Assessment and Disposal of Arsenic Treatment Residuals

SBRP/EPA Workshop

Feb. 28 - Mar. 01, 2005

Philosophy and Format

- Road test research
- Proactive environmental engineering
- Condense normal timeline
- Cut across conventional delineations
- Limited size
  - facilitate open discussion
  - narrow focus/broad expertise
  - solutions/directions beyond the problems

Changes and Impacts

- **2001revised arsenic in D.W. standard**
  - **10 ppb MCL (from 50 ppb)**
  - **Implementation by 2006-2012**
- **Predicted impacts**
  - **4000 new utilities impacted (>95% small)**
  - **8M lb solid residuals annually (30,000 # As /yr)**
  - **Present and future Superfund/RCRA sites**
- **Residuals hazard assessment**
  - **Toxicity characteristic leaching procedure (TCLP)**
  - **Waste extraction test (WET)**

Next Steps for As Residuals

S1. Simulate landfills/repositories to determine appropriate performance bar

S2. Develop tractable protocols based on engineering critical leaching mechanisms to clear bar

S3. Evaluate (technically & economically) treatment options, including stabilization, alternative sorbents, etc.

S4. Develop and evaluate hybrid (conventional & innovative) disposal options

Test/Landfill Characteristics

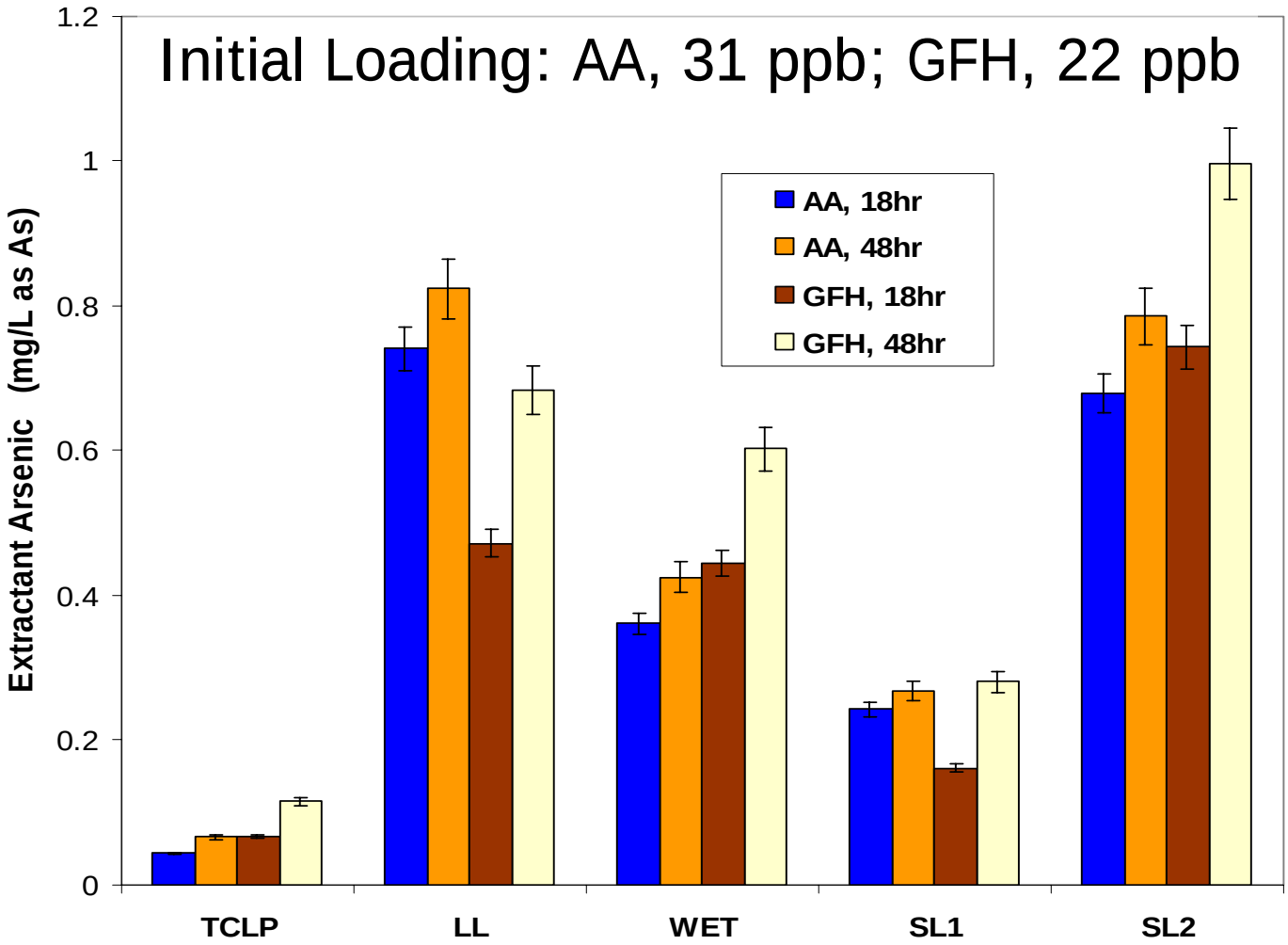
Test	pH	ORP (mV)	Alkalinity (mg/L as $CaCO_3$)	TOC (mg/L)	TDS (mg/L)	Ionic Strength (M)
TCLP	4.95	103.5	766	38.6	1480	0.08
WET	5.05	74	7940	55.8	5160	0.10
SL1	7.03	121.4	1500	1050	5200	0.03
SL2	7.55	-37	12500	1310	8600	0.49
LL[1]	6.82	36.1	1100	160	3600	0.33
LL[2]	4.5-9.0	N/R*	300-11500	30-29000	2000-60000	N/R
LL[3]	6.5-8.2	N/R	1250-8050	N/R	1960-16800	N/R
LL[4]	6.2-7.1	N/R	N/R	236-3160	N/R	N/R

N/R* - Values Not Reported
LL[1] – Leachate collected from Tangerine Road Landfill, Tucson, AZ.
LL[2] – Leachate composition reported in Christensen et al, 2001 (21)
LL[3] – Leachate composition reported in Jang et al, 2003. (22)
LL[4] – Leachate composition reported in Hooper et al, 1998. (5)

Our Corollary Research

- **Treatment systems evaluation (IHS funding)**
- **Removal technology development (State of AZ/ SBRP)**
- **Residuals assessment (SBRP/AZ State funding)**
  - **Adequacy of TCLP and WET**
  - **What is adequate?**
  - **Alternative test development**
  - **Other contaminants and scenarios**
- **Residuals stabilization (SBRP/AWWARF/AZ State funding)**

Solid Media Leaching



Residuals Assessment Tests

Guiding Premise: test induces leaching as or more aggressively than conditions of non-hazardous waste disposal

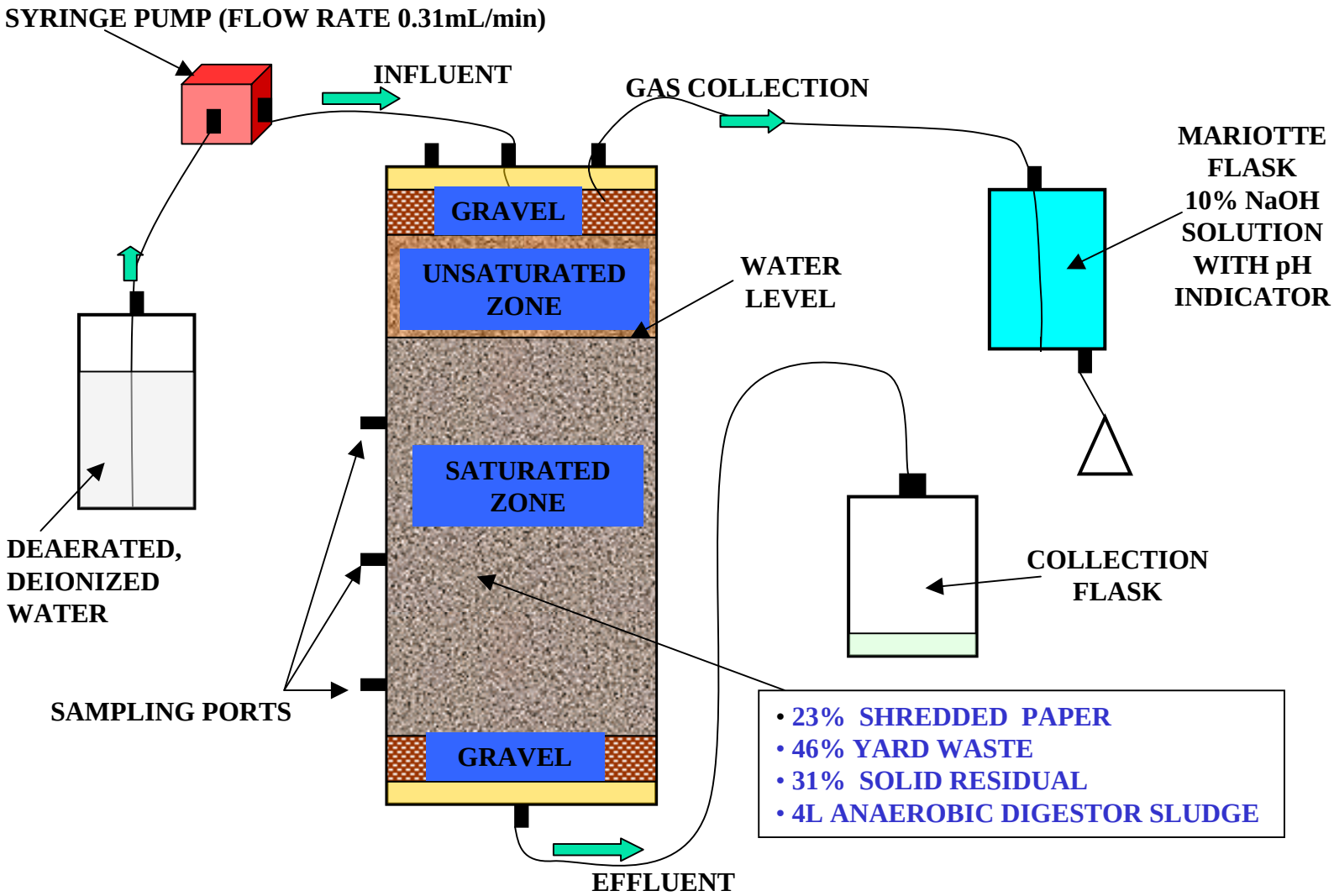
	TCLP	WET	Mature Landfill
pH	4.95	5.05	7-9
Bioactivity	abiotic	abiotic	biotic
Duration	18 hr	48hr	weeks/months
Active Reagent	acetate	citrate	Mix of organics & inorganics
Redox Condition	oxidizing	neutral	reducing

Immediate Findings

- **TCLP vs. WET Variables (batch test mode)**
  - **agitation method (tumbler (T) > shaker (W))**
  - **headspace (N_2 (W) > air (T))**
  - **duration (48 hr (W) > 18 hr (T))**
  - **reagent (citrate (W) > acetate (T))**
- **Landfill vs. Standard Variables (batch test mode)**
  - **pH (6.8 (LL) > ~5 (T&W))**
  - **TOC (above 160 ppm (LL) > below 60 ppm (T&W))**
  - **ORP (below 50 mV (LL) > above 50 mV (T&W))**
- **Study limitations**
  - **batch vs. continuous flow**
  - **abiotic vs. biotic**
  - **excess (non-reactive) vs. limiting (reactive) substrate**

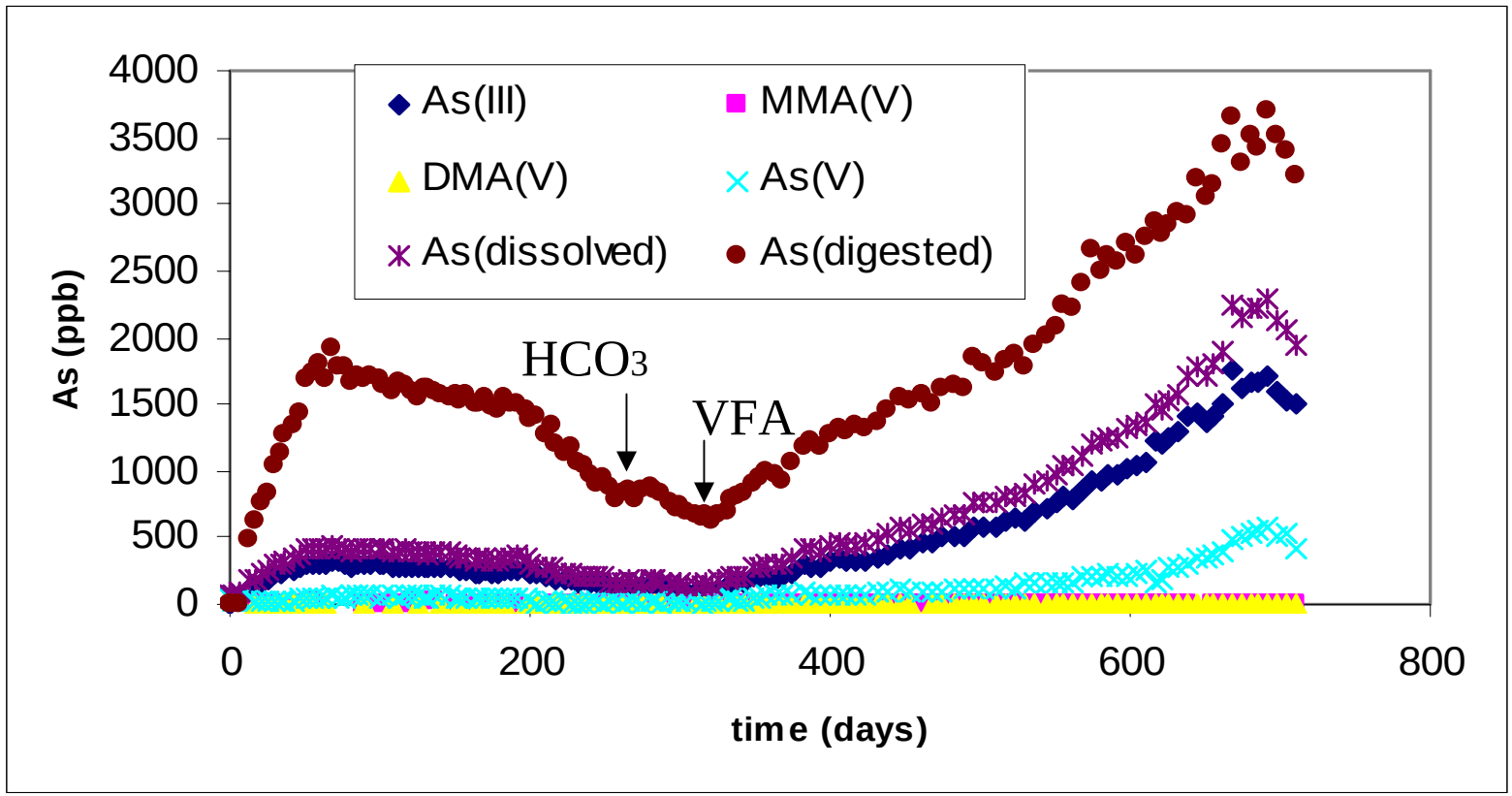
S1. Setting the bar

Landfill Simulation Columns



S1. Setting the bar

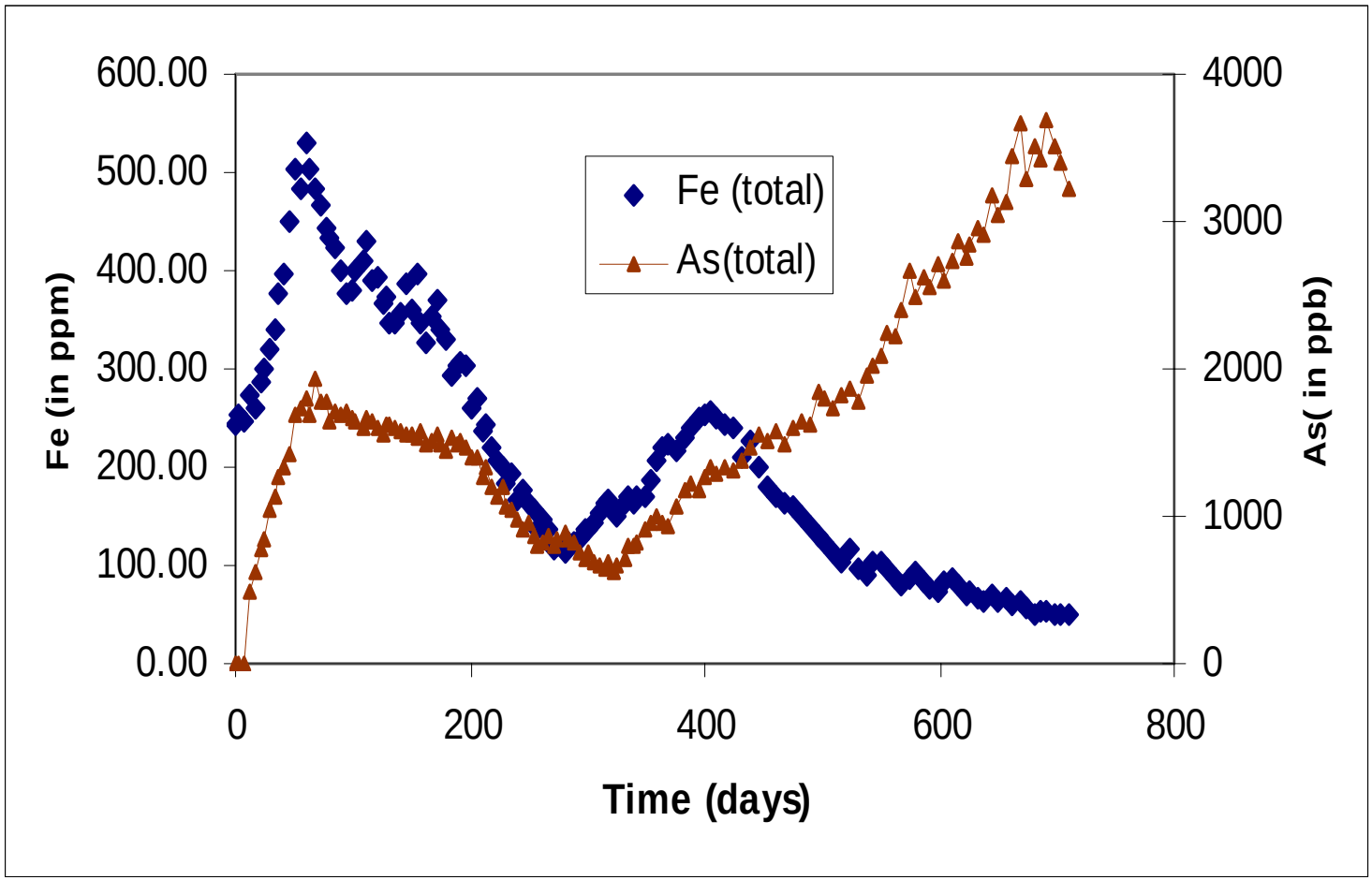
GFH Column Leachate



Equilibrium As Concentration : 25.66ppb

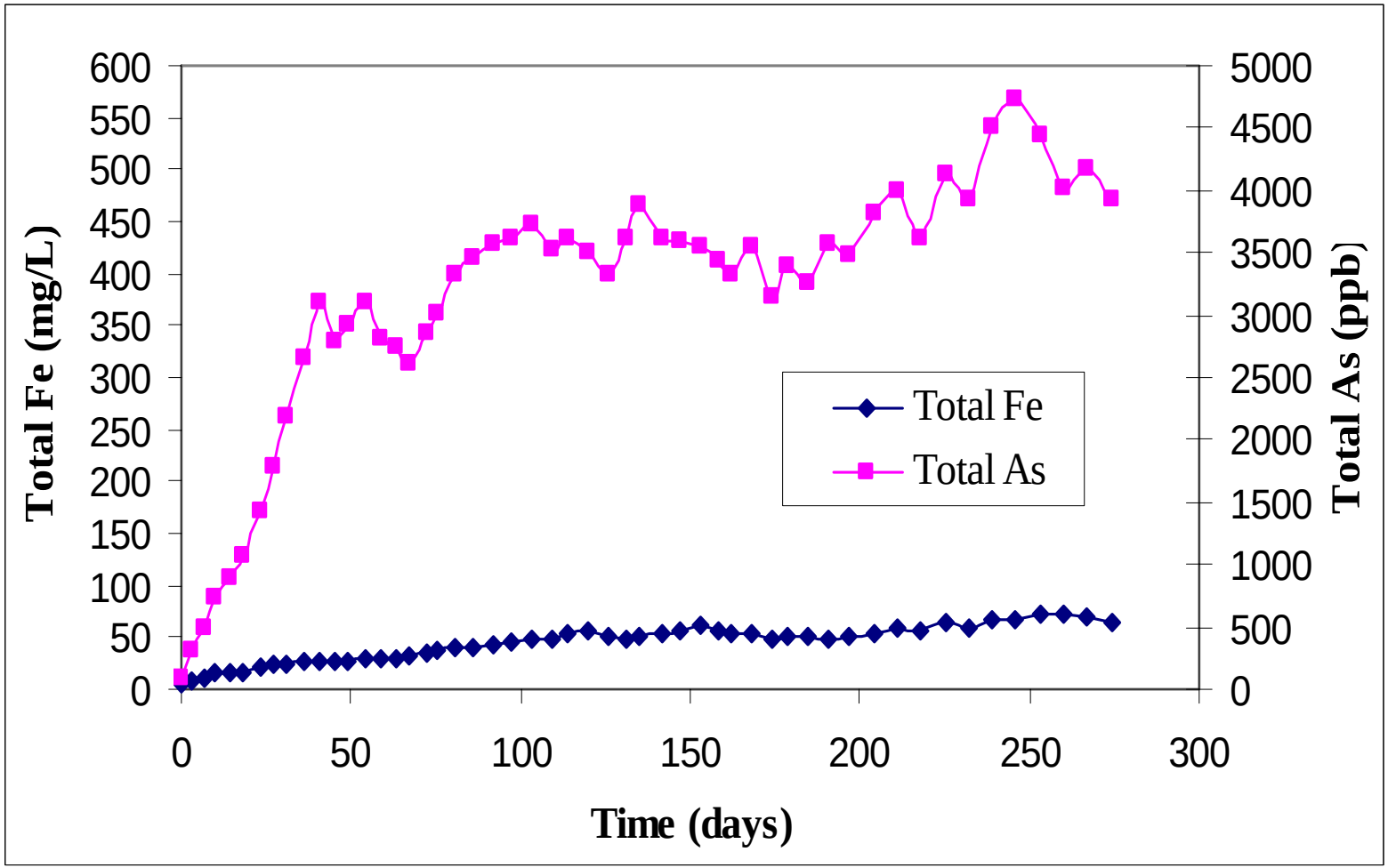
S1. Setting the bar

GFH Column Leachate



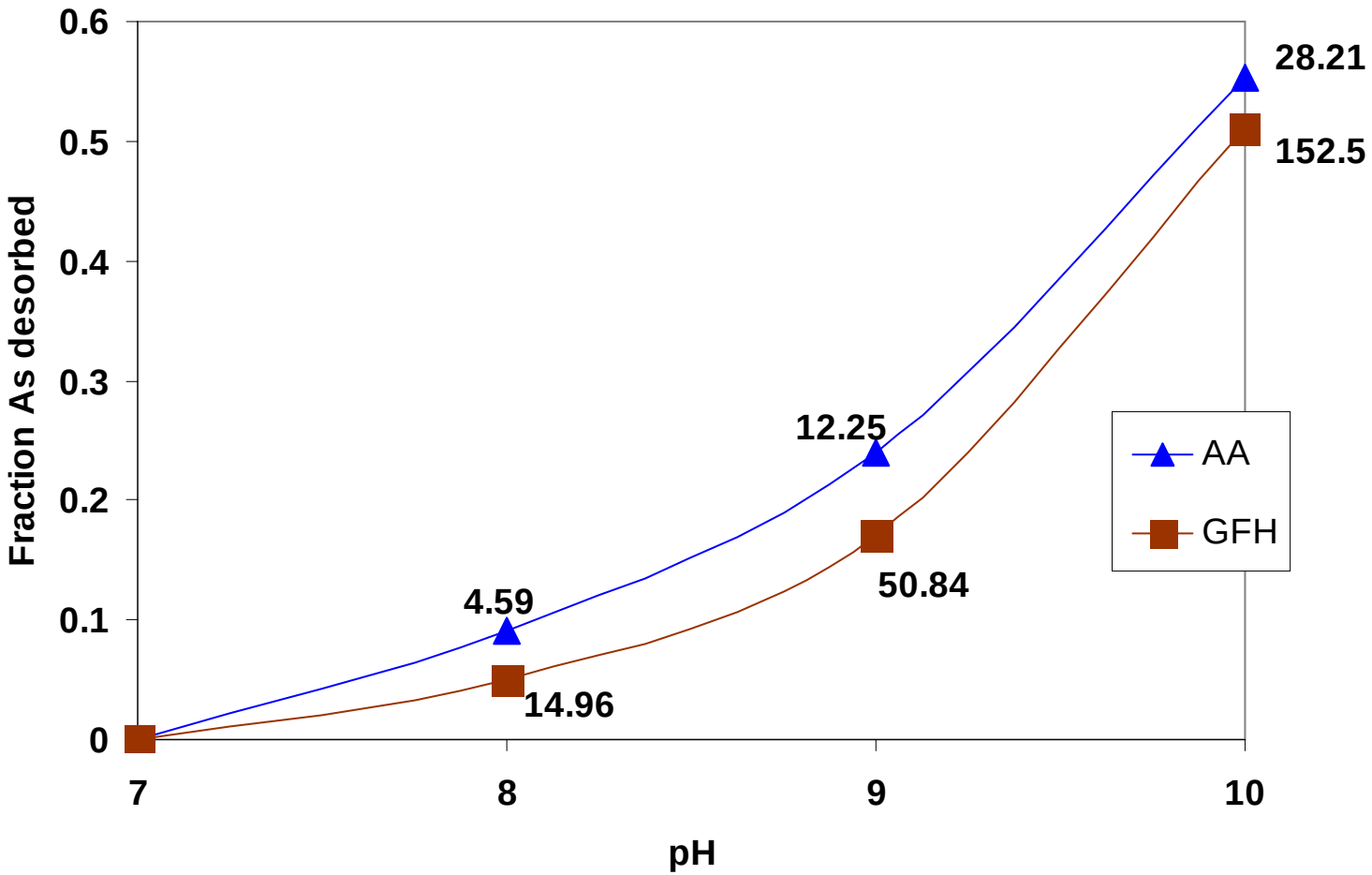
S1. Setting the bar

Sorb-33 Column Leachate



S2. New Protocol Development

pH Effects



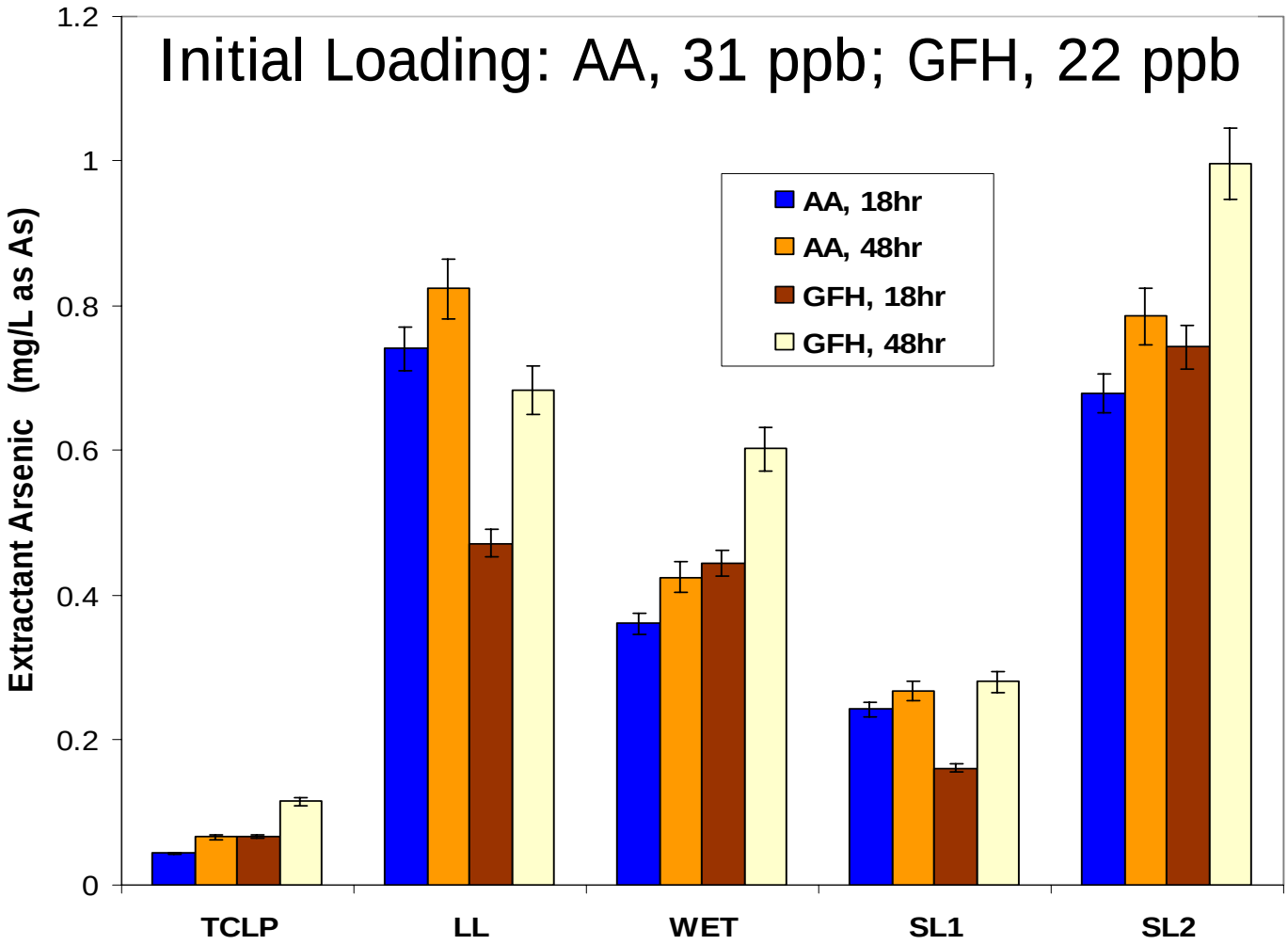
S2. New Protocol Development

Anion's Effects

Anion	Landfill Leachate Range (in mg/L) (Bagchi, 1994)	Concentration Used in Competition Trials (in mg/L)	Fraction As expected to leach due to concentration of anion in LL	Fraction of total leaching attributable to each anion in the SLL-theo
Activated Alumina				
Phosphate	0.11- 234	20	0.002	0.04
Bicarbonate	34- 15,050	1,200	0.008	0.15
Sulfate	105- 4,900	500	0.002	0.04
Silicate	5.1-51	10	0.001	0.02
NOM	76-40,000	200	0.04	0.75
Granular Ferric Hydroxide				
Phosphate	0.11- 234	20	0.0007	0.03
Bicarbonate	34- 15,050	1,200	0.012	0.48
Sulfate	105- 4,900	500	0.0008	0.03
Silicate	5.1-51	10	0.0013	0.05
NOM	76-40,000	200	0.01	0.4

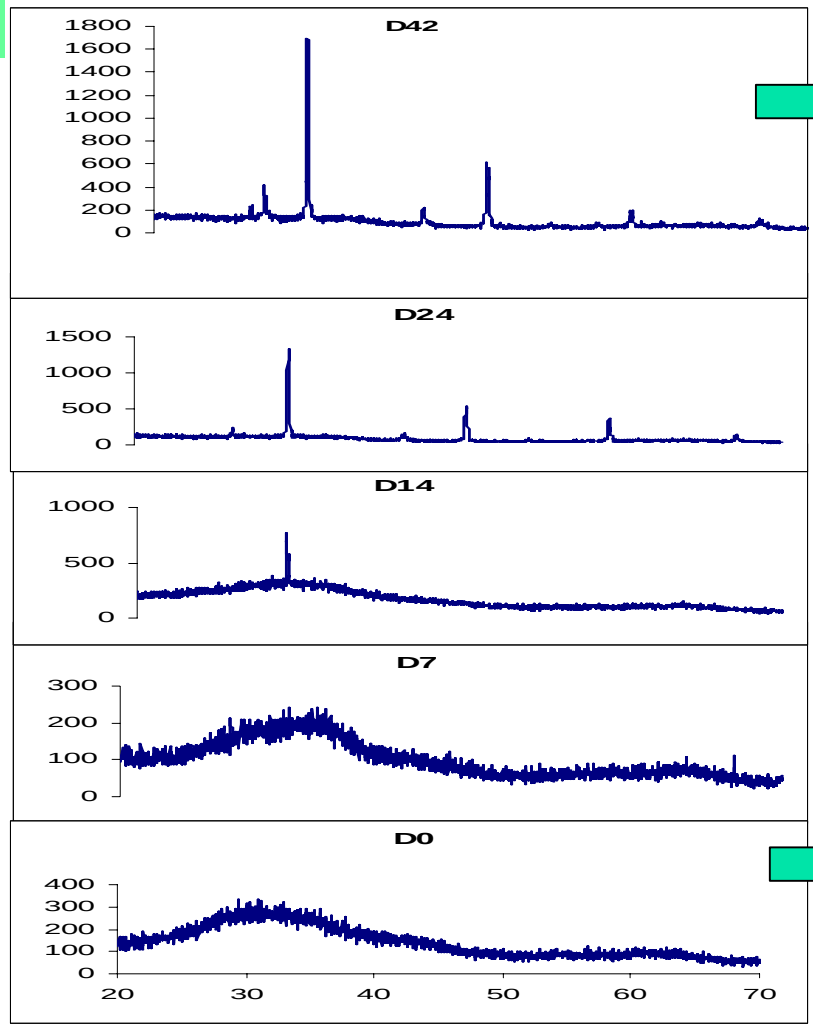
S2. New Protocol Development

Reductant + TOC Effect



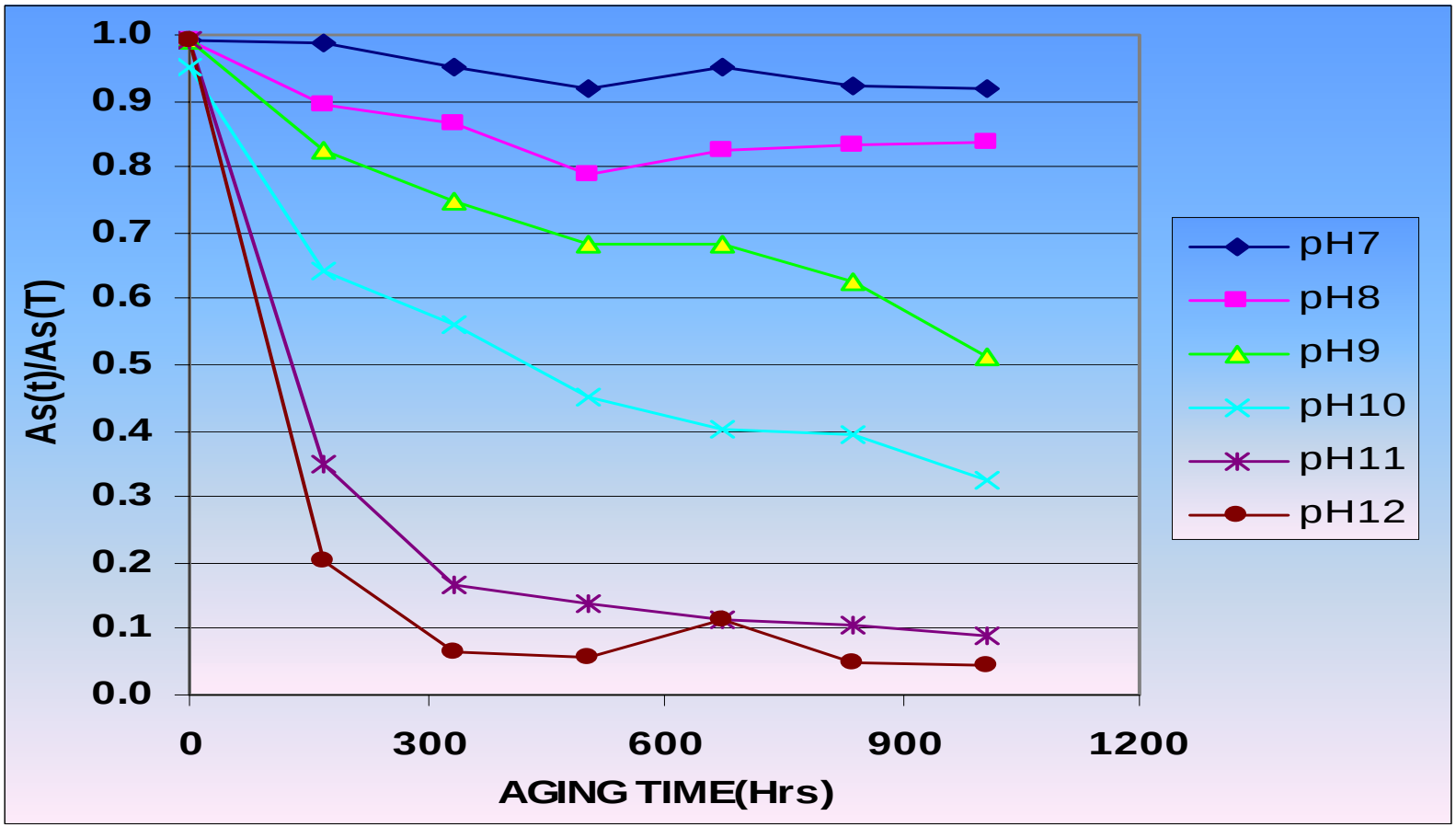
S3. Treatment & Stabilization Options

AFH Crystallization



S3. Treatment & Stabilization Options

As Release & Crystallization

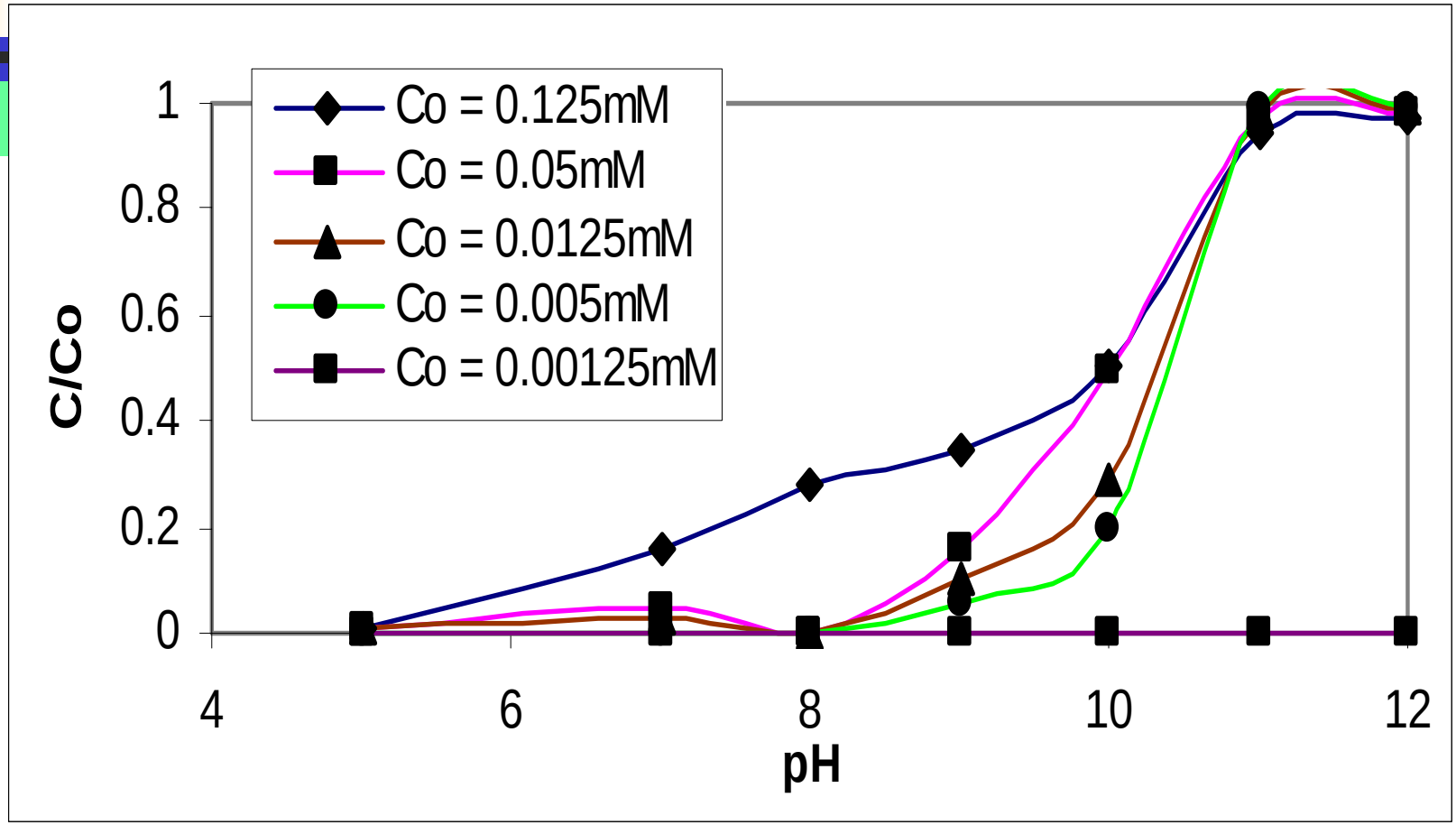


Broader Implications

- **Arsenic as an elemental contaminant**
  - **no destructive technologies**
  - **media and speciation transformations only**
  - **surrogate for heavy metals, metalloids, radionuclides**
- **Arsenic as a redox-sensitive, oxyanion**
  - **inverse pH behavior to metals**
  - **microbially mediated fate and transport**
  - **typically most mobile in reduced form**
  - **surrogate for V, Mo, Se, S, Cl, N, P**
- **Arsenic as a 'natural' contaminant**
  - **primarily non-anthropogenic sources**
  - **naturally diffuse but anthropogenically concentrated**
  - **surrogate for Rn, U, Se, S, F, Br, V**

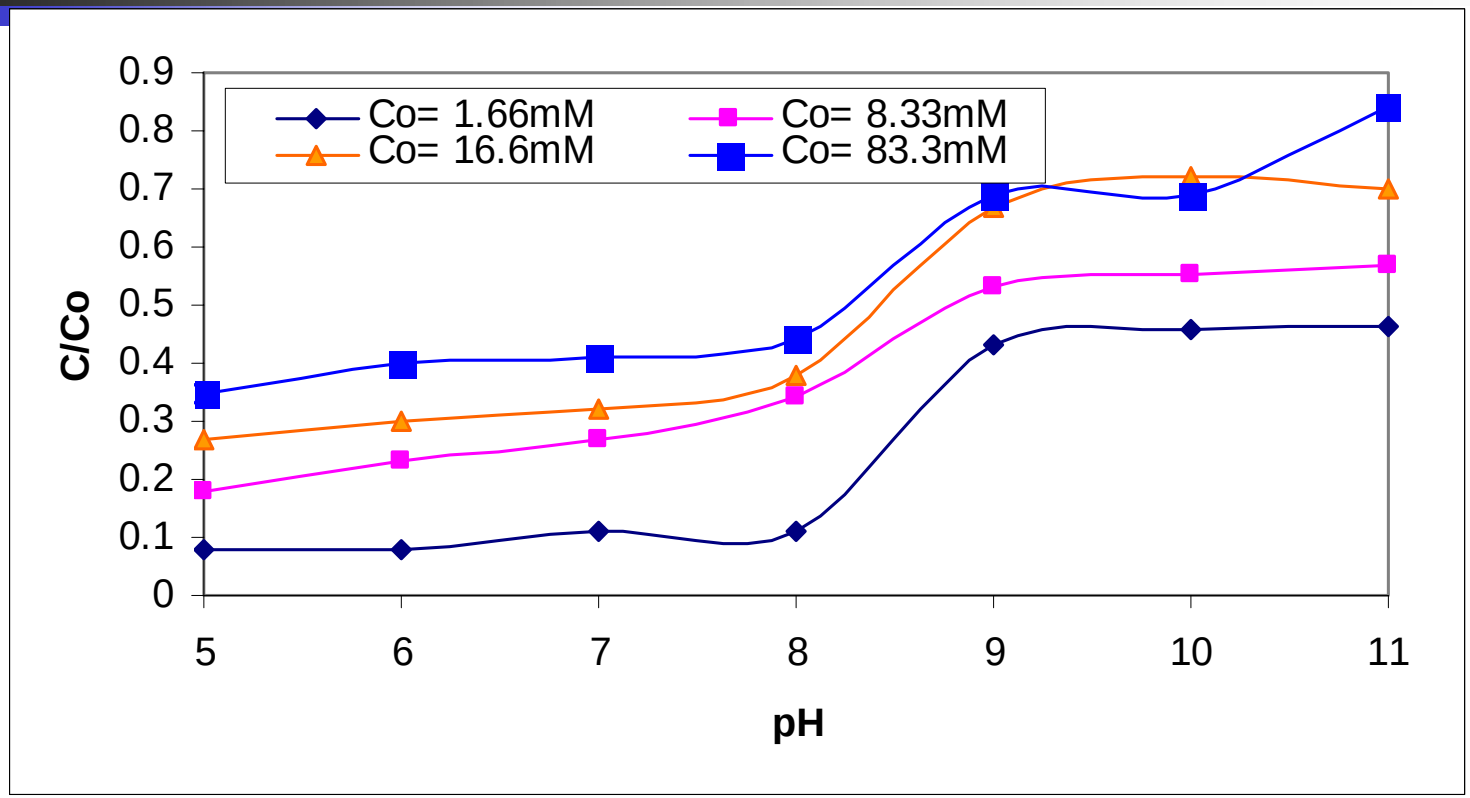
Batch Adsorption Experiments

AA Adsorption Edge



- Co - Initial arsenic concentration in solution
- C - Equilibrium arsenic concentration in solution

GFH Adsorption Edge



Co = Initial concentration of As in solution (total As in the system)

C = Concentration of As in solution at equilibrium

Solid Loading = 25g/L

Comparative Leaching Tests

TABLE 1. Characteristics of the Synthetic Extractants and Landfill Leachates

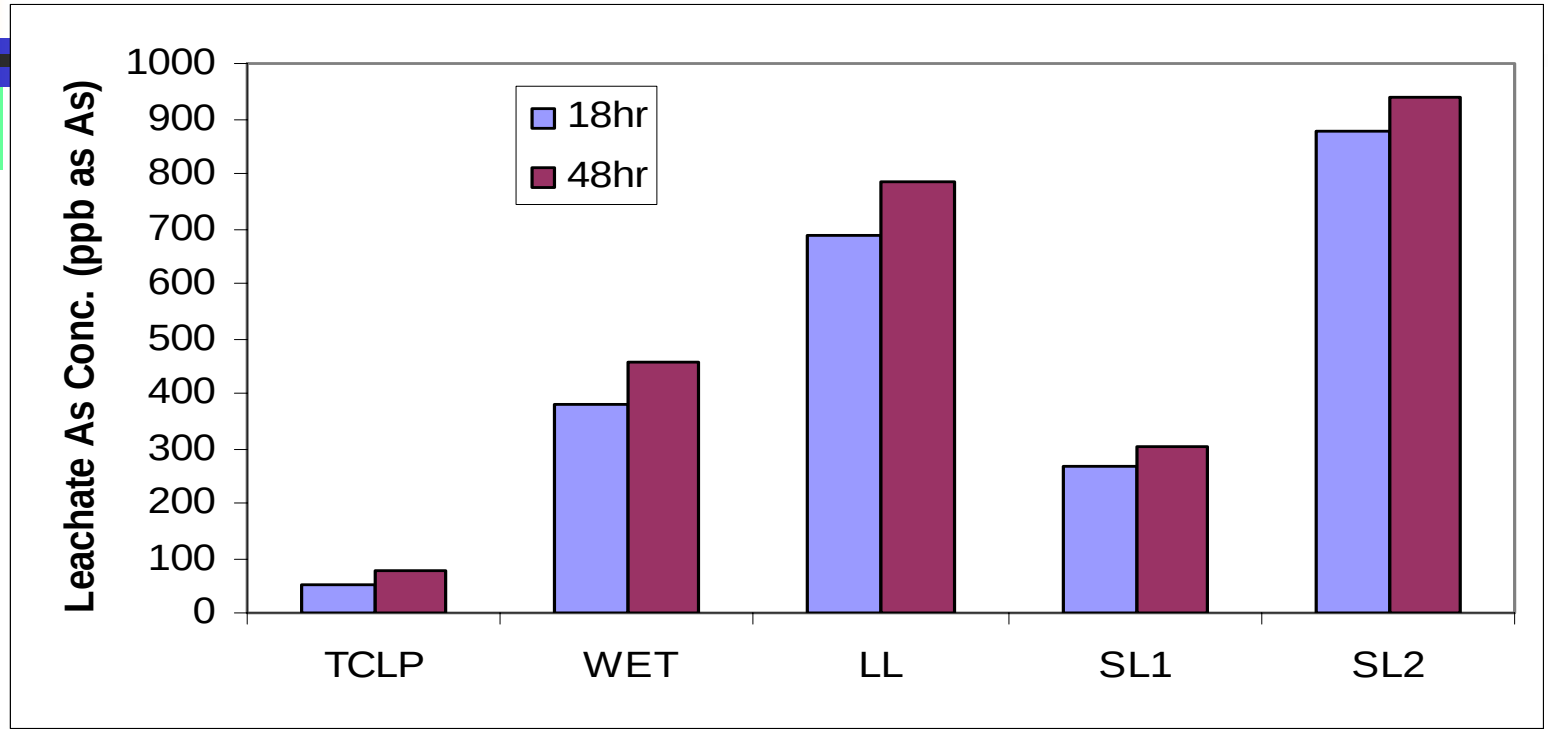
test	pH	ORP (mV)	alkalinity (mg/L as $CaCO_3$)	TOC (mg/L)	TDS (mg/L)	ionic strength (M)
TCLP	4.95	103.5	766	38.6	1480	0.08
WET	5.05	74	7940	55.8	5160	0.10
SL1	7.03	121.4	1500	1050	5200	0.03
SL2	7.55	−37	12 500	1310	8600	0.49
LL[1]	6.82	36.1	1100	160	3600	0.33
LL[2]	4.5−9.0	N/R*	300−11 500	30−29000	2000−60000	N/R
LL[3]	6.5−8.2	N/R	1250−8050	N/R	1960−16800	N/R
LL[4]	6.2−7.1	N/R	N/R	236−3160	N/R	N/R

N/R*: Values Not Reported. LL[1]: Leachate collected from Tangerine Road Landfill, Tucson, AZ. LL[2]: Leachate composition reported in Christensen et al., (*21*). LL[3]: Leachate composition reported in Jang et al. (*22*). LL[4]: Leachate composition reported in Hooper et al. (*5*).

TABLE 2. Composition of Simulated Leachate 1 (SL1) and Simulated Leachate 2 (SL2). the VFA Mixture in SL2 Is Identical to that in SL1

SL1	concentration (mg/L)
acetic acid	576
propionic acid	192
butyric acid	422
valeric acid	163
caproic acid	232
ammonium chloride	2680
sodium bicarbonate	2520
TOC	1050
pH	7.0
SL2	
calcium carbonate	1100
sodium carbonate	11 500
ammonium chloride	650
TOC (VFA mixture)	1310
sodium citrate	46 400
hydroxylamine hydrochloride	31.7
pH	7.5

Activated Alumina

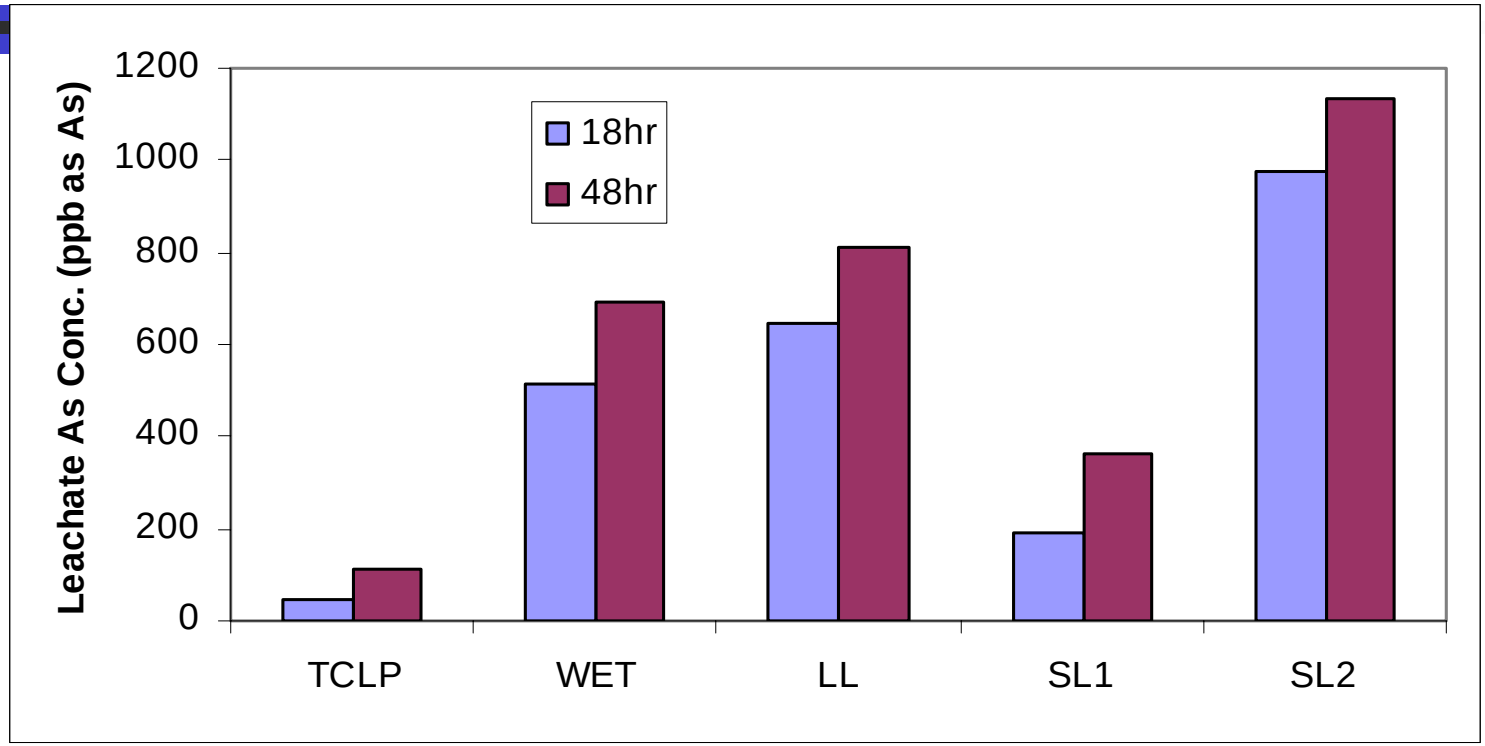


Concentration of As in solution at equilibrium prior to leaching tests = 21.8ppb

Sorbed concentration of As = 1.27mgAs/gAA.

Test conditions: No N2 headspace, end-over-end tumbler.

Granular Ferric Hydroxide

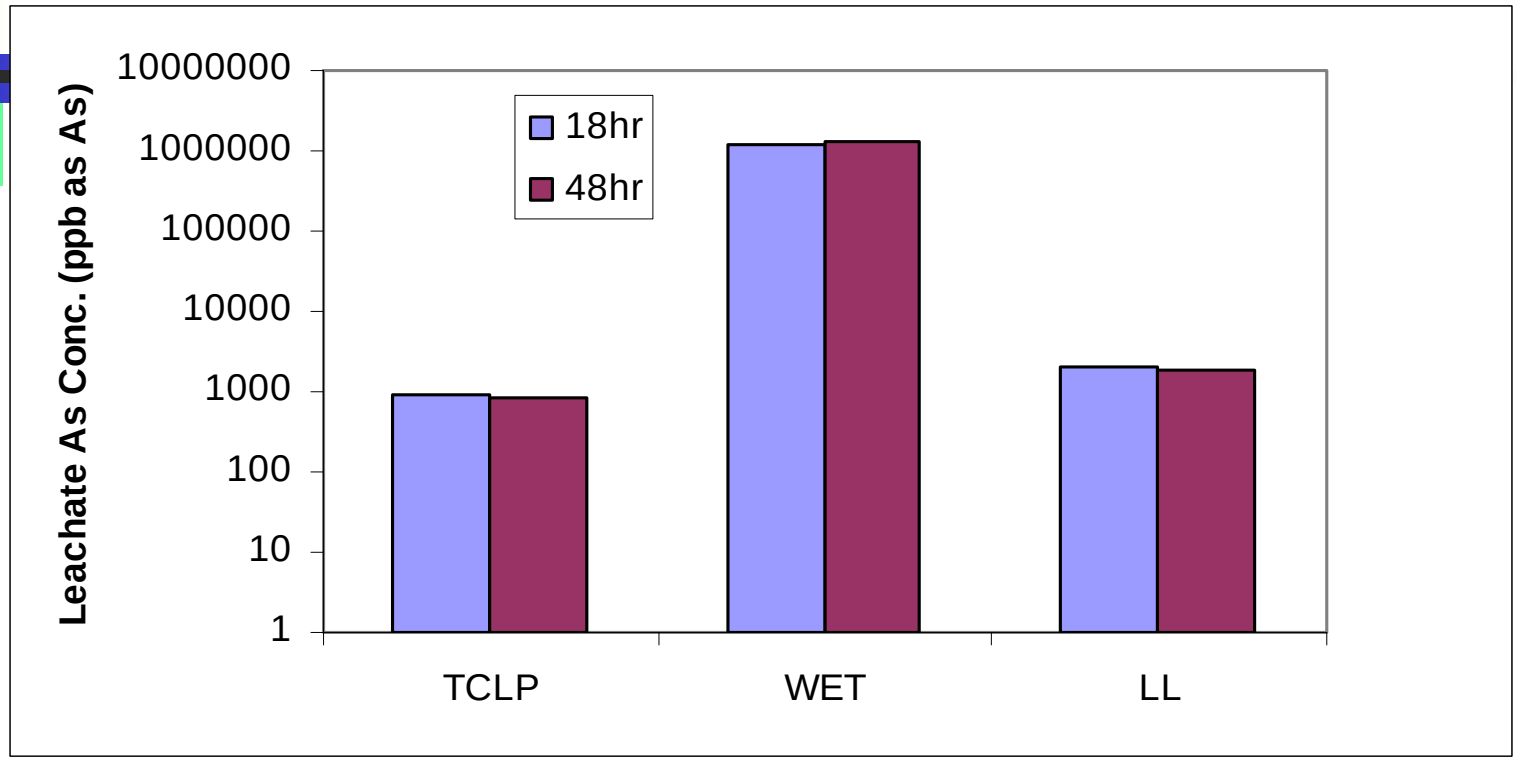


Concentration of As in solution at equilibrium prior to leaching tests = 31ppb

Sorbed concentration of As = 7.2mgAs/gGFH.

Test conditions: No N2 headspace, end-over-end tumbler.

Ferric Hydroxide Sludge



Concentration of As in solution at equilibrium prior to leaching tests = 1040ppb

Sorbed concentration of As = 20.3mgAs/gFe.

Test conditions: No N2 headspace, end-over-end tumbler.

Competitive Anion Effects

Activated Alumina Anion Effect

Anion	(Moles As released/ mole anion)high		(Moles As released/ mole anion)low		(Moles As released/ mole anion)average		Fraction sorbed As expected to leach due to concentration of anion in LL
	pH7	pH9	pH7	pH9	pH7	pH9	
Phosphate	279	113	3.05	1.52	9.24	4.69	0.002
Bicarbonate	0.92	0.58	0.014	0.007	0.043	0.025	0.008
Sulfate	0.352	0.143	0.017	0.014	0.045	0.028	0.002
Silicate	12	8.6	0.56	0.68	2.6	2	0.001
NOM	391	336	0.41	0.23	2.35	1.13	0.04

GFH Anion Effect

Anion	(Moles As released/ mole anion)high		(Moles As released/ mole anion)low		(Moles As released/ mole anion)average		Fraction sorbed As expected to leach due to concentration of anion in LL
	pH7	pH9	pH7	pH9	pH7	pH9	
Phosphate	357	244	4.02	2.09	10.5	6.07	0.0007
Bicarbonate	8	4	0.027	0.023	0.24	0.11	0.012
Sulfate	0.698	0.458	0.021	0.005	0.098	0.054	0.0008
Silicate	32	21	2.1	0.62	5.4	3.7	0.0013
NOM	1064	374	0.7	0.19	3.9	0.97	0.01

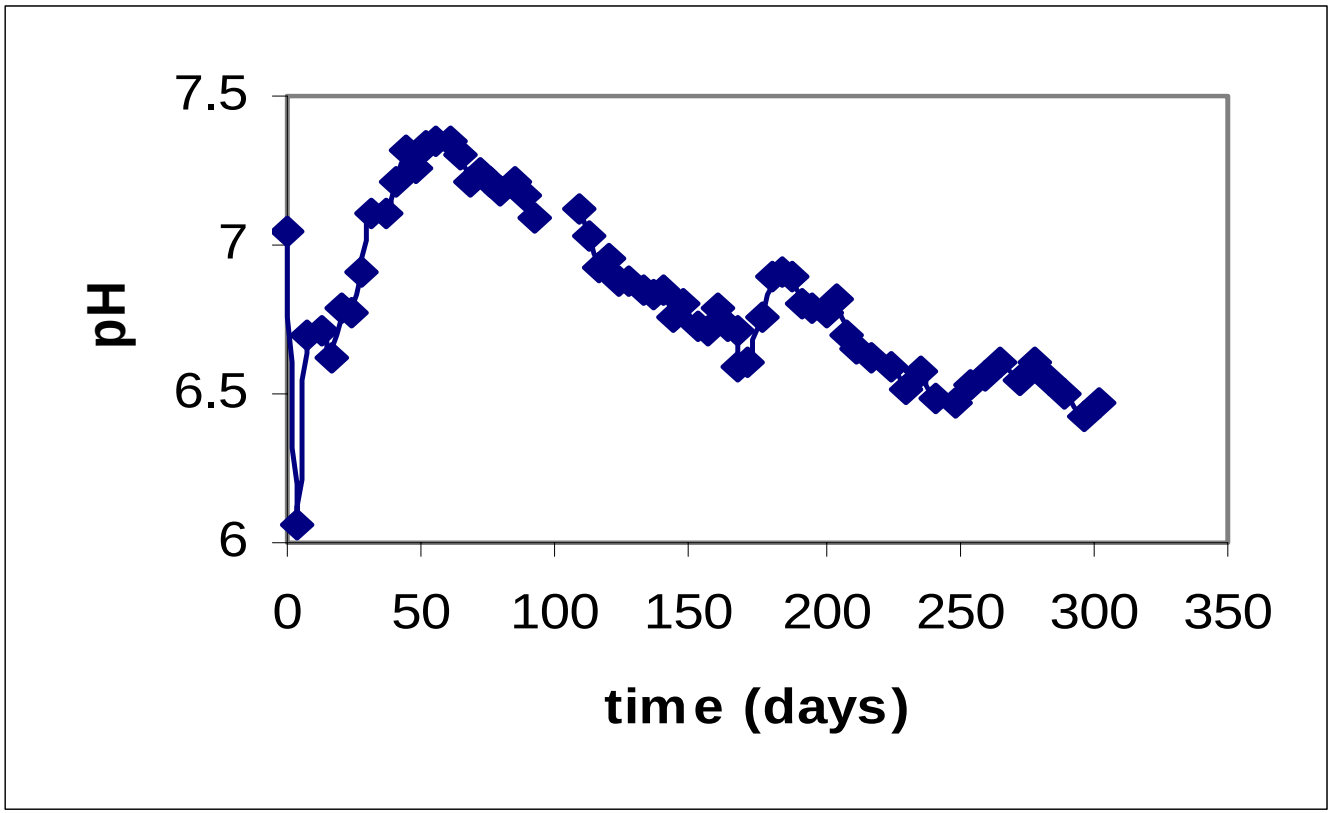
Column Experiment Methods

Column Packing Composition

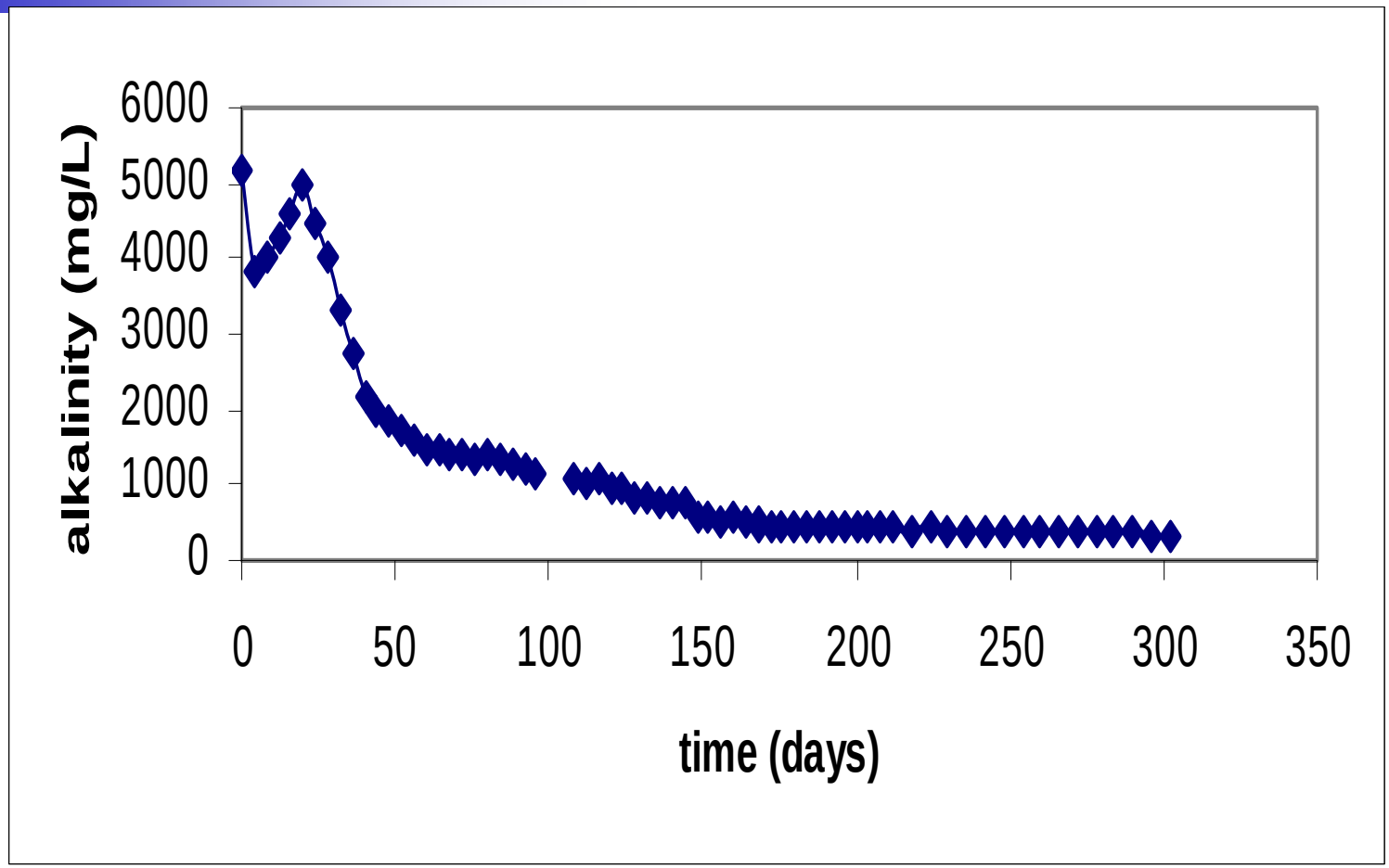
Specifications	Activated Alumina	GFH	E-33
Mass of Residual	1017g	527g	509g
Total Amount of As	1.29g	2.86g	2.61g
Initial Sorbed As Conc.	1.27mgAs/gAA	5.42mgAs/gGFH	5.13mgAs/gE33
Initial equilibrium As conc.	193ppb	25.6ppb	11ppb
Duration of run	302 days	808 days	274 days

Activated Alumina Column

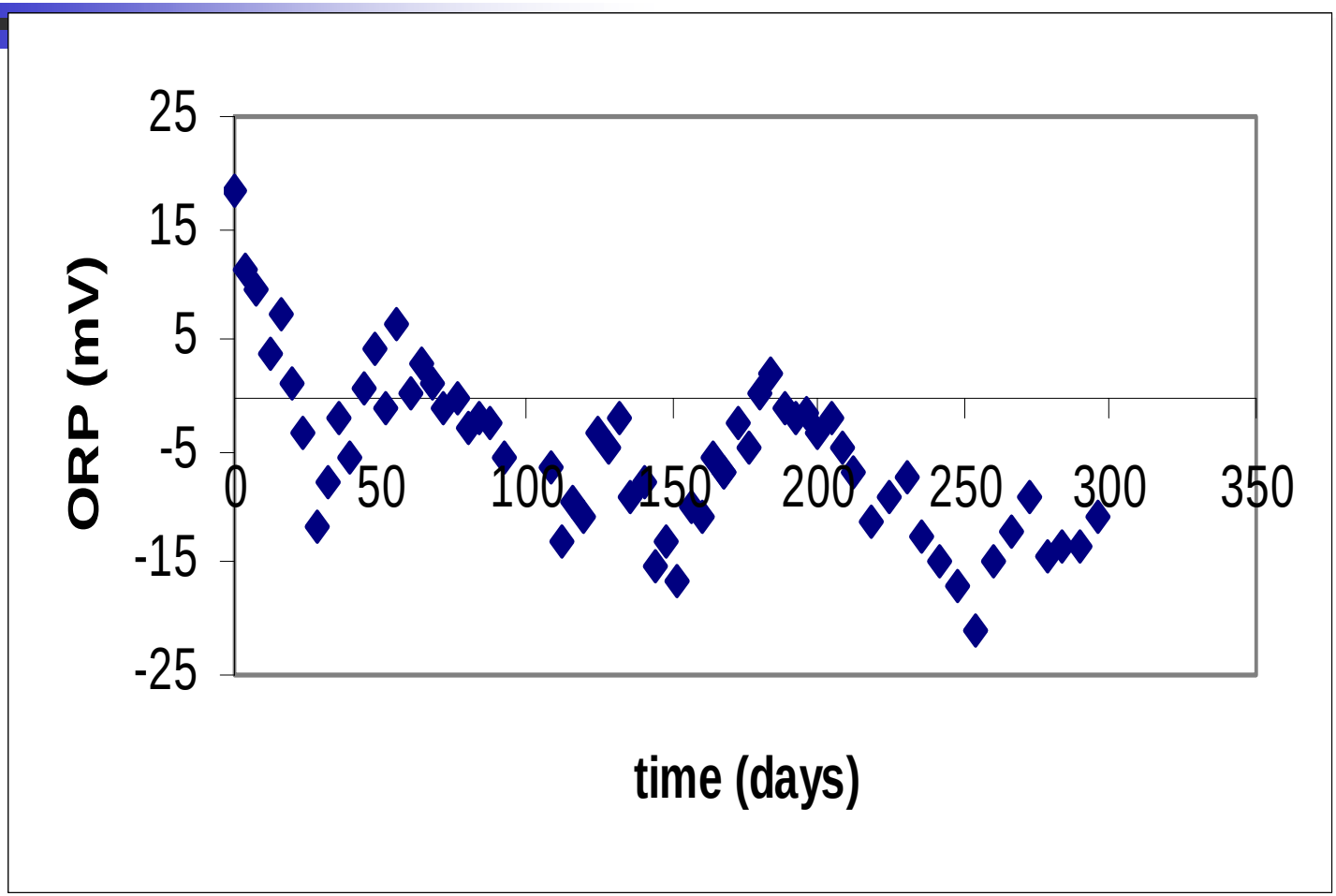
pH



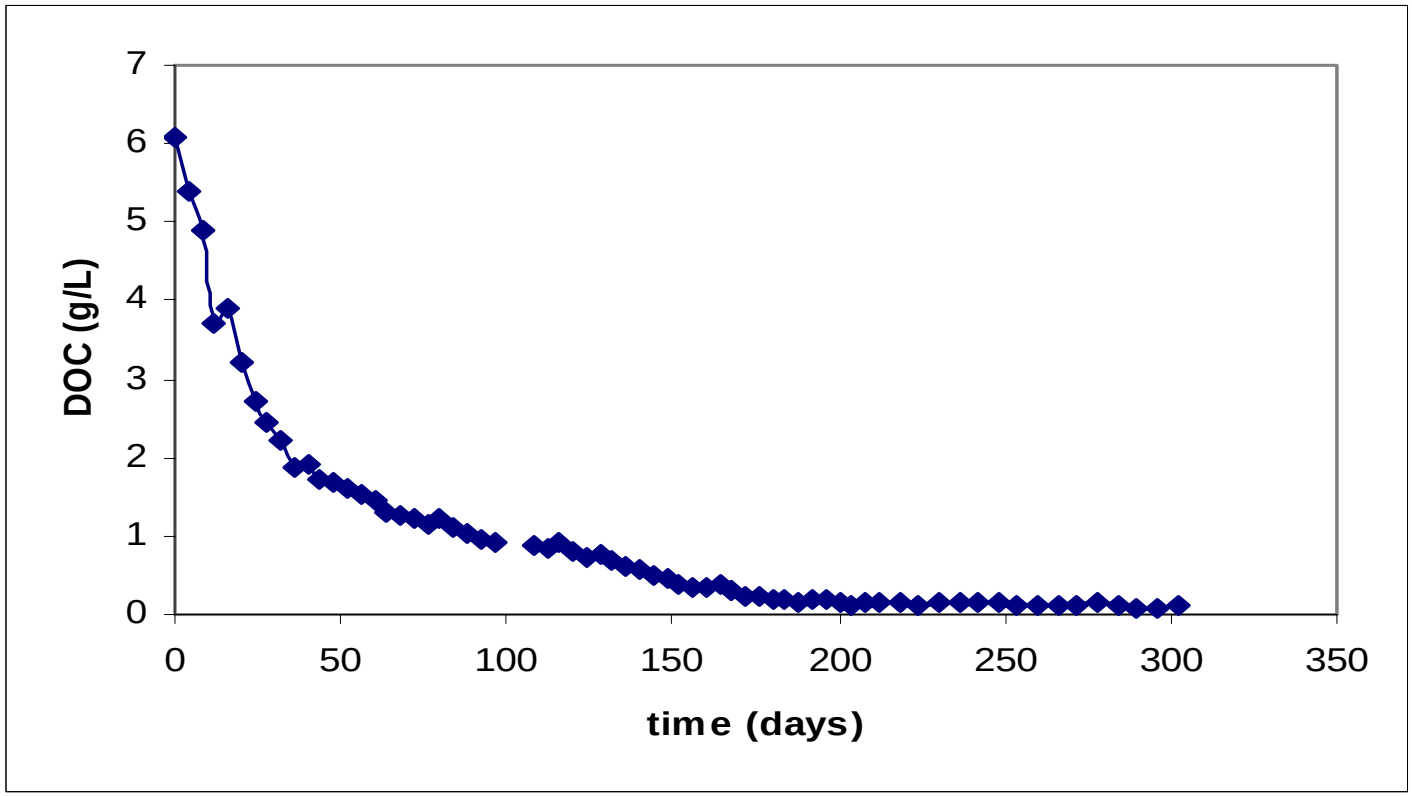
Alkalinity


alkalinity (mg/L)
6000
5000
4000
3000
2000
1000
0
0
50
100
150
200
250
300
350
time (days)

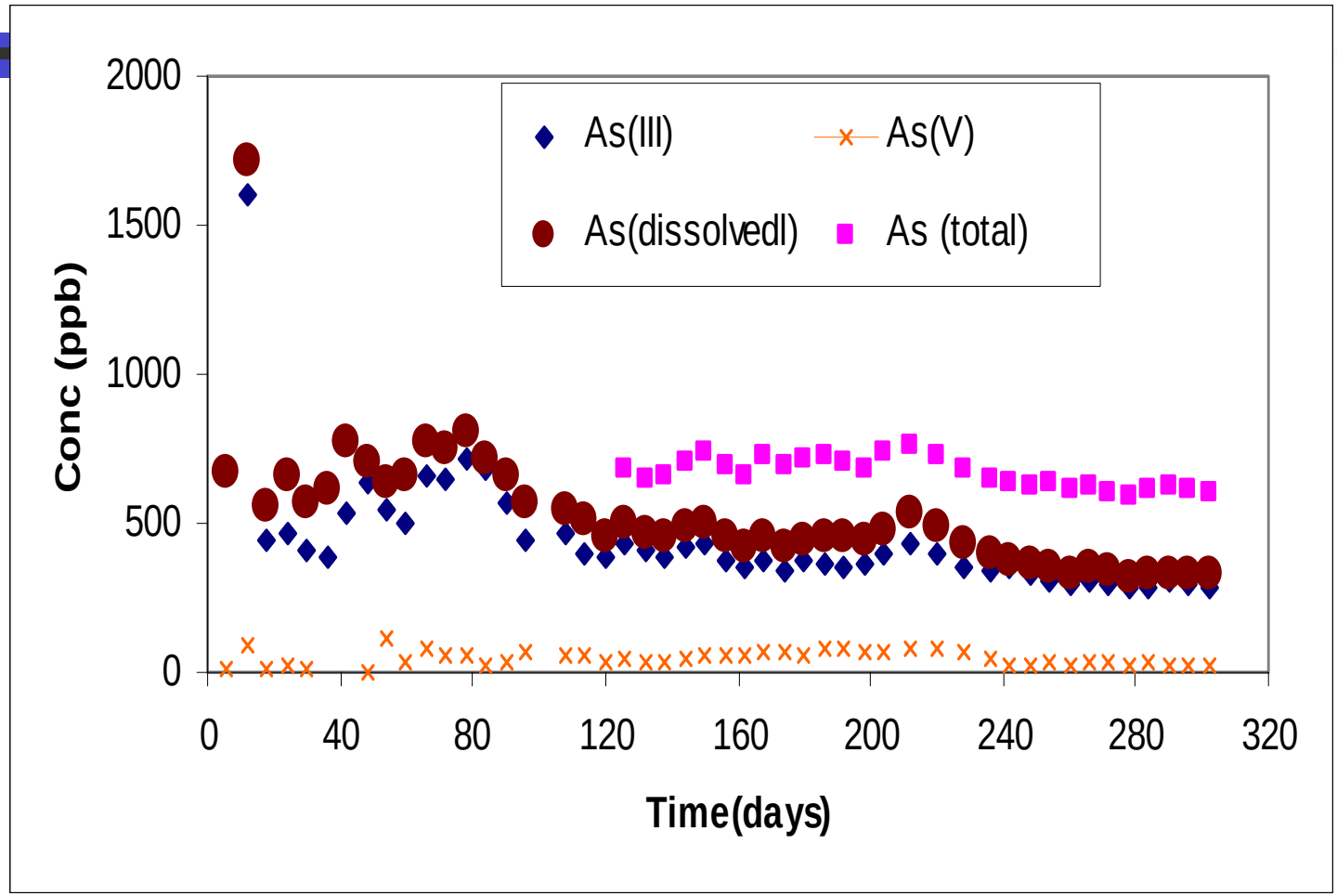
ORP



DOC

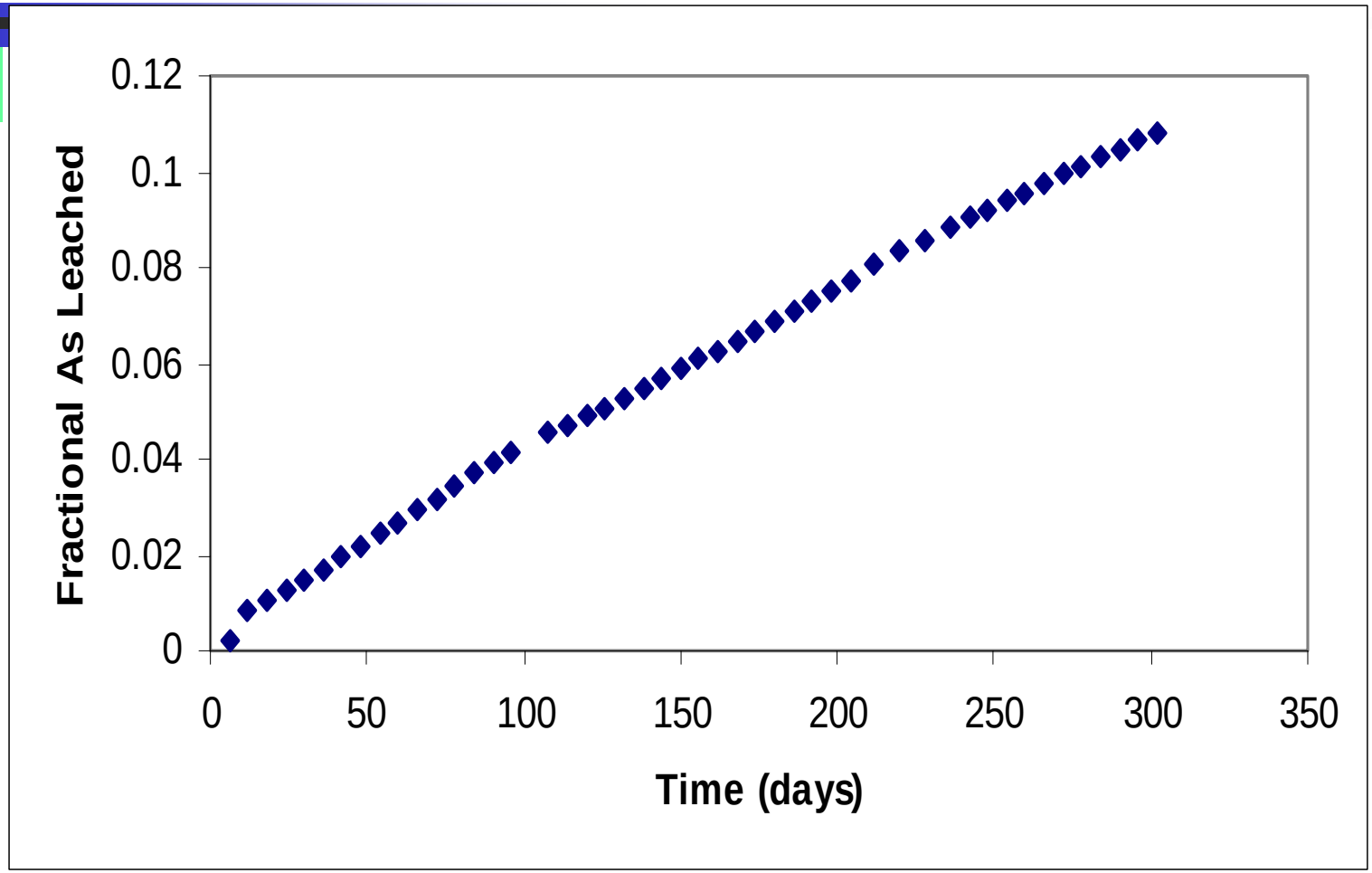


Arsenic



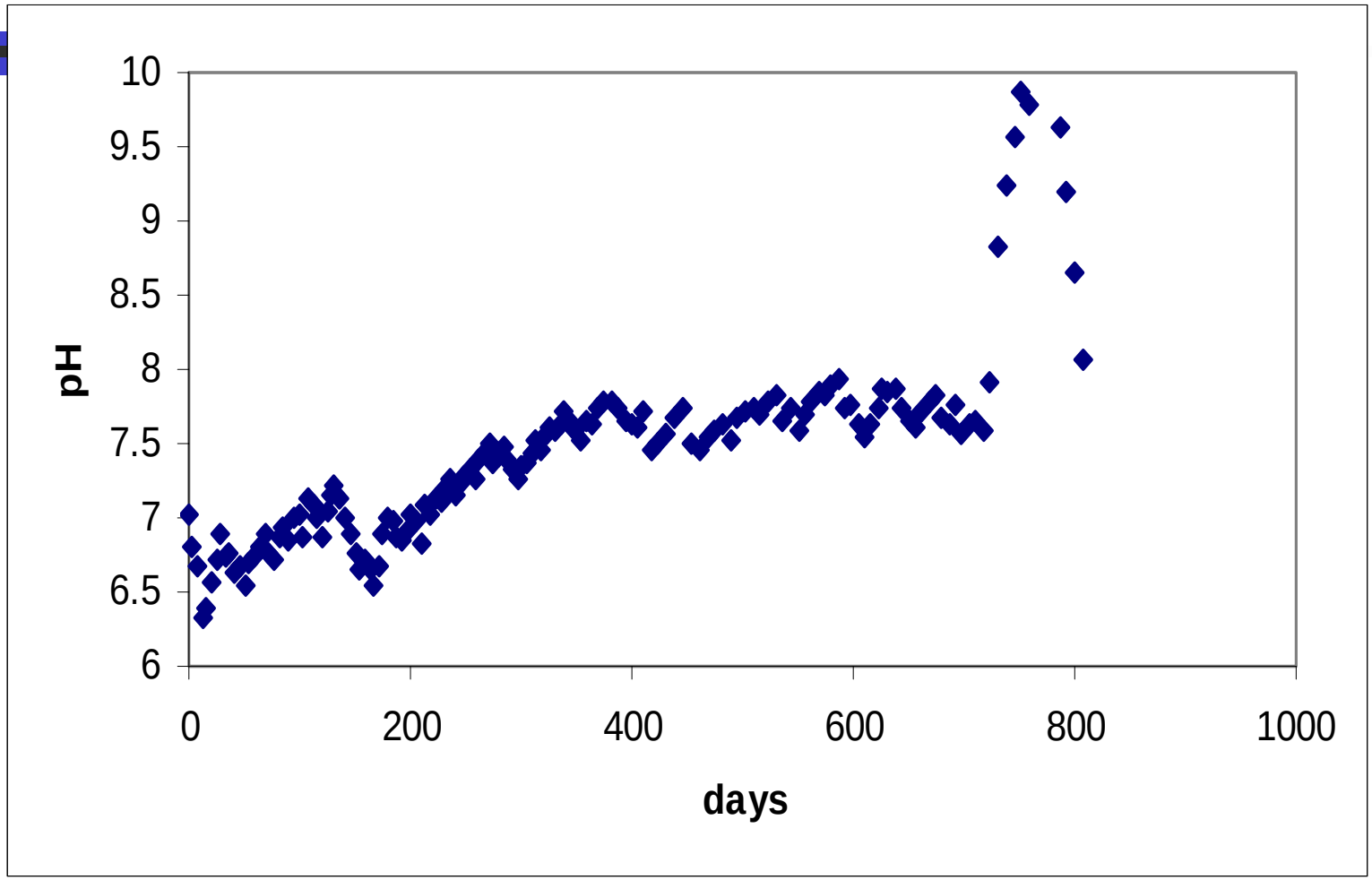
* Small amounts of MMA(V), DMA(V) and MMA(III) were also observed in the effluent.

Fractional Arsenic Leached

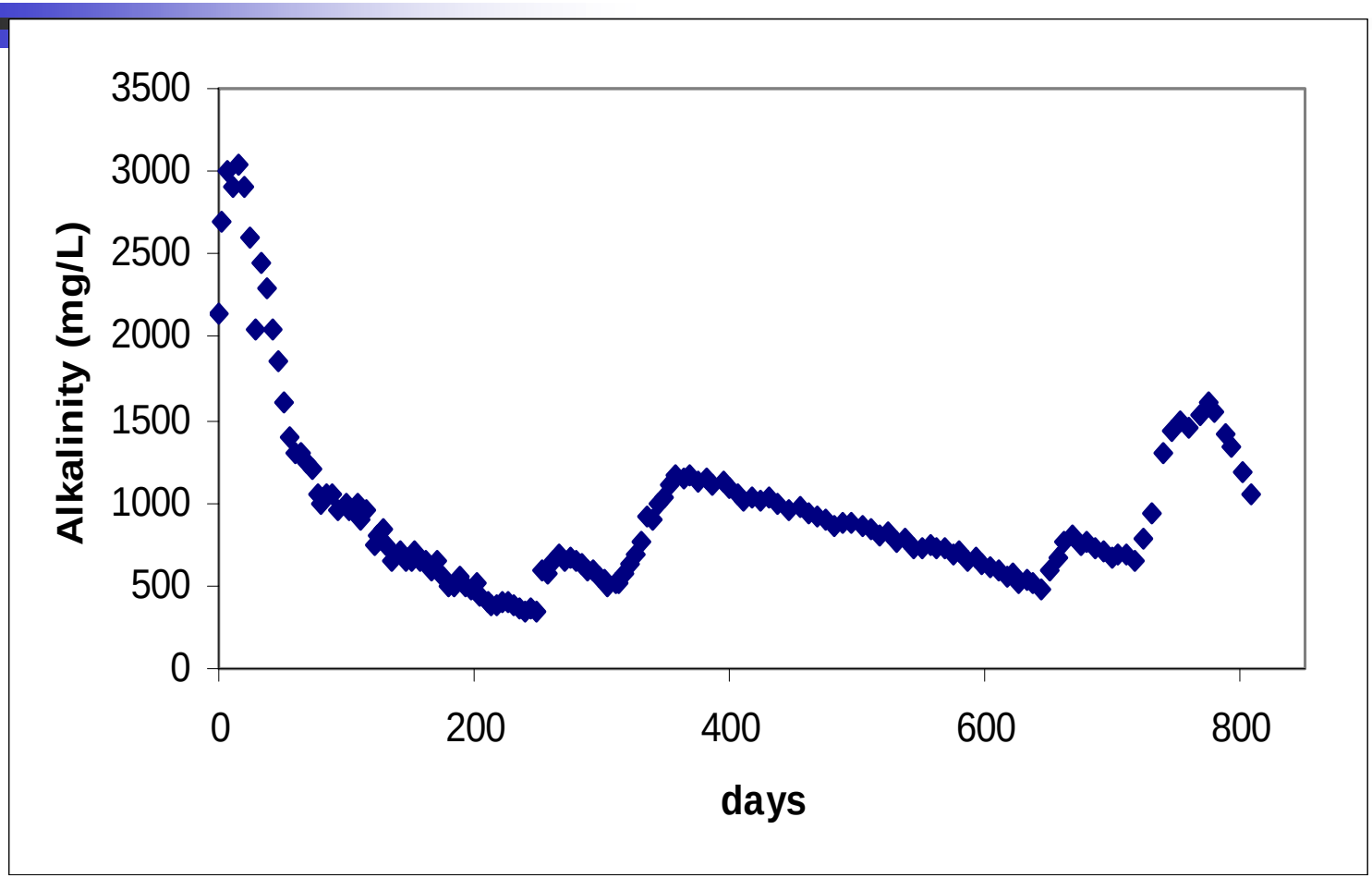


GFH Column Results

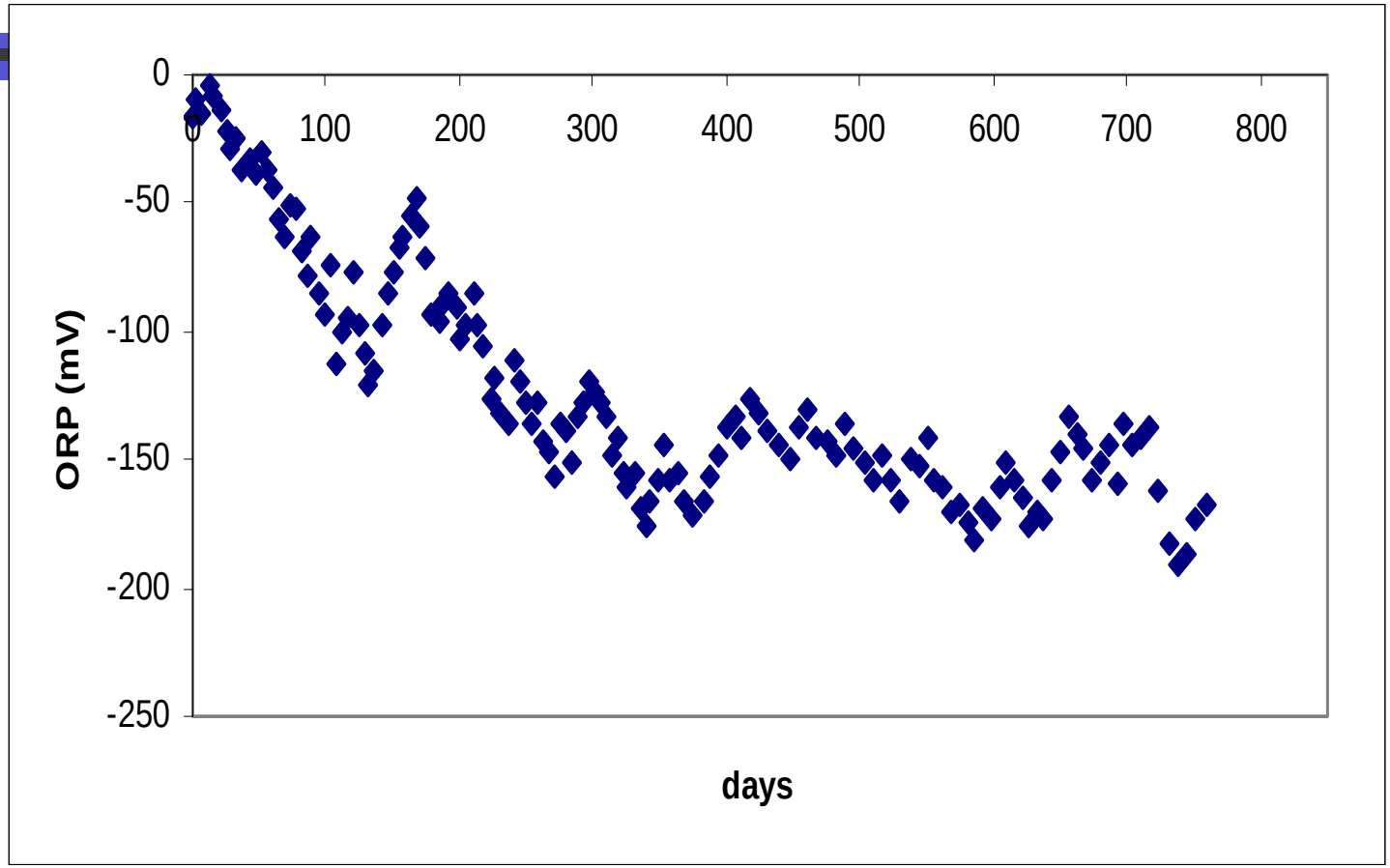
pH



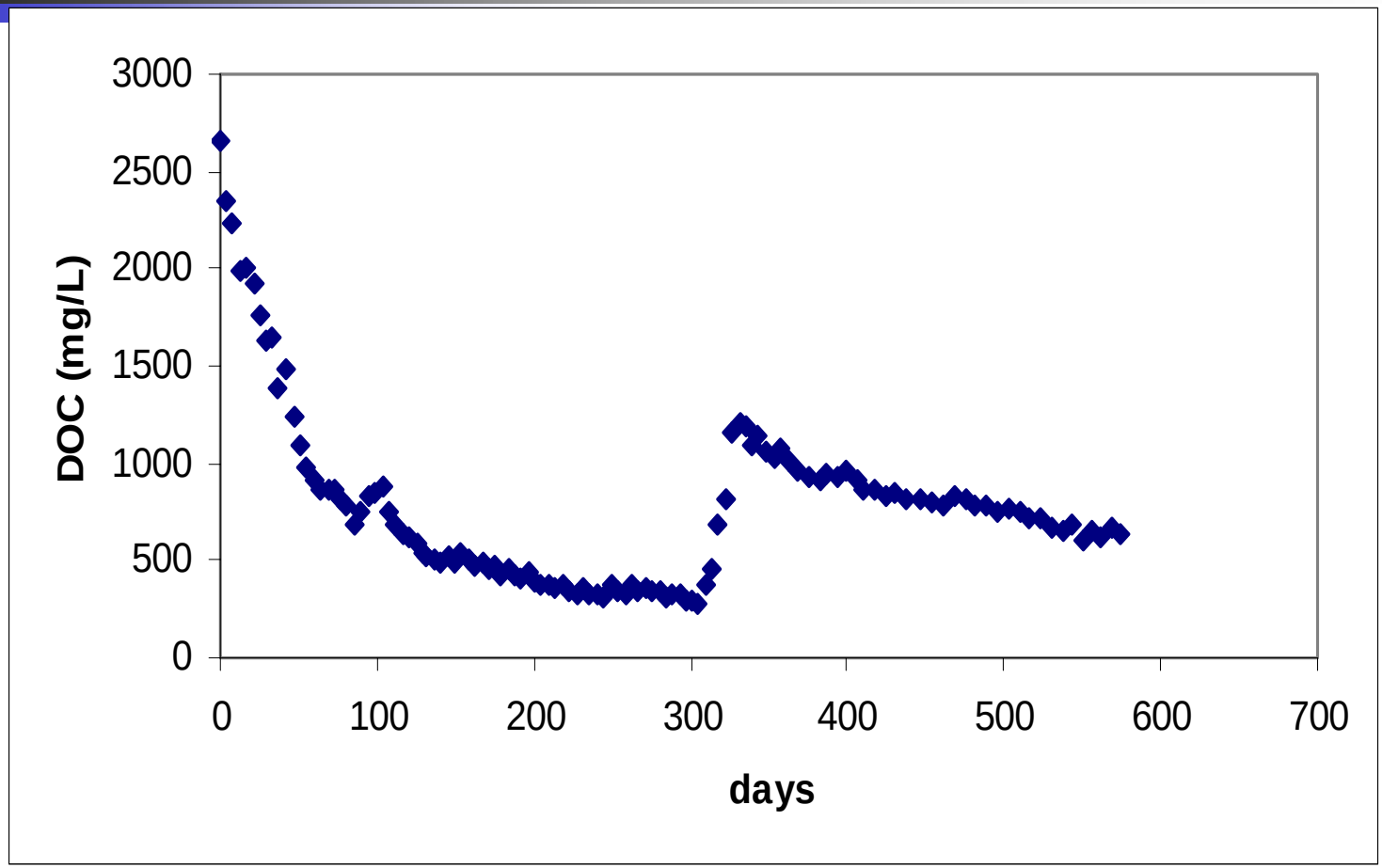
Alkalinity


Alkalinity (mg/L)
3500
3000
2500
2000
1500
1000
500
0
0
200
400
600
800
days

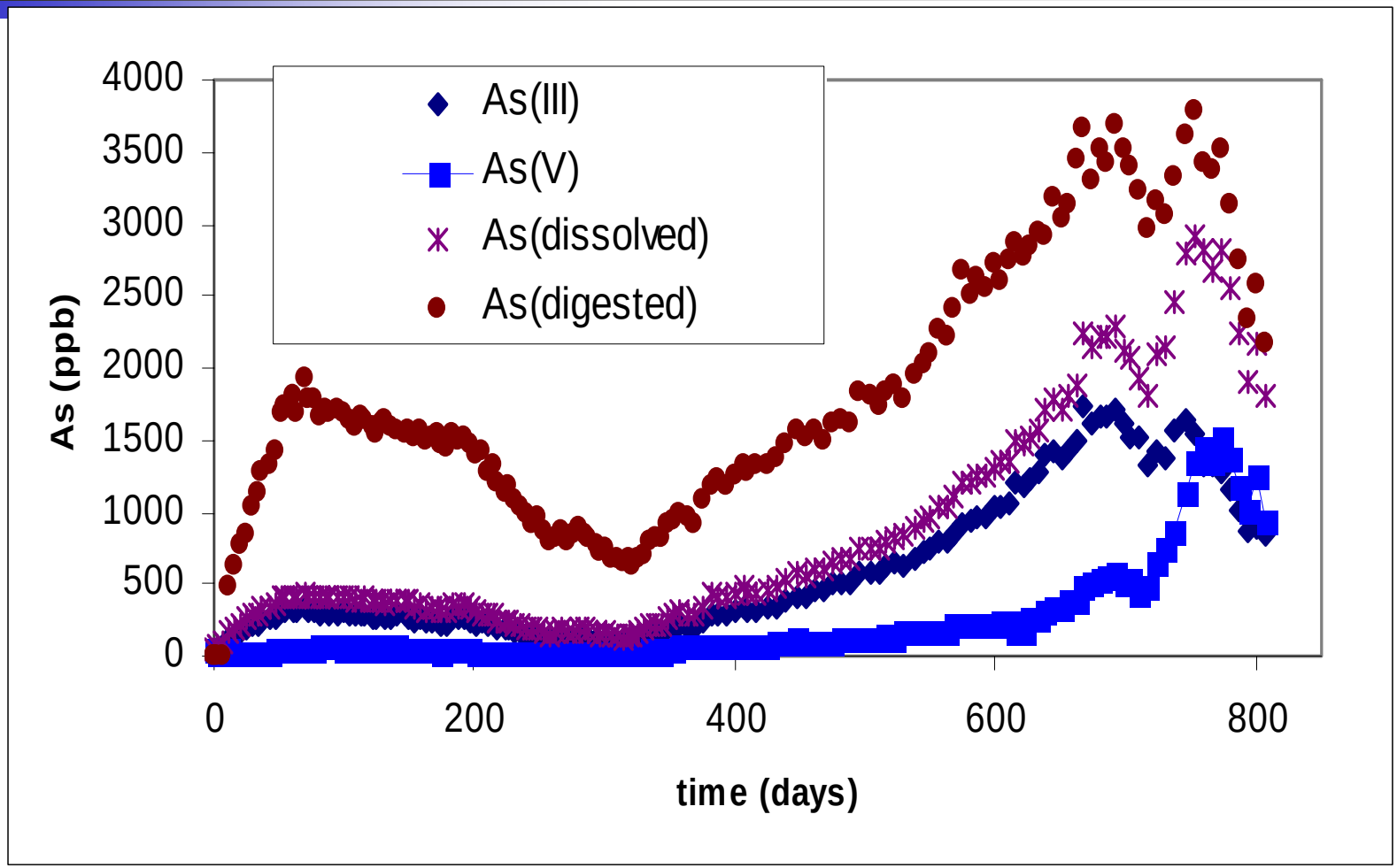
ORP



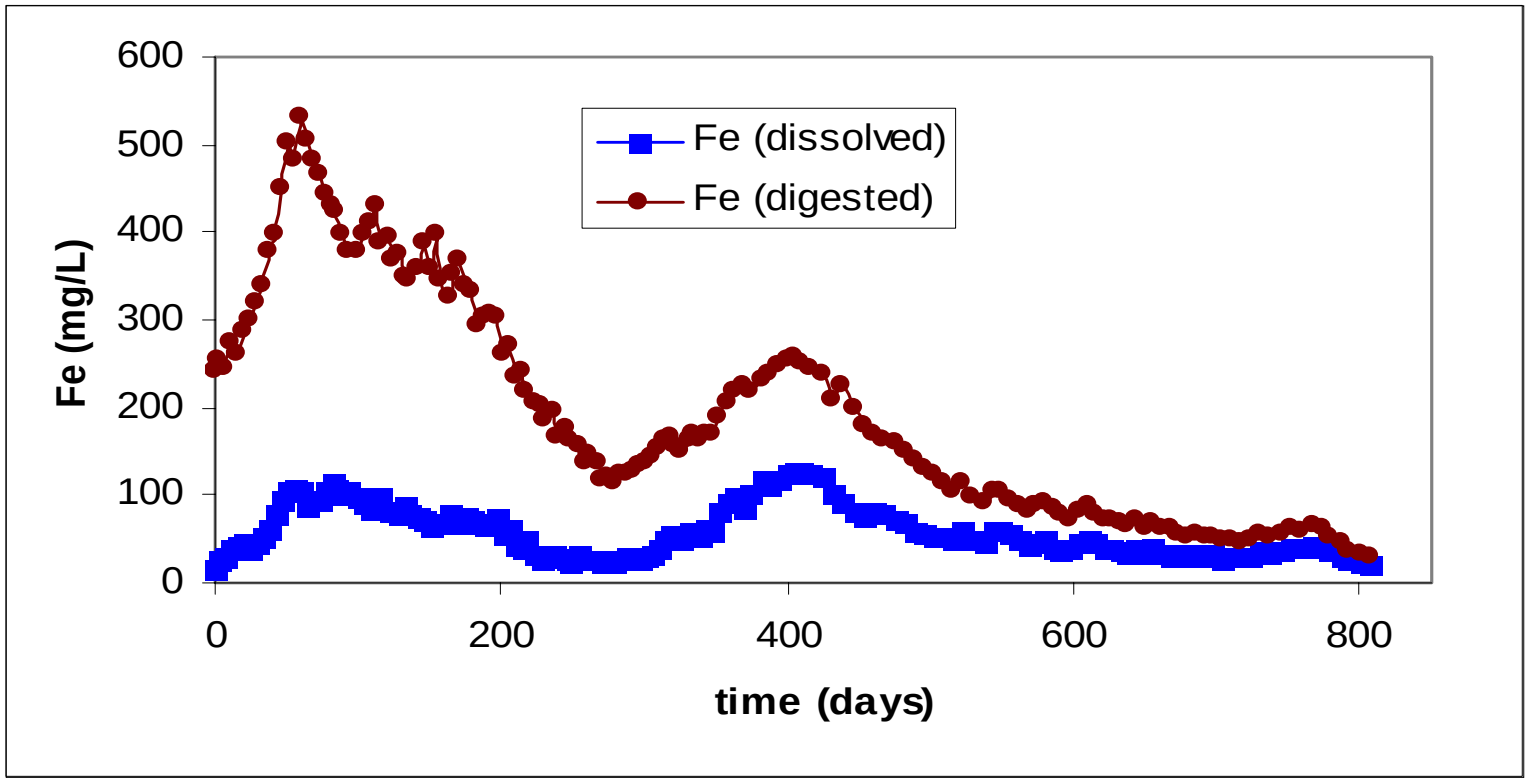
DOC


3000
2500
2000
1500
1000
500
0
DOC (mg/L)
0
100
200
300
400
500
600
700
days

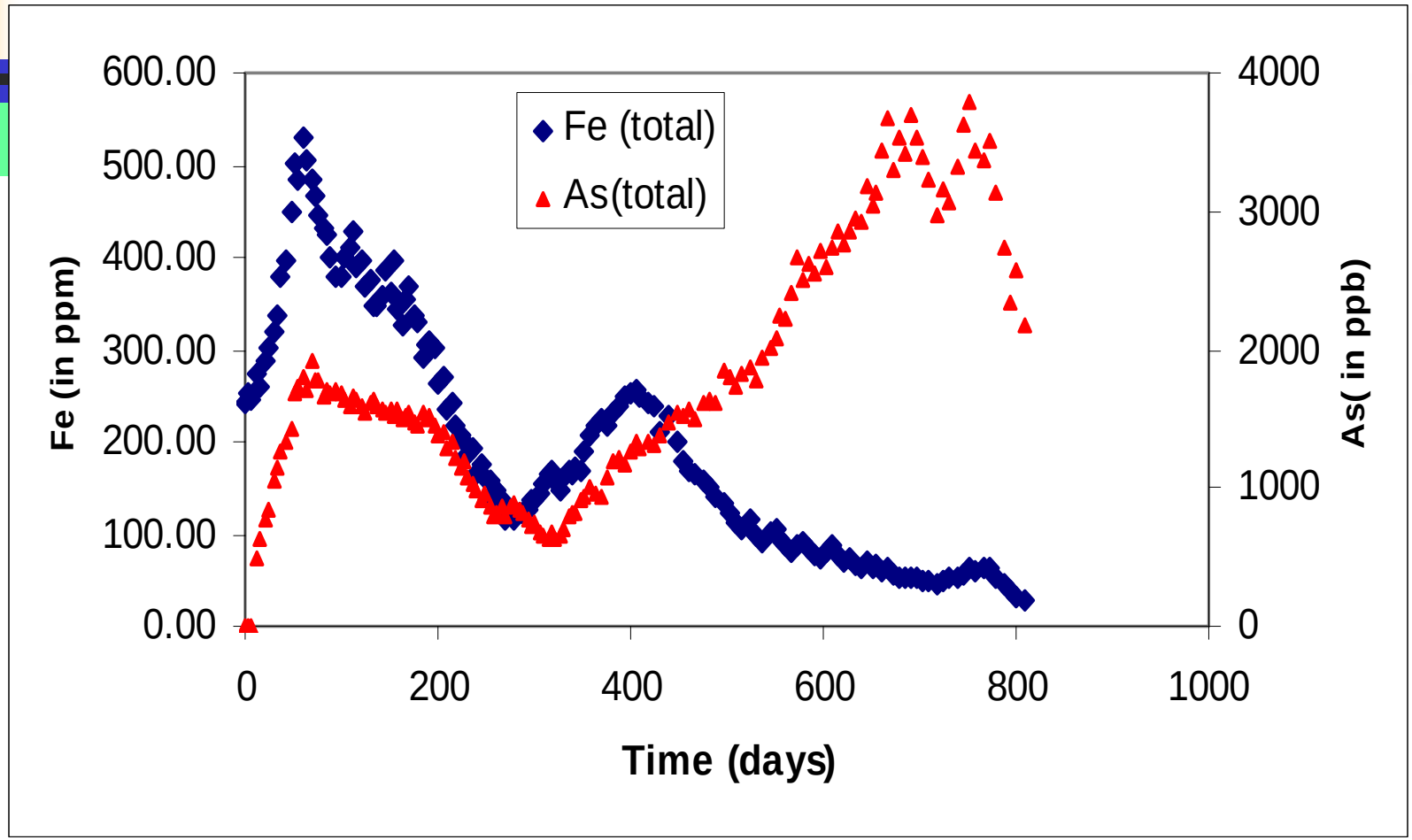
GFH Column Results



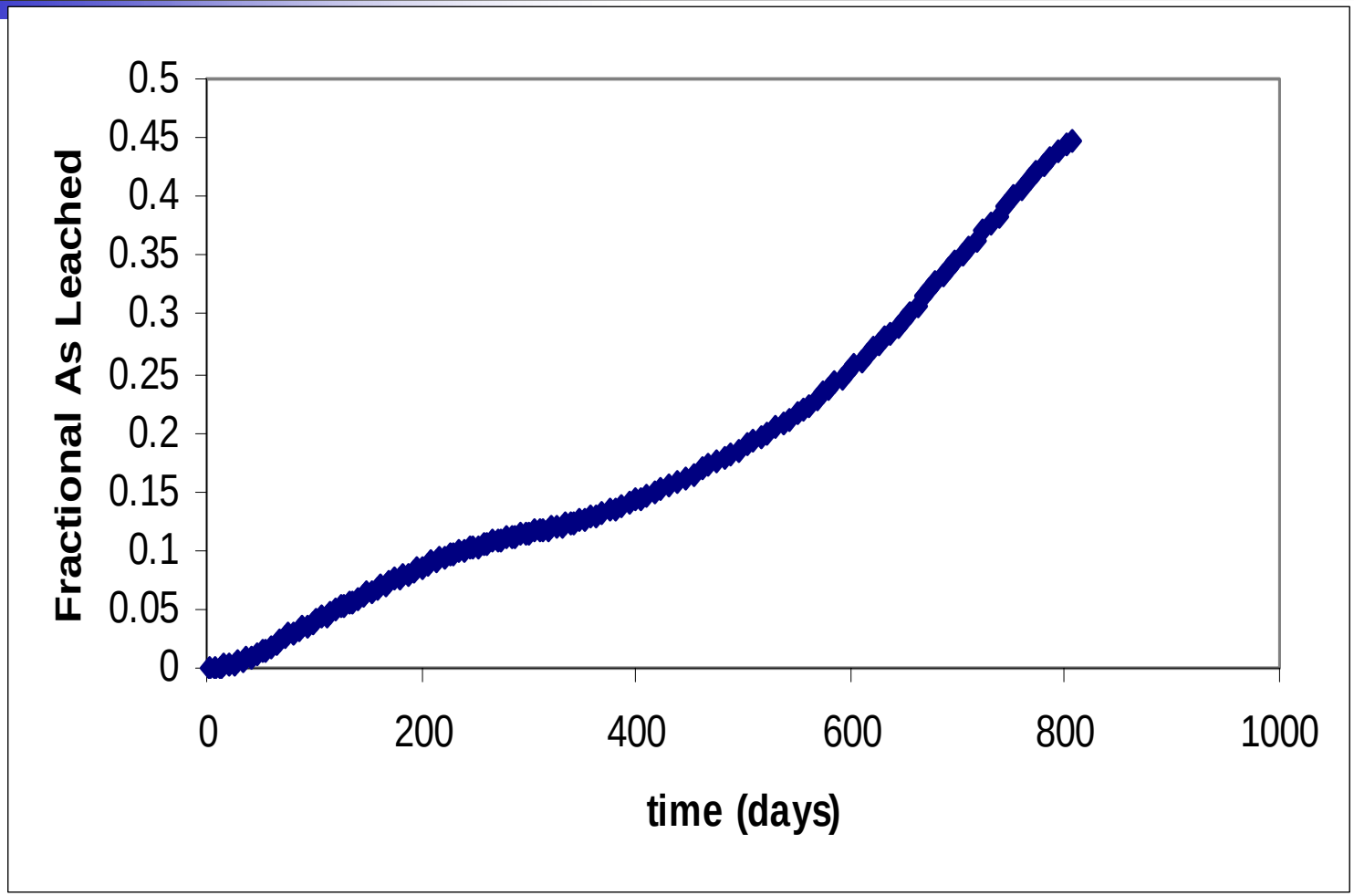
GFH Column Results



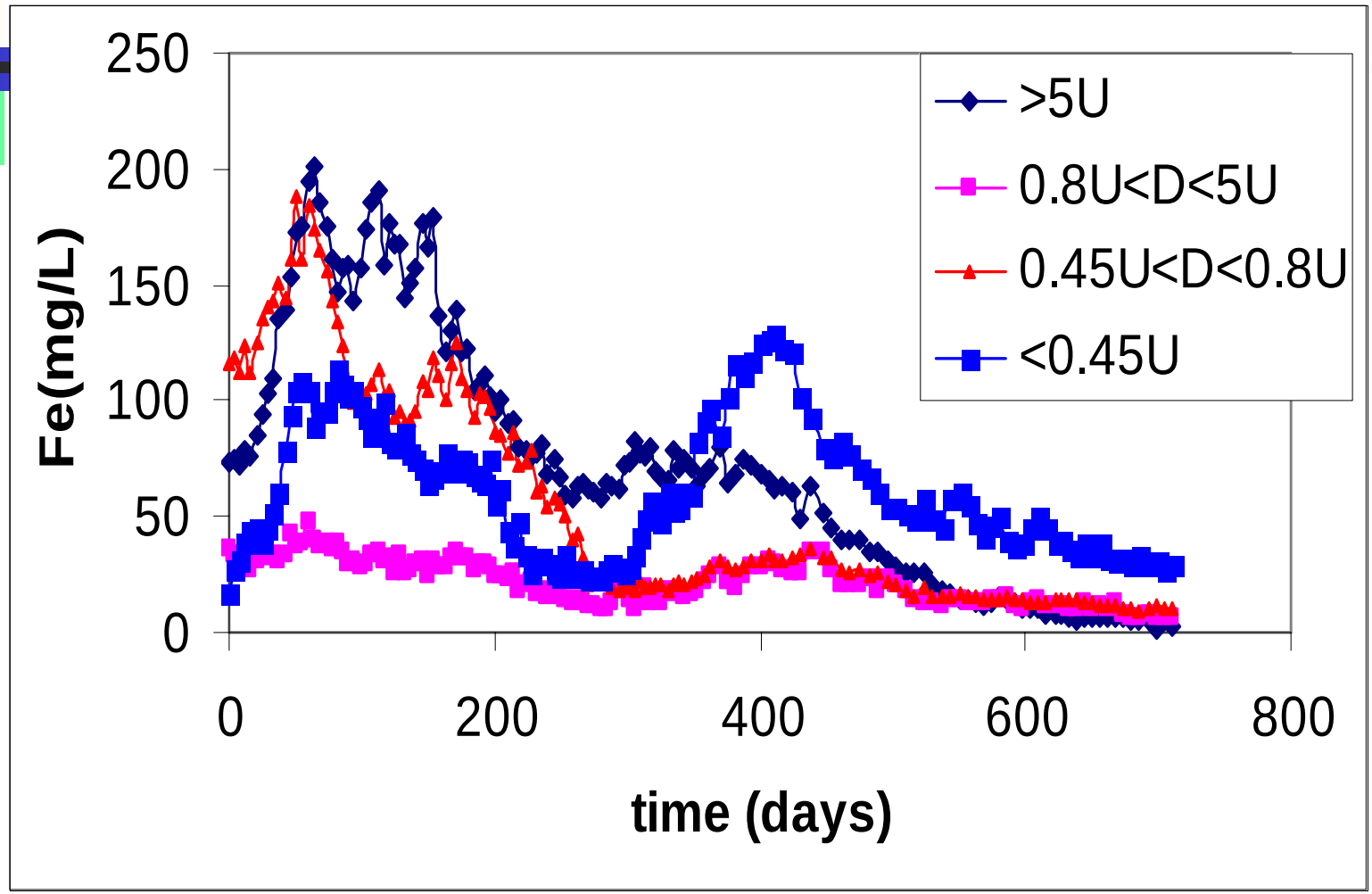
Overall Picture



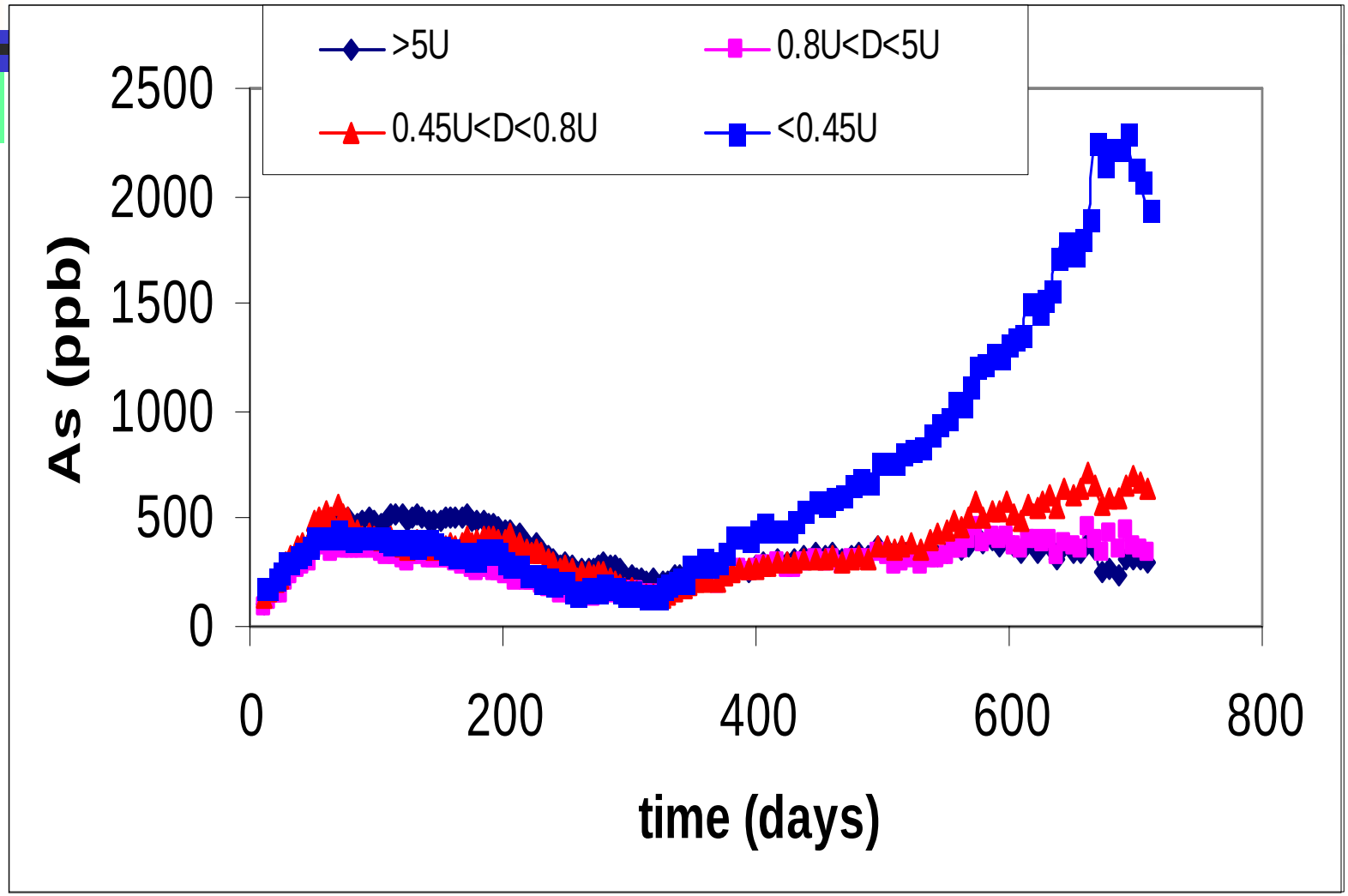
Fractional Arsenic Leached



Particulate Analysis

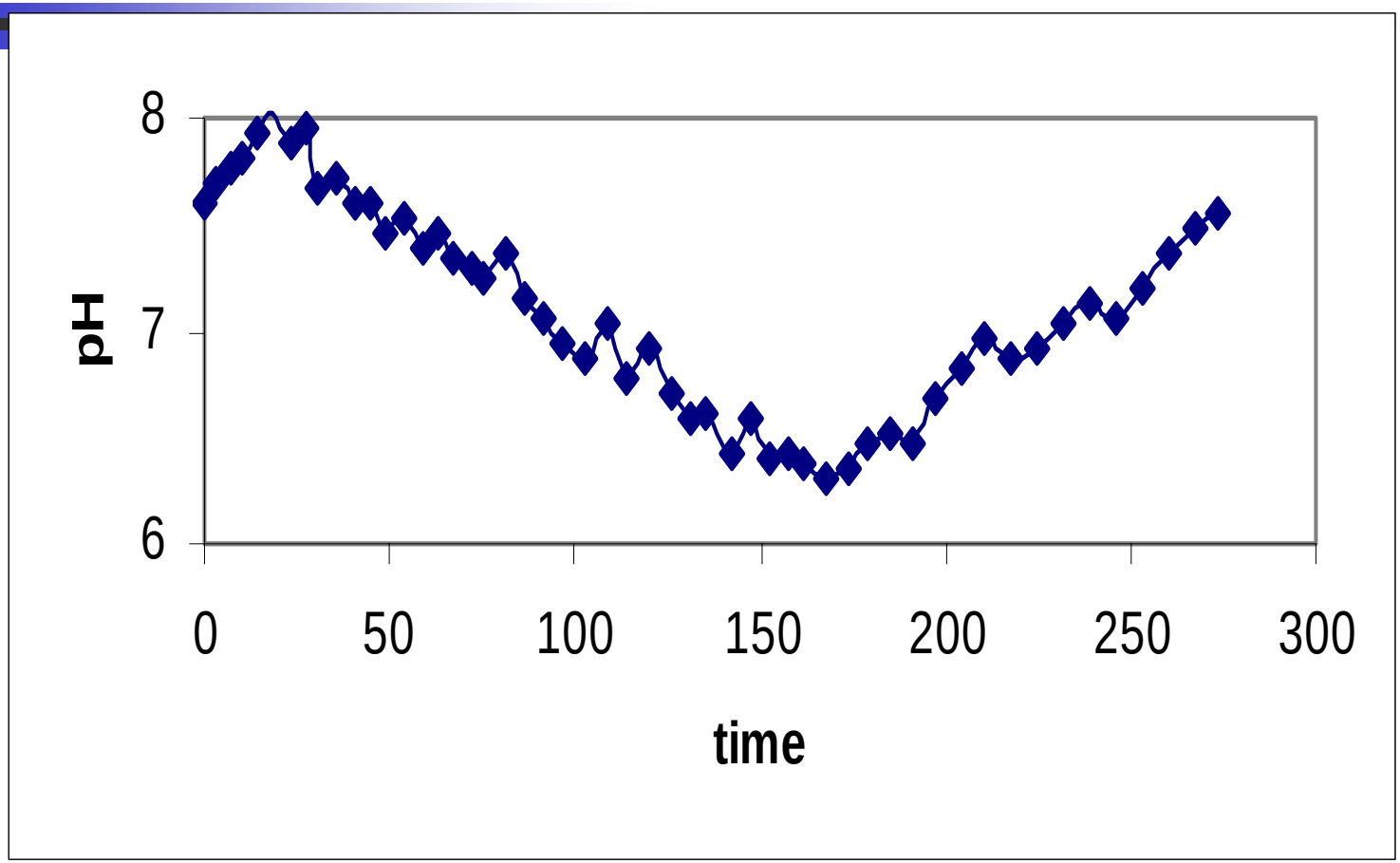


Particulate Analysis

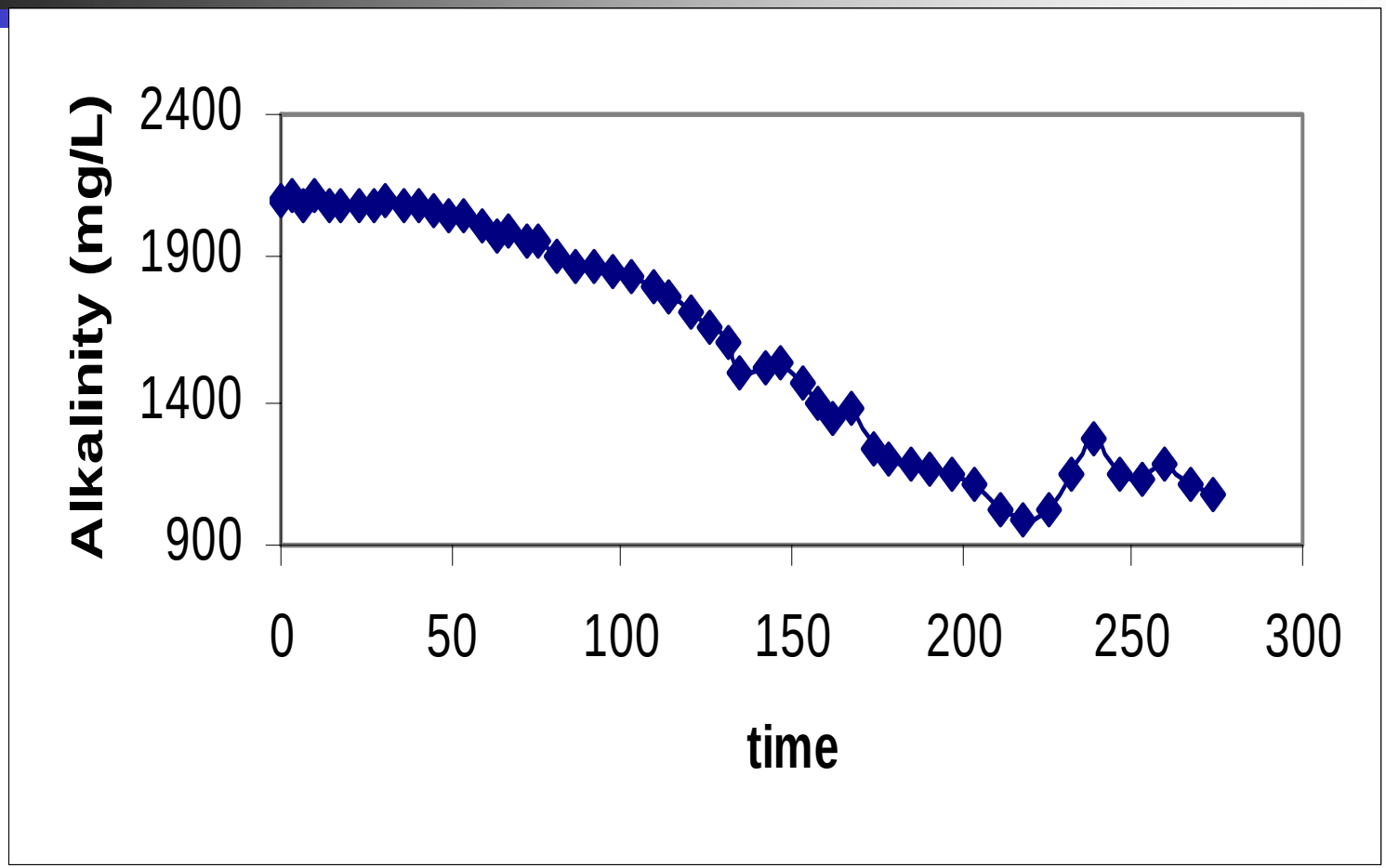


E-33 Column Results

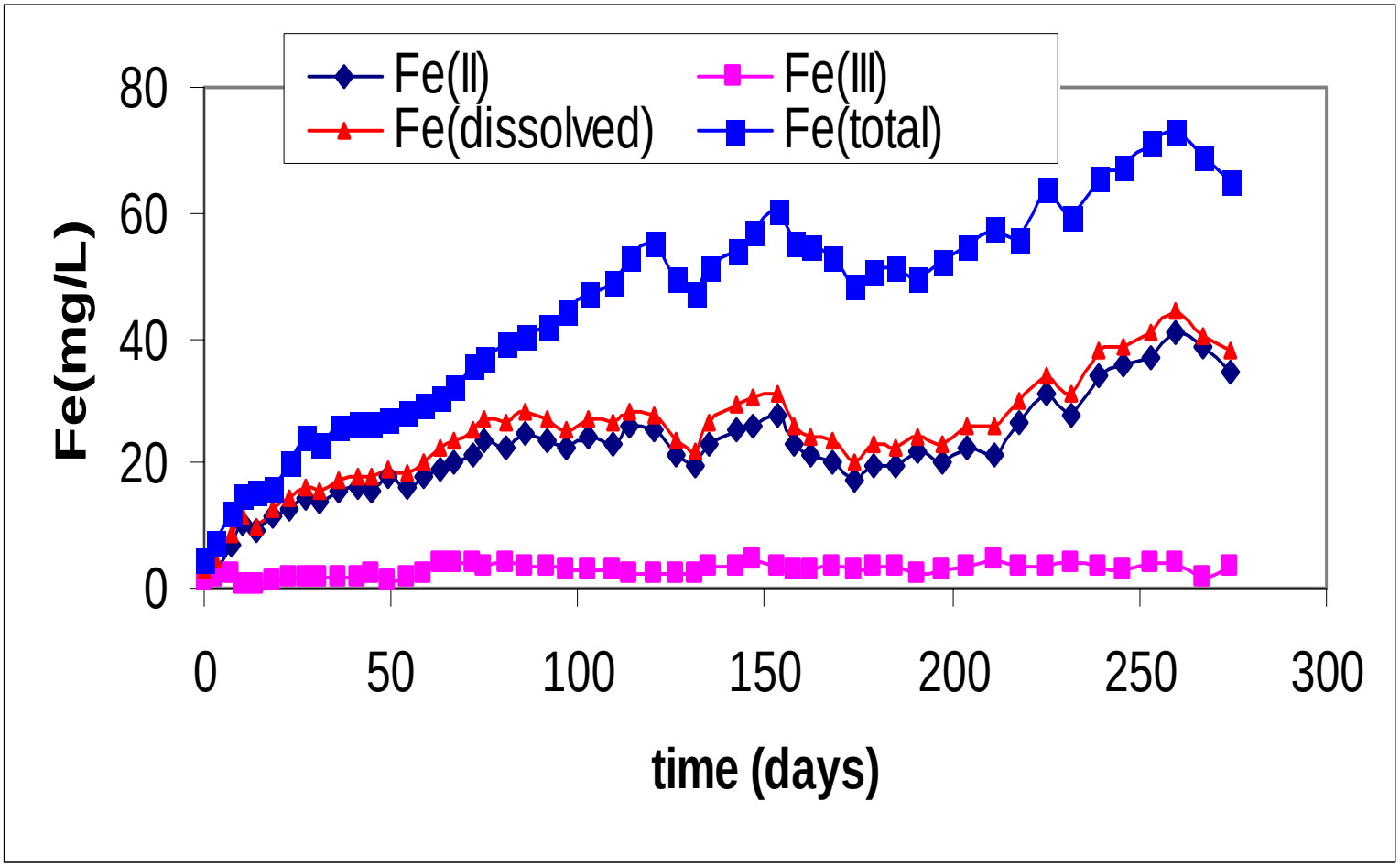
pH



Alkalinity


Alkalinity (mg/L)
2400
1900
1400
900
0
50
100
150
200
250
300
time

E-33 Column Results



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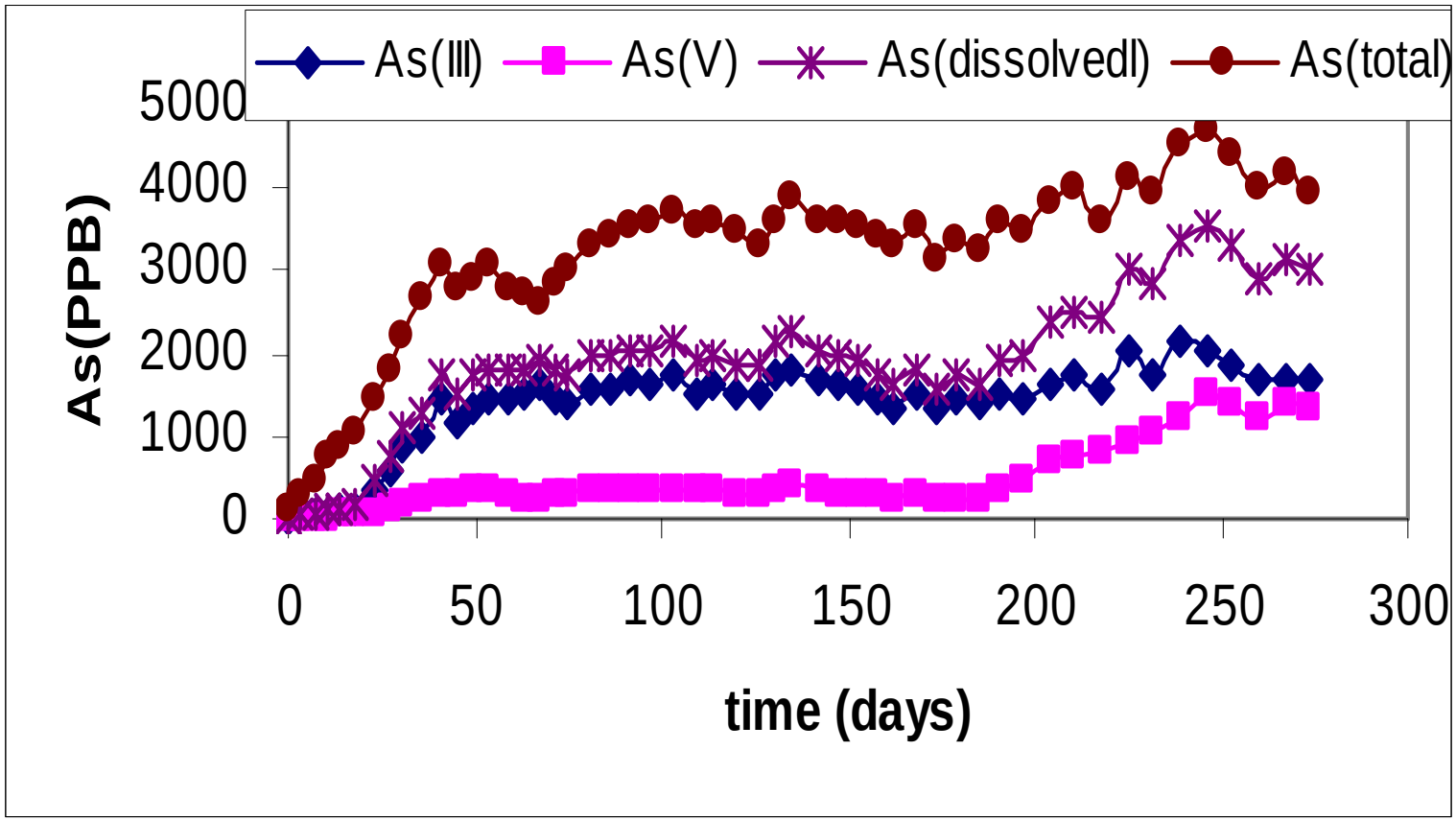
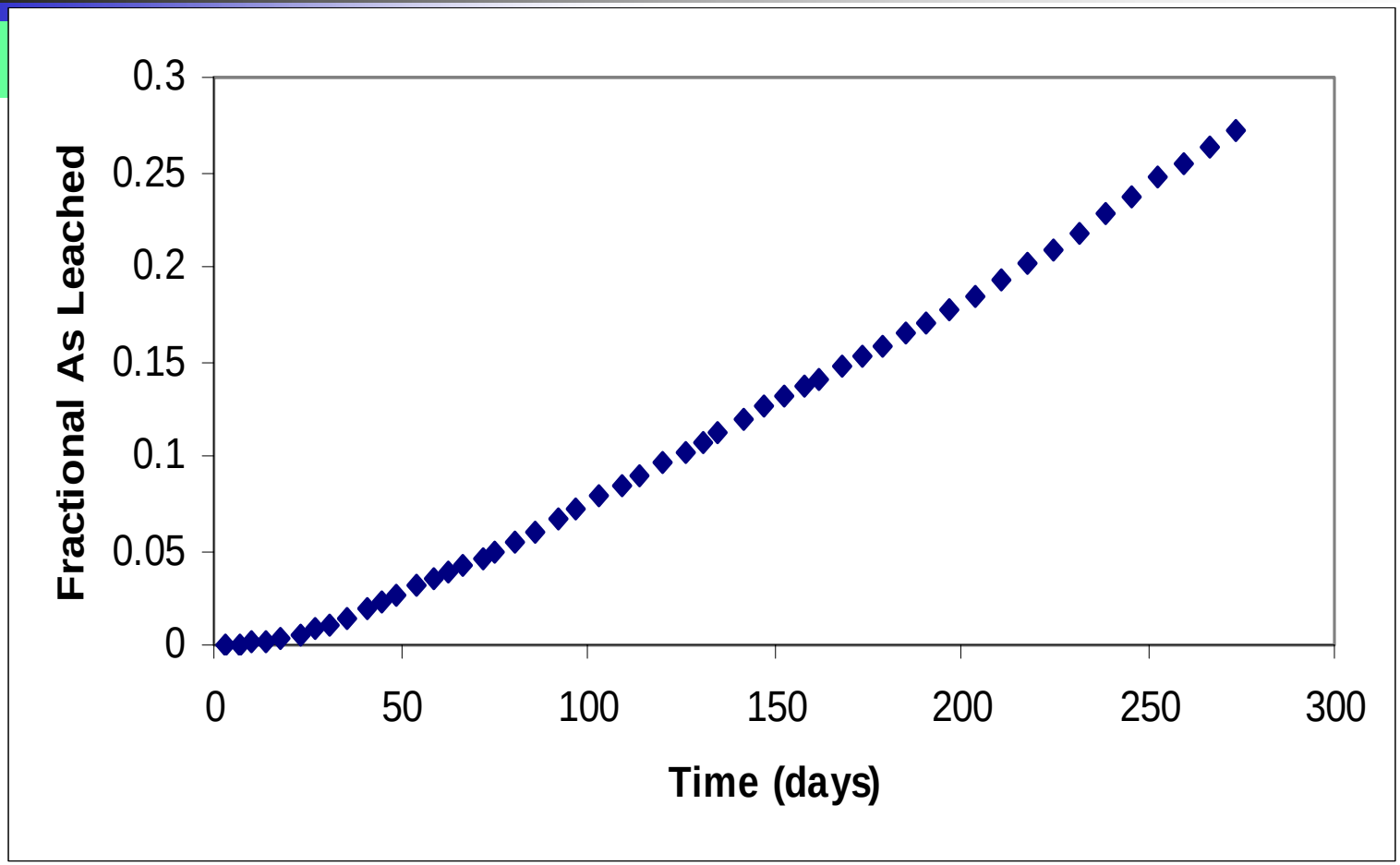
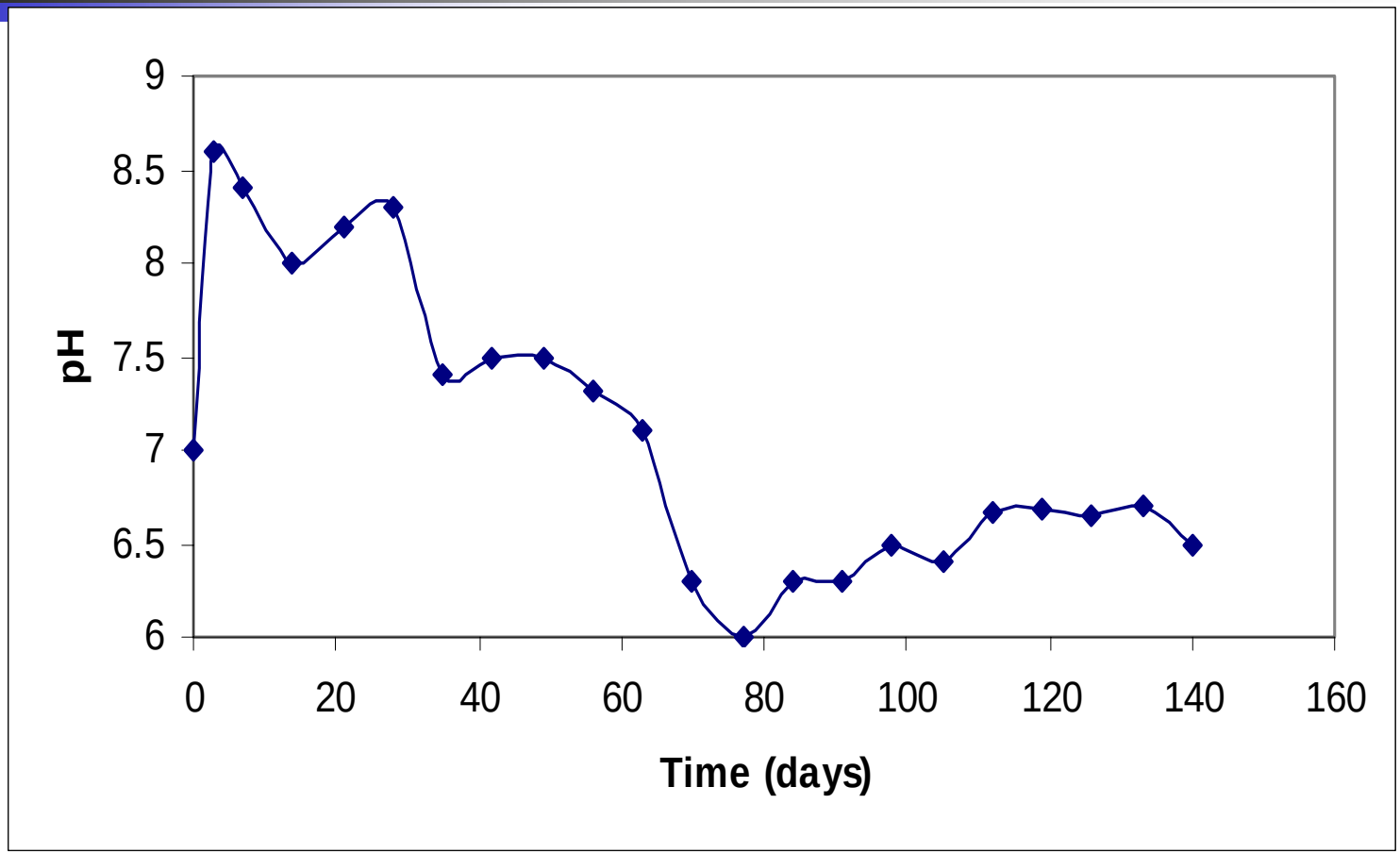


Fractional Arsenic Leached

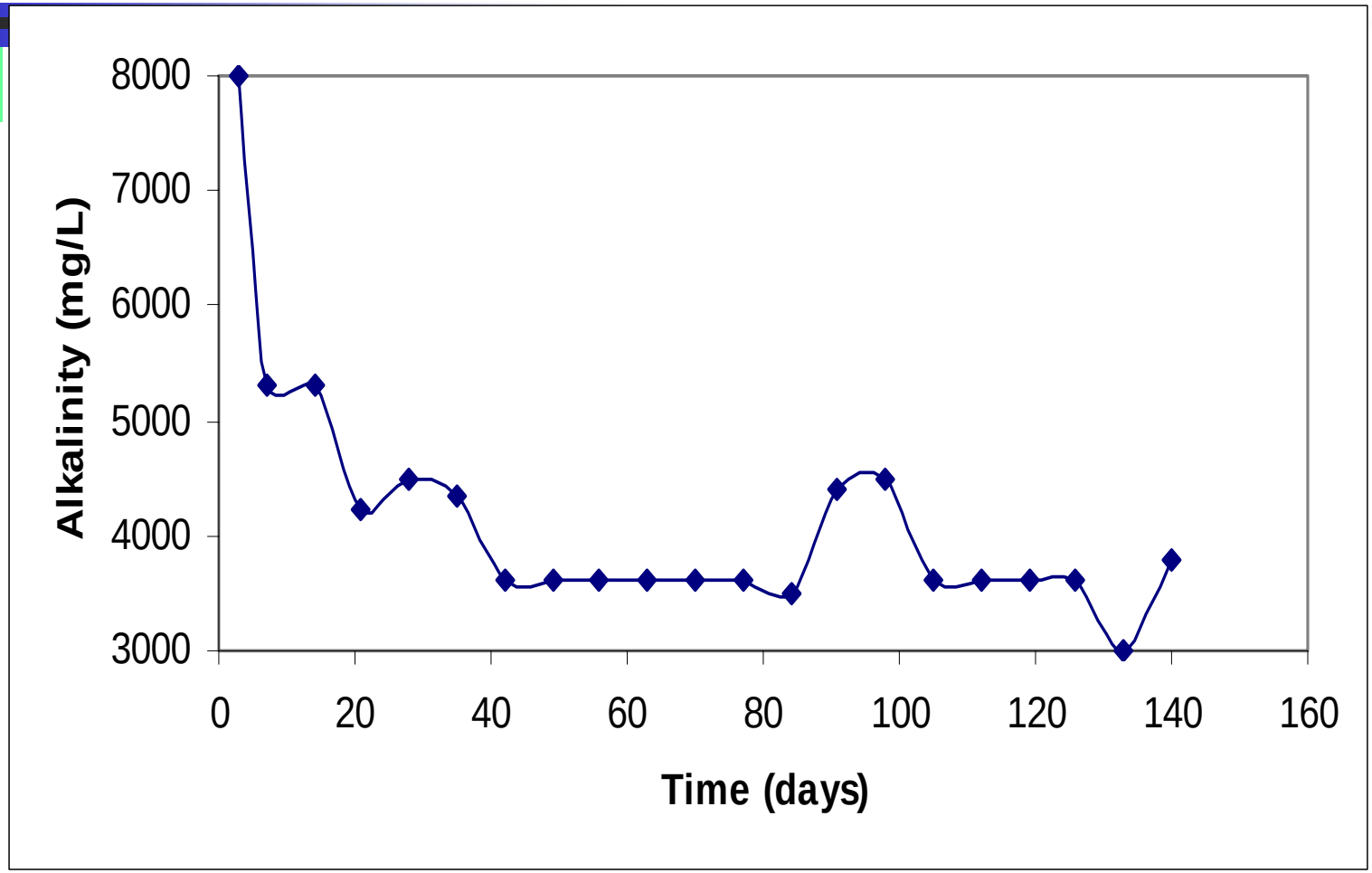


Iron Sludge Column Results

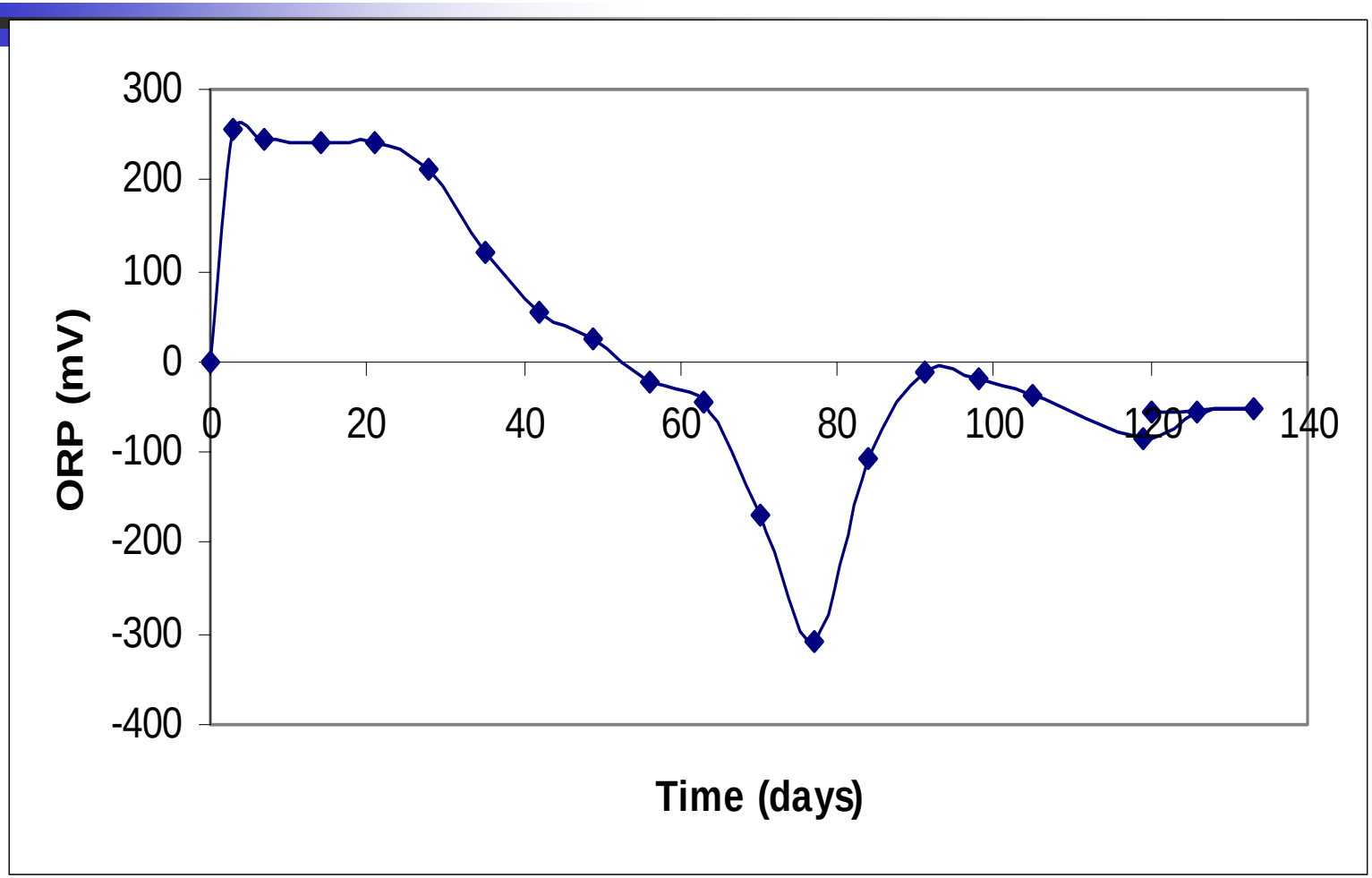
pH



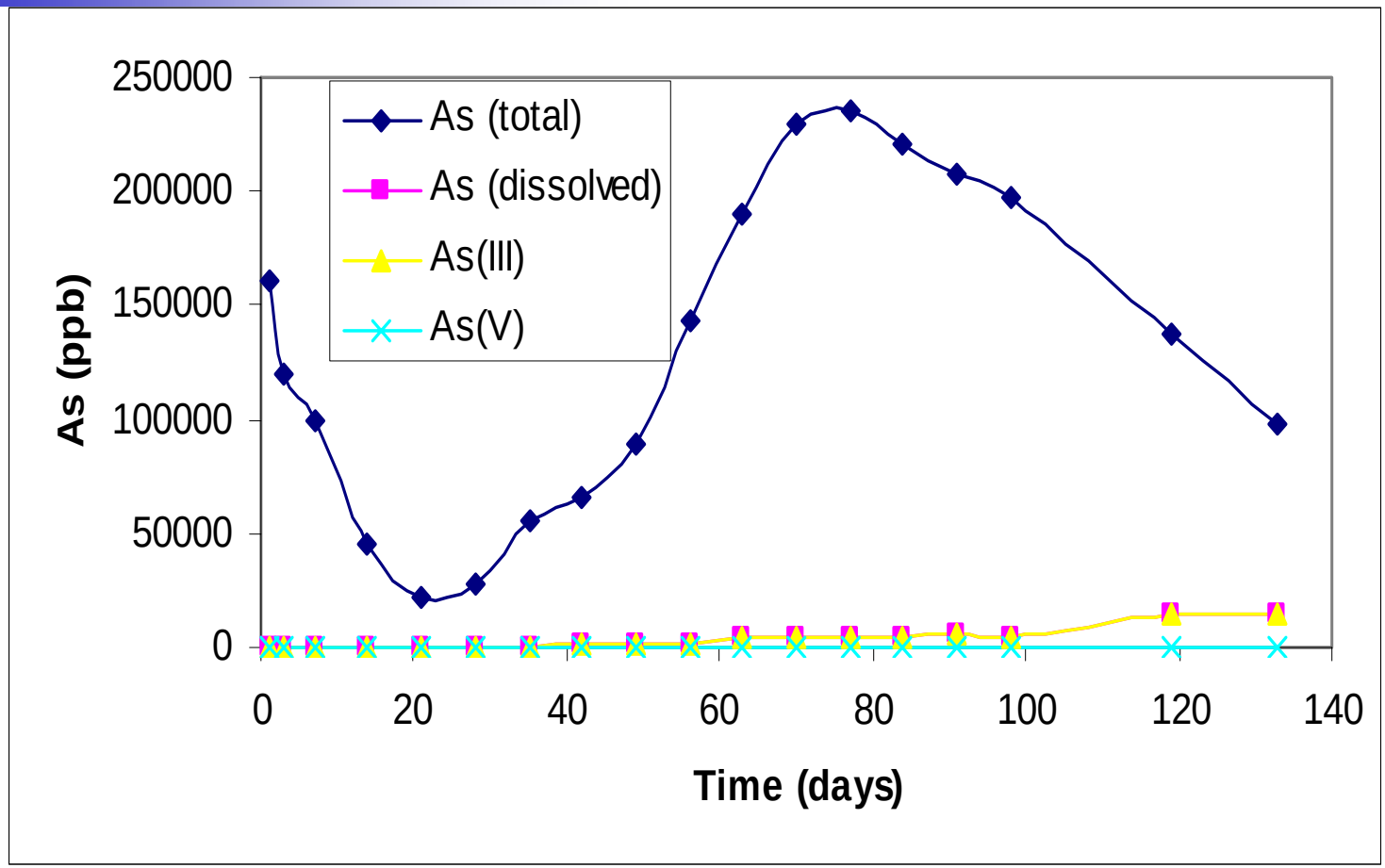
Alkalinity


8000
7000
6000
5000
4000
3000
Alkalinity (mg/L)
0
20
40
60
80
100
120
140
160
Time (days)

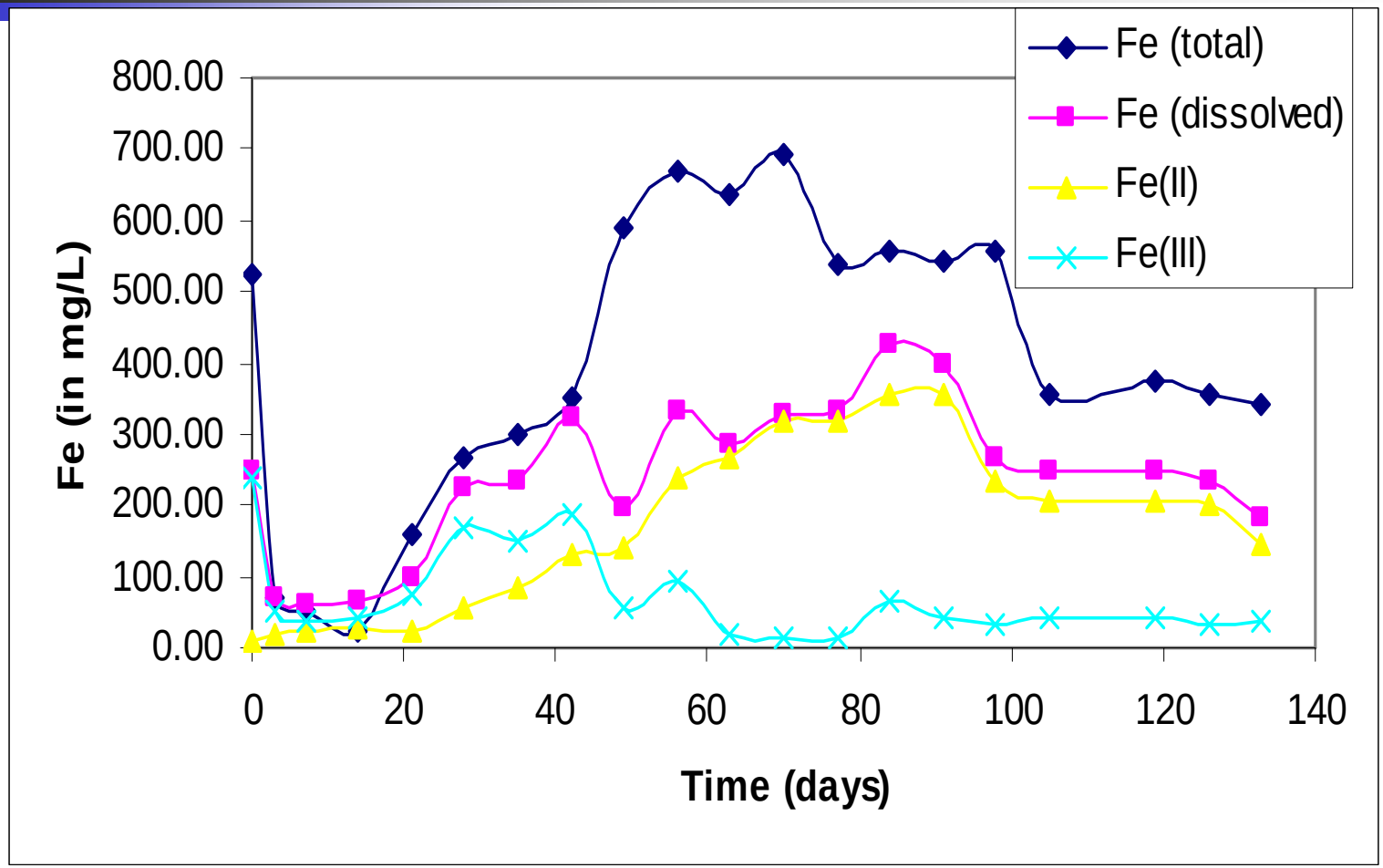
ORP


300
200
100
0
-100
-200
-300
-400
ORP (mV)
0
20
40
60
80
100
120
140
Time (days)

Arsenic


250000
200000
150000
100000
50000
0
As (ppb)
As (total)
As (dissolved)
As(III)
As(V)
0
20
40
60
80
100
120
140
Time (days)

Iron


Fe (total)
Fe (dissolved)
Fe(II)
Fe(III)
800.00
700.00
600.00
500.00
400.00
300.00
200.00
100.00
0.00
Fe (in mg/L)
0
20
40
60
80
100
120
140
Time (days)