

# The Use of Waste Mussel Shells in Sulfate-Reducing Bioreactors treating Acid Mine Drainage

31<sup>st</sup> ASMR

Oklahoma City – June 2014

Benjamin Uster - Ph.D. Candidate

M. Milke, A. O'Sullivan, B. Caruso, J. Webster-Brown (University of Canterbury)

J. Pope and D. Trumm (CRL Energy Ltd)

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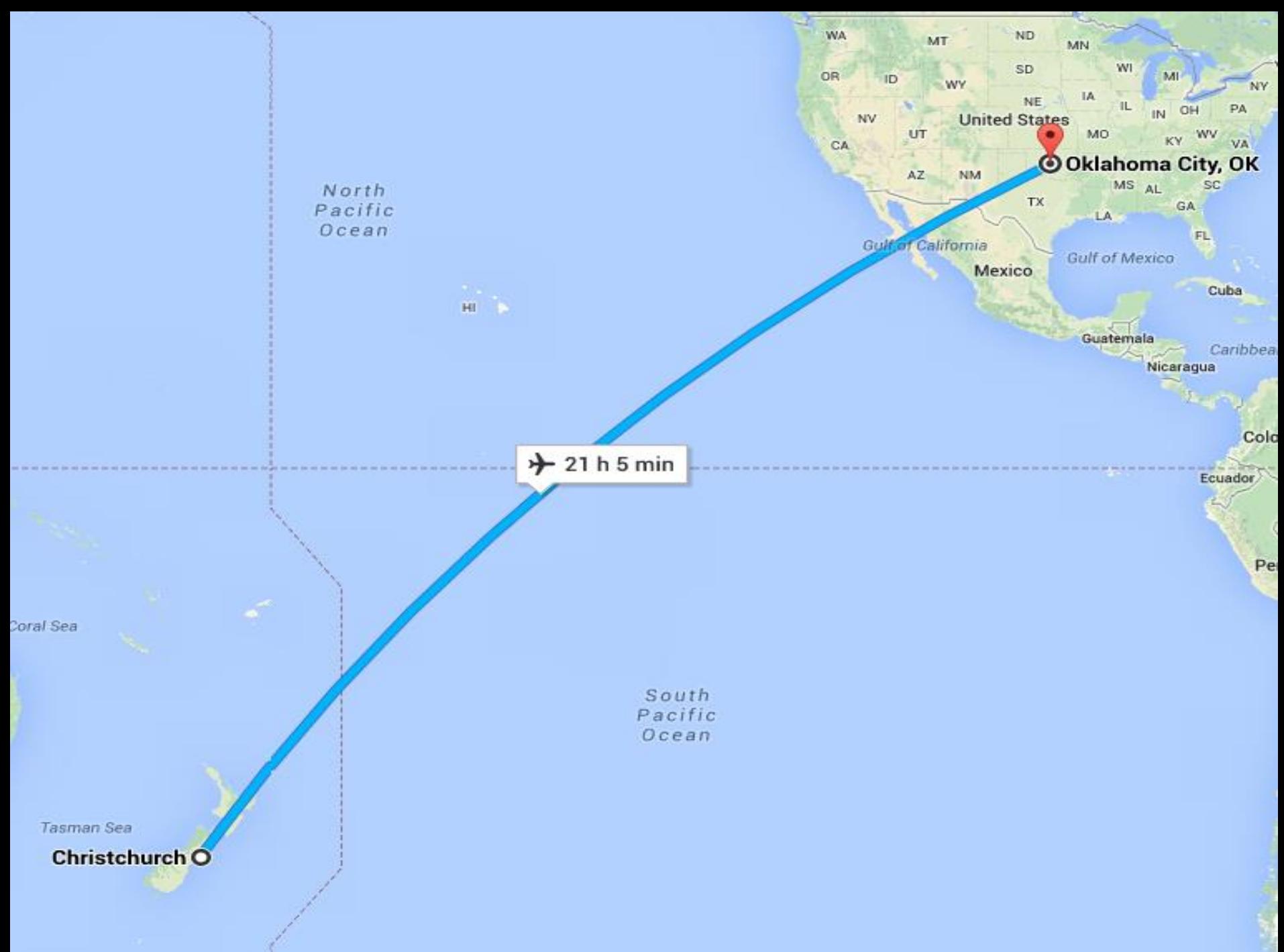
Oklahoma City – June 2014

**Bob**

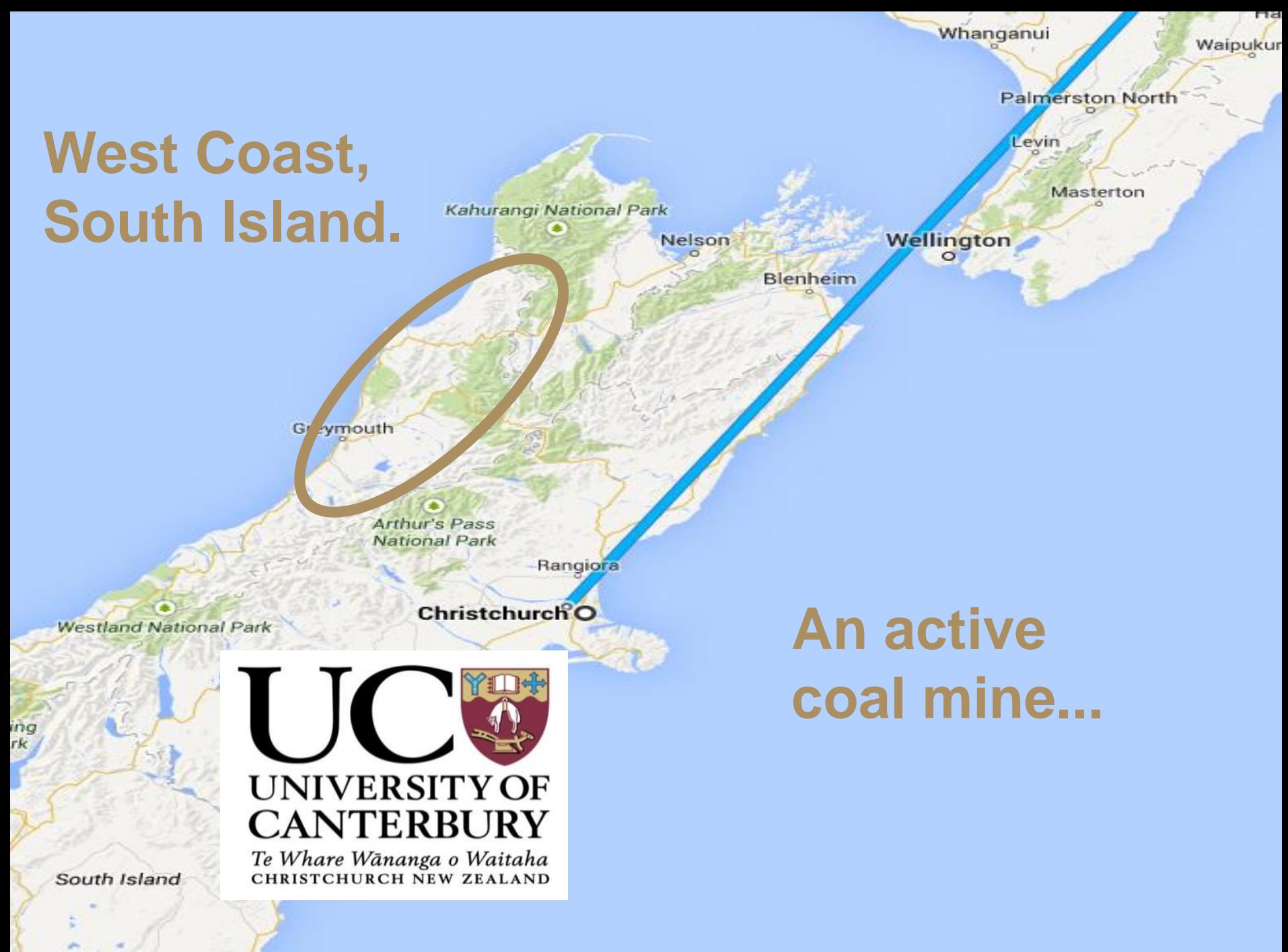
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# West Coast, South Island.



An active  
coal mine...





A wide-angle photograph of a large-scale open-pit coal mine. The image shows the massive, stratified rock walls of the excavation site, which are dark grey and black with distinct horizontal layers and patches of orange and yellow oxidation. The bottom of the pit contains a large, stagnant pool of brownish-yellow water. A network of grey dirt roads winds through the site, connecting different parts of the mine. In the background, a dense forest of green trees covers a hillside, with some mist or fog visible in the distance.

**Bituminous coking coal**









**4x 1m<sup>3</sup> AMD collected  
Mar – Dec 2013**



**4x 1m<sup>3</sup> AMD collected  
Mar – Dec 2013**

### **Median AMD characteristics (mg/L)**

|                |                     |           |               |
|----------------|---------------------|-----------|---------------|
| <b>pH</b>      | 2.89<br>(2.76-2.98) | <b>Fe</b> | 32<br>(17-73) |
| <b>Sulfate</b> | 1650<br>(1470-1990) | <b>Al</b> | 18<br>(10-26) |
| <b>Acidity</b> | 360<br>(257-475)    | <b>Mn</b> | 17<br>(13-21) |

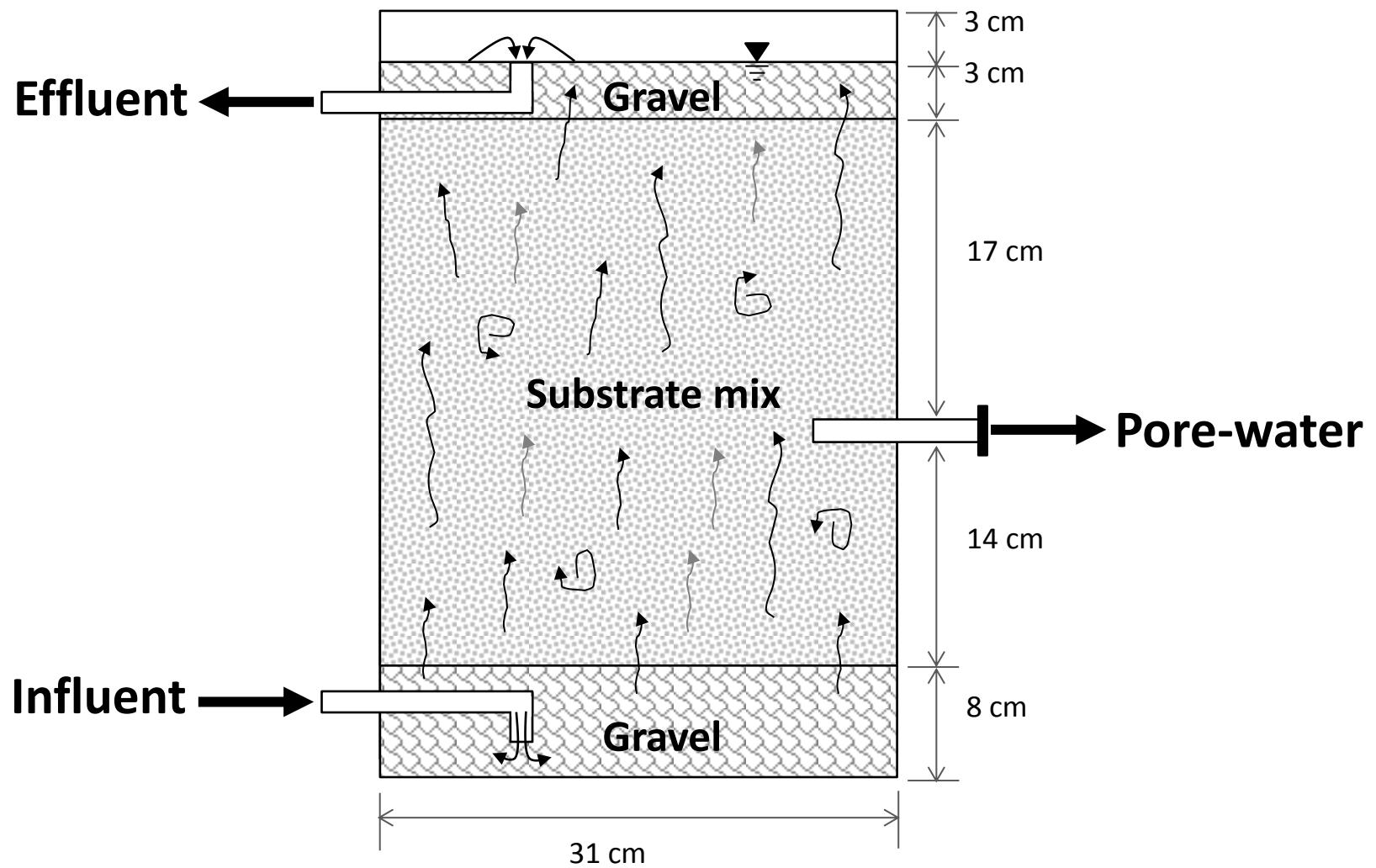
Zn, Ni, Cu,  
Cd, Pb,  
As,...

4x 1m<sup>3</sup> AMD collected  
Mar – Dec 2013

### Median AMD characteristics (mg/L)

|         |                     |    |               |
|---------|---------------------|----|---------------|
| pH      | 2.89<br>(2.76-2.98) | Fe | 32<br>(17-73) |
| Sulfate | 1650<br>(1470-1990) | Al | 18<br>(10-26) |
| Acidity | 360<br>(257-475)    | Mn | 17<br>(13-21) |







30% vol. BARK (*Pinus Radiata*)



20% vol. COMPOST



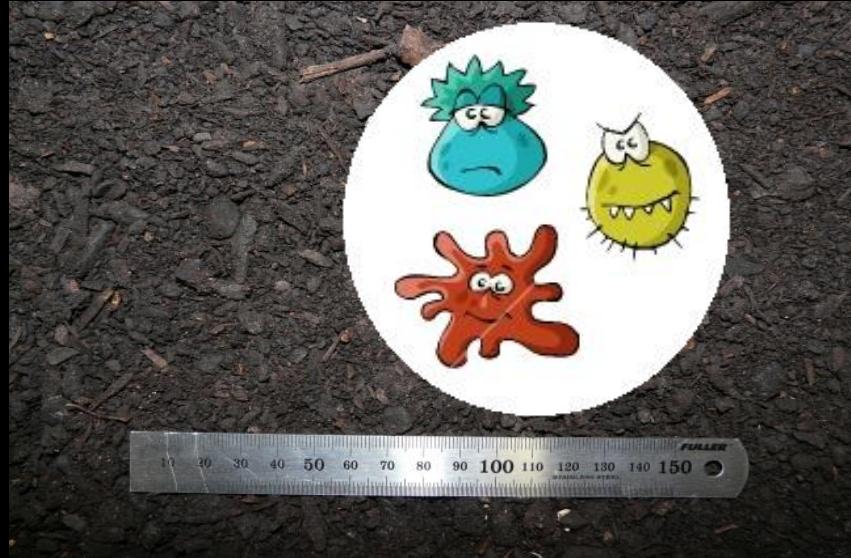
20% vol. BARK MULCH



30% vol. ALKALINE MAT.



30% vol. BARK (*Pinus Radiata*)



20% vol. COMPOST



20% vol. BARK MULCH



30% vol. ALKALINE MAT.

# Limestone Mix



# Mussel Shells Mix



# Mussel shells

# Limestone

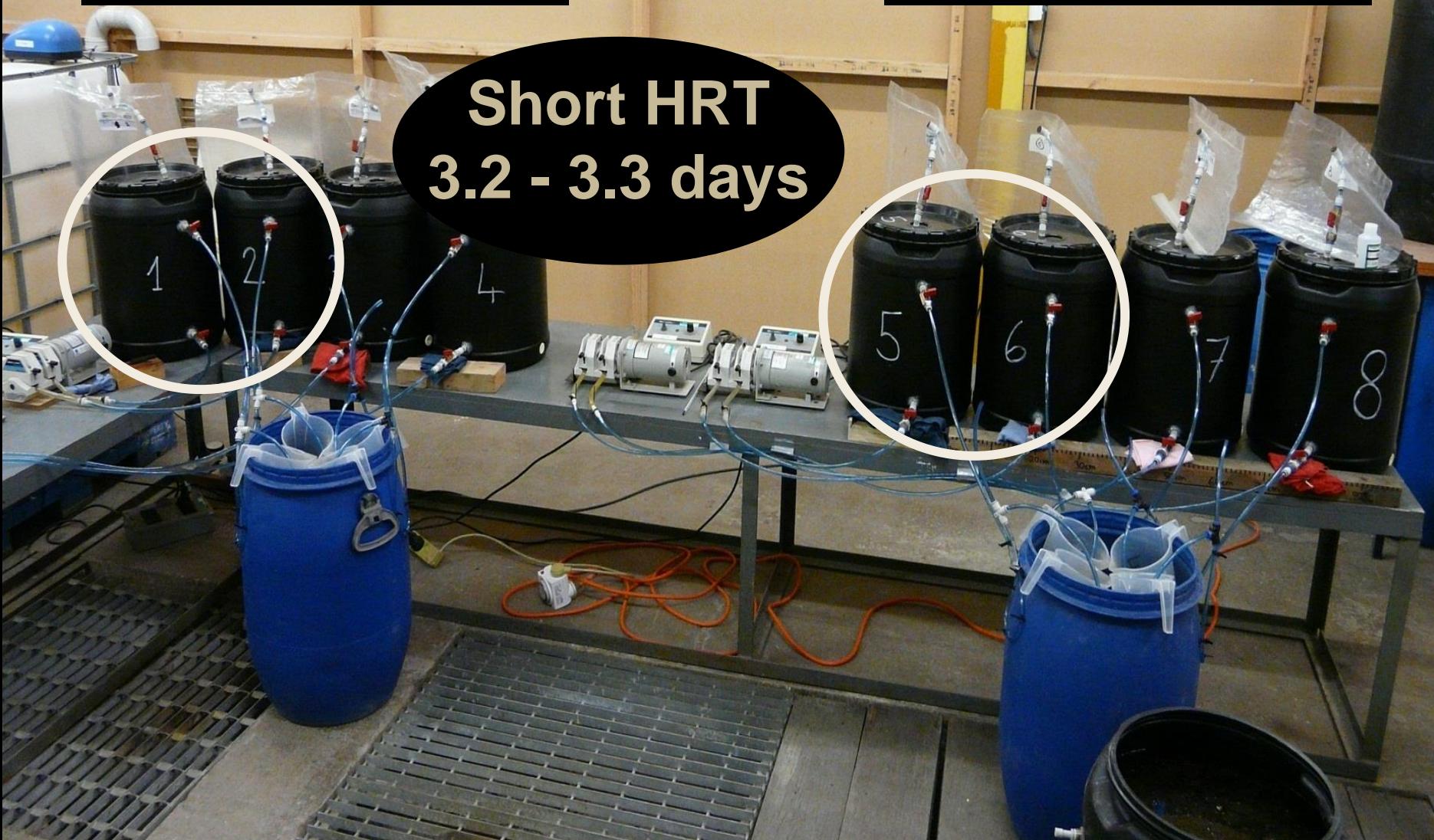
Research in progress  
PLEASE DO NOT  
DISTURB



# Mussel shells

# Limestone

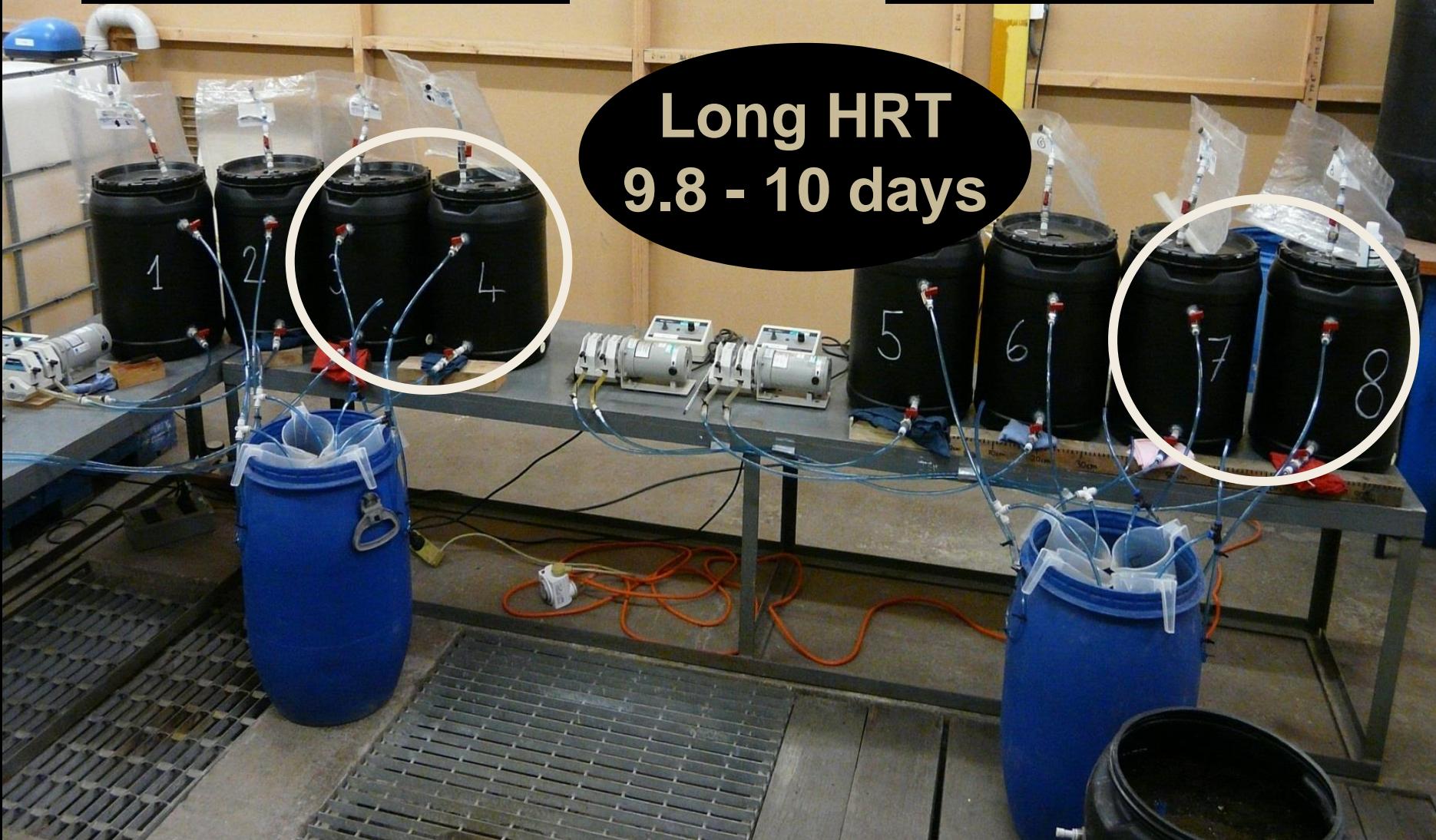
Short HRT  
3.2 - 3.3 days



Mussel shells

Limestone

Long HRT  
9.8 - 10 days





**Upward flow reactors**

**3 weeks acclimation (ORP, S<sup>2-</sup>)**

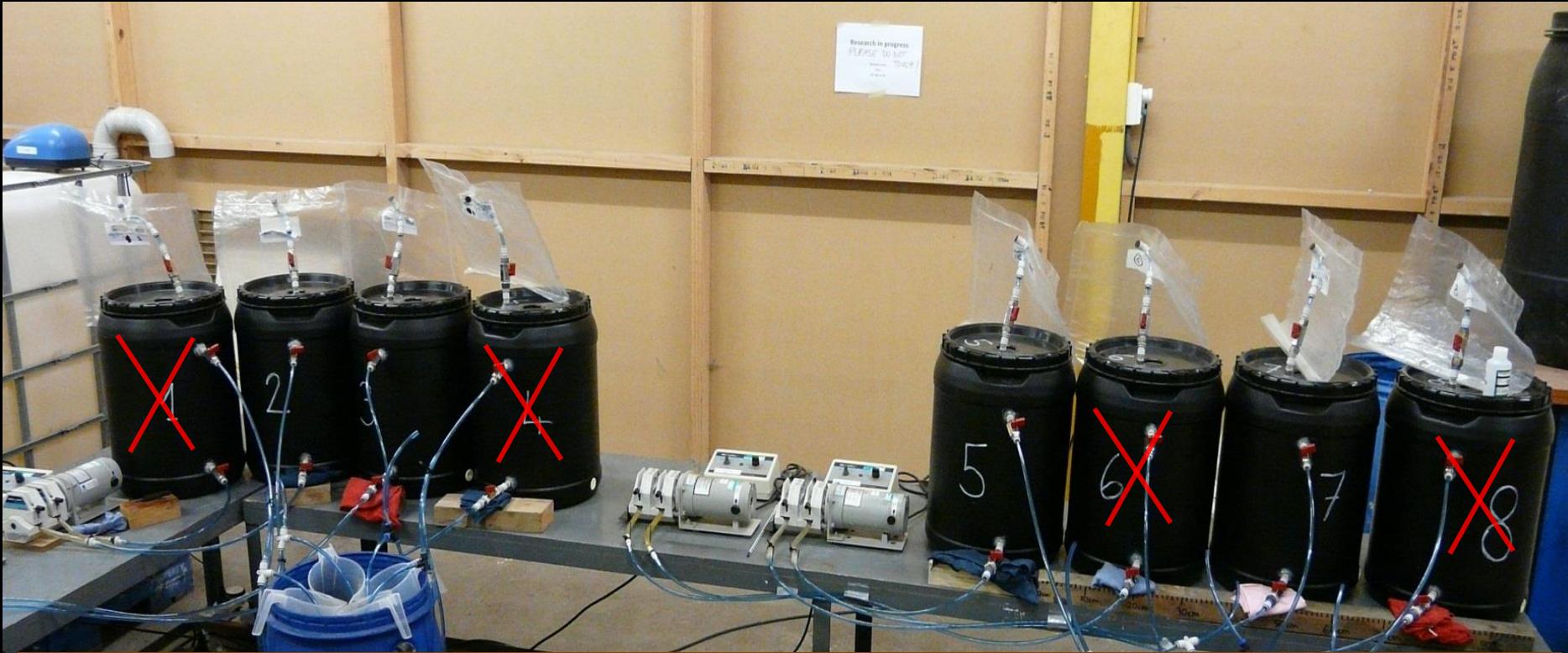
**20 weeks flow-through treatment**

**Weekly sampling**

**Tedlar bags...**



2 months interruption ( $\uparrow \text{SO}_4^{2-}$  ?!)  
21 supplementary weeks treatment  
*4 reactors only*  
Fortnight sampling  
Additional Nutrients and TOC/DOC analyses



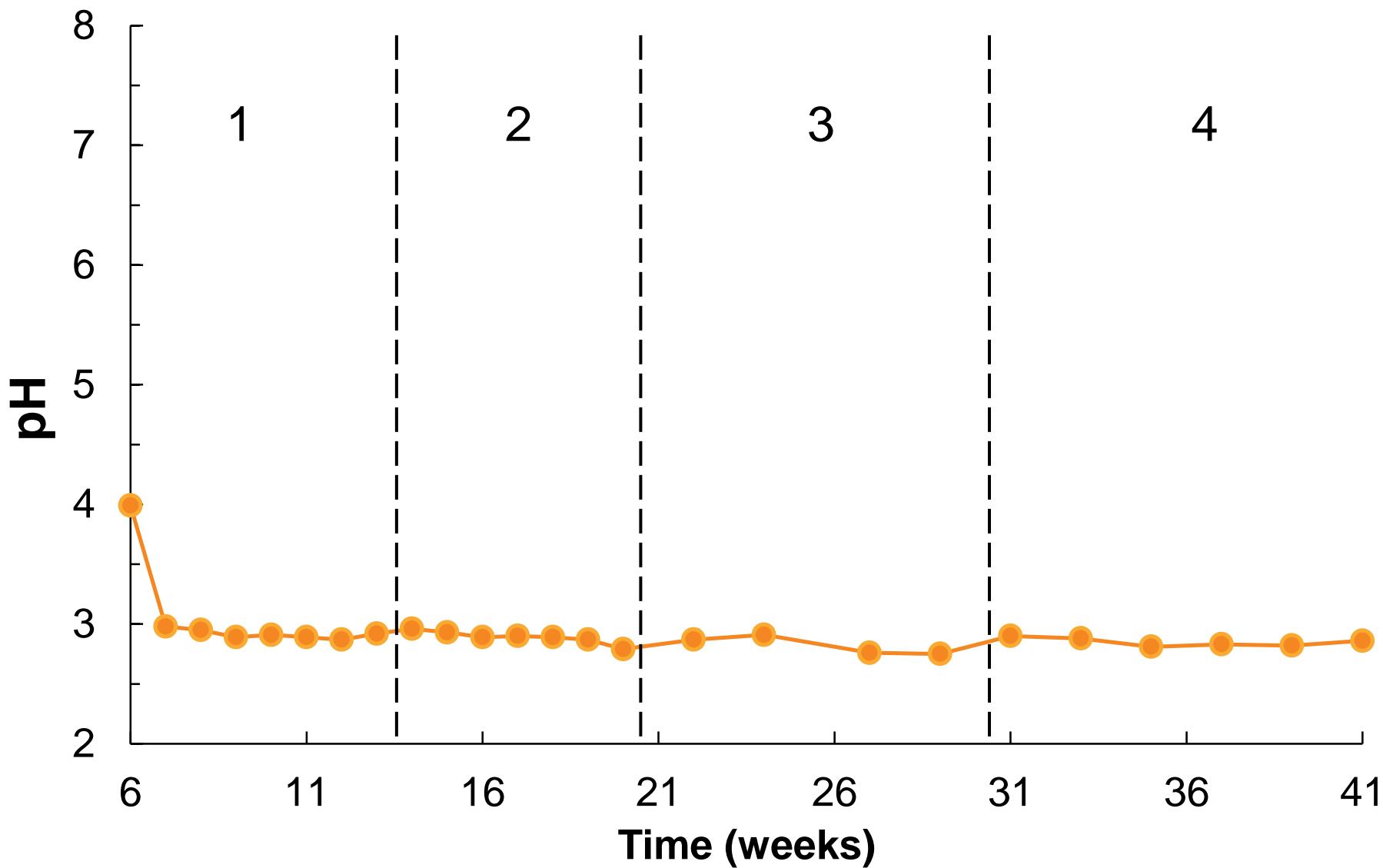
2 months interruption ( $\uparrow \text{SO}_4^{2-}$  ?!)  
21 supplementary weeks treatment

*4 reactors only*

Fortnight sampling  
Additional Nutrients and TOC/DOC analyses

● AMD (influent)

2.87

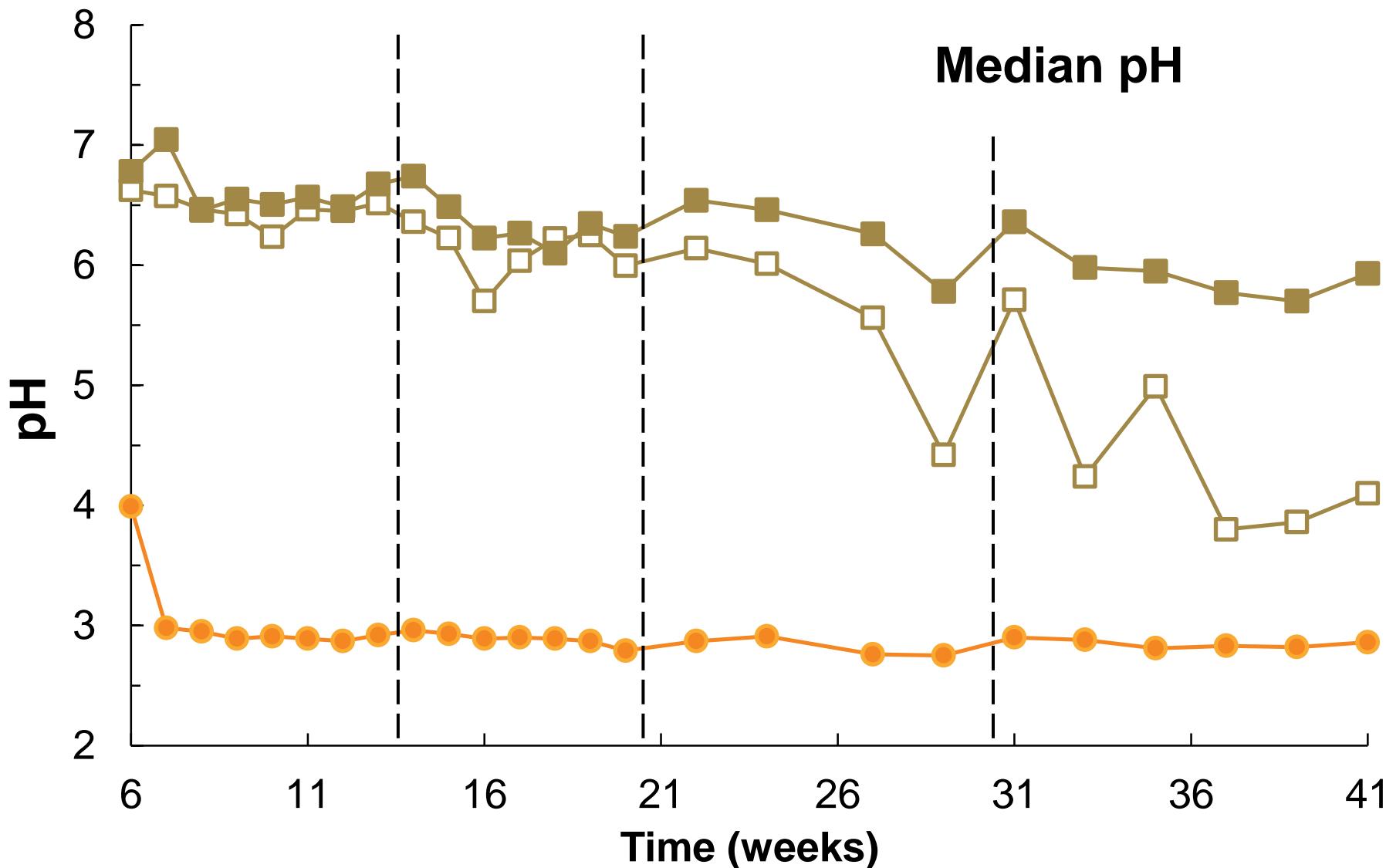


● AMD (influent) □ LS-Short HRT - 6.14

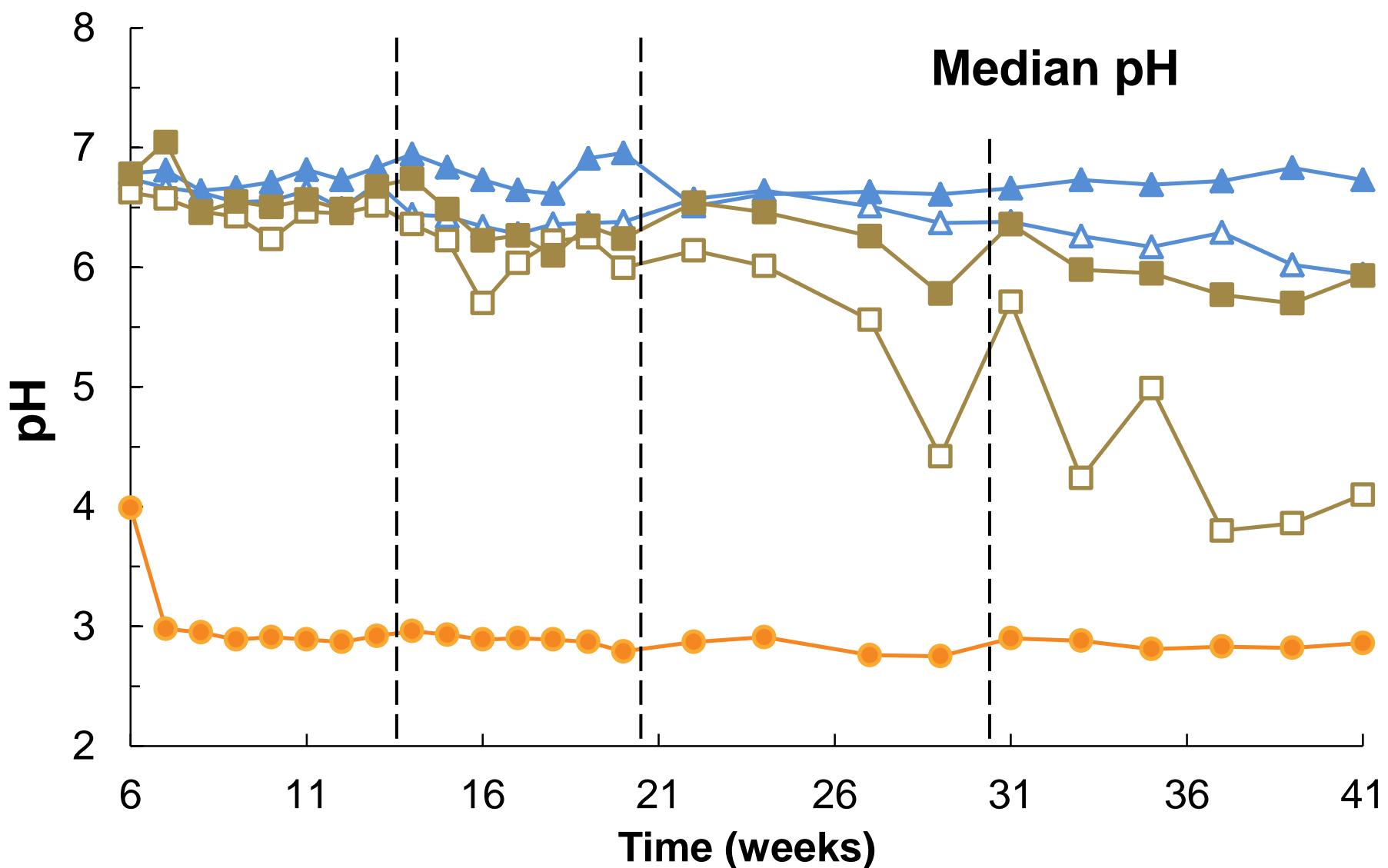
2.87

■ LS-Long HRT - 6.36

Median pH

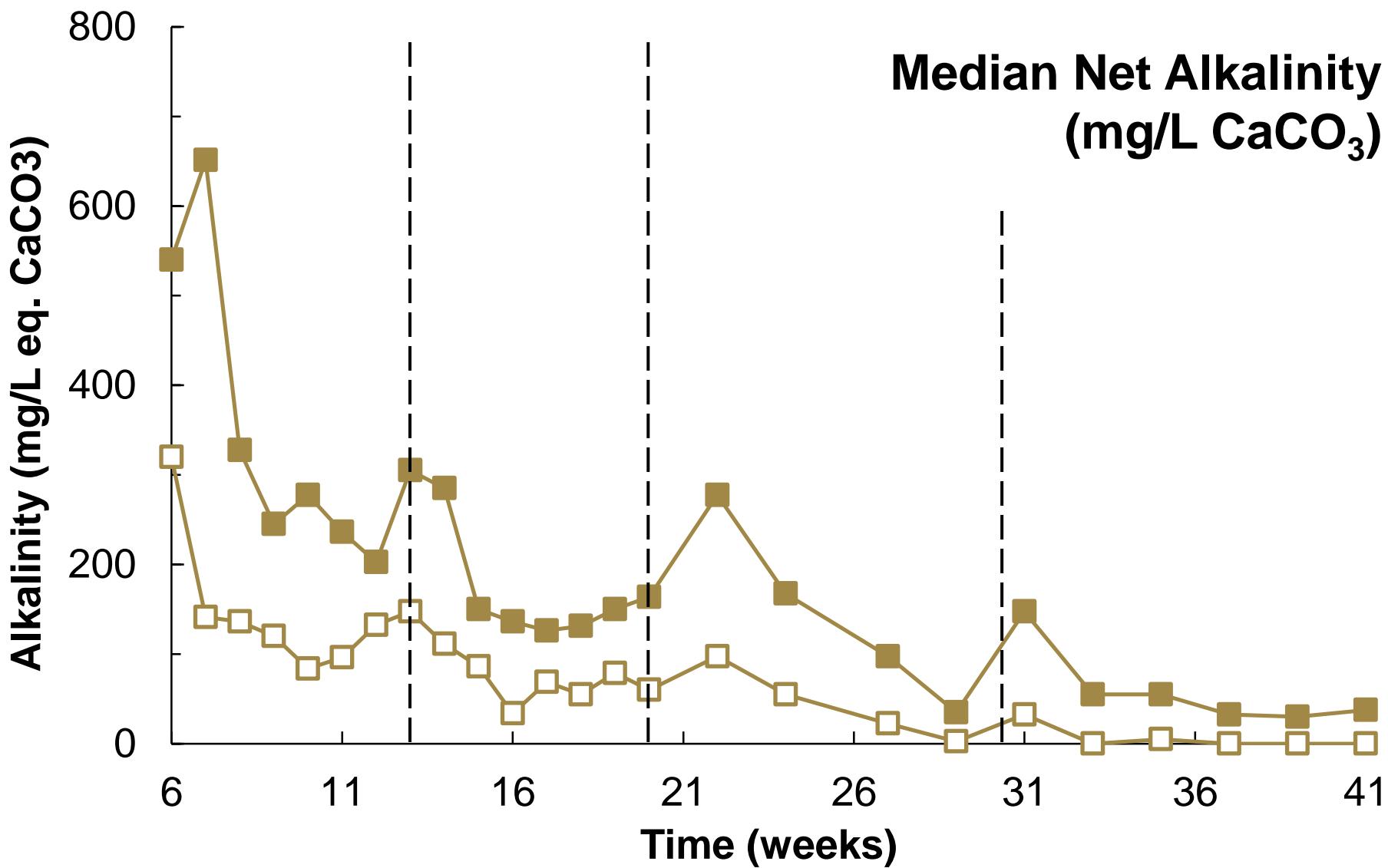


● AMD (influent) 2.87      □ LS-Short HRT - 6.14      ▲ MS-Short HRT - 6.43  
■ LS-Long HRT - 6.36      ▲ MS-Long HRT - 6.73



■ LS-Short HRT - 12.7  
■ LS-Long HRT - 123.4

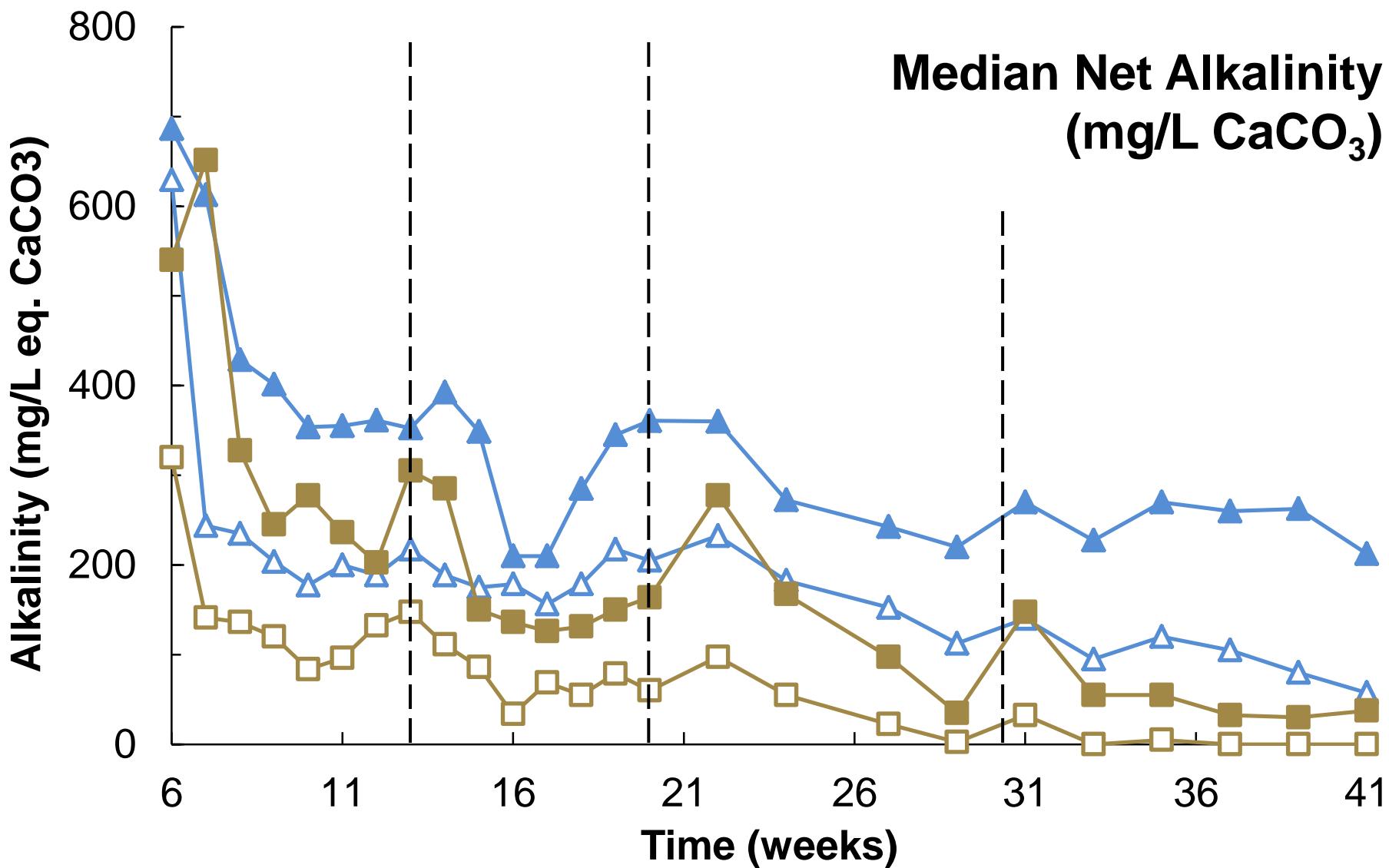
**Median Net Alkalinity**  
**(mg/L CaCO<sub>3</sub>)**



■ LS-Short HRT - 12.7  
■ LS-Long HRT - 123.4

▲ MS-Short HRT - 142.7  
▲ MS-Long HRT - 266.9

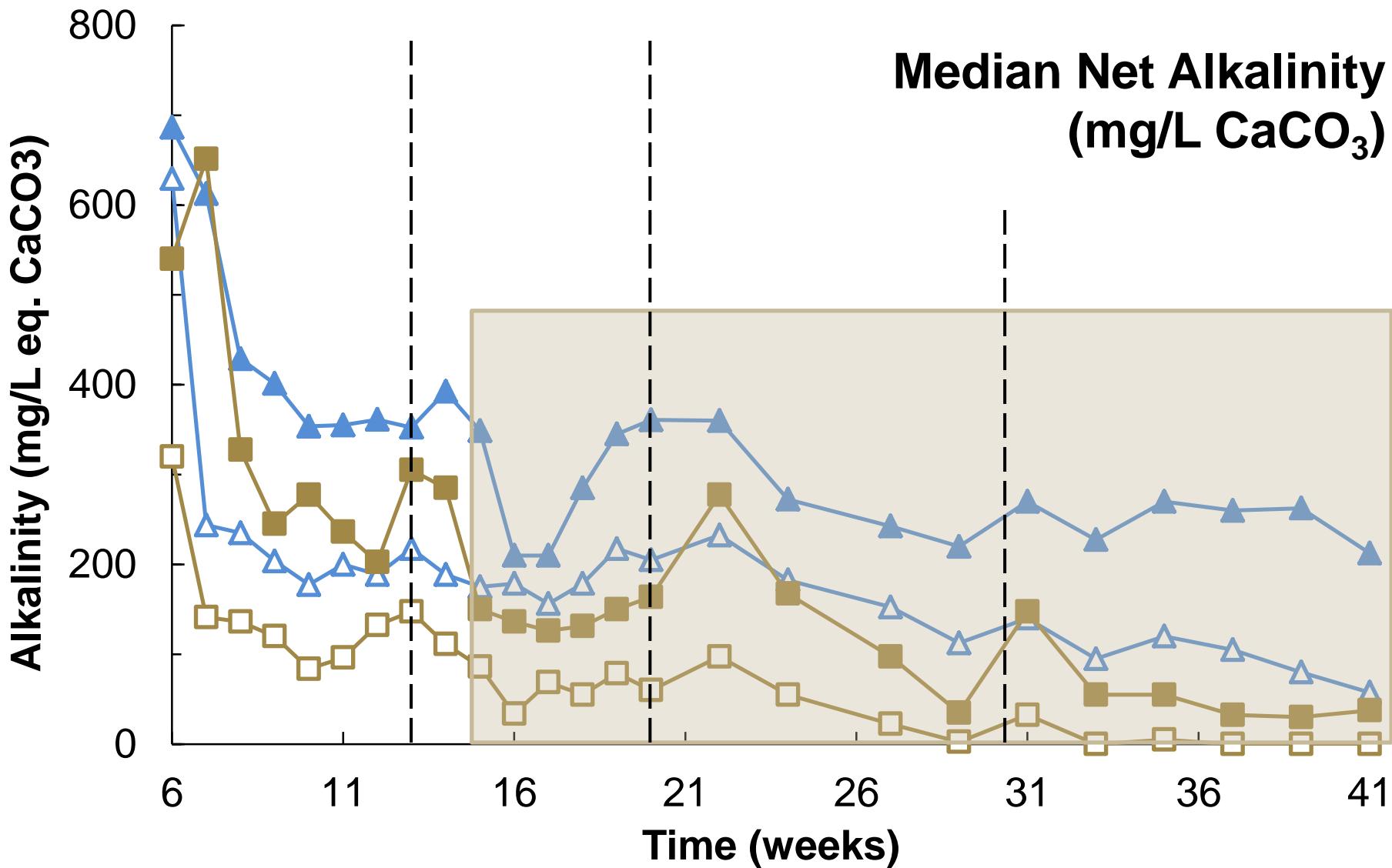
## Median Net Alkalinity (mg/L CaCO<sub>3</sub>)



■ LS-Short HRT - 12.7  
■ LS-Long HRT - 123.4

▲ MS-Short HRT - 142.7  
▲ MS-Long HRT - 266.9

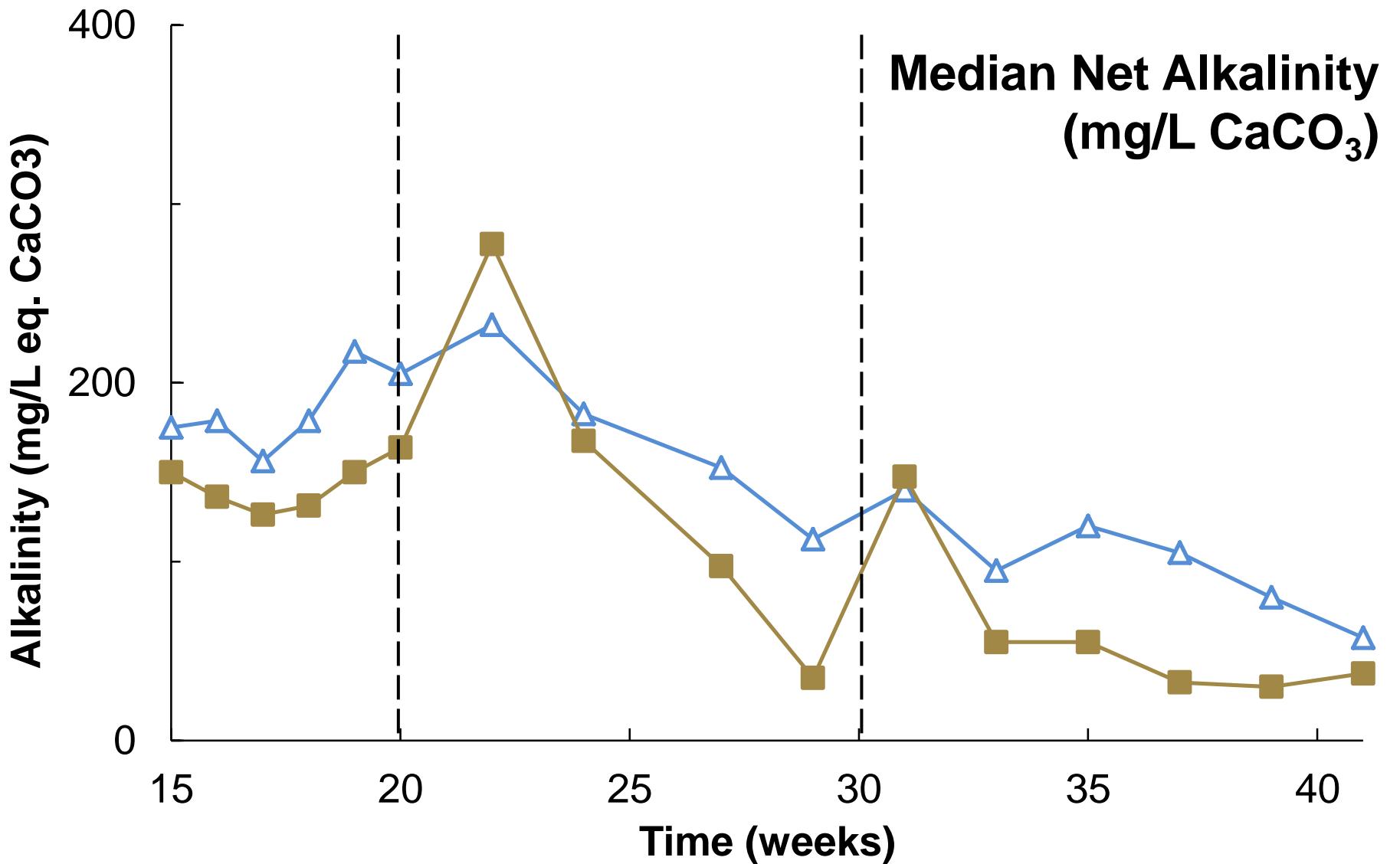
## Median Net Alkalinity (mg/L CaCO<sub>3</sub>)



▲ MS-Short HRT - 139.4

■ LS-Long HRT - 118.2

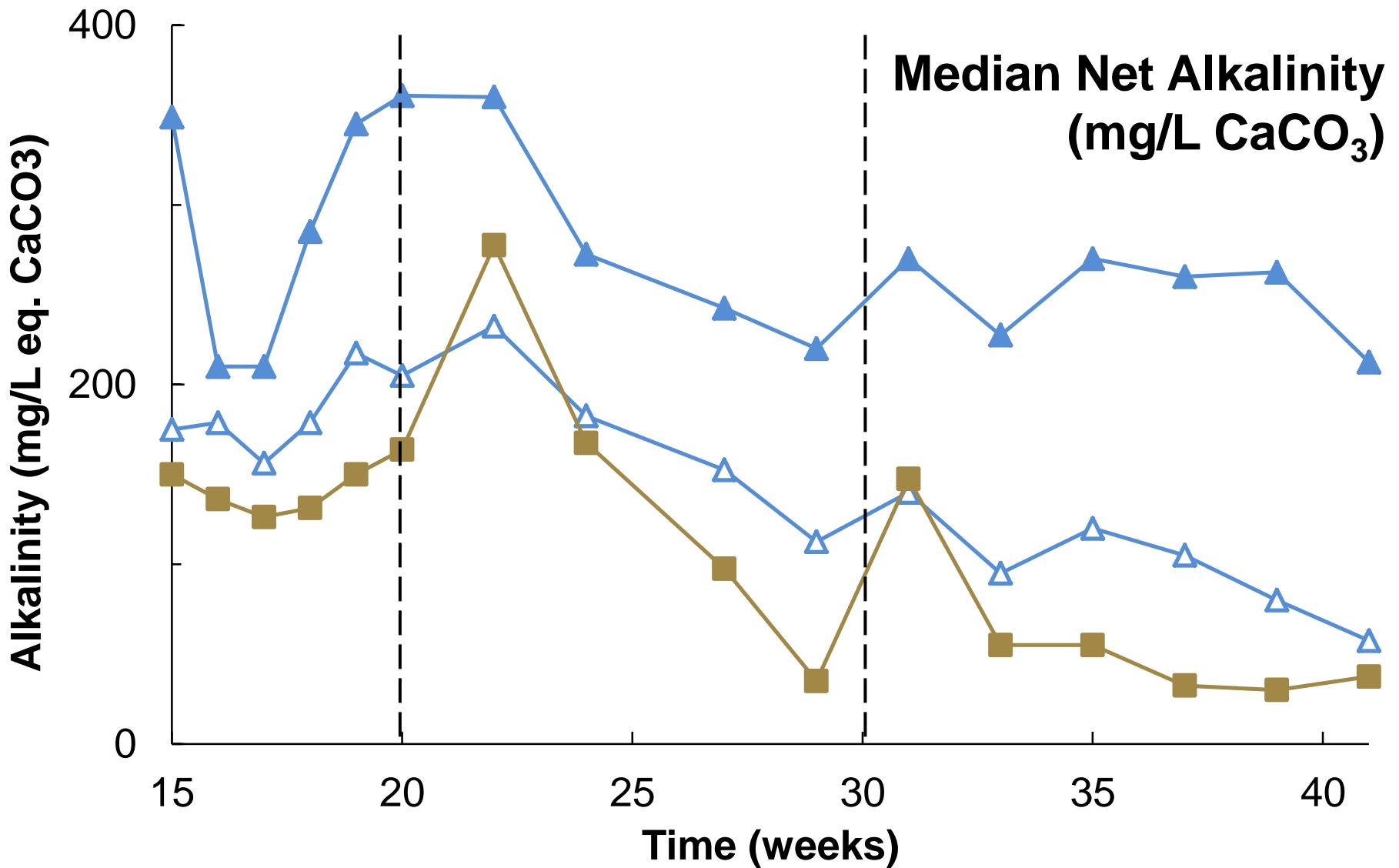
**Median Net Alkalinity  
(mg/L CaCO<sub>3</sub>)**



■ LS-Long HRT - 118.2

▲ MS-Short HRT - 139.4  
▲ MS-Long HRT - 250.2

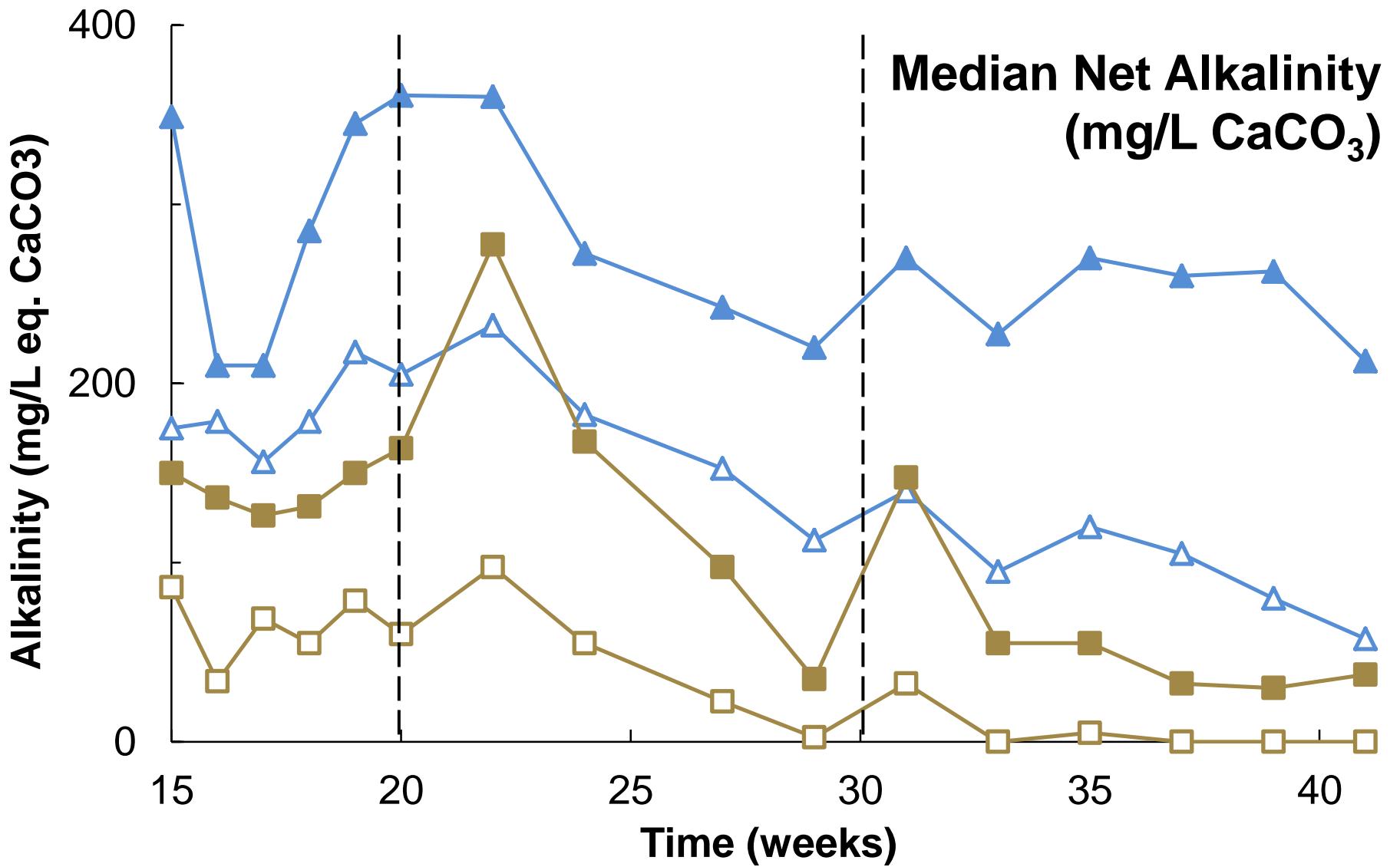
**Median Net Alkalinity  
(mg/L CaCO<sub>3</sub>)**



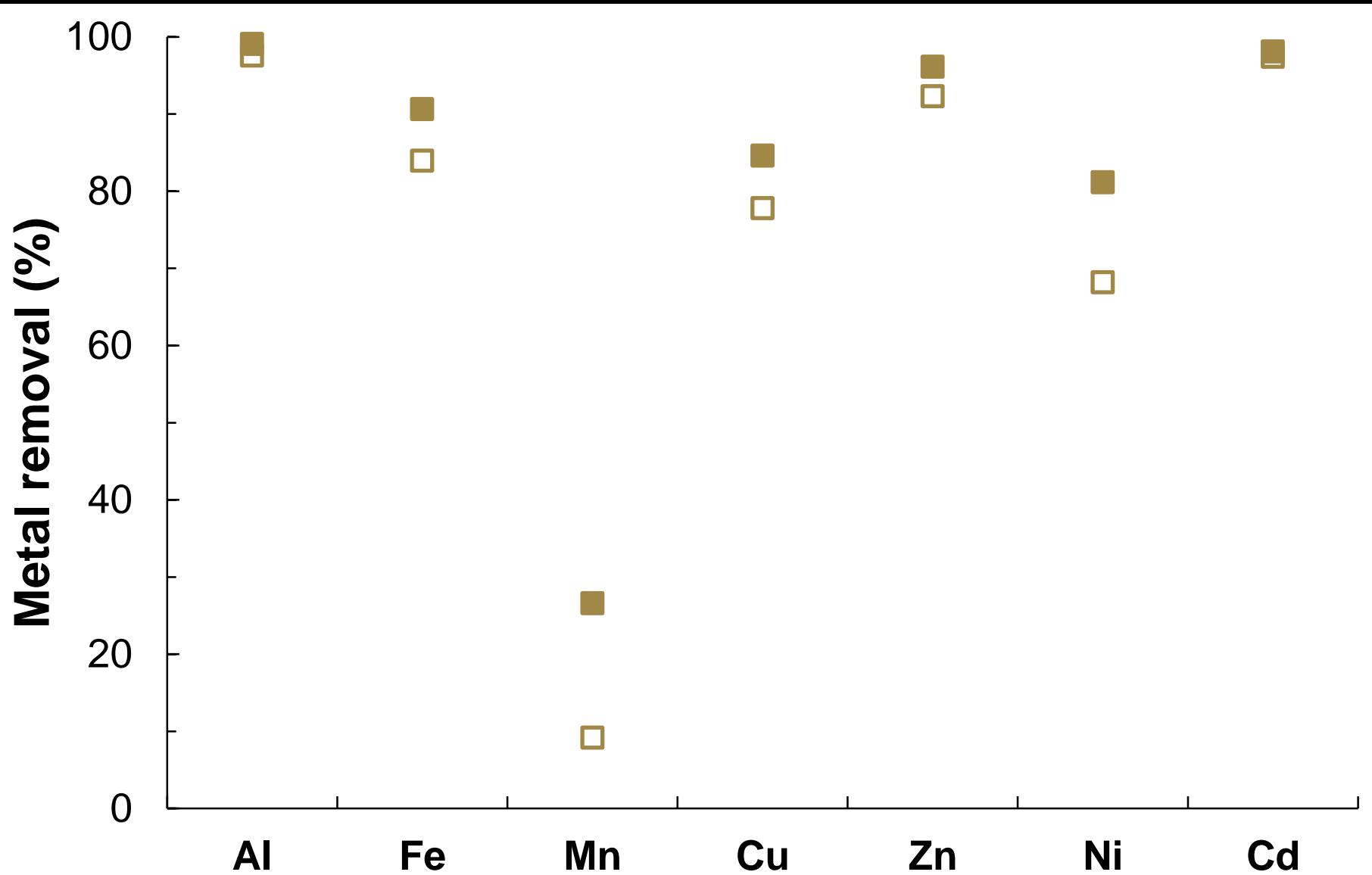
■ LS-Short HRT - -1.3  
■ LS-Long HRT - 118.2

▲ MS-Short HRT - 139.4  
▲ MS-Long HRT - 250.2

**Median Net Alkalinity  
(mg/L CaCO<sub>3</sub>)**

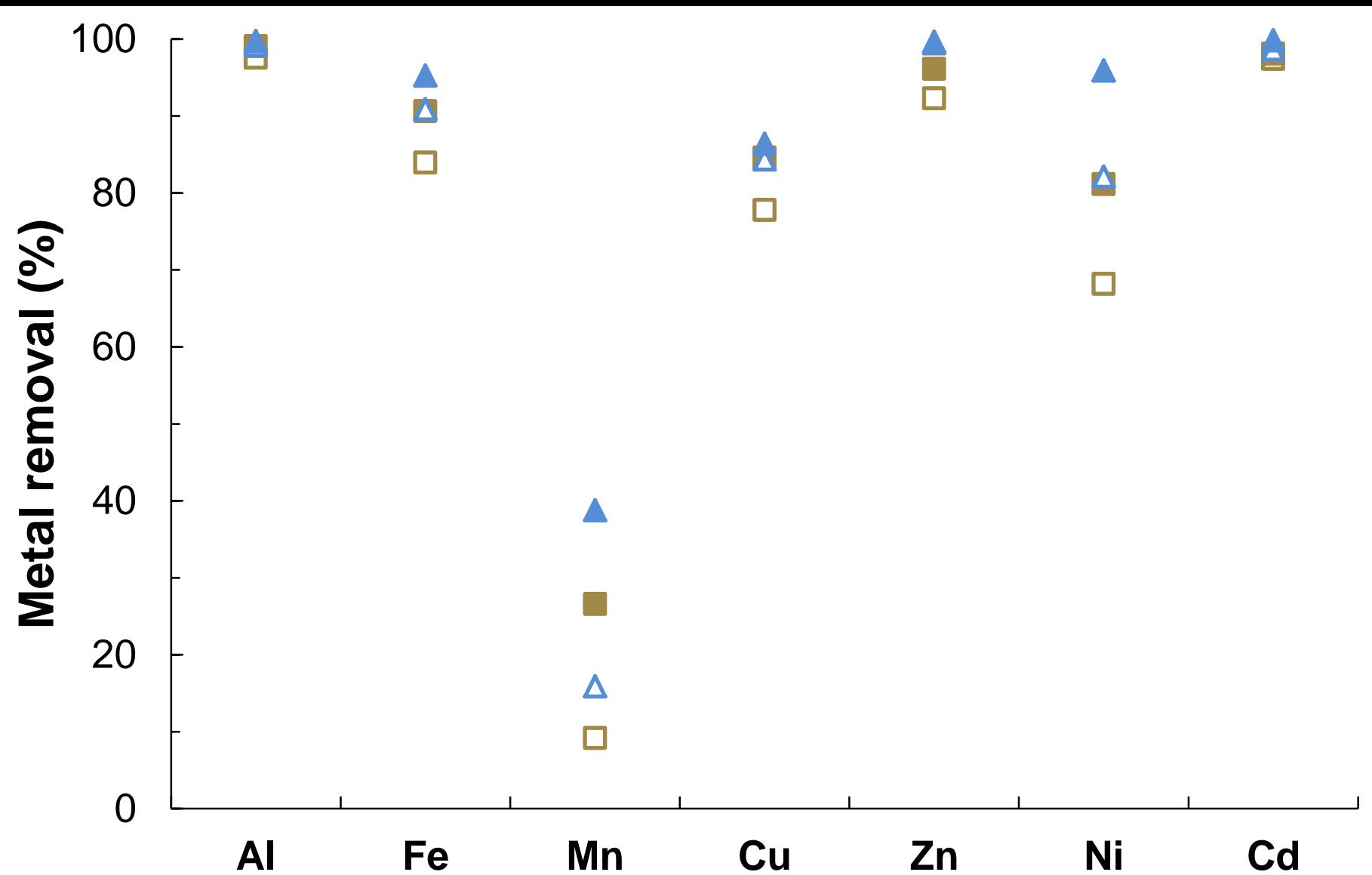


■ LS-Short HRT > 68%  
■ LS-Long HRT > 81%



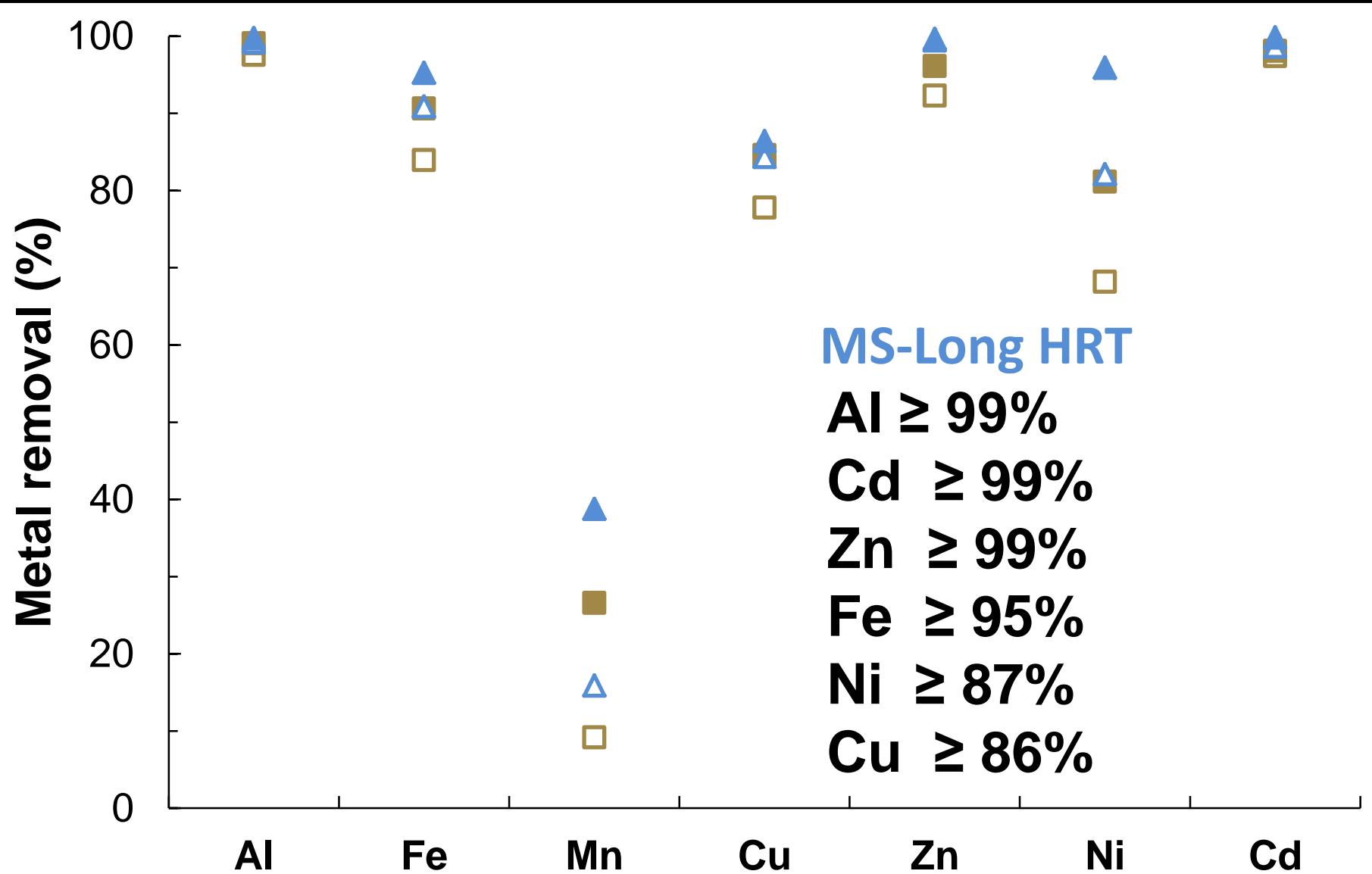
■ LS-Short HRT > 68%  
■ LS-Long HRT > 81%

▲ MS-Short HRT > 82%  
▲ MS-Long HRT > 86%



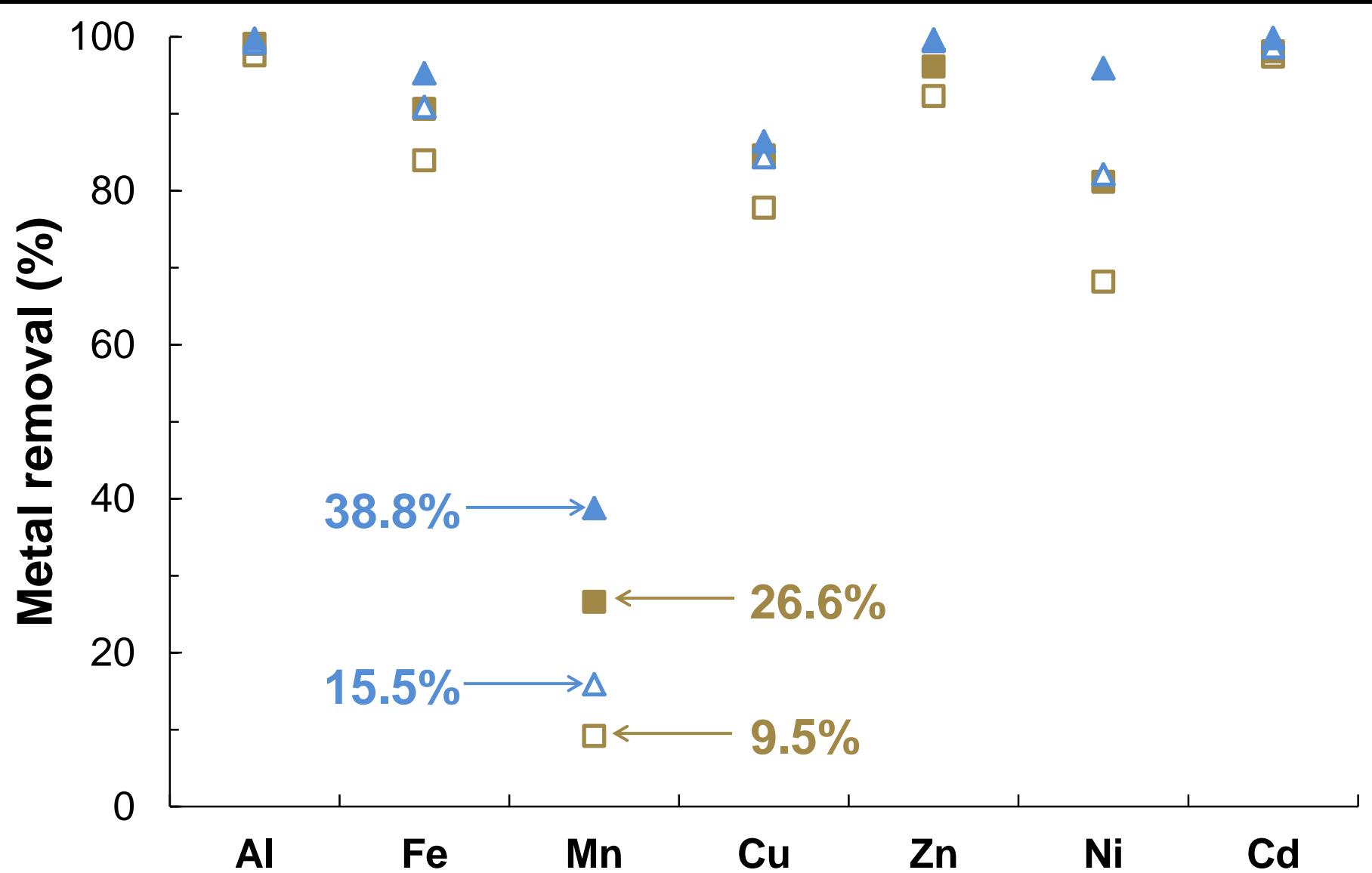
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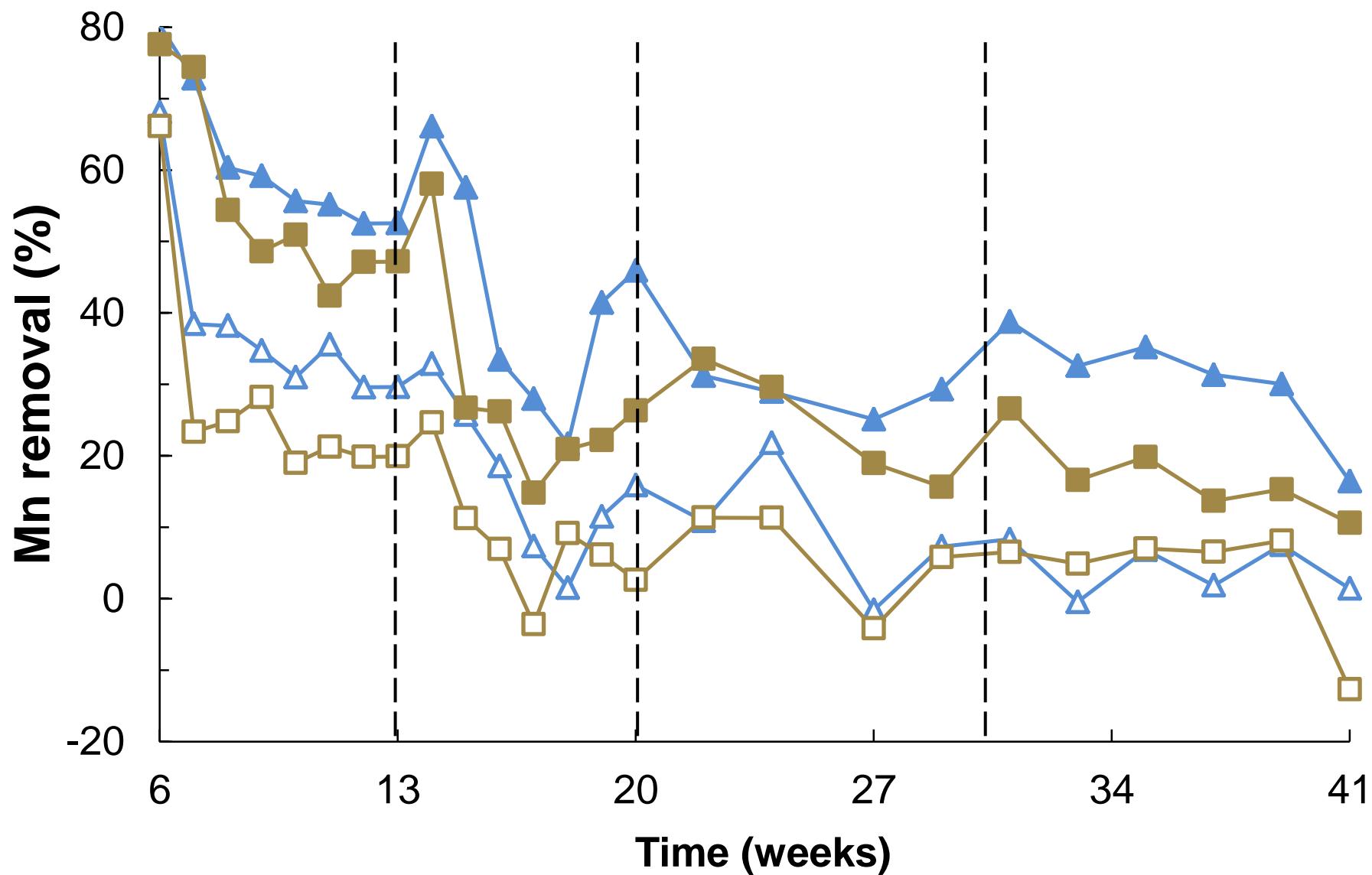
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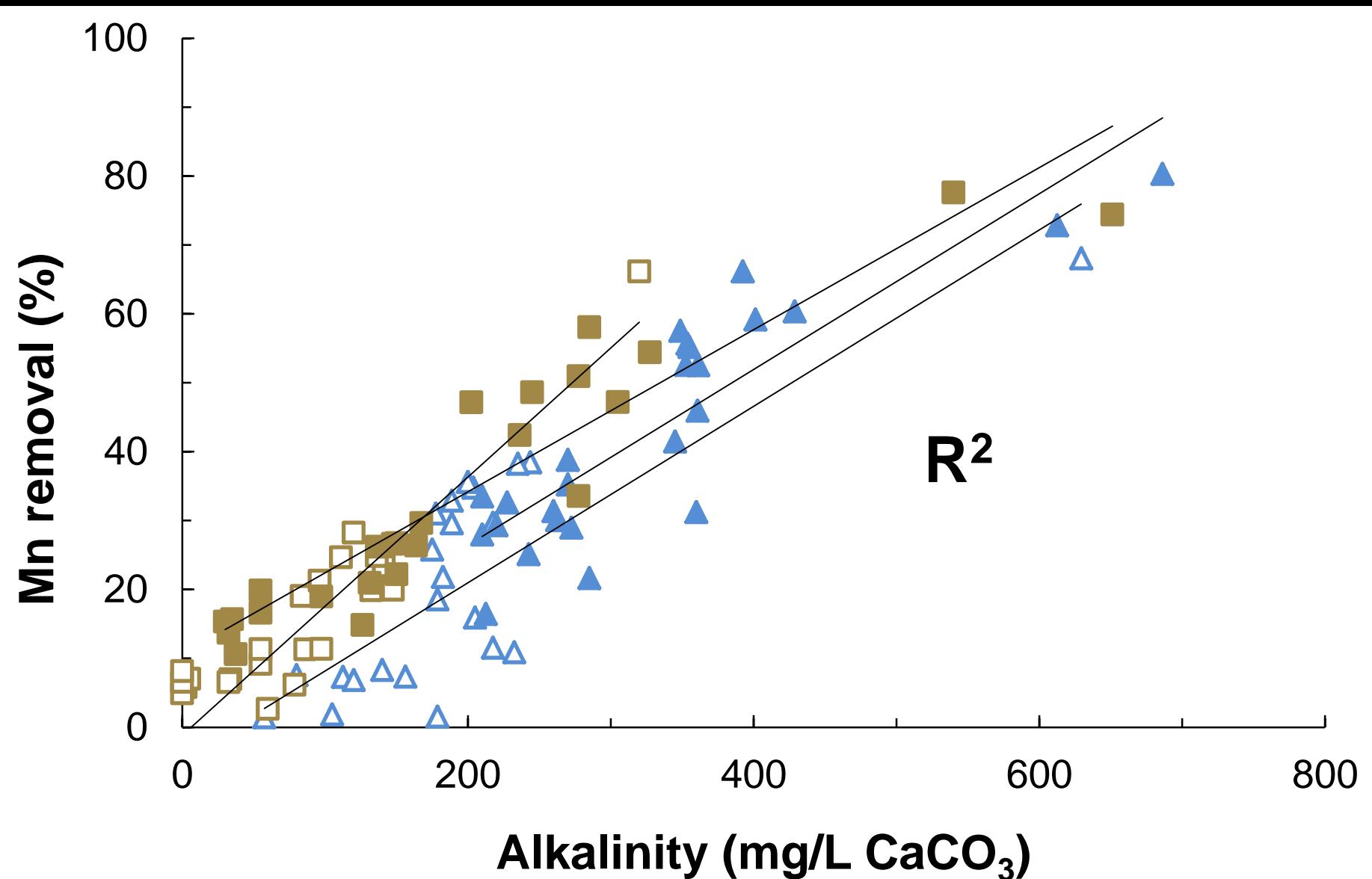
■ LS-Short HRT  
■ LS-Long HRT

▲ MS-Short HRT  
▲ MS-Long HRT



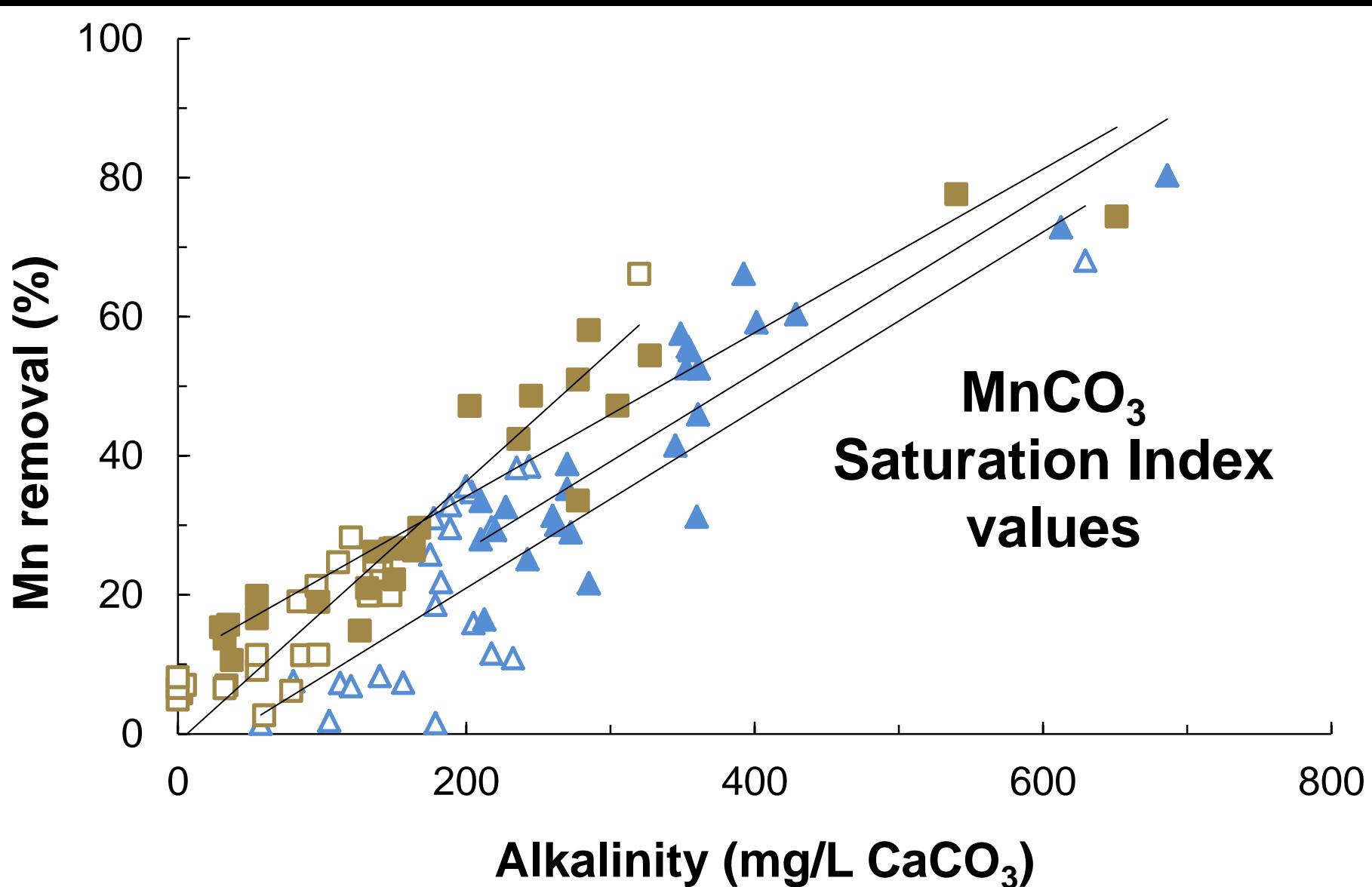
■ LS-Short HRT - 0.79  
■ LS-Long HRT - 0.88

▲ MS-Short HRT - 0.63  
▲ MS-Long HRT - 0.76



■ LS-Short HRT - 0.03  
■ LS-Long HRT - 0.47

▲ MS-Short HRT - 0.40  
▲ MS-Long HRT - 0.85



**Pre-treatment**



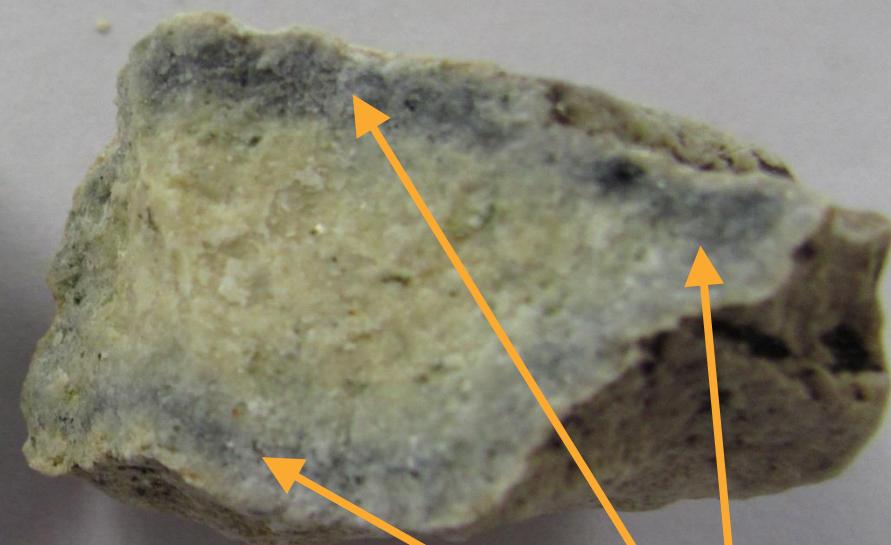
**Post-treatment**



**Pre-treatment**



**Post-treatment**



?!  
?



**Tedlar bags acted  
like 'lungs'**

**Strong H<sub>2</sub>S smell  
during sampling  
events**

**GC analysis...**

Gas Sample Report of Analysis  
Tedlar gas bags sampled by Client.

**N<sub>2</sub> = 75-80%    O<sub>2</sub> = 14-20%    CO<sub>2</sub> = 3-6%**

| Sample Reference:             |   | Sample #1 | Sample #2 | Sample #3 | Sample #4 |
|-------------------------------|---|-----------|-----------|-----------|-----------|
| CH <sub>4</sub>               | % | 0.0039    | 0.0071    | 0.0090    | 0.0099    |
| CO <sub>2</sub>               | % | 2.60      | 4.52      | 5.89      | 5.91      |
| C <sub>2</sub> H <sub>6</sub> | % | <0.0010   | <0.0010   | <0.0010   | <0.0010   |
| C <sub>3</sub> H <sub>8</sub> | % | <0.0010   | <0.0010   | <0.0010   | <0.0010   |
| H <sub>2</sub>                | % | <0.0010   | <0.0010   | <0.0010   | <0.0010   |
| O <sub>2</sub>                | % | 20.03     | 13.66     | 14.59     | 17.59     |
| N <sub>2</sub>                | % | 76.58     | 81.63     | 78.84     | 75.50     |
| CO                            | % | <0.0040   | 0.0112    | <0.0040   | <0.0040   |
| H <sub>2</sub> S*             | % | n/d       | n/d       | n/d       | n/d       |

Values expressed on a mole/mole % basis

Measurement standard:

The test was conducted with an Agilent 3000A TCD micro gas chromatograph, using CRL Energy Ltd's In-house procedures and BOC Alpha and Beta calibration gasses.

\*H<sub>2</sub>S tested with a Crowcon Tetra 3 with no detectable H<sub>2</sub>S present.

Gas Sample Report of Analysis  
Tedlar gas bags sampled by Client.

H<sub>2</sub>S ≤ 0.001%

N<sub>2</sub> = 75-80%    O<sub>2</sub> = 14-20%    CO<sub>2</sub> = 3-6%

| Sample Reference:             |   | Sample #1 | Sample #2 | Sample #3 | Sample #4 |
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| C <sub>2</sub> H <sub>4</sub> | % | <0.0010   | <0.0010   | <0.0010   | <0.0010   |
| C <sub>2</sub> H <sub>6</sub> | % | <0.0010   | <0.0010   | <0.0010   | <0.0010   |
| H <sub>2</sub>                | % | <0.0010   | <0.0010   | <0.0010   | <0.0010   |
| O <sub>2</sub>                | % | 20.03     | 13.66     | 14.59     | 17.59     |
| N <sub>2</sub>                | % | 76.58     | 81.63     | 78.84     | 75.50     |
| CO                            | % | <0.0040   | 0.0112    | <0.0040   | <0.0040   |
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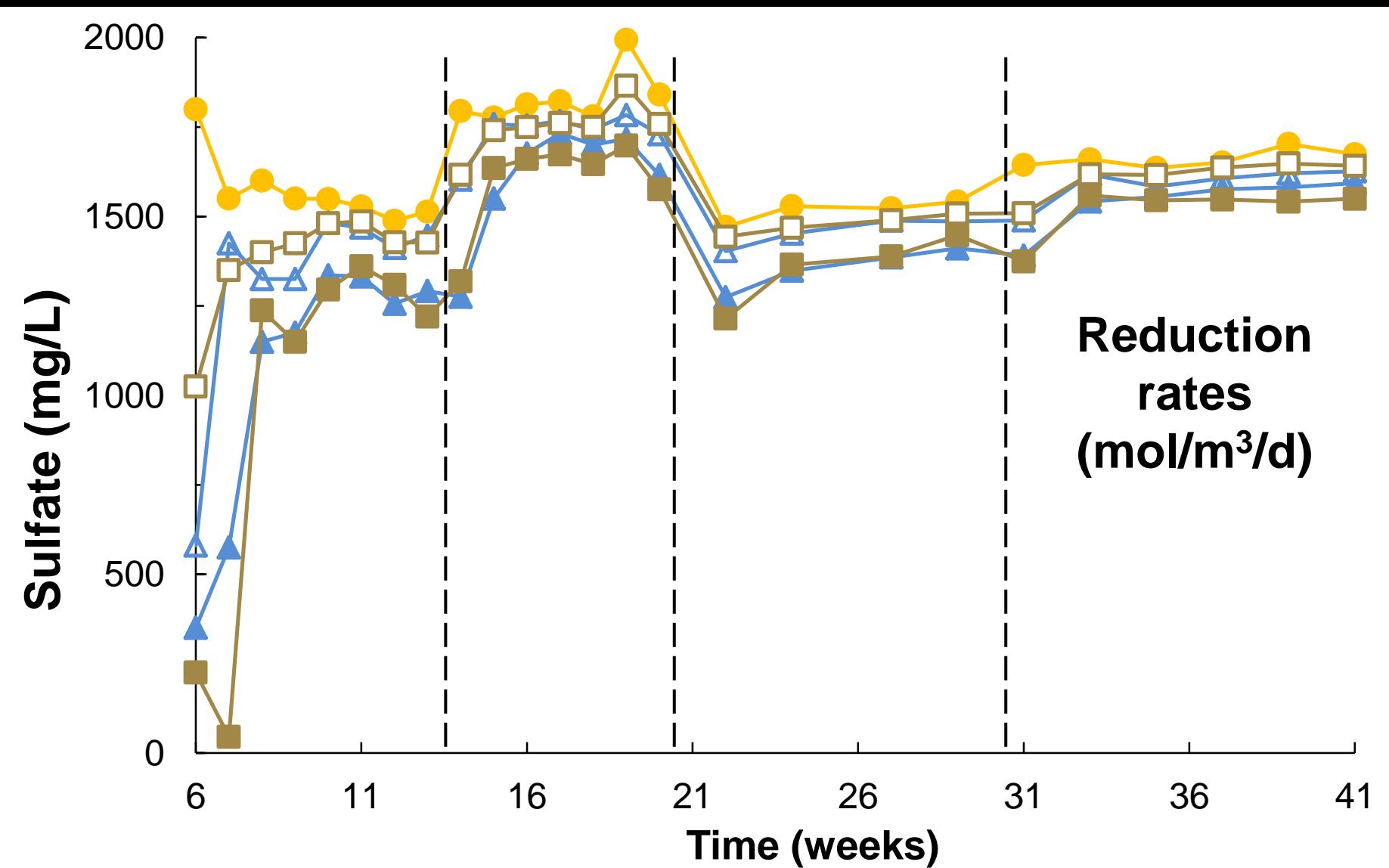
\*H<sub>2</sub>S tested with a Crowcon Tetra 3 with no detectable H<sub>2</sub>S present.



**H<sub>2</sub>S gas and  
dissolved species  
escaped with  
effluent**

**Quantification  
for mass balance  
budget ?!#%**

● AMD (influent)    □ LS-Short HRT - 0.13    ▲ MS-Short HRT - 0.13  
■ LS-Long HRT - 0.12    ▲ MS-Long HRT - 0.14



● AMD (influent)

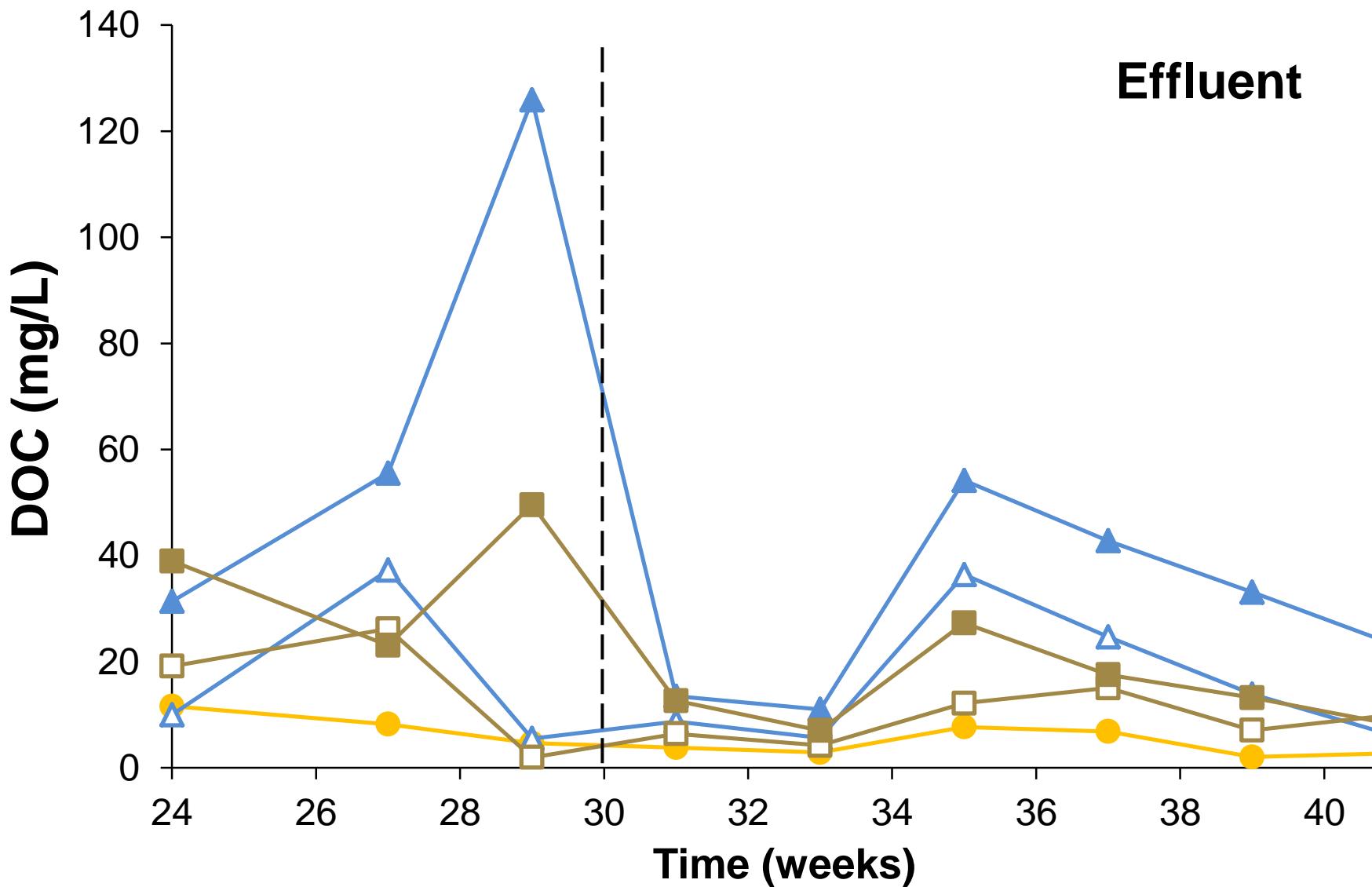
□ LS-Short HRT

▲ MS-Short HRT

■ LS-Long HRT

▲ MS-Long HRT

**Effluent**



# Substrate autopsies





MS-Short



MS-Long



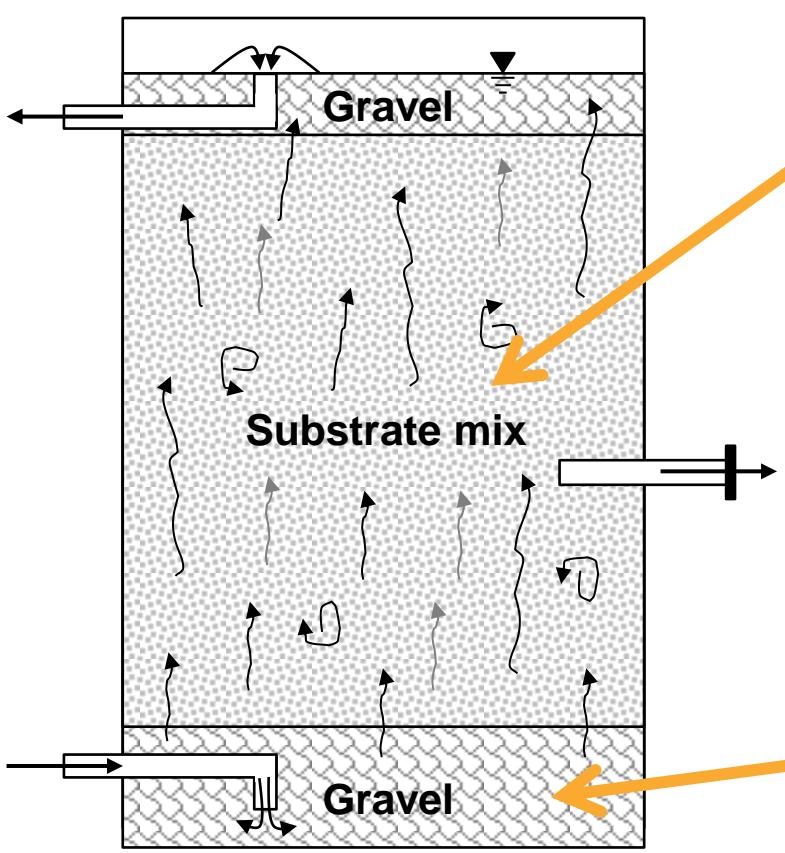
# LS-Short



# LS-Long

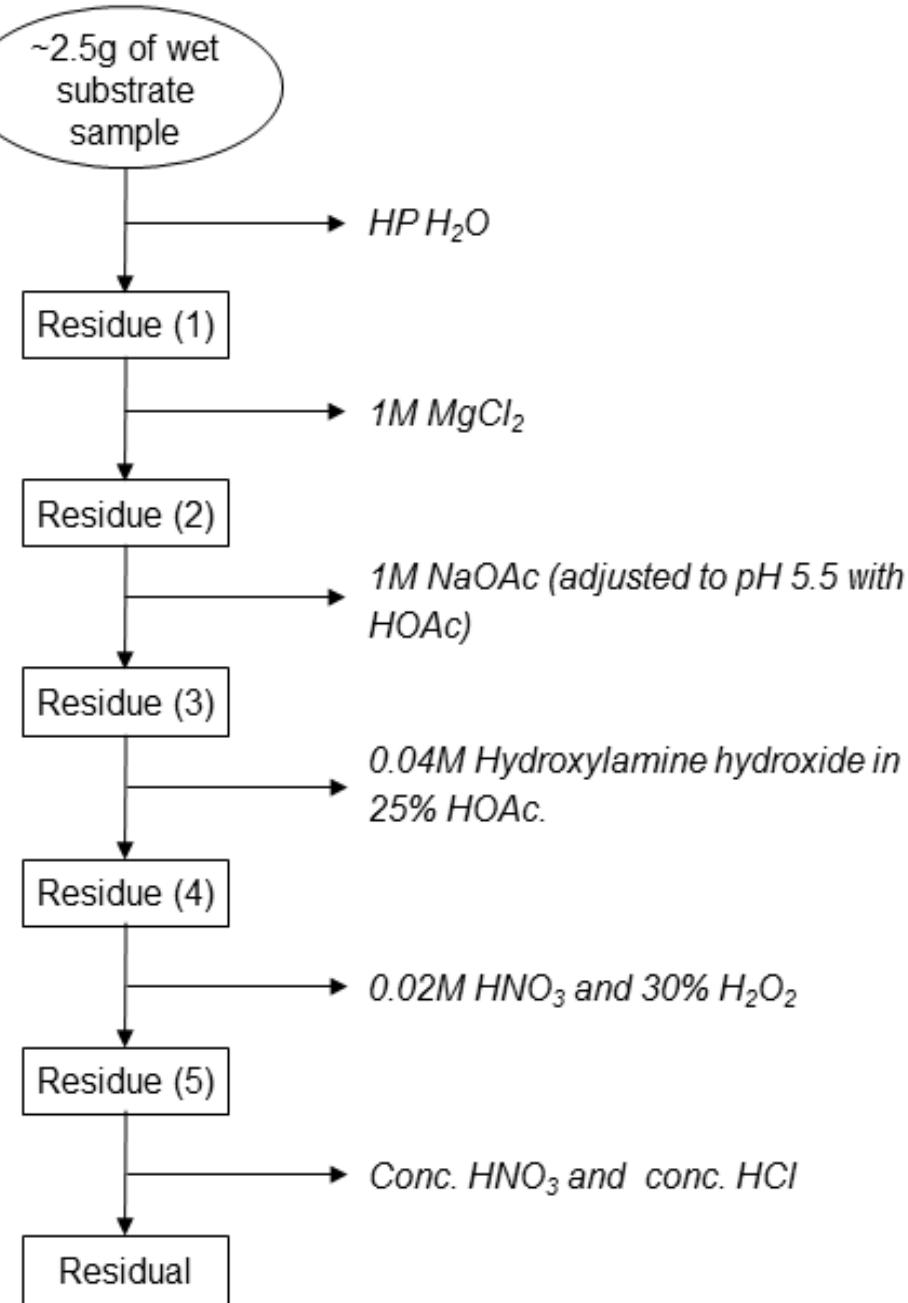


# Limestone post-treatment



# Sequential extractions

6-steps extraction process



Operational fractions:

(1) Water soluble species

(2) Ion exchangeable from FeO, MnO, Org's

(3) Carbonate bound

(4) FeO-MnO bound

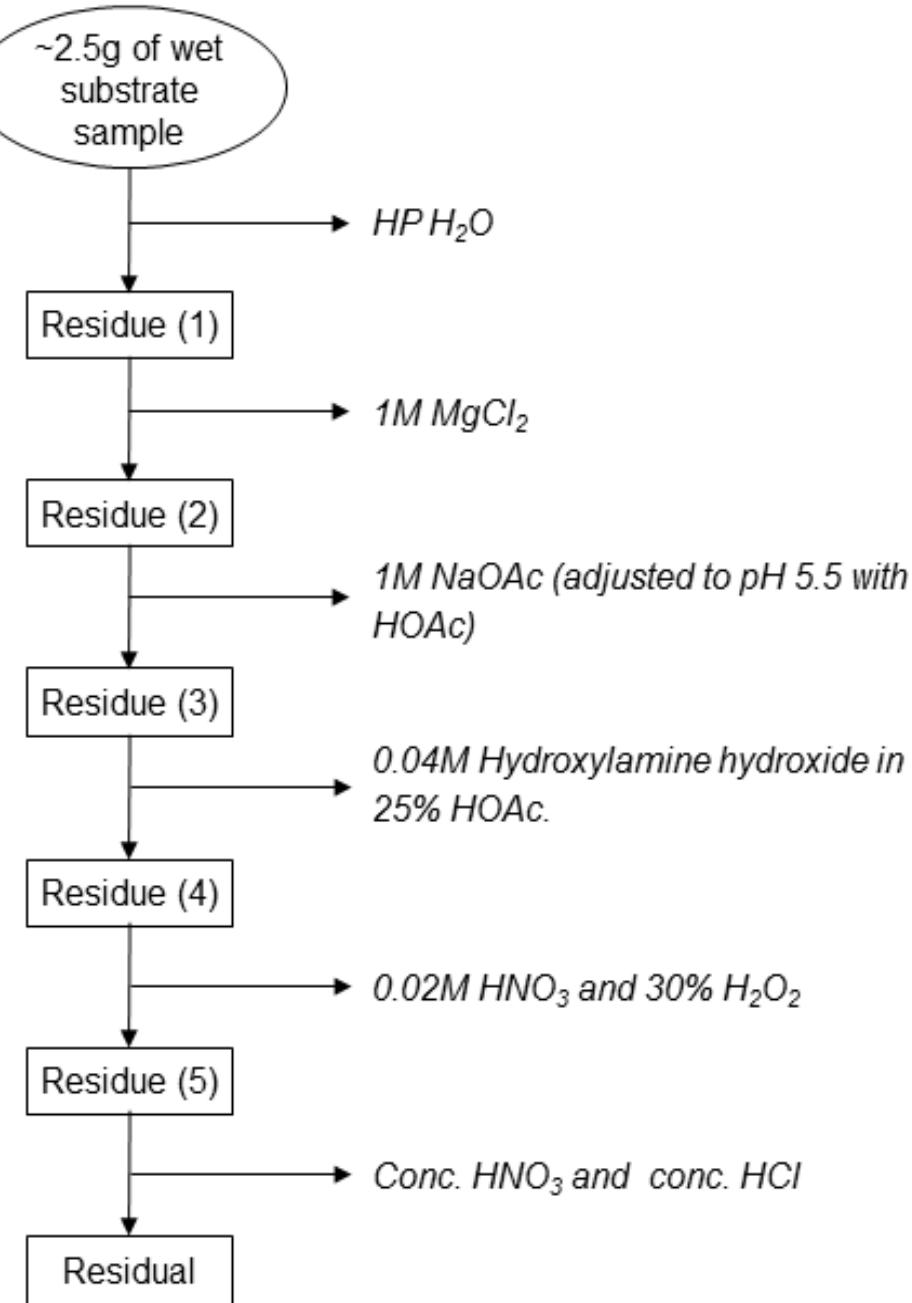
(5) Org/Sulfide bound

(6) Residual

(4) Am. & “fresh” O(OH)  
(6) Cryst. & “old” O(OH)

# Sequential extractions

6-steps extraction process



Operational fractions:

(1) Water soluble species

(2) Ion exchangeable from  $FeO$ ,  $MnO$ , Org's

(3) Carbonate bound

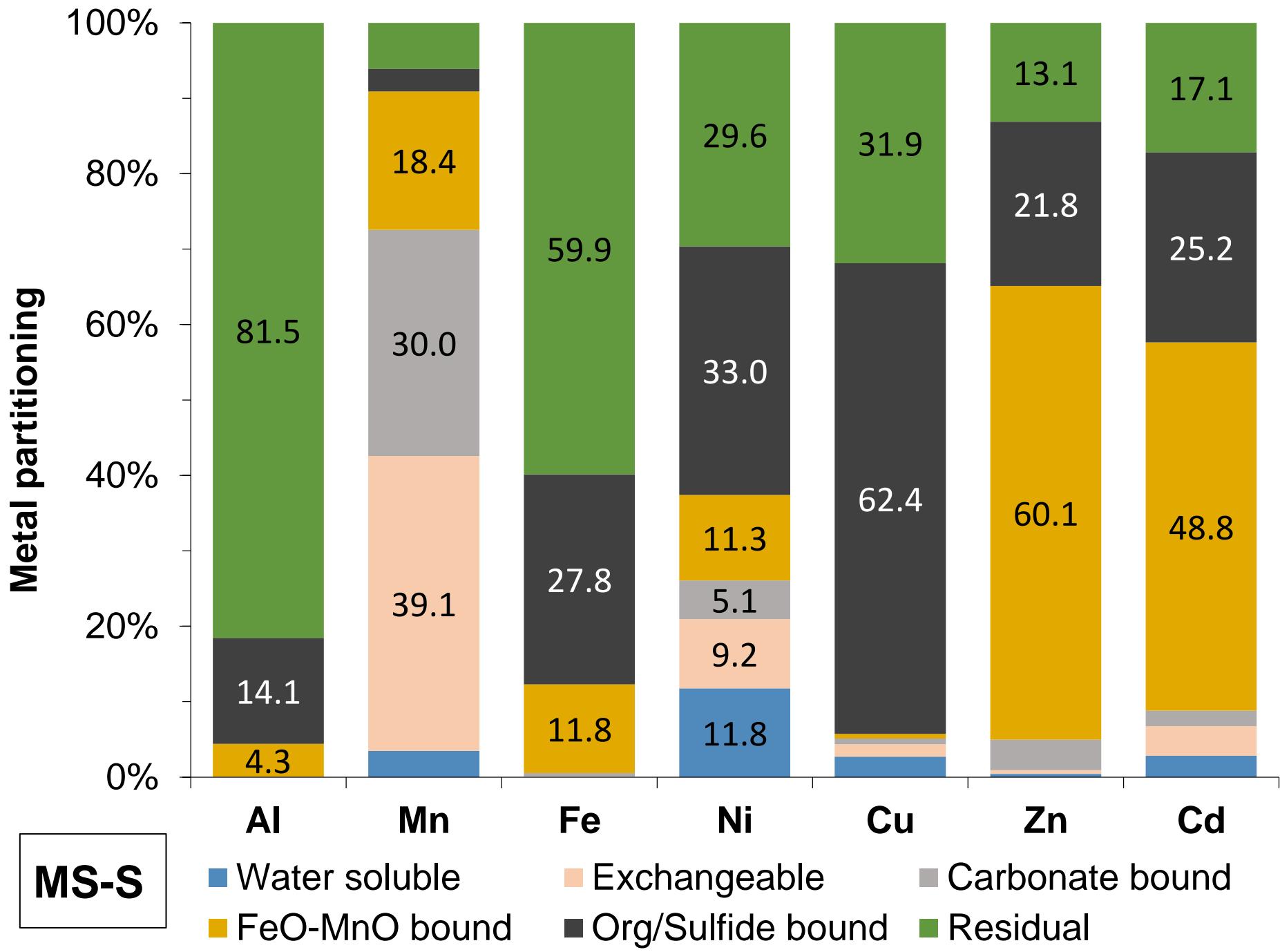
(4)  $FeO$ - $MnO$  bound

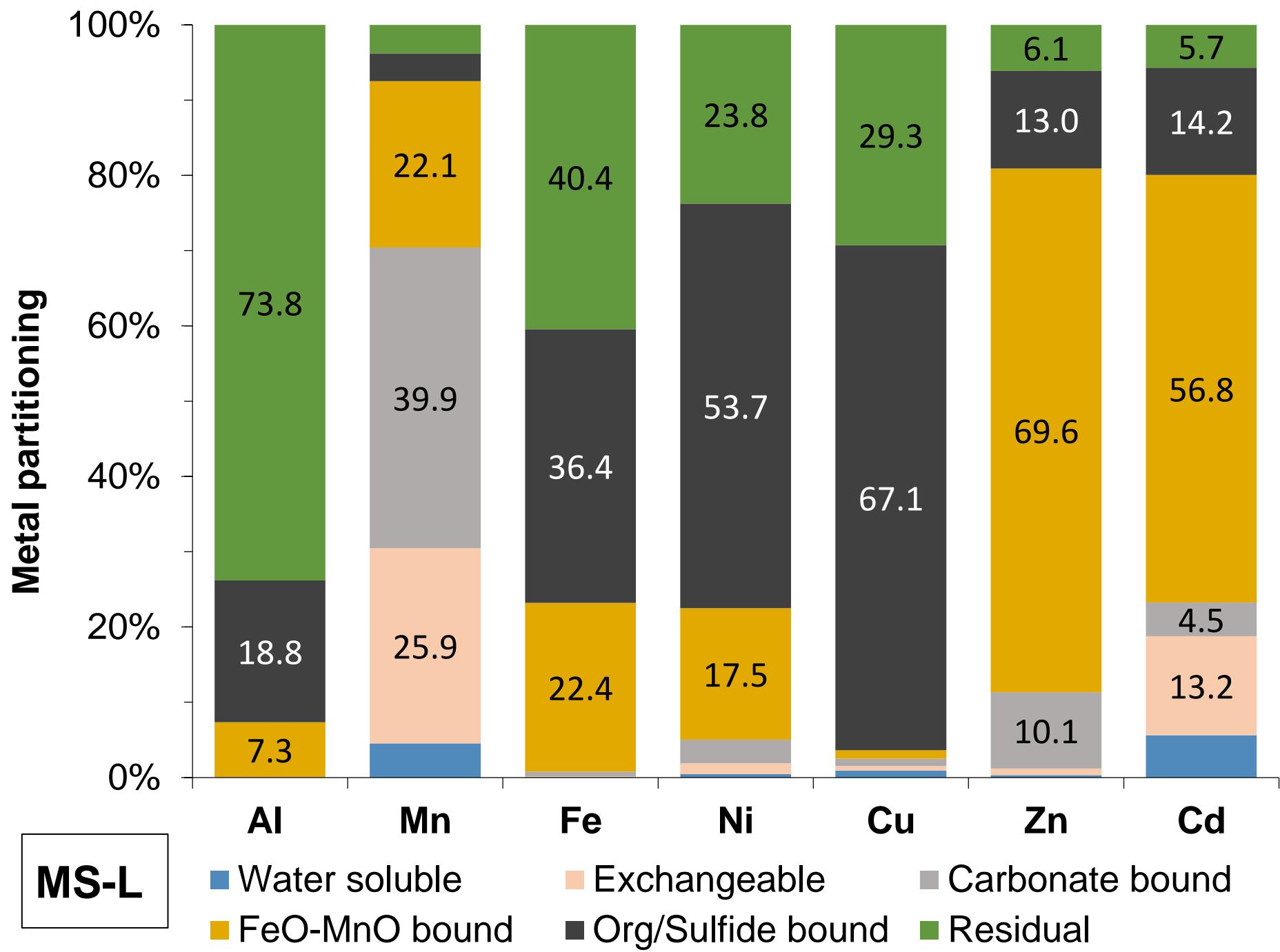
(5) Org/Sulfide bound

(6) Residual

(4) Am. & “fresh” O(OH)

(6) Cryst. & “old” O(OH)





# What's next ?!

- Scanning Electron Microscopy (with EDS)
- Sorption tests
  - batch experiments, pH control,  
modelling (?)
- “Carbon species” extractions
  - EAS, cellulose - hemicellulose, lignin

# Conclusions

Waste mussel shells are a **sustainable** and effective alternative to limestone in passive treatment systems.

- Greater alkalinity generation
- Better metal removal (e.g. Mn)
- Greater nutrient and organic carbon source

Long HRT resulted in a better overall treatment.  
Short HRT (i.e. mussel shells) was sufficient to remove > 80% metals and raise pH > 6 for more than 40 weeks -> **intermediate HRT** ?

**Upward-flow** design maintained reducing conditions



# Thank you for your attention!

**Peter McGuigan – ENG.**  
**Dave McPherson – ENG.**  
**Su Ko Young – ENG.**  
**Alex Evans – ENG.**  
**Robert Stainthorpe – CHEM.**  
**Matt Cockcroft – GEOL.**  
**Mine staff**



# Thank you for your attention!



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Dave McPherson – ENG.  
Su Ko Young – ENG.  
Alex Evans – ENG.  
Robert Stainthorpe – CHEM.  
Matt Cockcroft – GEOL.  
Mine staff**

# Extra Slides

# Substrate

|                    | Mussel shells mix | Limestone mix   | Recom.              |
|--------------------|-------------------|-----------------|---------------------|
| Porosity           | 0.51              | 0.49            | 0.35 - 0.65         |
| $K_{sat}$ (cm/sec) | $6.3 * 10^{-2}$   | $9.7 * 10^{-2}$ | $10^{-2} - 10^{-3}$ |
| nHRT(days)         | MS–Short          | MS–Long         | LS–Short            |
|                    | 3.3               | 10              | 3.2                 |
|                    |                   |                 | 9.8                 |
|                    |                   |                 | variable            |

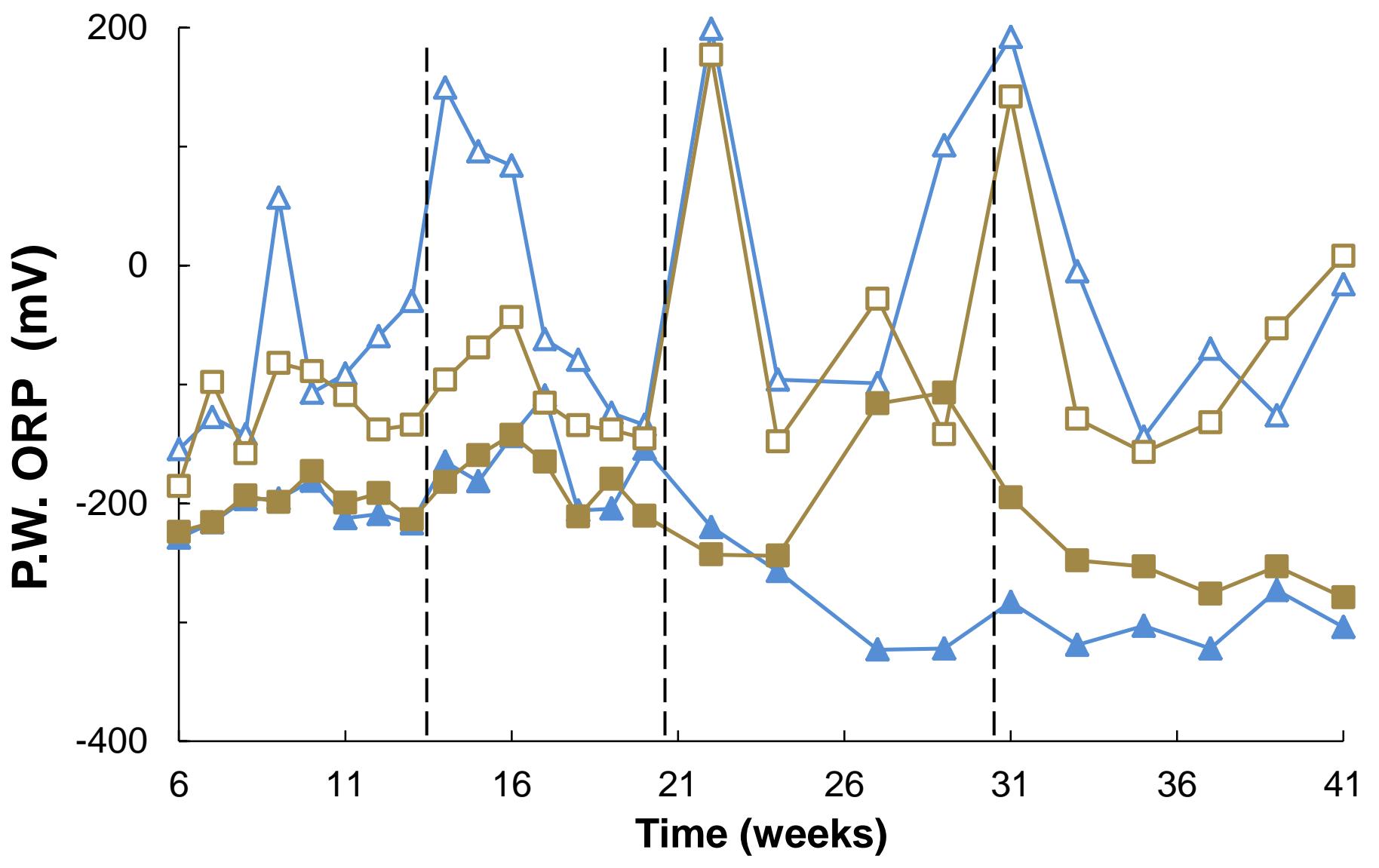
- **3 weeks batch-mode**
  - **Microbial population growth and acclimation period**
- **41 weeks flow-through experiment**
  - **weekly sampling of influent, effluent and pore-water**

# Water Quality Guidelines

|                                 | AI          | Fe          | Mn           | Ni     | Cu     | Zn     | Cd       | $\text{SO}_4^{2-}$ | pH      |
|---------------------------------|-------------|-------------|--------------|--------|--------|--------|----------|--------------------|---------|
| Recreational purpose values     | 0.2         | 0.3         | 0.1          | 1      | 5      | 0.1    | 0.005    | 400                | 6.5-8.5 |
| Trigger values (80% protection) | ID          | ID          | 3.6          | 0.0025 | 0.03   | 0.0017 | 0.0008   | n/d                | n/d     |
| <b>Median effluents</b>         |             |             |              |        |        |        |          |                    |         |
| <b>MS-S</b>                     | 0.08        | <b>1.85</b> | <b>10.16</b> | 0.1685 | 0.0258 | 0.0204 | 3.86E-05 | <b>1483</b>        | 6.5     |
| <b>MS-L</b>                     | 0.04        | <b>0.66</b> | <b>6.70</b>  | 0.0449 | 0.0203 | 0.0175 | 1.75E-05 | <b>1333</b>        | 6.8     |
| <b>LS-S</b>                     | <b>0.19</b> | <b>2.62</b> | <b>11.88</b> | 0.1955 | 0.0375 | 0.0433 | 5.12E-05 | <b>1486</b>        | 6.4     |
| <b>LS-L</b>                     | 0.08        | <b>1.53</b> | <b>8.69</b>  | 0.1805 | 0.0279 | 0.1668 | 3.34E-05 | <b>1319</b>        | 6.5     |

ID = insufficient data  
n/d = not defined

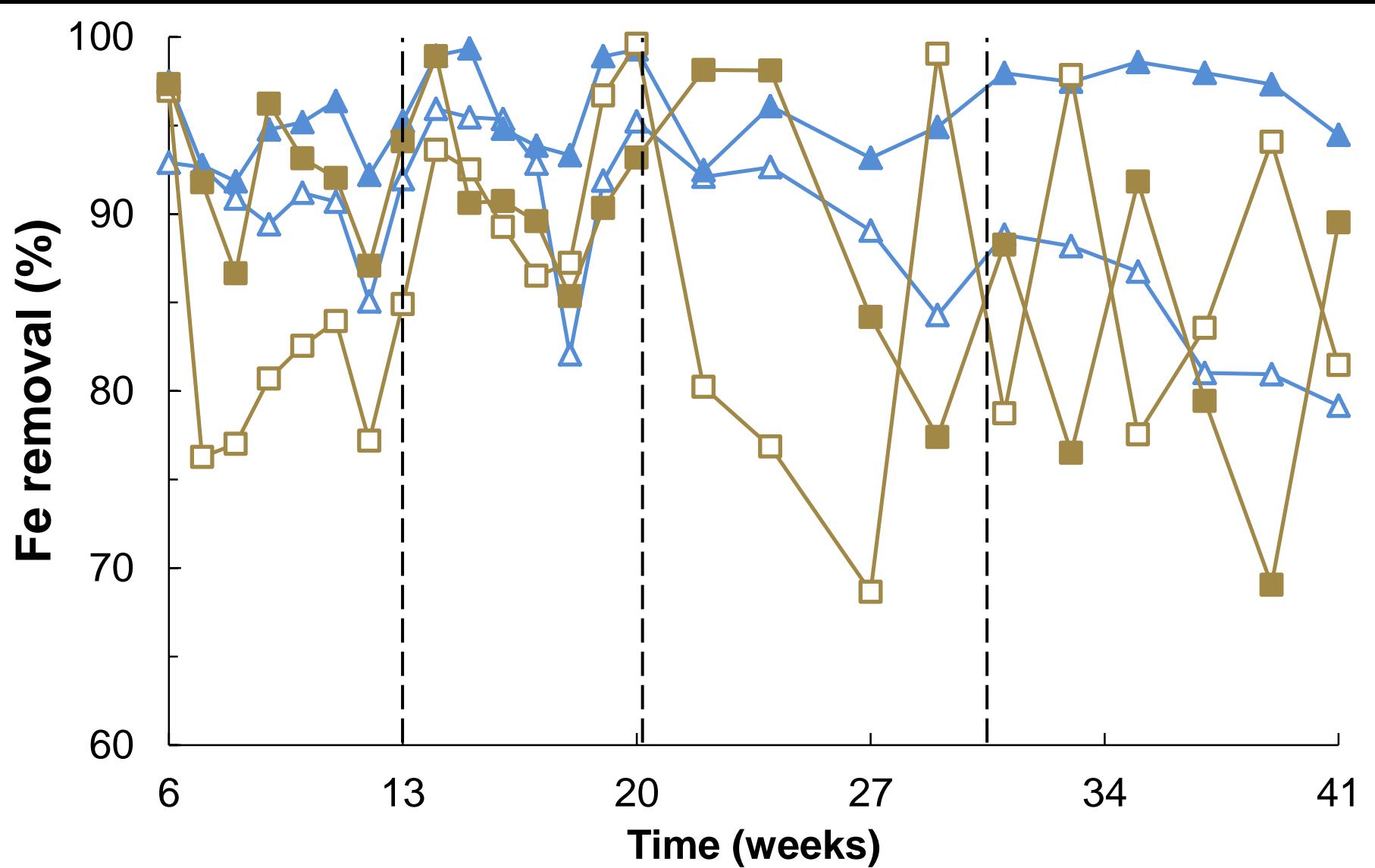
TV = in-stream concentrations

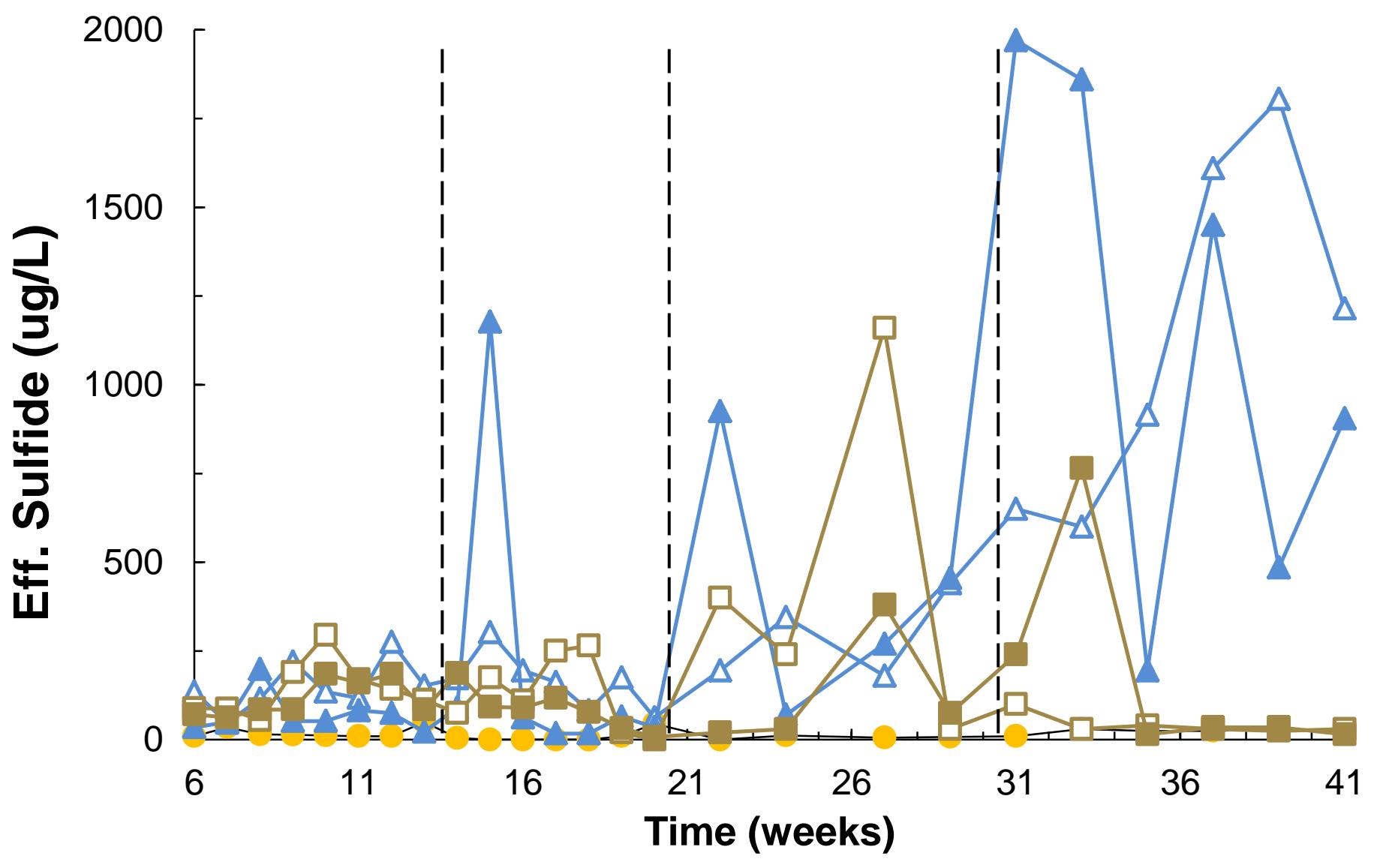


- AMD (influent)    □ LS-Short HRT - -115    ▲ MS-Short HRT - -70  
465                  ■ LS-Long HRT - -199    ▲ MS-Long HRT - -216

■ LS-Short HRT - 83.9%  
■ LS-Long HRT - 90.6%

▲ MS-Short HRT - 90.9%  
▲ MS-Long HRT - 95.2%





● AMD (influent)

■ LS-Short HRT

▲ MS-Short HRT

■ LS-Long HRT

▲ MS-Long HRT

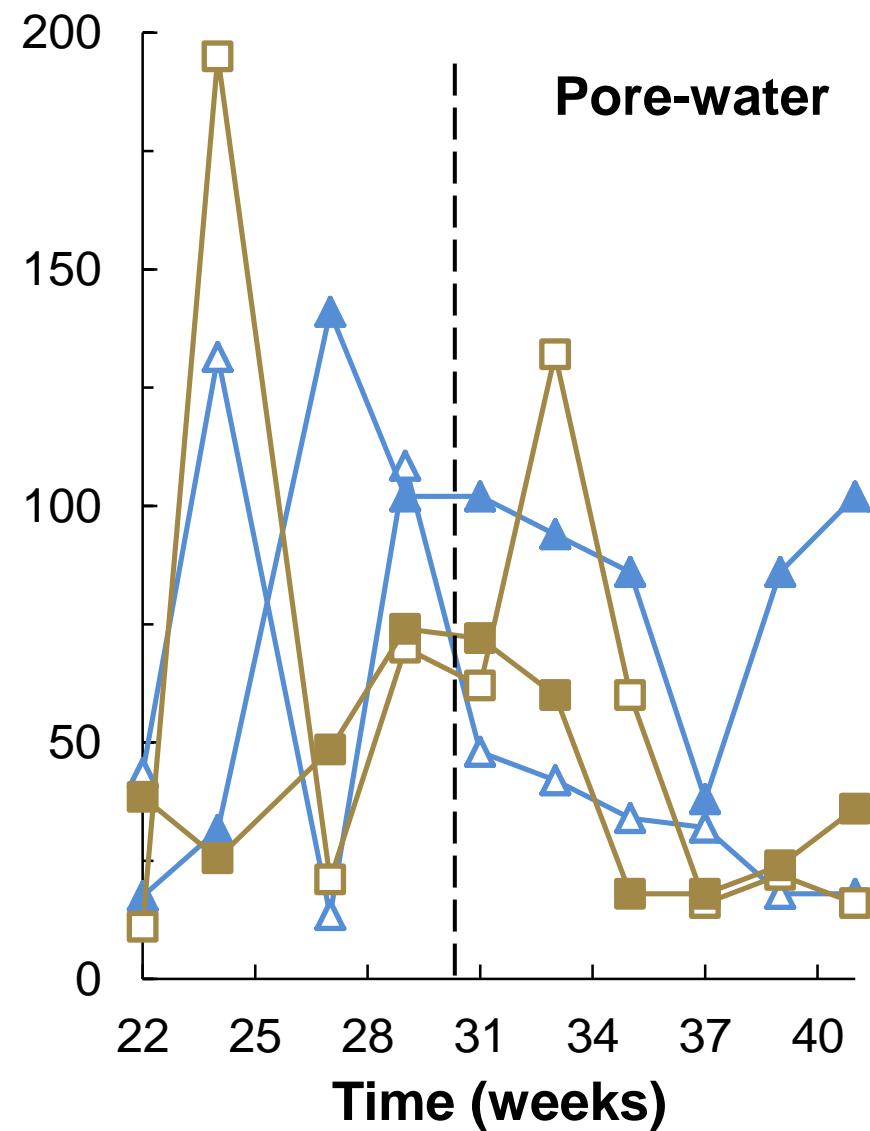
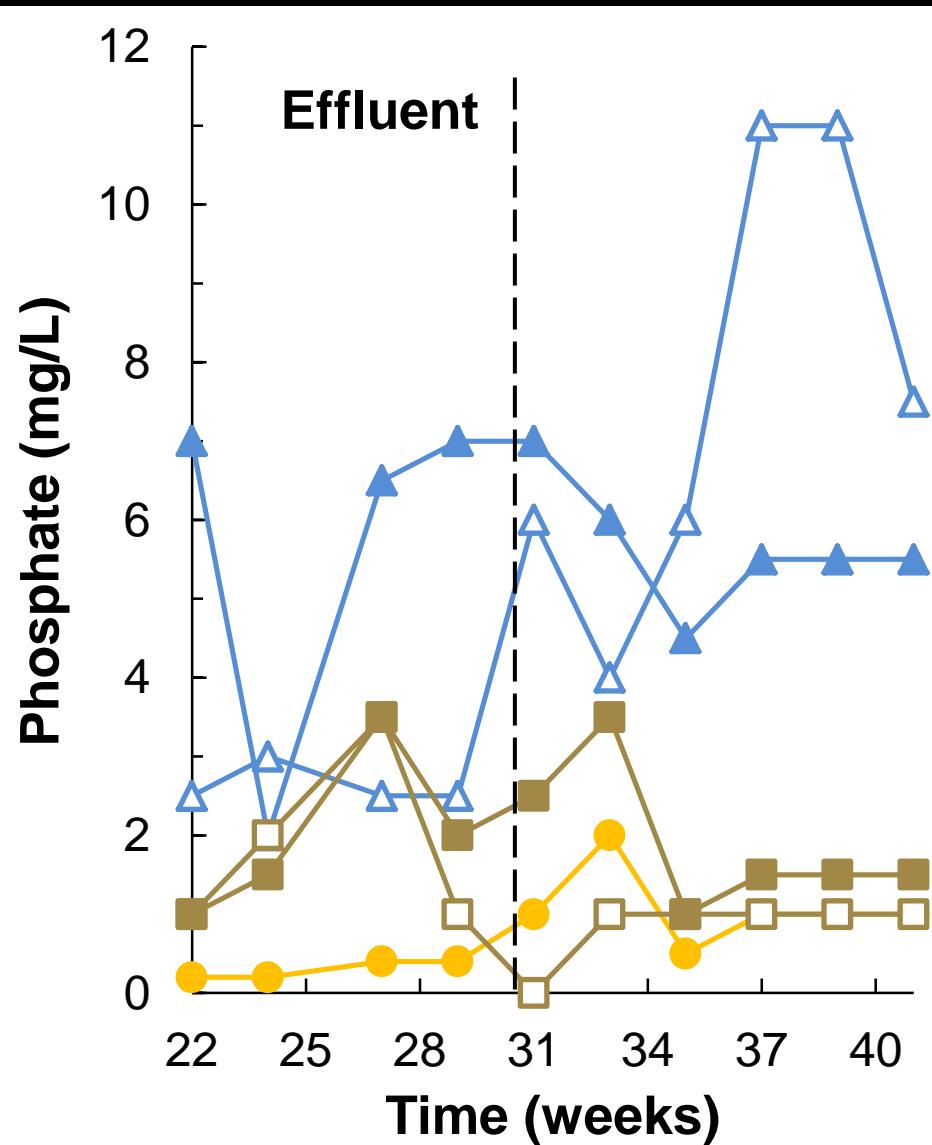
● AMD (influent)

□ LS-Short HRT

△ MS-Short HRT

■ LS-Long HRT

▲ MS-Long HRT



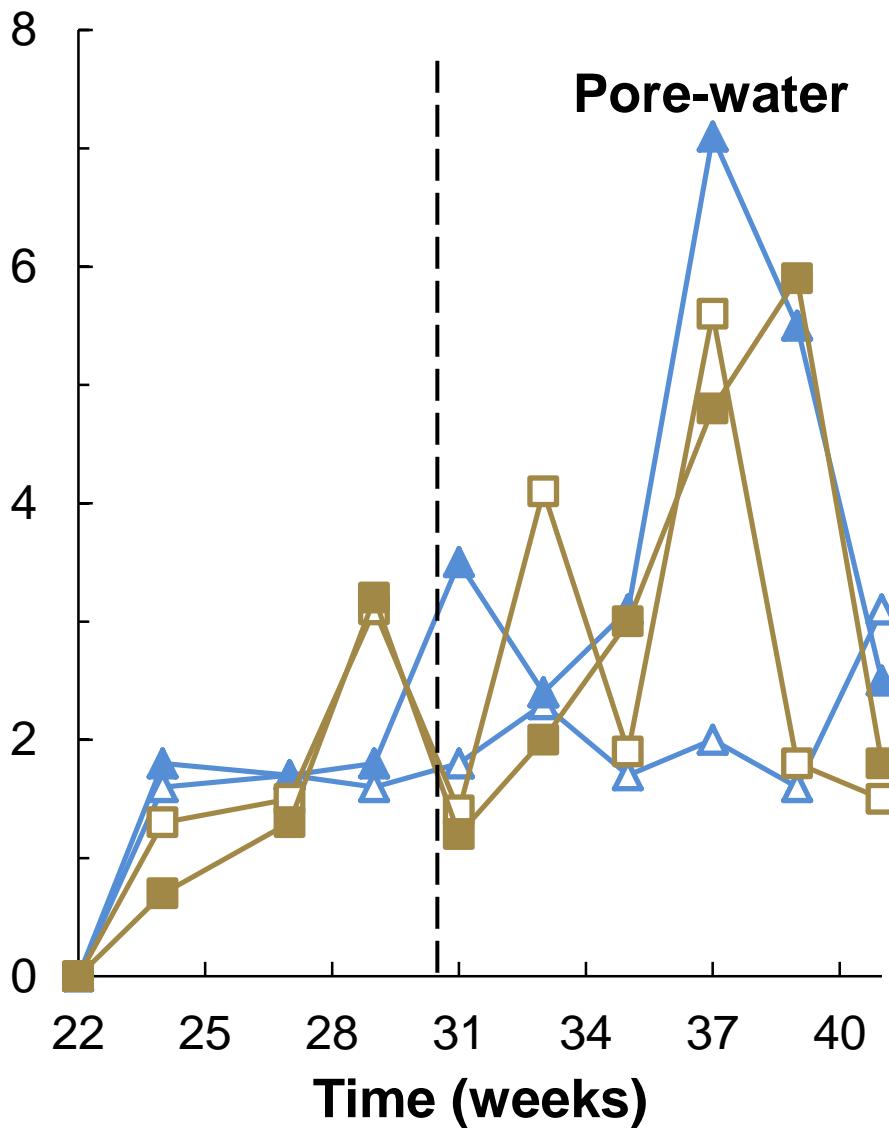
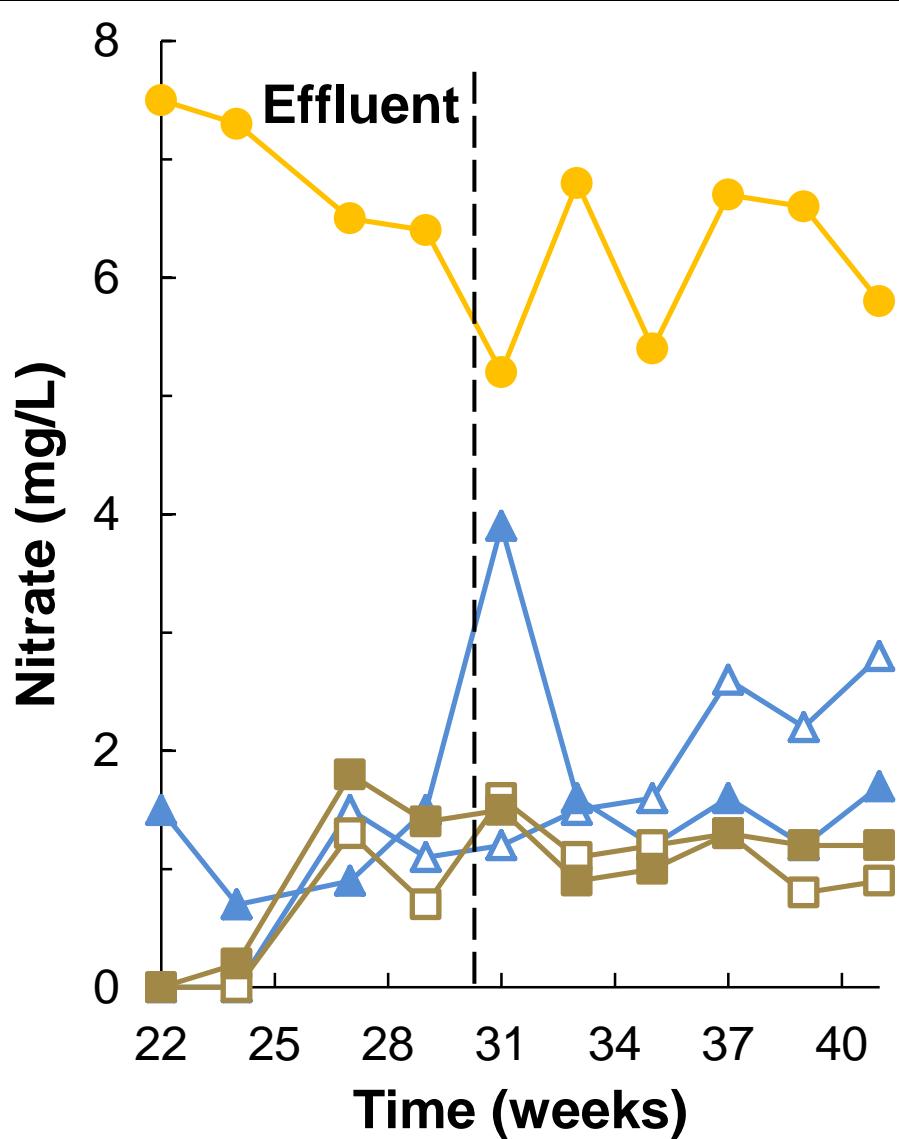
● AMD (influent)

□ LS-Short HRT

▲ MS-Short HRT

■ LS-Long HRT

▲ MS-Long HRT



● AMD (influent)

□ LS-Short HRT

▲ MS-Short HRT

■ LS-Long HRT

▲ MS-Long HRT

**Effluent**

