Underwater Mass Spectrometry: Applications of NEREUS in Lake Geochemistry

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BIOGEOCHEMICAL CYCLES:WHY THEY ARE IMPORTANT

- Direct Life Support (C, N, P, micronutrients)
- Toxic Chemicals, both Natural and Anthropogenic (Hg, As, PCBs, PAHs, pesticides, etc.)
- Planetary Regulation (C, N, P, Fe, O)

1) Many key chemicals are gases, and their cycles are coupled

Mass spectrometry ideally suited to multi-species analysis of gases

TABLE 2-6 Common Environmental Redox Half-Reactions[a]

Half-reaction	log K, ($\Delta G°$, kcal/mol)
$\frac{1}{4}O_2(g) + H^+ + e^- \rightarrow \frac{1}{2}H_2O$	20.75 (−28.22)
$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- \rightarrow \frac{1}{10}N_2(g) + \frac{3}{5}H_2O$	21.05 (−28.63)
$\frac{1}{2}MnO_2(s) + 2H^+ + e^- \rightarrow \frac{1}{2}Mn^{2+} + H_2O$	21.00 (−28.56)
$Fe(OH)_3(s) + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$	16.5 (−22.44)
$\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^+ + e^- \rightarrow \frac{1}{8}H_2S(g) + \frac{1}{2}H_2O$	5.25 (−7.14)
$\frac{1}{8}SO_4^{2-} + \frac{9}{8}H^+ + e^- \rightarrow \frac{1}{8}HS^- + \frac{1}{2}H_2O$	4.25 (−5.78)
$\frac{1}{8}CO_2(g) + H^+ + e^- \rightarrow \frac{1}{8}CH_4(g) + \frac{1}{4}H_2O$	2.87 (−3.90)
$\frac{1}{4}CH_2O + \frac{1}{4}H_2O \rightarrow e^- + H^+ + \frac{1}{4}CO_2(g)$	1.2 (−1.63)

[a]Stumm and Morgan (1981).

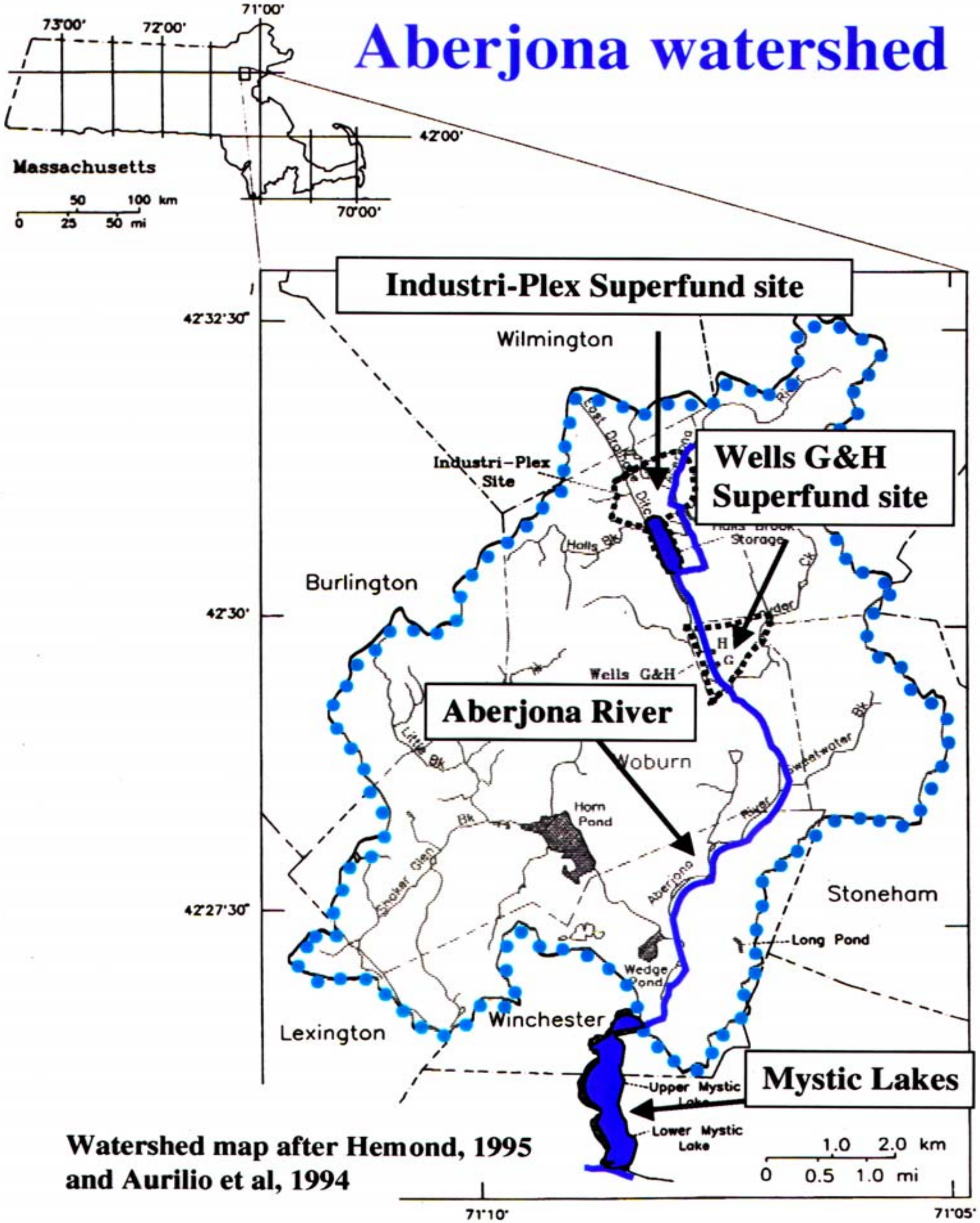
2) High temporal and spatial variability requires high resolution measurements

Need for an autonomous, mobile platform for biogeochemical sensor systems

Investigation of coupled biogeochemical cycles by traditional methods of sampling:

An example in the Mystic Lakes, Aberjona Watershed, eastern MA

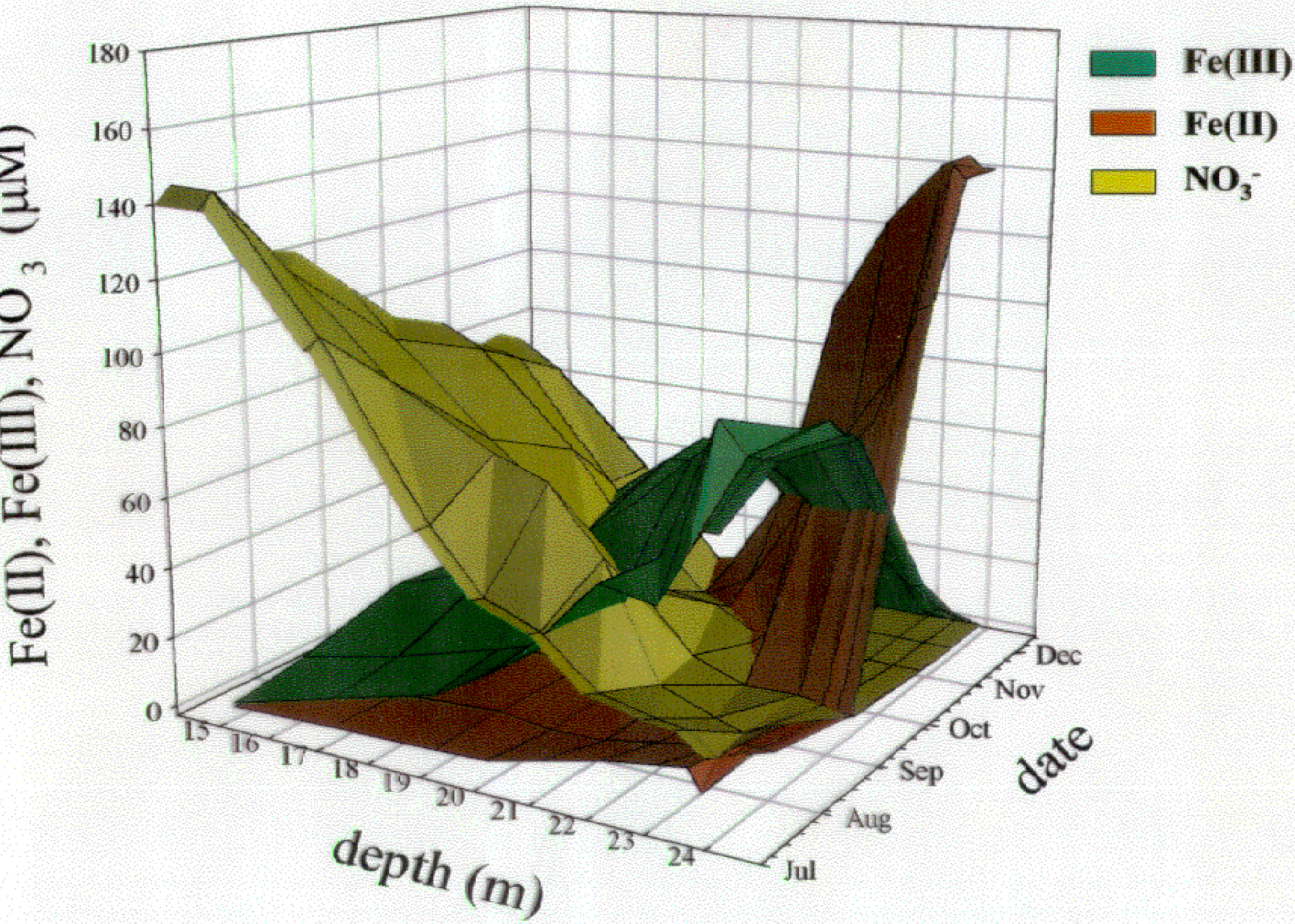
Aberjona watershed



Watershed map after Hemond, 1995
and Aurilio et al, 1994

An Example:
Testing the hypothesis that nitrate controls the speciation of iron and arsenic in a stratified lake with anoxic hypolimnion

- **Test 1-Spatial and temporal correlations**
- *Test 2-Microcosm studies*
- *Test 3-Mass and electron balance studies*
- *Test 4-Thermodynamic feasibility*



Fe(III)
Fe(II)
NO_3^-
Fe(II), Fe(III), NO_3^- (μM)
180
160
140
120
100
80
60
40
20
0
15
16
17
18
19
20
21
22
23
24
depth (m)
Jul
Aug
Sep
Oct
Nov
Dec
date

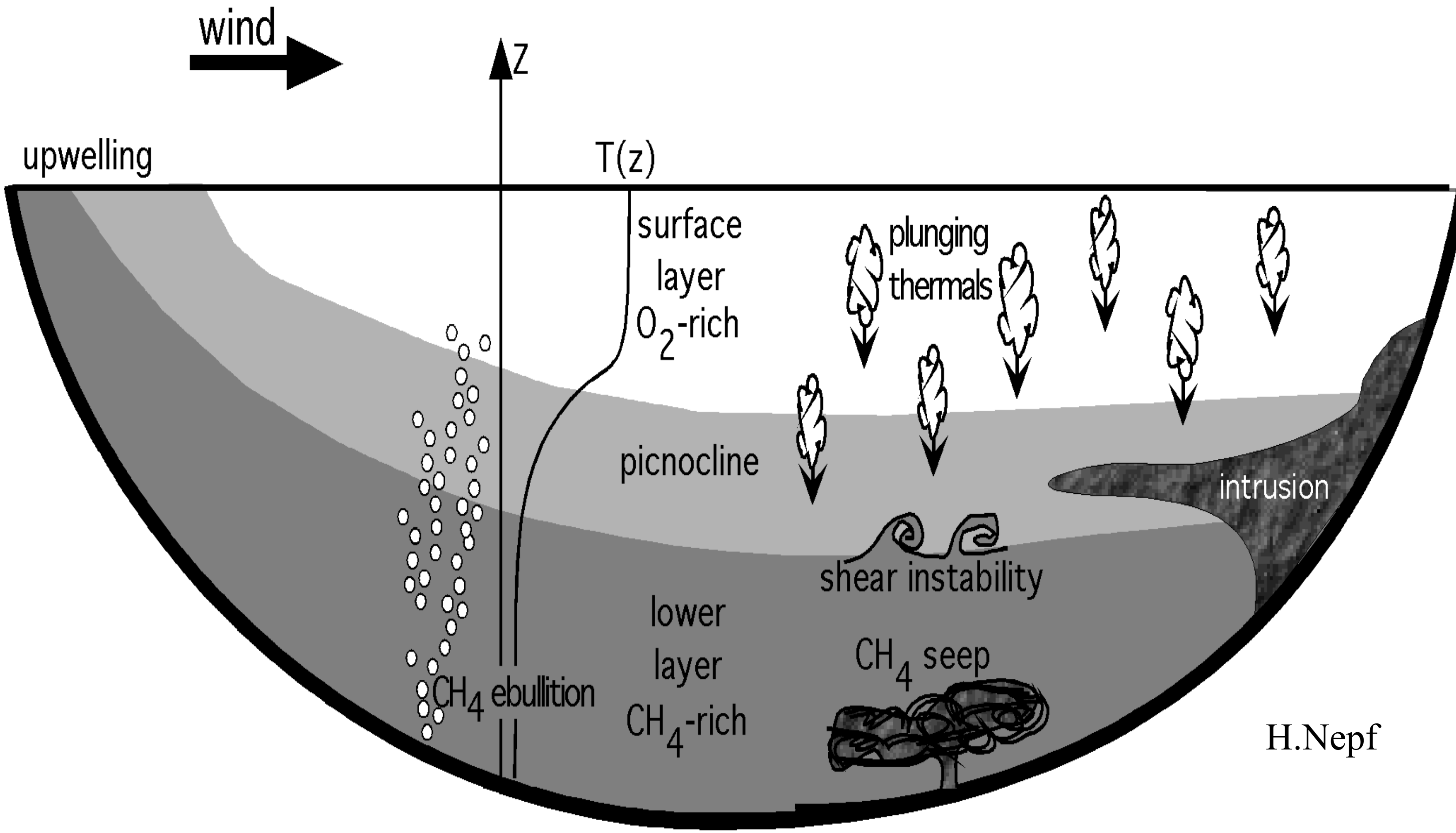
Dave Senn

The biogeochemical cycling of Methane

- Climate
- Carbon cycle
- Stratospheric chemistry
- Ecosystem energetics
- Transport via ebullition
- Energy source for humans

Broad Hypotheses:

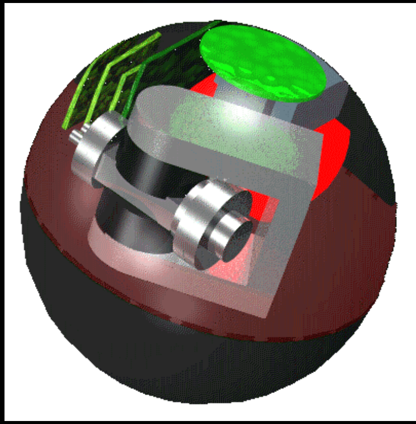
- Methane transfer from ecosystems to atmosphere is governed by the competition of physical transport and bacterial metabolism
- Relative importance of each process can be determined on the basis of **time series of synoptic data**



Physical and chemical processes hypothesised to control methane geochemistry in a stratified lake

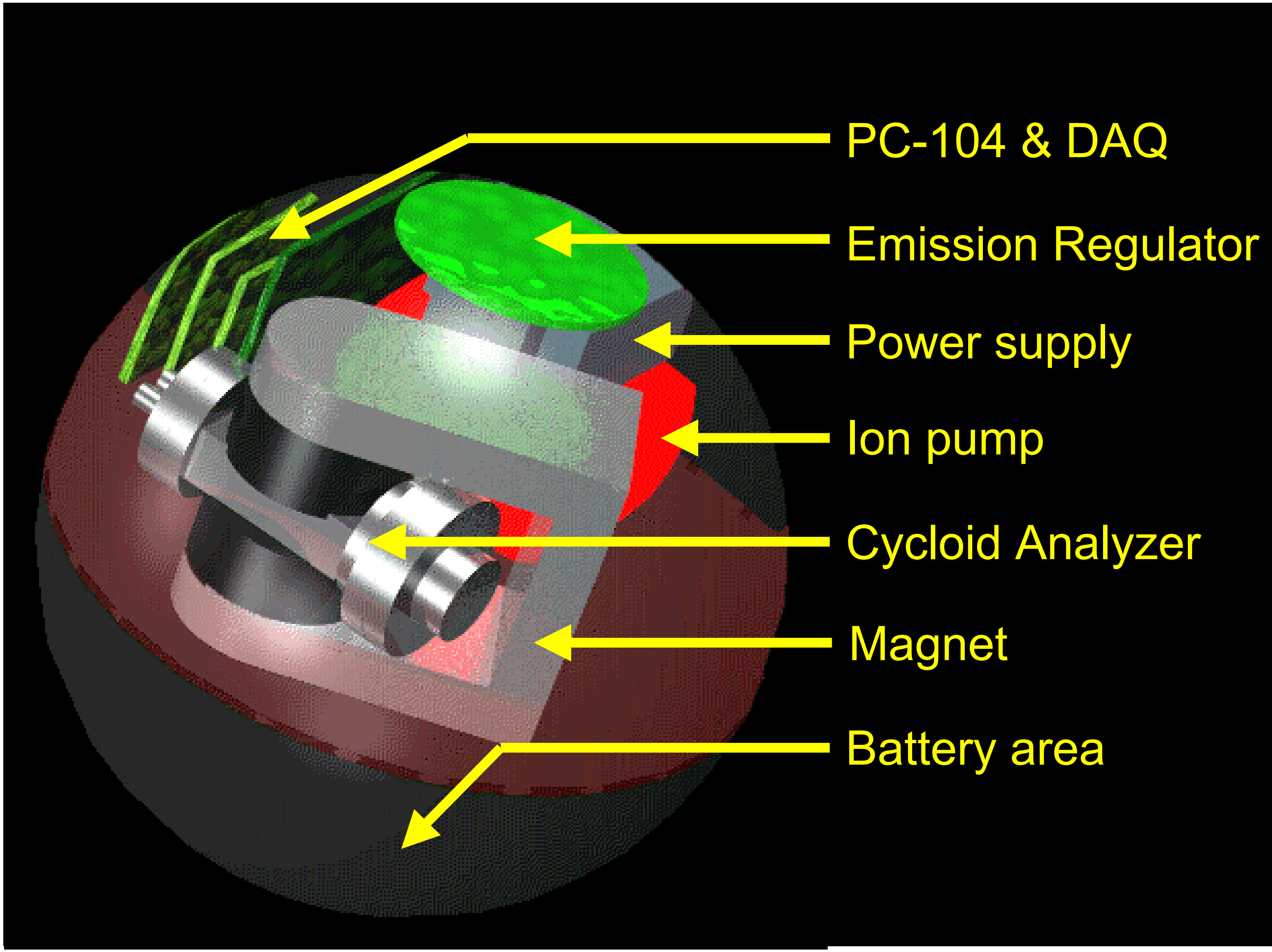
NEREUS CONCEPT

A compact, low power, cycloidal type membrane inlet mass spectrometer for deployment onboard an Odyssey class Autonomous Underwater Vehicle (AUV)

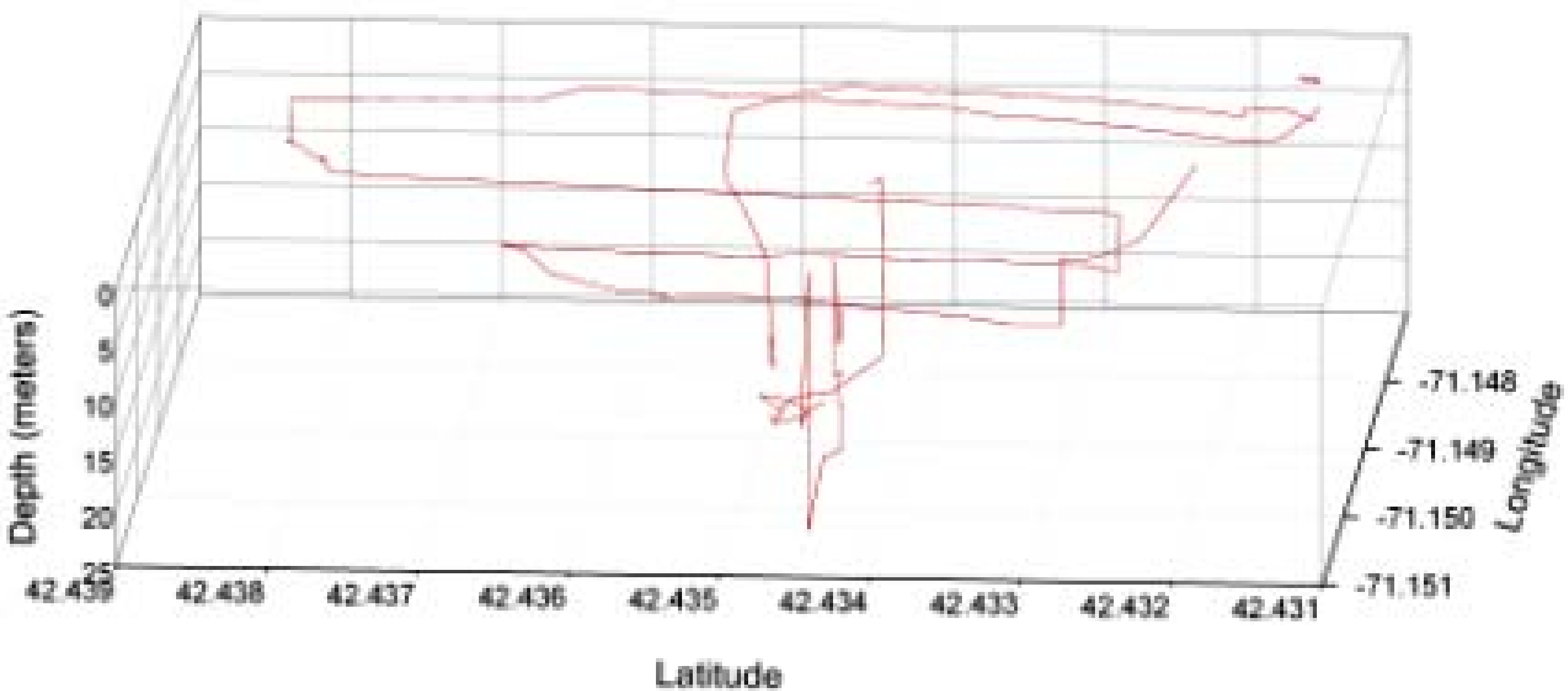


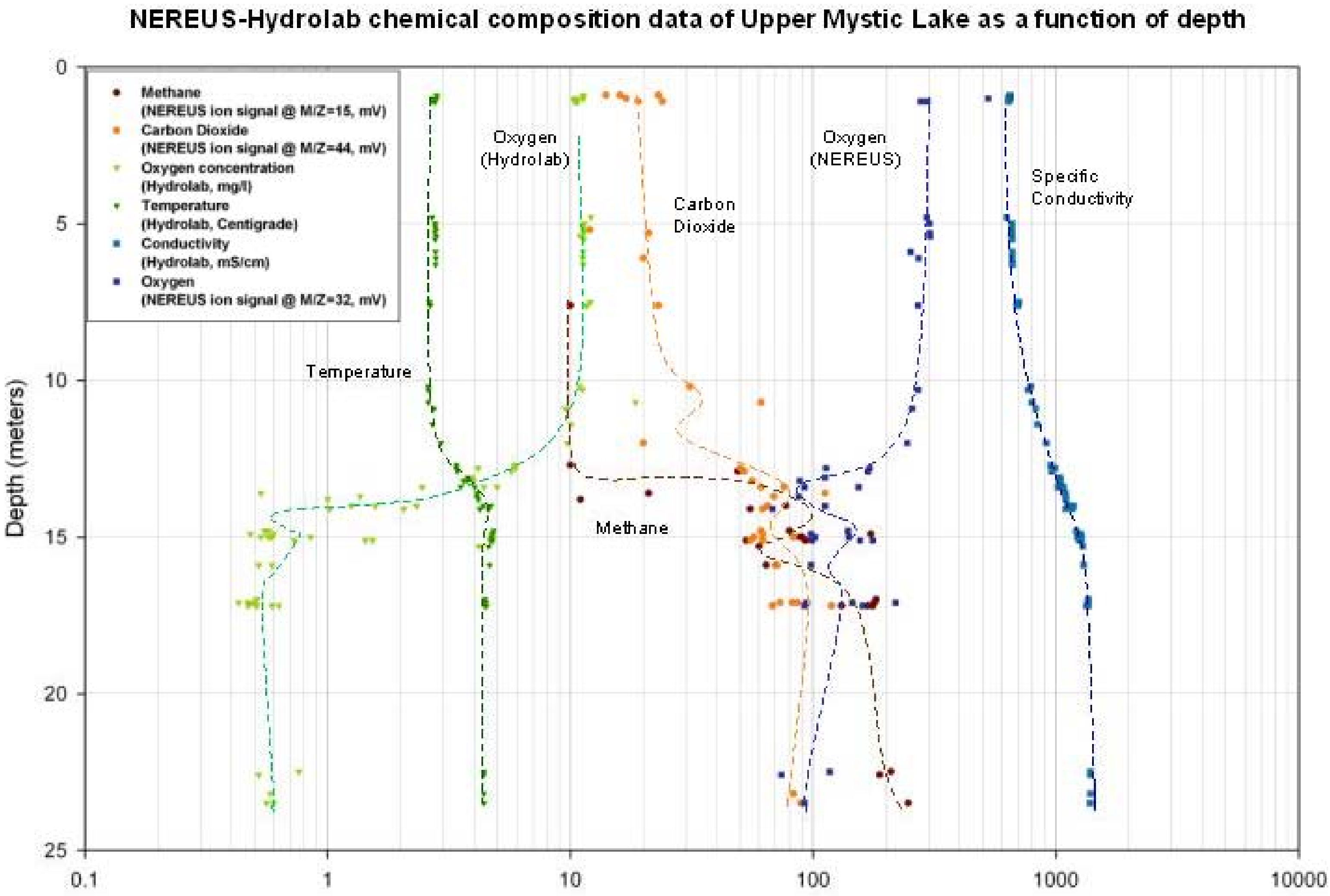
DESIGN SPECIFICATIONS

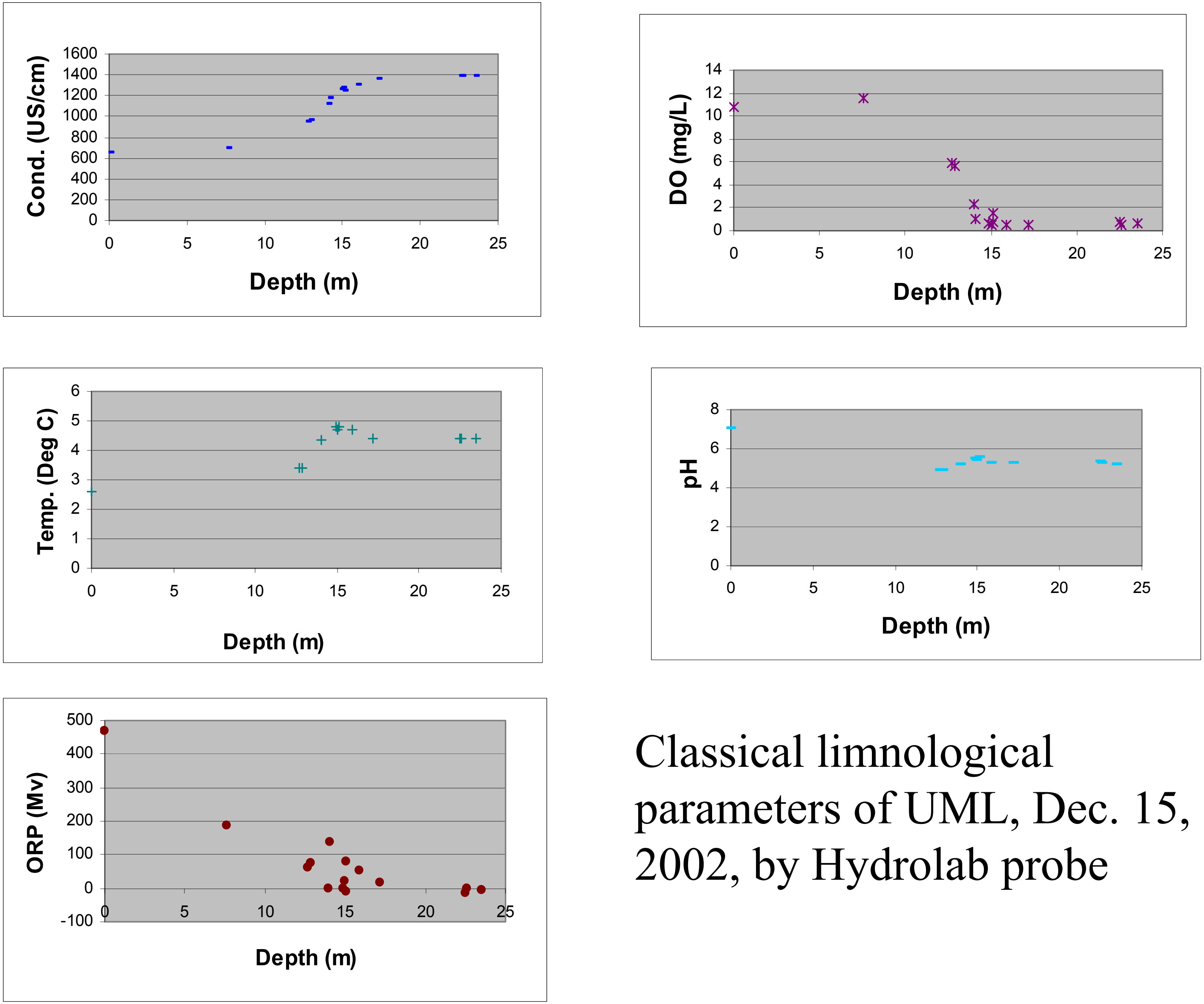
	Goal	As Built
Mass range	2 -100 AMU	2-150 AMU
Mass resolution	1 AMU	<1 AMU
Data handling	RS232	RS232, RF
Power	25 w	2-18 w
Maximum depth	300 m	100 m
Response time	~10 sec	~ 10 sec
Sensitivity	~10 ppb	~10 ppb
Weight	25.5 kg	22 kg
Volume	9,200 cc	3,600 cc


PC-104 & DAQ
Emission Regulator
Power supply
Ion pump
Cycloid Analyzer
Magnet
Battery area

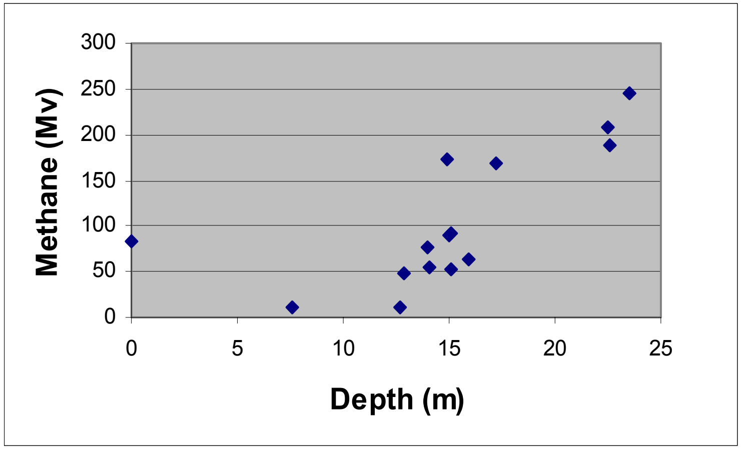
Track of Upper Mystic Lake NEREUS towed body deployment December 13 and 15, 2002

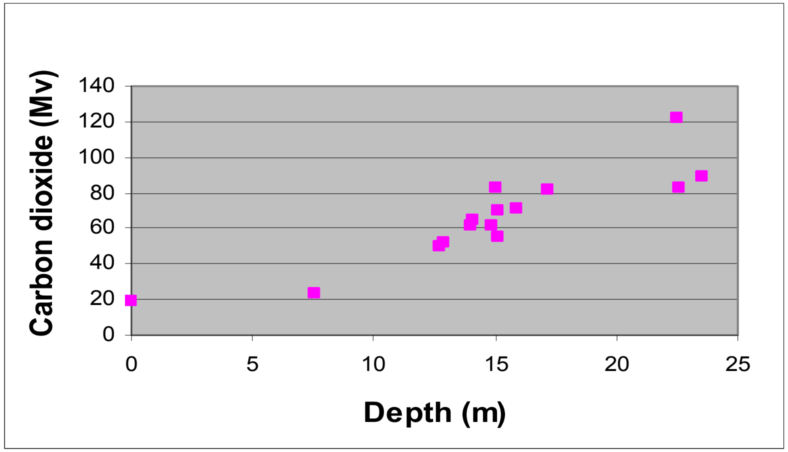


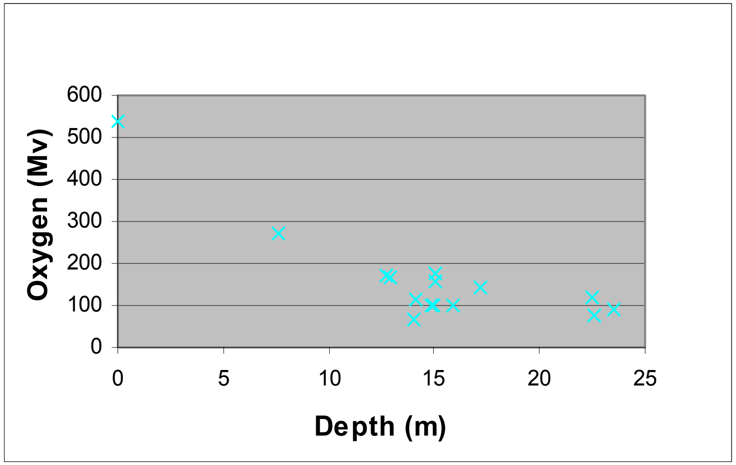

NEREUS-Hydrolab chemical composition data of Upper Mystic Lake as a function of depth
Methane
(NEREUS ion signal @ M/Z=15, mV)
Carbon Dioxide
(NEREUS ion signal @ M/Z=44, mV)
Oxygen concentration
(Hydrolab, mg/l)
Temperature
(Hydrolab, Centigrade)
Conductivity
(Hydrolab, mS/cm)
Oxygen
(NEREUS ion signal @ M/Z=32, mV)
Oxygen
(Hydrolab)
Carbon
Dioxide
Oxygen
(NEREUS)
Specific
Conductivity
Temperature
Methane
Depth (meters)
0
5
10
15
20
25
0.1
1
10
100
1000
10000

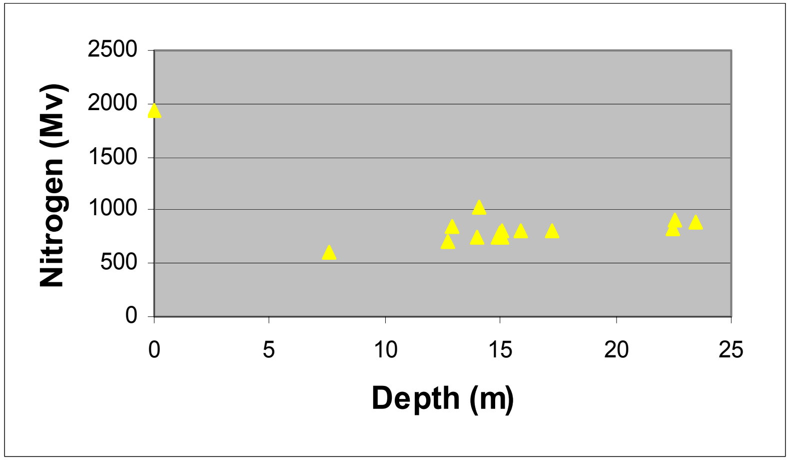


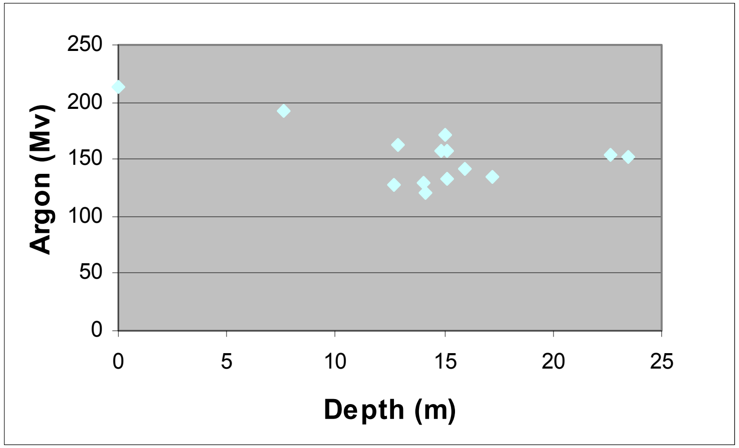
Classical limnological parameters of UML, Dec. 15, 2002, by Hydrolab probe





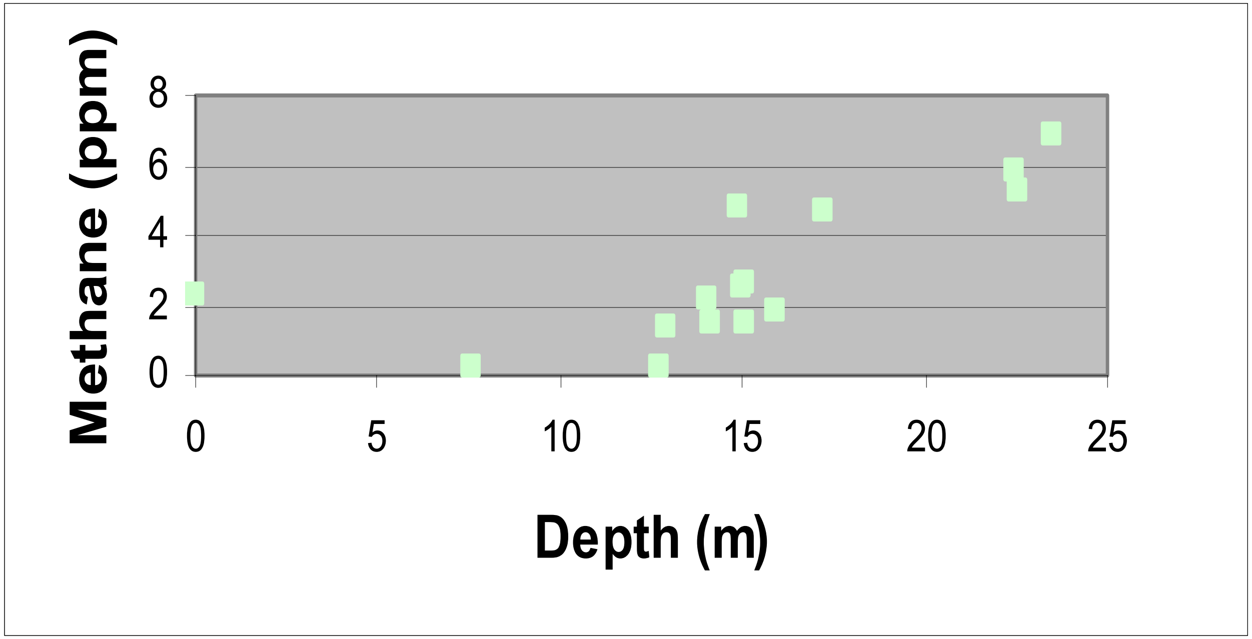






Gas profiles in UML, Dec. 15, 2002 as measured by NEREUS

Estimating methane production rate in UML



Approximate mass of methane = 10^6 grams
Accumulation time estimate = 1 month
Possible production O{10 g/(m^2-y)}

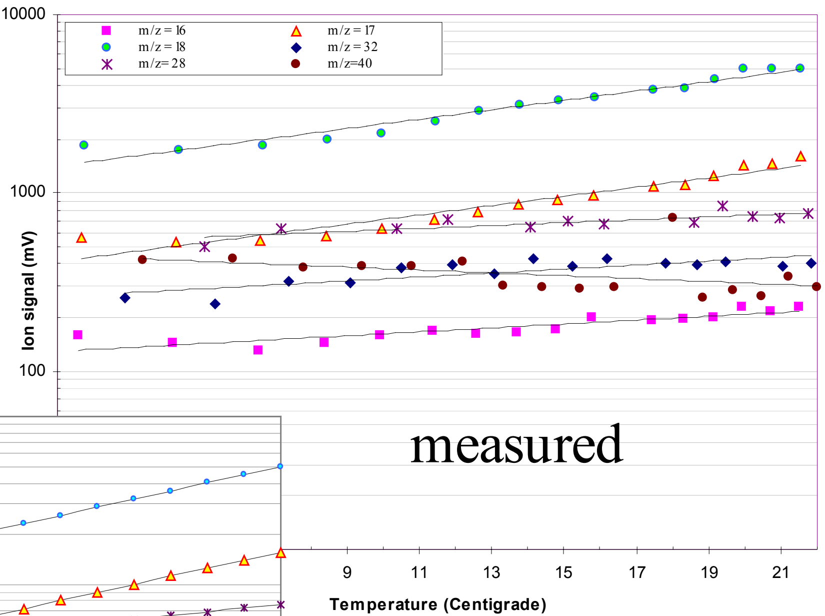
Summary of UML observations

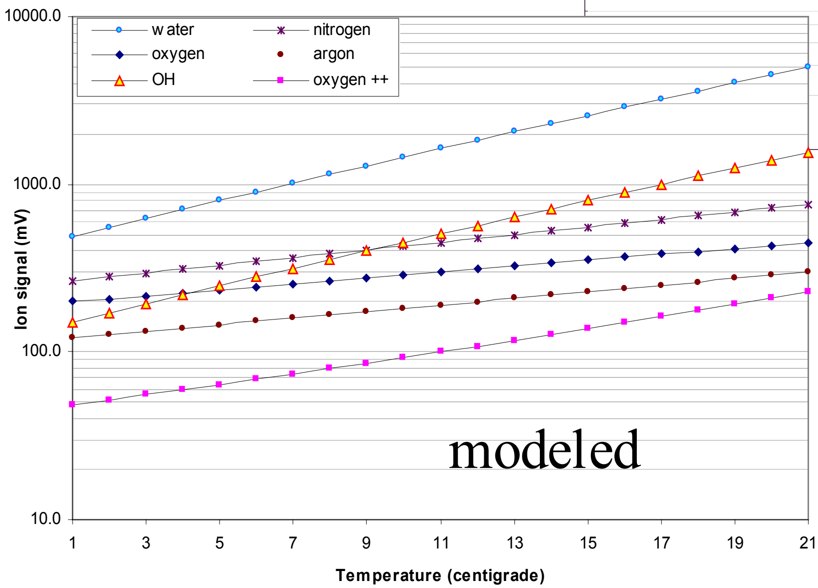
- Very weak thermal stratification is sufficient to produce chemical stratification
- Results compatible with classical parameters
- Carbon dioxide and methane correlated
- Methane anticorrelated with oxygen
- First estimate of methane production rate

Additional Needs: Calibration

- Both **temperature** and **pressure** effects expected with membrane inlet
- Possible fouling effects with long-term deployment
- Instrument drift correction

NEREUS ion signal temperature dependence





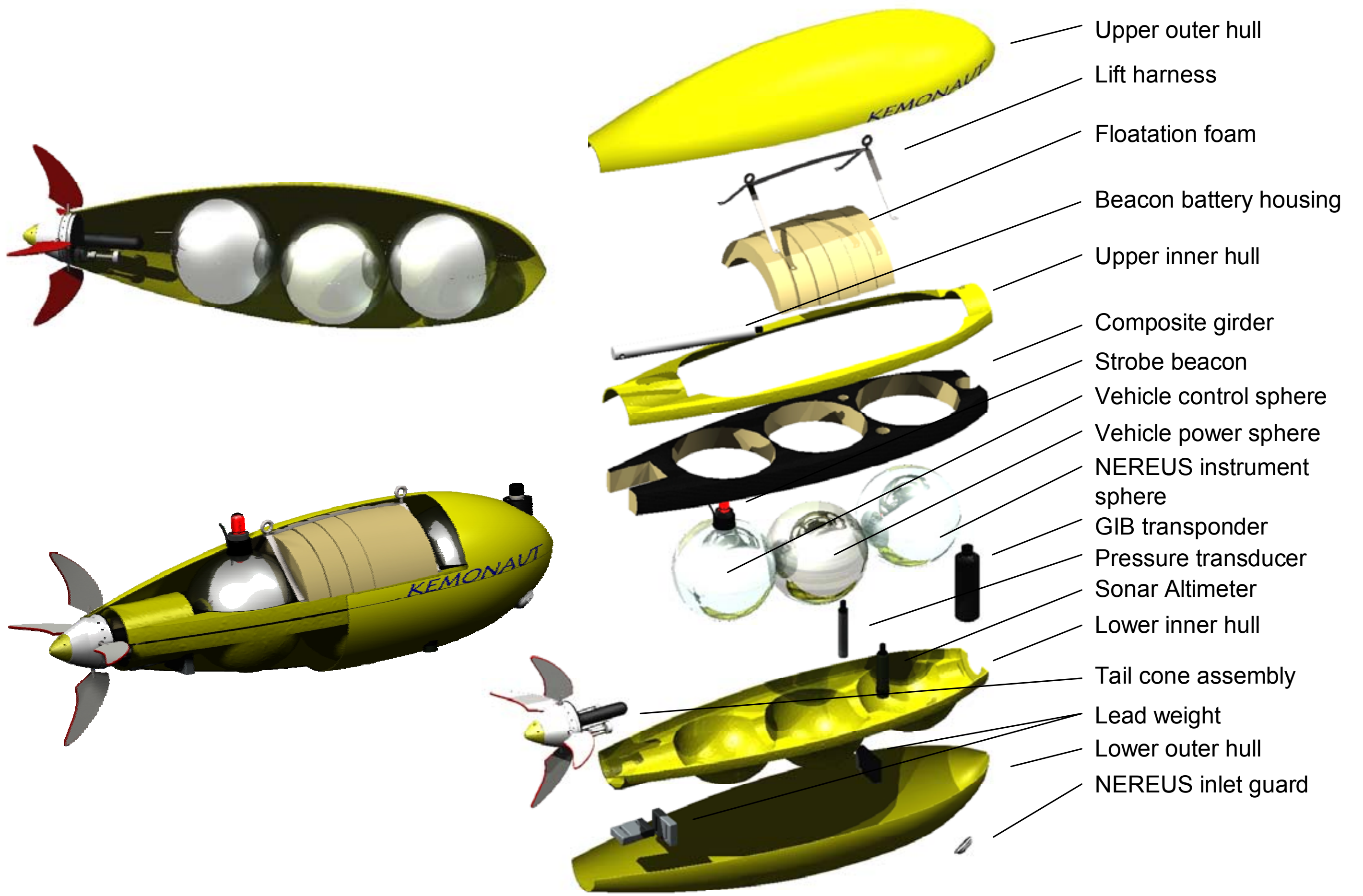
$$P = P_0 \times e^{-E_p / RT}$$

$$Q = \frac{P\,A}{l}(p_1 - p_2)$$

A mobile platform for NEREUS: the KEMONAUT AUV

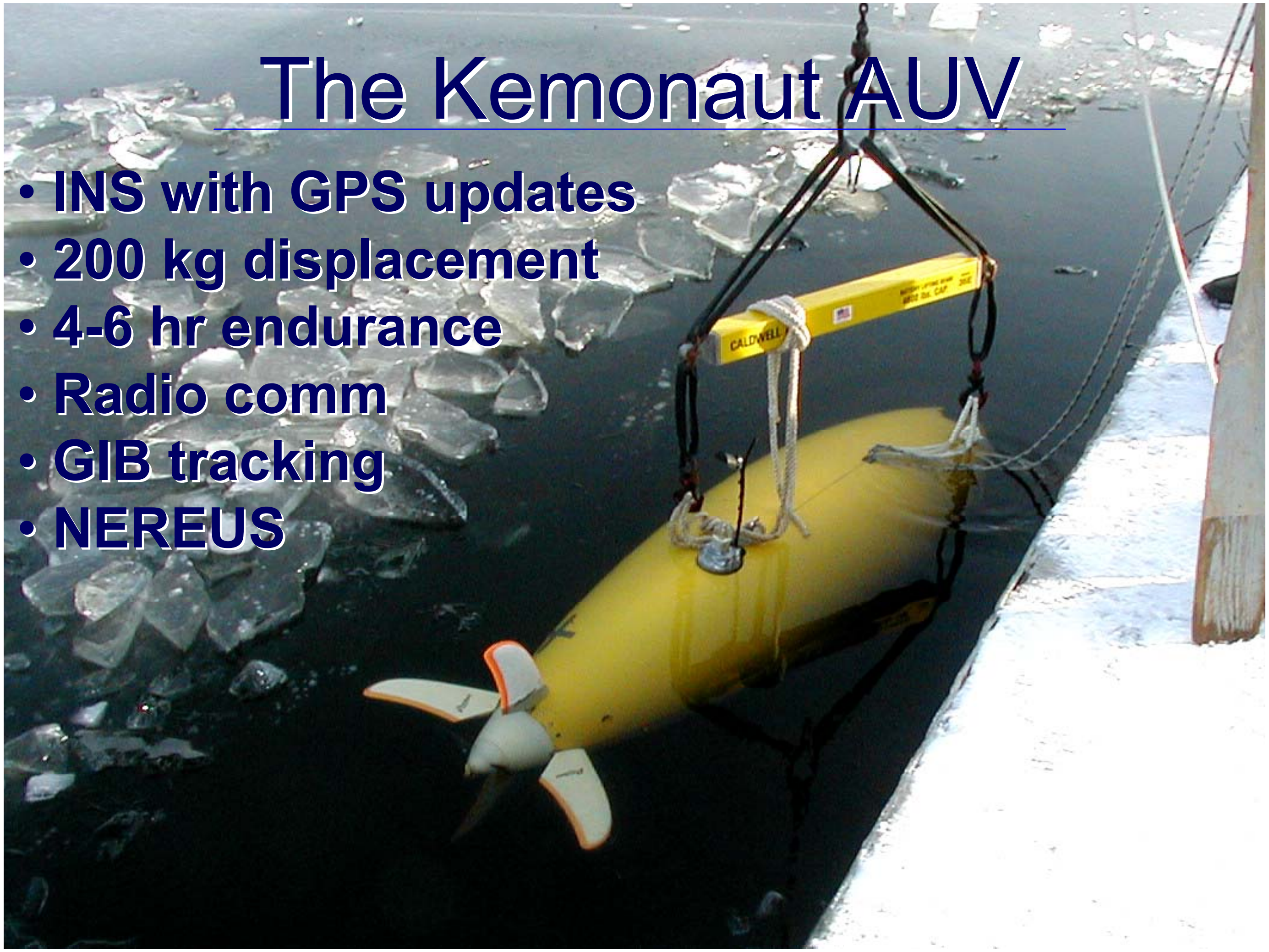
Tests moved to Boston Harbor due to ice

The Kemonaut Autonomous Underwater Vehicle



The Kemonaut AUV

- INS with GPS updates
- 200 kg displacement
- 4-6 hr endurance
- Radio comm
- GIB tracking
- NEREUS




KEMONAUT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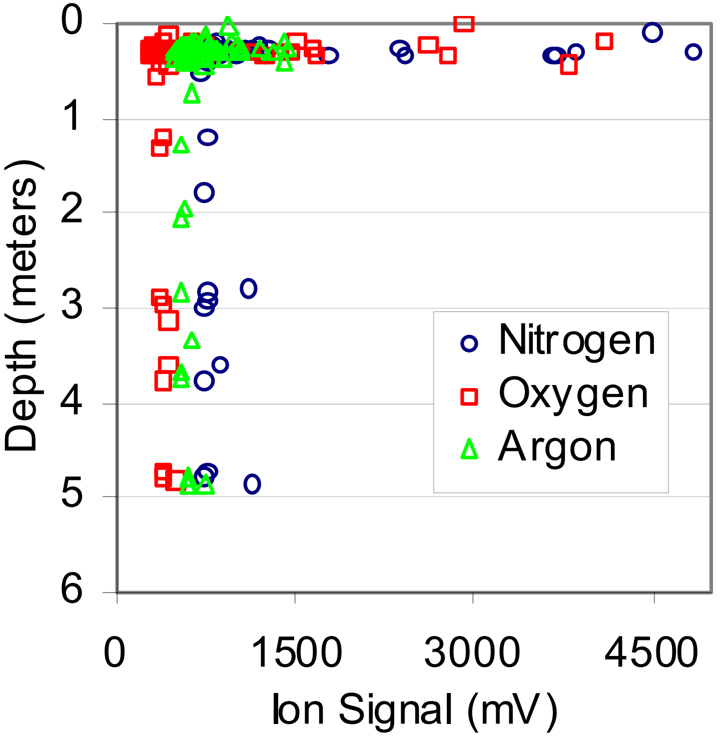
NEREUS/Kemonaut data in Boston Harbor'

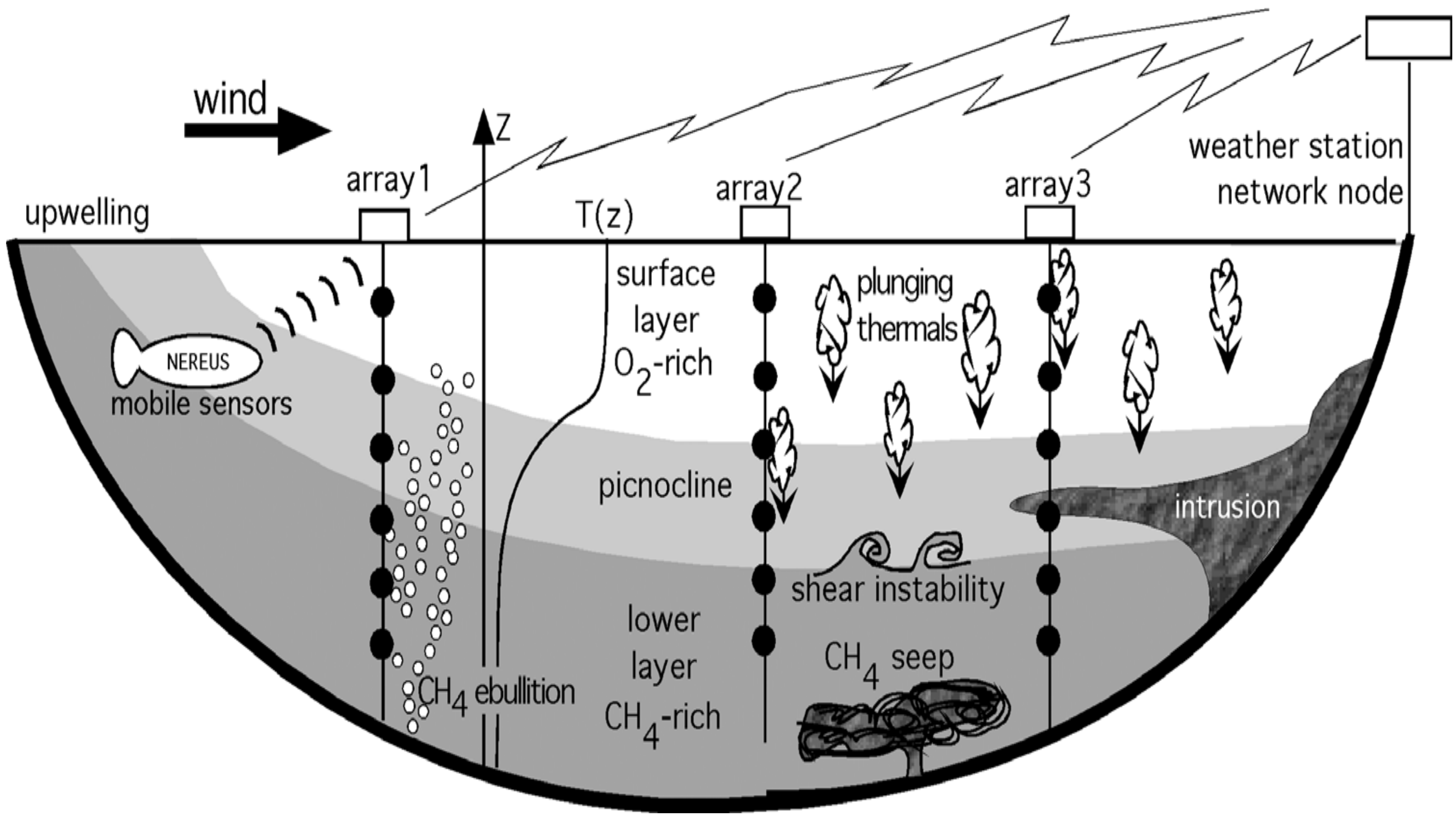
December 19, 2002

- **Dissolved atmospheric gases present in expected ratios**
- **No hydrocarbons detected**
- **High apparent variability in surface waters, likely due to entrained bubbles**

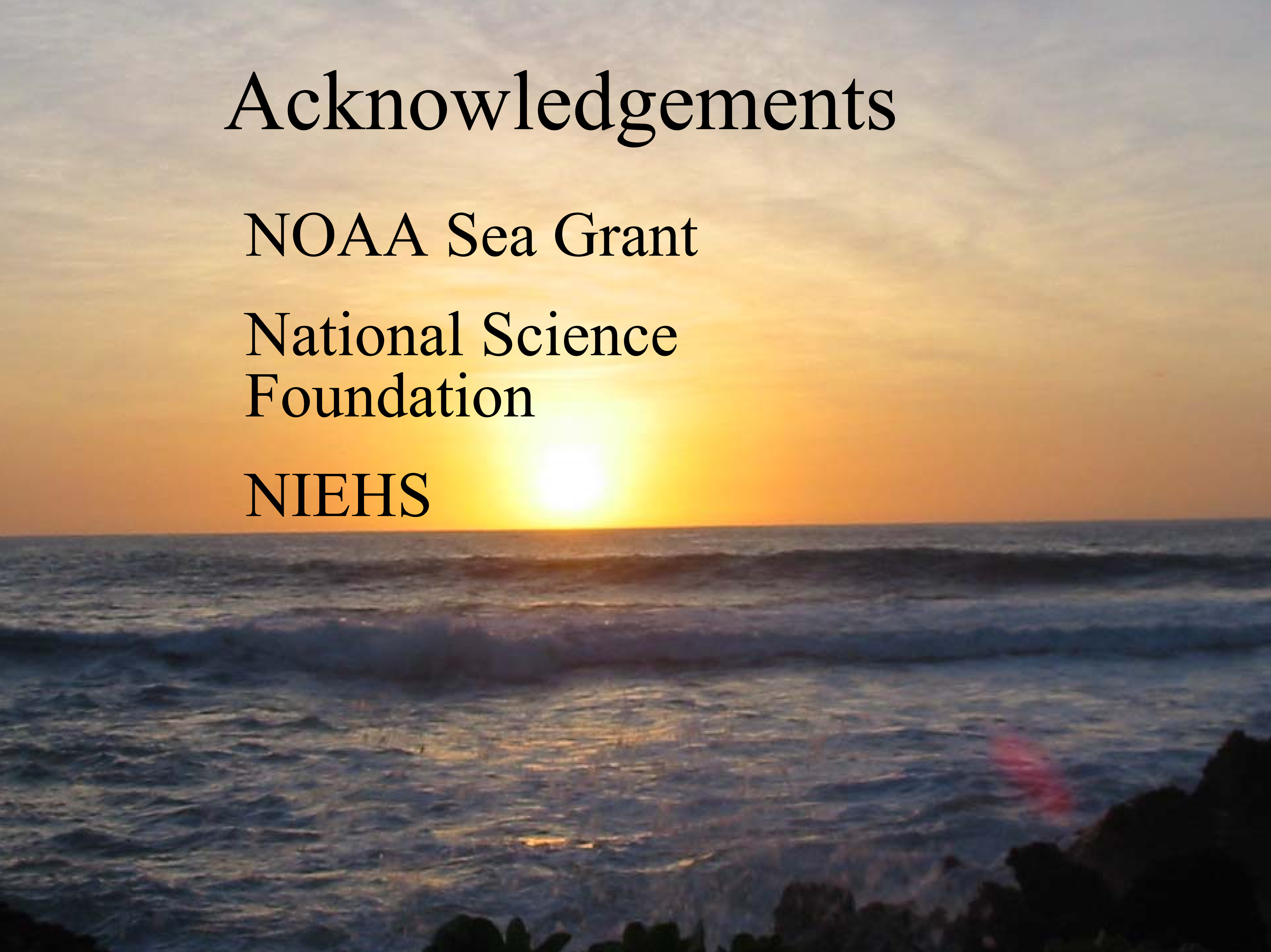


Integration of AUV/Mass Spec into a networks of sensors for Biogeochemical Analysis

Maximization of ability to test hypotheses about biogeochemistry that are imposed by need for high resolution chemical data



Proposed sensor network to observe biogeochemical processes in a stratified lake



Acknowledgements

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NIEHS