Determining a Total Dissolved Solids Release Index from Overburden Using Laboratory Weathering Experiments

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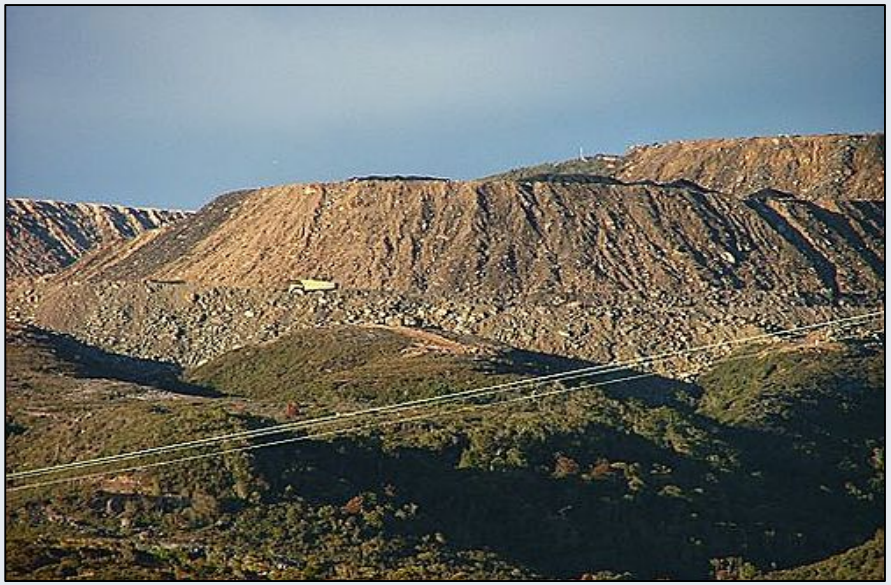


The Acid Base Account

- **Developed at WVU by Richard M. Smith**
  - **To understand the chemical production potential of rocks**

The Acid Base Account

ACID <---------> BASE

MPA <----------> NP

% S

- **Carbonates**
- **Exchangeable bases**
- **Weatherable silicates**

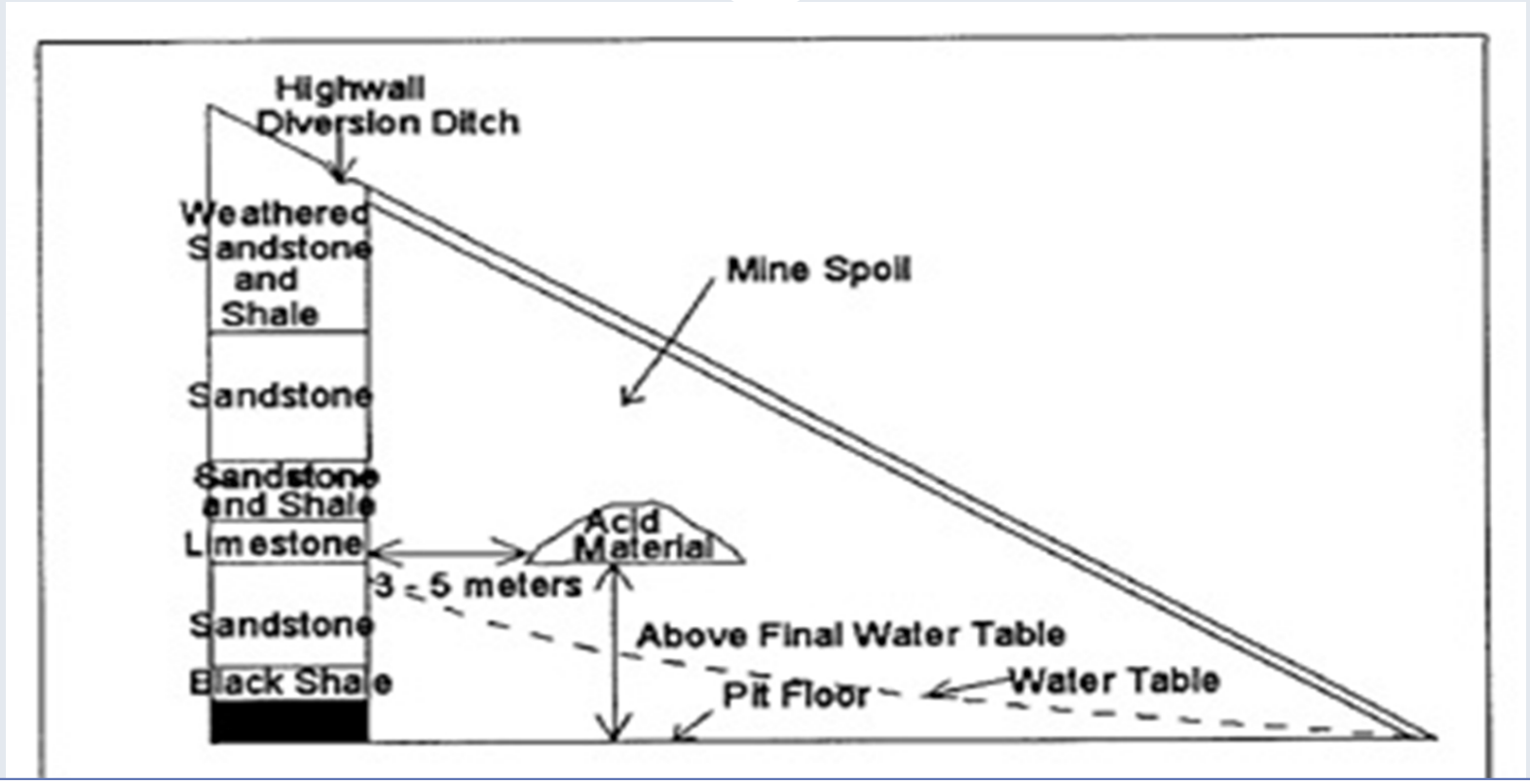
The Acid-Base Account

Excess Acidity **Excess Alkalinity**

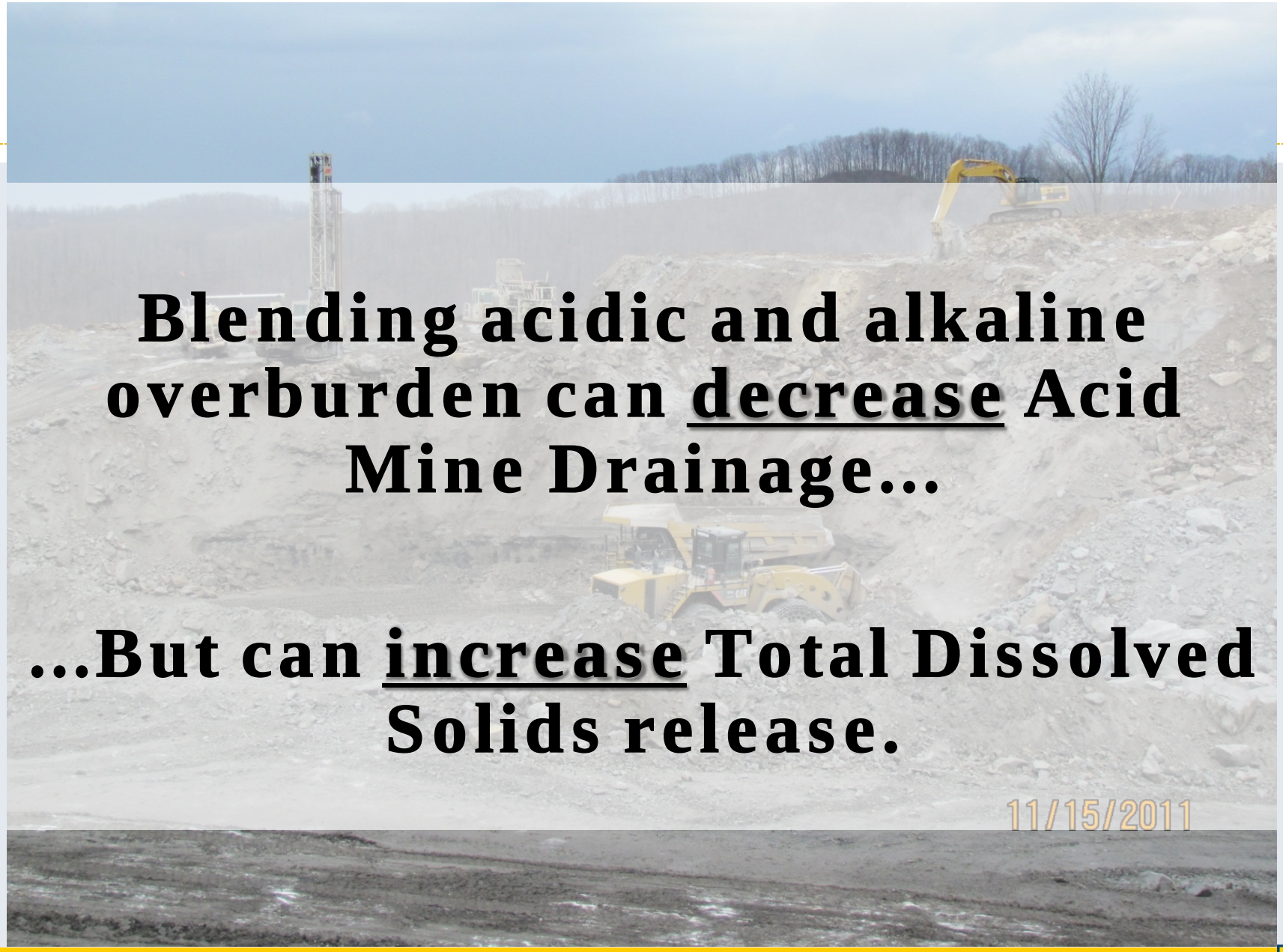
$CaCO_3$ equivalent - tons/1000 tons of material

Sample Number	Bottom depth (feet)	Rock type	Fizz	Color	%S	Max. from %S	Amount present (NP)	Max. needed (pH7)	Excess	Paste pH
1	3	Soil	0	7/3	.035	1.09	3.52		2.53	4.4
2	6	SS	0	8/6	.029	0.91	-1.51	2.42		4.3
3	6	SS	0	8/2	.023	0.72	-1.59	2.31		4.6
4	14	SH	0	7/4	.009	0.28	-0.60	0.88		4.6
5	17	SS	0	7/4	.009	0.28	-0.09	0.37		4.7
6	20	SH	0	8/3	.011	0.34	-0.17	0.51		4.5
7	24	MS	0	7/1	.263	8.22	-0.94	9.16		4.8
8	28	MS	1	7/1	.179	5.59	78.33		72.74	7.8

The Acid-Base Account



It would be ideal to have a technique similar to the ABA for predicting TDS release from overburden material.



Blending acidic and alkaline overburden can <u>decrease</u> Acid Mine Drainage…

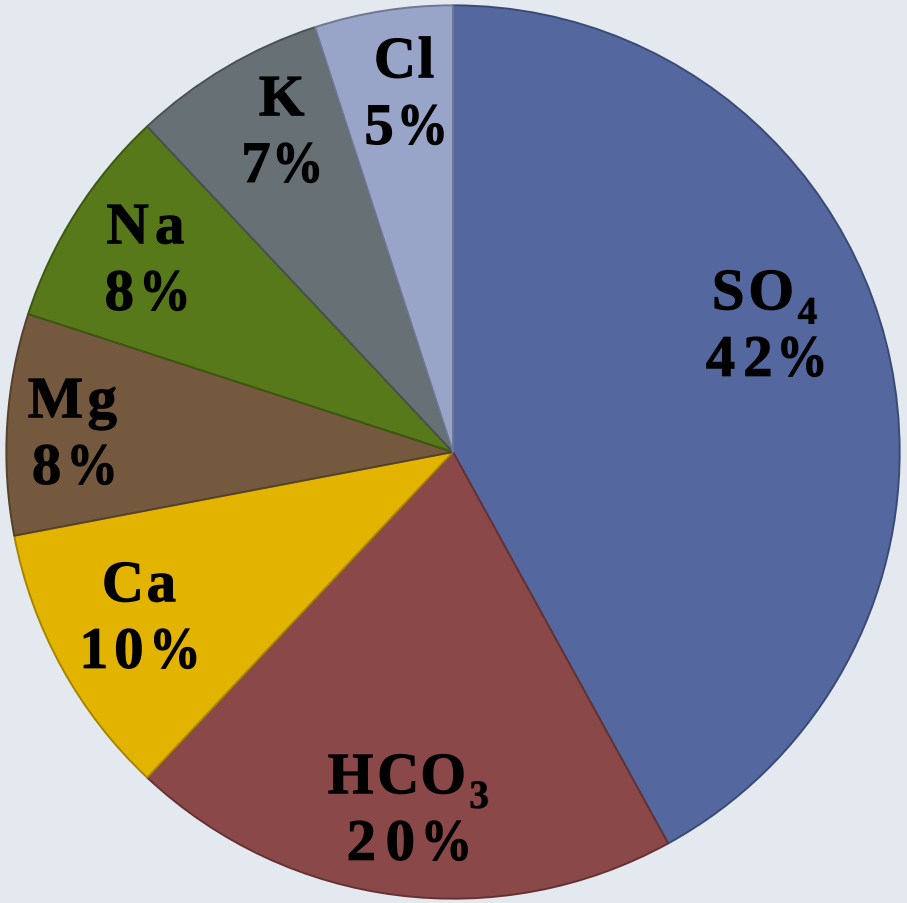
…But can <u>increase</u> Total Dissolved Solids release.

Total Dissolved Solids (TDS)

- All inorganic and organic substances contained in water that can pass through a 2 micron filter.

- Gravimetrically:
  - Filter water sample
  - Evaporate at 180°C in a pre-weighed dish
  - The increase in weight (the dried residue) represents TDS measured in (mg L^{-1})

TDS Composition



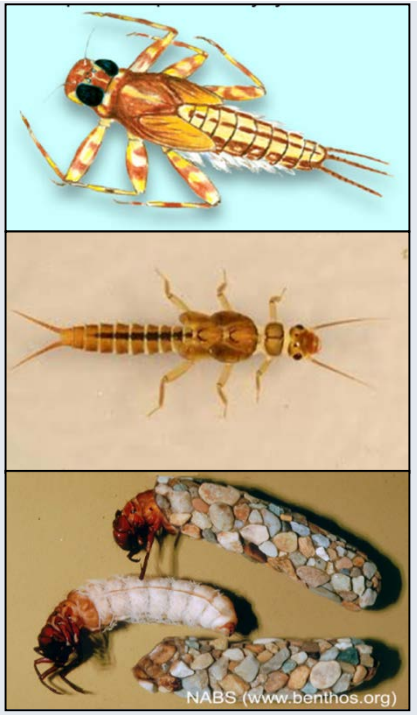
Total Dissolved Solids (TDS)

Why do we care?

- **Human Health**
  - **Secondary Maximum Contaminant Limit:**
    - **500 mg L^{-1}**

Total Dissolved Solids (TDS)

Why do we care?



- **Aquatic Health**
  - **The number of EPT taxa had a strong negative correlation to TDS (Timpano et al., 2010).**

Metric	Ca^{2+}	SO_4^{2-}	Mg^{2+}	TDS	Cond	K^+
EPT	-0.81	-0.81	-0.79	-0.76	-0.76	-0.64

Purpose

With a quick laboratory experiment, we hope to be able to identify overburden as producing:

High, Moderate, or Low TDS

so that operators can properly treat, isolate, and/or handle their overburden in a manner that will decrease TDS runoff from their site.

Appalachian Research Initiative for Environmental Science (ARIES)

WVU, VT, UK, OSU, PSU, UP

Area 3

1. **Develop and Collect Regional Sample Set**
   - VT and WVU

2. **Laboratory Analyses of Mine Spoils**
   - VT and WVU

3. **Field Screening Techniques for EC and Se**
   - UK

4. **Kinetic Testing of Spoils**
   - VT, WVU, and UK

Objective

- To determine an index for TDS release from overburden material using three laboratory weathering techniques:

1. Dilute nitric acid (HNO_3)
2. Ethylenediaminetetraacetic Acid (EDTA)
3. Microwave Digestion

Materials & Methods

- 41 samples from WV, VA, and KY
- Specific type of rock with varying TDS potential:
  - High (Shales or Sandstones with high %S and/or high NP)
  - Medium
  - Low (oxidized/weathered sandstones)

Overburden ABA

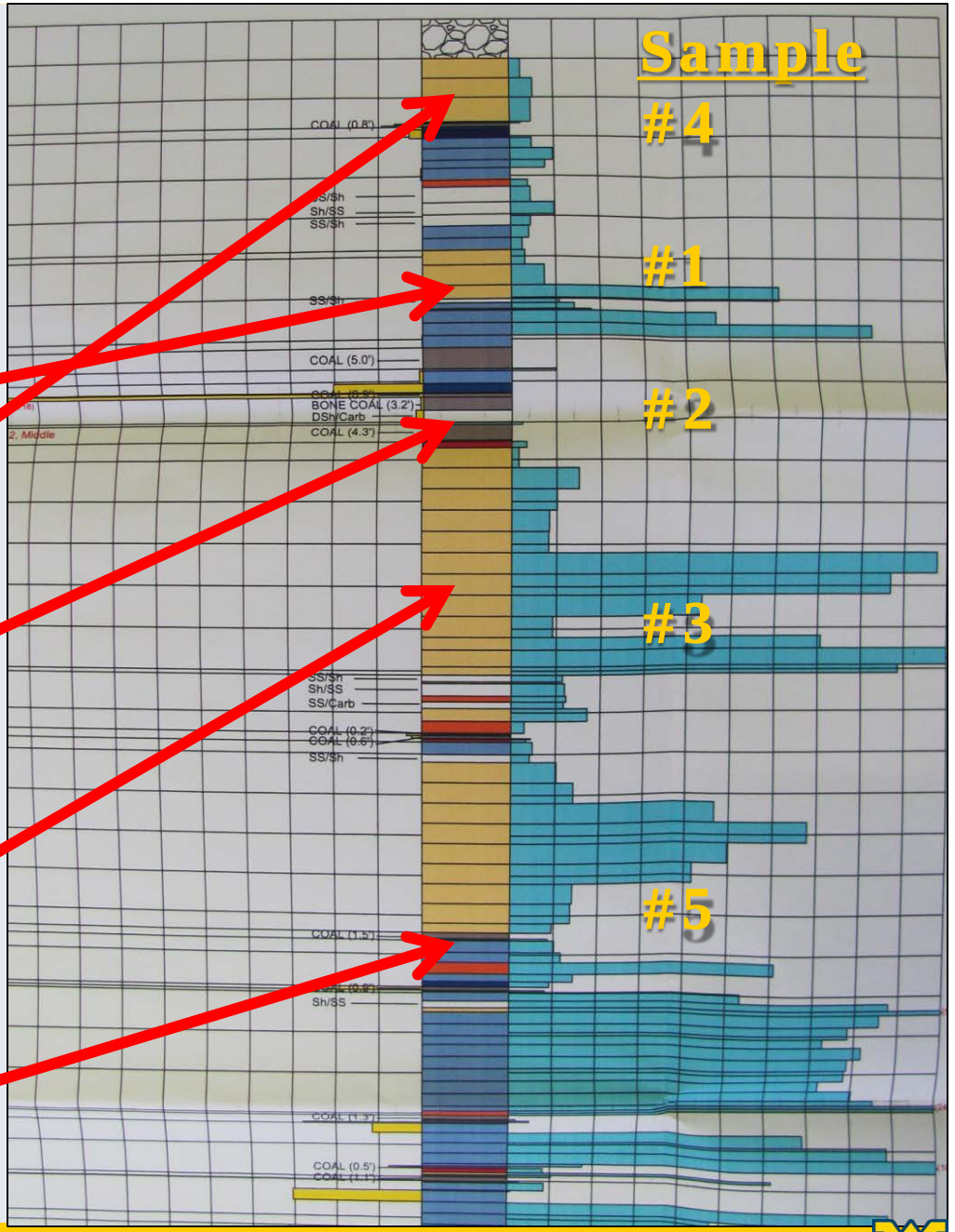
Low TDS

Medium TDS

High TDS

High Alkalinity

High Acidity



Materials & Methods

- 1 g overburden + 200 mL Dilute HNO_3 or EDTA
- The bottles were placed on a Wrist Action Shaker
- Bottles removed and analyzed after 6, 24, 72,…hrs of shaking
- pH & EC
- ($Al^{3+,}$ Fe^{3+}, Mn^{2+}, Mg^{2+}, Ca^{2+} and K^{+}) by ICP-OES

Materials & Methods

Microwave Digestion

- 0.5 g overburden + 9 mL HNO_3 + 3 mL HCl
- 175°C and increased pressure

Dilute Nitric Acid (HNO_3)

- **1/1000 Dilution of trace metal grade HNO_3**
  - **0.016 M**
  - **pH: 2.0**
  - **EC: 6.17 mS cm^{-1}**

- **Proton-Promoted Dissolution**
  - **Acid conditions: protons can promote mineral dissolution by binding to surface oxide ions, causing bonds to weaken**
    - **The metal species is detached into solution.**

EDTA

- **Chelating Ligand: 1+ ions form multiple bonds to a central metal atom.**
  - **0.5 M**
  - **pH: 8.0**
  - **EC: 47.1 mS cm^{-1}**

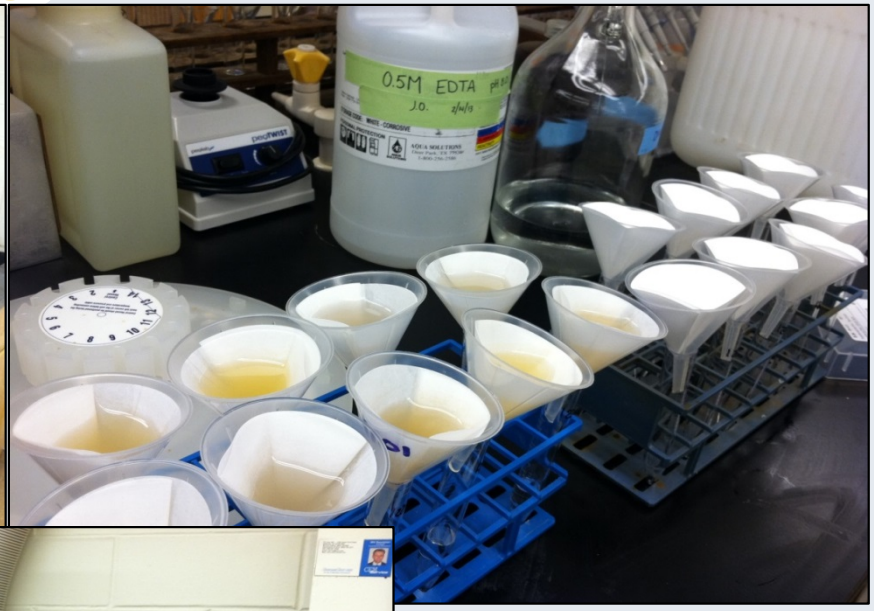
- **Ligand-Promoted Dissolution**

Microwave Digestion
USEPA Method 3051

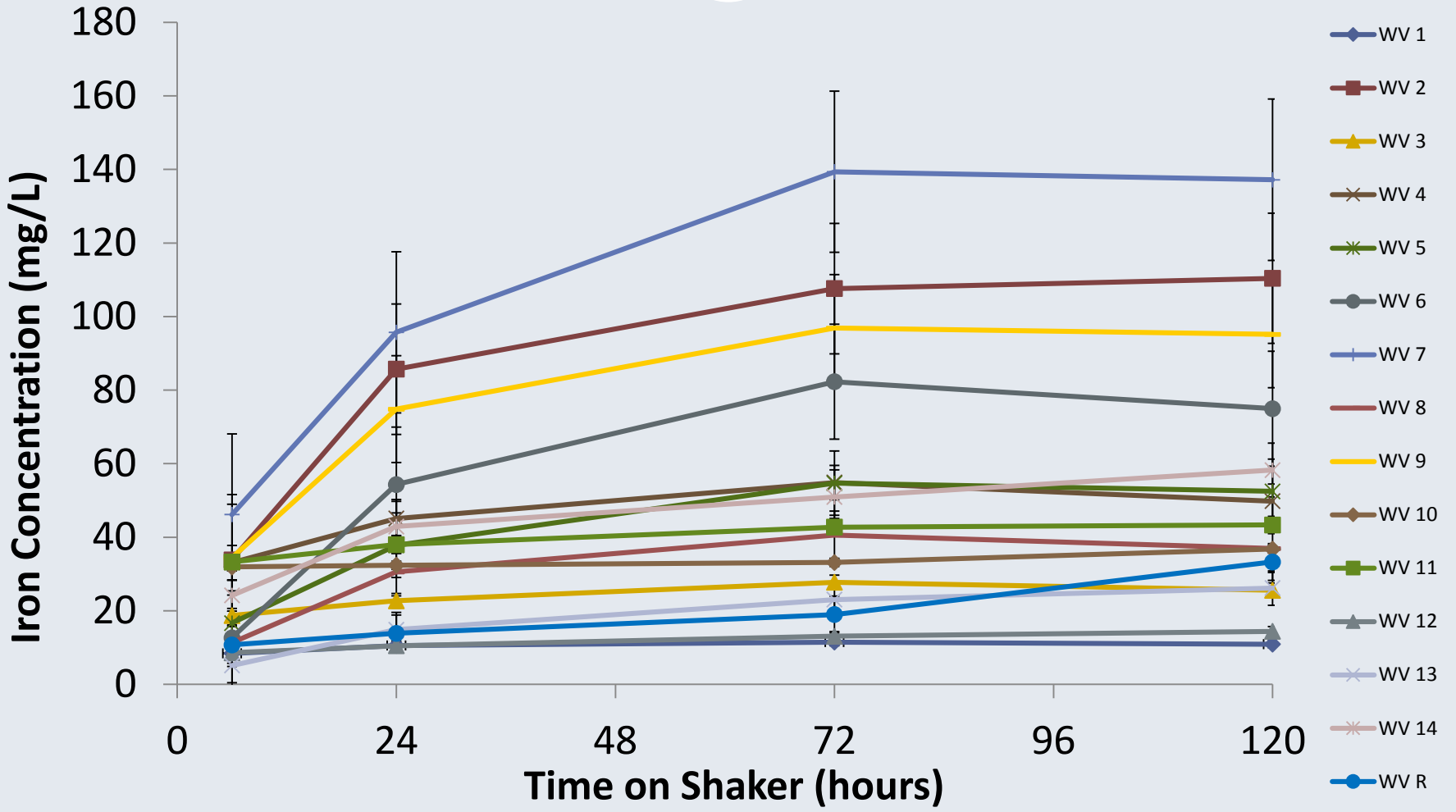
- **Will provide the upper limit on constituent release**

- **May provide a quicker prediction of potential TDS release than the shaking techniques**

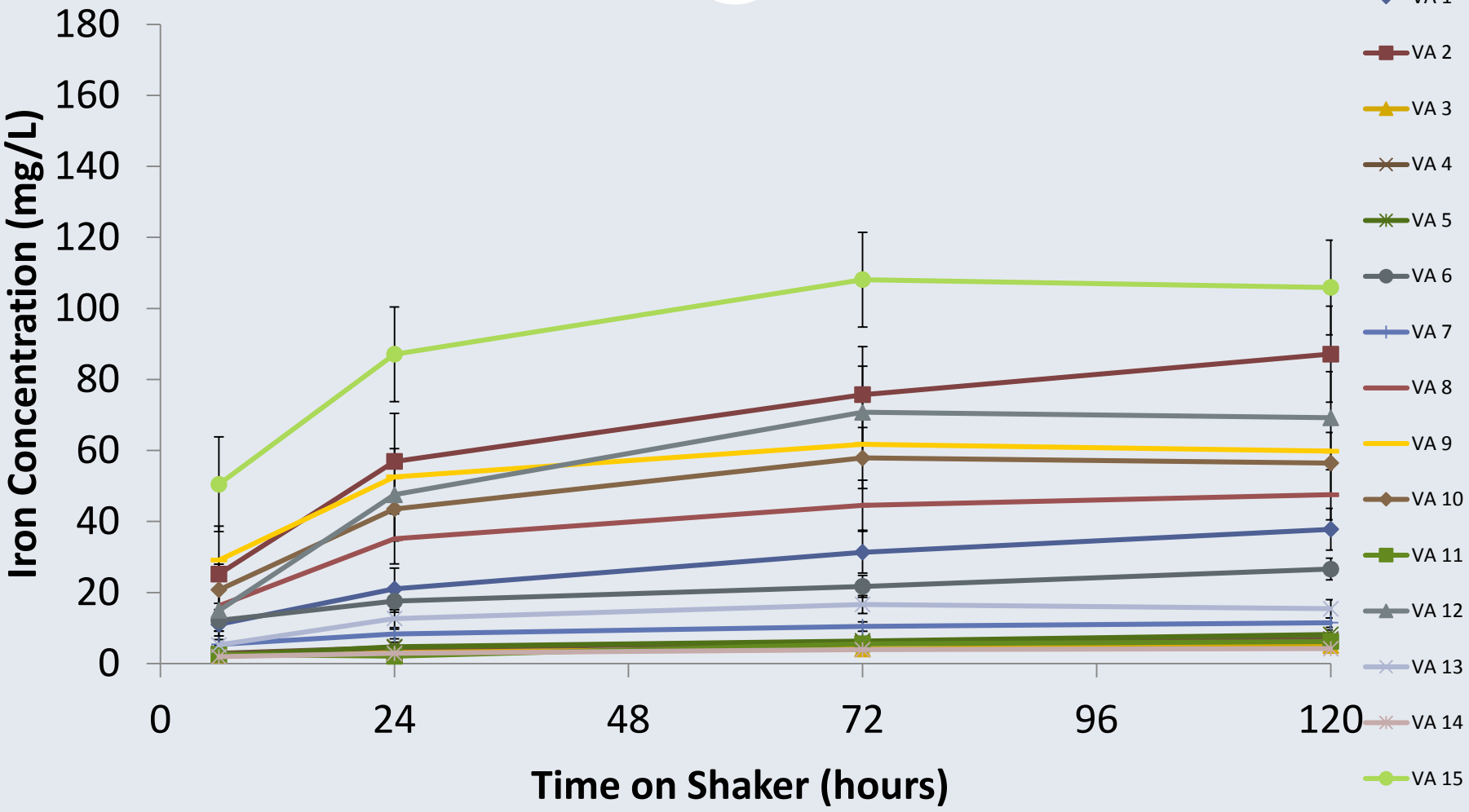
Results



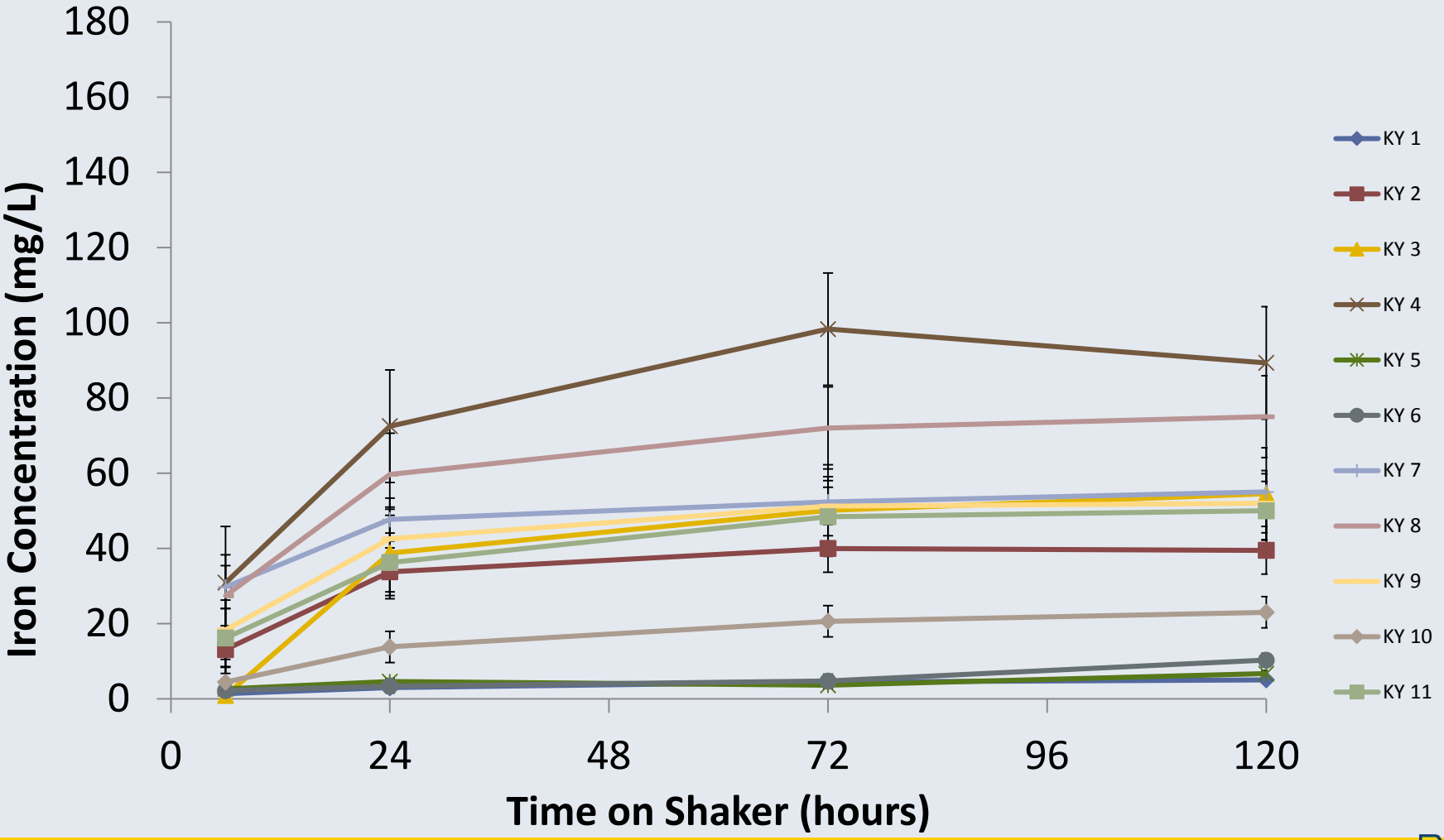
Iron Released from WV Samples Shaken in Dilute HNO_3



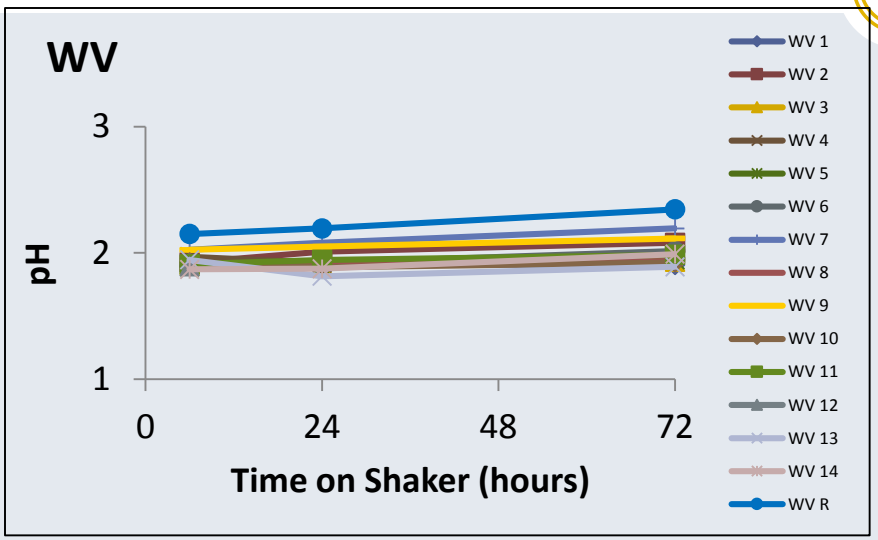
Iron Released from VA Samples Shaken in Dilute HNO_3

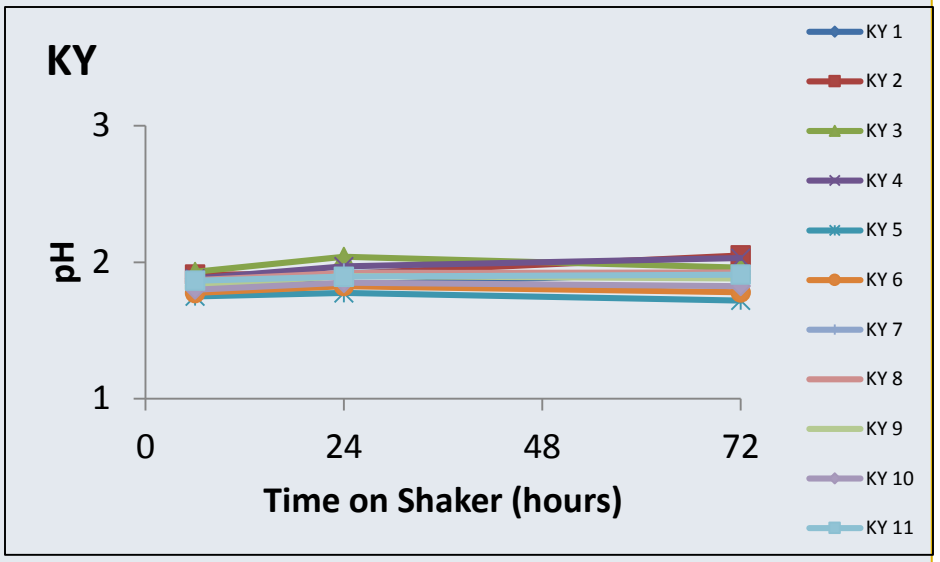


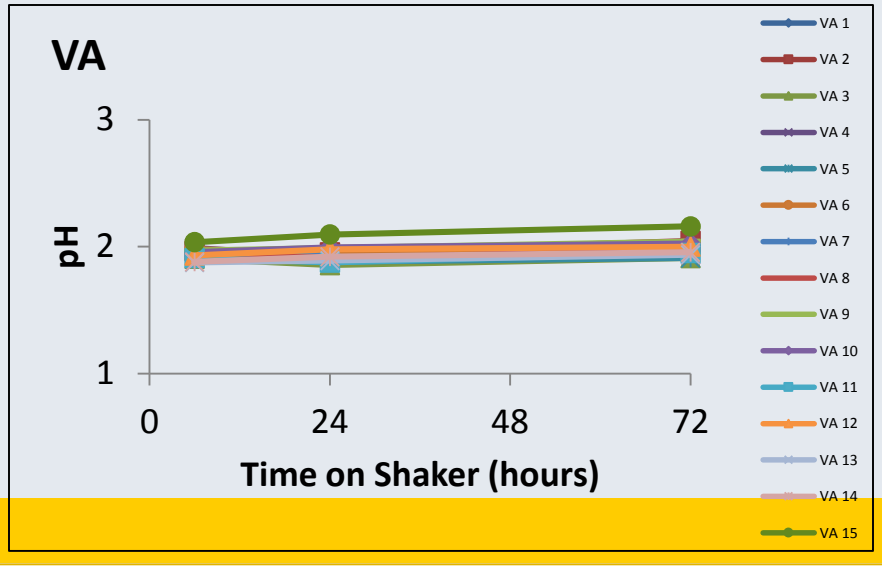
Iron Released from KY Samples Shaken in Dilute HNO_3



pH of Dilute HNO_3 Samples



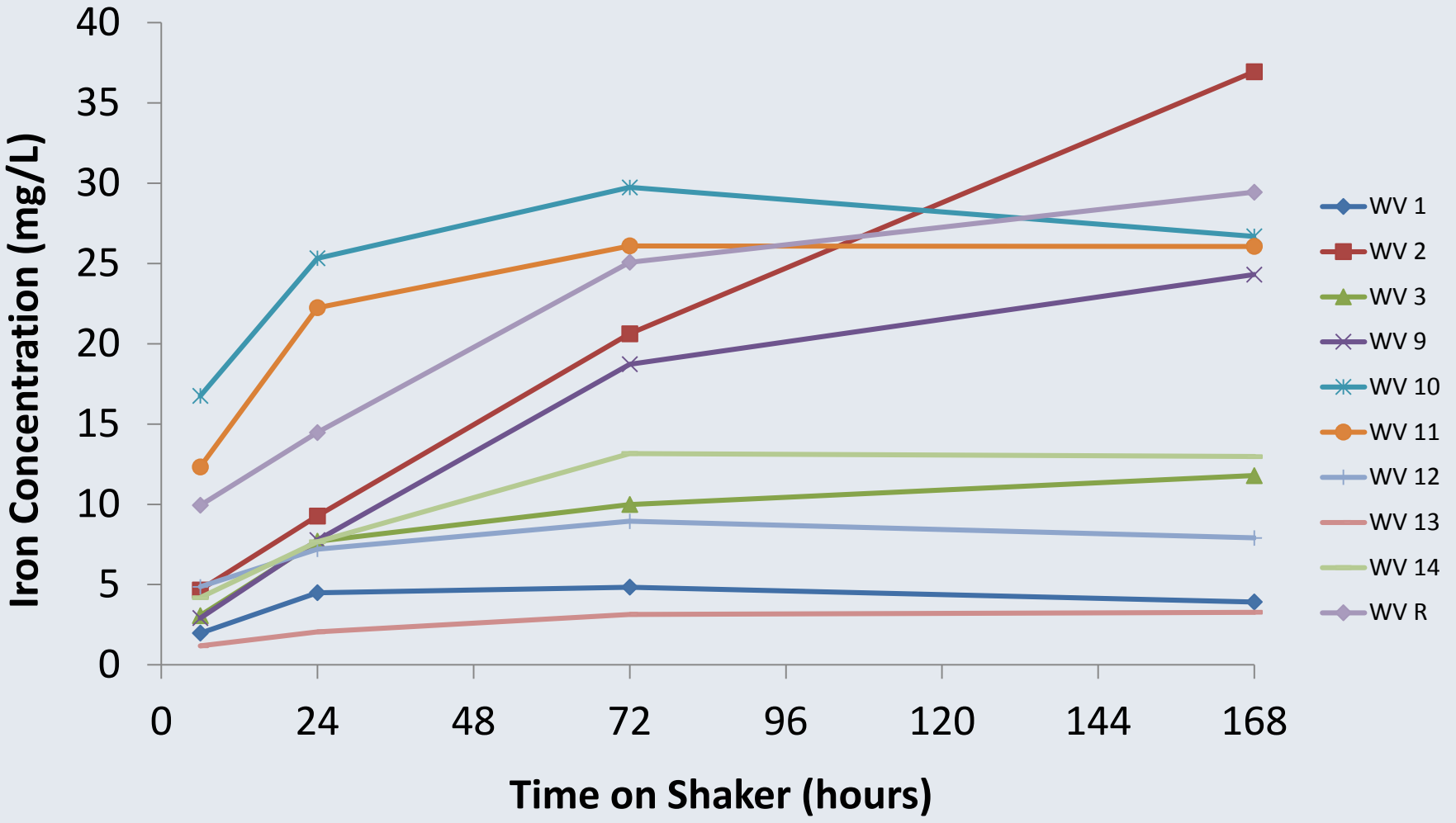




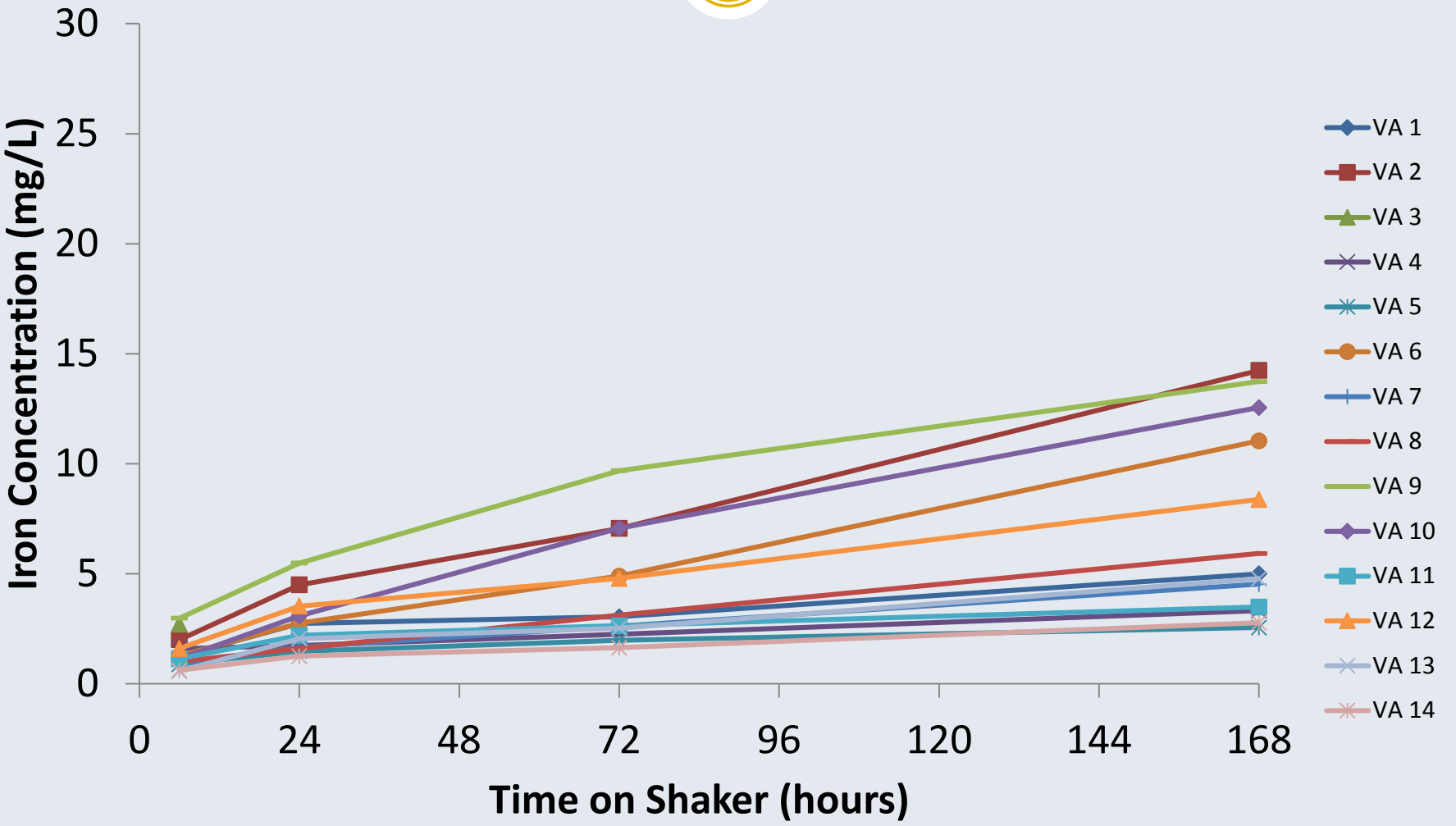
Summary Dilute HNO3

- Concentrations level off after 72 hours of shaking
- pH is stable around 2.0
- Similar pattern for all elements

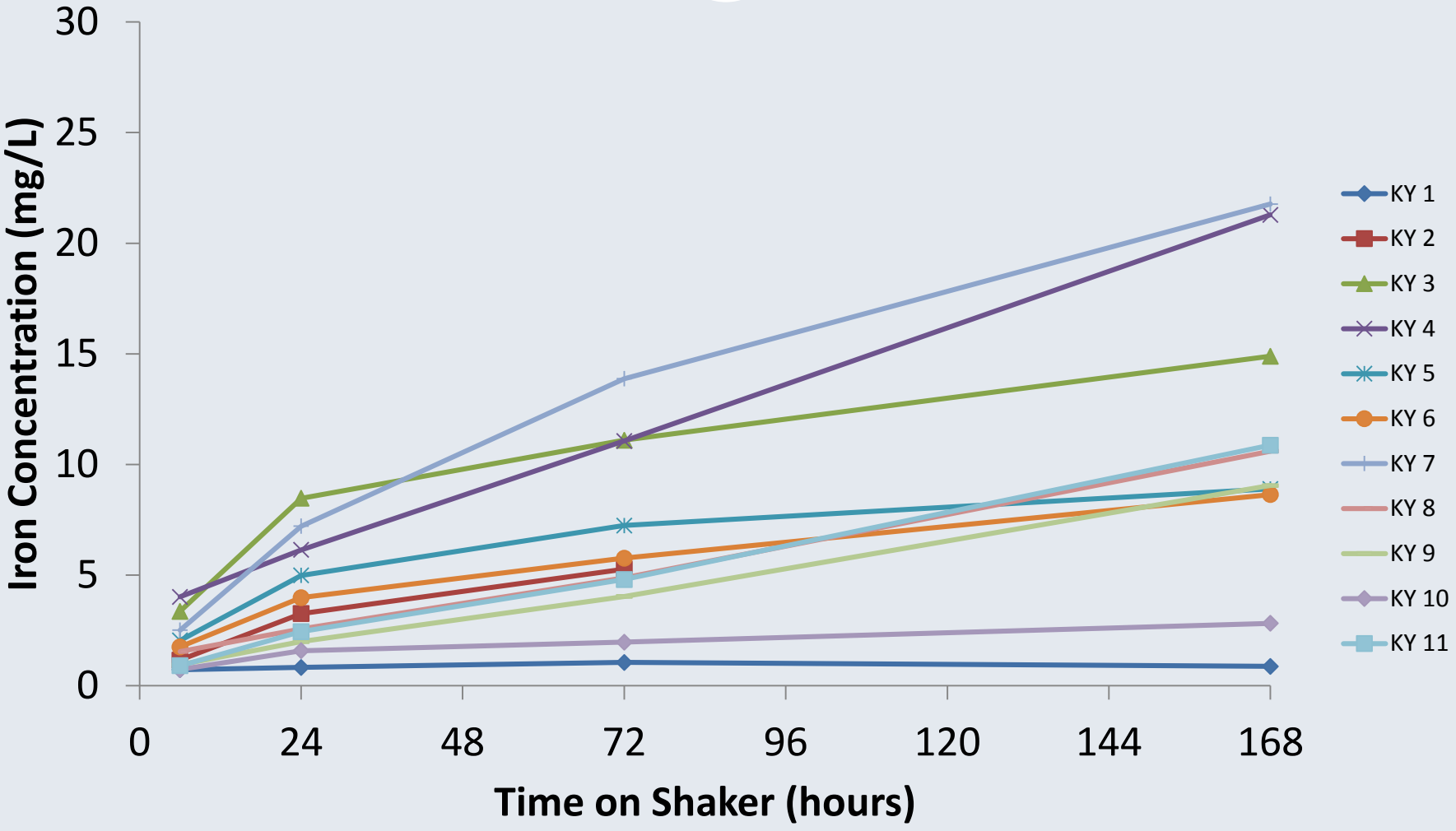
Iron Released from WV Samples Shaken in EDTA



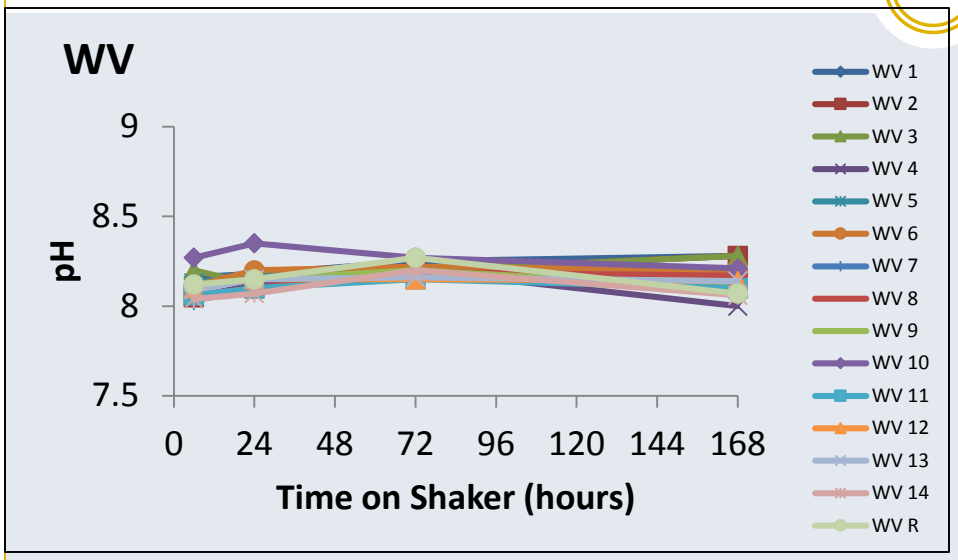
Iron Released from VA Samples Shaken in EDTA

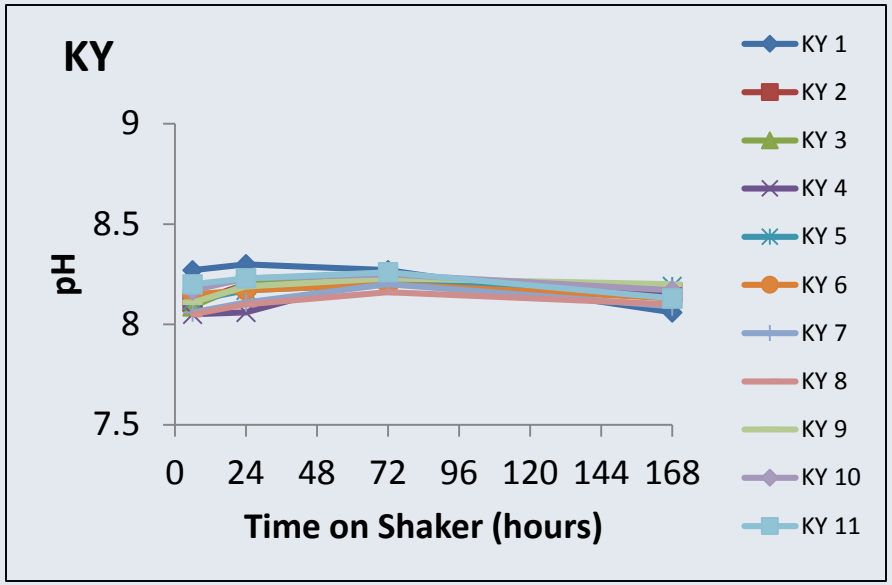


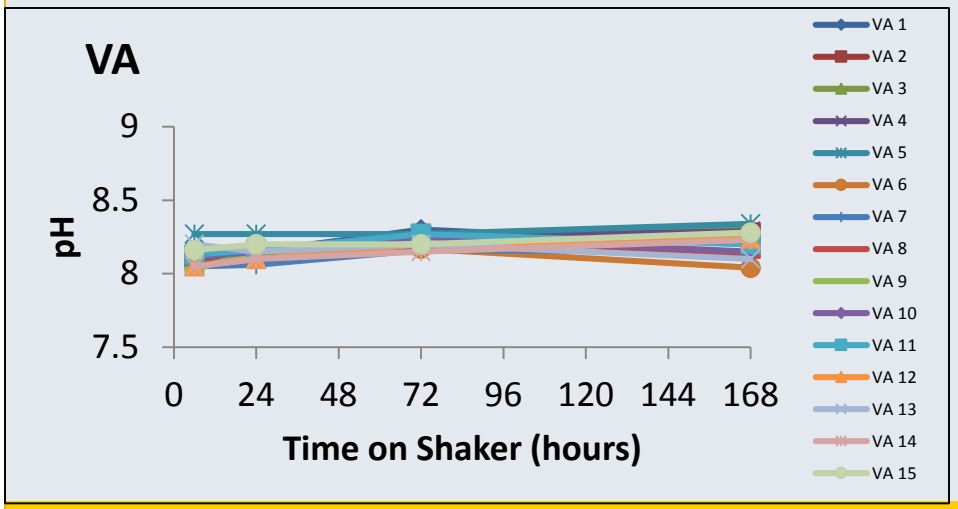
Iron Released from KY Samples Shaken in EDTA



pH of EDTA Samples







Summary EDTA

- About 50% of the samples level off after 168 hours (1 week) of shaking.
  - Same samples kept increasing after one month of shaking
- The pH is stable around 8.0.

Microwave Digestion

Sample	Iron Concentration		
	mg kg^{-1}	---------- mg L^{-1} ----------	
	Digestion	HNO_3	EDTA
VA 1	644,448	31.3	5.0
VA 2	1,268,520	75.7	14.2
WV 3	468,216	27.8	11.8
WV 4	824,208	54.9	22.3
KY 5	809,328	3.6	8.9
KY 6	1,726,080	4.7	8.6

Summary Microwave Digestion

- **Microwave Digestion breaks the mineral structure providing almost a total elemental analysis.**

- **The concentration of elements released from Microwave Digestion ranges from 4 to 5 orders of magnitude more than the dilute HNO_3 and EDTA shaking solutions.**

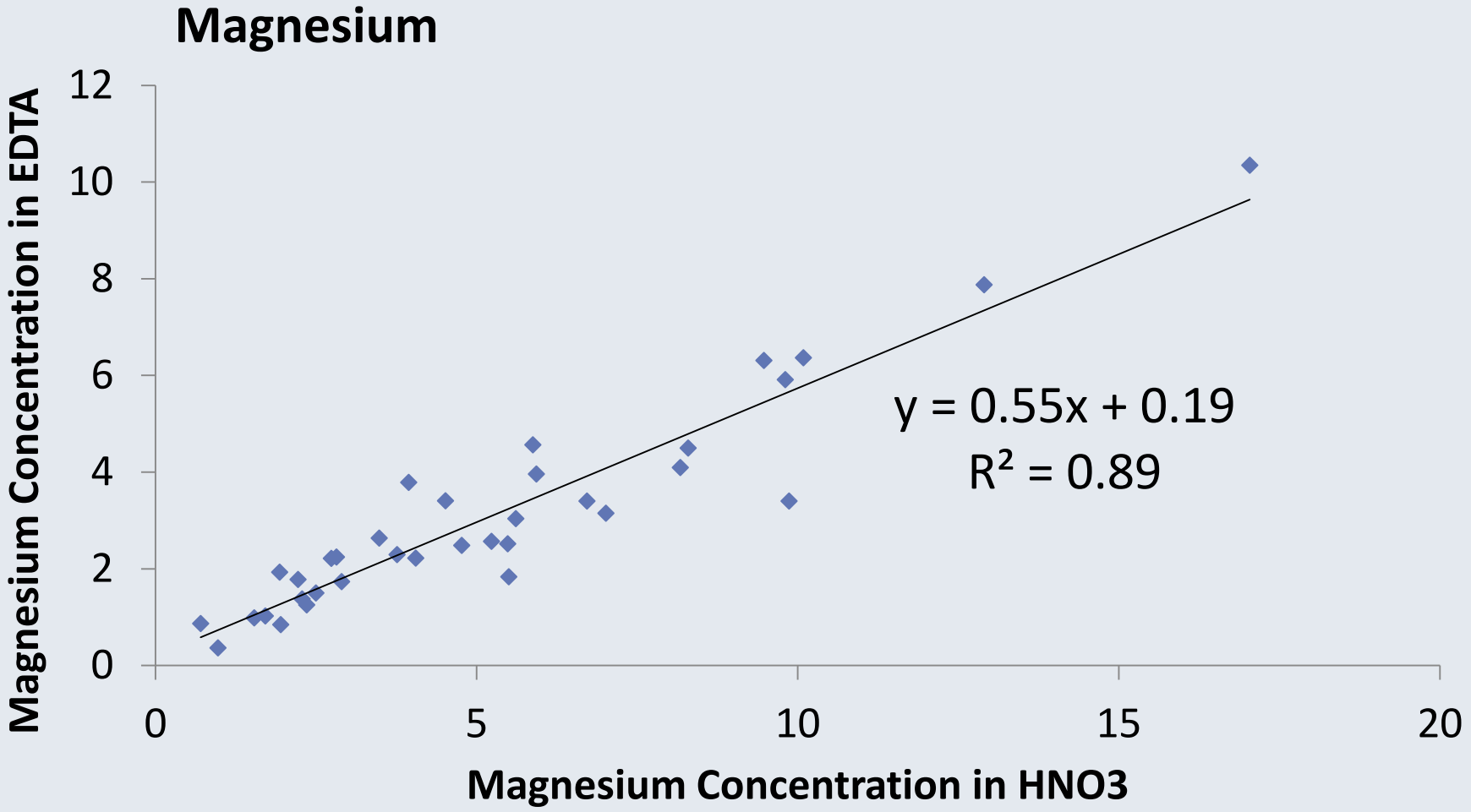
Correlation Between the Two Shaking Methods

- **Is there a relationship between the two methods?**
  - Dilute HNO_3 versus EDTA
    - Perhaps one is better than the other
    - Perhaps one is better correlated to field-scale scenarios
- **Comparison of all 41 samples at their respective "endpoints"**
  - (72 hrs and 168 hrs)

R^2 of Elements Extracted from the Dilute HNO3 and EDTA Solutions

Element	R^2	Trend
Aluminum	0.43	logarithmic
Iron	0.60	linear
Manganese	0.69	power
Magnesium	0.89	linear
Calcium	0.91	linear

Correlation Between Dilute HNO_3 and EDTA



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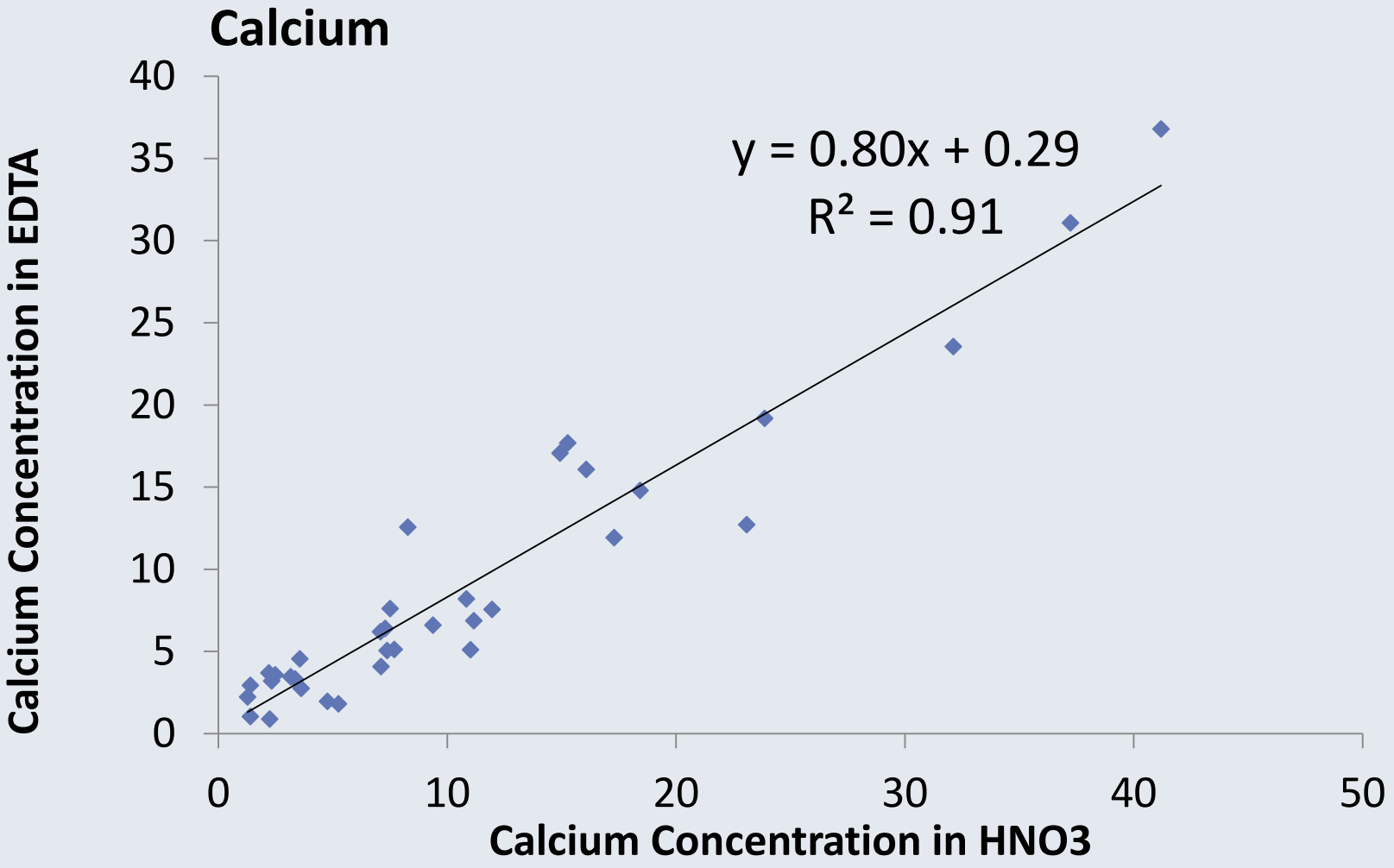

Relationship Between Dilute HNO3 and EDTA

- Strong linear relationship between the two methods in respect to Calcium and Magnesium concentrations (r^2=0.91, 0.89)

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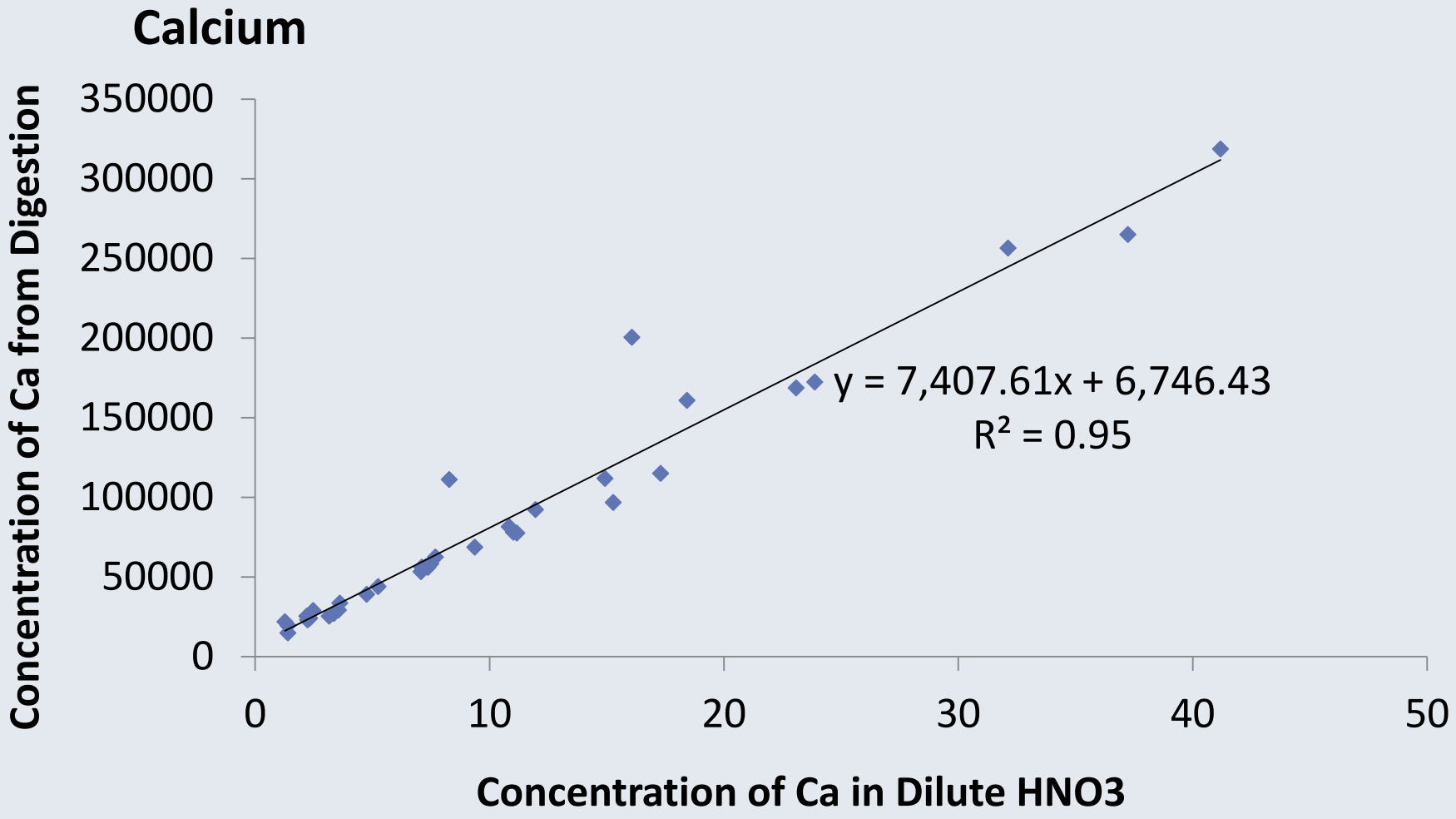
Iron	0.60	linear
Manganese	0.69	power
Magnesium	0.89	linear
Calcium	0.91	linear

Relationship Between Digestion and the Two Shaking Methods

Microwave Digestion vs. Dilute HNO_3

Element	R^2	Trend
Aluminum	0.19	linear
Iron	0.21	polynomial
Manganese	0.86	power
Magnesium	0.58	linear
Calcium	0.95	linear

Correlation of Microwave Digestion and Dilute HNO_3

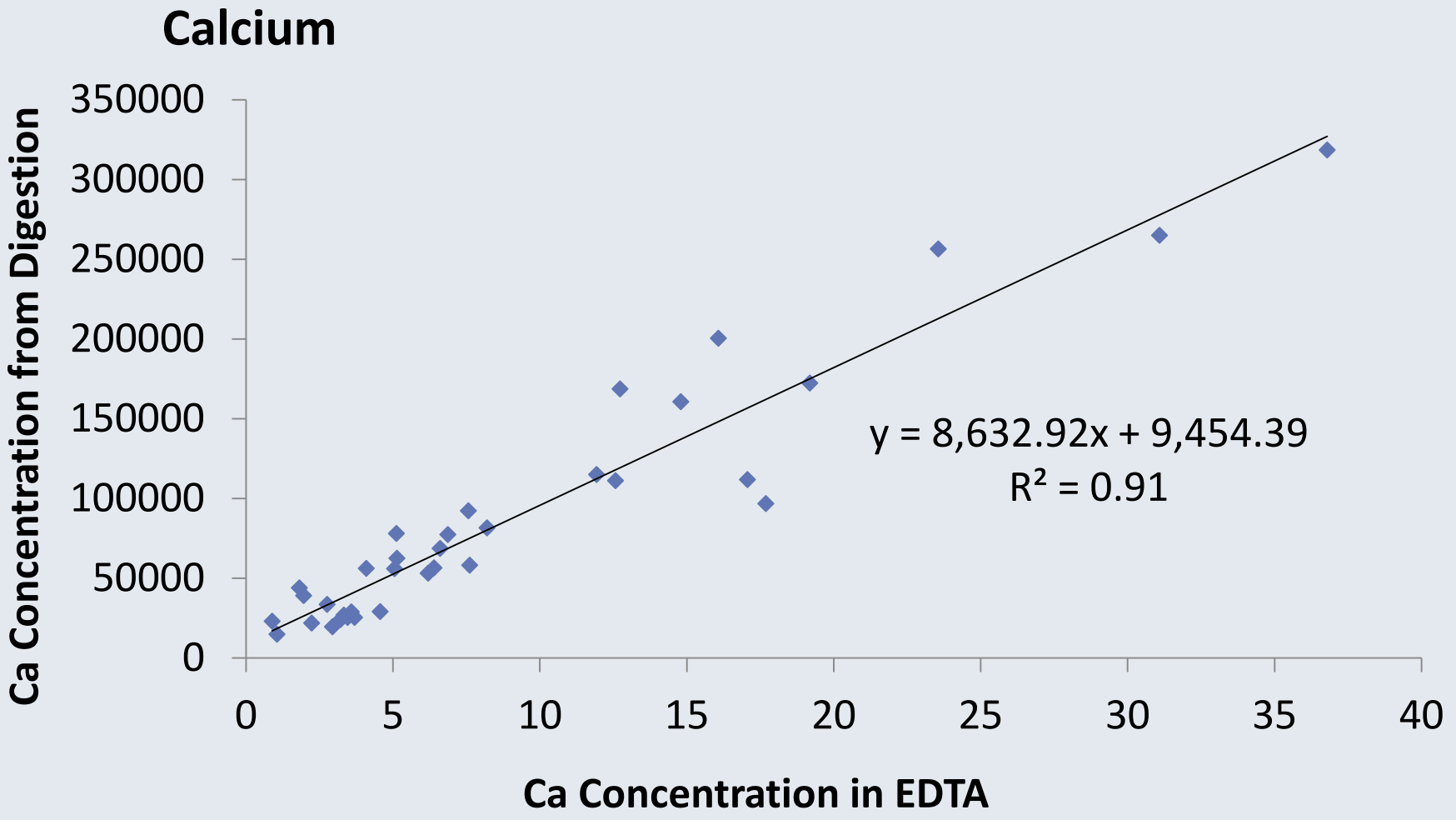


Relationship Between Digestion and the Two Shaking Methods

Microwave Digestion vs. EDTA

Element	R^2	Trend
Aluminum	0.20	logarithmic
Iron	0.20	power
Manganese	0.67	linear
Magnesium	0.59	linear
Calcium	0.91	linear

Correlation of Microwave Digestion and EDTA



Summary of the Three Methods

- **The three weathering techniques can be used interchangeably when specifically analyzing Calcium** ($r^2 > 0.91$)**.**
- **Shaking with dilute HNO3 and EDTA can be used interchangeably when specifically analyzing Magnesium and Calcium** ($R^2 = 0.89, 0.91$)**.**
- **Microwave Digestion and shaking with dilute HNO_3 had an R^2 of 0.86 in regards to manganese.**
- **Microwave Digestion and shaking with EDTA had an R^2 of 0.67 in regards to manganese.**

Correlation with % Sulfur

Sample Number	Bottom depth (feet)	Rock type	Fizz	Color	%S	$CaCO_3$ equivalent - tons/1000 tons of material: Max. from %S	Amount present (NP)	Max. needed (pH7)	Excess	Paste pH
1	3	Soil	0	7/3	.035	1.09	3.52		2.53	4.4
2	6	SS	0	8/6	.029	0.91	-1.51	2.42		4.3
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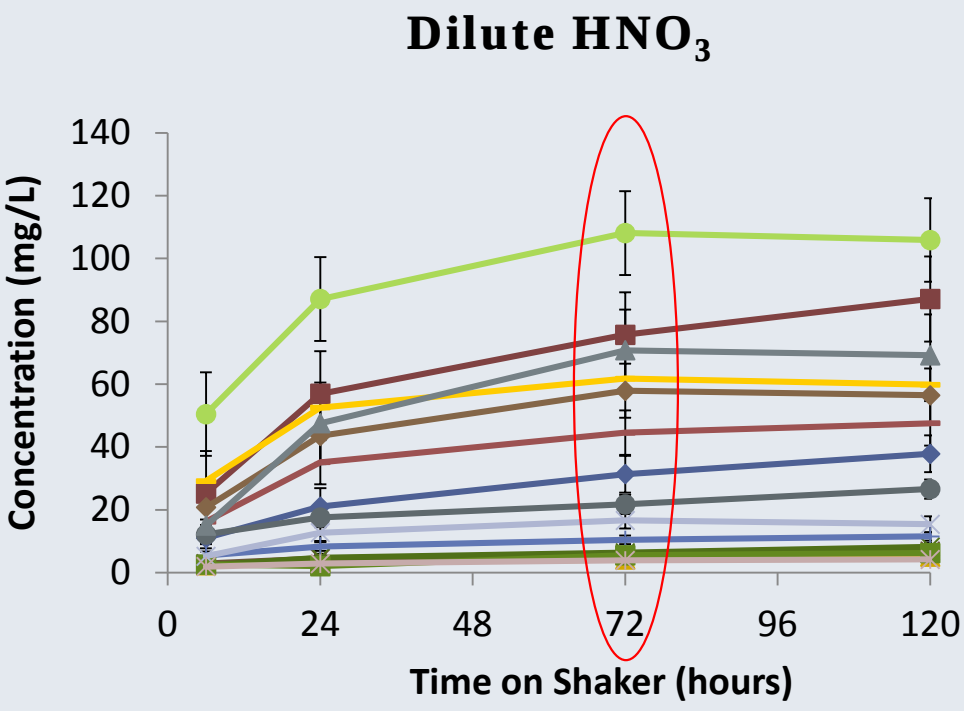
7	24	MS	0	7/1	.263	8.22	-0.94	9.16		4.8
8	28	MS	1	7/1	.179	5.59	78.33		72.74	7.8

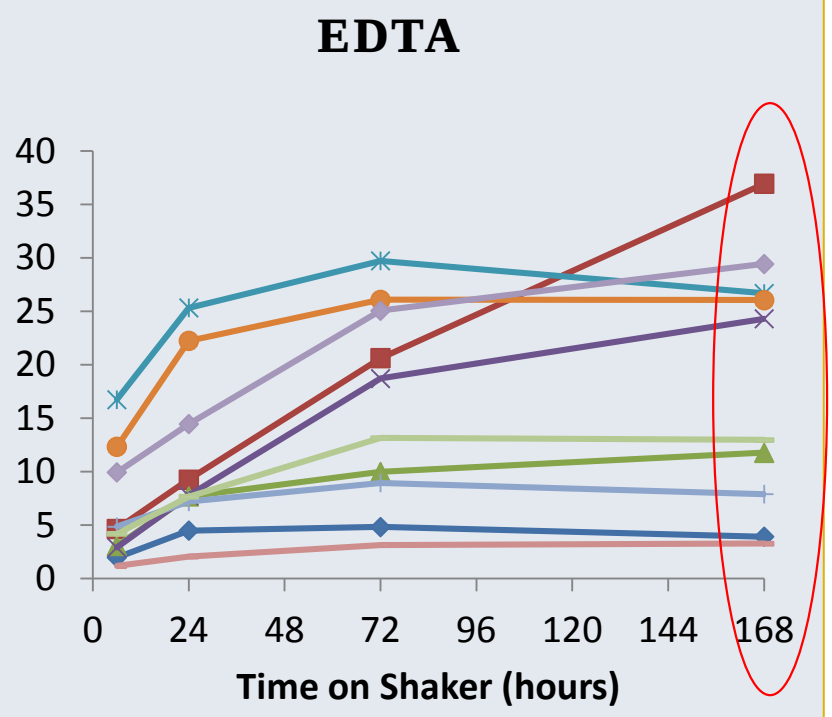
- **Can ABA data predict constituent release?**

Correlation with % Sulfur

- 9 VA Samples
- Compared concentrations extracted from the dilute HNO_3 samples and the EDTA samples to % S
  - Al, Fe, Mn, Mg, and Ca
- Microwave Digestion

Correlation with % Sulfur





Al, Fe, Mn, Mg, Ca

Relationships Between %S and Constituents Released

	Method			
	HNO_3	Trend	EDTA	Trend
Element	----------R^2 ----------			
Aluminum	0.06	polynomial	0.07	polynomial
Iron	0.53	polynomial	0.57	polynomial
Manganese	0.28	logarithmic	0.58	exponential
Magnesium	0.17	polynomial	0.32	polynomial
Calcium	0.50	polynomial	0.56	polynomial

Summary of % Sulfur Correlation

- **Can we use % S to predict constituent release from overburden material?** --Not quite.
- **Iron and Calcium are best correlated with % S ($r^2 \approx 0.50 - 0.57$).**
- **Samples shaken with EDTA have better correlation with % S than samples shaken with dilute HNO3.**

Future Research

- **Determine a TDS release index for overburden material (high, medium, low).**

- **Acid-Base Account Analysis:**
  - **Complete % Sulfur analysis for all samples**
  - **Neutralization Potential (NP) analysis**

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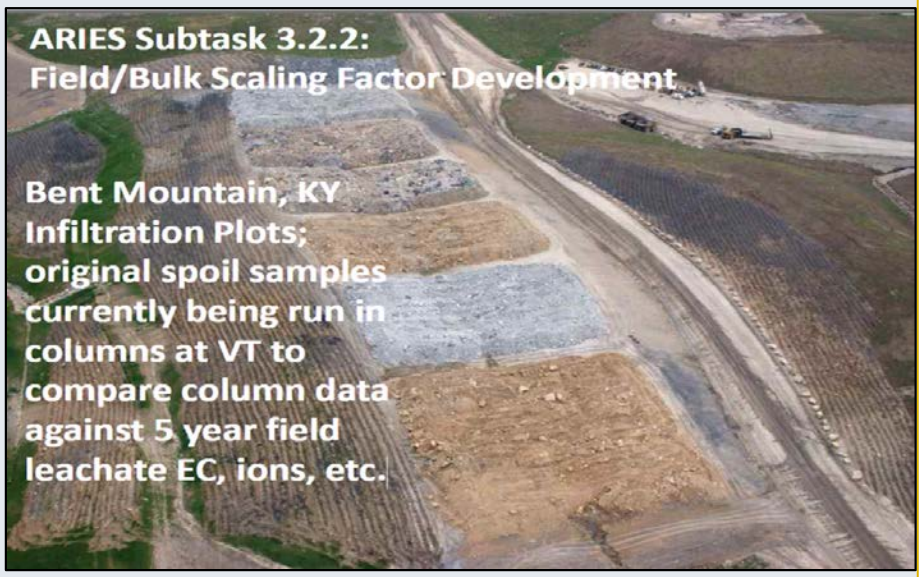
Future Research

- **Can we correlate our shaking data with VT column leaching data and/or UK data?**



ARIES Statement

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