Sub-Project A2: Simultaneous Removal of Inorganic Contaminants, DBP Precursors, and Particles in Alum and Ferric Coagulation

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Introduction

- *Brief Description:* Use enhanced alum or ferric coagulation for simultaneous inorganic and natural organic matter removal, and develop a mechanistic understanding of the interrelationships between NOM, inorganic contaminants, and metal precipitation. Inorganic contaminants of interest include:
  - Fluoride
  - Arsenic
  - Chromium
  - Manganese
- *Anticipated target utility characteristics:*

  - Small water systems using surface waters with elevated inorganic contaminant concentrations that may already be applying alum or ferric coagulation as part of their treatment process
- *Continuum of technology development:*

Outputs and Outreach

Completed:

- “Mechanisms of fluoride removal: adsorption and co-precipitation with aluminum hydroxide in the presence and absence of NOM” ACS National Meeting, Denver, March 2015
- “Impact of ligands on co-precipitation and adsorption with aluminum” ACS National Meeting, Boston, March 2016

Scheduled:

none

Anticipated:

White paper for WINSSS website, late Spring 2016.
Manuscript for submission to a technical Journal, Fall 2016.

WINSSS or US EPA Small Systems Webinar – late 2016 or 2017

Outline

- Alum Coagulation for Fluoride Removal (Isabella Gee)
  - Bench- Scale Testing
    - Synthetic Water
    - Natural Water
  - Pilot Study Testing
    - MacKenzie Lake, TX
    - Manitou Springs, CO
- Fe Coagulation for Fluoride Removal (Ki Yeo)
  - Bench- Scale Testing
    - Synthetic Water
- Al and Fe Coagulation for Trace Metal Removal (Lynn Katz)

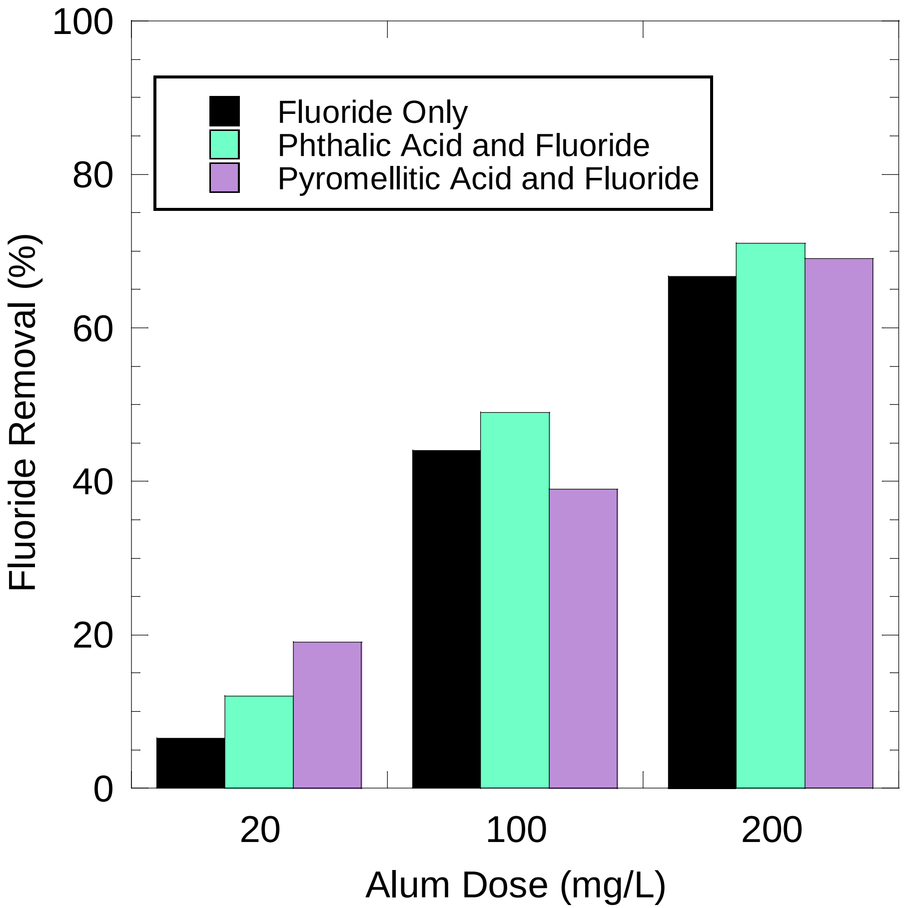
Synthetic Water Tests

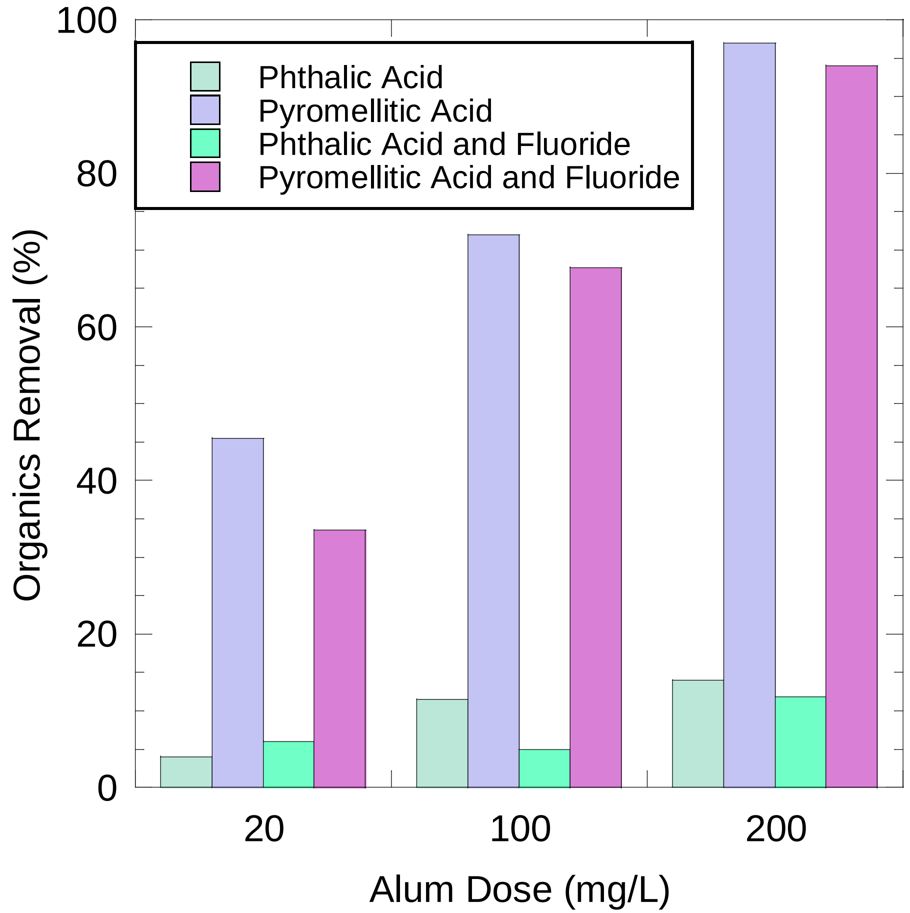
Synthetic Water Test Conditions

Reagent	Quantity	Unit	Purpose
$CaCl_2$	336	mg	Hardness
$NaHCO_3$	504	mg	Alkalinity
NaCl	Variable	mg	Ionic Strength
HCl (1N)	6	mL	Acidification
H_2O	1.994	L	Background

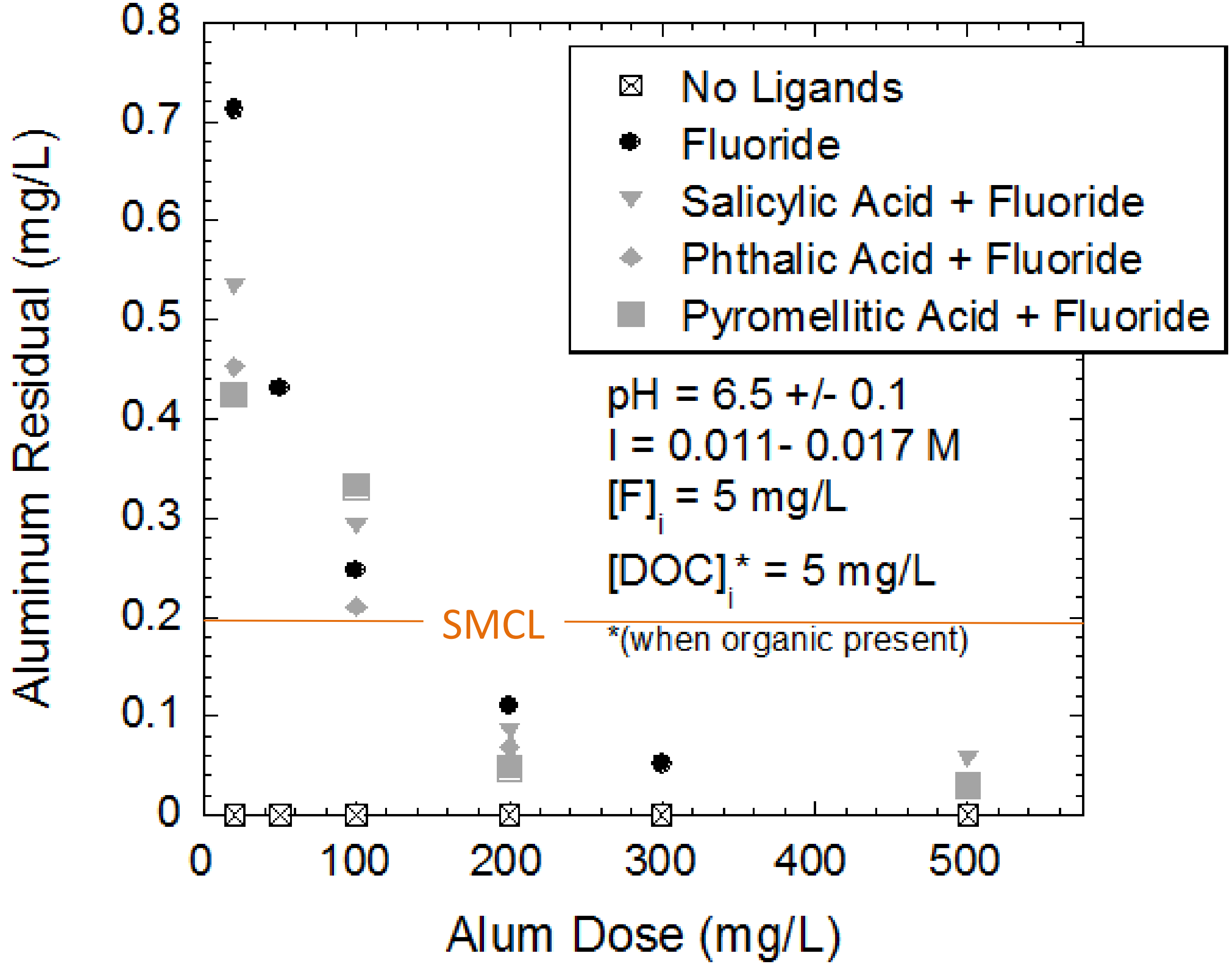
- Three NOM surrogates
  - Pthallic Acid
  - Pyromellitic Acid
  - Salycylic Acid
- pH varied
  - Between 4 and 9
- Coagulant dose varied
  - Between 20 – 500mg/L

Removal of Fluoride & Organic Acids





Aluminum Residuals



Natural Water Tests

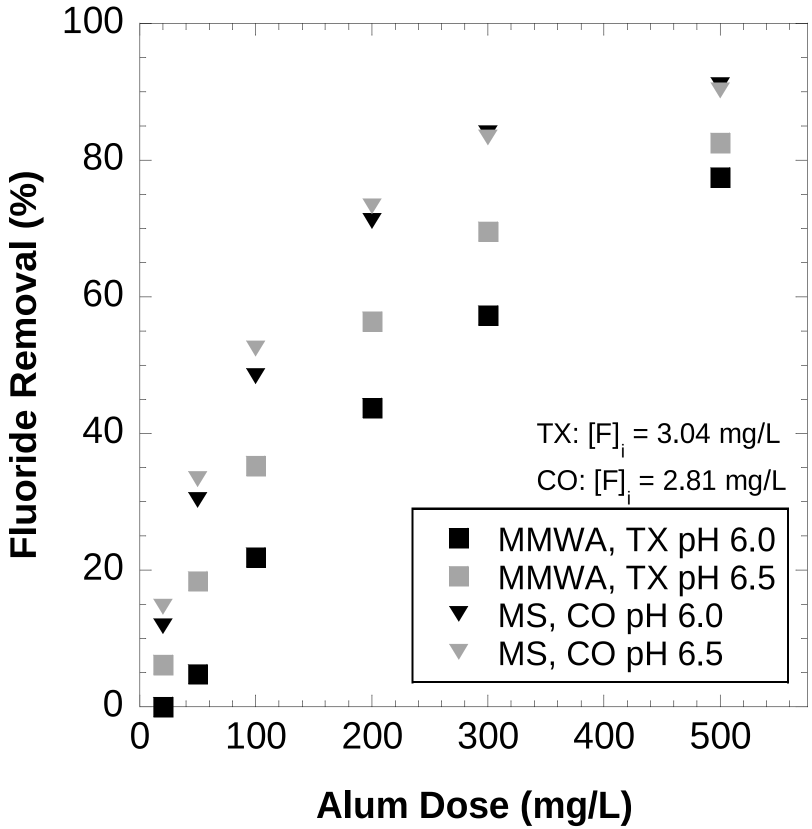
Natural Water Tests

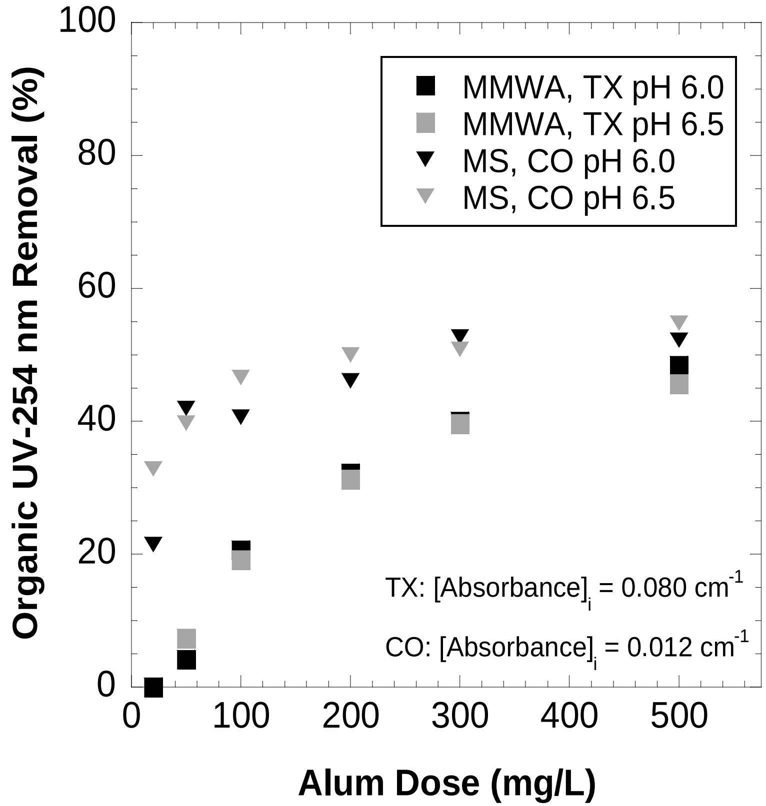
- Two Waters
  - MacKenzie Lake, TX
  - Manitou Springs, CO
- pH controlled
  - pH 6.5
  - Using Na_2CO_3, NaOH, and HCl
- Alum dose varied between each jar
  - Between 20 – 500mg/L

Natural Water Characteristics

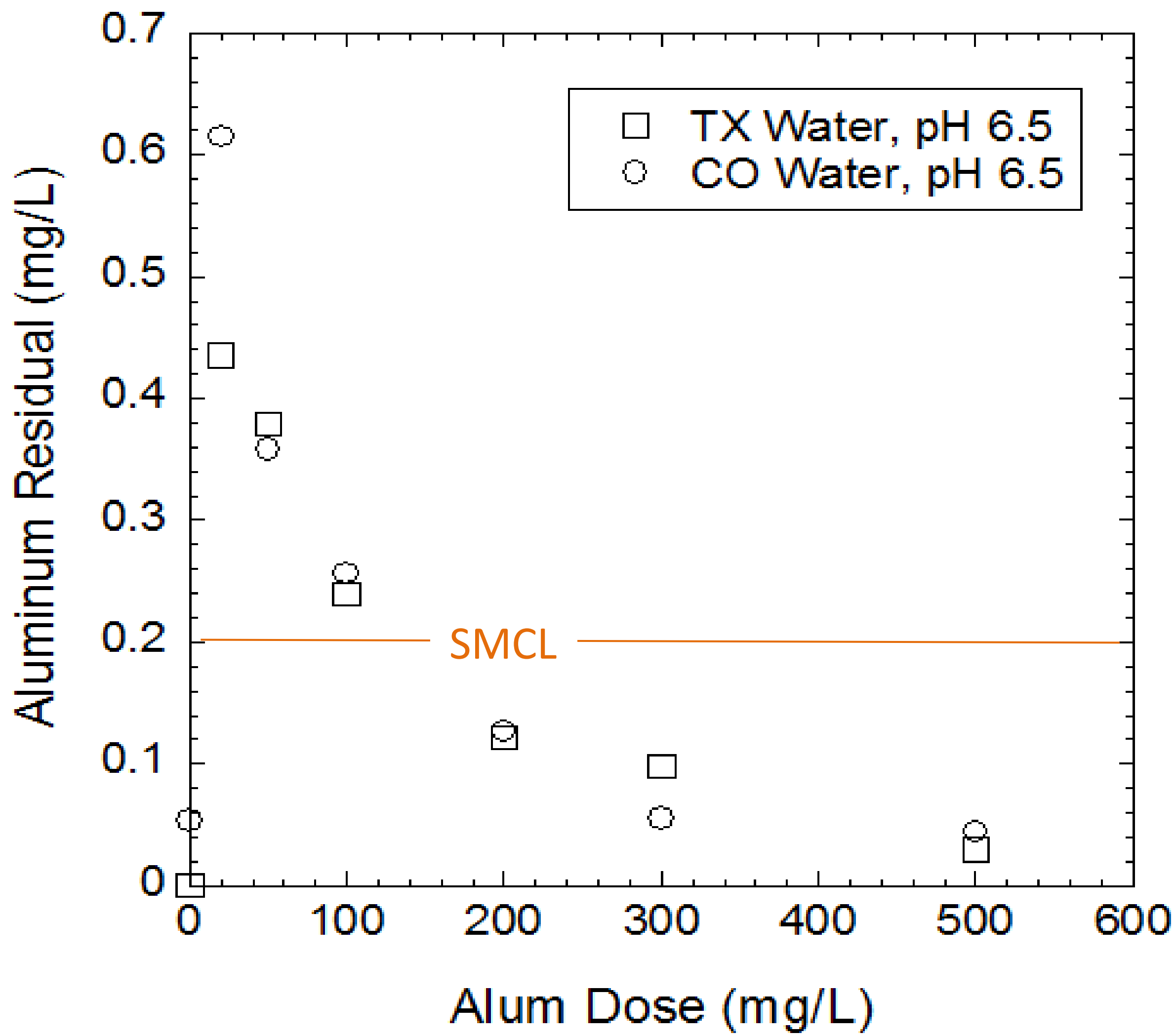
Parameter	Natural Waters	
	TX Water Site	CO Water Site
Water Source	SW	SW
pH	8.60	7.58
[F] (mg/L)	3.04	3.15
DOC (mg/L Carbon)	9.20	1.18
SUVA (L/mg-m)	0.87	1.76
Alkalinity (mg/L $CaCO_3$)	294.6	16.8

Natural Waters from TX and CO - Fluoride and Organic Removal





Aluminum Residuals



Pilot Studies

Pilot Studies

MacKenzie Lake, TX

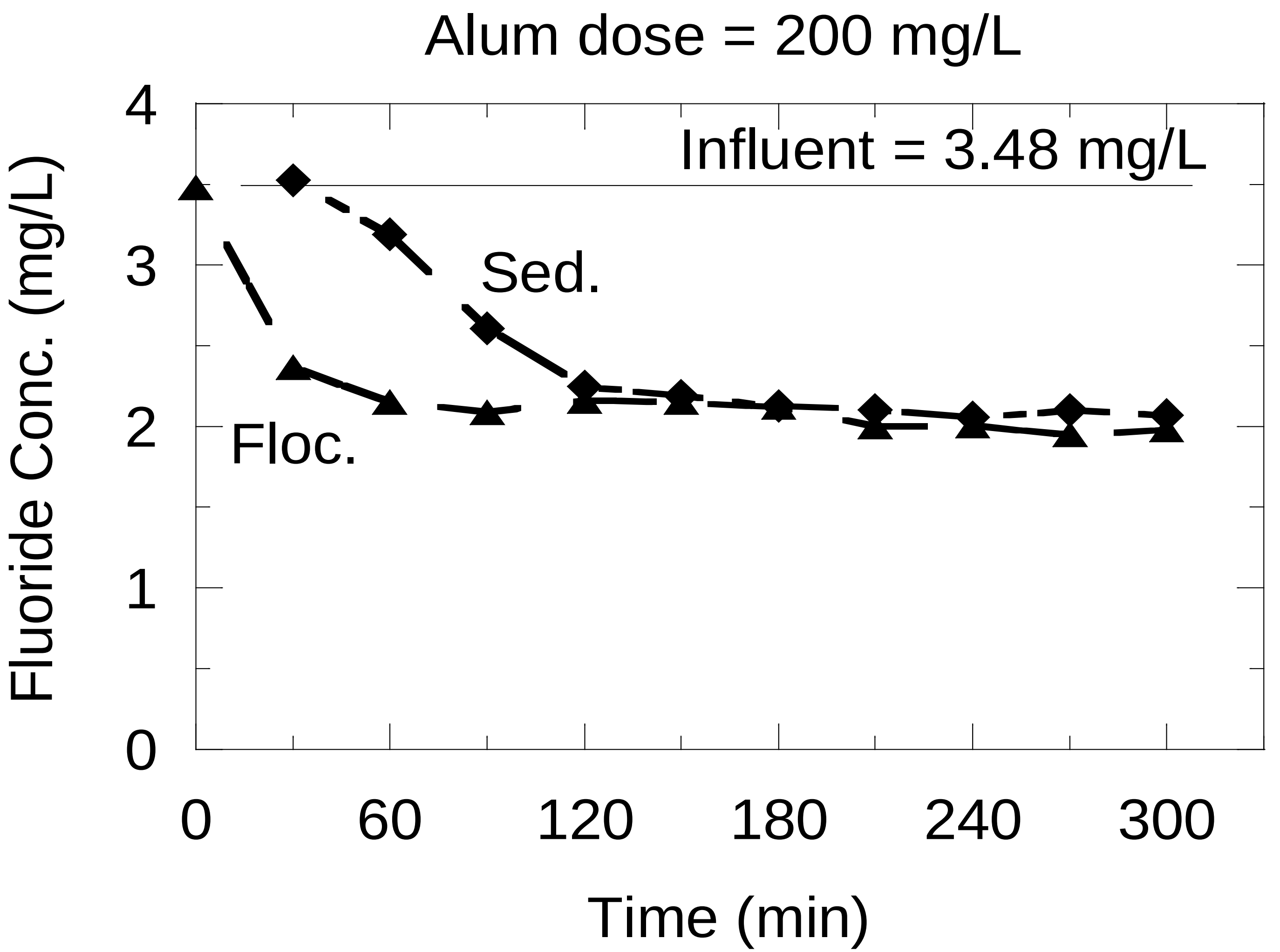
- pH varied with alum dose (High Alk water)
- Alum dose varied between 100—300 mg/L

Manitou Springs, CO

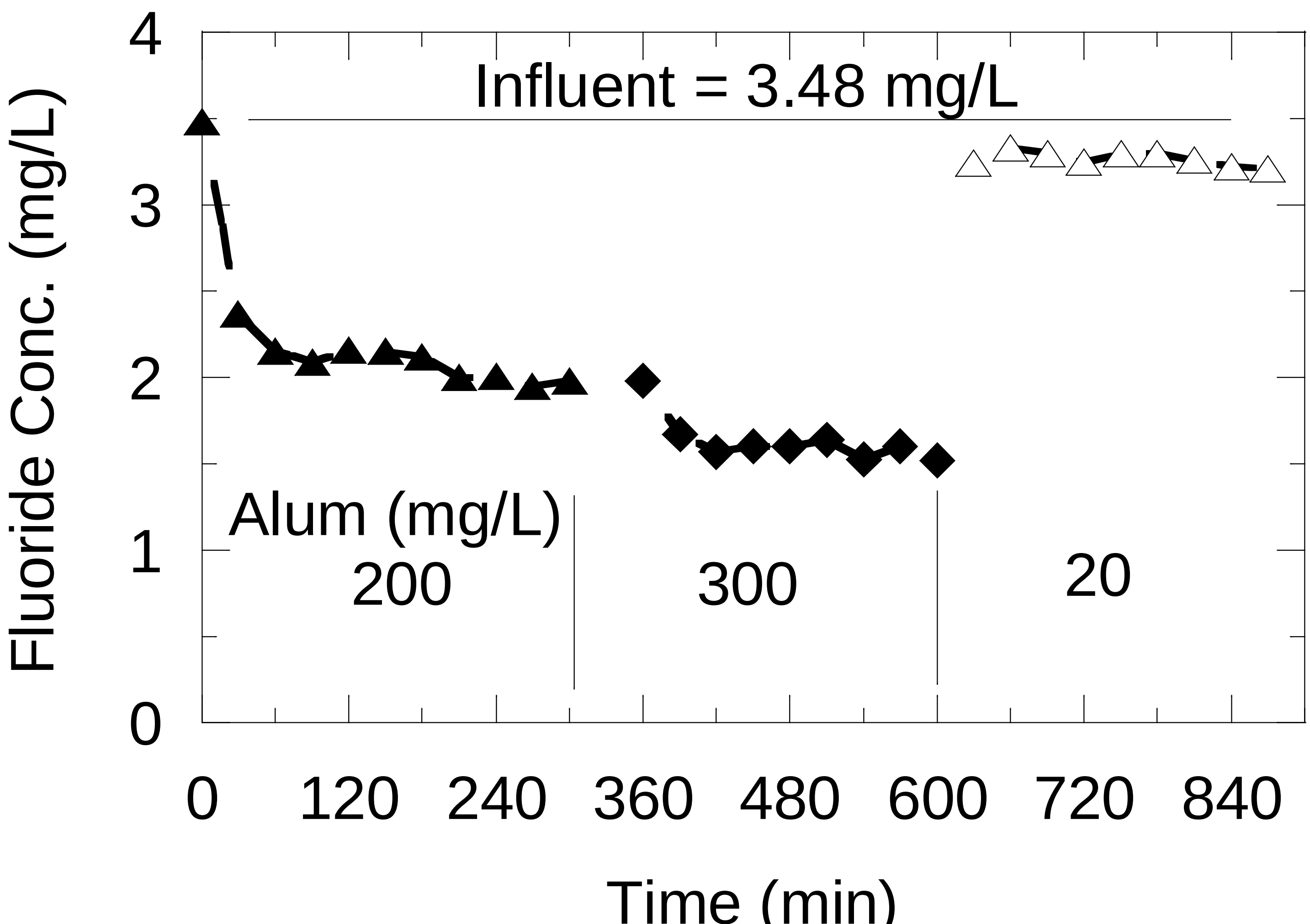
- pH control required for low Alk water (6.5,7.5)
- Alum dose varied between 20 – 300 mg/L

MacKenzie Lake, TX

TX Pilot Studies: Approach to Steady State



TX – Fluoride Removal



MMWA, TX Steady State Values in Flocculation Effluent

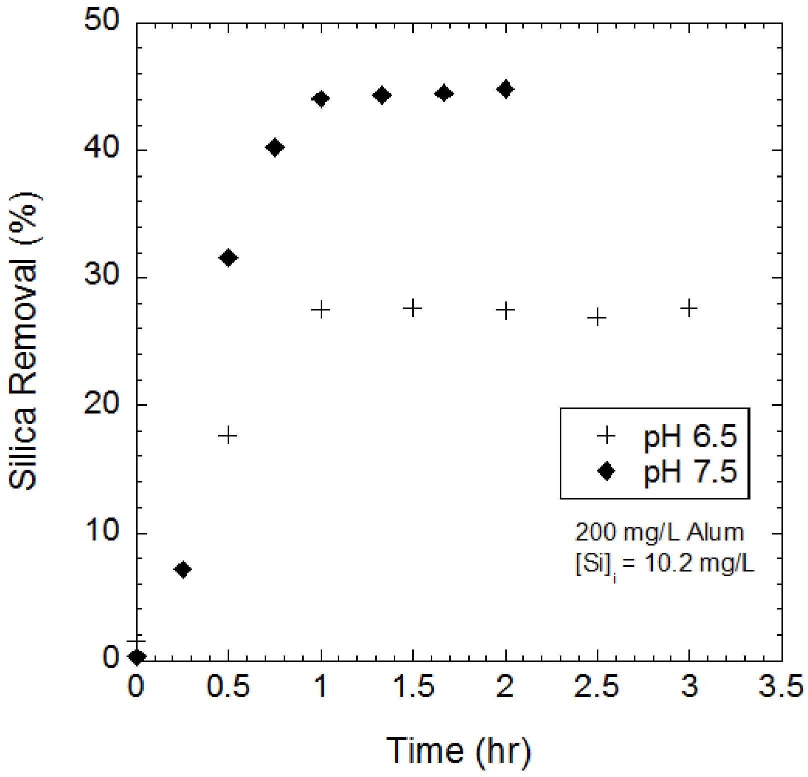
Alum Dose (mg/L)	pH	F (mg/L)	% Removal	DOC (mg/L)	% Removal
20	8.32	3.24	6	8.9	1
50	7.98	3.14	10	8.9	1
100	7.72	2.88	21	8.4	7
150	7.35	2.42	30	8.0	11
200	7.20	1.98	43	7.4	18
300	6.89	1.57	56	6.8	24

Manitou Springs, CO

Colorado Pilot Results

Alum Dose (mg/L)	F Removal (%)	Si Removal (%)	Al Residual (mg/L)	UV-254 Removal (%)
20	14.3	4.8	0.475	53
50	33.9	11.5	0.229	62
100	52.8	16.7	0.074	65
150	63.6	21.2	0.056	64
200	71.2	27.4	0.038	65
300	79.8	34.0	0.031	66

Effect of pH on Removals



pH	F Removal (%)	UV-254 Removal (%)
6.5	71	65
7.5	51	54

Fluoride Removals

Alum Dose (mg/L)	Synthetic Water	CO Jar Test	CO Pilot	TX Jar Test	TX Pilot
20	17	12	14	6	6
50	30	34	34	18	10
100	46	48	53	35	21
150	71	74	64	56	30
200	80	81	71	70	43
300	86	87	80	83	56

Conclusions for Al Coagulation

- Alum coagulation can be an effective treatment process for lowering fluoride concentrations to acceptable levels. The optimum pH is 6.5.
- The impact of NOM on F removal is minimal.
- Pilot tests of the Colorado Water were consistent with Jar Tests and Synthetic water tests
- Pilot tests for the TX water showed lower removals of F than Jar tests due to differences in pH
- F removal in jar tests with TX water were also lower than the synthetic water tests due to differences in background water chemistry (e.g. low SUVA, high TOC, high alkalinity)

$FeCl_3$ Coagulation

Objectives

- Quantify Fluoride Removal in iron coagulation systems
- Determine the effect of NOM surrogates on fluoride removal
- Determine the effect of NOM on fluoride removal
- Determine the effect of fluoride on removal of NOM

Bench-Scale Testing

- Synthetic Water
- pH varied
  - pH 4.0 – 6.5 (ΔpH=0.5)
  - Using NaOH, and HCl
- $FeCl_3$ dose controlled

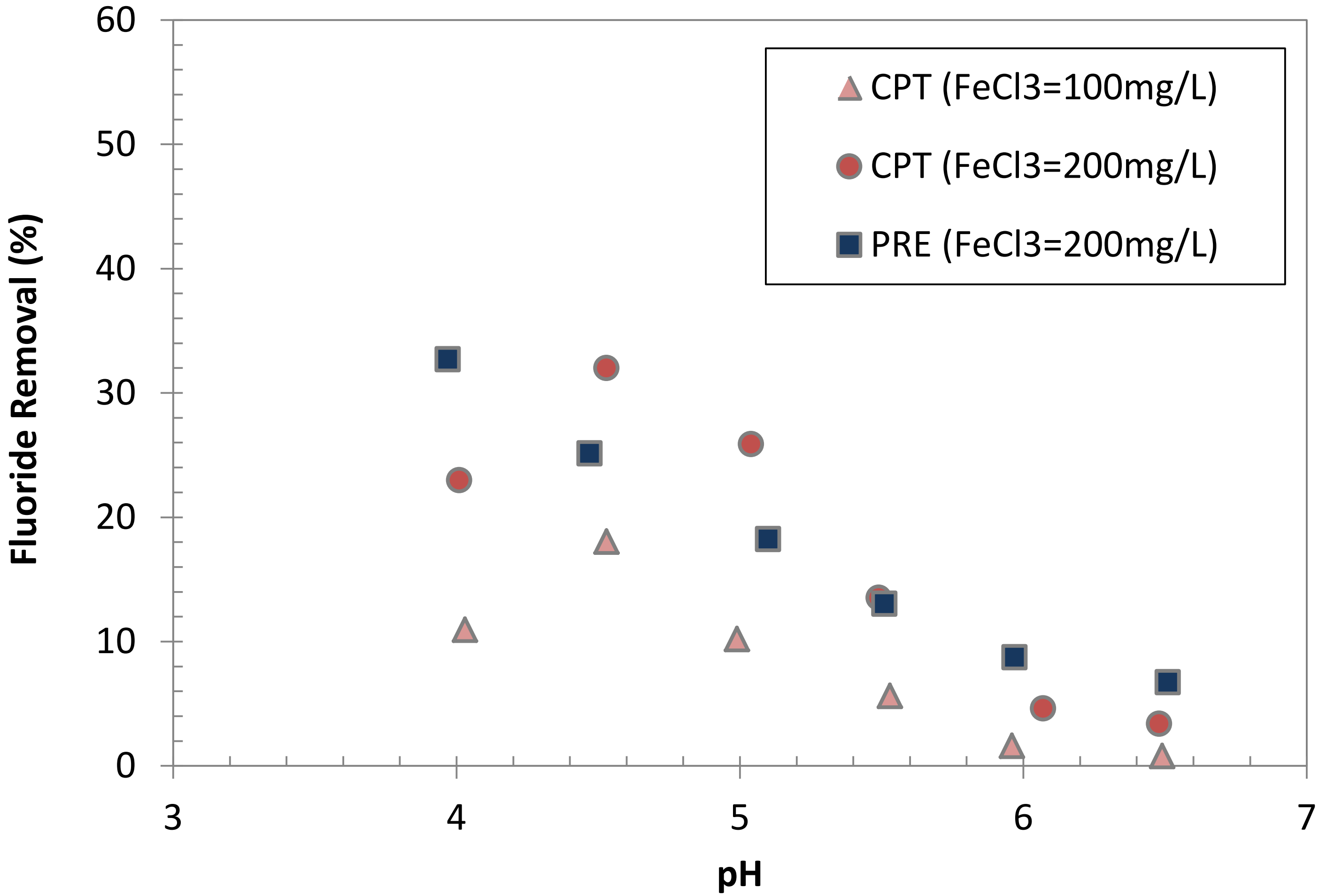
  = 100mg/L and 200mg/L
- Organic acids

  - Pyromellitic acid

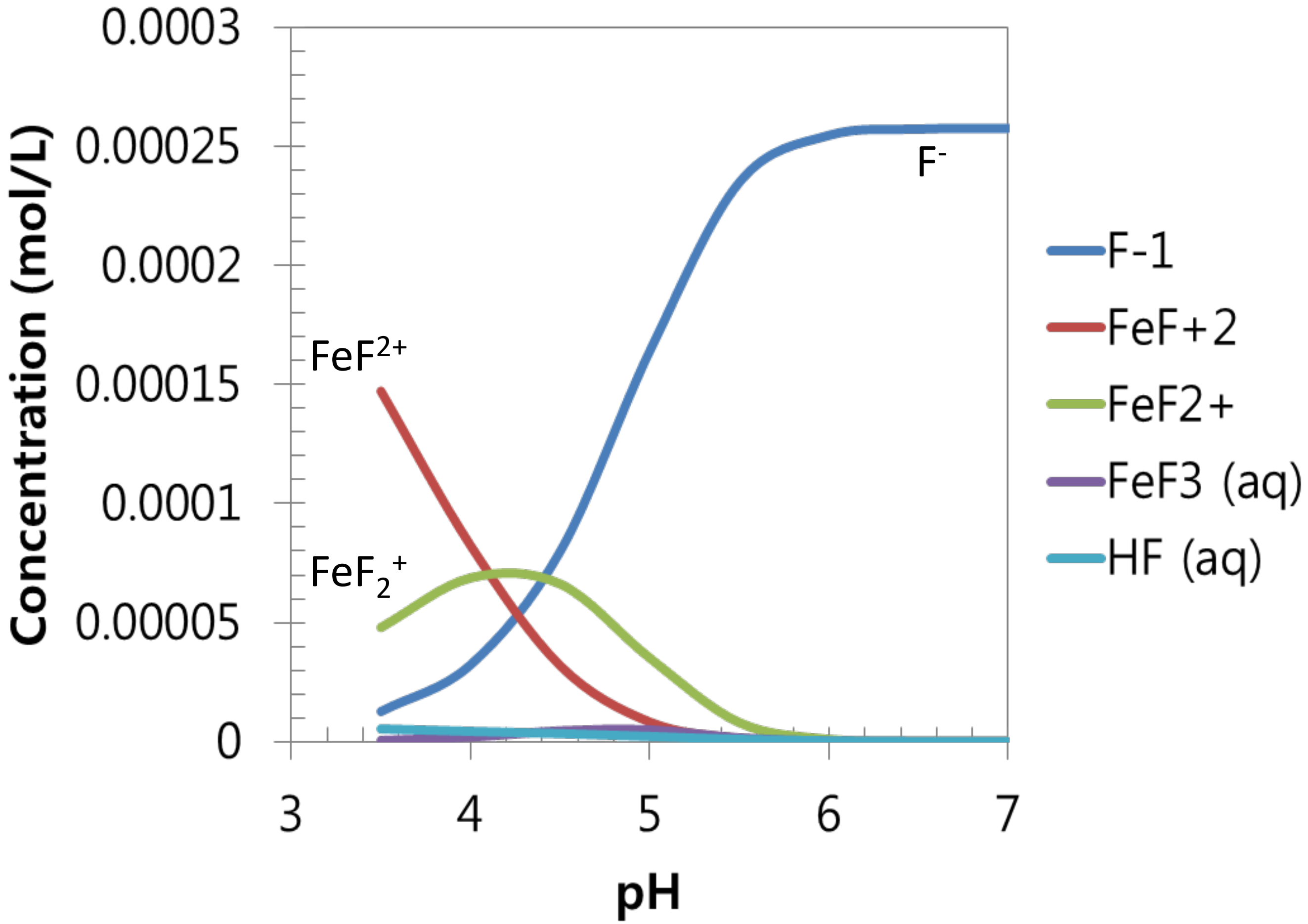
  - Phthalic acid

  - NOM

Comparison of Co-precipitation vs Pre-formed $Fe(OH)_{3(s)}$

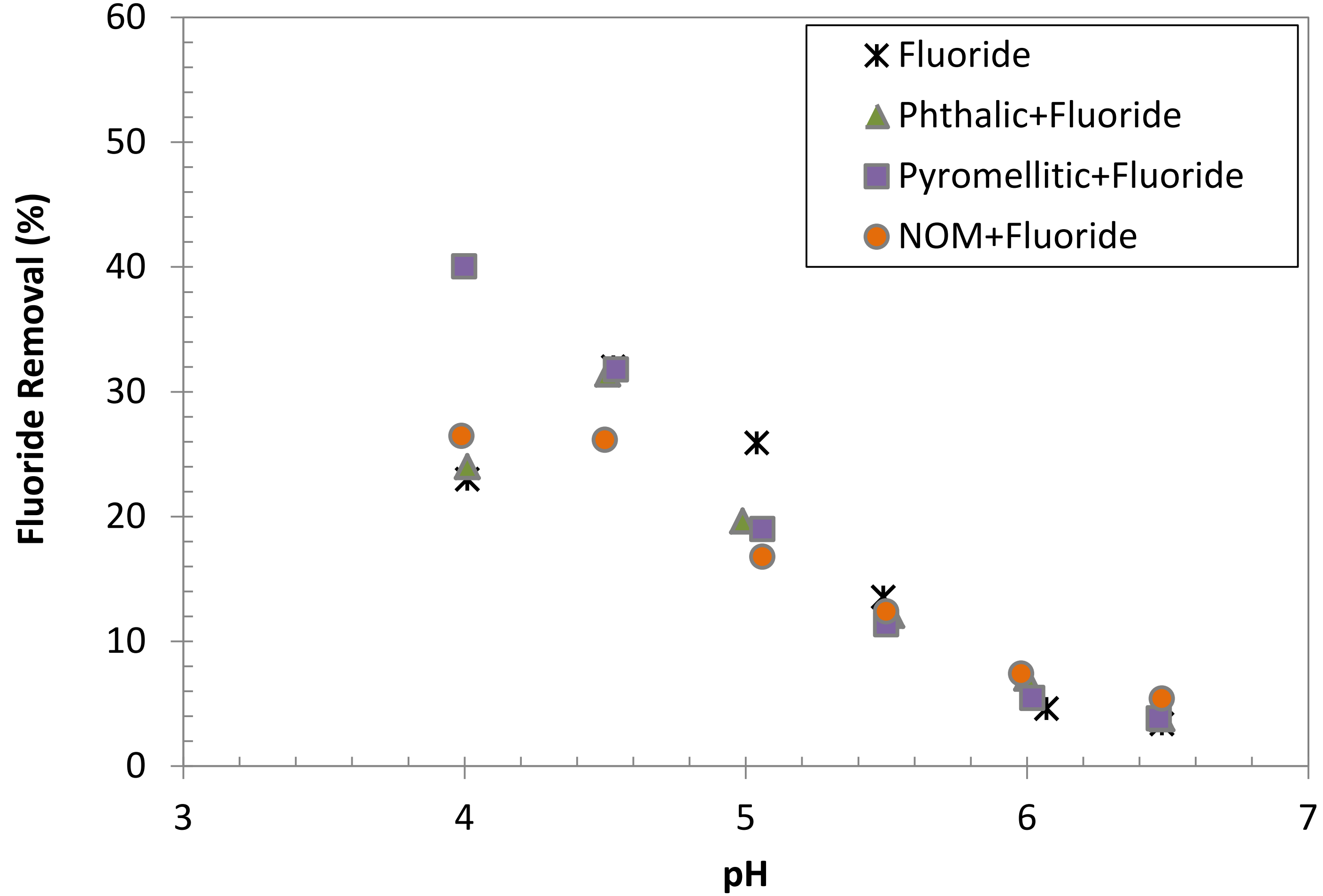


FeF_x Complexation

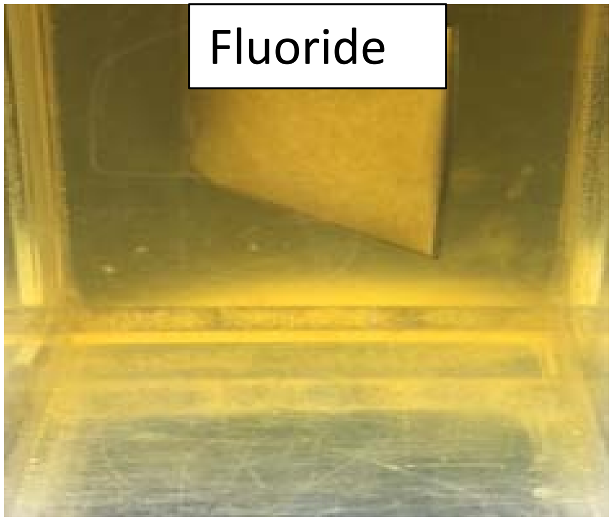


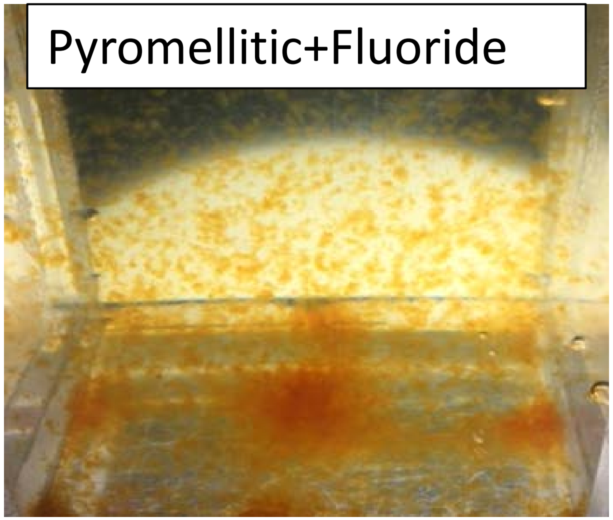
FeF_2^+ is a Key Player of Fe Coagulation

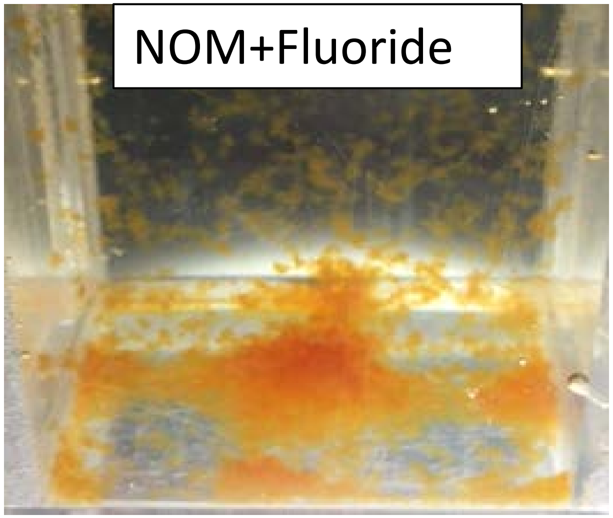
Fluoride Removal

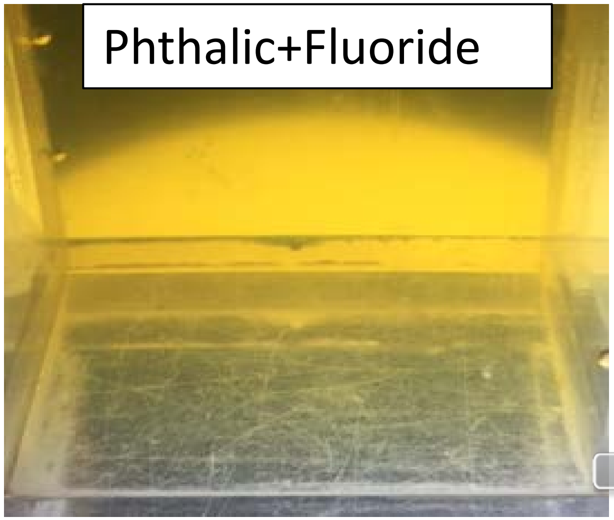


Fluoride Removal at **pH 4.0**

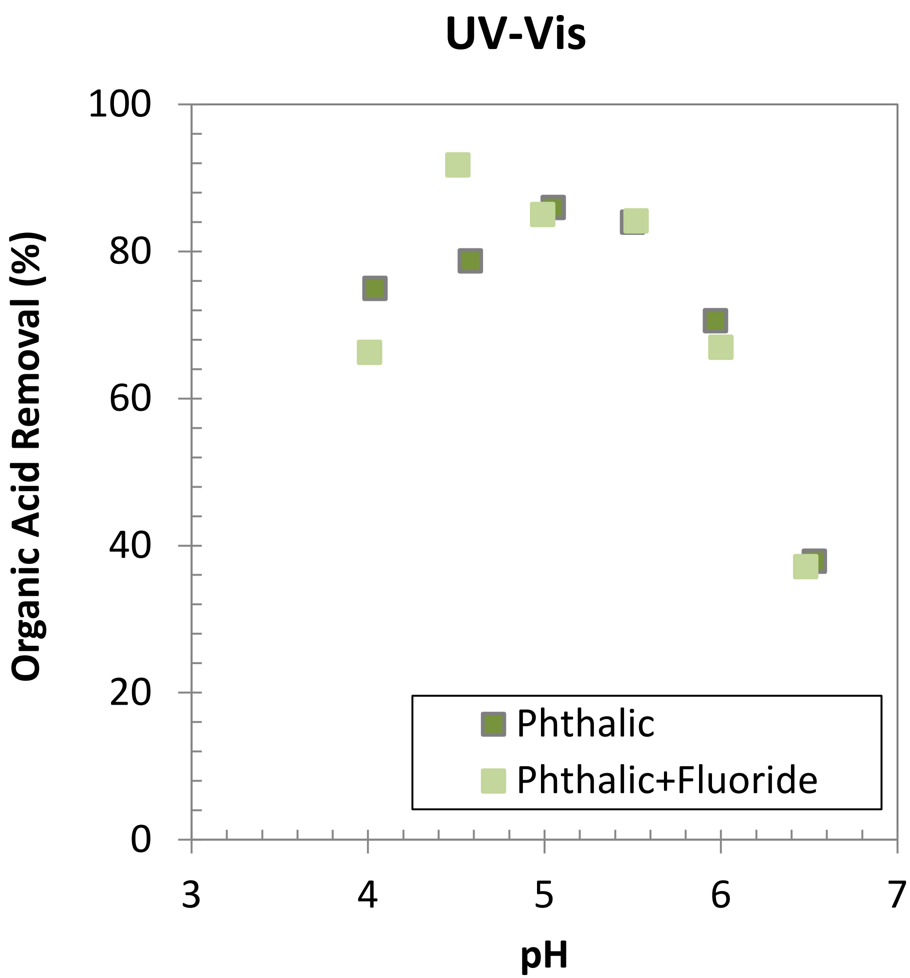


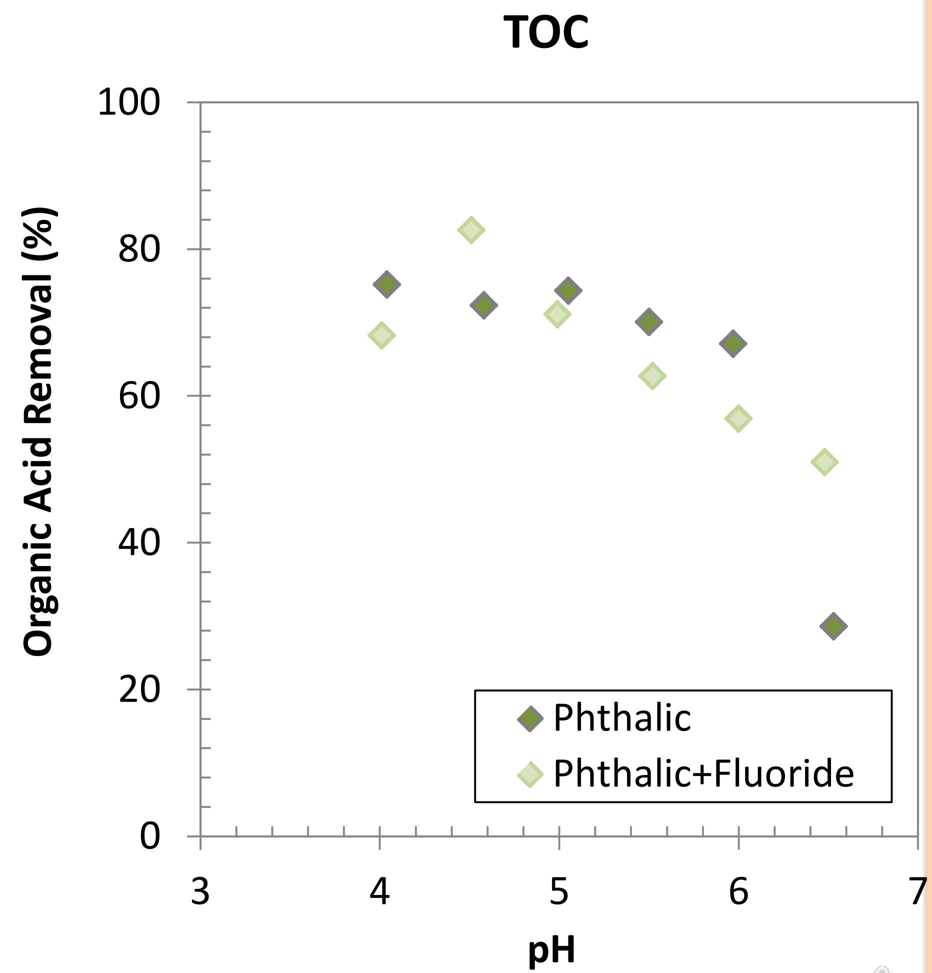




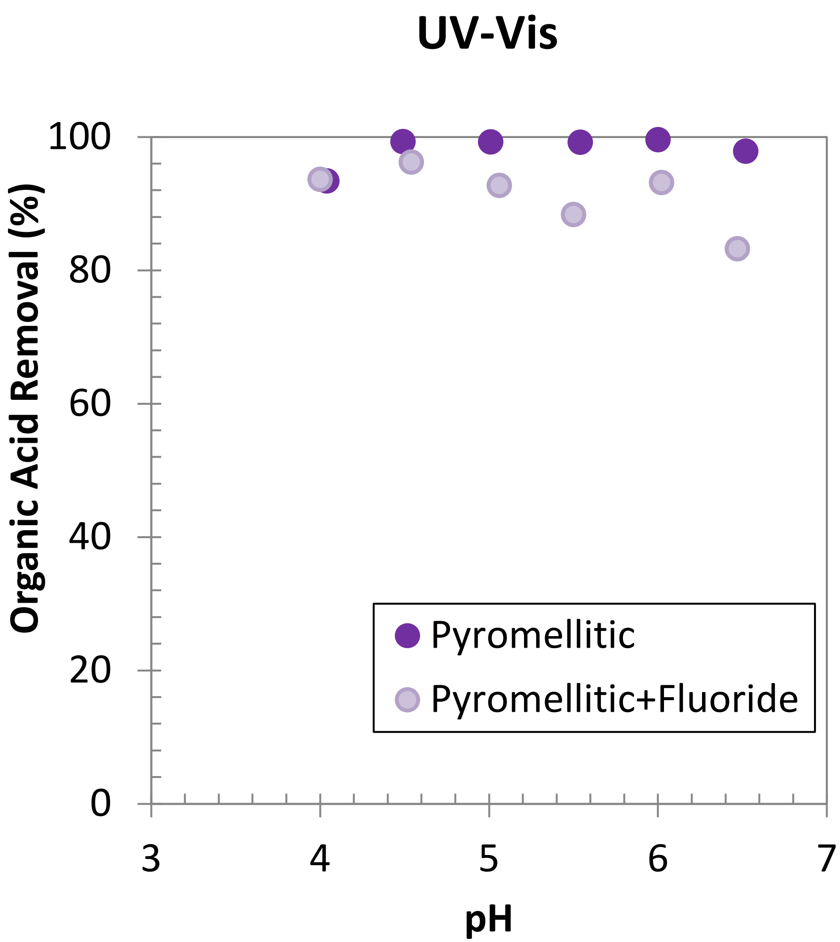


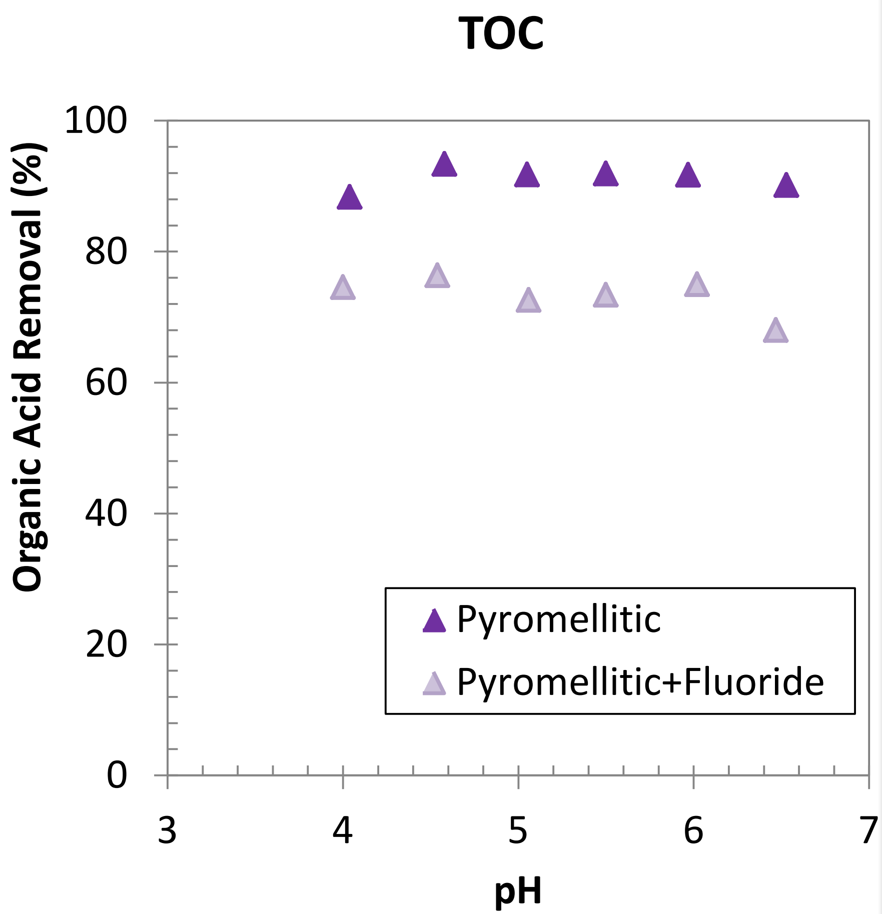
Organic Removal – **Phthalic acid**



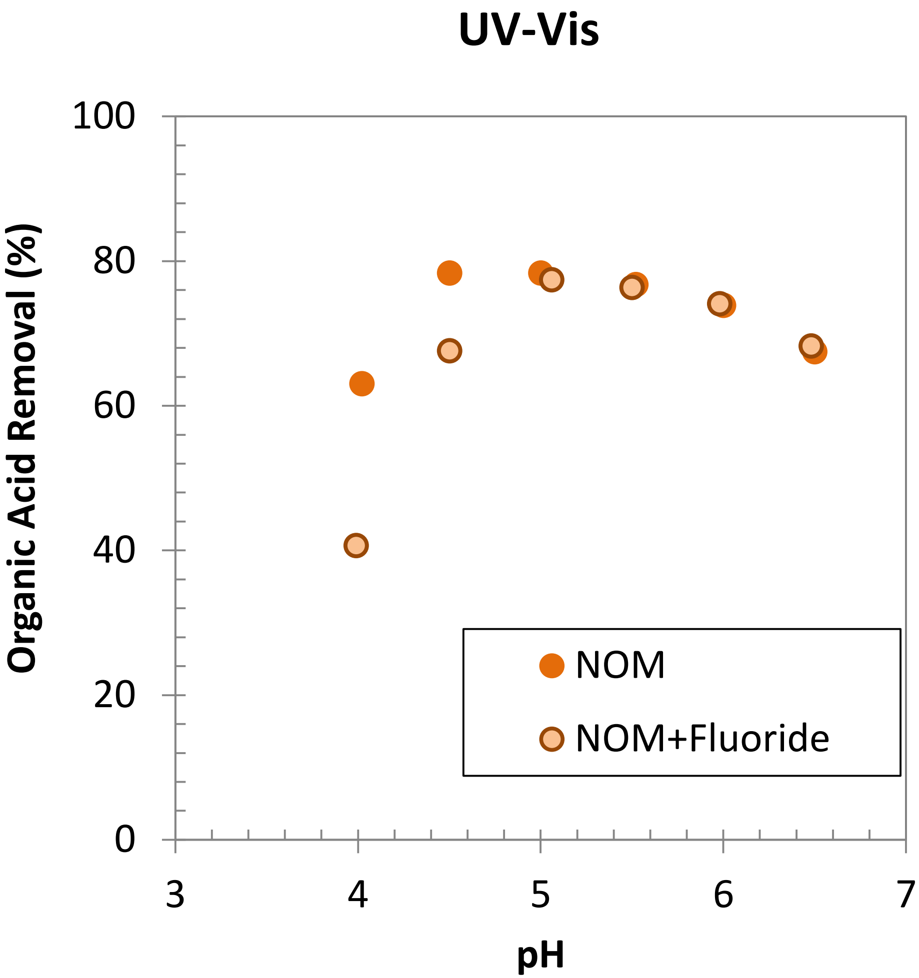


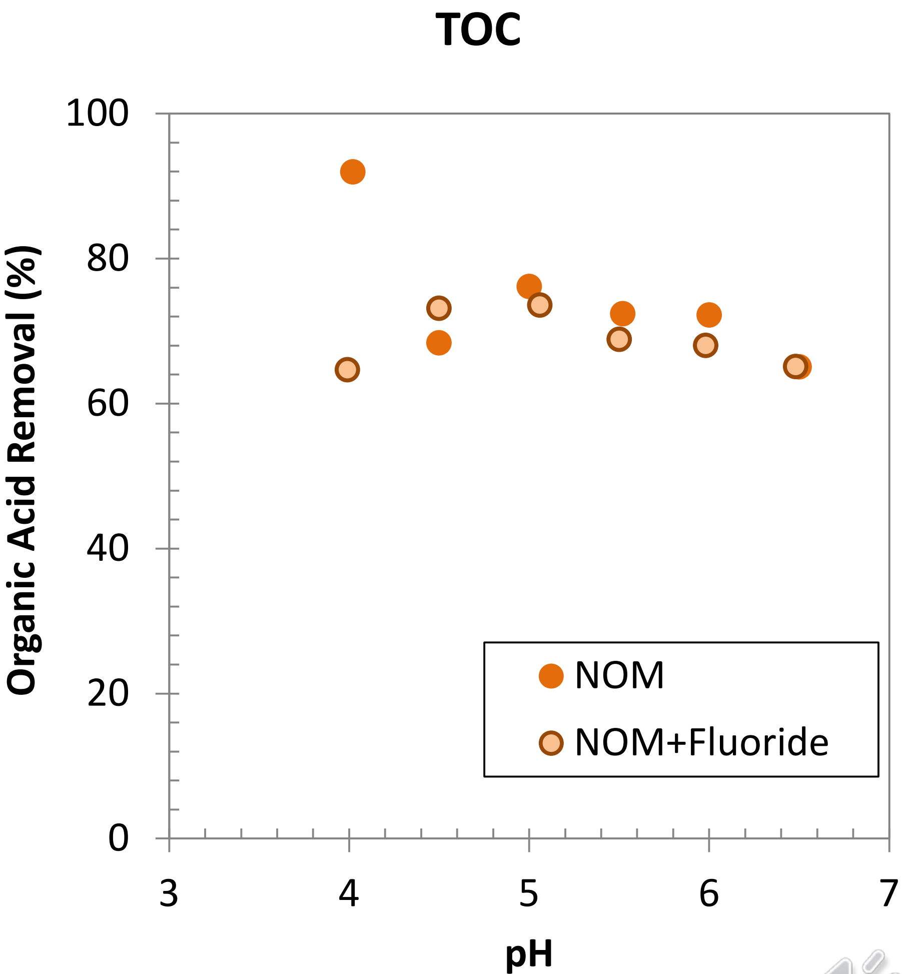
Organic Removal – **Pyromellitic acid**





Removal of NOM in Fe Coagulation





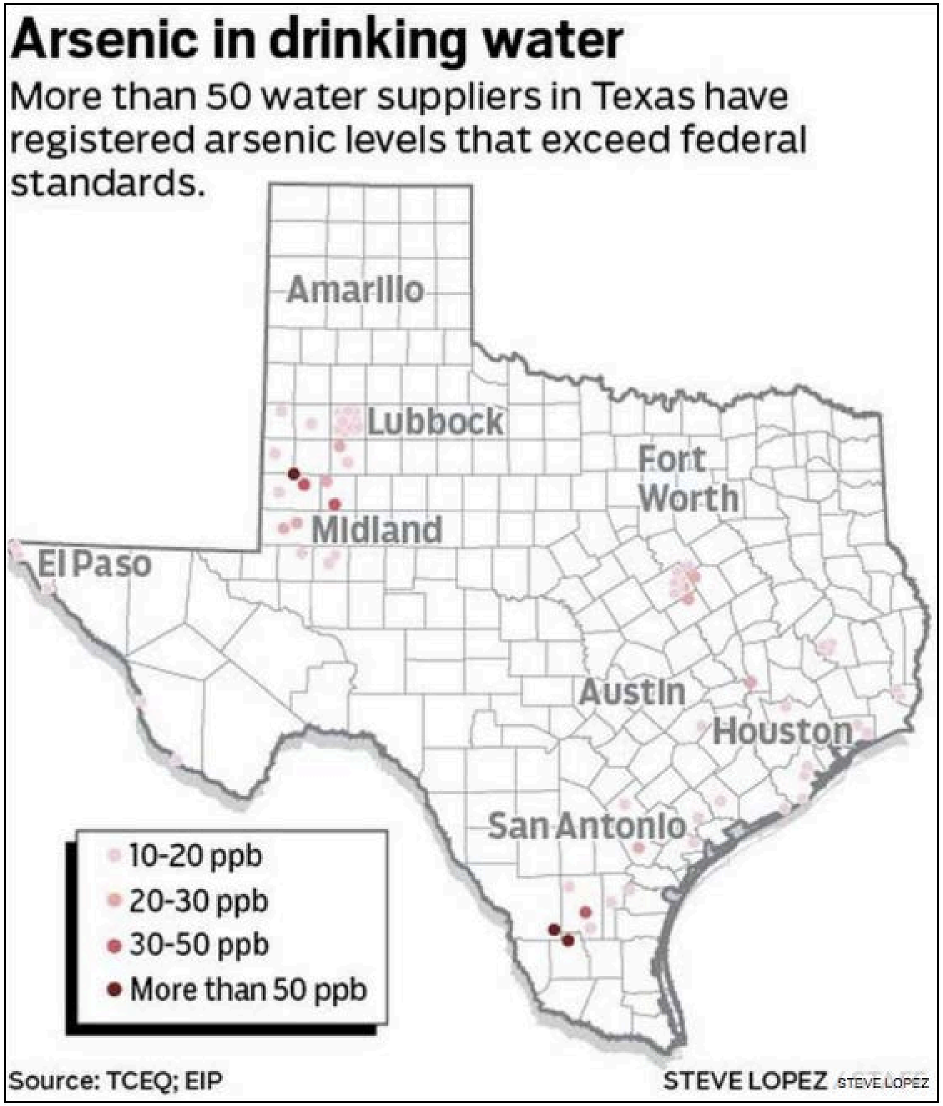
Conclusions

- **Fe coagulation**
  - Fluoride removals up to about 30% were observed.
    - Max removal at pH 4.5
    - No reduction in removal in the presence of organic acids
  - Effect of fluoride on organic acid removal is dependent on the organic acid and the pH/

- Compared to **Alum coagulation**
  - **More** organic removal over the pH range
  - **Max.** fluoride removal at **lower pH**

    $FeCl_3$=pH 4.5 , Alum=pH 6.5

Removal of Trace Metals in Enhanced Coagulation



Texas Statesman: Arsenic persists in some Texas water supplies

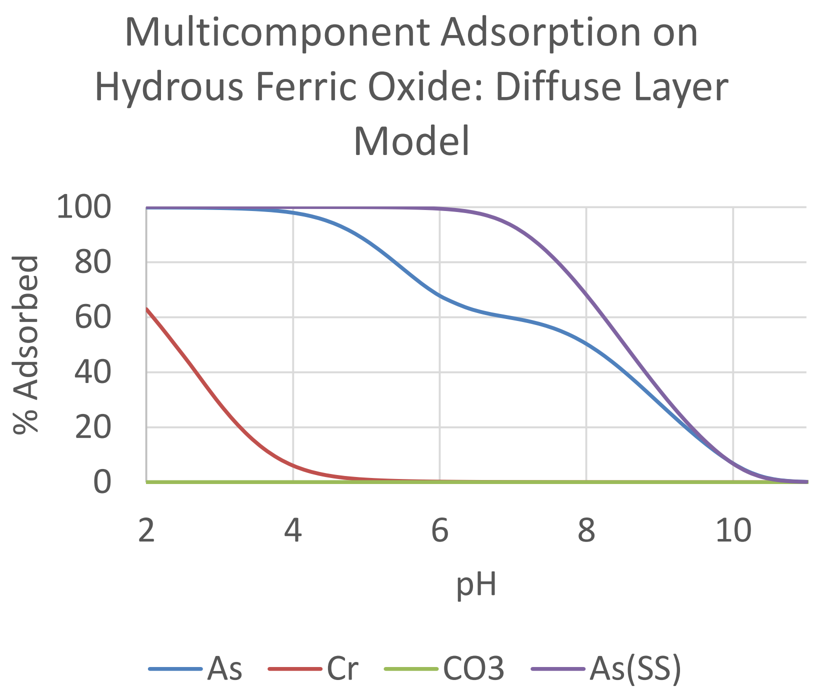
- Recent report found elevated levels of arsenic throughout Texas drinking water systems
- **Chromium-6 Found in Tap Water of 31 U.S. Cities (Dec. 2010)**
- Enhanced Coagulation could be applied for Arsenic and Chromium removal

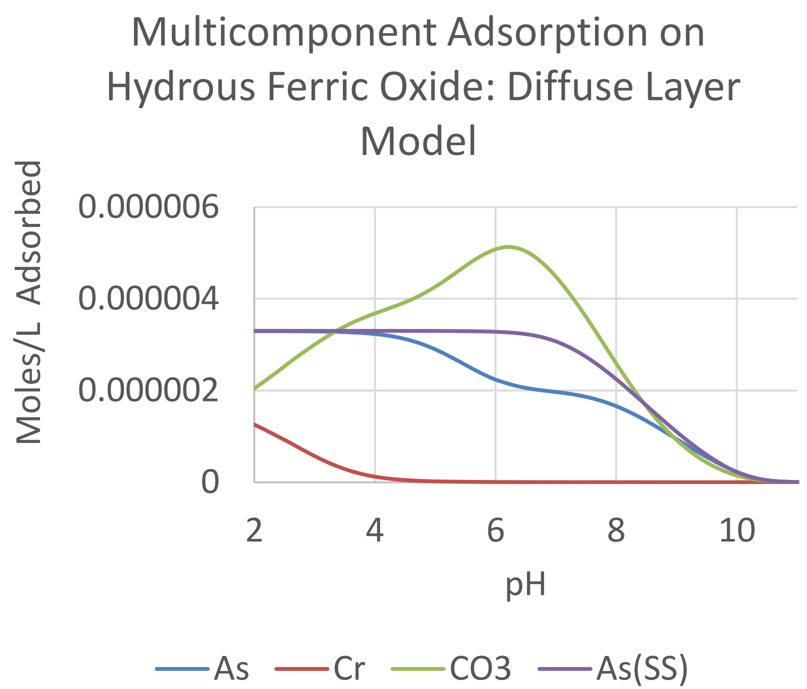
Methodology

- Evaluate Removals in Freshly Precipitated and Pre-precipitated Systems in Increasingly Complex Systems
  - Single-Solute
  - Bi-Solute
  - Tri-Solute
  - Natural Systems
- Assess the Potential of DLM Surface Complexation Model for Predicting Removal

Predictions of Adsorption onto Hydrous Ferric Oxide

AsT = 3.3e-6M, CrT = 2e-6M, CO3T = 0.01M





Adsorption Experiments on GFH

Single Solute arsenate pH sorption edge surface coverages (µmol/g) corresponding to 100 percent removal from solution

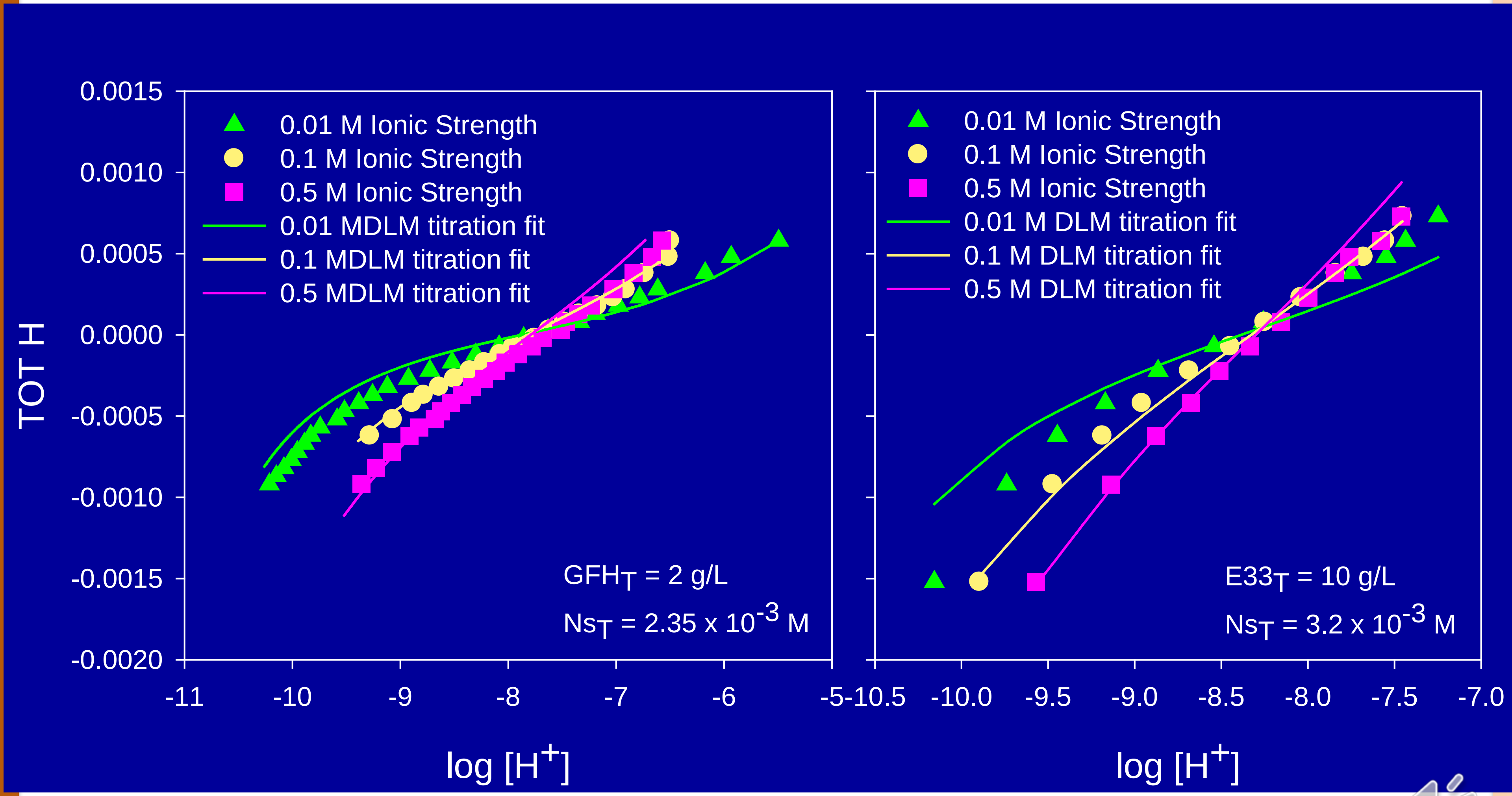
Solid	(g/L)	I.S. (M)	Sorbate	Max. Γ (µmol/g)	Buffer	(M)
GFH	0.01	0.01	As SiO_2 Ca^{2+}	133 111 2495	$NaHCO_3$	0.01
GFH	0.01	0.01	As SiO2 Ca2+	133 1113 2495	NaHCO3	0.01
E33	0.01	0.01	As SiO_2 Ca^{2+}	133 111 2495	$NaHCO_3$	0.01
E33	0.01	0.01	As SiO_2 Ca^{2+}	133 1113 2495	$NaHCO_3$	0.01

Estimation of Site Density

	E33*	GFH*
Surface area from surface charge density comparisons (m^2/g)	350	600
SSD, tritium exchange (sites/nm^2)	2.51	1.43
SSD, anion maximum sorption (sites/nm^2)	0.55	1.18
SSD, cation maximum sorption (sites/nm^2)	1.90	1.70

Surface protolysis:

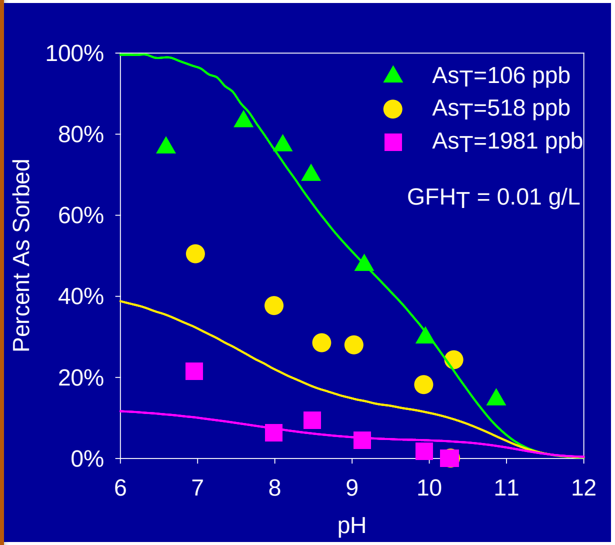
DLM Fits to Titration Data

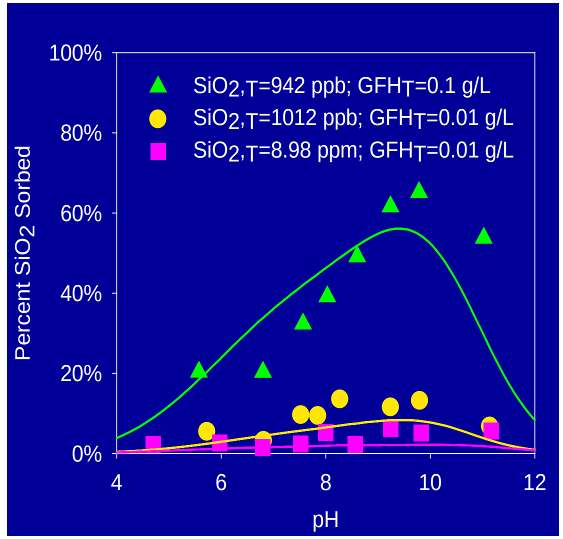


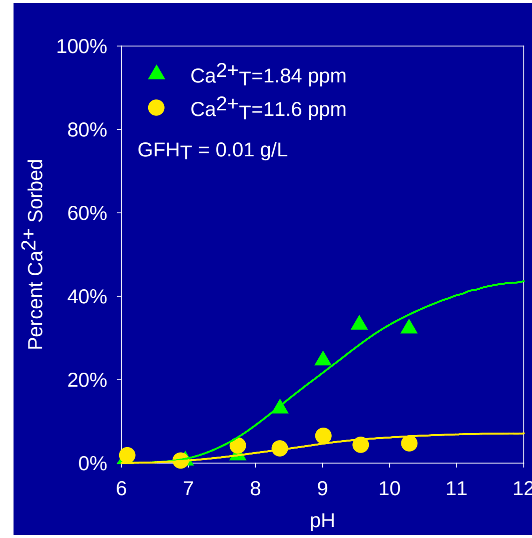
log K$^+$ = 6.90; log K$^-$ = -8.96

As(V) Si Ca

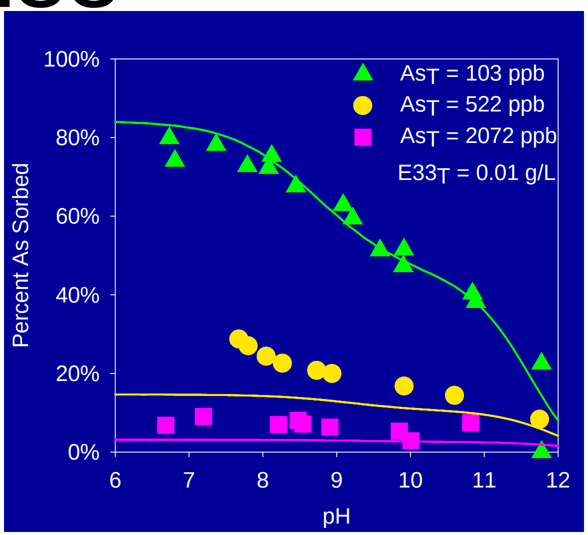
GFH

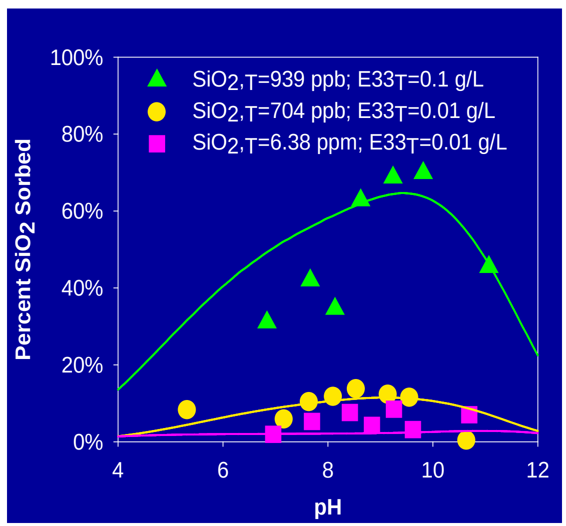


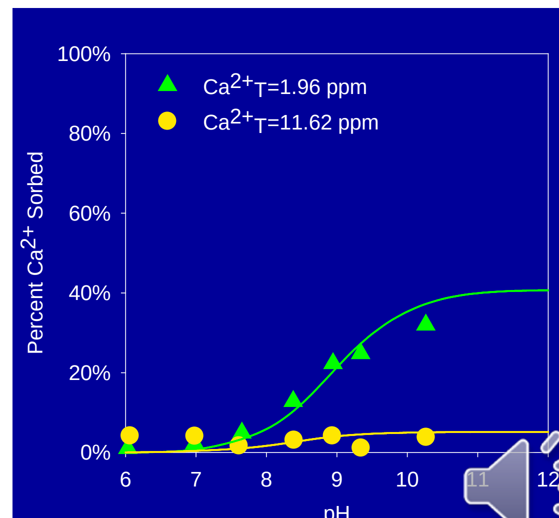




E33



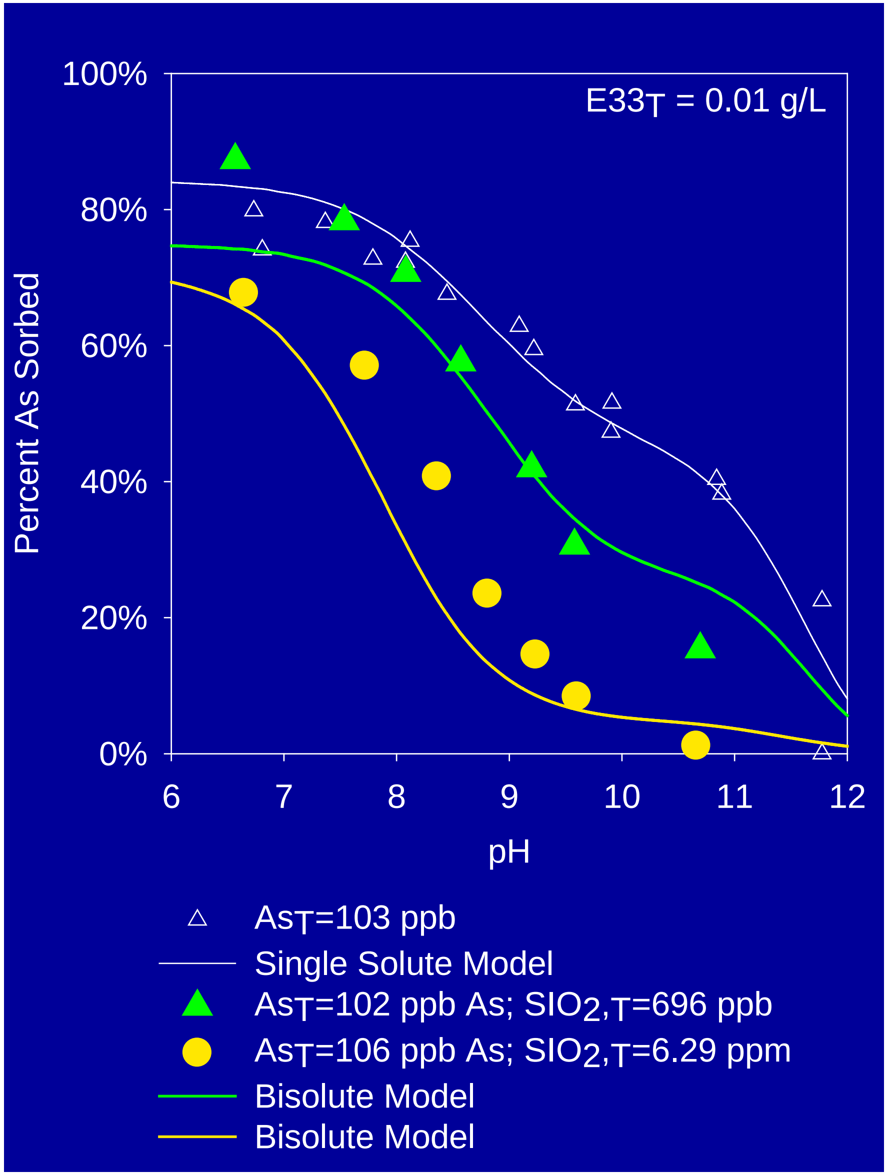




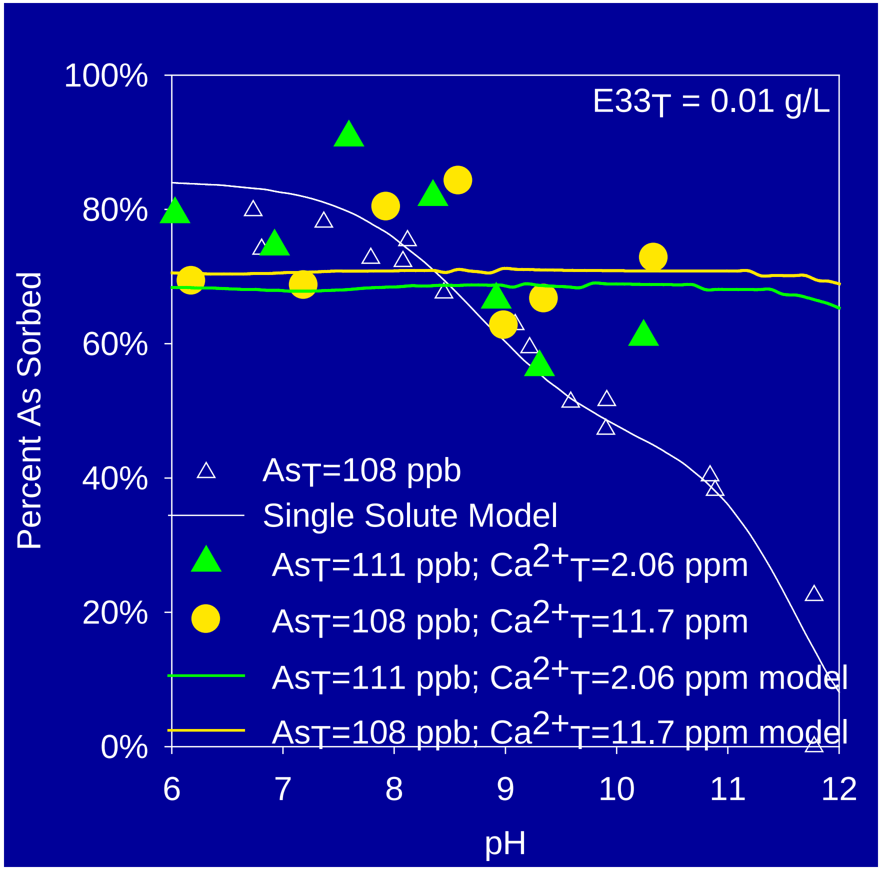
I.S. = 0.02M

Bisolute Predictions on E33

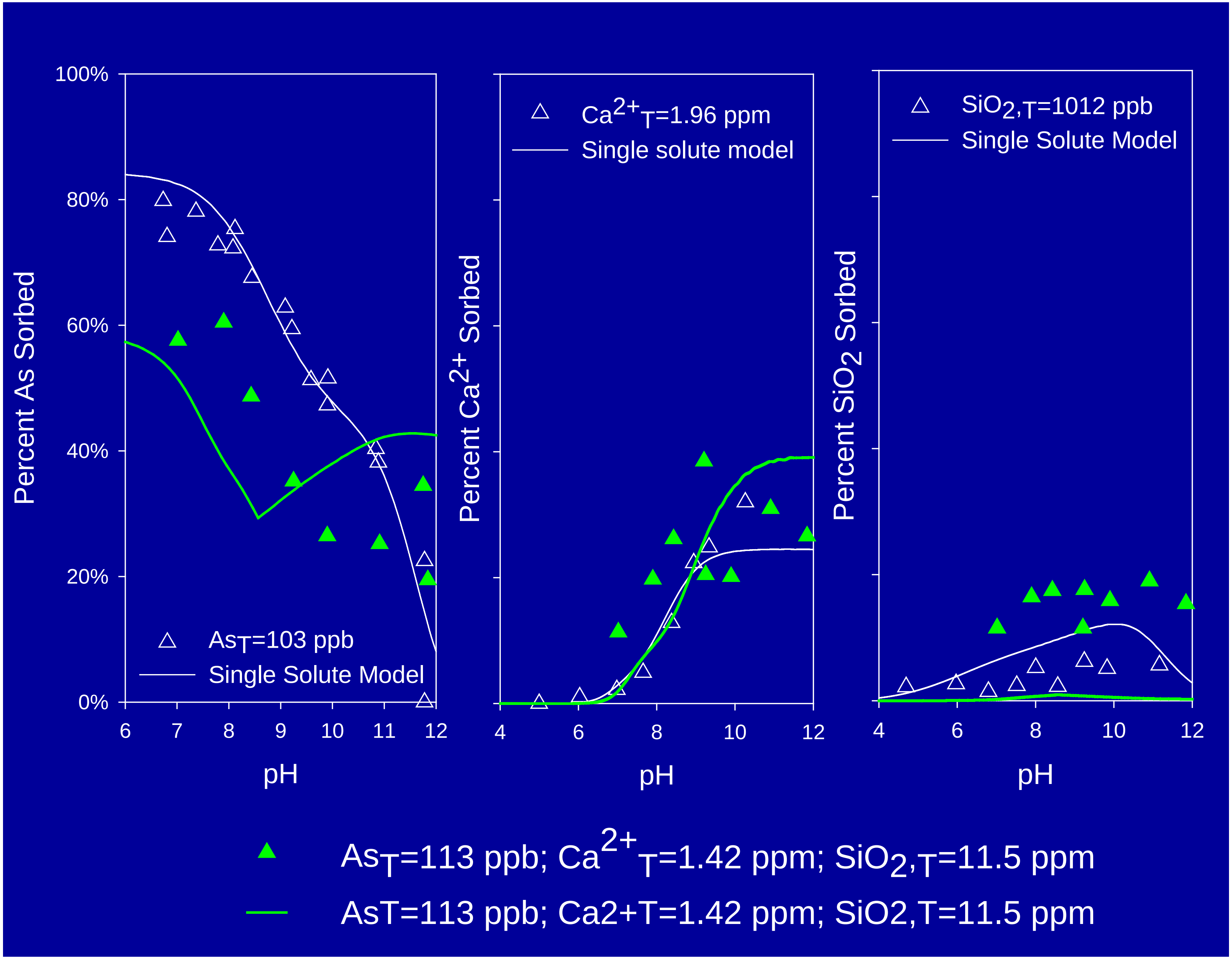
As/Si



As/Ca



Tri-Solute Predictions on E33

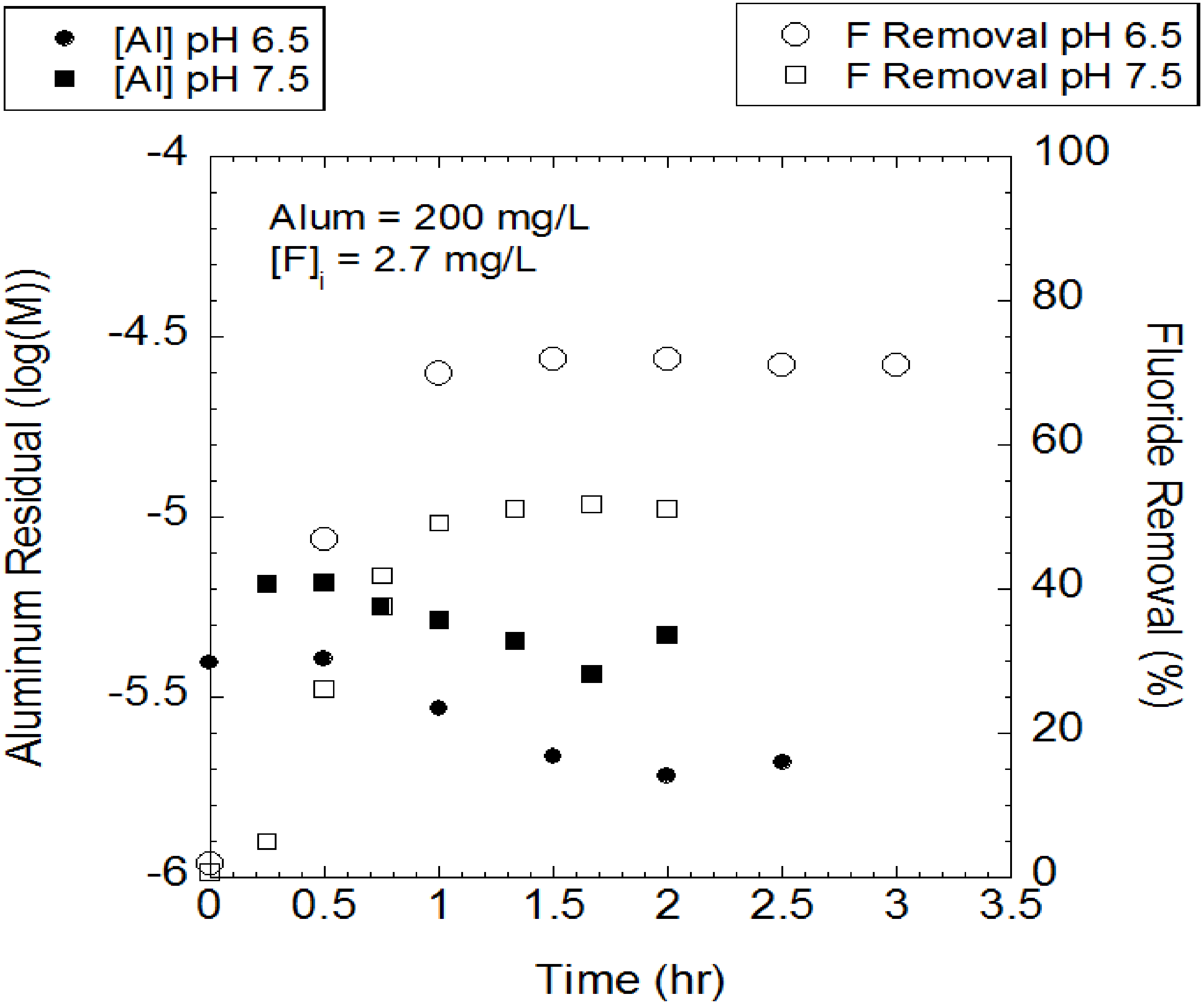


Summary

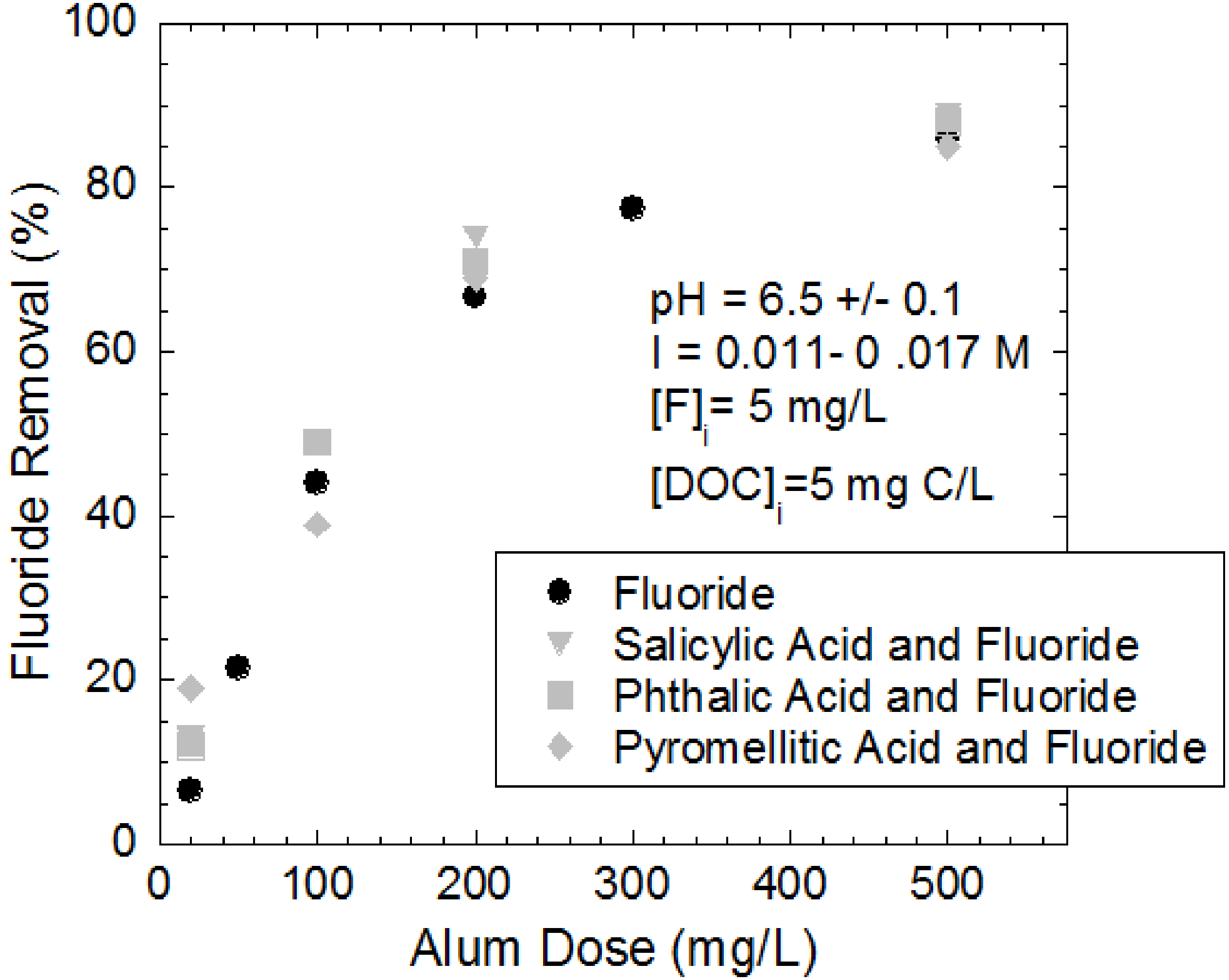
- Precipitation, complexation and adsorption in alum coagulation are intricately linked
- Most adsorption models examine aged precipitates
- Most precipitation models do not evaluate short term effects of adsorption
- Understanding the mechanisms of these precipitation and adsorption processes will allow better estimation of removals of contaminants in coagulation systems

Extra Slides

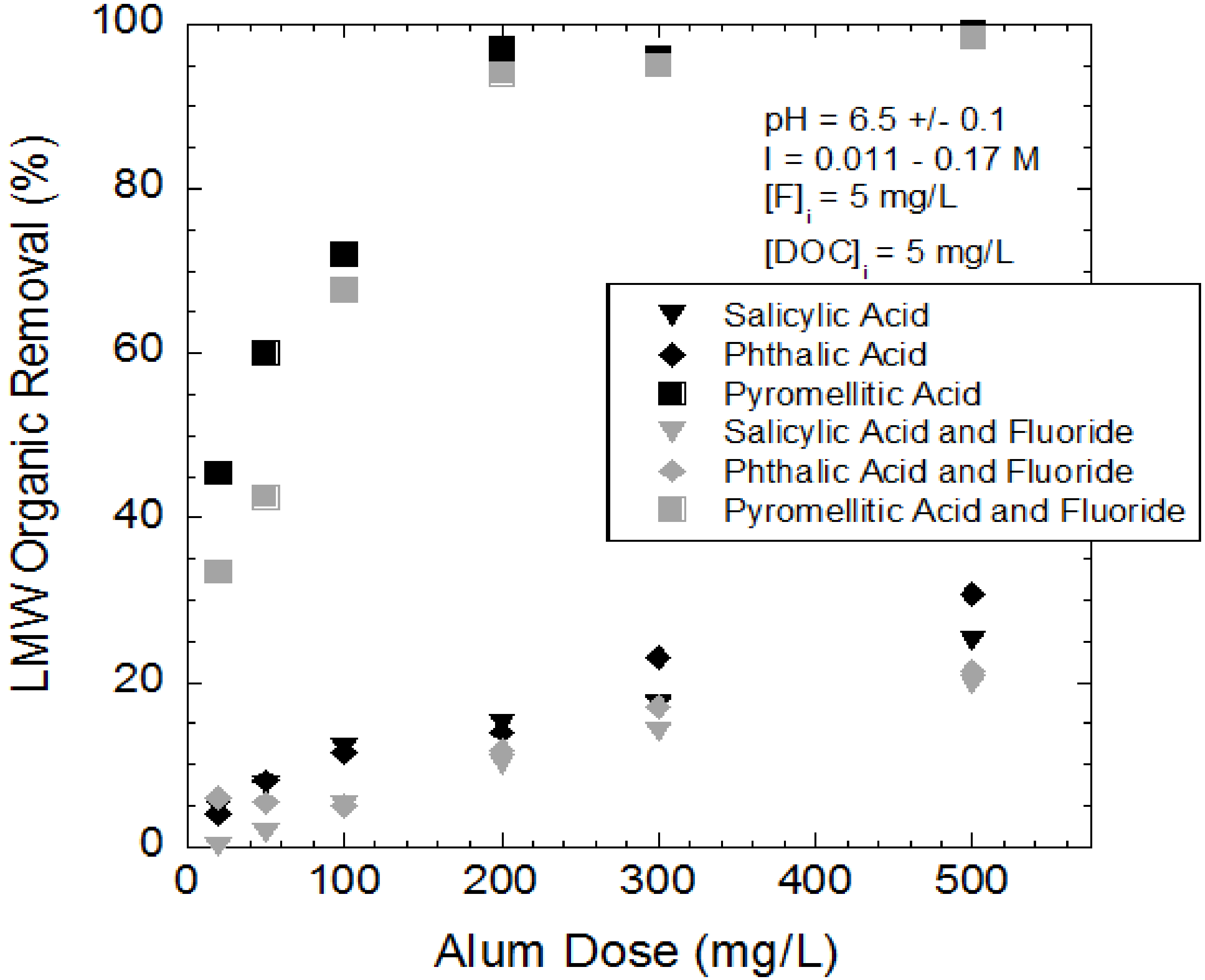
Effect of pH on Al Residuals



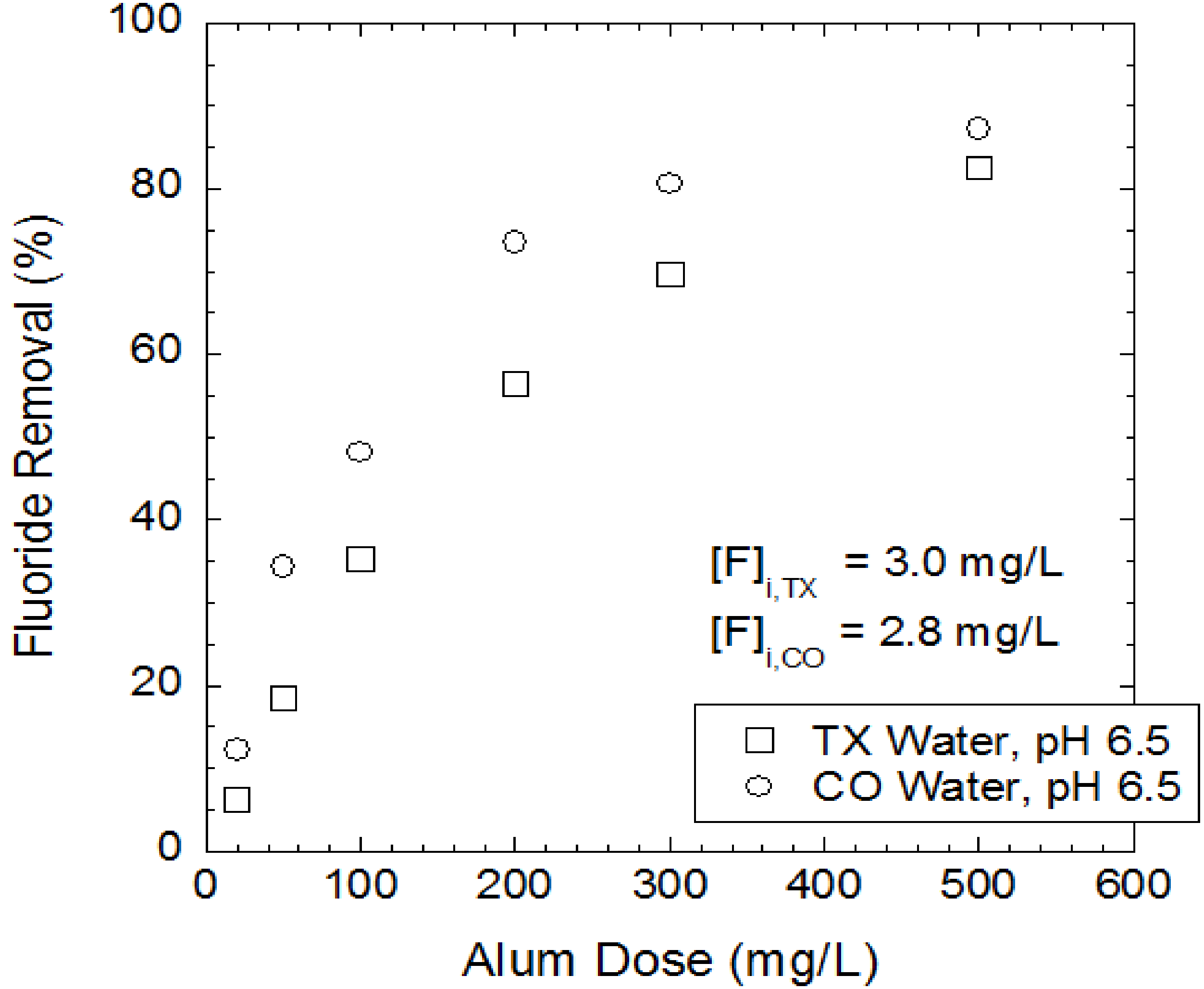
Fluoride Removal



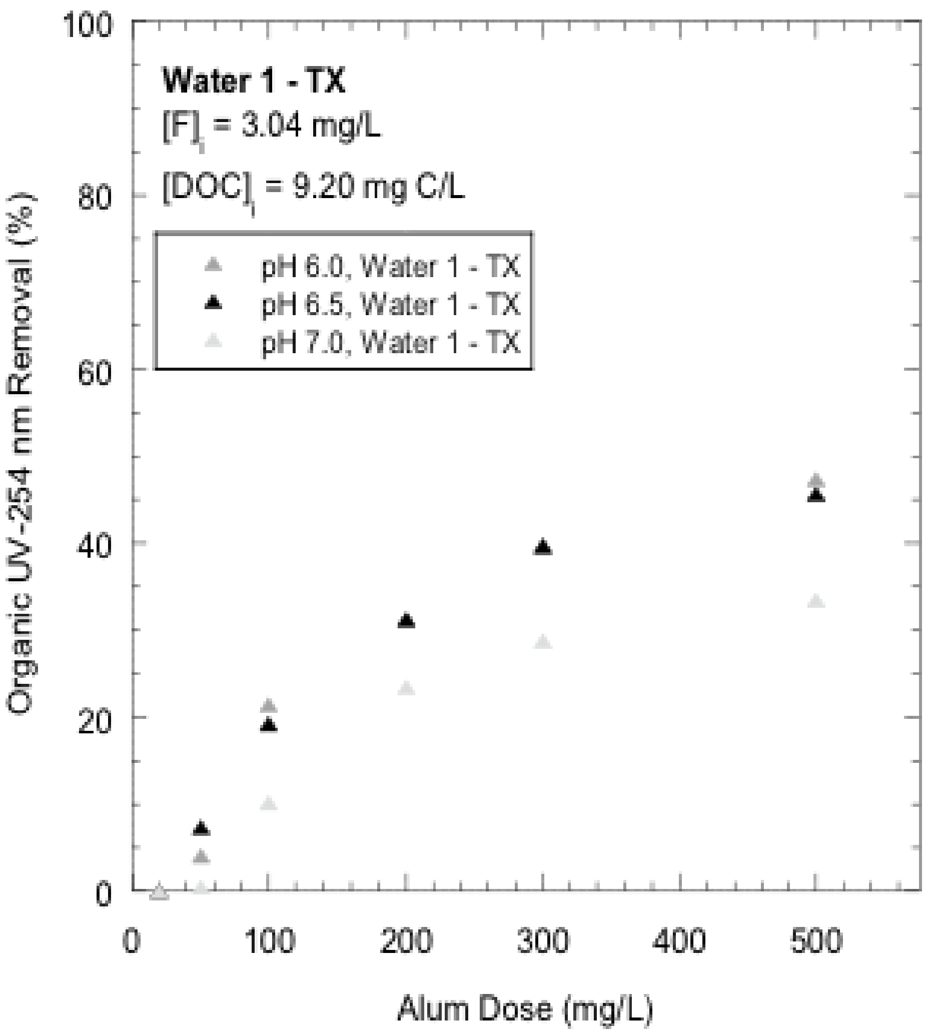
Organic Removal



Fluoride Removal



Organic Removal



CO Water UV-254 Removal	
Alum Dose (mg/L)	Removal (%)
20	33
50	40
100	47
150	50
200	51
300	55