Column Study Treatability Testing for *In Situ* Remediation of Mining-Influenced Water

Nathan Smith, Nick Anton, David Reisman, Angela Frandsen, Roger Olsen **(CDM Smith)**

Mike Sieczkowski, Donovan Smith **(JRW Bioremediation)**

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CDM Smith

MIW Treatment Overview

- Treatment often performed using active methods (treatment plants) or passive/semi-passive methods (biochemical reactors [BCRs], wetlands, limestone drains)
  - Treatment plants often require continuous operation and maintenance
- Treatment is often limited to where drainage exits the mine, including: adits, seeps, or pumped
  - Typically requires multiple points for treatment, or complex piping/transport of the MIW
  - Can be limited by available space for passive / semi-passive locations in remote, mountainous areas

In Situ Application Overview

- *In situ* treatment involves generation of sulfate-reducing conditions within the abandoned mine – simulates a BCR
  - Treats the MIW at the source, rather than the discharge location
  - Utilizes the same geochemical principles as BCRs
  - Utilizes pH adjustment and organic amendment / substrate addition
  - Includes application to mine voids, shafts, and fractures within bedrock groundwater systems and PRB-type application for alluvial groundwater systems
  - Can also include source control methods such as mine bulkheading, grouting, and groundwater controls

2012 Study – Static Bench-Scale Tests

- Utilized batch reactors to simulate MIW present within a mine void
  - Cubitainers containing:
    - *MIW*
    - *Site sediments*
    - *Manure (extract)*
    - *Inert material (sand/pea gravel)*
      - Roughly 2/3 of each container was freeboard MIW to simulate open voids
  - pH adjustment (NaOH addition to pH 4.5 su)
  - Added carbon substrate
  - Test length 3 months with periodic sampling and injection

2012 Study – Electron Donors and Water Types

- Selected carbon sources that could be easily injected (either liquids or solids that could be slurried):
  - Ethanol
  - Methanol
  - Beer
  - ChitoRem® (no NaOH)
  - Antifreeze (ethylene glycol)
- Three MIW types:
  - Two strongly acidic (pH <3), high metals (Al, As, Cd, Cu, Fe, Mn, Zn)
  - One near-neutral (pH 5.5), moderate metals (Cd, Pb, Zn)

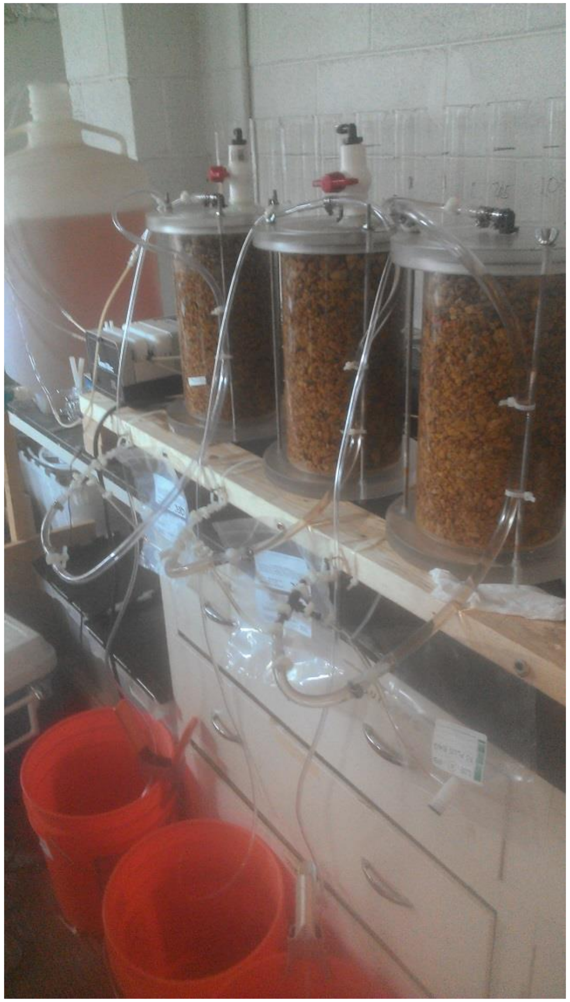
2012 Study Test Results

- Best metal removal by ChitoRem®
- Ethylene glycol and ethanol also provided promising results
- Sulfide production mostly limited to ChitoRem® and ethanol

2013 Study – Phase 1

- Objective: Can we inject amendments into a simulated mine environment and generate necessary conditions to improve water quality?
- Column study comparing propylene glycol + NaOH, ChitoRem® (suspended in guar gel slurry), and control
- Columns packed with site waste rock and inert pea gravel
- Acidic MIW pumped through columns (pH approx 3; Sulfate: 16,000 mg/L; Iron: 1,400 mg/L; Nickel: 1.3 mg/L; Copper: 45 mg/L)
- Periodic injections of amendment through injection port in column

2013 Study – Phase 1 – Lessons Learned



- Gravity feed of guar slurry does not work
- Pressurization of guar slurry with inert gas required careful management
- Gravity feed of liquid substrates - PG and NaOH - led to short-circuiting
- Gas generation led to draining of columns
- Injection through one small port means minimal distribution throughout column

2013 Study – Phase 1 - Results

Metal Removal Efficiency			
	PG + NaOH	ChitoRem®	Control
Aluminum	91%	24%	-7%
Arsenic	99%	58%	30%
Cadmium	85%	13%	-6%
Copper	94%	26%	-11%
Iron	100%	46%	30%
Zinc	87%	-2%	-12%
Sulfate	60%	19%	0%

- Column 1: pH 5.58; ORP 230.5 mV
- Column 2: pH 3.07; ORP 385.9 mV

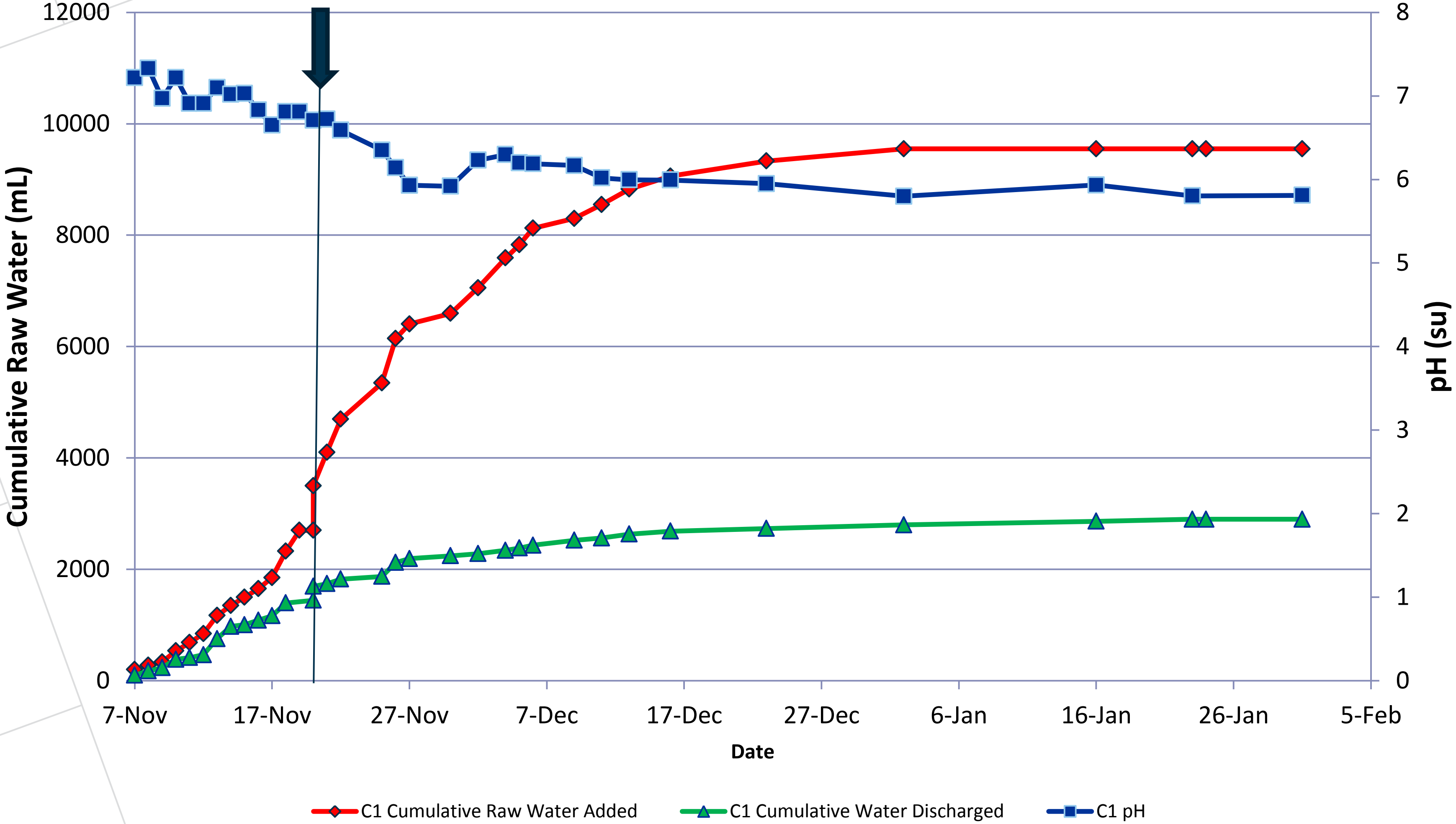
2013 Study – Phase 2

- Objectives:
  - Can we treat this MIW using ChitoRem® alone?
  - Does pumping treated MIW into a simulated mine environment improve conditions in the mine?
- Column 1: ChitoRem® (15%) mixed into column packed with pea gravel (70%) and sand (15%)
- Column 2: Site waste rock (33%) with pea gravel (67%)
- Raw MIW in Columns 1 and 2 (2 – 2.5 liters pore volume)
- Once treated by Column 1, transfer treated water into Column 2

2013 Study – Phase 2

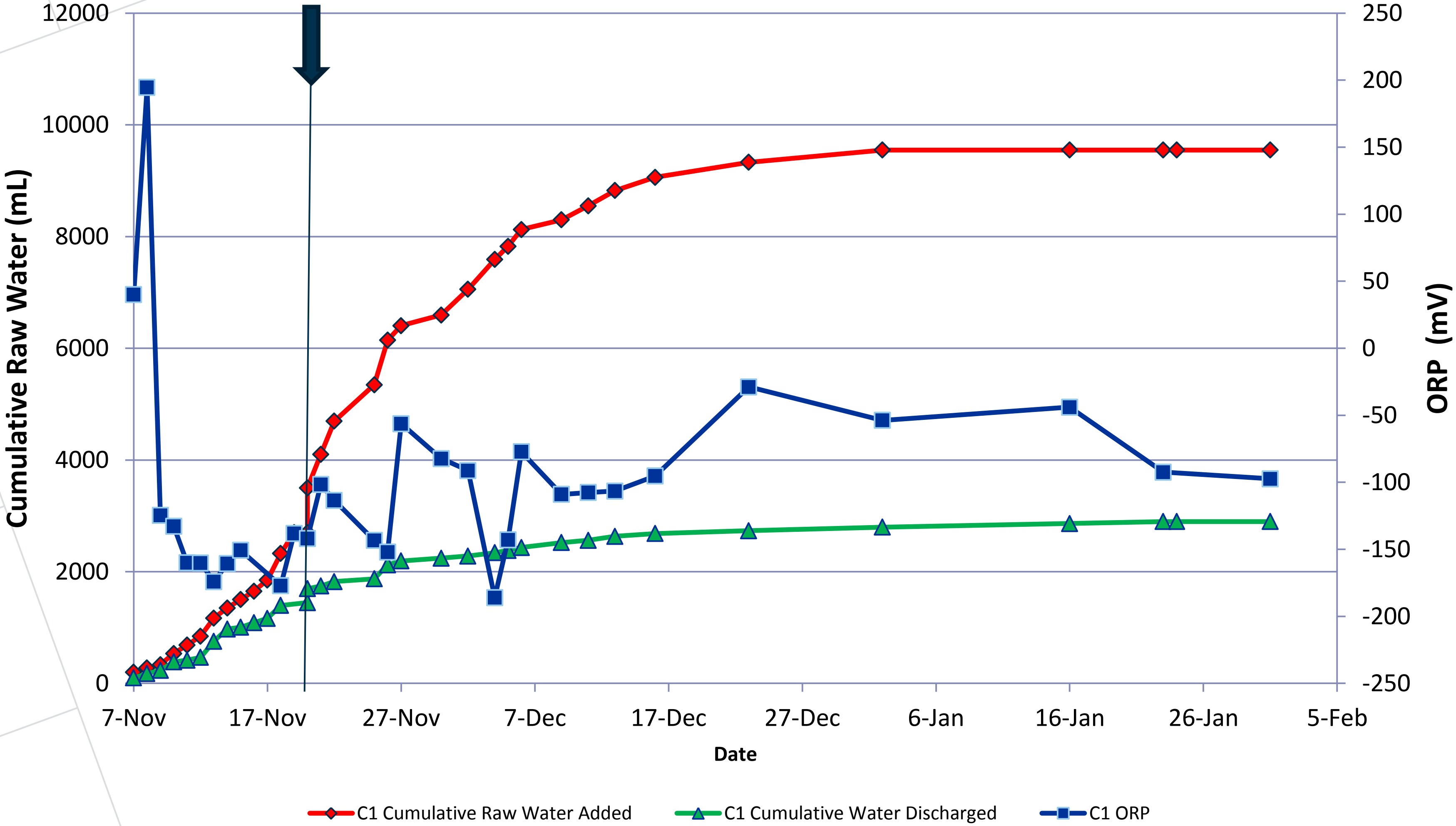
- Raw MIW recirculated in C1 and C2 until pH, ORP stabilized
- Once C1 stable, began transferring effluent to C2 in roughly 5-10% batches (by pore volume)
  - Provides a treated MIW containing alkalinity and soluble carbon, proteins, and SRB from ChitoRem®
  - Simulates gradual replacement of mine pool, either actively or due to flushing events

Column 1 - pH



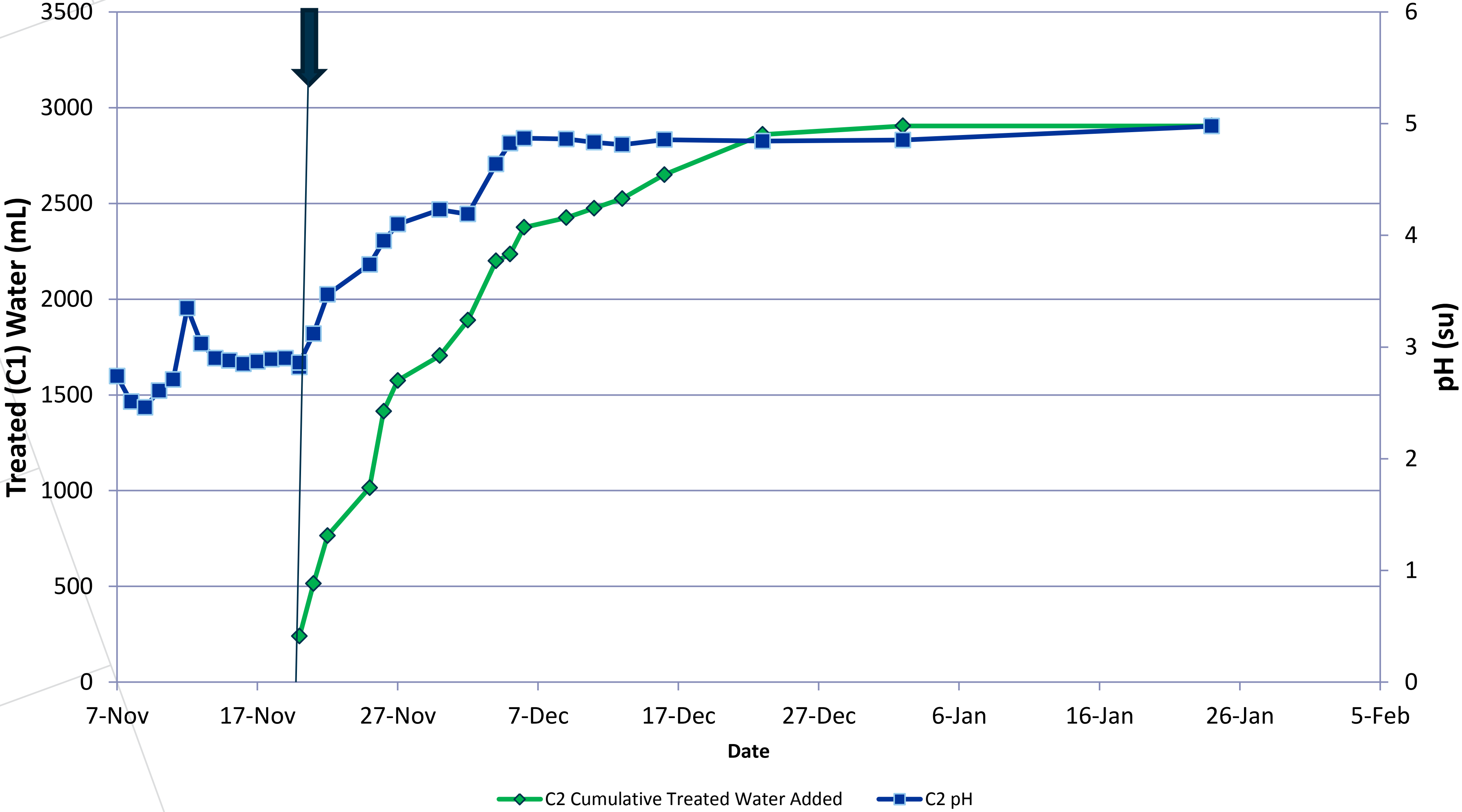
12000
10000
8000
6000
4000
2000
0
8
7
6
5
4
3
2
1
0
Cumulative Raw Water (mL)
pH (su)
7-Nov
17-Nov
27-Nov
7-Dec
17-Dec
27-Dec
6-Jan
16-Jan
26-Jan
5-Feb
Date
C1 Cumulative Raw Water Added
C1 Cumulative Water Discharged
C1 pH

Column 1 - ORP



12000
10000
8000
6000
4000
2000
0
Cumulative Raw Water (mL)
250
200
150
100
50
0
-50
-100
-150
-200
-250
ORP (mV)
7-Nov
17-Nov
27-Nov
7-Dec
17-Dec
27-Dec
6-Jan
16-Jan
26-Jan
5-Feb
Date
C1 Cumulative Raw Water Added
C1 Cumulative Water Discharged
C1 ORP

Column 2 - pH



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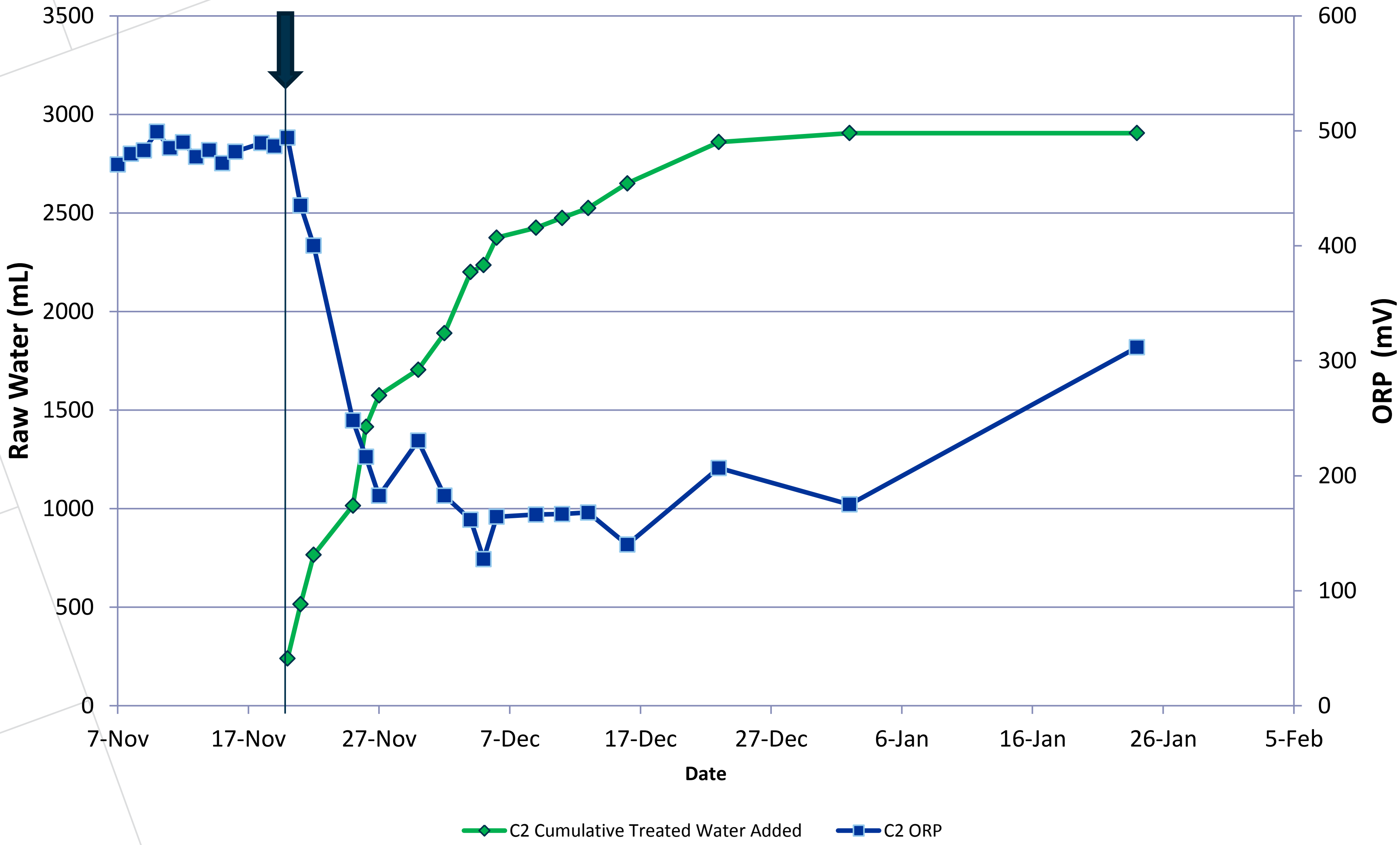
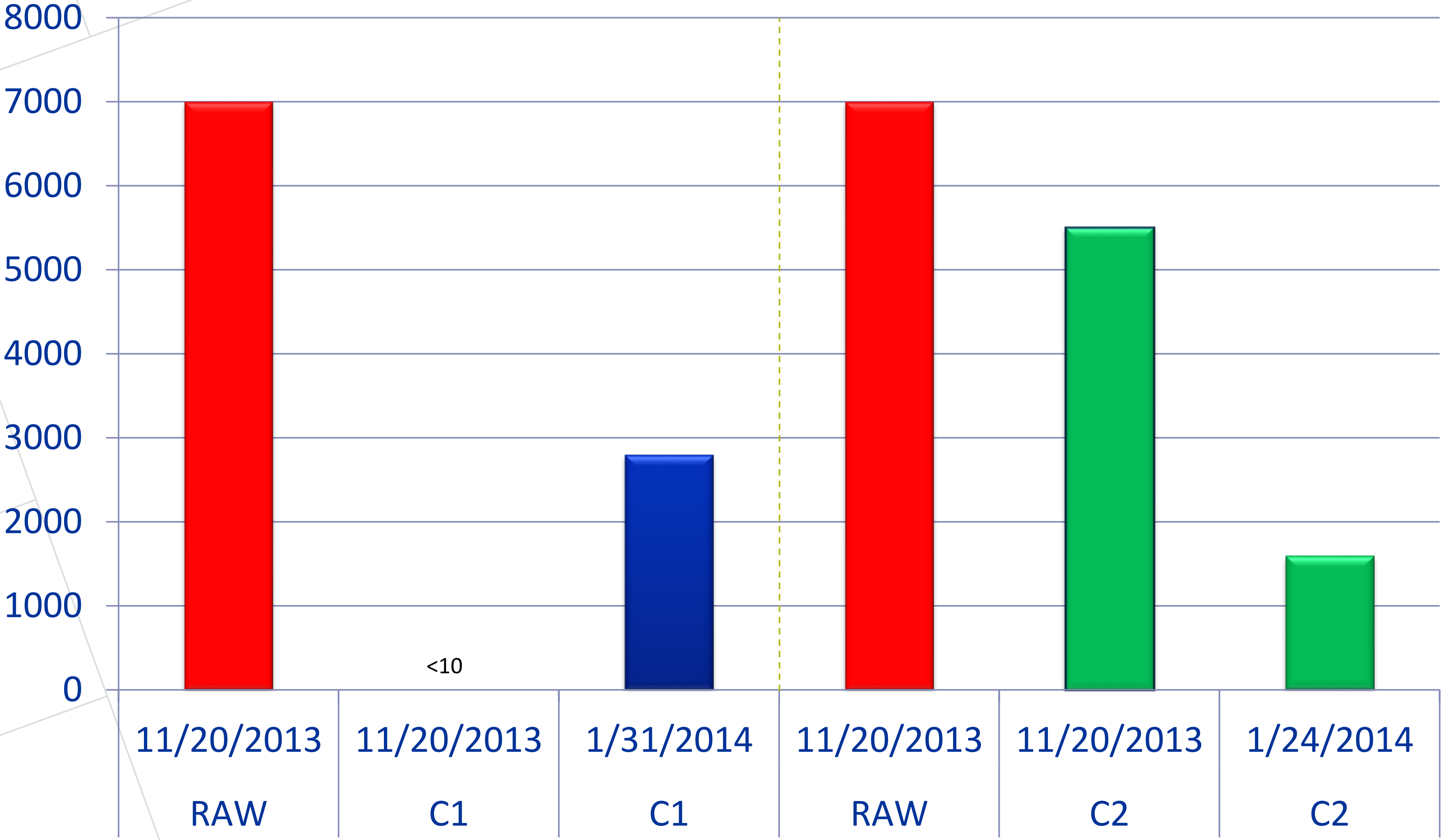
Column 2 - ORP



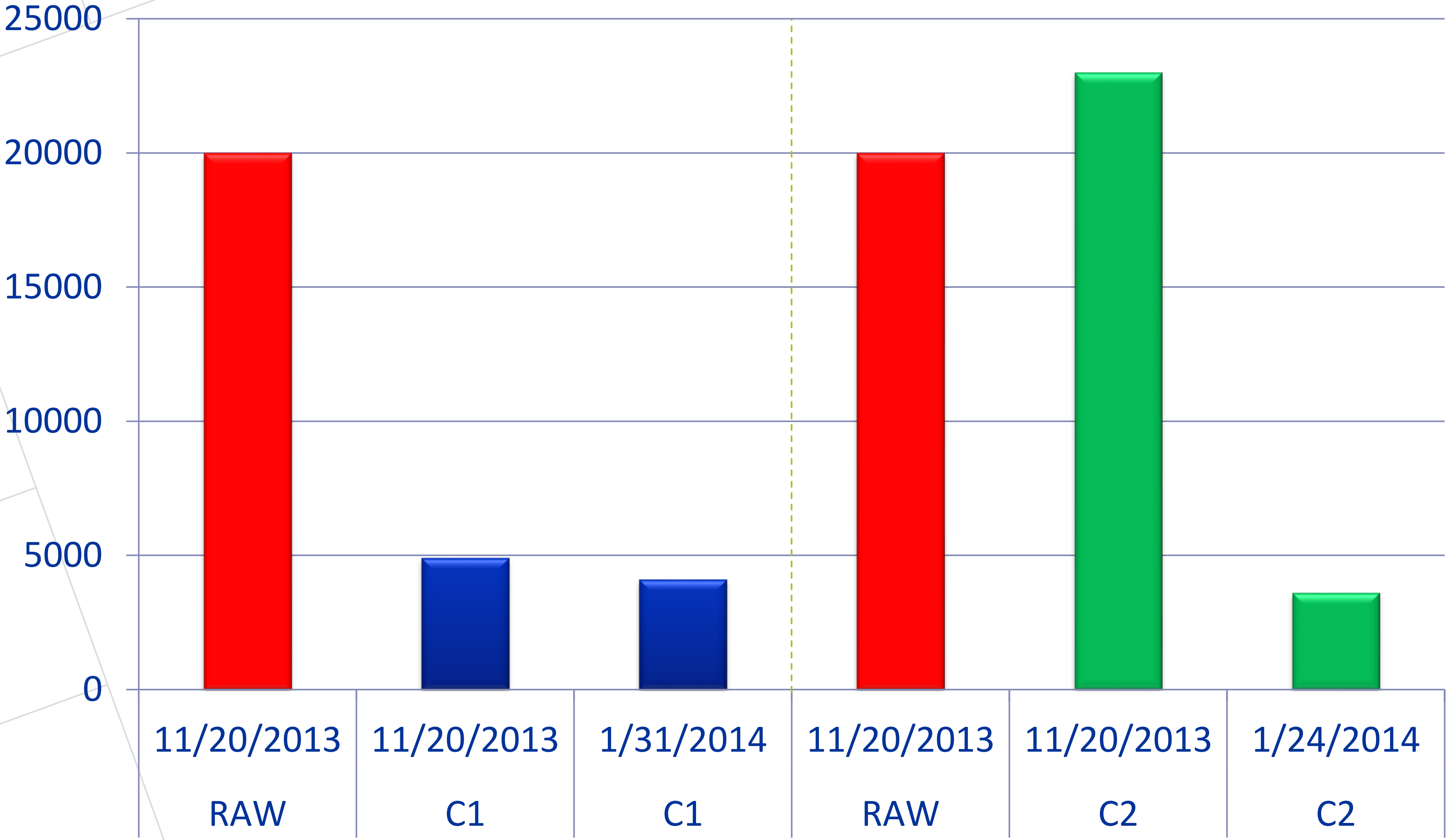
Raw Water (mL)
3500
3000
2500
2000
1500
1000
500
0
600
500
400
300
200
100
0
ORP (mV)
7-Nov
17-Nov
27-Nov
7-Dec
17-Dec
27-Dec
6-Jan
16-Jan
26-Jan
5-Feb
Date
C2 Cumulative Treated Water Added
C2 ORP

Acidity (mg/L)

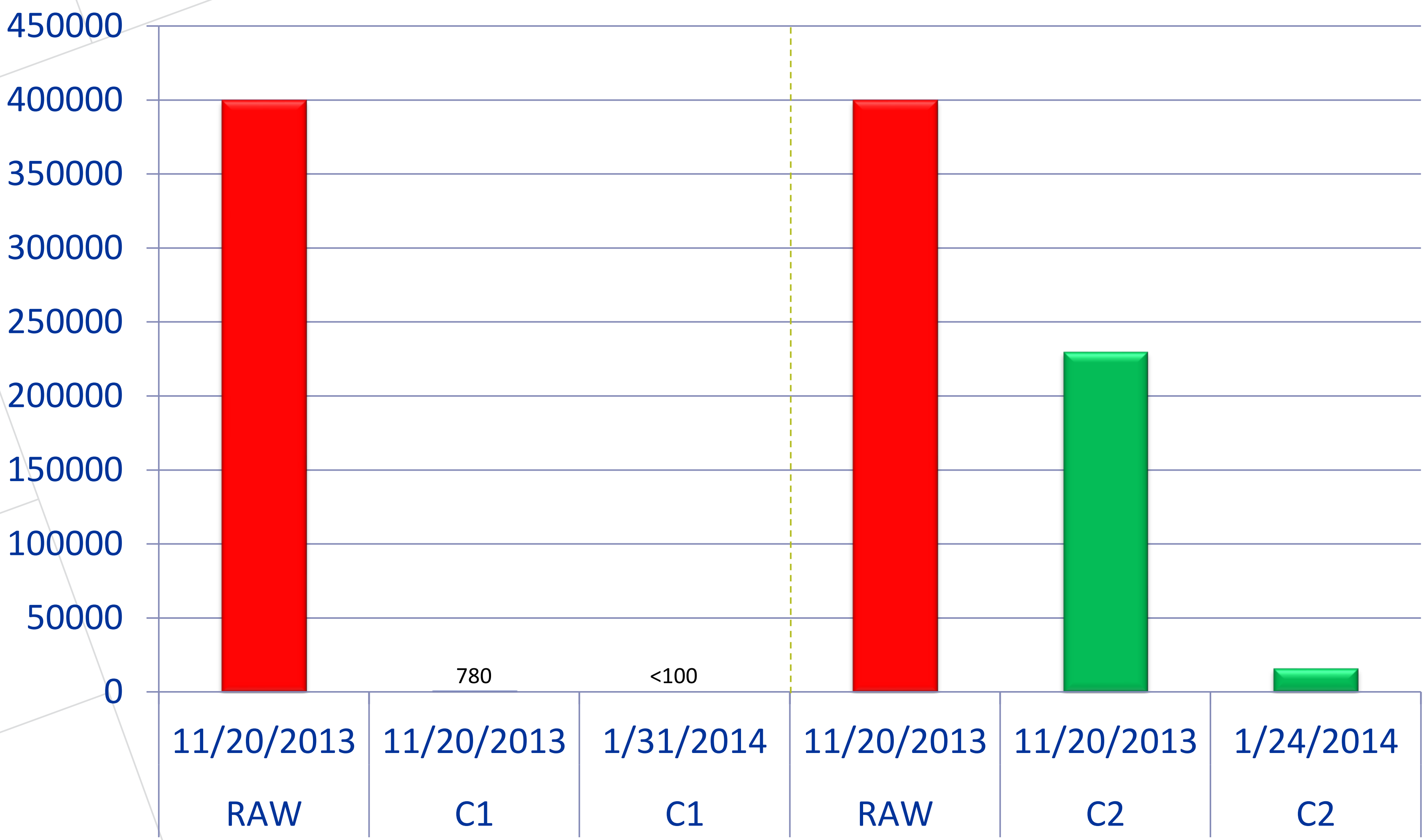


8000
7000
6000
5000
4000
3000
2000
1000
0
<10
11/20/2013 RAW
11/20/2013 C1
1/31/2014 C1
11/20/2013 RAW
11/20/2013 C2
1/24/2014 C2

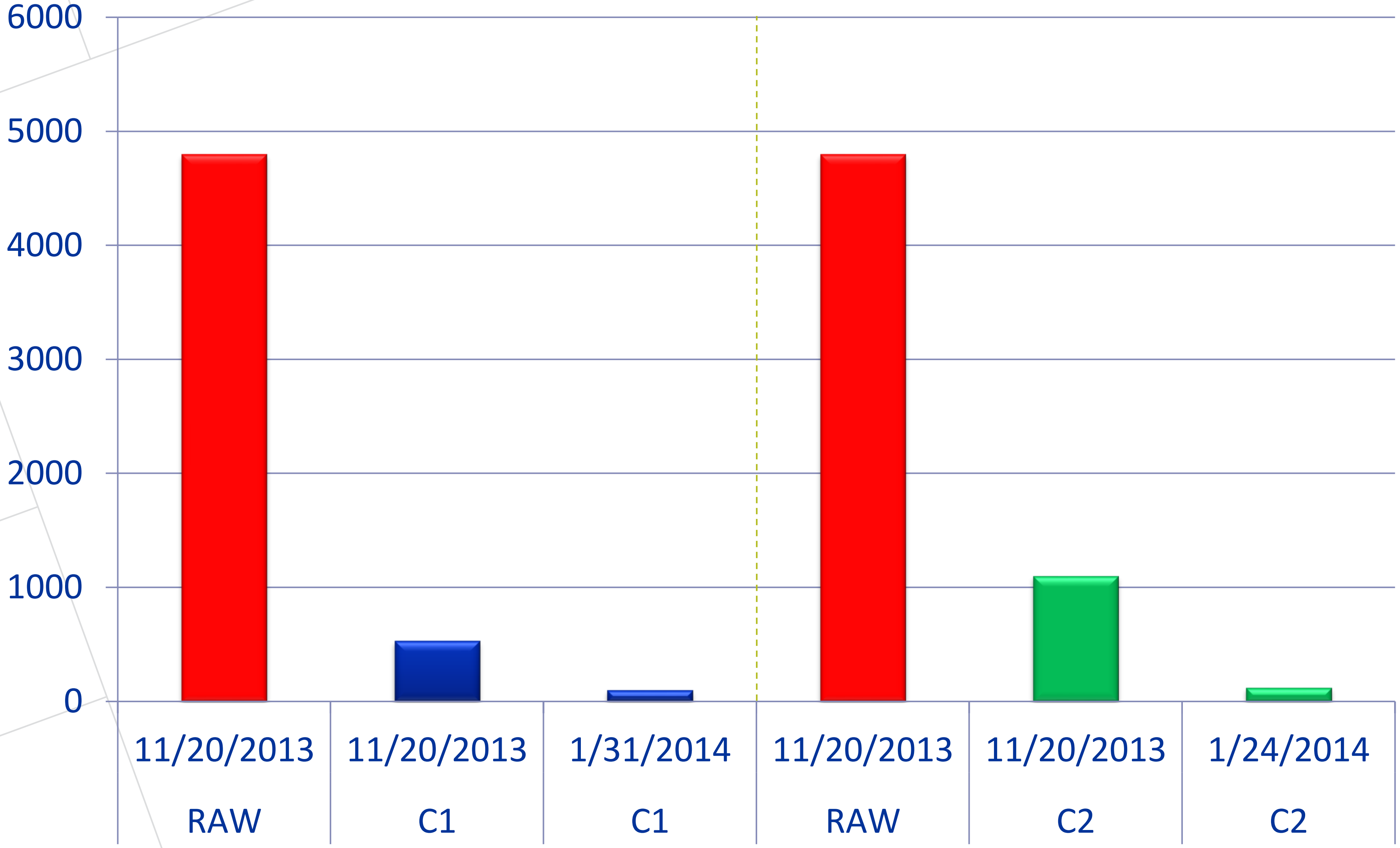
Sulfate (mg/L)


25000
20000
15000
10000
5000
0
11/20/2013 RAW
11/20/2013 C1
1/31/2014 C1
11/20/2013 RAW
11/20/2013 C2
1/24/2014 C2

Aluminum (ug/L)

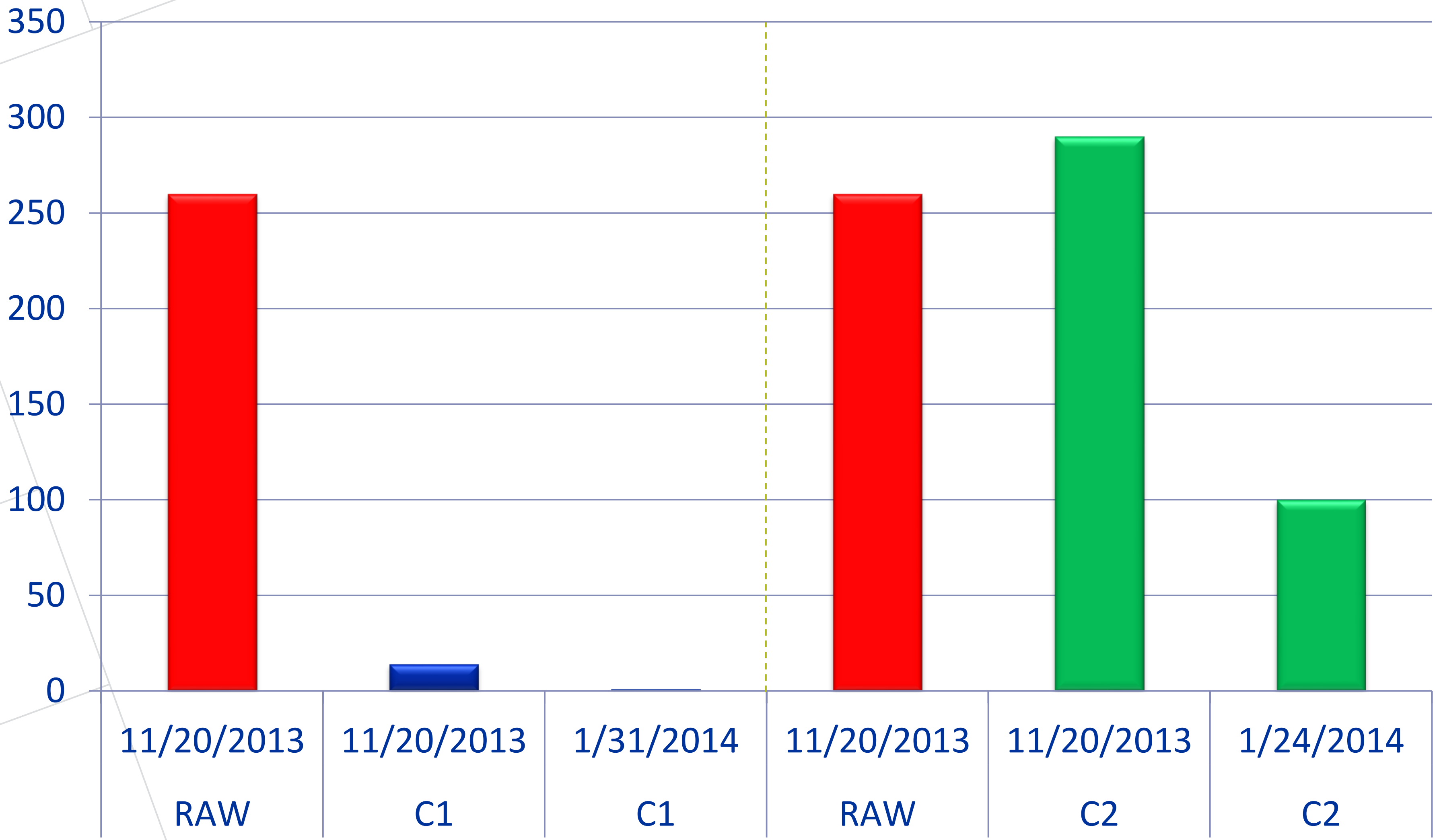


Arsenic (ug/L)



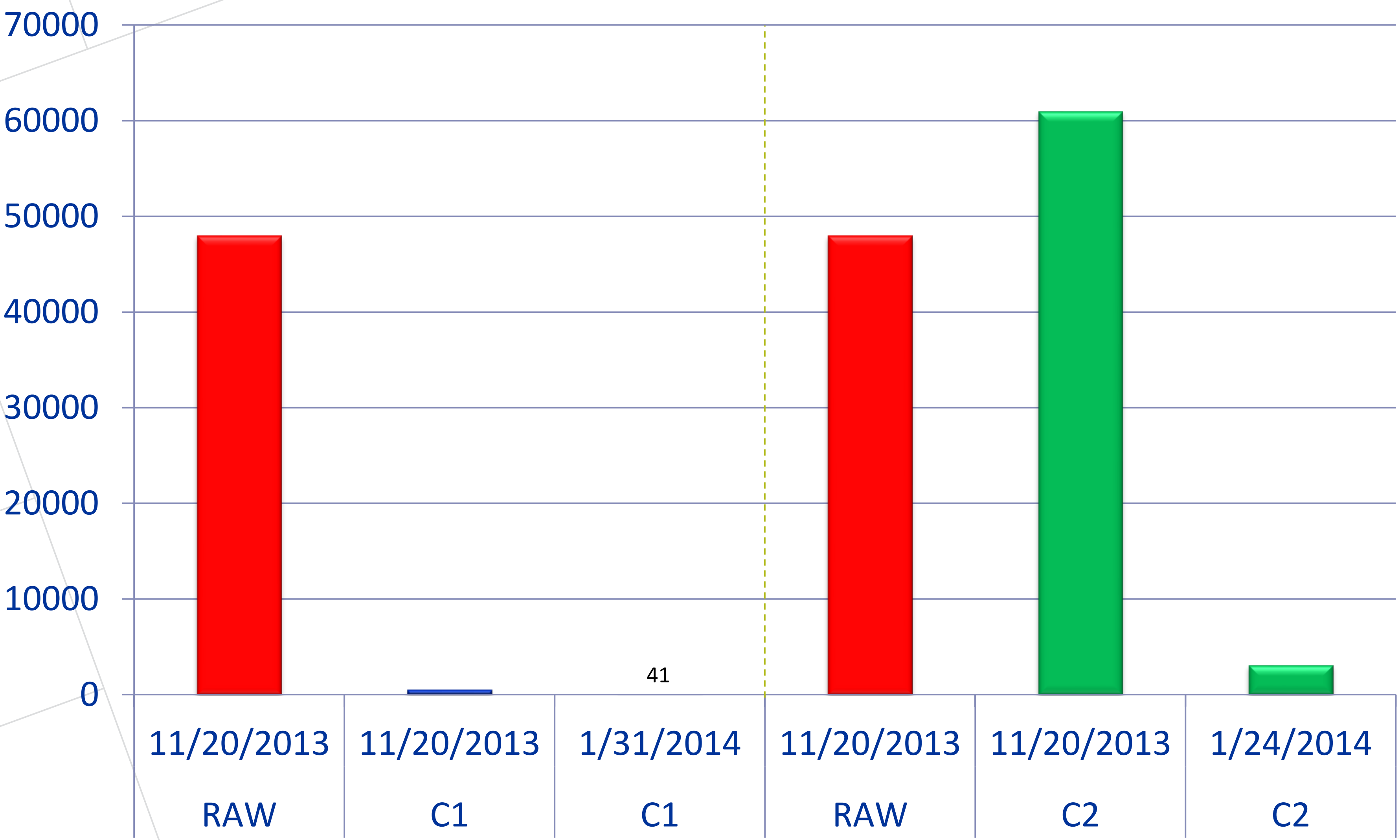
6000
5000
4000
3000
2000
1000
0
11/20/2013
RAW
11/20/2013
C1
1/31/2014
C1
11/20/2013
RAW
11/20/2013
C2
1/24/2014
C2

Cadmium (ug/L)



350
300
250
200
150
100
50
0
11/20/2013
RAW
11/20/2013
C1
1/31/2014
C1
11/20/2013
RAW
11/20/2013
C2
1/24/2014
C2

Copper (ug/L)



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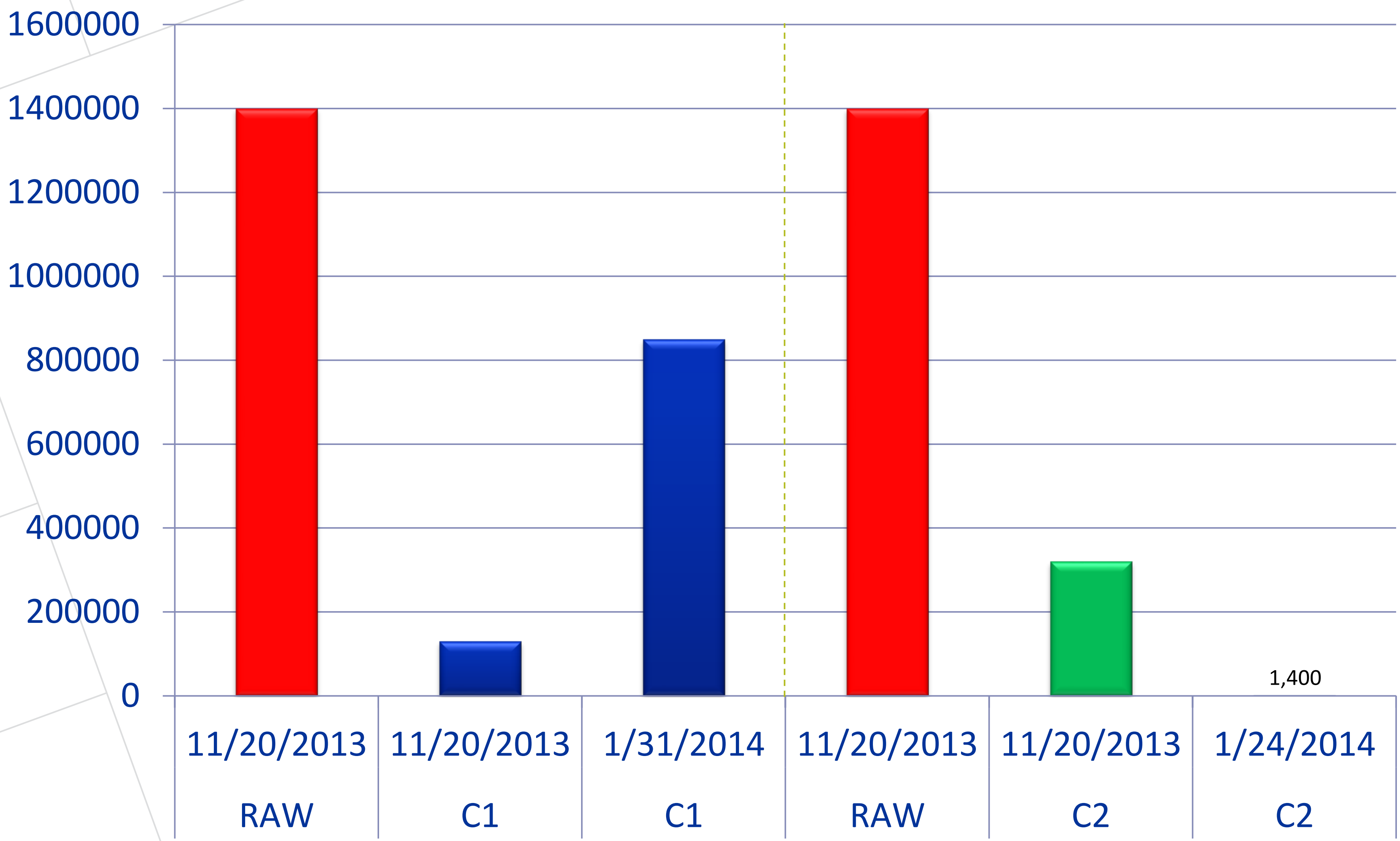
Iron (ug/L)



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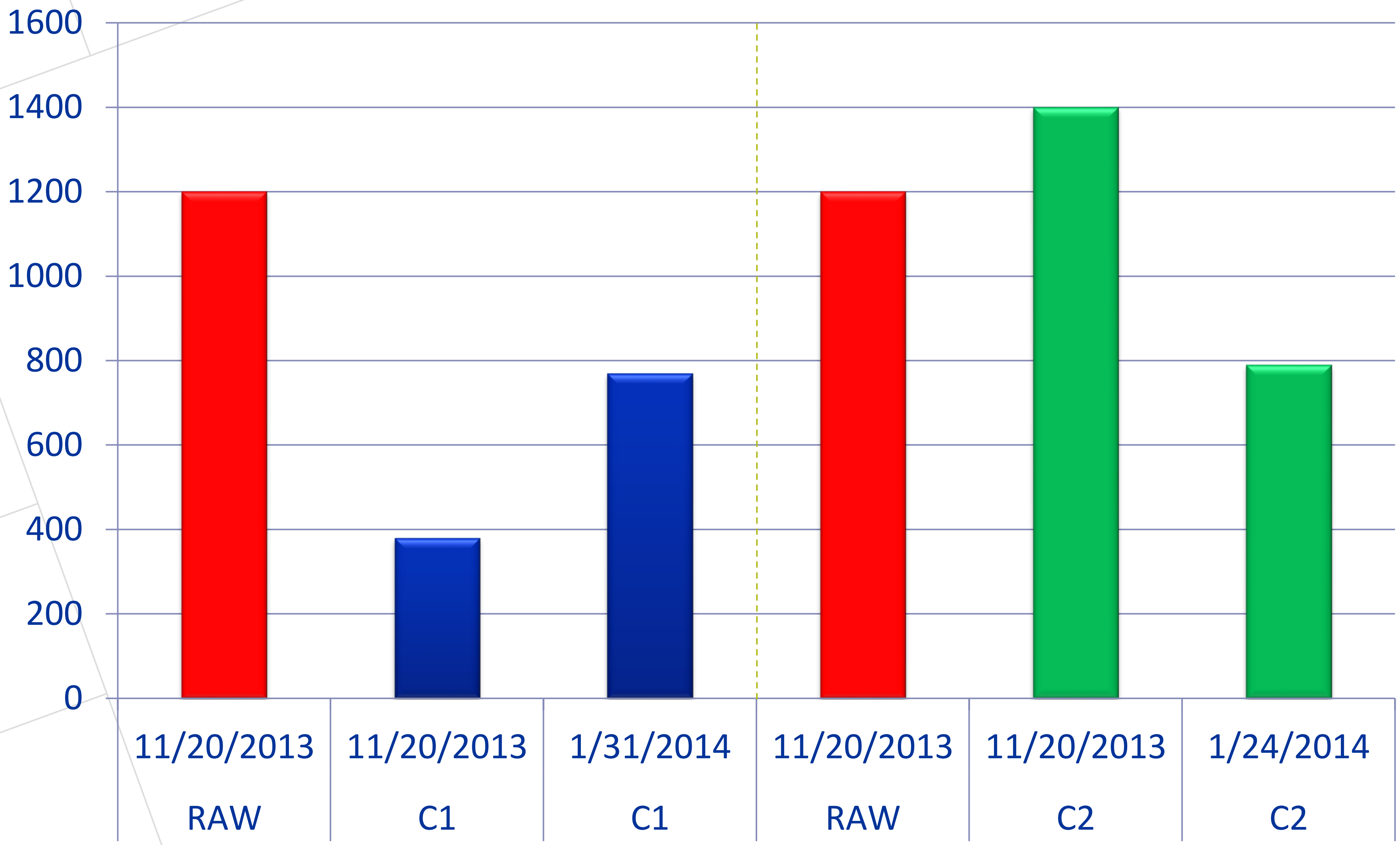
Nickel (ug/L)


1600
1400
1200
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800
600
400
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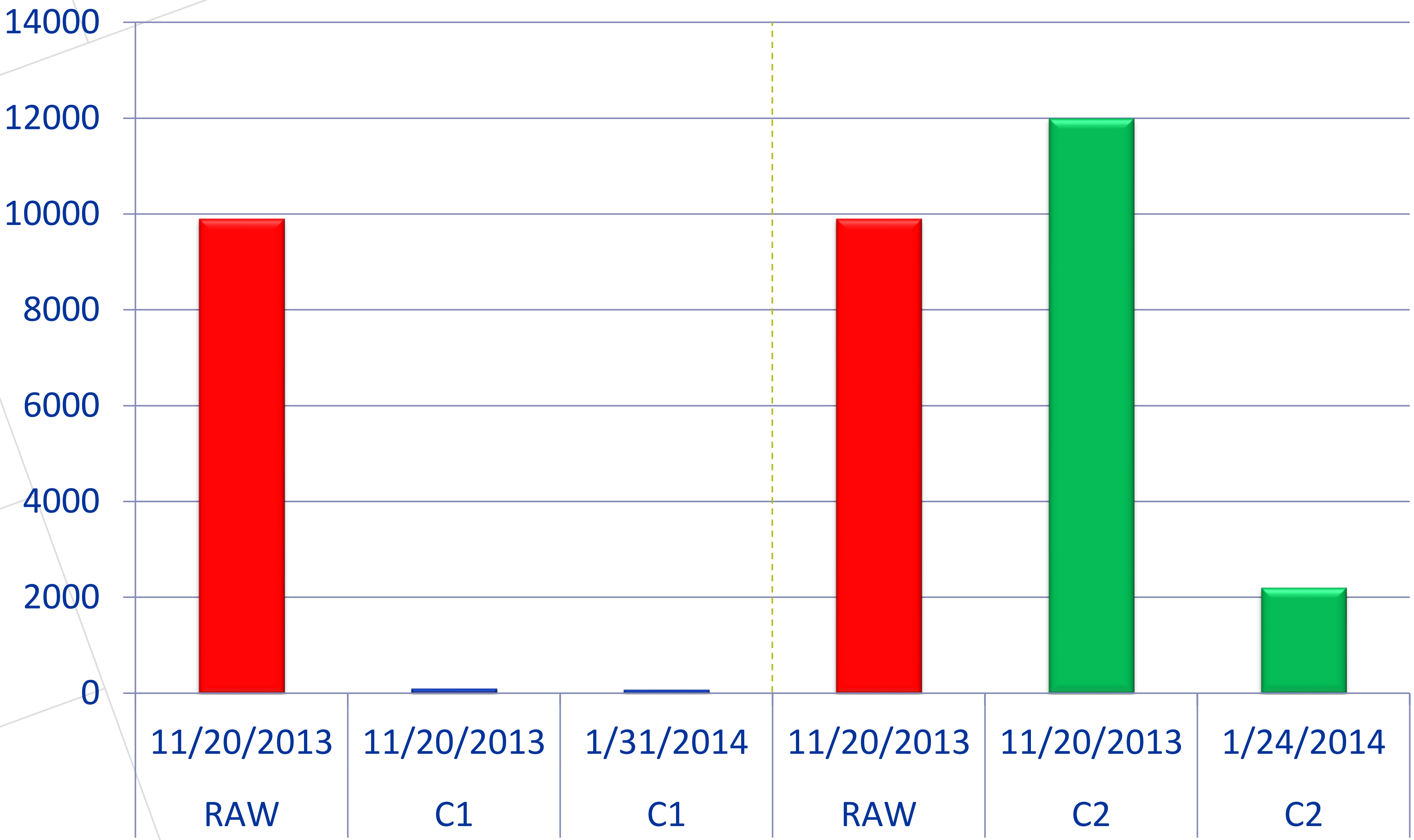
11/20/2013
RAW
11/20/2013
C1
1/31/2014
C1
11/20/2013
RAW
11/20/2013
C2
1/24/2014
C2

Zinc (ug/L)



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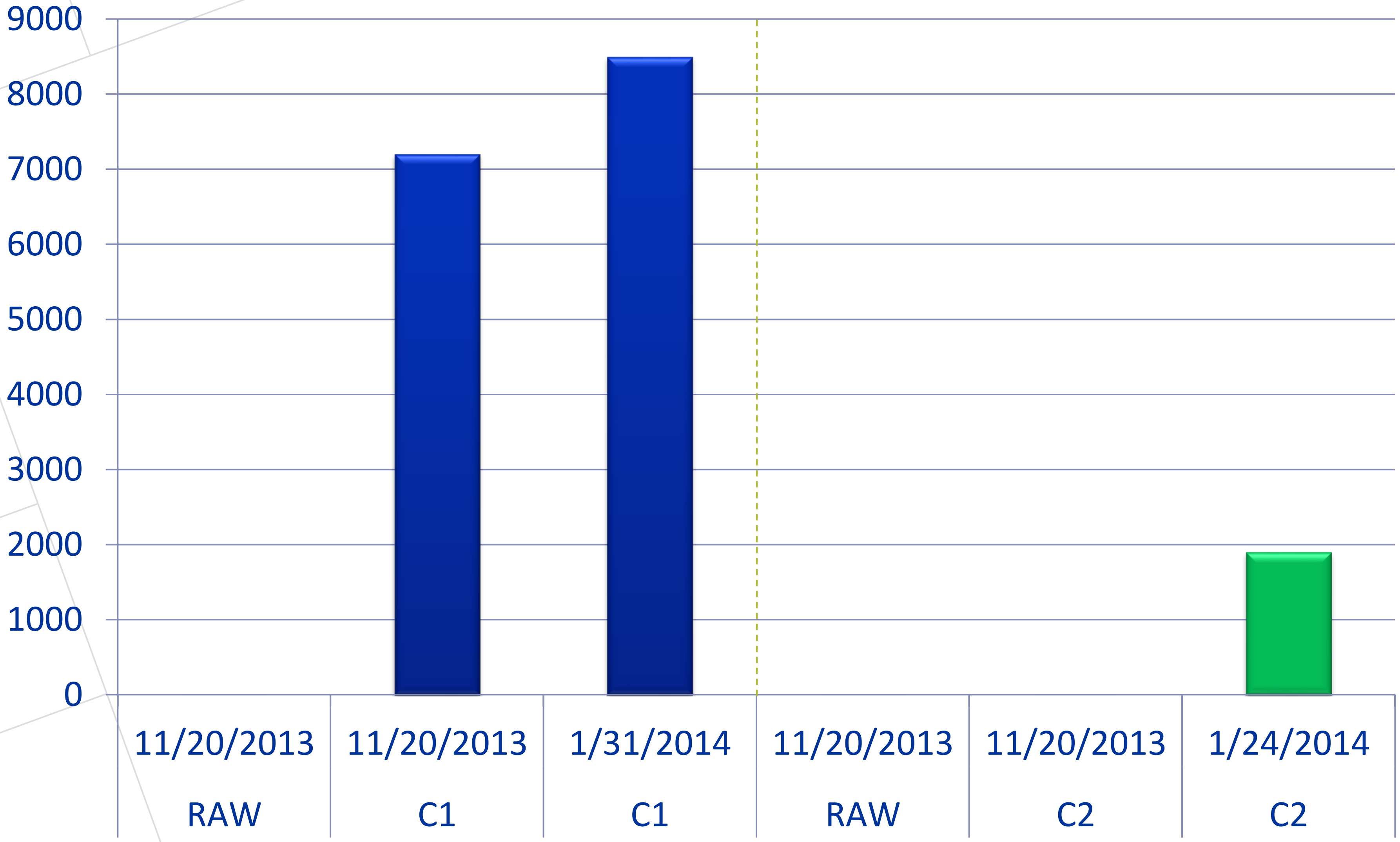
Alkalinity (mg/L)



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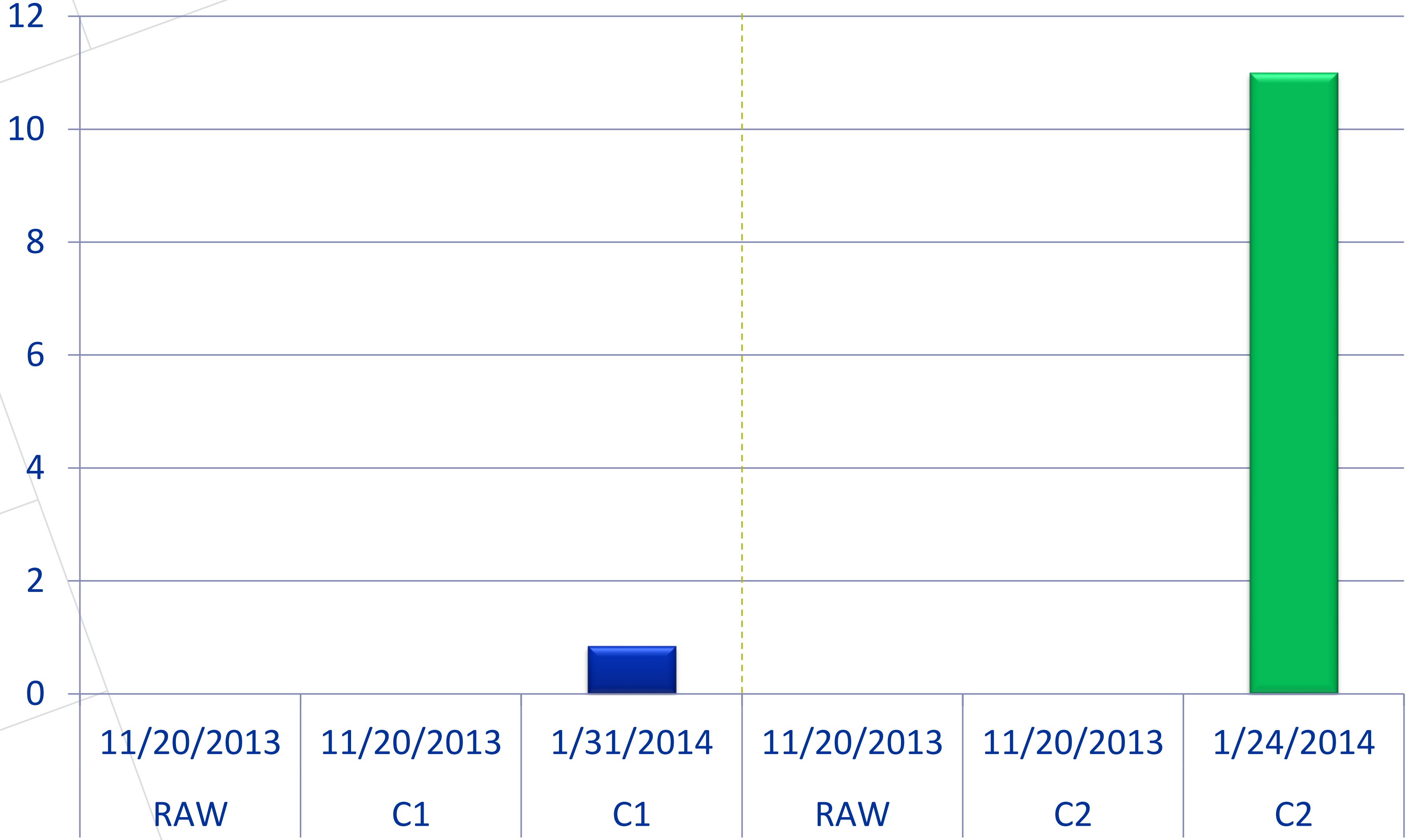
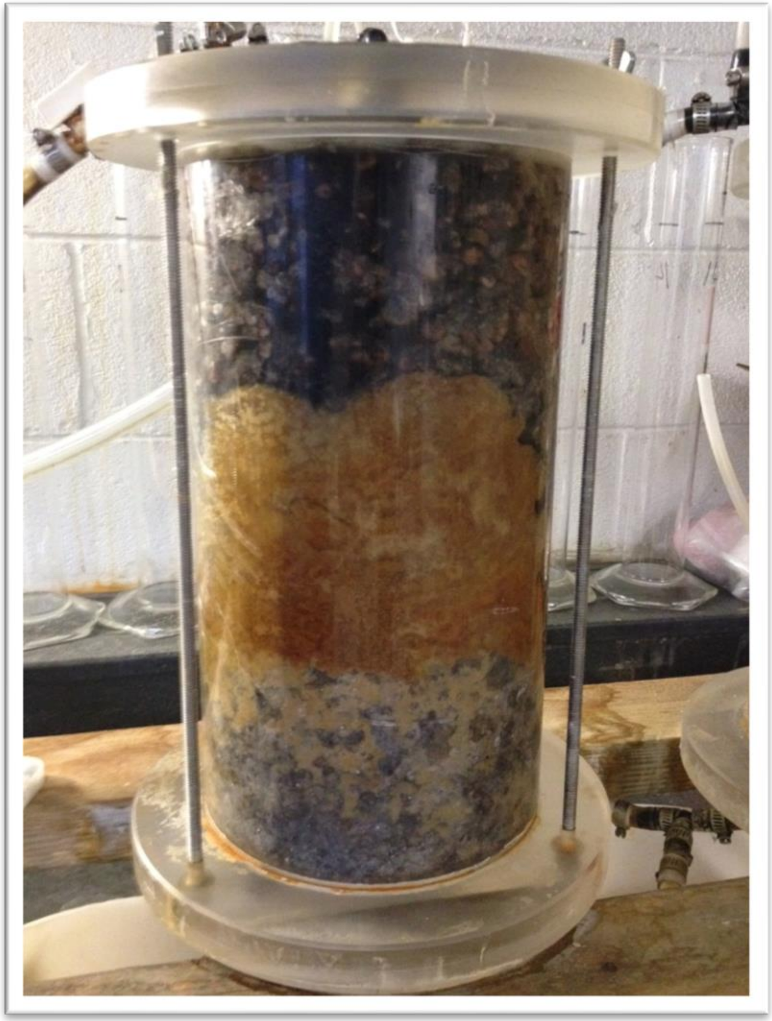
Sulfide (mg/L)



12
10
8
6
4
2
0
11/20/2013 RAW
11/20/2013 C1
1/31/2014 C1
11/20/2013 RAW
11/20/2013 C2
1/24/2014 C2

Conclusions

- Column 1 (ChitoRem®-treated)
  - Treated over 4 pore volumes of MIW
  - pH buffered to approximately 6 or higher; ORP negative
  - Considerable metal removal
  - Sulfide produced



Conclusions

- Column 2 (contained waste rock; received treated water)
  – Prior to treatment, metals and sulfate increased, pH decreased due to waste rock
  – Just over *one* pore volume replaced
  – pH buffered to approximately 5; ORP declined 300 mV
  – Substantial reduction in metals despite lack of direct treatment (Al, As, Cd, Cu, Fe, Zn)

Conclusions

- Emplacement of ChitoRem® is effective at buffering acidity; reducing metals
  - Emplaced in mine workings to intercept flow
  - Used in reactive barrier
  - Treat and reinject extracted groundwater
- Transfer of treated water buffered acidity and reduced metals in non-treated column
  - Suggests that passivation of waste rock may have occurred
  - Downgradient MIW has the potential to be treated as secondary effect of source zone treatment

Lessons Learned

- Use high-quality valves to prevent leaks
- Need vent hoses / pressure relief for gas generation
- Minimize tubing length connecting columns
- Use narrow columns to minimize short-circuiting
- *In situ* parameter measurement could potentially minimize stress associated with sample collection

Questions?