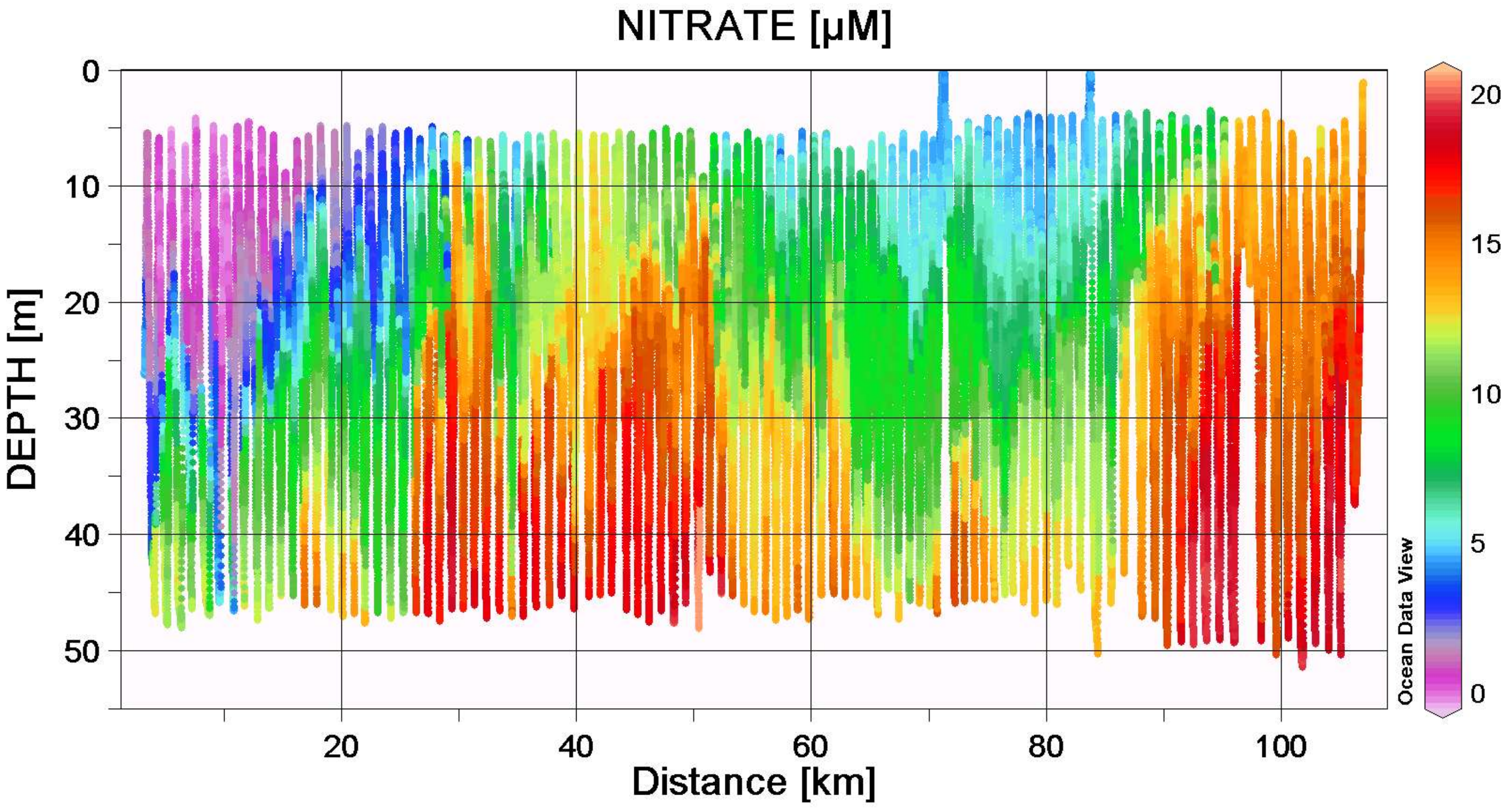
Chemical Sensors for Autonomous and Lagrangian Platforms

Ken Johnson, Monterey Bay Aquarium Research Institute



CHEMICAL SENSORS

Examples:

1. **Oxygen electrode.**
2. **pH electrode.**

Principles:

1. **Diffusion of analyte to active surface. Requires a reversible chemistry, detectable physical property or a reaction rate measurement.**

Advantages:

1. **Simplicity - no moving parts in simplest realizations.**
2. **Electronics can be remote if based on fiber optics.**
3. **Low cost.**
4. **Low power consumption.**

Limitations:

1. **Requires development of new, reversible chemistries or kinetic methods of analysis.**
2. **Difficult to maintain calibration**
3. **Usually a trade-off between sensitivity and response rate.**

CHEMICAL ANALYZERS

Examples:

1. NAS-2E,
2. Submersible Chemical Analyzer (SCANNER, DigiSCANNER),
3. OSMOAnalyzer

Principles:

1. Mechanical system used to obtain sample, add reagents and transport mixture to detector.

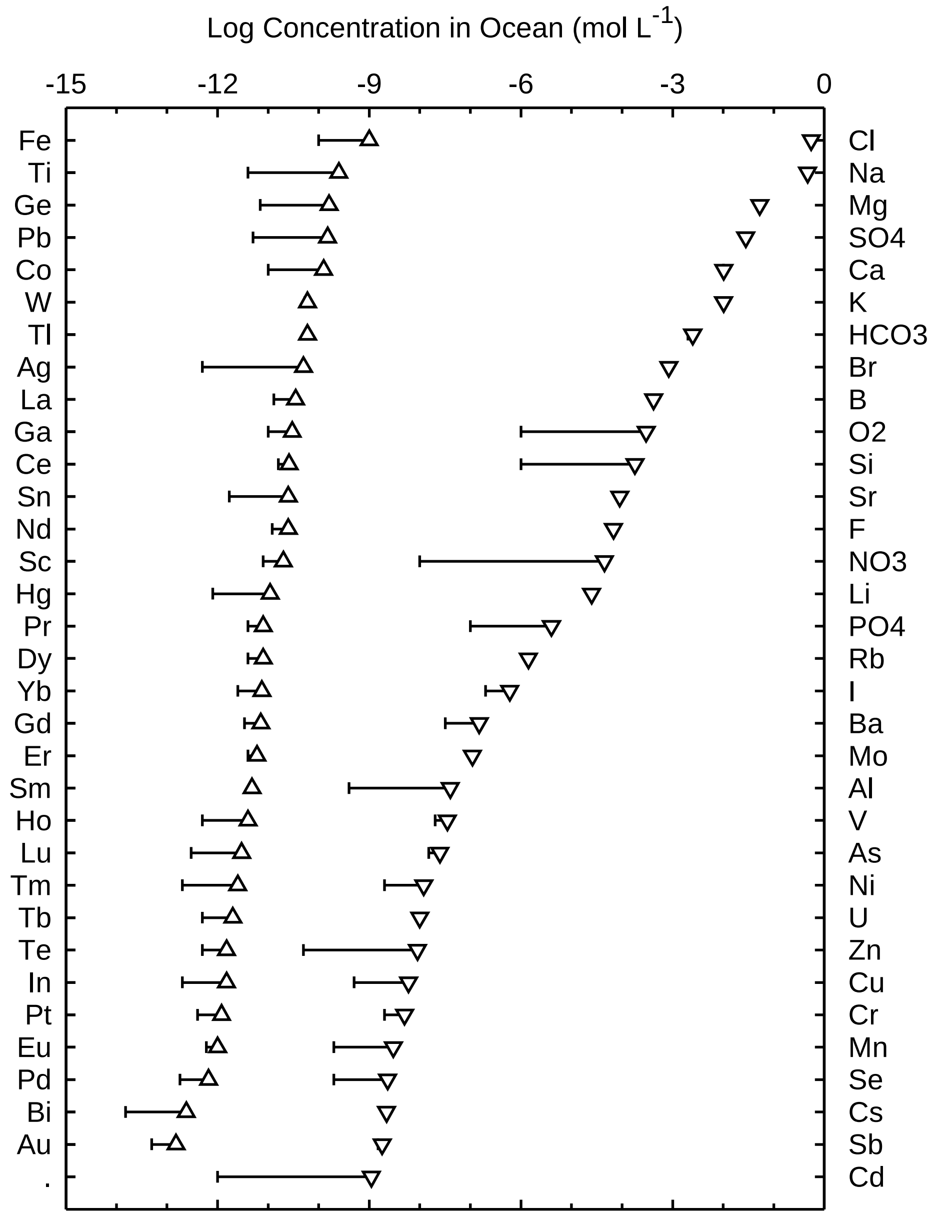
Advantages:

1. Many existing chemistries with a long track record can be used.
2. Easy to calibrate in situ.
3. Resistant to biofouling.
4. More complex chemical manipulations possible.

Limitations:

1. Mechanically more complex.
2. Potentially high power consumption.
3. Generally larger than sensors.

- Gases other than CO_2
  - Oxygen
  - Total Gas Pressure
  - Methane
  - Hydrogen sulfide
- Nutrients
  - Macro-nutrients (NO_3^-, PO_4^{3-}, Si)
- Carbon Dioxide
  - pCO_2
  - ΔpCO_2
  - Particulate Organic Carbon



Oxygen:

The Clark electrode is widely used, albeit problematic. Here, the sensor is used on a mooring at HOT. Monthly cruises are used to recalibrate the sensor, which may drift 15%.

Gas Tension Device:

Much more stable (<1% drift) but slow due to thick membrane.

(Emerson et al.,, 2002)

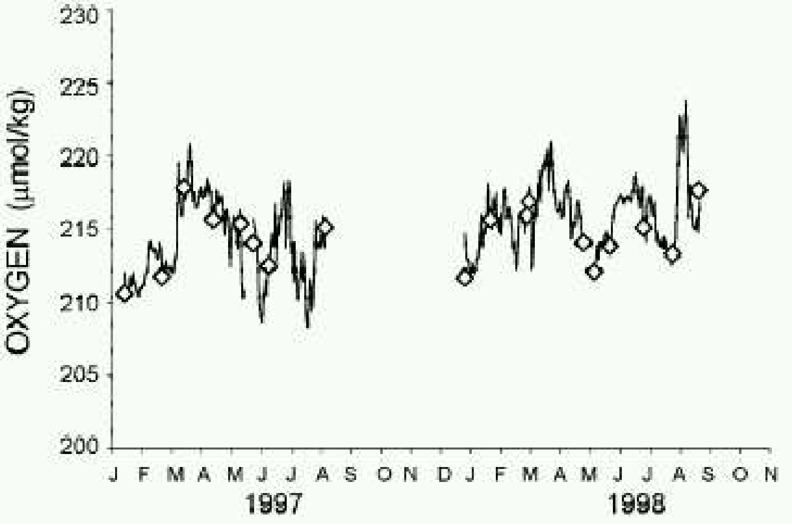
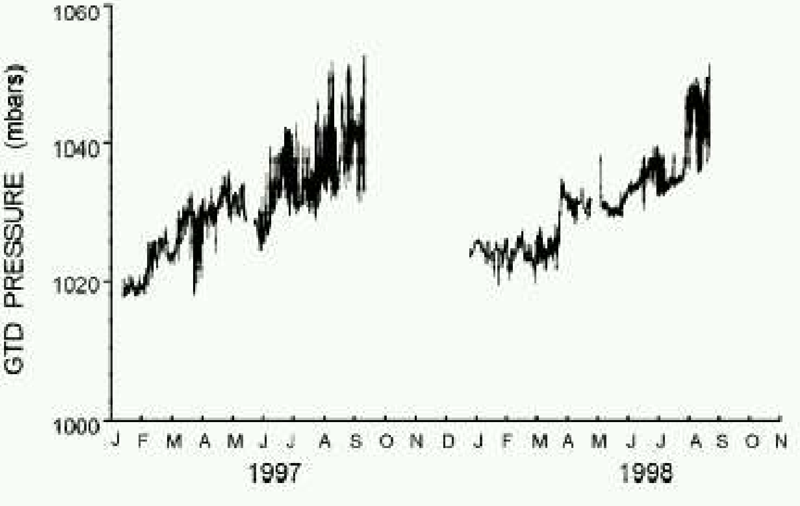
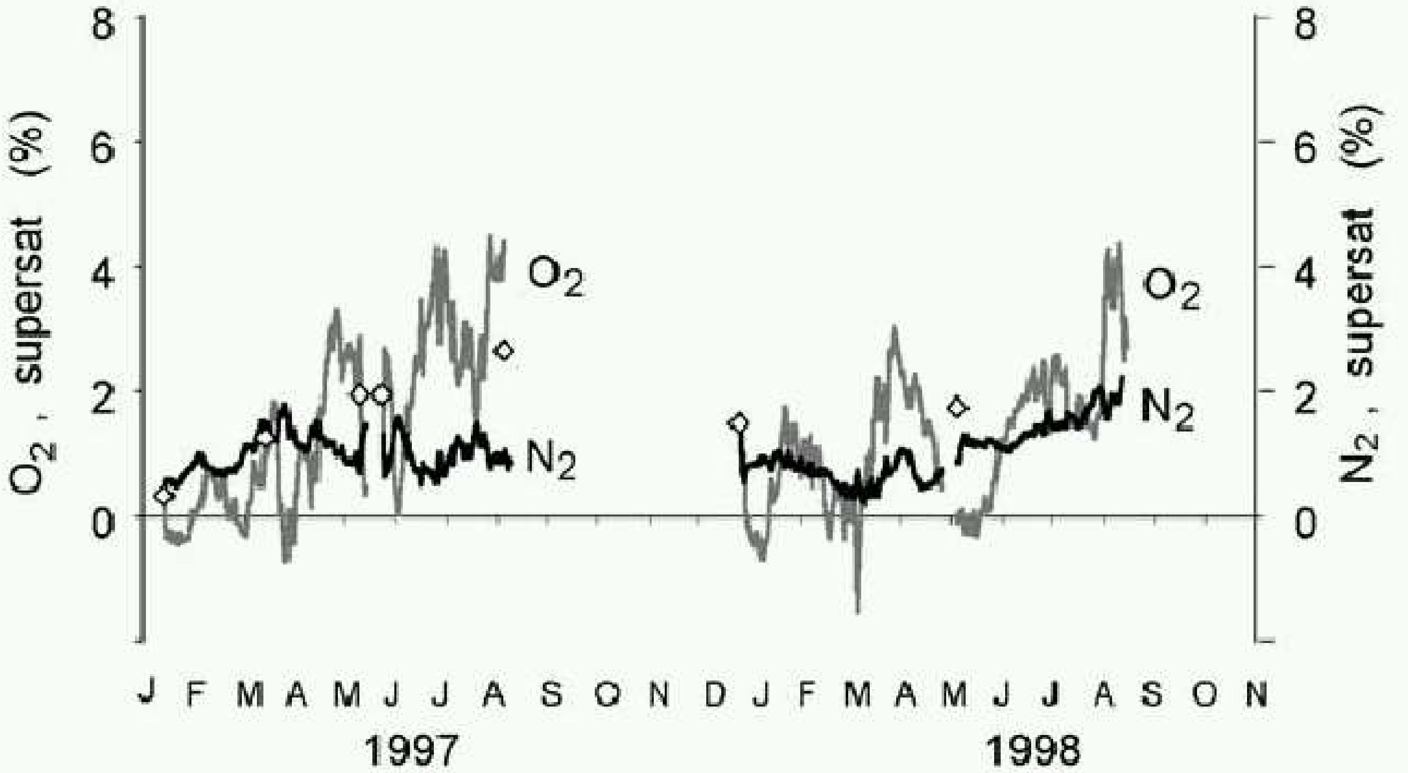


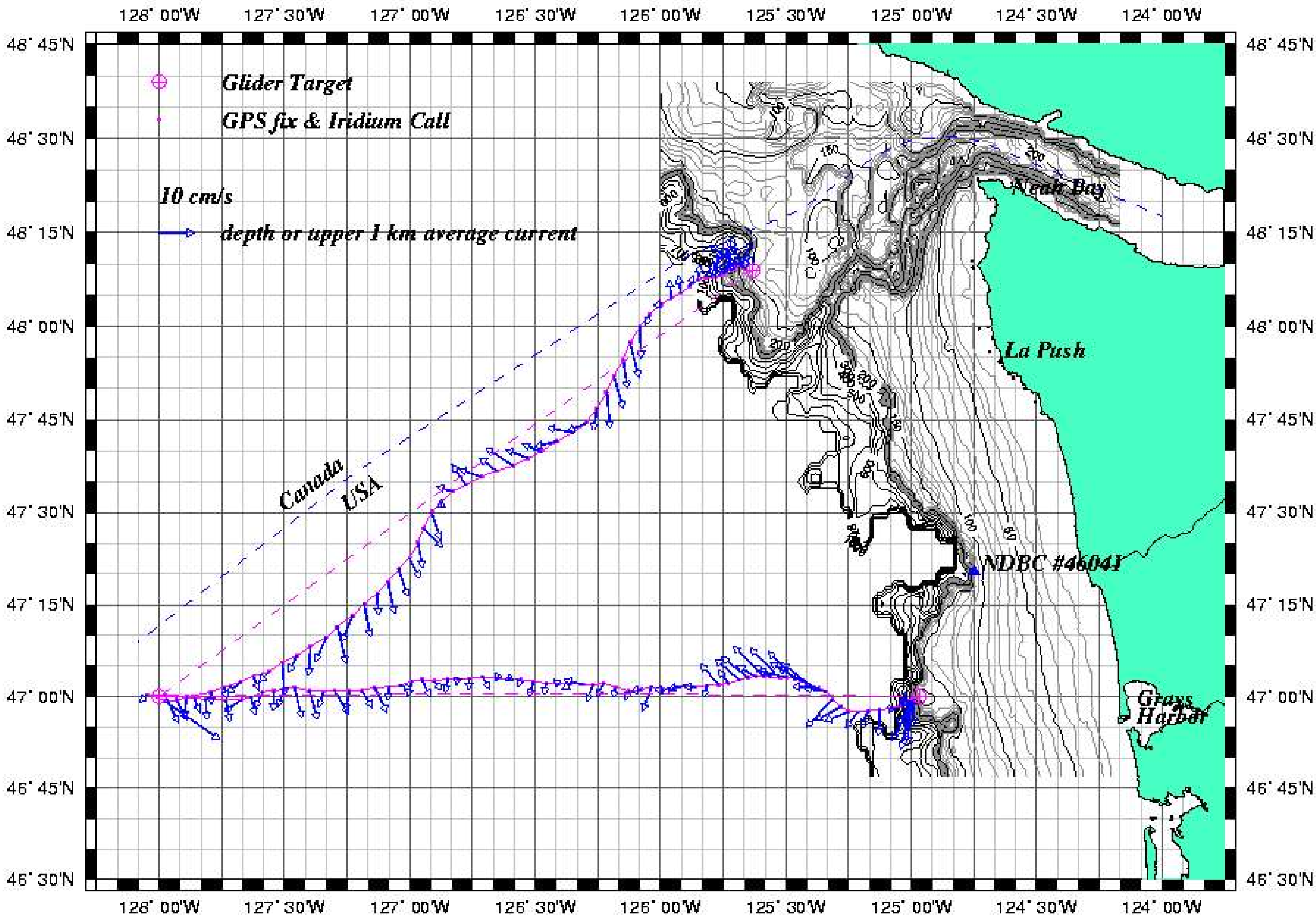
Fig. 3. Daily averaged oxygen concentrations determined from measurements every 2 h at 50 m by the GTD–CTD-O_2 instrument (lines) during HALE 1–4 deployments for the years 1997 and 1998. Diamonds are oxygen measurements from the same density as the instrument determined by Winkler titrations. The O_2 sensor is calibrated to the Winkler titrations to correct for instrument drift (see Table 1).



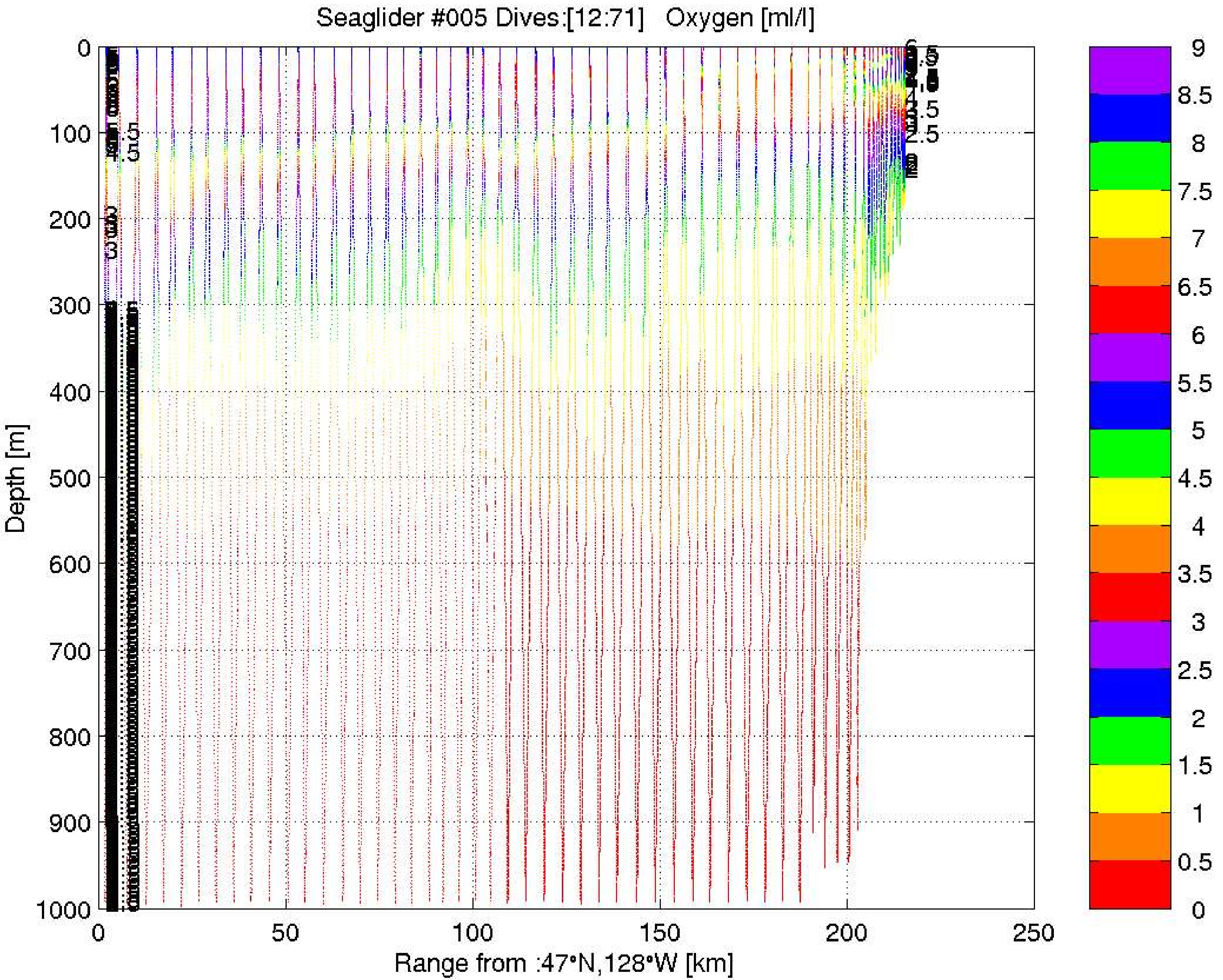
If one can solve the drift problems (e.g. operation on a vertically profiling platform that spends most of its time out of the euphotic zone), the O2 electrode and GTD can provide nearly direct measurements of primary production by change in oxygen concentration, relative to N_2 change measured with GTD (Emerson et al., 2002).



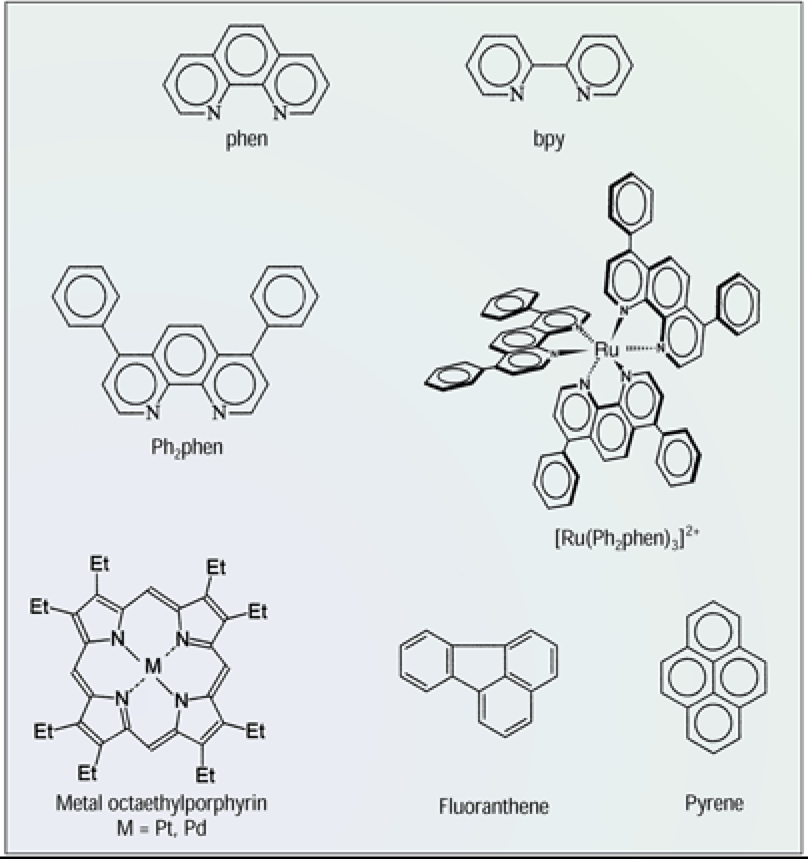
Seaglider #005 12 September - 9 October 2002

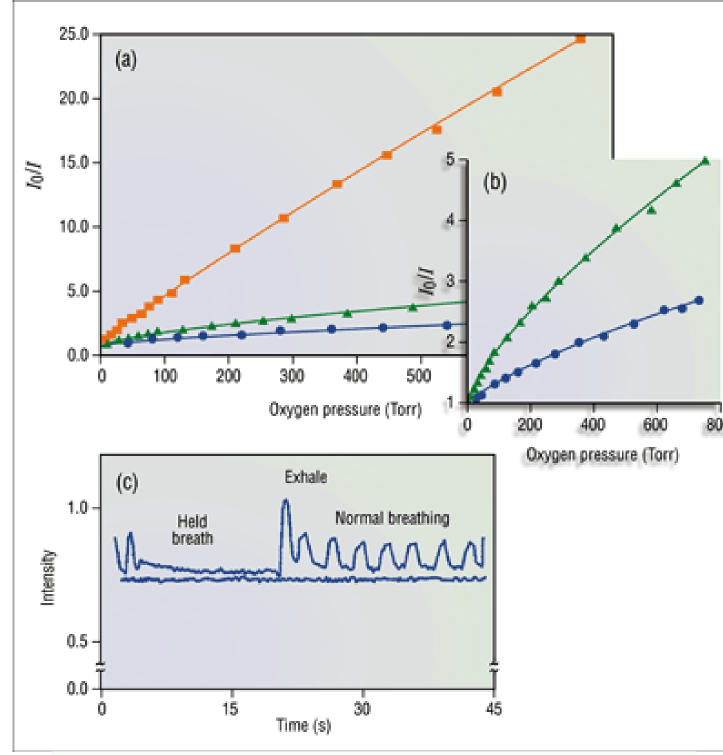


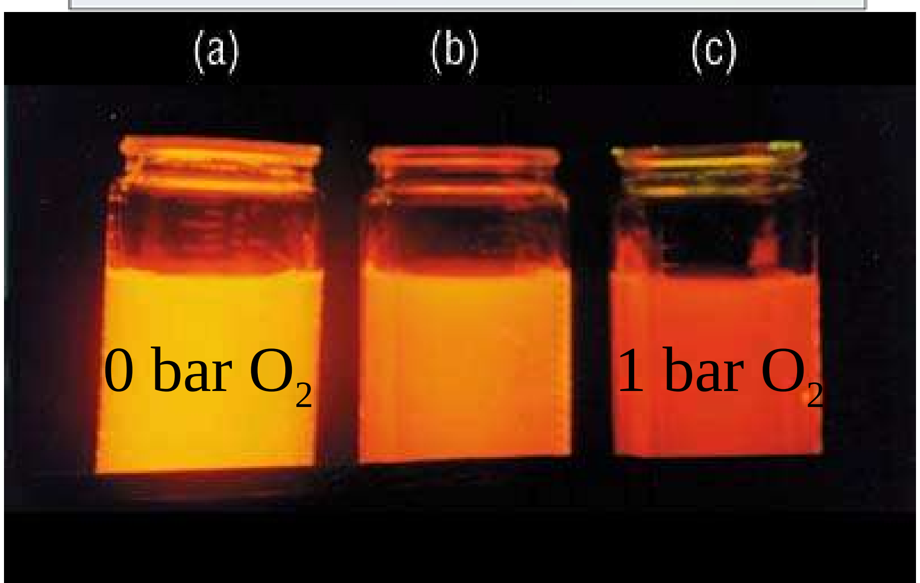
U.W. School of Oceanography / Applied Physics Laboratory


Seaglider #005 Dives:[12:71] Oxygen [ml/l]
Depth [m]
Range from :47°N,128°W [km]
0
100
200
300
400
500
600
700
800
900
1000
0
50
100
150
200
250
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0

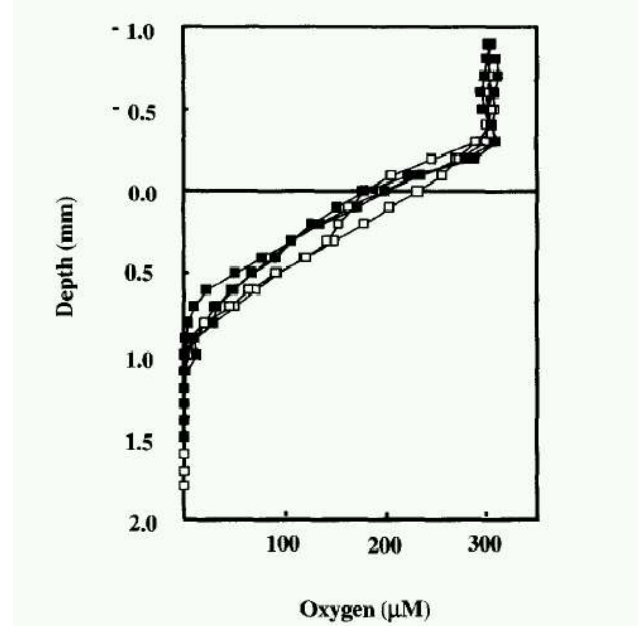
Fluorescence quenching based oxygen sensors are an alternative with some strengths and also some issues (Demas et al., 1999).



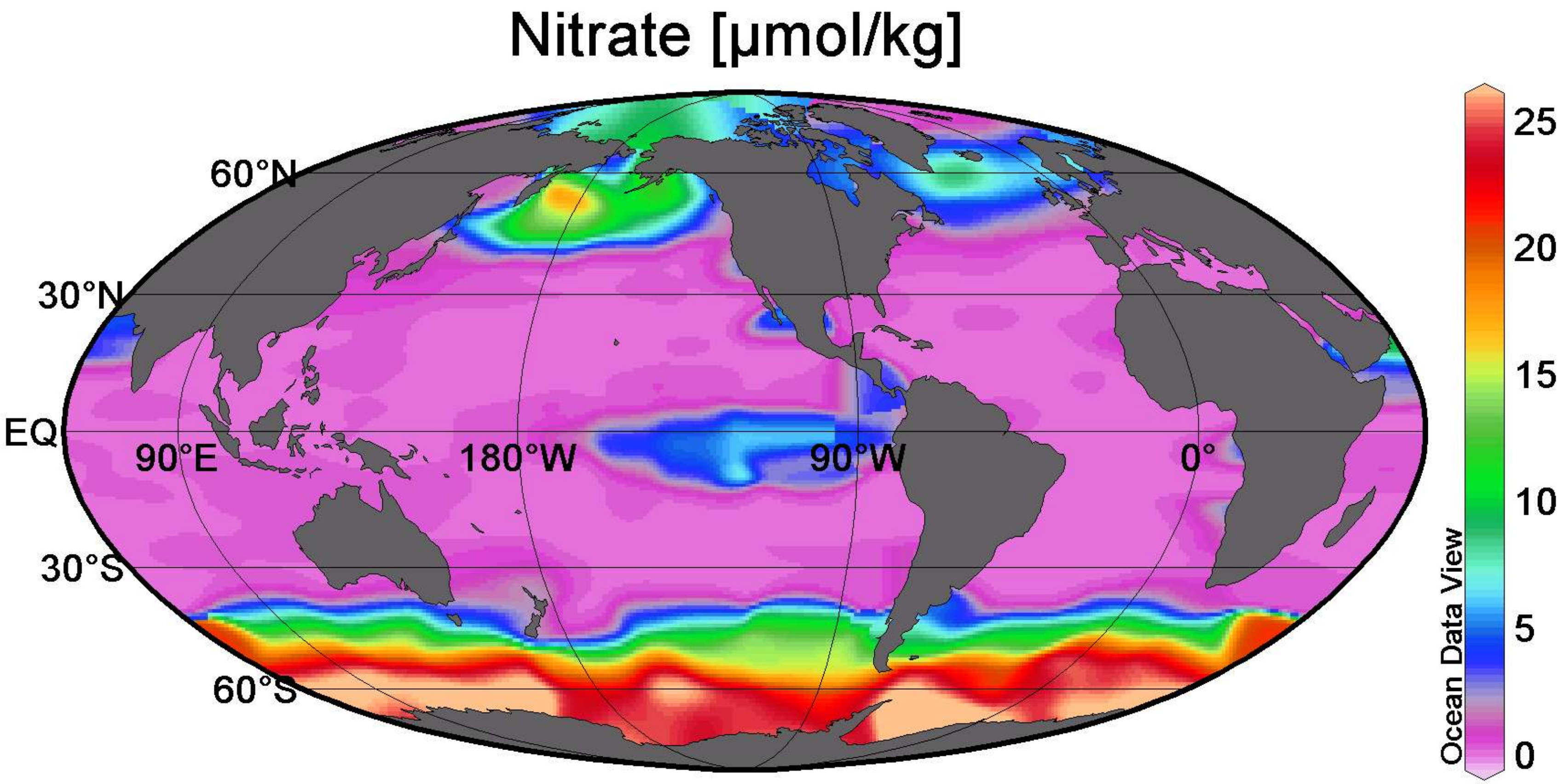




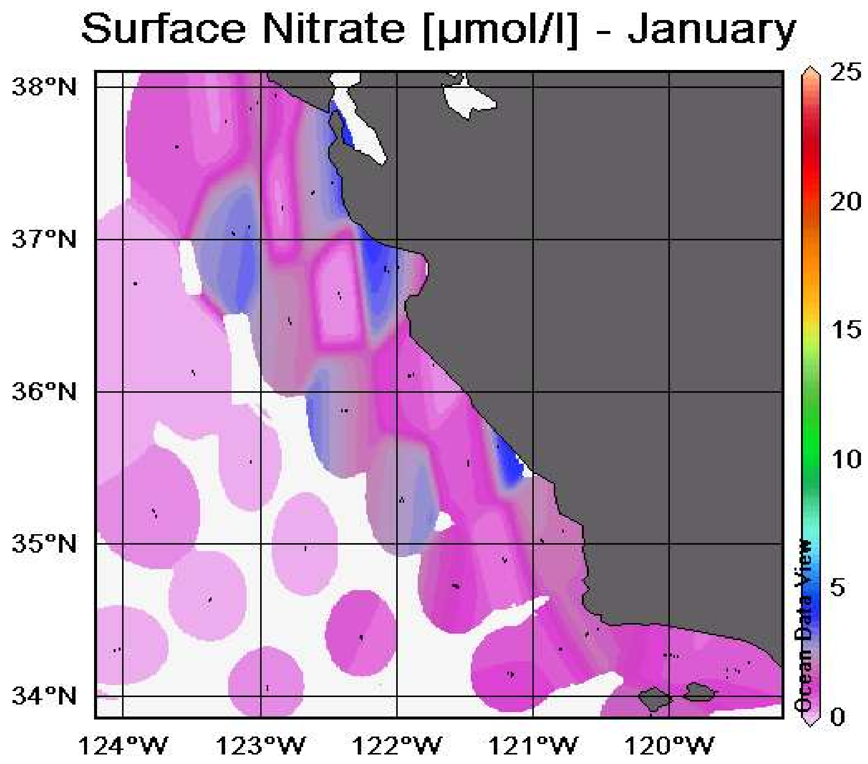
R.N. Glud et al. / Deep-Sea Research I 46 (1999) 171–183

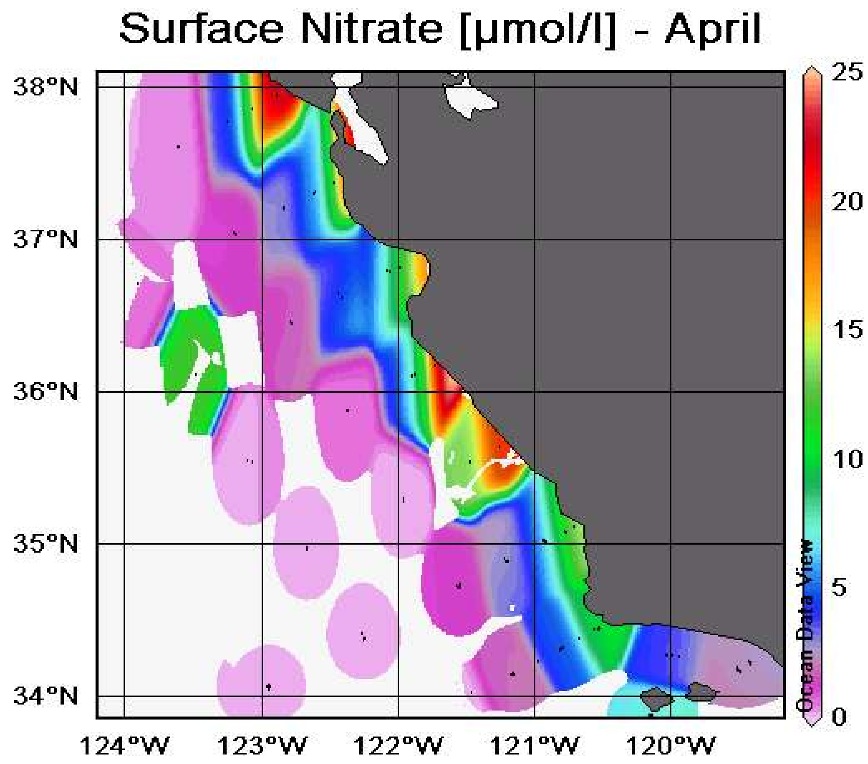


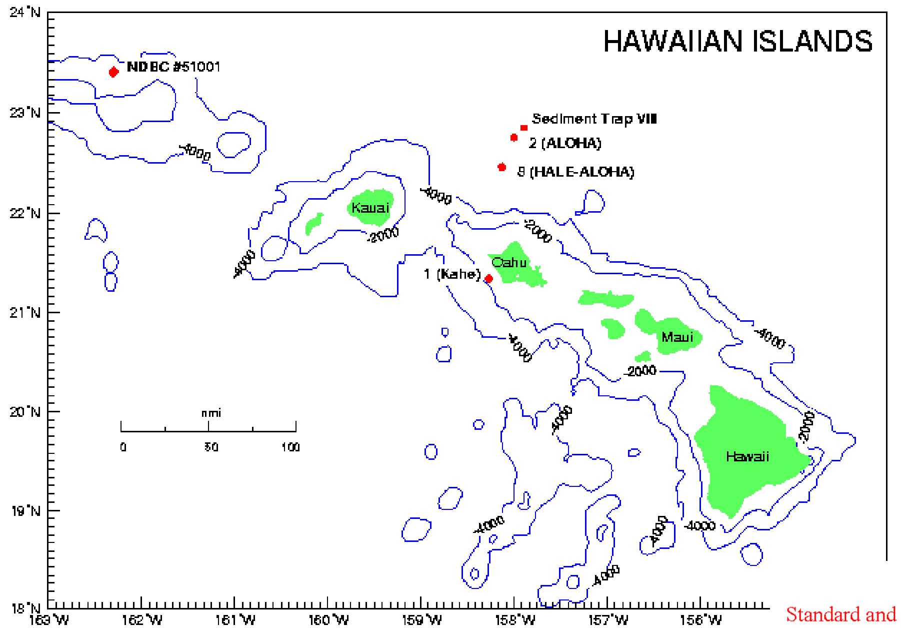
Nutrient concentrations are a key to understanding processes regulating primary production and carbon transport.



Coastal nutrient concentrations highly variable: CalCOFI Data - Mean 1954-1997

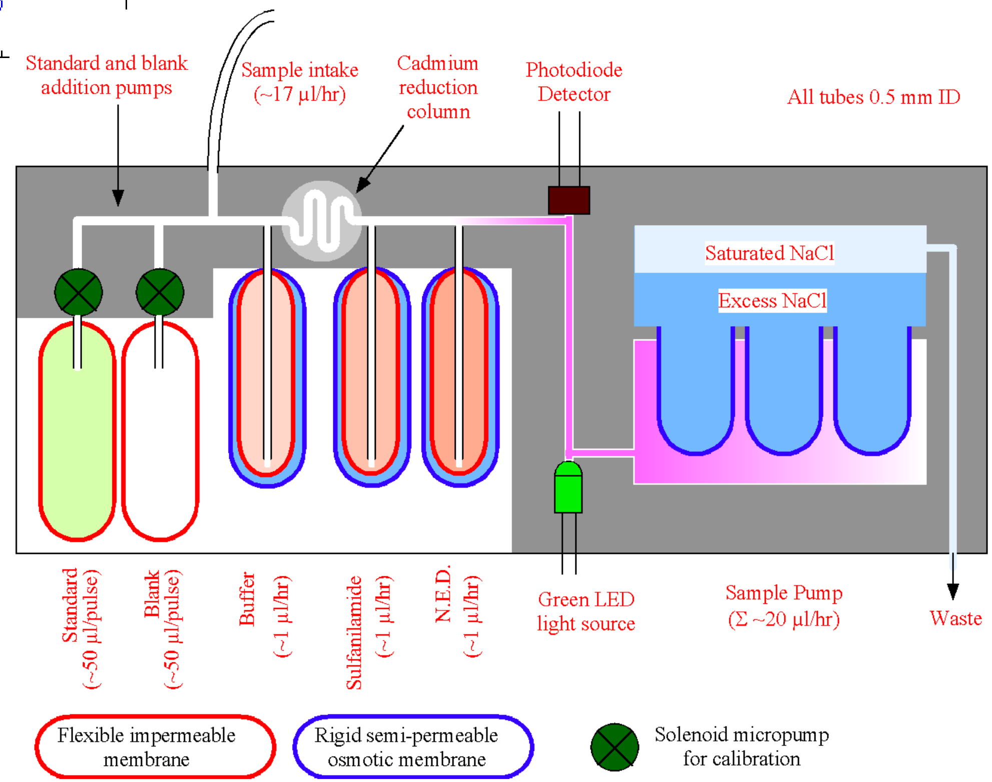




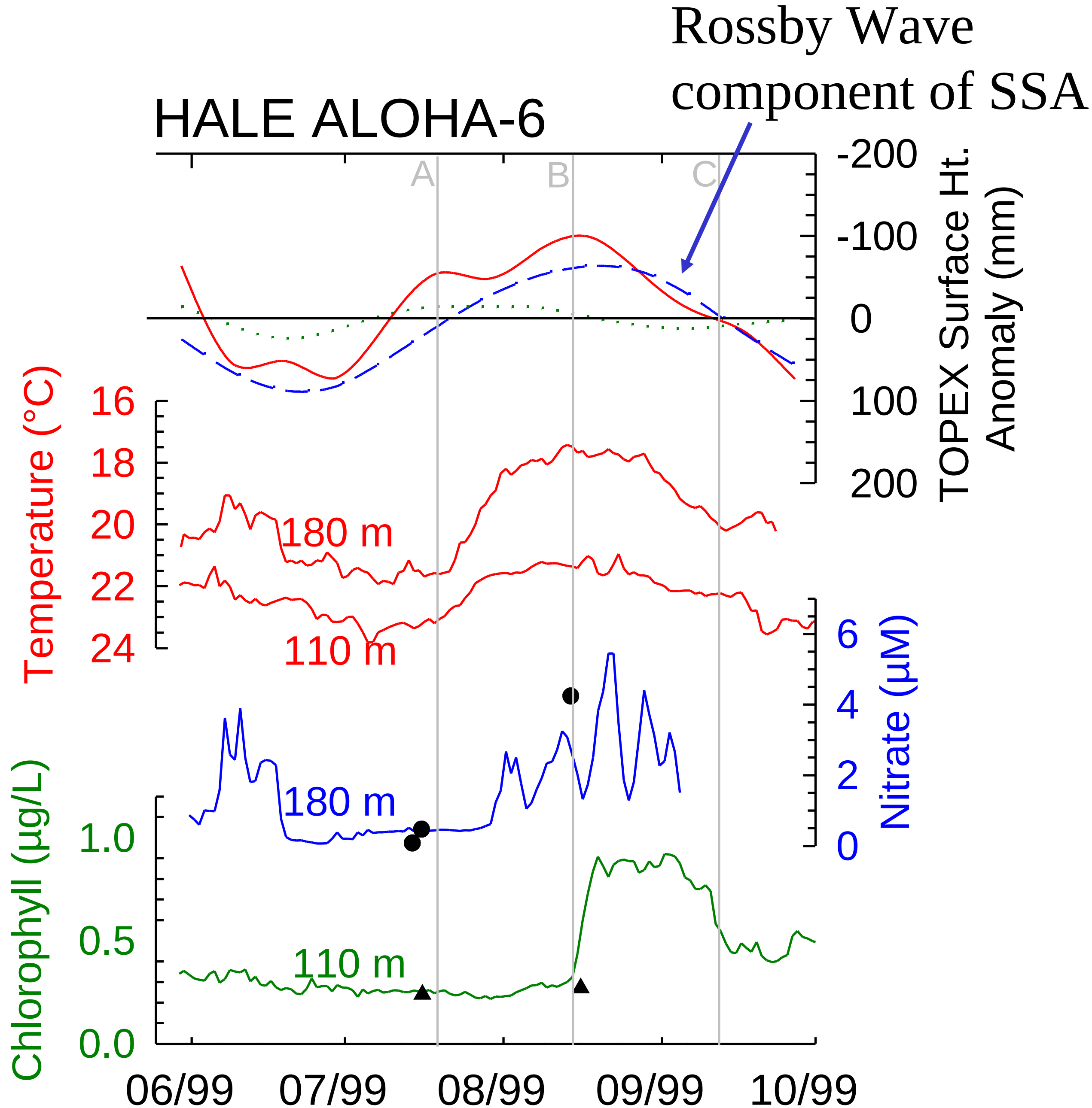


Analyzers have been the only practical systems nutrients such as nitrate, phosphate, Si, Fe... on autonomous platforms such as the HOT mooring.

Example: the OSMOAnalyzer (Jannasch et al., 1994)



Eddies and, in this case, Rossby Waves alter the nutrient field periodically in the open ocean and may account for most of the vertical nutrient flux (Sakamoto et al., submitted).



Deployments up to 12 mo. now being achieved with analyzers.

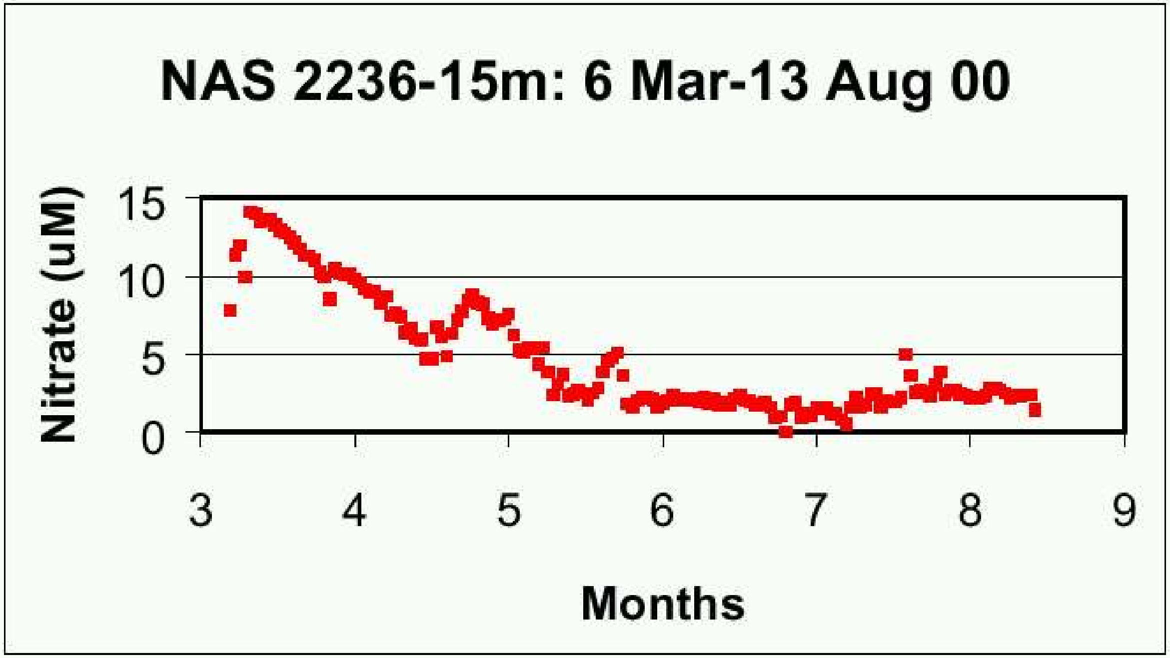
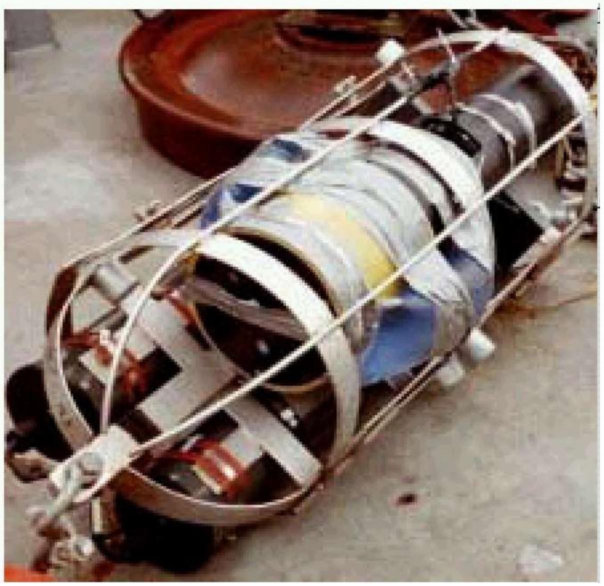


Figure 2 Daily mean nitrate concentrations (uM) at 15m depth on the Gulf of Alaska shelf (GAK4) for 6 March-13 August 2000.

T. Whitledge, UAF, results using NAS-2E Analyzer in the Gulf of Alaska [arctic.bio.utk.edu/ SBI%20meeting%20abstracts%5CSession%203%5CWhitledge.pdf]



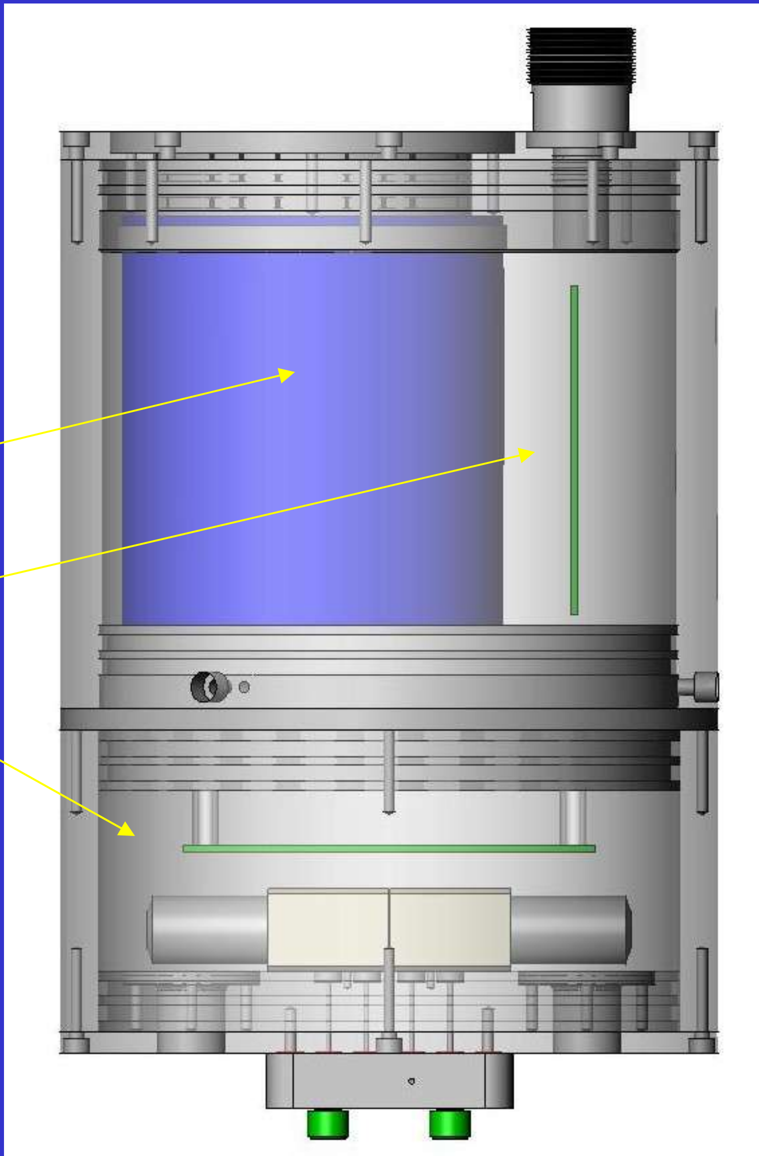
Analyzers continue to get smaller and a variety of commercial units are becoming available.

E.g., a DigiSCAN ready for 2 month deployment in Elkhorn Slough (Chapin et al., submitted).

YSI Nitrate Monitor Design

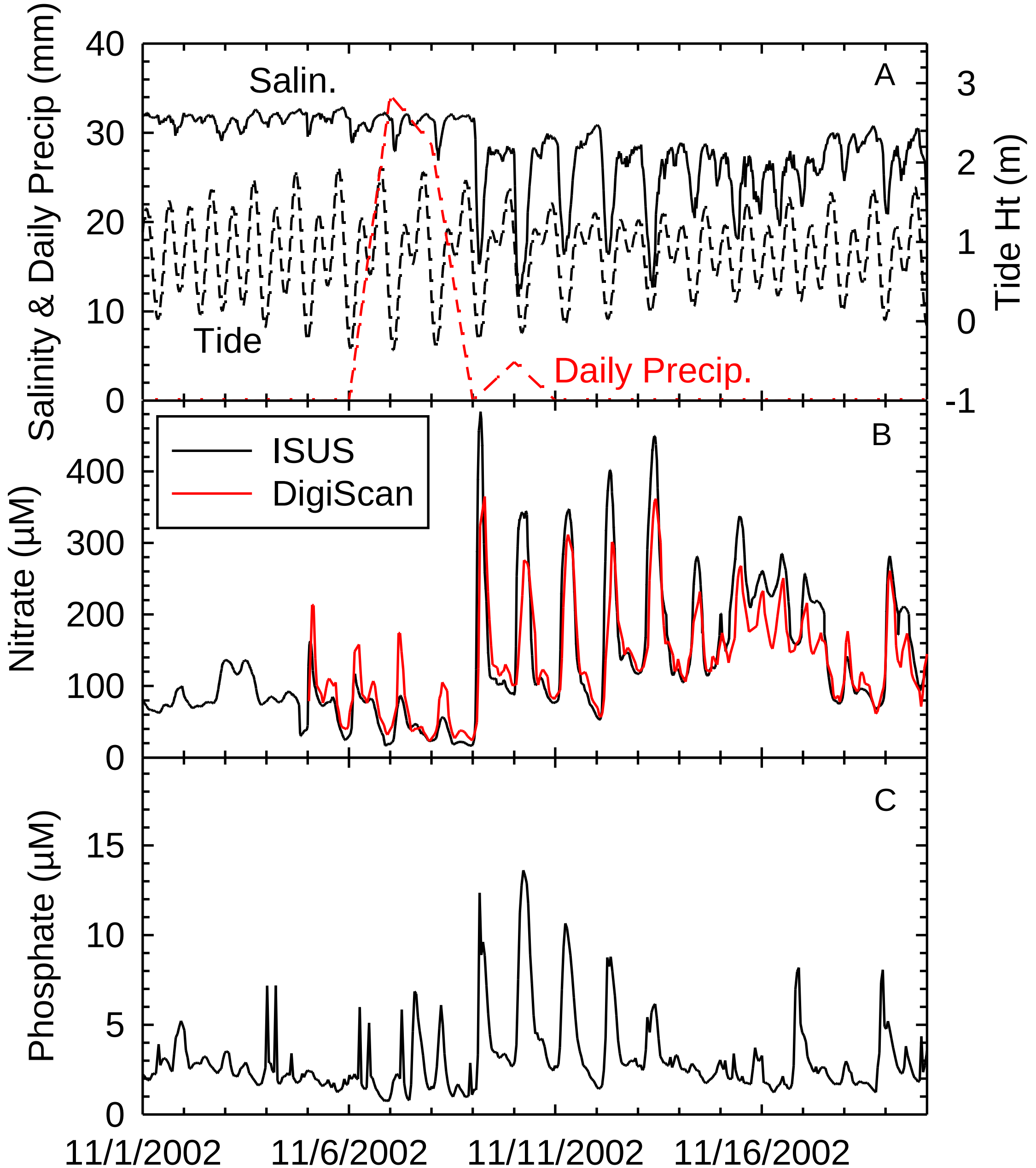
- Single pressure casing for electronics and pumps
- Sealed Battery Compartment
- Sealed air filled electronics housing
- Pressure compensated oil filled pump chamber
- Instrument size:

  Entire assembly including reagents and clamshell (not shown) 12” dia. x 24” long

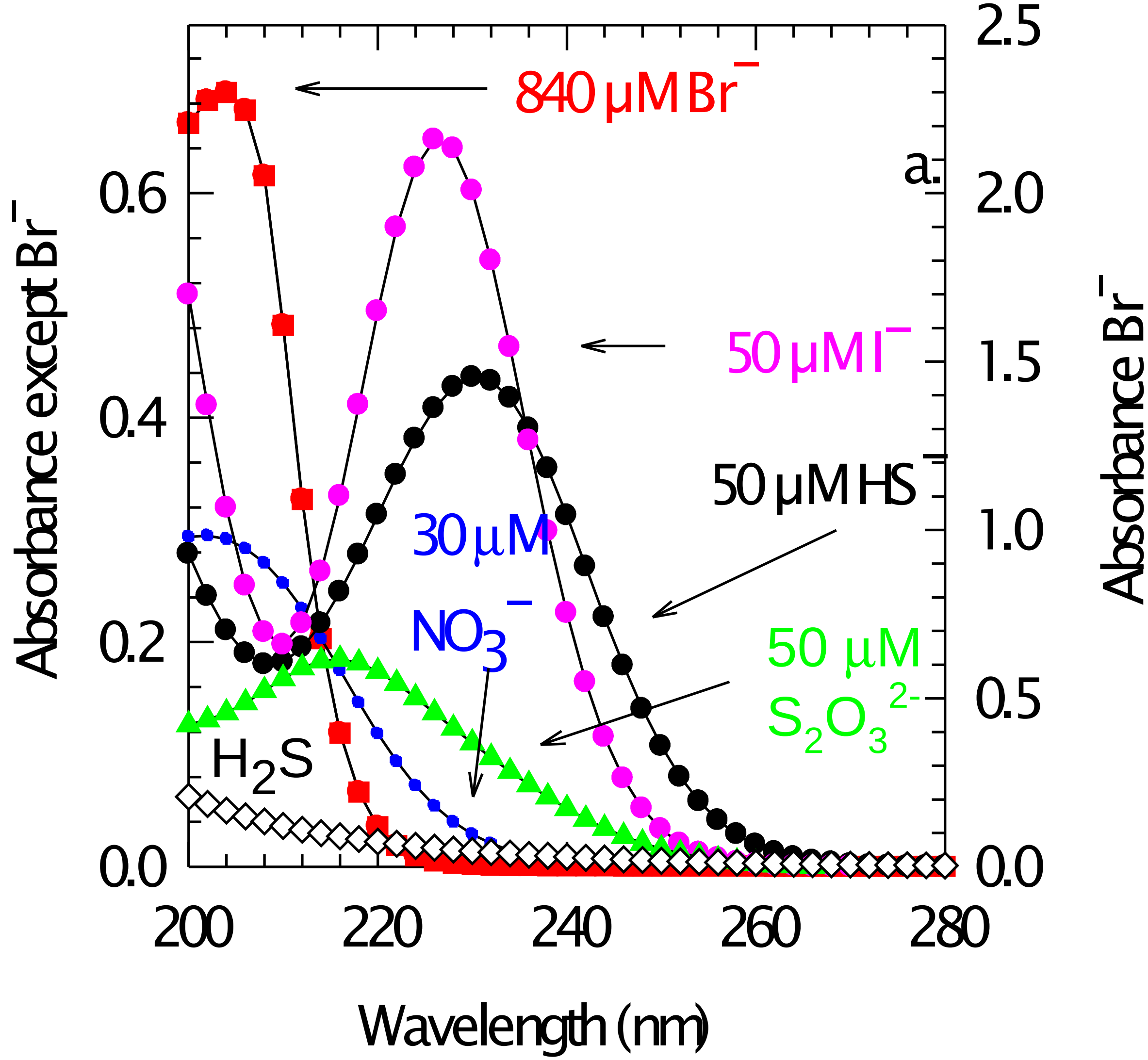


Measurements of nitrate and phosphate with DigiSCAN's in ML Harbor during the first rain event of the year.

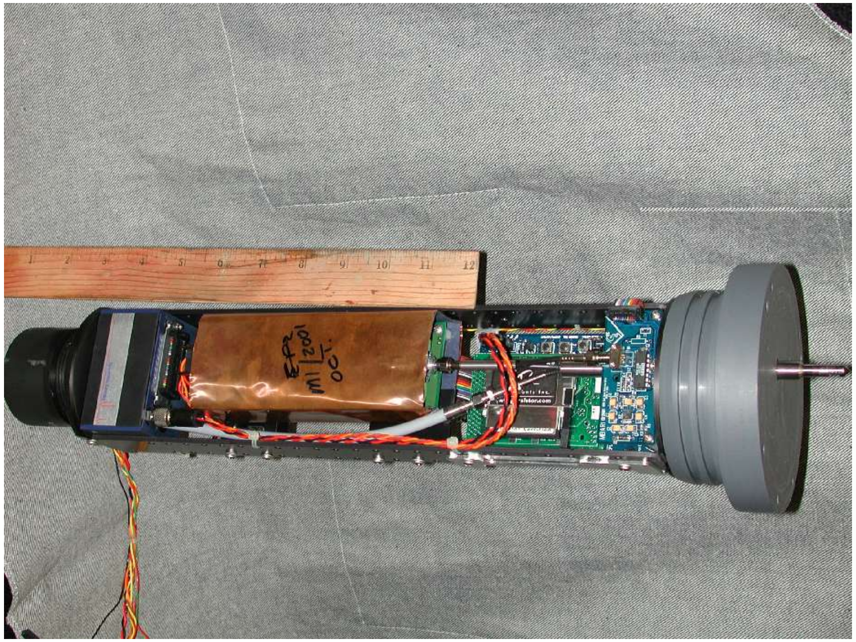
Analyzers remain the only practical systems available in a research or operational mode for other nutrients such as phosphate, Si, and Fe, but....

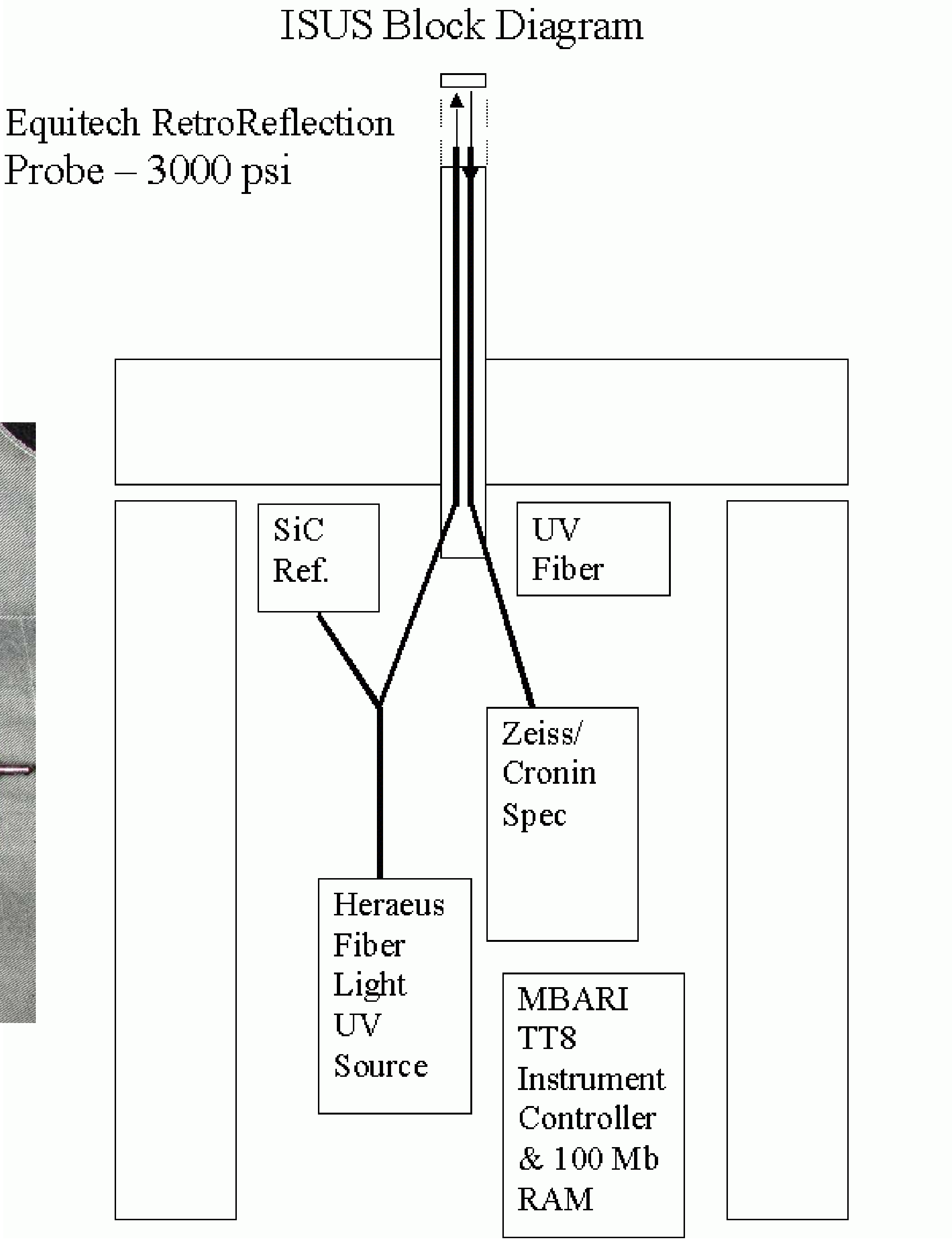


Advances in opto-electronics now make it possible to measure nitrate and bisulfide directly in seawater using their UV absorption spectrum (Johnson and Coletti, 2002).

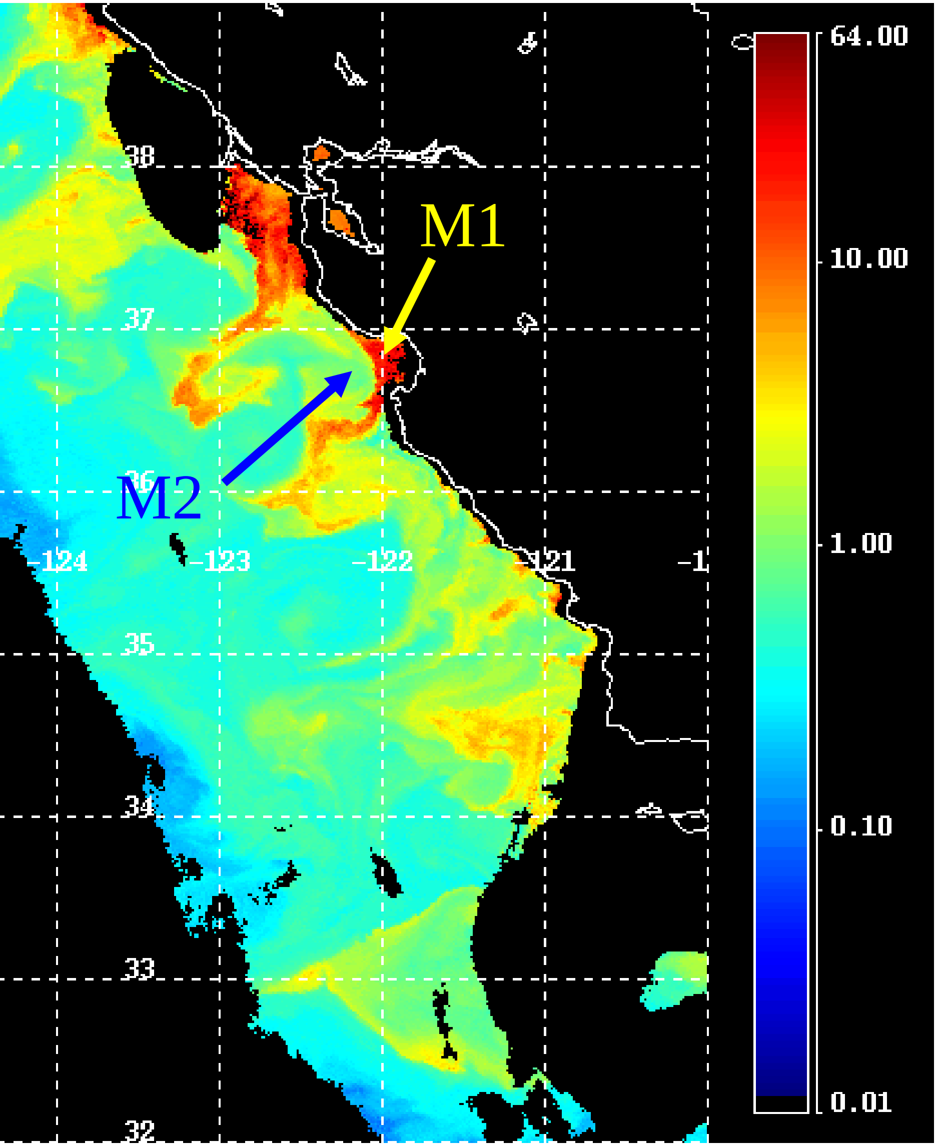


In Situ Ultraviolet Spectrophotometer - ISUS

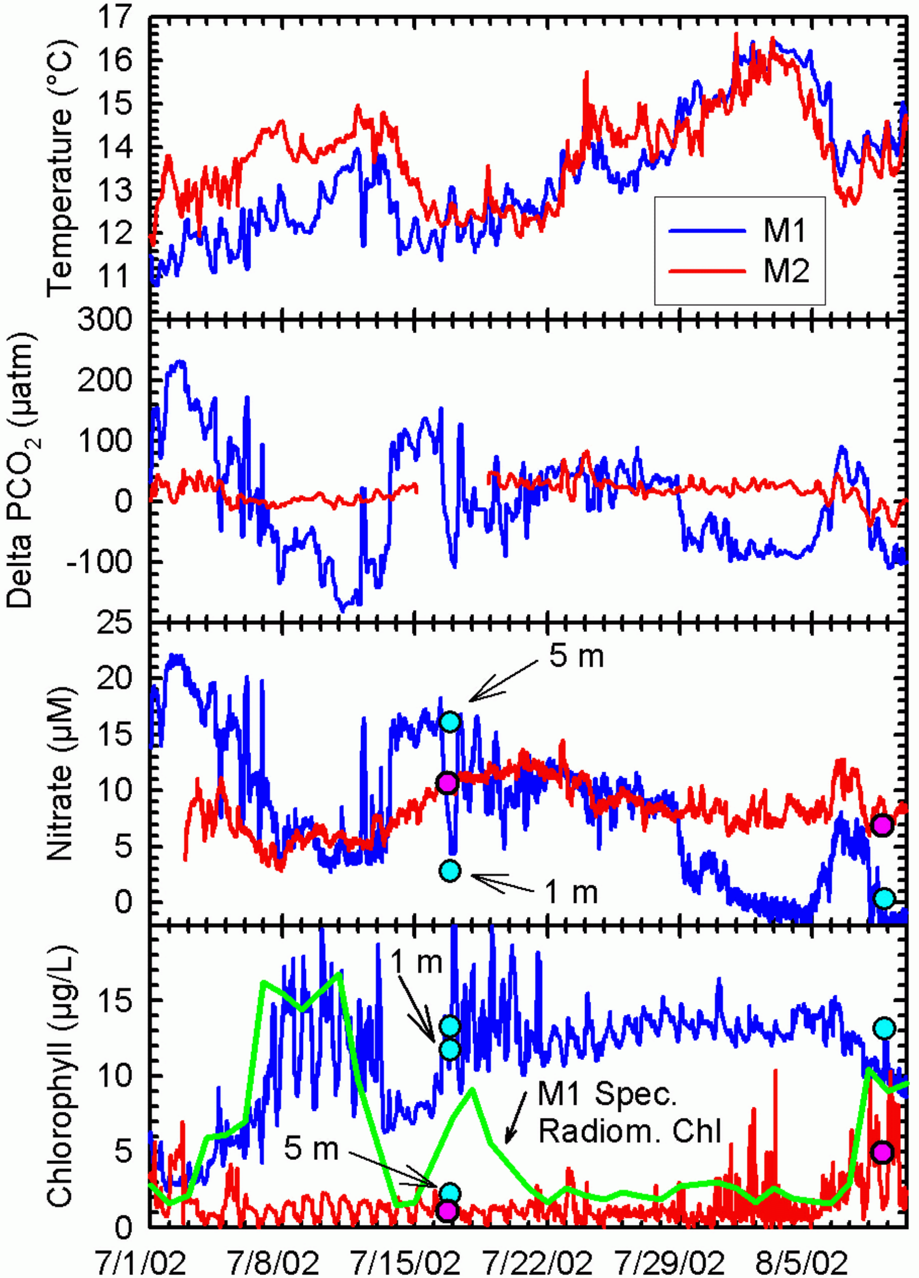




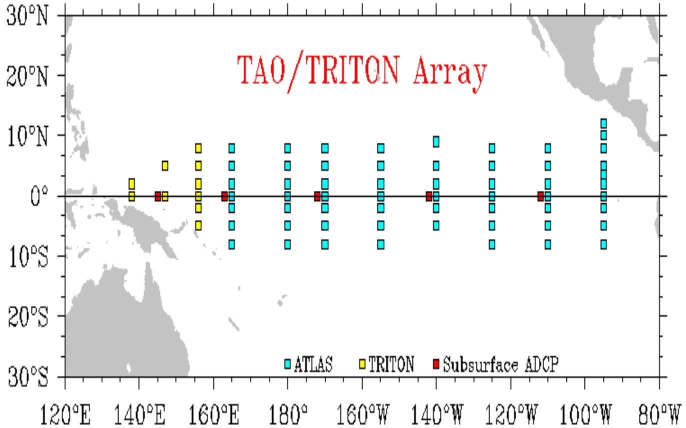
July 10, 2002 SeaWIFS Chlorophyll

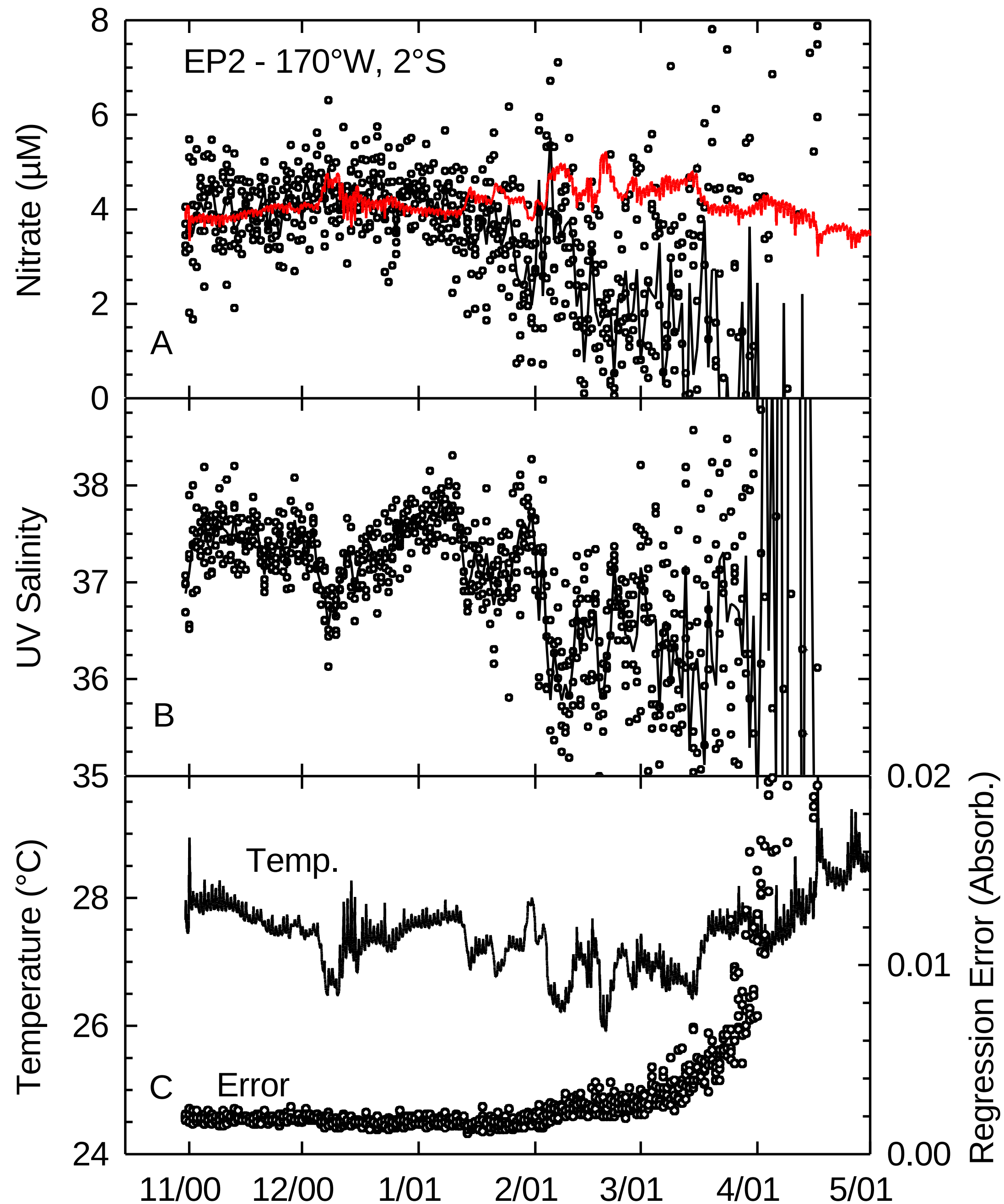


M1 & M2 Sensors July 2002



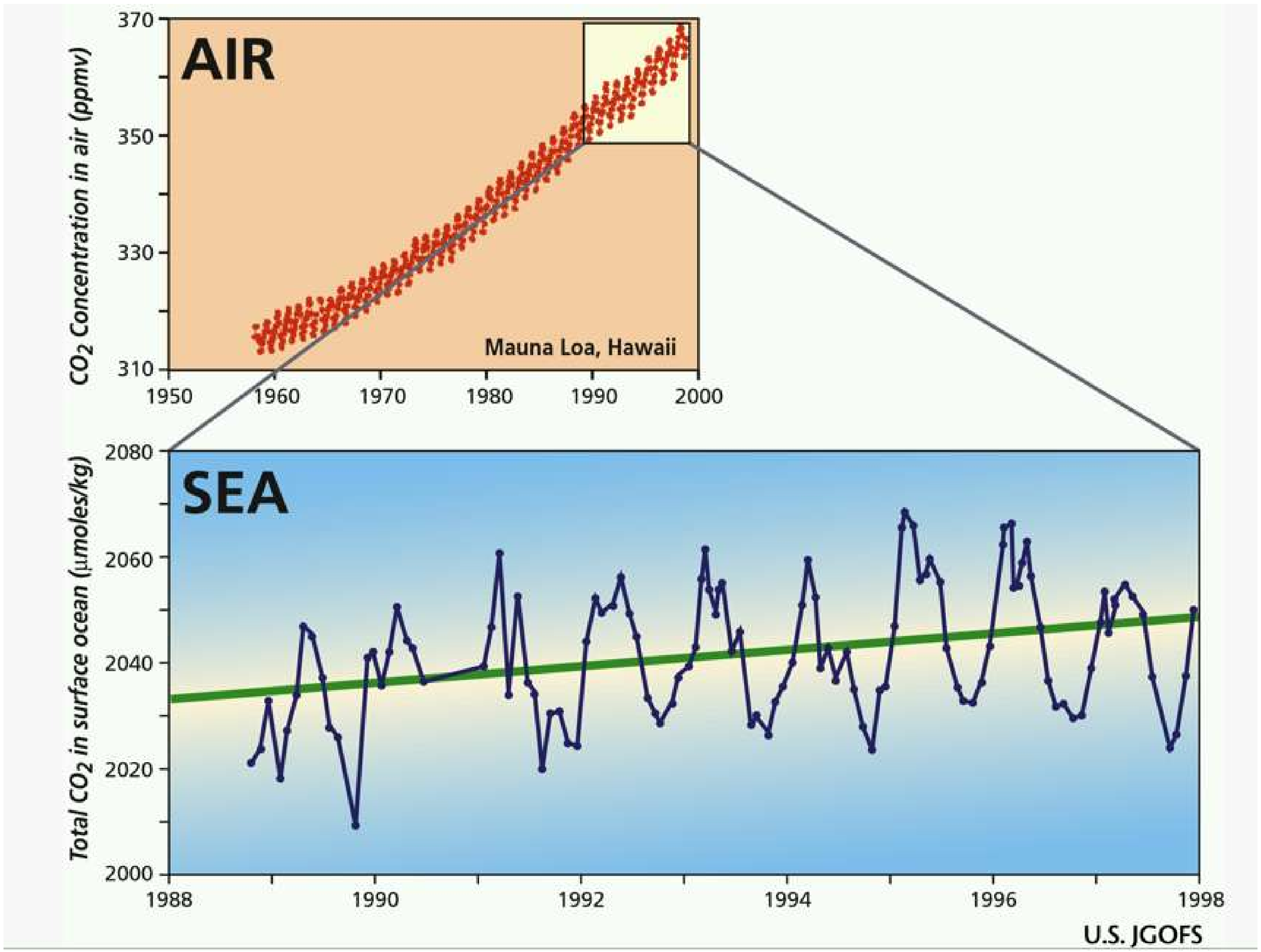
ISUS on a TAO/ TRITON mooring





The error term of the spectral fit reveals biofouling - an unfitted component of the spectrum

Measurements of carbon dioxide are key to understanding the role of the ocean in regulating composition of the atmosphere and uptake of anthropogenic carbon dioxide.



Instruments we routinely deploy on fixed moorings and surface drifters - M. Degrandpre

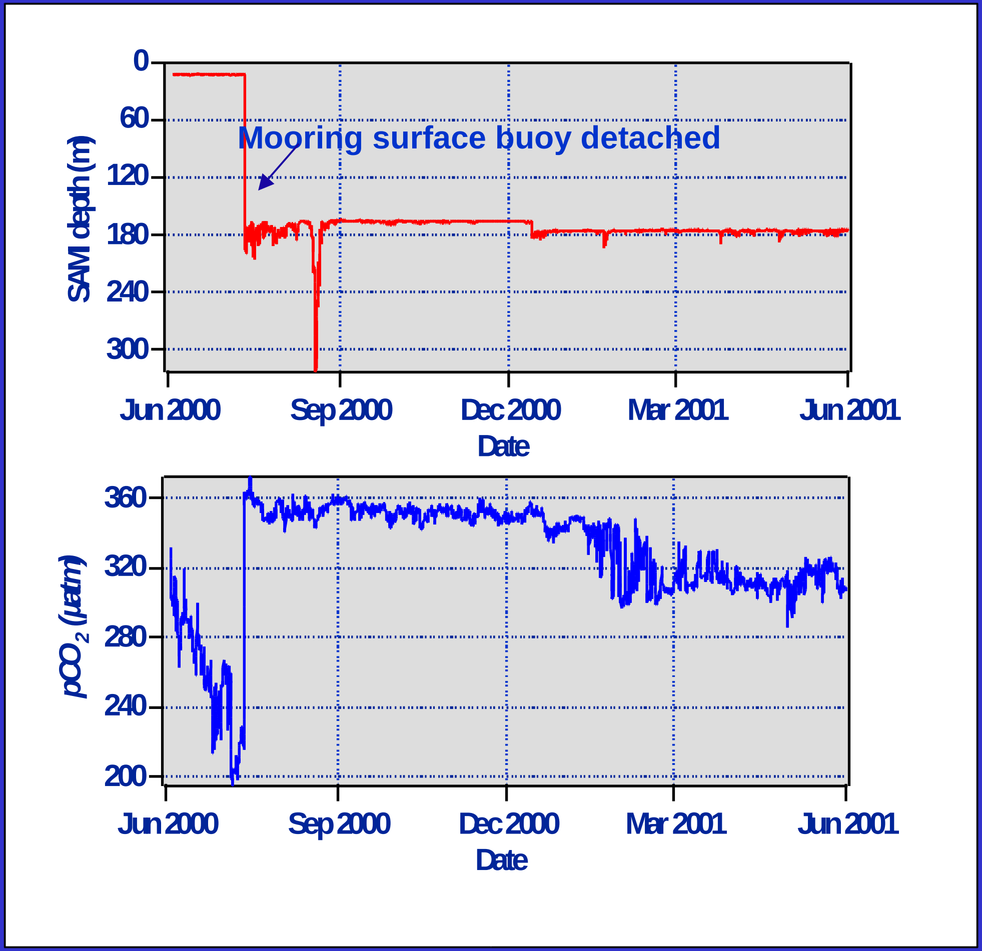
- Submersible Autonomous Moored Instrument for CO_2 (SAMI-CO_2)
- Dissolved O_2 sondes (YSI, Inc.)
- Chlorophyll-a fluorometers
- PAR, T, C, P

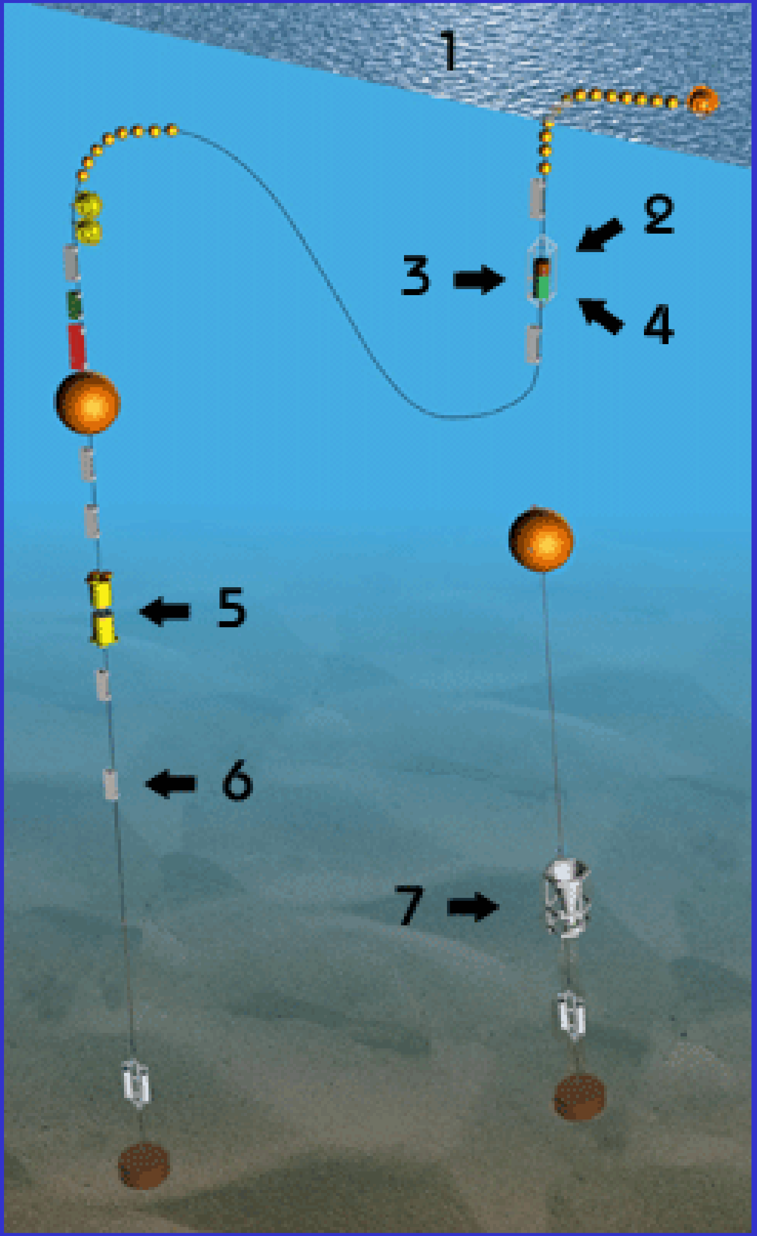
SAMI-CO_2

Labrador Sea mooring

SAMI was located at position 2 at right

(M.DeGrandpre in collaboration with U. Send, D. Wallace)





pCO$_2$ measured with the CARIOCA drifting buoy in the equatorial Atlantic. June 20 - Sept. 15, 1997 (Bakker et al., 1997).

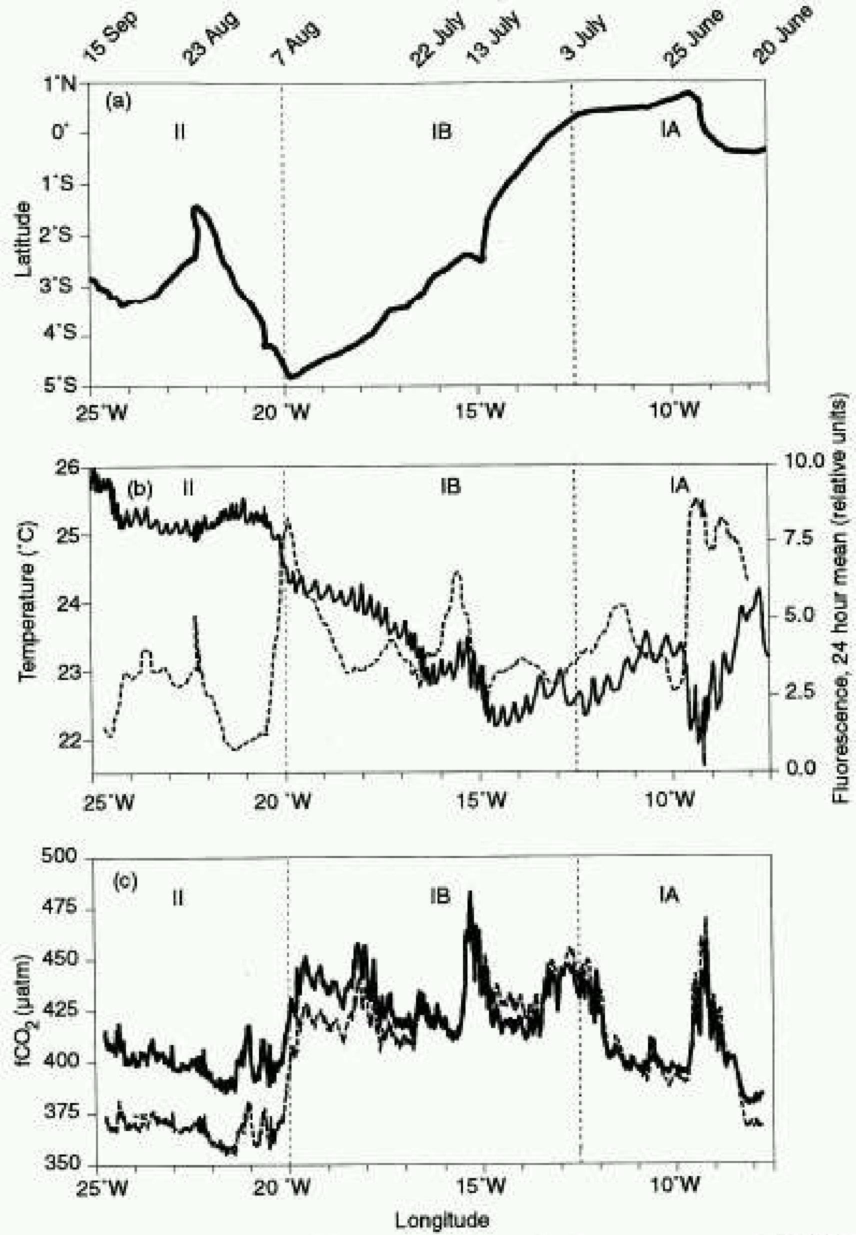
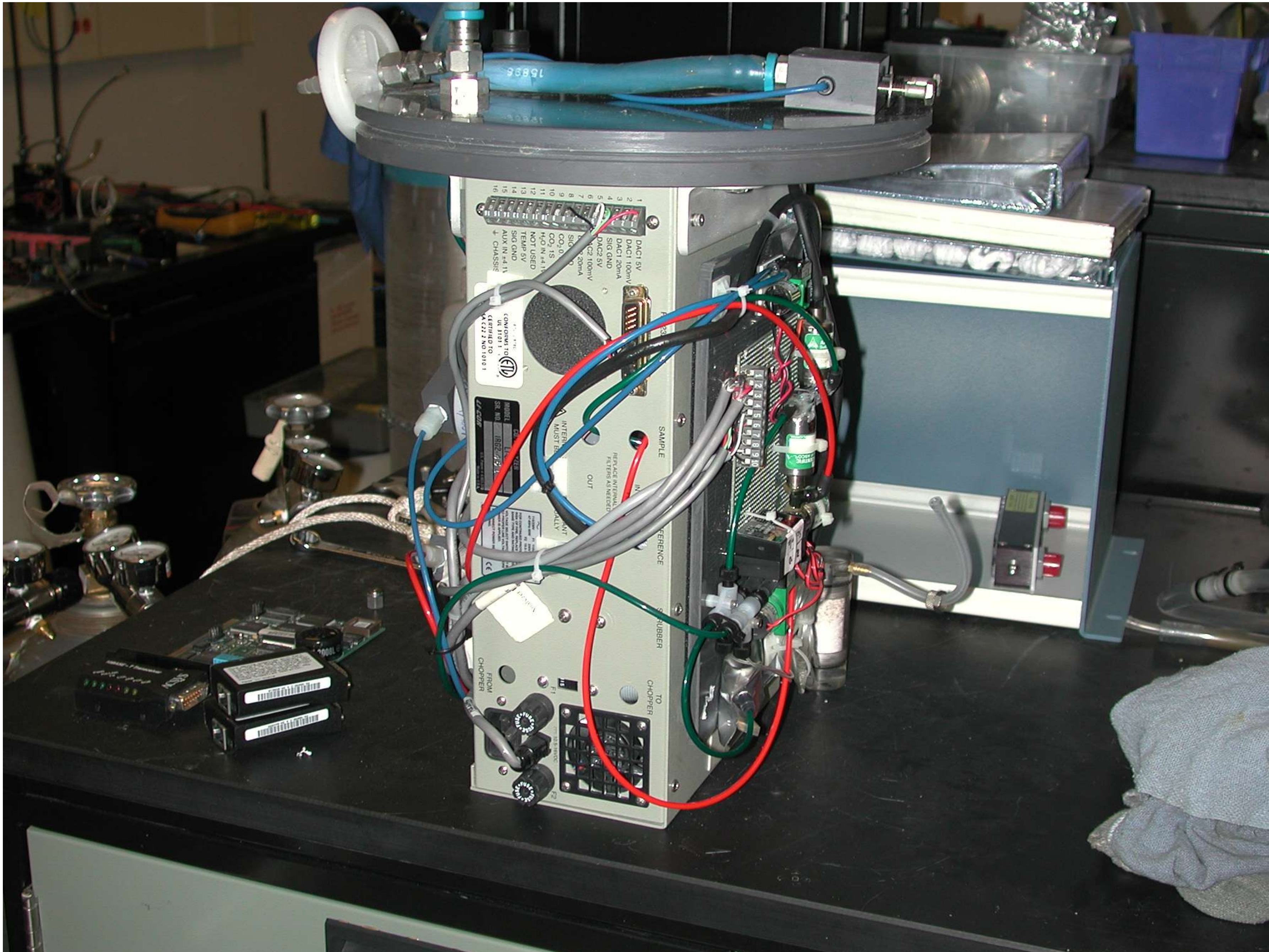
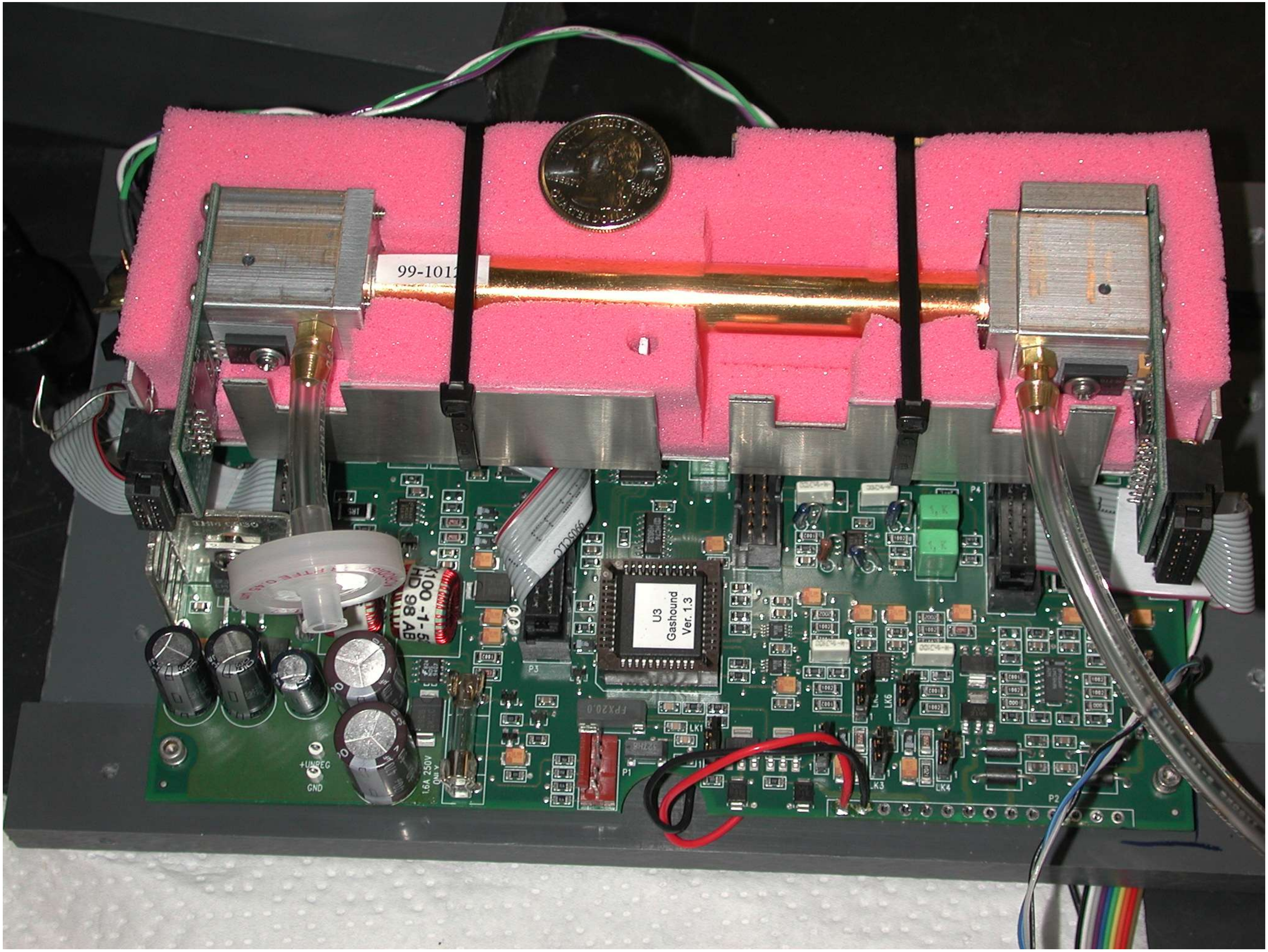
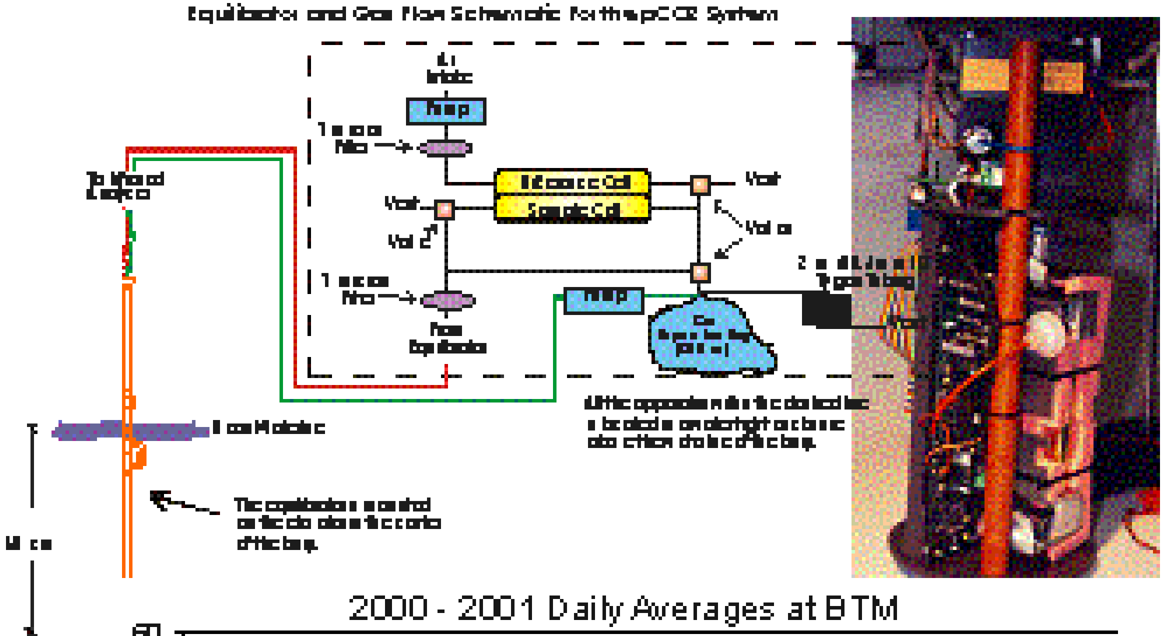
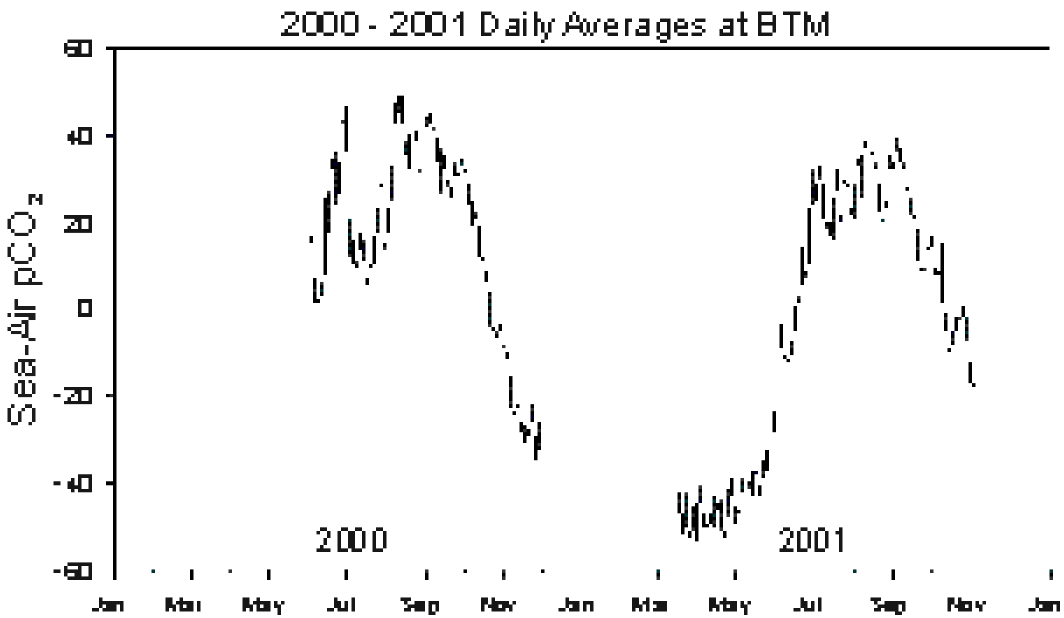


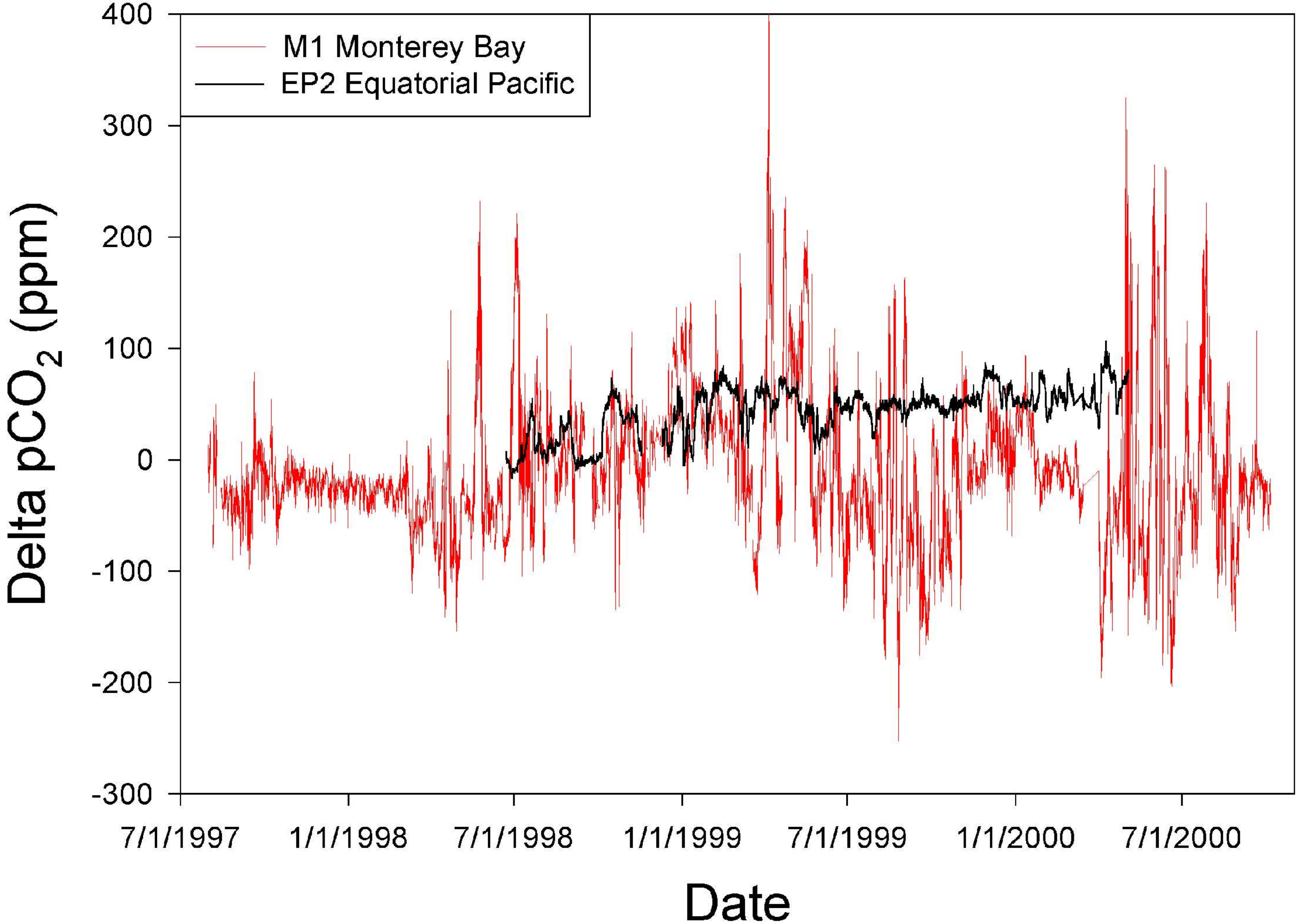
Figure 4. (a) The westward trajectory of the CARIOCA buoy, (b) the water temperature (thick line) and the 1 day running average of fluorescence (dashed line), and (c) fCO$_2$ (thick line) and fCO$_2$ at 23°C (dashed line) against longitude from June 20 to September 15, 1997. Vertical lines separate the zones IA, IB, and II.


DAC1 5V
DAC1 100mV
DAC1 20mA
SIG GND
DAC2 5V
NOT USED
TEMP 5V
SIG GND
SAMPLE
REPLACE INTERNAL FILTERS AS NEEDED
OUT
FROM CHOPPER
TO CHOPPER


99-1012
U3
Gashound
Ver. 1.3
+UNREG
GND
1.6A 250V
P1
P2
P3
P4
LK1
LK3
LK4
LK6

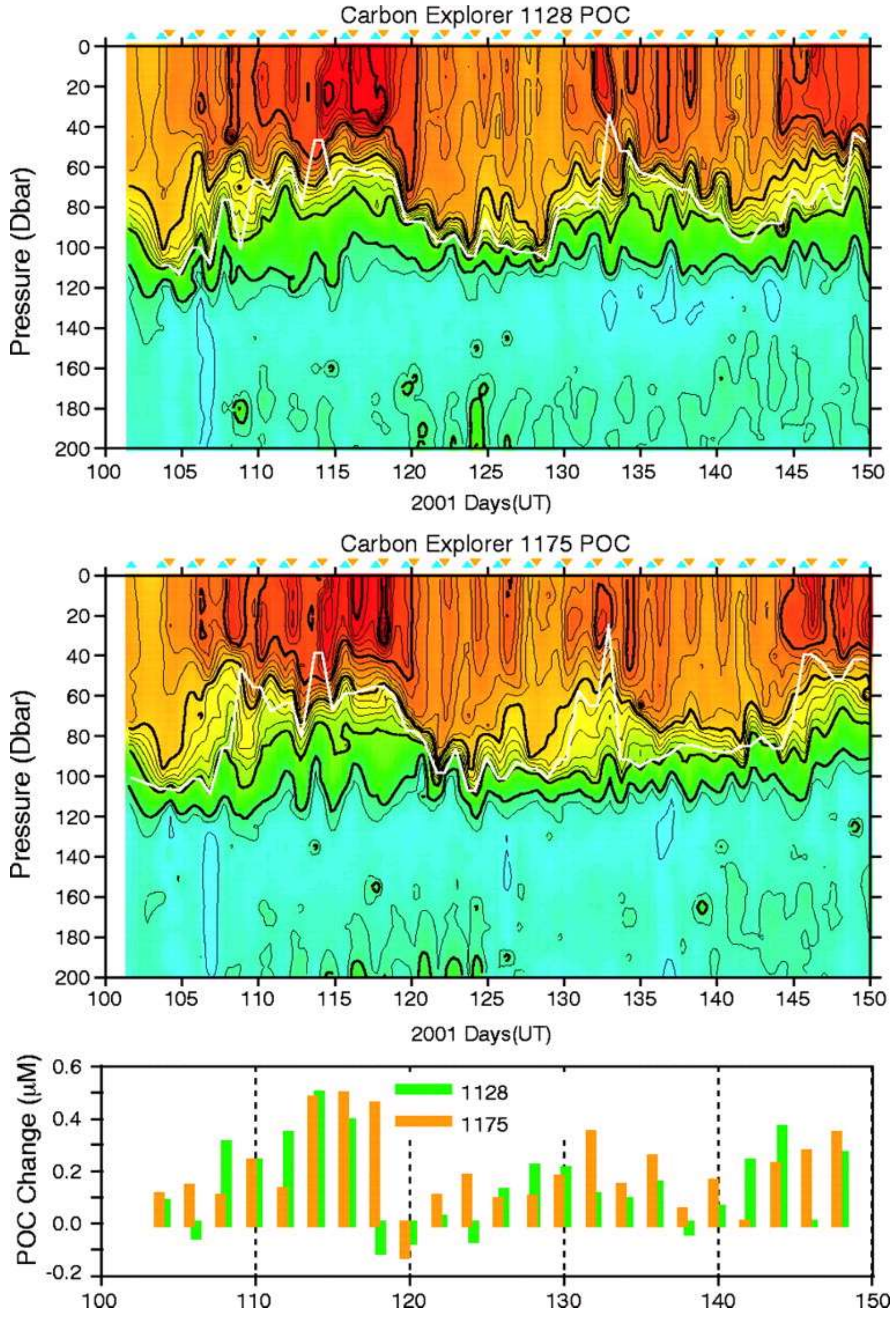

Equilibrator and Gas Flow Schematic for the pCO2 System
Pump
Reference Cell
Sample Cell
Vent
Vent
Pump


2000 - 2001 Daily Averages at BTM
Sea-Air pCO2
60
40
20
0
-20
-40
-60
2000
2001
Jan
Mar
May
Jul
Sep
Nov
Jan
Mar
May
Jul
Sep
Nov
Jan

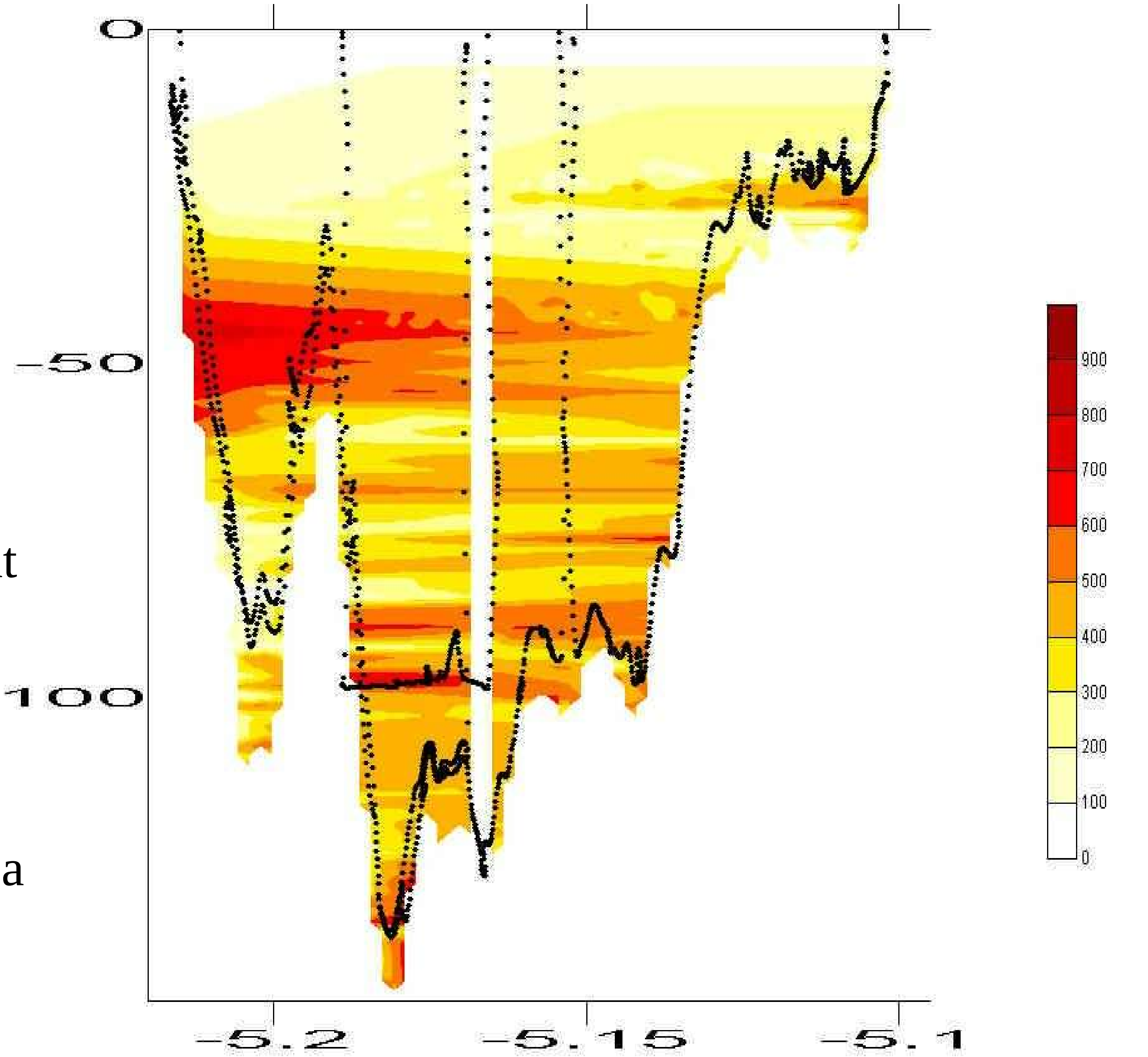


M1 Monterey Bay
EP2 Equatorial Pacific
400
300
200
100
0
-100
-200
-300
Delta pCO_2 (ppm)
7/1/1997
1/1/1998
7/1/1998
1/1/1999
7/1/1999
1/1/2000
7/1/2000
Date

Time series of POC variability from SOLO1128 and SOLO1175 in Subarctic N. Pacific inferred from transmissometer measurements (Bishop et al., 2002)

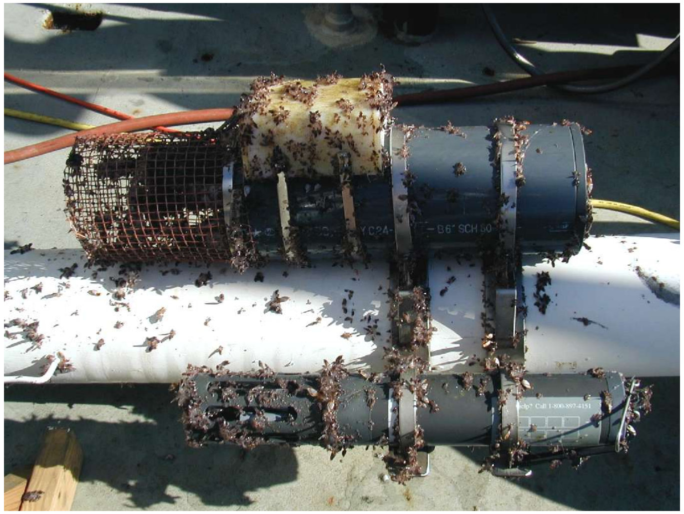


Some progress is being made with metal measurements. e.g. Mn (nM) determined with SCANNER type instrument on AutoSub AUV in a Scottish Loch (D. Connelly, IOS). This area is still researchy!

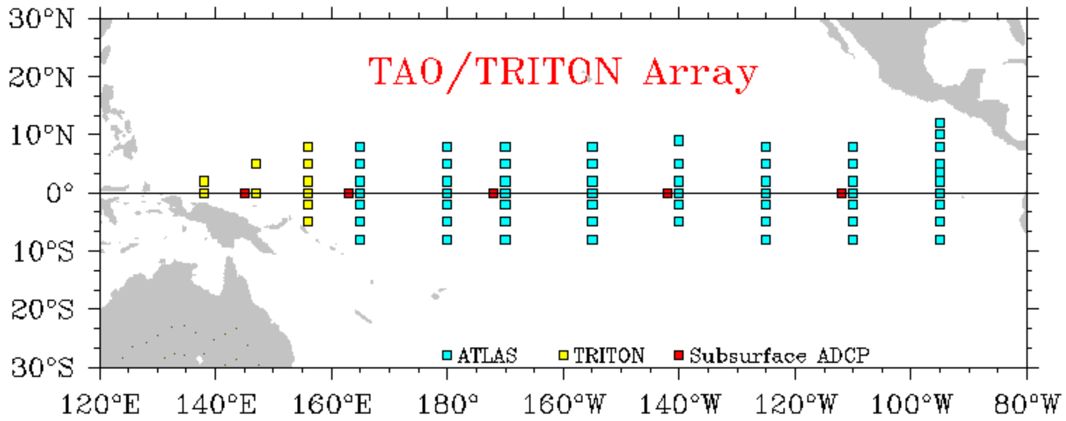


What are the issues with present technology?

- sensors
  - resistance to fouling
  - calibration
  - few chemicals
- analyzers
  - complexity
  - cost
  - high operator skill
  - size
  - power

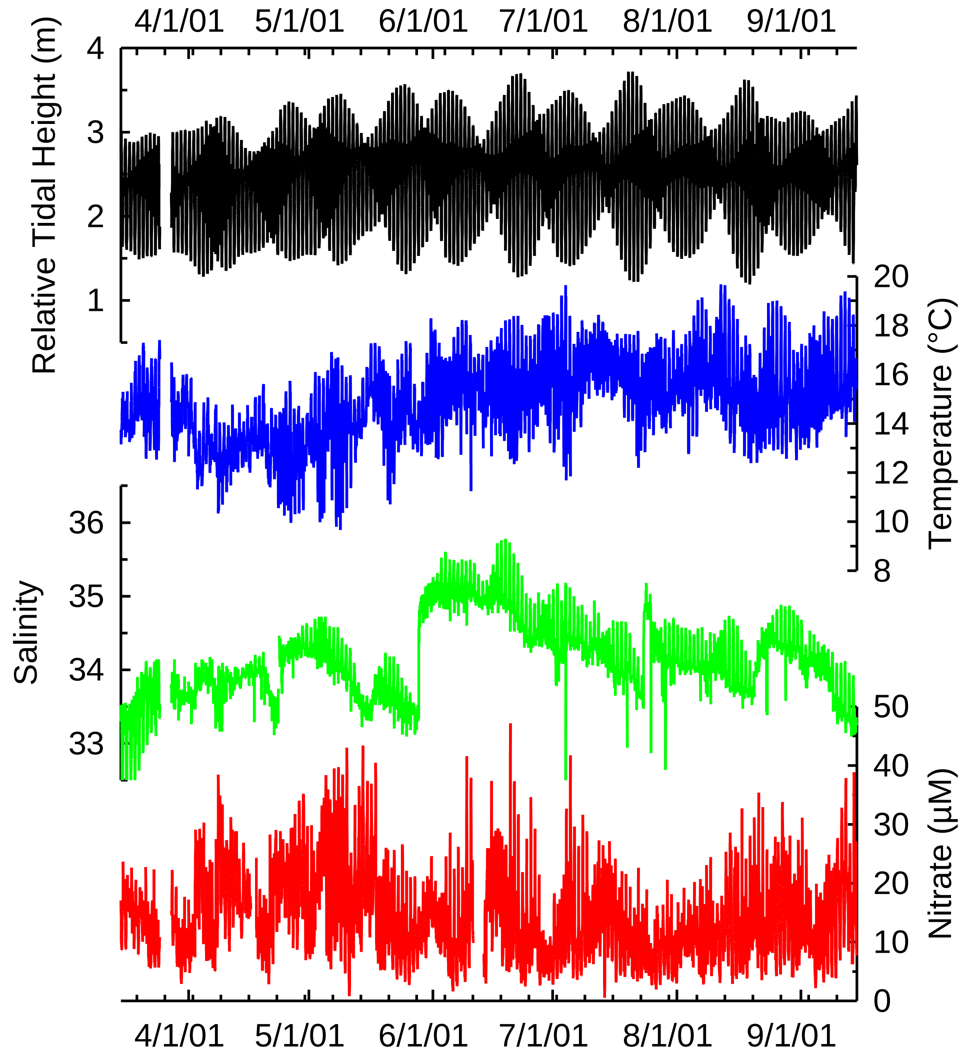


New Millenium science is not just one mooring!



Analyzers can be highly resistant to fouling and still generate quality data:

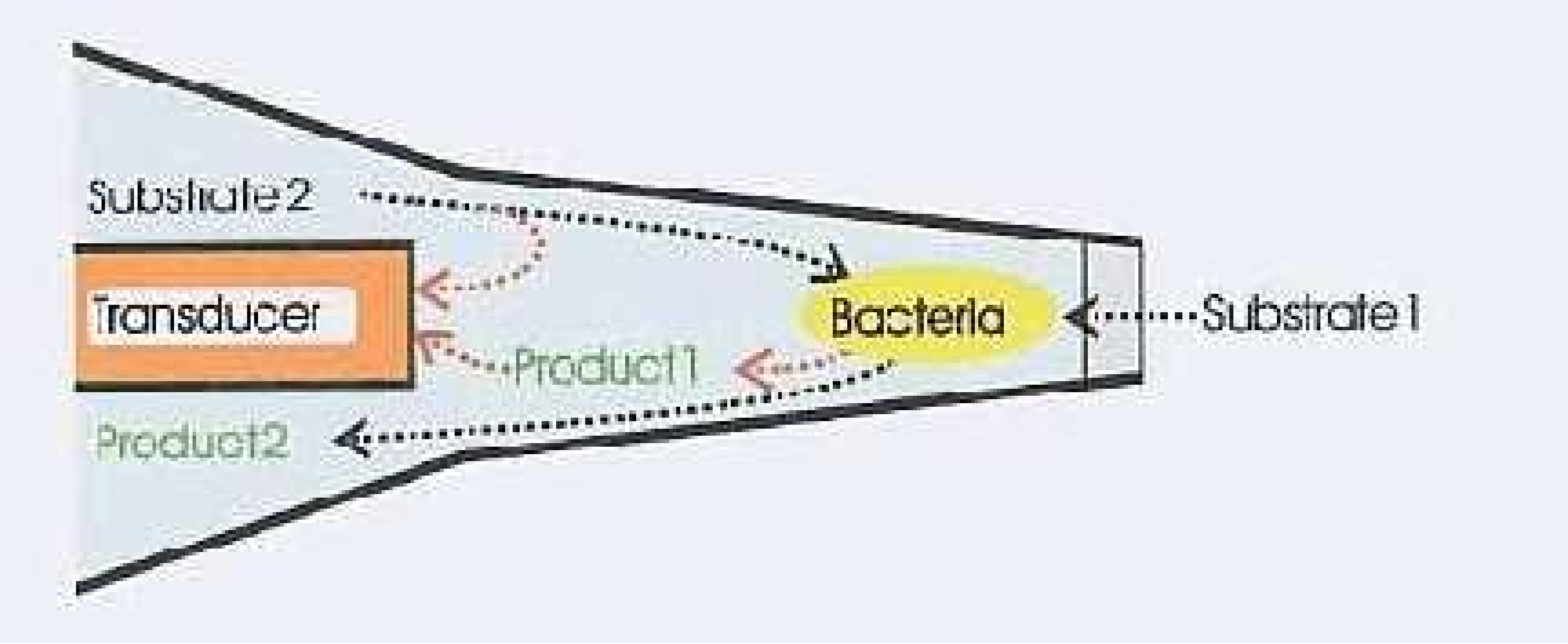
During several 2 month long deployments in Elkhorn Slough nitrate is robust, salinity is not.



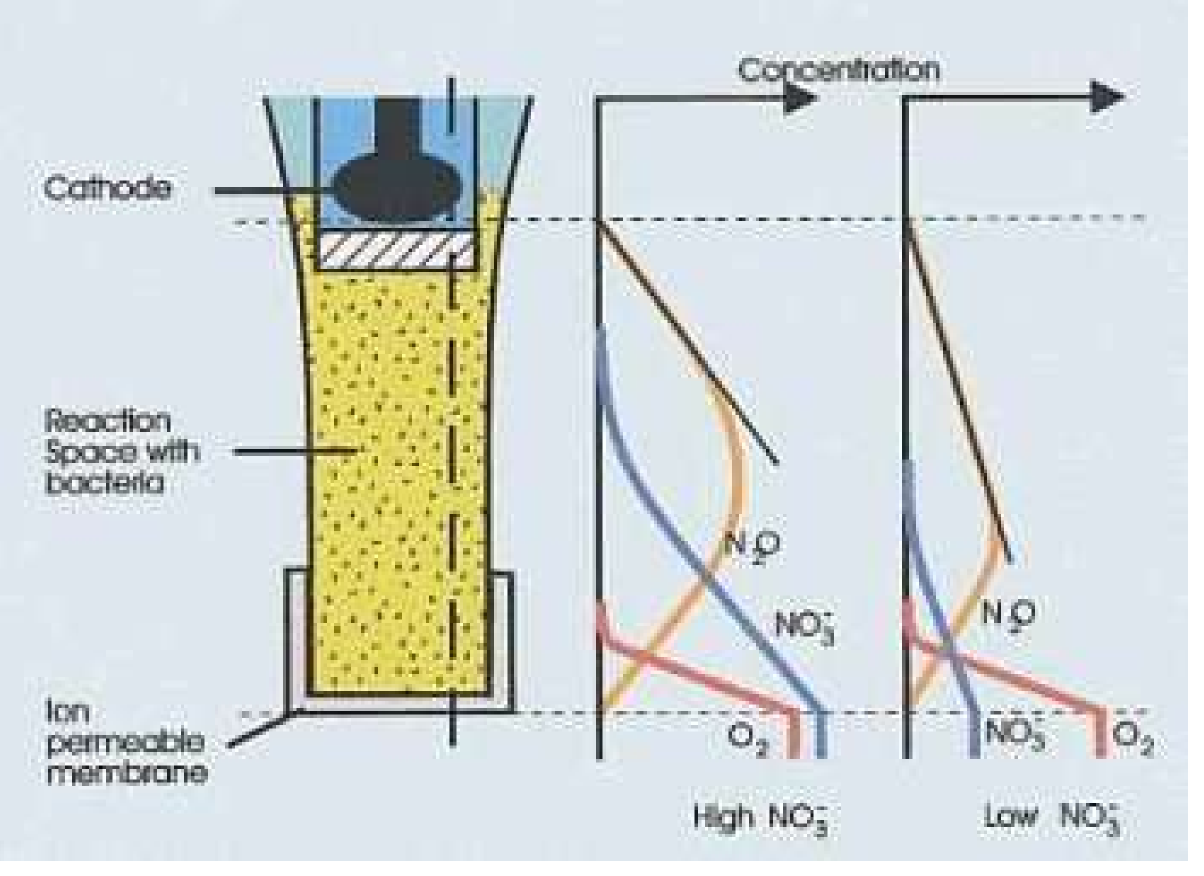
What's coming?

- Biosensors

- Niels Peter Revsbech, Department of Microbial Ecology, Institute of Biology, University of Aarhus, DK



Nitrate and nitrite biosensors using genetically modified bacteria



Smaller, cheaper, more robust analyzers are required:

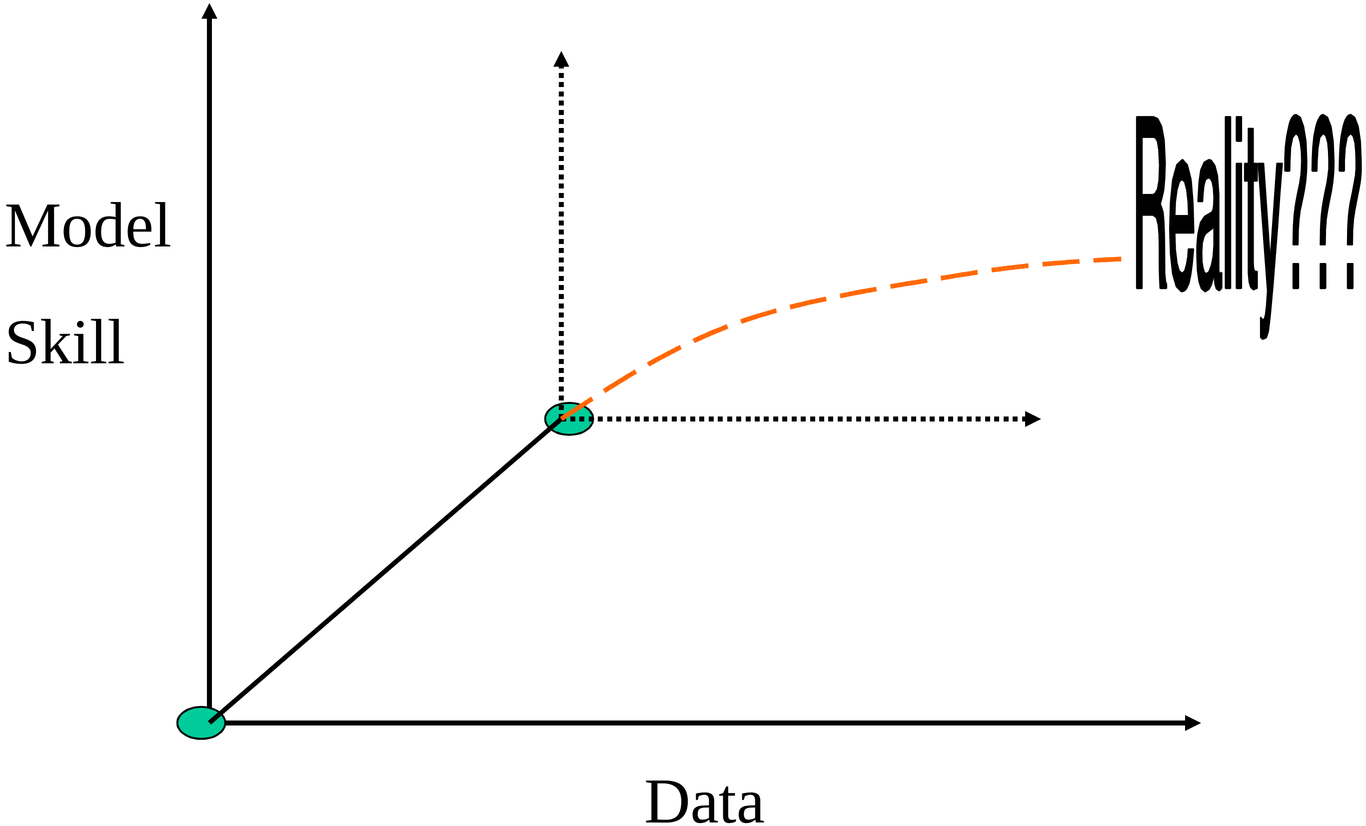
- Is micro-fluidics the answer, or will "milli-fluidics" do?
    - MBARI Solid State Analyzer (Jannasch et al., 2002)
- What do we do about low response rates dictated by chemical reactions?
    - Only measure in mixed layer with vertically profiling devices?

Are any chemical sensor systems ready for global programs?

Probably not today! They have to be deployable in numbers of >100's. Most current systems have << 10 instruments deployed by any one laboratory or require a lot of TLC.

The challenge is to move from research to a global monitoring program!

BUT WE DON'T NEED DATA - WE'LL JUST MODEL "IT"!!!



MORE DATA = BETTER MODELS