IEUA Sulfide Formation Sampling Campaign

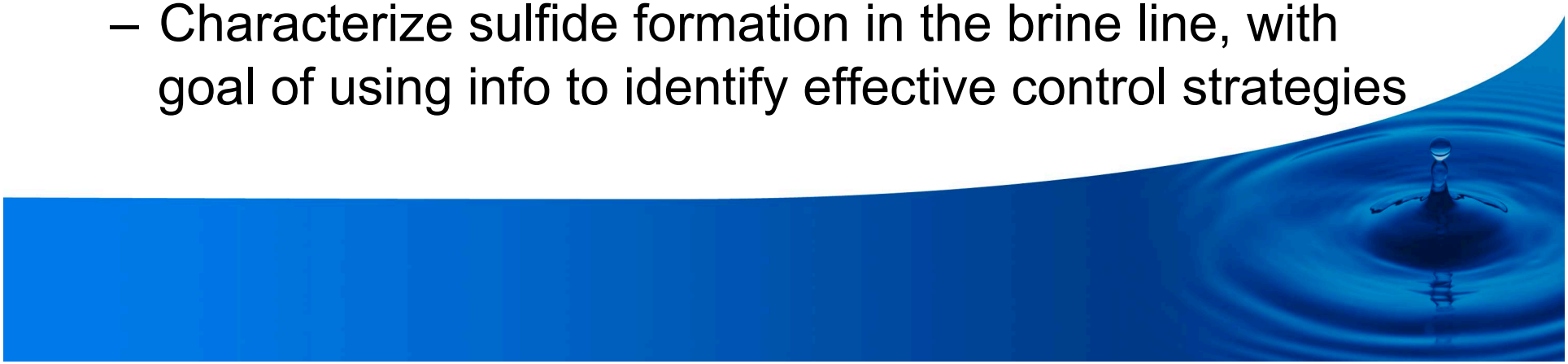
Brian Pecson

October 2012

Project overview

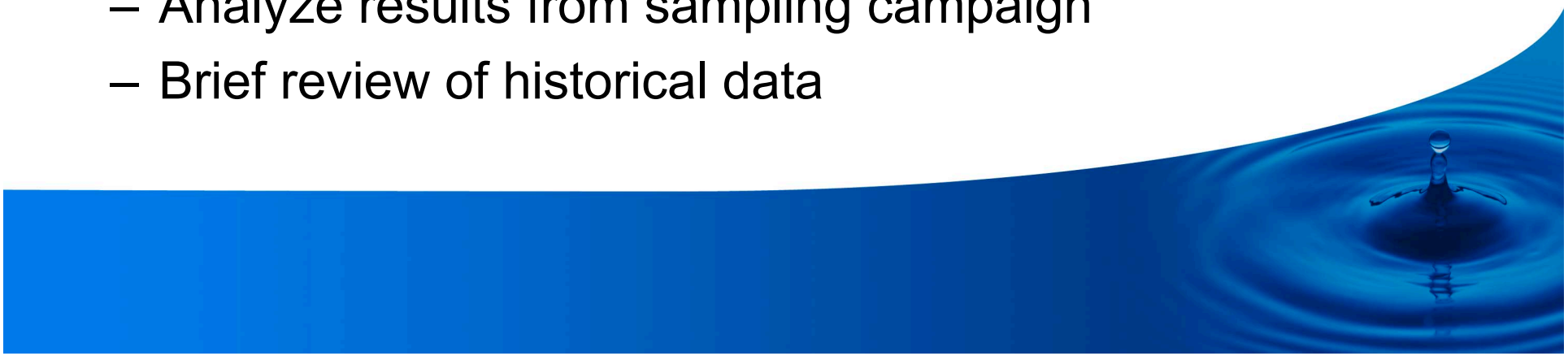
- **Problem statement**
  - Sulfide generated within Reach IVA of the brine line exceeding acceptable levels
    - Total sulfide (TS) limit: 5.0 mg/l
    - Dissolved sulfide (DS) limit: 0.5 mg/l
  - Issues: sulfide hazardous for workers, malodorous

- **Project objectives**
  - Characterize sulfide formation in the brine line, with goal of using info to identify effective control strategies



Project Scope

- **Task 1**
  - Develop a sampling campaign to characterize sulfide formation in brine line
- **Task 2**
  - Discuss water quality issues and operational constraints with dischargers
- **Task 3**
  - Analyze results from sampling campaign
  - Brief review of historical data



History of IEUA sulfide issues

2010

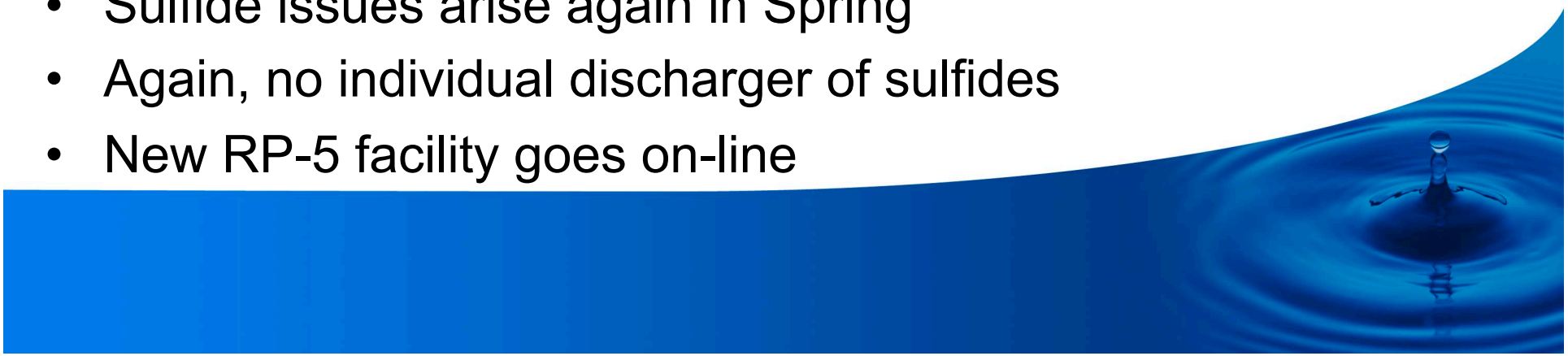
- Sulfide problems arise, though no direct discharger of sulfides
- Physical cleaning of the line resolves issue

2011

- Relined section with cured-in place piping (Oct to Mar 2012)

2012

- Sulfide issues arise again in Spring
- Again, no individual discharger of sulfides
- New RP-5 facility goes on-line



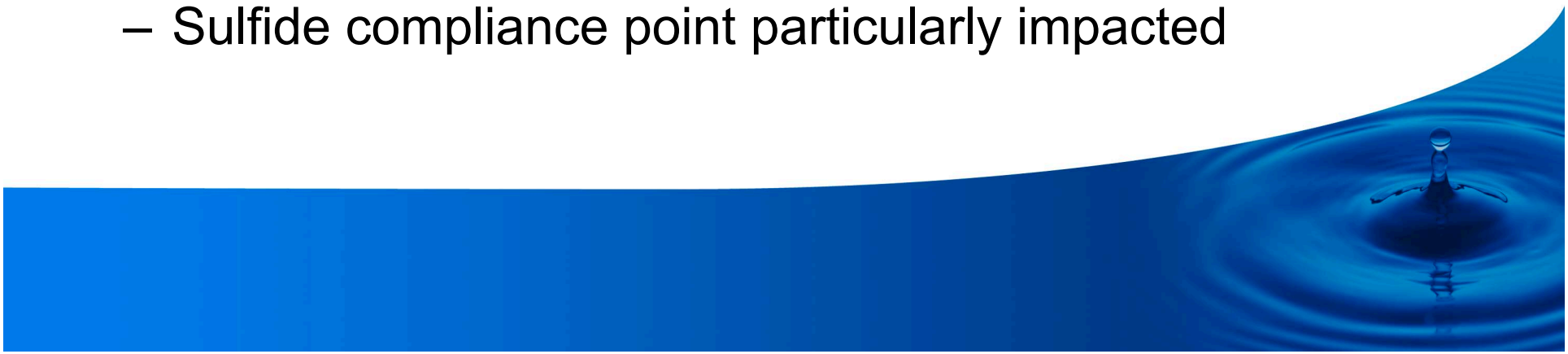
Potential causes of sulfide formations

- Biological growth
  - Requirements
    1. Sulfate-reducing bacteria (SRB)
    2. Energy source (e.g., BOD)
    3. Sulfate
    4. Absence of other electron acceptors (e.g., O_2, nitrate)
    5. Surface for attachment and development of biofilm?
  - Influence of new CIPP lining: a preferential surface for biofilm growth?
- Abiotic mechanisms: less common

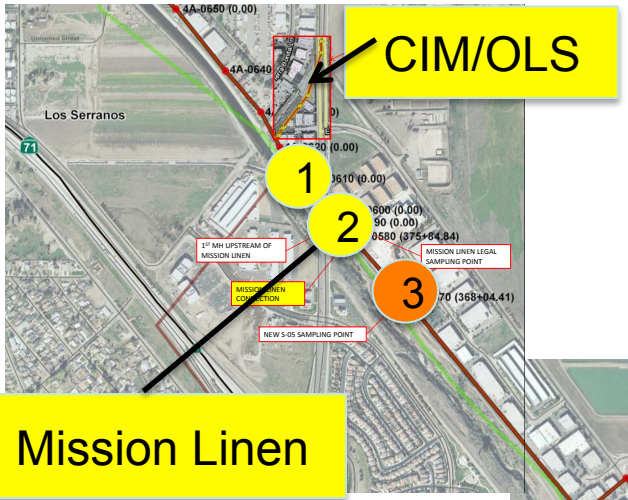
Historical data

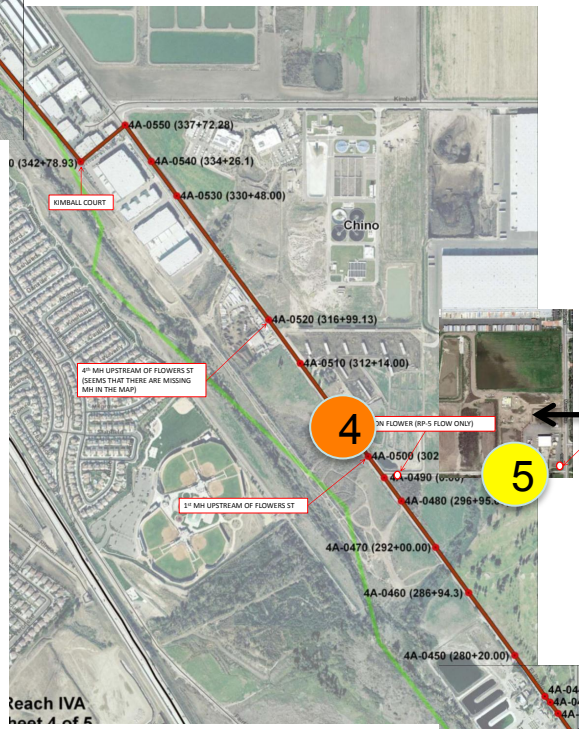
- Sulfide violations in 2012
  - TS: 39% of dates with at least one violation
  - DS: 77% of dates with at least one violation

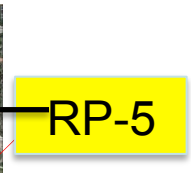
- Location of violations
  - Never at any of the 4 dischargers
  - Occurs in blended flow with increasing likelihood as flow moves downstream
  - Sulfide compliance point particularly impacted

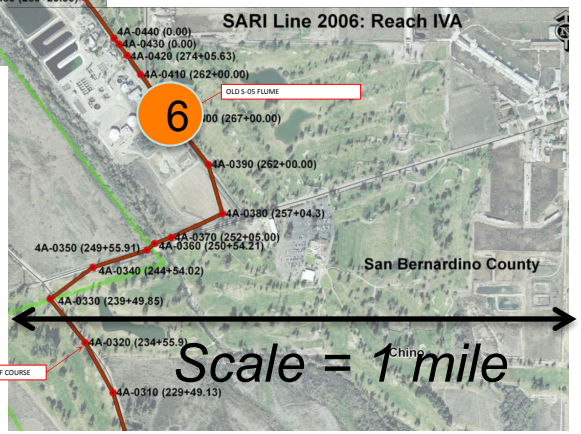


SAMPLING CAMPAIGN









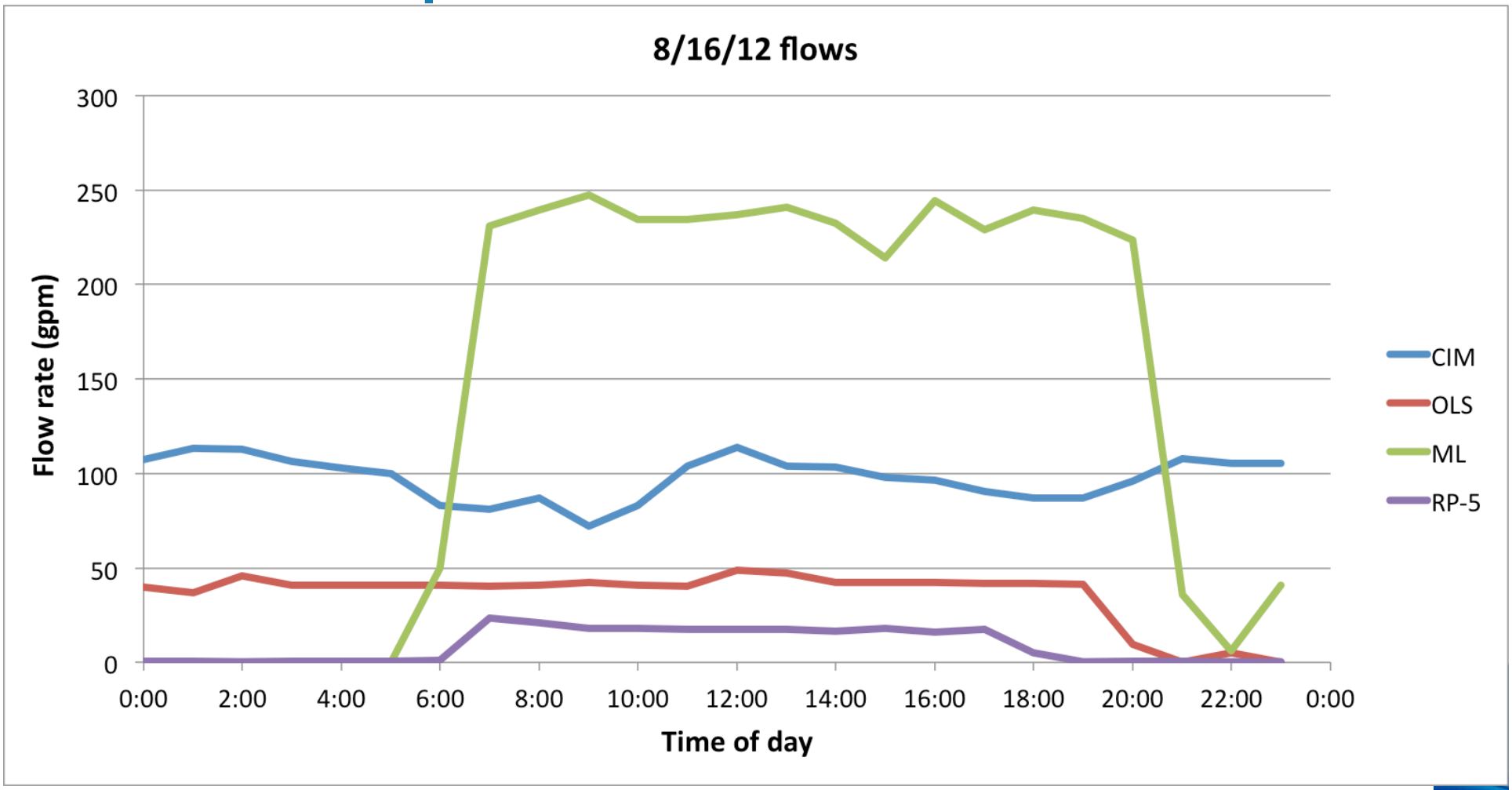
6 sampling locations

1. CIM/OLS alone
2. Mission Linen
3. Blend of 1 & 2
4. Blend of 1 &2
5. RP-5 alone
6. Blend of all dischargers

Sampling dates:

- 8/6: Monday
- 8/8: Wednesday
- 8/14: Tuesday
- 8/16: Thursday
- 8/19: Sunday

Flow patterns in Reach IVA



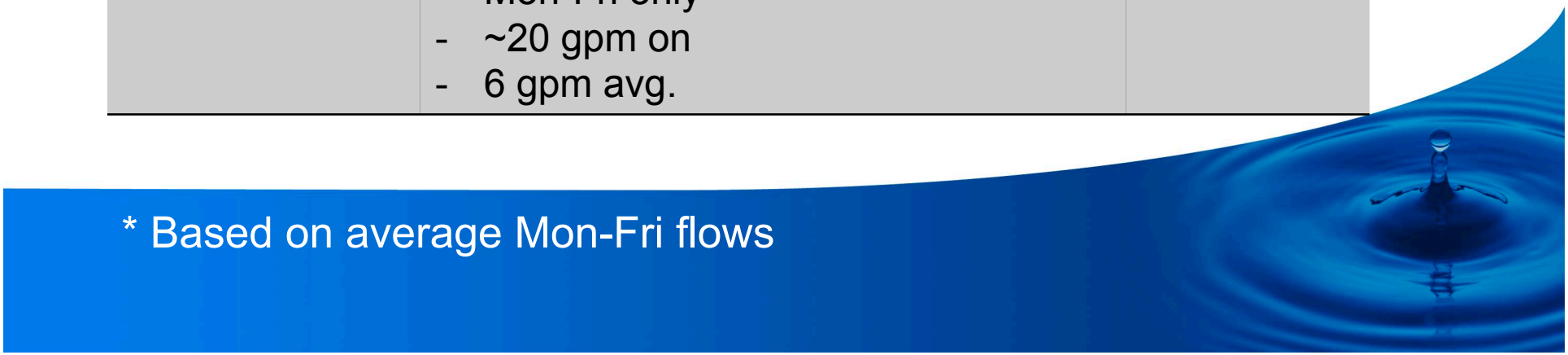
Mission Linen: major contributor during the day

CIM/OLS: ~constant flowrate 24/7

RP-5: minor contributor during the day

Flow summary

Site	Flow pattern	% of daily flow*
CIM/OLS	- Constant 24/7 - 140 gpm	49%
Mission Linen	- On/off over 24h - Mon-Fri w/ limited flows Sat-Sun - ~240 gpm on - 140 gpm avg.	49%
RP-5	- On/off over 24h - Mon-Fri only - ~20 gpm on - 6 gpm avg.	2%



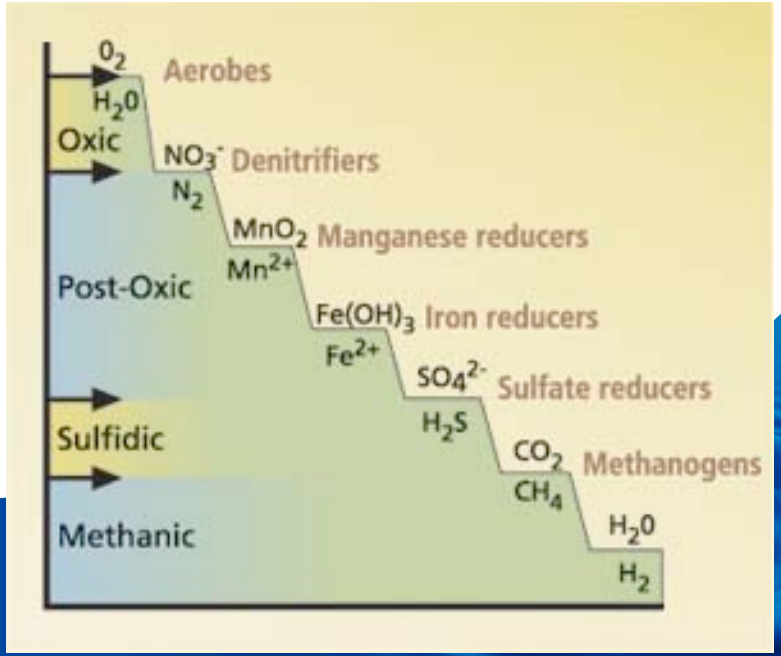
* Based on average Mon-Fri flows

Sampling campaign overview

- Measured the following parameters:
  - pH
  - Temperature
  - Dissolved oxygen (DO)
  - Sulfate
  - Alkalinity
  - Nitrate
  - BOD

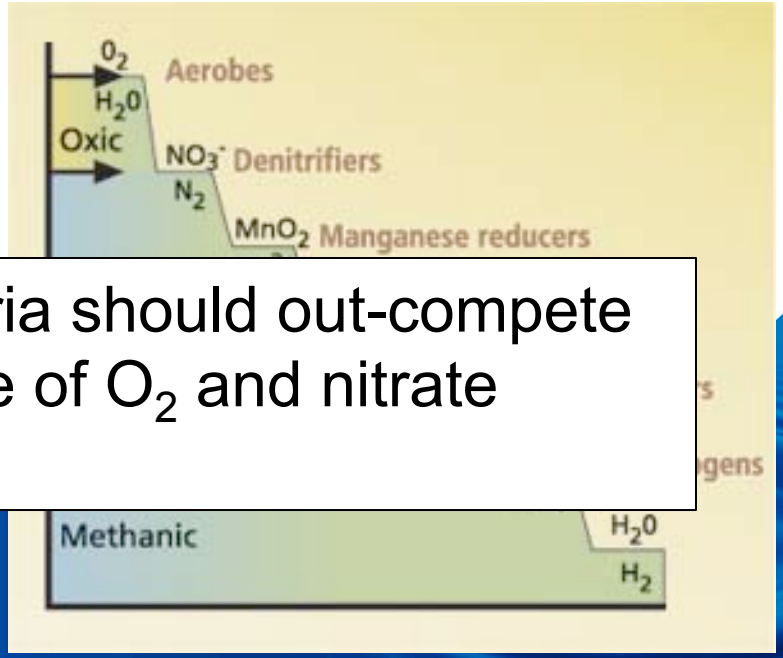
Biological growth + Energy

- Energy generated by bacteria is a good predictor of who will be present
  - More energy created → higher chance of survival
- Energy ladder (assuming BOD as food source):
  - Oxygen (aerobic) – highest
  - Nitrate (anoxic) – high
  - Sulfate (anaerobic) – low



Biological growth + Energy

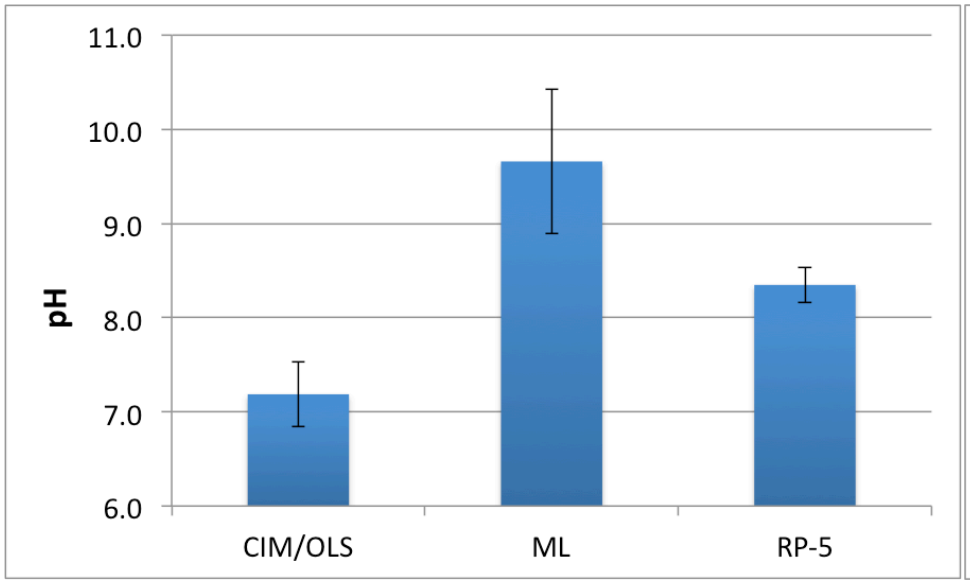
- Energy generated by bacteria is a good predictor of fitness
  - More energy created → higher chance of survival
- Energy ladder (assuming BOD as food source):
  - Oxygen (aerobic) – highest
  - Nitrate (anoxic) – high
  - Sulfate (anaerobic) – low



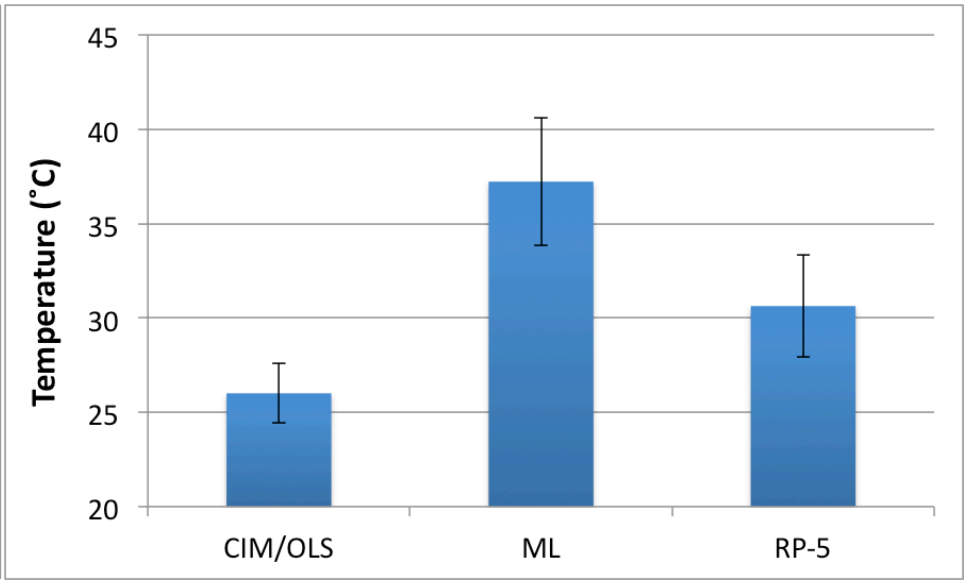
Aerobic and nitrate-reducing bacteria should out-compete → NO sulfide formation in presence of O_2 and nitrate

Water quality: pH, temp, DO

pH

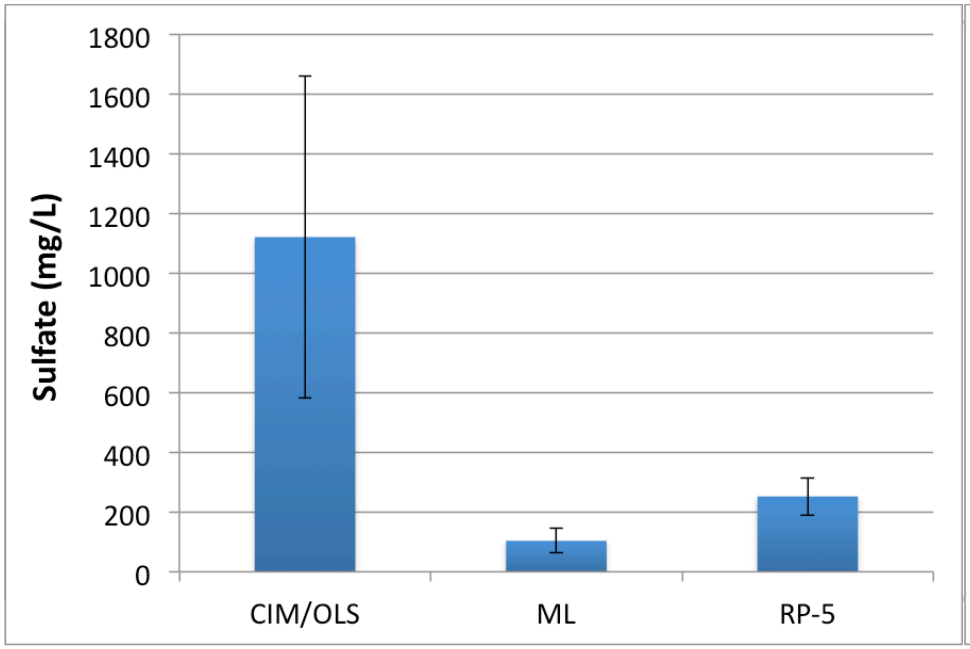


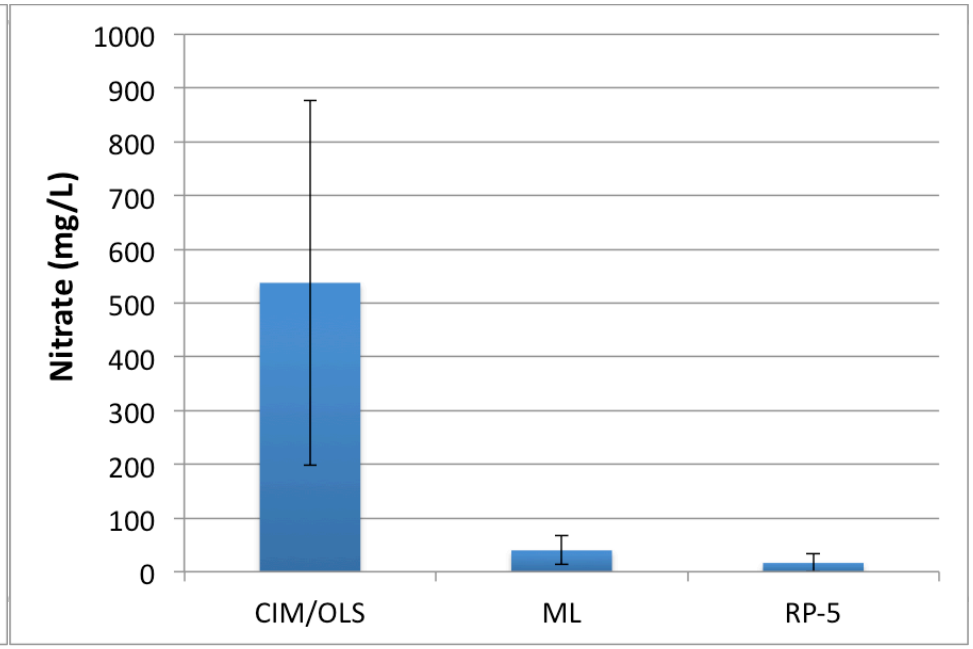
Temperature



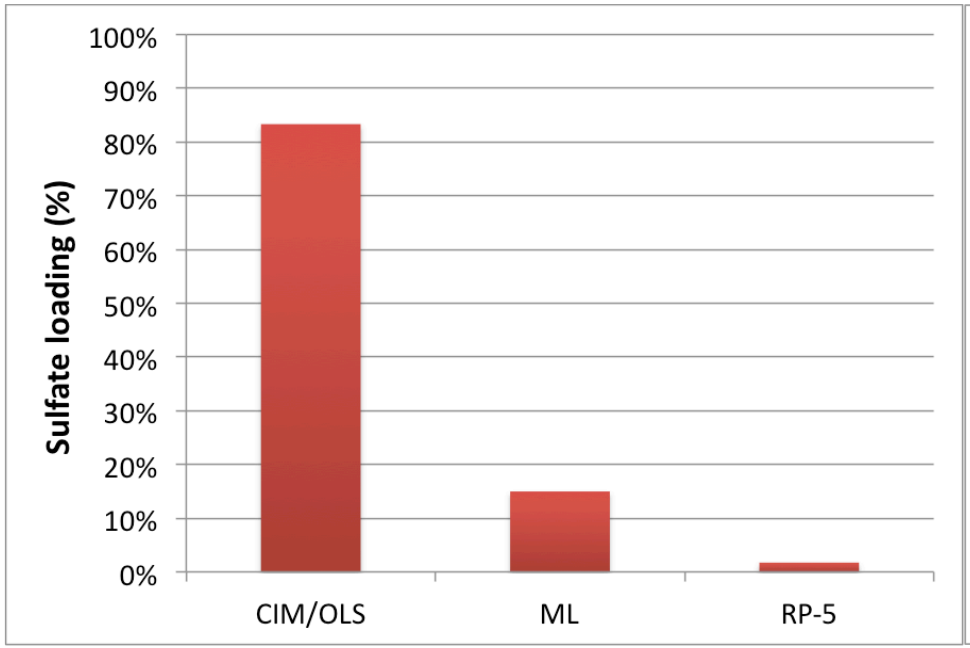
- Findings:
  - Mission significantly different (high pH, high temp)
  - DO present in all discharges at all testing periods

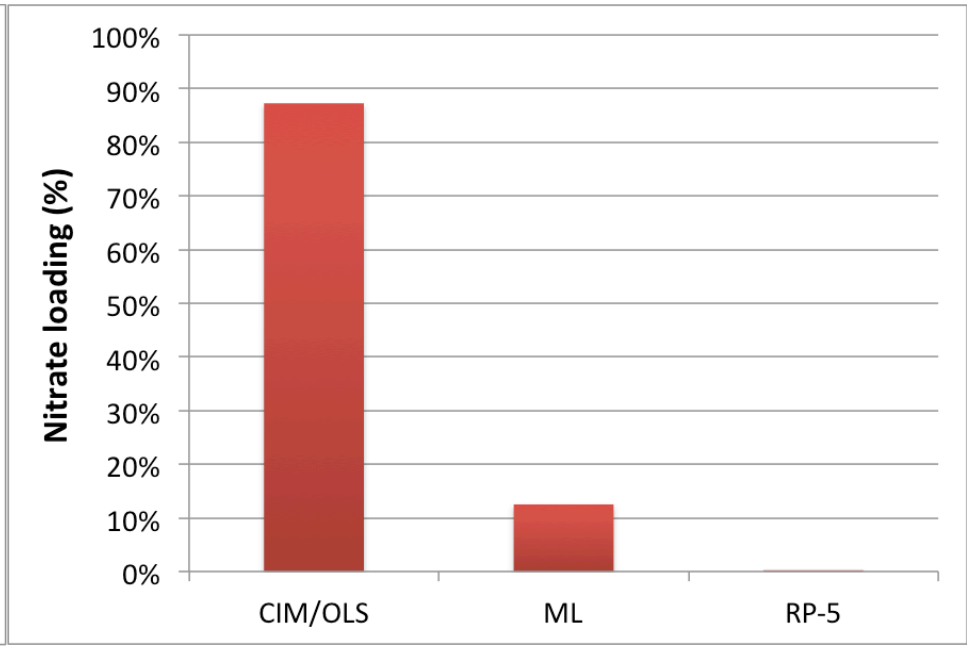
Water quality: sulfate and nitrate





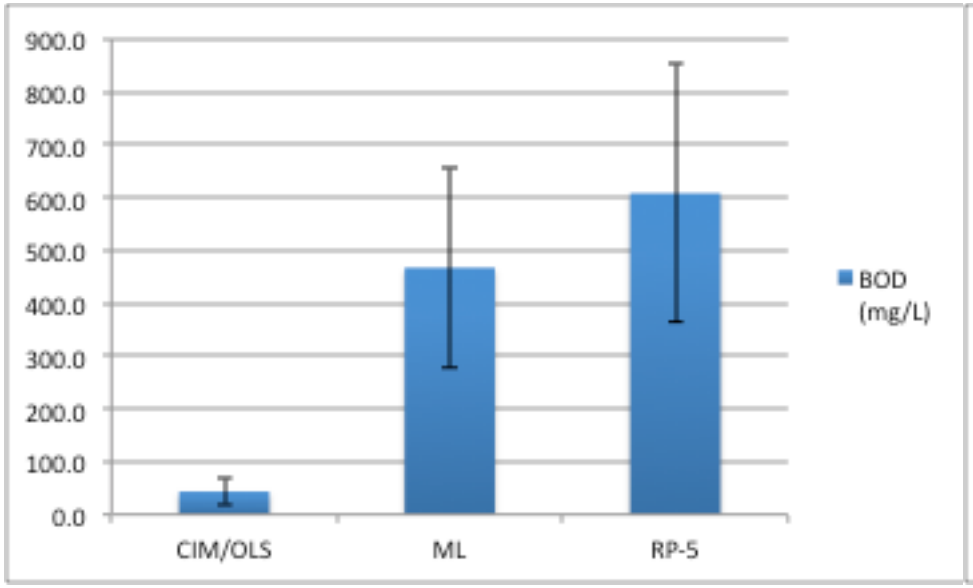
Water quality: sulfate and nitrate

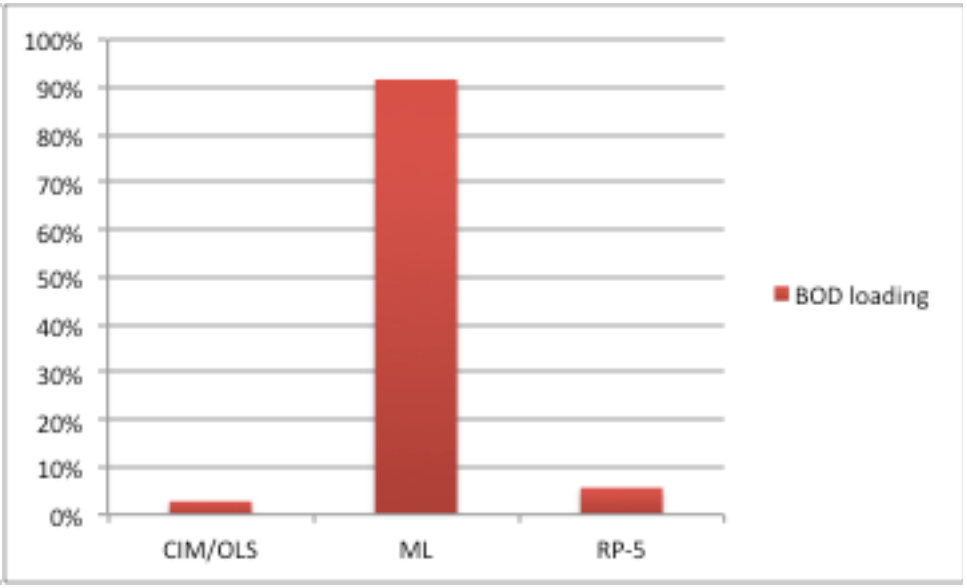




- Findings:
  - CIM/OLS dominate both sulfate and nitrate inputs (>80%)
  - Alkalinity more evenly distributed

Water quality: BOD





- Findings:
  - Mission Linen dominant source of BOD (>90%)
  - ***But***…ML only inputting around 10-12 h per day…

Water quality and flow summary

Site	Flow pattern	% of daily flow*	Average WQ	Main source of:
CIM/OLS	- Constant 24/7 - 140 gpm	49%	pH 7.2 Temp: 26C DO > 2.5 mg/l	- SO_4^{2-} - NO_3^{2-}
Mission Linen	- On/off over 24h - 7 days/wk - ~240 gpm on - 140 gpm avg.	49%	pH 8.9 Temp: 37C DO > 4.2 mg/l	- BOD
RP-5	- On/off over 24h - Mon-Fri - ~20 gpm on - 6 gpm avg.	2%	pH 8.3 Temp: 31C DO > 0.9 mg/l	

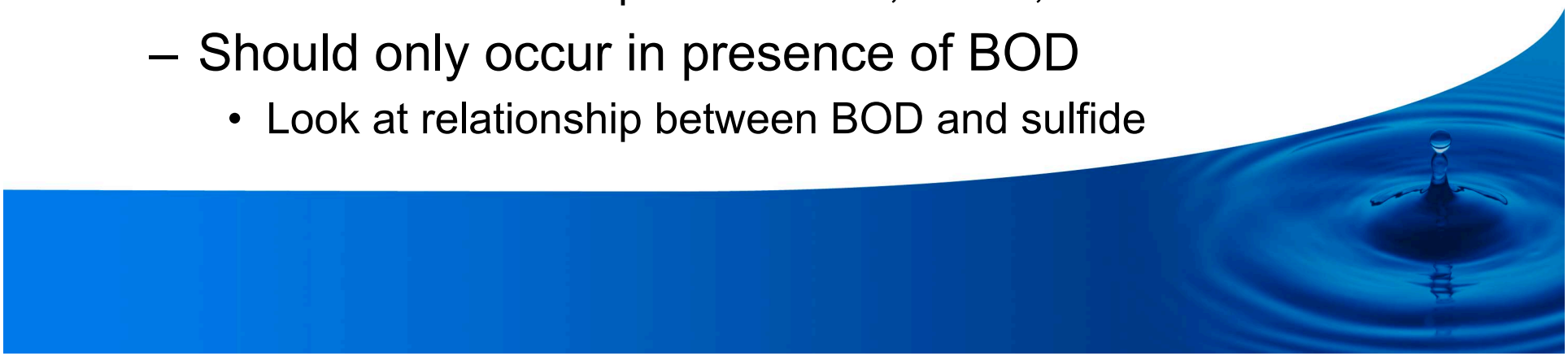
* Based on average Mon-Fri flows

SULFIDE FORMATION

Sulfide violations

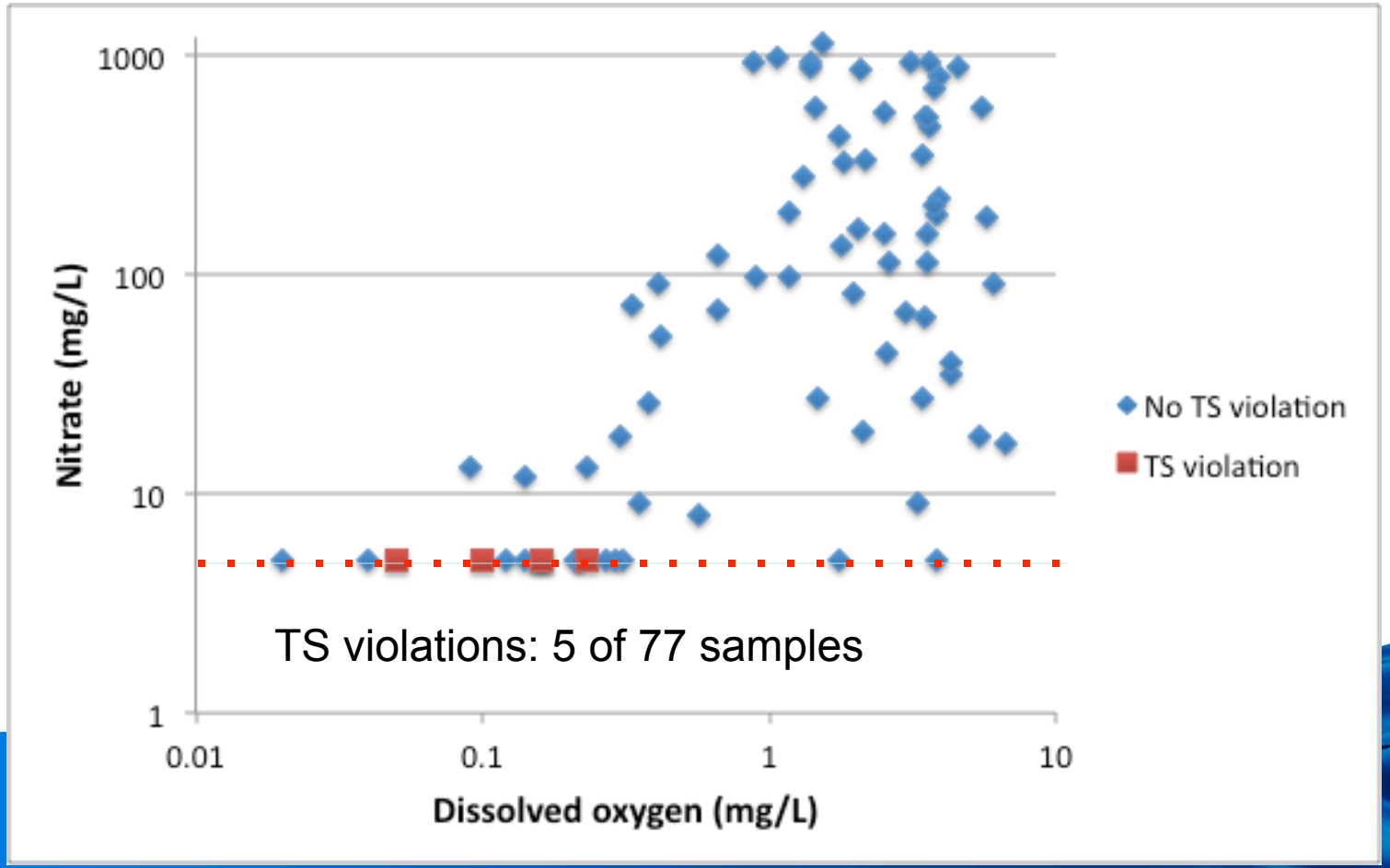
- Of the 77 samples collected during the campaign:
  - 5 TS violations
  - 10 DS violations

- Working hypothesis: SRB consume BOD with sulfate to generate sulfide
  - Significant mechanism only if O2, nitrate used up
    - Look at relationship between O2, nitrate, and sulfide
  - Should only occur in presence of BOD
    - Look at relationship between BOD and sulfide



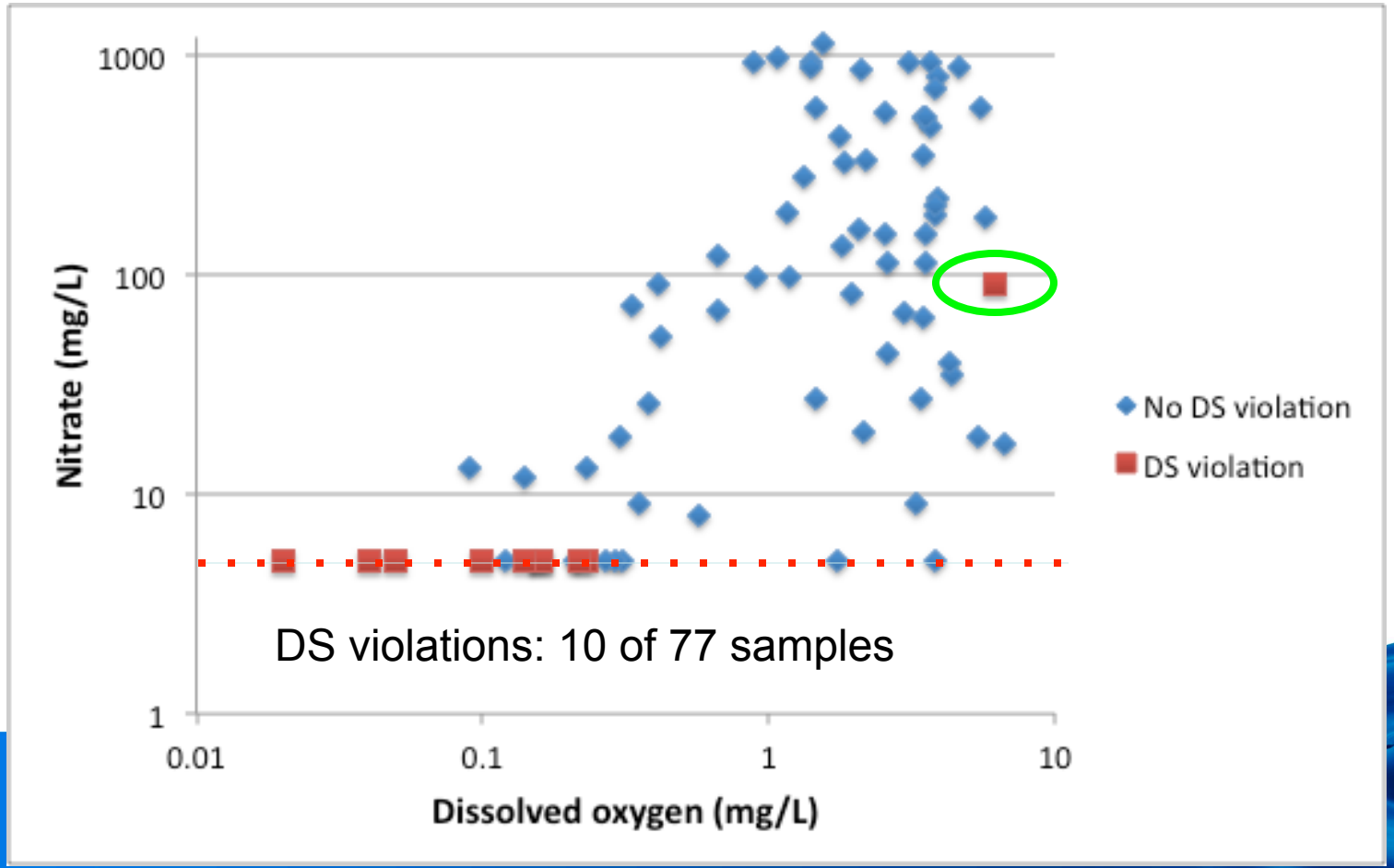
Total Sulfide violations

- TS violations occur only when both DO and nitrate are low



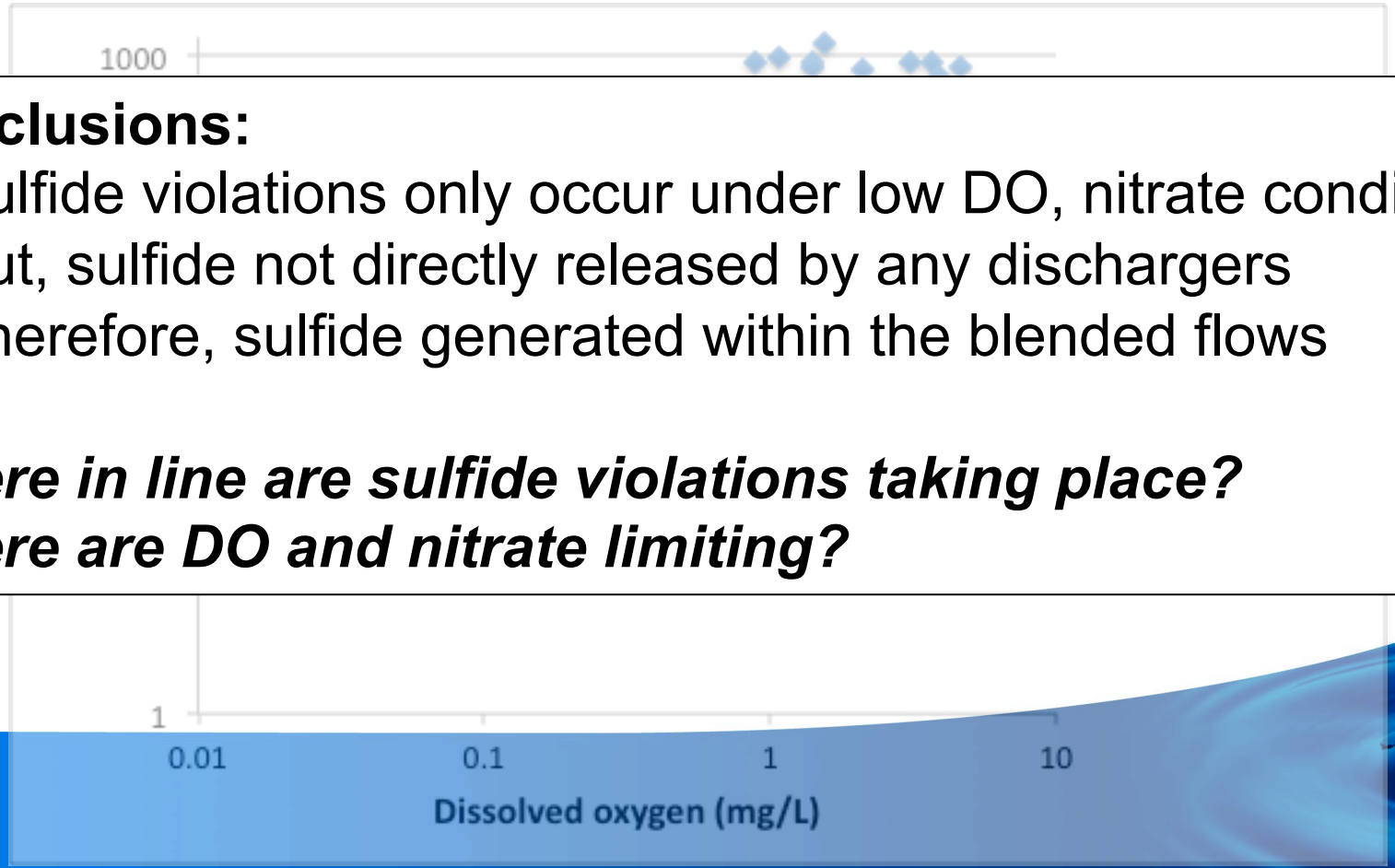
Dissolved Sulfide violations

- DS violations occur only when both DO and nitrate are low



Dissolved Sulfide violations

- DS violations occur only when both DO and nitrate are low



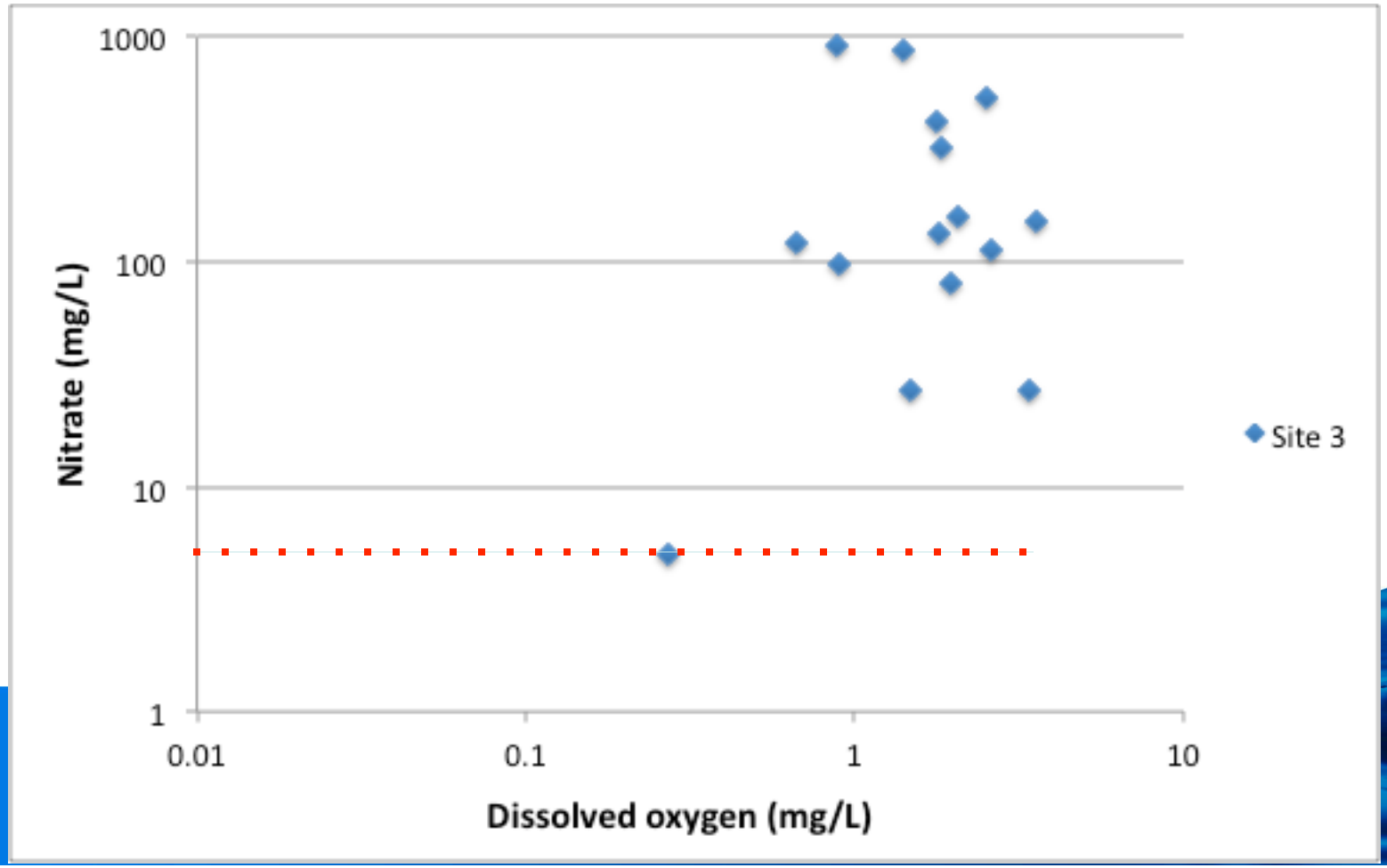
Conclusions:

- Sulfide violations only occur under low DO, nitrate conditions
- But, sulfide not directly released by any dischargers
- Therefore, sulfide generated within the blended flows

Where in line are sulfide violations taking place?
Where are DO and nitrate limiting?

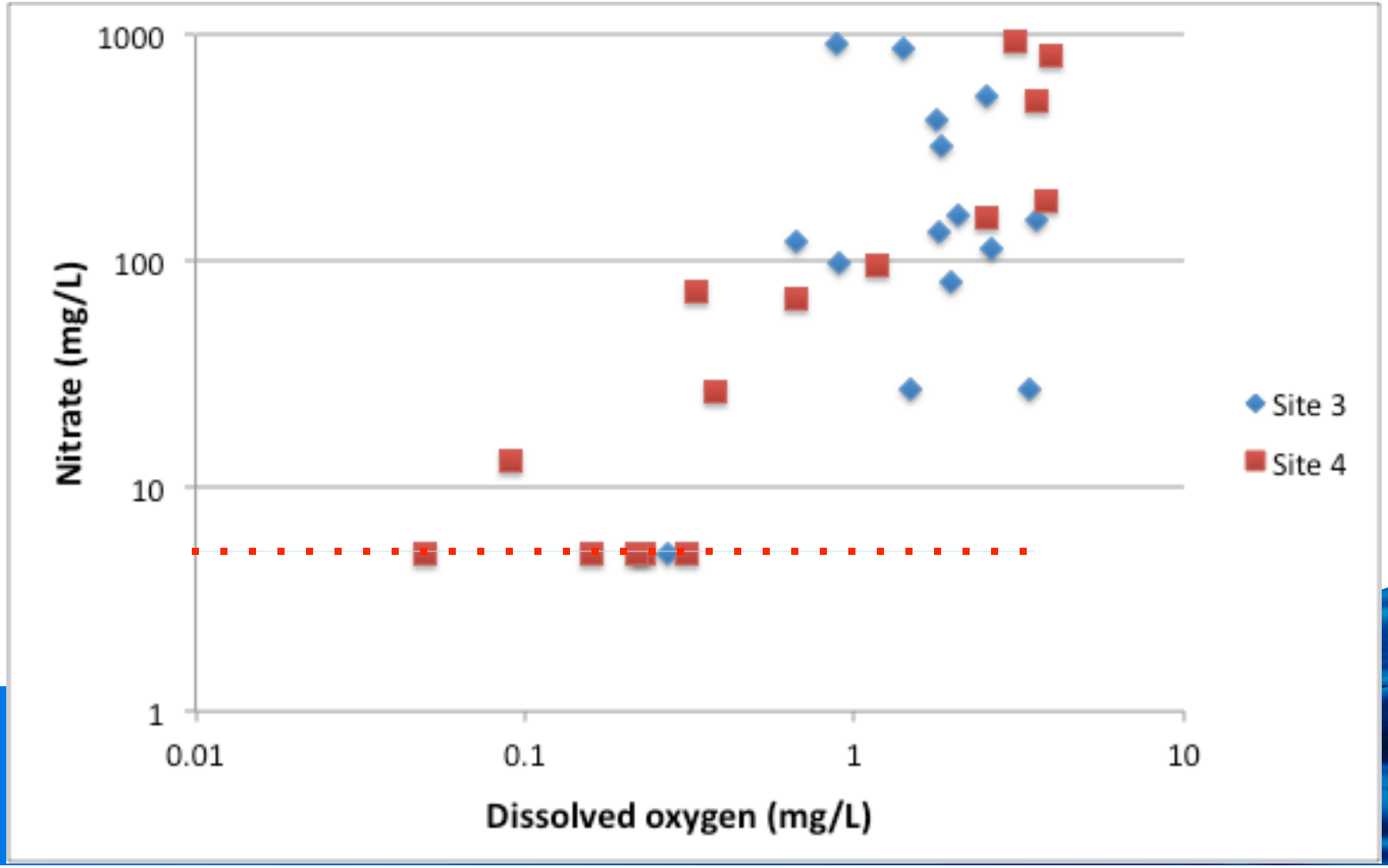
DO, nitrate in blended flows

- Site 3: upstream blend CIM/OLS & Mission Linen



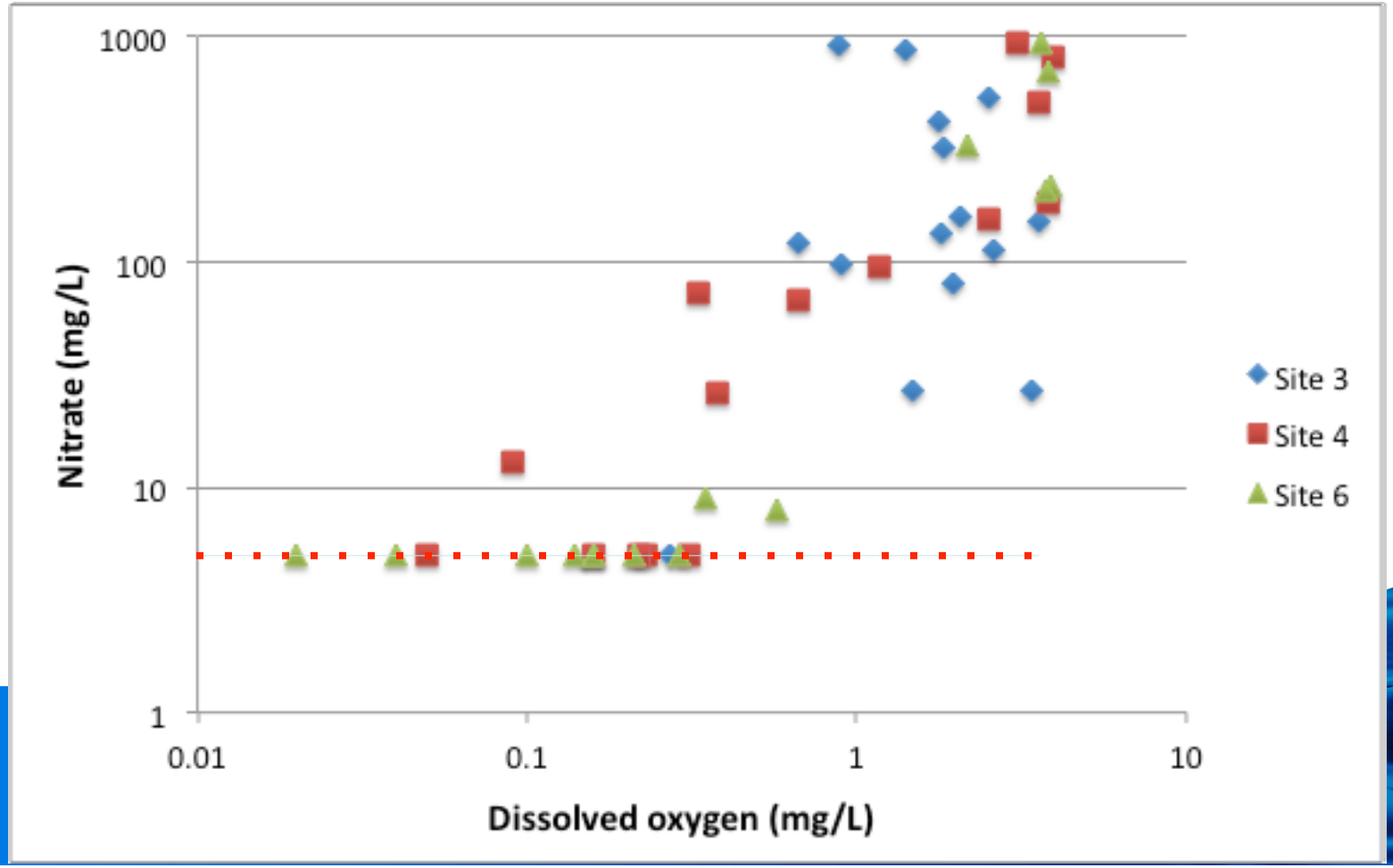
DO, nitrate in blended flows

- Site 4: downstream blend CIM/OLS & Mission Linen

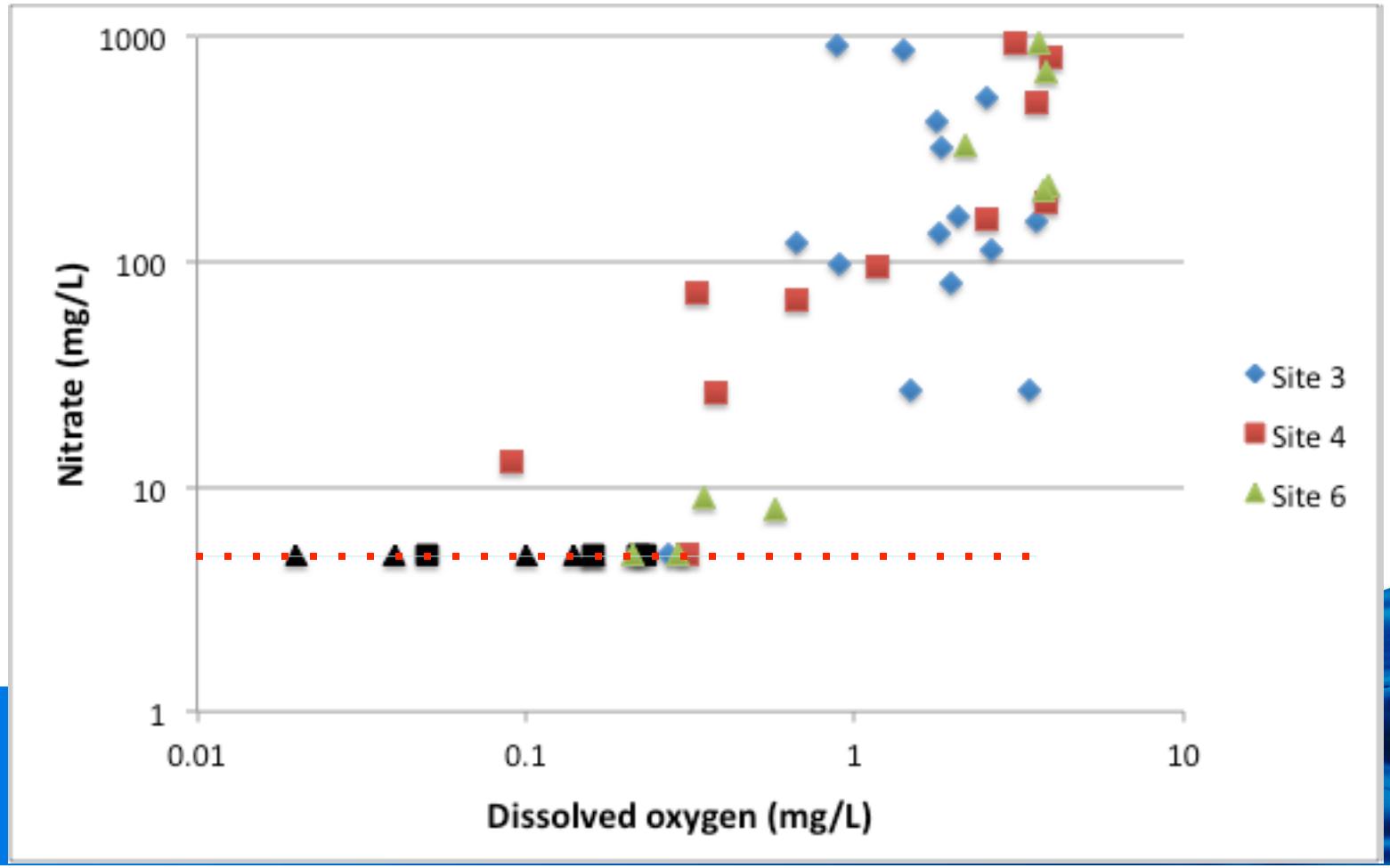


DO, nitrate in blended flows

- Site 6: downstream blend of all discharges (compliance point for sulfide)

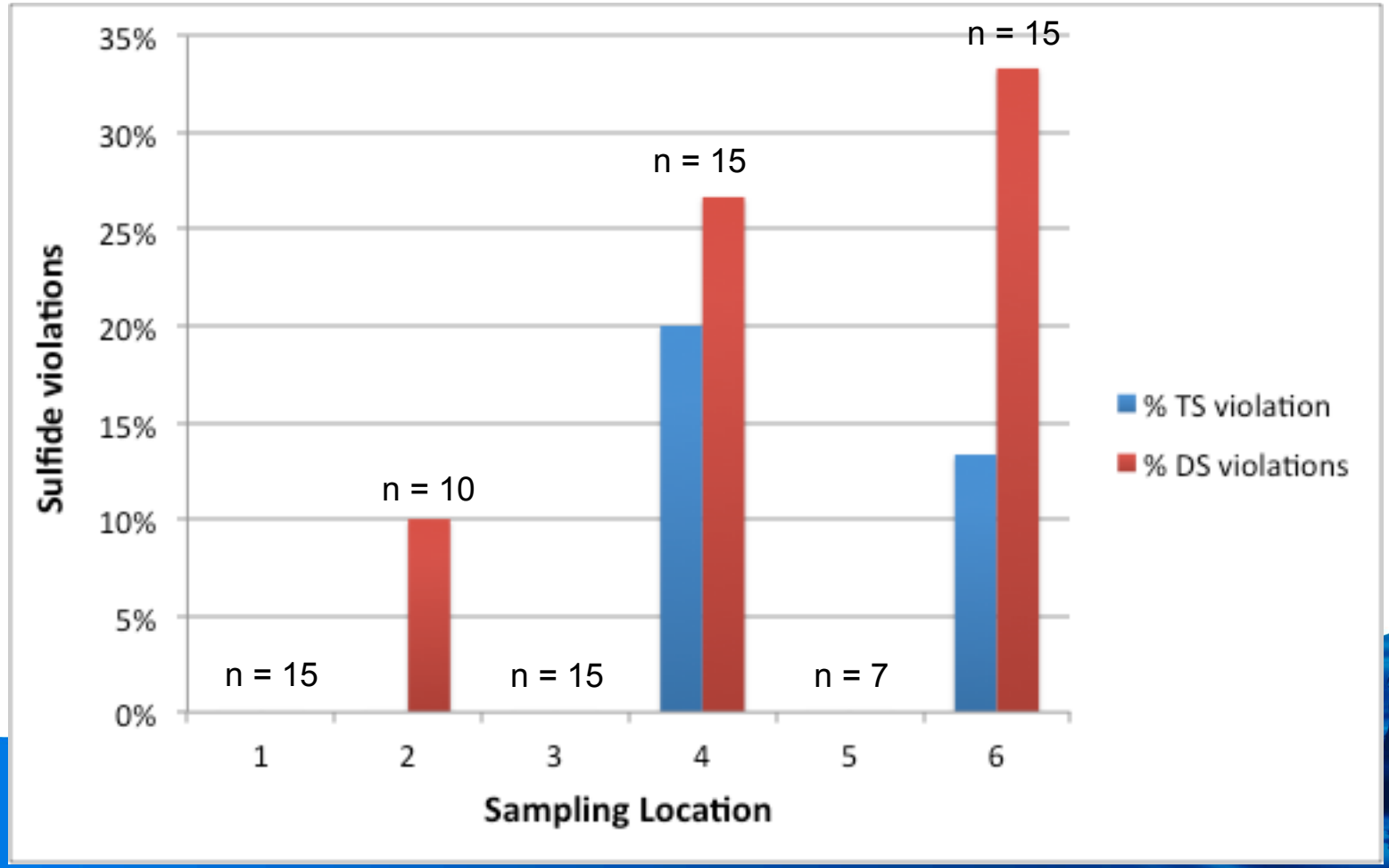


DS violations in blended flows



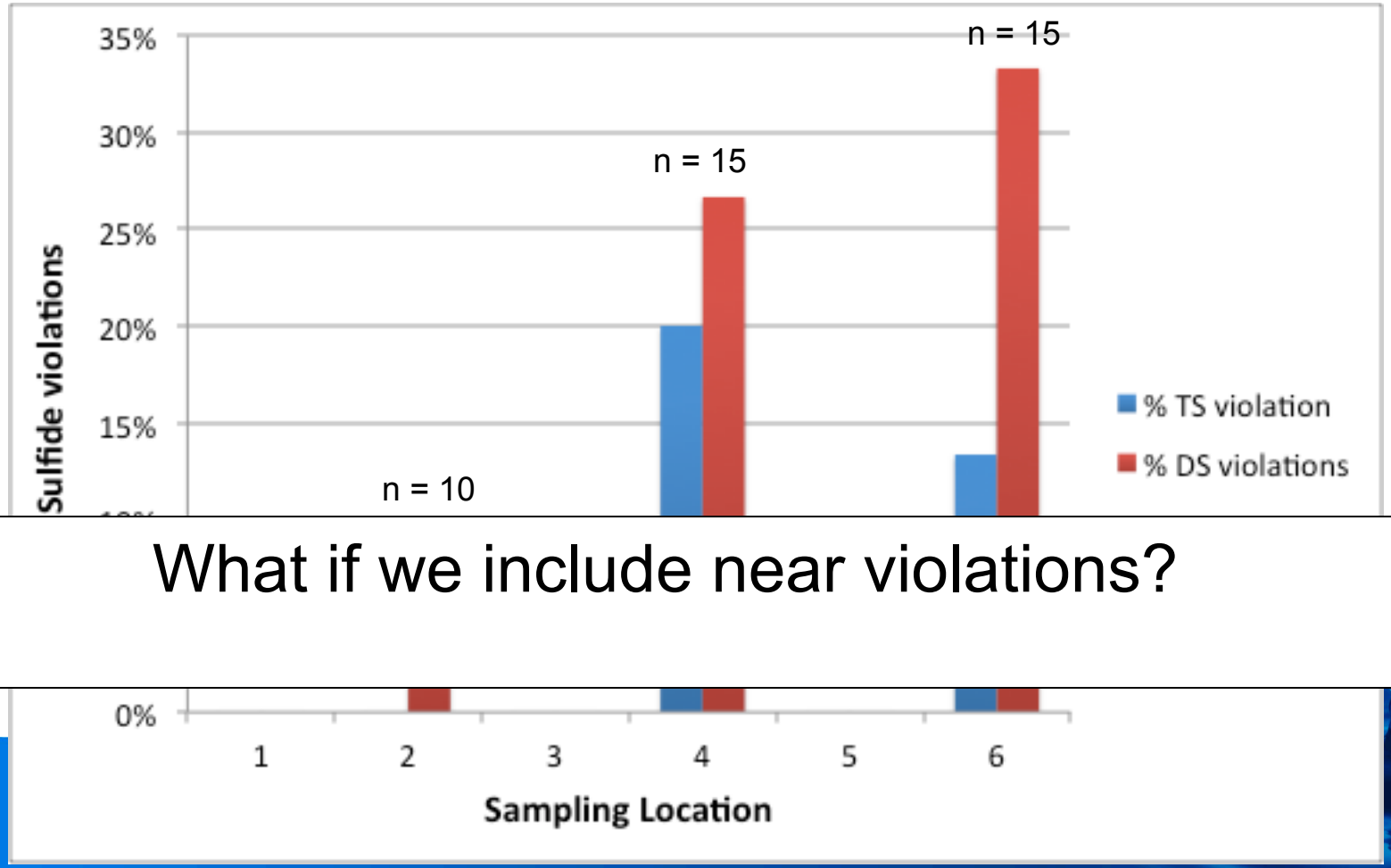
Location of sulfide violations

- Violations occur only at downstream sites 4 and 6



Location of sulfide violations

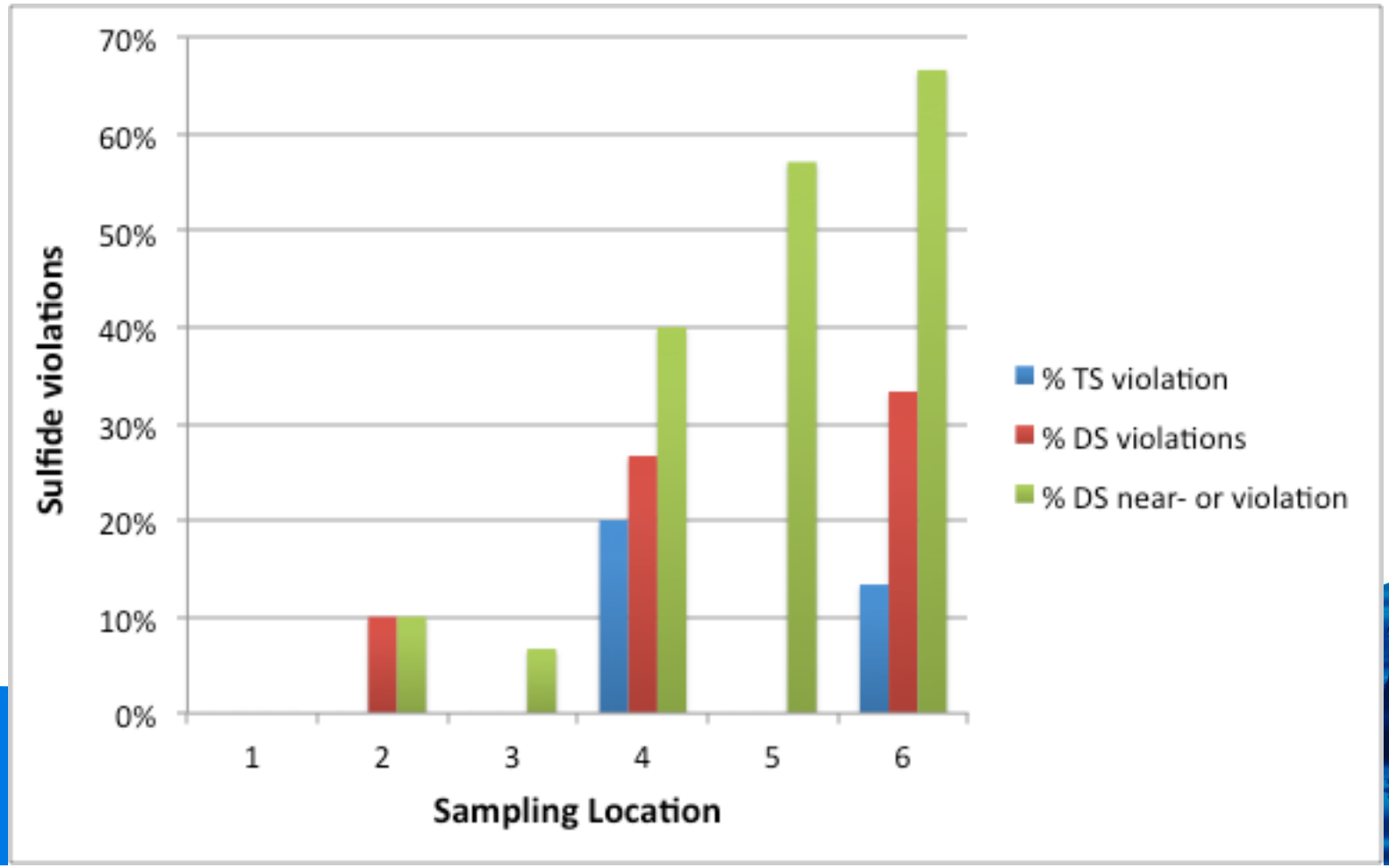
- Violations occur only at downstream sites 4 and 6



What if we include near violations?

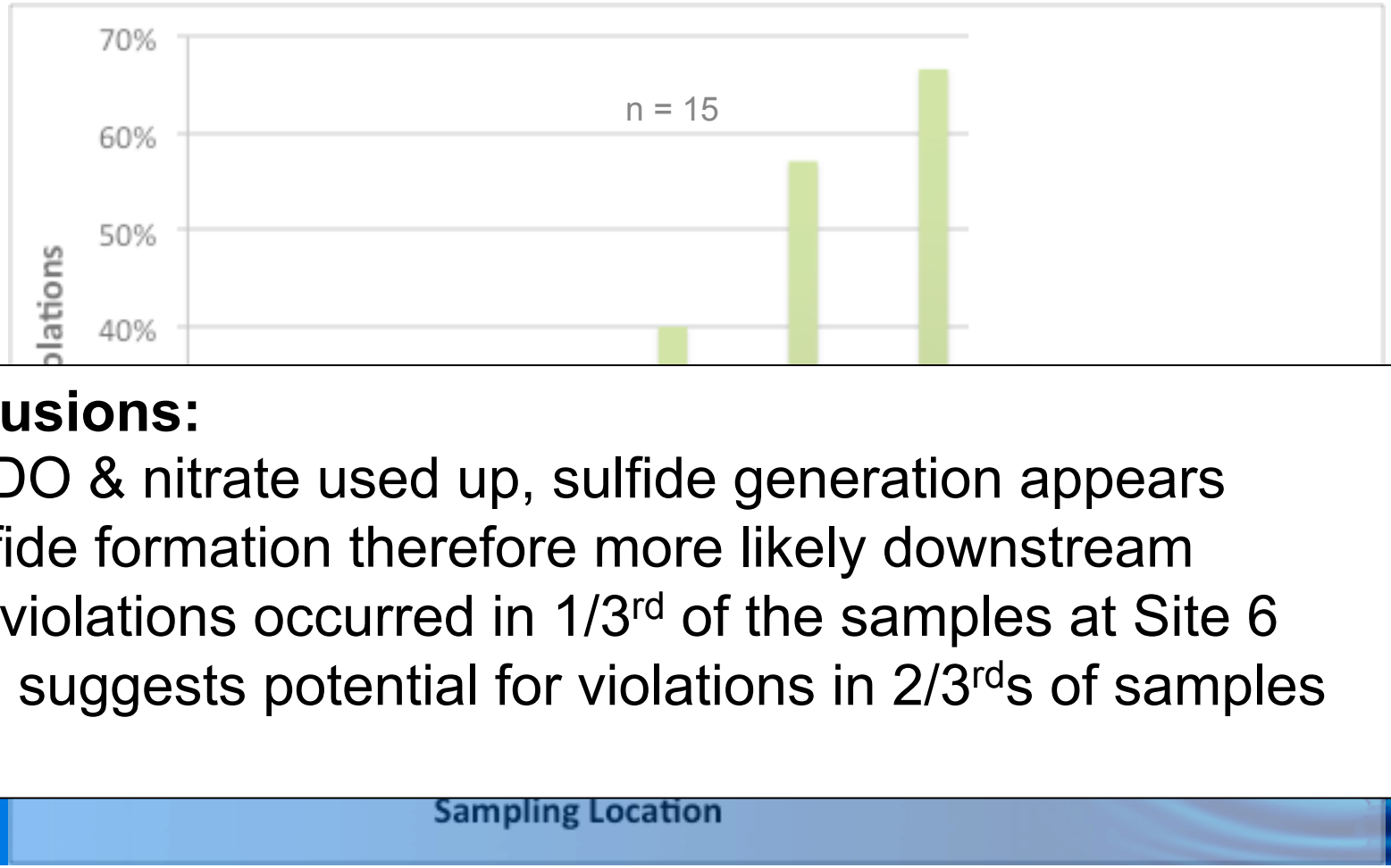
Potential sulfide violations

- <u>Near violations</u>: (1) DO < 1 mg/L, (2) NO_3^{2-} < 20 mg/L



Potential sulfide violations

- Near violations: (1) DO < 1 mg/L, (2) NO_3^{2-} < 20 mg/L



Conclusions:

- As DO & nitrate used up, sulfide generation appears
- Sulfide formation therefore more likely downstream
- DS violations occurred in 1/3rd of the samples at Site 6
- WQ suggests potential for violations in 2/3rds of samples

Impact of BOD on sulfide

- Main BOD source: Mission Linen = 90% of BOD
  - BOD in blended flow with Mission Linen: ~200 mg/L
  - BOD without Mission Linen: ~45 mg/L

- Sulfide formation in absence of ML flows
  - Early morning flows and weekend flows
  - No sulfide violations in absence of ML
- Sulfide formation with ML flows
  - Violations in 6 of 10 events when ML flowing

Biological sulfide formation?

- Requirements (from intro):
  1. Sulfate-reducing bacteria
  2. Energy source (e.g., BOD)
  3. Sulfate
  4. Absence of other electron acceptors (e.g., O_2, nitrate)
  5. Surface for attachment and development of biofilm?

Biological sulfide formation?

- Requirements (from intro):
  1. Sulfate-reducing bacteria
     - Biological analysis not included in sampling campaign
  2. Energy source (e.g., BOD)
  3. Sulfate
  4. Absence of other electron acceptors (e.g., O_2, nitrate)
  5. Surface for attachment and development of biofilm?

Biological sulfide formation?

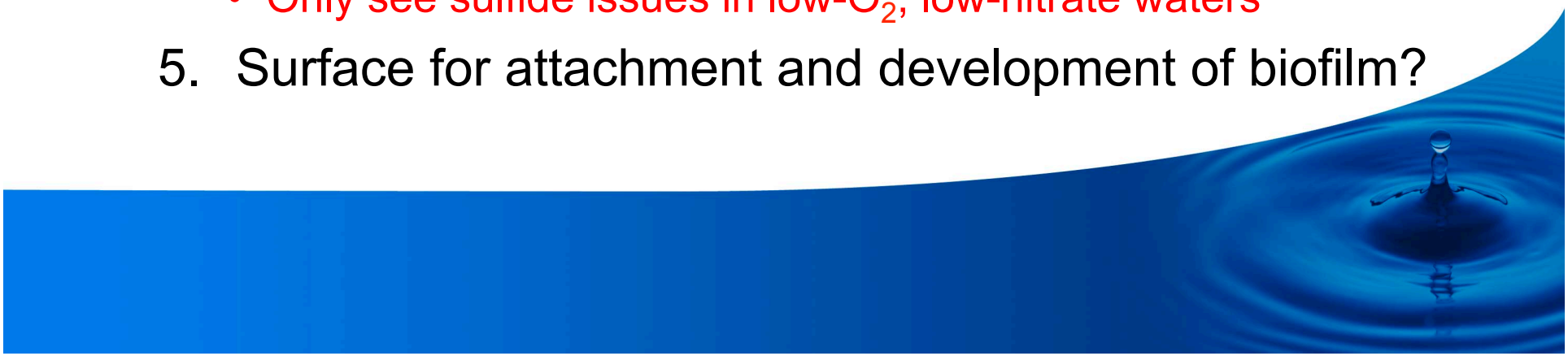
- Requirements (from intro):
  1. Sulfate-reducing bacteria
     - Biological analysis not included in sampling campaign
  2. Energy source (e.g., BOD)
     - Sulfide only generated in blended water with high BOD
  3. Sulfate
  4. Absence of other electron acceptors (e.g., O_2, nitrate)
  5. Surface for attachment and development of biofilm?

Biological sulfide formation?

- Requirements (from intro):
  1. Sulfate-reducing bacteria
     - Biological analysis not included in sampling campaign
  2. Energy source (e.g., BOD)
     - Sulfide only generated in blended water with high BOD
  3. Sulfate
     - High concentration of sulfate in blended flows (>600 mg/L)
  4. Absence of other electron acceptors (e.g., O_2, nitrate)
  5. Surface for attachment and development of biofilm?

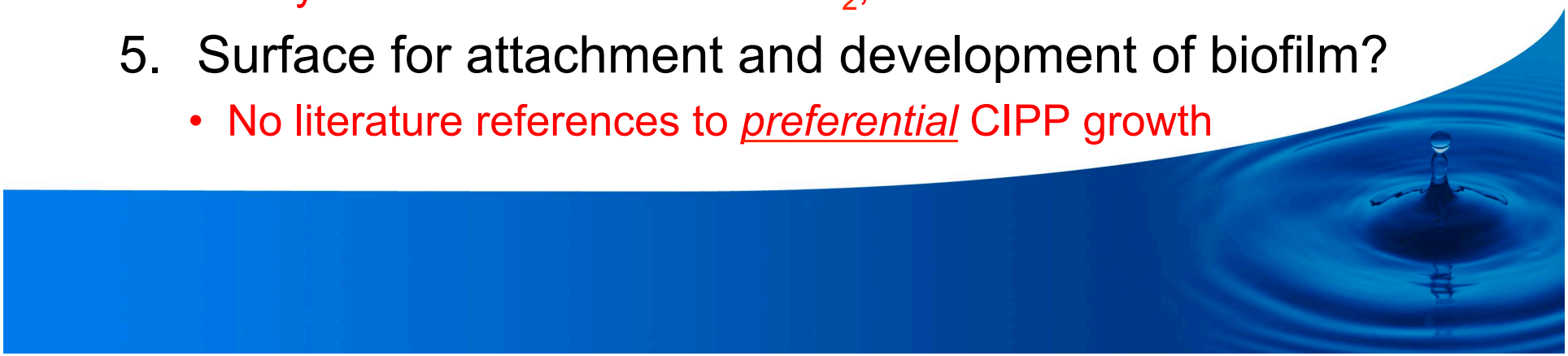
Biological sulfide formation?

- Requirements (from intro):
  1. Sulfate-reducing bacteria
     - Biological analysis not included in sampling campaign
  2. Energy source (e.g., BOD)
     - Sulfide only generated in blended water with high BOD
  3. Sulfate
     - High concentration of sulfate in blended flows (>600 mg/L)
  4. Absence of other electron acceptors (e.g., O_2, nitrate)
     - Only see sulfide issues in low-O_2, low-nitrate waters
  5. Surface for attachment and development of biofilm?



Biological sulfide formation?

- Requirements (from intro):
  1. Sulfate-reducing bacteria
     - Biological analysis not included in sampling campaign
  2. Energy source (e.g., BOD)
     - Sulfide only generated in blended water with high BOD
  3. Sulfate
     - High concentration of sulfate in blended flows (>600 mg/L)
  4. Absence of other electron acceptors (e.g., O_2, nitrate)
     - Only see sulfide issues in low-O_2, low-nitrate waters
  5. Surface for attachment and development of biofilm?
     - No literature references to *preferential* CIPP growth



Biological sulfide formation?

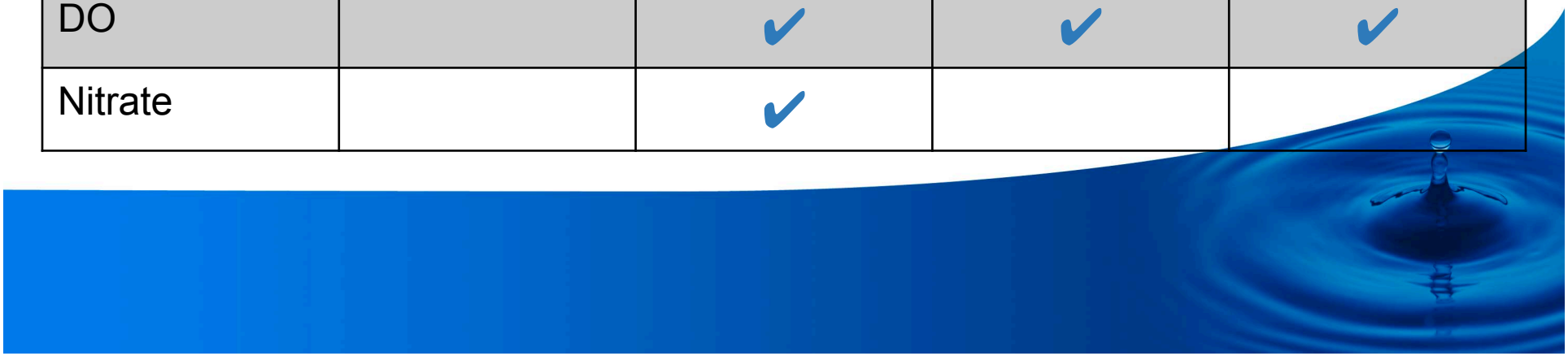
- Requirements (from intro):
  1. Sulfate-reducing bacteria
     - Biological analysis not included in sampling campaign
  2. Energy source (e.g., BOD)
     - Sulfide only generated in blended water with high BOD
  3. Sulfate
     - High concentration of sulfate in blended flows (>600 mg/L)
  4. Absence of other electron acceptors (e.g., O_2, nitrate)
     - Only see sulfide issues in low-O_2, low-nitrate waters
  5. Surface for attachment and development of biofilm?
     - No literature references to *preferential* CIPP growth

Conclusions

- What causes sulfide formation?
  - BOD
  - Sulfate
  - Absence of electron acceptors
  - Temperature?
- All of these factors need to be satisfied
- No one discharger alone adds all of these components
- Problem is the result of ***blended*** flows

Conclusions

	Worst-case	CIM/OLS	Mission Linen	RP-5
Factors favoring sulfide development				
High BOD	✔		✔	✔
Sulfate	✔	✔		✔
High temperature?	✔		✔	
Factors limiting sulfide development				
DO		✔	✔	✔
Nitrate		✔		



SITE VISITS

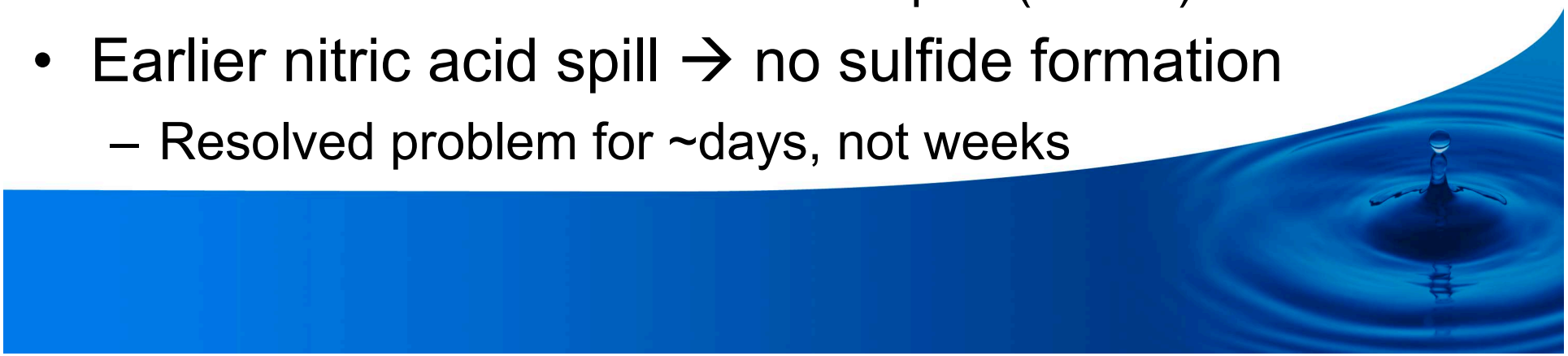
CIM

Current configuration

- CIM is sole source of BOD in CIM/OLS blended flow
- BOD source: citric acid (control of precipitation)

Expected changes

- Planning to switch from citric to nitric acid
  - Reduces BOD loading in line
  - Adds an additional electron acceptor (nitrate)
- Earlier nitric acid spill → no sulfide formation
  - Resolved problem for ~days, not weeks



Mission Linen

- **Discharge schedule**
  - Monday – Friday: 5 a.m. to 10:30 p.m.
  - Saturday – Sunday: 5 a.m. to 1:30 p.m.
  - Overtime: rare, potentially additional 1 h (beginning or end)
  - Definite periods when zero flow from Mission Linen
- **No pattern of material to be washed**
- **$FeCl_3$ tank present on-site, but unused**

NEXT STEPS

Next Steps

- Select control strategies for evaluation
- Develop costs and feasibility of alternative strategies
- Select and implement preferred alternative
- Perform sampling campaign to monitor sulfide control

Control Strategies

- Three main categories for chemical/biological options
  - Increasing redox potential
  - Inhibition of sulfate-reducing bacteria
  - Chemical removal of sulfide

Control Strategies

- Three main categories for chemical/biological options
  - Increasing redox potential
    - Alternatives: add DO, nitrate, etc.
    - Evaluate dosing requirements, costs
  - Inhibition of sulfate-reducing bacteria
  - Chemical removal of sulfide

Control Strategies

- Three main categories for chemical/biological options
  - Increasing redox potential
  - Inhibition of sulfate-reducing bacteria (two main options)
    - pH adjustment: shock treatment
    - Inhibit / eliminate SRB populations: biocides, chlorine
  - Chemical removal of sulfide

Control Strategies

- Three main categories for chemical/biological options
  - Increasing redox potential
  - Inhibition of sulfate-reducing bacteria
  - Chemical removal of sulfide (two main options)
    - Precipitation by metal salts
    - Addition of oxidizing chemicals (H_2O_2, chlorine, permanganate)