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EectroChemical GeoOxidation (ECGO) *In Situ* Sediment Treatment Technology

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RTDF Sediments Workshop
Baltimore, MD
February 18, 2004

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Introduction

- The Technology
- Current Projects
  - New Jersey
  - Georgia
  - Duluth
    - Intro
    - 2002 Results
    - 2003 Preliminary Results
    - Current Testing
- Test Facilities

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The Technology

- ElectroChemical GeoOxidation is a patented electrochemical process which uses Direct Current for the mineralization of organic materials either insitu or exsitu in soils and sediments.
- The process may be used to treat inorganic contaminants using Induced Complex process.

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Direct Current Technologies
DCT: Electrochemical Cell

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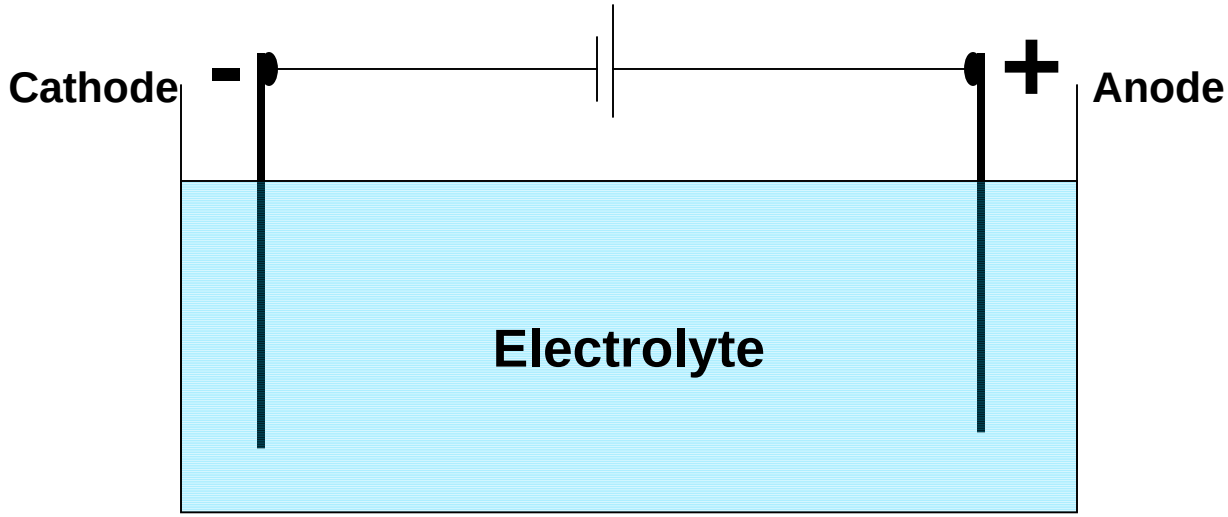
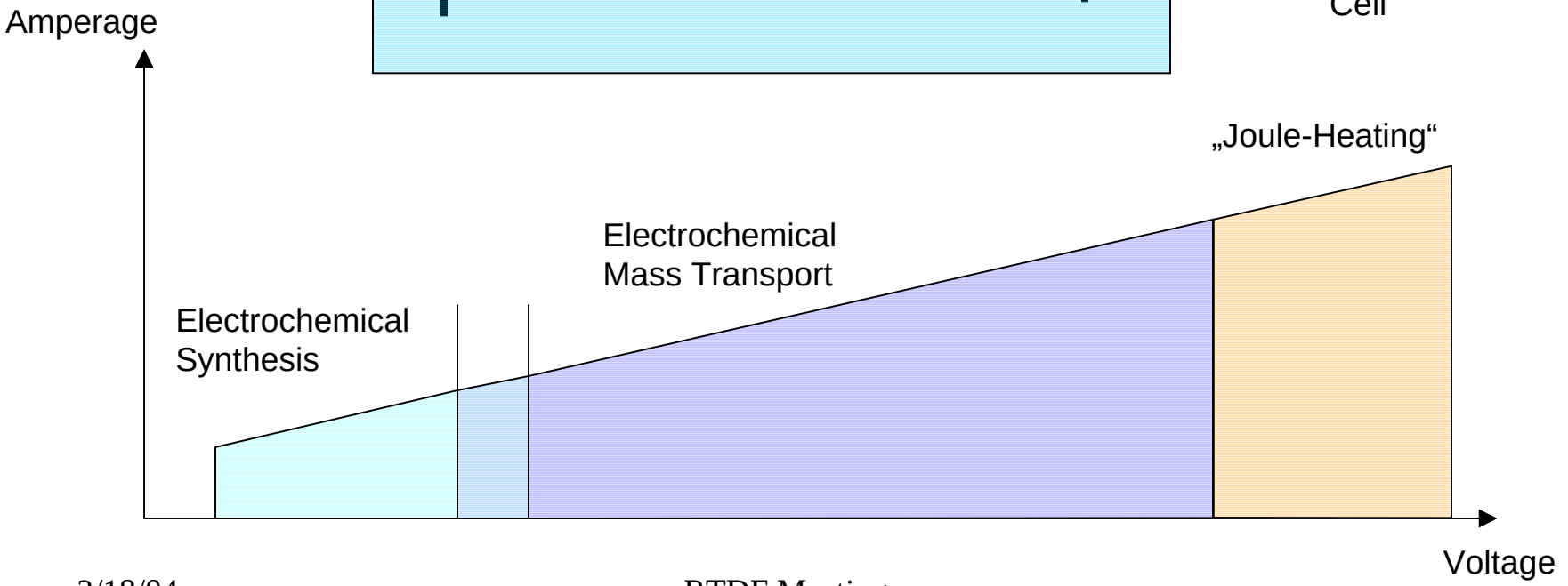


Electrochemical Cell



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The Flow of Electrical Current in Soils

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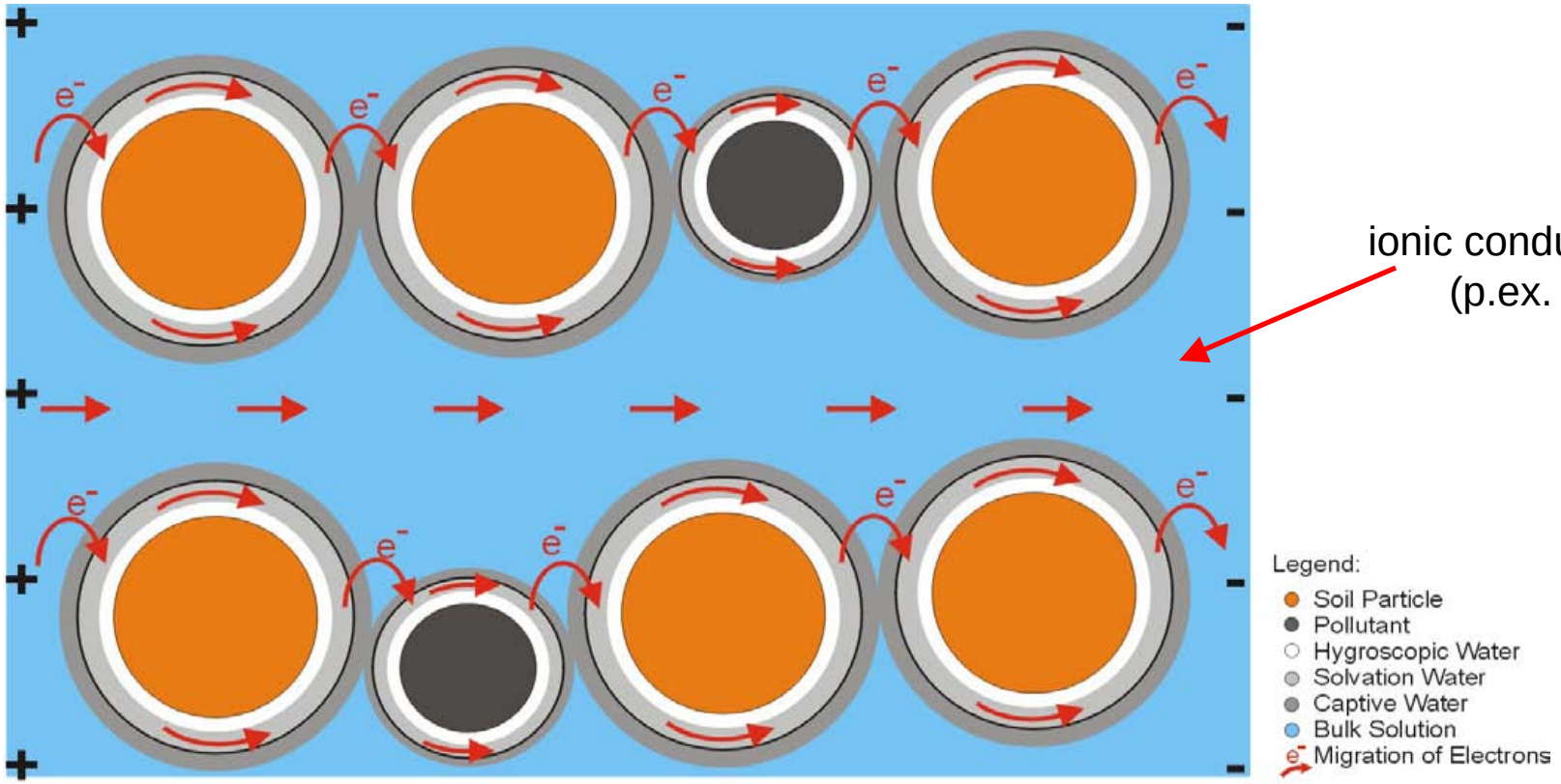
colloid conductivity (p.ex. 0.9 Ω)



ionic conductivity
(p.ex. 8.4 Ω)

0.0001 in.

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Places of Electrochemical Reactions

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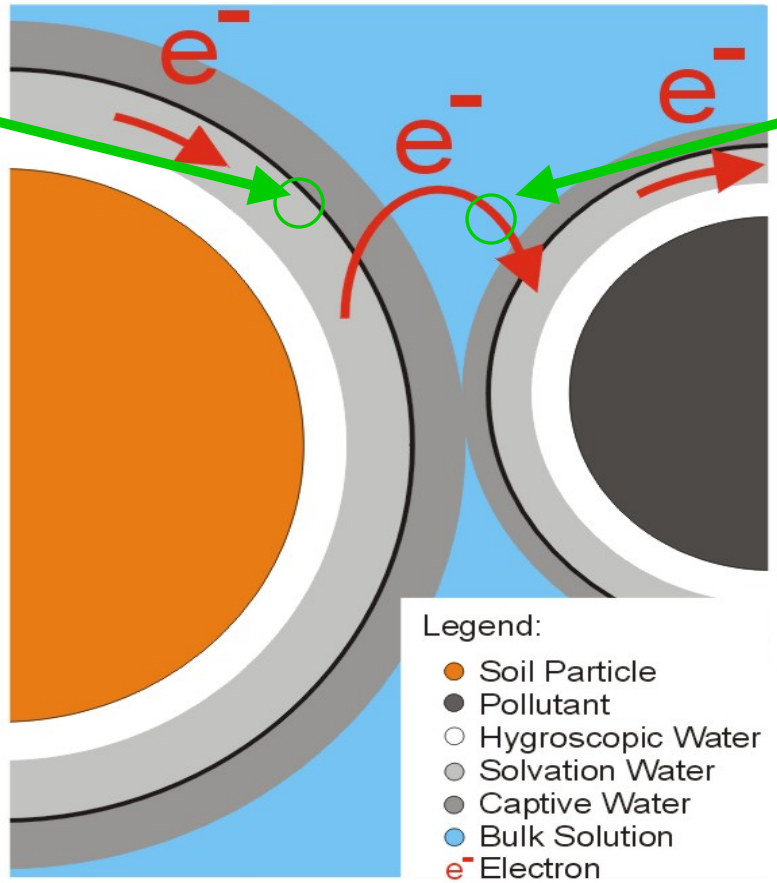
Oxidation: donation of electrons (e-)

$Fe \rightarrow Fe^{2+} + 2\ e^-$

$2\ H_2O \rightarrow 4\ H^+ + O_2 + 4e^-$

$C_6H_6 + 12\ H_2O \rightarrow 6\ CO_2 + 3\ OH^+ + 30\ e^-$



Reduction: acceptance of electrons (e^-)

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

$2\ H_2O + 2e^- \rightarrow H_2 + 2\ OH^-$

$C_6H_6 + 18\ H^+ \rightarrow 6\ CH_4$

(ring opening)

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New Jersey Site

- Pesticides
  - Aldrin
  - Lindane
  - Chlordane
  - 4,4’-DDD, 4,4’ DDE, 4,4’-DDT
  - Heptachlor
  - Methoxychlor
- Xylene
- 415,800 Cubic Feet

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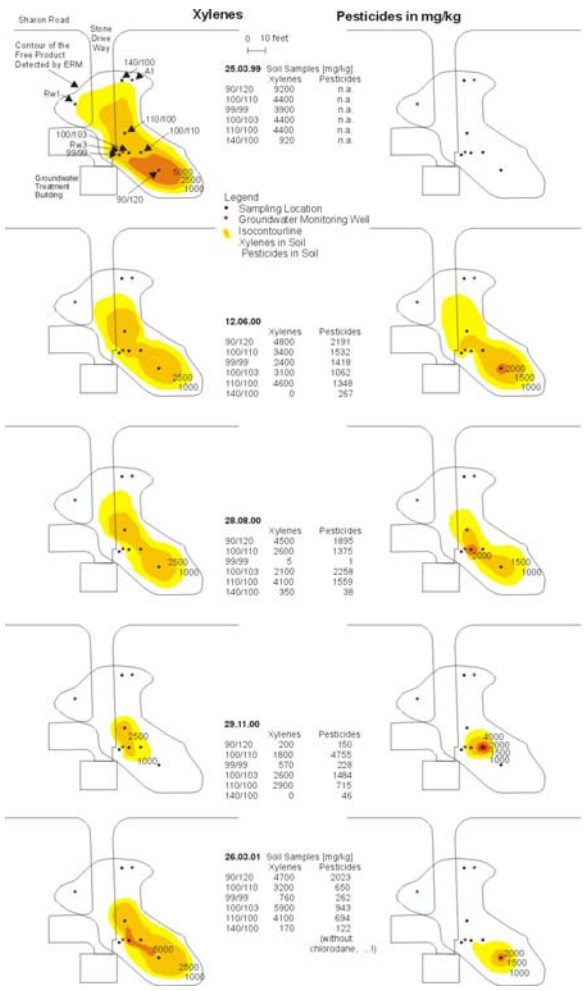
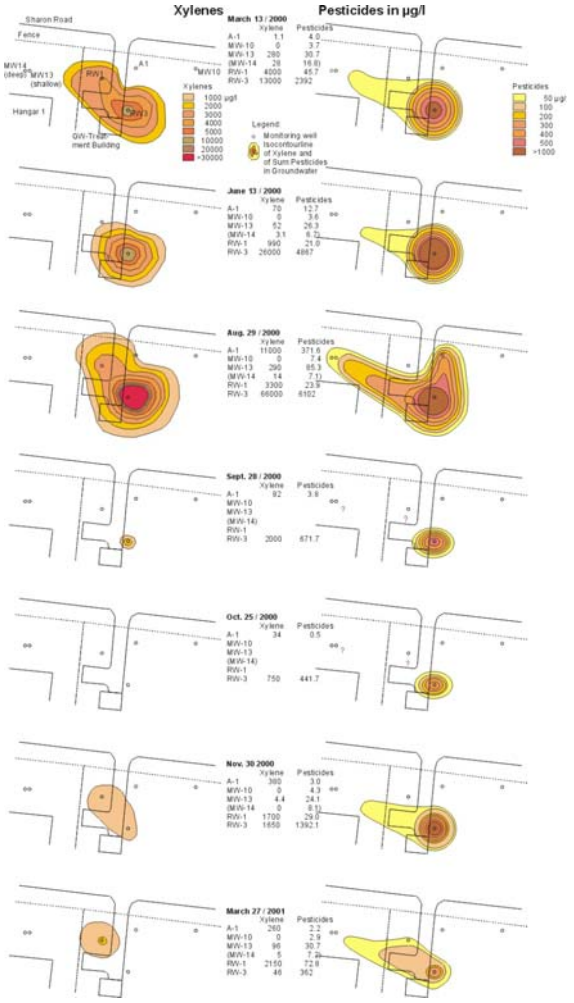
Results New Jersey





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Georgia Site

- TCE
- Contaminated Soil
- Cleanup levels reached within 210 days

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Purpose of Erie Pier Demonstration

- The Purpose of this Study is to Investigate the ECGO Technology for Sediments Treatment in a Demonstration Test at the Erie Pier CDF, Duluth MN. This is an independent evaluation on the technology in a controlled and monitored test at sufficient scale to provide realistic information on costs, effectiveness and ease on implementation.

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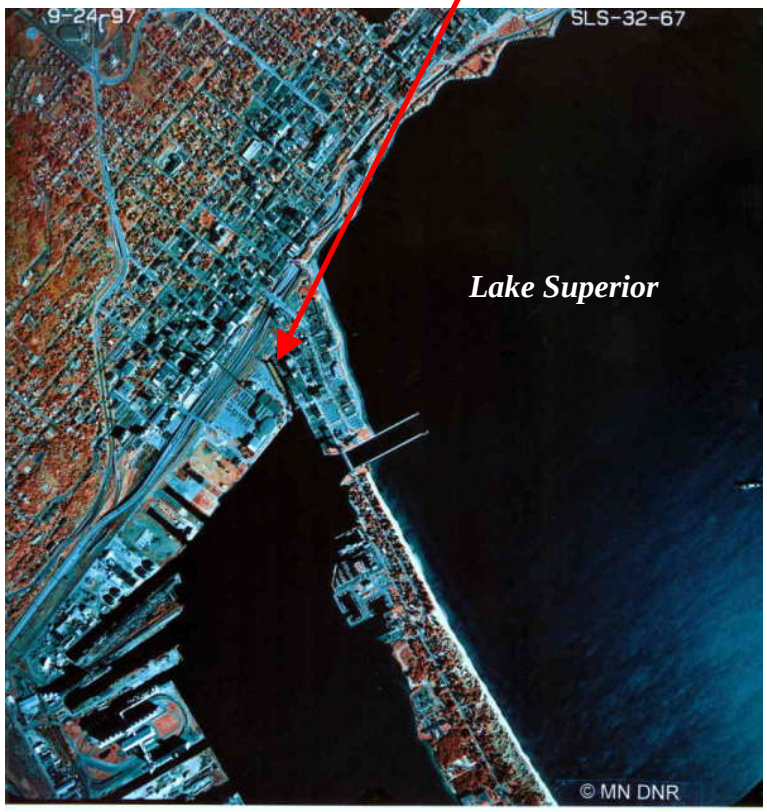
Minnesota Slip and Erie Pier



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Program Participants

- U.S Army Corps of Engineers (CELRE- Detroit Office – Funding Organization
- U.S Army Corps of Engineers – Duluth Office
- U.S Army Corps of Engineers – Vicksburg – Funding and Chemical Analysis
- Great Lakes National Program Office (GLENPO) of U.S. EPA - Funding
- University of Minnesota – NRRI- Project Management- Sampling
- Minnesota Pollution Control Authority (MPCA)
- EPI and ecp, llc – Technology Provider- Funding
  - U of Minnesota
  - Service Environmental
  - Harrison Marine
- Remediation Technologies Development Forum (RTDF)
- EPA Site Program

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Dredging of the Slip

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Cell Construction

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Cells Filled with Sediments

East Cell

West Cell

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Electrode Installation

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Power Supply and Test Cell

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Monitoring Parameters

- Power input
- PAHs in Control Cell and Treatment Cell
- Temperature
  - Control cell
  - Treatment cell
  - Ambient temperature
- pH
- Biological Changes

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Monitoring Equipment

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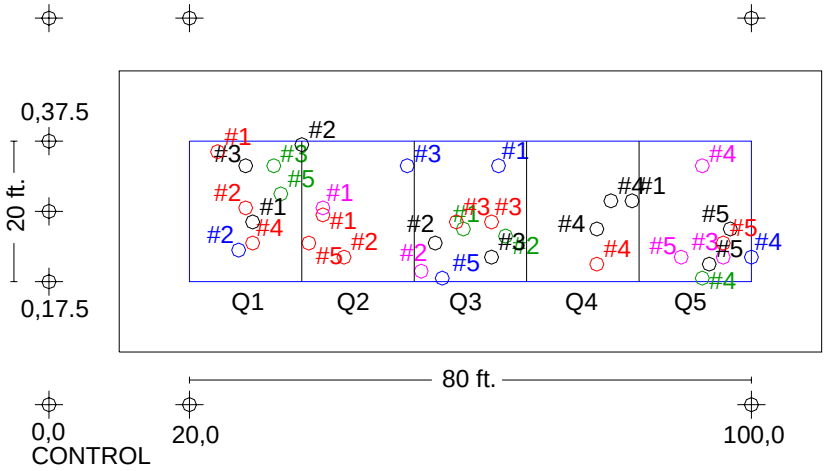
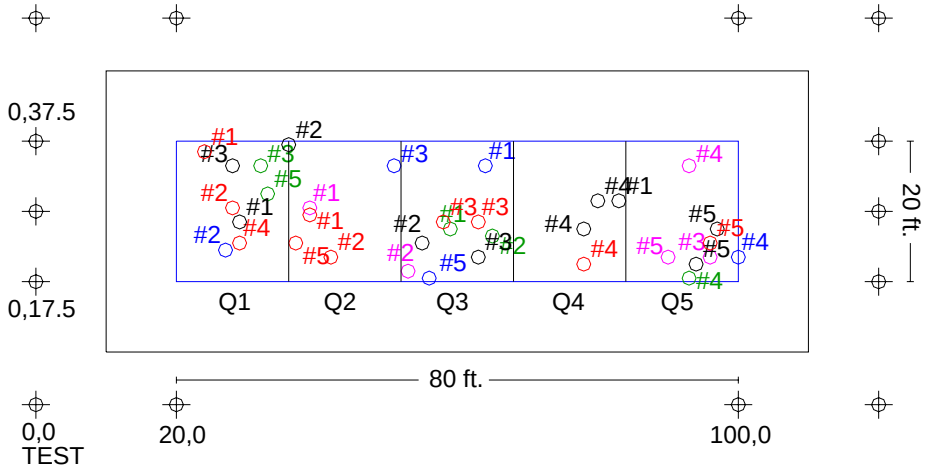
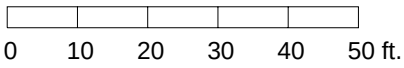
CONTROL CELL



TEST CELL





GRID
"NORTH"

#2 SAMPLING POINT

REFERENCE POINTS

Q4 SAMPLE ZONE QUINTILE (2003)

2002-3 sample locations

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Sampling and Analysis

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Sampling Crew

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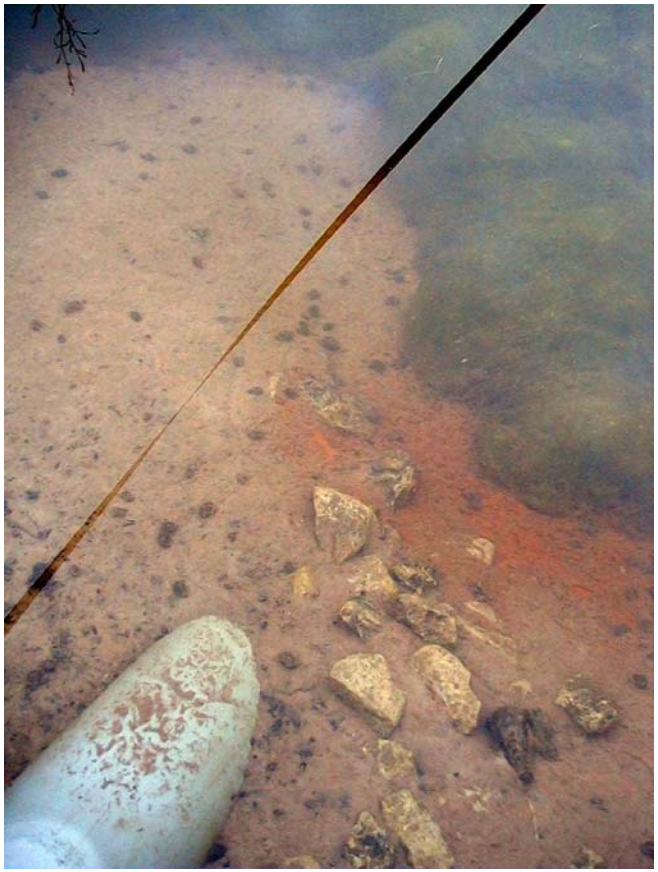
Sampling of Snails in Test Cell



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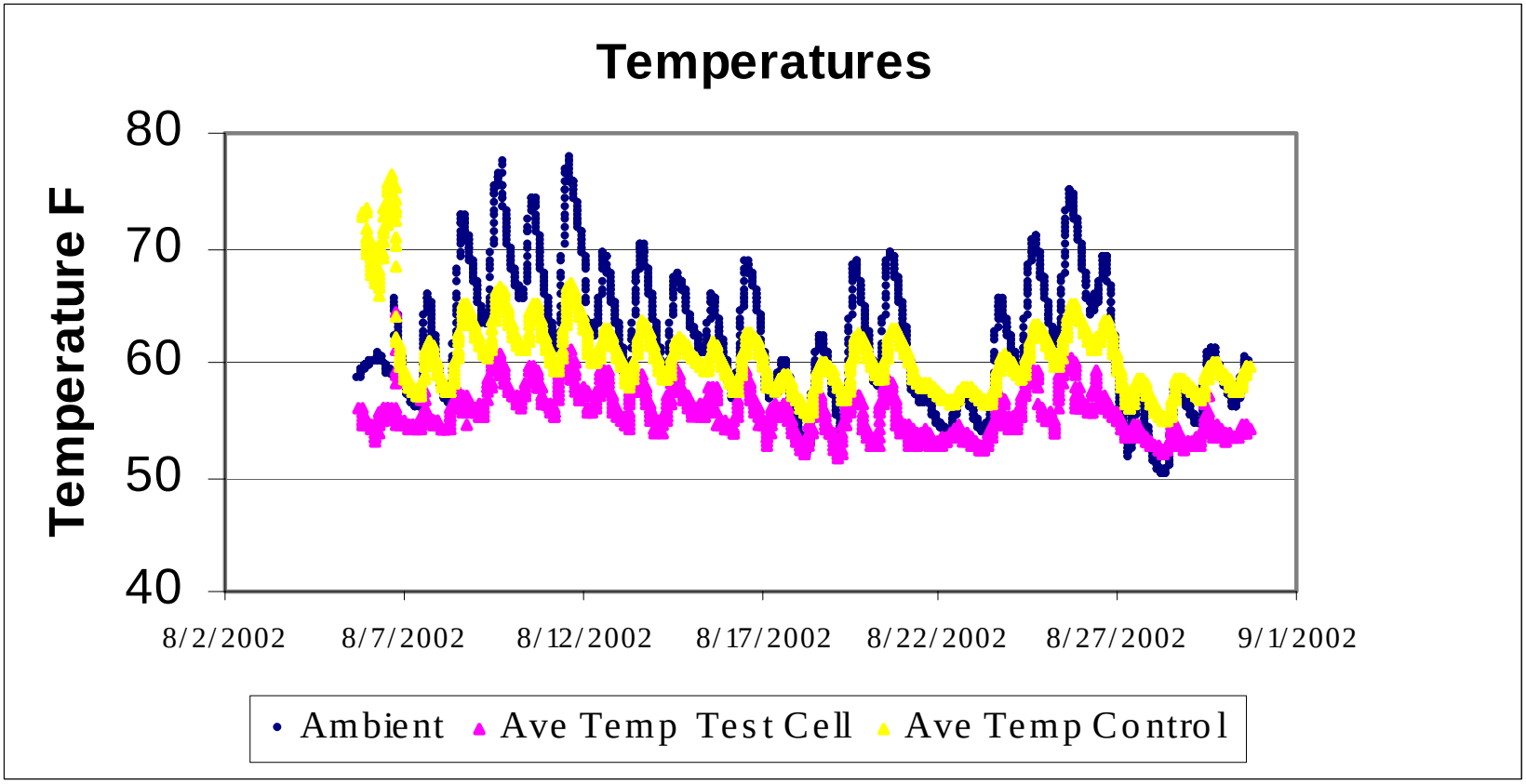
Cell Temperatures



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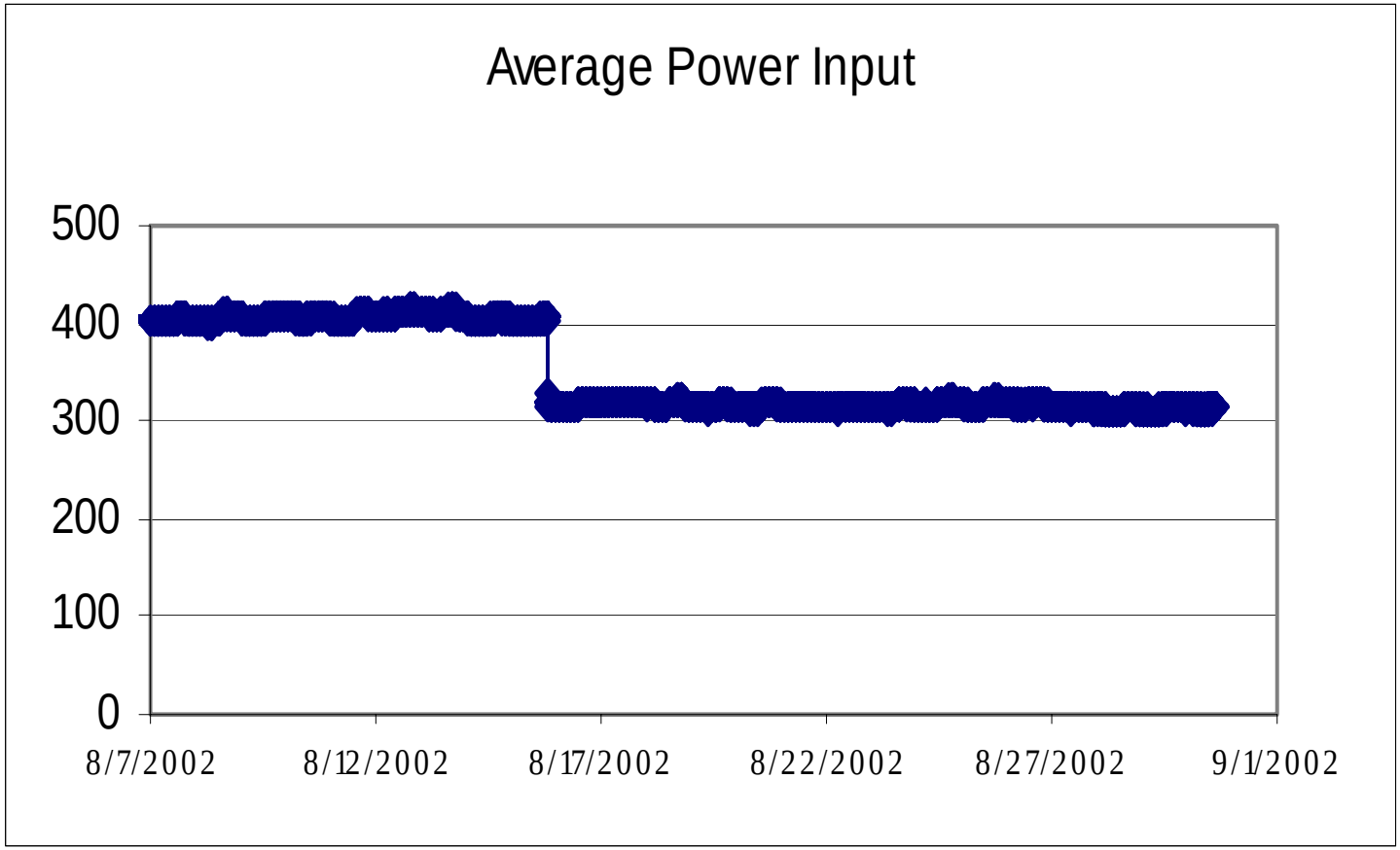
Power Input



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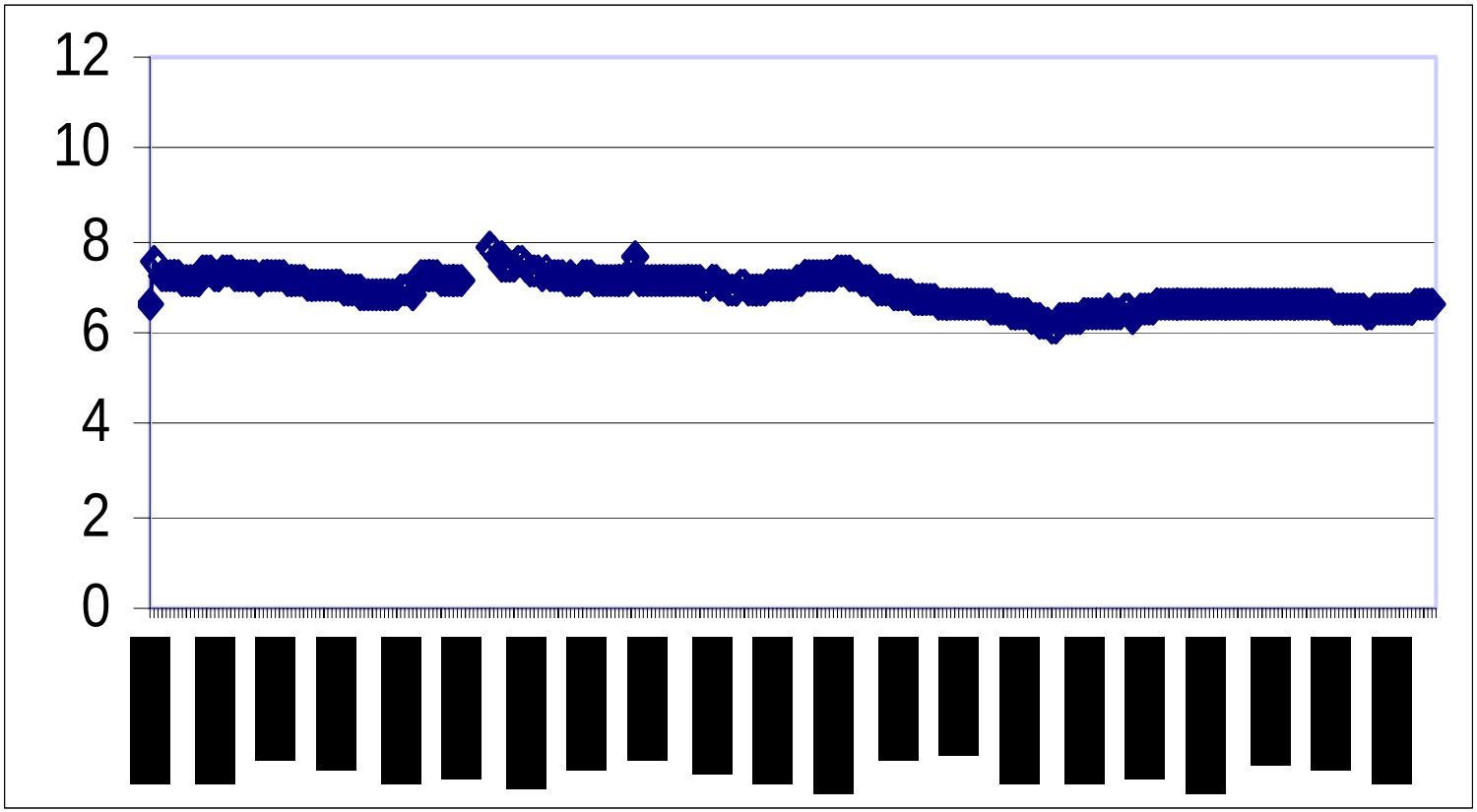
pH



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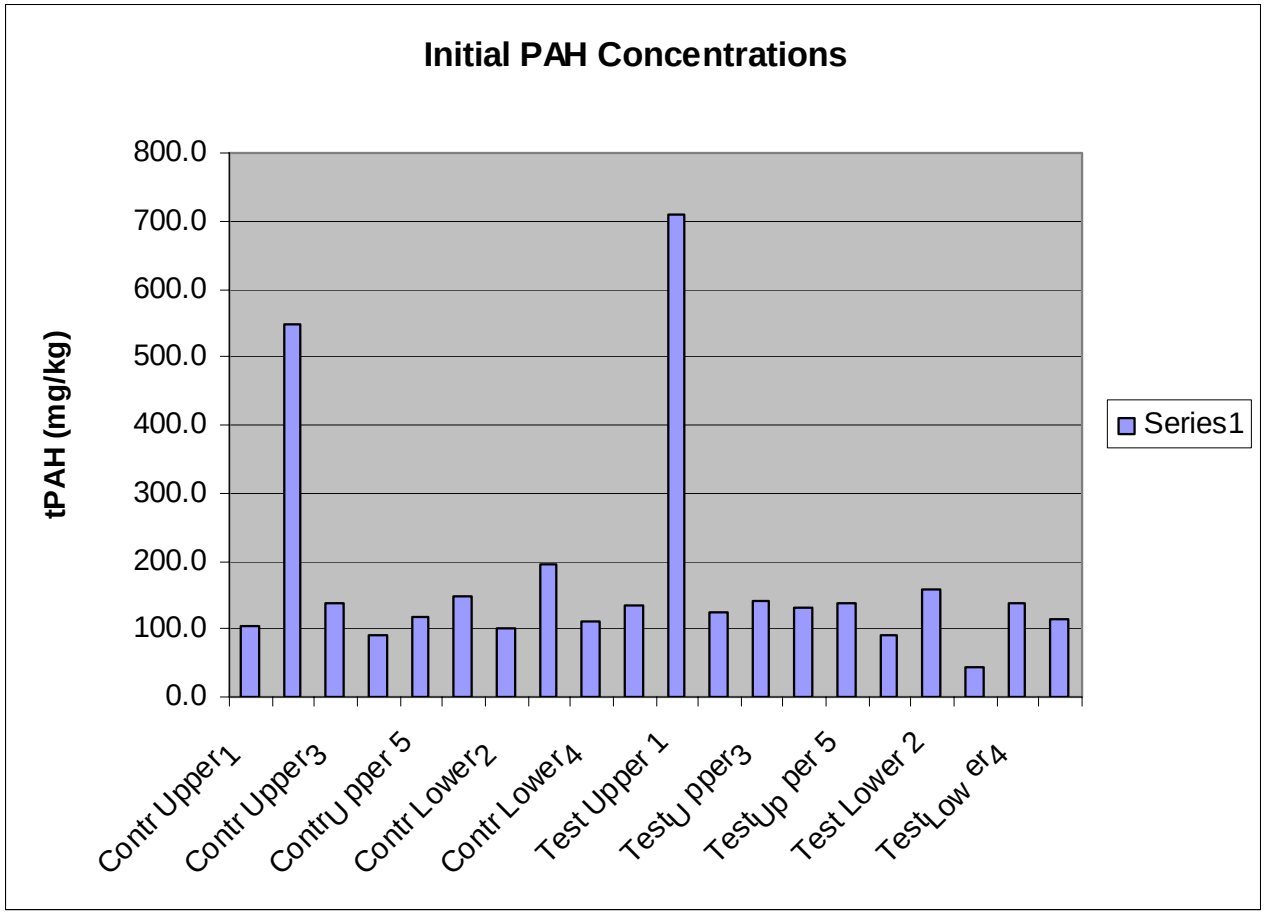
Sediments Analysis



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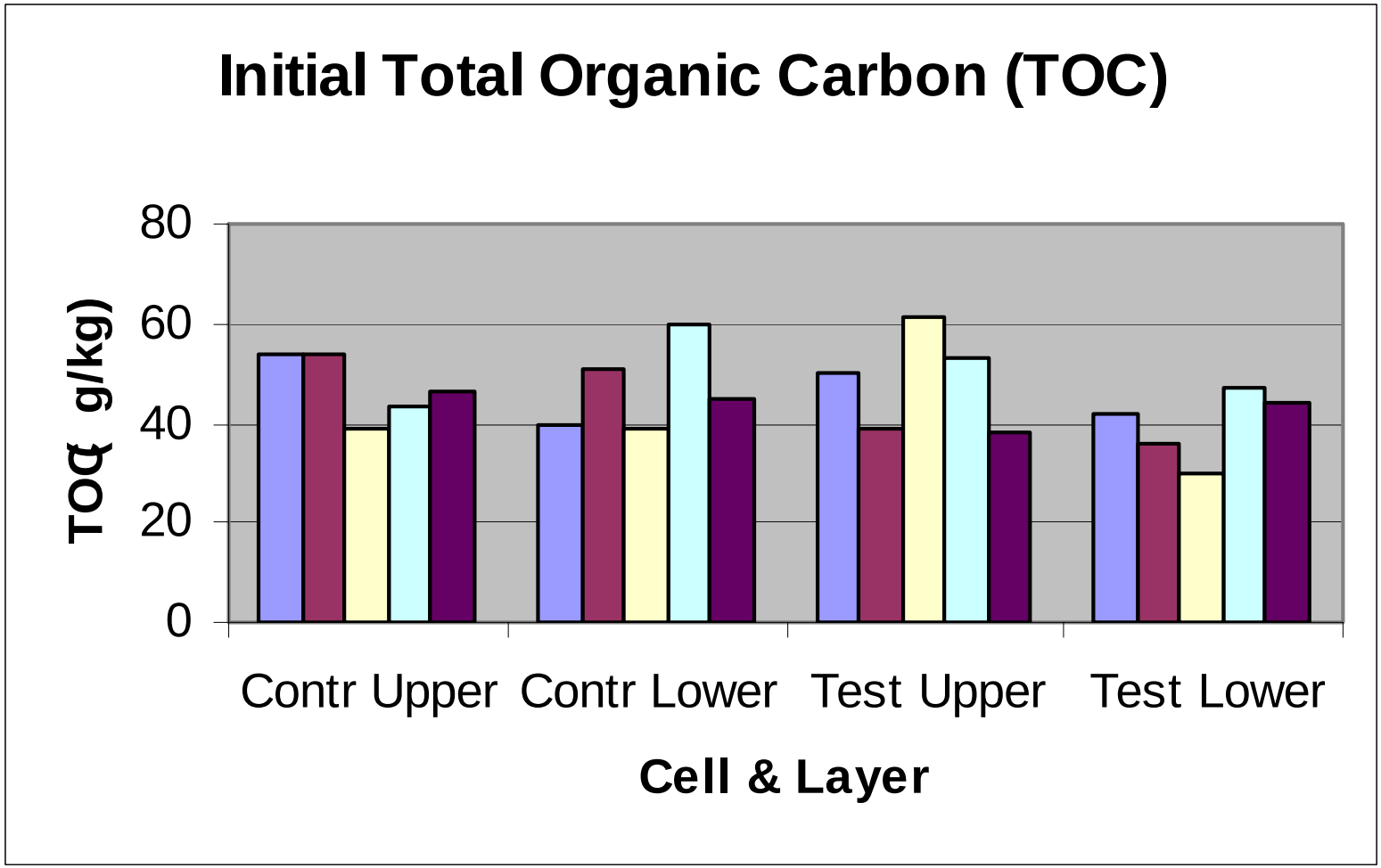
Sediments Analysis



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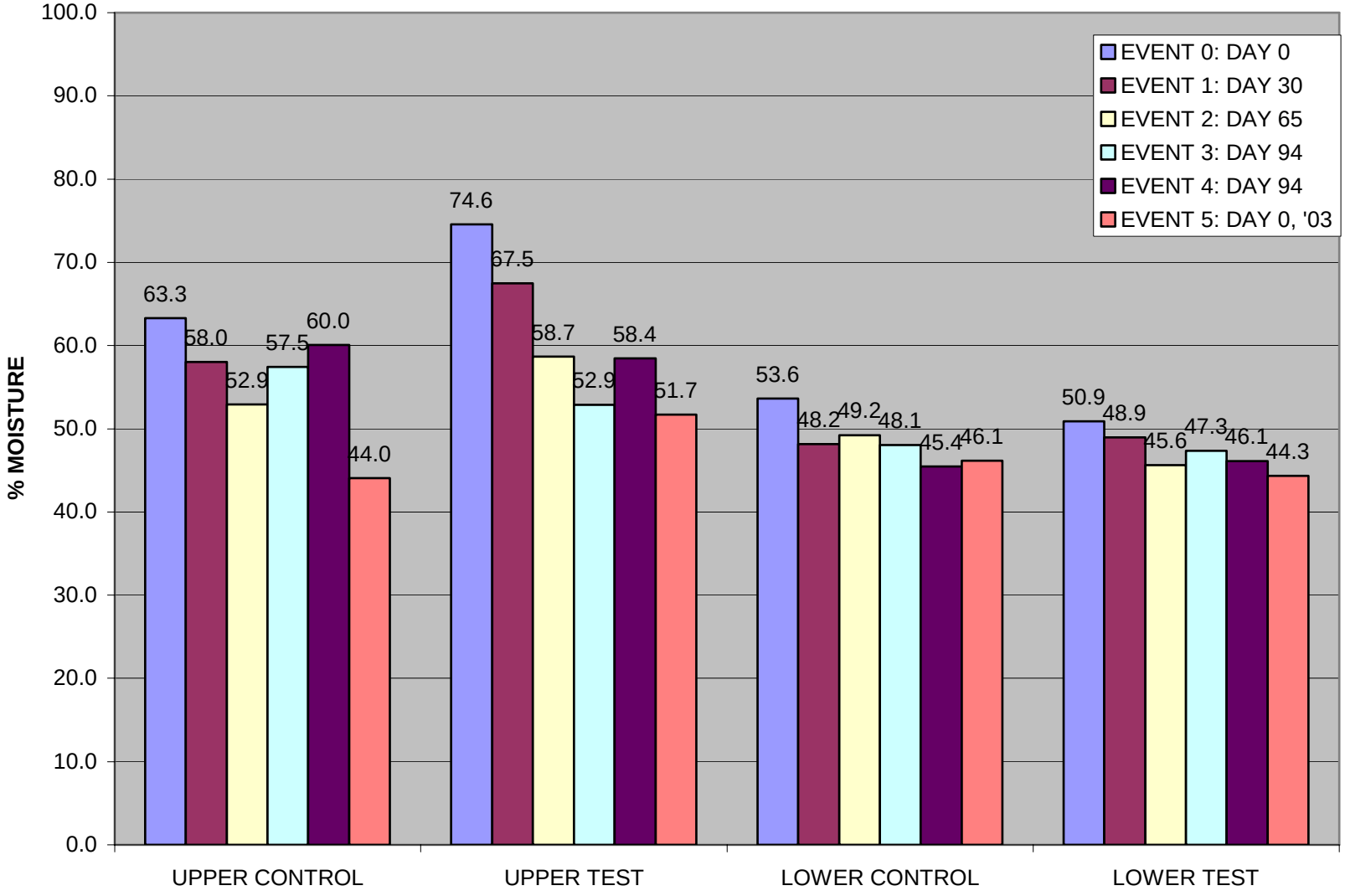
SAMPLE MOISTURE CONTENT



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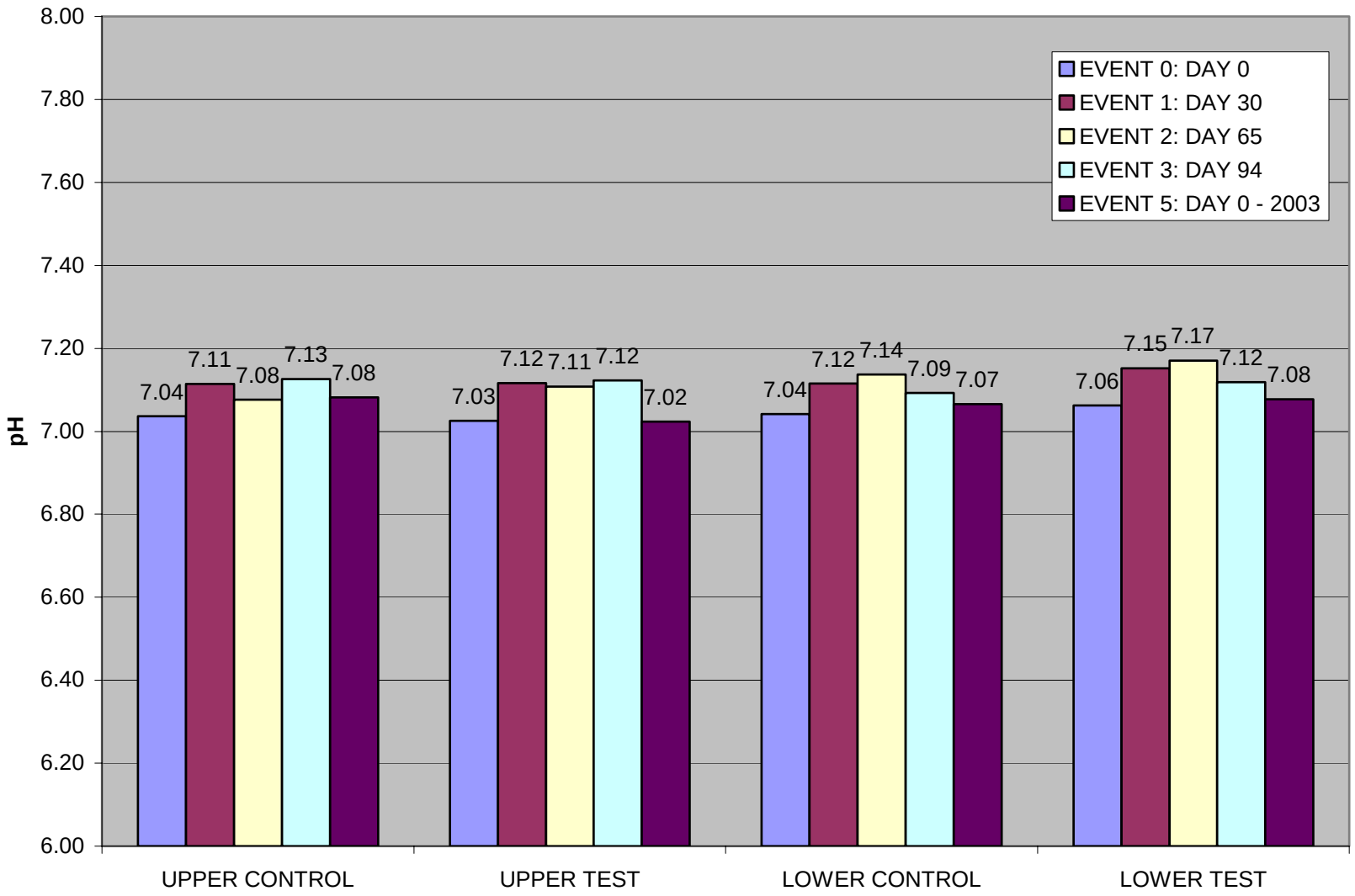
SAMPLE pH



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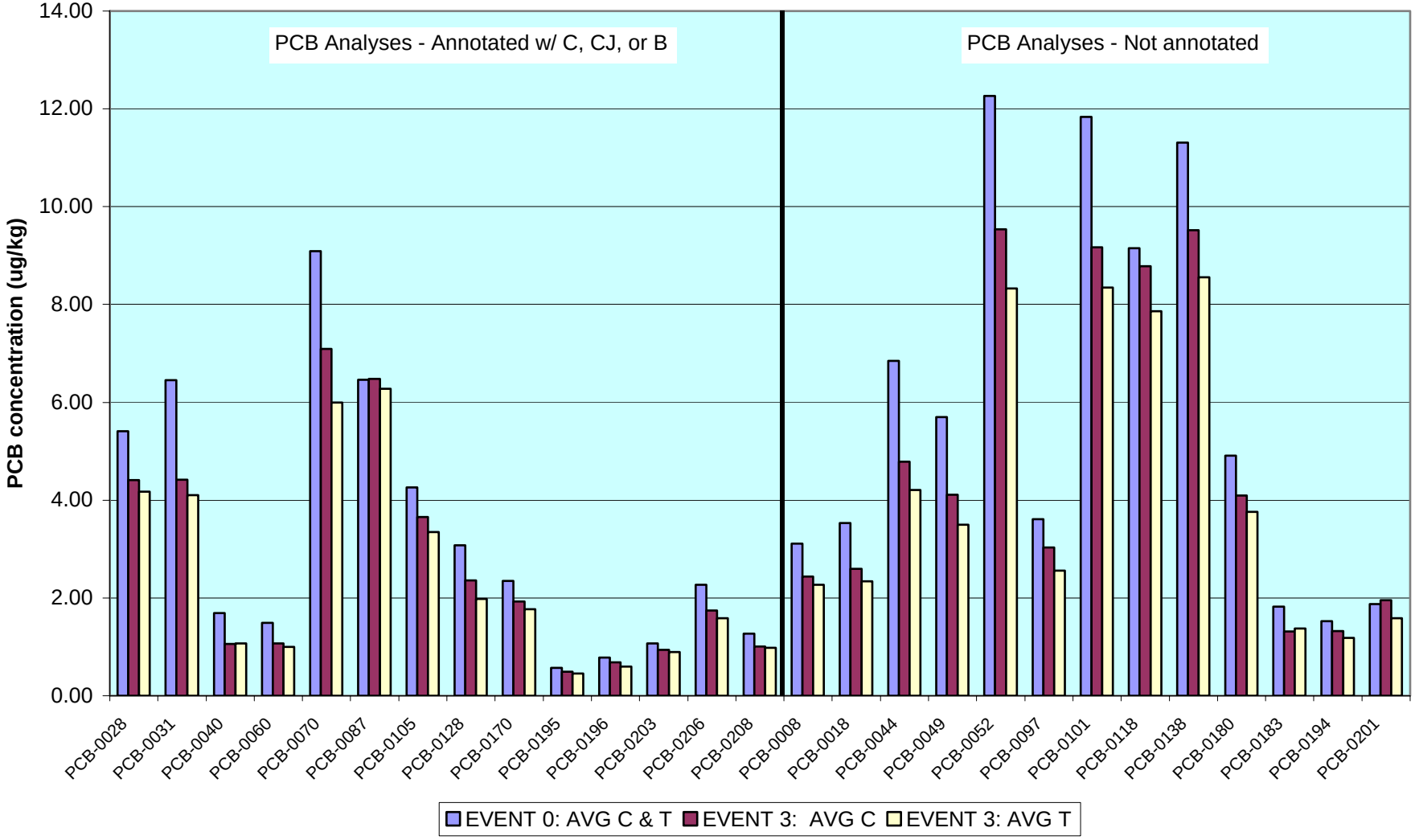
PCB Congener Averages (Aroclors not included)
Event 0 Control & Test Combined as "baseline" Control



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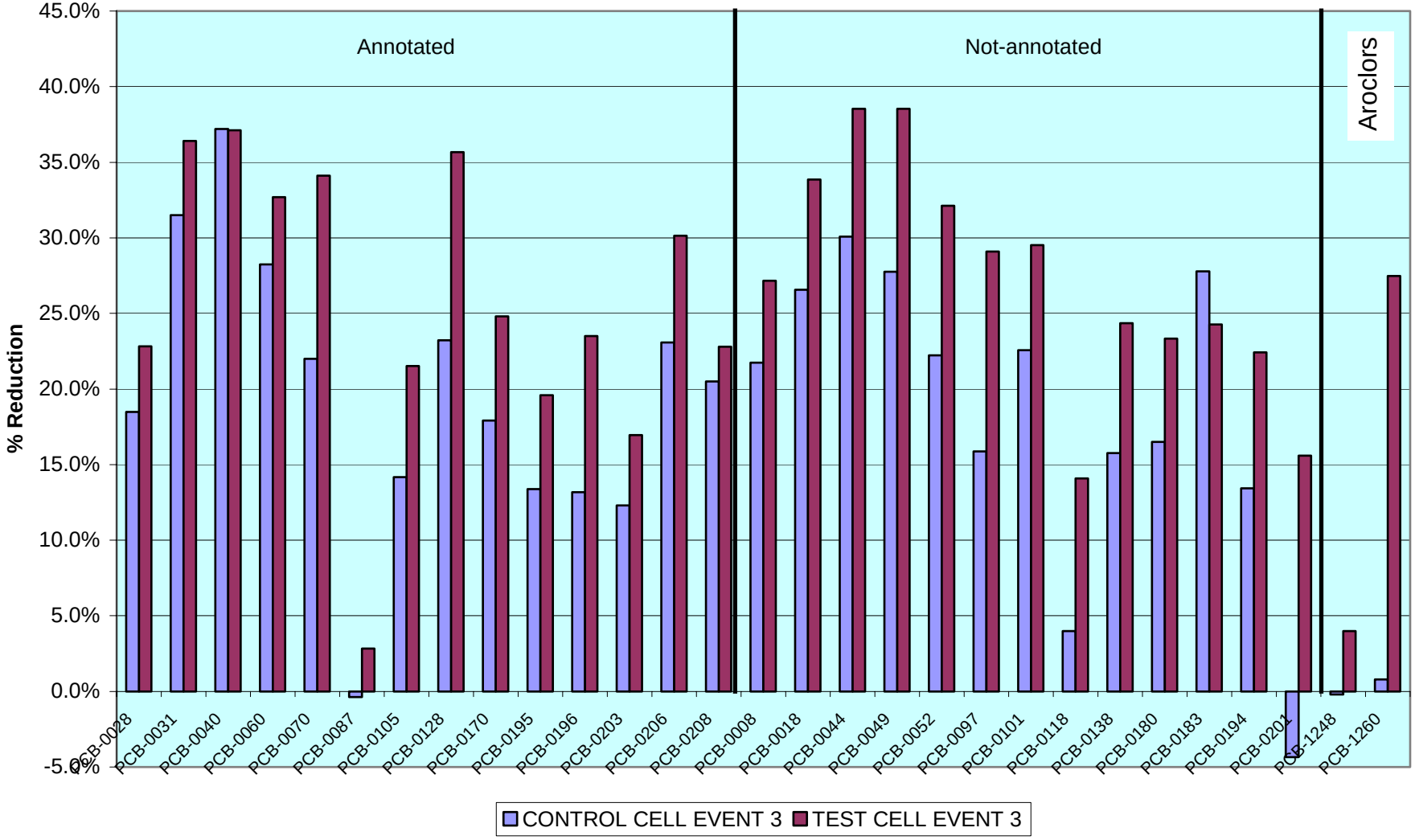
Percent PCB reduction from baseline average
(Control 0 & Test Event 0 combined = baseline average)



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2002 Issues

- PAHs were not being destroyed as anticipated.
- PCBs in low concentrations were being reduced in concentration.
- pH was not being changed by the ECGO process
- Plants and animals continued to live in the test and control cell.

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2003 Program

- Continue Testing at Erie Pier
- Use Pyrolysis GC-MS Dr. Philps, University of Oklahoma
- Contracted with Dr. Jay Means Western Michigan University for additional PAH analysis.
- Instituted Redox Monitoring
- Evaluated Impact of Humates on PAHs
- Initiated additional sediments characterization
- Build Test Facility at NRRI

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Plant Growth 2003

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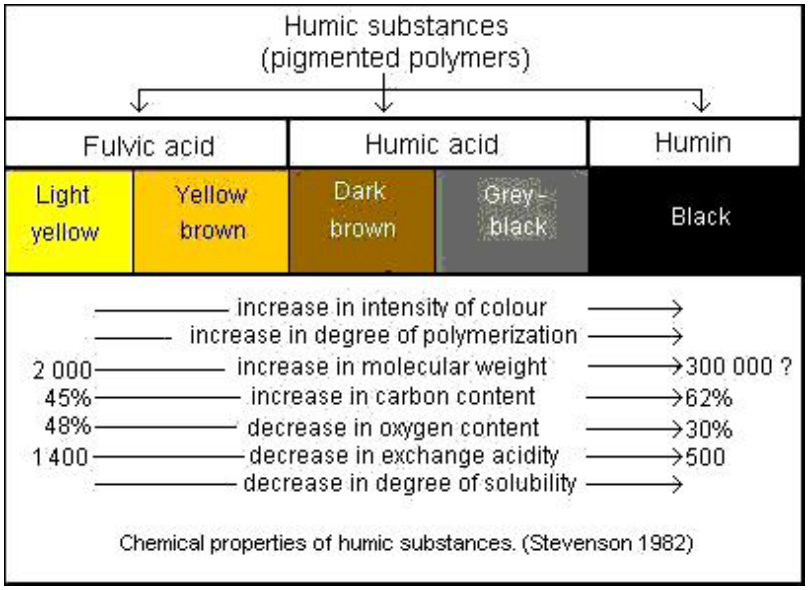
Color Change During Treatment



Chemical properties of humic substances. (Stevenson 1982)

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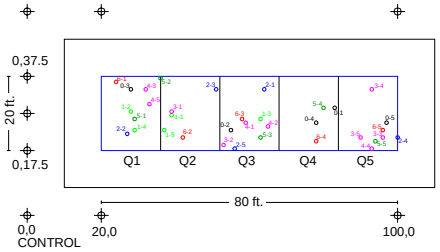
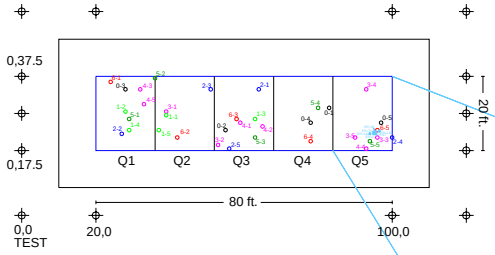
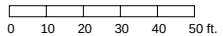
CONTROL CELL



TEST CELL



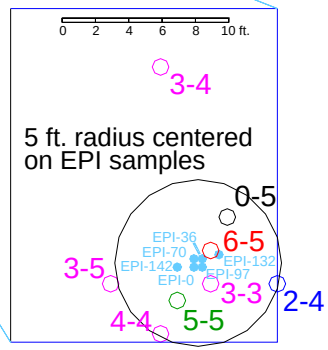


GRID "NORTH"

#2 SAMPLING POINT
REFERENCE POINTS
Q4 SAMPLE ZONE QUINTILE (2003)

EPI SAMPLING

SAMPLE #	X COORD	Y COORD
EPI-0	95	22
EPI-36	95.5	22.5
EPI-70	95	22.5
EPI-97	95.5	22
EPI-132	96.5	22.75
EPI-142	94	22



Q5

EVENT	SAMPLE #	X COORD	Y COORD
0	SAMPLE 0-1	83	29
0	SAMPLE 0-2	55	23
0	SAMPLE 0-3	28	34
0	SAMPLE 0-4	78	25
0	SAMPLE 0-5	97	25

EVENT	SAMPLE #	X COORD	Y COORD
1	SAMPLE 1-1	39	27
1	SAMPLE 1-2	28	28
1	SAMPLE 1-3	63	26
1	SAMPLE 1-4	29	23
1	SAMPLE 1-5	37	23

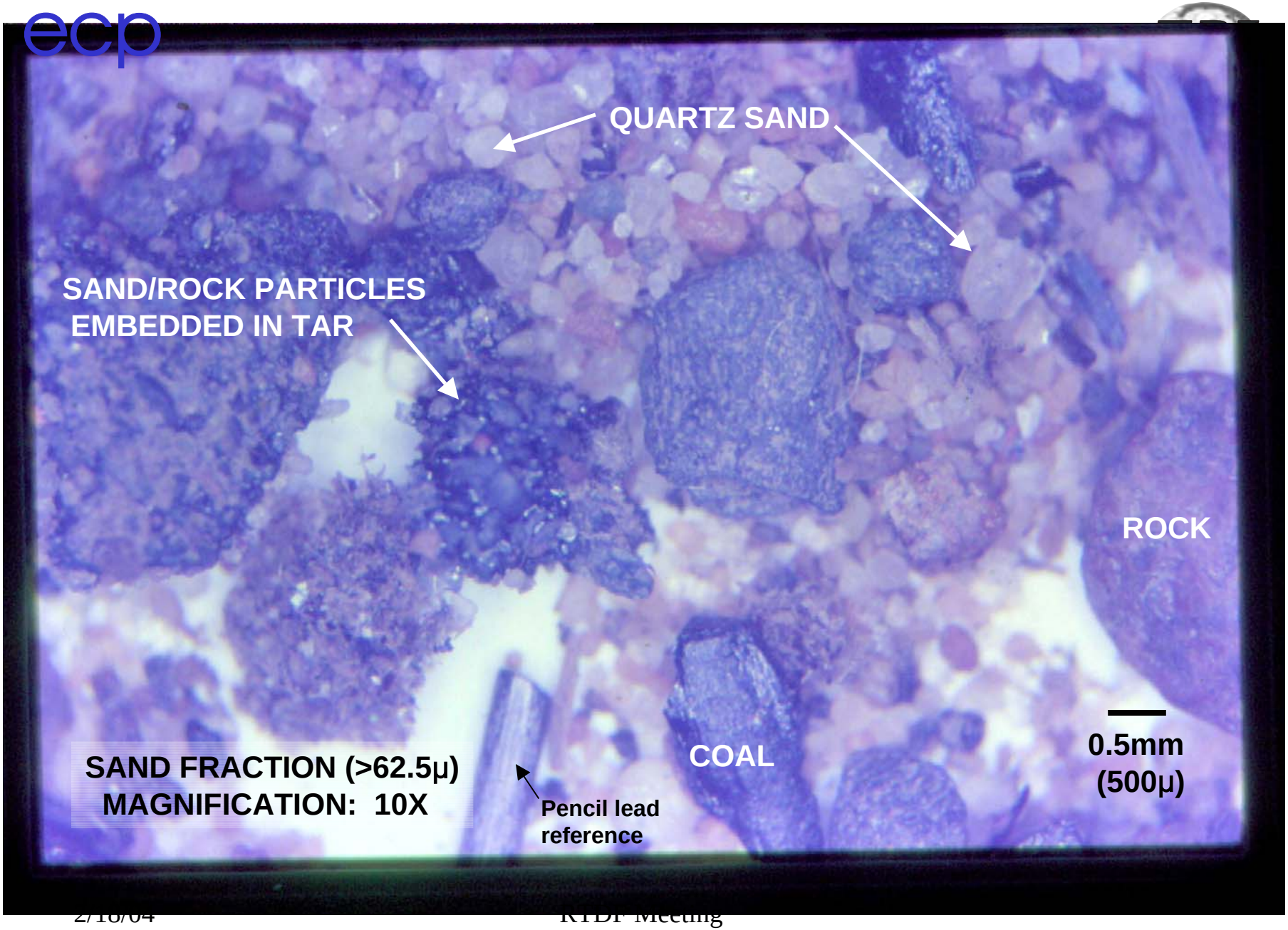
EVENT	SAMPLE #	X COORD	Y COORD
2	SAMPLE 2-1	64	34
2	SAMPLE 2-2	27	22
2	SAMPLE 2-3	51	34
2	SAMPLE 2-4	100	21
2	SAMPLE 2-5	56	18

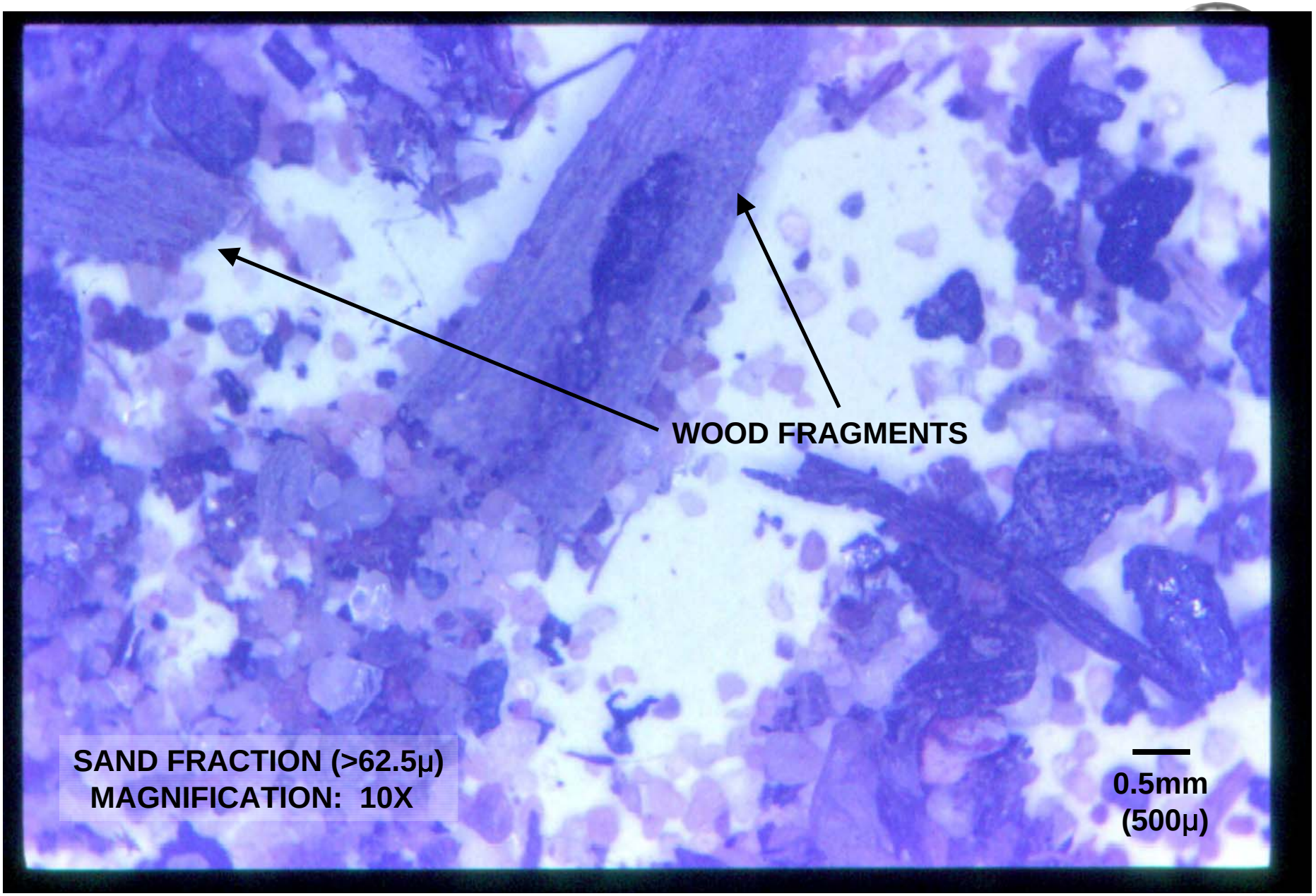
EVENT	SAMPLE #	X COORD	Y COORD
3/4	SAMPLE 3-1	39	28
3/4	SAMPLE 3-2	53	19
3/4	SAMPLE 3-3	96	21
3/4	SAMPLE 3-4	93	34
3/4	SAMPLE 3-5	90	21

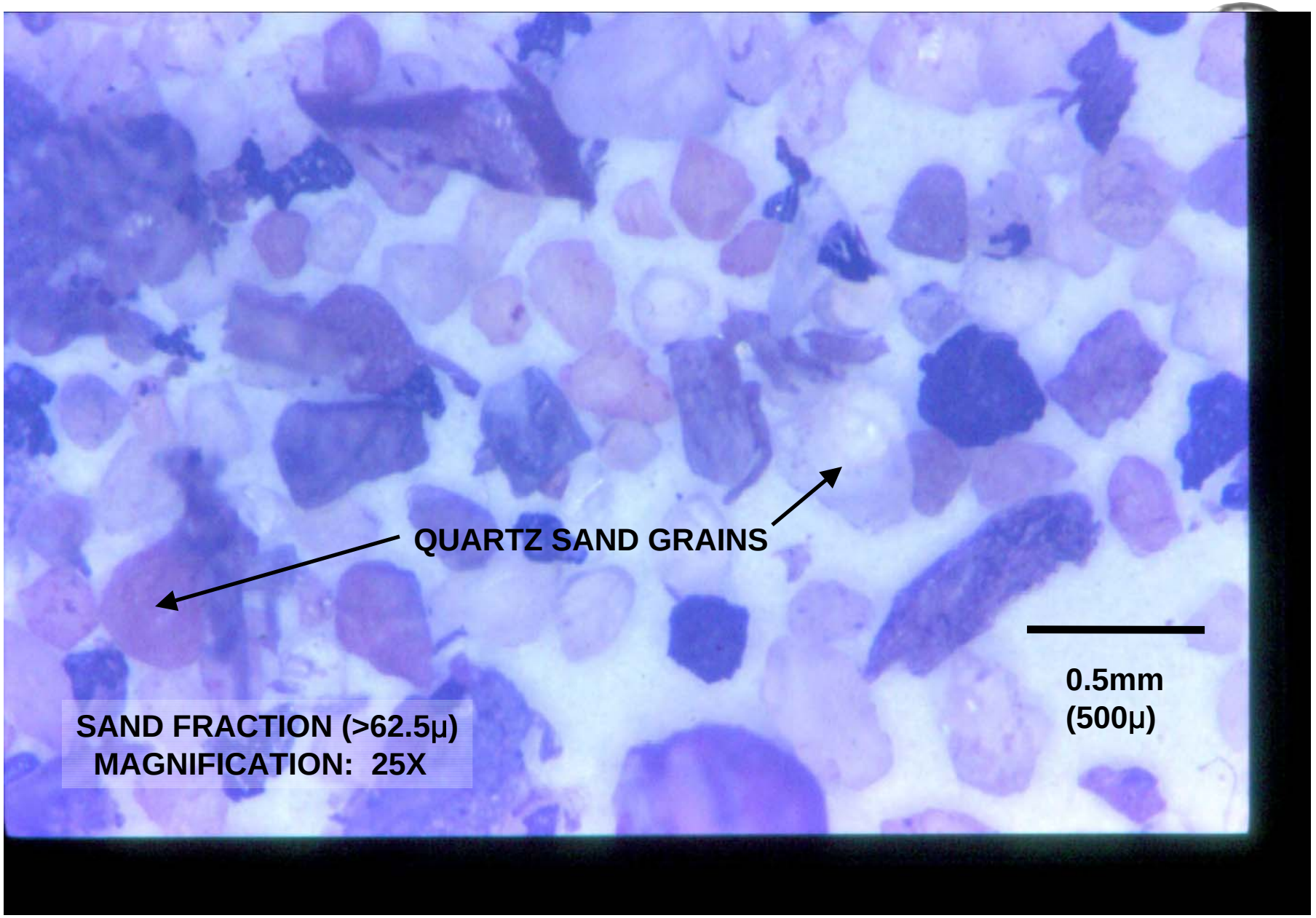
EVENT	SAMPLE #	X COORD	Y COORD
3/4	SAMPLE 4-1	59	25
3/4	SAMPLE 4-2	65	24
3/4	SAMPLE 4-3	32	34
3/4	SAMPLE 4-4	93	18
3/4	SAMPLE 4-5	33	30

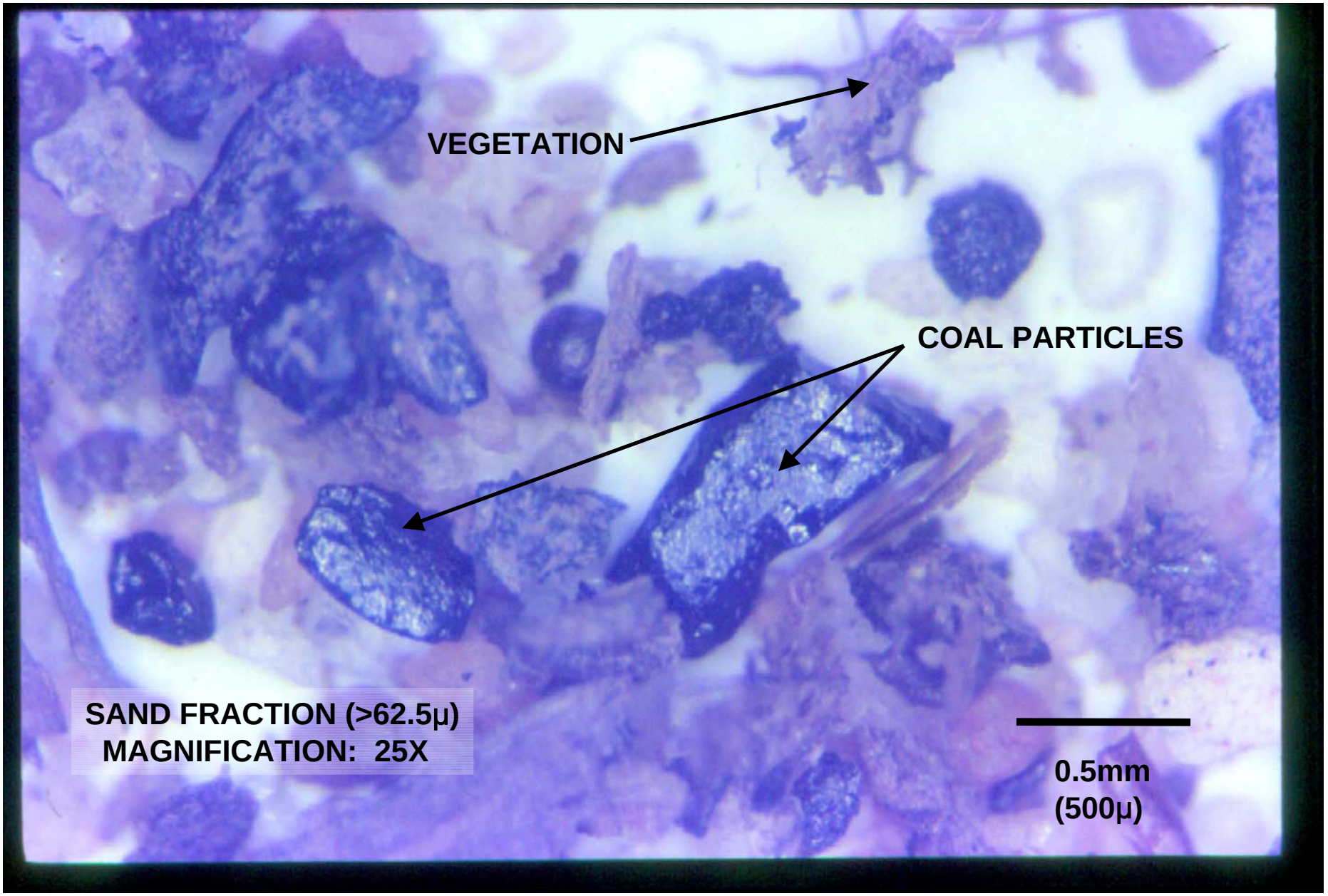
EVENT	SAMPLE #	X COORD	Y COORD
5	SAMPLE 1	29	26
5	SAMPLE 2	36	37
5	SAMPLE 3	63	21
5	SAMPLE 4	80	29
5	SAMPLE 5	94	20

EVENT	SAMPLE #	X COORD	Y COORD
6	SAMPLE 1	24	36
6	SAMPLE 2	42	21
6	SAMPLE 3	58	26
6	SAMPLE 4	78	20
6	SAMPLE 5	96	23


QUARTZ SAND
SAND/ROCK PARTICLES
EMBEDDED IN TAR
ROCK
COAL
0.5mm
(500µ)
SAND FRACTION (>62.5µ)
MAGNIFICATION: 10X
Pencil lead
reference


WOOD FRAGMENTS
SAND FRACTION (>62.5µ)
MAGNIFICATION: 10X
0.5mm
(500µ)


QUARTZ SAND GRAINS
0.5mm
(500µ)
SAND FRACTION (>62.5µ)
MAGNIFICATION: 25X


VEGETATION
COAL PARTICLES
SAND FRACTION (>62.5µ)
MAGNIFICATION: 25X
0.5mm
(500µ)

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Preliminary Test Results 2003

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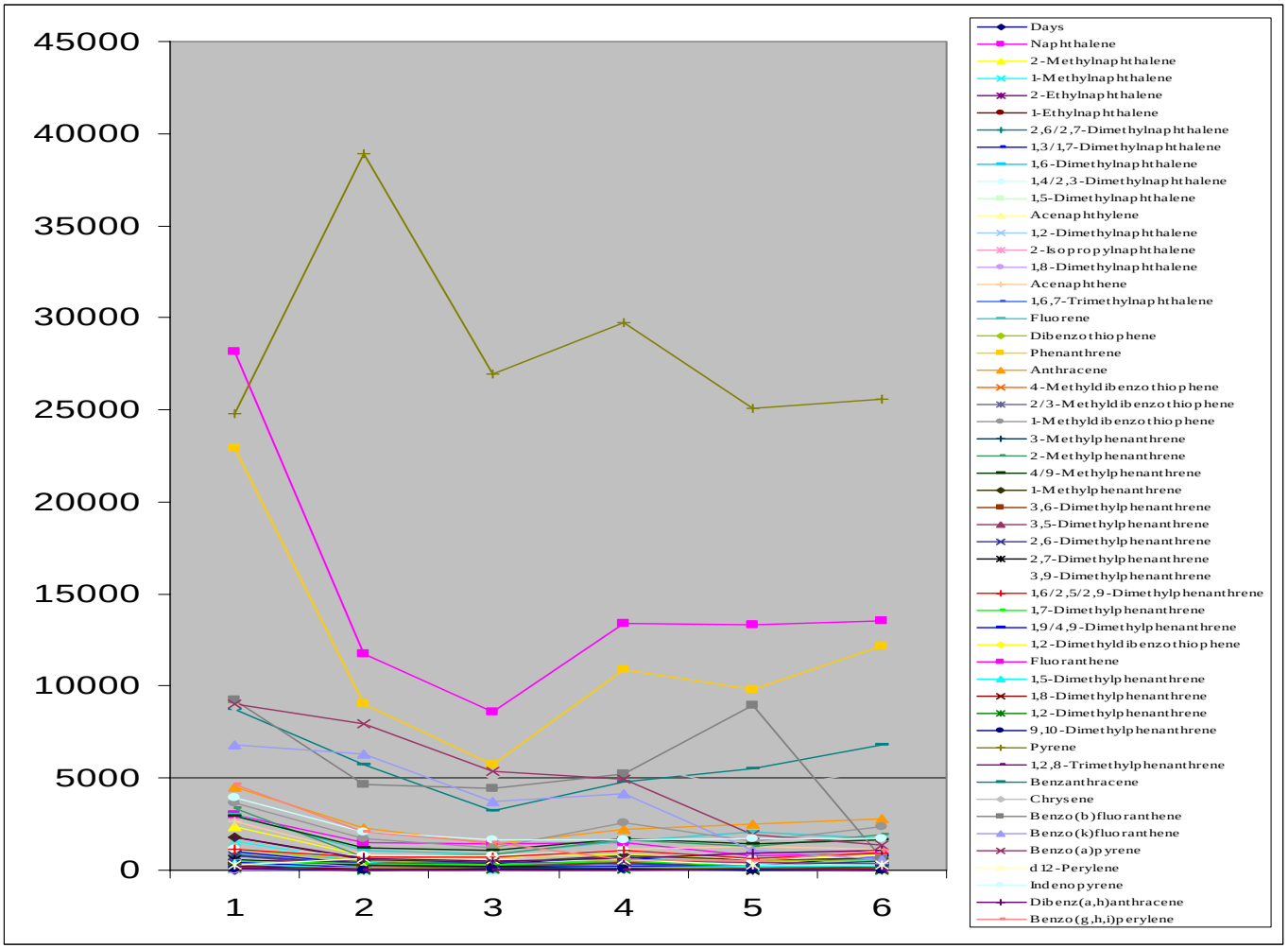

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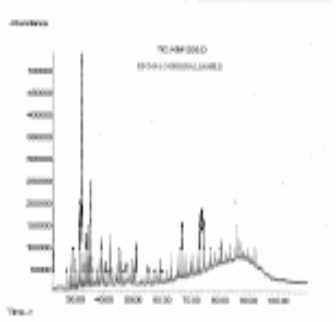
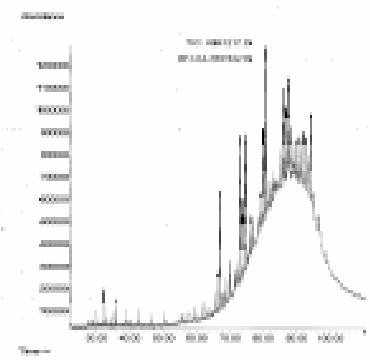
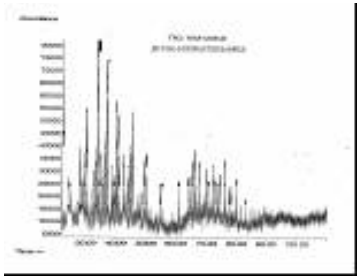
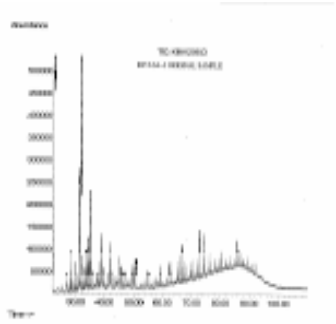
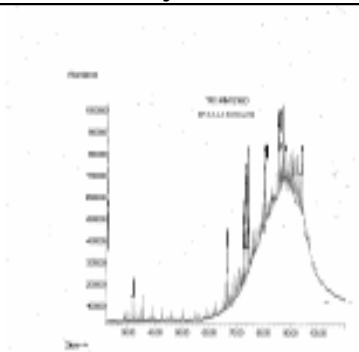
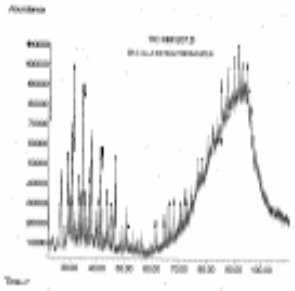
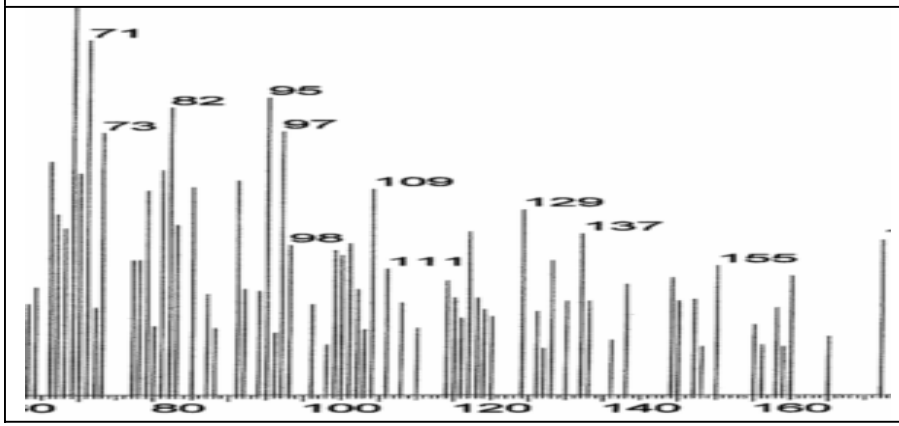
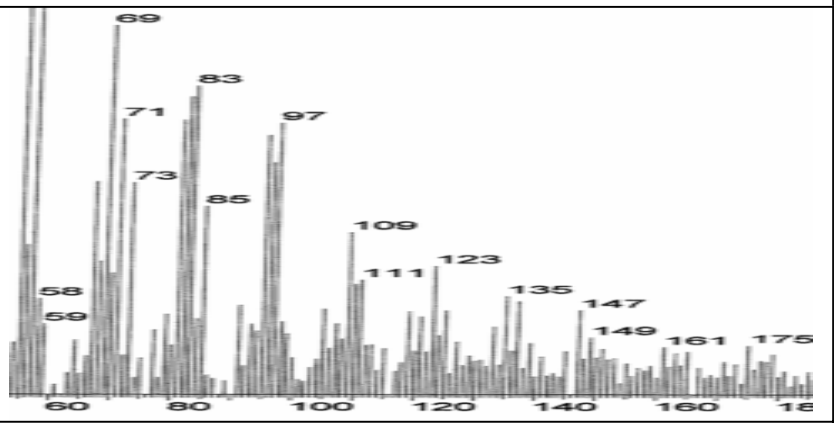
Pyrolysis GC-MS Day 0 to 100

Original Sample	Extract	Extracted Sample
Day 0	Day 0	Day 0
		
Day 100	Day 100	Day 100
		

Ion Current Time 81 min
Ion Mass 90

Extracted Sample 0 Days	Extracted Sample 100 Days
Time 81 min	Time 81 min
	

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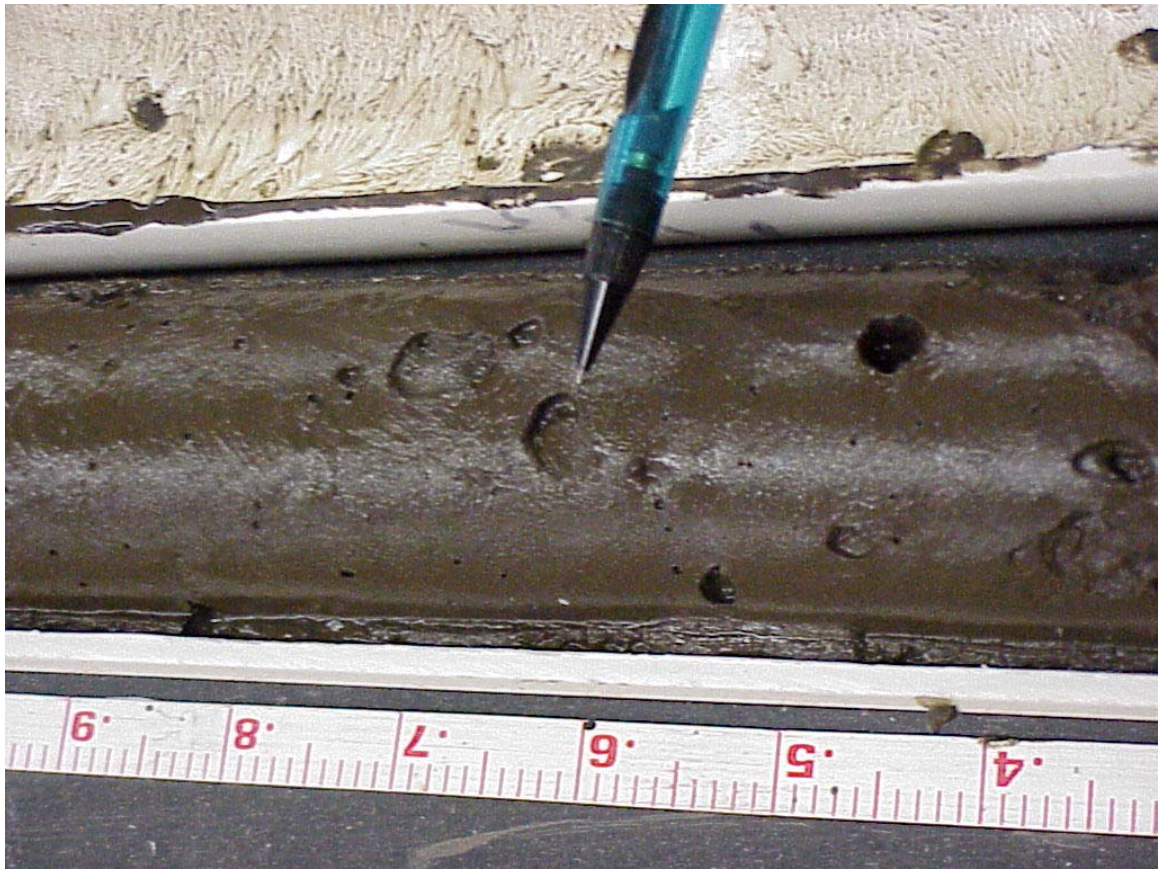
Gas Pockets 2003



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What we learned 2003

- Sediments in Erie Pier were very reductive
- Pyrolysis GC-MS indicates redox activity in the sediment
- Sediment contained coal, tar, wood and vegetation fragments, slag, humic acids, oil, and a variety of foreign objects.
- Analysis of samples for 66 PAHs taken from one confined area of the test cell shows reduction of PAHs during 2003.

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What we learned 2003 (cont'd)

- Persistent gas formation (bubbling) in the ECGO treatment cell indicated that electrochemical reactions were occurring.
- The combination of reducing conditions, sediment heterogeneity, presence of humic substances, and relatively high organic carbon content likely contributed to the treatment inefficiencies that were experienced.

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What we learned 2003 (cont'd)

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- Traditional sampling and analytical techniques may be inadequate for assessing how alternative sediment treatment technologies may (or may not) be working in the field, particularly when one takes into account the "acceptable" range of analytical variability assigned to substances like PAHs, e.g., RPD of ∗40% between laboratory duplicates, *plus* the typically heterogeneous nature of sediments and contaminant distribution.

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SUMMARY

- ECGO technology may need to be tailored and/or augmented to meet the specific characteristics of each treatment site, and to optimize performance. Alternatively, significant reduction of PAH contaminant levels within complex and organic-rich sediments using ECGO may be too difficult to achieve efficiently in-situ. In either case, the NRRI test facility will aid in making future assessments.

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The Research Facility Coleraine, MN

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Test Cell Coleraine

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Web Site

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Welcome to the Coleraine Testing Facility

Volts	Amps	Water Level	RH	Center Temp	Electrode	Indoor	Outdoor	Power Supply
102 %	88 %	60.5 "	8 %	23.1 C° 73.7 F°	15.0 C° 59.1 F°	15.0 C° 59.1 F°	-7.9 C° 17.7 F°	27.3 C° 81.2 F°

Cell 1 Volts = 3 % Amps = 1 % Temp = 158.8	Cell 4 Volts = 80 % Amps = 92 % Temp = 17.6		System Sand Volts = 109 % Amps = 52 % Temp = 17.8	Cell 10 Volts = 0 % Amps = 2 % Temp = 158.9
Cell 2 Volts = -1 % Amps = 1 % Temp = 158.9	M. S. Erie Pier Volts= 80 % Amps = 90 % Temp = 21.4	Temp X	Cell 8 Volts = 84 % Amps = 97 % Temp = 19.5	Cell 11 Volts = 0 % Amps = 1 % Temp = 158.9
Cell 3 Volts = 0 % Amps = 1 % Temp = 158.9	N. B. H. Volts = 12 % Amps = 137 % Temp = 18.4		Hog Island Volts = 56 % Amps = 97 % Temp = 157.0	Cell 12 Volts = 0 % Amps = 1 % Temp = 158.9

Thu Feb 5 06:28:05 CST 2004 up 77 days 16:03

Webcam image from Coleraine

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Capabilities

- Can Test one cubic yard samples
- Six Test Cells or more
- Monitoring Equipment
- Flexible to address individual client issues
- Sediments analysis
  - Particle characterization
  - Chemical analysis
  - Gas analysis

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Montana Research Facility

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Test Cell Configuration

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Oil Sand

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Crude Oil Sample

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PAH Concentrations				
Name	Day 1	Day 50	Day 74	Day 124
Naphthalene	2.24	049		ND
Acenaphthylene	ND			ND
Acenaphthene	6.5			ND
Fluorine	ND 1.38			ND
Phenanthrene	5.2 1.97			ND
Anthracene	ND			ND
Fluoranthene	ND			ND
Pyrene	5.6 1.22	4.5 0.66	1.9	ND
Benzo(a)anthacene	ND 0.21	0.59		ND
Chysene	7.2 0.74	6.7 0.57	2.4	ND
Benzo(b)fluoranthene	ND 0.16	ND		ND
Benzp(k)fluoranthene	ND 0.19	ND 0.11		ND
Benzo(a)pyrene	ND 0.32	ND 0.24		ND
Indeno(1,2,3-cd)pyrene	ND	ND		ND
Dibenzo(a,h) anthracene	ND	ND		ND
Benzo(ghi)perylene	ND 0.12	ND		ND

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Extraction Efficiency
Erie Pier