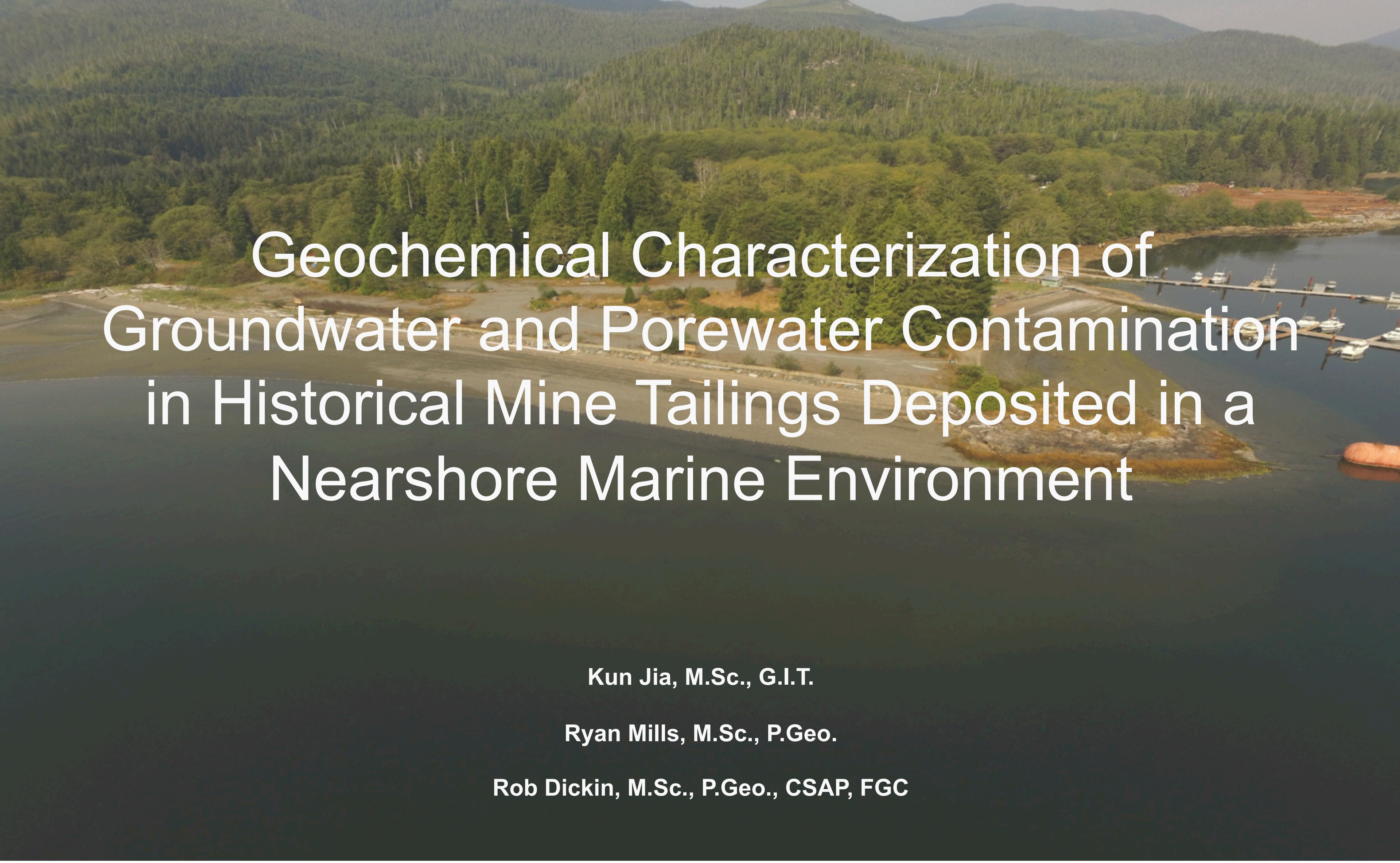

Geochemical Characterization of Groundwater and Porewater Contamination in Historical Mine Tailings Deposited in a Nearshore Marine Environment

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Overview

1. Background
2. Problem Definition
3. Hydrogeological Conceptual Model
4. Geochemical Characterization
5. Conclusions

Background - Site Location

- Located on the west coast of Vancouver Island near Ucluelet, British Columbia
- Tofino and Ucluelet are international tourist destinations
- Former Brynnor Mine located approximately 10 km northwest of Toquaht Bay Tailings Site

Background – Brynnor Iron Mine

- Mine operated in 1960's and produced very high grade iron ore (Fe_3O_4)
- Ore mechanically processed and magnetically separated prior to tailings discharge to ocean shoreline
- Site used as campground and boat launch for several decades
- High arsenic and cobalt levels identified in beach sand samples and porewater in 2013
- Campground closed for further investigation and remediation

Problem Definition – Local Study Area

Defined Three Areas:

Upland / Campground Area

- Above high tide mark (> +2m asl)

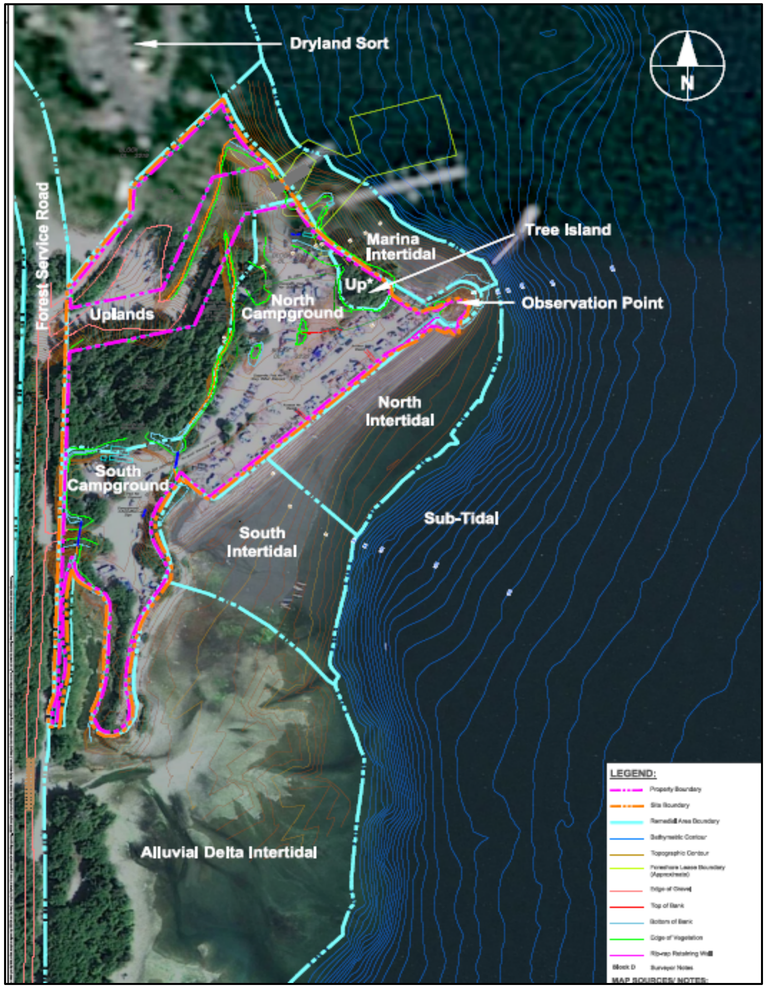
Shoreline and Intertidal Zone

- Between high tide mark (+2m asl) and low tide mark (-2m asl)

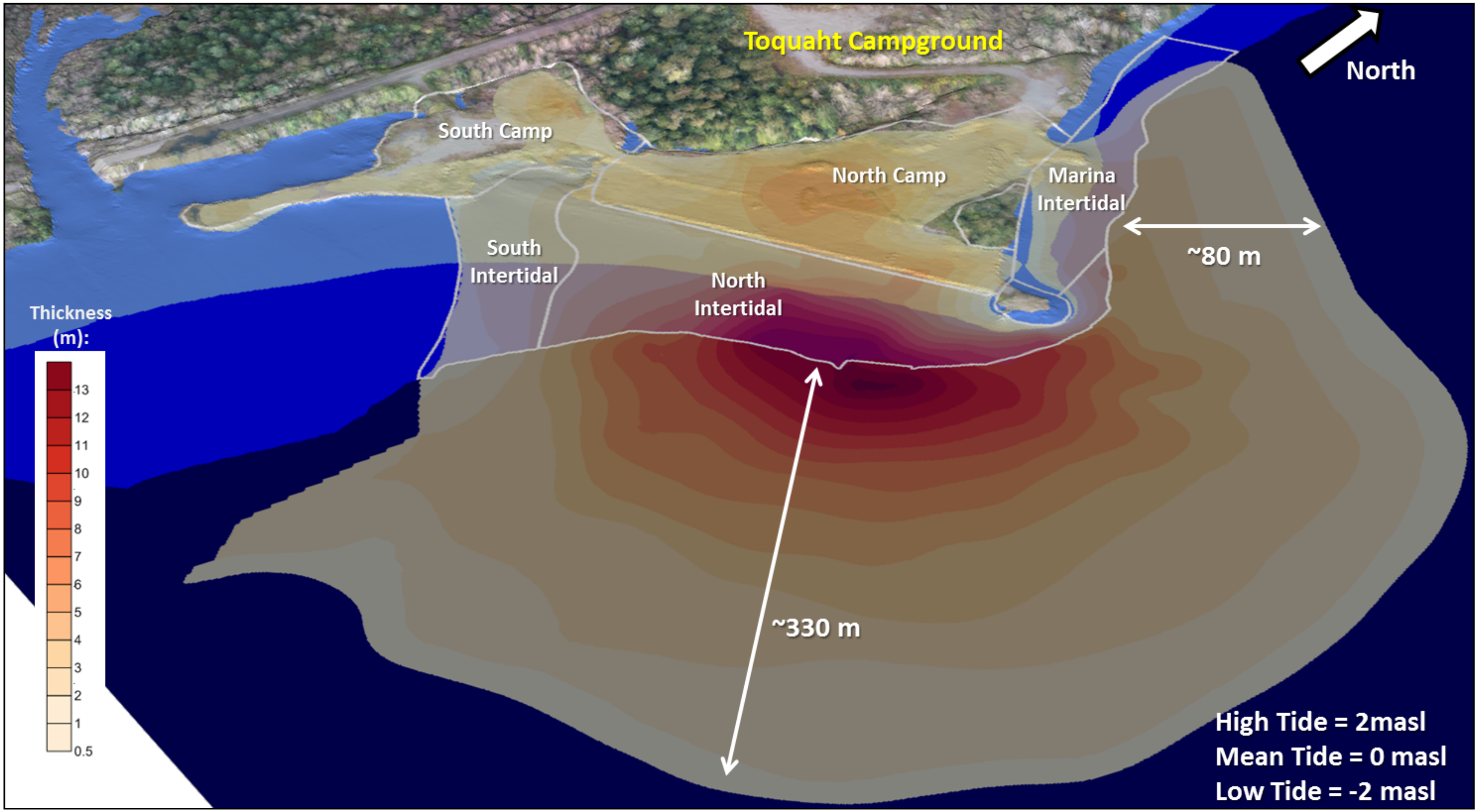
Sub-Tidal Area

- Below low tide mark (< -2m asl)



Problem Definition – Magnitude and Extent of Tailings



- Drilling, bathymetry and sub-bottom profiling surveys produced 3D model
- Found tailings to range from 0.5 - 13 meters thick (>1,000,000 m^3)

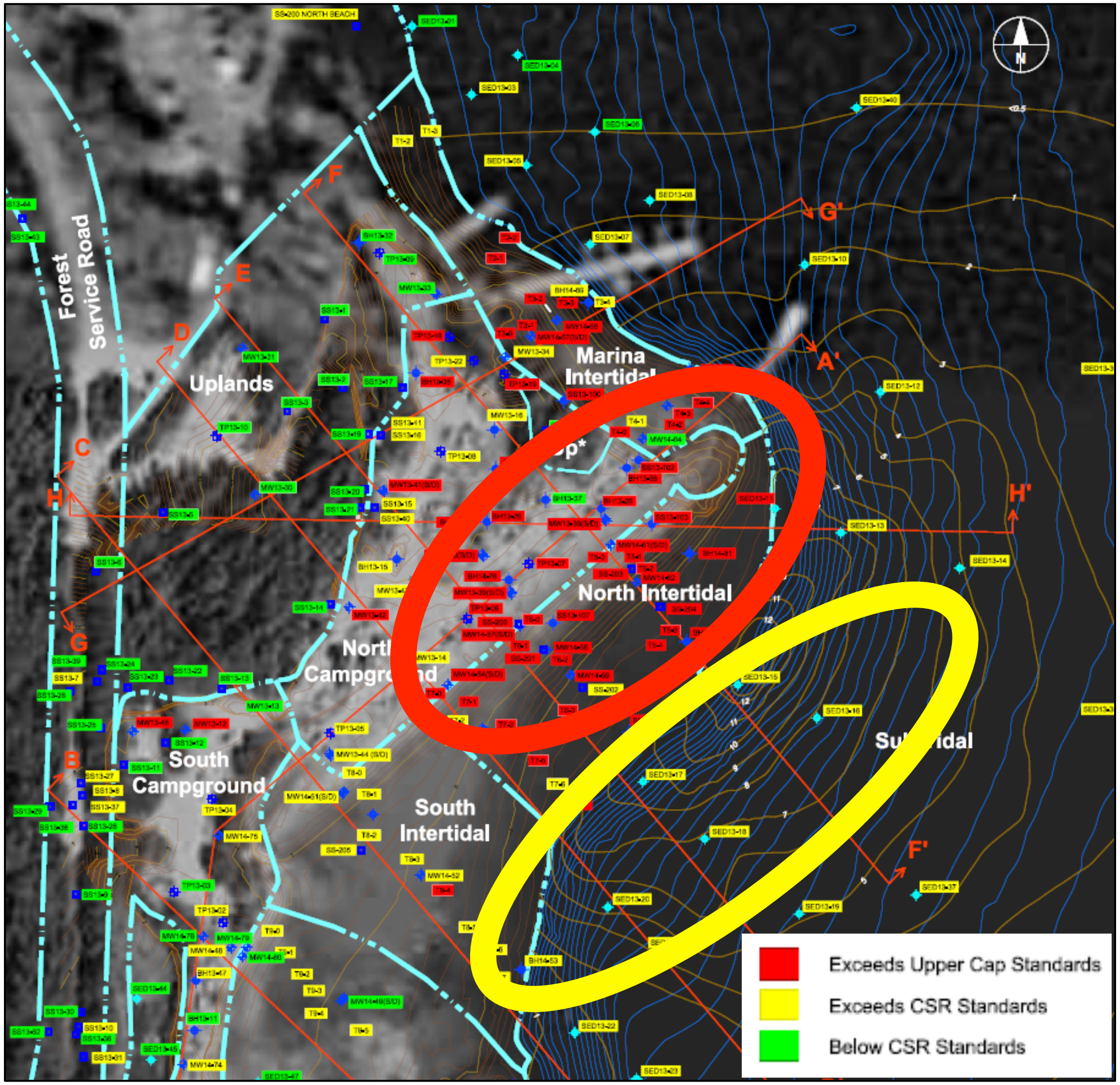
Problem Definition – Soil and Sediment Quality

Identified CoPCs:

- Arsenic
- Cobalt
- Copper
- Zinc

Major CoPCs:

- Arsenic
- Cobalt

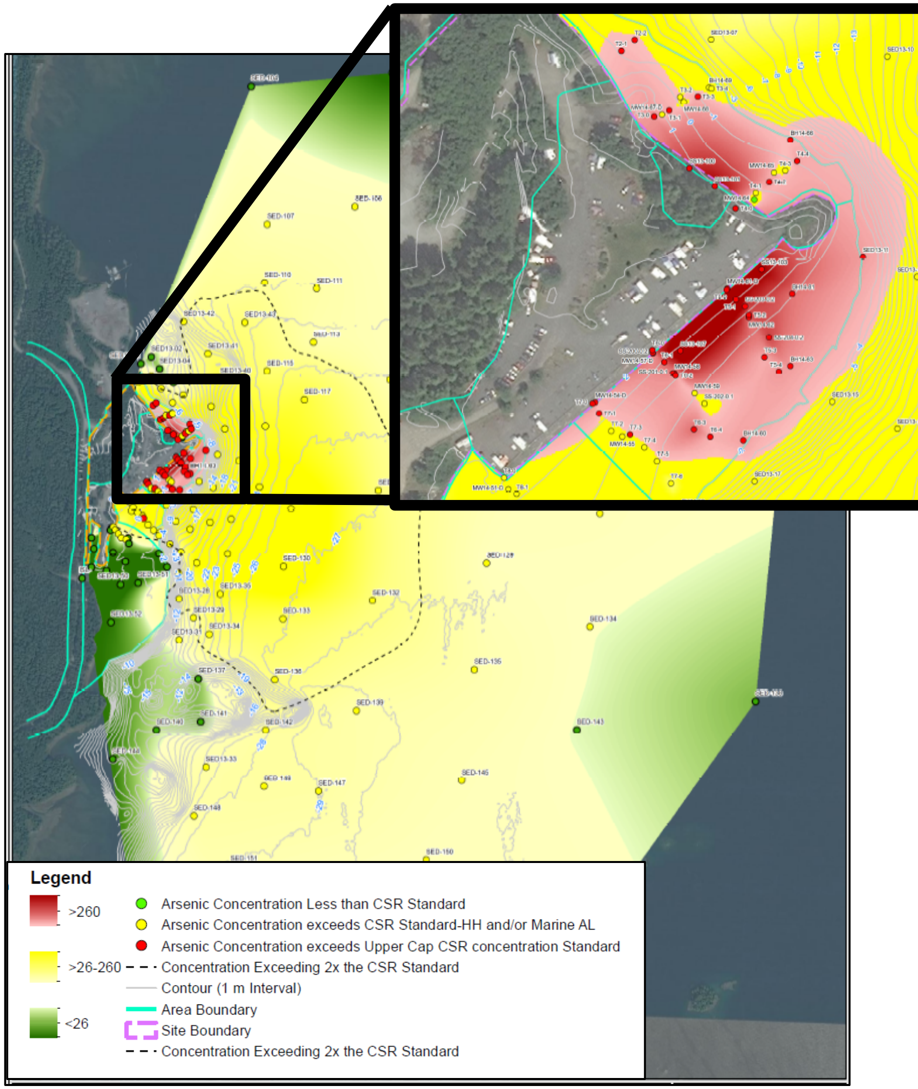


Problem Definition – Arsenic Impacted Sediments

- Highest in soil and sediment
- As > CSR Upper Cap (260 µg/g) in campground and intertidal (red)
- As > CSR (26 µg/g) extends up to 350m into subtidal (yellow)
- Cobalt follows similar patterns

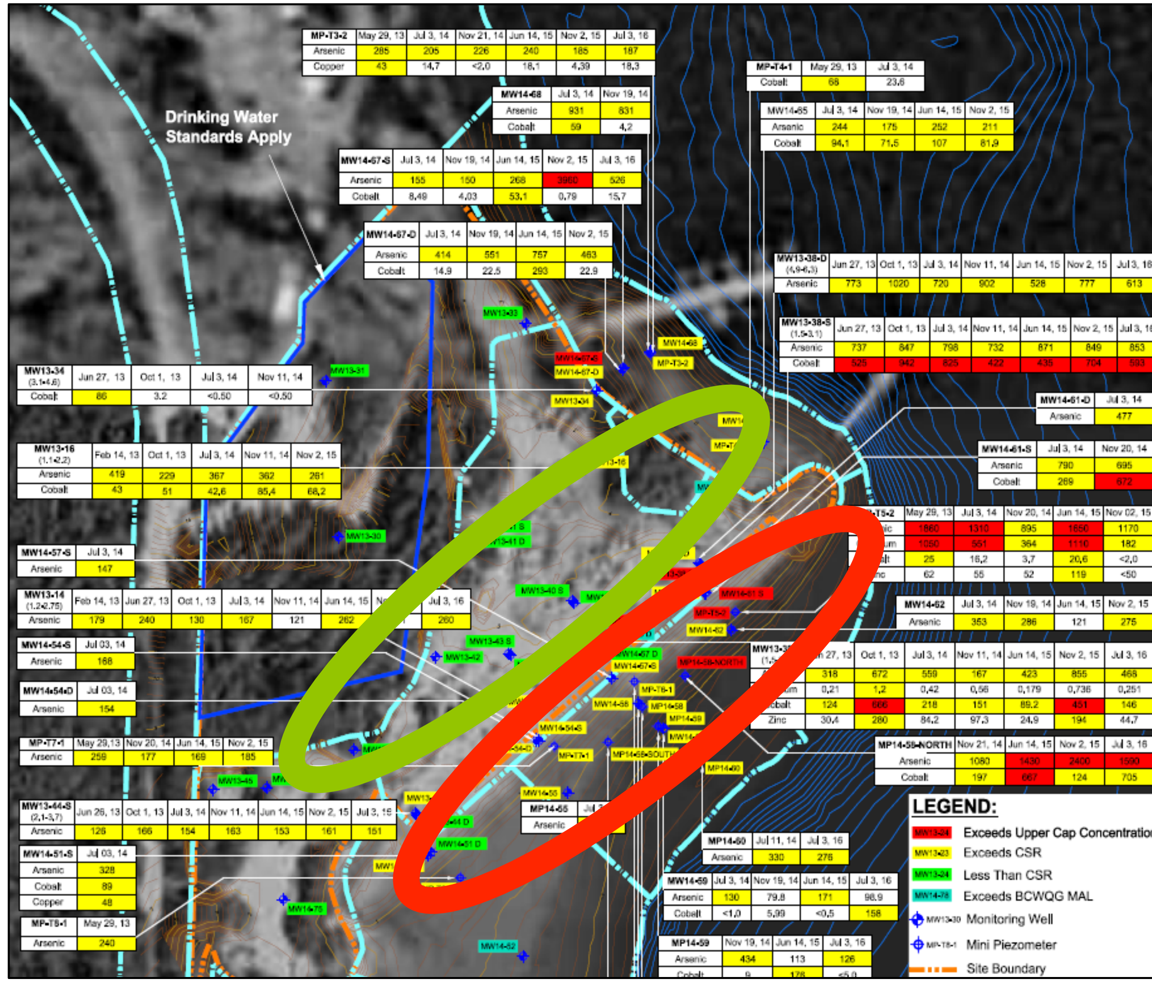
Overall:

Campground > Intertidal>Subtidal



Problem Definition – Groundwater Quality

- As in groundwater generally <CSR in Campground Area
- As in groundwater generally >CSR along shoreline and in Intertidal Zone
- Minimal to no impact on groundwater quality in deep confined aquifer
- Co issue over smaller footprint.



Problem Definition – Solid vs. Aqueous Concentrations

- No statistical correlation between concentrations of total metals in solid and aqueous phase.
- Dissolved As and Co concentrations are highest in groundwater in the Intertidal Zone.
- Dissolved metals concentrations more than 10x lower in Campground Area

Location	Mean Arsenic Concentration		Mean Cobalt Concentration	
	Groundwater (µg/L)	Soil/Sediment (µg/g)	Groundwater (µg/L)	Soil/Sediment (µg/g)
North Campground	16.1	1151	7.23	299
Intertidal Zone	340	420	76.9	124
Subtidal Zone	-	68.2	-	26.4

Problem Definition - Key Geochemical Questions

1. How does the groundwater flow regime change in response to tidal cycling?

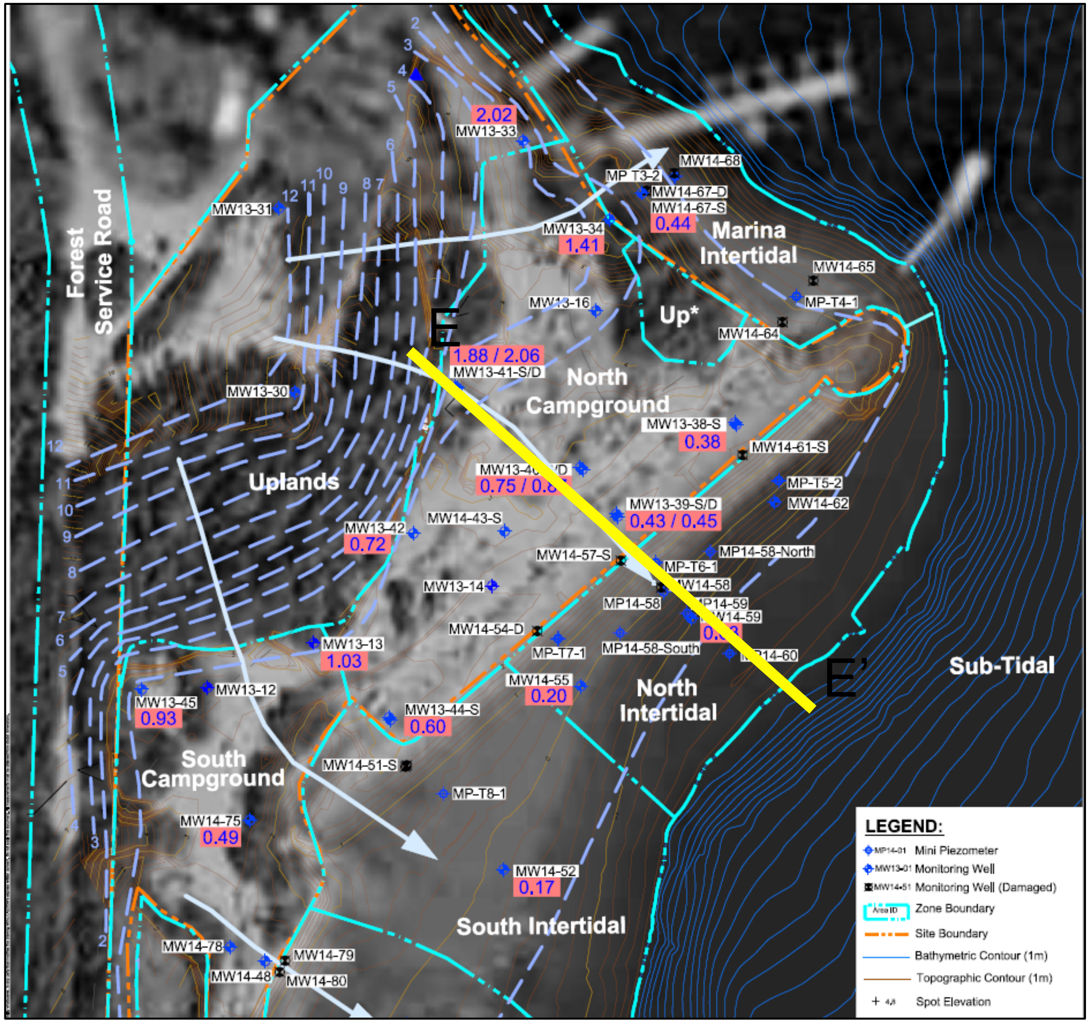
2. What minerals in the tailings produce elevated concentrations of As and Co in groundwater?

3. What geochemical reactions primarily control the release of As and Co from tailings in near-shore and Intertidal Zone groundwater?

4. How do redox conditions (e.g., DO, ORP and pH) and salinity affect the geochemical reactions that release or attenuate As and Co?

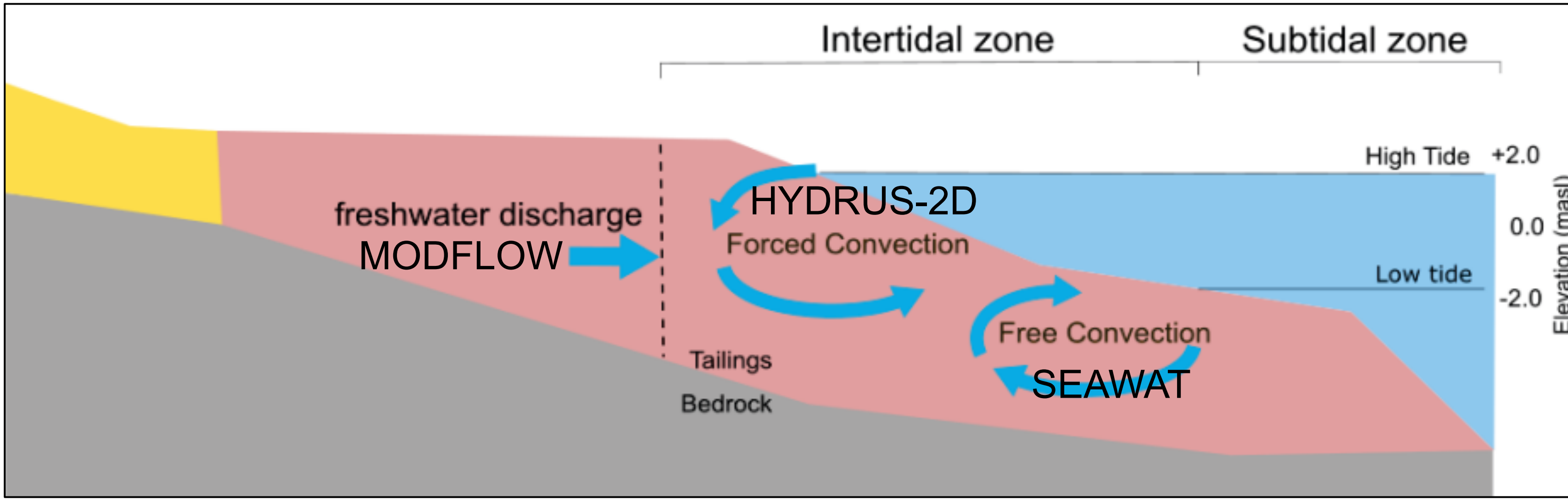
Conceptual Hydrogeological Model

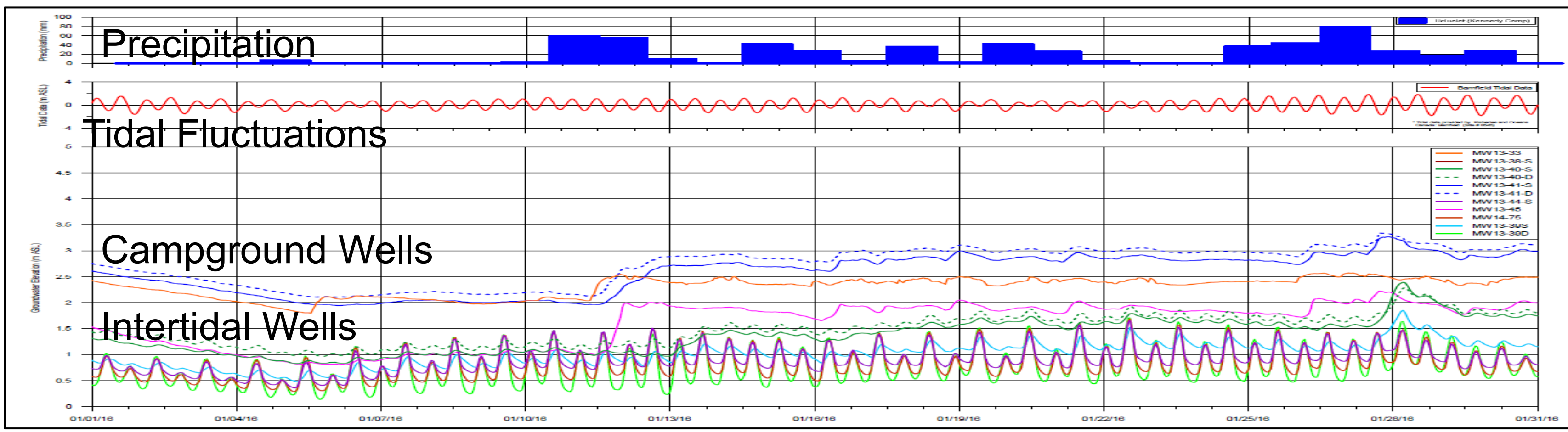
- Monitoring well network consists of 26 groundwater monitoring wells and 5 drive point piezometers
- Groundwater flow from northwest to southeast across the site towards the ocean.
- Groundwater flow generally through the tailings with discharge to the intertidal zone.



Conceptual Shallow Groundwater Flow in Tailings Aquifer

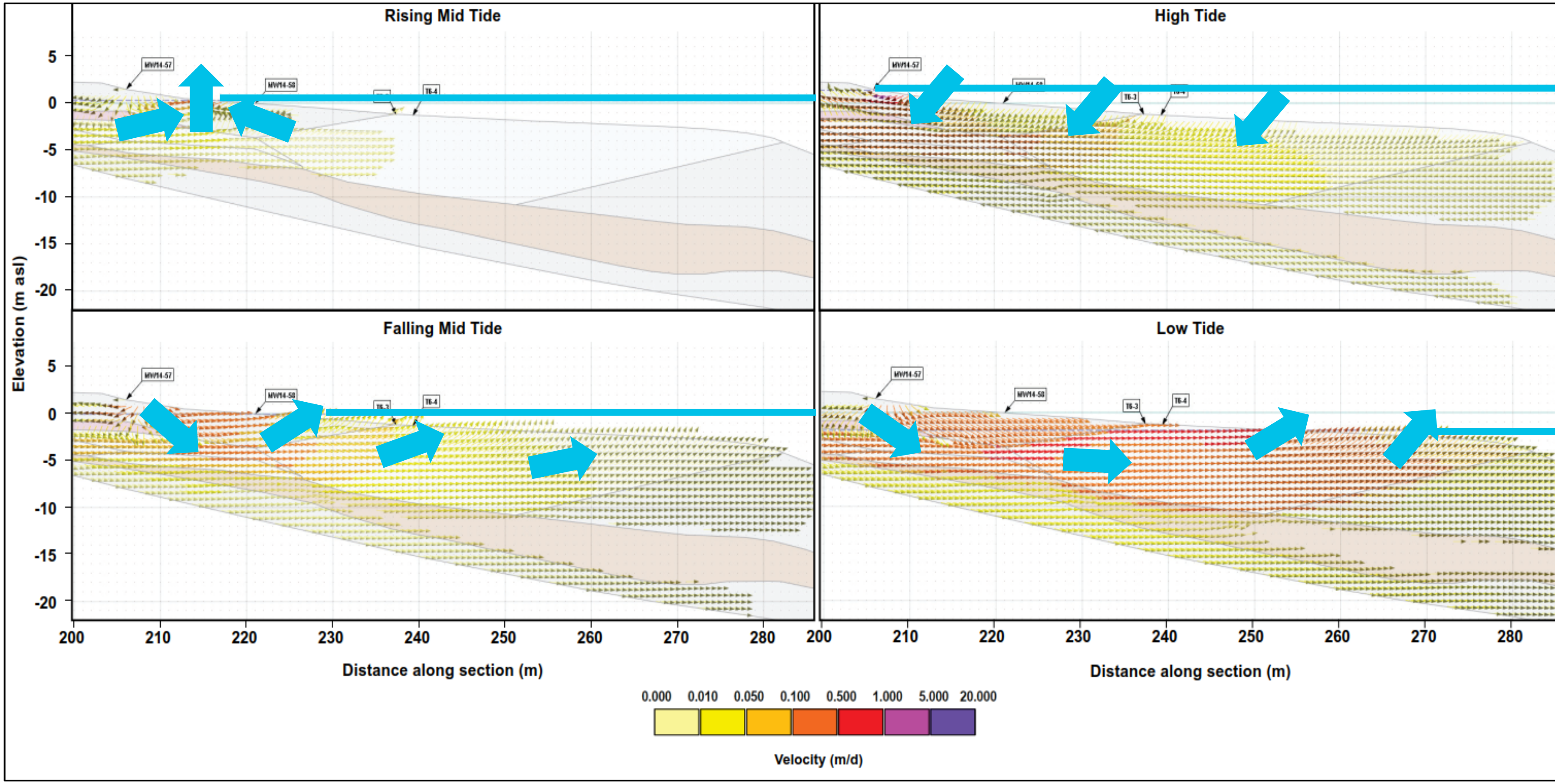
Hydrogeological Conceptual Model





Groundwater Elevations over Lunar Cycles (January 1-31, 2016)

Hydrogeological Conceptual Model – Tidal Cycling



HYDRUS 2D (sat/unsat) used to investigate impact of tidal cycling to aid in interpreting geochemistry. Calibrated to transient groundwater levels.

Geochemical Characterization - Solid Phase

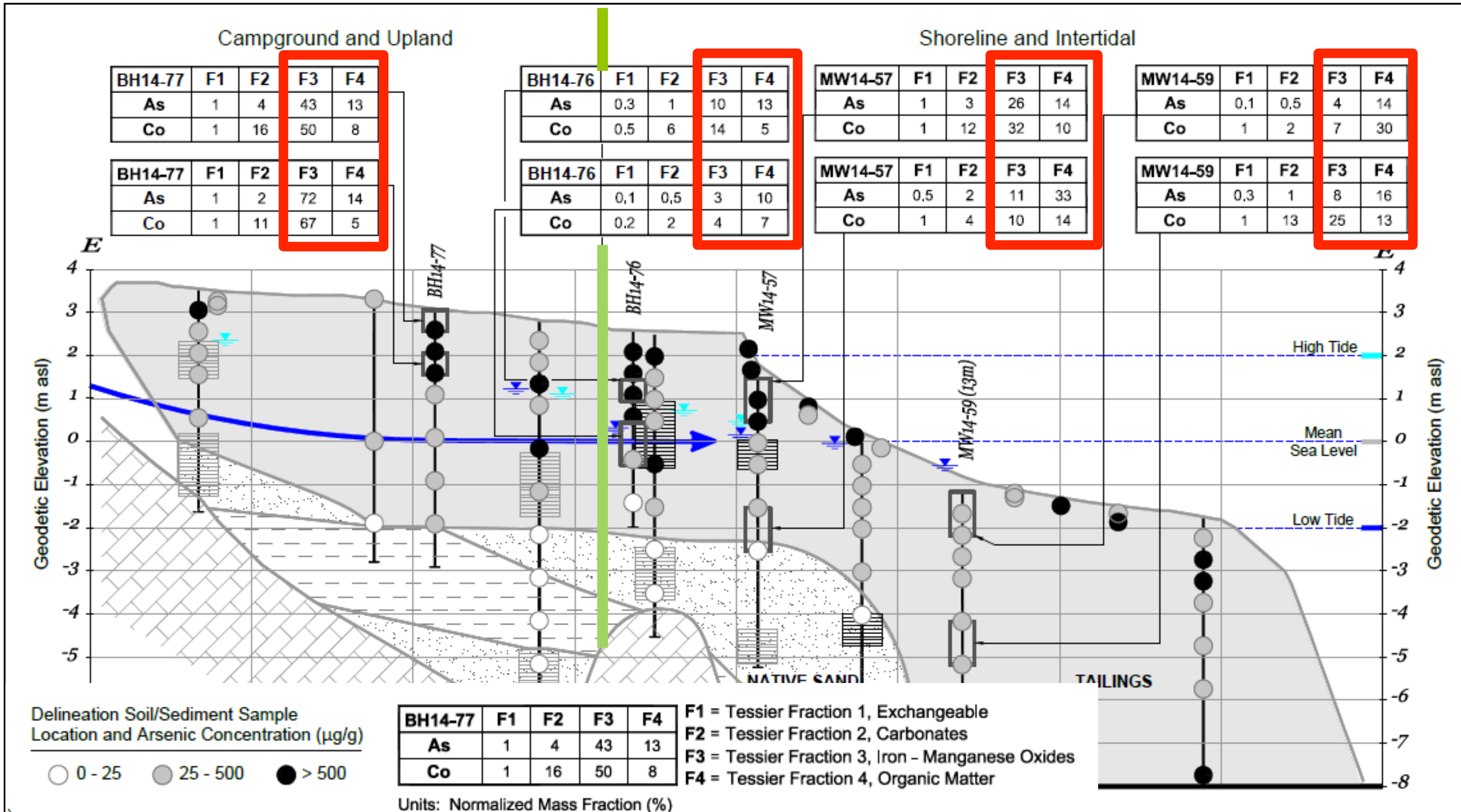
- Mineralogy Analysis on samples collected from mine wall rocks, waste dump and tailings.
- Sequential Leach Tests (Tessier et al. 1979) conducted to determine fraction of As and Co associated with various fractions:
  - Fraction 1 – Exchangeable ($MgCl_{2}$)
  - Fraction 2 – Bound to Carbonates (NaOAc)
  - Fraction 3 – Bound to Iron and Manganese Oxides ($NH_4OH \cdot HCl$)
  - Fraction 4 – Bound to Organic Matter (HNO_3, H_2O_2 and NH_4OAc)
  - Fraction 5 – Residual Forms (HF): Not completed
- Shake Flask Extraction with distilled water and seawater.
- Sequential Leach Tests and Shake Flask Extractions conducted on 8 samples collected from different geochemical (oxidation-reduction) zones and salinity zones.

Geochemical Characterization - Mineralogy

- Mineral sources for the main metal contaminants in the tailings (i.e., As, Co, Cu and Zn) are trace (<0.1%) amounts of the following sulphide minerals, present primarily in the skarn host rock:
  - Arsenic: Arsenopyrite ($FeAsS$)
  - Cobalt: Cobaltite ($CoAsS$)
  - Copper: Chalcopyrite ($CuFeS_2$)
  - Zinc: Sphalerite ($(ZnFe)S$)
- The host rocks include limestone and marble. There are sufficient carbonate minerals in the tailings to neutralize any acidity released during the oxidation of the trace quantities of sulphide minerals.
- Acid rock drainage is not an issue at this Site.

Geochemical Characterization - Sequential Leach Tests

- Campground Area: As and Co are more enriched in iron and manganese oxyhydroxides
- Shoreline and Intertidal zone: As and Co are generally less associated with iron and manganese oxyhydroxide, and more bound to organic matter



BH14-77	F1	F2	F3	F4
As	1	4	43	13
Co	1	16	50	8

BH14-77	F1	F2	F3	F4
As	1	2	72	14
Co	1	11	67	5

BH14-76	F1	F2	F3	F4
As	0.3	1	10	13
Co	0.5	6	14	5

BH14-76	F1	F2	F3	F4
As	0,1	0,5	3	10
Co	0.2	2	4	7

MW14-57	F1	F2	F3	F4
As	1	3	26	14
Co	1	12	32	10

MW14-57	F1	F2	F3	F4
As	0,5	2	11	33
Co	1	4	10	14

MW14-59	F1	F2	F3	F4
As	0,1	0,5	4	14
Co	1	2	7	30

MW14-59	F1	F2	F3	F4
As	0,3	1	8	16
Co	1	13	25	13

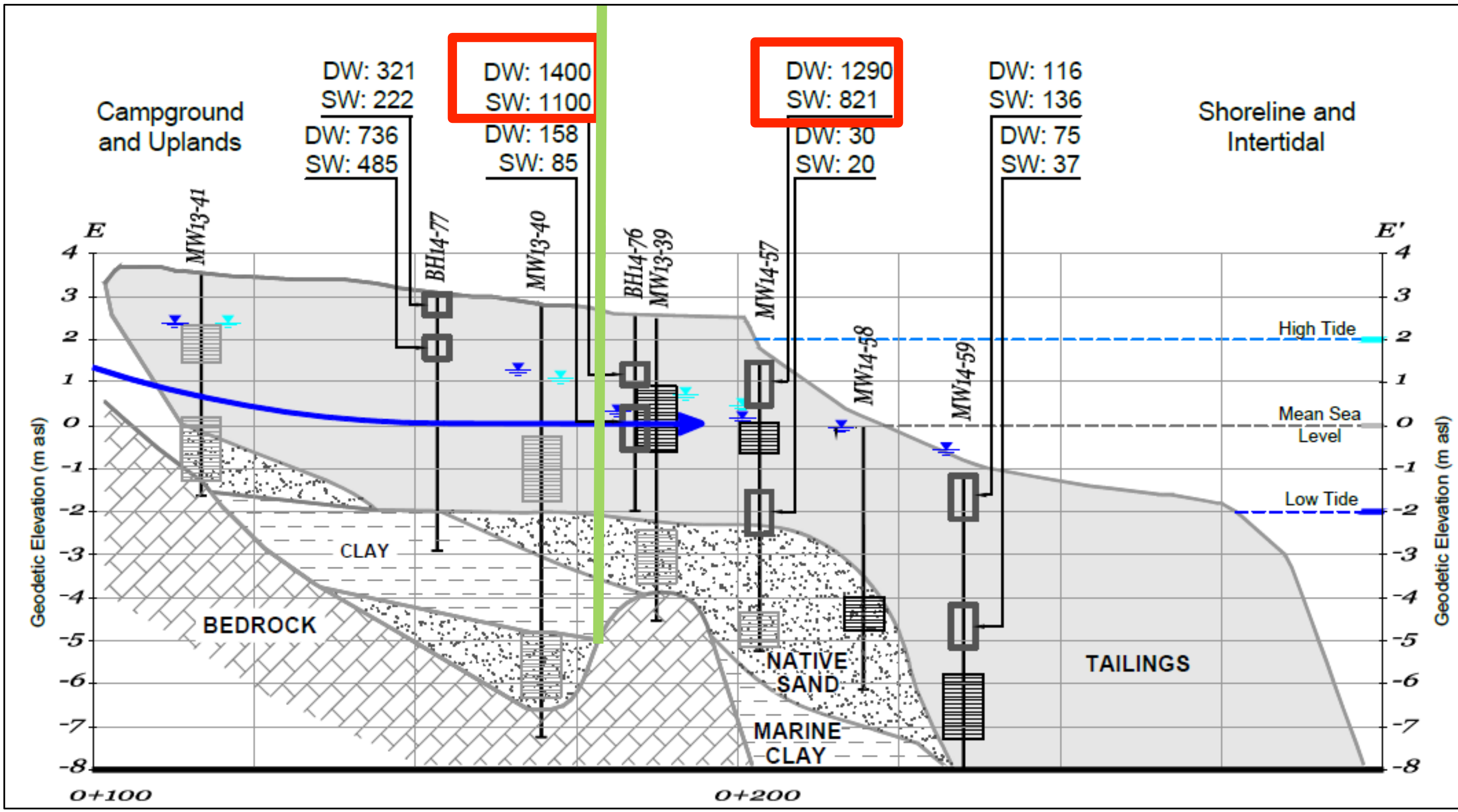
BH14-77	F1	F2	F3	F4
As	1	4	43	13
Co	1	16	50	8

Units: Normalized Mass Fraction (%)

F1 = Tessier Fraction 1, Exchangeable
F2 = Tessier Fraction 2, Carbonates
F3 = Tessier Fraction 3, Iron – Manganese Oxides
F4 = Tessier Fraction 4, Organic Matter

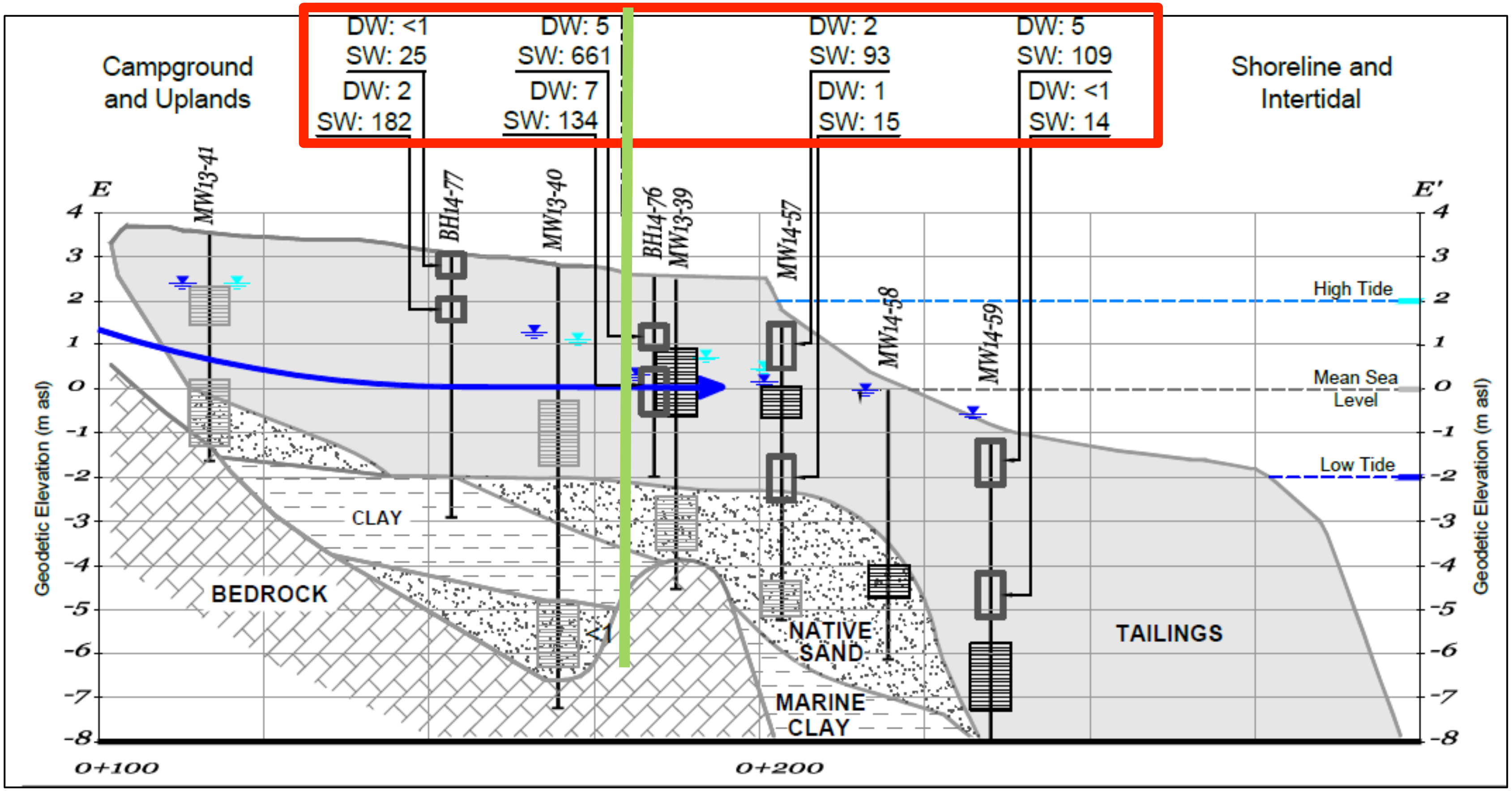
Geochemical Characterization – Shake Flask Extraction (As)

- Arsenic more leachable in shallow Shoreline and Intertidal Zone than Campground Area
- Salinity is NOT likely a key factor controlling arsenic mobilization



Geochemical Characterization - Shake Flask Extraction (Co)

- Cobalt more leachable in Shoreline and Intertidal Zone than Campground Area
- Salinity enhances cobalt mobility in Shoreline and Intertidal Zone



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Geochemical Characterization - Campground

Vadose Zone: Oxidizing conditions; sulphide oxidation

Shallow Tailings Aquifer: relatively oxidizing conditions, elevated dissolved Fe and As; *positive correlation between As/Fe (R^2>0.75)*

Deep Confined Aquifer: relatively reducing condition, lower Fe and As; *positive correlation between As/Fe (R^2>0.70)*

Area		pH	DO (mg/L)	ORP (mV)	Salinity (ppt)	Fe (ug/L)	As (ug/L)
Campground	Vadose Zone	Oxidizing Condition					
	Shallow (Tailings)	6.3 to 7.8	0.08 ~2.0	-25.2 ~ 97.4	0.23~0.41	220 ~ 7470	2.02 ~ 39.8
	Deep (confined)	6.15 to 8.8	0.03 ~ 0.2	-145 to ~ -0.2	0.19~0.36	10.3 ~ 1150	3.96 ~ 21
Shoreline	Shallow (Tailings)	7.03~8.0	0.35 ~ 1	-60.3 ~ 225	0.23~0.59	14.9 ~ 41.9	423 ~ 871
	Deep (Tailings)	6.9~7.5	0.1 ~ 1	-106.3~ -45	0.26~0.83	1610 ~ 5090	15.5 ~ 777
Intertidal Zone	Shallow (Tailings)	7.2~8.6	<0.05~ 1.0	-148 ~ 148	0.98 ~ 22.1	<5 ~ 1560	113 ~ 2400
	Deep (Tailings)	7.5~8.6	<0.05 ~0.8	-128 ~ -42	3.3 ~ 30	15 ~ 10800	62 ~ 353
Subtidal	Reducing Condition						

Geochemical Characterization - Shoreline Area

Shallow Tailings Aquifer: Dynamic oxidizing/reducing conditions; low dissolved Fe, elevated As; but no correlation between As/Fe

Deep Tailings Aquifer: relatively reducing condition, elevated dissolved Fe, and variable dissolved As (temporal and spatial variations); no correlation between As/Fe

Area		pH	DO (mg/L)	ORP (mV)	Salinity (ppt)	Fe (ug/L)	As (ug/L)
Campground	Vadose Zone	Oxidizing Condition					
	Shallow (Tailings)	6.3 to 7.8	0.08 ~2.0	-25.2 ~ 97.4	0.23~0.41	220 ~ 7470	2.02 ~ 39.8
	Deep (confined)	6.15 to 8.8	0.03 ~ 0.2	-145 to ~ -0.2	0.19~0.36	10.3 ~ 1150	3.96 ~ 21
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	Deep (Tailings)	7.5~8.6	<0.05 ~0.8	-128 ~ -42	3.3 ~ 30	15 ~ 10800	62 ~ 353
Subtidal	Reducing Condition						

Geochemical Characterization - Intertidal Zone

<u>Shallow Tailings :</u> Variable salinity, circumneutral to alkaline pH; dynamic oxidizing/reducing conditions; low to non-detect dissolved Fe, and highly elevated As; no correlation between As/Fe

<u>Deep Tailings:</u> Variable salinity, circumneutral to alkaline pH, relatively reducing conditions, variable dissolved Fe and As, no correlation between As/Fe

Area		pH	DO (mg/L)	ORP (mV)	Salinity (ppt)	Fe (ug/L)	As (ug/L)
Campground	Vadose Zone	Oxidizing					
	Shallow (Tailings)	6.26 to 7.82	0.08 ~2.0	-25.2 to~ 97.4	0.23~0.41	220 ~ 7470	2.02 ~ 39.8
	Deep (confined)	6.15 to 8.8	0.03 ~ 0.2	-145 to ~ -0.2	0.19~0.36	10.3 ~ 1150	3.96 ~ 21
Shoreline	Shallow (Tailings)	7.03~8.0	0.35 ~ 1	-60.3 ~ 225	0.23~0.59	14.9 ~ 41.9	423 ~ 871
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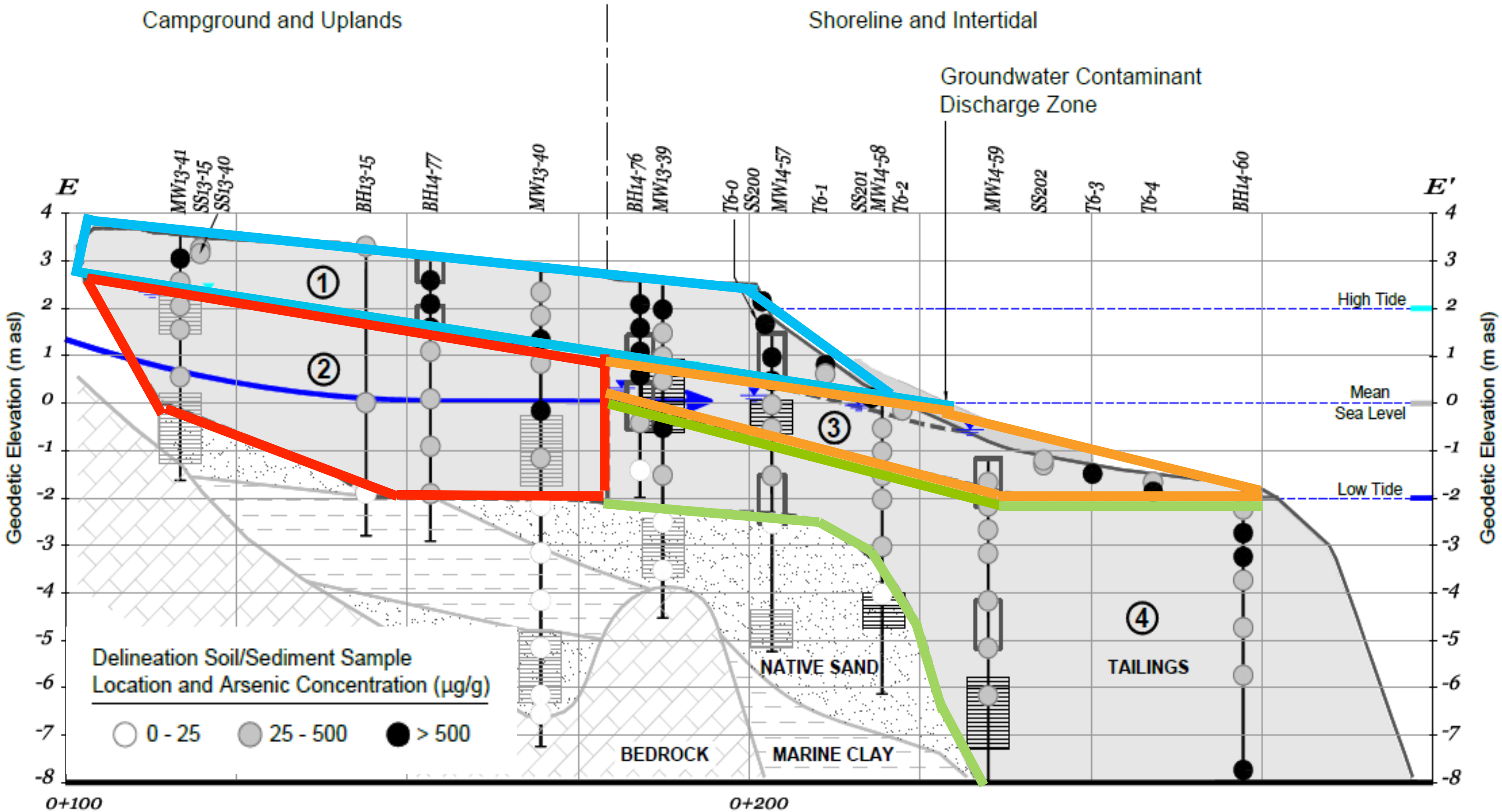
	Deep (Tailings)	7.5~8.6	<0.05 ~0.8	-128 ~ -42	3.3 ~ 30	15 ~ 10800	62 ~ 353
Subtidal	Reducing Condition						

Conclusions - Geochemical Conceptual Model



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Conclusions - Geochemical Conceptual Model

Zone 1 (Vadose Zone):

- Unsaturated, oxidizing, most sulphides oxidized, freshwater infiltration, metals leach downward to water table

Zone 2 (Campground Area):

- Positive correlation between As and Fe; precipitation/dissolution of iron and manganese oxyhydroxides control arsenic transport in groundwater

Zone 3 (Shallow Shoreline and Intertidal Zone):

- Variable redox conditions; variable salinity; highest dissolved As and Co concentrations; low to non-detect dissolved Fe concentrations; adsorption/desorption controls arsenic transport in groundwater.

Zone 4 (Deep Shoreline and Intertidal Zone):

- Relatively more reducing conditions; variable salinity; elevated dissolved As and Fe; arsenic is governed by multiple geochemical mechanisms, including sorption/desorption and dissolution of iron and manganese oxyhydroxides

Conclusions - Key Factors Governing As Cycling

1. *Spatially and Temporally Variable Redox Conditions*

- Arsenic speciation As(III) and As (V)
  Sorption: As(V) > As (III)
  Mobility: As(III) > As (V)

- Sulphide Oxidation (vadose zone and shallowest tailings aquifer)

$$FeAsS + 9H_2O \rightarrow FeOOH + H_2AsO_3^- + 15H^+ + SO_4^{2-} + 12e^-$$

- Iron/Manganese precipitation/reduction dissolution (tailings aquifer)

$$CH_2O + 4Fe(OH)_3 + 7H^+ \rightarrow 4Fe^{2+} + HCO_3^- + 10H_2O$$

2. *Dynamic Adsorption/Desorption Processes:*

- Dependent on grain size/surface area, pH, salinity, etc.
- As Speciation

Conclusions - Challenges and Limitations

- Redox conditions in tidal environment introduces variability in oxygen concentrations that may affect speciation and mobility of arsenic
- Dynamically Changing Environment and Kinetic Reactions: Field measured DO and ORP may not always be representative of field conditions; multiple redox pairs undergoing simultaneous reactions
- Accounting for dynamic nature of sorption / desorption processes under influence of changing pH and salinity
- Heterogeneity of Tailings: Distribution and abundance of sulphide minerals, iron oxides and reactivity (older vs. younger tailings)
- Groundwater Sampling: Samples represent “snap shot” in tide cycle primarily during falling tide due to access limitations

Complexity of geochemical processes and groundwater flow must be considered during development of remedial solutions.

Acknowledgements

Crown Contaminated Sites Program

Toquaht Nation

AECOM was contracted by the Crown Contaminated Sites Program of the Government of British Columbia, Ministry of Forests, Lands, Natural Resource Operations and Rural Development, for the Toquaht Bay Marina and Tailings Investigation project.

Contributors to this Project

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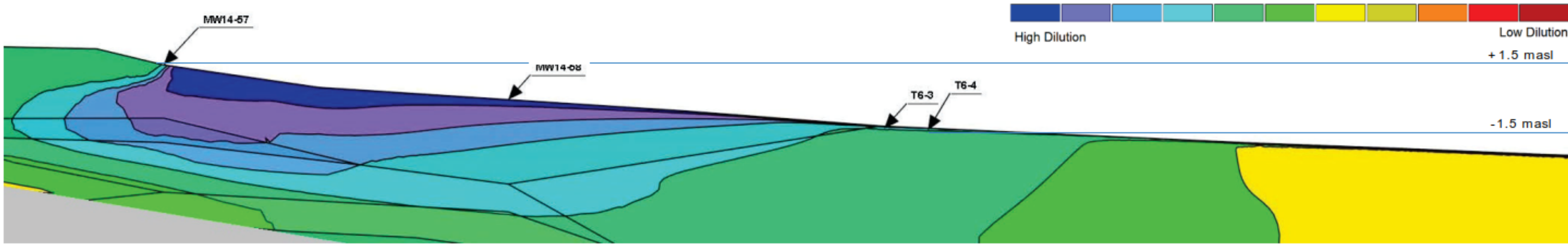
- Mike Sanborn

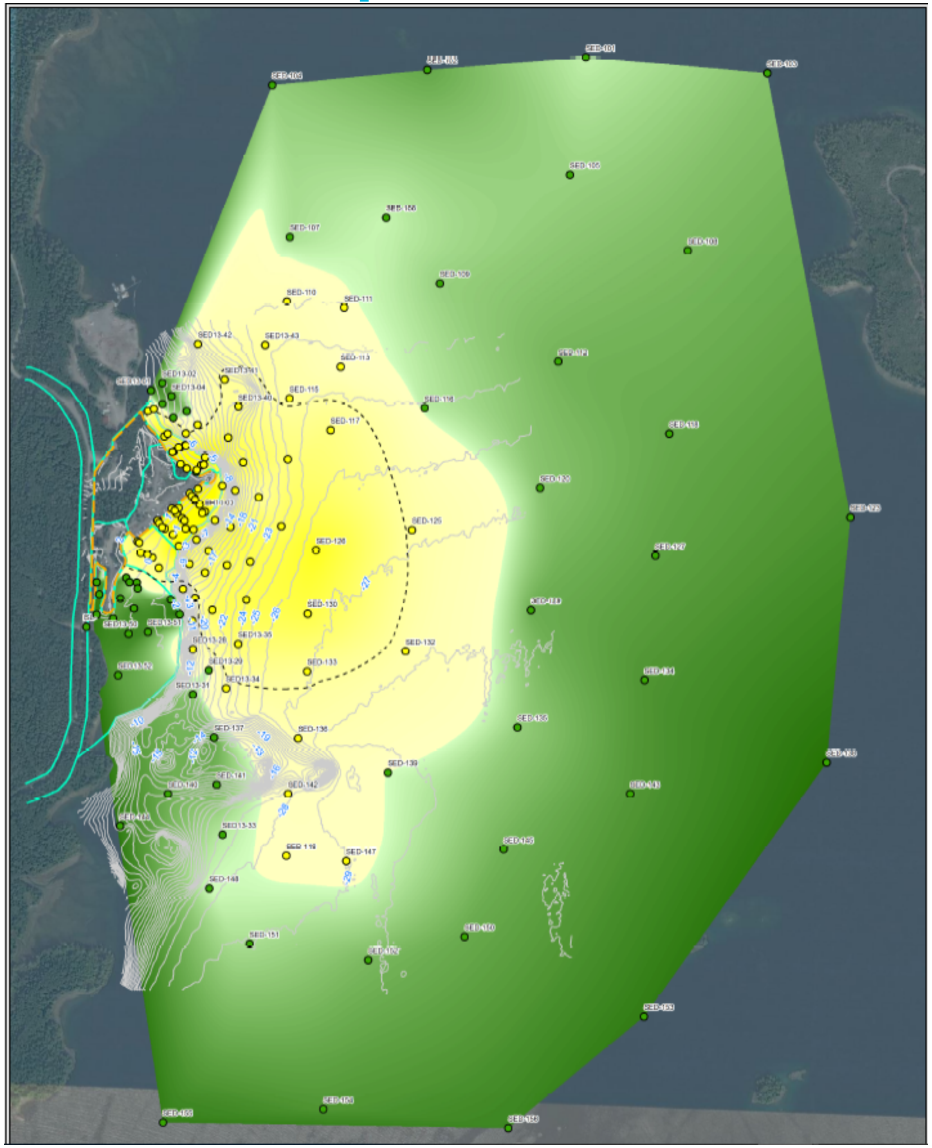
Questions?

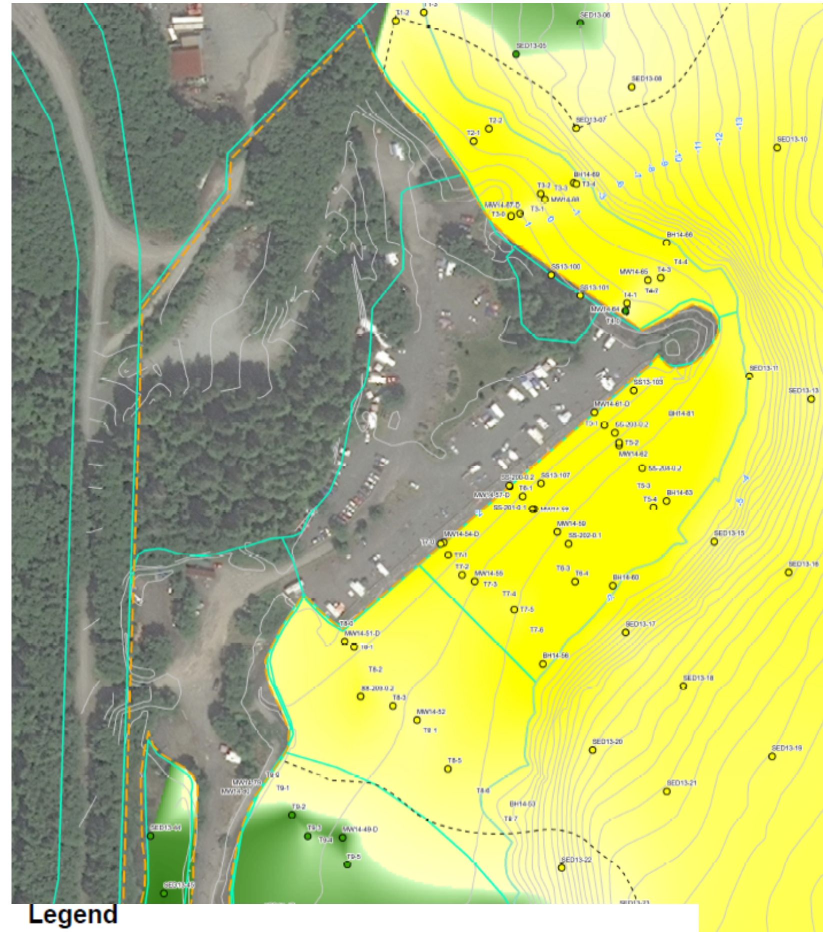
VANCOUVER ISLAND
N
Kennedy Lake
4
Toquaht Bay marina and campground
Toquaht Bay
LONG BEACH
4
PACIFIC RIM NATIONAL PARK
Ucluelet
Loudoun Channel
PACIFIC OCEAN
Broken Islands
8 km

Figure 4.1: Mixing with marine water in intertidal sediments under current conditions.



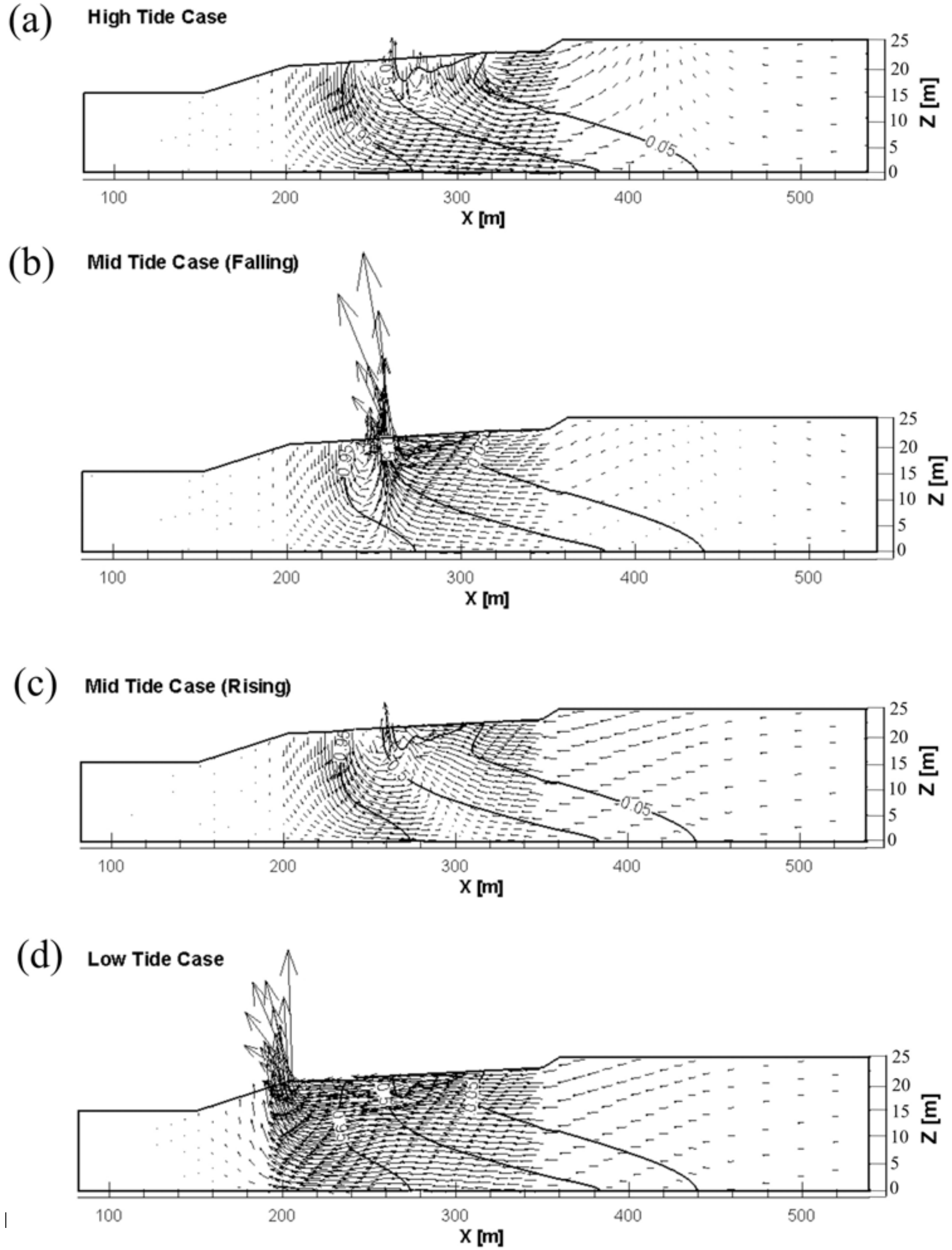
Cobalt Impacted Sediment



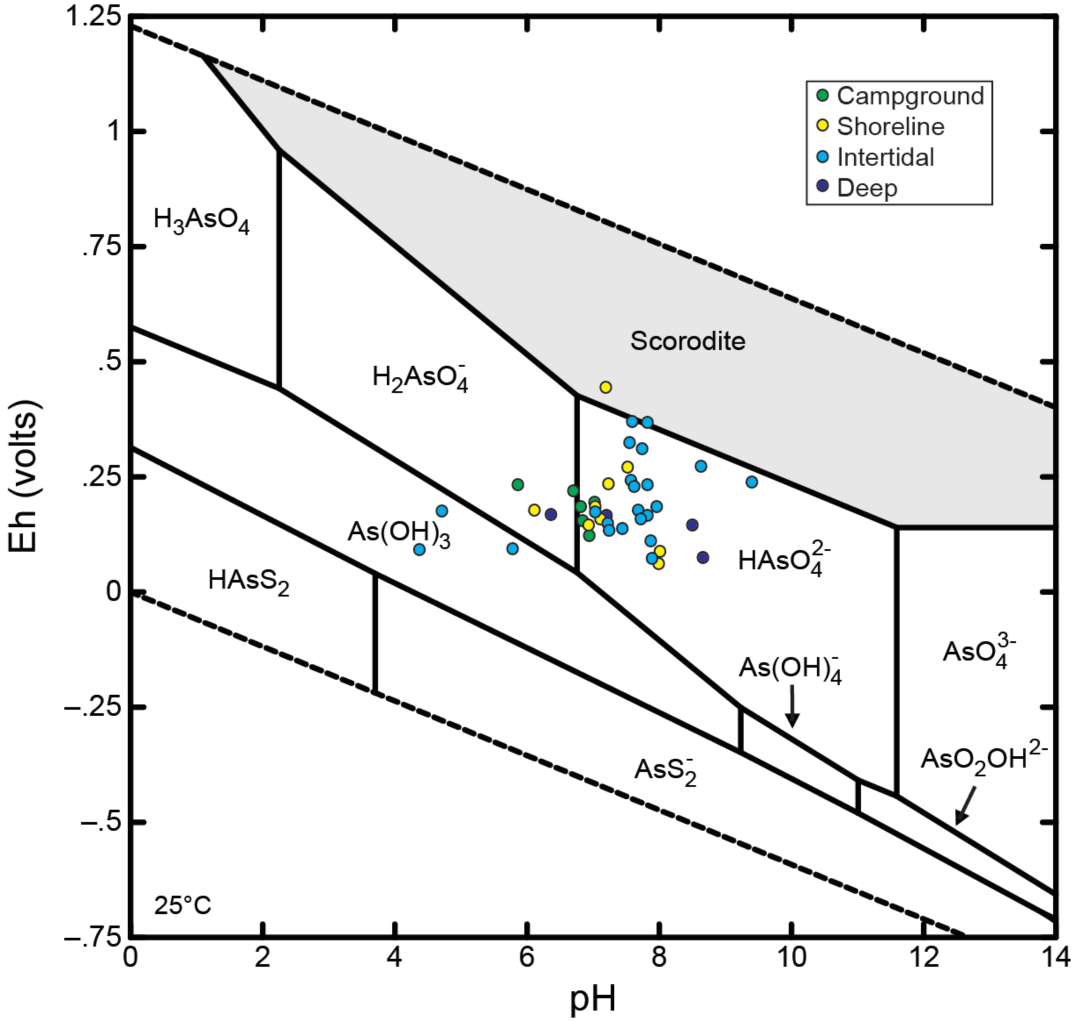


Legend

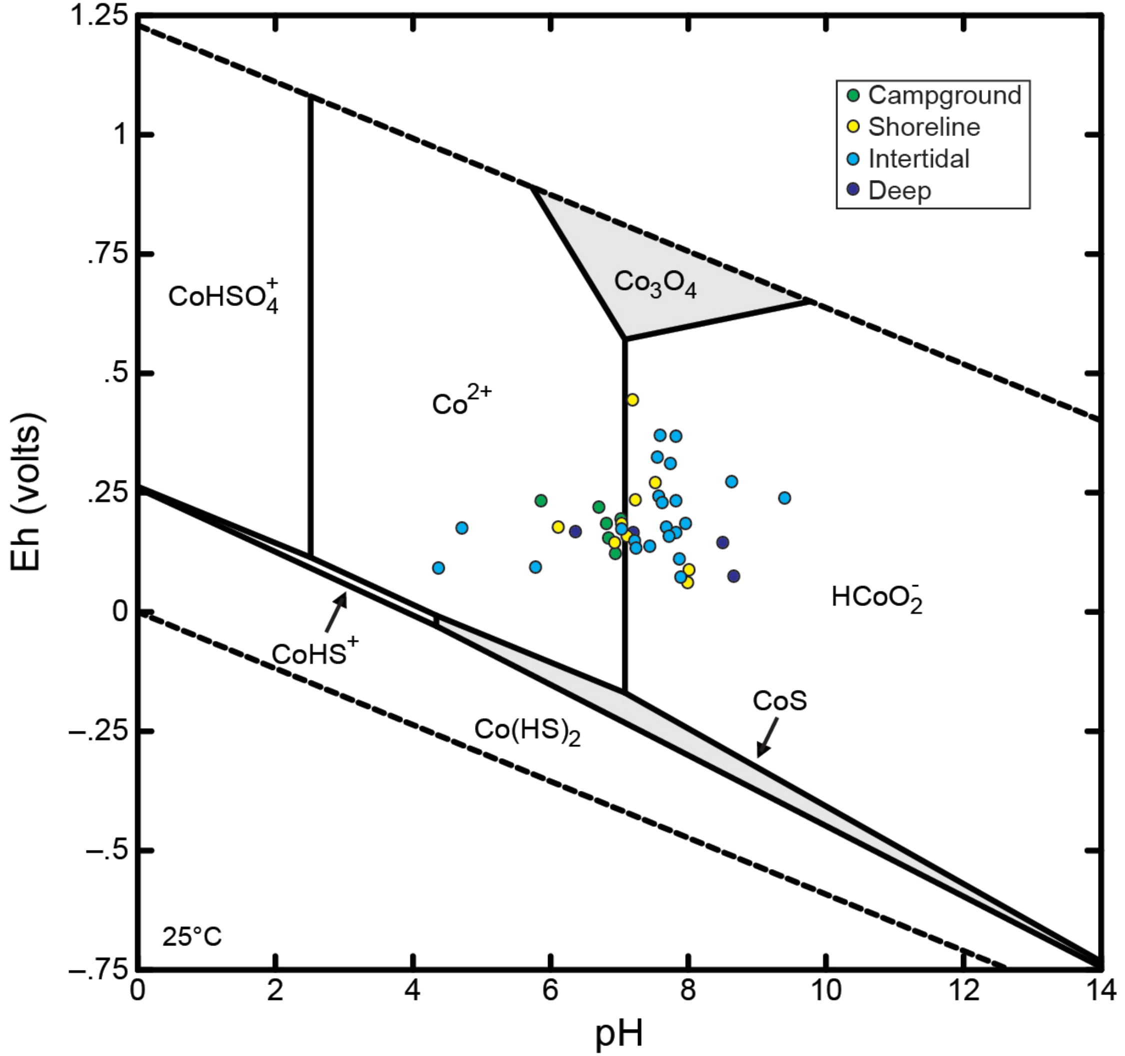
- > 15.38
- < 15.38
- Below Average Background
- Above Average Background
- Site Boundary
- Contour (1 m Interval)
- Area Boundary
- 95% Upper Tolerance Limit (with 90% Coverage)


(a)
High Tide Case
0.05
X [m]
Z [m]
(b)
Mid Tide Case (Falling)
X [m]
Z [m]
(c)
Mid Tide Case (Rising)
0.05
X [m]
Z [m]
(d)
Low Tide Case
X [m]
Z [m]

As Speciation



Cobalt Speciation



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