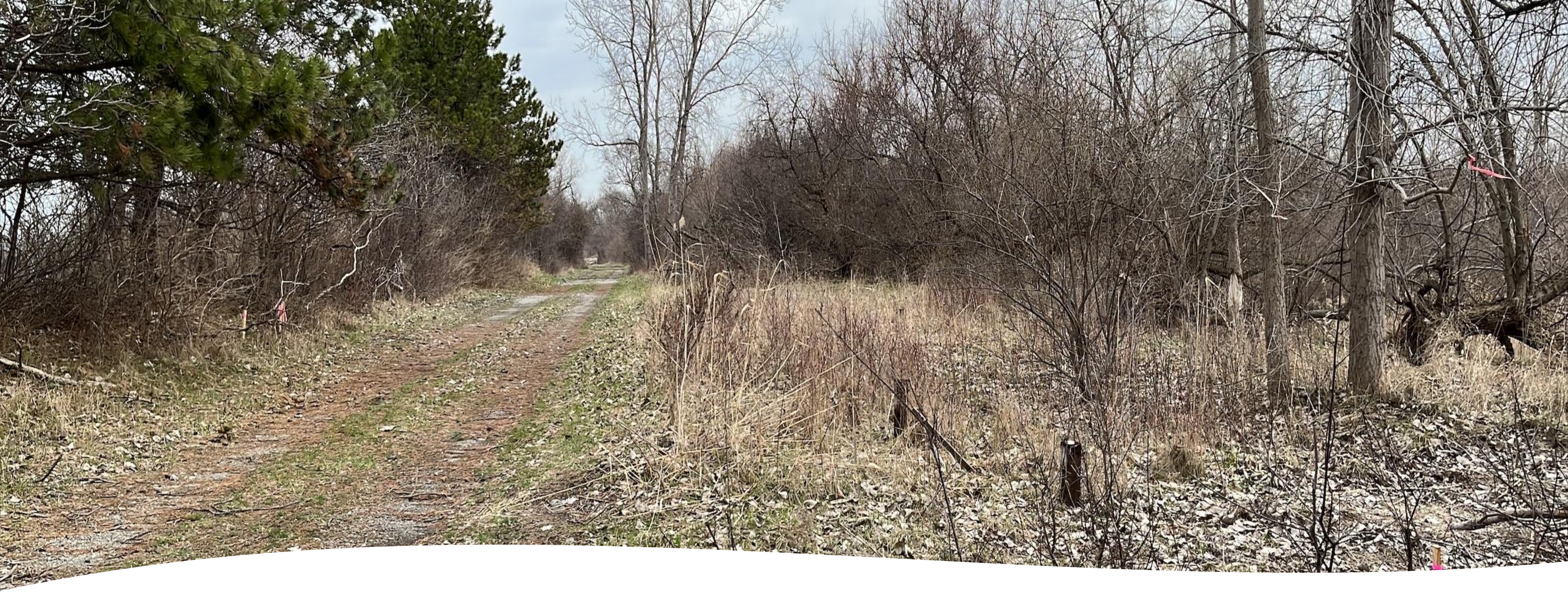
Point Hennepin Update

December 4, 2024



Agenda

- Phase I Approach
- Sampling Results
- Biogeochemcial Assessment
- Summary and Path Forward

Phase I Approach

- Channel hydraulic evaluation and close data gap
  - Could not retrieve transducer in PZ-11 so redeployed transducers on 7/8. Removed 10/11 and analysis ongoing.

- Evaluate COC concentrations at the perimeter of the island in areas of higher priority. Monitoring 10 piezometers quarterly
  - PZ-01S/D, PZ-02S/D, PZ-03S/D, PZ-08S/D, and PZ-09S/D sampled.
  - Q3 2024 - event completed in July and presented for discussion in this presentation
  - Q4 2024 - event completed in October. Data undergoing validation
  - Q1 2025 – as early in the quarter a possible, weather dependent

- Evaluate biological and geochemical conditions

Basis for Sampling Locations

Higher Priority

Response to surface water visible in groundwater data
Consistent outward gradient
Consistent GW levels higher than SW
Higher K zones; Higher estimated potential GW flux

Lower Priority

Limited or no response to SW in GW
Inward gradient or seasonal/low outward gradient
SW seasonally higher than GW levels
Lower K zones; Lower potential GW flux

SAMPLING RESULTS

VOCs

- Detections but no FAV or GSI exceedances of VOCs
- Elevated RLs in PZ-03D, will work with lab on lowering RLs during subsequent sampling

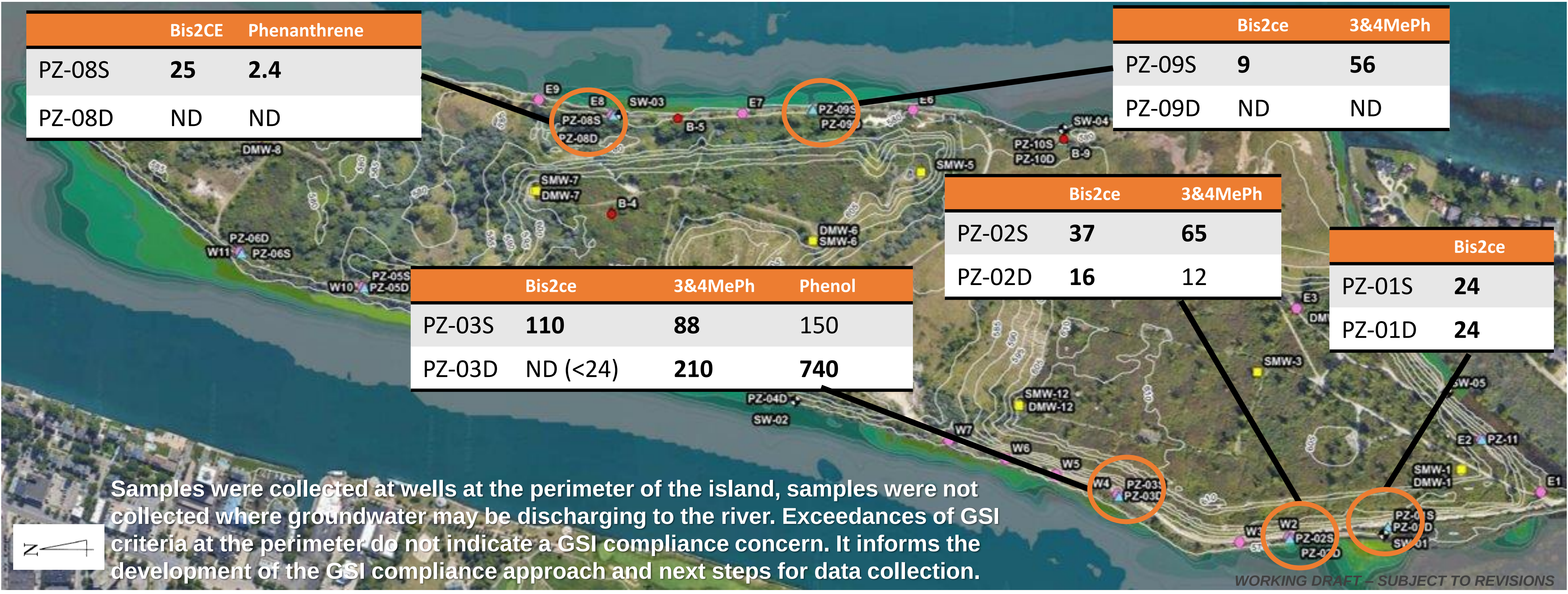
Samples were collected at wells at the perimeter of the island, samples were not collected where groundwater may be discharging to the river. Exceedances of GSI criteria at the perimeter do not indicate a GSI compliance concern. It informs the development of the GSI compliance approach and next steps for data collection.

SVOCs

BOLD = GSI criteria exceedance
Underline = FAV exceedance
All concentration units are μg/L
ND = non-detect

Criteria	GSI	FAV
Bis(2-chloroethyl)ether (Bis2ce)	**1.0**	680
3 & 4 Methylphenol (3&4MePh)	**30**	2500
Phenanthrene	**2.0**	240
Phenol	**450**	8500

No FAV Exceedances



	Bis2CE	Phenanthrene
PZ-08S	**25**	**2.4**
PZ-08D	ND	ND

	Bis2ce	3&4MePh
PZ-09S	**9**	**56**
PZ-09D	ND	ND

	Bis2ce	3&4MePh
PZ-02S	**37**	**65**
PZ-02D	**16**	12

	Bis2ce
PZ-01S	**24**
PZ-01D	**24**

	Bis2ce	3&4MePh	Phenol
PZ-03S	**110**	**88**	150
PZ-03D	ND (<24)	**210**	**740**

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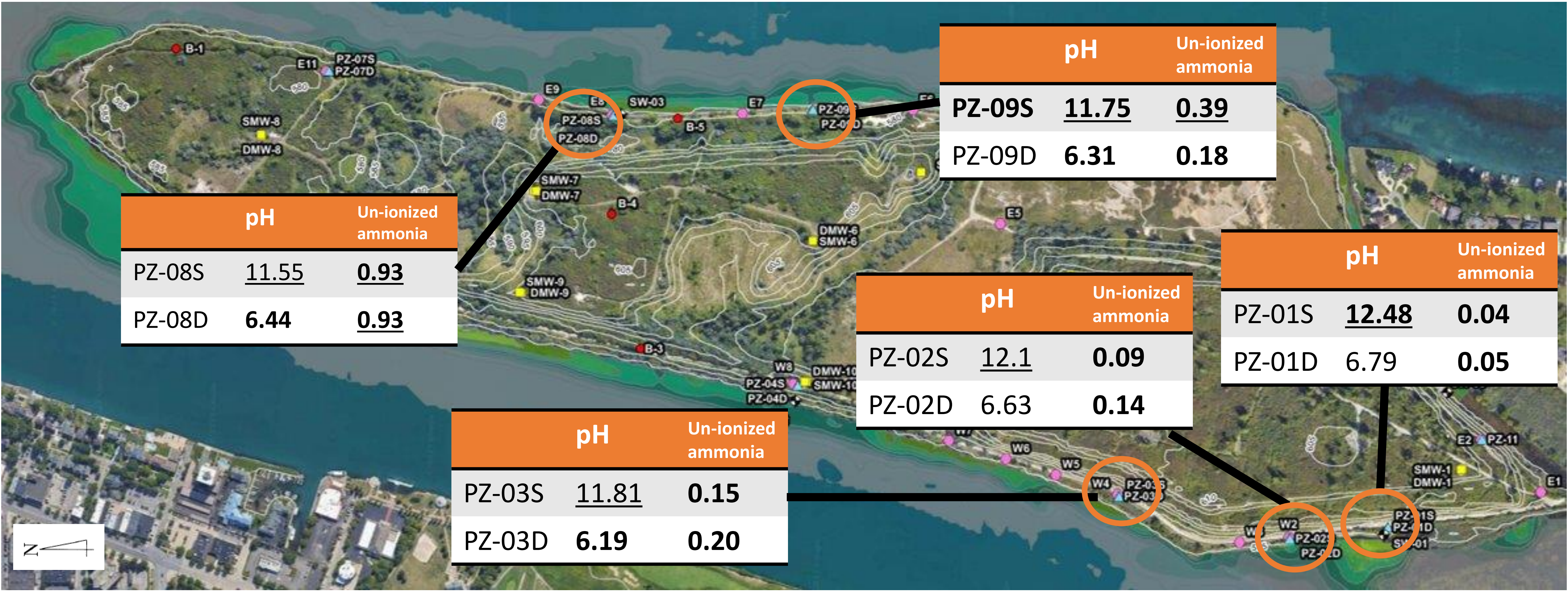
pH and Un-ionized Ammonia

ARCADIS

BOLD = GSI criteria exceedance
<u>Underline</u> = FAV exceedance
Un-ionized Ammonia concentration units are µg/L

Criteria	GSI	<u>FAV</u>
pH	**6.5-9**	<u>>9</u>
Un-ionized ammonia	**0.029**	<u>0.32</u>



	pH	Un-ionized ammonia
PZ-09S	<u>**11.75**</u>	<u>**0.39**</u>
PZ-09D	**6.31**	**0.18**

	pH	Un-ionized ammonia
PZ-08S	<u>11.55</u>	<u>**0.93**</u>
PZ-08D	**6.44**	<u>**0.93**</u>

	pH	Un-ionized ammonia
PZ-01S	<u>**12.48**</u>	**0.04**
PZ-01D	6.79	**0.05**

	pH	Un-ionized ammonia
PZ-02S	<u>12.1</u>	**0.09**
PZ-02D	6.63	**0.14**

	pH	Un-ionized ammonia
PZ-03S	<u>11.81</u>	**0.15**
PZ-03D	**6.19**	**0.20**

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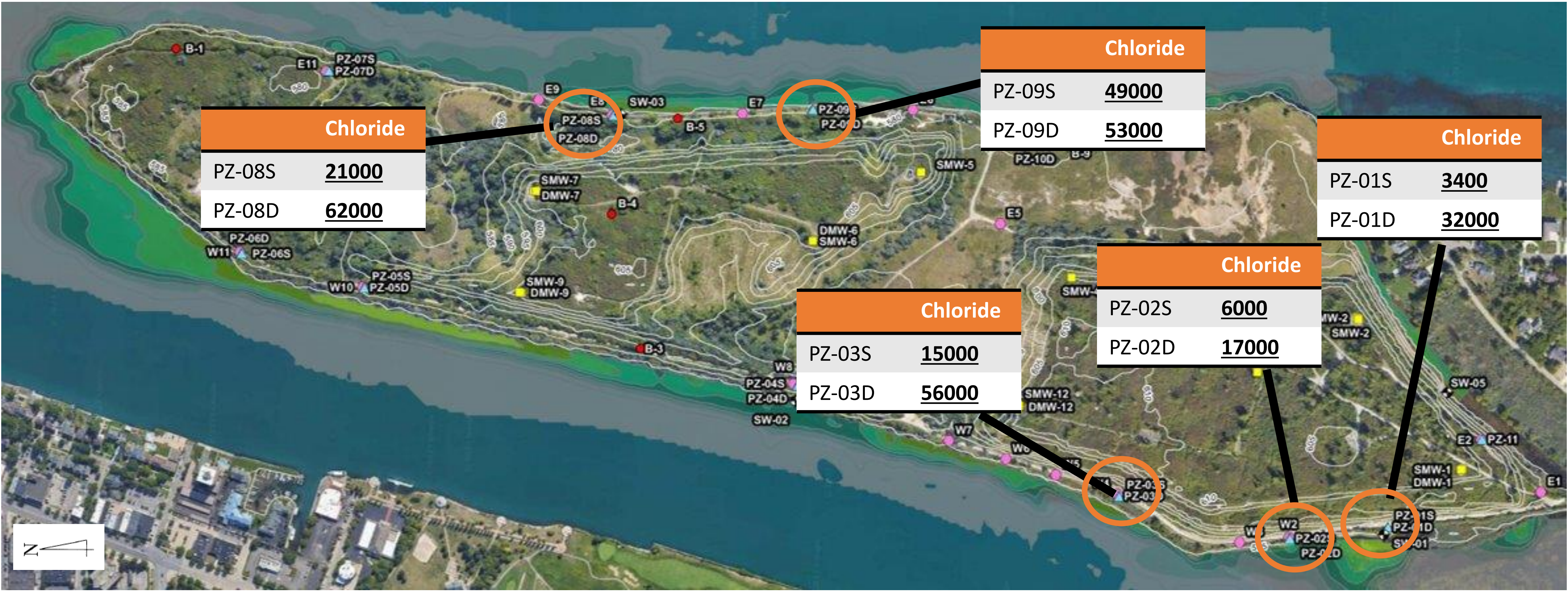
Chloride

ARCADIS

BOLD = GSI criteria exceedance
Underline = FAV exceedance
All concentration units are mg/L

Criteria	GSI	FAV
Chloride	**50**	640



	Chloride
PZ-08S	**21000**
PZ-08D	**62000**

	Chloride
PZ-09S	**49000**
PZ-09D	**53000**

	Chloride
PZ-01S	**3400**
PZ-01D	**32000**

	Chloride
PZ-02S	**6000**
PZ-02D	**17000**

	Chloride
PZ-03S	**15000**
PZ-03D	**56000**

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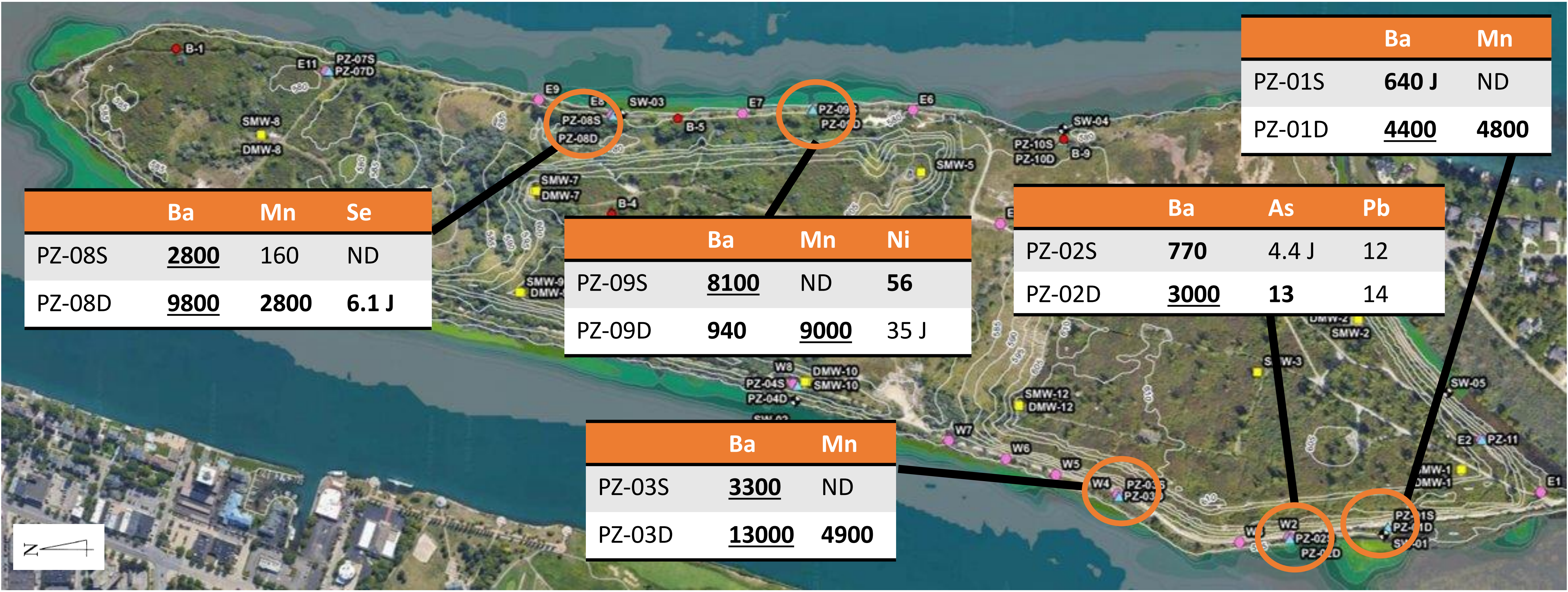
ARCADIS

Metals -Total

Criteria	GSI	FAV
Arsenic (As)	**10**	680
Barium (Ba)	**440**	2500
Lead (Pb)	**14**	240
Manganese (Mn)	**1300**	8500
Nickel (Ni)	**52**	940
Selenium (Se)	**5**	120

BOLD = GSI criteria exceedance
Underline = FAV exceedance
ND = Non-detect
J = estimated concentration less than the quantitation limit
All concentration units are μg/L



	Ba	Mn
PZ-01S	**640 J**	ND
PZ-01D	**4400**	**4800**

	Ba	Mn	Se
PZ-08S	**2800**	160	ND
PZ-08D	**9800**	**2800**	**6.1 J**

	Ba	Mn	Ni
PZ-09S	**8100**	ND	**56**
PZ-09D	**940**	**9000**	35 J

	Ba	As	Pb
PZ-02S	**770**	4.4 J	12
PZ-02D	**3000**	**13**	14

	Ba	Mn
PZ-03S	**3300**	ND
PZ-03D	**13000**	**4900**

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GSI Compliance Approach

- Potential GSI compliance approaches may include (but are not limited to):
  - ★ **Mixing zones** for COCs that are not bioaccumulative and do not exceed the final acute value for aquatic life;
  - ★ **Alternative monitoring points** designed to measure COCs in groundwater that is venting at the GSI;
  - – **Ecological assessments** to evaluate the likelihood of adverse ecological effects as a result of exposure of aquatic life and/or wildlife to COCs in venting GW;
  - ★ **Modeling assessments** to determine compliance with the GSI pathway using scientifically valid modeling approaches that are calibrated and verified with site-specific field data;
  - ★ **Natural attenuation** demonstration in accordance with published reference documents;
  - ★ **Technical Impracticability** is the inability to achieve certain requirements based on engineering feasibility / reliability, cost, and risk-based considerations;
  - ★ **Passive or active remediation** where treatment is required to reduce concentrations of COCs to below applicable GSI criteria prior to groundwater venting to surface water.
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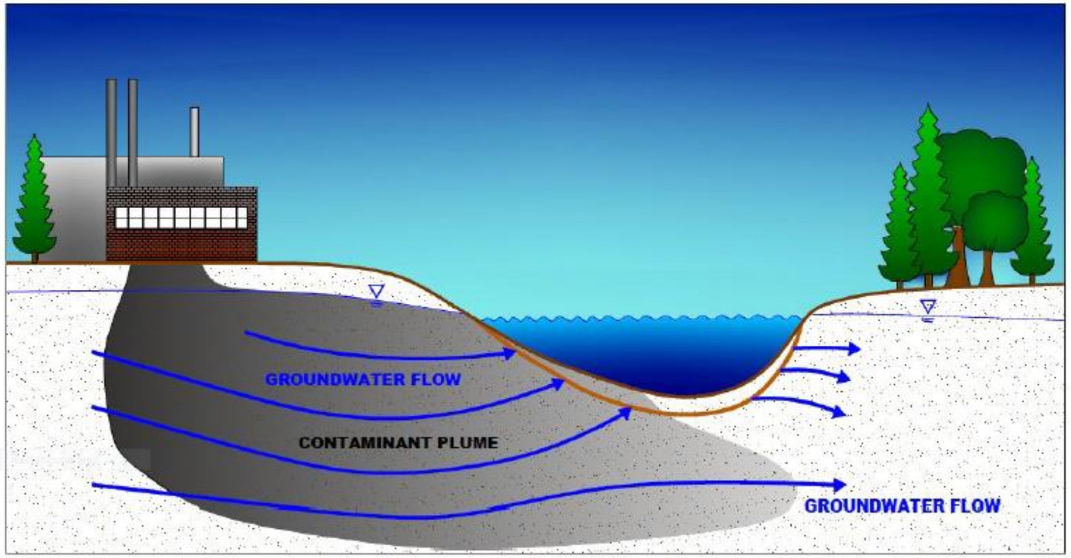
GROUNDWATER-SURFACE WATER INTERFACE PATHWAY COMPLIANCE OPTIONS

REMEDIATION AND REDEVELOPMENT DIVISION
RESOURCE MATERIALS



Adapted from US EPA, Proceedings of the Groundwater/Surface-Water Interactions Workshop, EPA/542/R-00/007, July 2000

EGLE GSI TAPs Team Input will be critical during the development of Phase 2

Q3 2024 Analytical Data Summary

GSI Compliance Approach - Utilize a mixing zone for COCs that exceed GSI but are not bioaccumulative and do not exceed the final acute value for aquatic life.

Remaining locations with COCs above FAV:

PZ	pH	Un-Ionized Ammonia	Chloride	Ba	Mn
PZ-01S	✓		✓		
PZ-01D			✓	✓	
PZ-02S	✓		✓		
PZ-02D			✓	✓	
PZ-03S	✓		✓	✓	
PZ-03D			✓	✓	
PZ-08S	✓	✓	✓	✓	
PZ-08D		✓	✓	✓	
PZ-09S	✓	✓	✓	✓	
PZ-09D			✓		✓

Mercury- Was not on the Work Plan COC List and not analyzed in Q3 but will be included in subsequent quarterly events

BIOGEOCHEMICAL ASSESSMENT

Biogeochemical Assessment

Over time, the Site has established a population of microbes that have adapted to the Site conditions

Purpose of the biogeochemical evaluation is to identify the microbial populations present (to the extent practical) and evaluate the processes they are undergoing.

By understanding these microbial populations and processes, we can:

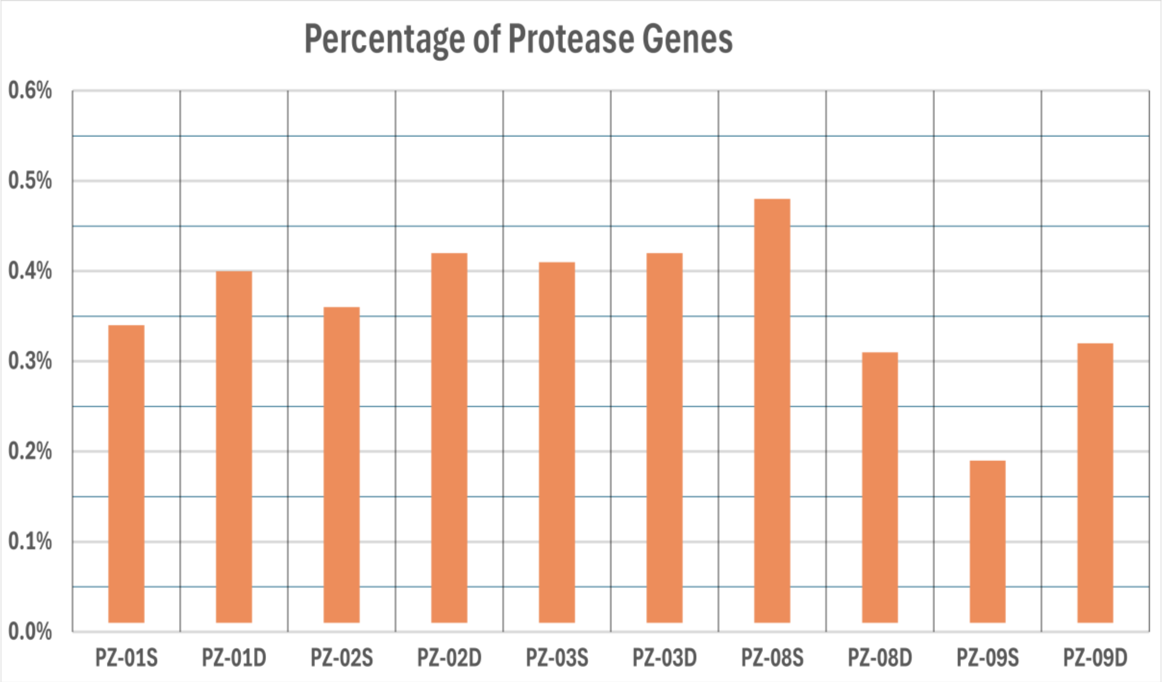
- Enhance our understanding of the Conceptual Site Model
- Evaluate how the microbial community relates to the COCs on Site, specifically those that exceed FAV
- Explore sustainable approaches utilizing the naturally occurring microbial processes to achieve GSI compliance

Tri-valent Nitrogen Production

Un-ionized ammonia – NH_3, toxic to aquatic life, generally present at higher pH
Ammonium or Ionized Ammonia = NH_4^+, generally present at neutral pH

} Tri-valent nitrogen

- Protease is an enzyme that allows microbes to biodegrade proteins, generating tri-valent nitrogen as a by product
- All wells have microbes with protease
- This process likely generates dissolved phase tri-valent nitrogen concentrations observed in the groundwater at the site
- Proteins are available from peat, organic materials used to fill in the sinkholes, and river sediments

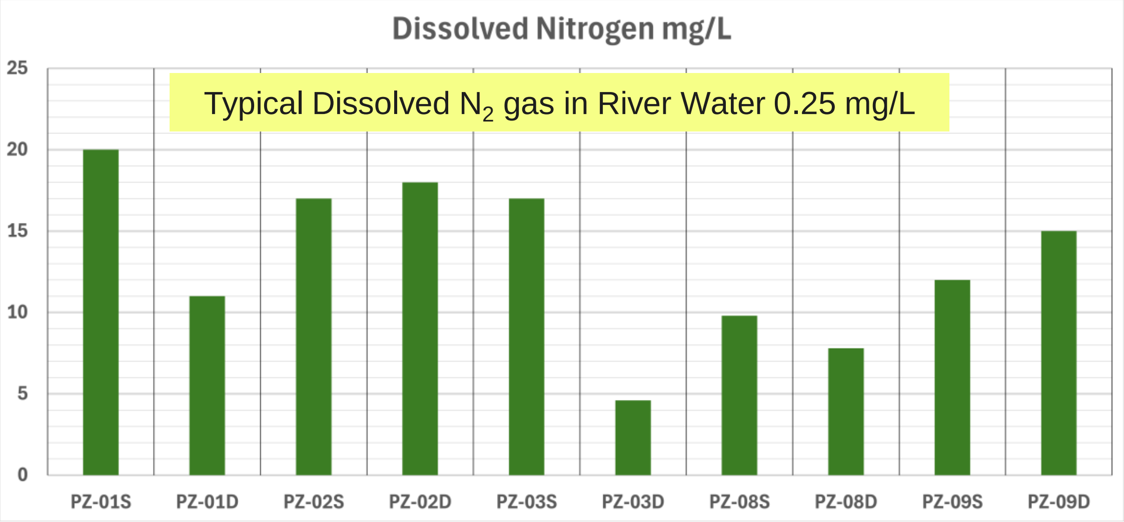


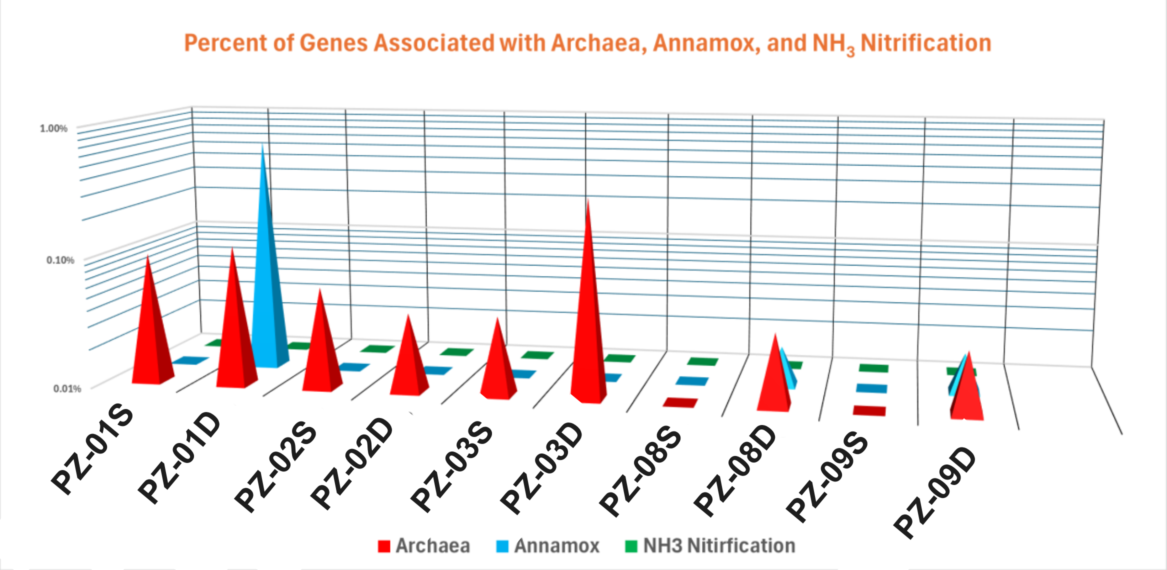
Tri-valent nitrogen is being produced at all well locations – why do we not have high levels (ie exceeding FAV) at all locations?

Tri-valent Nitrogen Utilization

Tri-valent nitrogen is currently being utilized in a variety of ways!

- Nitrification Process - Tri-valent nitrogen (ammonia/ammonium) can react with oxygen to form nitrate. Microbes can use nitrate for energy and form nitrogen gas.
  - Presence of nitrogen gas above typical river levels indicates that nitrification is occurring
  - However – we did not see the markers we expected related to nitrification
- Anamox - anaerobic process where bacteria convert tri-valent nitrogen to nitrogen gas (relatively newly discovered process), identified in PZ-01D, PZ-08D, and PZ-09D
- Archea – microbes that thrive in extreme environments (i.e high TDS and pH), they can transform tri-valent nitrogen into nitrate and through assimilation consume tri-valent nitrogen,
  - Archaea is present at all wells with the exception of PZ-08S and PZ-09S where we see the highest un-ionized ammonia concentrations

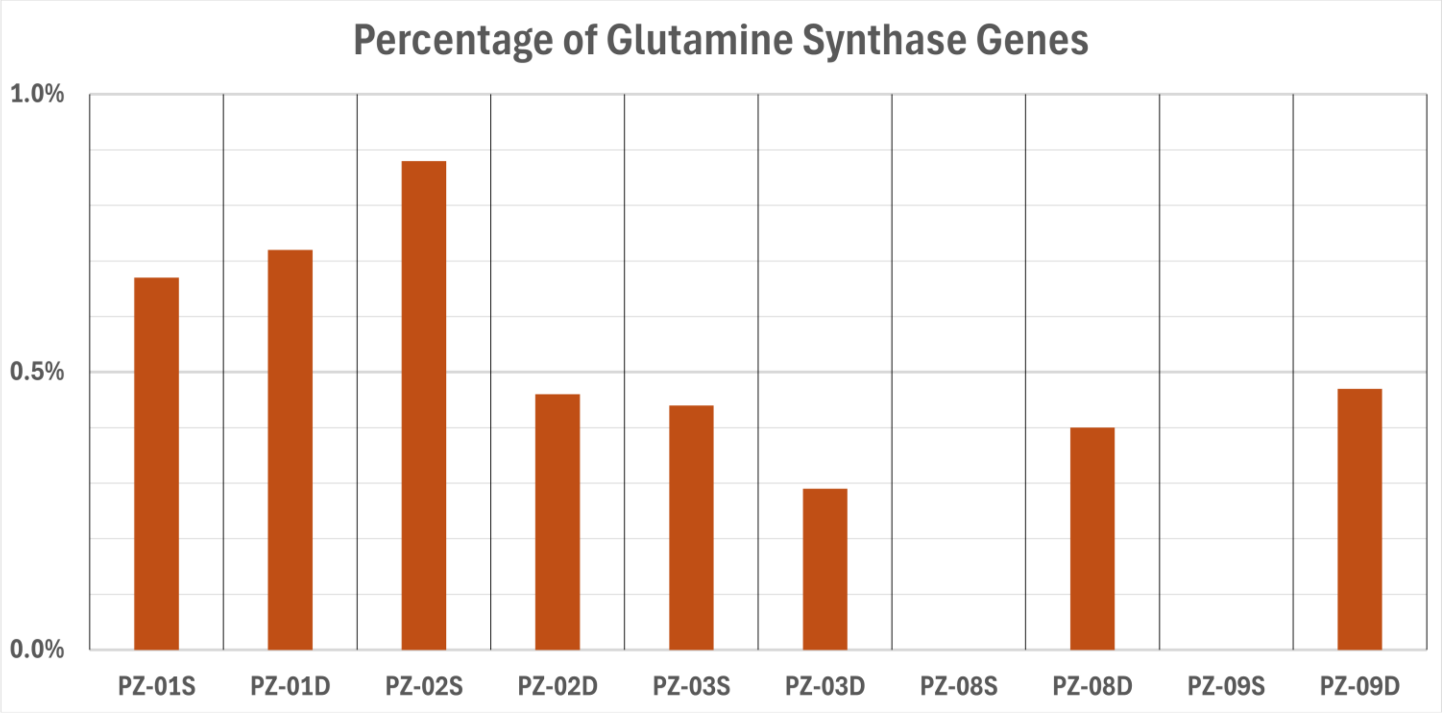




Tri-valent Nitrogen Utilization (cont)

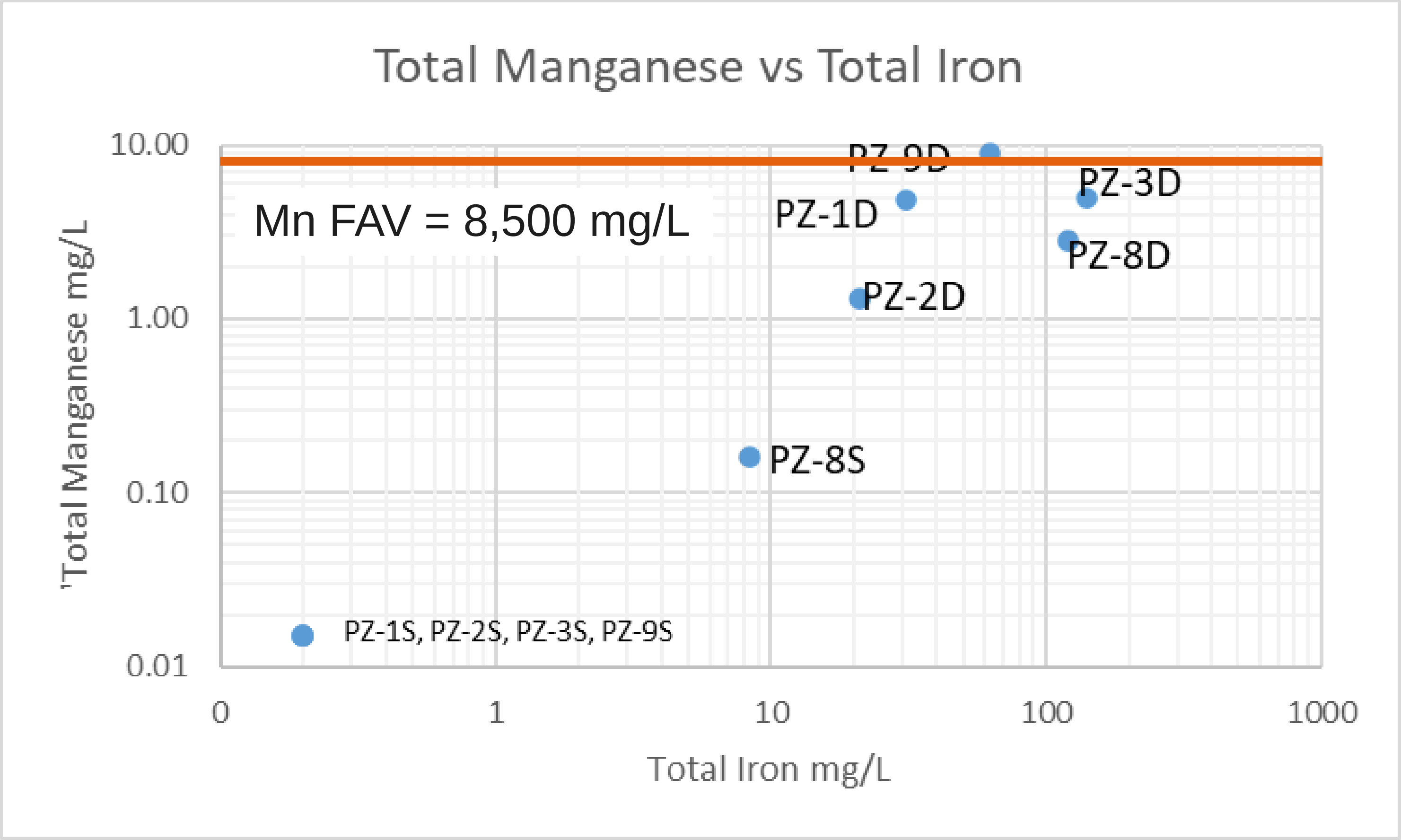
Trivalent nitrogen is currently being generated and utilized in a variety of ways!

- Assimilative Process – Microbes consume the trivalent nitrogen and incorporate it into their biomass.
- Allows microbes to thrive and reproduce
- Glutamine Synthase is a key enzyme used in the assimilative process
- Glutamine Synthase is present in all locations except PZ-08S and PZ-08D



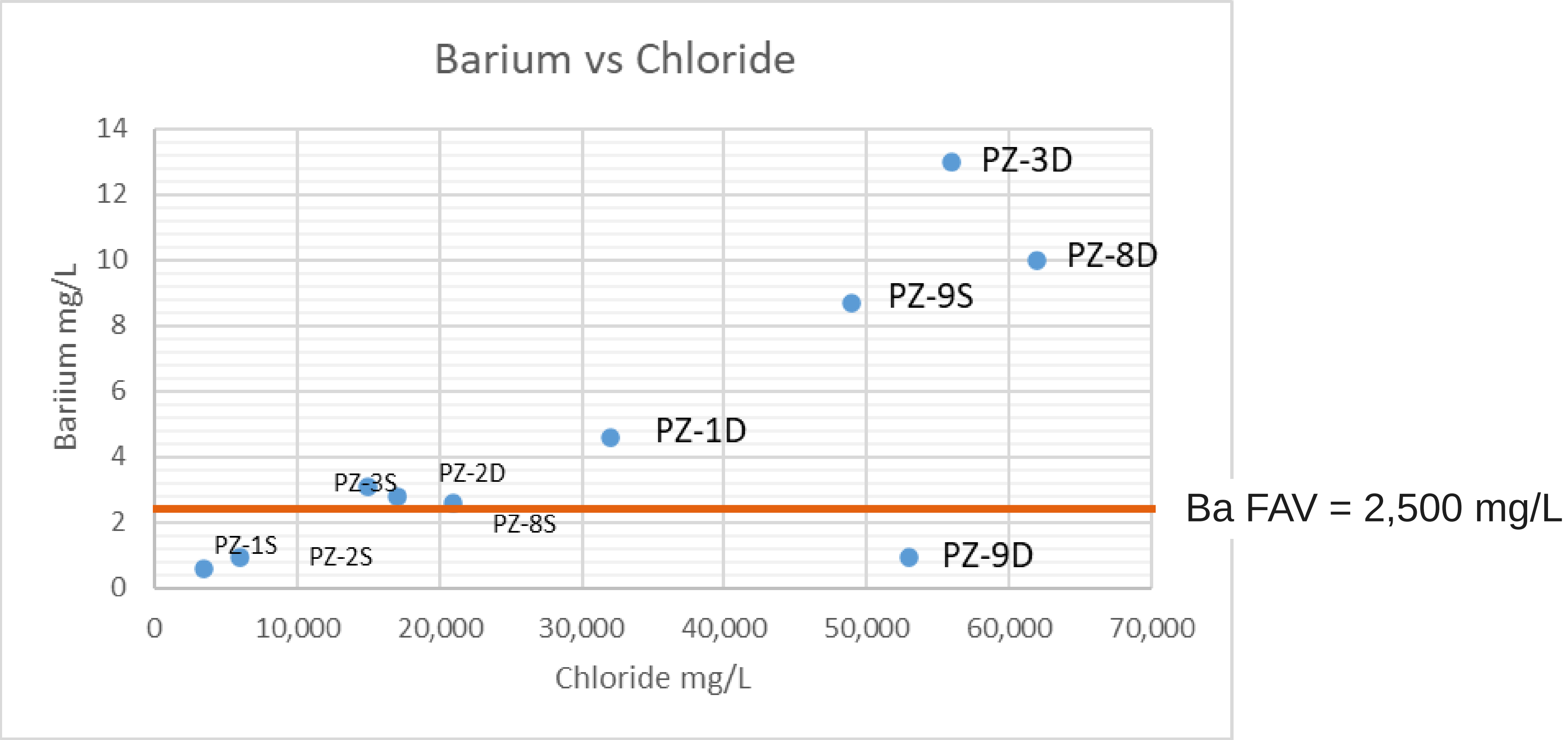
Iron and Manganese Relationship

- Manganese is associated with iron reduction.
- Native iron oxides are being reduced by indigenous iron reducing microbes, increasing dissolved iron concentrations
- Under Site conditions dissolved manganese is produced along with dissolved iron



Barium Solubility Influenced by Dissolved Chlorides

The solubility of barium sulfate (associated with salt mining activities) is enhanced by the presence of chlorides (also associated with salt mining)



SUMMARY AND PATH FORWARD

Summary

- Limited exceedances of FAV criteria for un-ionized ammonia and manganese
  - Native microbe population is creating tri-valent nitrogen from organic materials (peat, organic material used to fill sinkhole, river sediment).
  - Native microbe population is utilizing tri-valent nitrogen. Utilization processes (nitrification, Anamox, Archea, and assimilation) are the reason that tri-valent ammonia is not elevated across the Site.
  - Manganese is associated with iron reduction. Native iron oxides are being reduced by indigenous iron reducing microbes, which releases manganese
- Elevated pH limited to shallow interval
- Chloride and barium is likely associated with salt mining activities. Solubility of barium in enhanced by presence of chloride.

Path Forward

- Evaluate hydraulic data from PZ-11
- Quarterly monitoring will continue Q1 and Q2 2025 (including Hg) to evaluate trends
- Considering additional genomic sequencing to try to identify nitrification markers:
  - Do we need to understand the exact microbes/processes that are responsible for nitrification?
- Isotopic evaluation of tri-valent nitrogen:
  - Is the tri-valent nitrogen being generated from native or anthropogenic sources?
- Evaluation of next steps as it relates to the FAV exceedances and GSI compliance:
  - Consider relevance and/or information needed for other GSI compliance strategies (i.e. natural attenuation, modeling, etc.)
  - Potential alternate GSI sampling
  - Is there something missing (e.g. oxygen, sulfate) that the microbial population needs for tri-valent nitrogen conversion at PZ-08S, PZ-08D, and PZ-09S locations that we can address easily/sustainably?