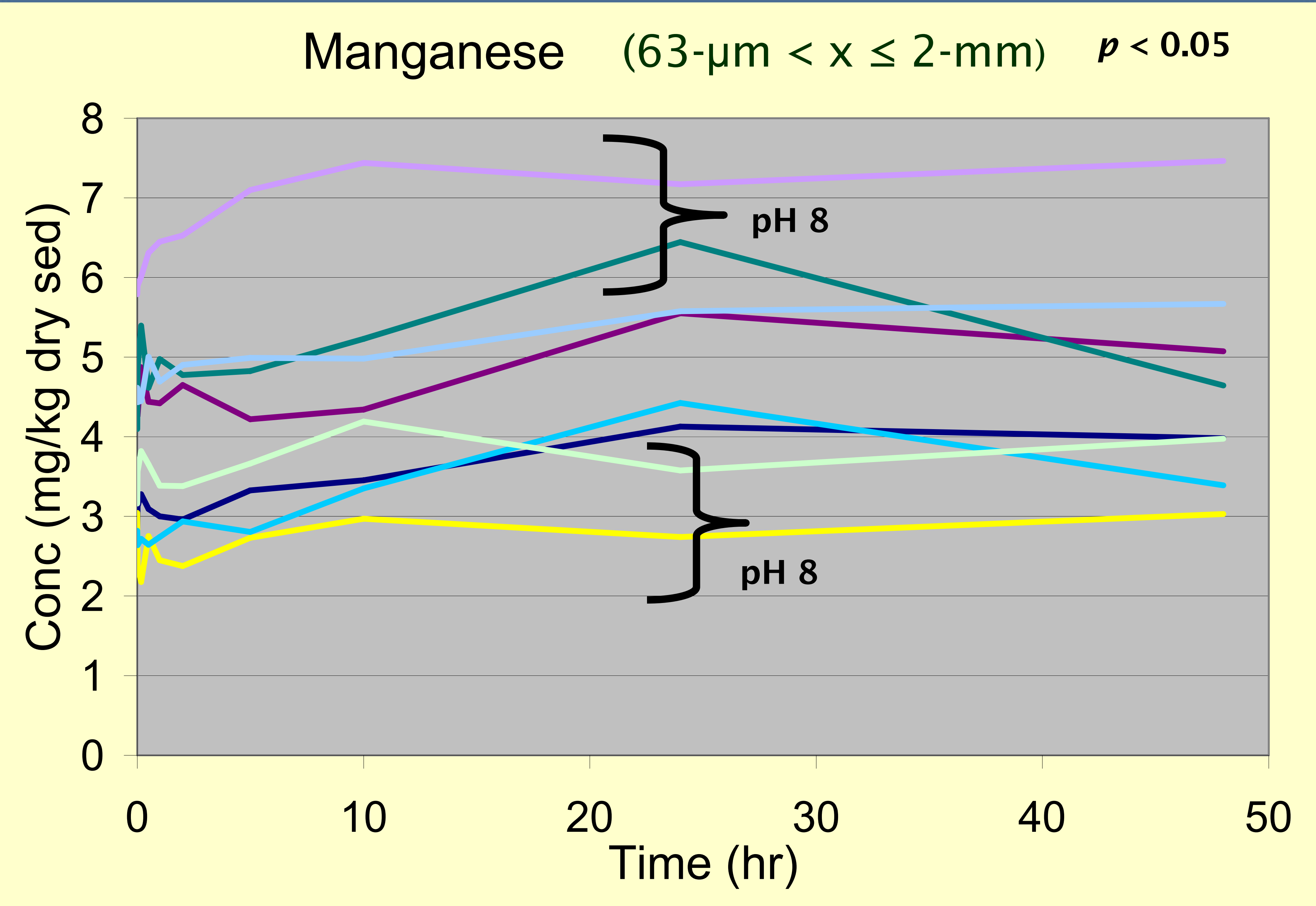

Manganese
$p < 0.05$
Conc (mg/kg dry sed)
140
120
100
80
60
40
20
0
0
10
20
30
40
50
Time (hr)



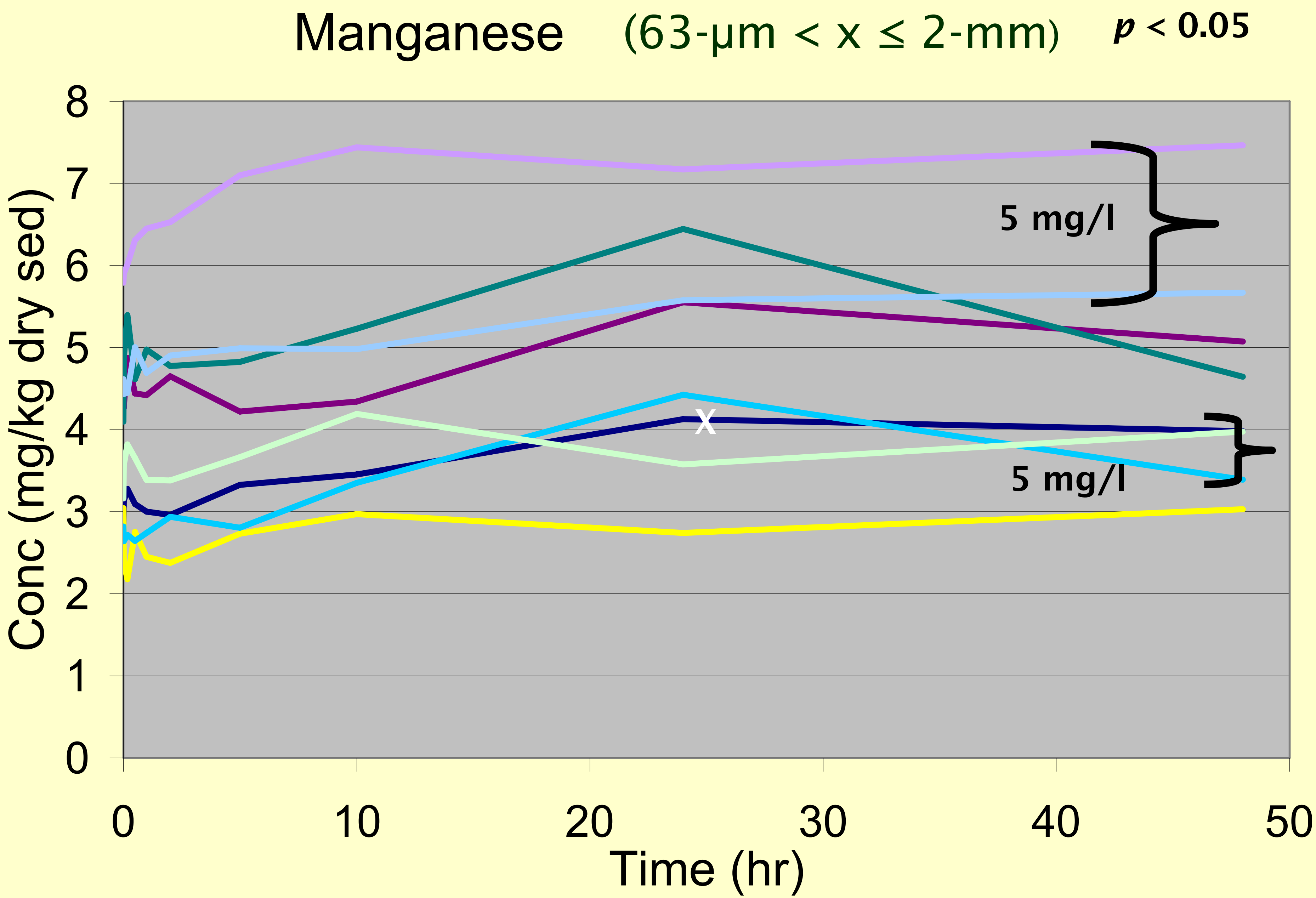
Manganese (< 63-μm)
p < 0.05
Conc (mg/kg dry sed)
140
130
120
110
100
90
80
70
60
0
10
20
30
40
50
Time (hr)
2 mM ionic strength
0.7 mM ionic strength



Manganese
(63-µm < x ≤ 2-mm)
p < 0.05
Conc (mg/kg dry sed)
8
7
6
5
4
3
2
1
0
2 mM ionic strength
0.7 mM ionic strength
0
10
20
30
40
50
Time (hr)

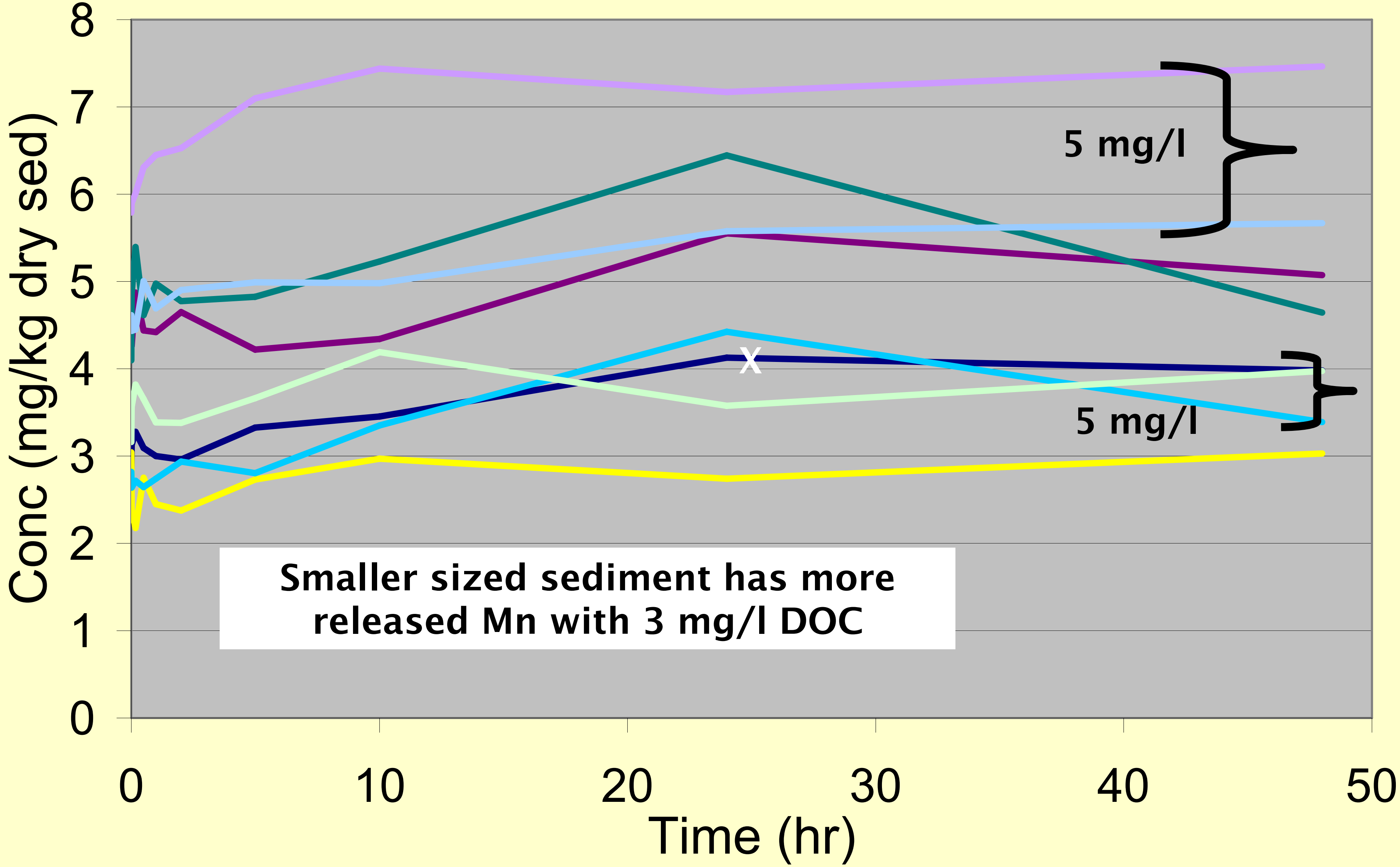


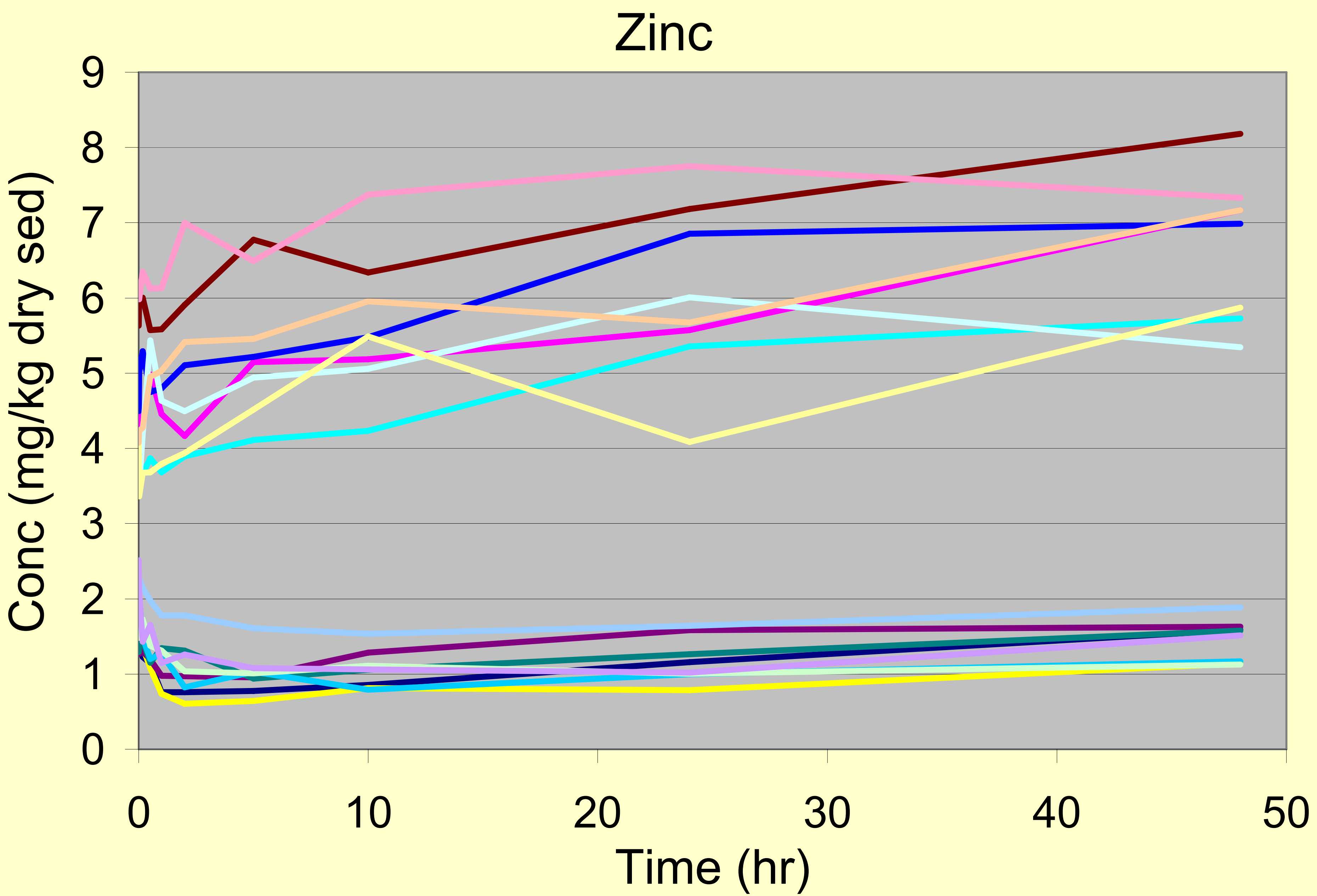
Manganese (63-µm < x ≤ 2-mm) p < 0.05
pH 8
pH 8
Conc (mg/kg dry sed)
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
Time (hr)

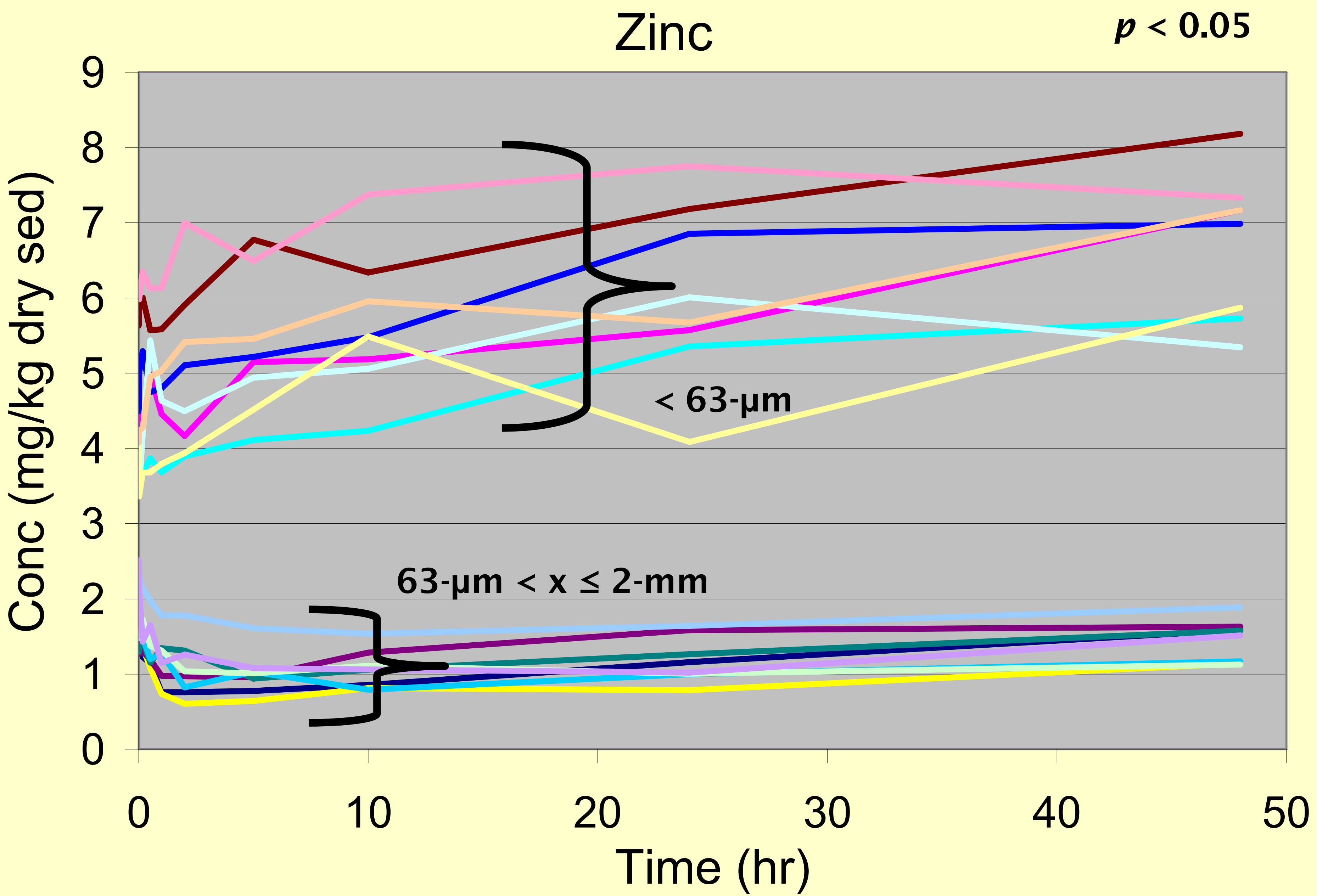


Manganese (63-µm < x ≤ 2-mm) p < 0.05
Conc (mg/kg dry sed)
8
7
6
5
4
3
2
1
0
0
10
20
30
40
50
Time (hr)
5 mg/l
5 mg/l
X

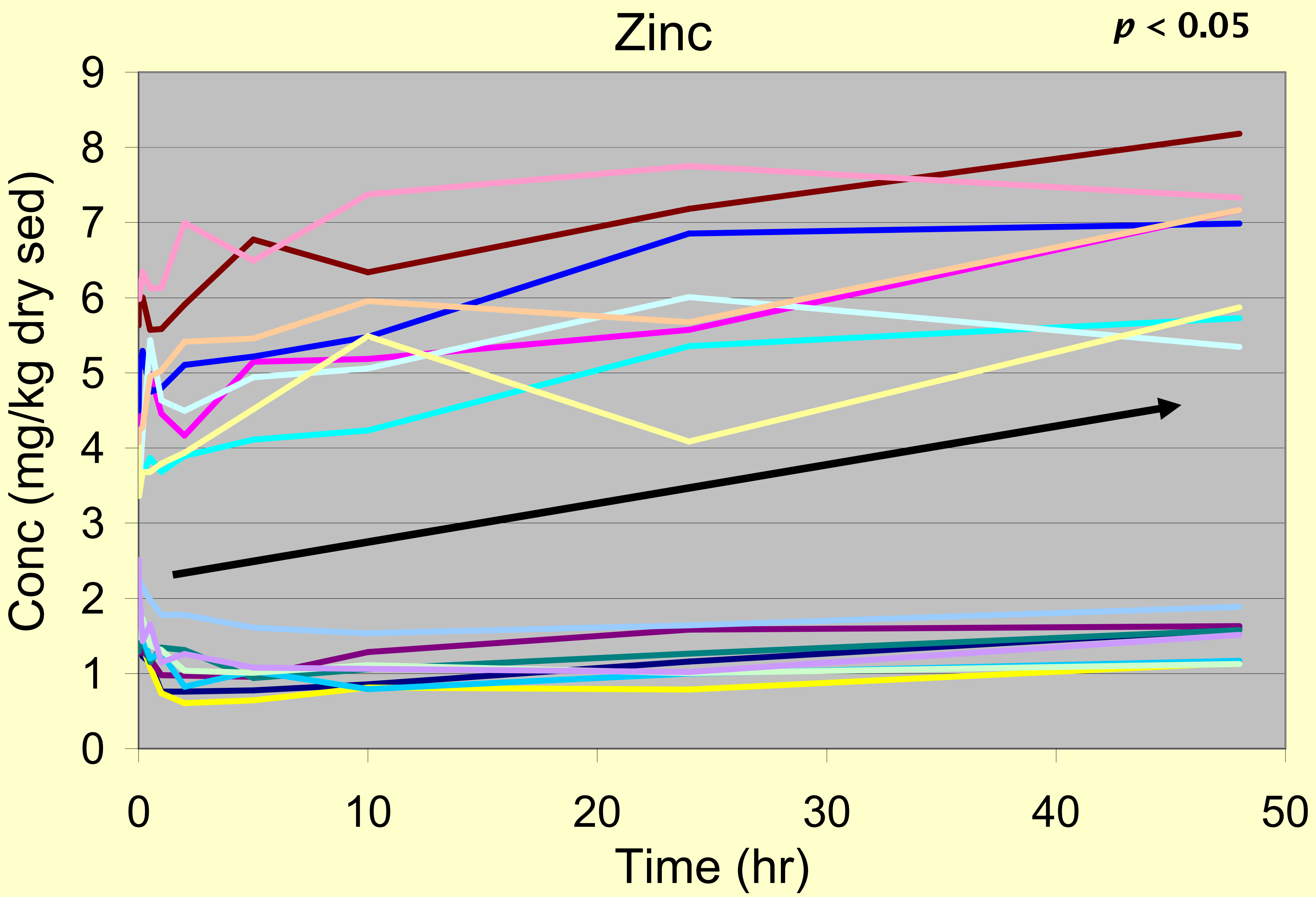
Manganese (63-µm < x ≤ 2-mm) $p < 0.05$

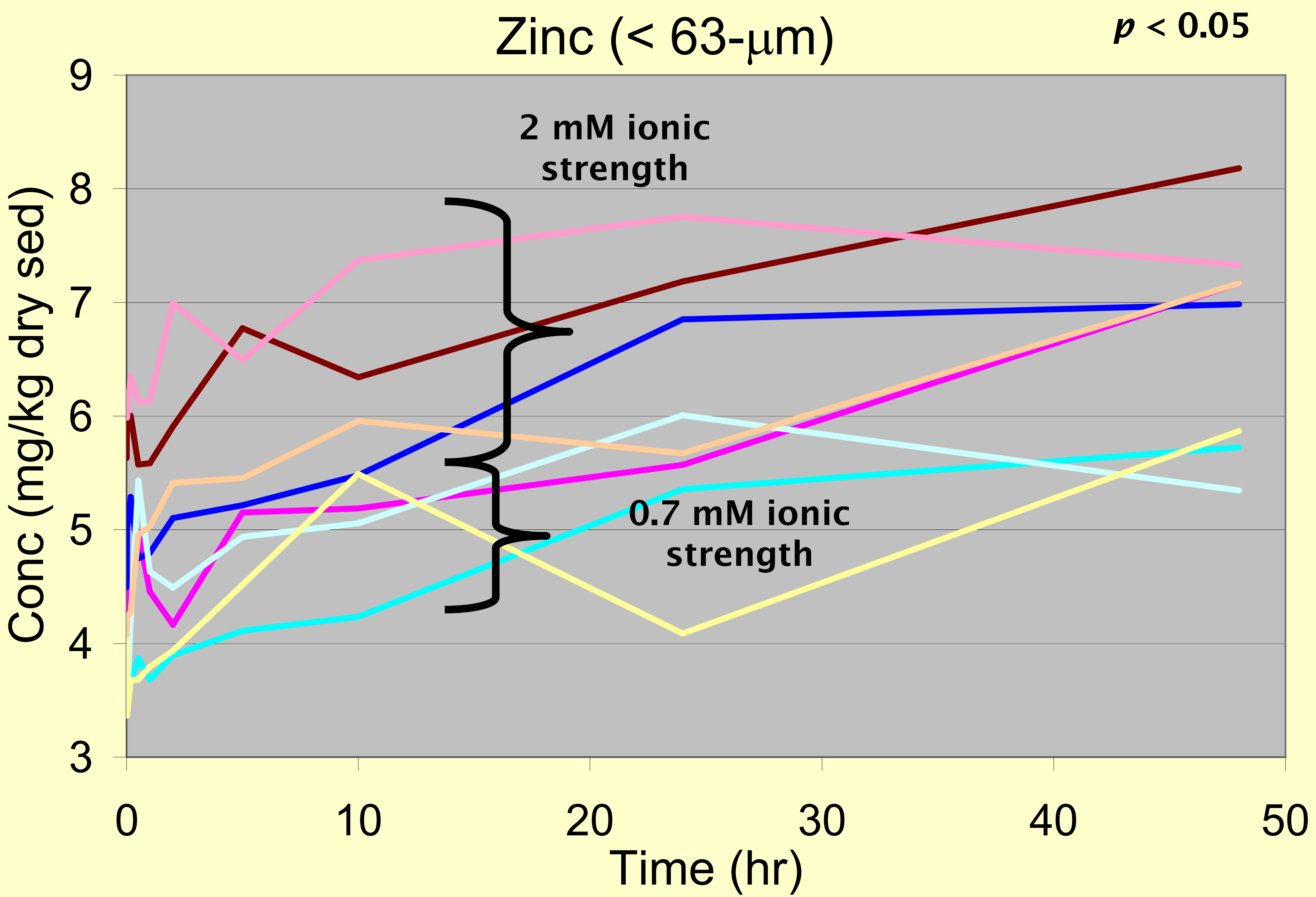



Zinc
Conc (mg/kg dry sed)
0
1
2
3
4
5
6
7
8
9
0
10
20
30
40
50
Time (hr)

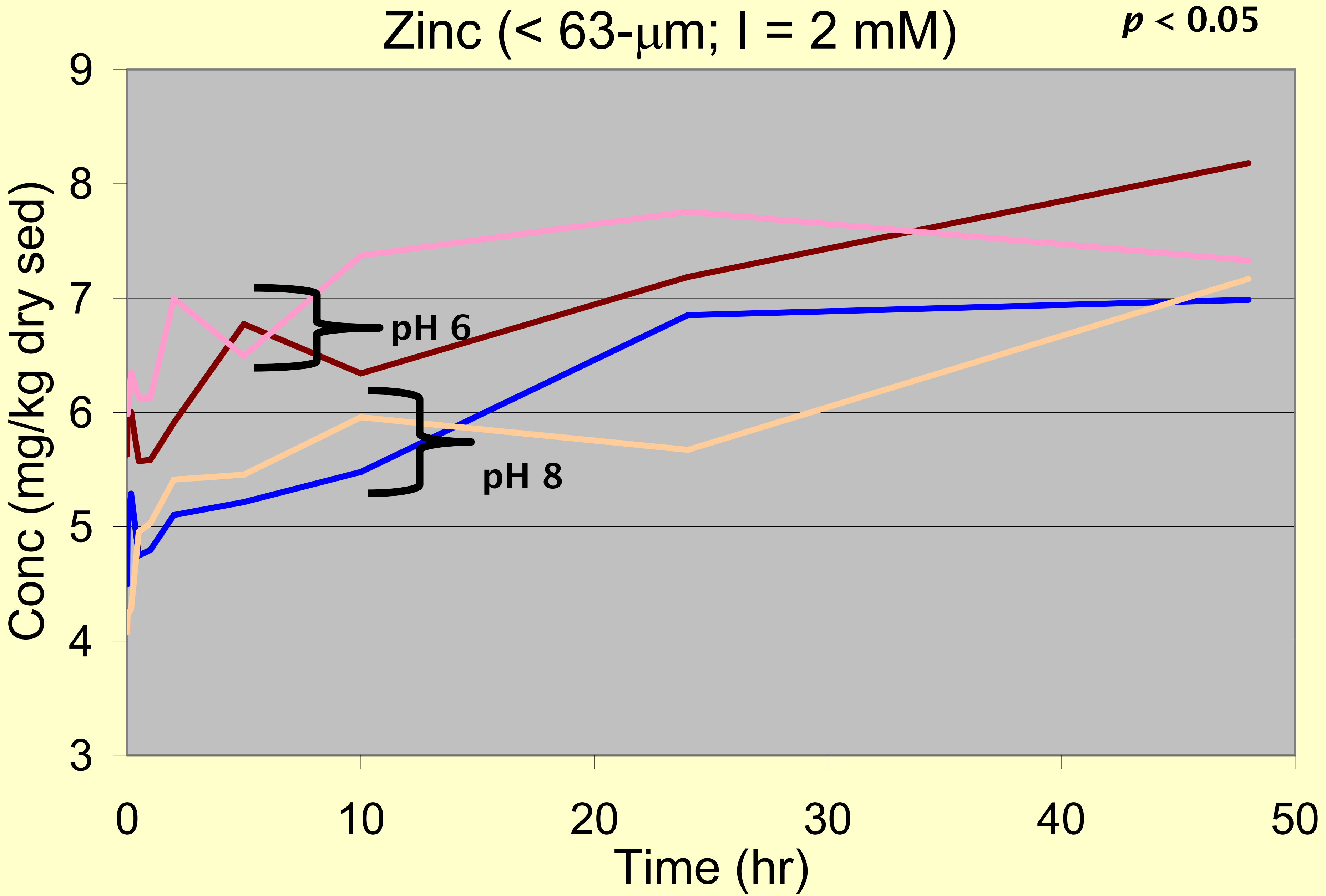


Zinc
p < 0.05
Conc (mg/kg dry sed)
9
8
7
6
5
4
3
2
1
0
< 63-µm
63-µm < x ≤ 2-mm
0
10
20
30
40
50
Time (hr)

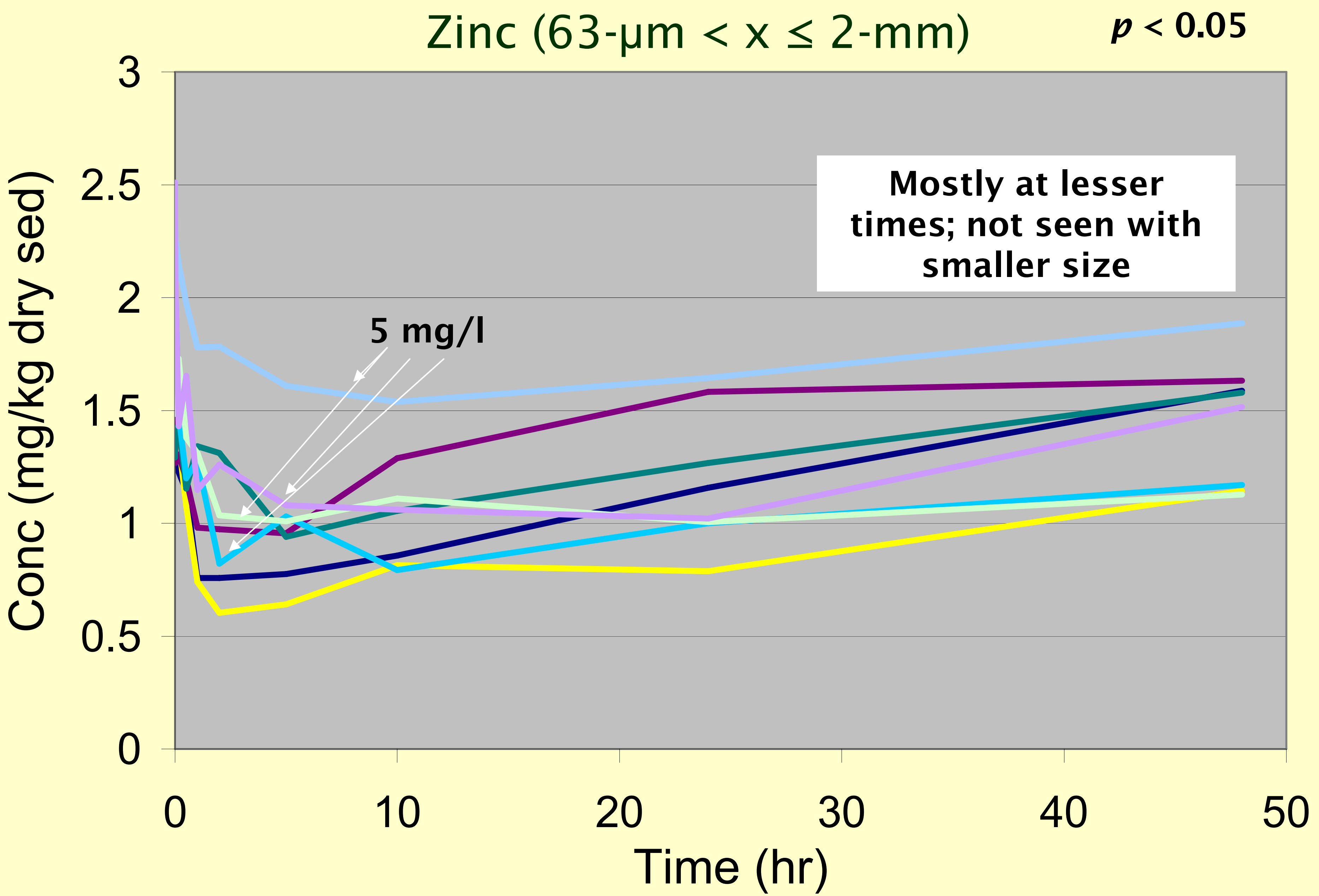

Zinc
p < 0.05
Conc (mg/kg dry sed)
0
1
2
3
4
5
6
7
8
9
Time (hr)
0
10
20
30
40
50



Zinc (< 63-μm)
p < 0.05
2 mM ionic strength
0.7 mM ionic strength
Conc (mg/kg dry sed)
Time (hr)
9
8
7
6
5
4
3
0
10
20
30
40
50



Zinc (< 63-μm; I = 2 mM)
p < 0.05
Conc (mg/kg dry sed)
9
8
7
6
5
4
3
pH 6
pH 8
0
10
20
30
40
50
Time (hr)



Zinc (63-µm < x ≤ 2-mm)
p < 0.05
Mostly at lesser times; not seen with smaller size
5 mg/l
Conc (mg/kg dry sed)
Time (hr)
0
0.5
1
1.5
2
2.5
3
10
20
30
40
50

Bed Sediment Research

- Question:
  - Is the amount released as a function of size simply due to there being more present for release?

Bed Sediment Research

- Test:
  - Compare amount of metal released versus amount ‘bioavailable’
    - 0.6 M HCl digestion for 2-hours*

*Luoma et al. (1995). Marine Pollution Bulletin. 31(1-3):44-54; Hornberger et al. (1999). Marine Chemistry. 64:39-55; Giddings et al. (2001). USGS Water Resources Investigations Report 01-4213.

Bed Sediment Research

- Answer:
  - Fraction released follows same trend for Cd, Cu, and Mn
  - Fraction released is opposite to trend for Fe and Zn

Fraction released = amount released / amount ‘bioavailable’

Bed Sediment Research

- Answer:
  - Fraction released follows same trend for Cd, Cu, and Mn
  - Fraction released is opposite to trend for Fe and Zn
  - < 1% Cd, Cu, Fe, Zn; 4-7% Mn

Fraction released = amount released / amount ‘bioavailable’

Bed Sediment Research

- Answer:
  - Fraction released follows same trend for Cd, Cu, and Mn
  - Fraction released is opposite to trend for Fe and Zn
  - < 1% Cd, Cu, Fe, Zn; 4-7% Mn
  - Release due to size is not *simply* due to there being more metal *for* release

Fraction released = amount released / amount 'bioavailable'

Bed Sediment Research

- Summary
  - Time
    - Increased metal released with time
    - Cu increased to 10 hours, then decreased

Bed Sediment Research

- Summary
  - Time
    - Increased metal released with time
    - Cu increased to 10 hours, then decreased
  - Size
    - 63-µm < x ≤ 2-mm
      - More Cu released; less Cd, Fe, Mn, and Zn
        - Greater fraction for Cu, Fe, and Zn
    - < 63-µm
      - More Cd, Fe, Mn, and Zn released; less Cu
        - Greater fraction for Cd and Mn

Bed Sediment Research

- Summary
  - DOC
    - More Cu released with higher DOC from both sizes of sediment
    - More Mn released with higher DOC from larger sized sediment; more with lower DOC from smaller sized sediment
    - More Zn released with higher DOC from larger sized sediment only

Bed Sediment Research

- Summary
  - Ionic Strength (I)
    - More Cd, Mn, and Zn released with higher I
      - Not statistically significant for Cd from larger sized sediment

Bed Sediment Research

- Summary
  - pH
    - More Cd and Zn released at lower pH
    - More Mn released at higher pH for larger sediment size
    - More Mn released at lower pH for smaller sediment size

Bed Sediment Research

- Indications and implications…
  - Cu bound by inner-sphere mechanism (no dependence on ionic strength)
  - Cd, Mn, and Zn bound by outer-sphere mechanism (strong dependence on ionic strength, and pH)

Bed Sediment Research

- Indications and implications…
  - Sediments will release metals
    - Perhaps less than current for Cd, Mn, and Zn (with lower I)
    - Perhaps more than current for Cu and for Zn associated with larger sediment particles (with higher DOC)

Bed Sediment Research

- Indications and implications…
  - Sediments will release metals
    - 2 mm – 63 µm
      - 83% of total sediment (mass)*
    - < 63 µm
      - 17% of total sediment (mass)*
        - The majority of this material comes from precipitation of AMD-inputs

*April 2007…sampling in April 2008 had 7% small sized particles

Bed Sediment Research

- Indications and implications…
  - Acute national water quality criteria (WQC) for each metal were exceeded at most time points
    - But these would be diluted by stream water flow

Bed Sediment Research

- Indications and implications…
  - Acute national water quality criteria (WQC) for each metal were exceeded at most time points
    - But these would be diluted by stream water flow
    - The smaller-sized particles (precipitated metal oxyhydroxides) won't be formed to the same extent

Bed Sediment Research

- Indications and implications…
  - Acute national water quality criteria (WQC) for each metal were exceeded at most time points
    - But these would be diluted by stream water flow
    - The smaller-sized particles (precipitated metal oxyhydroxides) won't be formed to the same extent
    - Hardness-based…would not be the same

Acknowledgements

- Dr. Jim Ranville (Colorado School of Mines) – sampling assistance
- Many folks in LRPCD – SSMB and RRB
- Folks at T&E for running sulfate and DOC analyses and for use of the ICP-AES

Thank you!