Voltammetry: an in situ multi-analyte tool to monitor the health of estuaries

10th International Biogeochemistry Symposium on Estuaries in a Changing World, Xiamen, China, May 22, 2008

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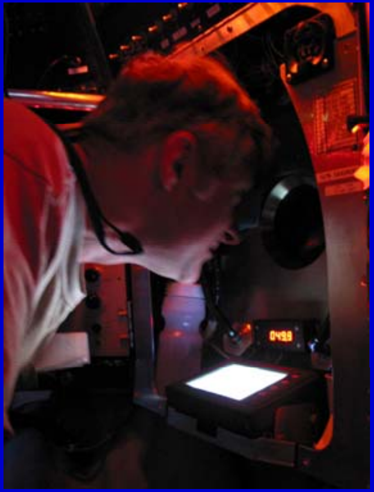

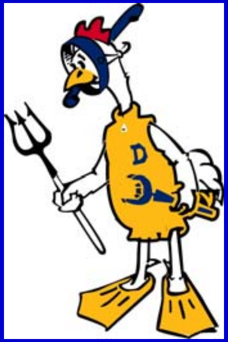

Acknowledgments

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Analytical Instrument Systems

Funding sources

Outline

In situ techniques are necessary to study the environment – voltammetry as a good *non-selective* analytical method

Show capability in a variety of estuarine environments

Inland Bays – lab equipment brought to the field

Chesapeake Bay – field equipment

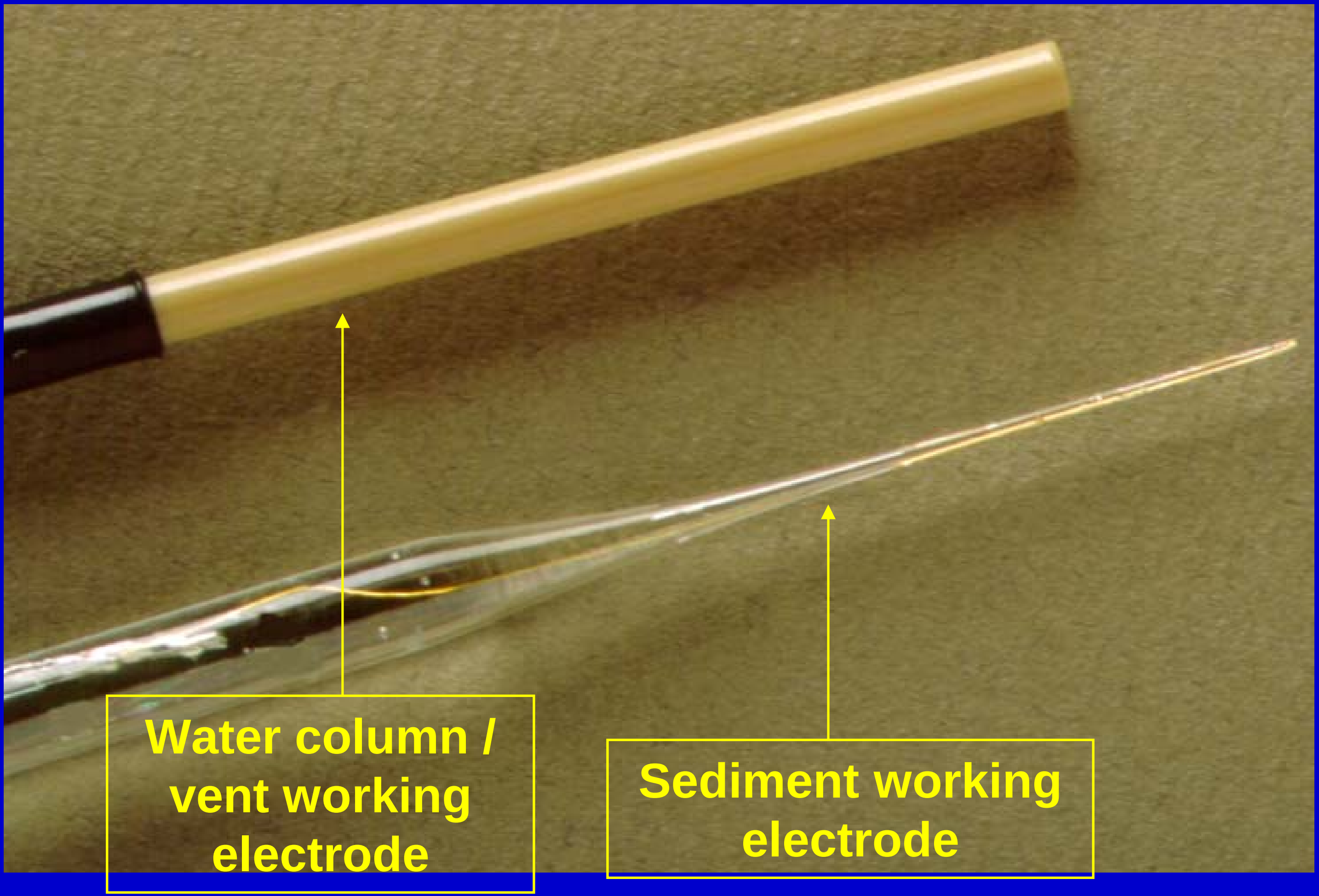
Field equipment on moorings:

Salt marsh / sediment work

Delaware Bay

A story on O_2, Fe, S biogeochemistry coupled with physical forcing

PEEK & Glass encased electrodes in marine epoxy



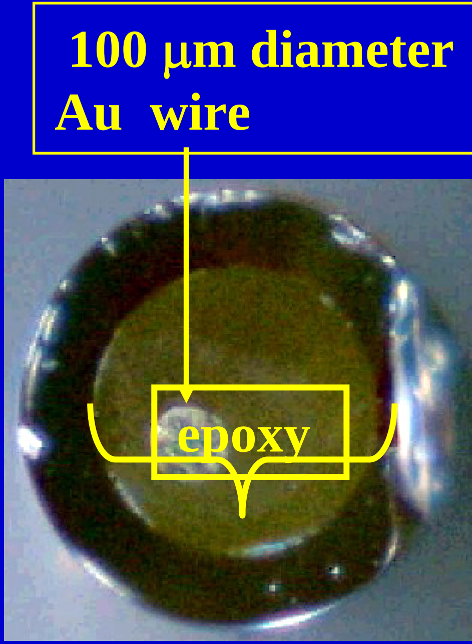


Plate with Hg film

O_2, Fe^{2+}, Mn^{2+}, H_2S, H_2O_2, I^-, S_x^{2-}, $S_2O_3^{2-}$, FeS_{aq}, Fe(III) are all measurable in one scan, if present

Tested to 2700 m and 120 °C

Solid state (micro)electrodes for the analysis of biologically relevant compounds and ions

Chemistry Drives Biology

Rationale for design and use

Fine scale resolution - mm in sediments; micrometer in biofilms and mats

determine sediment heterogeneity vs. homogeneity

use to prospect for life forms and understand ecosystem health

Use in sedimentary porewaters of bays, oceans and lakes

in water column; e.g., Chesapeake Bay, Black Sea

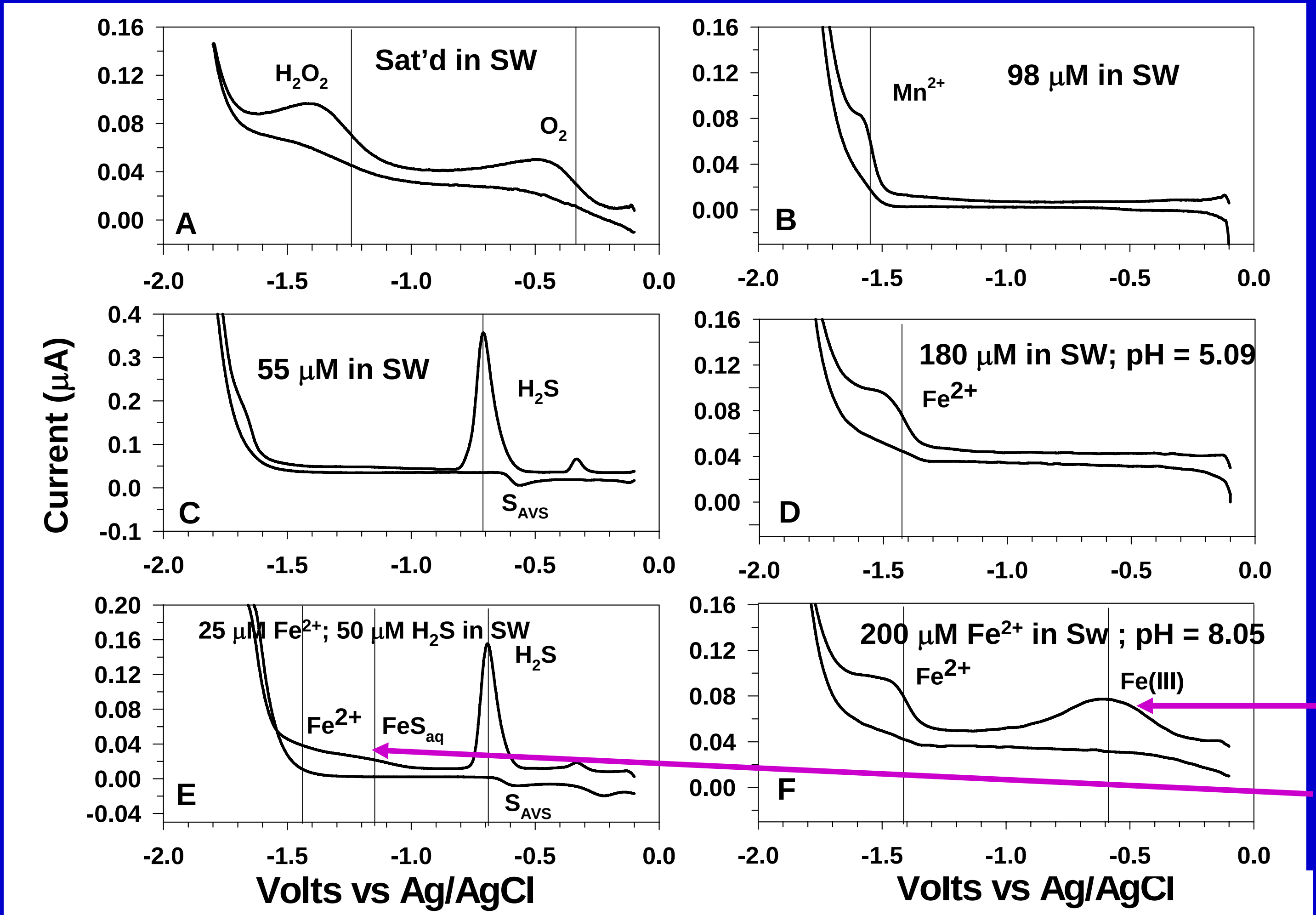
at Hydrothermal Vents, Yellowstone hot springs,

in corrosion studies

VOLTAMMETRY I vs E plots [similar to A vs λ plots]

Vertical lines indicate the half-wave potential for the reduction of each analyte at the Au/Hg electrode

Potential scans and Hg tip prevent (bio)fouling



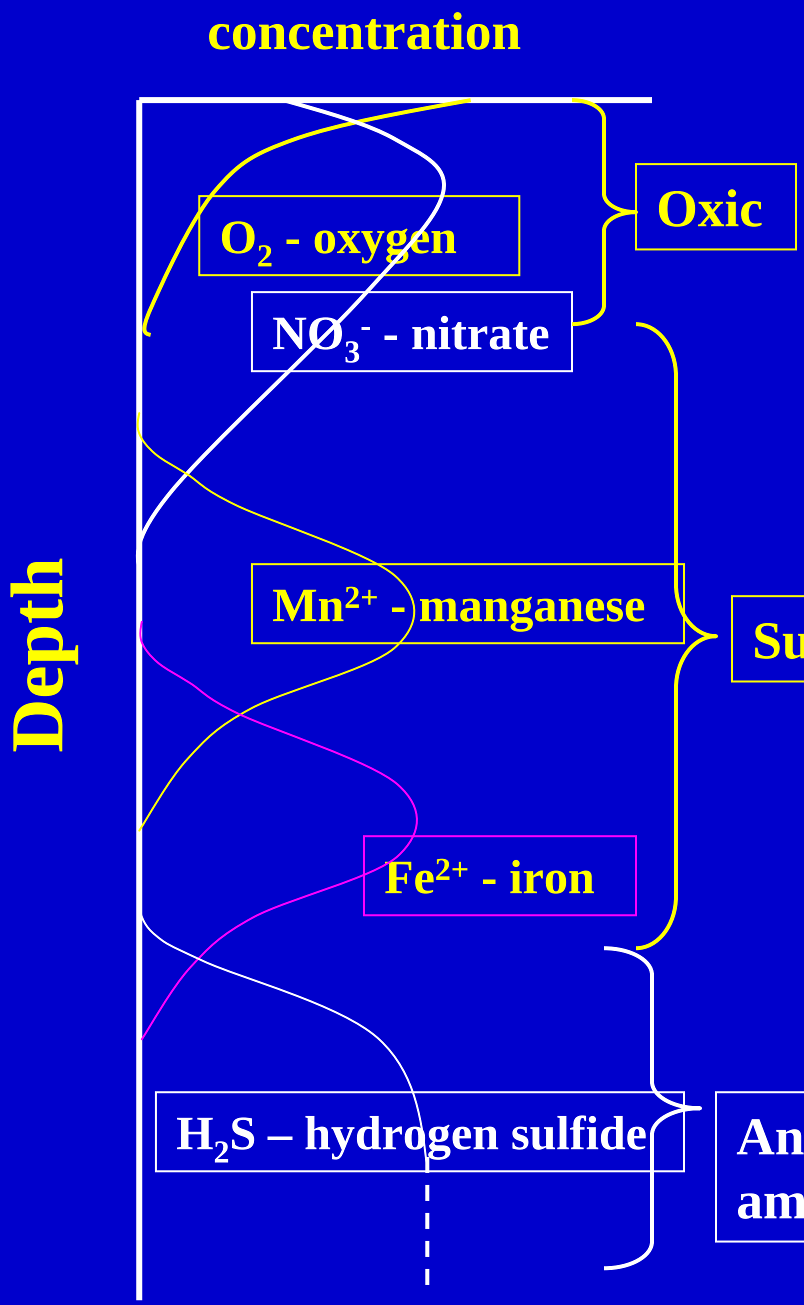
Detection limits
3 μM for O_2,
5 μM Mn^{2+}
10 μM Fe^{2+}
0.1 μM H_2S

Multi-analyte sensor

No standards for Fe(III) and FeS

Luther et al, 2008

Where is the oxygen?



concentration

Depth

O_2 - oxygen

NO_3^- - nitrate

Oxic

Mn^{2+} - manganese

Fe^{2+} - iron

H_2S – hydrogen sulfide

Suboxic – no oxygen and no hydrogen sulfide

Anoxic – no oxygen BUT also rich in ammonia and phosphate (nutrients)

Profiles for the sequence of some major chemical components in sediments and stagnant waters

Due to Organic matter decomposition by oxidants [oxygen, nitrate, manganese and iron oxides (rust), sulfate]

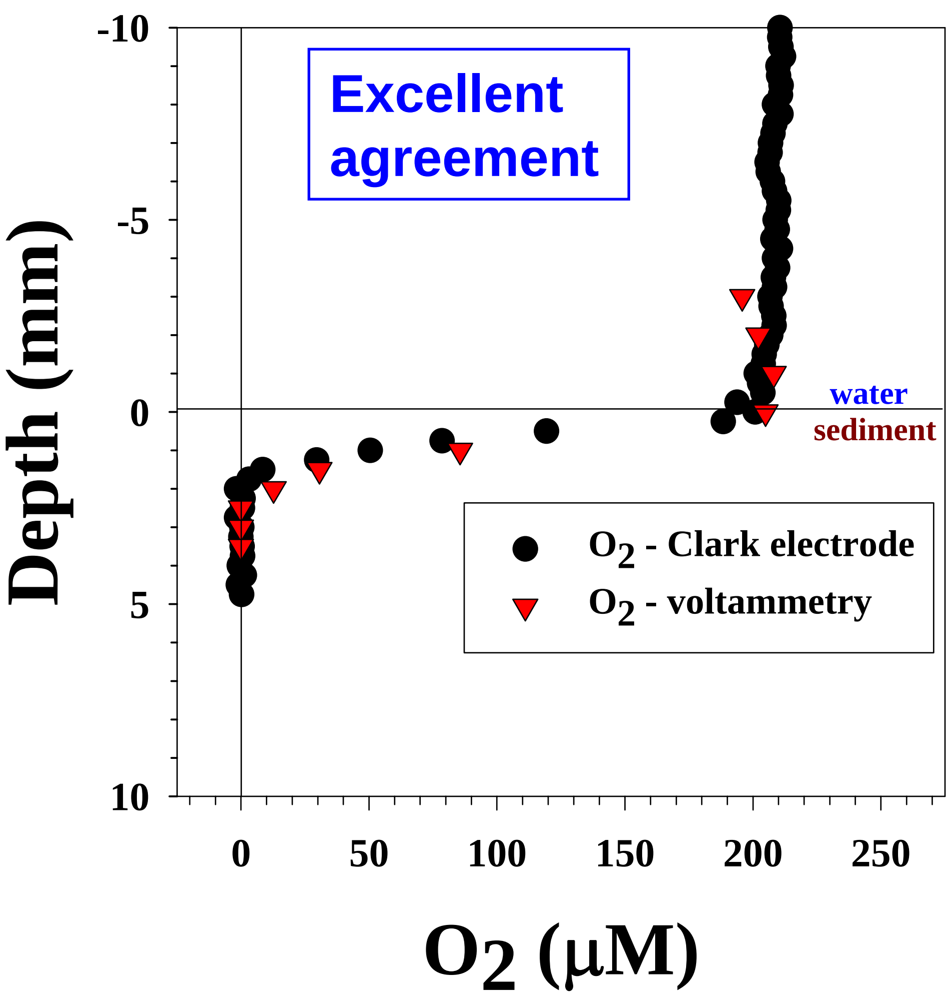
$$Fe^{2+} + H_2S \rightarrow FeS + 2\ H^+$$

$$FeS + H_2S \rightarrow FeS_2 + H_2$$

fools' gold

In situ comparison of O_2 Clark vs voltammetric Au/Hg in sediments from a ROV

*R*eal time voltammetry of porewaters



Raritan Bay 1997 - Dive 6

Excellent agreement

Free Benthic Lander for Depth Profiles and Flux Measurements

Remote micromanipulator

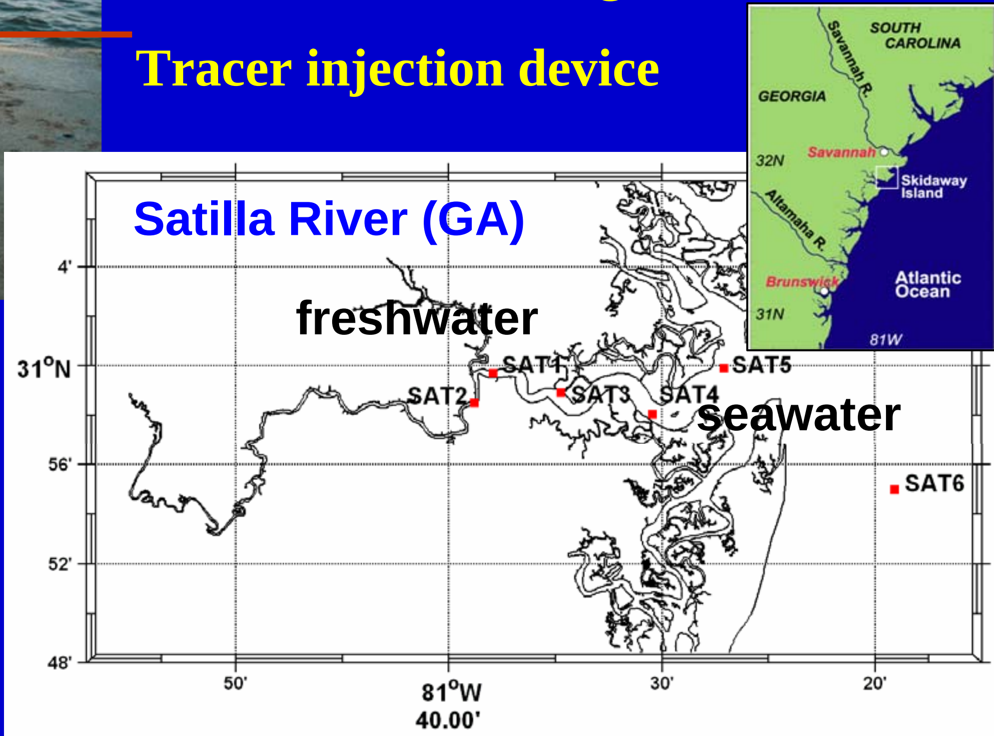
Potentiostat: ISEA II™

AIS
Analytical Instrument Systems, Inc.

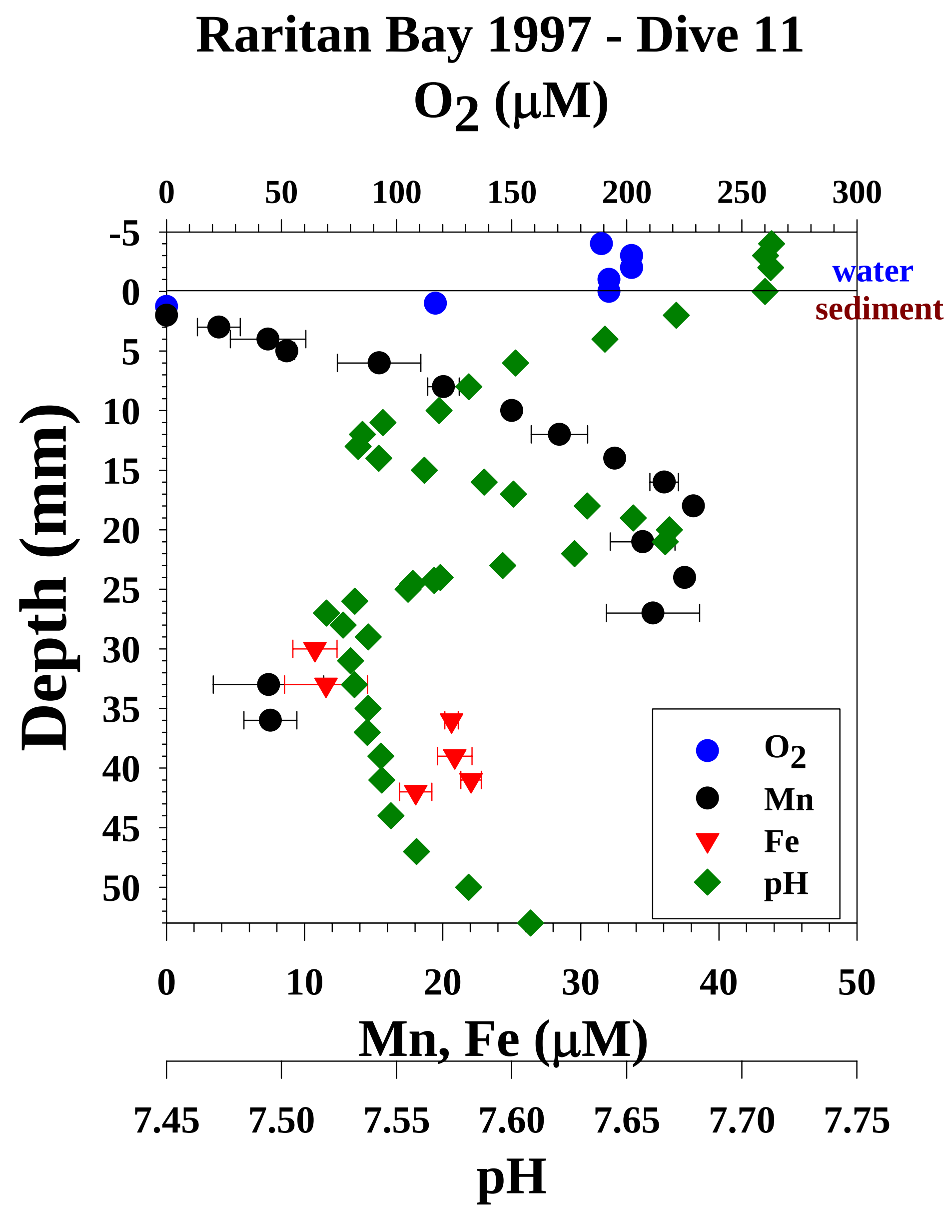
Cable for all 4 Au/Hg electrodes

Tracer injection device

Benthic chamber with Au/Hg microelectrode



SEDIMENT DIAGENESIS



Raritan Bay 1997 - Dive 11

pH reflects processes

$138\,O_2 + C_{106}H_{263}O_{110}N_{16}P \rightarrow 106\,HCO_3^- + 16\,NO_3^- + HPO_4^{2-} + 16\,H_2O + 124\,H^+$

O_2, NO_3^- electron acceptor; lowers pH

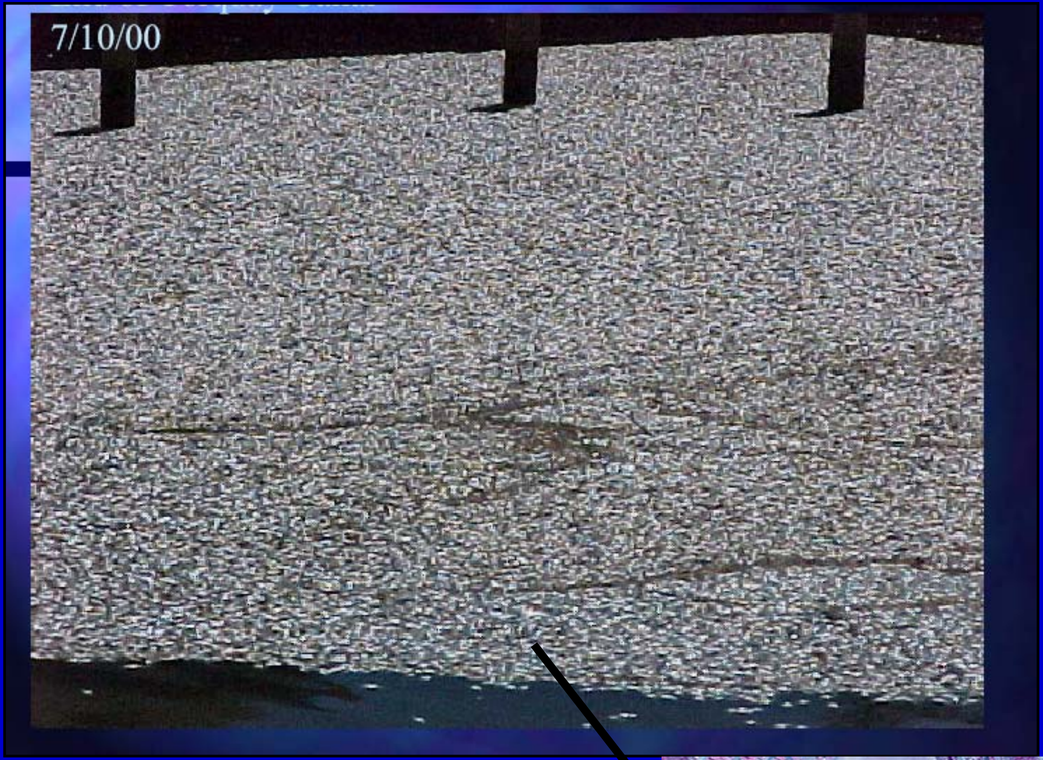
Mn^{2+} inc.; MnO_2 electron acceptor; raises pH

$Ca(Mn)CO_3$ precipitation; lowers pH

$236\,MnO_2 + C_{106}H_{263}O_{110}N_{16}P + 364\,H^+ \rightarrow 8\,N_2 + 106\,HCO_3^- + HPO_4^{2-} + 236\,Mn^{2+} + 636\,H_2O$

Luther et al, 1999

Tourquay Canal DE – July 10, 2000 benthic processes at their worst?



Close-up

End of canal

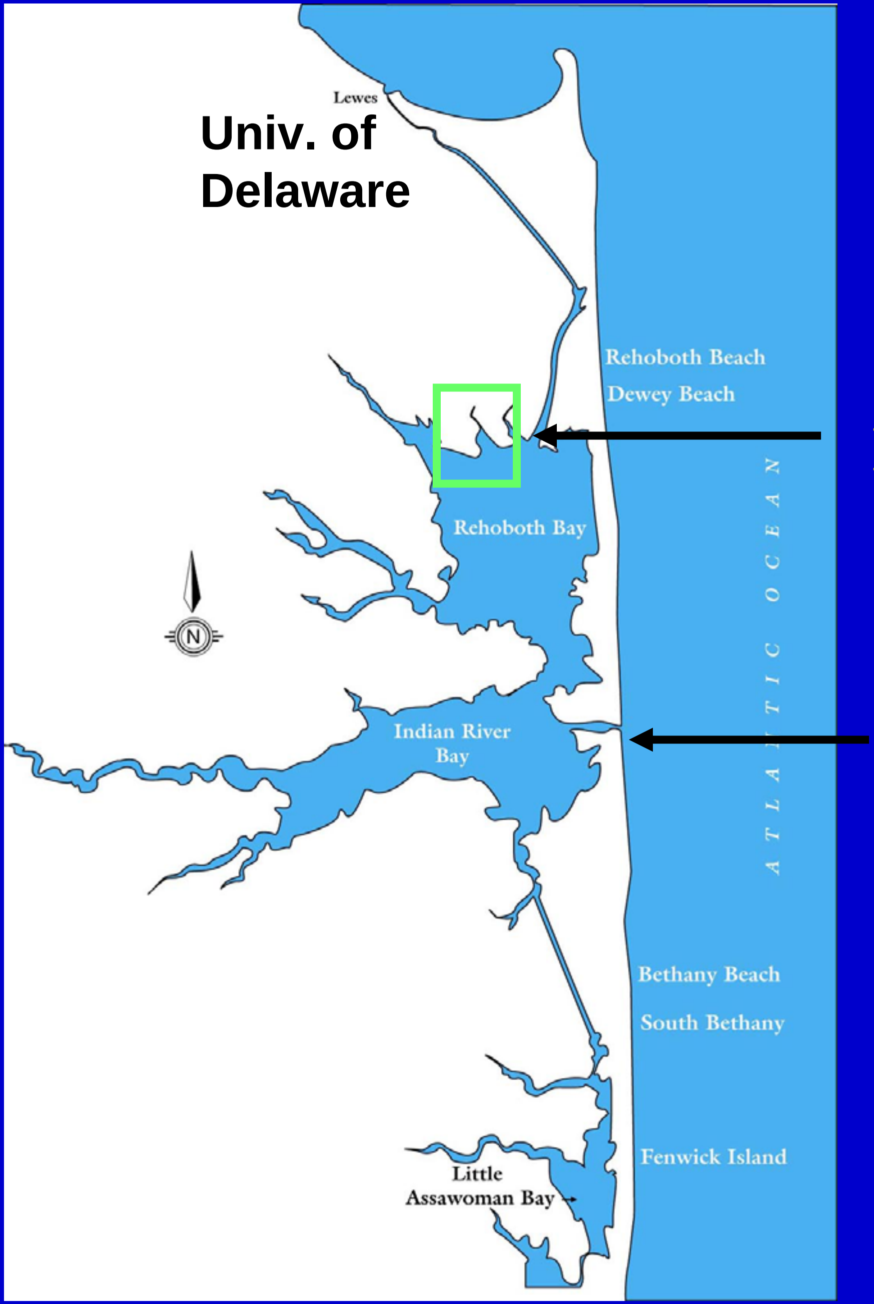
Fish found at end of canal at control sites, brought in with the tide

Electrodes on wire for *in situ* work

Blue crabs stressed in early August 5, 2004 –

there were small amounts of oxygen in the surface waters along with H_2S

Delaware's Inland Bays

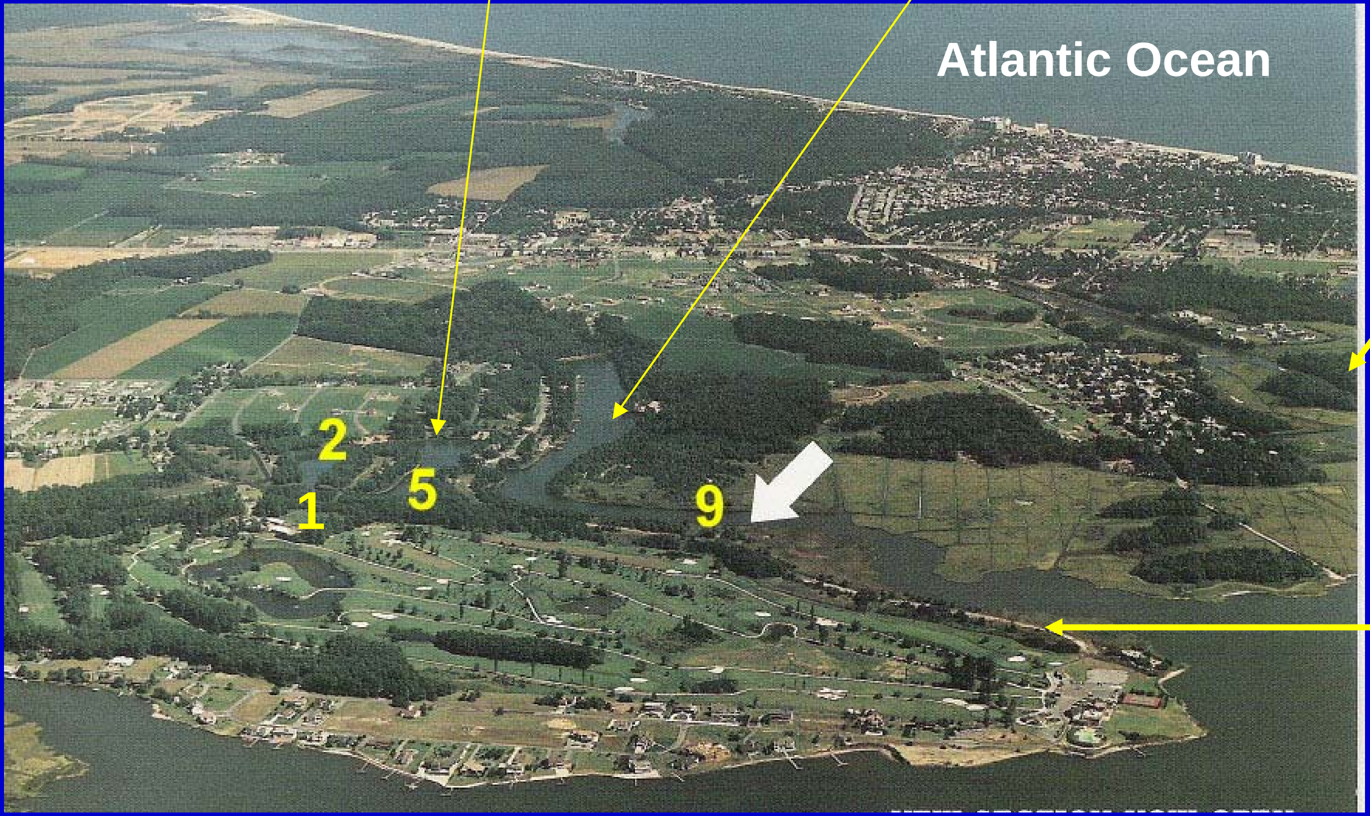


Bald Eagle Creek area - residence time 90 days

Only One Inlet

System with significant eutrophication

Torquay Canal / Bald Eagle Creek Sites



Nutrients from

Waste water treatment plant

Golf course

Torquay Canal / Bald Eagle Creek Sites

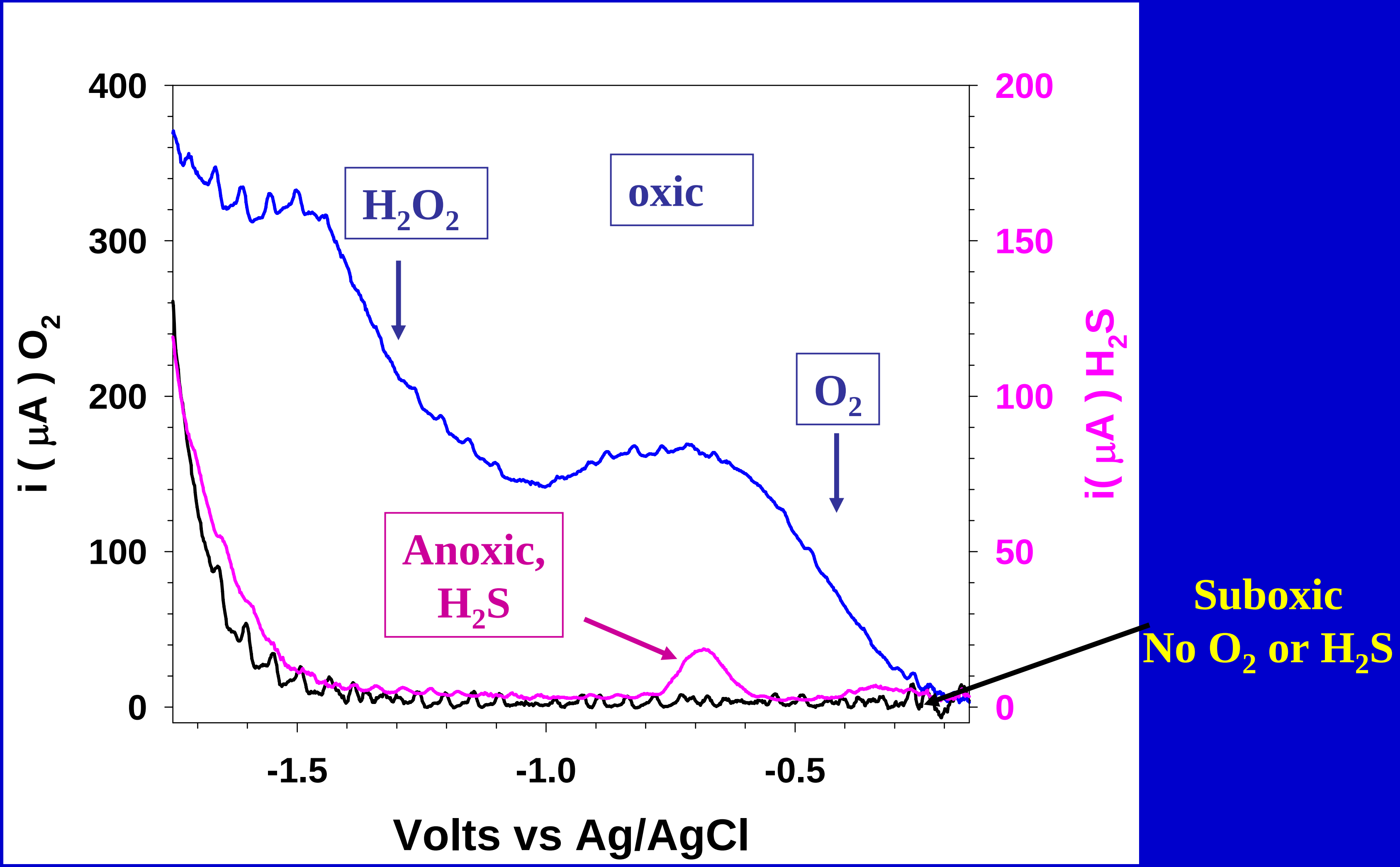
sites 2 and 9 are larger than a FOOTBALL FIELD IN AREA

Torquay canal control sites = 1, 5

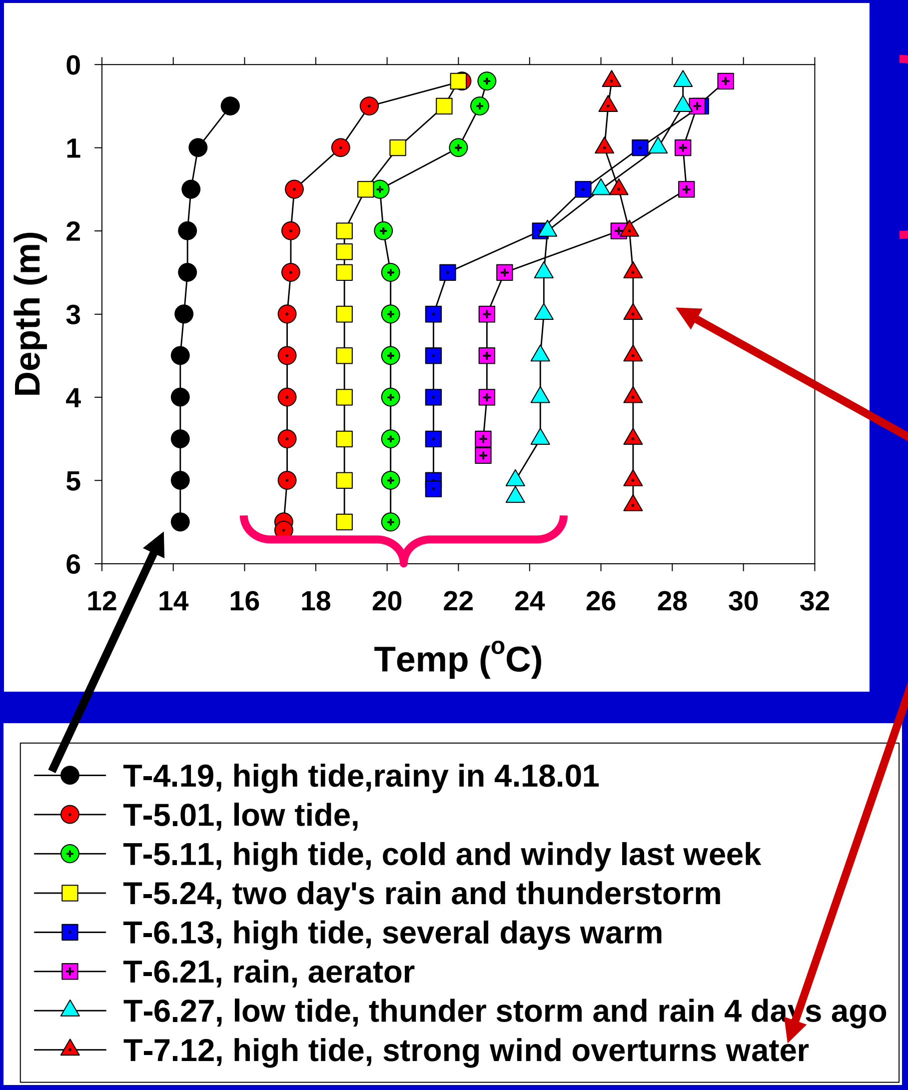
Circles indicate holes in this ecosystem with depths of 5 meters.

Squares have normal depth of 2 m

In situ Voltammograms



Temperature change from Spring to Summer, 2001
SITE #2



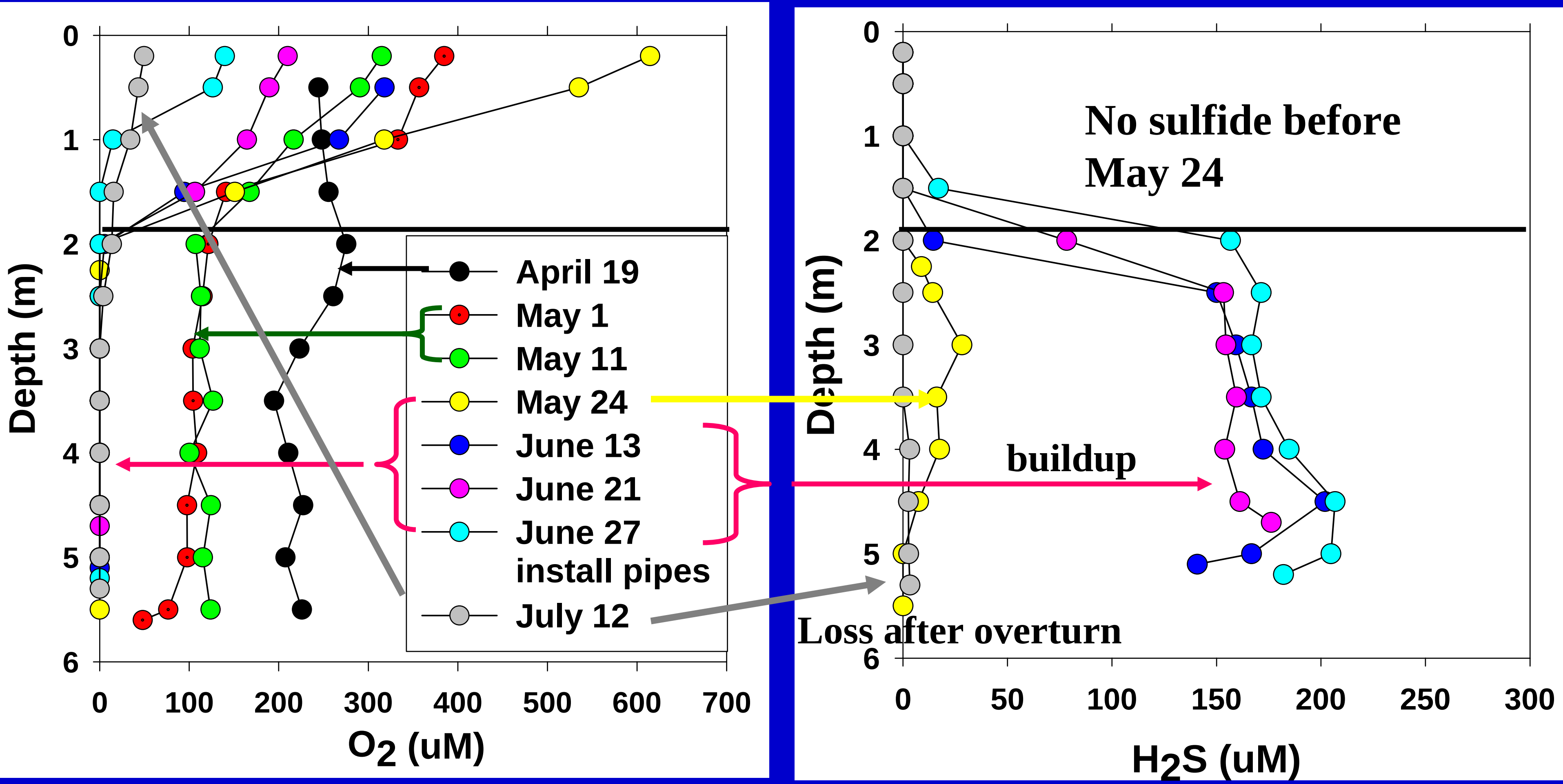
2 m mixed layer depth in summer STRONG PHYSICAL STRATIFICATION !

STRONG WINDS CAN OVERTURN THIS !

Mixed layer changes with season in 2001 for hole at site 2

O_2 change over time at Site #2, Tourquay Canal

H_2S change over time at Site #2, Tourquay Canal



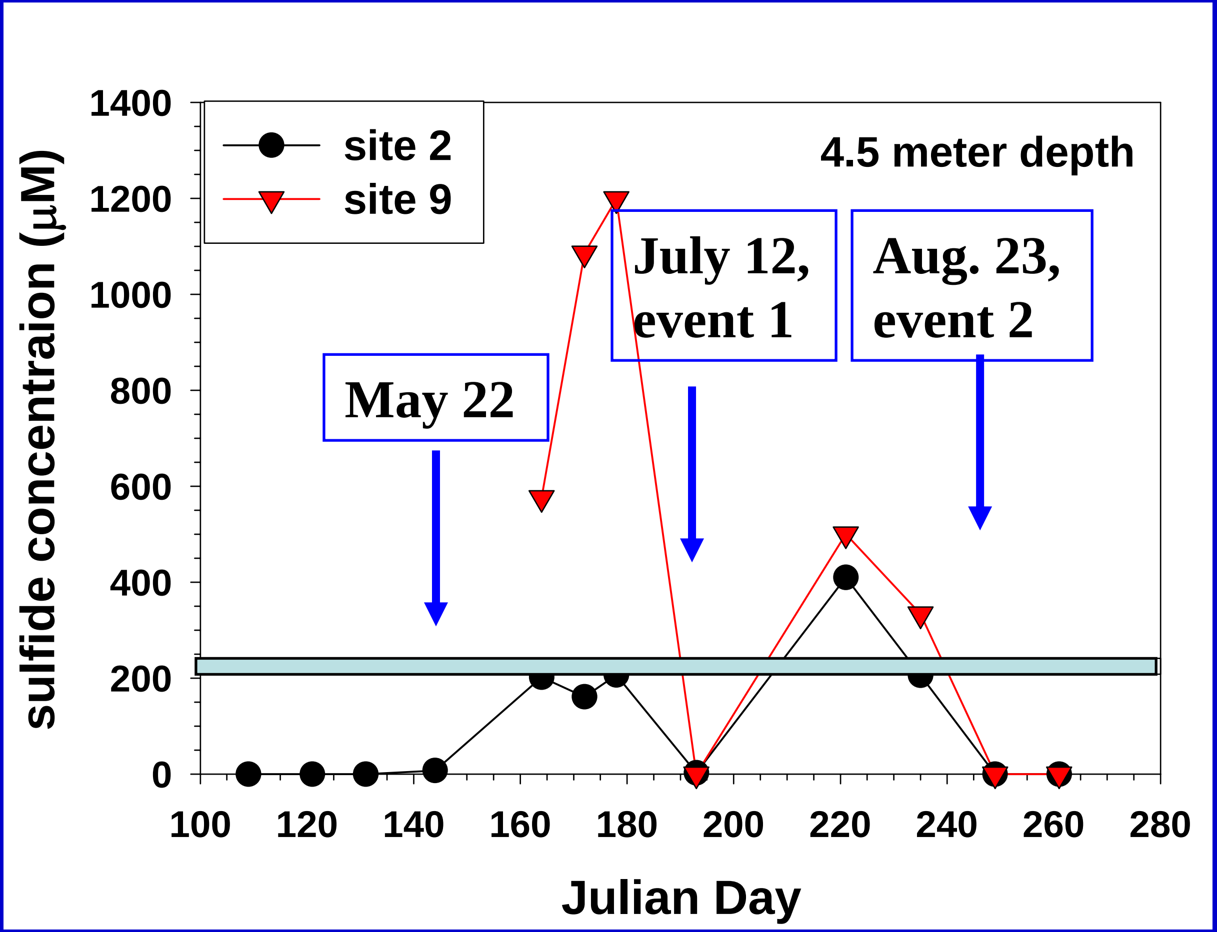
No sulfide before May 24

buildup

Loss after overturn

Strong PHYSICAL AND CHEMICAL stratification.
Mixed layer ~ 2 meters

Sulfide change with season in bottom waters at 4.5 meter depth.



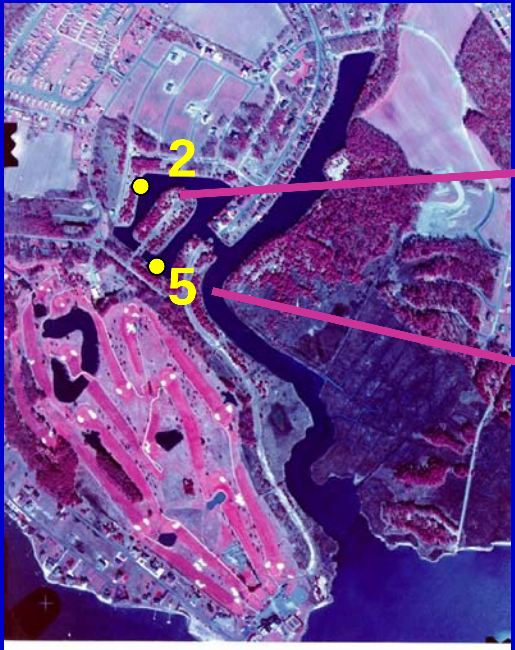
oxygen saturation level

Sulfide levels are among the highest reported in anoxic basins

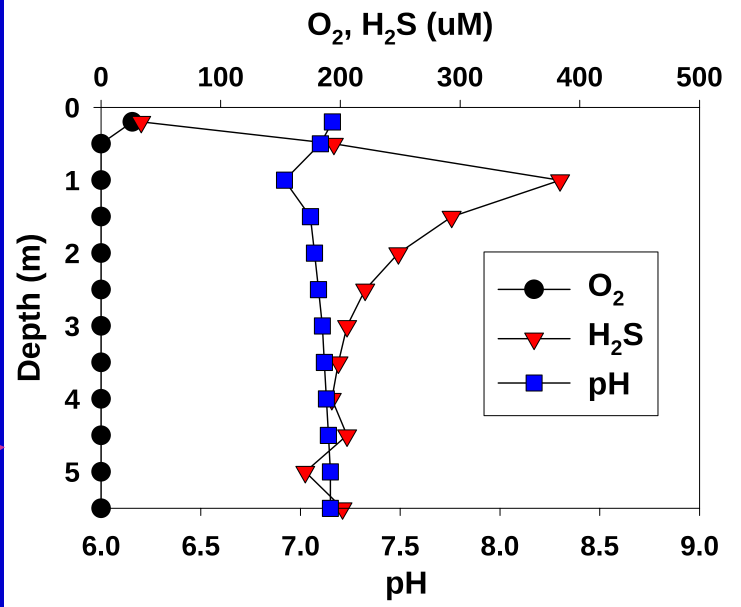
Luther et al, 2004; Ma et al 2006a, b

Tourquay Canal after event #2 – bottom water overturn

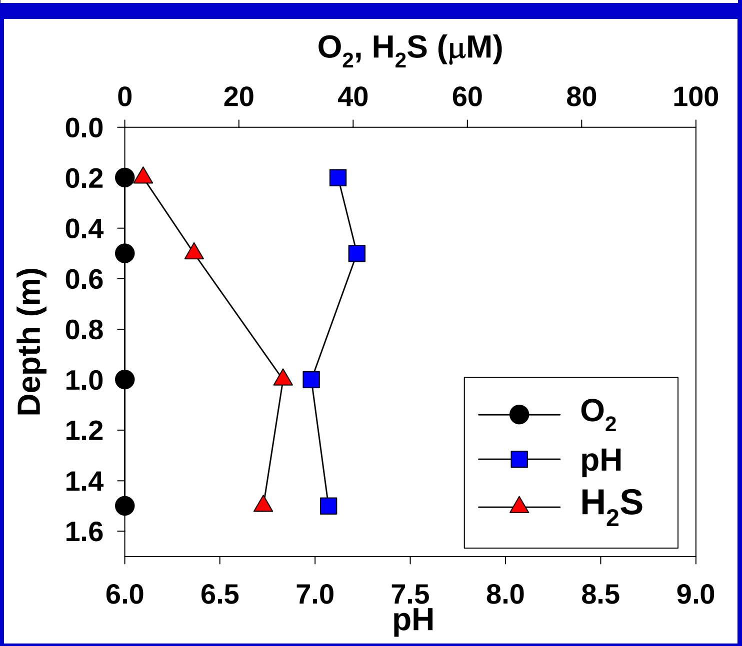
H_2S in surface waters! O_2 low or not detectable



site with hole



Control - no hole



NH_4^+ and PO_4^{3-} also go to surface waters and cause harmful algal blooms; e.g., *Heterosigma* and *Prorocentrum*

Fe^{2+} is ND-10 μM (below Au/Hg detection limit); FeS_{aq} is present; Mn^{2+} is < 0.2 μM

Fe catalytic cycle

$HS^- \rightarrow HS + e^-$ $E^o = -1.08$ V

$O_2 + e^- \rightarrow O_2^-$ $E^o = -0.16$ V

$O_2 + HS^- \rightarrow HS + O_2^-$ $E^o = -1.24$ V (overall)

Reaction is thermodynamically unfavorable!

Thus, Oxygen does NOT directly oxidize hydrogen sulfide!

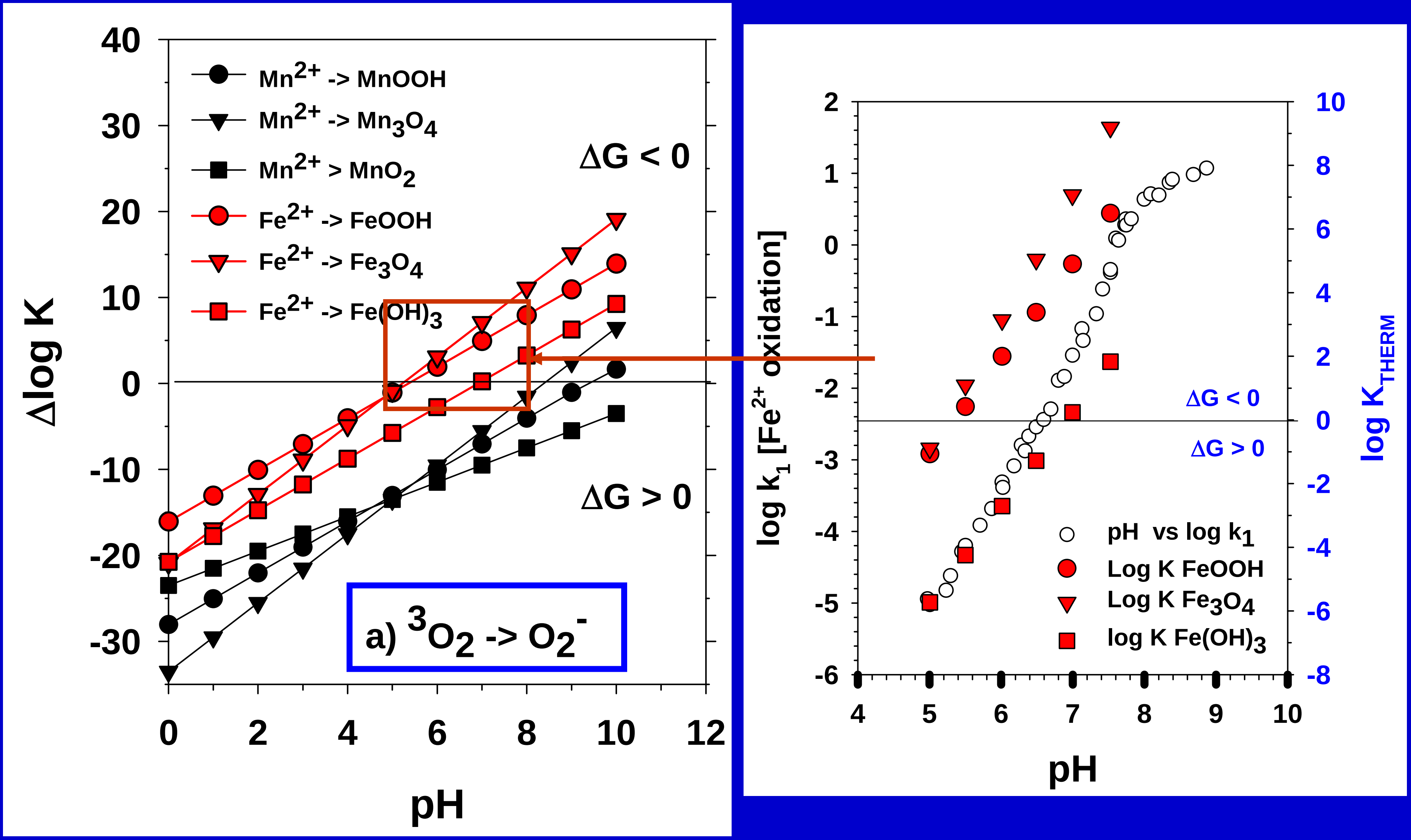
BUT

$2\,Fe^{2+} + O_2 + 4\,H^+ \rightarrow 2\,Fe^{3+} + 2\,H_2O_2$

$2\,Fe^{3+} + HS^- \rightarrow 2\,Fe^{2+} + S^o + H^+$

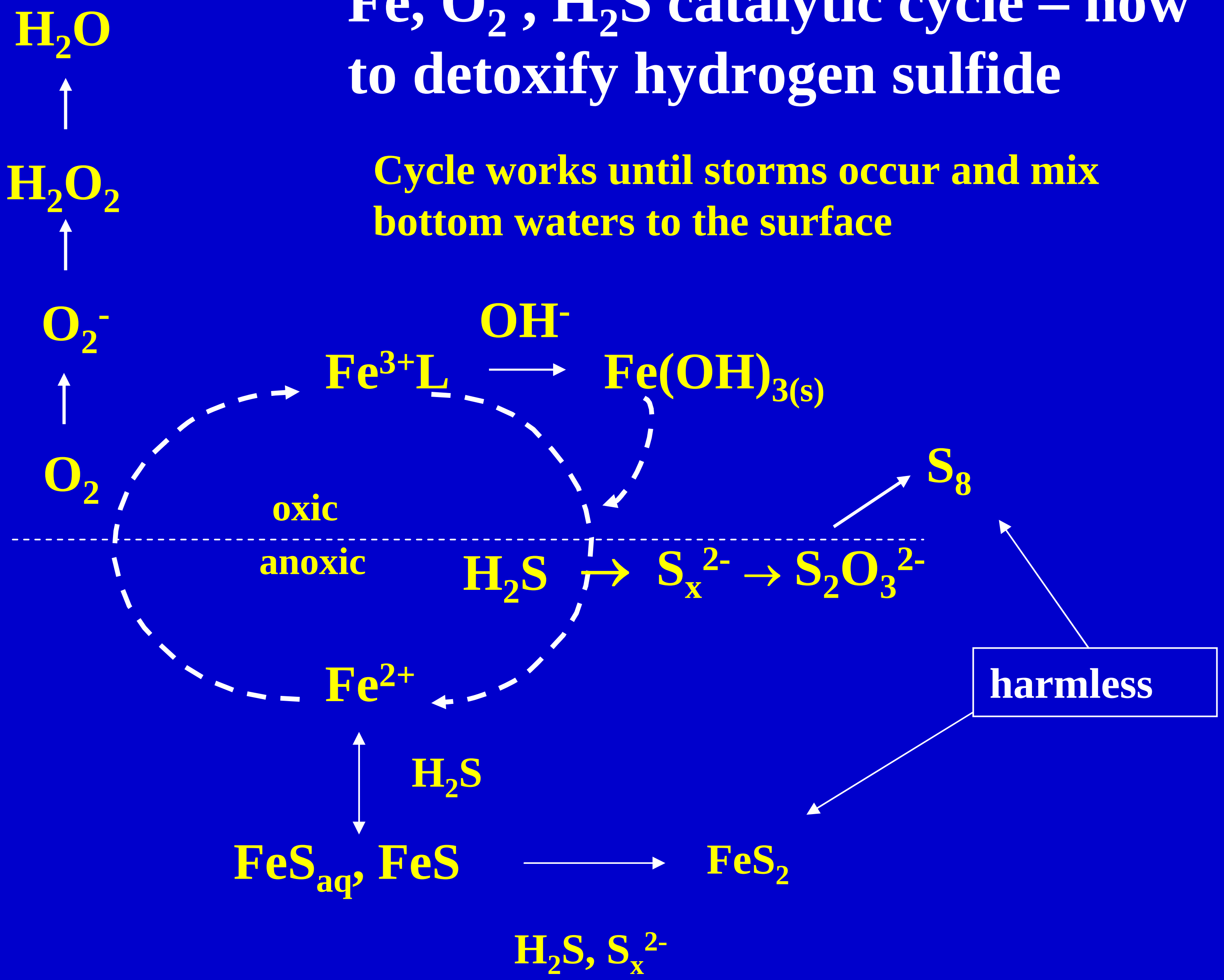
S^o concentrations were as high as 30 micromolar and should be added to the H_2S data for total reduced sulfur.

Thermodynamics and kinetics of Fe^{2+} and Mn^{2+} oxidation in freshwater (25 ºC) at O_2 saturation predicts abiotic reaction



Fe, O_2 , H_2S catalytic cycle – how to detoxify hydrogen sulfide

Cycle works until storms occur and mix bottom waters to the surface



H_2O

H_2O_2

O_2^-

O_2

$Fe^{3+}L$ $\xrightarrow{OH^-}$ $Fe(OH)_{3(s)}$

oxic

anoxic

$H_2S \rightarrow S_x^{2-} \rightarrow S_2O_3^{2-}$

S_8

harmless

Fe^{2+}

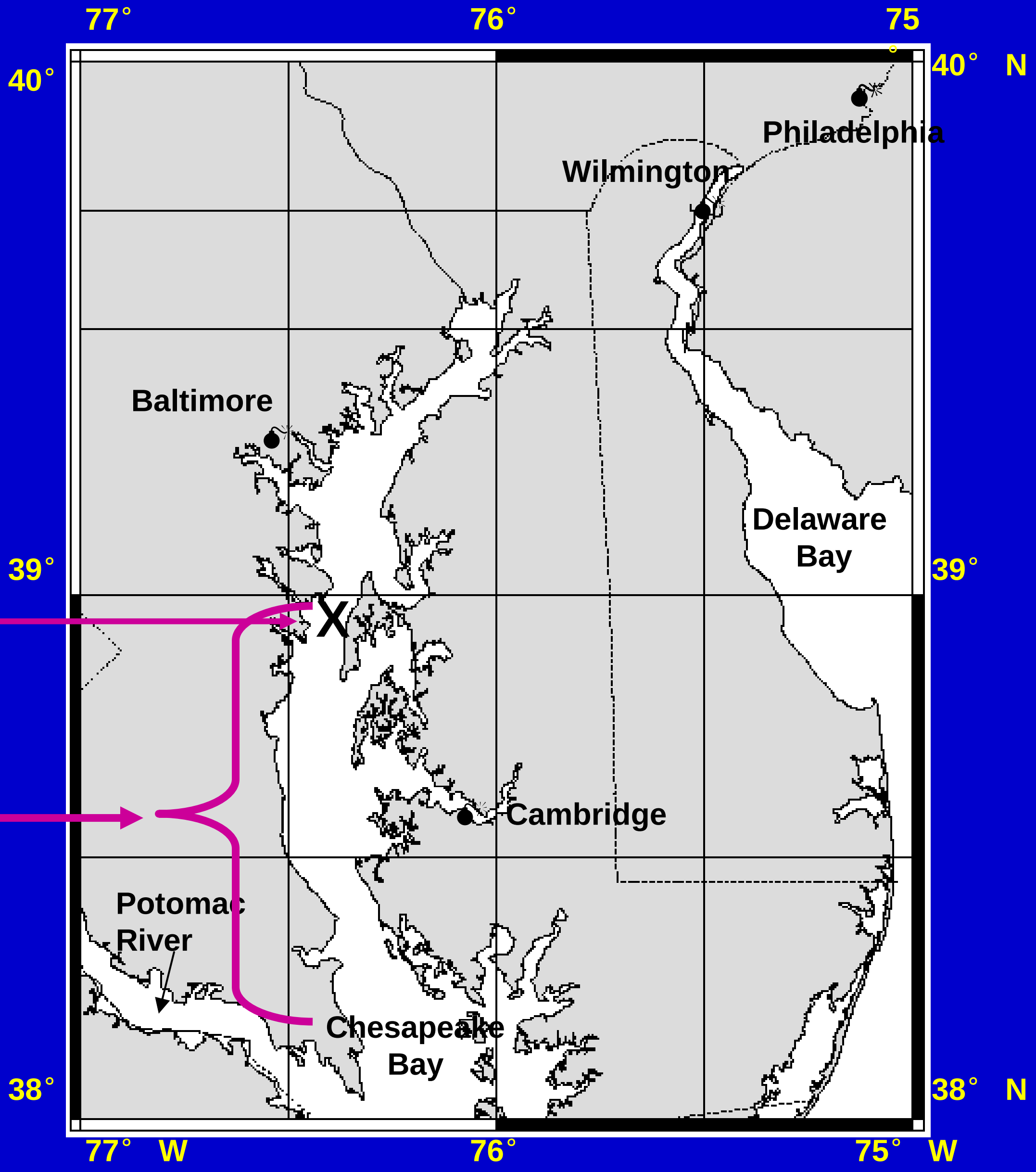
H_2S

FeS_{aq}, FeS $\rightarrow$ FeS_2

H_2S, S_x^{2-}

Ma et al, 2006a, b

Chesapeake Bay Map

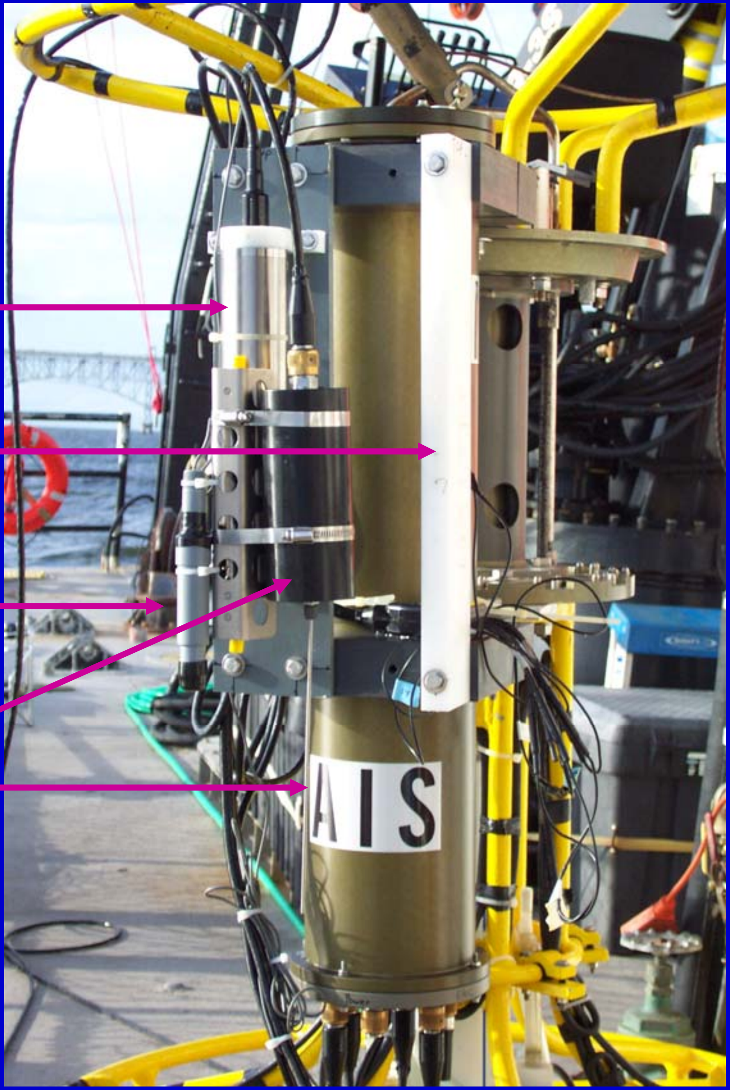


Sampling Site, July 2002

Extent of bottom water anoxia

Lewis et al, 2007

Submersible Electrochemical Analyzer on Deck



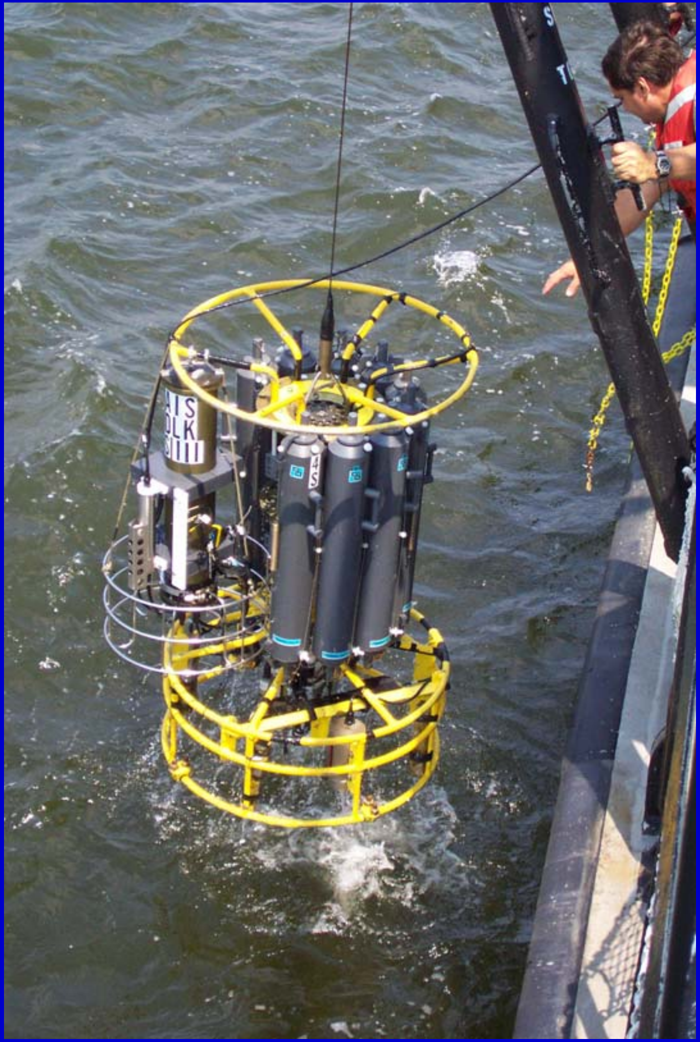
SeaBird MicroCat CTD

Voltammetric electrode holder for 4 working electrodes

pH probe

Extra temperature sensor

Deploying Submersible Electrochemical Analyzer

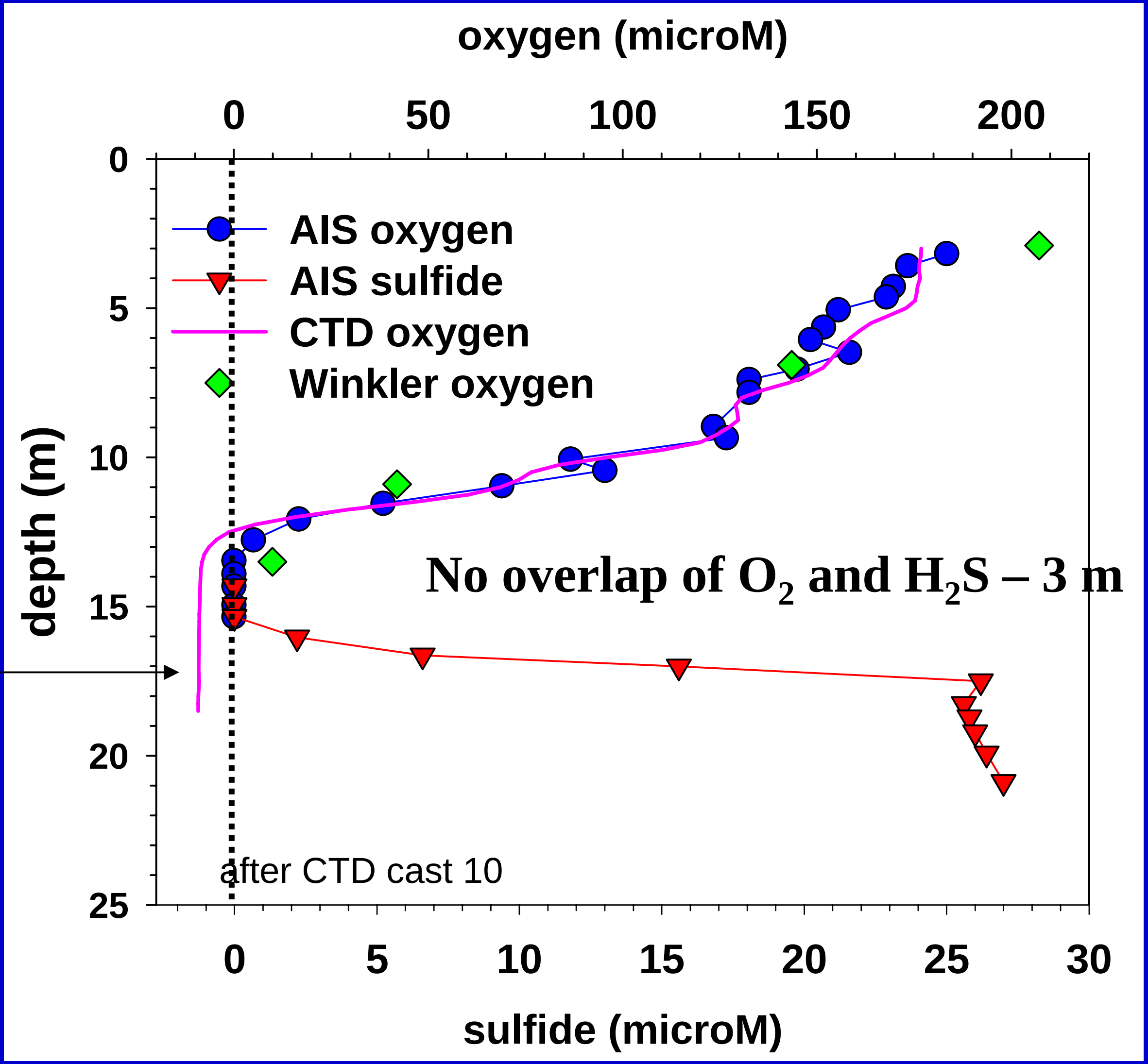


Mated to a ship CTD/rosette

Stand Alone

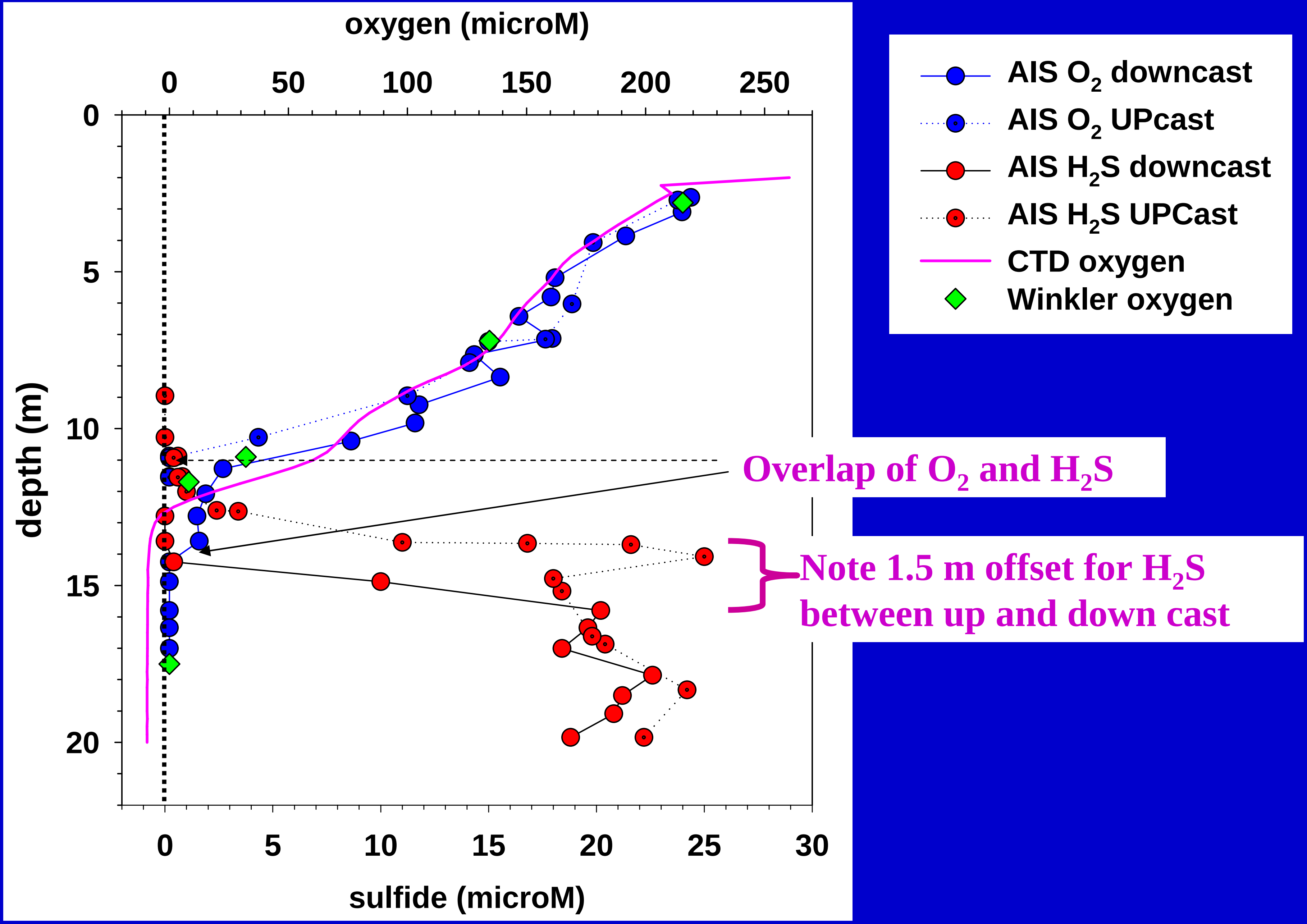
July 28, 2002 @ 0900 – high slack water

CTD sensor was found to have a hole in the membrane



No overlap of O_2 and H_2S – 3 m

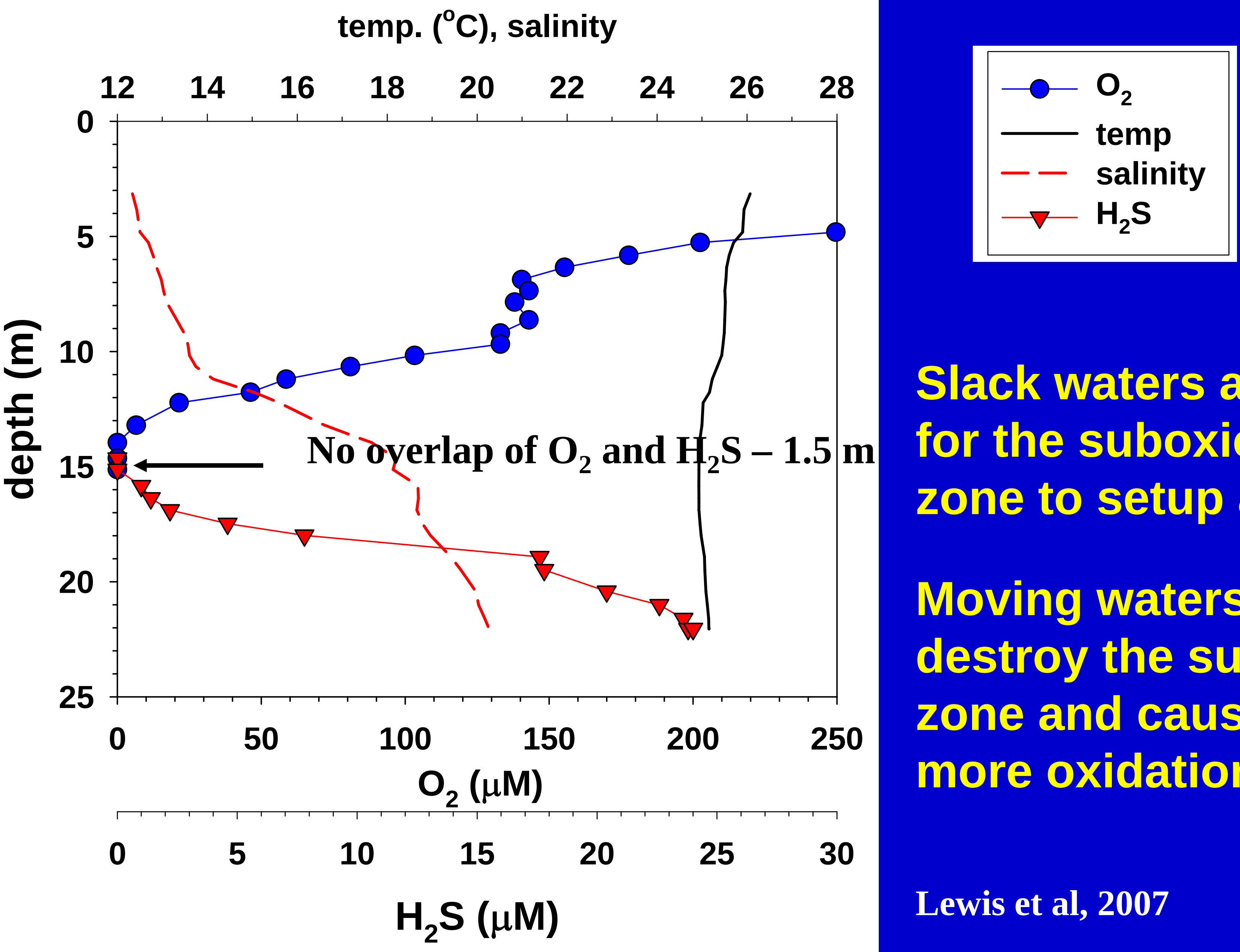
Upcast vs Downcast July 28, 2002 @ 1230 – mid ebb tide



Overlap of O_2 and H_2S

Note 1.5 m offset for H_2S between up and down cast

July 28 2002 @ 1600 low slack water



No overlap of O_2 and H_2S – 1.5 m

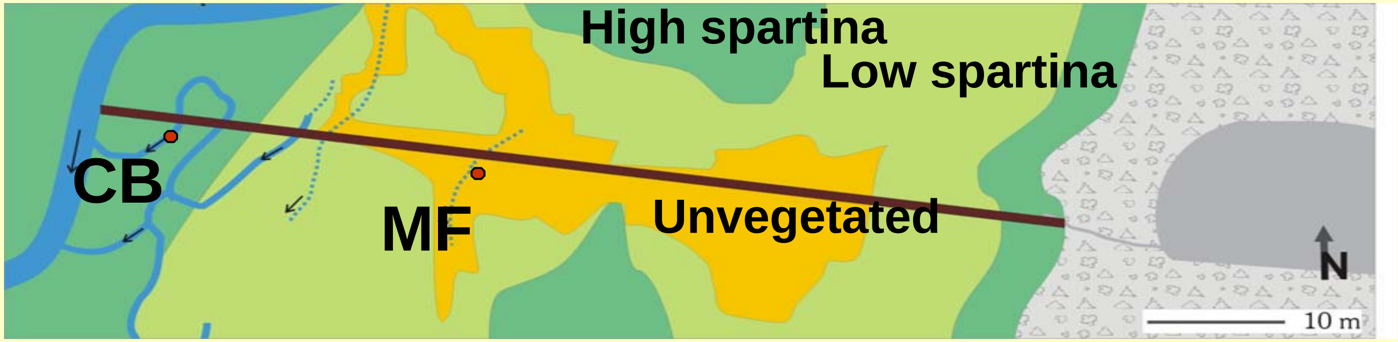
Slack waters allow for the suboxic zone to setup again

Moving waters destroy the suboxic zone and cause more oxidation

Lewis et al, 2007

Skidaway Island Salt Marsh Environmental Research Facility (SERF)

Difference between high and low tide = 2.5 m



Remote Sensing of Salt Marsh Geochemistry

Wind generator **Solar panels**

Monitoring wells

Four Au/Hg voltammetric electrodes positioned at different depths

Microcat (Seabird)

900 MHz VHF radio

ISEA-III potentiostat

VHF Antenna

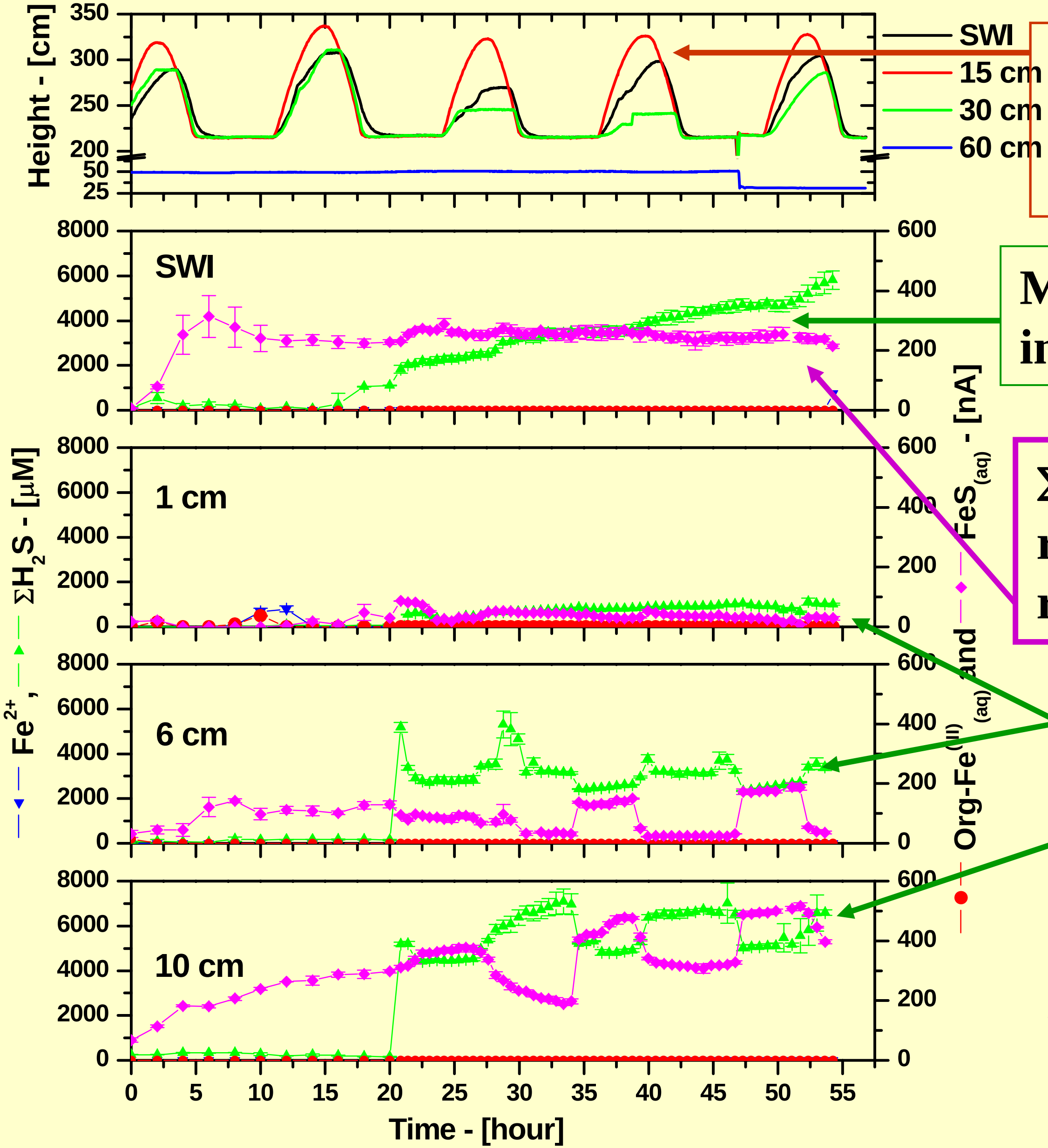
UNIVERSITY OF DELAWARE

AIS
Analytical Instrument Systems, Inc.

Taillefert et al. (2007)

GT

In Situ Measurements in Mud Flat Sediments



6/16/06
at 11h:15m:00s

2.38 Days

6/18/06
at 20h:05m:00s

Wells show preferential H_2O intrusion near 15 cm deep on a rising tide

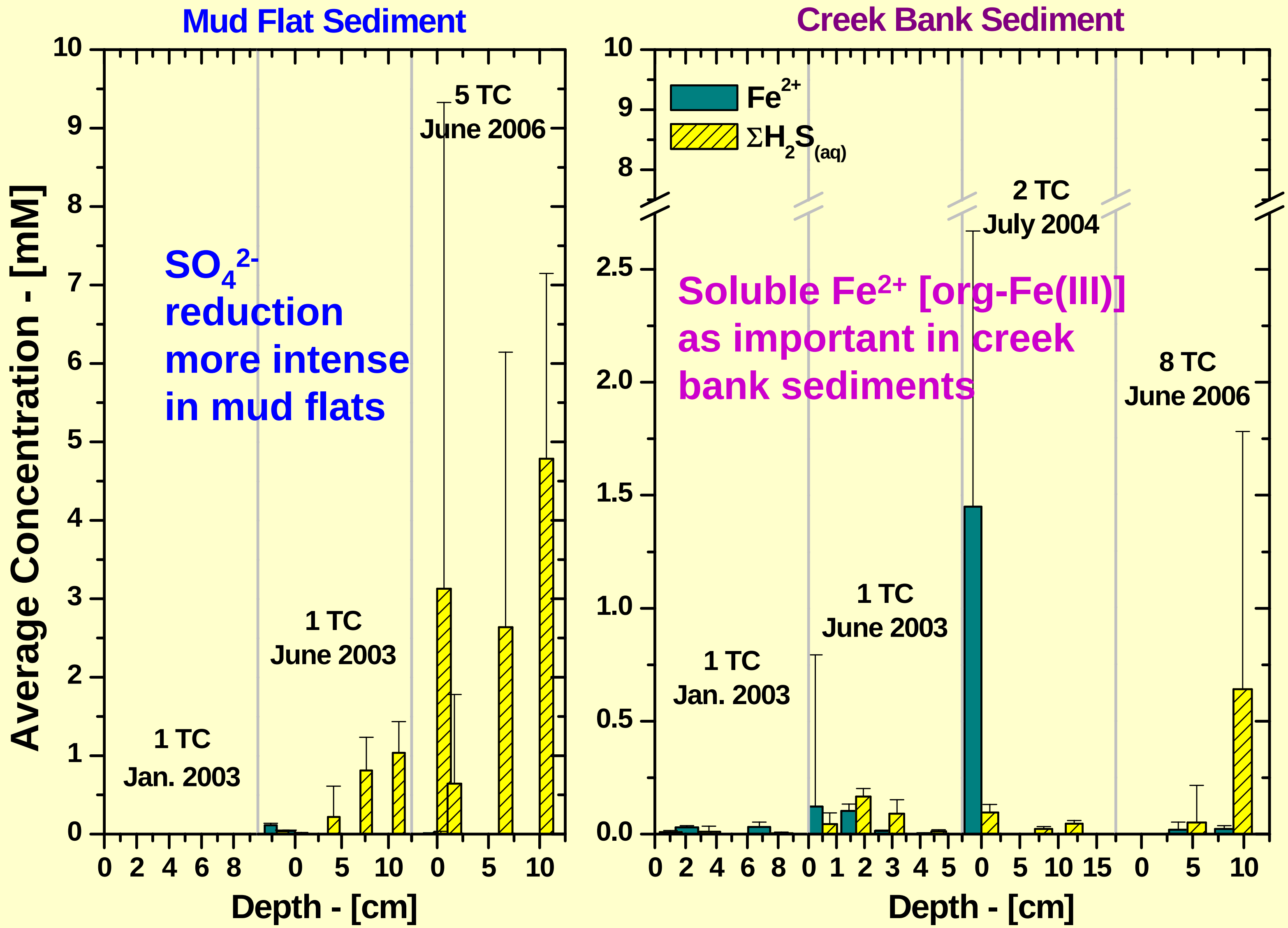
Mud flat sediments show intense SO_4^{2-} reduction to H_2S

ΣH_2S produced by SO_4^{2-} reduction generates FeS_{aq} by reduction of Fe(III) oxides

Variations in Σ H_2S concentrations and FeS_{aq} intensities are related to advection during tides

***In situ* measurements using 4 electrodes placed at fixed depths compared to water levels in nearby wells**

Average Fe^{2+} and ΣH_2S Concentrations Measured *In Situ* as a Function of Depth


Mud Flat Sediment

Creek Bank Sediment

SO_4^{2-} reduction more intense in mud flats

Soluble Fe^{2+} [org-Fe(III)] as important in creek bank sediments

TC = Tidal Cycle

Taillefert et al. (2007)

Conclusions

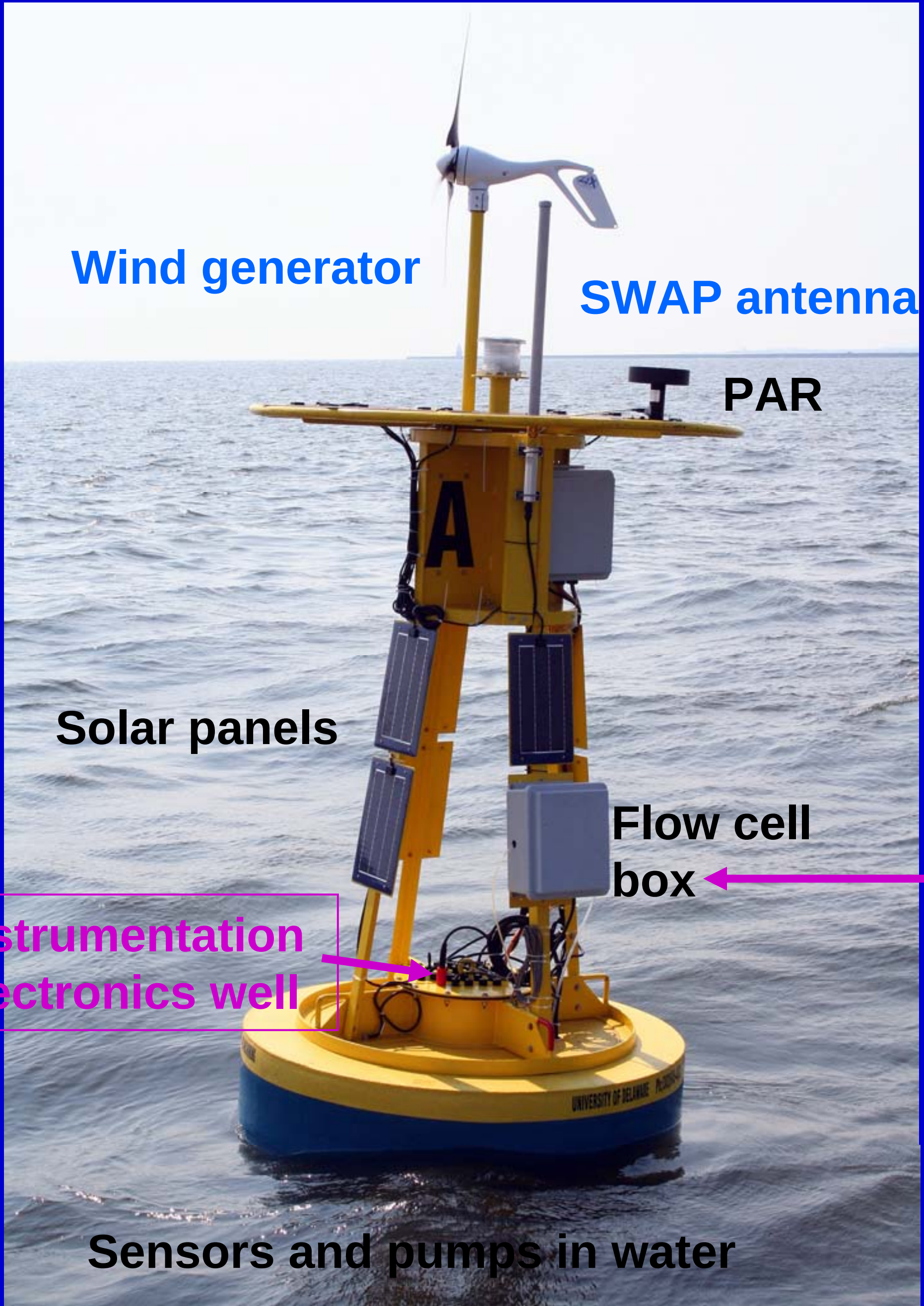
Ex situ core measurements cannot capture the dynamics of biogeochemical processes in sediments affected by tidal forcing

Overall, mud flat sediments are dominated by sulfate reduction, while creek bank sediments are dominated by metal reduction

- Hydrostatic pressure is higher in creek bank than in mud flat sediments
- Creek bank sediments are more oxidized (brownish sediments)

Voltammetry can be used *in situ* to determine the effect of tidal forcing on biogeochemical processes

Moorings with physical, chemical and biological sensors



Wind generator

SWAP antenna

PAR

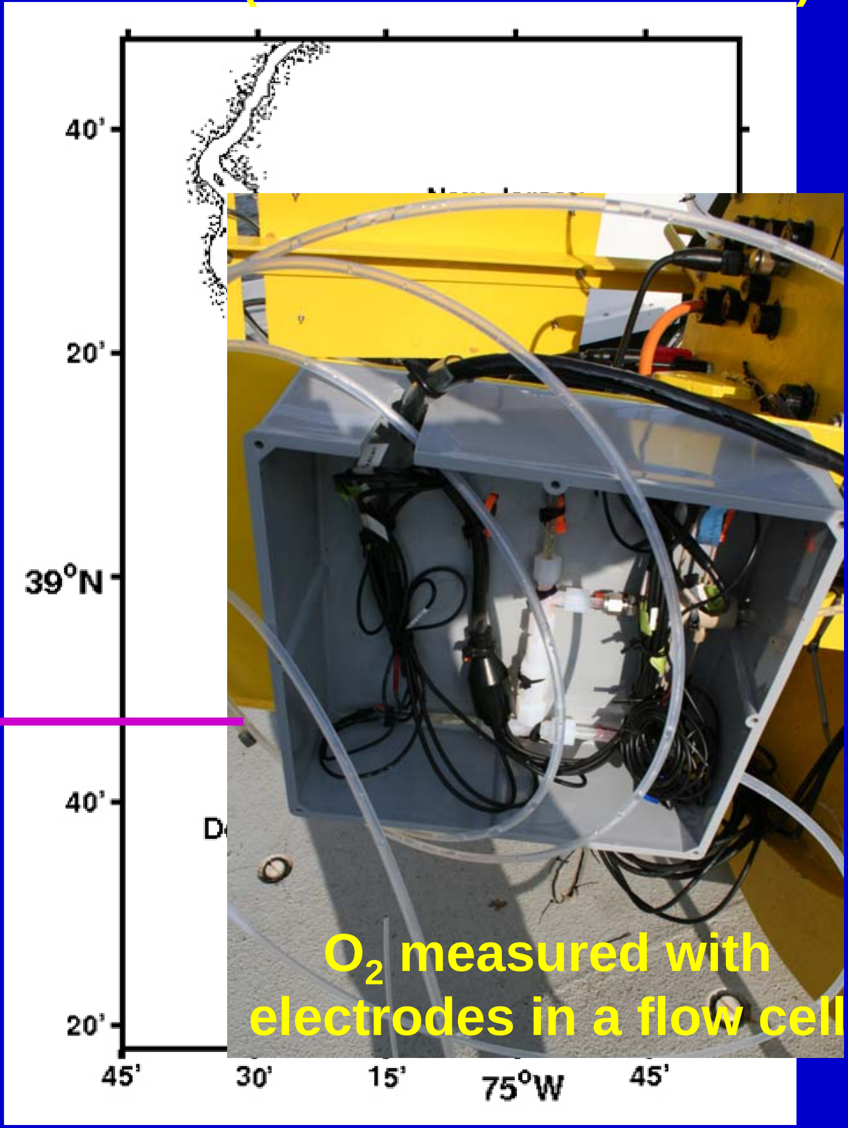
Solar panels

Flow cell box

Instrumentation electronics well

Sensors and pumps in water

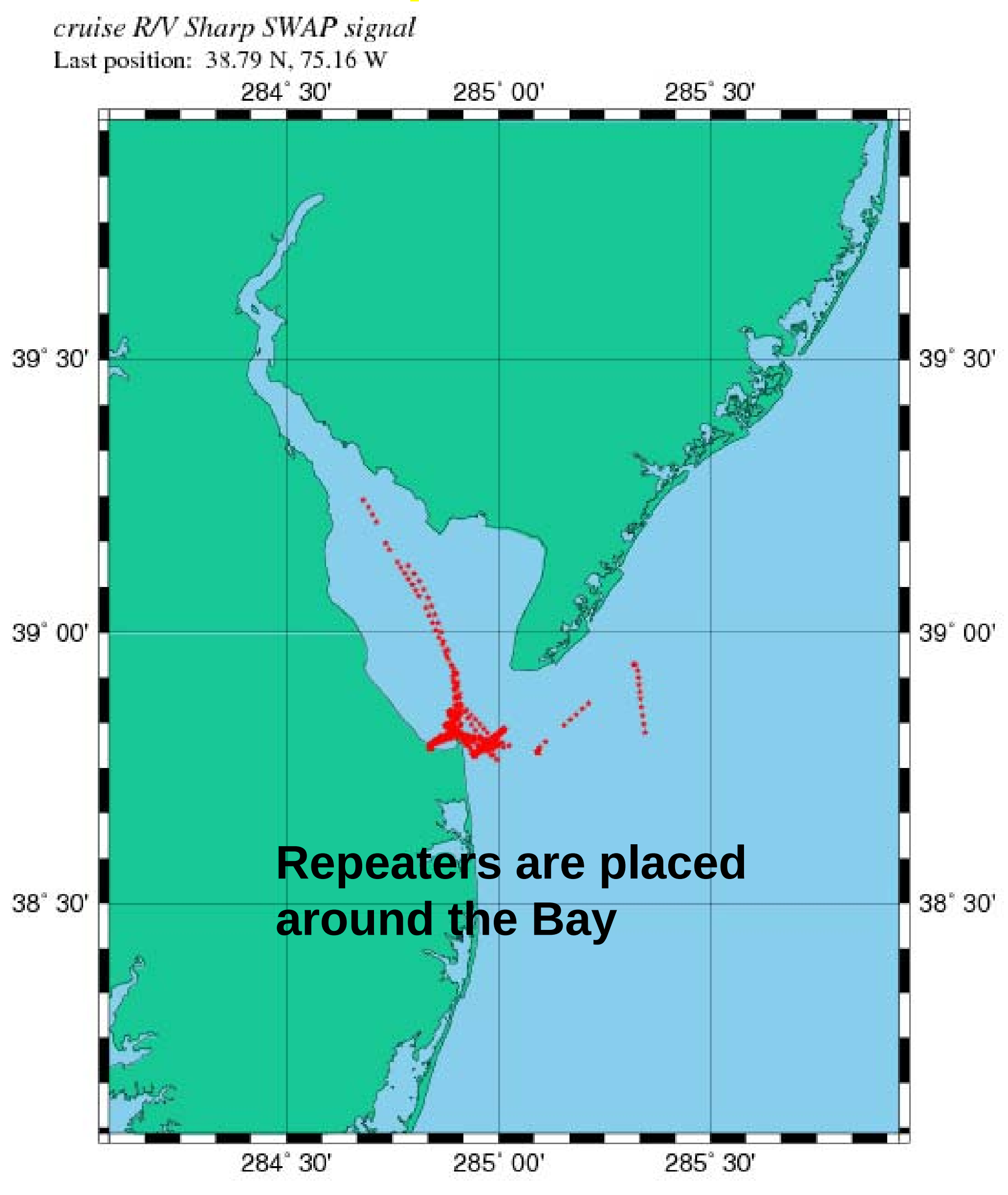
Measures salinity, temperature, O_2, fluorescence, transmissometry, light irradiance – (data to shore via SWAP)



O_2 measured with electrodes in a flow cell

Data Transmission via

SWAP: Shipboard Wireless Access Protocol



Repeaters are placed around the Bay

Ship to ship

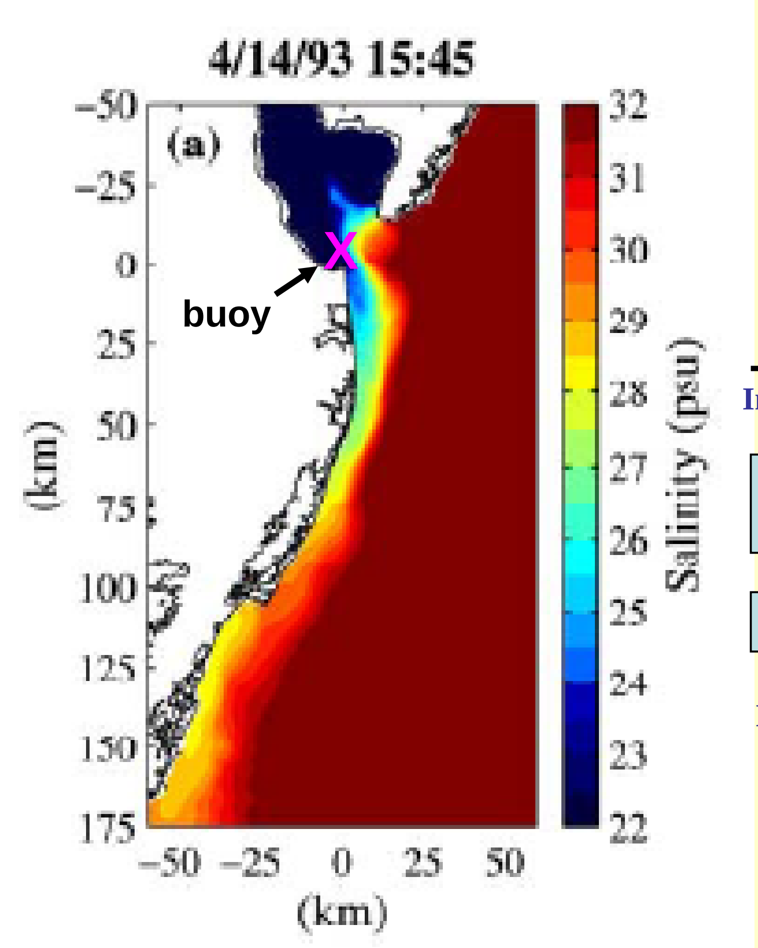
Ship to shore

Shore to shore

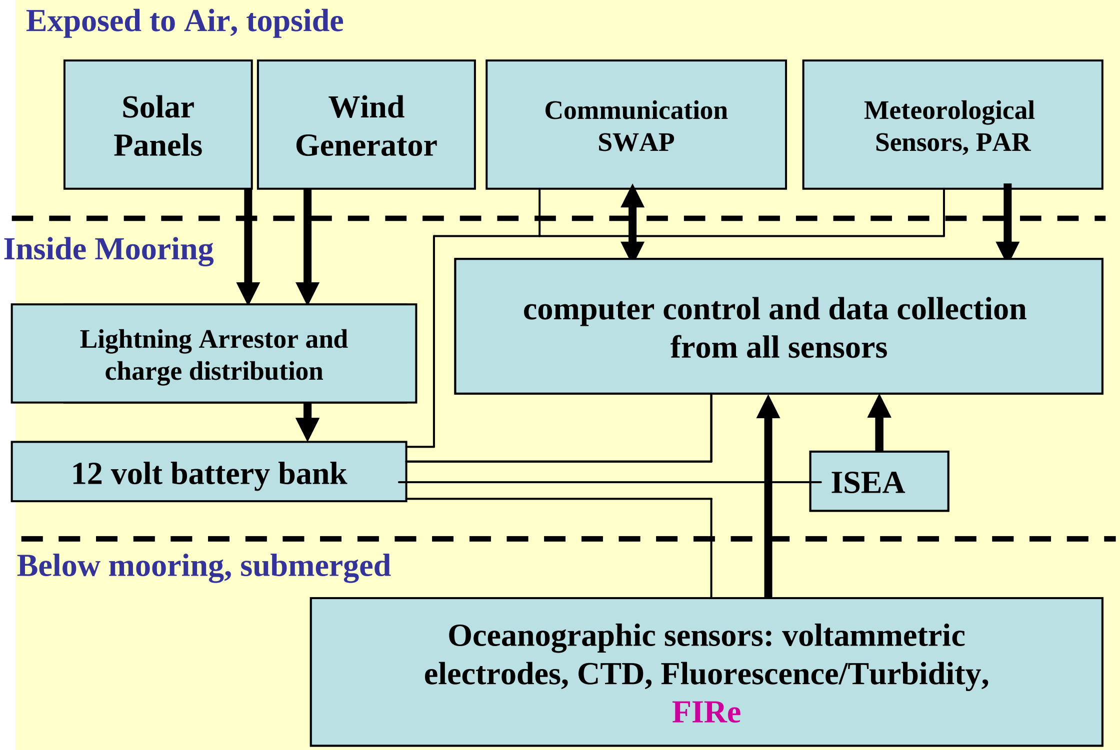
with 2.4 gHz radio

About 15 km

Delaware Bay Mooring Location



Mooring Block Diagram



Exposed to Air, topside

Solar Panels

Wind Generator

Communication SWAP

Meteorological Sensors, PAR

Inside Mooring

Lightning Arrestor and charge distribution

computer control and data collection from all sensors

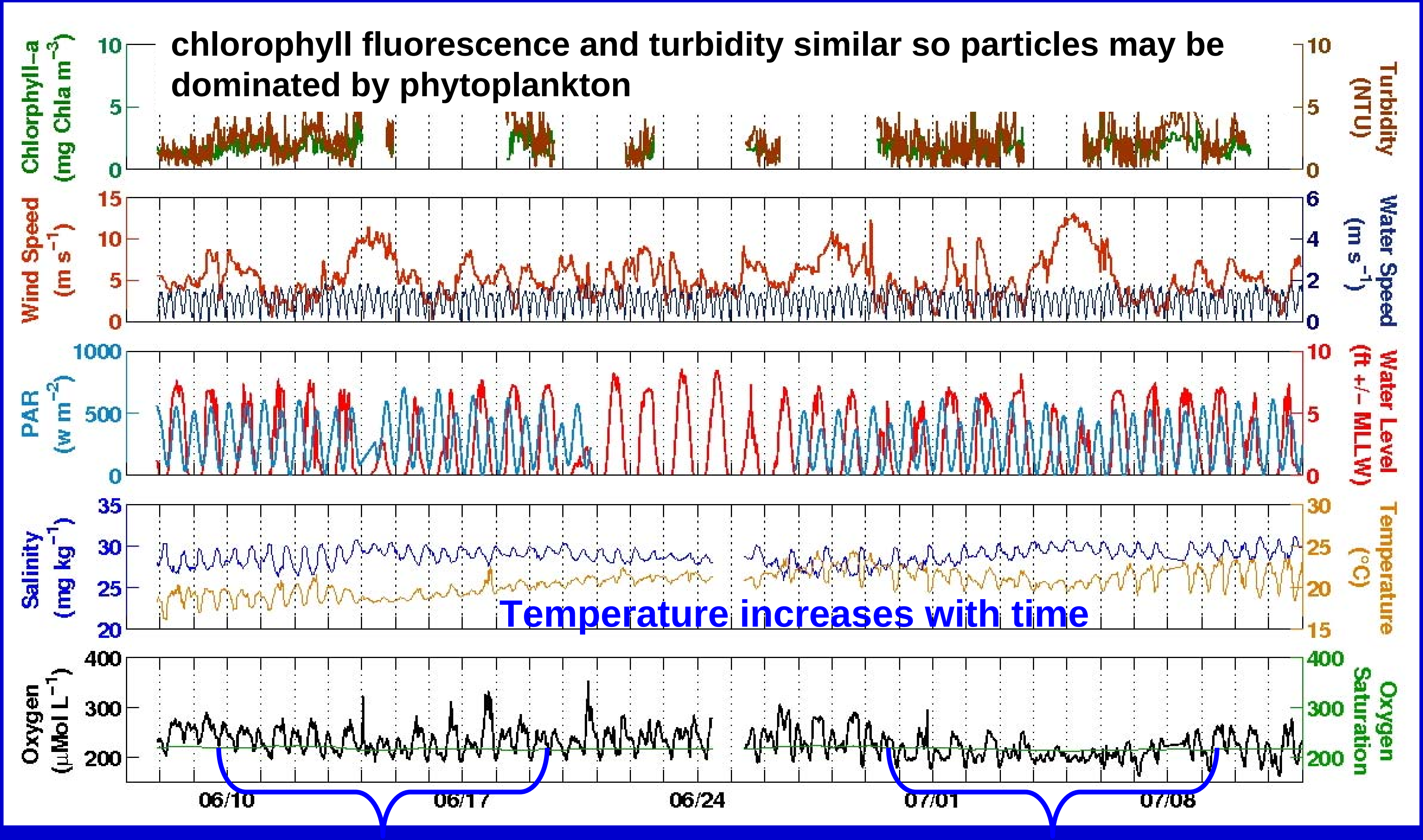
12 volt battery bank

ISEA

Below mooring, submerged

Oceanographic sensors: voltammetric electrodes, CTD, Fluorescence/Turbidity, FIRe

Time course data for 1 month; 0.5 hr data collection



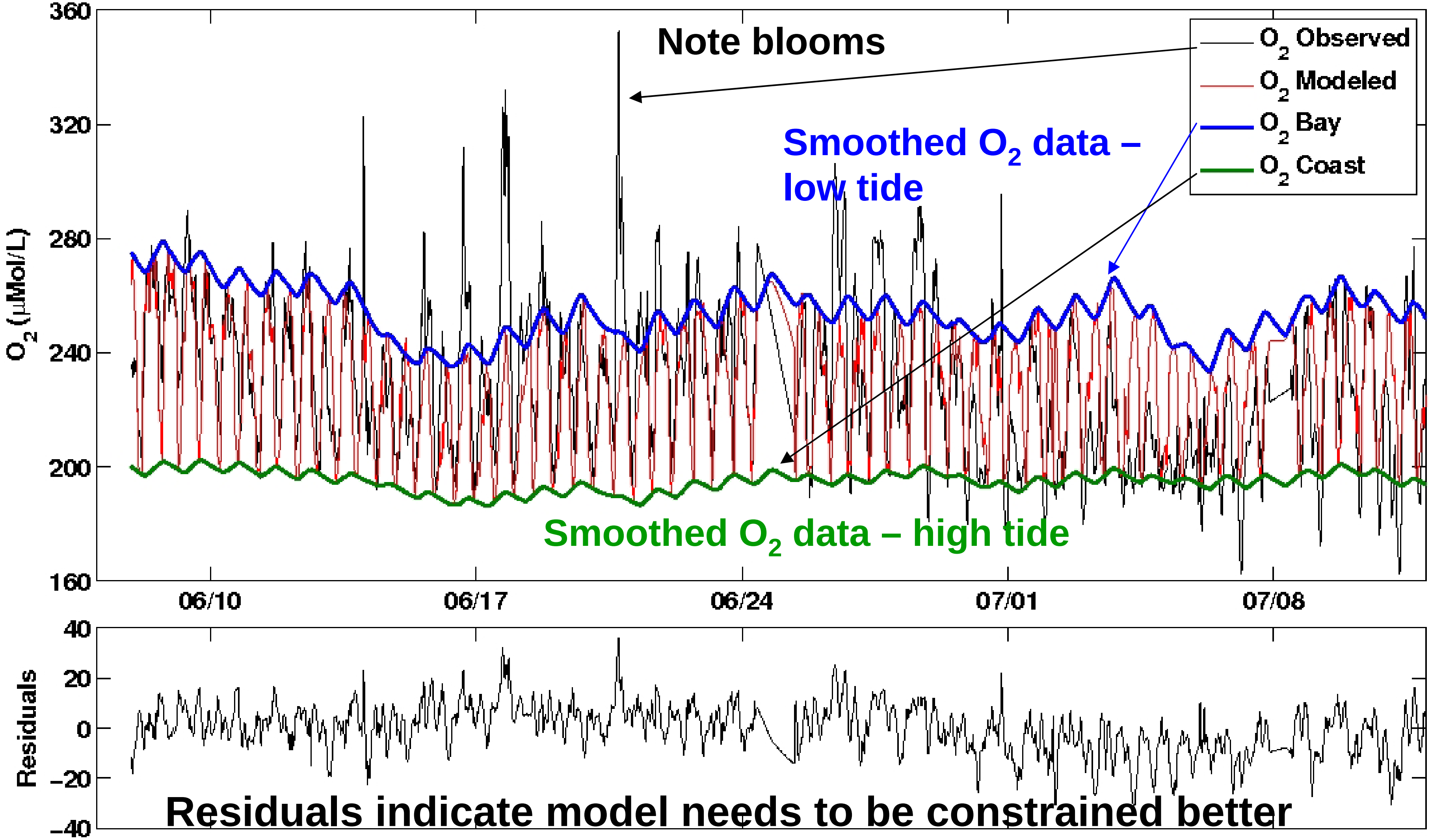
chlorophyll fluorescence and turbidity similar so particles may be dominated by phytoplankton

Temperature increases with time

Higher O_2 / higher productivity

Lower O_2 so lower productivity / higher respiration or photoinhibition?

Productivity and Respiration model from Chapra (1997)



Note blooms

Smoothed O_2 data – low tide

Smoothed O_2 data – high tide

Residuals indicate model needs to be constrained better

Productivity and Respiration model from Chapra (1997)

P (productivity) = $r_{oa}G_{max}1.066^{T-20}\,\phi_{l}a$

R (respiration) = $r_{oa}\,k_{ra}1.08^{T-20}a$

Physical processes accounted for with wind speed

r_{oa} = O_2 generated from unit mass of plant biomass produced (mg-O_2 / mg-Chl*a*)

G_{max} = maximum plant growth rate for optimal light and excess nutrient conditions

T = water temperature (° C)

a = concentration of plant biomass (mg-Chl*a* m^{-3})

ϕ_{l} = attenuation of growth due to light

k_{ra} = plant respiration rate

The model is not fully constrained but can be

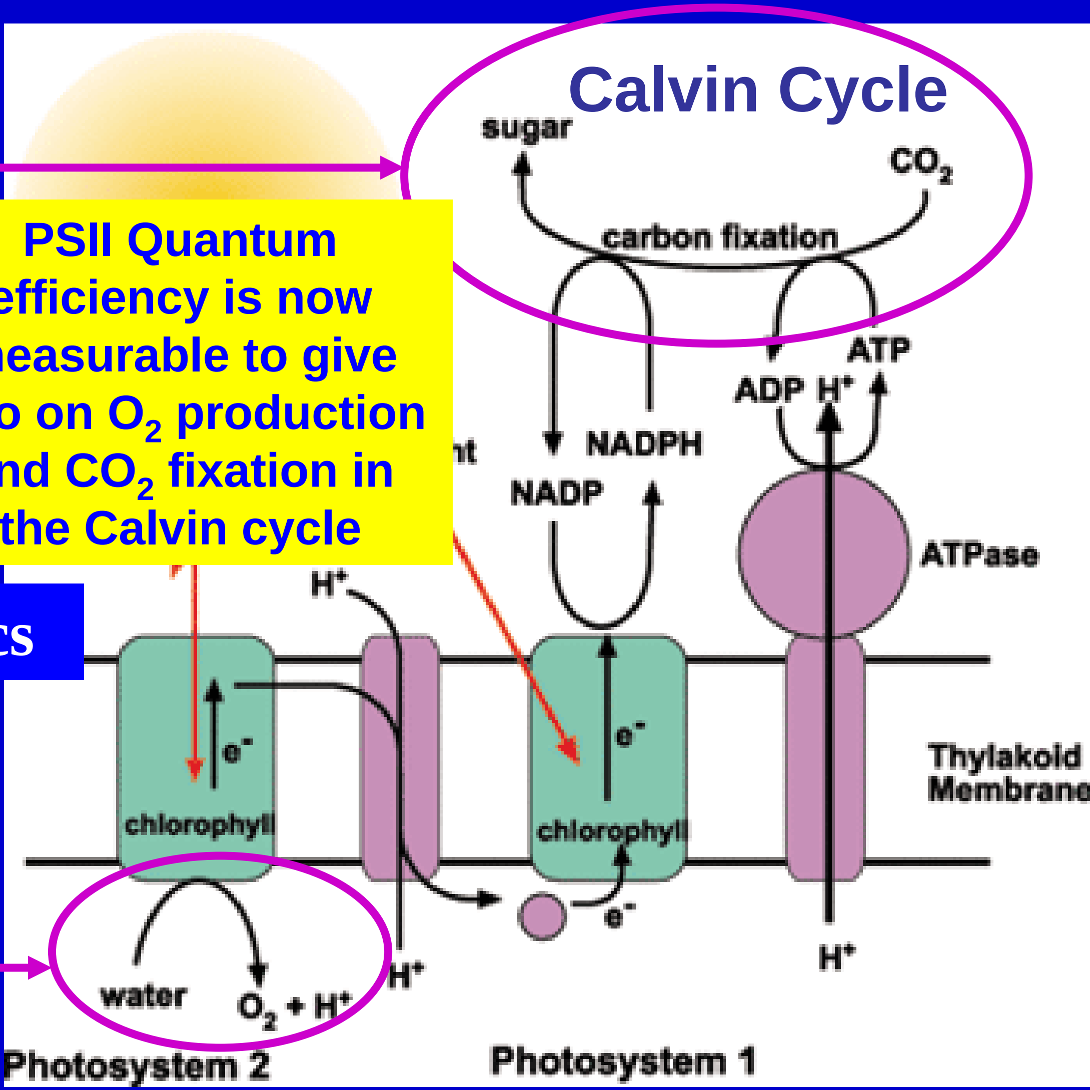
r_{oa} and G_{max} are unknown conversion factors from chl a to O_2 and light to growth

These can be measured or estimated with an *in situ* device known as the Fluorescence Induction Relaxation system (FIRe) - (Gorbunov and Falkowski, 2004)

FIRe measures the variable fluorescence of the photosystem center II, and thus is an indicator of how efficient a photosynthetic organism can utilize light energy to fix inorganic carbon and produce O_2.

Oxygenic photosynthesis

Photosystem 1 (PSI) produces organic carbon from CO_2, electrons and protons



PSII Quantum efficiency is now measurable to give info on O_2 production and CO_2 fixation in the Calvin cycle

FIRe measures PSII dynamics

Photosystem 2 (PSII) produces O_2 from water and electrons for photosystem 1

IMPACT OF ELECTRODES ON THE FIELD

Multi-analyte Environmental chemistry tool

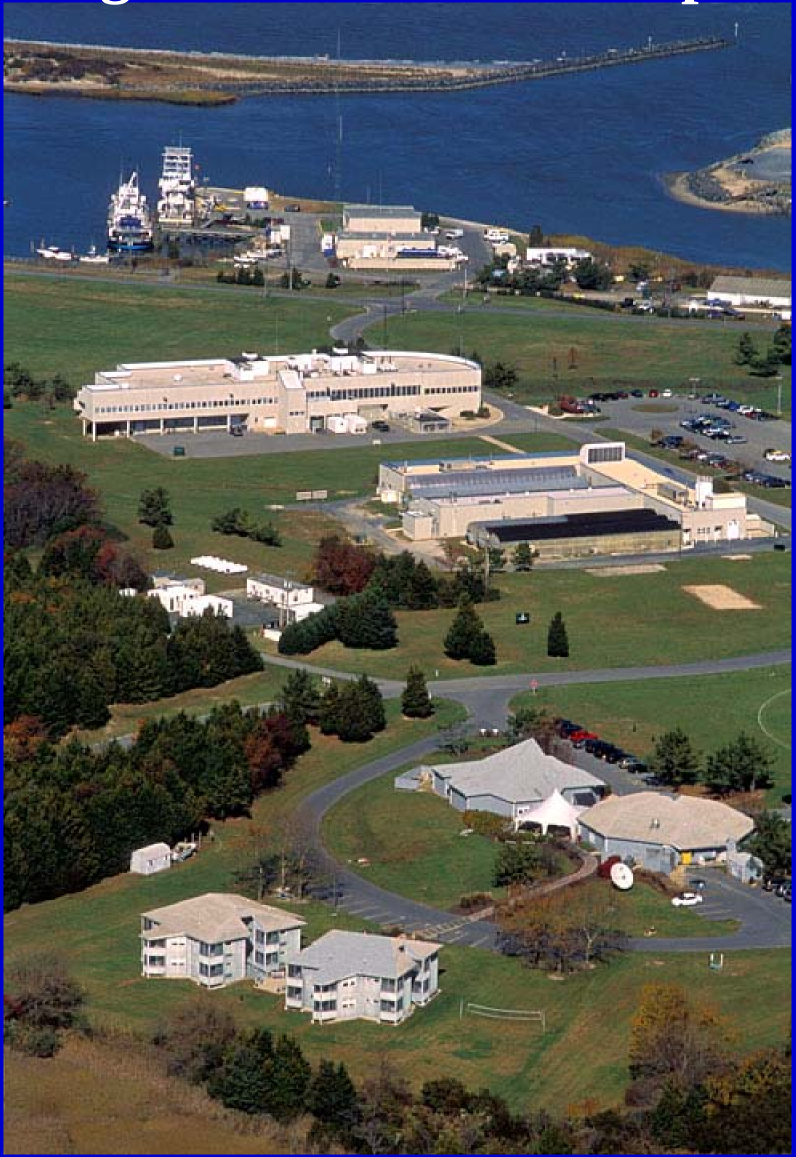
Sediment Diagenesis better described with finer resolution

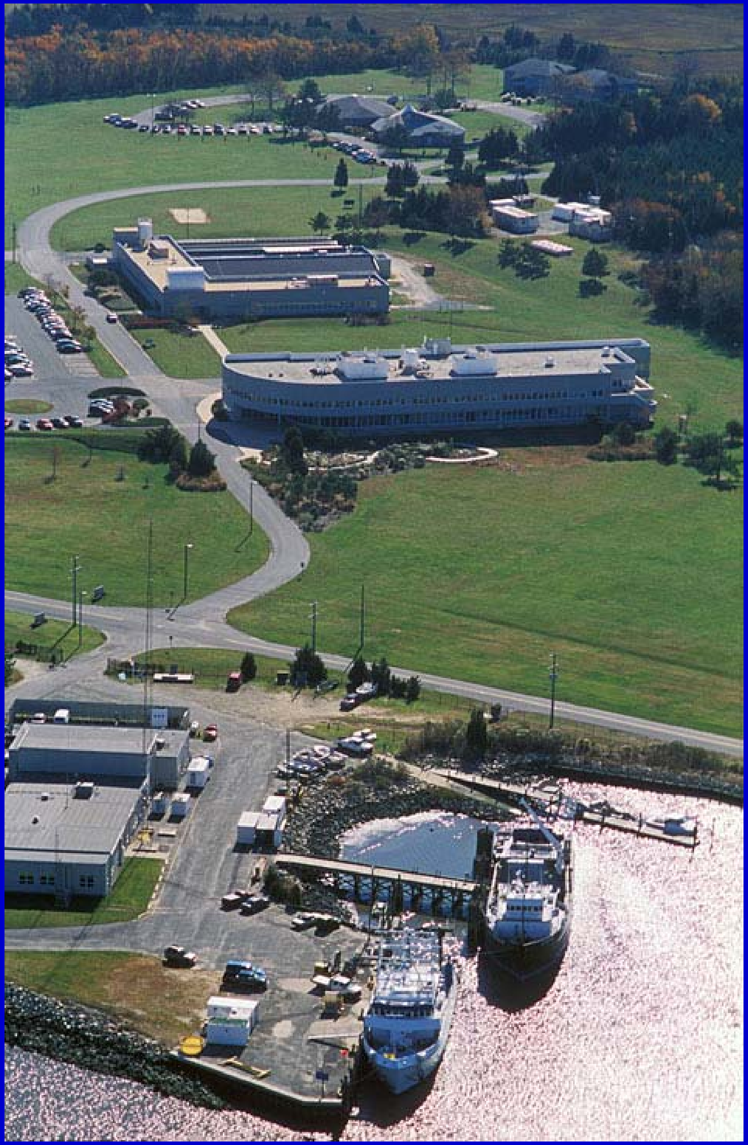
Describe ecosystem health - why do fish kills and HABs occur?
Benthic – pelagic coupling;

Must combine several tools/data to understand physics, chemistry and their role on biology: need newer biological sensors (FIRe) to Assess planktonic health at molecular level

Increased collaboration with government officials and industry with recommendations for improvement

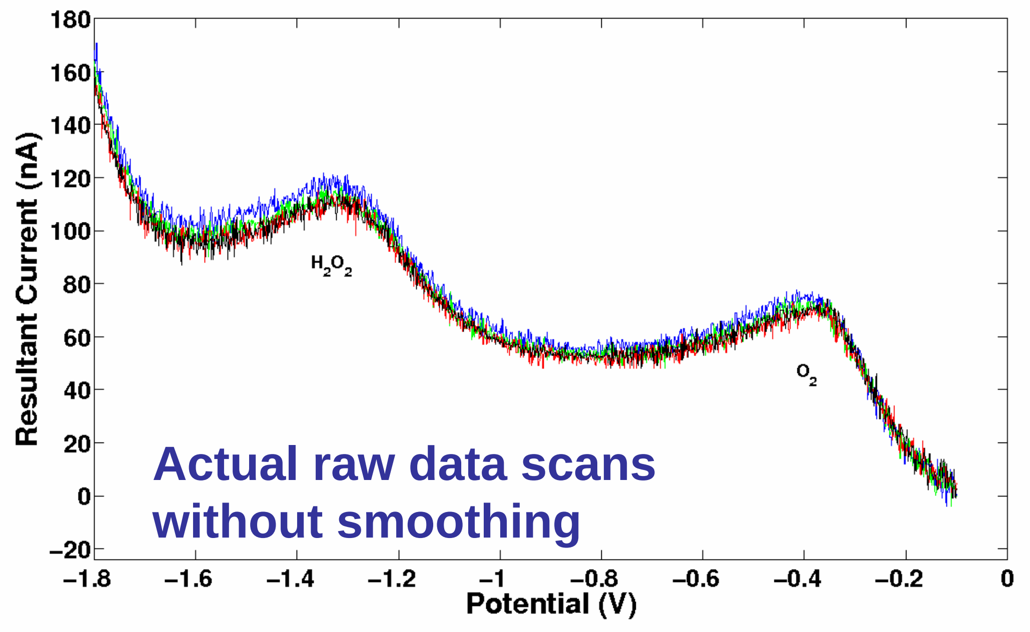
Xiè Xie Ni to Prof. Minahn Dai, Ms. Vera Shi and the rest of the organizers for their hospitality and a stimulating conference



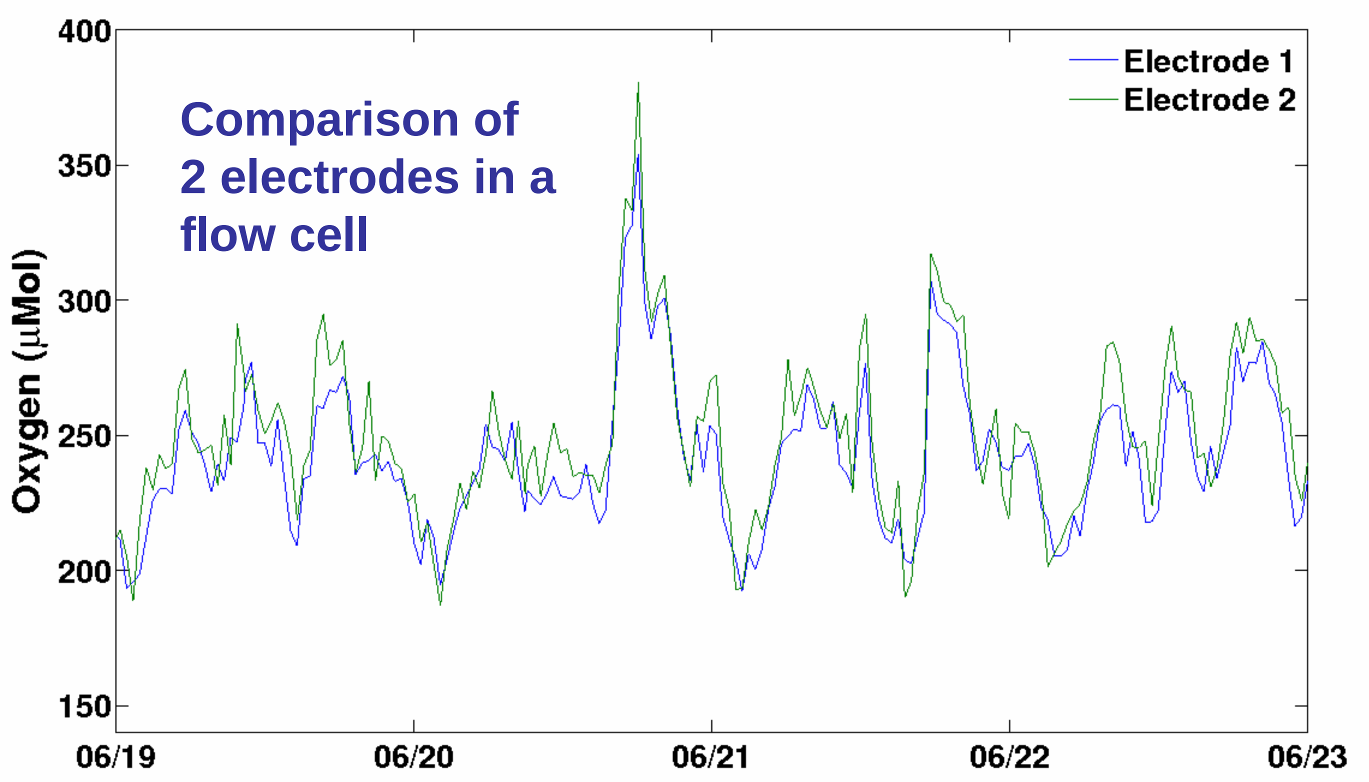


University of Delaware Marine Campus in Lewes

Voltammetric O_2 data

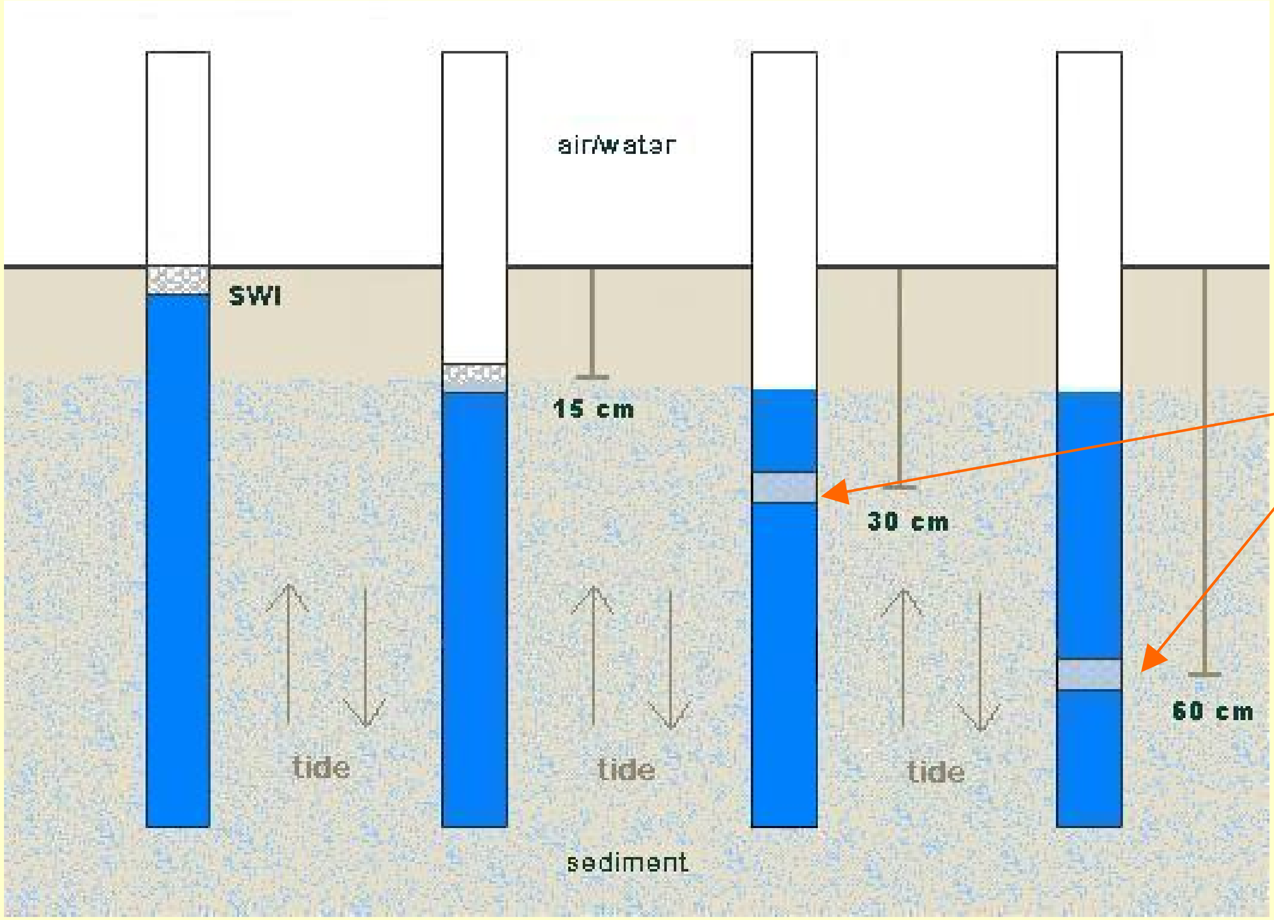


Actual raw data scans without smoothing



Comparison of 2 electrodes in a flow cell

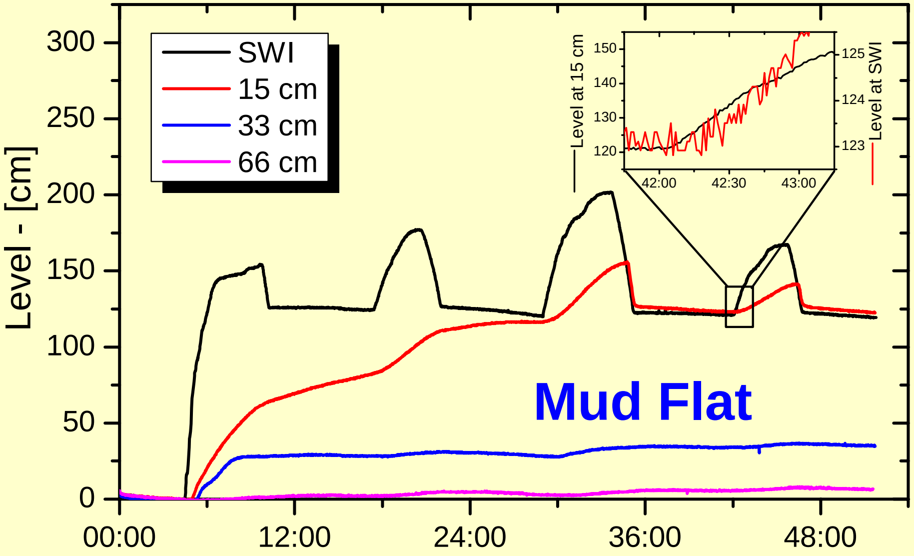
Monitoring Wells to Measure Water Levels in Sediments

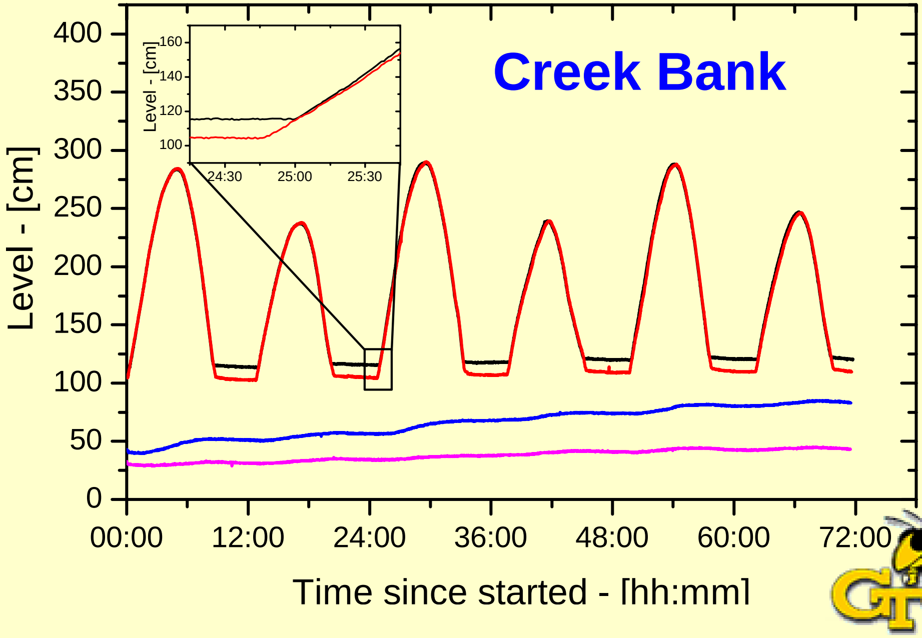


5 cm screens set at 0, 15, 30, and 60 cm deep in the sediment.

Taillefert et al. (2007)

Tidal Advection in Sediments





- **Tidal forcing affects porewater advection over 30 cm only**
- **Compared to mud flat sediments, creek bank sediments display:**
  - **higher hydrostatic pressure**
  - **faster advection rates**
- **Water infiltrates mud flat sediments from the surface, while deep wells fill first in creek bank sediments**

Taillefert et al. (2007) Geochem. Trans.

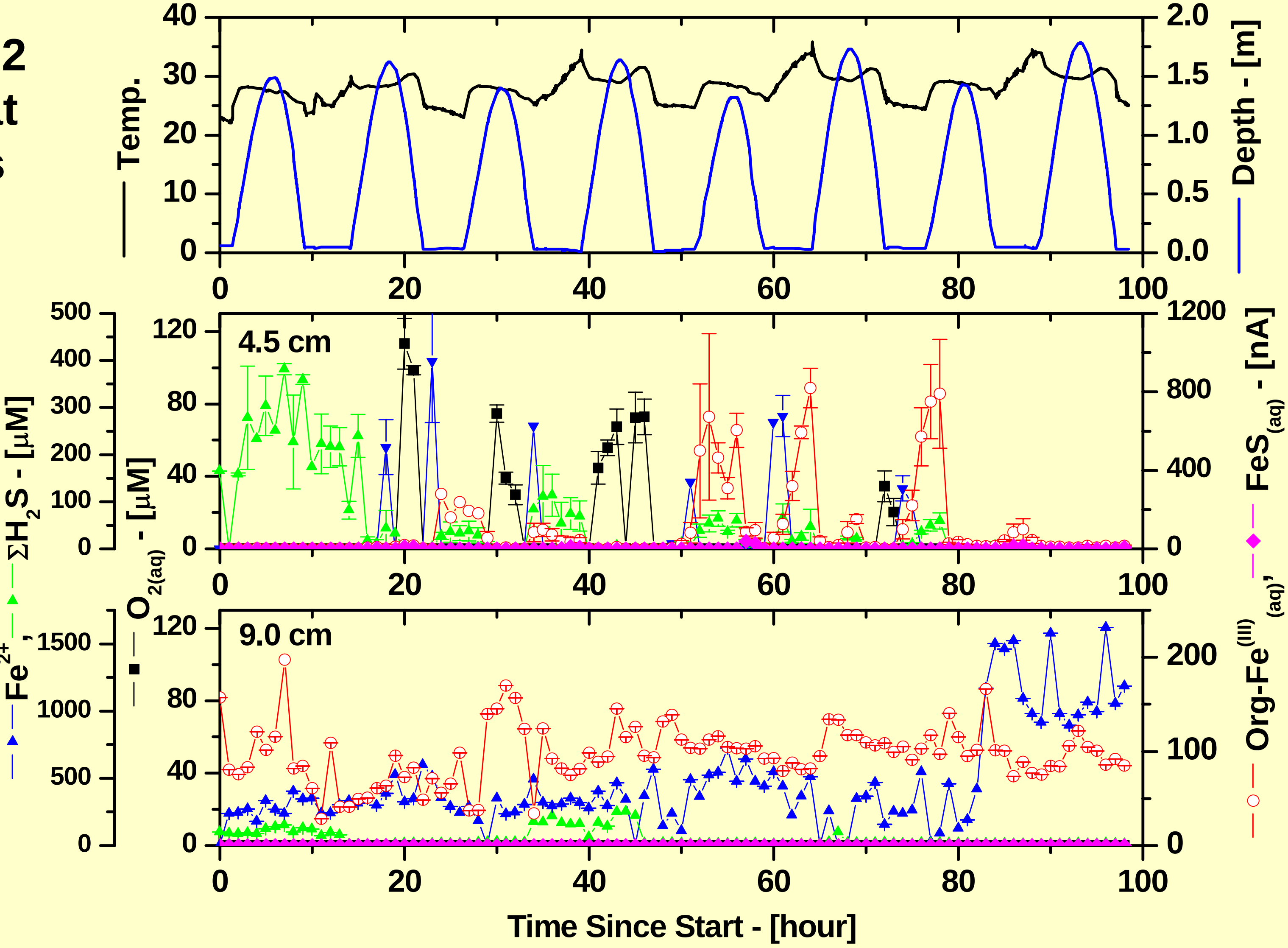
In Situ Measurements in Creek Bank Sediments

In situ data for 2 electrodes at fixed depths in the creek

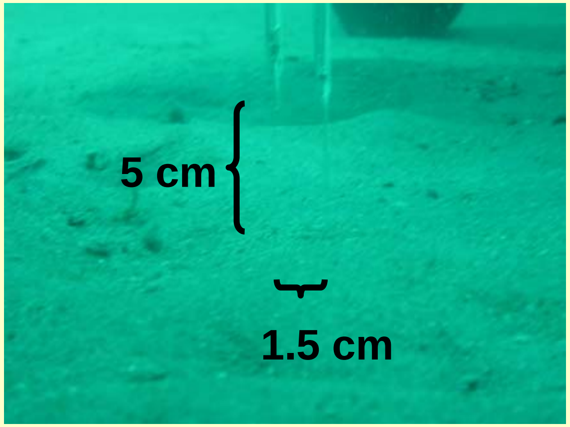
T fluctuates slightly

Reduced species generally produced at low tide

At rising tide, reduced species diffuse to SWI



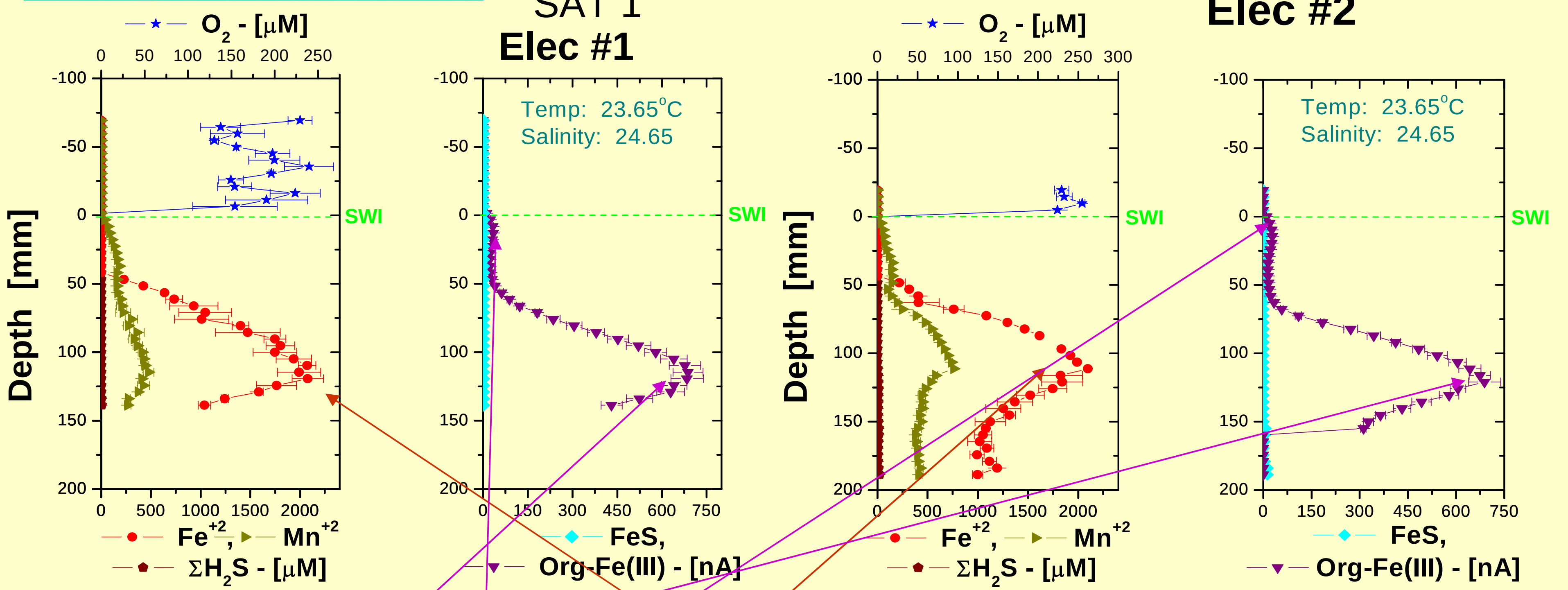
- At ebb tide, species diffuse away or are oxidized by $O_{2(aq)}$ that can penetrate from the overlying waters.



In Situ Profiles with Two Electrodes in Estuarine Sediments

Fe^{2+} oxidation appears important near the sediment-water interface

SAT 1



Good reproducibility between electrodes; O_2 penetrates about 2 mm

Organic-Fe(III) complexes and Fe^{2+} dominate until the onset of ΣH_2S later

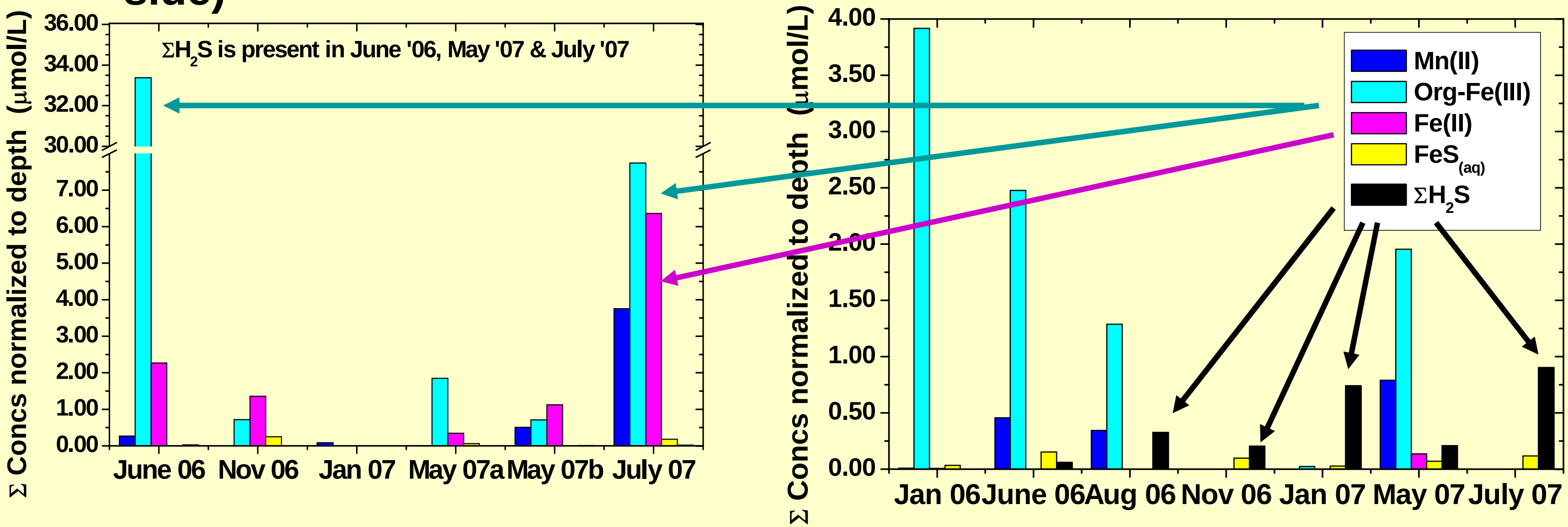
Soluble organic-Fe(III) complexes seem to flux out of the sediment

Nonreductive dissolution of Fe(III) solids forms soluble Fe(III) prior to Fe^{2+}

Seasonal Variations in Biogeochemical Processes at SAT2 and SAT4

SAT 2 (freshwater side)

SAT 4 (marine side)



Fe(III) production and reduction to Fe^{2+} are more prevalent in SAT1 and SAT 2 sediments

SO_4^{2-} reduction becomes more prevalent in SAT 4, SAT5, and SAT 6 sediments during late summer and fall only: based on porewater data