Hyper-alkaline Waters in Calumet Wetlands (South Chicago, IL):

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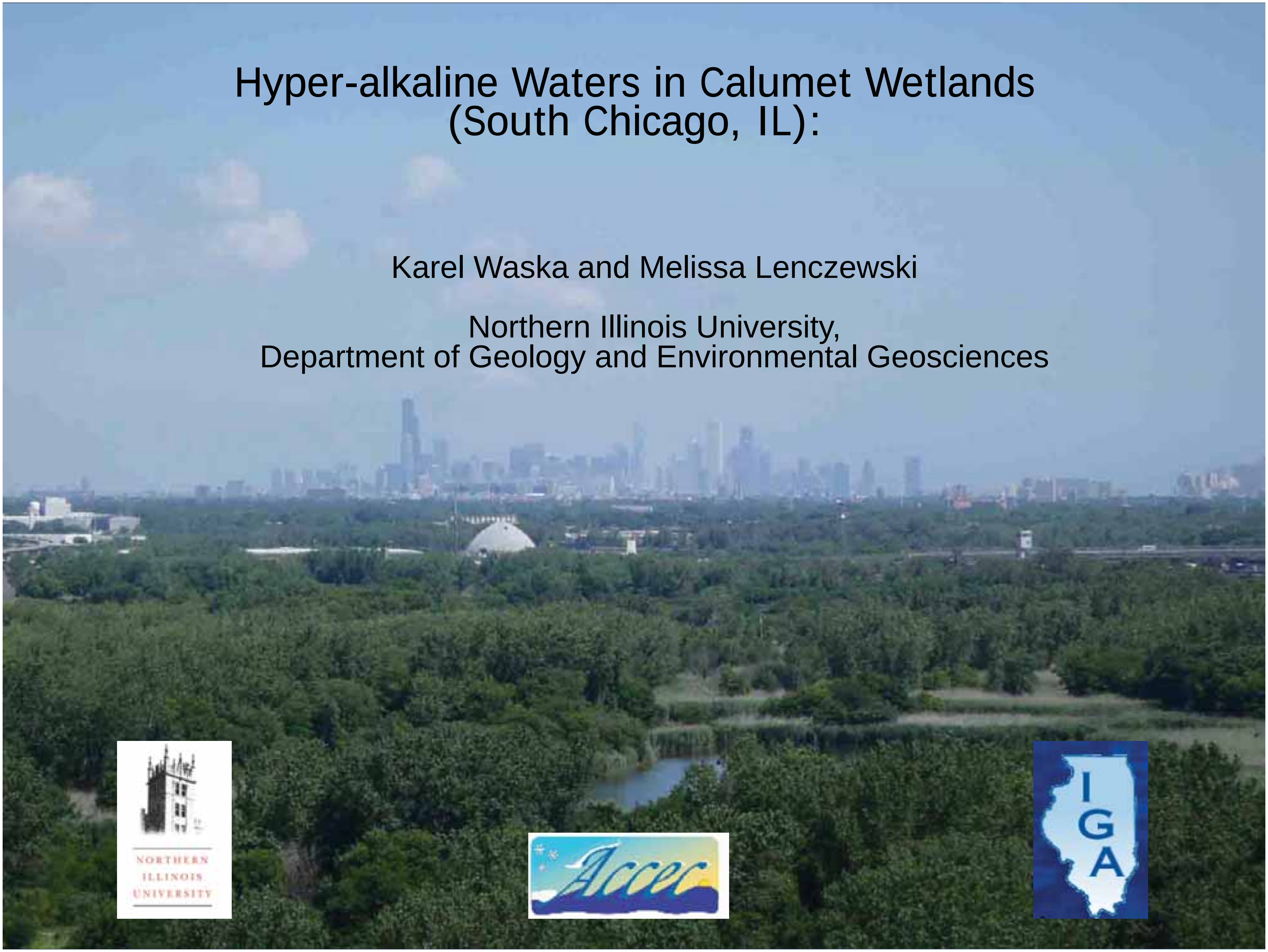

Acknowledgements

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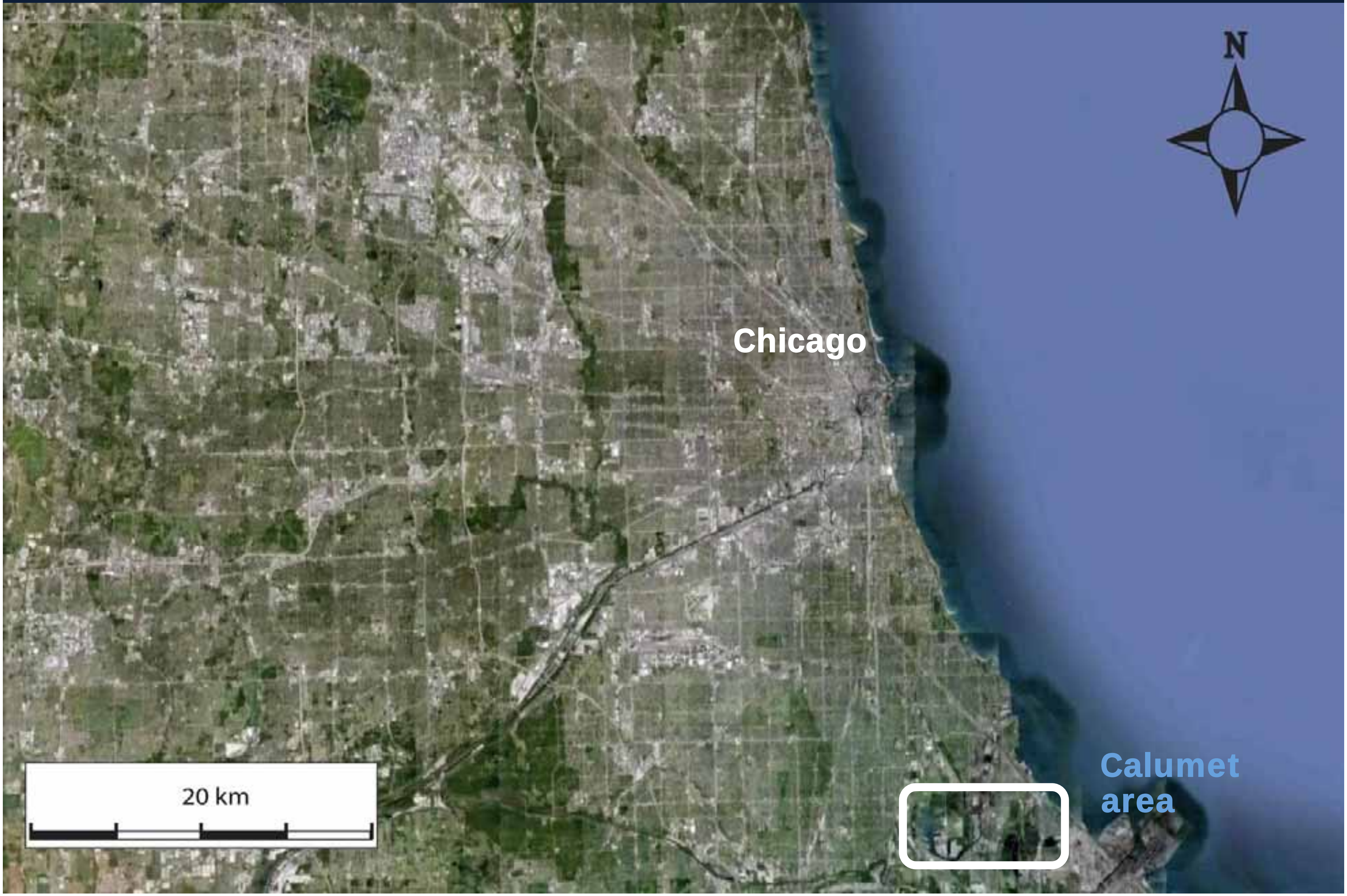
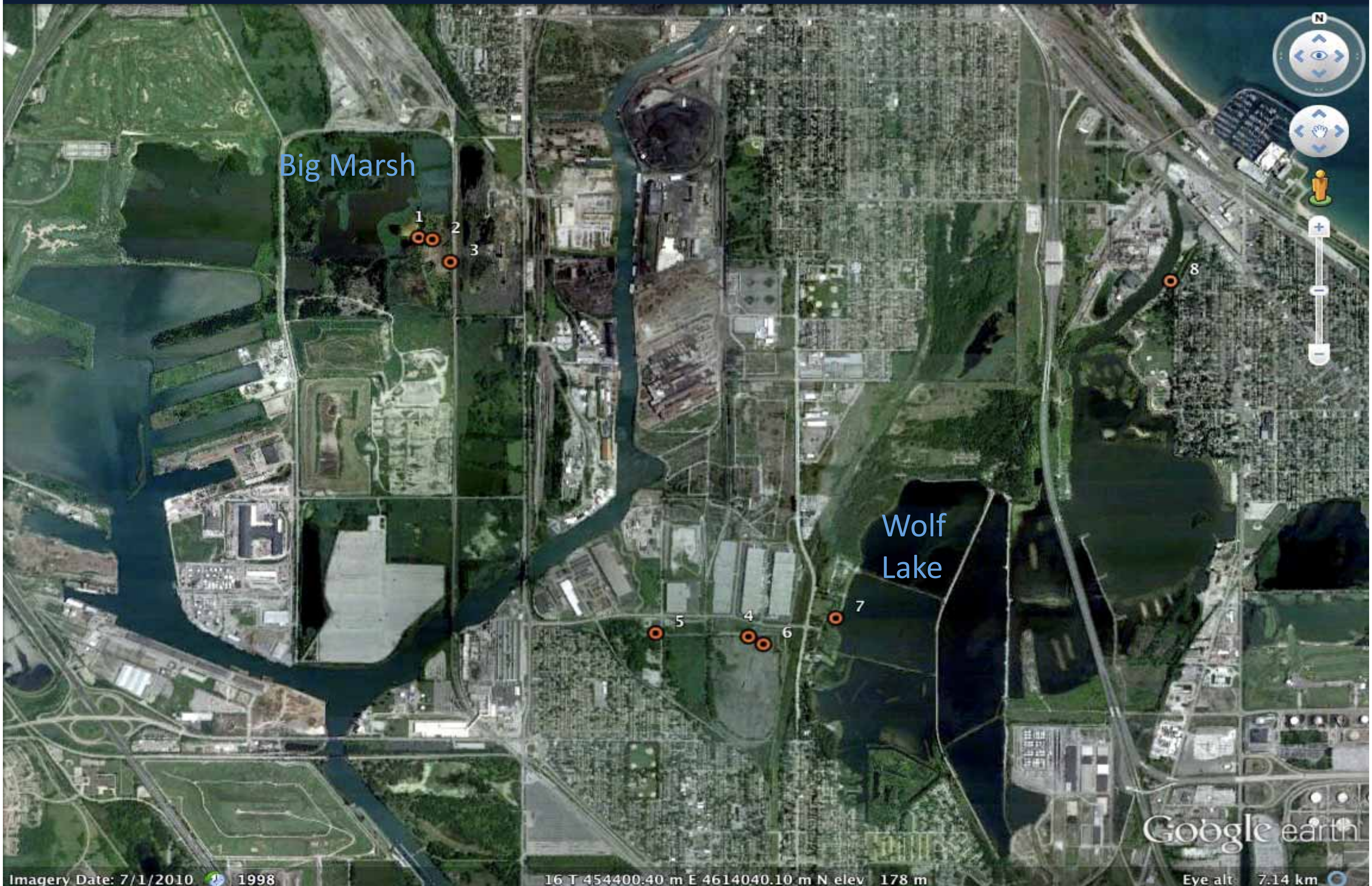
- Special thanks belong to Dr. George S. Roadcap from Illinois State Water Survey for his advices on site selection
- Professor Melvin R. Duvall, Anni Moore, and Andrew Thompson from NIU Department of Biology
- Undergraduate researchers: Richard Lauderdale and Hugh Fritz

Introduction

- Hyper-alkaline (pH up to 13.3) surface and groundwater habitats
- Seasonal and site-specific differences in pH (9-13) and heavy metal concentration
- Unique site for study of alkaliphilic and alkalitolerant organisms


N
Chicago
Calumet
area
20 km


Big Marsh
1
2
3
4
5
6
7
8
Wolf
Lake
Google earth
Imagery Date: 7/1/2010
1998
16 T 454400.40 m E 4614040.10 m N elev 178 m
Eye alt 7.14 km

What happened? History...

- Geology: periglacial plain at southern tip of Lake Michigan
- Industrial history:
  - From 1850s: railroad tracks
  - 1870s: building of Calumet Harbor
    - – large scale industrial development
  - Steel production, railroad cars manufacture, brick and tile production; mining of sand, gravel, and clay; processing of coal and petroleum; and meat packaging
  - Dumping of waste products: largely slags

- Infilling of wetlands: disposing of unwanted wastes, creating new land, eliminating breeding grounds for insects

What happened? Geochemistry...

- Slags composed mainly of high temperature Ca-Si minerals, up to 50% of metallic Fe and Mn and other steel additives (Cr, Mo, V, Zn)
- Long term weathering:
  - Rankinite: $Ca_3Si_2O_7 + 7H_2O = 3Ca^{2+} + 2H_4SiO_4 + 6OH^-$
  - Larnite: $Ca_2SiO_4 + 4H_2O = 2Ca^{2+} + H_4SiO_4 + 4OH^-$
  - Akermanite: $Ca_2MgSi_2O_7 + 7H_2O = 2Ca^{2+} + Mg^{2+} + 2H_4SiO_4 + 6OH^-$
- On contact with atmosphere: $CO_2 + H_2O = 2H^+ + CO_3^{2-}$

  $Ca^{2+} + CO_3^{2-} = CaCO_3$


Big Marsh
1
2
3
N
100 m
166 m
Imagery Date: Jul 1, 2010
16 T 452892.67 m E 4615519.27 m N elev 178 m
Eye alt 753 m
©2009 Google


7
N
5
Squaw Creek
4
6
Wolf Lake
300 m

Why we care?

Why we care?

Endangered Species

- Great blue heron
- Black-crowned night heron
- Tree swallow
- Blue spotted salamander
- Common mudpuppy
- Northern leopard frog
- Eastern spiny soft shell
- Plains garter snake

What we know?

- Aquatic environment with high pH (pH=13.3; Site2, 07/2011)
- Buffering system of Ca-OH, potentially dependent on temperature
  - ↓ T => ↑pH
- High chemical variability due to slag variations between sites
- Evidence of microbial activity at these alkaline environments:
  - Alkaliphiles closely related to known extreme alkaline environments (e.g., Lake Magadi, Kenya; Mono Lake, CA)

Roadcap *et al.*,2006, Groundwater 44(4): 511-517.

Objectives

- Aquatic environment with high pH
  - Study of alkaliphilic and alkalitolerant microbial communities
- Buffering system of Ca-OH, potentially dependent on temperature
  - Monitor pH over different seasons
- High chemical variability due to slag differences between sites
  - Compare the geochemistry of the water and sediment
- Evidence of microbial activity at these alkaline environments
  - Compare the microbial diversity of sediment and water at particular sites

  - Examine possible remediation methods in laboratory column experiment (bioreactor) and observe the response of microbial communities

Environmental field study

- Sampling and monitoring of *in-situ* conditions at all 7 sites performed seasonally

- Field work:
  - Monitoring of physicochemical parameters
  - Collection of 14 micro-filter samples, and 6 sediments (#2, #6 = wells)

- Lab work:
  - Geochemistry: concentrations of dissolved cations
  - Sample processing and analysis: DNA extraction and PCR-fingerprinting

Physicochemical monitoring and sampling

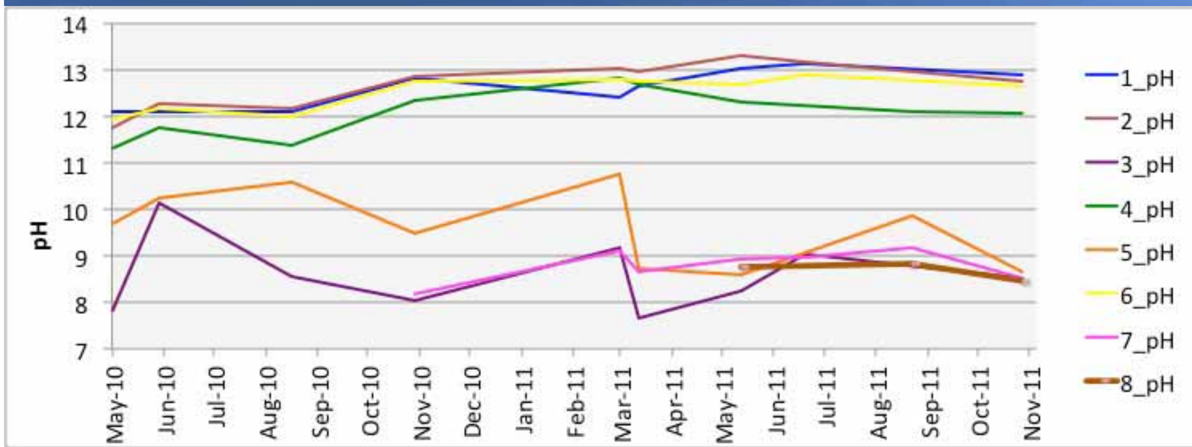
- Hydrolab MiniSonde
- Temperature and pH

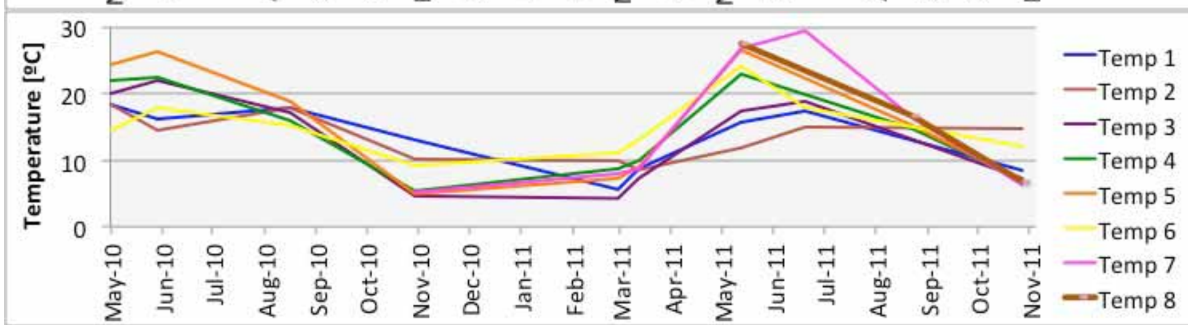
- Digging the bottom of water body
- 2 sterile tongue depressors
- Whirl-pak bag
- ~200 g per site

- Sterile filters (45μm pores)
- Peristaltic pump
- 2 filters per site

All samples transported in ~ 5ºC and processed within one day

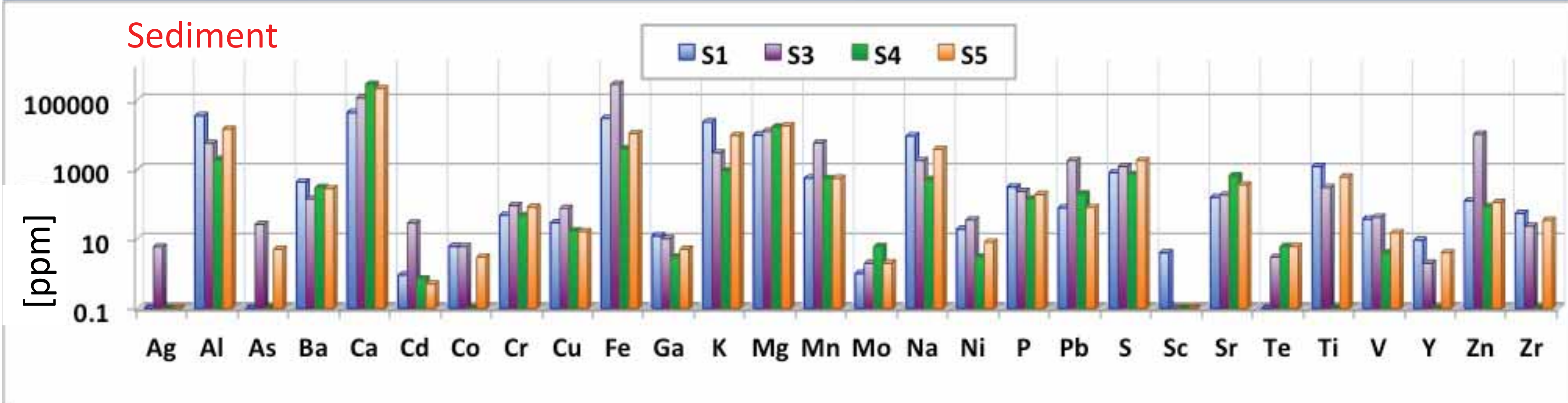
pH and Temperature measurements

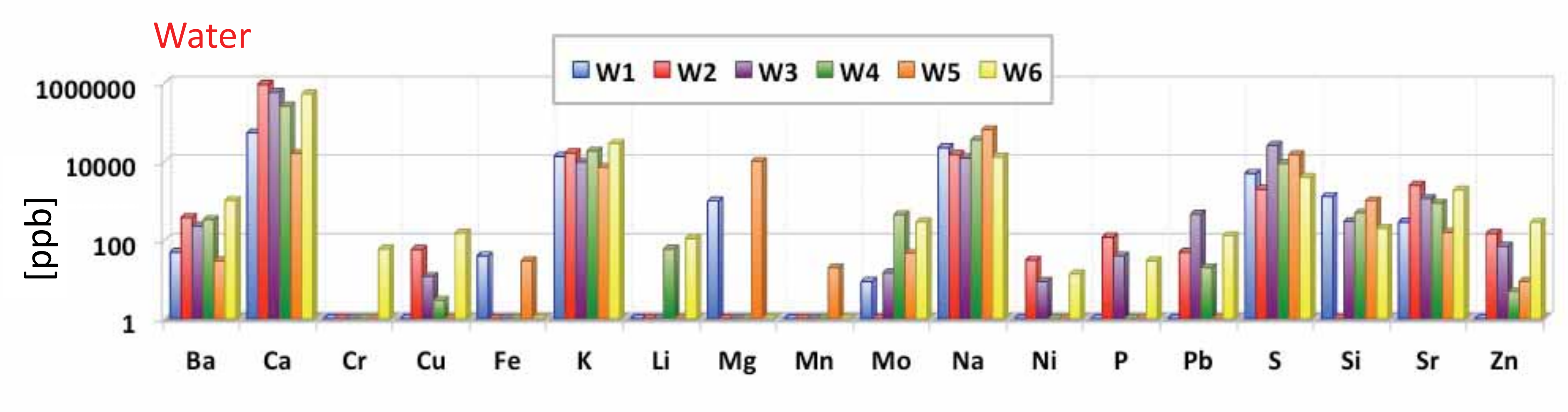




Other Factors – Hydraulic Conductivity (K) = 1.4 x 10^{-3} cm/s (= 121 cm/day)

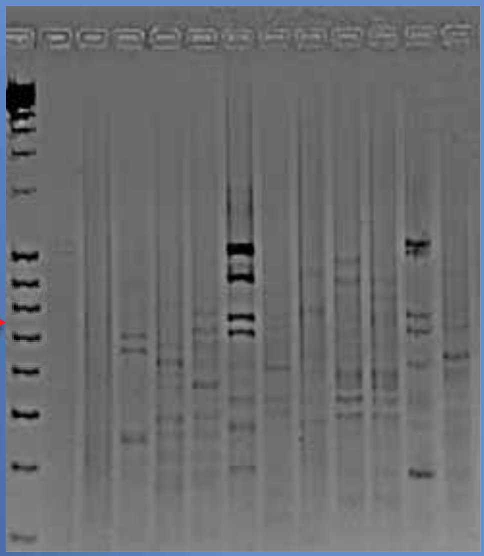
Heavy metals



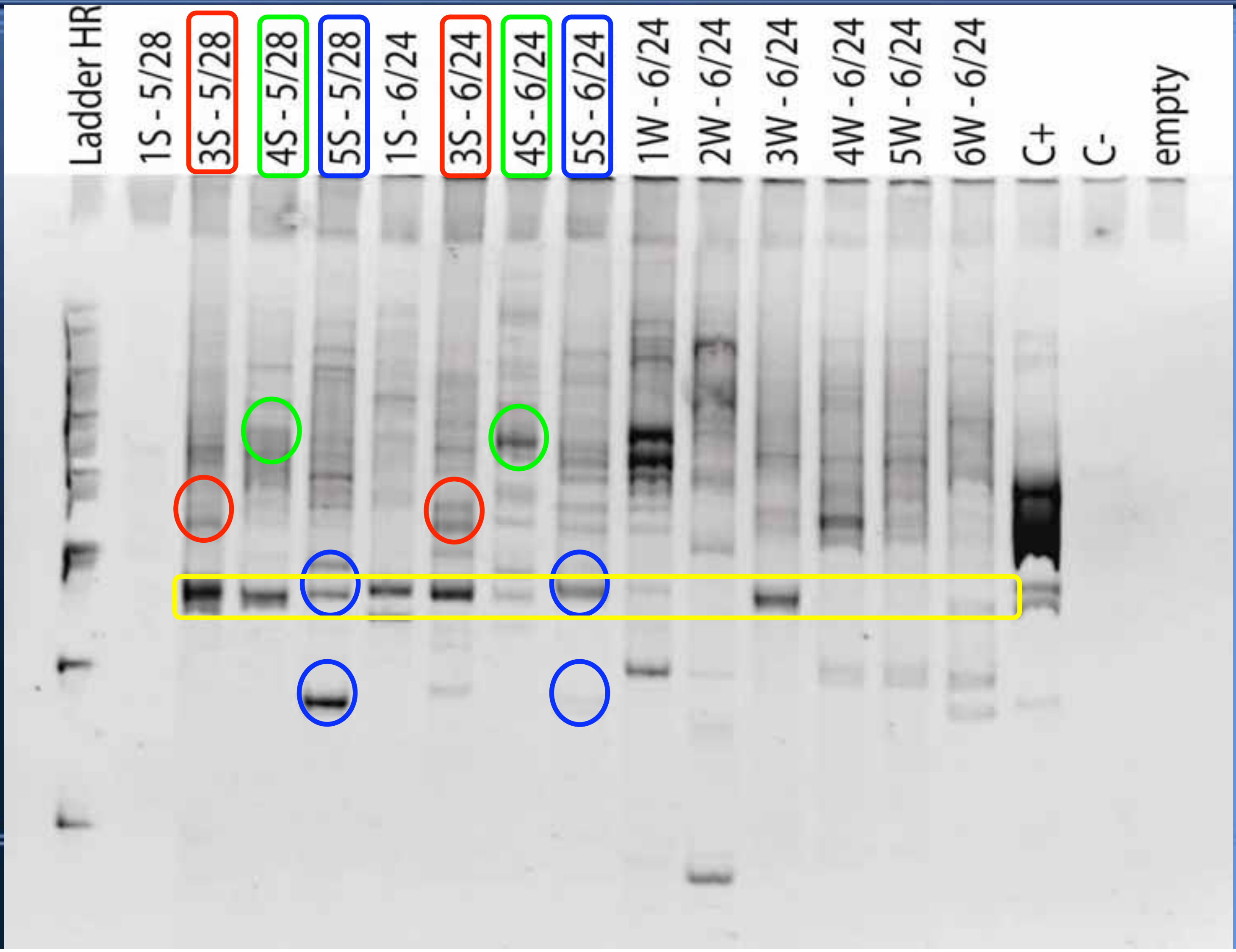


PCR-fingerprinting

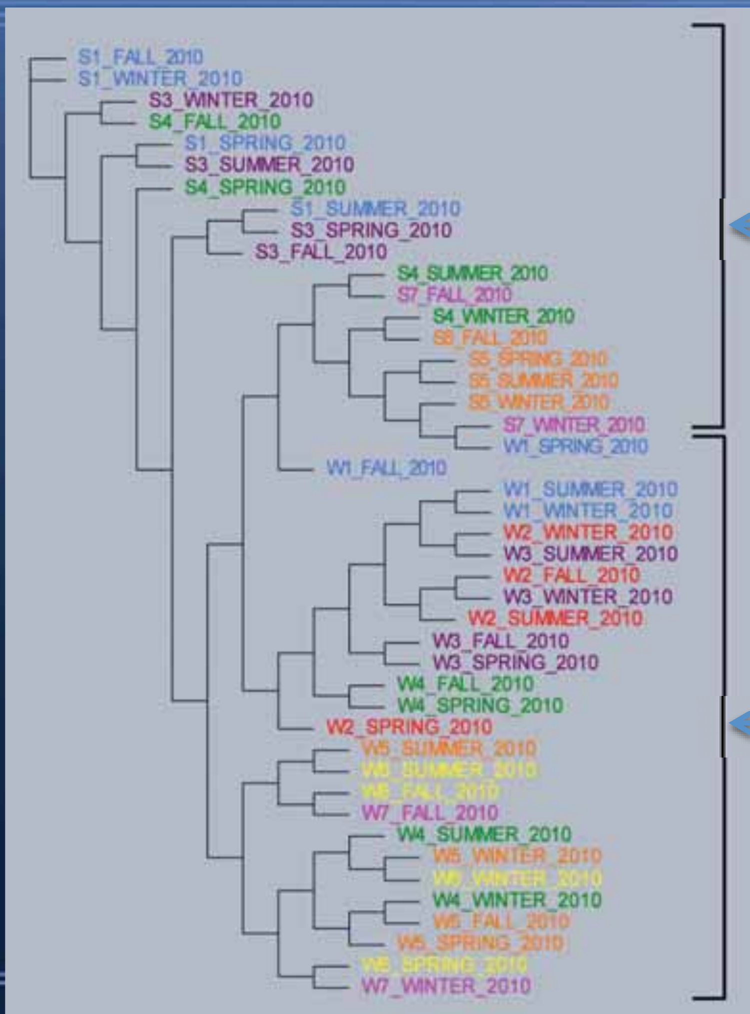
- Environmental DNA extracted using MoBio Powersoil™ DNA isolation kit from filters
- DNA extracts purified by PCR (Polymerase Chain Reaction) using RISA1406f and RISA23Sr primers
- RISA = Ribosomal Intergenic Spacer Analysis
- Products of PCR subjected to gel electrophoresis on 2% TAE agarose gel – visualization of results
- Gel analyzed using GelQuest (Sequentix)
- Statistical analysis performed using modified Jaccard index (Nei and Li, 1979)



PCR-fingerprinting



Microbial community variations



… DNA fingerprints

Summary

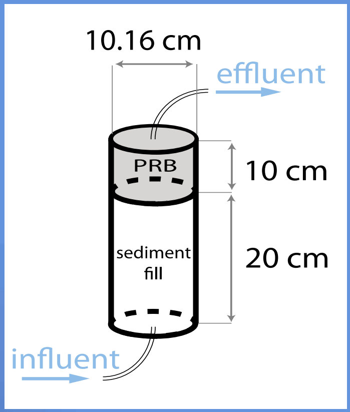
- Unique sites with widely differing conditions
  - heavy metal concentrations varying between sites and between water and soil

- Significant pH variations among sites and seasons
  - other environmental factors likely contributing: Hydraulic conductivity K = 1.4 x 10^{-3} cm/sec => fast motion of groundwater even with small change in hydraulic gradient

- DNA fingerprint analysis indicated:
  - microbial communities differ between water and soil
  - effect of season changes less pronounced than substrate or location effect =>
  - geographically related communities clustered closer together

What is next?

- Remediation column experiment in progress:
  - testing 3 Permeable Reactive Barriers (dolomite, quartz, Apatite II^{TM})
    - controls: without PRB and killed
  - sediment from site 1 and groundwater from site 2
  - two different incubation temperatures (4° & 25°C)
  - monitoring influent and effluent on pH, temperature, geochemistry, and microbial community



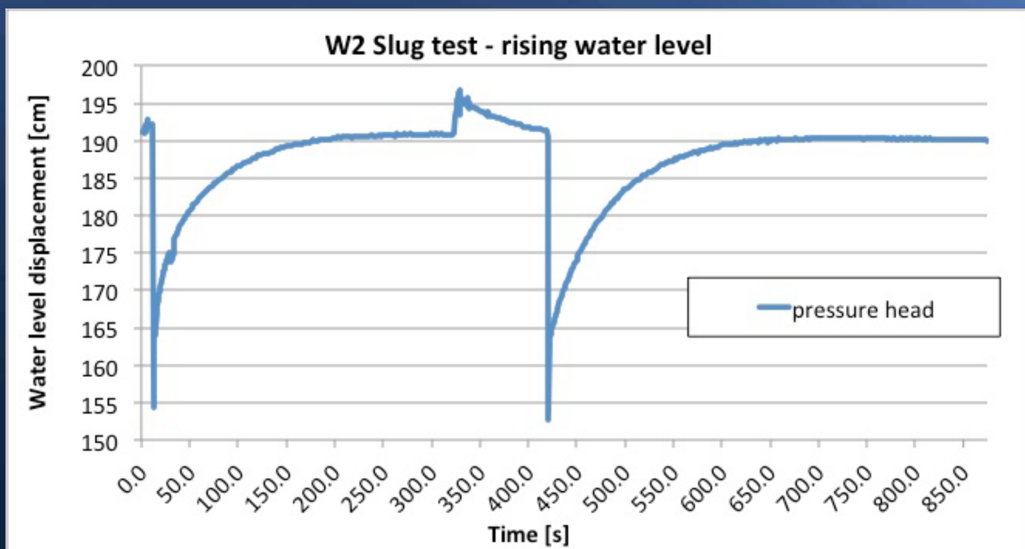
- Analyses of samples from "mineral-trap" *in-situ* incubation experiment
  - 11 different minerals incubated in water and sediment of Big Marsh and Wolf Lake sites for comparison of newly developing microbial communities

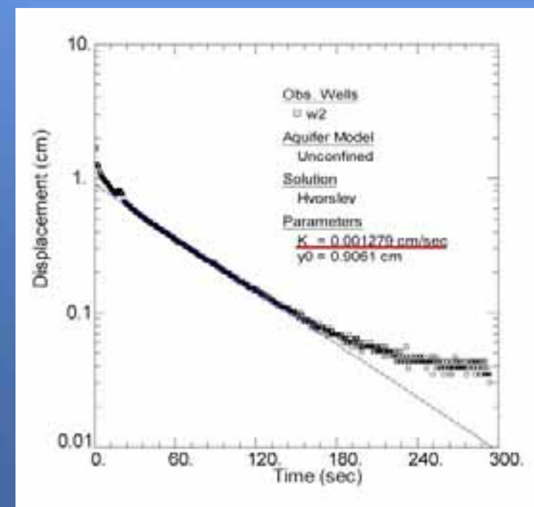
- Further environmental data collection

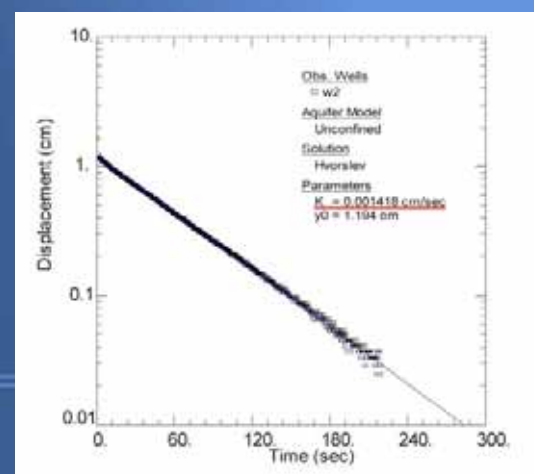
Thank you.

Slug Test data

- Hvorslev 1957; AQTeslov







Remediation Experiment

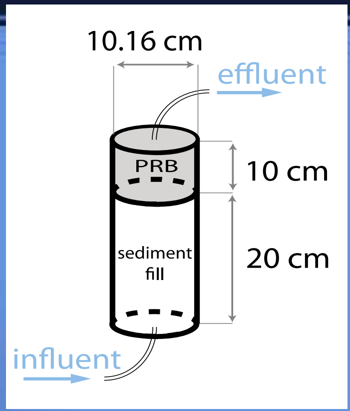
Remediation of the high pH examined by G.S. Roadcap (Dissertation Thesis 2004):

- acid addition
- air sparging
- dolomite
- quartz sand

Remediation of heavy metal contamination:

- dolomite (Roadcap, 2004, Reardon et al., 1993)
- Apatite II^{TM} (fish bones; PIMS = phosphate induced metal stabilization, Conca and Wright, 2006; Martinez et al., 2005)
- and wide variety of chelation methods (Lo and Yang, 2003; Papassiopi et al, 1997; Tandy et al., 2006; Wang et al., 2007), phytoremediation (Gremion et al., 2004), lime ($CaCO_3$) addition (Lee et al., 2006), etc…

Remediation Experiment



- CONSTRUCTED COLUMN EXPERIMENT:
- Started in December 2012
- To determine remediation strategies

- Columns filled with sediment from site 1 and flushed with water from site 2
- Different PRB (Permeable Reactive Barrier: dolomite gravel, quartz sand, Apatite II™) in different position inside the column (top or bottom)
- Incubation in two temperatures T = 4ºC and 25ºC

Remediation Experiment

- CONSTRUCTED COLUMN EXPERIMENT:
- 8 columns in duplicates for the two temperature incubations:
  - 1 natural control column
  - 1 autoclaved ("kill") control column
  - 2 dolomite incubations (top or bottom of column)
  - 2 quartz sand incubations
  - 2 Apatite II^{TM} incubations

- Monitoring influent and effluent on pH, geochemistry, and microbial activity

Remediation Experiment

Site 1 soil

Dolomite-top column design

Quartz-top column design

Apatite II^{TM}-bottom column design

Remediation Experiment

Remediation Experiment

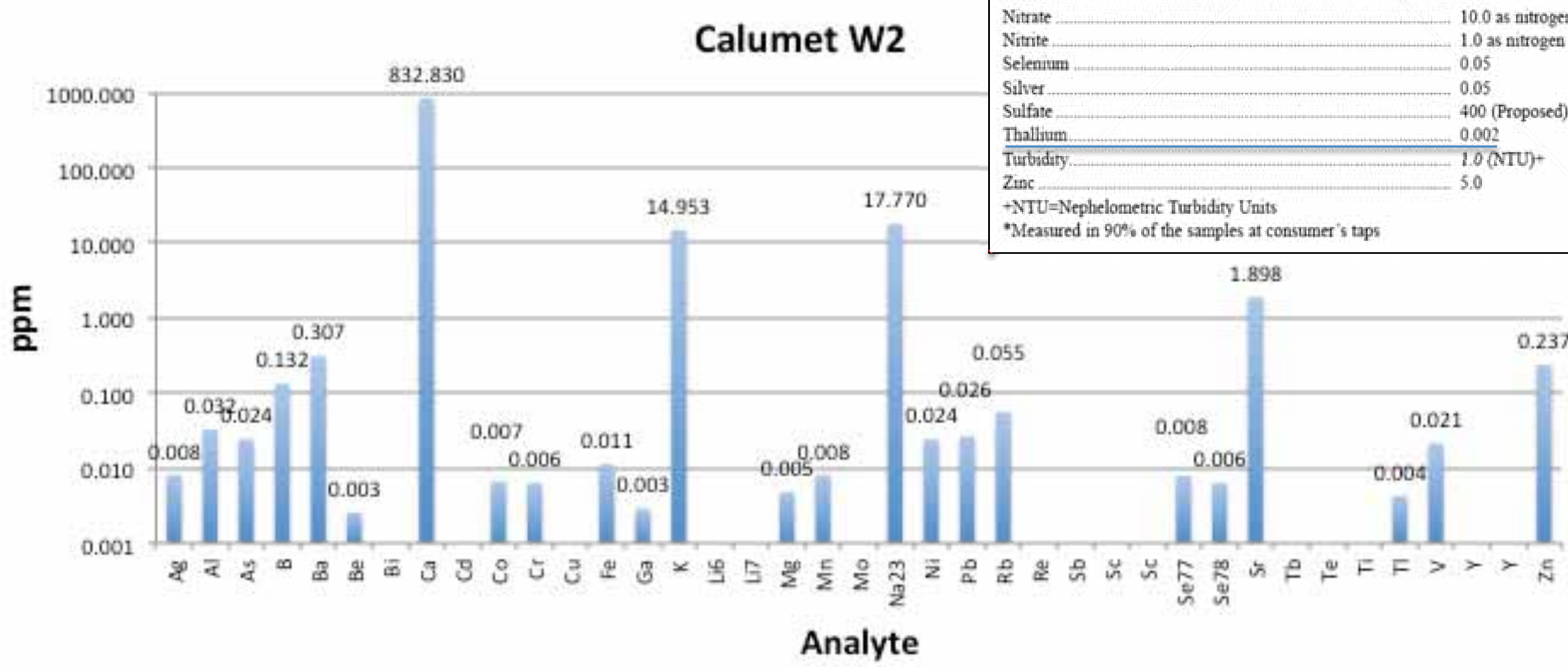
Influx and effluent water monitored on:

- pH and temperature (Corning bench top pH meter)
- dissolved anions (HPLC – Dionex)
- dissolved cations = earth metals and heavy metals (ICP-MS
- microbial community composition (DNA fingerprinting – future work, collection of water filters in progress)

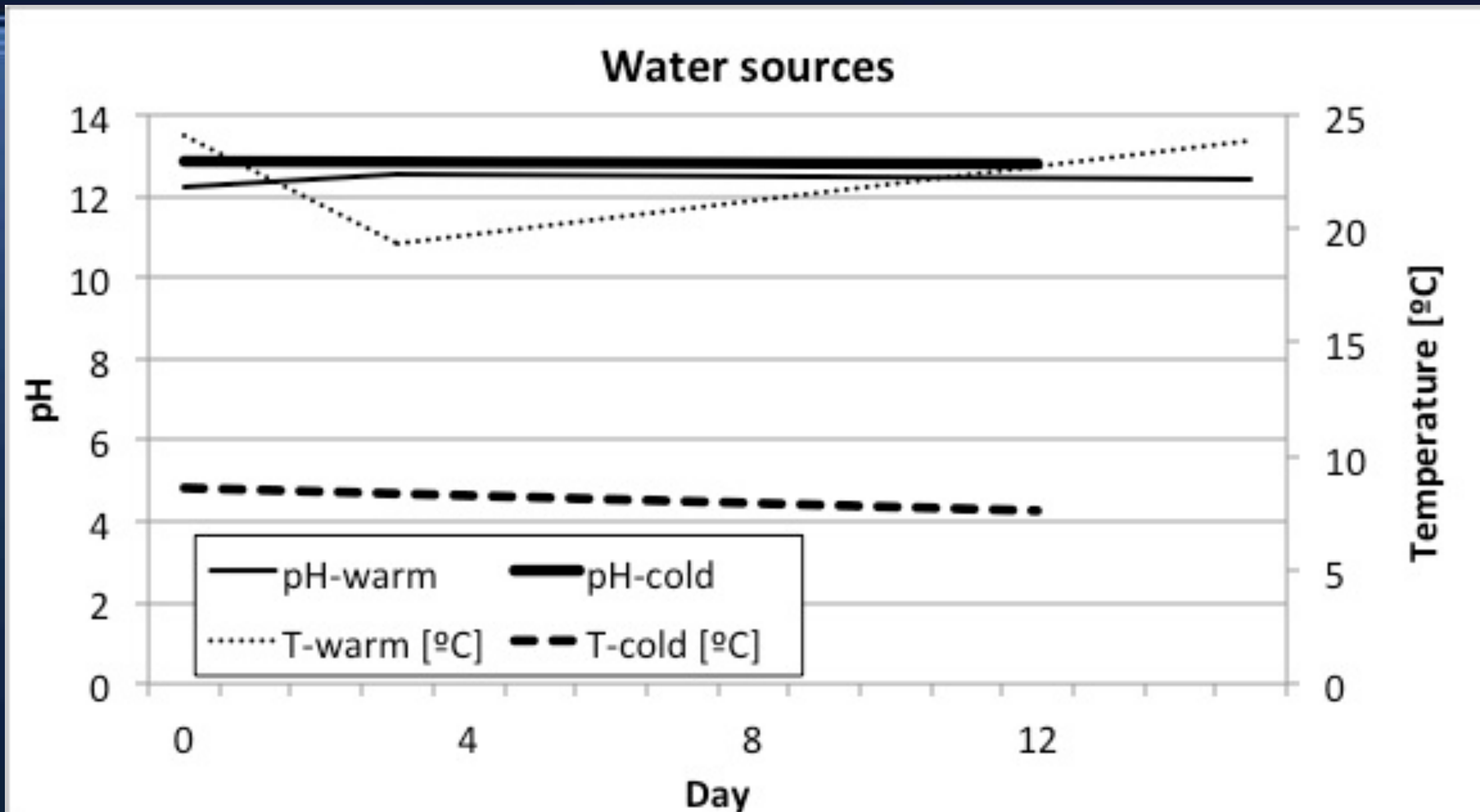
Heavy Metal concentration

Substance Inorganics	Maximum Contaminant Level (MCL) parts per million
Arsenic	0.05
Antimony	0.006
Asbestos	7 million fibers/liter
Barium	2.0
Beryllium	0.004
Cadmium	0.005
Chromium	0.1
Copper*	1.3
Cyanide	0.2
Fluoride	4.0
Iron	1.0
Lead*	0.015
Manganese	0.15
Mercury	0.002
Nickel	0.1
Nitrate	10.0 as nitrogen
Nitrite	1.0 as nitrogen
Selenium	0.05
Silver	0.05
Sulfate	400 (Proposed)
Thallium	0.002
Turbidity	1.0 (NTU)+
Zinc	5.0

+NTU=Nephelometric Turbidity Units
*Measured in 90% of the samples at consumer's taps



pH measurements



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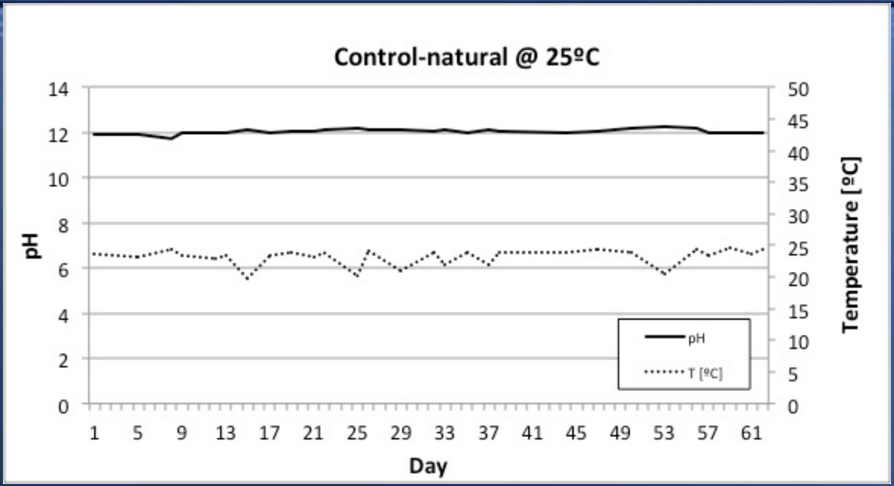

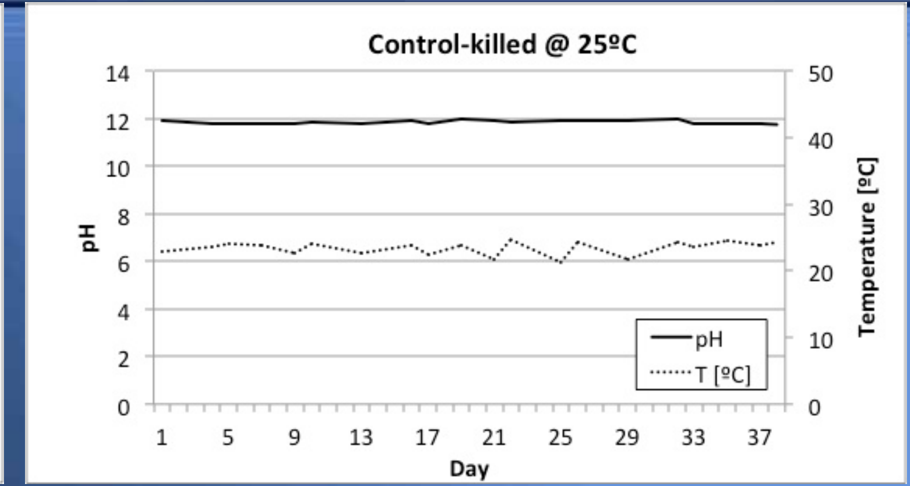

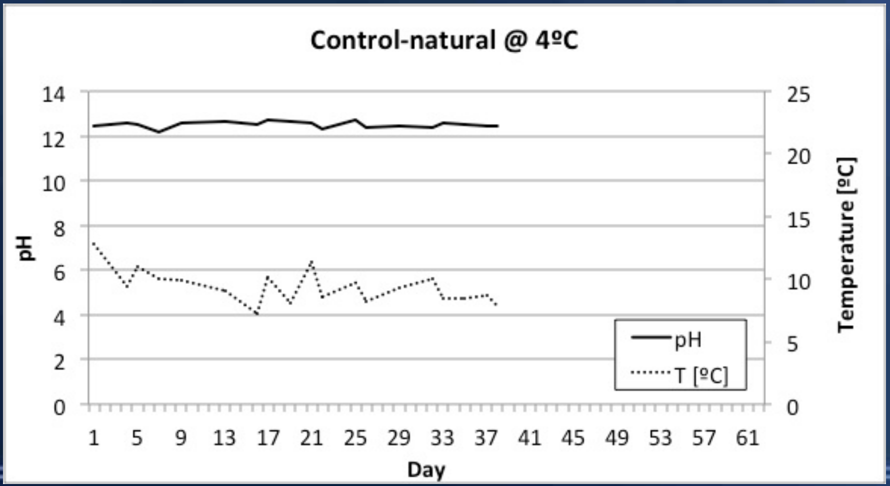

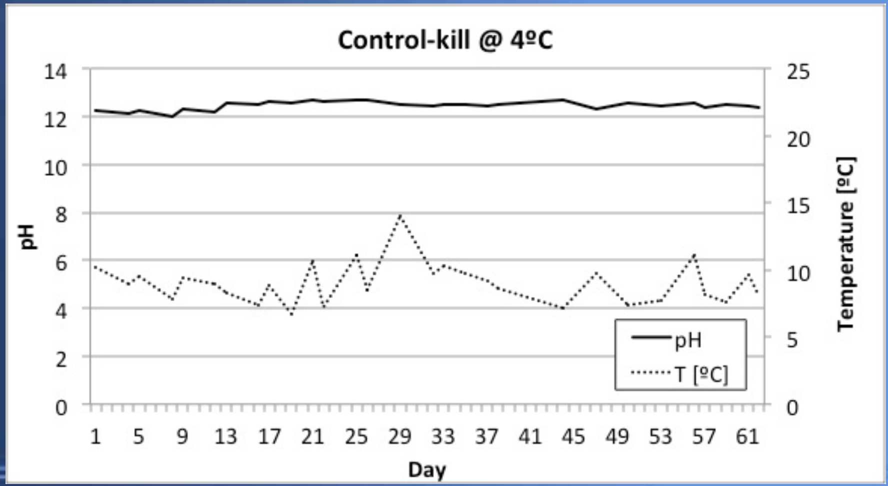

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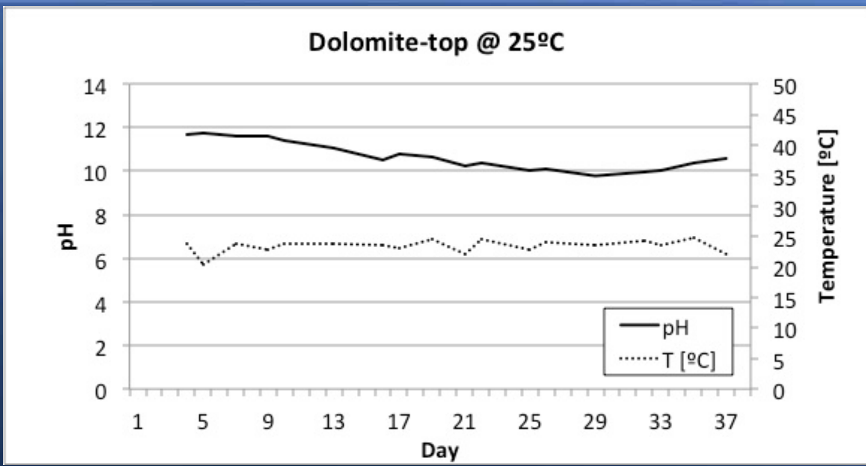
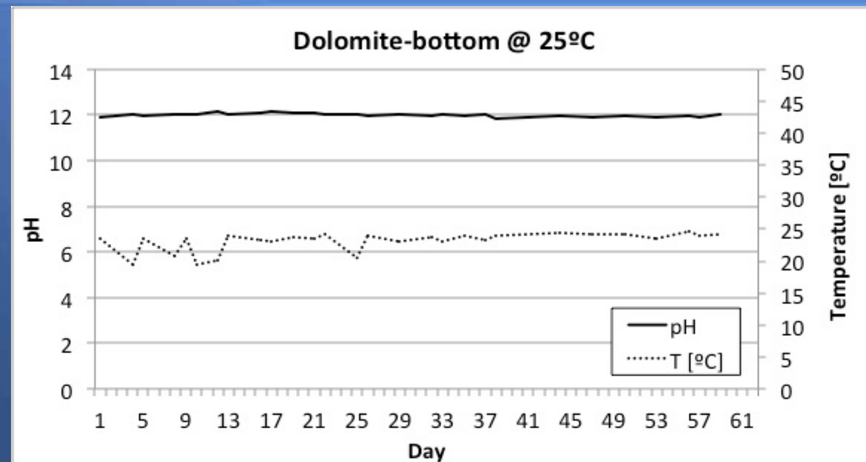
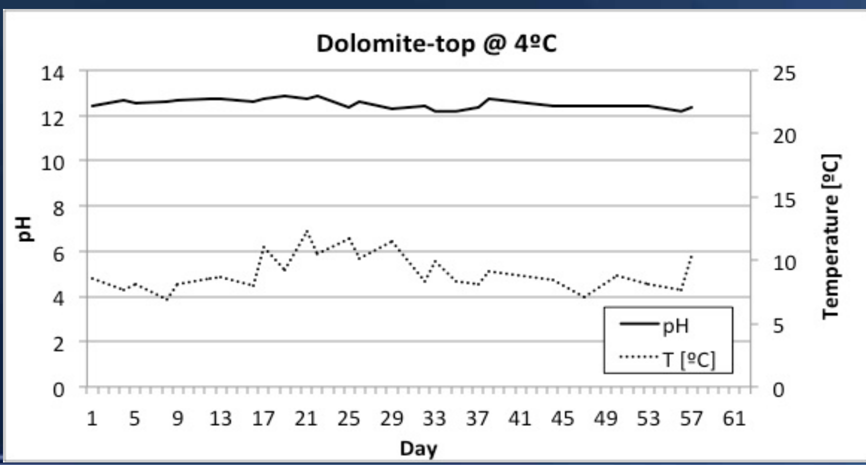
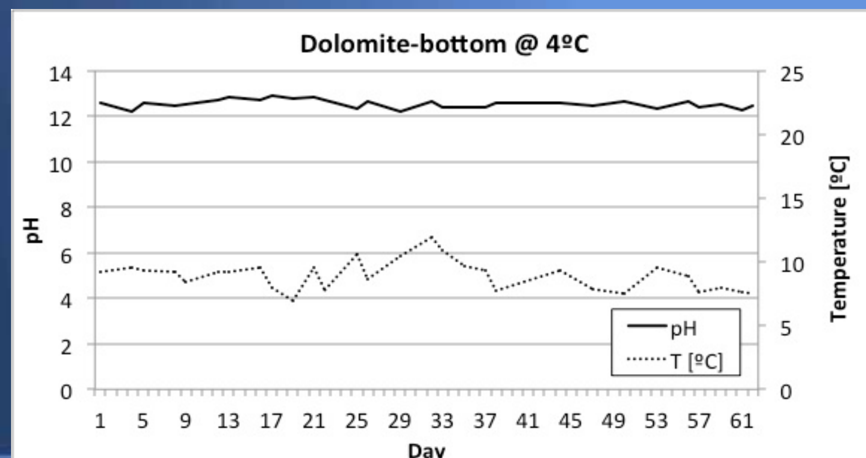
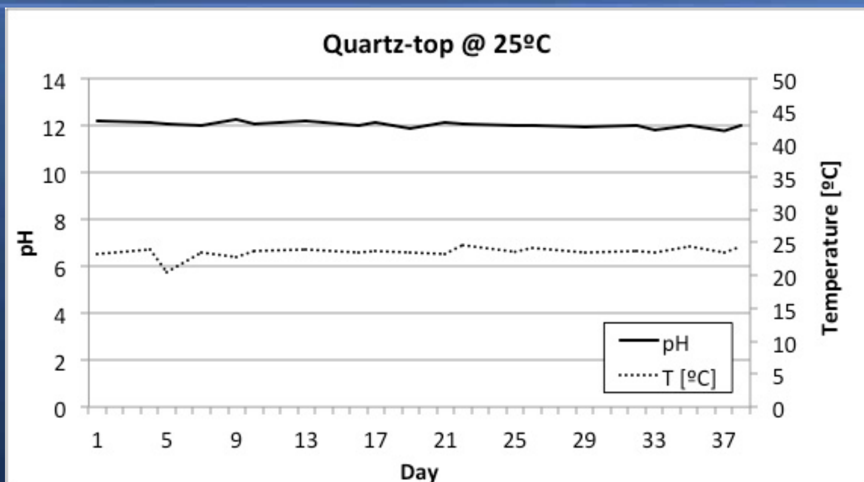


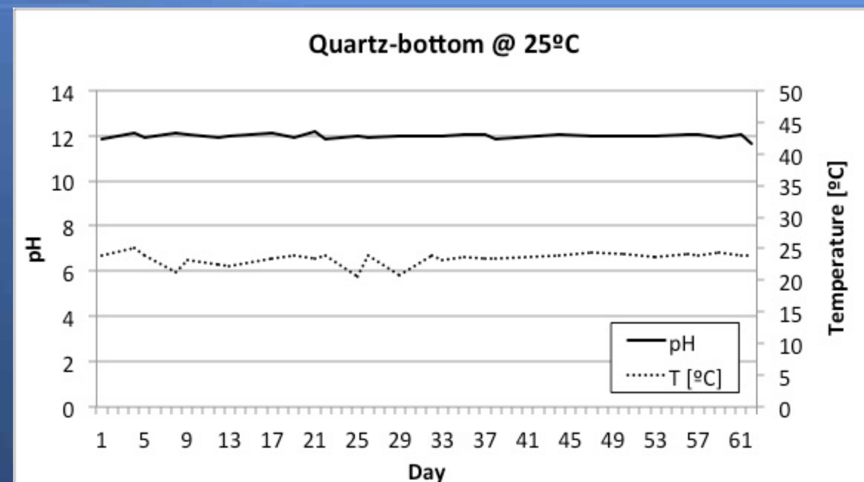


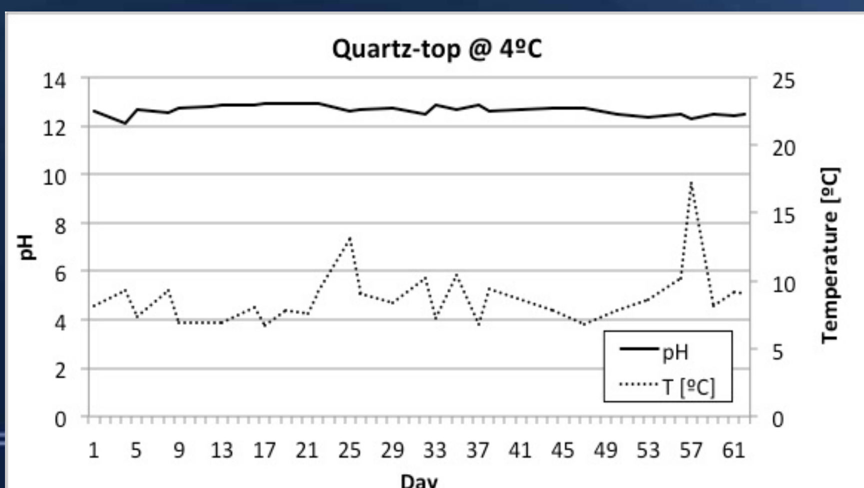


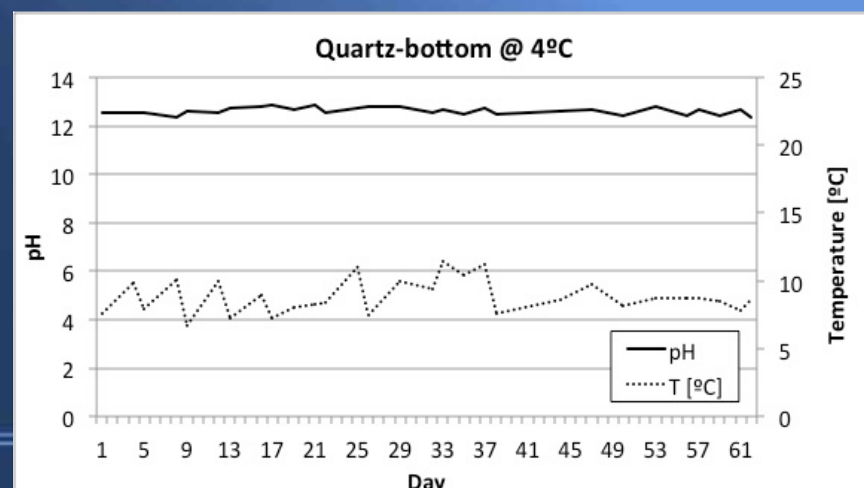


pH measurements









pH measurements

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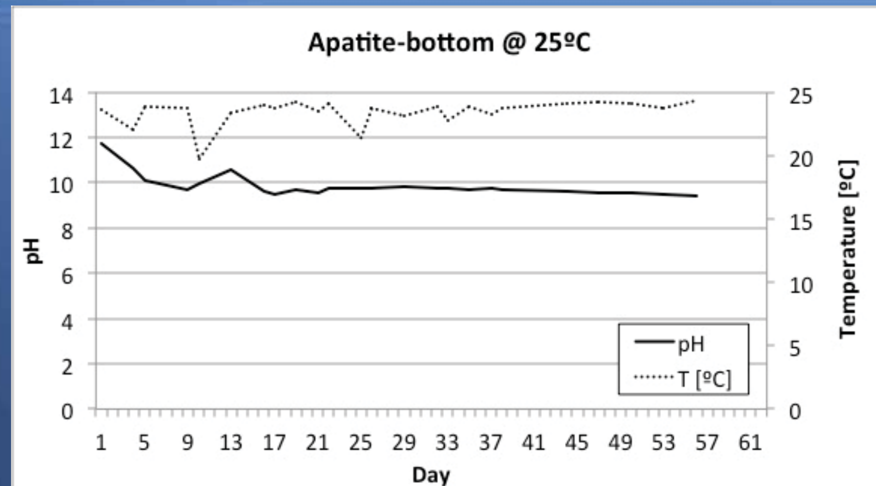

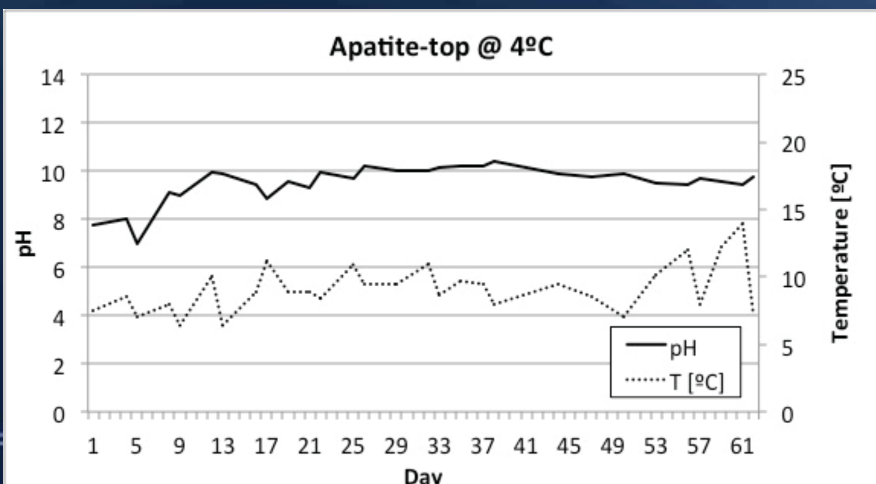

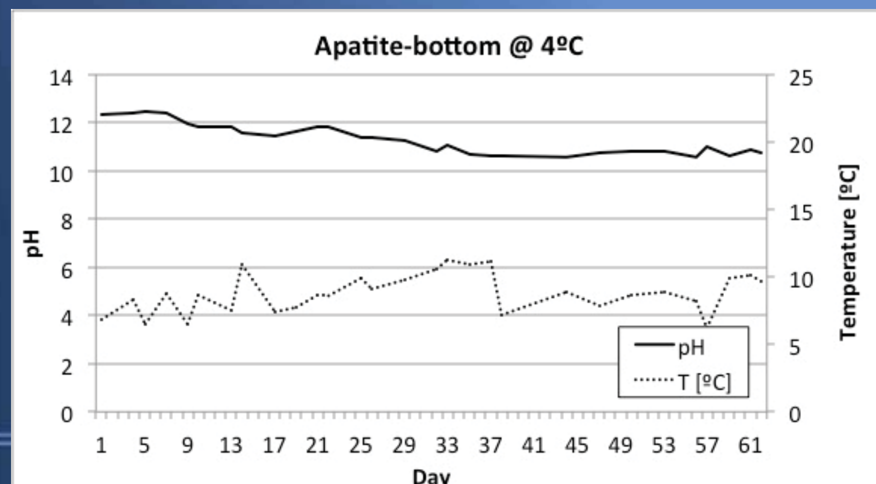

What is next?

Continuing analyses:

- pH and temperature – further measurements
- HPLC – Dionex: data collection, processing, and interpretation of dissolved anion concentrations, drawing conclusions about chemical conditions inside the columns, geochemical modeling (PhreeqC) for better description of the systems
- ICP-MS: data collection, processing, and interpretation of cation concentrations, evaluation of PRB effectiveness

Future analyses:

- titrations of carbonate species in the samples
- spectrophotometric analysis of NH_3 and H_2S concentrations (Hach DR5000)
- DNA fingerprinting of selected samples from column experiment

Summary

Continuing experiment

Cation analysis shows rather lower concentrations of heavy metals present in the source water, possibly due to its high pH (HM mobility decreases with increasing pH) => more attention needs to be given to the columns with lowered pH as HM could become mobilized

pH measurements indicate changes in pH due to varying temperatures as well as due to different PRBs

Anion analyses (data not shown) suggest on different conditions developing inside the columns according to incubation conditions (PRB and temperatures)

The study posses good potential for comparison of alkaliphilic and/or alkalitolerant microbial communities developed under varying conditions (future work)