USE OF A SEQUENTIAL EXTRACTION PROCEDURE TO REVEAL ARSENIC SORPTION AND TRANSLOCATION KINETICS IN AN OXYGENATED SEDIMENT

Outline

- Introduction – Why is this significant for Arsenic?
  - Purpose
  - Approach
  - Applications
- Results/Discussion – Depletion Kinetics
  - Translocation Kinetics
  - Environmental Applications
- Conclusions
- Future Work – additional kinetics experiments
  - solid phase analysis
  - speciation extraction method validation
- Acknowledgements

Introduction

Why is this significant for Arsenic?

- Arsenic oxidation and sorption is often rapid in many natural environments, but matrix dependant
- Arsenic mobility and toxicity is redox sensitive
- The dynamic nature of hydrologic environments induces redox changes with substrates in contact with water
- During aging, Arsenic translocations may increase the solid phase retention strength
- Knowing Arsenic translocation rates and related retention strengths helps to predict release rates when environmental conditions change

Purpose

1) Determine dissolved arsenate and arsenite removal rates from an oxygenated circumneutral sediment suspension

2) Determine arsenic translocation rates in an oxygenated circumneutral sediment suspension during aging, as defined by a sequential extraction procedure

Approach

Top 3 cm of sediment collected with an Ekman grab sampler

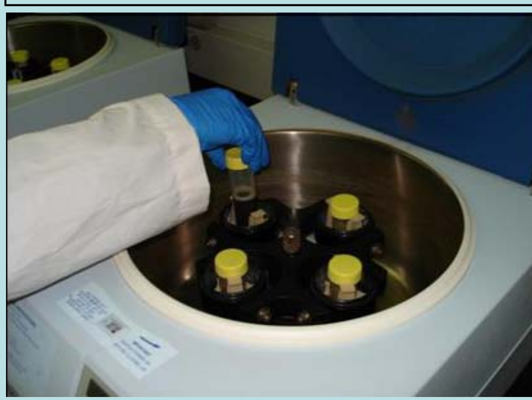
Freeze Dried

Depletion Kinetics

0.4g sediment + 25mL of 50μg/L As(III) or As(V) and shaken for 0, 8, 24, 49, 73, 169, 406, 550, and 739hrs

Batch Reactions

Centrifuge
20 minutes at 3000 rpm



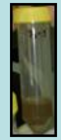
Dissolved Fraction

ICP-MS

Solid Fraction

4 Step Sequential Extraction Procedure

archived for solid phase analysis



5 replicates

Step 1 - 0.05M $(NH_4)_2SO_4$, 4hrs

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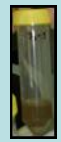

Step 2 - 0.05 $NH_4H_2PO_4$, 16hrs

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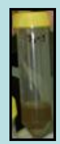
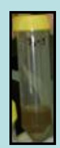


Step 1 applied to 4 samples

Step 3 – 0.2M $COONH_4$, 4hrs in dark

archived for solid phase analysis



Step 4 – 12N HCL, 30 minutes

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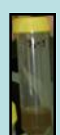
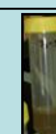




SEP

centrifuge

HG-AAS

ICP-OES

Applications

Answers the questions when environmental redox conditions change:

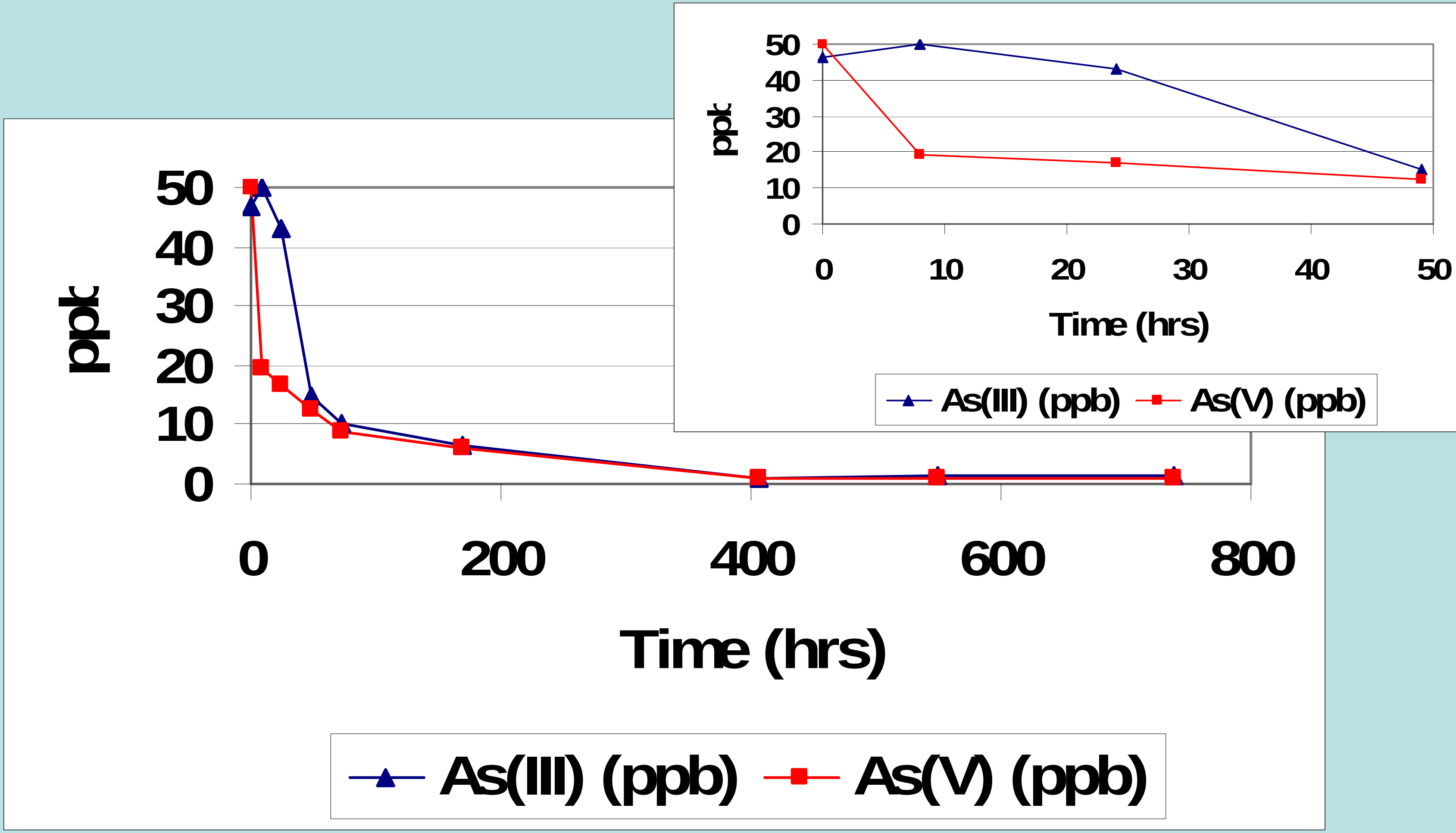
- **How long before dissolved As is retained or released?**
- **How strongly is it retained after specific durations?**
- **What conditions will remobilize it?**

Examples of redox condition changes that may last days to months:

- **Groundwater draw down/recharge cycling**
- **Surface water level changes**
- **Hypolimnion growth/depletion**
- **Sub-surface horizontal flow across redox gradients (e.g. tailings amended organic covers)**
- **Upwelling groundwater through lake sediments**

Results/Discussion

Depletion Kinetics



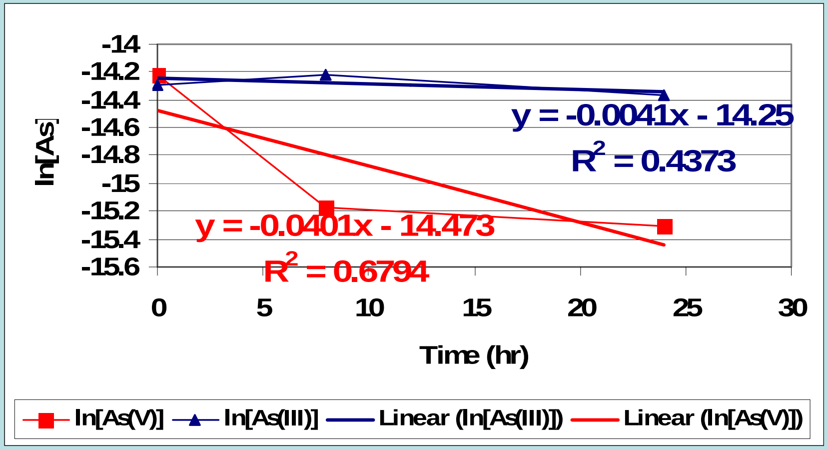
As(III) and As(V) solution depletion rates reacted with oxygenated lake sediment for 740hrs (50ppb solution).

Reaction Order and Kinetic Coefficients (k)

First Order

$k_{As(III)}$ $4.1x10^{-3}$ –hr (slower)

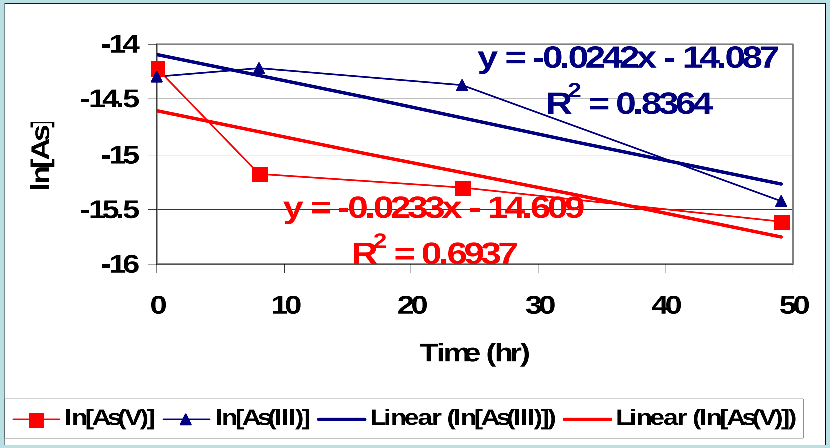
$k_{As(V)}$ $4.0x10^{-2}$ –hr (faster)



First Order

$k_{As(III)}$ $2.4x10^{-2}$ –hr

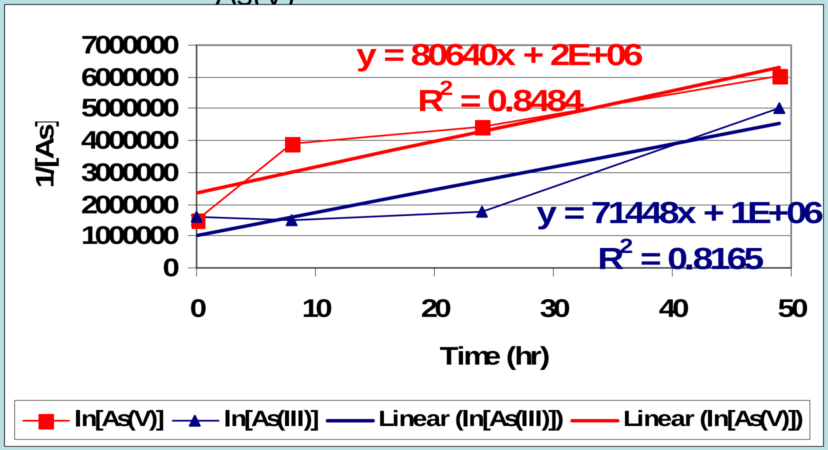
$k_{As(V)}$ $2.3x10^{-2}$ -hr



Second Order

$k_{As(III)}$ $7.1x10^{4}$ –mole –hr

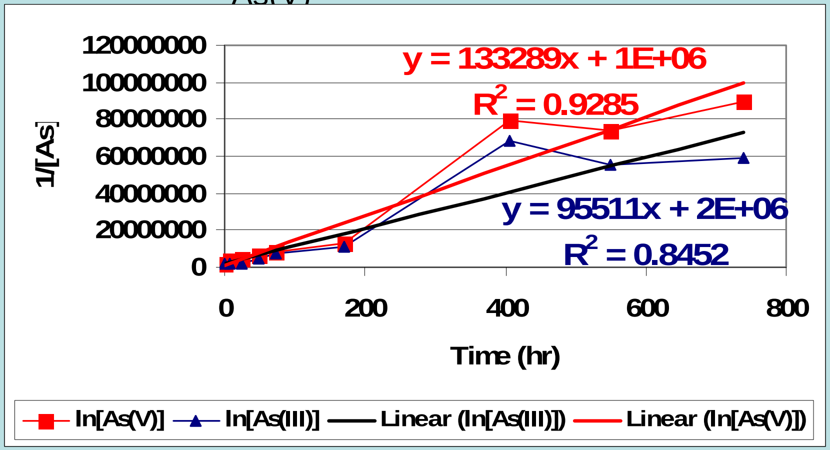
$k_{As(V)}$ $8.1x10^{4}$ –mole -hr



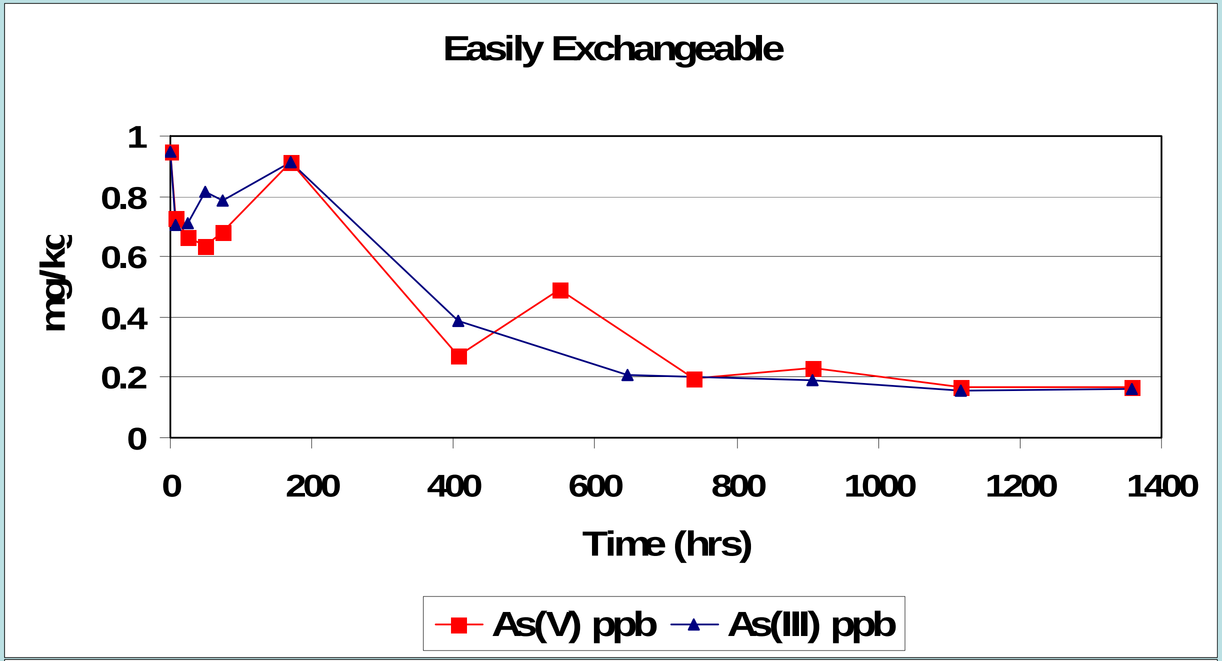
Second Order

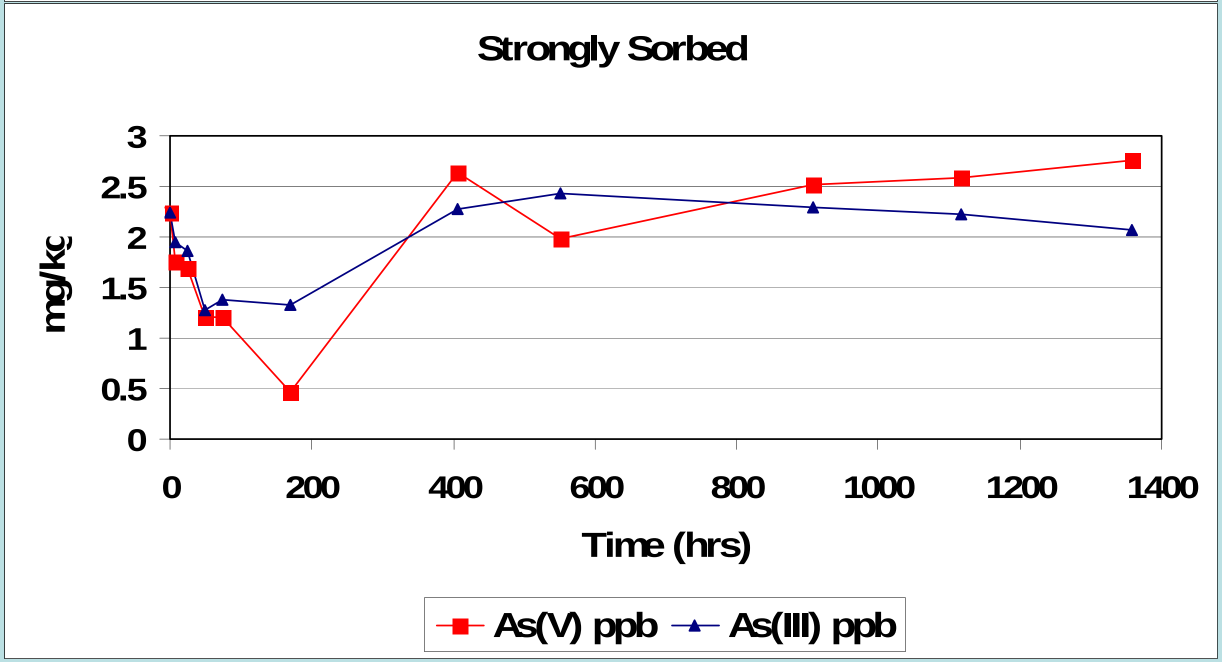
$k_{As(III)}$ $9.6x10^{4}$ –mole –hr

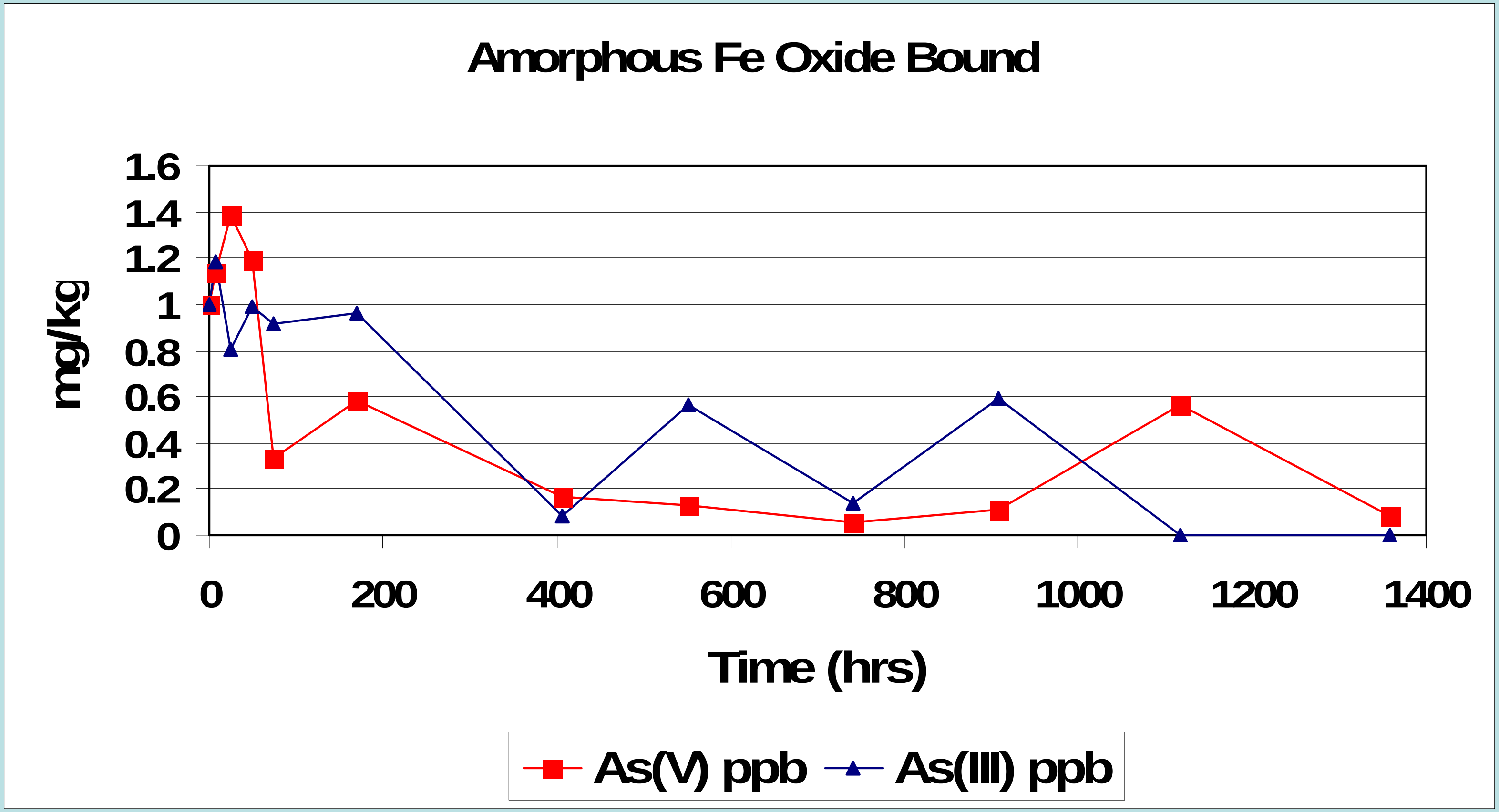
$k_{As(V)}$ $1.3x10^{5}$ –mole -hr



Translocation Revealed Through a SEP

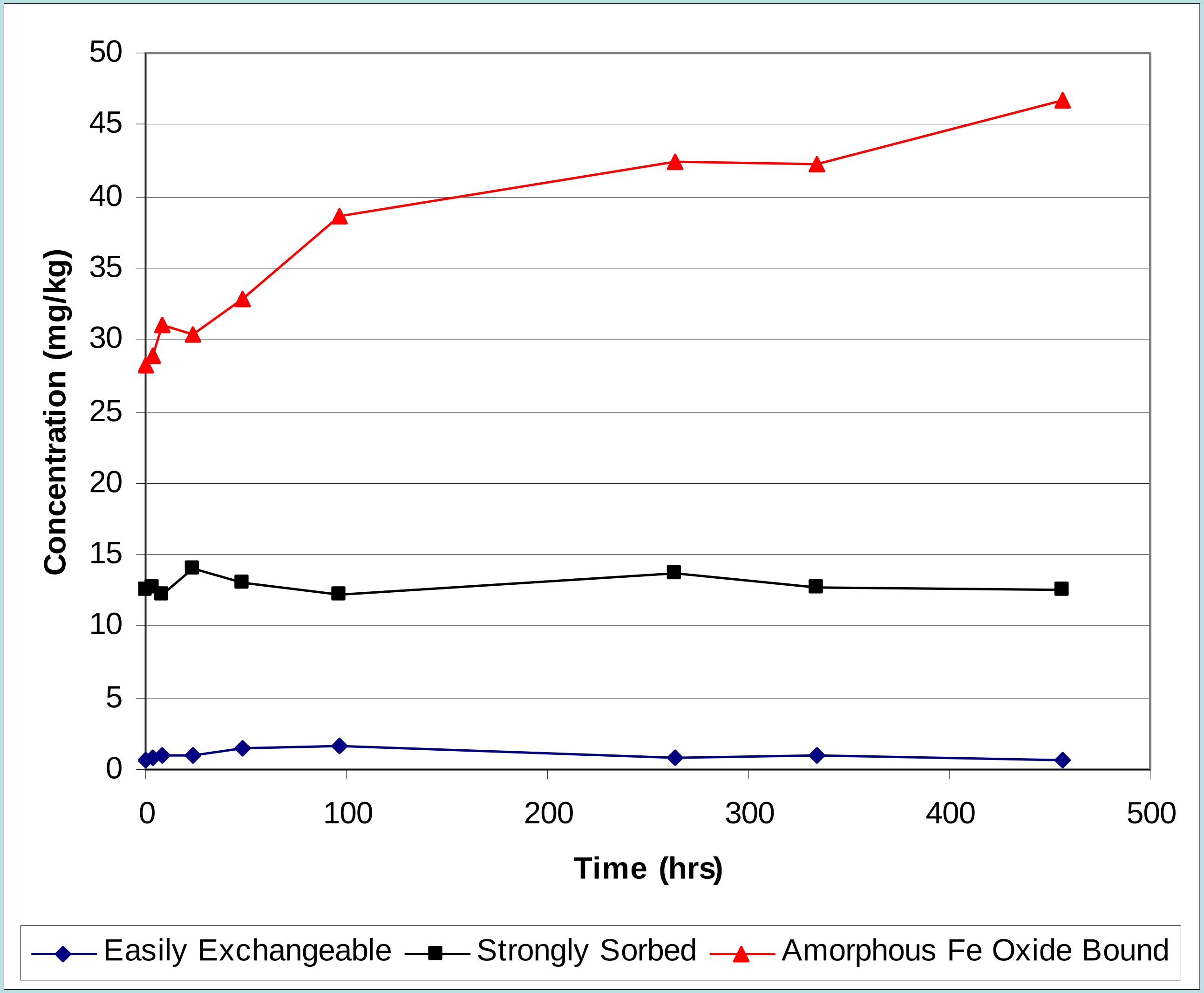






Amorphous Fe Oxide Bound
mg/kg
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
200
400
600
800
1000
1200
1400
Time (hrs)
As(V) ppb
As(III) ppb

Preliminary SEP Experiment



Environmental Applications

- Dissolved As(V) sorbs in hours, whereas dissolved As(III) remains in solution for 2 days, therefore with potential to travel further
- The easily exchangeable fraction binds As rapidly, but should be considered bioavailable as increased conductivity mobilizes it (e.g. road salt enrichment in lakes)
- After 200hrs As is strongly sorbed, but may be mobile in nutrient rich lakes

Conclusions

- Depletion kinetics – Dissolved As(V) starts depleting in less than 8hrs, but As(III) removal is delayed by 2 days, likely due to oxidation kinetics
- As(III) depletion kinetics are 1st order during the first 48hrs and 2nd order for longer periods
- As(V) depletion kinetics are 2nd order
- As rapidly binds to the weakly sorbed fraction
- Translocation of As from weakly sorbed to strongly bound appears to occur after 200hrs
- Amorphous Fe oxide binds As after 100hrs

Future Work

- Resolve analytical issues with salty matrices
- Conduct same experiment with higher As concentrations (100ppb and 300ppb) and use different substrates (possibly tailings)
- Analyse solid phases with XANES, XRD and SEM
- Validate SEP that does not alter As speciation and analyse samples for As species

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