Natural Attenuation at a High Energy GSI, St. Joseph, MI

ISAS, Initiative in Sustainable Aqueous Systems

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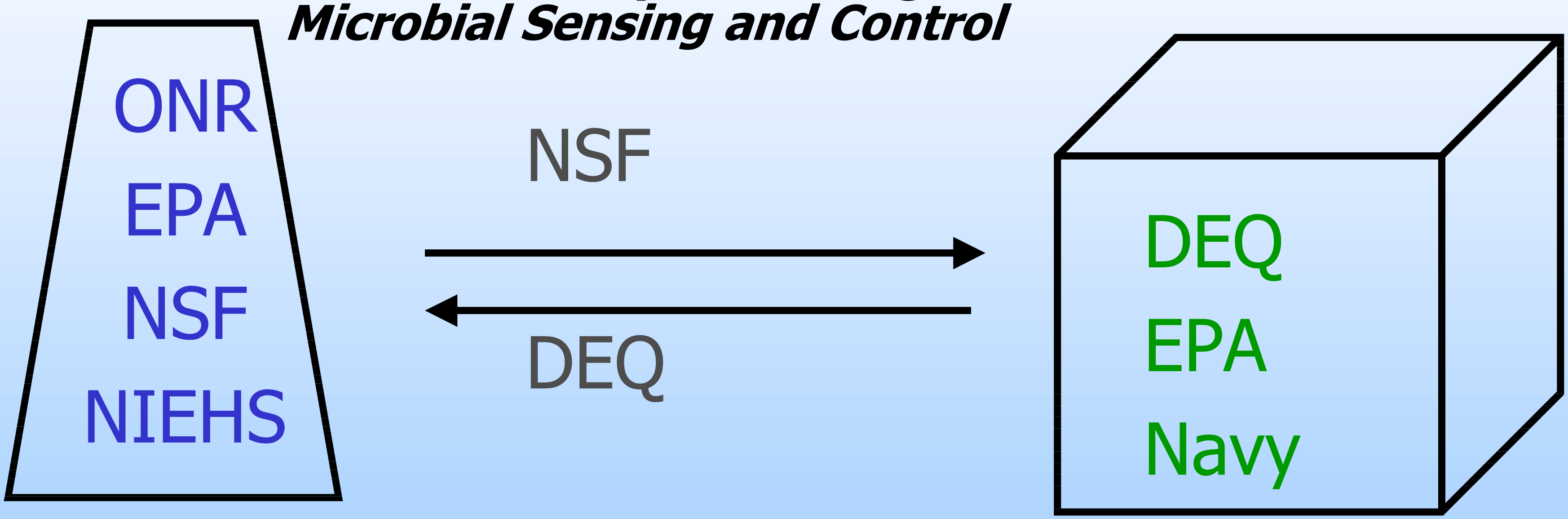
From Flask to Field (and Back Again!)

<u>Research Themes</u>

Monitored Natural Attenuation
Remediation System Design
Microbial Sensing and Control



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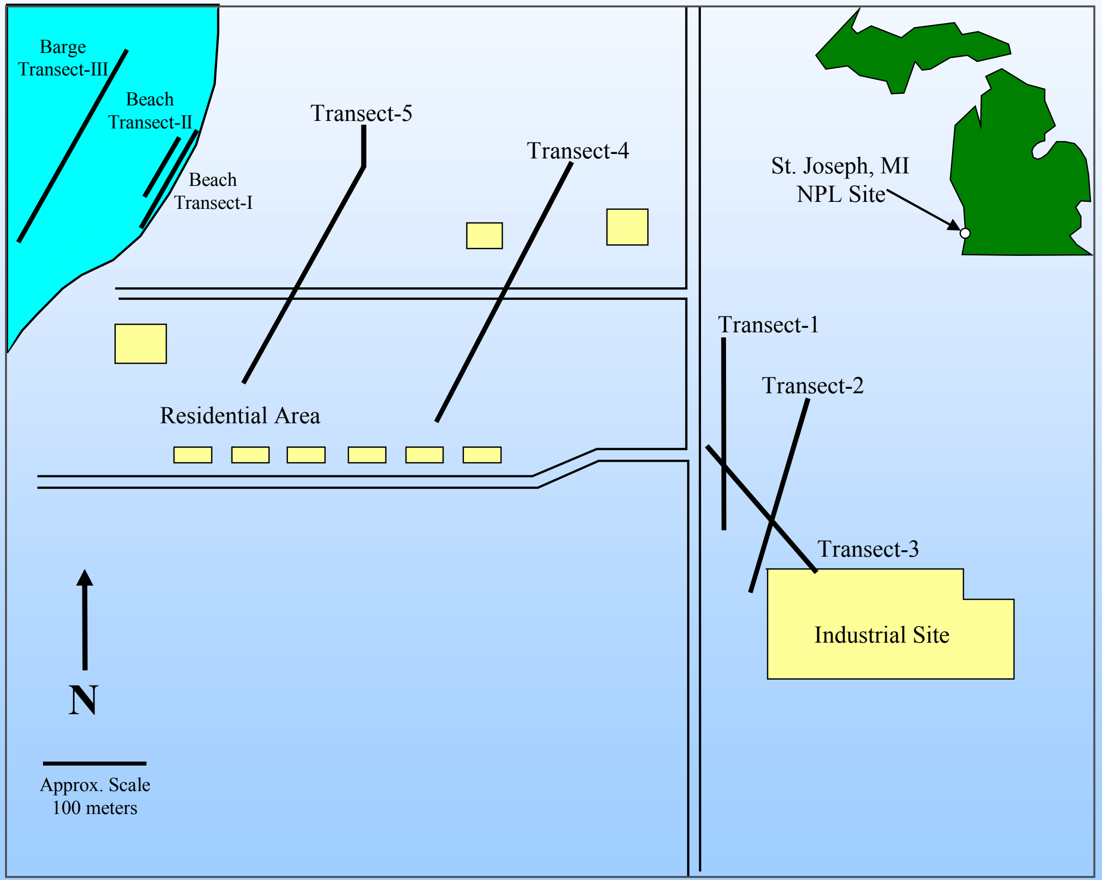
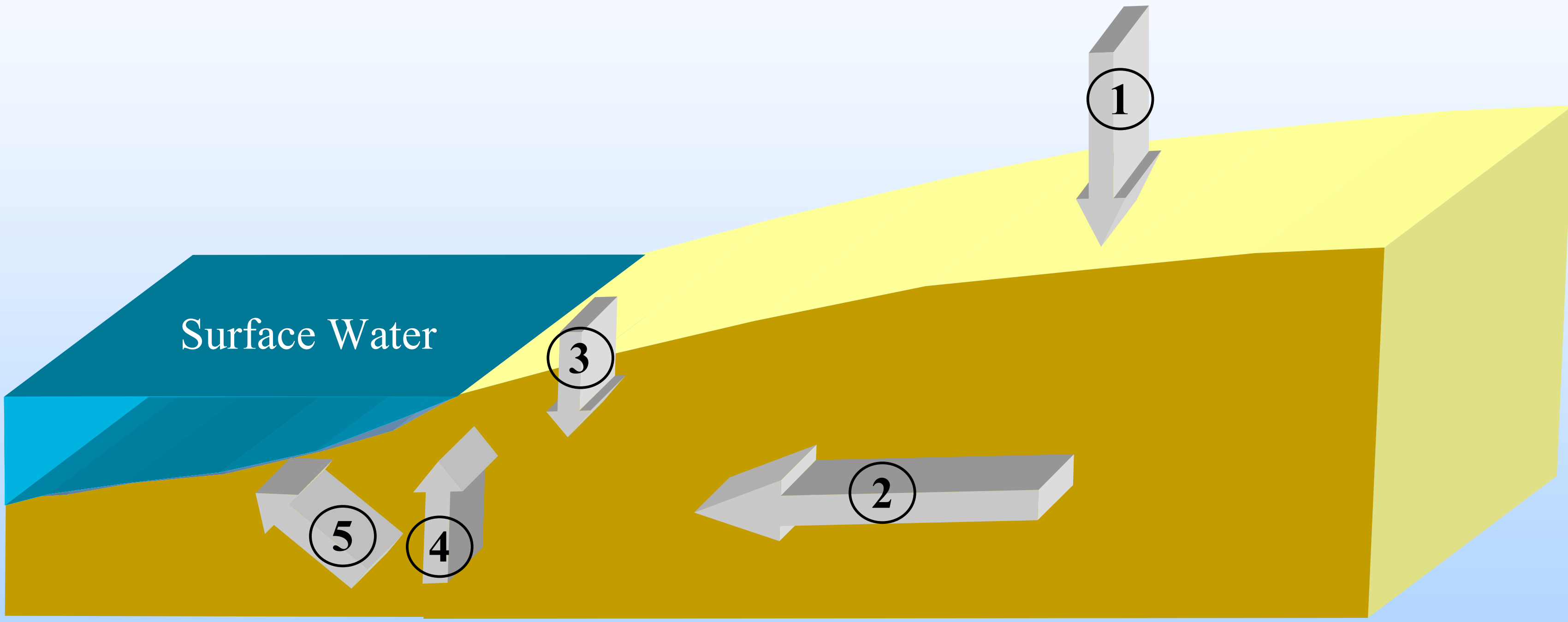
Shiang Fu	**Cyndee Gruden**	**Peter Yung**
Andrei Barkovskii	**Babu Fathepure**	**Erik Petrovskis**
Aksay Kumar	**Tim Towey**	

St. Joseph MI Superfund Site: Groundwater-Surface Water Interface (GSI)



- Chlorinated solvents (> 500 mg/kg); vinyl chloride at > 16 mg/kg; Hydrocarbons (< 1 mg/kg)
- Contaminant flux in Lake Michigan estimated at 8.4-17 kg/yr.

Hydrodynamic Processes at the GSI



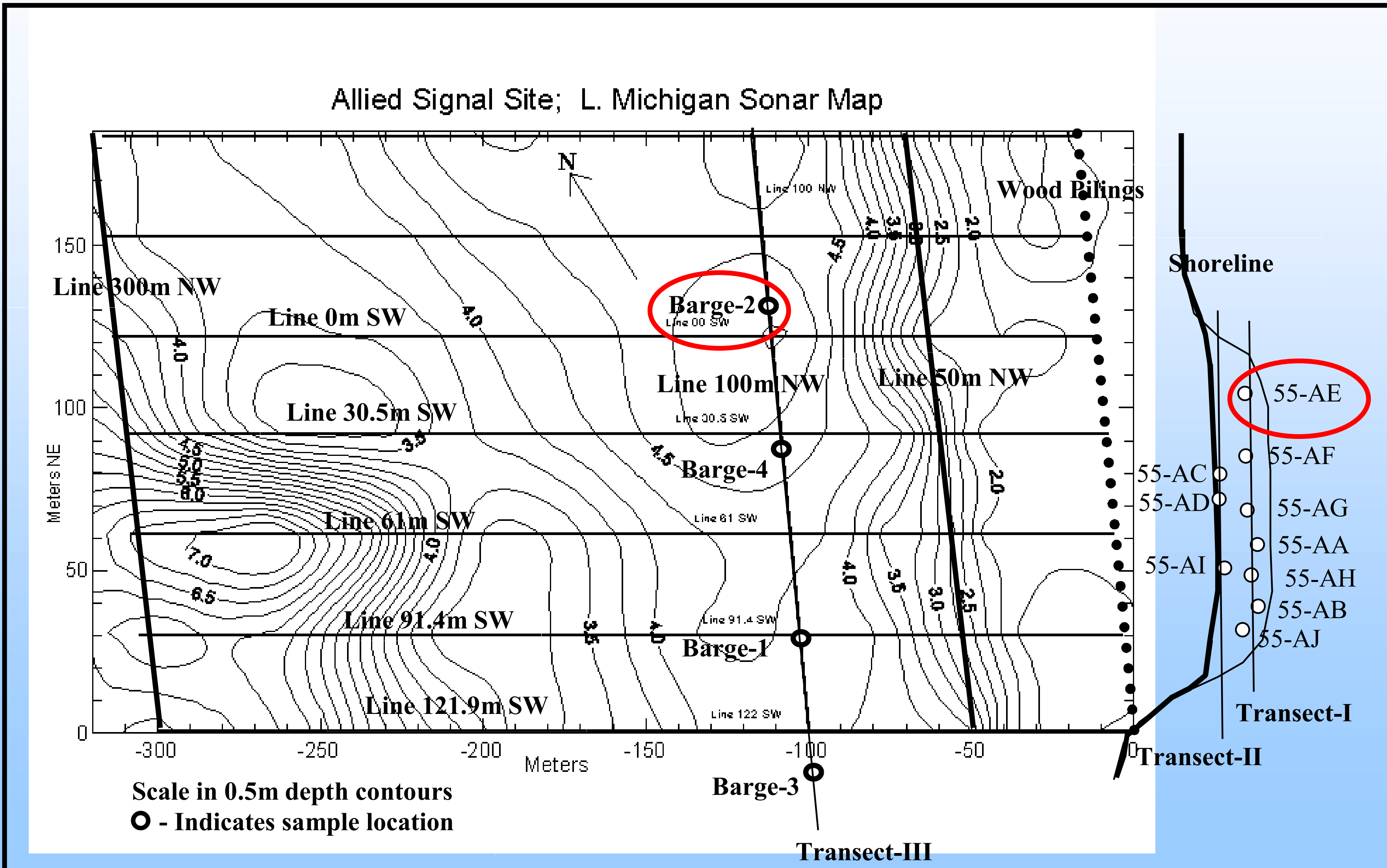
1. Recharge and infiltration.
2. Hydraulically driven flow.
3. Wave setup and infiltration.
4. Ebullition processes.
5. Hydraulically driven flow into surface water.

Hypothesis

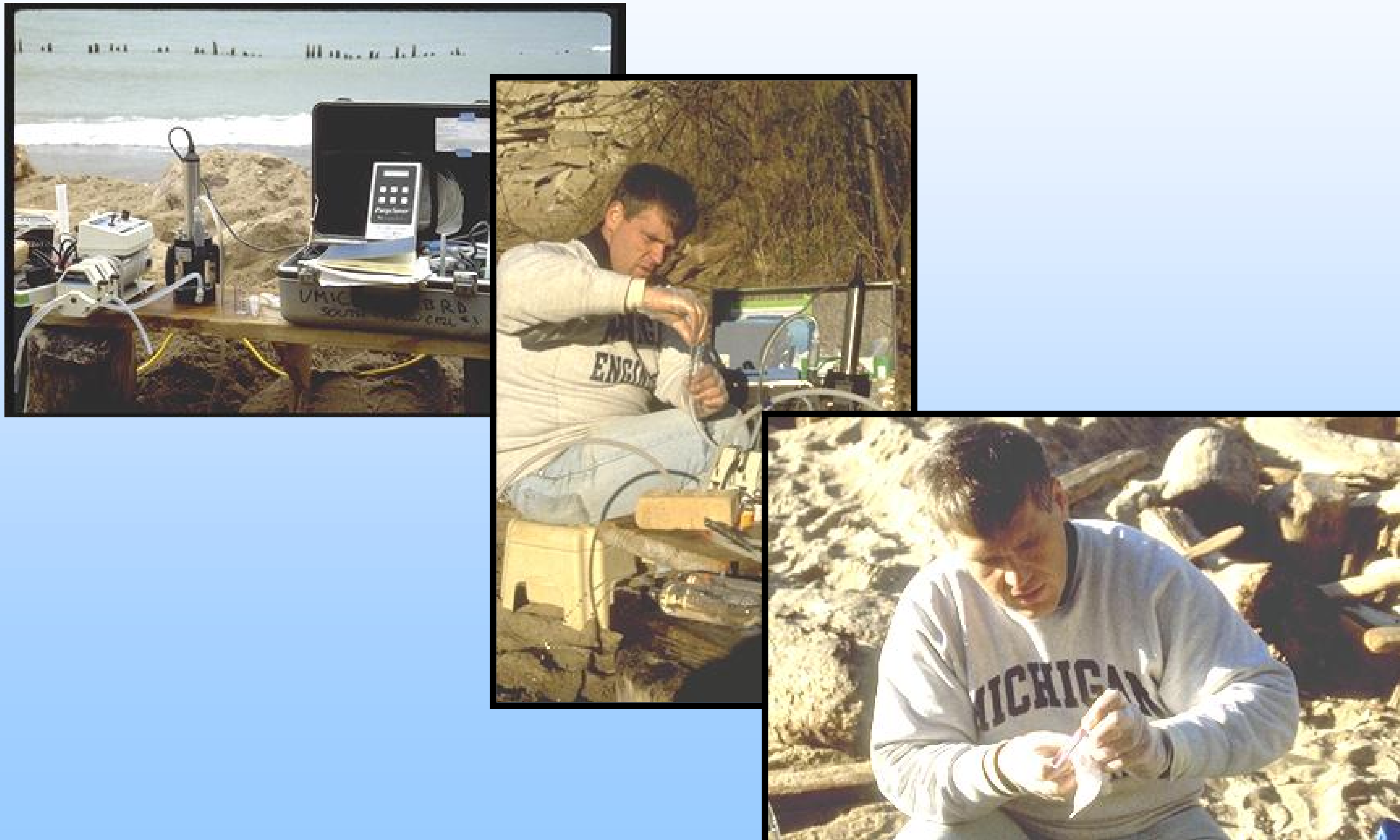
"Biogeochemical changes resulting from hydrological interactions between anaerobic groundwater and aerobic surface water facilitate *in situ* (bio)transformation processes."

<u>Specific Objective</u>: demonstrate vinyl chloride attenuation at GSI or "Are the biogeochemical processes sufficient to mitigate contaminant fluxes into L.M.?"

Plan View of Sample Locations

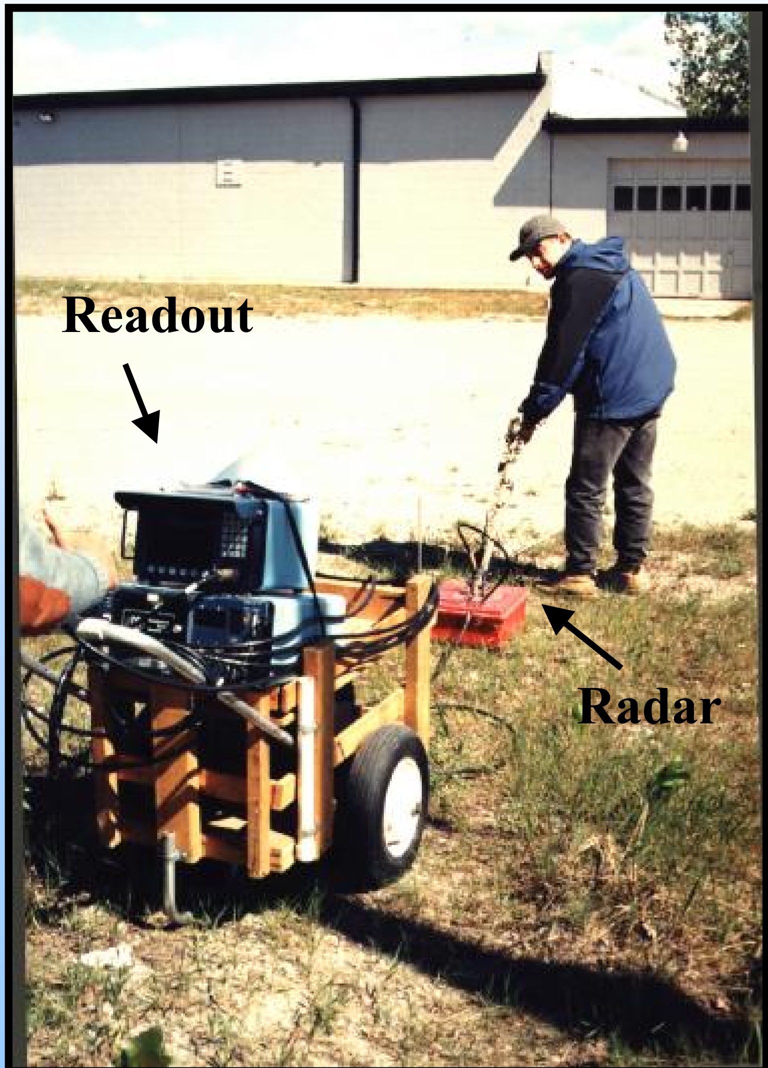


Groundwater Analyses



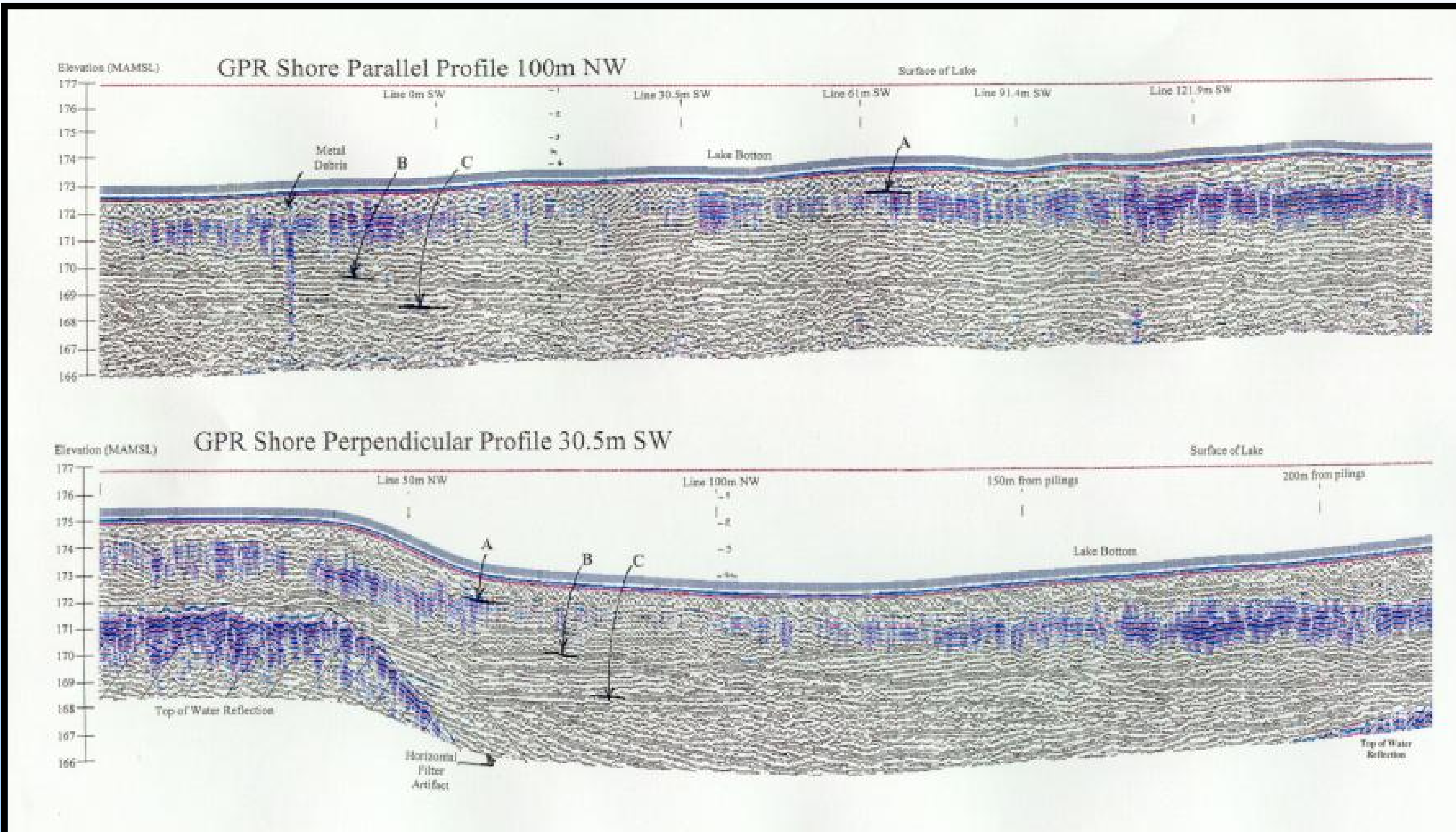
Offshore Sampling Procedures

Geophysical Characterization:
Ground Penetrating Radar

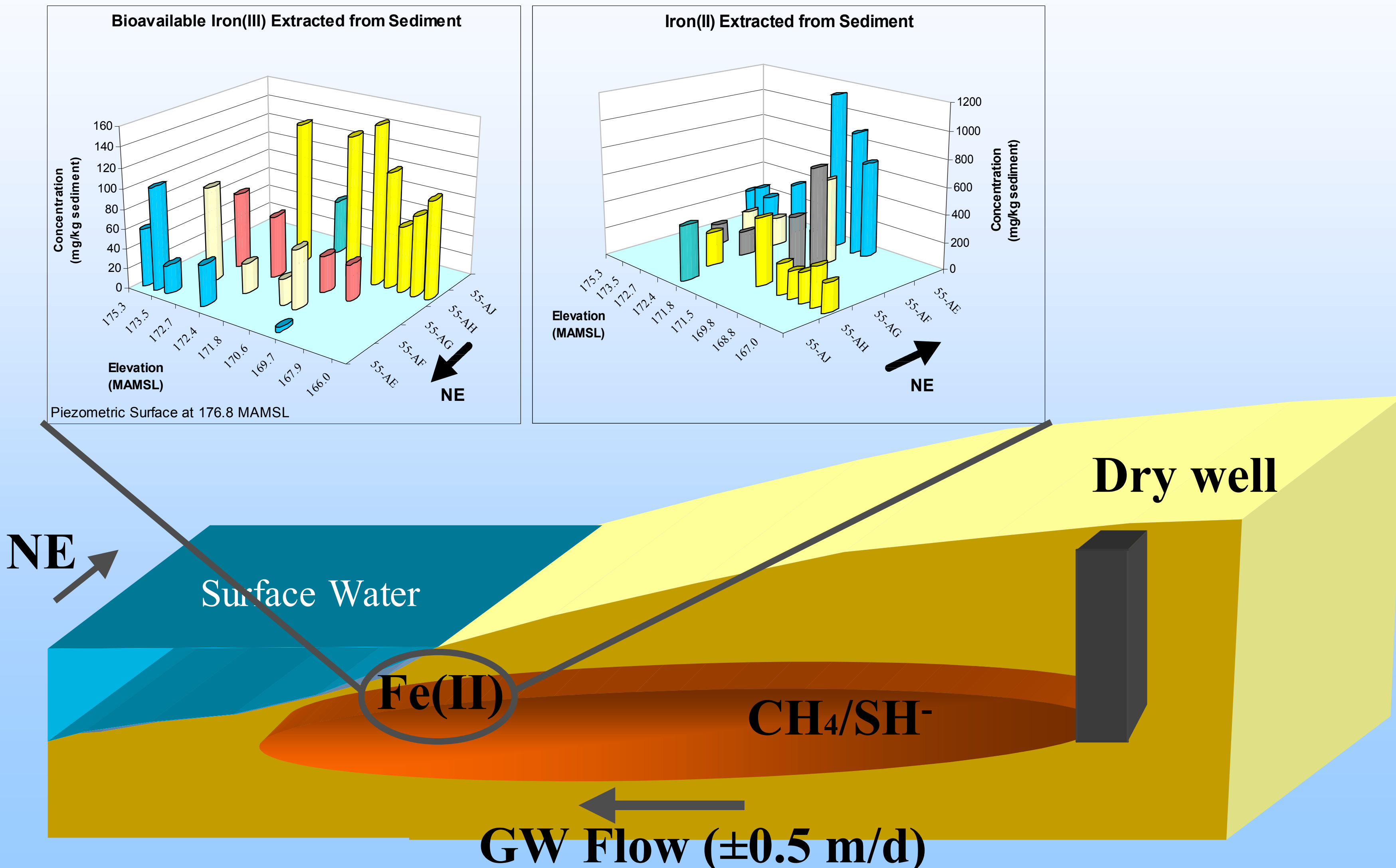


- Principle: Short term emission of electro-magnetic pulses, and longer term reception of reflected waves results in "reflection patterns" from the interaction of the pulses with features of the subsurface.
- Electrical conductivity (σ) of the subsurface controls the wave attenuation; the higher the conductivity, the less is the penetration.
- Electrical permittivity (ε_r) in the subsurface varies from 2-5 for soils and rocks, to ~ 9 for moist sand and to ~25 for saturated sand . The water table is thus a clear conductivity boundary
- Magnetic permeability (μ_r) becomes relevant when minerals exhibit magnetic properties, e.g. magnetite.

Contaminant Plume GPR Profiles

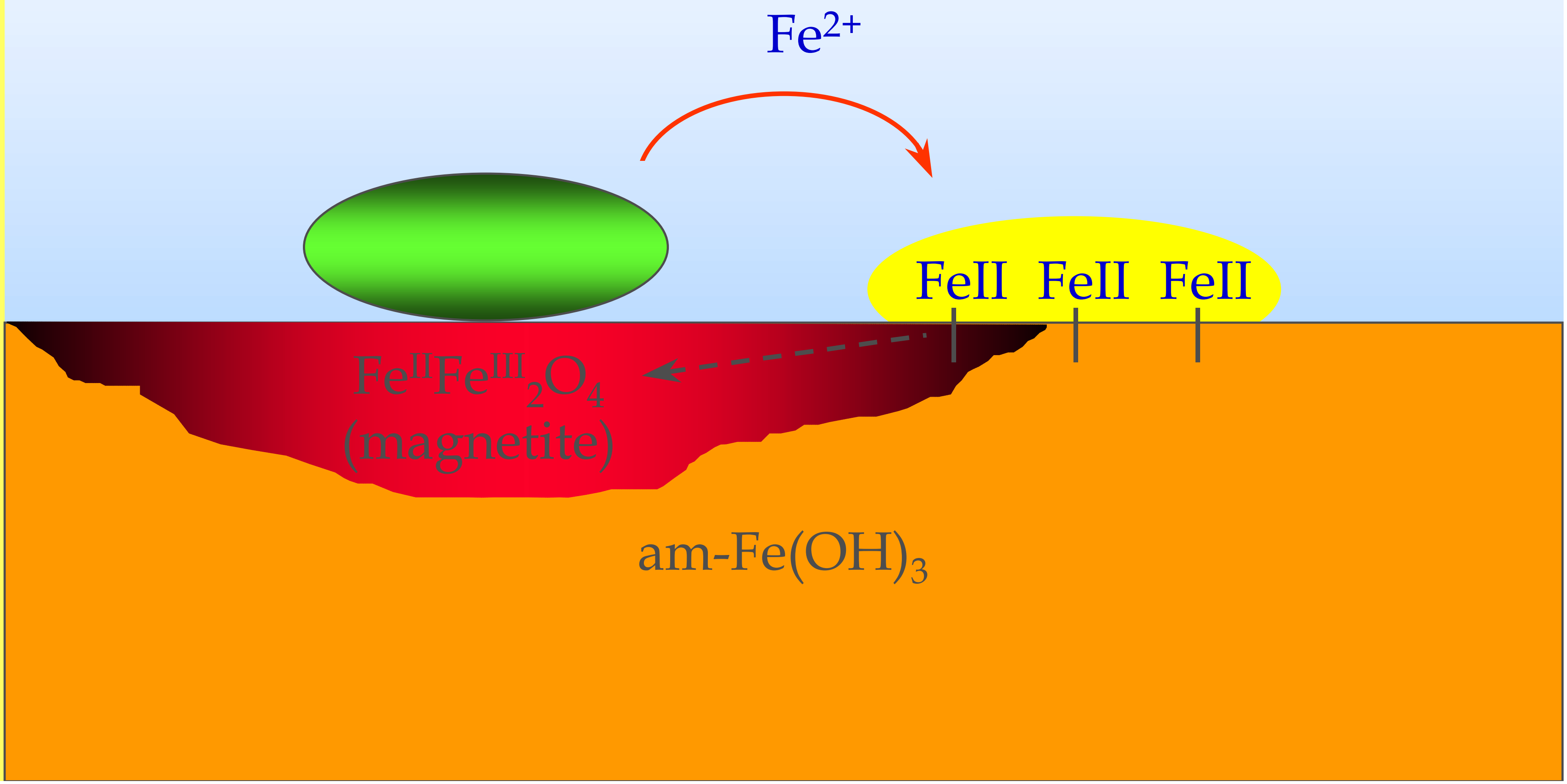


Macroscale Phenomena:
Respiratory Depletion of Iron (III) Minerals

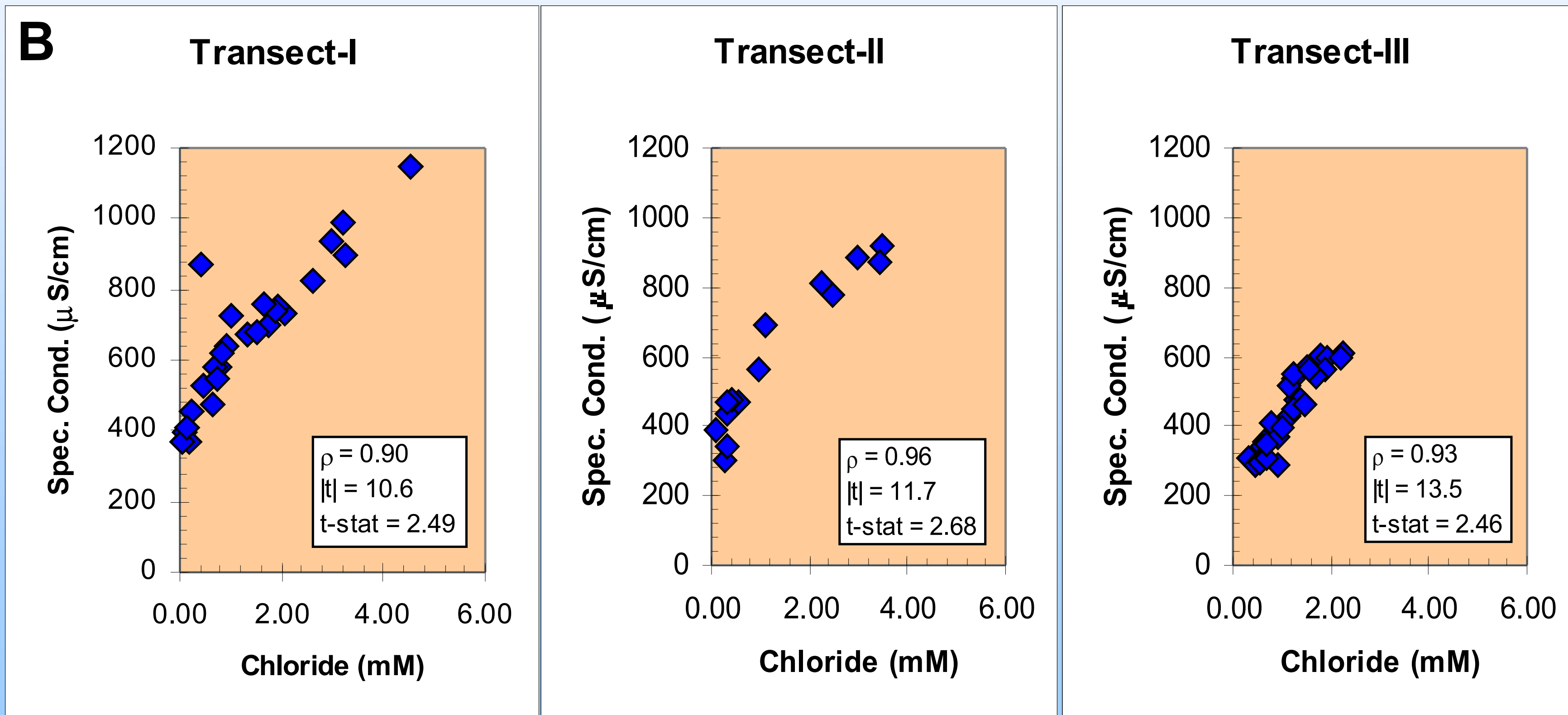


Iron Transformation as a Consequence of Microbial Iron Reduction

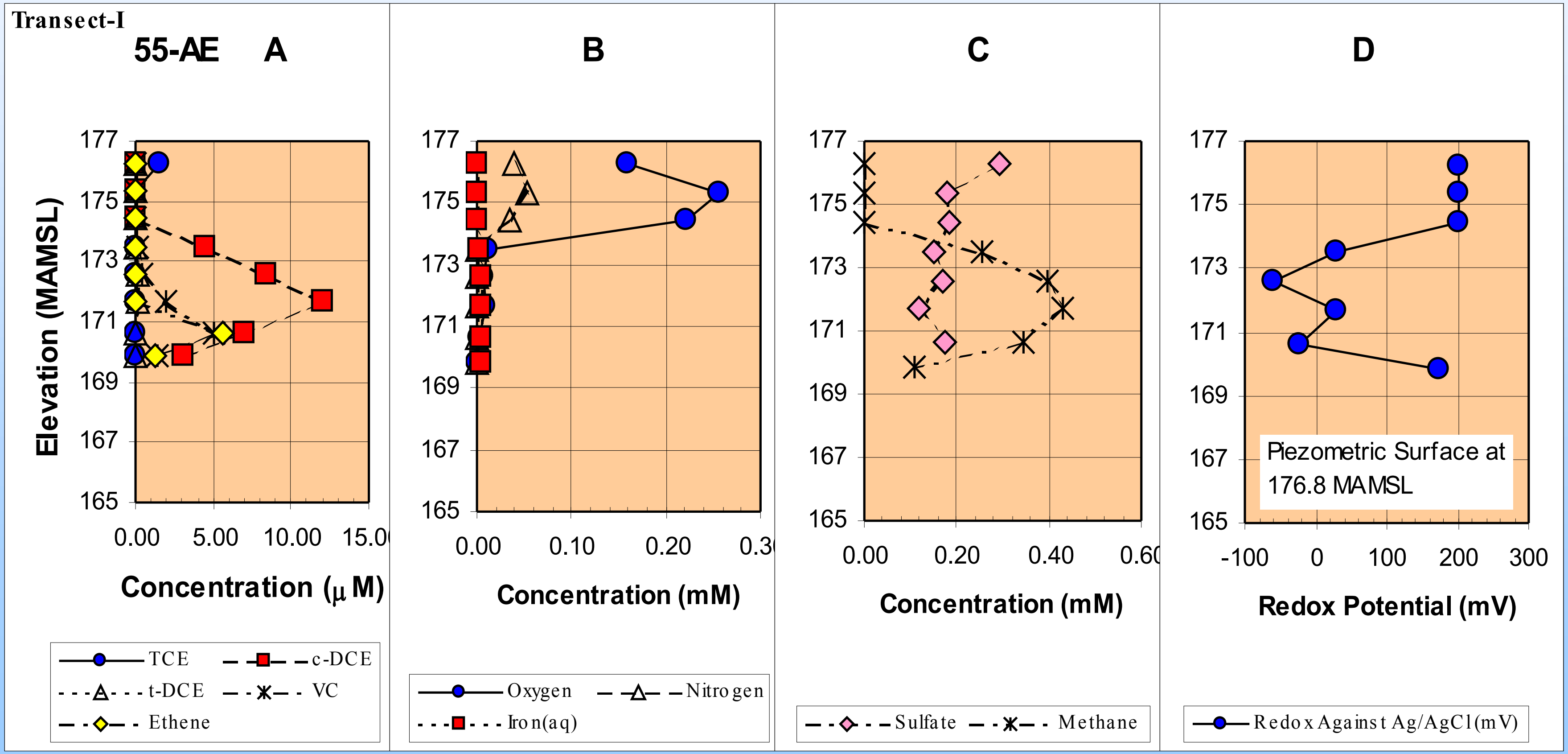
$$2\ \text{am-Fe(OH)}_3\ (s) + Fe^{2+}\ (aq) \rightarrow Fe_3O_4\ (s) + 2\ H_2O + 2\ H^+$$



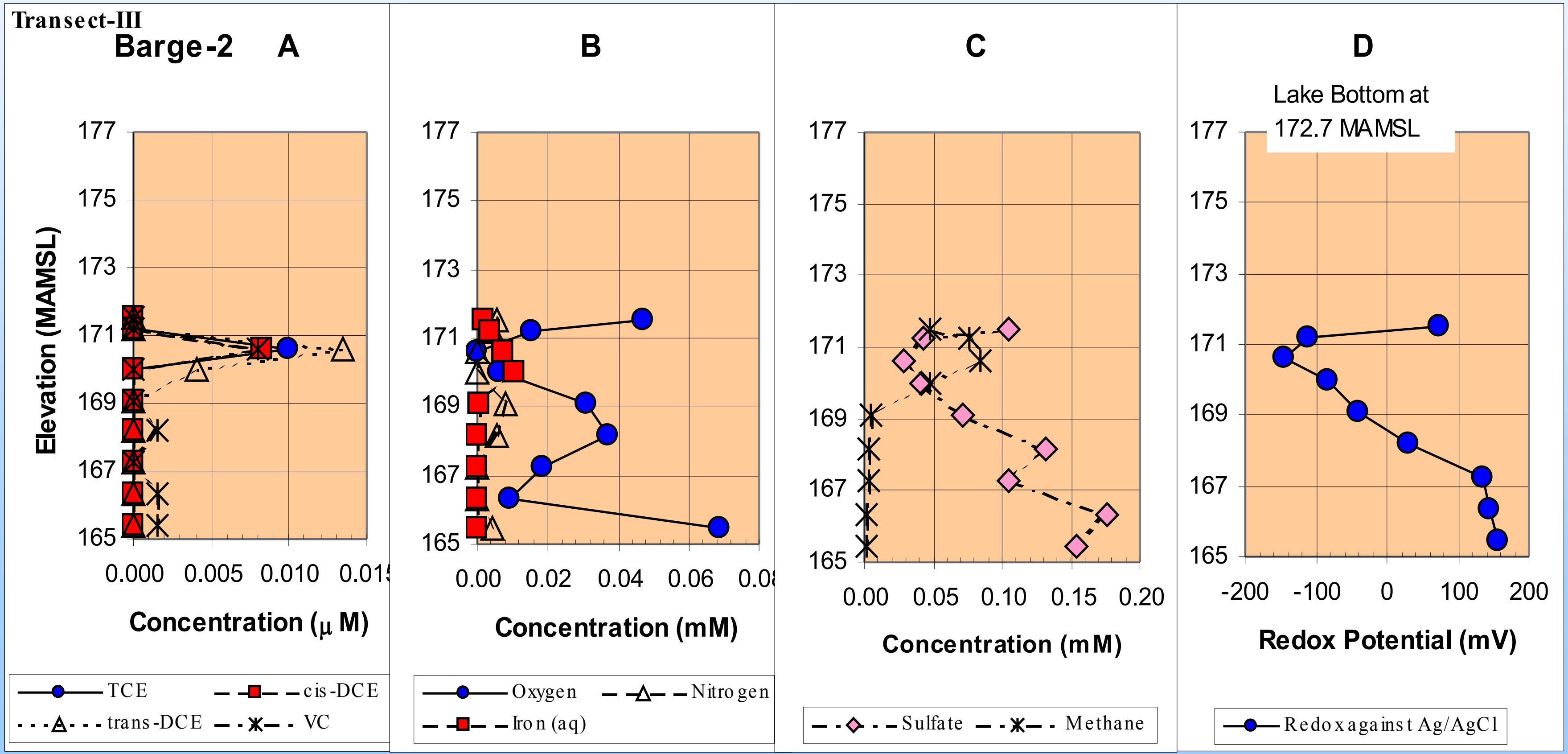
Specific Conductance and Chloride Scatter-grams



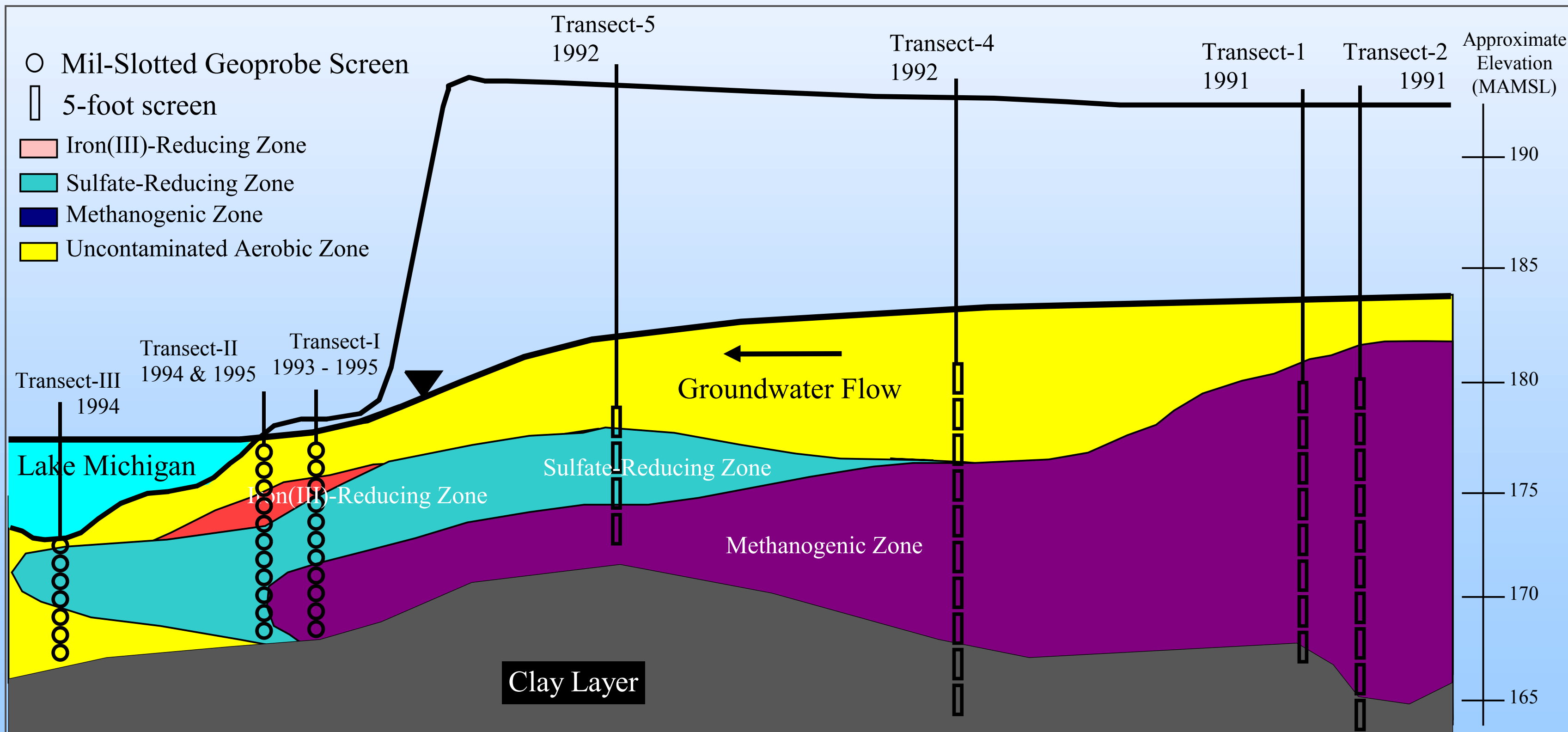
Contaminant & Geochemical Profiles for 55-AE



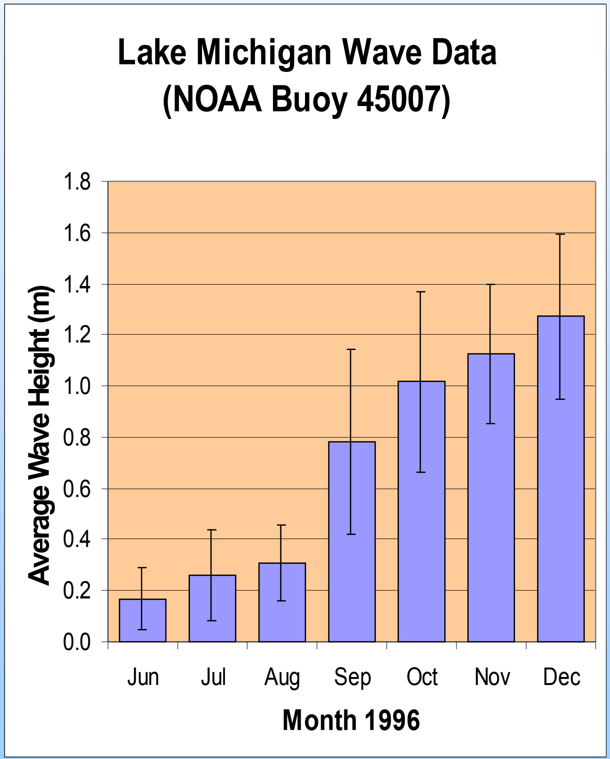
Contaminant & Geochemical Profiles for Barge-2



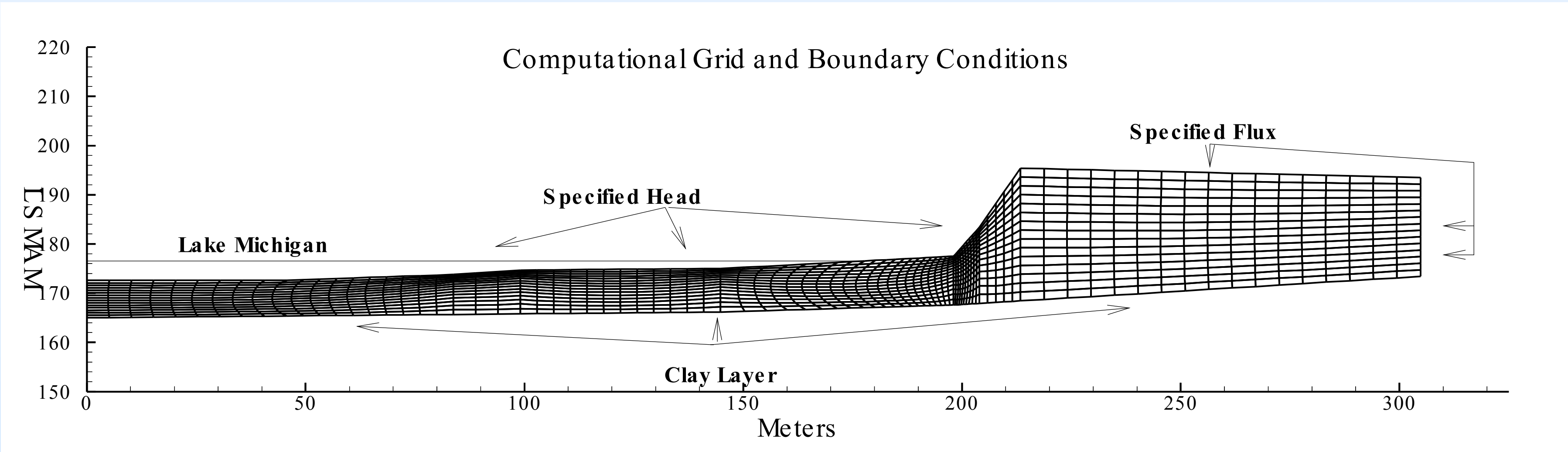
Conceptual Diagram of Plume



Temporal Effects: Storm Activity

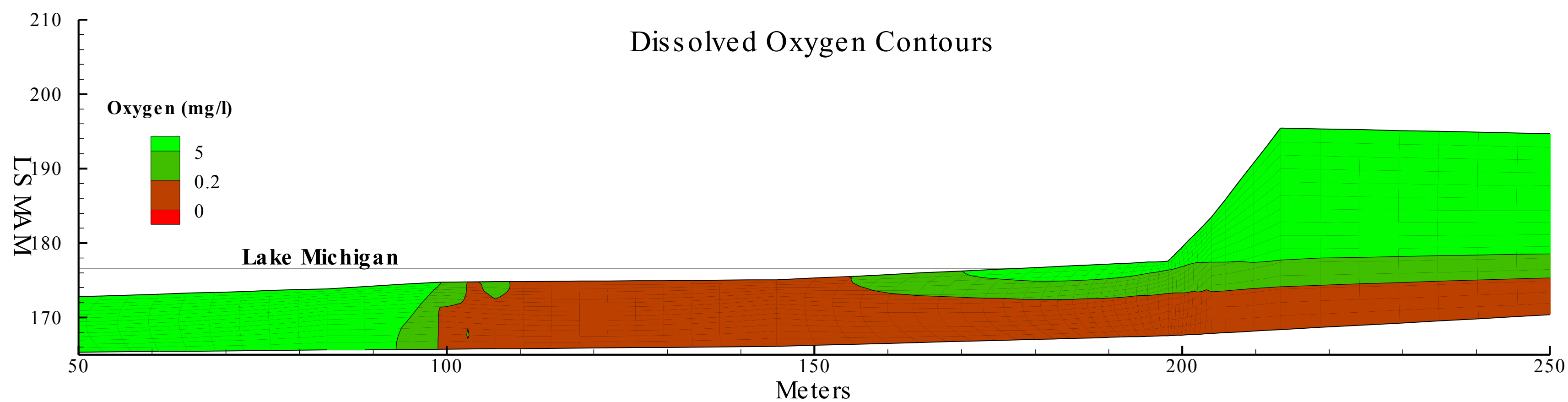


Computational Grid for the GSI



1408 Nodes	1325 Elements

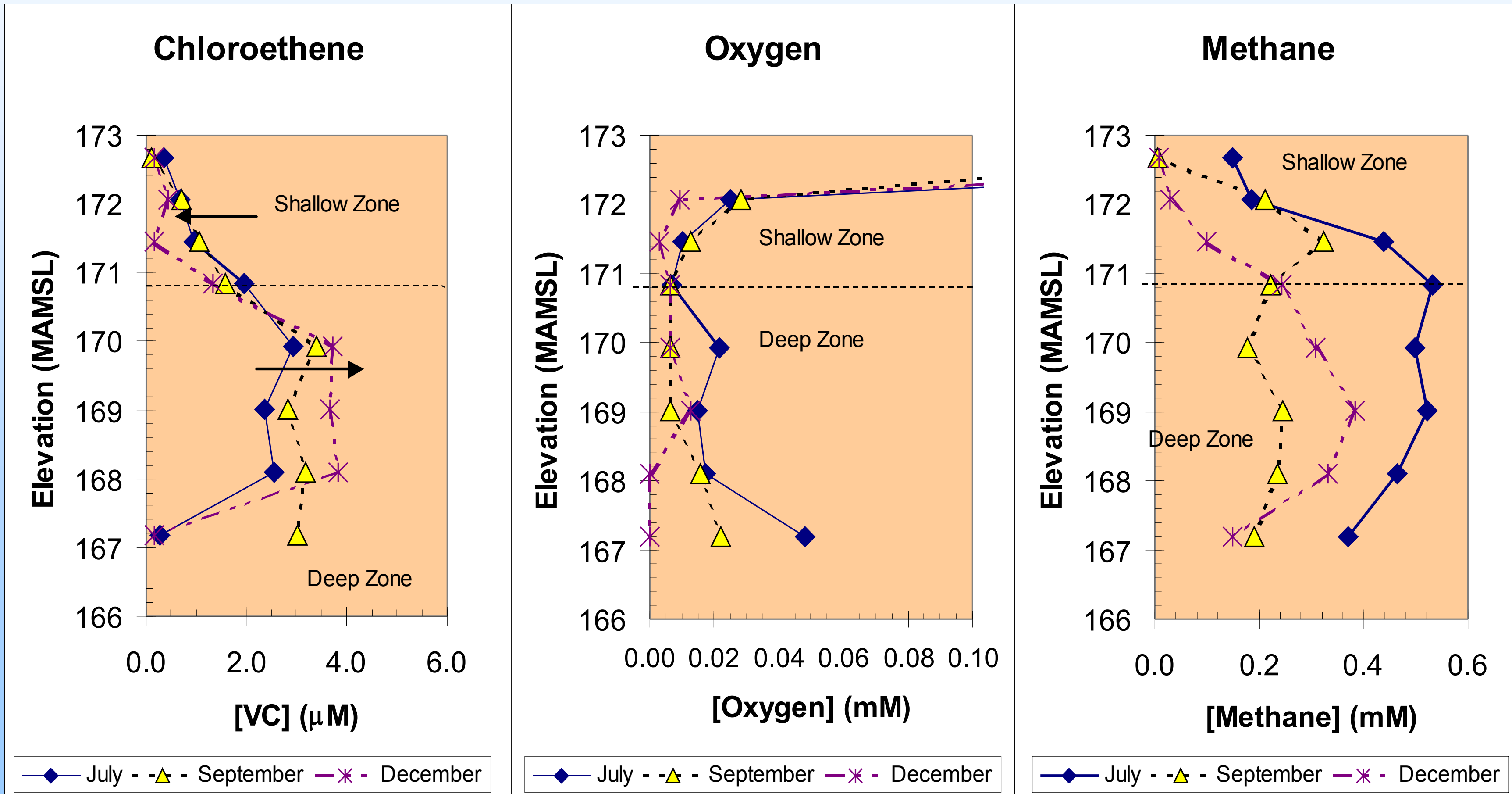
Predicted Oxygen Profiles in Response to Storm/Wave Activity



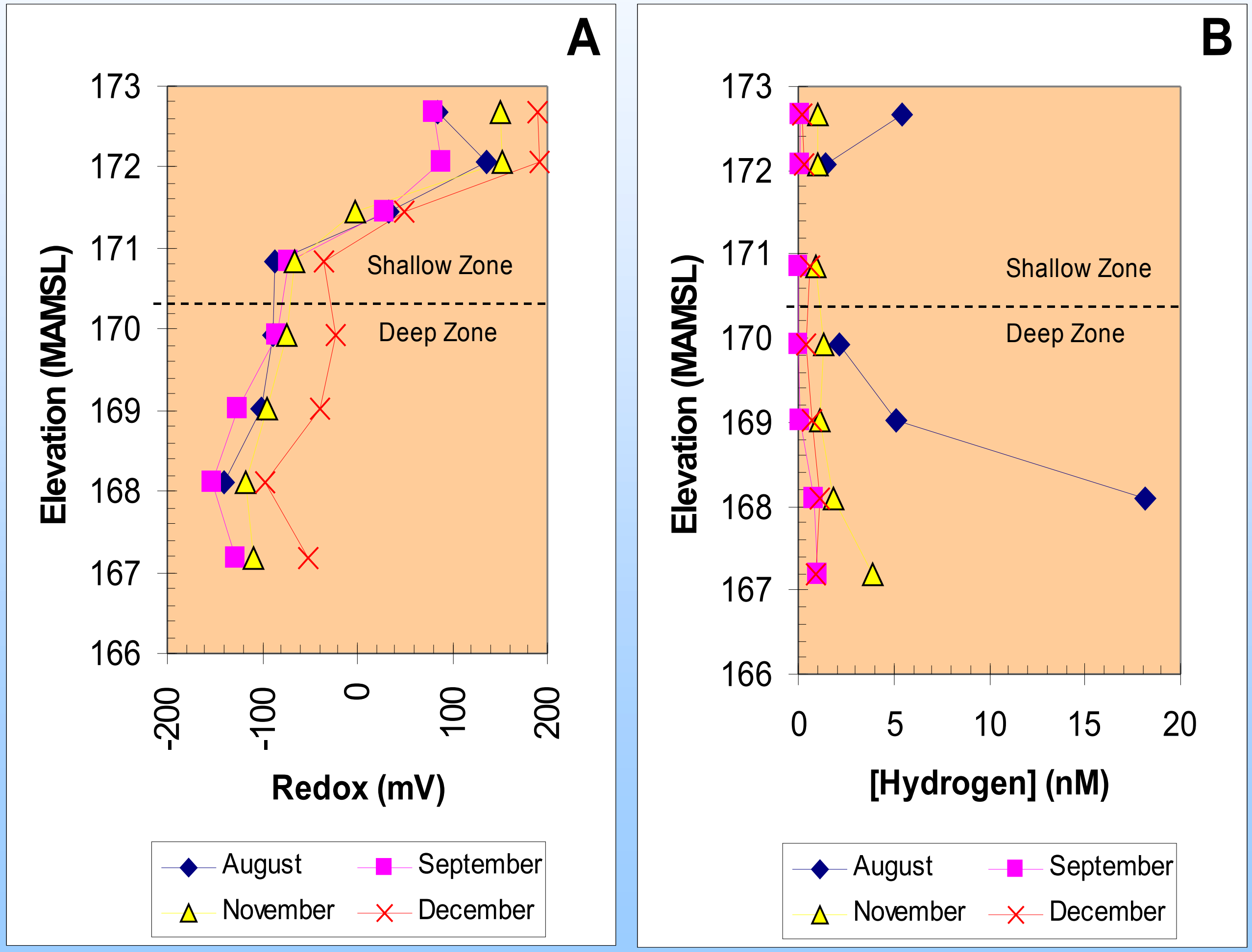
Initial Conditions:	Oxygen present at 12 mg/l throughout aquifer.
Boundary Conditions:	Aerobic lake water (12 mg/l). Aerobic rainwater infiltration (12 (mg/l). Anaerobic groundwater inflow from inland (0 mg/l).
Velocity Field:	4 day cycle - 1 stormy day followed by 3 calm days
Storm:	1.5 meter waves 0.75 meter rise in lake level

Installation of Multilevel Samplers on the Beachhead

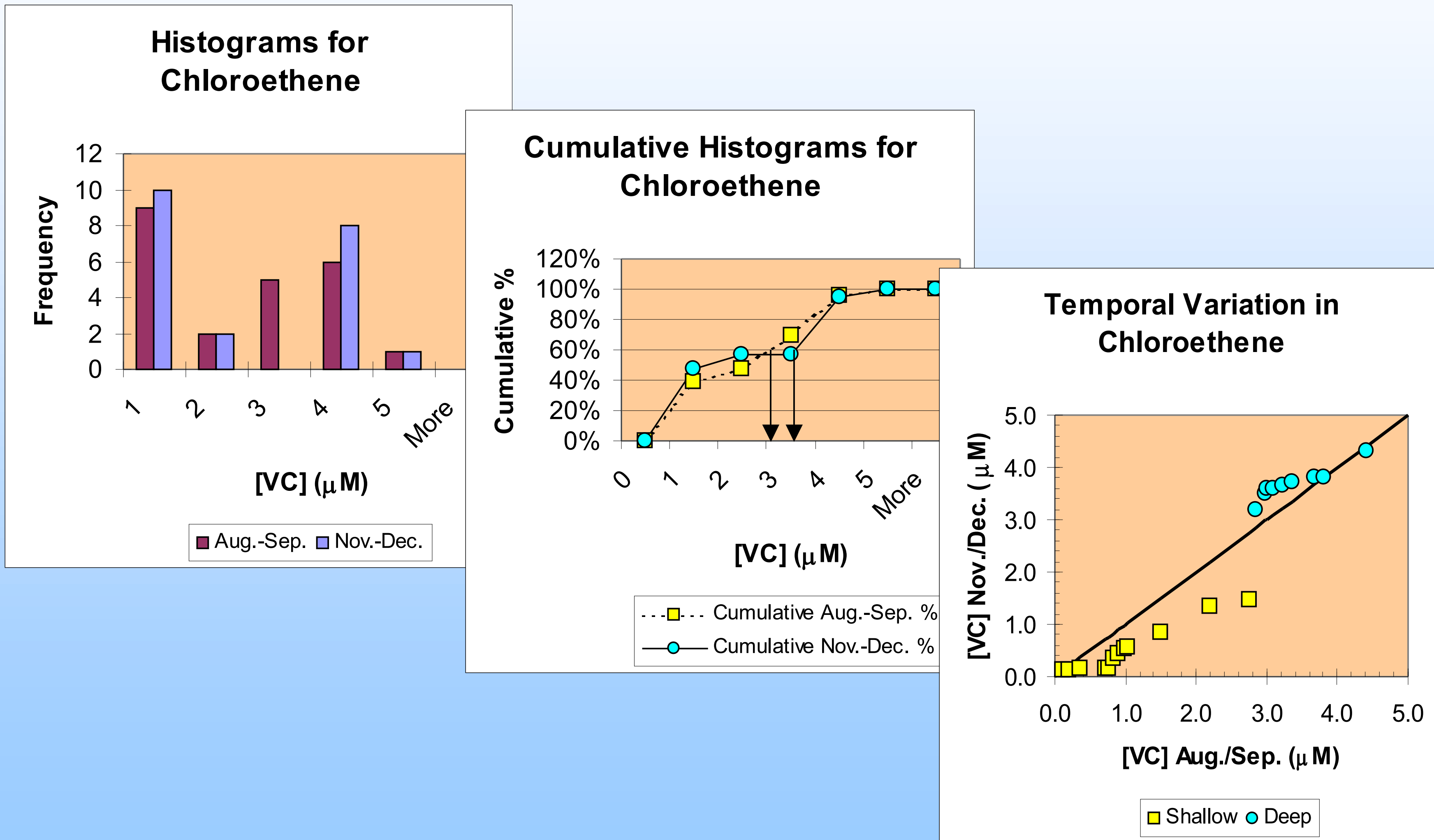
Contaminant & Geochemical Profiles at the GSI



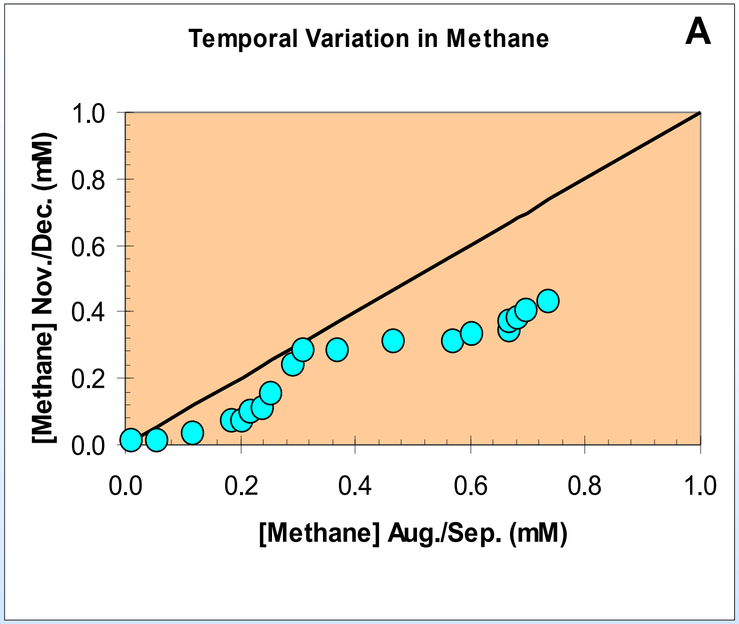
Redox and Hydrogen Profiles

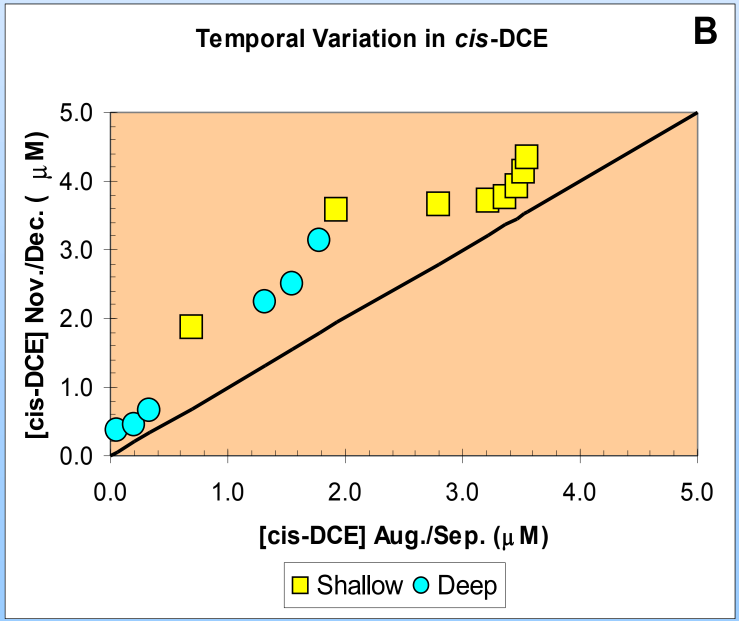


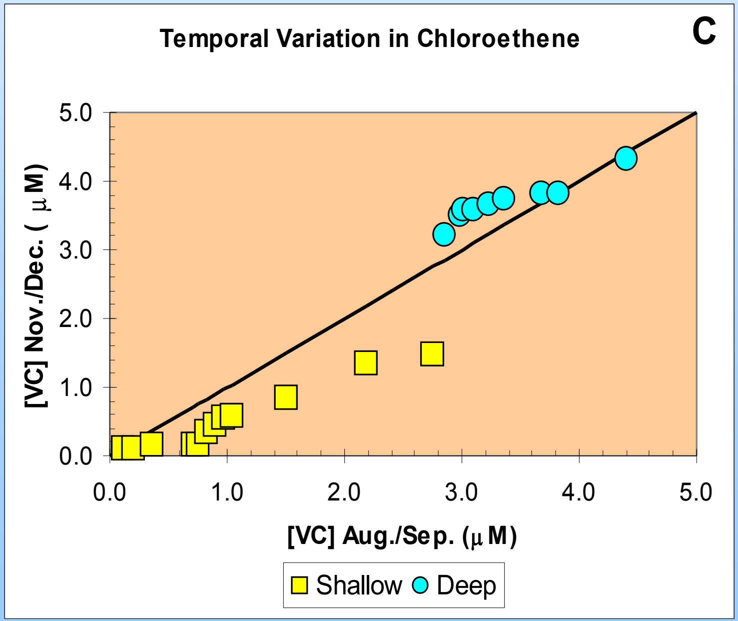
Construction of Quantile-Quantile (q-q) Plot



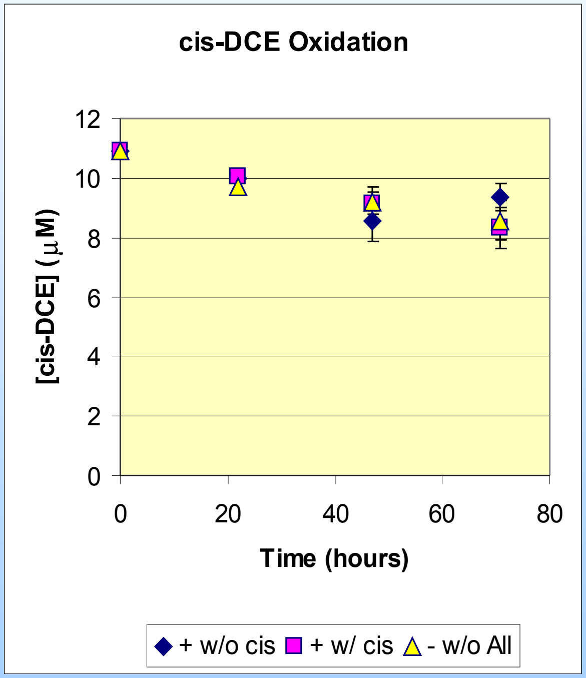
Temporal Variations

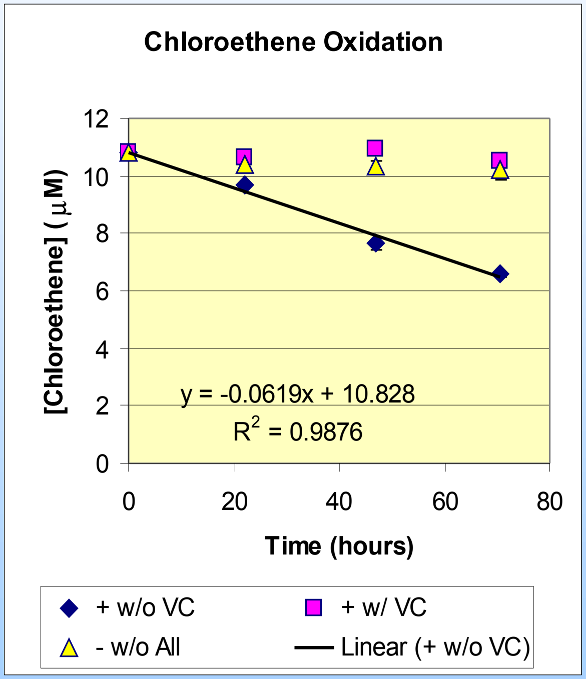


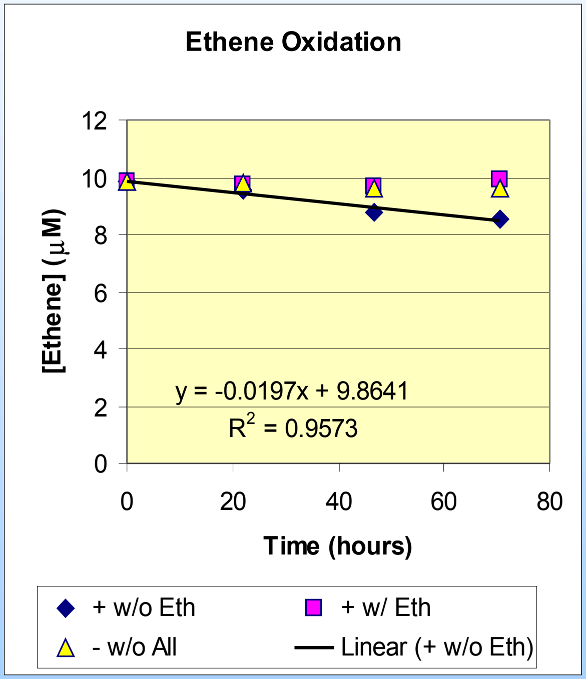




Activity of Aquifer Solid-Eluted Cell Suspensions: Methanotrophs

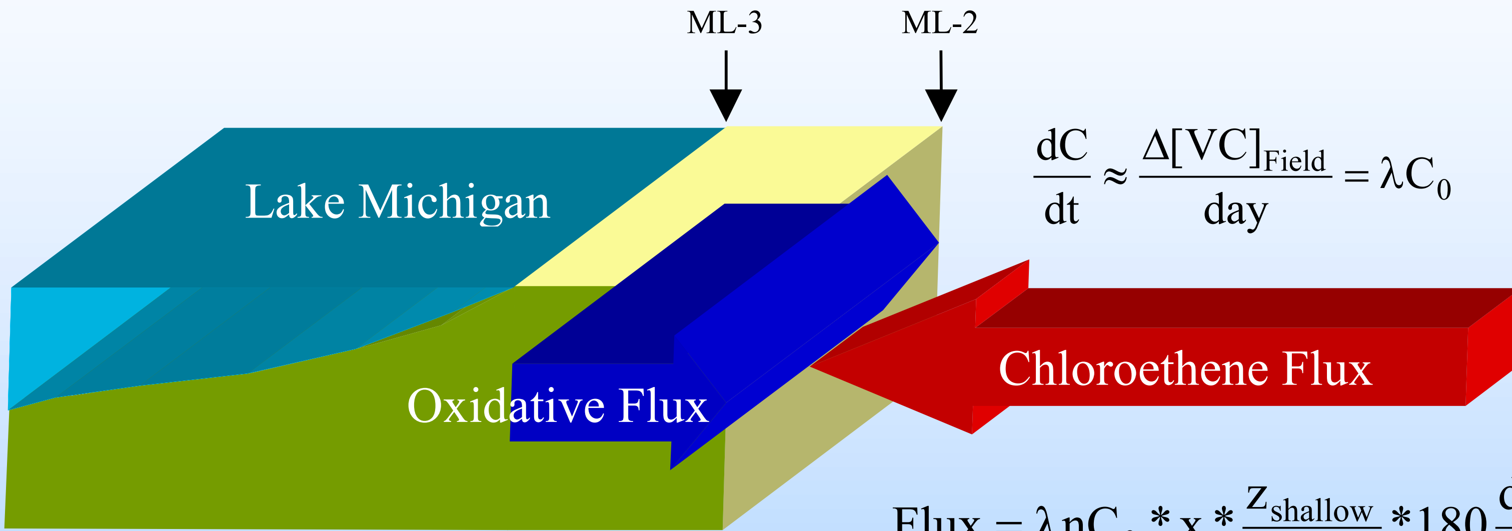






- *cis*-DCE: > zero relative to Control
- Chloroethene: -2.94 nMoles / (day-mg protein)
- Ethene: -0.85 nMoles / (day-mg protein)

Sediment Oxidation Potential



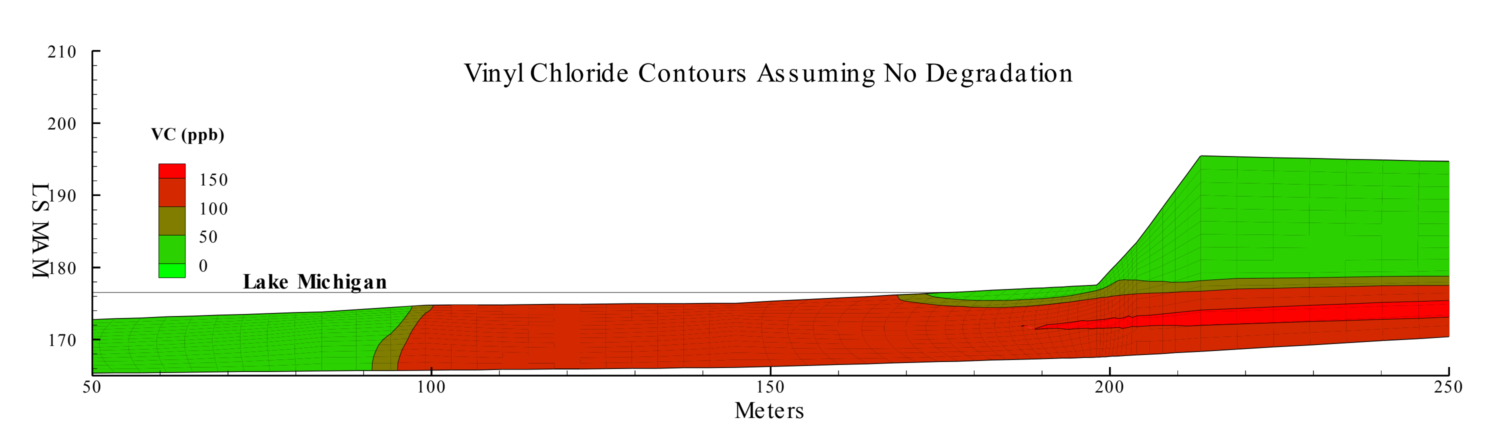
$$\frac{dC}{dt} \approx \frac{\Delta[VC]_{Field}}{day} = \lambda C_0$$

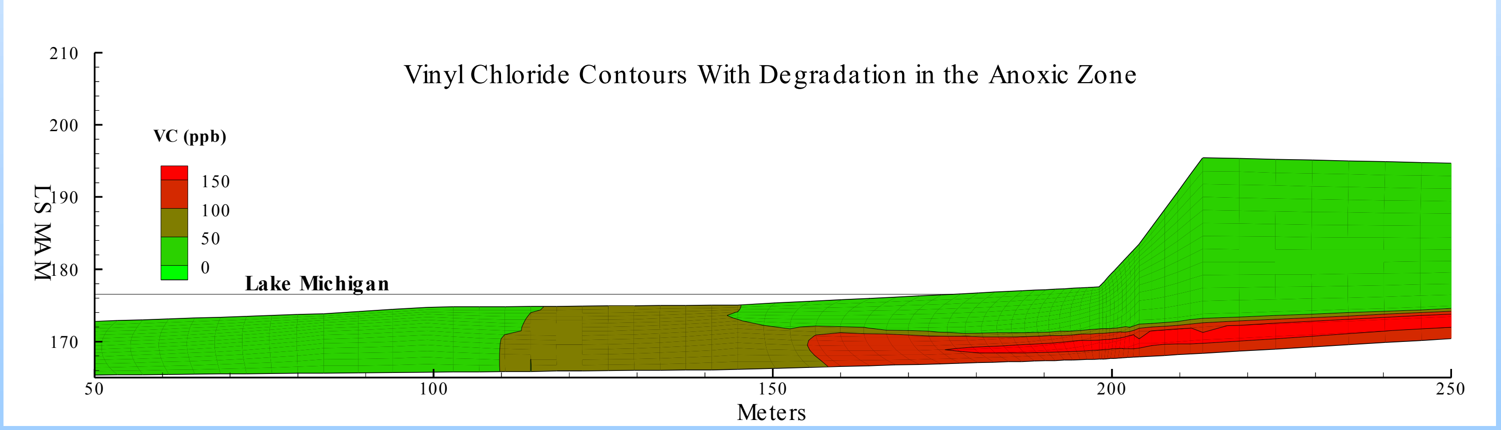
$$Flux = \lambda n C_0 * x * \frac{z_{shallow}}{z_{total}} * 180 \frac{days}{year}$$

- *Effect of Oxidation:*
  - ✓ *Chloroethene Flux at Transect-5 is 0.86g/(yr-m^2).*
  - ✓ *Oxidative Flux by Field Measurement is 0.063g/(yr-m^2) (~7%).*
  - ✓ *Oxidative Flux by Lab Measurement is 0.0007g/(yr-m^2) (~0.1%).*

Modeling Bioremediation at the GSI:

Methanotrophic Vinyl Chloride Oxidation at GSI During Storm Events





Degradation:	If oxygen > 0.1 mg/l	k = 1.5/day
	If oxygen < 0.1 mg/l	k = 0.

Implications for Intrinsic Bioremediation at GSI

- **The contaminant plume has migrated to the lake and discharges into Lake Michigan between the shoreline and 100 meters from shore.**
- **Surface water activity oxidizes the shallow and deep portions of the GSI, however, this effect is greatest in the shallow zone.**
- **Contaminants are transformed via oxidative processes in the shallow zone and reductive processes in the deep zone.**
- **Aerobic natural attenuation is insufficient to prevent flow of chloroethene into Lake Michigan.**

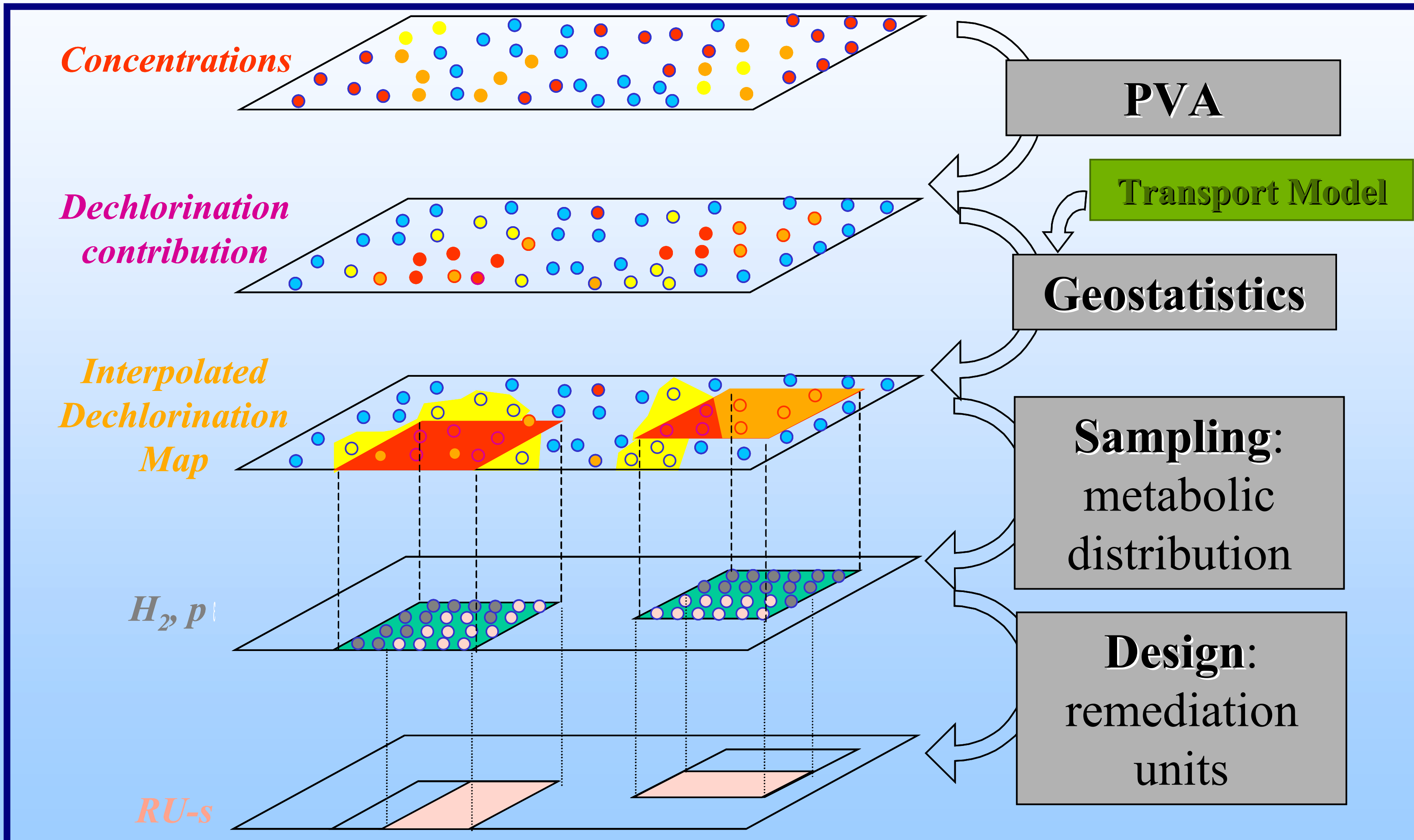
“Heads Up”: CLEANER (NSF Collaborative Large-Scale Engineering Assessment Network for Environmental Research)

- Backbone: A series of well-instrumented field facilities (EFFs) representing distinctive stressed environments or environments that are representative of a common set of conditions or anthropogenic stressors

- Enabling Technologies: Remote and on-site sensors, as well as local and off-site sample analysis. Real-time data acquisition and wireless transmission. Distributed parameter models. Geostatistical integration of monitoring data and GIS layers

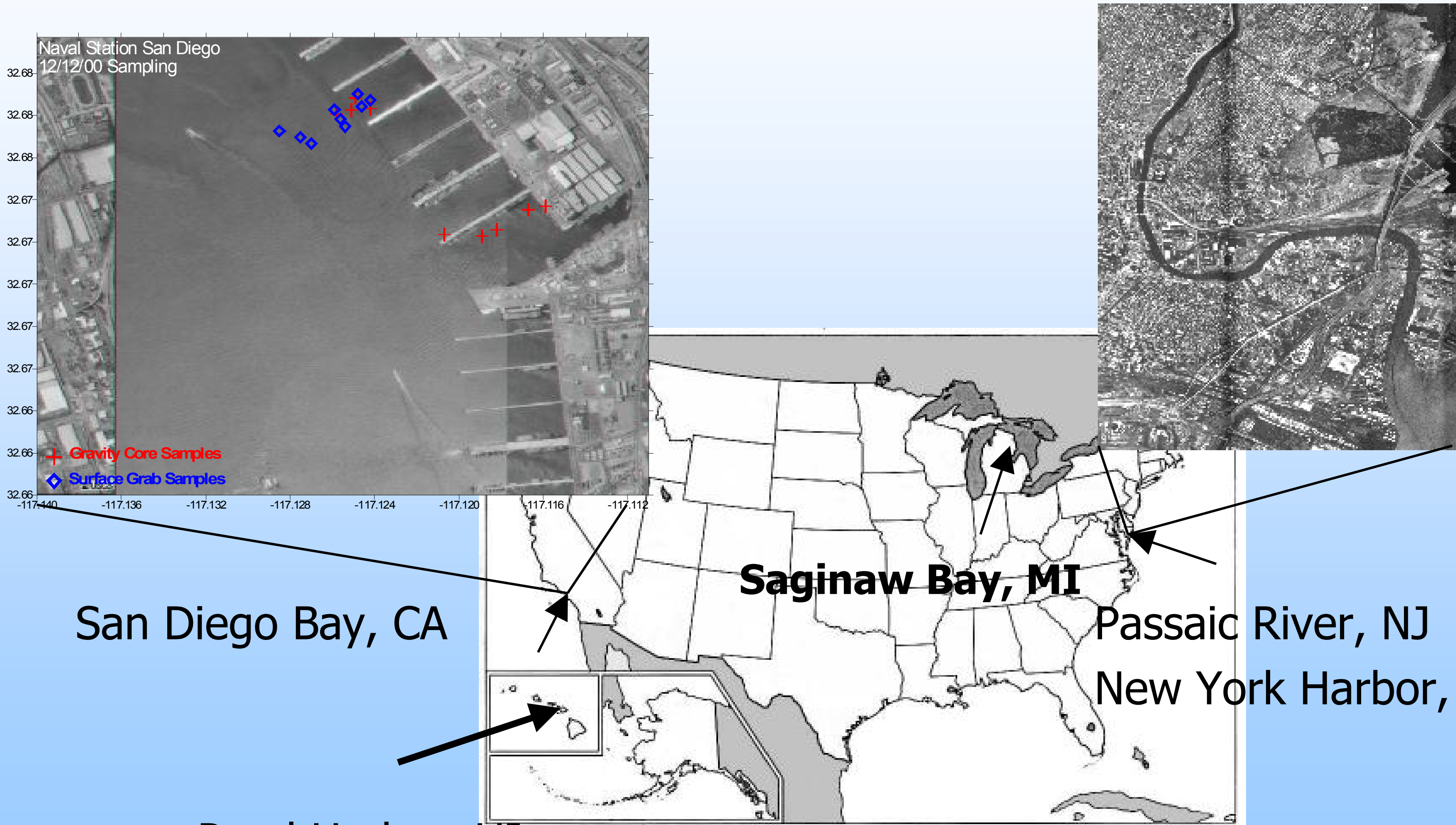
- Objective: Systematic and dynamic evaluation of ecosystems conditions and flows across and within media. Improved management strategies for ecosystems by controlling anthropogenic inputs and applying remediation techniques.

Layered Information Approach for Contaminated Sediments: Incorporating Uncertainty Analysis in Remedial Unit Design



PVA: Polytopic Vector Analysis – An Environmental Forensics Tool for Source Apportionment

Contaminated Sediment Sites



San Diego Bay, CA

Saginaw Bay, MI

Passaic River, NJ

New York Harbor, NY

Pearl Harbor, HI