Optimizing Floc Formation and Arsenic Removal in Drinking Water Supplies Containing Interfering Compounds

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Topic Overview

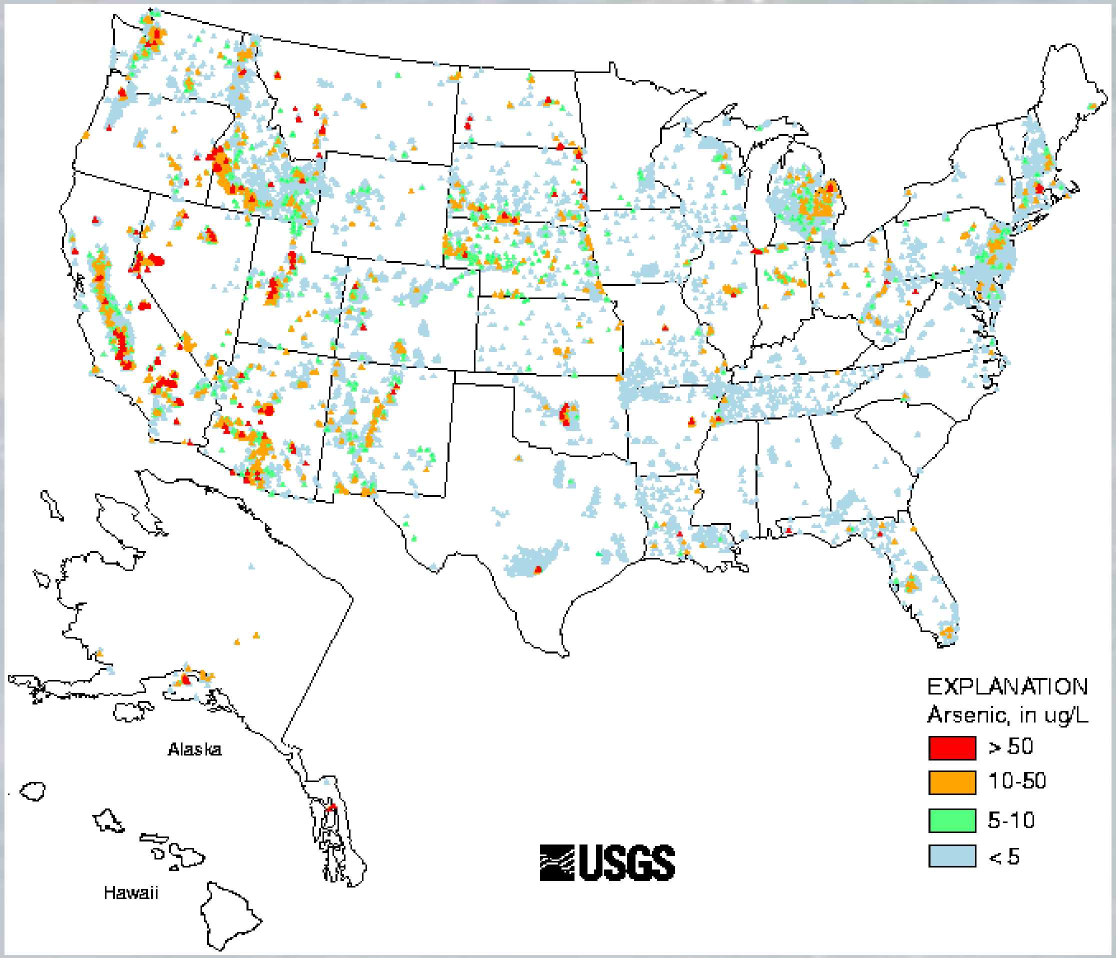
- Background
- Methods and Materials
- Results and Discussion
- Conclusion

Significance of Arsenic Contamination

- Acute and Chronic Toxicity, Class I Carcinogen
- Effective 2006, MCL was lower from 50 to 10 μg/L.
-  = 

Background

Location of Problem

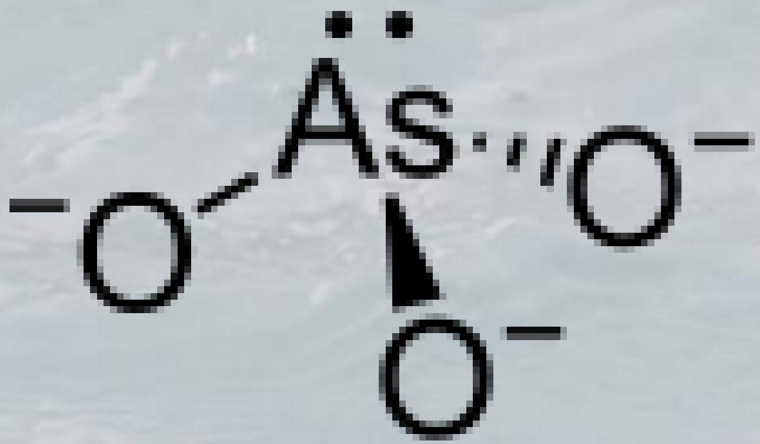


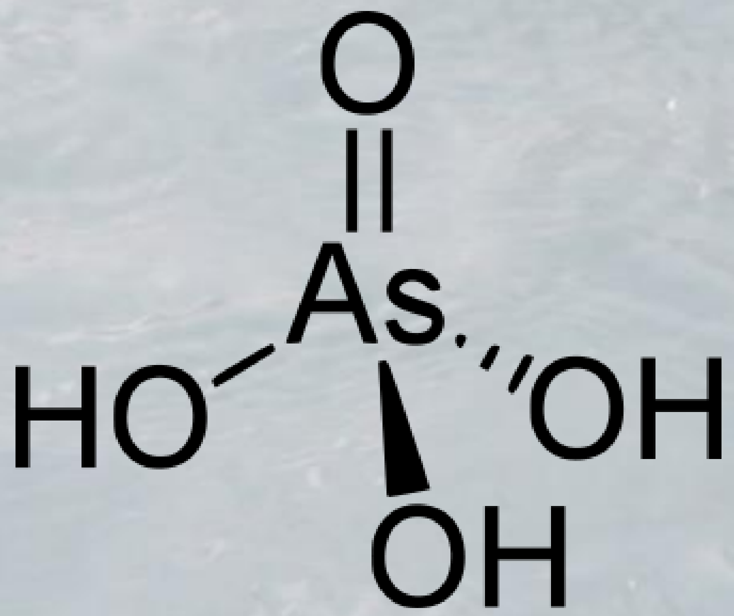
Background

- Isolated locations
- Automated systems
- Variable source water quality
- Challenging treatment

Background

- Arsenic Chemistry As(III) vs. As(V).
- As(III) is 60x more toxic (Ciardelli et al. 2008)





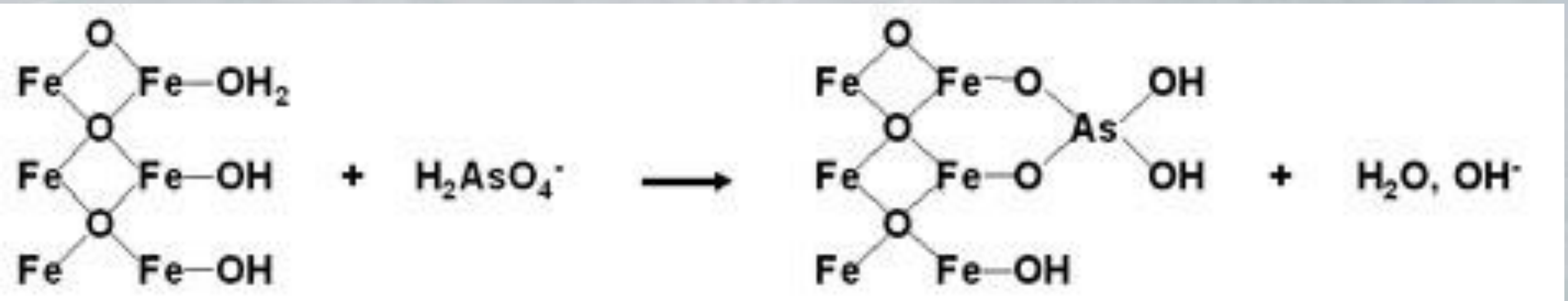
Background

- Ferric Chloride coagulation/flocculation

$$FeCl_3 \cdot 6H_2O + 3(HCO_3^-) \rightarrow Fe(OH)_{3(am)} + 3Cl^- + 3CO_2 + 6H_2O$$

Background

- Ferric hydroxide polymerization and arsenate adsorption



Loeppert, 2005.

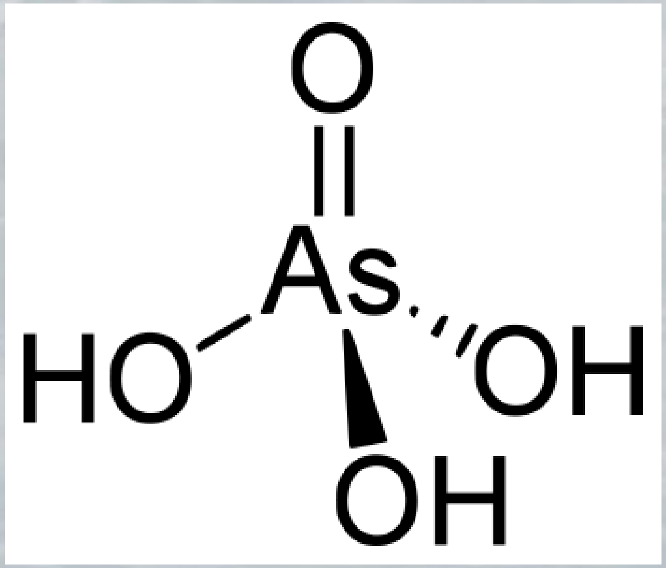
Background

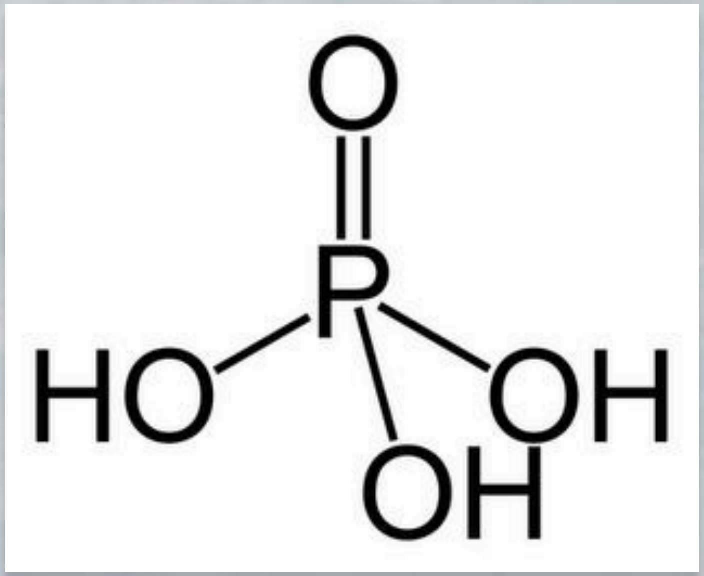
Interfering of Compounds:

- Phosphate (PO_4^{3-}) => H_3PO_4 or $H_2PO_4^-$
- Silicate (SiO_4^{4-}) => H_4SiO_4

Background

- Phosphate – competitive inhibitor (Laky et al, 2011; Guan et al, 2009; Roberts et al, 2004)

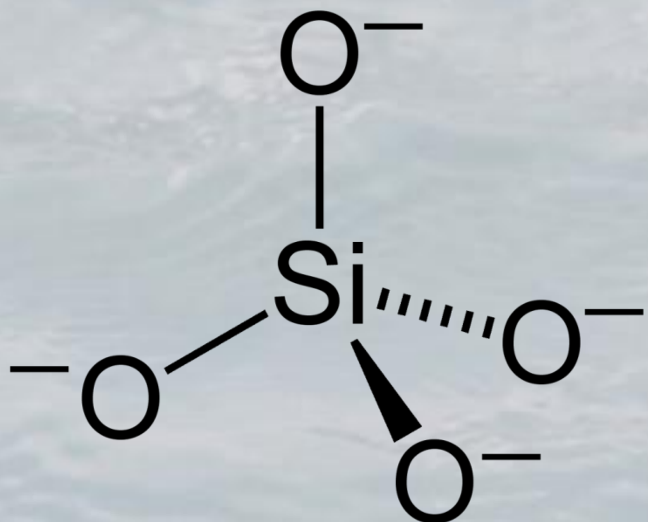




Background

- Silicate - Floc polymerization inhibitor

  (Ruiping et al, 2007; Pokrovski et al, 2003)

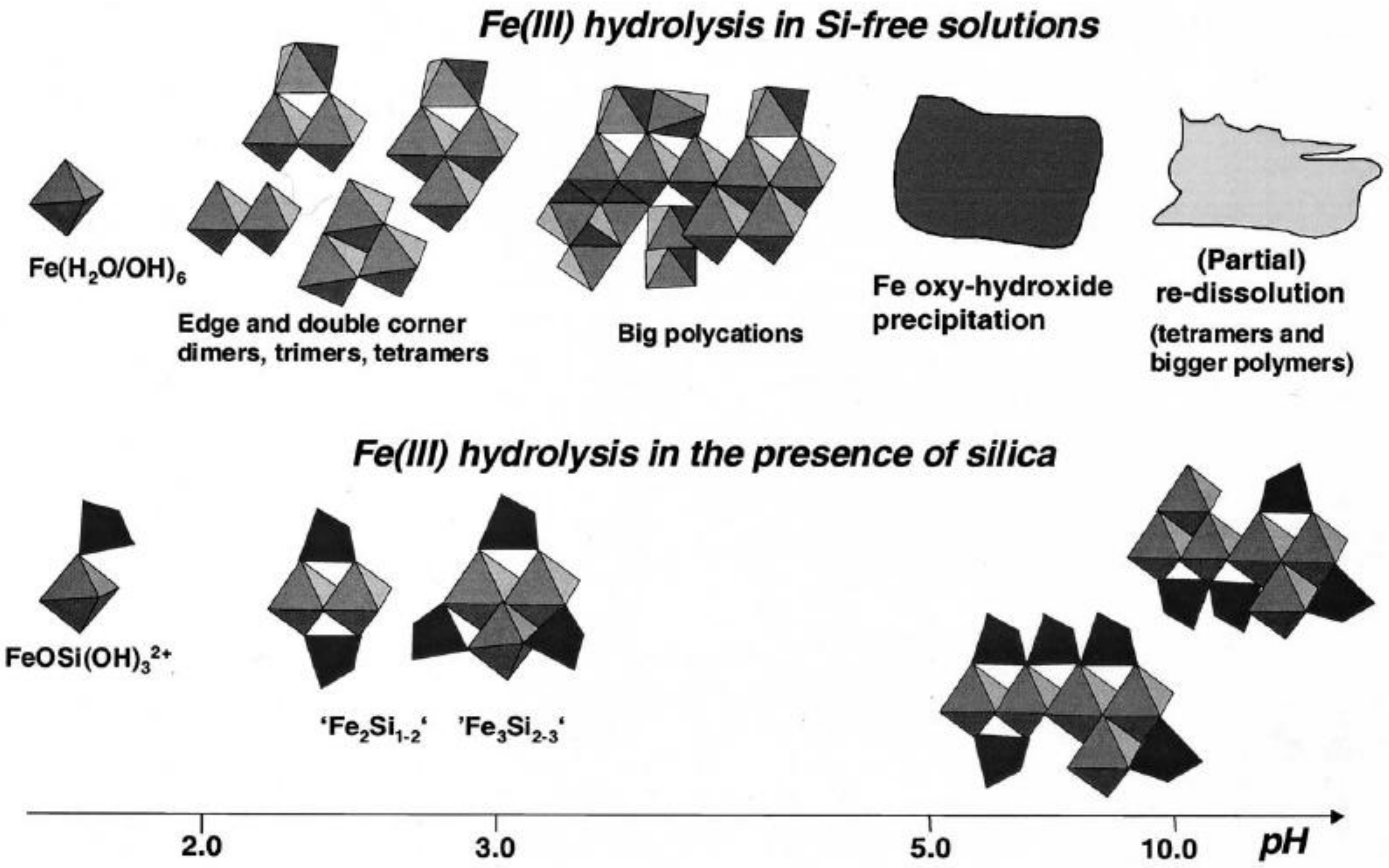


Silicate (SiO_4^{4-}) → Orthosilicic Acid (H_4SiO_4)

Quartz (SiO_2)

Background

XAFS (Pokrovski et al, 2003)



Objective

- Evaluate arsenic removal as a function of:

  ferric chloride dose,

  phosphate concentration,

  silicate concentration,

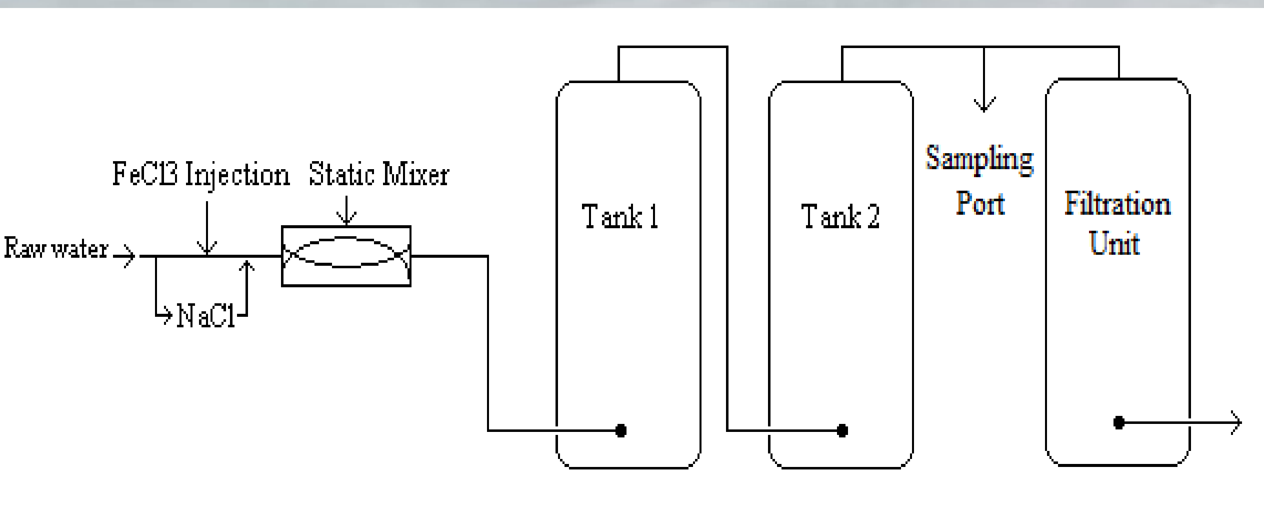
  in a representative groundwater of Island County, WA.

Methods and Materials

- Chemicals
- Field Tracer Study
- Synthetic Groundwater
- Jar Testing Conditions
- Chemical Analysis
- Factorial Experimental Design.
  - Two level, three factor

Field Tracer Study

- NaCl impulse input tracer study Brutus system



$$\bar{t} \cong \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} \quad (1)$$

t_i = *discrete time*

C_i = *tracer concentration leaving system at* t_i

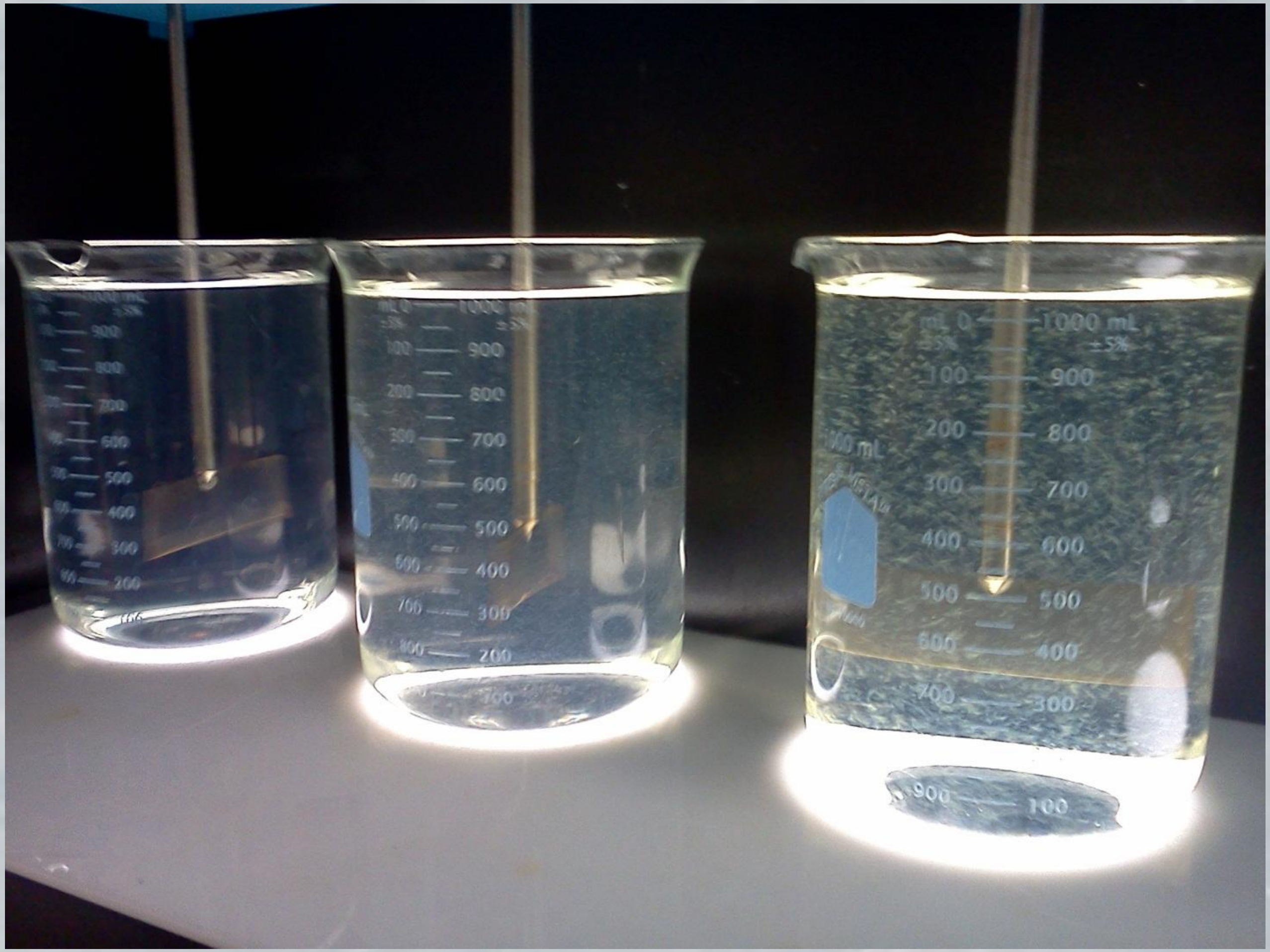
Δt_i = *time interval between* t_i *and* t_{i-1}

Synthetic Groundwater

Chemical characteristics of synthetic and Island County groundwater.

	Synthetic Water	Natural Water
pH	8.2 ± 0.1	8
Conductivity [µS/cm]	1060	400
Alkalinity[mg/L as $CaCO_3$]	125	136
Inorganic Species	[mg/L]	[mg/L]
Cl^-	100	30
NO_3^-	1.3	1.3
SO_4^{2-}	20	20
CO_3^{2-}	136	140
Na^+	105	60
K^+	3.3	3.3
Mg^{2+}	14.2	14.2
Ca^{2+}	40	40
Arsenic	0.075	-

Jar Testing

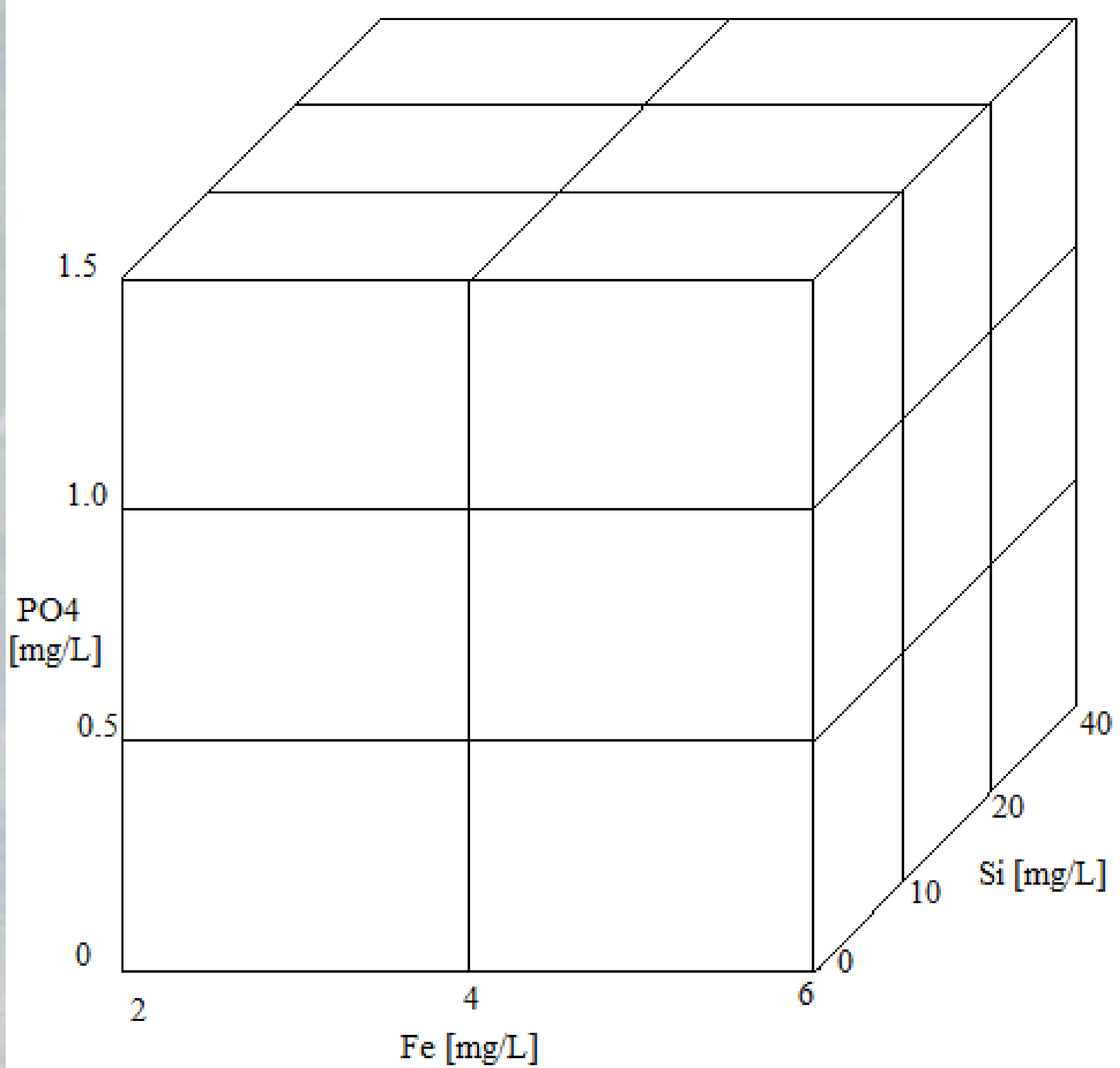


Jar Testing

- Arsenic removal under a range of
  - iron doses (2, 4 and 6 mg/L as Fe)
  - silicate concentrations (0, 10, 20, 40 mg/L as Si)
  - and phosphate concentrations (0, 0.5, 1.0, 1.5 mg/L as PO_4^{3-})
  - Variations form factorial analysis 36 cubes
- Coagulation/Flocculation Procedure
  - ferric chloride was added
  - flash mixed for 1 minute at 100 rpm a mean velocity gradient (G) of $G = 106\ s^{-1}$
  - 20 minutes of slow mixing (30 rpm; $G = 42\ s^{-1}$)
  - 10 minutes of quiescent settling. The mixing intensity (G) values were calculated using data supplied by (Jones et al, 1978).

Chemical Analysis

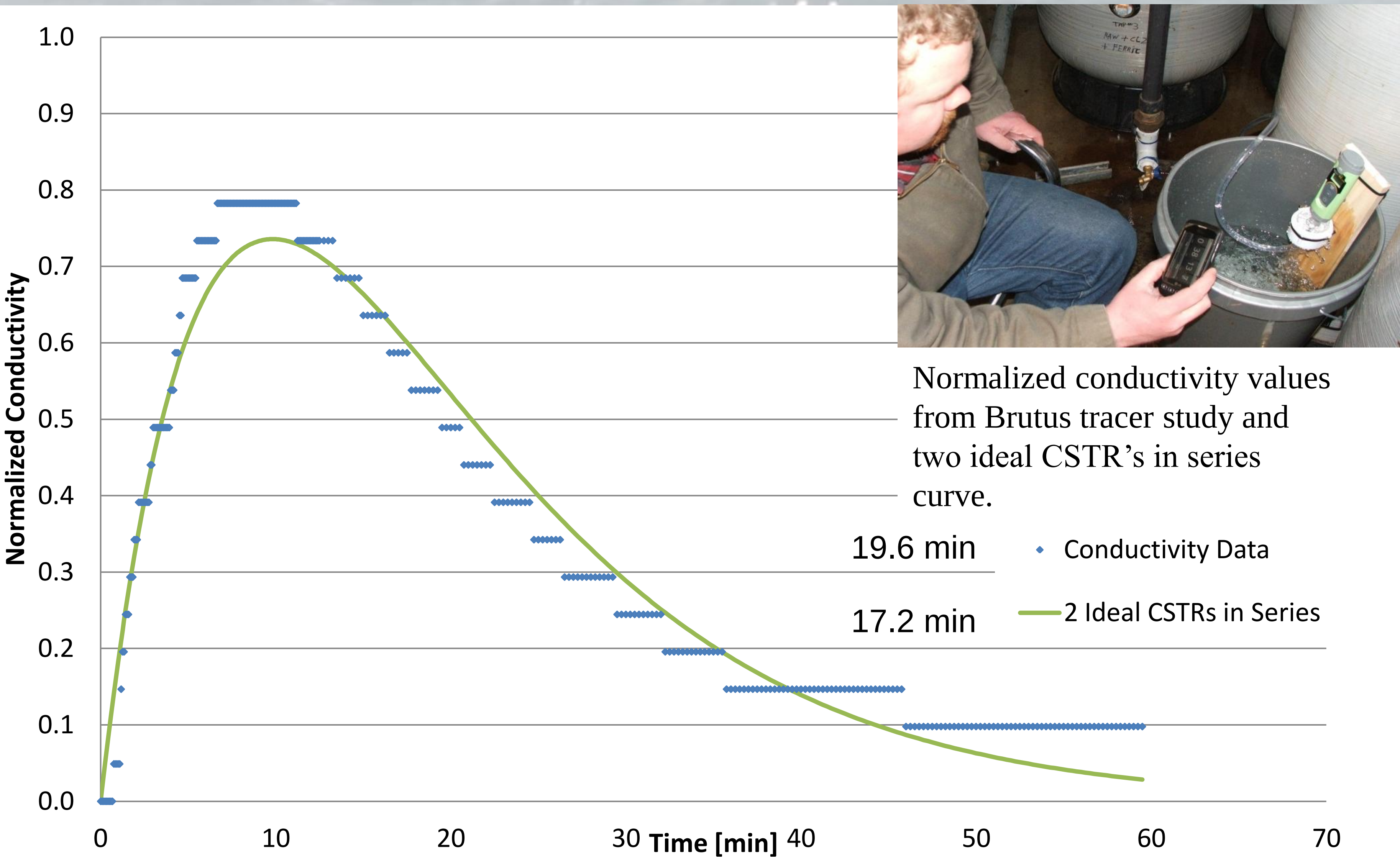
- Arsenic concentration - Inductively Coupled Plasma Mass Spectrometry (ICP-MS)
- PO_4^{3-} concentrations - Stannous chloride method 4500 – P D (Standard Methods, 2005)
- Fe concentrations - HACH method 8008 with a spectrophotometer set at a wave length of 510 nm.


1.5
1.0
PO4 [mg/L]
0.5
0
2
4
6
Fe [mg/L]
0
10
20
40
Si [mg/L]

Results

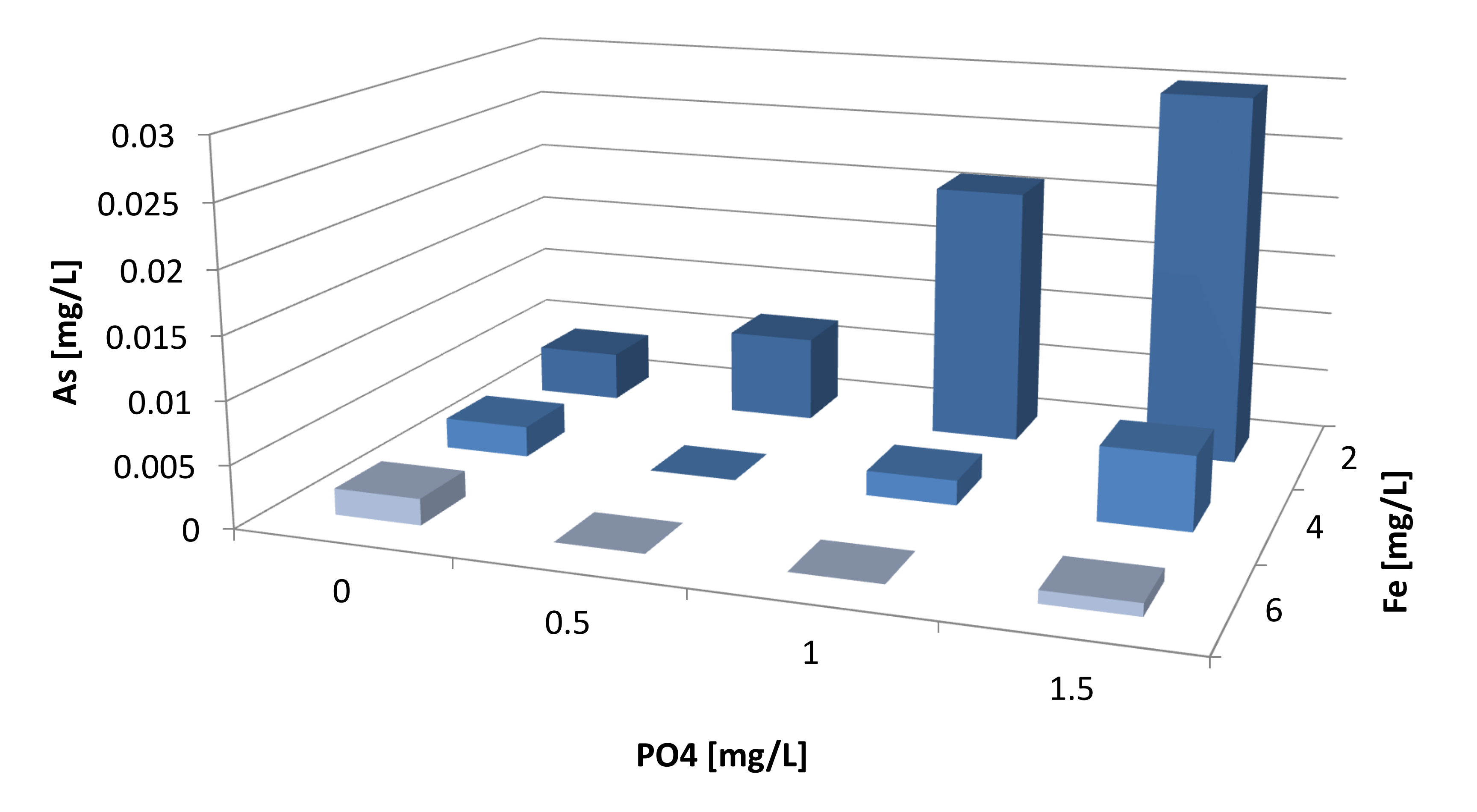
- Field Tracer Study
- Phosphate Interference
- Silicate Interference
- Combined Effect of Phosphate and Silicate

Tracer Results



Normalized conductivity values from Brutus tracer study and two ideal CSTR's in series curve.

Phosphate Interference

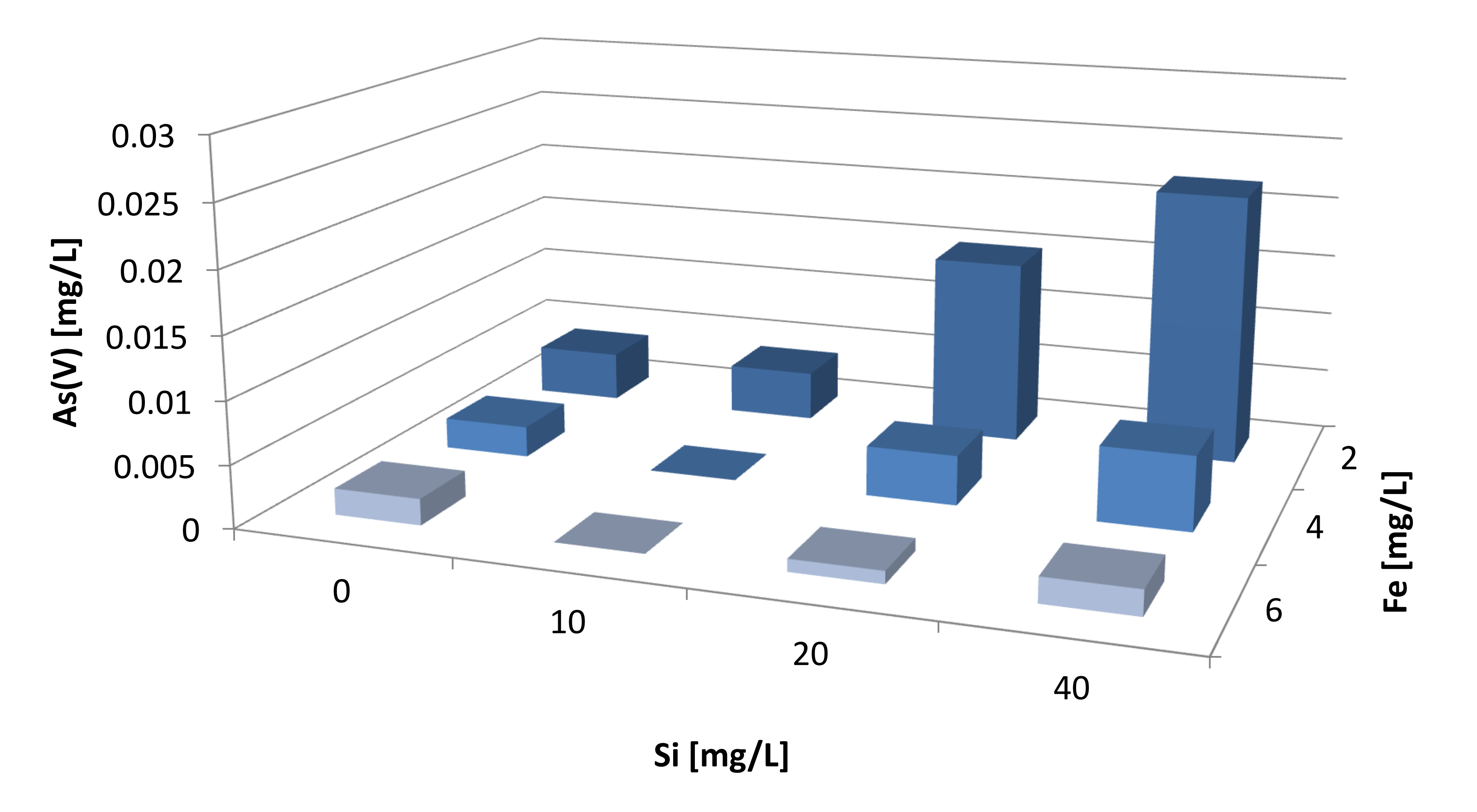


The effect of phosphate interference on arsenic removal.

Phosphate Interference

- This Study – Floc formation was not effected
  - Dosed at 2 mg/L iron
  - Phosphate levels of 1.0 and 1.5 mg/L,
  - Arsenic concentration was 0.021 and 0.030 mg/L, respectively
  - Dosed at 4 mg/L iron (100% increase) yielded arsenic concentration below MCL
- Similar to Laky et al, (2011)
  - In the presence of 1.2 mg/L phosphate
  - An 80% increase in iron dose reduced the arsenic concentration below MCL

Silicate Interference

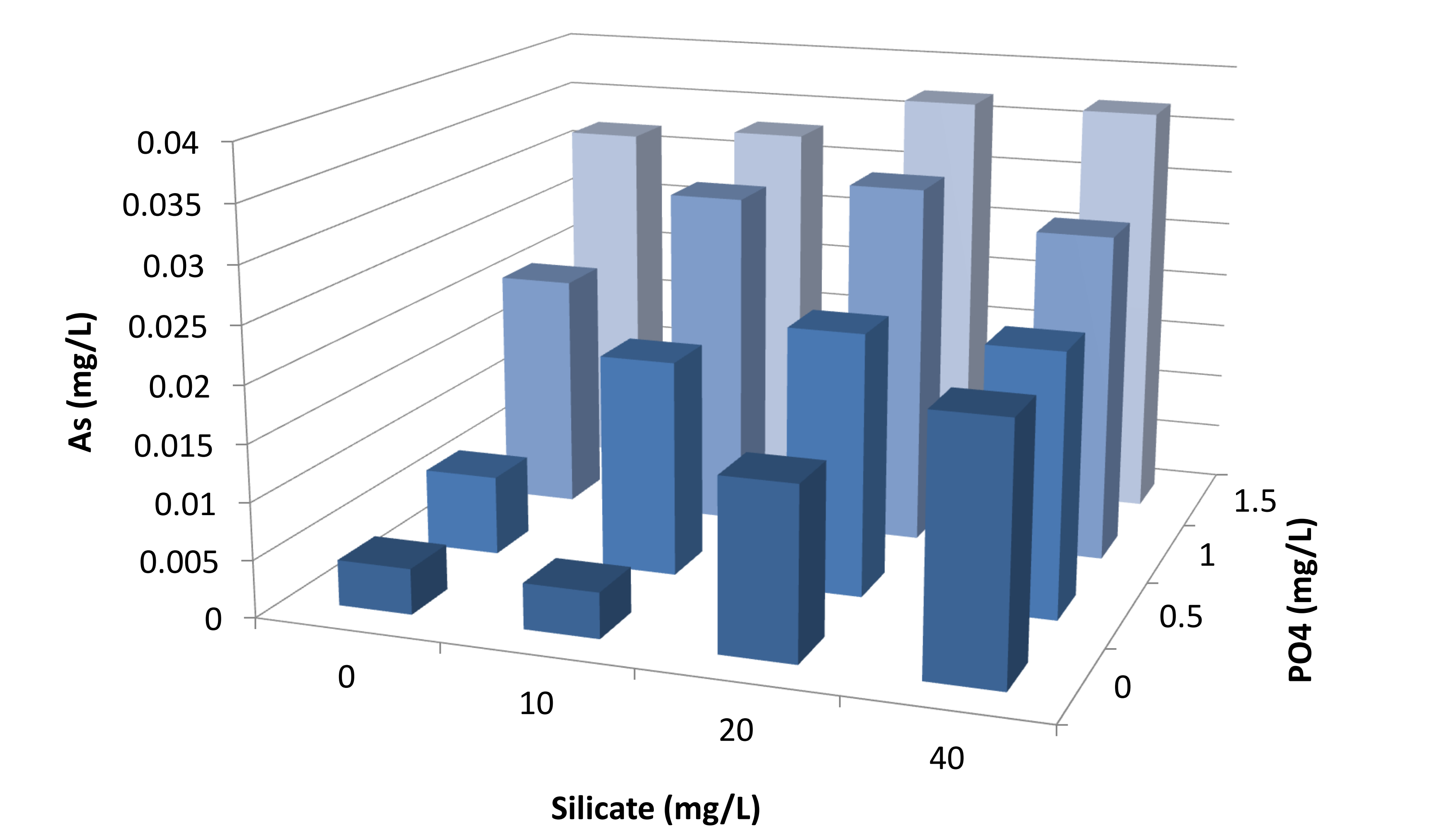


The effect of silicates interference on arsenic removal.

Silicate Interference

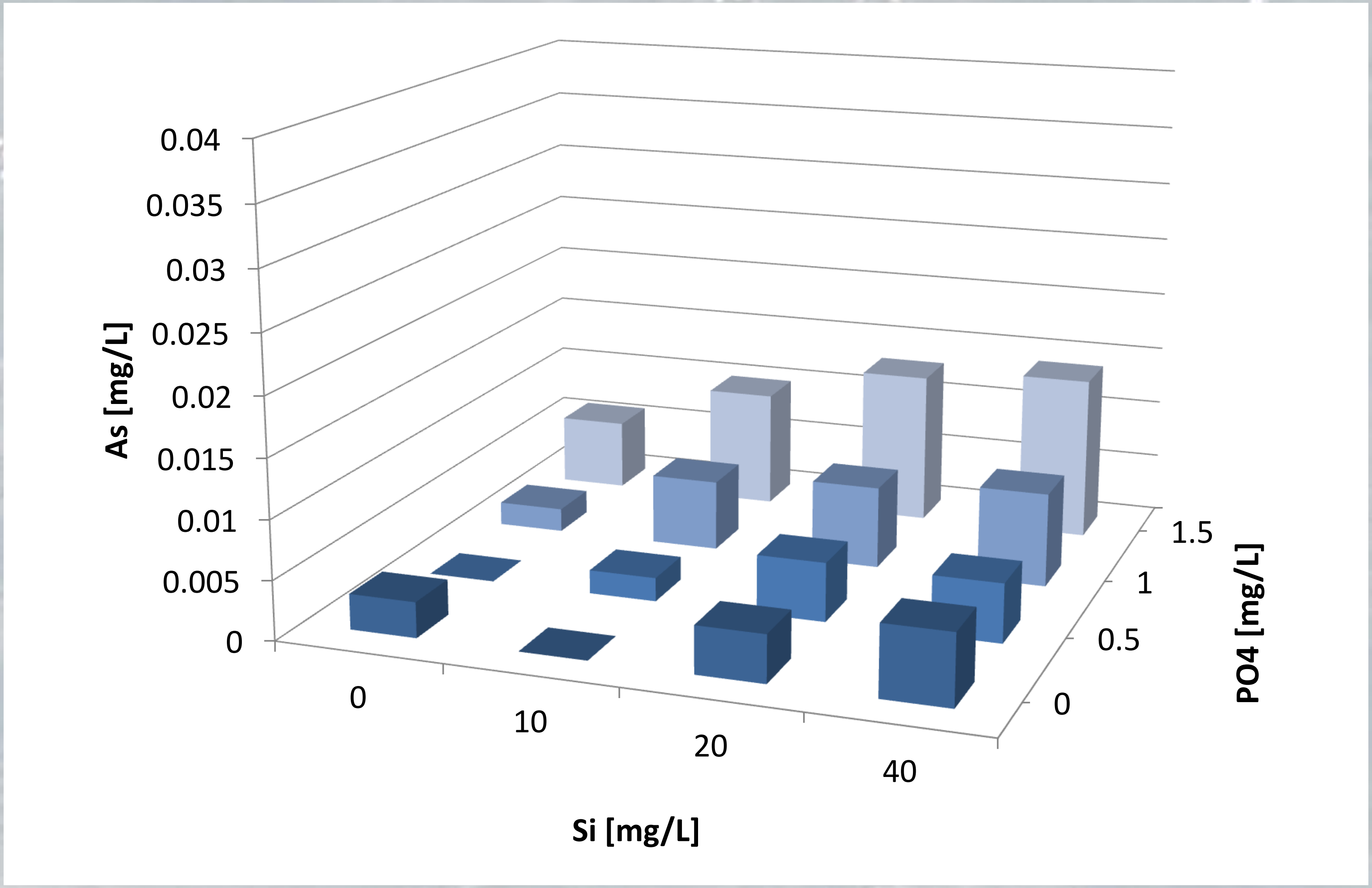
- This Study – Floc formation was delayed, decreased floc size (more pin floc)
  - In the presence of 10 mg/L silicate at 2 mg/L iron dose, 95% arsenic removal was exhibited
- Guan et al, (2009)
  - 80 percent arsenic removal in the presence of 10 mg/L silicate and iron dose of 2.5 mg/L
- Laky et al, (2011)
  - Even lower arsenic removal (55 %) was observed at similar low range of iron (Fe = 1.5 mg/L) and silicate (Si = 10 mg/L) levels
- The decrease in arsenic removal could be due to the lack of Ca^{2+} ions in the Laky and Guan synthetic test water
- Calcium and magnesium, aids in ferric hydroxide formation in the presence of silicate (Ruiping et al, 2007)

Combined Phosphate and Silicate Interference



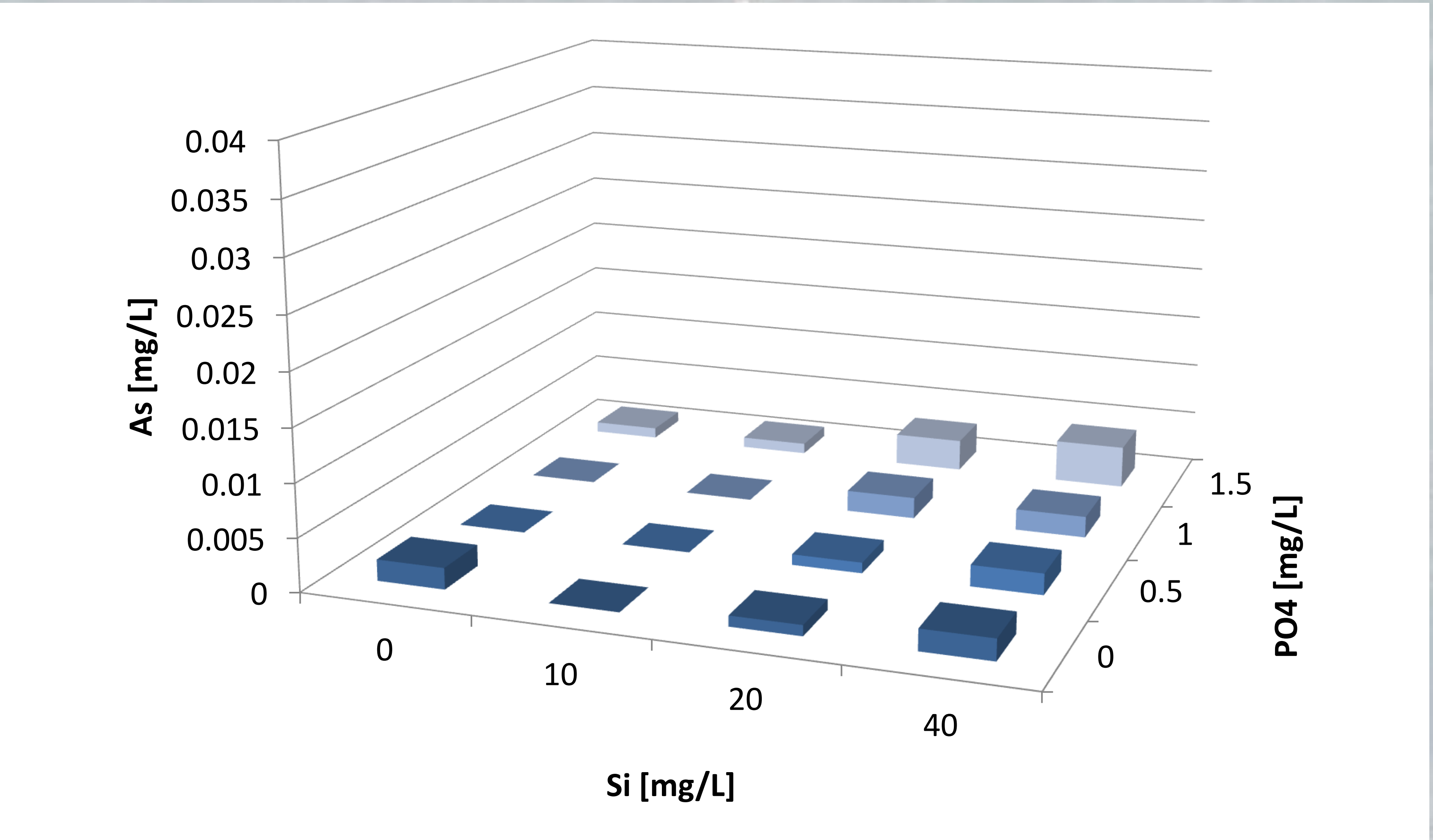
Arsenic concentrations in filtrate as a function of varying phosphate and silicate concentrations and a fixed dose of 2 mg/L Fe.

Combined Phosphate and Silicate Interference



Arsenic concentrations in filtrate as a function of varying phosphate and silicate concentrations and a fixed dose of 4 mg/L Fe.

Combined Phosphate and Silicate Interference



Arsenic concentrations in filtrate as a function of phosphate and silicate concentrations and a fixed dose of 6 mg/L Fe.

Statistical Significant Main Effects and Interactions

- 36 Factor increase variations (cubes)
  - iron doses (2 and 4 mg/L as Fe)
  - silicate concentrations (0, 10, 20, 40 mg/L as Si)
  - and phosphate concentrations (0, 0.5, 1.0, 1.5 mg/L as PO_4^{3-})
- Only one significant phosphate-silicate interaction
  - increase of phosphate from 0 to 0.5 mg/L and increase of silicate from 0 to 10 mg/L, which increased arsenic concentration by an average of 0.003 mg/L (Equation 5)

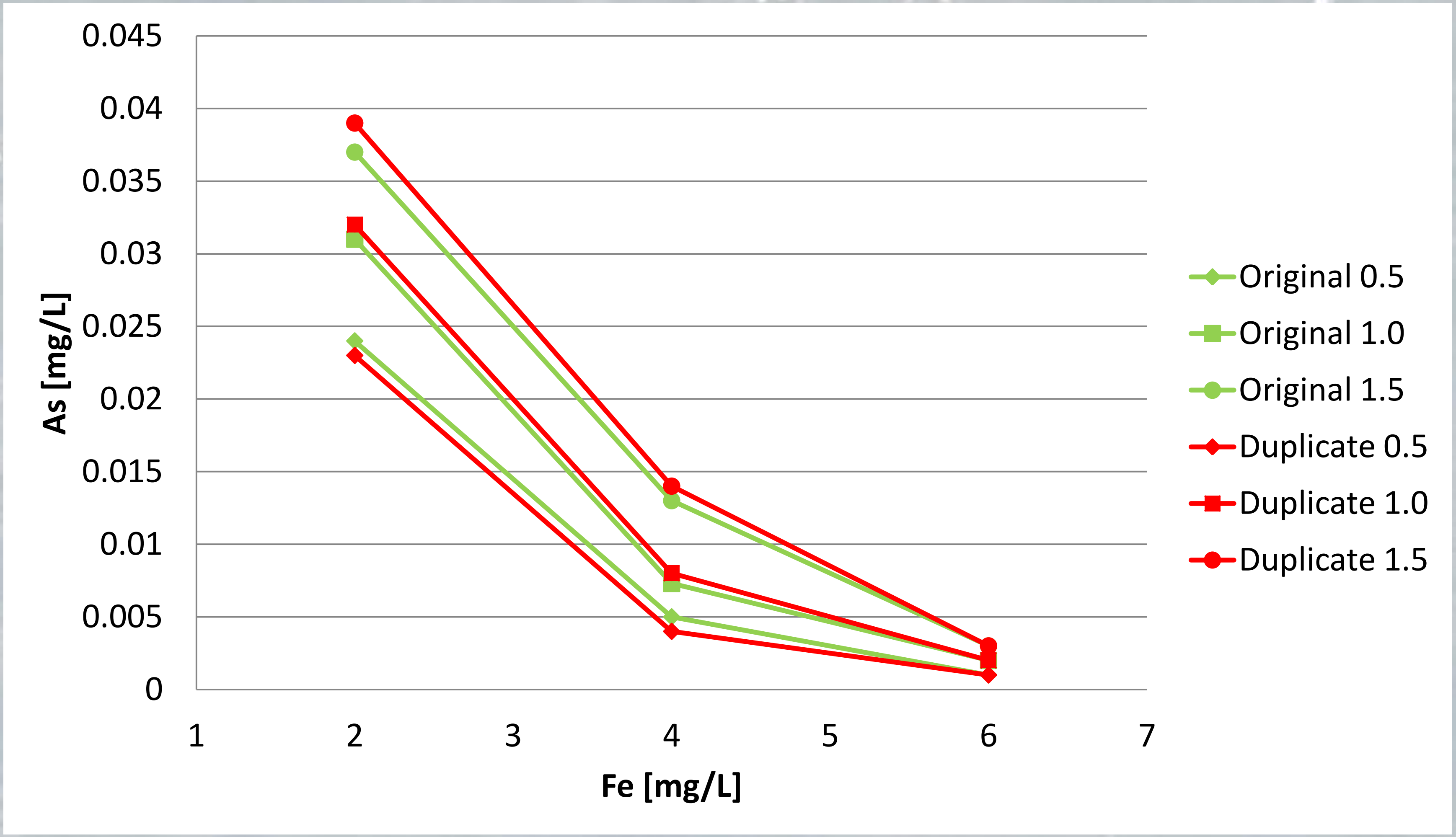
Statistical Significant Main Effects

- Phosphate Main Effects
- 29 of 36 conditions exhibited a significant main effect
- Increase of silicate from 0 to 10 mg/L and increase of phosphate from 0 to 1.5 mg/L resulted in increasing the arsenic concentration by an average of 0.017 mg/L (Equation 3)
- At all levels of silicate tested the increase of phosphate from 0 to 1.5 mg/L, resulted in a significant increase in average arsenic concentrations

Statistical Significant Main Effects

- Silicate Main Effects
- 15 of 36 conditions exhibited a significant main effects
- Increasing phosphate levels from 0 to 0.5 mg/L and increasing silicate from 0 to 40 mg/L, increased final arsenic concentration by an average of 0.011 mg/L (Equation 4)
- Over the range of phosphate levels, an increase of 0 to 40 mg/L silicate resulted in a significantly increased final arsenic concentrations

Between Run Precision



The original and replicate arsenic removal data, each pair was within 0.002 mg/L

Conclusions

- Lack of statistical significant PO_4^{3-} -Si interaction
- At low iron doses (e.g. 2 mg/L) phosphate and silicate can decrease arsenic removal from 97 to 59 percent.
- At a higher iron dose of 6 mg/L the interfering effects are significantly reduced.
- Over the range of concentrations studied, increasing iron dose can yield finished water that meets the 0.010 mg/L MCL
- Further Research

  -Humic interference and combined interferences

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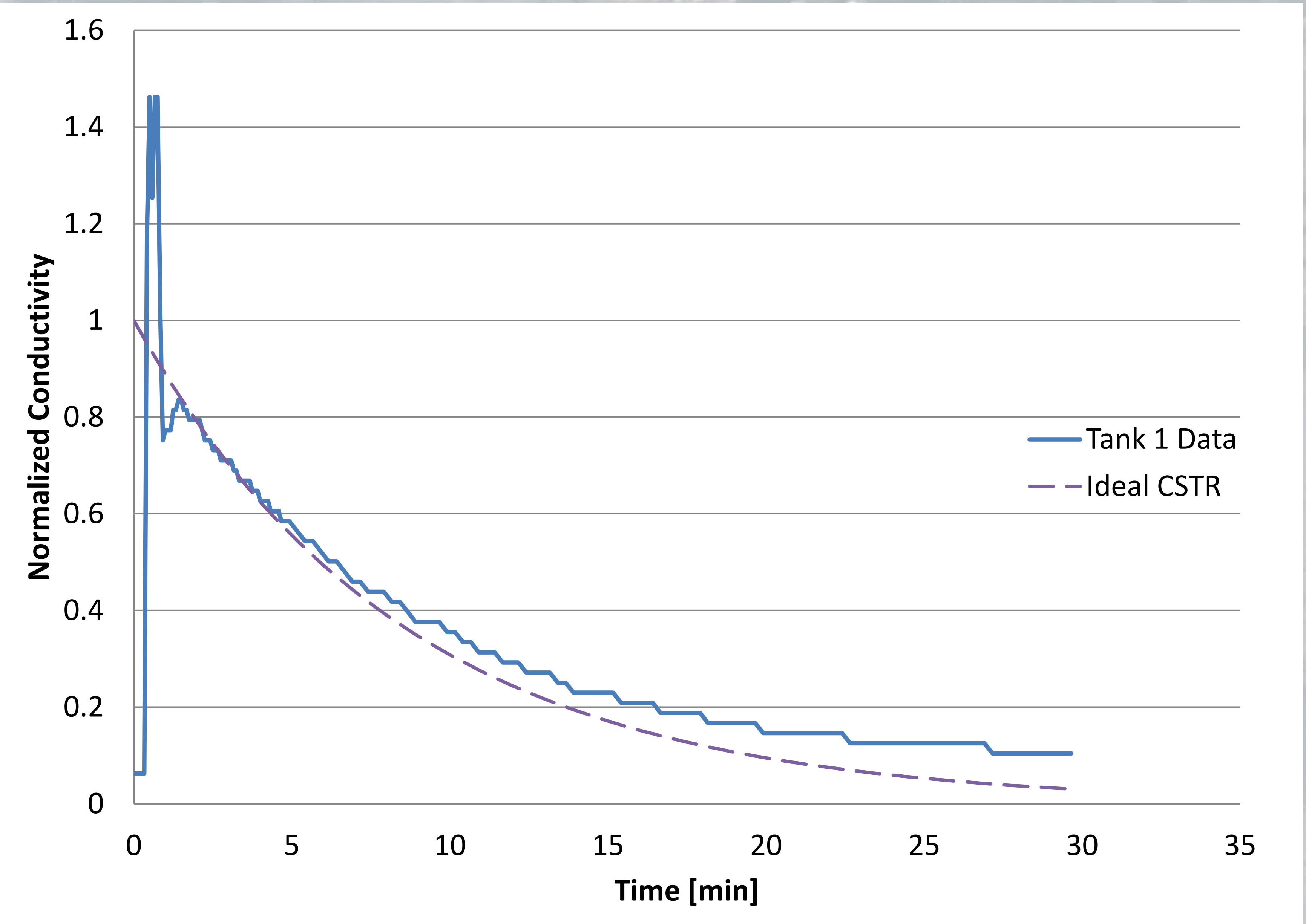

1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Normalized Conductivity
0
5
10
15
20
25
30
35
Time [min]
Tank 1 Data
Ideal CSTR