# Evaluating the Impact of Na-$SO_4^{2-}$ - Dominated Ionic Strength on Trace Metal Removal in Vertical Flow Bioreactors


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- **Background**
- **Methods**
- **Results**
- **Conclusions**

# Background

- Typical mine water
  - Elevated iron, trace metals, and sulfate
  - Often acidic (pH < 4.5)
- Passive treatment to treat mine water
  - Anoxic limestone drains generate alkalinity/neutralize acidity
  - Oxidation ponds precipitate iron
  - Vertical flow bioreactors may remove trace metals
    - In addition to generating alkalinity/neutralizing acidity

# Background

- Vertical flow bioreactors (VFBR)
  - Force water vertically through organic substrate
    - May overlay limestone layer or have limestone mixed throughout
  - Create anoxic, reducing conditions
    - Promote bacterial sulfate reduction and limestone dissolution
    - Remove divalent trace metals as insoluble sulfide minerals and increase pH

# Background

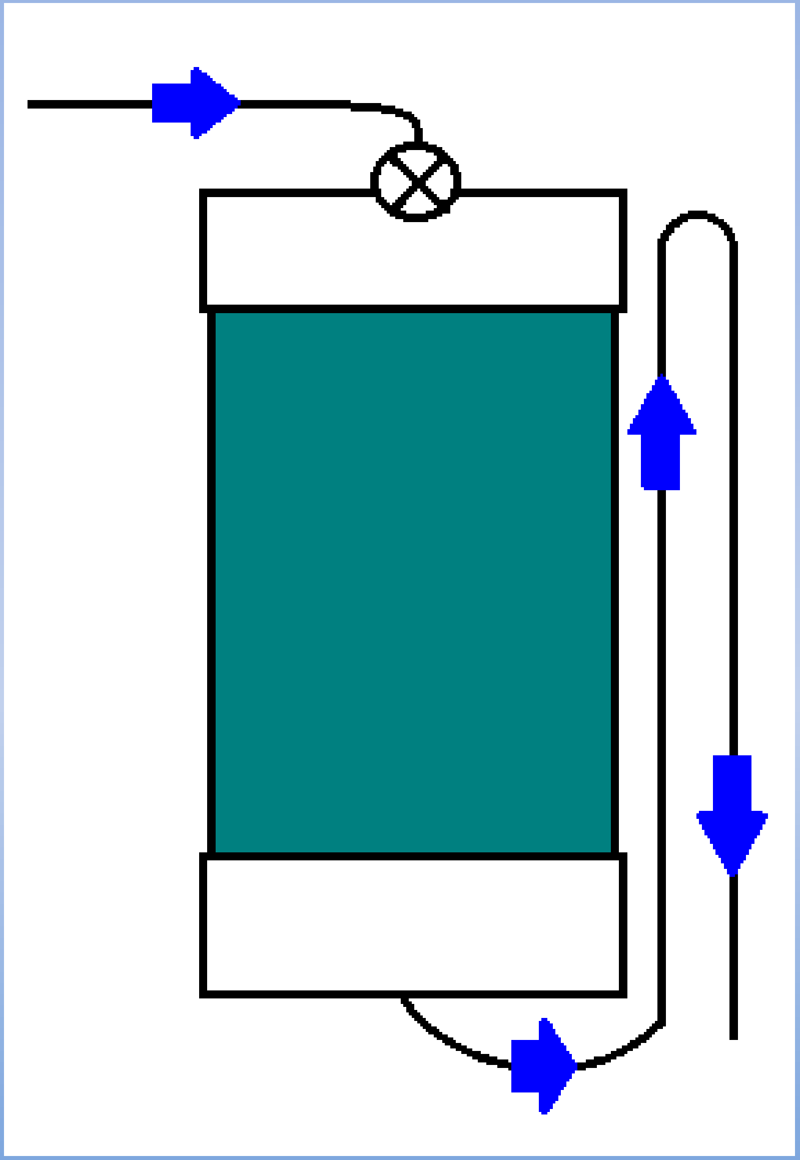
- Sulfide precipitation not only removal mechanism
  - Sorption, carbonates, complexation with OM
- Factors impacting trace metal removal/VFBR performance
  - pH, ORP, temperature, HRT, substrate
  - Ionic strength?
    - Impacts solubility of carbonates and sulfides
      - Increase in I generally correlates to *increase* in solubility
    - Impacts sorption capacity
      - Increase in I generally correlates to *decrease* in sorption

# Background

- Ionic strength of mine water varies a great deal
  - <0.01 M to 0.75 M
- Commonly dominated by sulfate anion and various cations (Ca, Mg, Fe)
- Sodium may occasionally be dominant cation
  - Geologic conditions or hydraulic connections to natural gas or oil wells
- **Does this impact trace metal removal in VFBR?**

# Methods

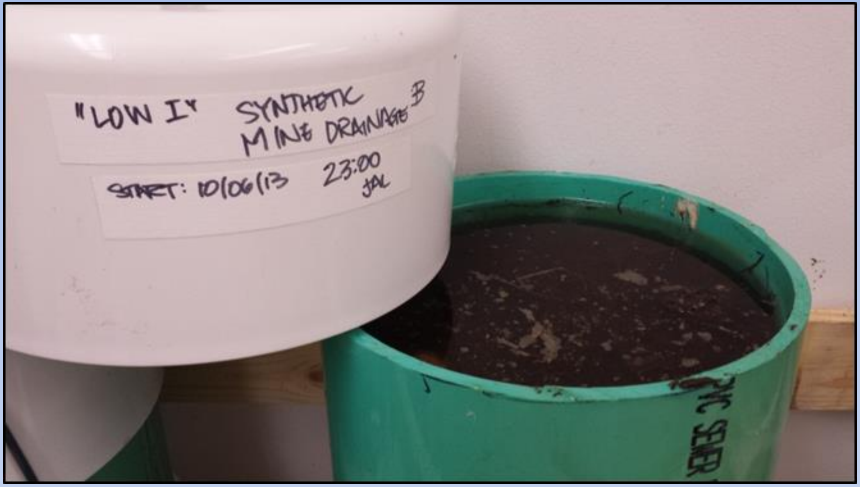
- Paired comparison
  - Two sets of columns
    - Spent mushroom compost
    - Same trace metals (Cd, Mn, Ni, Pb, Zn) concentrations
    - Different ionic strengths
      - $10^{-3}$ M vs. $10^{-1}$ M (LOW vs. HIGH)
      - Na-$SO_4^{2-}$ dominated
    - Three replicates in each set



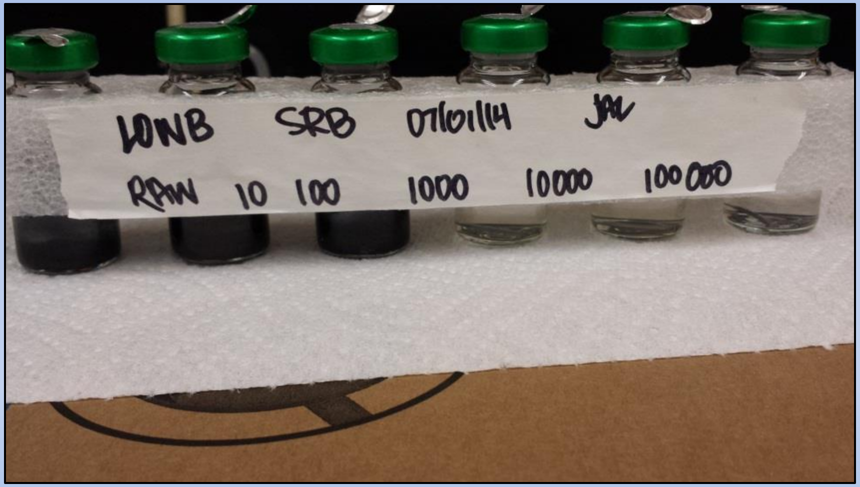
**H = 38.1 cm (15”)**
**r = 12.7 cm (5”)**
**Q ≈ 2.2 mL/min (3.15 L/d)**

# Methods

- Average HRT = 72 hours
- Sampled effluent biweekly
  - 100 pore volumes
- DO, ORP, pH, conductivity, alkalinity
- Total and dissolved metals
  - Cd, Mn, Ni, Pb, Zn
  - Ca, Mg, Na
- Sulfate and sulfide
- SRB presence/abundance




# Results

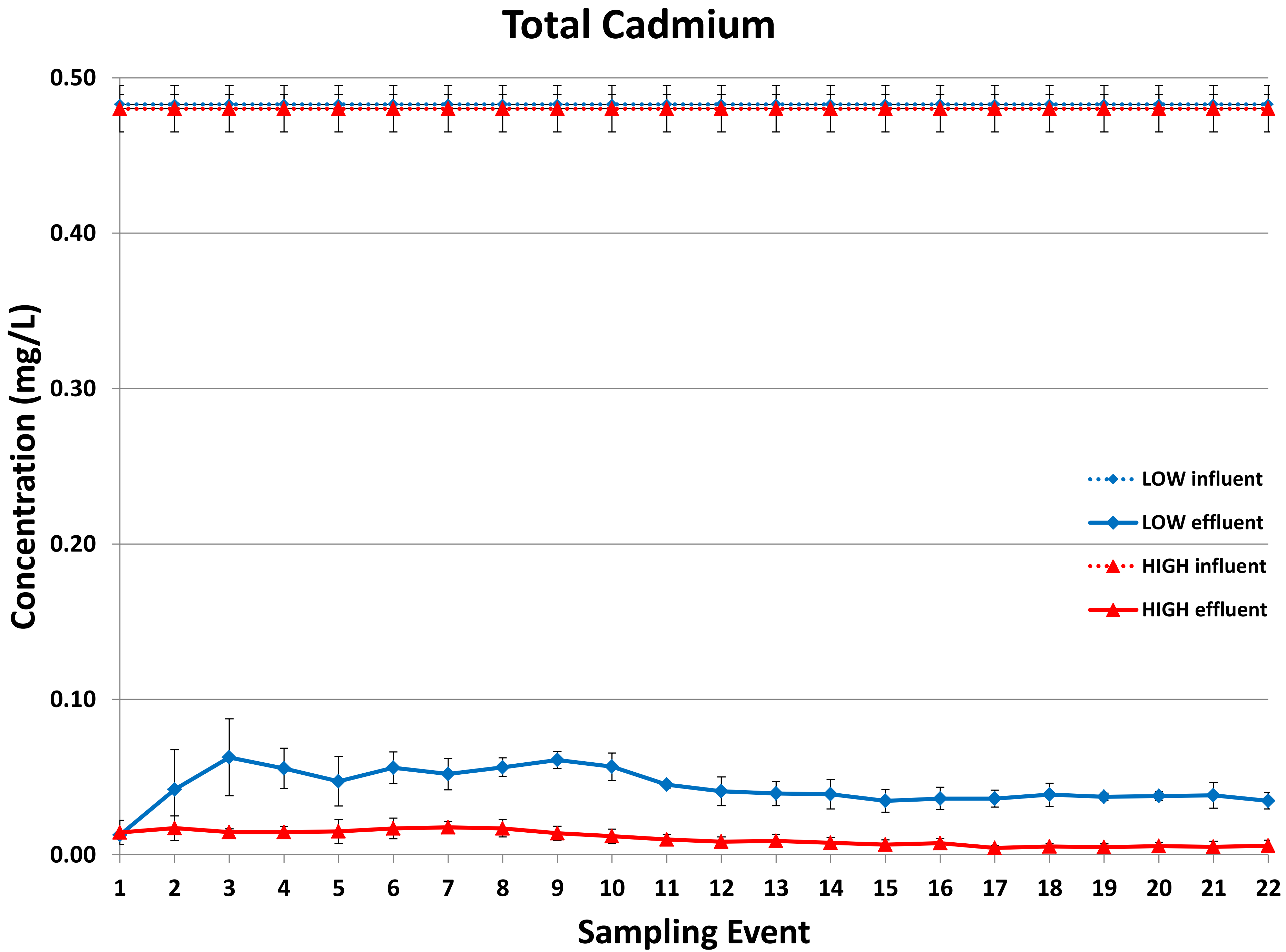



- Initial flush of cations (Ca, K, Mg, Na)
- Removal of dissolved oxygen
  - Establishment of reducing conditions
- Establishment of bacterial community
  - Growth in inoculated media
  - Removal of sulfate
  - Production of sulfide
- Increase in pH and alkalinity
  - Dissolution of gypsum in substrate
  - Bacterial sulfate reduction

# Results

## Mean Water Quality Data

| Parameter | LOW I | | HIGH I | |
|---|---|---|---|---|
| | IN | OUT | IN | OUT |
| T (°C) | 21.1 | 20.6 | 20.9 | 20.6 |
| pH | 6.3 | 7.4 | 5.9 | 7.6 |
| DO (mg/L) | 8.1 | 0.2 | 8.3 | 0.1 |
| ORP (mV) | 214 | -259 | 179 | -314 |
| Conductivity (mS/cm) | 0.3 | 0.6 | 4.96 | 4.88 |
| Alkalinity (mg/L as $CaCO_3$) | 5.7 | 171 | 3.2 | 255 |
| Sodium (mg/L) | 15.8 | 17.1 | 760 | 780 |
| Sulfide (mg/L) | - | 20.2 | - | 38.8 |
| Sulfate (mg/L) | 104 | 58 | 1827 | 1471 |


Total Cadmium
Concentration (mg/L)
0.50
0.40
0.30
0.20
0.10
0.00
1
2
3
4
5
6
7
8
9
10
11
12
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17
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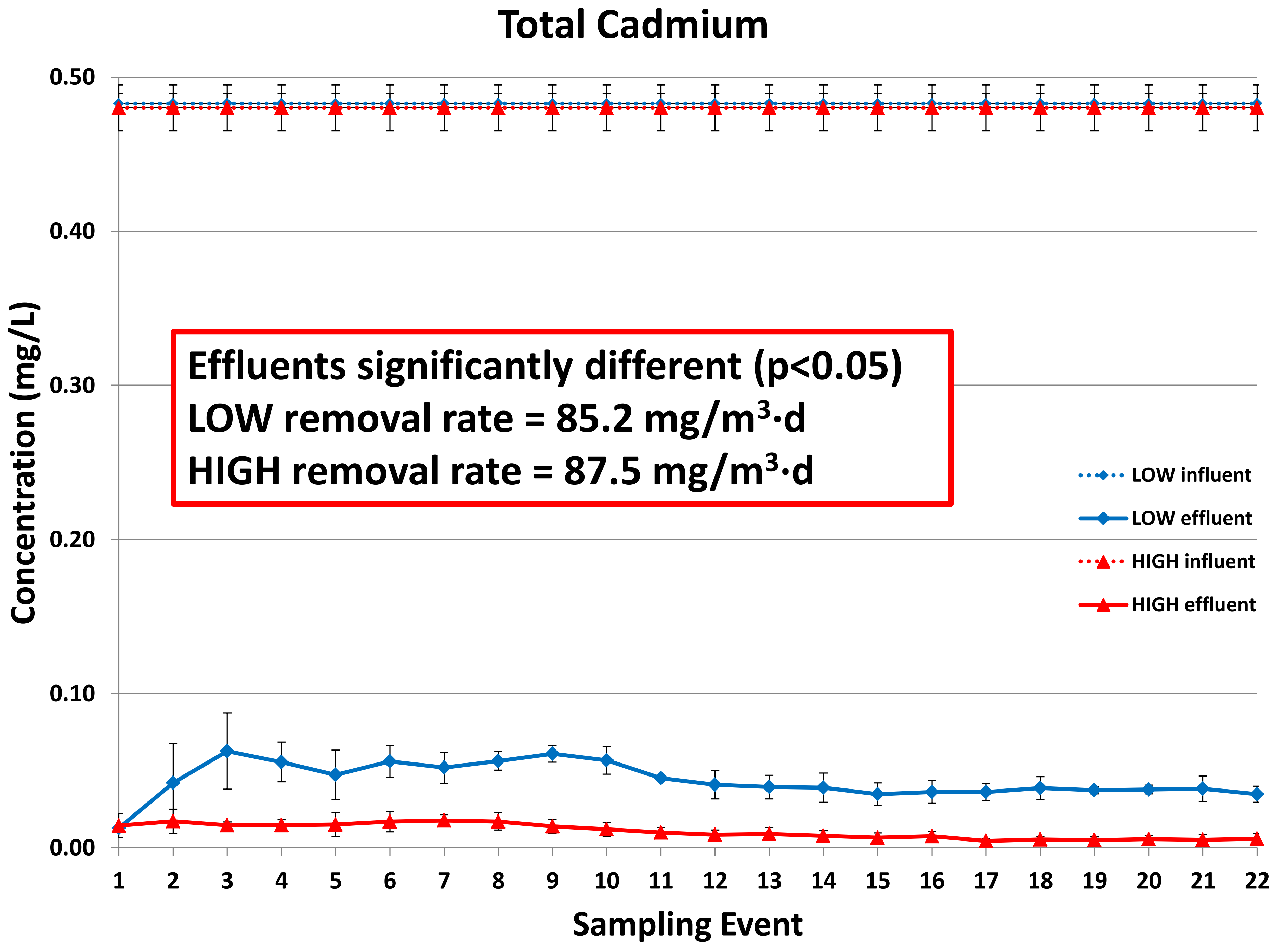
19
20
21
22
Sampling Event
LOW influent
LOW effluent
HIGH influent
HIGH effluent


Total Cadmium
Effluents significantly different (p<0.05)
LOW removal rate = 85.2 mg/m3·d
HIGH removal rate = 87.5 mg/m3·d
LOW influent
LOW effluent
HIGH influent
HIGH effluent
Concentration (mg/L)
0.50
0.40
0.30
0.20
0.10
0.00
1
2
3
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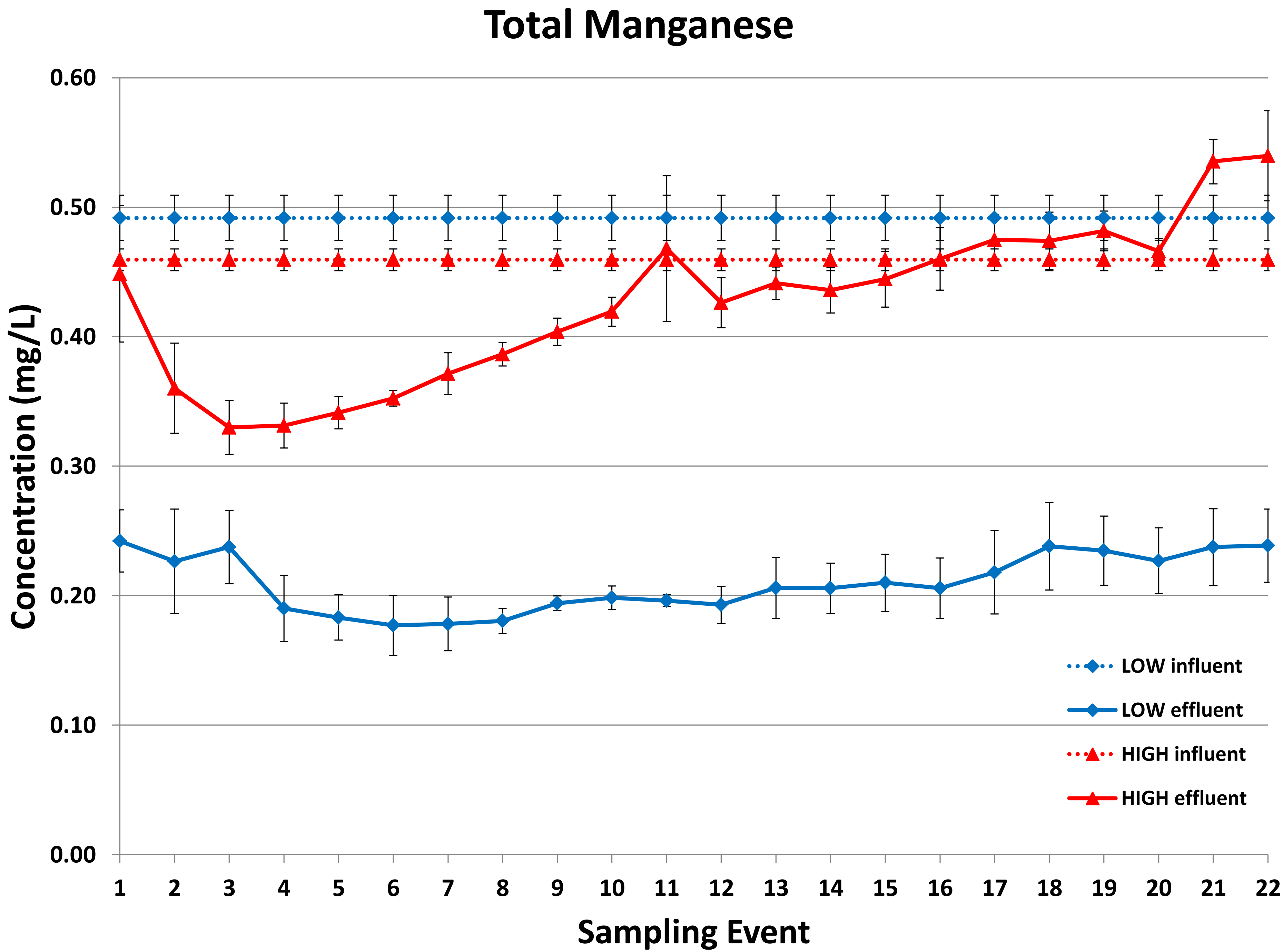
Sampling Event



Total Manganese
Concentration (mg/L)
0.60
0.50
0.40
0.30
0.20
0.10
0.00
1
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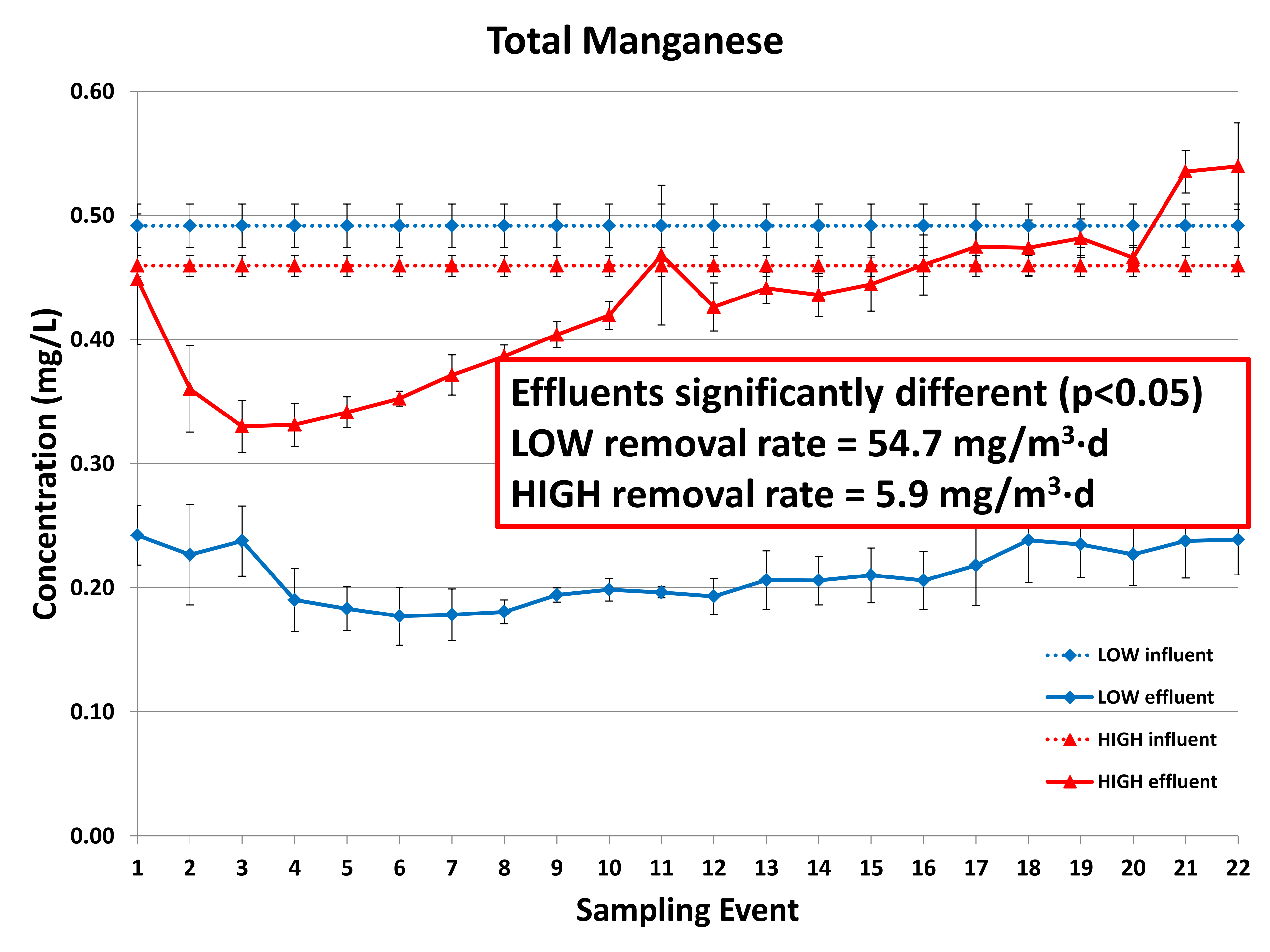
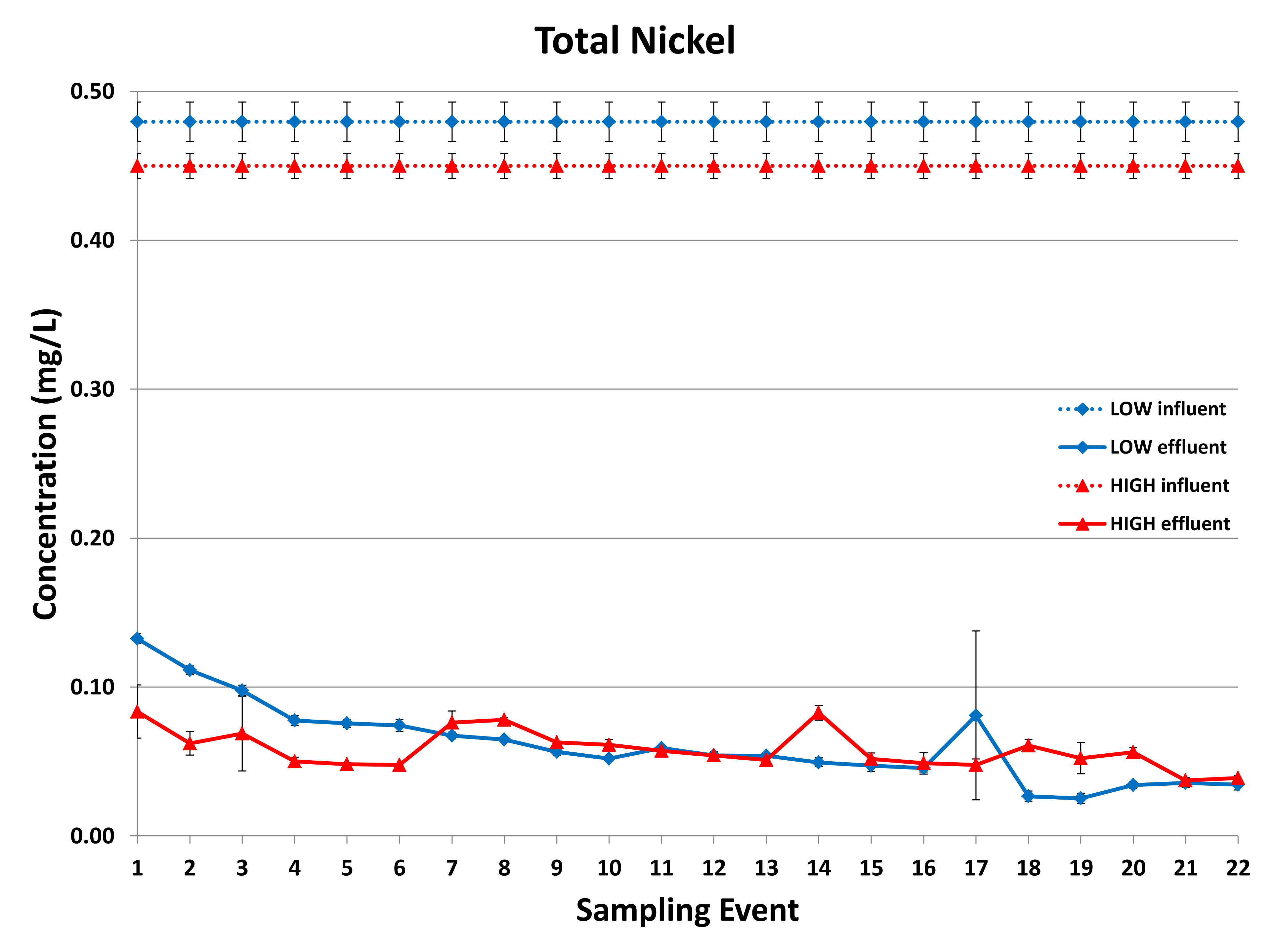
Sampling Event
LOW influent
LOW effluent
HIGH influent
HIGH effluent


Total Manganese
Effluents significantly different (p<0.05)
LOW removal rate = 54.7 mg/m³·d
HIGH removal rate = 5.9 mg/m³·d
Concentration (mg/L)
0.60
0.50
0.40
0.30
0.20
0.10
0.00
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
Sampling Event
LOW influent
LOW effluent
HIGH influent
HIGH effluent



Total Nickel
0.50
0.40
0.30
0.20
0.10
0.00
Concentration (mg/L)
1
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6
7
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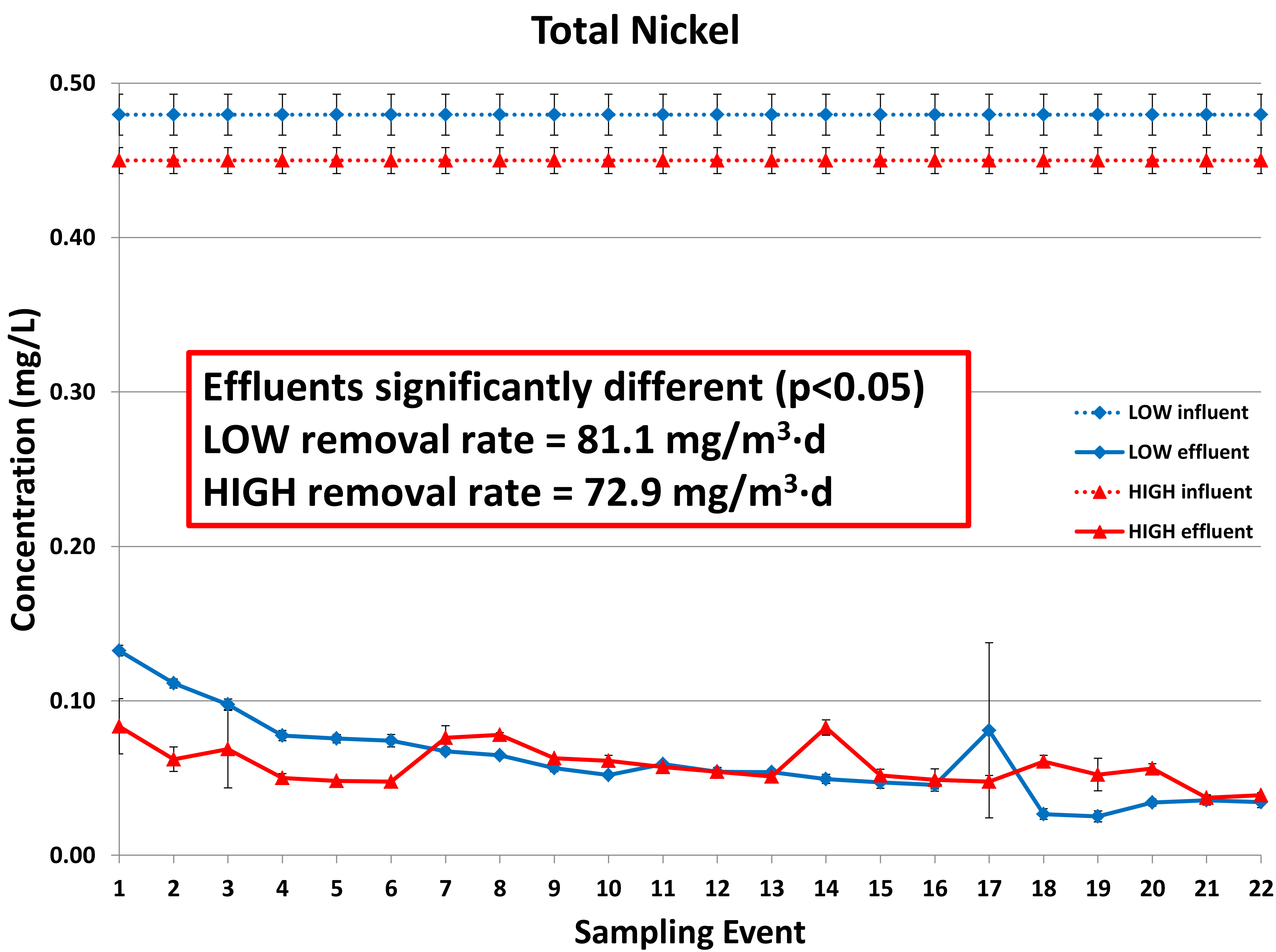
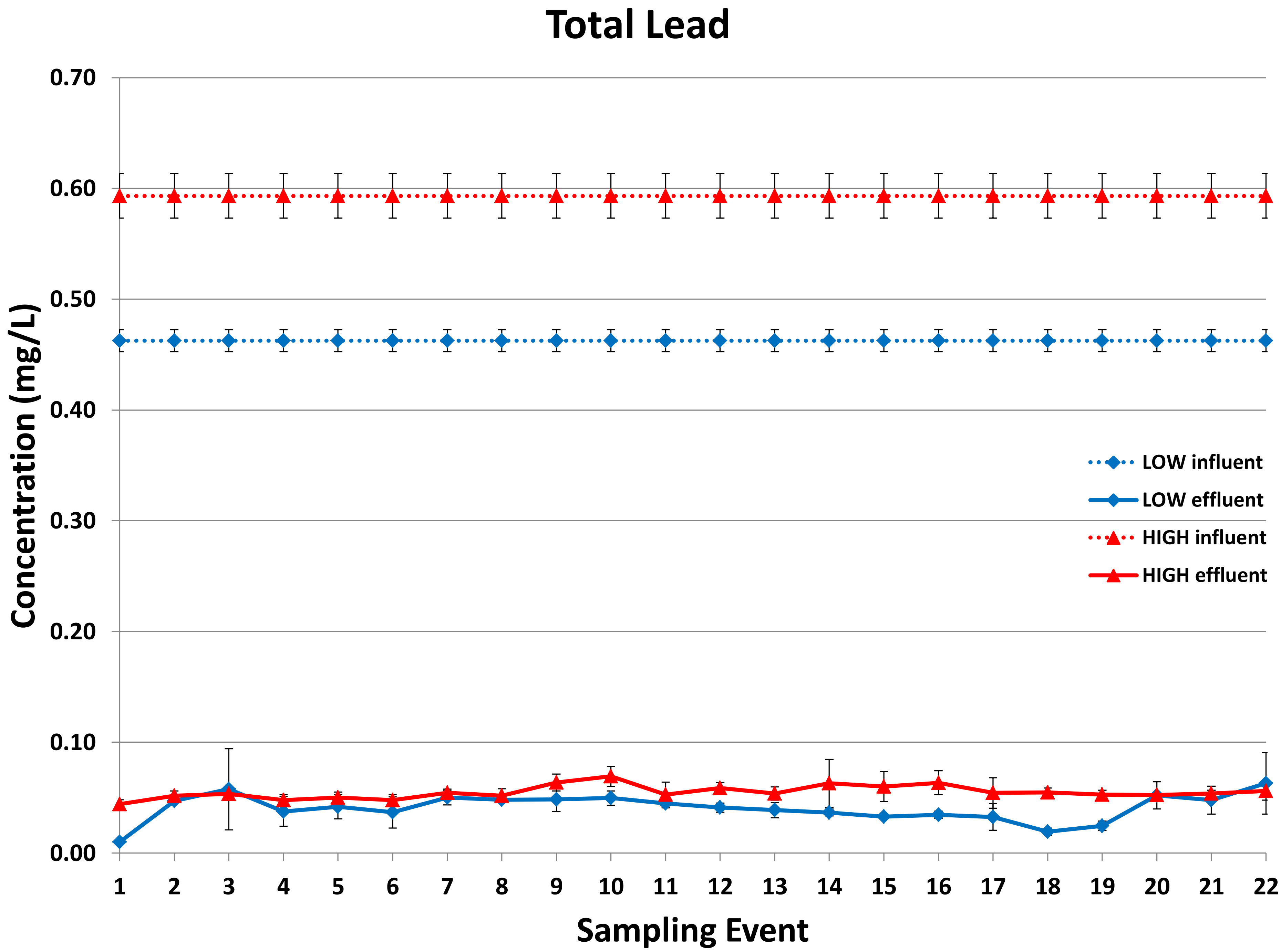
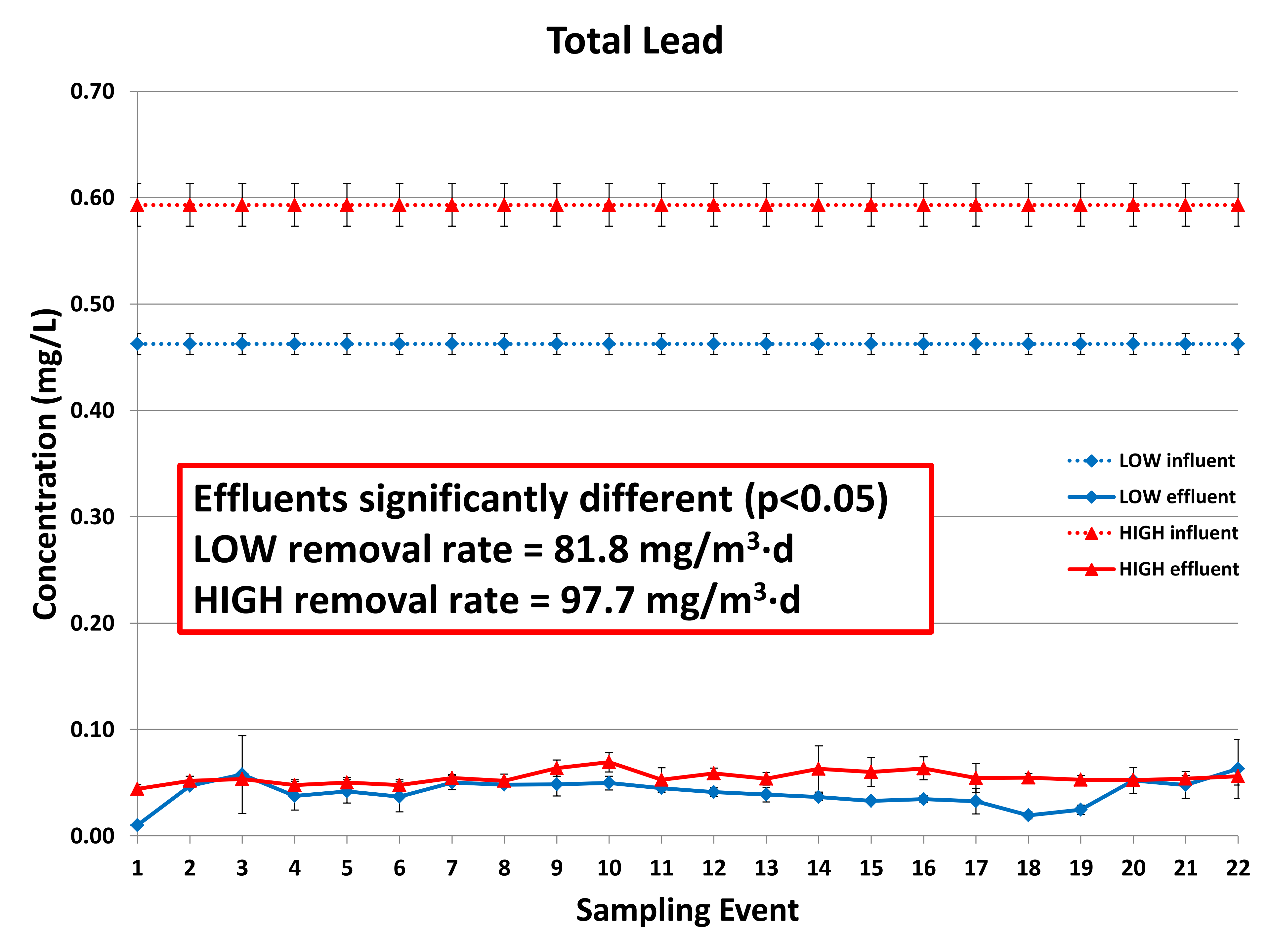
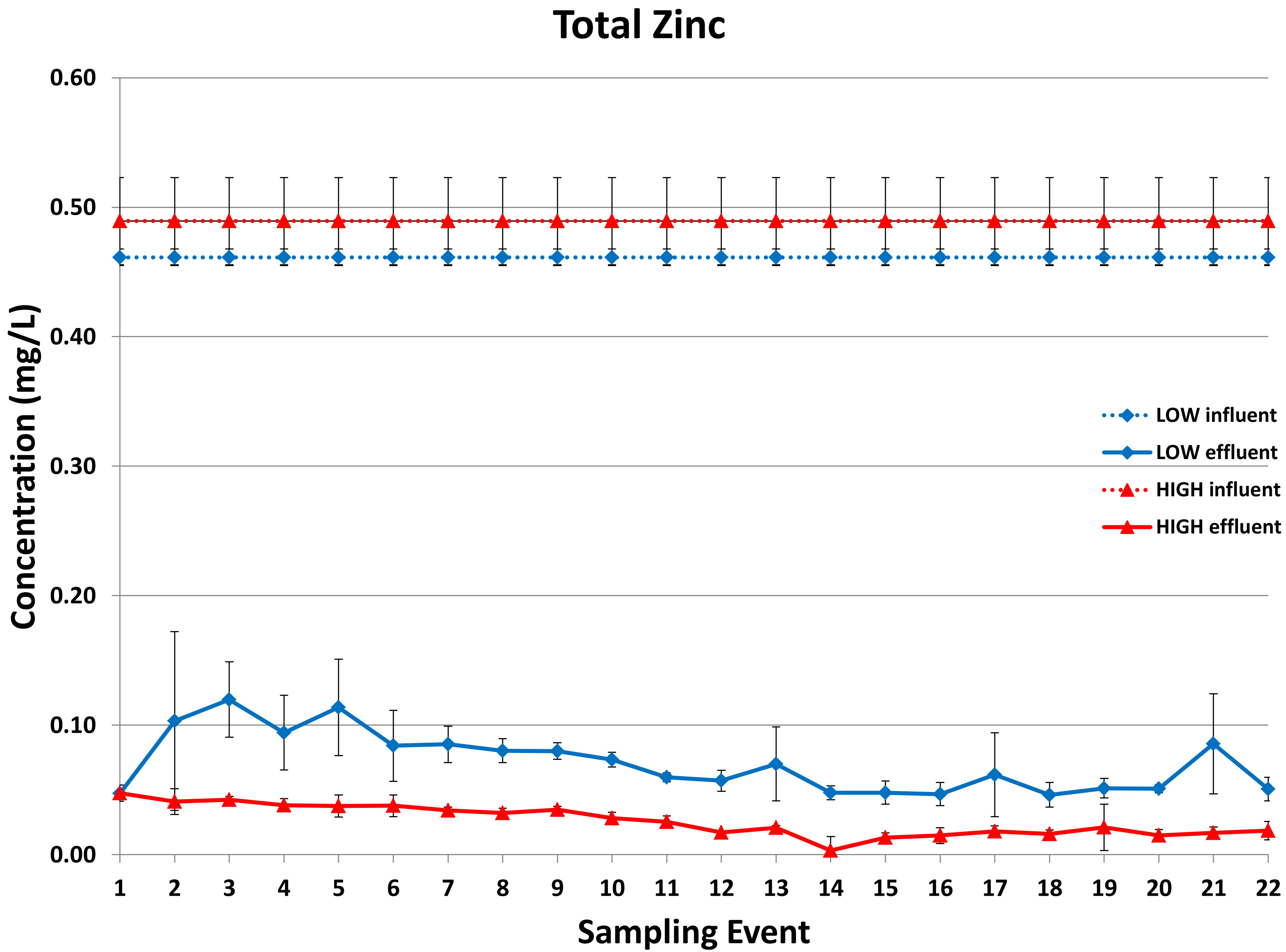
21
22
Sampling Event
LOW influent
LOW effluent
HIGH influent
HIGH effluent


Total Nickel
Concentration (mg/L)
0.50
0.40
0.30
0.20
0.10
0.00
Effluents significantly different (p<0.05)
LOW removal rate = 81.1 mg/m³·d
HIGH removal rate = 72.9 mg/m³·d
LOW influent
LOW effluent
HIGH influent
HIGH effluent
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
Sampling Event



Total Lead
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Concentration (mg/L)
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
Sampling Event
LOW influent
LOW effluent
HIGH influent
HIGH effluent


Total Lead
Concentration (mg/L)
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Sampling Event
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
LOW influent
LOW effluent
HIGH influent
HIGH effluent
Effluents significantly different (p<0.05)
LOW removal rate = 81.8 mg/m³·d
HIGH removal rate = 97.7 mg/m³·d


Total Zinc
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Concentration (mg/L)
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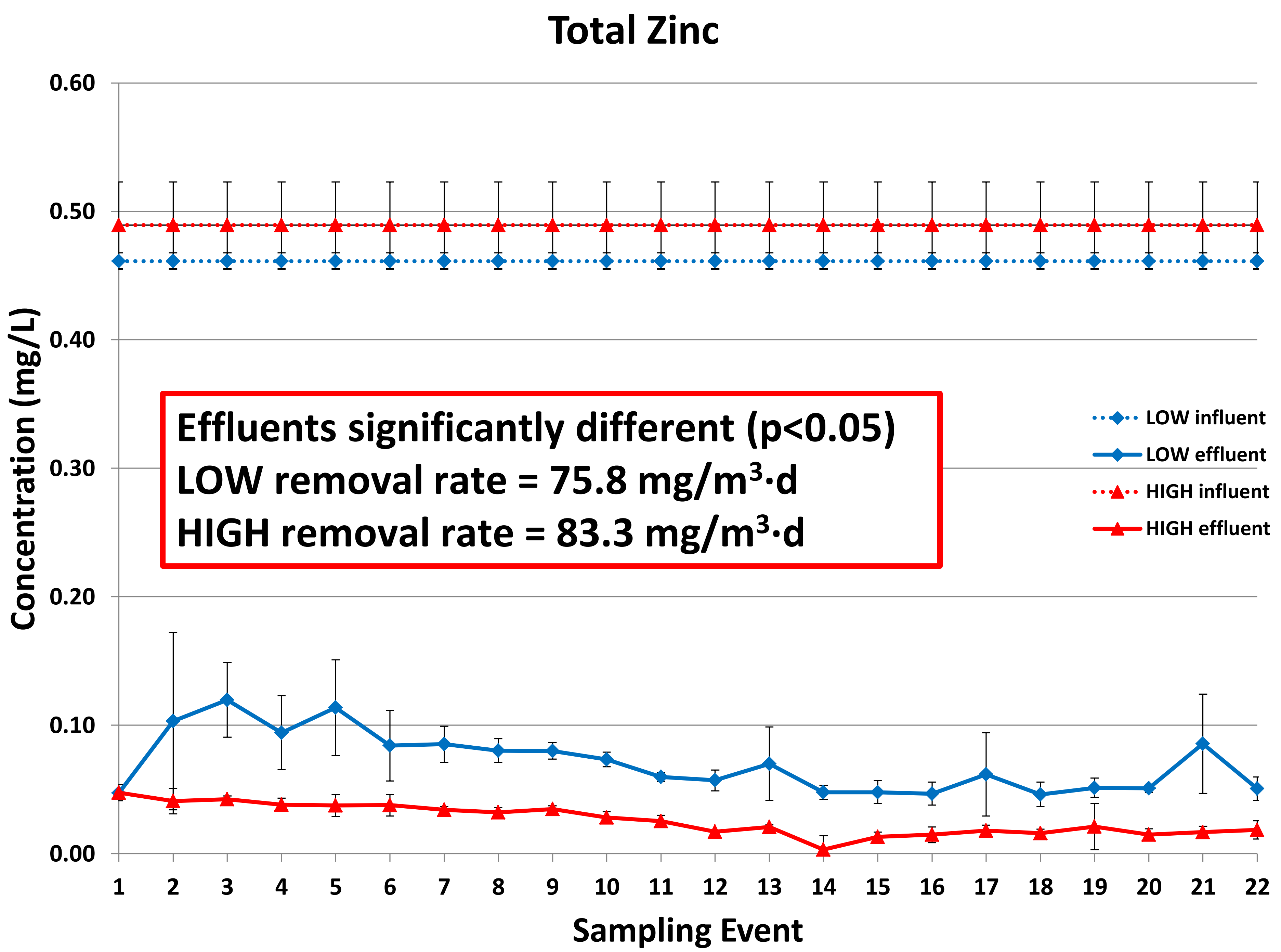
Sampling Event
LOW influent
LOW effluent
HIGH influent
HIGH effluent


Total Zinc
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Concentration (mg/L)
Effluents significantly different (p<0.05)
LOW removal rate = 75.8 mg/m³·d
HIGH removal rate = 83.3 mg/m³·d
LOW influent
LOW effluent
HIGH influent
HIGH effluent
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
Sampling Event

# Results

- Summary
  - Both sets of reactors removed >75% Cd, Ni, Pb, Zn
  - Significant difference ($p<0.05$) in mean effluent concentrations of Cd, Mn, Ni, Pb, and Zn
    - Lower concentrations of Mn and Pb in LOW
    - Lower concentrations of Cd and Zn in HIGH
    - Lower concentrations of Ni in HIGH at beginning and LOW at end

# Results

- Mean sulfate removal rate was greater in HIGH than LOW
  - 691 $mmol/m^3 \cdot d$ vs. 81 $mmol/m^3 \cdot d$
- Sulfate removal rate decreased over time in HIGH
  - Initial removal rate in HIGH ≈1100 $mmol/m^3 \cdot d$
  - Mean removal rate in HIGH in last four sampling events ≈375 $mmol/m^3 \cdot d$
  - Sulfide production continued as before

# Conclusions

- Significant differences ($p<0.05$) in removal rates for Cd, Mn, Ni, Pb, Zn
- Significant trends over time
  - LOW
    - Ni: 67.3 $mg/m^3 \cdot d$ – 86.4 $mg/m^3 \cdot d$
    - Pb: 87.8 $mg/m^3 \cdot d$ - 77.5 $mg/m^3 \cdot d$
  - HIGH
    - Ni: 68.2 $mg/m^3 \cdot d$ – 76.5 $mg/m^3 \cdot d$
    - Mn: 18.4 $mg/m^3 \cdot d$ - -15.1 $mg/m^3 \cdot d$
- May indicate a shift in removal mechanisms

# Conclusions

- Increased ionic strength does not have a consistent impact on divalent trace metal removal in VFBR
  - Positive impact for Cd, Pb, Zn
  - Negative impact for Mn, Ni
- Differences in removal rates likely due to effects on removal mechanisms
  - Exploring sorption, complexation, carbonate formation, sulfide precipitation
  - Sequential extractions, AVS/SEM, mineralogy, modeling

# Thank You

# Questions?

CREW
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