Bench-Scale Treatability Testing for *In Situ* Bioremediation of Mining-Influenced Water

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MIW Treatment Overview

- Treatment often completed using active methods (treatment plants) or passive/semi-passive methods (biochemical reactors [BCRs], wetlands, limestone drains)

- Treatment is completed where drainage exits the mine, including: adits, seeps, or pumped

  - Requires multiple points for treatment, or complex piping/transport of the MIW

Optimization Goals

- Reduce the number of locations where treatment is required
- Reduce capital cost
- Reduce operation and maintenance cost
- Passive or semi-passive technologies reduce cost, but do not solve the issue of conveyance of MIW from multiple locations

BCR Overview

- Significant advances have been made in optimization and performance of BCRs
- Utilize sulfate-reduction process to produce sulfide, generate alkalinity, and remove metals through adsorption and geochemical reactions (e.g., metal sulfide precipitation)

Advantages	Disadvantages
Passive or semi-passive Lower capital cost	Plugging Longevity Do not always remove COCs to below remediation goal Long retention times often necessary (low flow/volume)

In Situ Application Overview

- *In situ* treatment involves generation of sulfate-reducing conditions within the abandoned mine – simulates a BCR
  - Includes application to mine voids (bulk treatment), shafts, fractures (PRB-type application)
  - Utilizes pH adjustment and organic amendment addition
  - Utilizes the same geochemical principles of BCRs
  - Treats the MIW at the source, rather than the outlet

In Situ Application – Potential Challenges

- Requires detail of hydrogeology and hydraulic control
- Consists of permanently submerged areas, temporarily submerged areas, and vadose zone
- Amendment delivery methods

In Situ Application – Potential Benefits

- Opportunity to treat the MIW at the source
- Potential plugging could prevent continued fracture flow/ oxidation of acid-generating materials
- Create preferential pathways to minimize oxidation of vadose zone material

Bench-Scale Testing Design

- Utilized batch reactors to simulate MIW present within a mine void
  - Cubitainers containing:
    - MIW
    - Site sediments (simulate conditions in the mine, as well as provide native bacterial population)
    - Inert material (sand)
      - Roughly 2/3 of each container was freeboard MIW to simulate open voids
  - pH adjustment (NaOH addition to 4.5 su)
  - Added carbon amendment
  - Added manure to stimulate bacterial activity

Bench-Scale Testing Carbon Sources

- Selected carbon sources that could be easily injected (either liquids, or solids that could be slurried)
  - Ethanol (two doses – 50 mL and 150 mL)
  - Antifreeze (ethylene glycol; two doses – 50 mL and 150 mL)
  - Beer (50 mL)
  - ChitoRem® (no pH adjustment completed with NaOH)
  - Methanol (50 mL)

Water Types/Sites

- Three MIW types
  - MIW-1: strongly acidic (starting pH 2.51), high metals (450 mg/L Al, 250 ug/L Cd, 54 mg/L Cu, 6.2 mg/L Zn), high sulfate (14,000 mg/L)
  - MIW-2: near-neutral (starting pH 5.05), low metals, except Zn (36 mg/L), low sulfate (230 mg/L)
  - MIW-3: strongly acidic (starting pH 2.76), high metals (370 mg/L Al, 190 ug/L Cd, 62 mg/L Cu, 30 mg/L Zn), high sulfate (9,400 mg/L)
- Sediments from nearby ponds/streams were collected for addition to tests to simulate potential conditions within the mine void
- All water was collected in cubitainers with minimal headspace to attempt to preserve geochemical conditions

Test Startup

- Titrations with 25% NaOH solution completed for raw MIW to determine approximate dosing requirements to reach pH 4.5 (not necessary for MIW-2)
- MIW, site sediments, and inert materials added to cubitainers
- Added carbon amendment to each container
- Added NaOH to each container for pH adjustment (not completed for MIW-2)
- Compressed containers to minimize oxygen presence
- 21 tests total (3 MIW types x 7 carbon amendments)
- Test length: 3 months

Test Evaluation

- Metal removal efficiency (MRE)
- Sulfide production
- Sulfate reduction
- ORP decrease
- pH increase
- Alkalinity increase

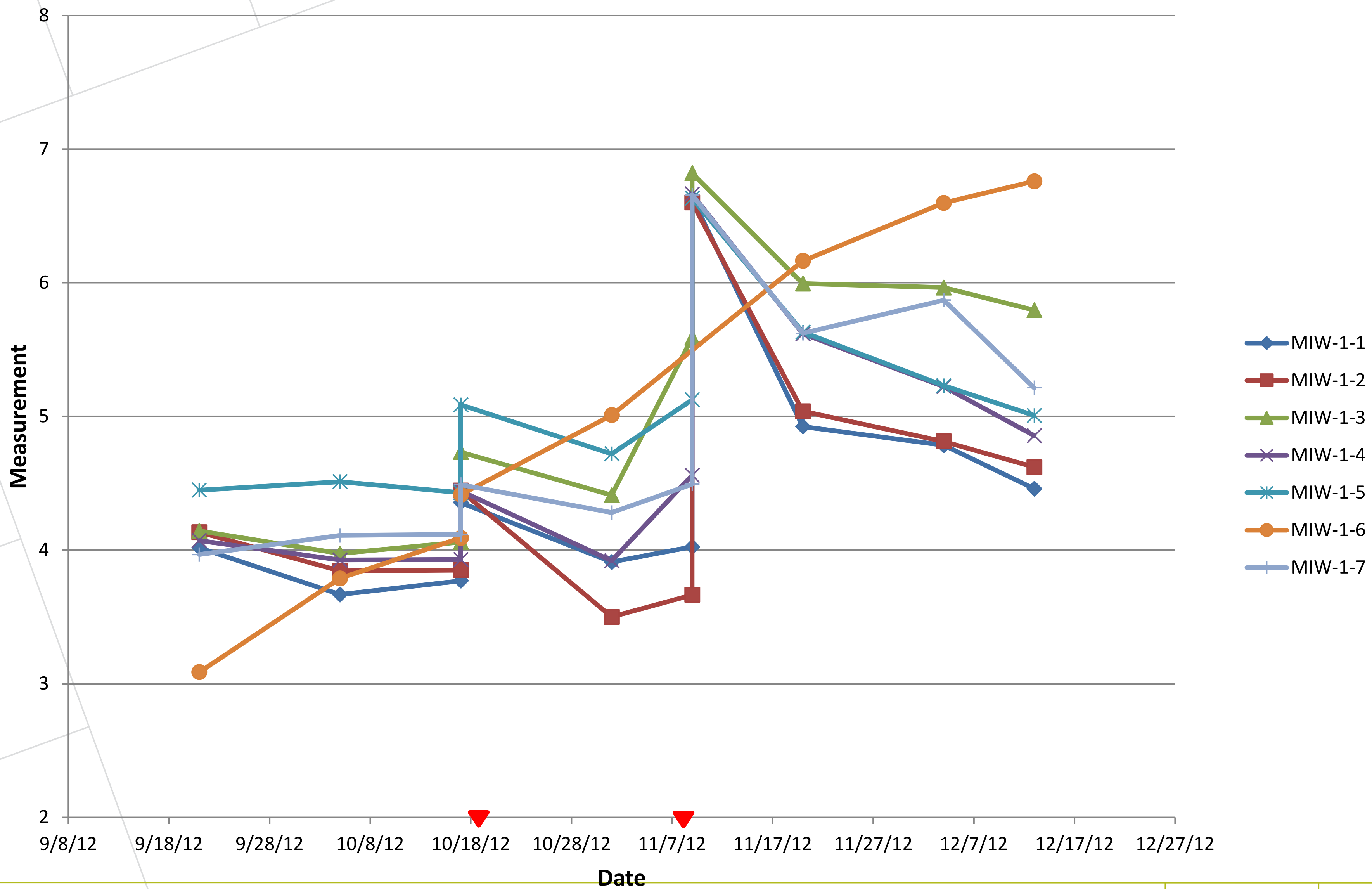
Test Operation

- Real-time parameter measurement during testing included:
  - pH
  - ORP
  - Conductivity
  - DO
  - Ferrous iron
  - Sulfide
  - Sulfate
  - Alkalinity

- Completed biweekly testing
- Added NaOH, amendments, and manure as necessary to increase sulfide production
- Sampling activities may have introduced oxygen stress

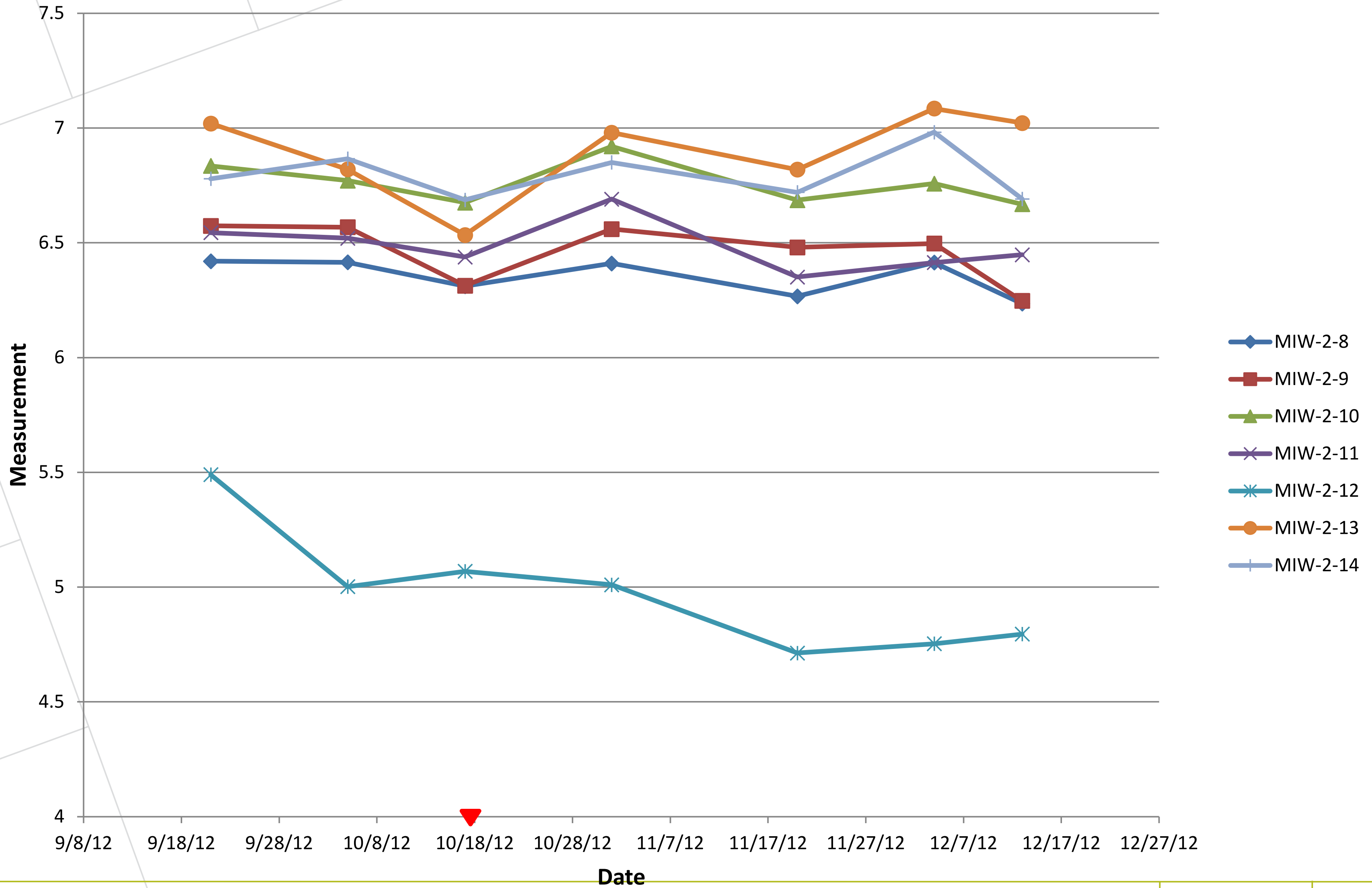
Sample ID	**Amendment**	**9/7/2012**		**10/1/2012**	**10/17/2012**			**11/9/2012**			**Cumulative**		
		NaOH (mL)	Organic	Organic	NaOH (mL)	Organic	Manure (mL)	NaOH (mL)	Organic	Manure (mL)	NaOH (mL)	Organic	Manure (mL)
MIW-1													
MIW-1-1	Ethanol (mL)	16.20	150		1	50	50	7	150	50	**24.20**	**350**	**100**
MIW-1-2	Ethanol (mL)	16.80	50		1	16.67	50	8.5	50	50	**26.30**	**116.67**	**100**
MIW-1-3	Ethylene glycol (mL)	16.75	150		1	50	50	3	150	50	**20.75**	**350**	**100**
MIW-1-4	Ethylene glycol (mL)	16.70	50		1	16.67	50	6	50	50	**23.70**	**116.67**	**100**
MIW-1-5	Beer (mL)	16.30	50		1	16.67	50	3	50	50	**20.30**	**116.67**	**100**
MIW-1-6	ChitoRem (g)		6.25	12.5		6.25			6.25		**0.00**	**31.25**	**0**
MIW-1-7	Methanol (mL)	15.00	50		1	16.67	50	7	50	50	**23.00**	**116.67**	**100**
MIW-2													
MIW-2-8	Ethanol (mL)		150			50	50				**0.00**	**200**	**50**
MIW-2-9	Ethanol (mL)		50			16.67	50				**0.00**	**66.67**	**50**
MIW-2-10	Ethylene glycol (mL)		150			50	50				**0.00**	**200**	**50**
MIW-2-11	Ethylene glycol (mL)		50			16.67	50				**0.00**	**66.67**	**50**
MIW-2-12	Beer (mL)		50			16.67	50				**0.00**	**66.67**	**50**
MIW-2-13	ChitoRem (g)		6.25	6.25							**0.00**	**12.5**	**0**
MIW-2-14	Methanol (mL)		50			16.67	50				**0.00**	**66.67**	**50**
MIW-3													
MIW-3-15	Ethanol (mL)	14.50	150		1	50	50	7	150	50	**22.50**	**350**	**100**
MIW-3-16	Ethanol (mL)	23.00	50		1	16.67	50	5	50	50	**29.00**	**116.67**	**100**
MIW-3-17	Ethylene glycol (mL)	16.15	150		1	50	50	2	150	50	**19.15**	**350**	**100**
MIW-3-18	Ethylene glycol (mL)	15.85	50		1	16.67	50	4	50	50	**20.85**	**116.67**	**100**
MIW-3-19	Beer (mL)	14.90	50		1	16.67	50	3	50	50	**18.90**	**116.67**	**100**
MIW-3-20	ChitoRem (g)		6.25	12.5		6.25			6.25		**0.00**	**31.25**	**0**
MIW-3-21	Methanol (mL)	15.70	50		1	16.67	50	5	50	50	**21.70**	**116.67**	**100**

MIW-1 pH



8
7
6
5
4
3
2
Measurement
9/8/12
9/18/12
9/28/12
10/8/12
10/18/12
10/28/12
11/7/12
11/17/12
11/27/12
12/7/12
12/17/12
12/27/12
Date
MIW-1-1
MIW-1-2
MIW-1-3
MIW-1-4
MIW-1-5
MIW-1-6
MIW-1-7

MIW-2 pH



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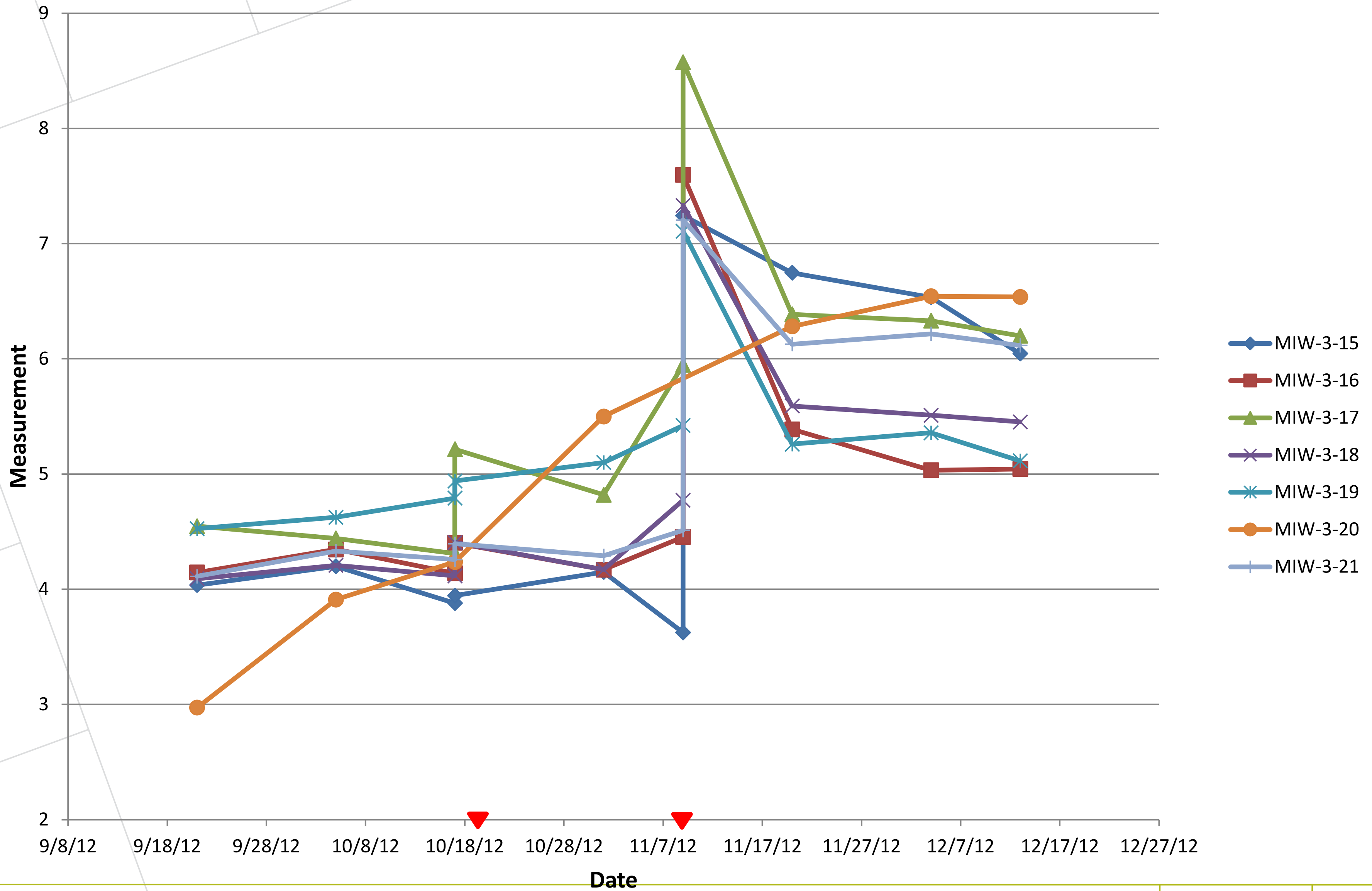
MIW-3 pH



Measurement
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8
7
6
5
4
3
2
9/8/12
9/18/12
9/28/12
10/8/12
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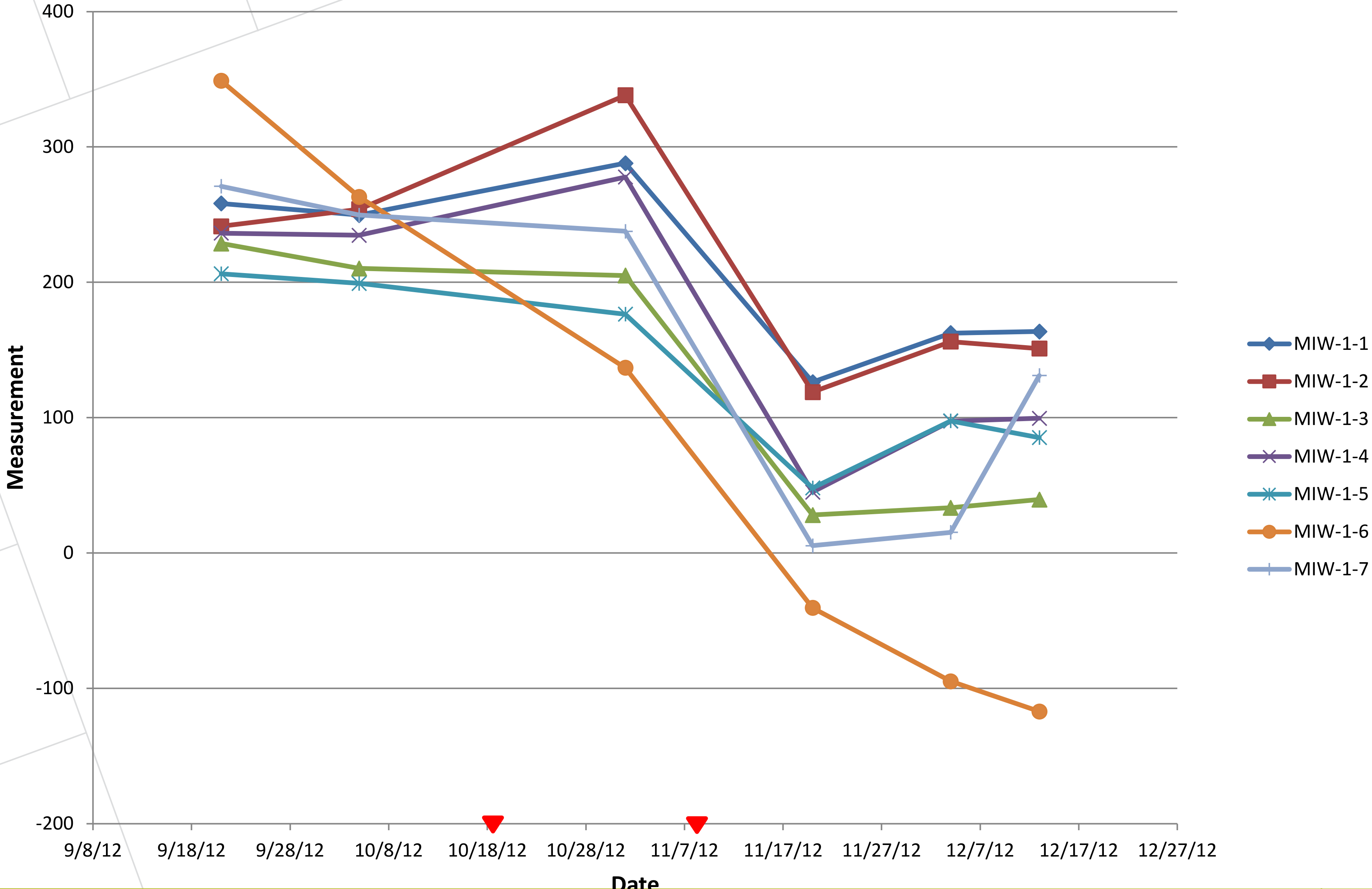
10/28/12
11/7/12
11/17/12
11/27/12
12/7/12
12/17/12
12/27/12
Date
MIW-3-15
MIW-3-16
MIW-3-17
MIW-3-18
MIW-3-19
MIW-3-20
MIW-3-21

MIW-1 ORP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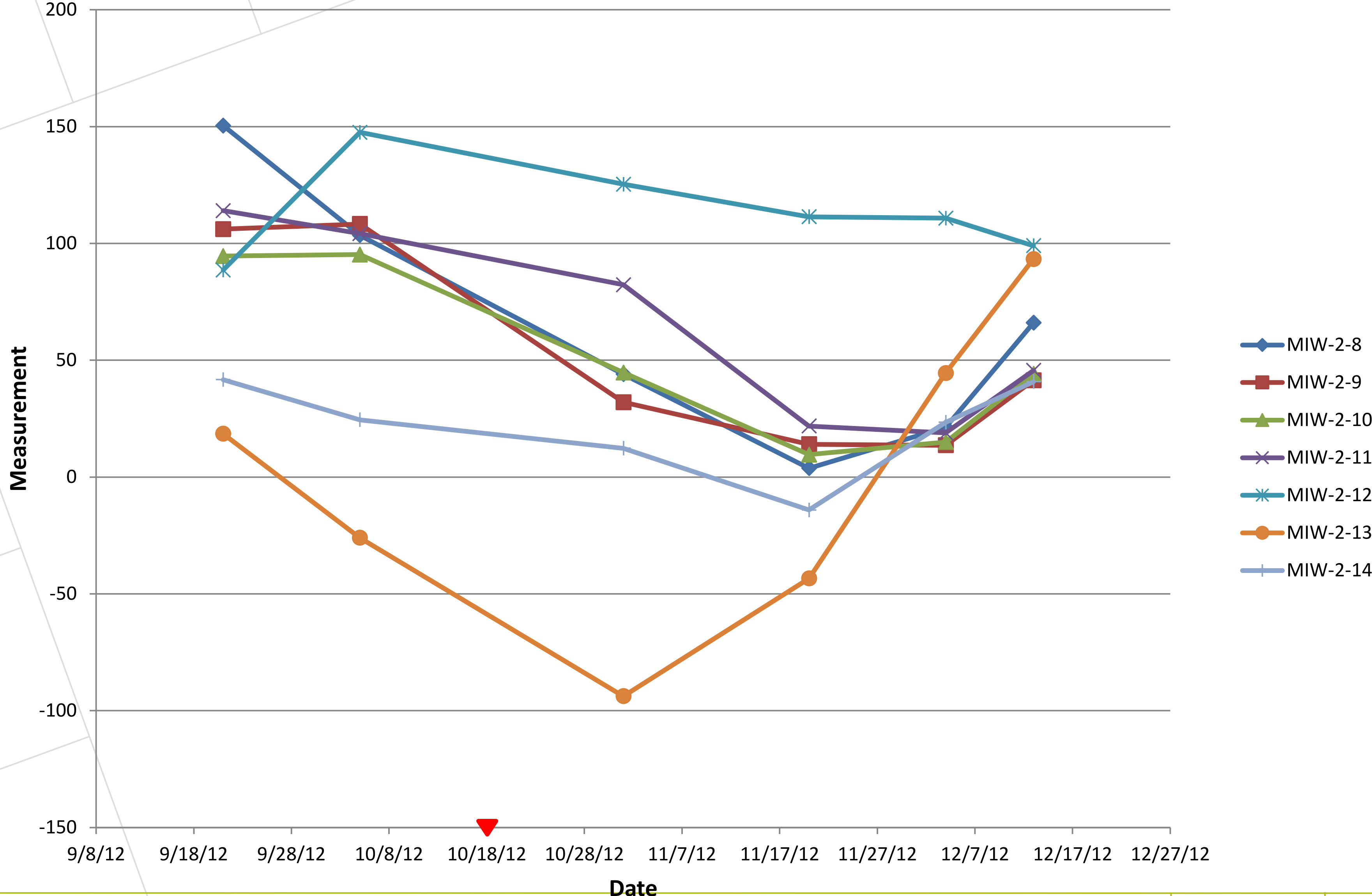
300
200
100
0
-100
-200
Measurement
9/8/12
9/18/12
9/28/12
10/8/12
10/18/12
10/28/12
11/7/12
11/17/12
11/27/12
12/7/12
12/17/12
12/27/12
Date
MIW-1-1
MIW-1-2
MIW-1-3
MIW-1-4
MIW-1-5
MIW-1-6
MIW-1-7

MIW-2 ORP



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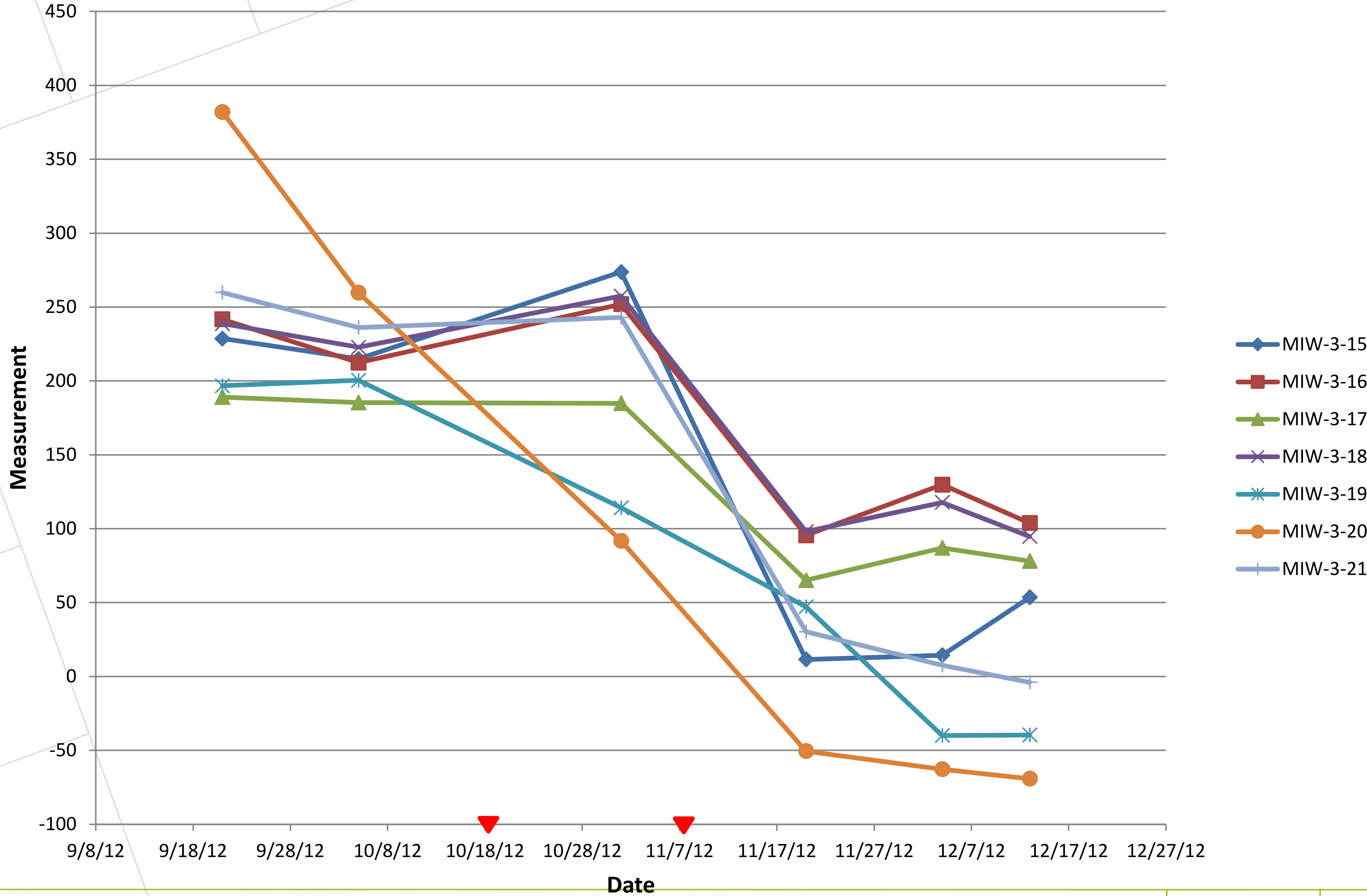
MIW-3 ORP



Measurement
450
400
350
300
250
200
150
100
50
0
-50
-100
9/8/12
9/18/12
9/28/12
10/8/12
10/18/12
10/28/12
11/7/12
11/17/12
11/27/12
12/7/12
12/17/12
12/27/12
Date
MIW-3-15
MIW-3-16
MIW-3-17
MIW-3-18
MIW-3-19
MIW-3-20
MIW-3-21

Sample ID	Donor	Aluminum % Reduction	Arsenic % Reduction	Cadmium % Reduction	Chromium % Reduction	Copper % Reduction	Iron % Reduction	Lead % Reduction	Nickel % Reduction	Zinc % Reduction
MIW-1										
MIW-1-1	Ethanol, 150mL	98%	99%	25%	100%	90%	89%	95%	31%	3%
MIW-1-2	Ethanol, 50 mL	98%	99%	21%	100%	96%	86%	100%	30%	-2%
MIW-1-3	Ethylene glycol, 150 mL	100%	99%	49%	99%	100%	83%	100%	77%	71%
MIW-1-4	Ethylene glycol, 50 mL	98%	99%	21%	99%	98%	82%	100%	14%	-7%
MIW-1-5	Beer, 50 mL	97%	98%	1%	99%	99%	31%	98%	28%	44%
MIW-1-5 (DUP-1)	Beer, 50 mL	97%	98%	9%	99%	99%	50%	98%	30%	24%
MIW-1-6	ChitoRem	100%	93%	100%	100%	100%	92%	100%	98%	100%
MIW-1-7	Methanol, 50 mL	98%	99%	-7%	100%	94%	85%	100%	24%	-13%
MIW-2										
MIW-2-8	Ethanol, 150mL	100%	NA	87%	NA	31%	100%	98%	74%	94%
MIW-2-9	Ethanol, 50 mL	100%	NA	100%	NA	75%	-14374%	99%	87%	100%
MIW-2-10	Ethylene glycol, 150 mL	100%	NA	77%	NA	46%	100%	79%	82%	84%
MIW-2-11	Ethylene glycol, 50 mL	100%	NA	57%	NA	64%	-295%	92%	19%	79%
MIW-2-12	Beer, 50 mL	-1107%	NA	100%	NA	46%	-197268%	87%	-573%	6%
MIW-2-13	ChitoRem	100%	NA	100%	NA	18%	-479%	99%	-223%	100%
MIW-2-14	Methanol, 50 mL	100%	NA	100%	NA	54%	-584%	93%	12%	92%
MIW-3										
MIW-3-15	Ethanol, 150mL	100%	97%	60%	100%	99%	99%	100%	57%	80%
MIW-3-16	Ethanol, 50 mL	100%	97%	61%	100%	99%	90%	100%	33%	88%
MIW-3-16 (DUP-2)	Ethanol, 50 mL	100%	97%	58%	100%	99%	91%	100%	23%	86%
MIW-3-17	Ethylene glycol, 150 mL	100%	100%	84%	69%	100%	100%	81%	95%	96%
MIW-3-18	Ethylene glycol, 50 mL	100%	93%	62%	87%	99%	99%	94%	6%	82%
MIW-3-19	Beer, 50 mL	100%	84%	100%	92%	100%	47%	100%	84%	100%
MIW-3-20	ChitoRem	100%	-86%	100%	100%	100%	93%	100%	80%	100%
MIW-3-21	Methanol, 50 mL	100%	98%	59%	100%	100%	91%	100%	39%	87%

Test Results, MIW-1

- Best metal removal by ChitoRem®
- Most tests did accomplish high removal of Al, As, Cr, Cu, Se
- Ethylene glycol appeared to provide the next best removal after ChitoRem®
- Best sulfate reduction in ChitoRem®, and only test with sulfide production
- Ethylene glycol produced promising results, with trends suggesting stronger reducing conditions developing by end of test

Test Results, MIW-2

- Primary metals of concern included Zn and Cd; best removal achieved by ChitoRem® and ethanol (50 mL dose)
- These tests also generated elevated sulfide
- Higher ethanol dose did not perform as well, possibly due to competing bacterial use of the donor

Test Results, MIW-3

- High metal removal achieved by ethanol, ethylene glycol, beer, and ChitoRem®
- ChitoRem® and beer generated the most sulfide, with production also by the ethanol 50 mL dose
- pH adjustment for MIW-3 may have resulted in generally favorable metal removal and sulfide production
  - Blue-green precipitate noticed following final pH adjustment

Conclusions

- ChitoRem® performed consistently well
  - No pH adjustment
  - No manure addition
- Low-dose ethanol also performed well for MIW 2 and 3
- Ethylene glycol performed well for MIW 1 and 3
- Testing indicates that MIW treatment can be accomplished through use of liquid substrates within the water column (saturated solid media not necessary)

Conclusions

- Oxygen stress may have hindered progress, based on observed DO, ORP values
  - May have influenced pH, and prevented sulfate reduction in some treatment tests
- Addition of site sediments provides native bacteria and site-specific conditions
  - Addition of site sediments increased total metals and acidity in the tests
    - Resulted in addition of more NaOH than anticipated based on titration testing

Future Work

- Completing additional bench testing activities using column studies

  – Reaction rates
  – Dosing requirements
  – Utilize columns packed with site waste rock to simulate *in situ* environment
  – Operate control column to determine the effect site waste rock has on the overall pH, acidity, and metal loading to the system

Questions