Bioremediation of a Dissolved Ammonia and Nitrate Plume Through In-Situ Denitrification

Remediation Technologies Symposium 2015

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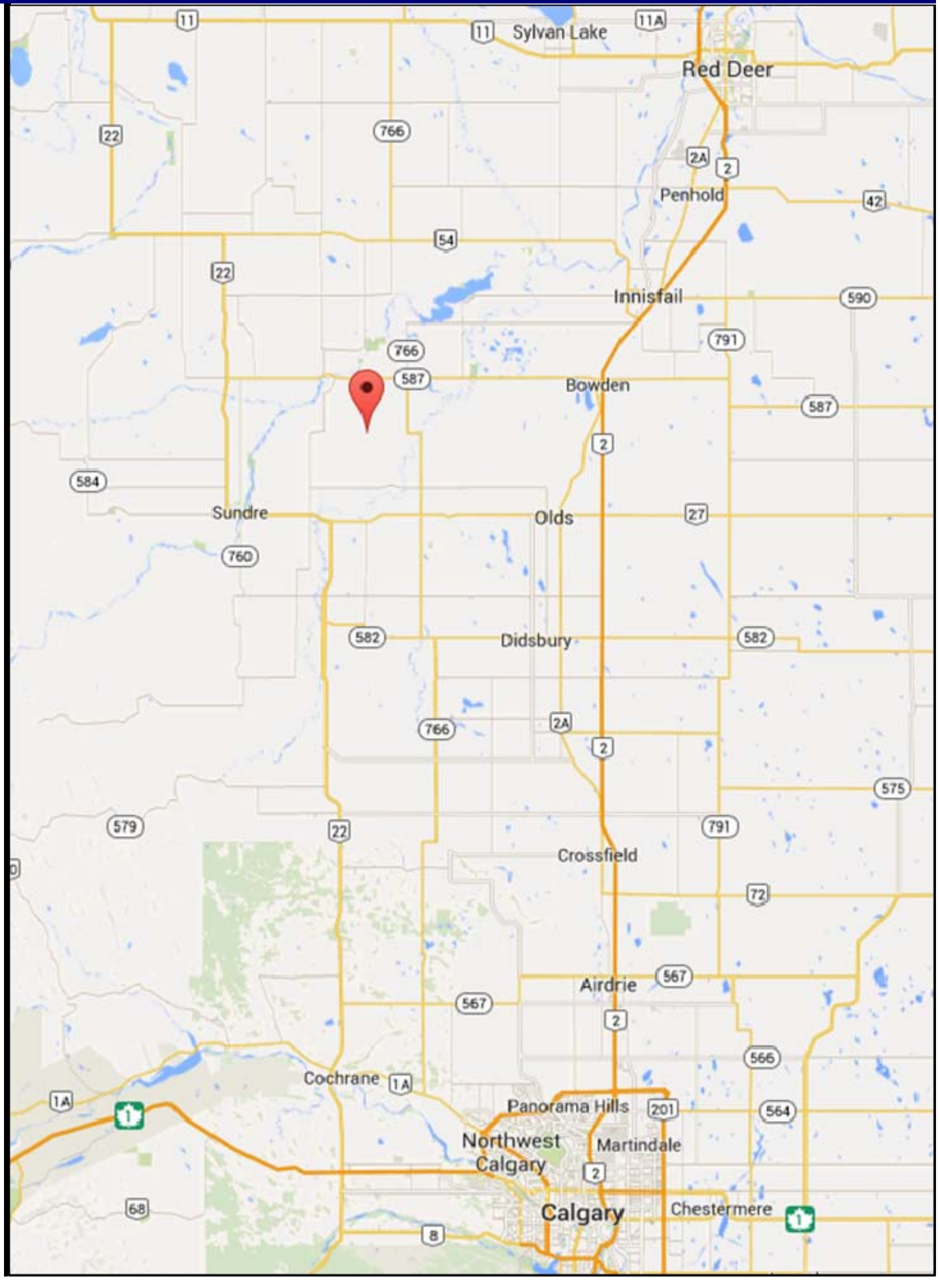
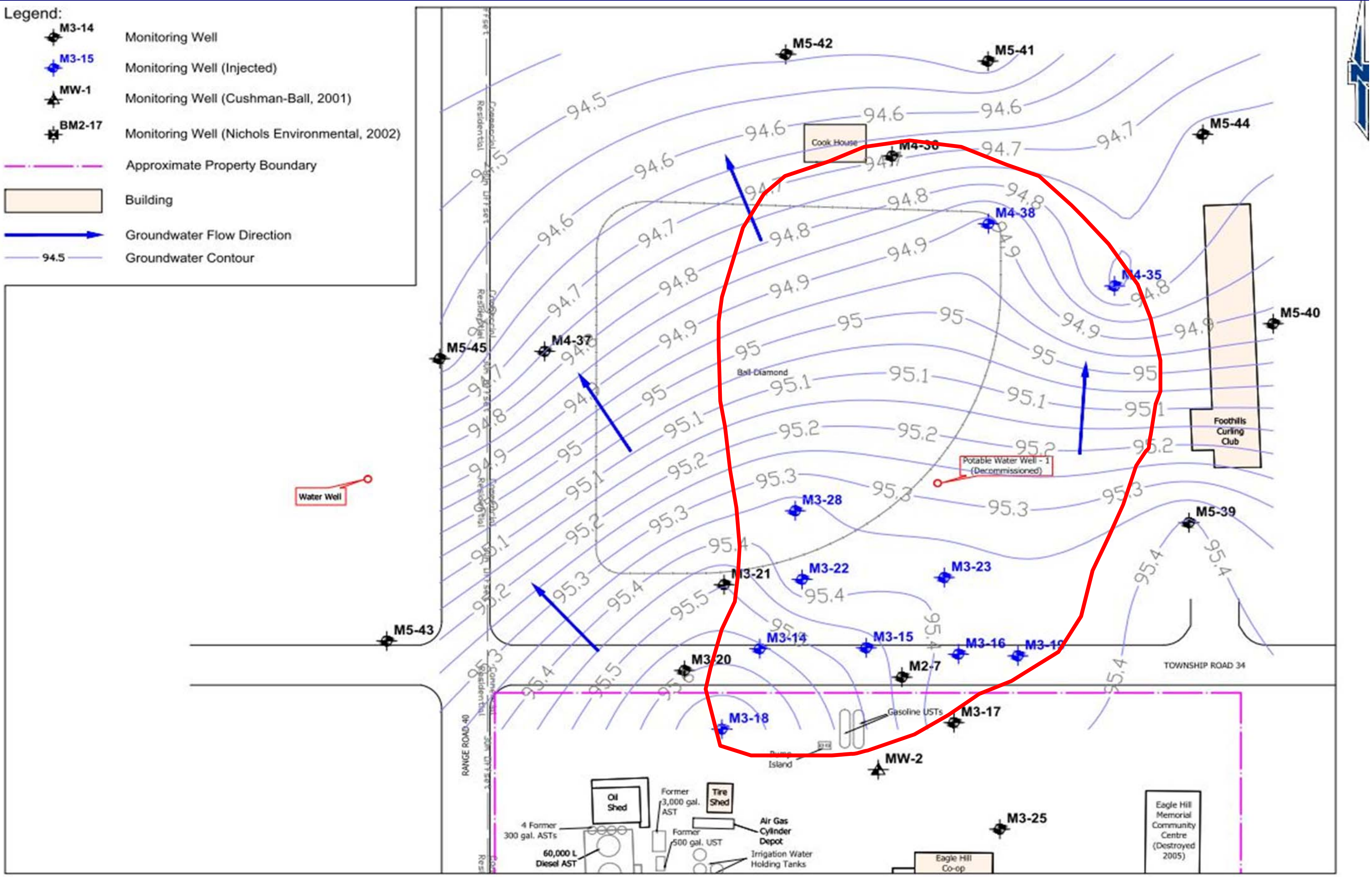
Background

- Small unincorporated community in central Alberta, Canada
- Petroleum facilities including gas bar and bulk fuel facility in operation since the 1930's
- Multiple ESAs since 2001 identifying PHC impacts in soil and groundwater
  - On-site
  - Off-site
- USTs were removed in 2006 and replaced with ASTs



Background



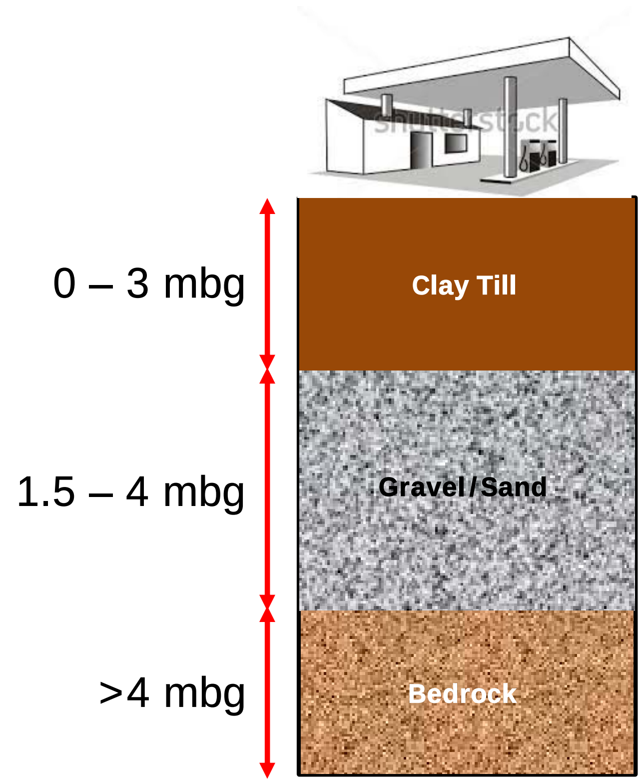
Legend:
M3-14 Monitoring Well
M3-15 Monitoring Well (Injected)
MW-1 Monitoring Well (Cushman-Ball, 2001)
BM2-17 Monitoring Well (Nichols Environmental, 2002)
Approximate Property Boundary
Building
Groundwater Flow Direction
94.5 Groundwater Contour
M5-42
M5-41
M5-44
M5-40
M5-39
M5-45
M5-43
M4-37
M4-38
M4-35
M4-36
M3-28
M3-22
M3-23
M3-21
M3-14
M3-15
M3-16
M3-19
M3-20
M3-18
M3-17
M3-25
M2-7
MW-2
Cook House
Ball Diamond
Potable Water Well - 1 (Decommissioned)
Water Well
Foothills Curling Club
TOWNSHIP ROAD 34
RANGE ROAD 40
Gasoline USTs
Pump Island
Oil Shed
Tire Shed
Former 3,000 gal. AST
4 Former 300 gal. ASTs
Former 500 gal. UST
60,000 L Diesel AST
Air Gas Cylinder Depot
Irrigation Water Holding Tanks
Eagle Hill Co-op
Eagle Hill Memorial Community Centre (Destroyed 2005)

Site Characteristics

Lithology
- Soil stratigraphy generally consists of clay till underlain by saturated gravel/sand followed by bedrock

Groundwater
- GW depth approximately 1.5 mbg
- Flow is toward the north

Gradient
- GW gradient 0.0086 m/m



Previous Remedial Efforts

Bio-Stimulation

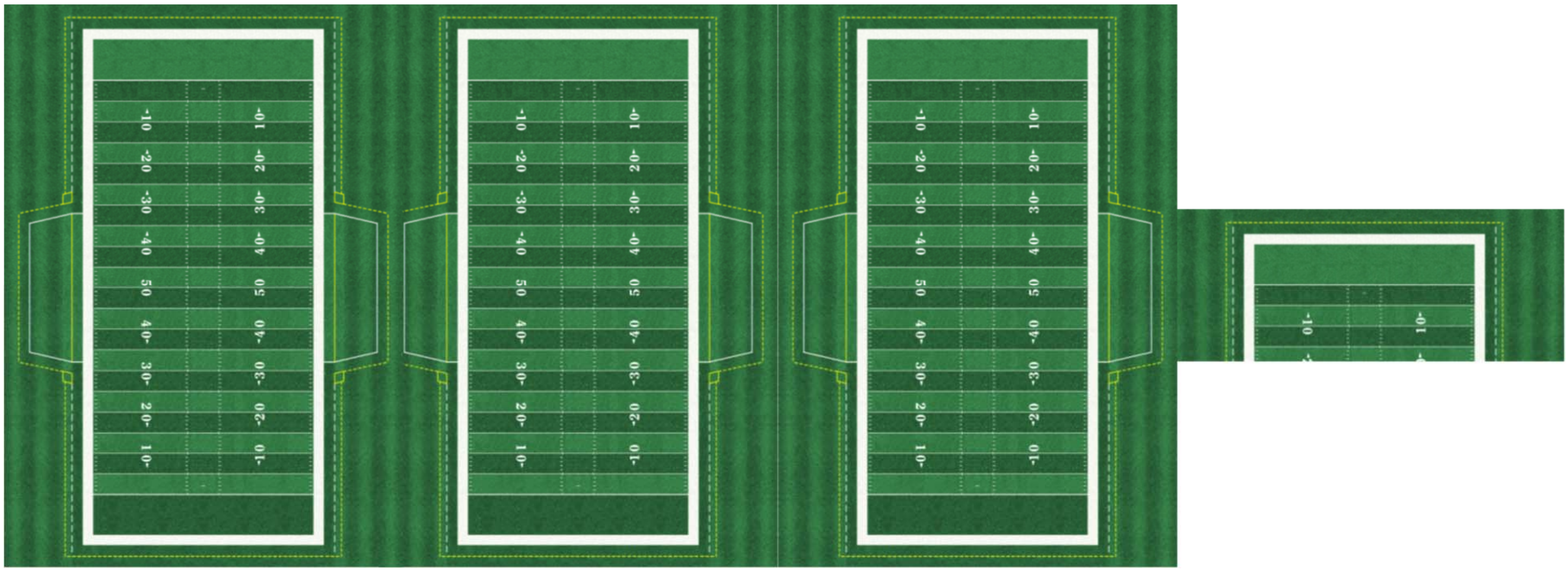
- Addition of nitrogen-based liquid fertilizer into the near-surface GW
- 500-L of 10-34-0 mixed with 500-L of 28-0-0 liquid fertilizer
    - Direct injected into nine monitoring wells and injection header

Previous Remedial Efforts

- As a result of limited carbon (low PHC impacts, coarse-grained geology), the added nutrients were not completely consumed
- GW nutrient concentrations (NO_3, NO_2, NH_4) exceed applicable regulatory guidelines
- Elevated concentrations of orthophosphate also present

Plume Characteristics

- Nutrient impact area estimated to be 16,850 m^2

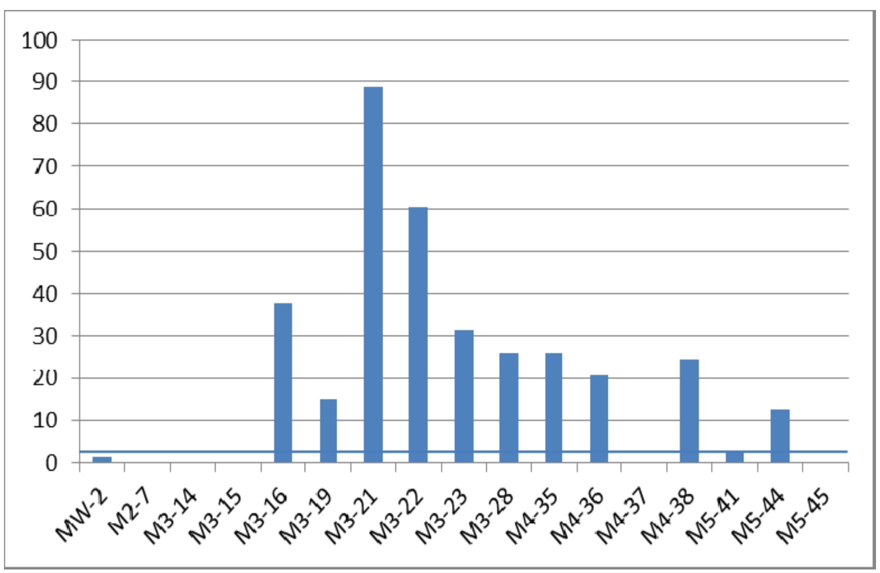


- Thickness of the impacted aquifer is approximately 2.5 m
- Porosity approximately 35%
- Estimated 14,745 m^3 of nitrate impacted groundwater requiring treatment

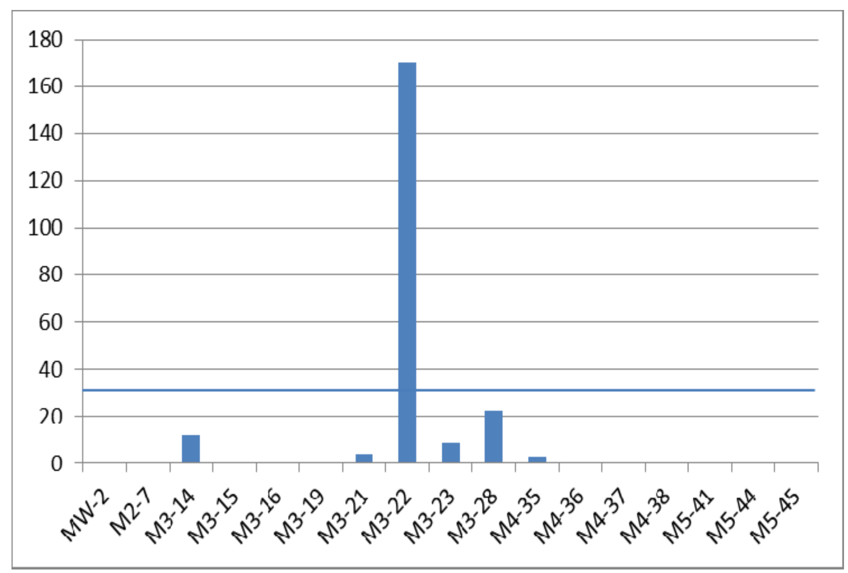
Remedial Approach

- Average nitrate concentration of 27 mg/L
- Average ammonia concentration 10.63 mg/L
- Estimated mass:
  - Nitrate estimated to be 398 kg (880 lbs)
  - Ammonia estimated to be 157 kg (350 lbs)

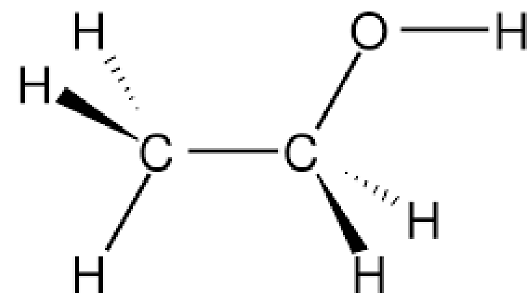
Nitrate (guideline = 3 ppm)



Ammonia (guideline = 34.2 ppm)



Remedial Approach



- Site has limited carbon
- Elected to use ethanol
  - Often used as a treatment for fertilizer impacts
  - Environmentally inert
  - Reasonable choice because of **low PHC concentrations**
- Ethanol is very labile and would have low toxicity

Balanced Stoichiometric Equation

$$NO_3^- + 5/12\ CH_3CH_2OH = 1/2\ N_2 + 5/6\ CO_2 + 3/4\ H_2O + OH^-$$

Remedial Approach

- Based on literature review, 1.4 mg of ethanol is required to denitrify 1 mg of nitrate
  - =1,088 kg of ethanol required

- Consideration also given to additional carbon consumption
  - Presence of iron (Fe^{3+})
  - Oxygen

- Recommendation to double the mass
  - =2,175 kg

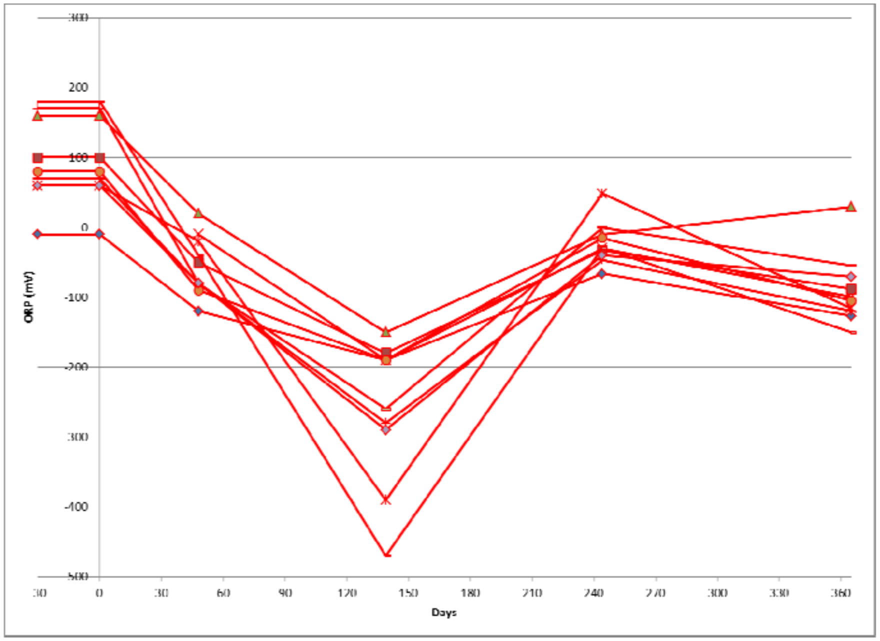
Injection Summary

- Ethanol added to the same wells which received fertilizer amendment
  - Approximately 20,600 litres of 15% ethanol injected
- GW monitoring and sampling programs completed pre- (-30 days) and post-amendment (48, 139, 244, 365 days)
  - Wells were developed by purging 100L per well

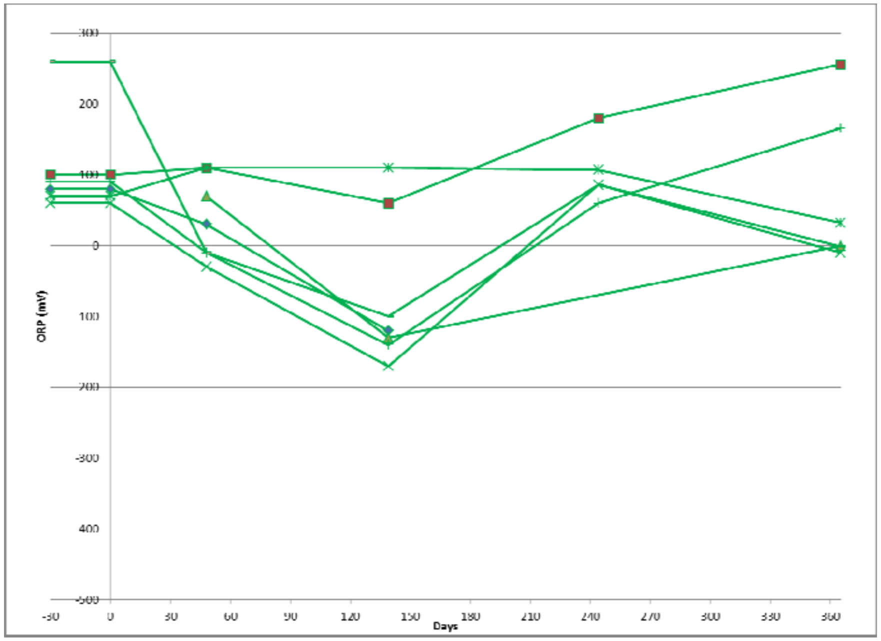
Results

Field Measured Oxidation Reduction Potential

Amended Wells



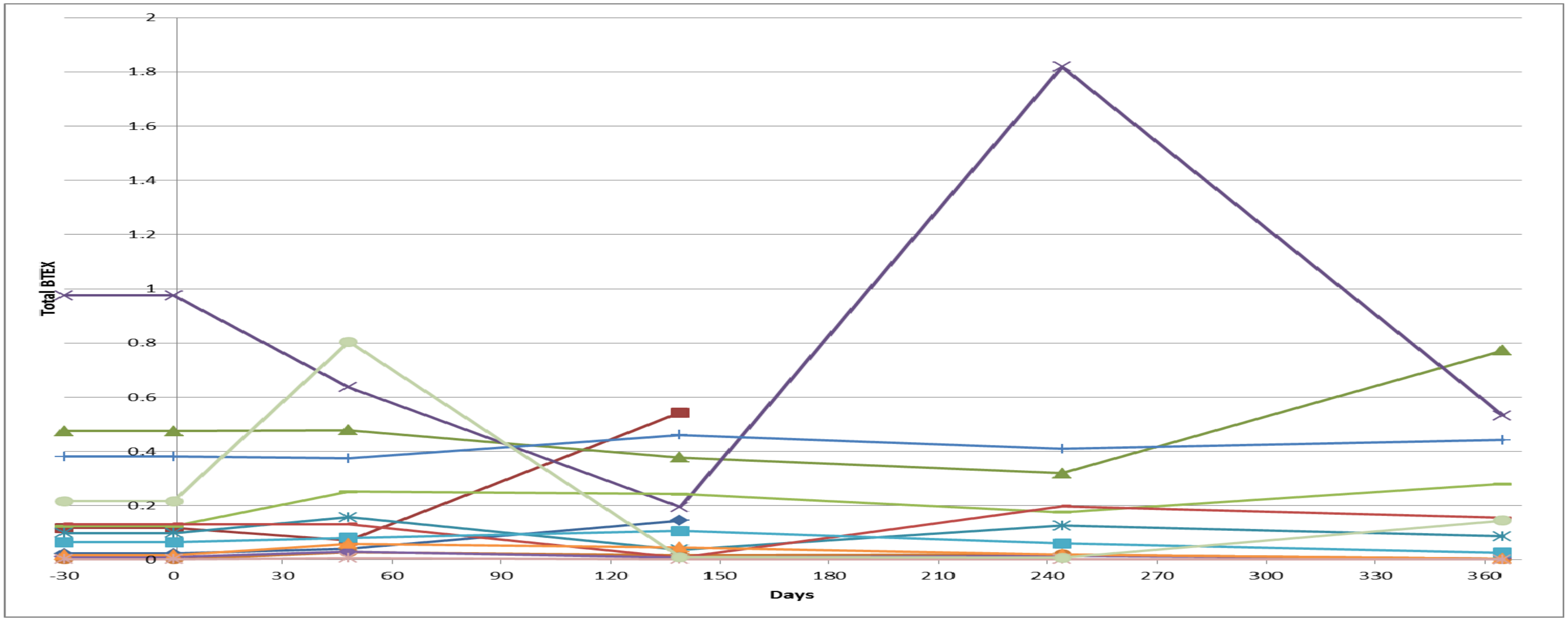
Non-amended Wells



- ORP decreased significantly following amendment
  - Reducing environment, returning close to baseline 240 days post amendment, but remains negative +1yr
- Larger decrease noted in wells receiving ethanol amendment versus non-amended wells

Results

Petroleum Hydrocarbons (Total BTEX)

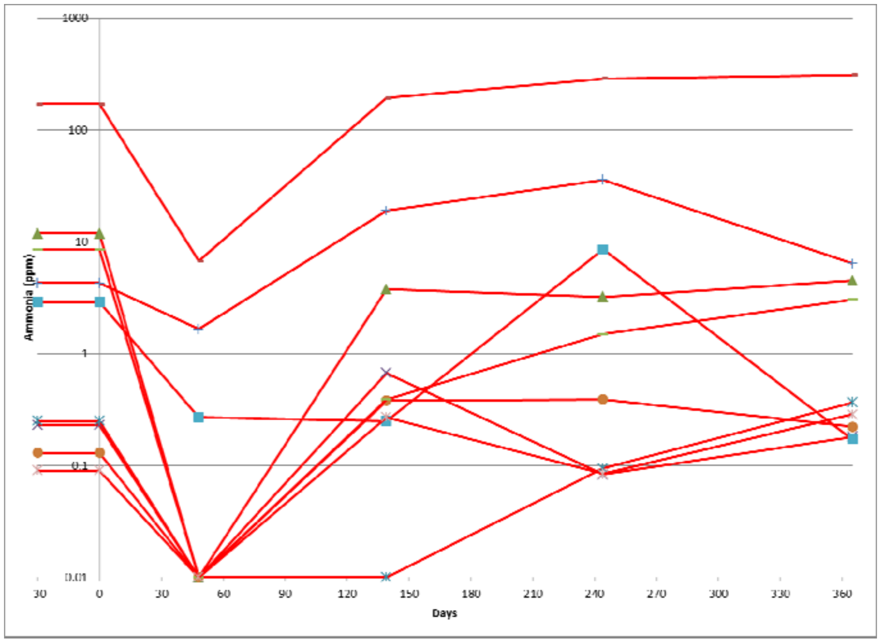


- PHC concentrations remained low between pre- and post-amendment
- EtOH is a simple carbon source, preferential consumption
- TOC (bioavailable carbon) increased

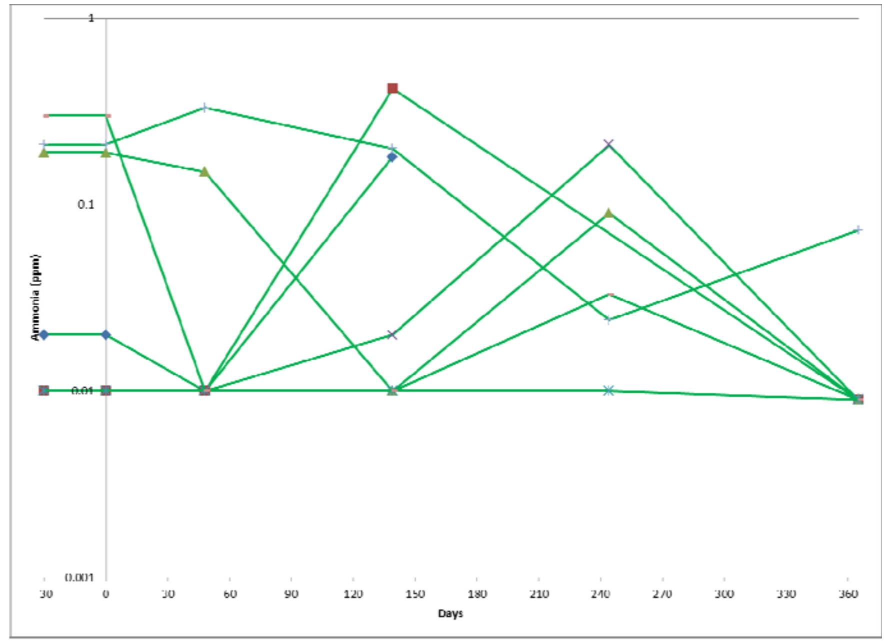
Results

Ammonia

Amended Wells



Non-amended Wells

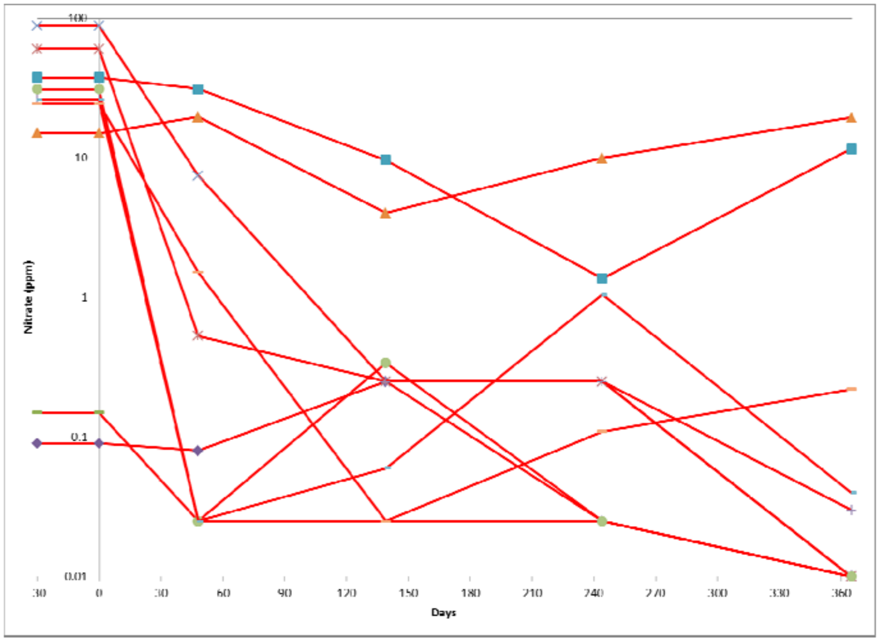


- Ammonia showed initial nitrification after 48 days (~96%)
- ~64% increase from baseline after 365 days (potentially diffused back into the area once carbon source was consumed)
- If we take out one well, ammonia concentrations were static

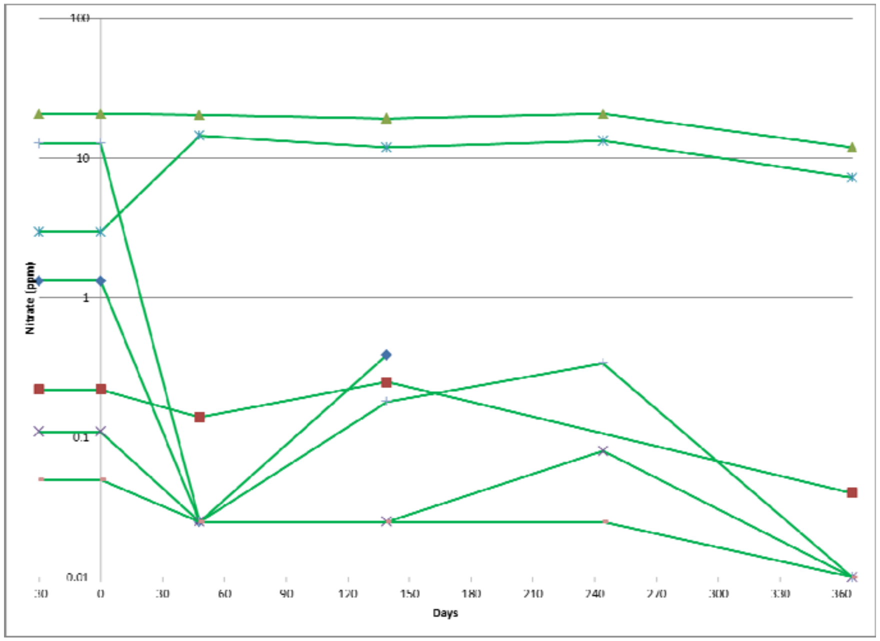
Results

Nitrate

Amended Wells



Non-amended Wells

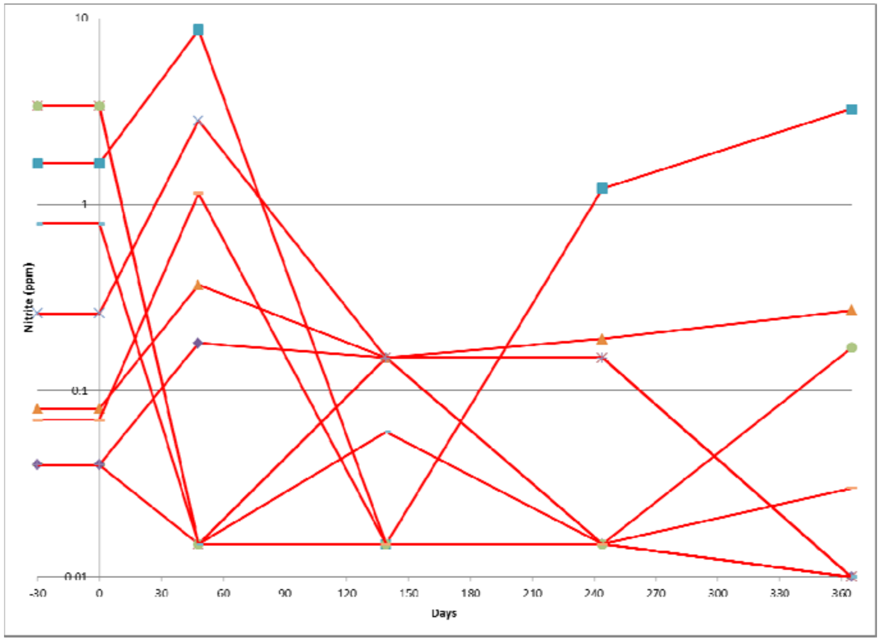


- Stable decreasing trend
  - ~90% reduction from baseline to final sampling event

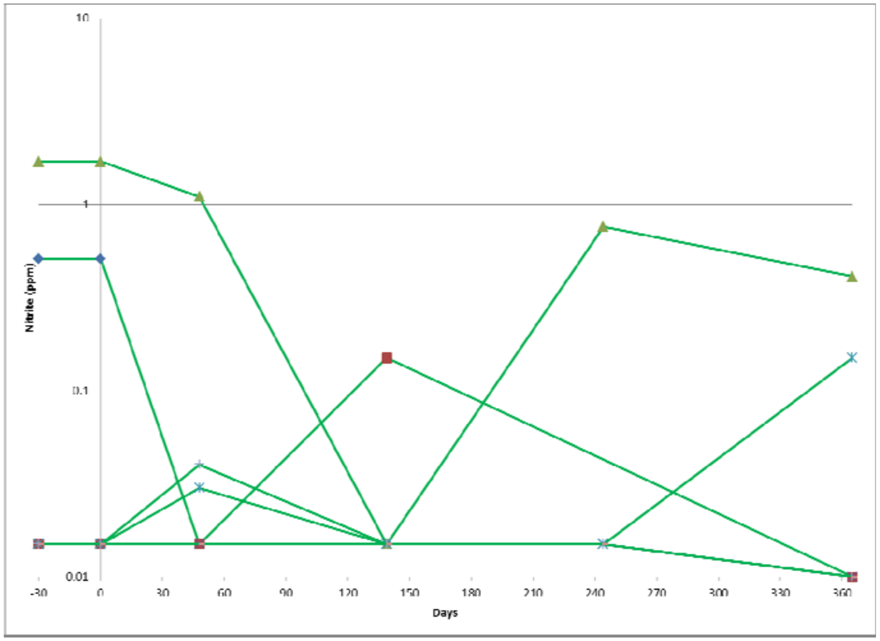
Results

Nitrite

Amended Wells



Non-amended Wells

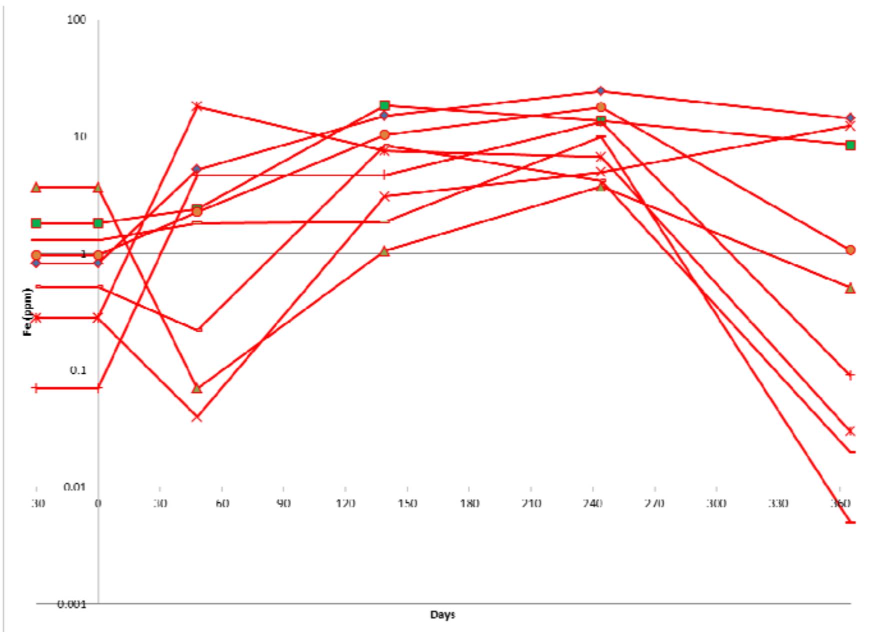


- Initial increase in nitrite concentrations a good indication of ammonia nitrification
- Decreasing concentrations of nitrite may indicate that the rate of nitrification is slowing

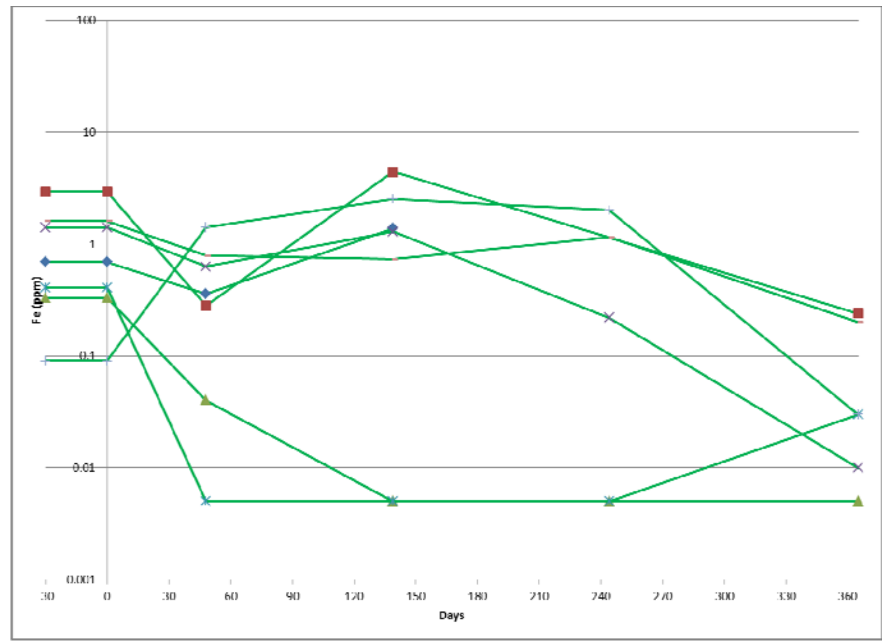
Results

Dissolved Iron

Amended Wells



Non-amended Wells



- Dissolved iron concentrations increased ~620% at third monitoring event and remains ~260% after 1 year
- The significant decrease in ORP resulted in the mobilization of metals
    - Evaluation of which metals were mobilized is still ongoing

Other Results

- Orthophosphate concentrations were below method detection limits
  - Orthophosphate may act as a rate limiting step in nitrogen compound degradation

- Bacteria concentrations
  - No discernable pattern for bacterial communities (SRB, IR, HA and SF)

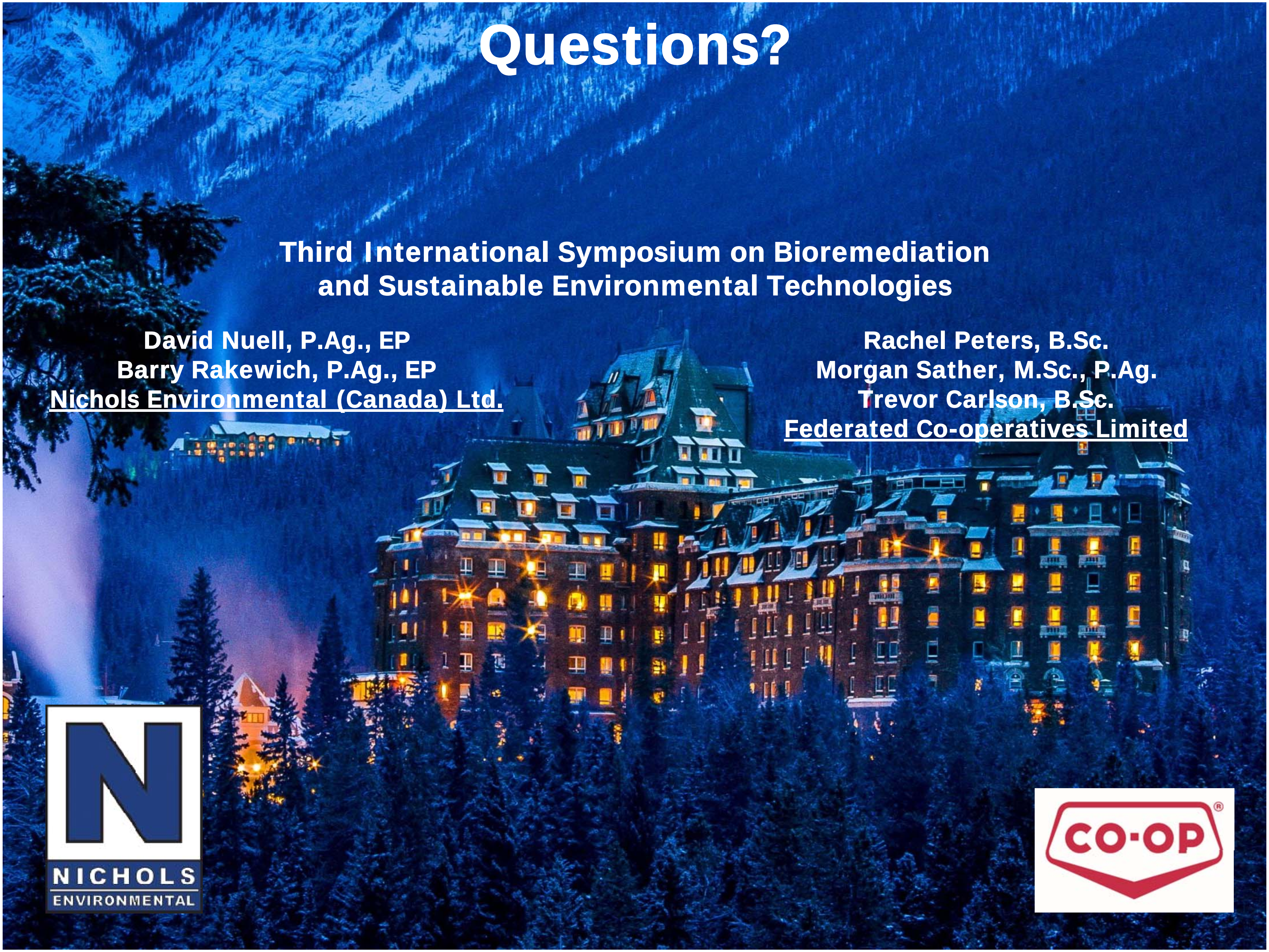
Conclusions

- Nitrification of ammonia would decrease DO and produce anaerobic conditions
  - Site was near anaerobic to begin. DO concentrations <1 ppm both pre and post amendment
  - Ethanol amendment forced redox negative environment
- Denitrifying bacteria would use nitrate as an electron acceptor during anaerobic respiration producing nitrogen gas
  - Nitrogen gas was not measured during investigation
  - Nitrogen gas likely increased based on reduction of nitrate concentrations throughout investigation area

Conclusions

- Nitrite concentrations would also increase
  - Initial increase in nitrite concentrations was a good indication of ammonia degradation – a 37% increase in nitrite concentration was noted
- Reduction of ammonia and nitrate via anammox process
  - Ammonia initially reduced, but rebounded (potentially the result of diffusion)
  - Average nitrate concentration went from 31 ppm in the baseline event to 1.3 ppm after third post amendment event
  - Anammox processes likely not taking place at the site

Questions?



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