Examples of how gliders/floats might be used to conduct experiments in low oxygen/denitrification zones

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Major Issues

-High resolution sediment records

-N_2O sources to atm

-Interesting biology

-Loss of fixed N (denitrification and/or Anammox)

-Low pH zones, carbonate dissolution zones

Possible Experimental Sites

#1--Black Sea--N budget
#2--California Borderland--$CaCO_3$ dissol.
#3--E. Tropical Pacific--denitrification vs. anammox
#4--Coastal Oregon--hypoxia

E. Tropical Pacific

Oxygen (µM)

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Oxygen at 400 m

Stramma et al. 2008

Gliders/Floats

--denitrification vs. anammox

N2 via denitrification involves C_{org} oxidation

N2 via anammox involves ammonia oxidation

First, the basic metabolic differences between the two groups of organisms involved (in Anammox and denitrification) mean that their activities might be differentially regulated and thus they might respond differently to environmental change,such as in oxygen or organic carbon supply.

Second, although the enzymatic pathway of anammox is not completely known, it is pretty clear that the powerful greenhouse gas nitrous oxide does not figure as an intermediate, as it does in denitrification.

Third, if anammox is established to be the quantitatively most significant pathway for N2 loss in some extensive marine environments (as currently suggested), it will change our view of how organic matter is remineralized under oxygen-limited conditions.

--B. Ward et al. 2007

Gliders/Floats

--denitrification vs. anammox final product is N_2

N_2 via denitrification involves C_{org} oxidation

-How much N_2 is present, where is is formed, can it be accounted for by nitrate deficiency with corresponding increase in TCO_2?

N_2 via anammox involves ammonia oxidation

-Where does the ammonia come from?

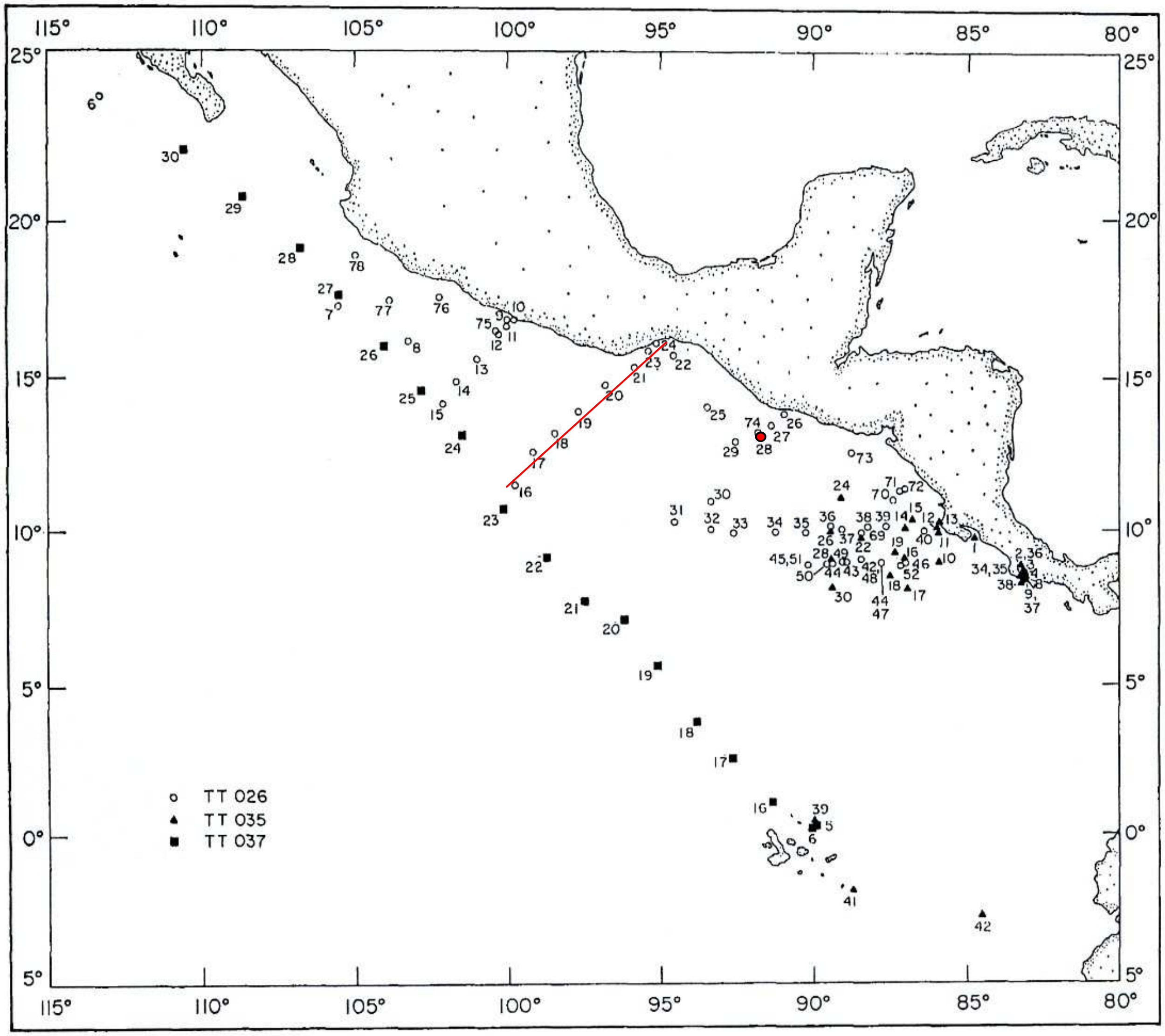


FIG. 1. Station locations for PONCHO (TT-026) and PISCO (TT-035, TT-037).

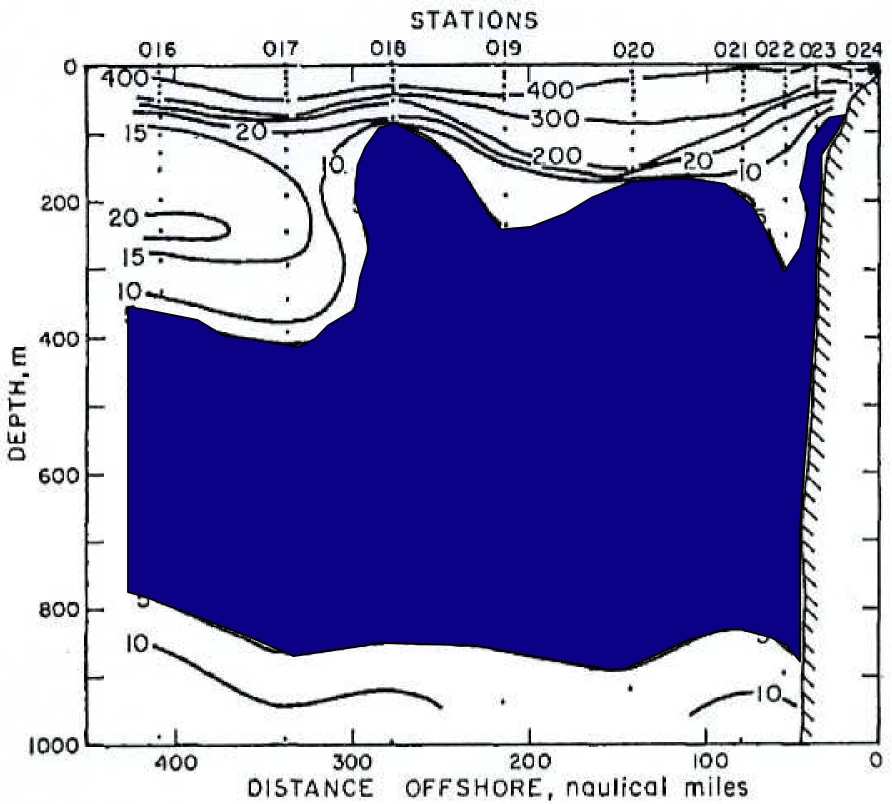


FIG. 2. Oxygen concentrations (μg-atoms/liter) along a section normal to the southern coast of Mexico (PONCHO, stations 16–24, TT-026). Oxygen concentrations less than ca. 25 μg-atoms/liter were measured by the colorimetric procedure of Broenkow and Cline (1969).

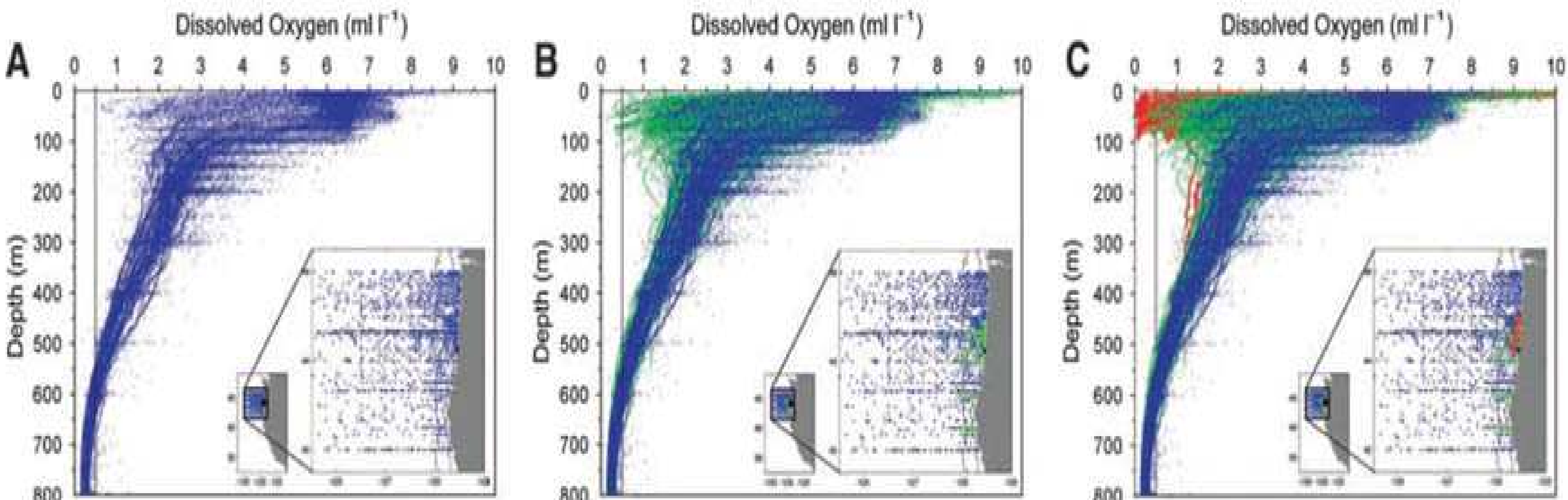
-Low O2 water in contact with shelf/slope sediments--> ammonia and Fe source

Oregon Coast Hypoxia

1950-1999

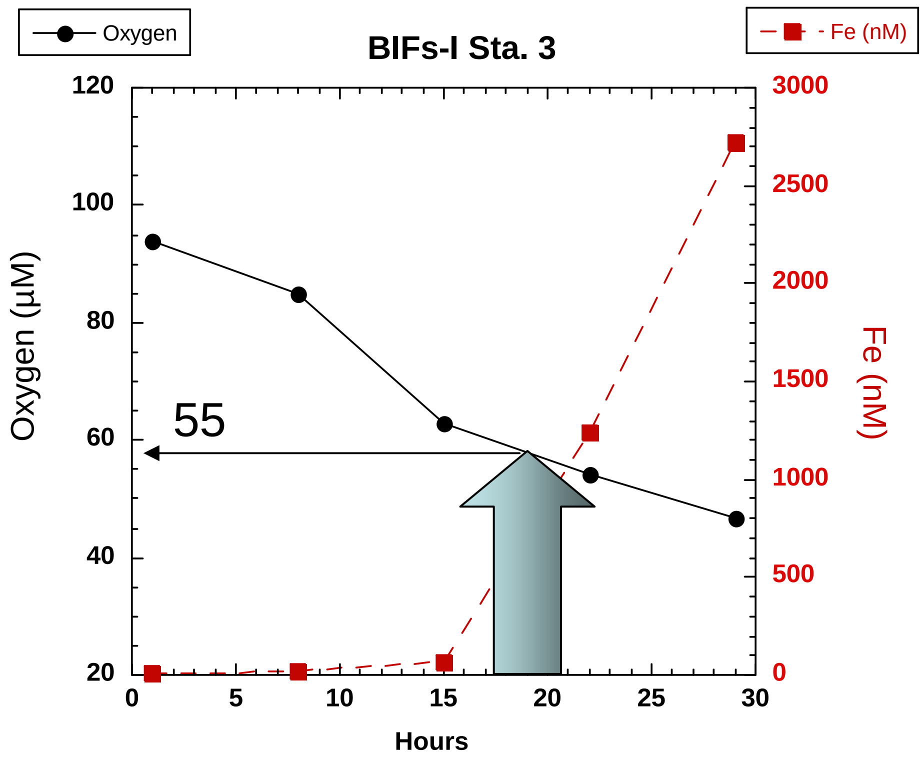
2000-2005

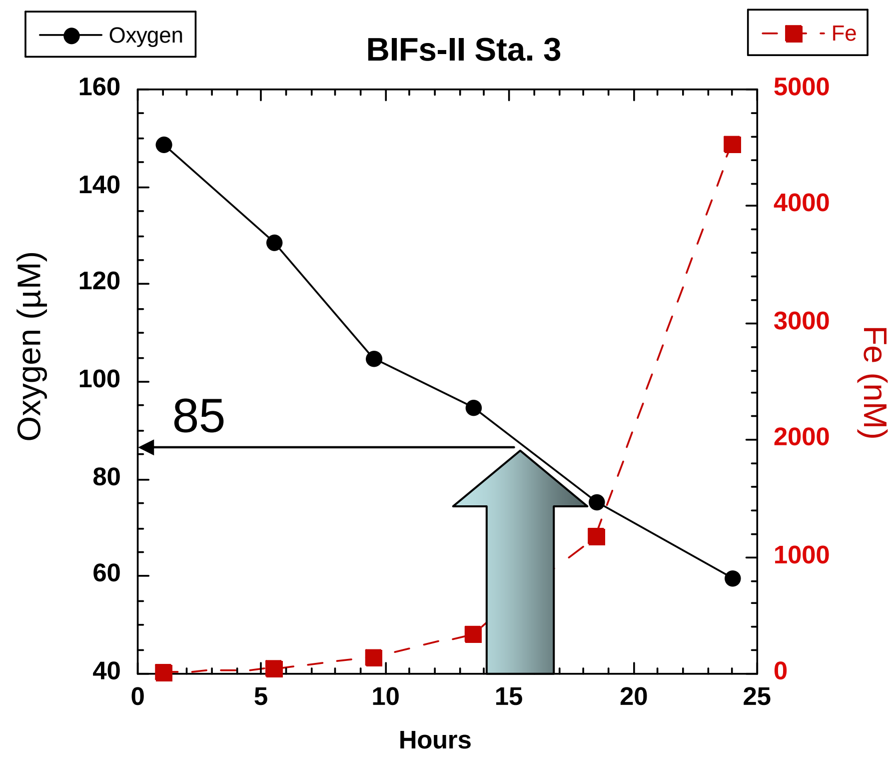
2006



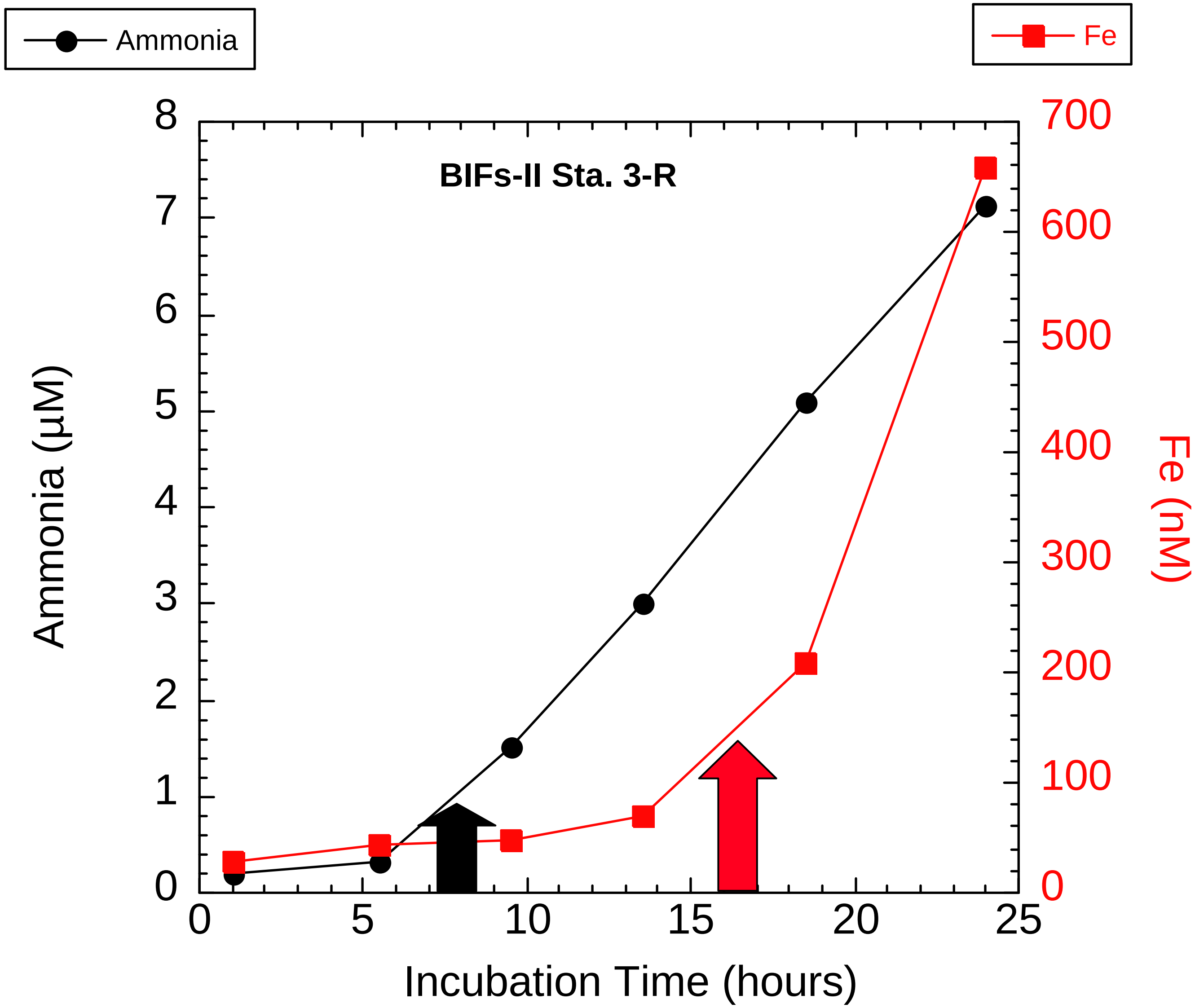
22 µM

Chan et al. 2008





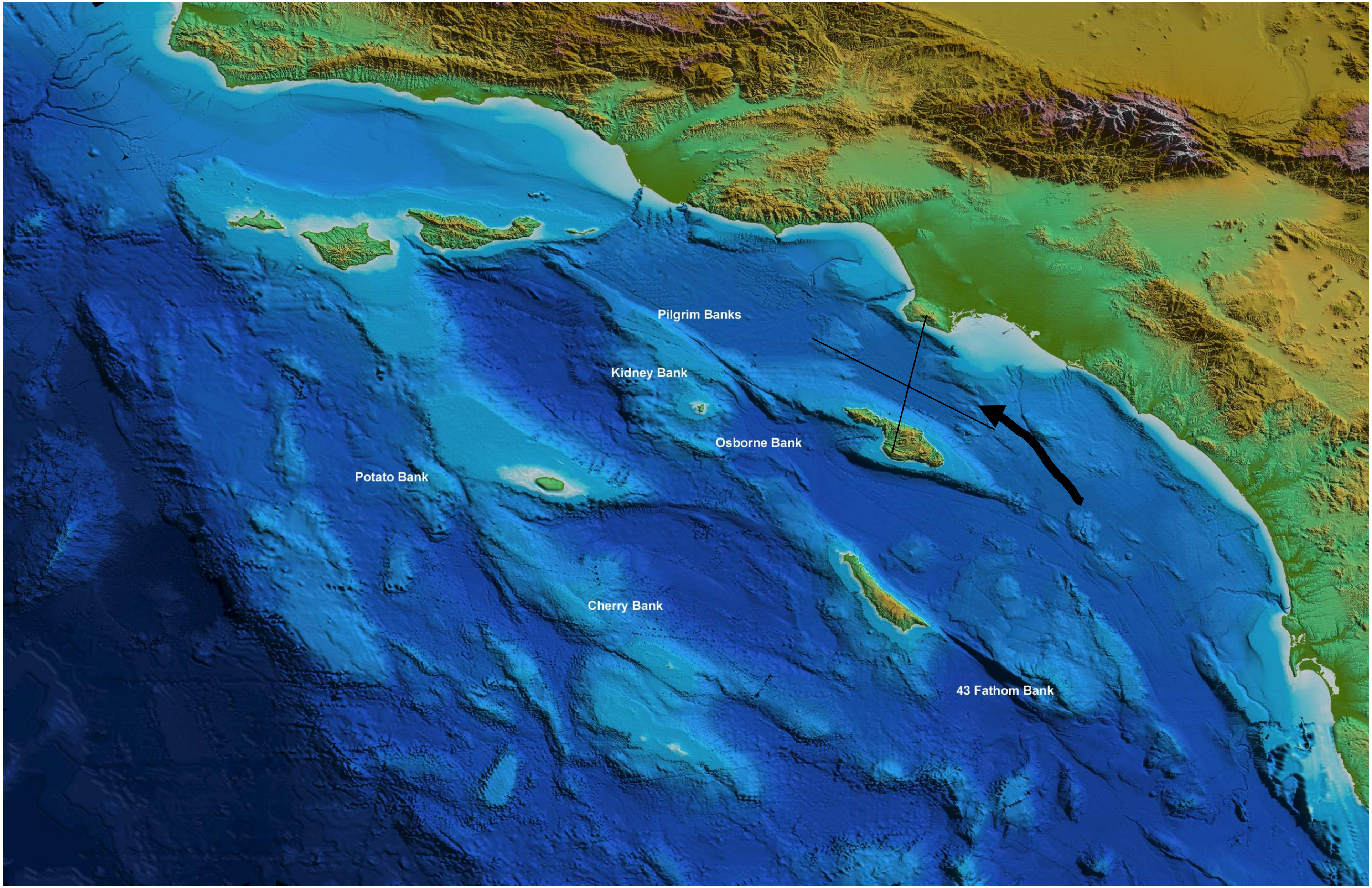
Berelson, McManus et al. in prep


Ammonia
Fe
BIFs-II Sta. 3-R
Ammonia (μM)
Fe (nM)
Incubation Time (hours)
0
1
2
3
4
5
6
7
8
0
100
200
300
400
500
600
700
0
5
10
15
20
25

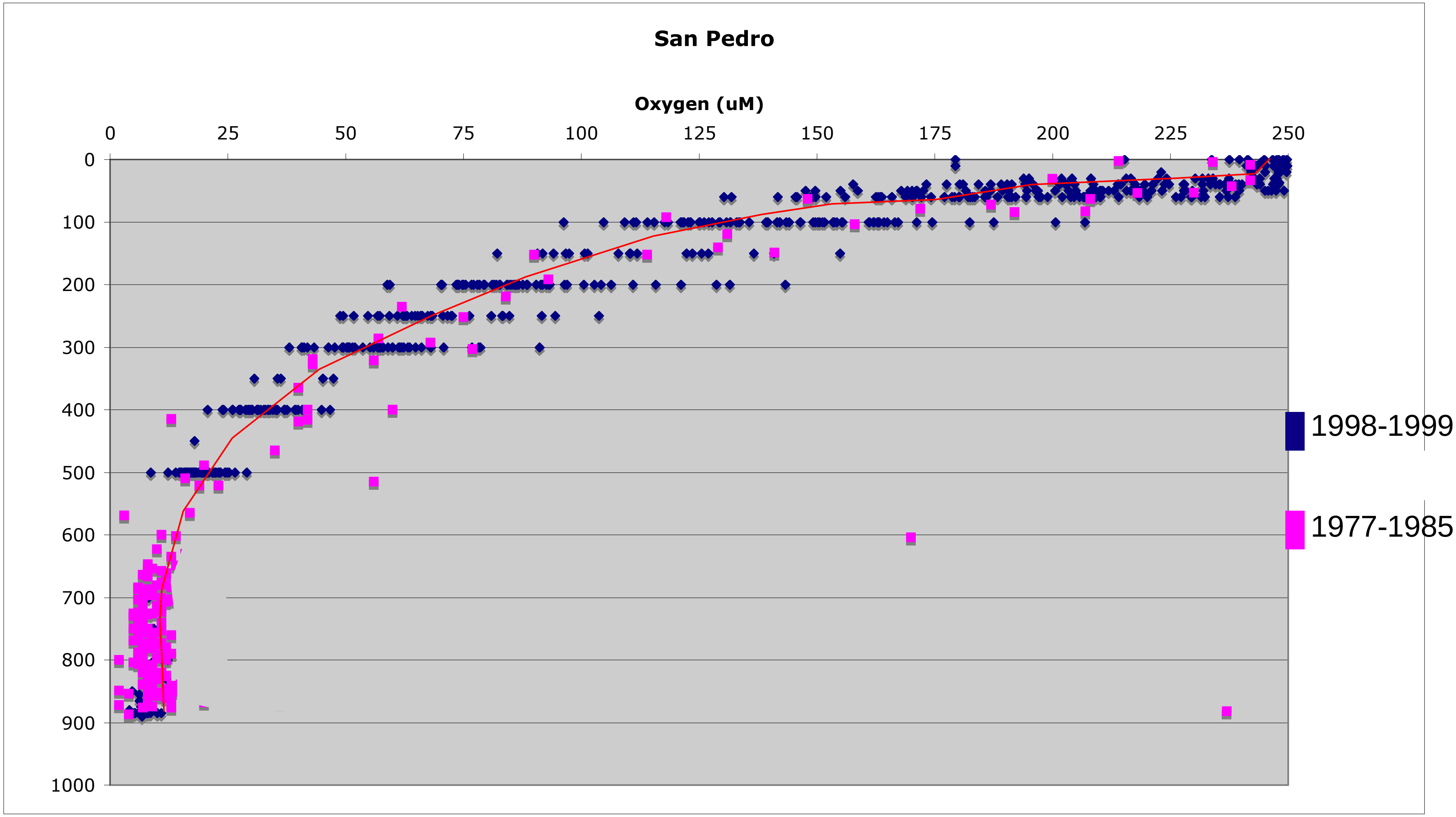
Low oxygen water in contact with sediments acquires ammonia and Fe

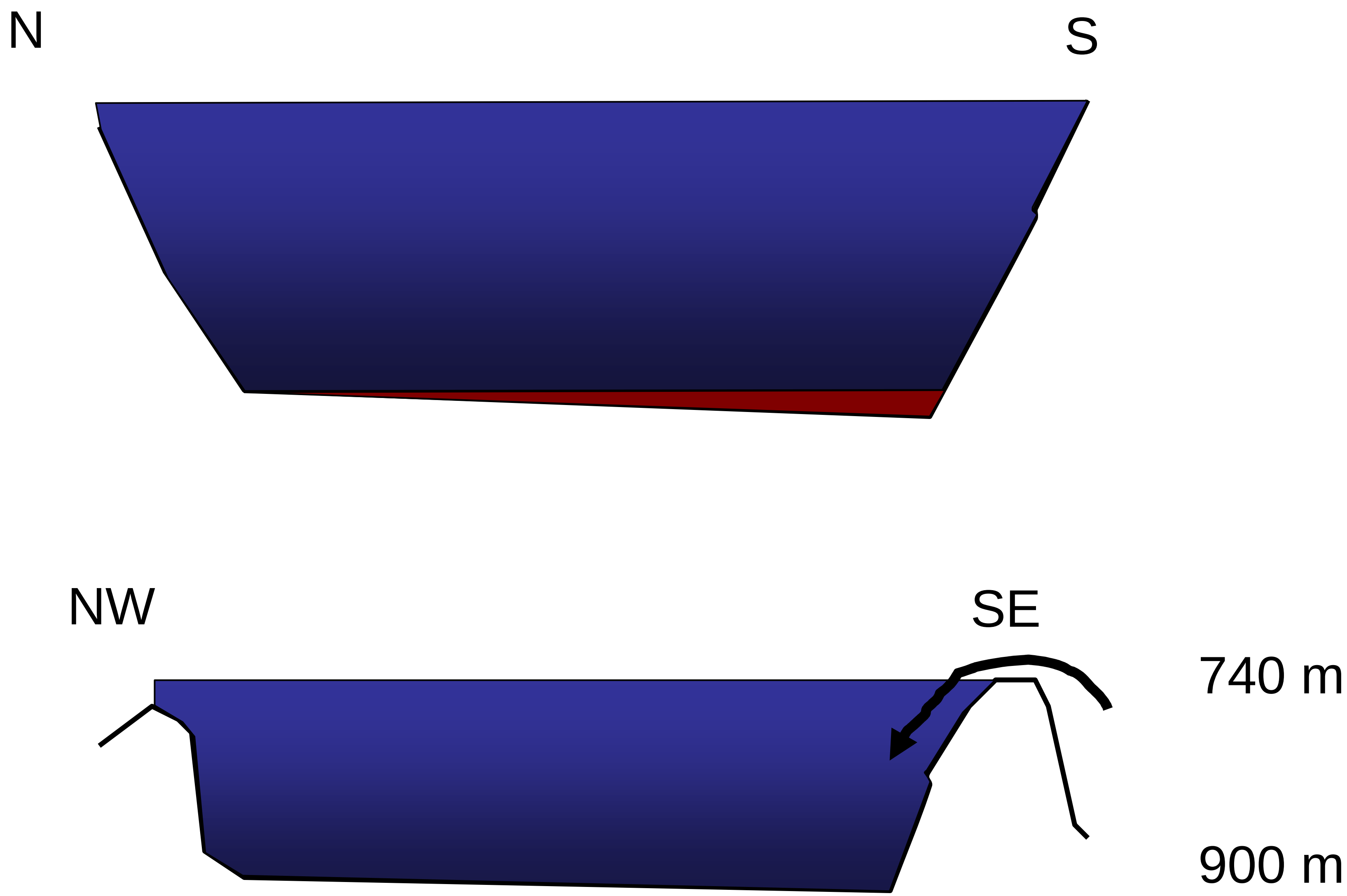
--these are important ingredients in seeding N-cycle reactions

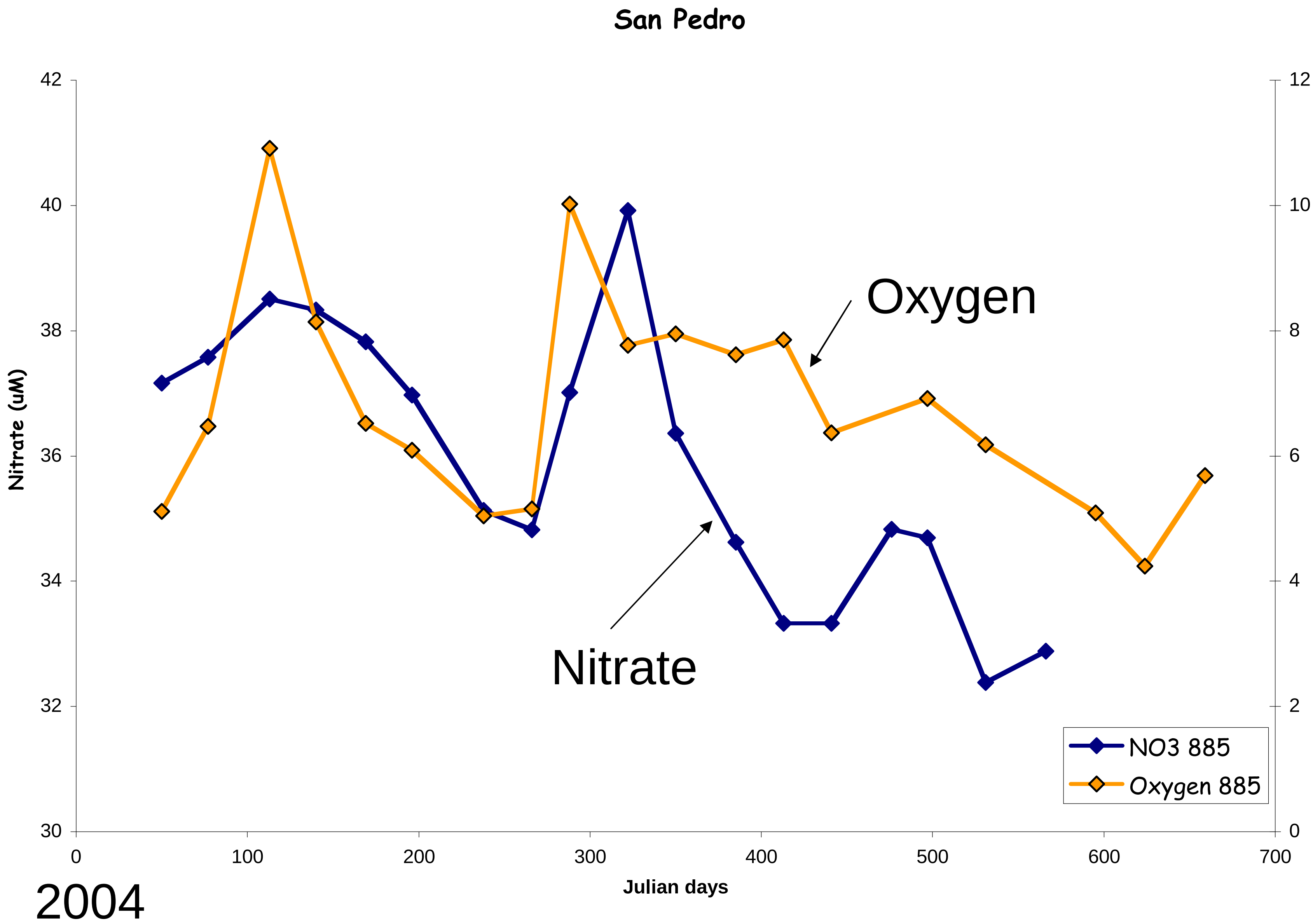
But can nitrate sensors on floats detect denitrification rates in the water column?



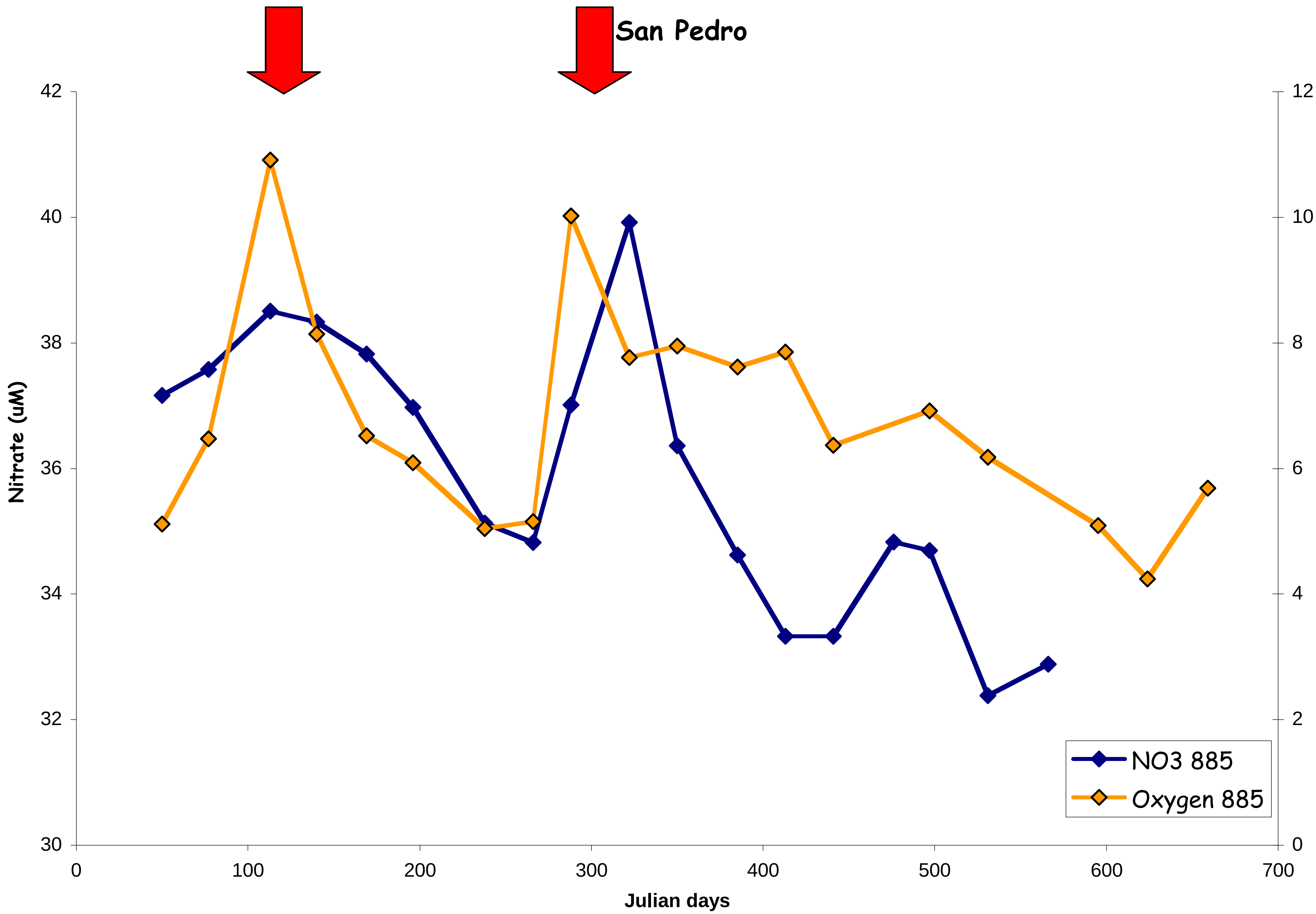
Pilgrim Banks
Kidney Bank
Osborne Bank
Potato Bank
Cherry Bank
43 Fathom Bank

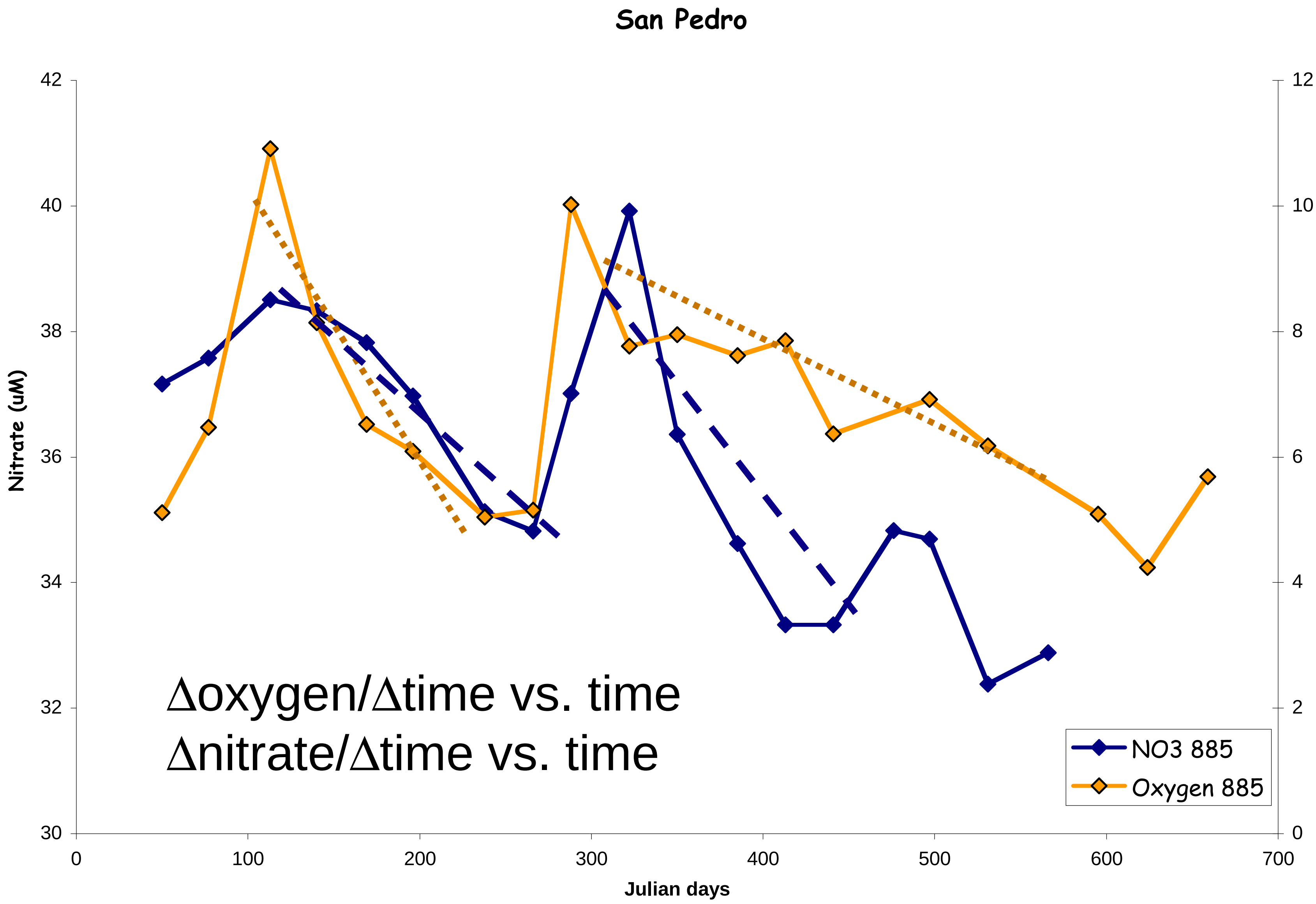

San Pedro
Oxygen (uM)
0
25
50
75
100
125
150
175
200
225
250
0
100
200
300
400
500
600
700
800
900
1000
1998-1999
1977-1985

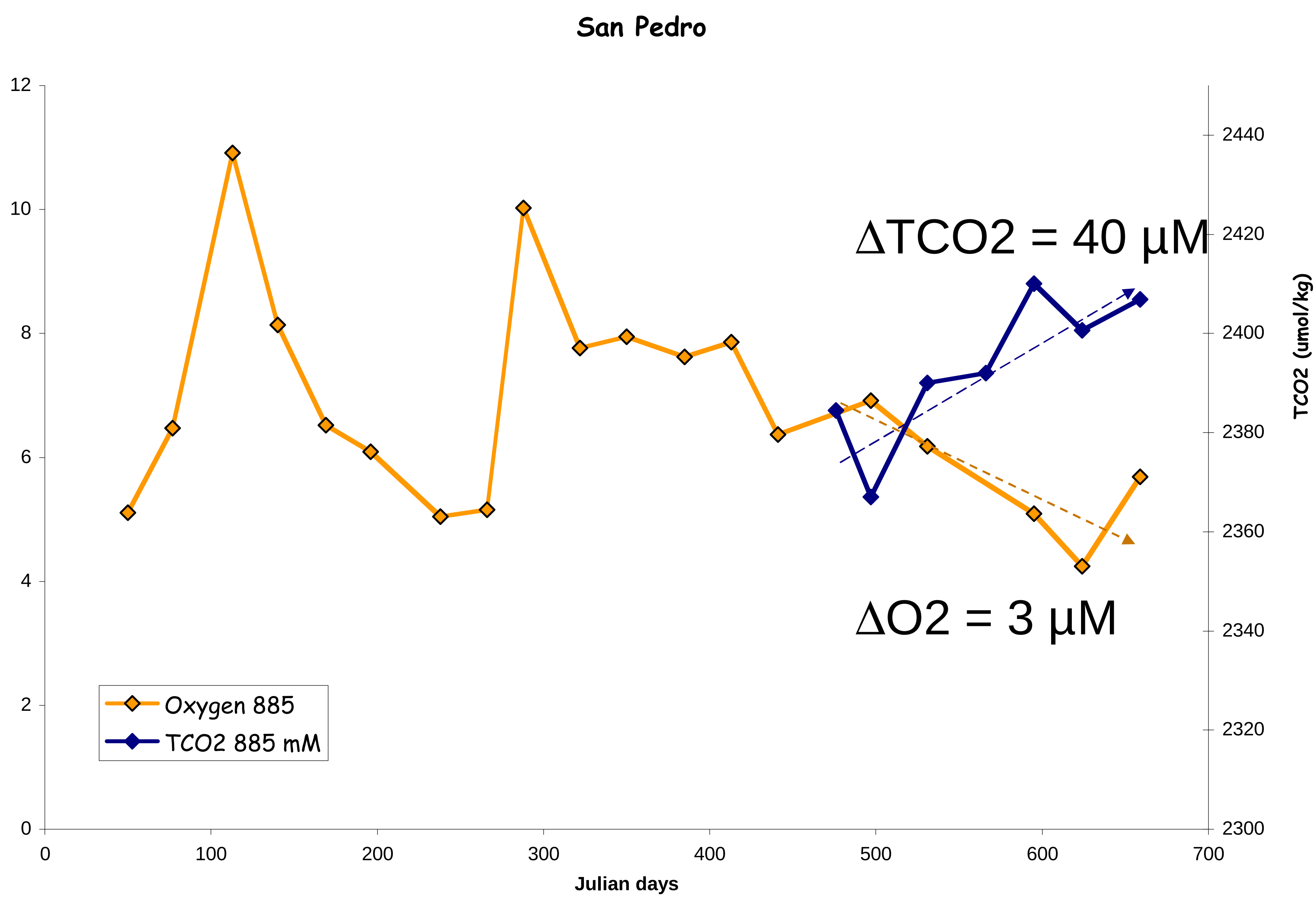

N
S
NW
SE
740 m
900 m

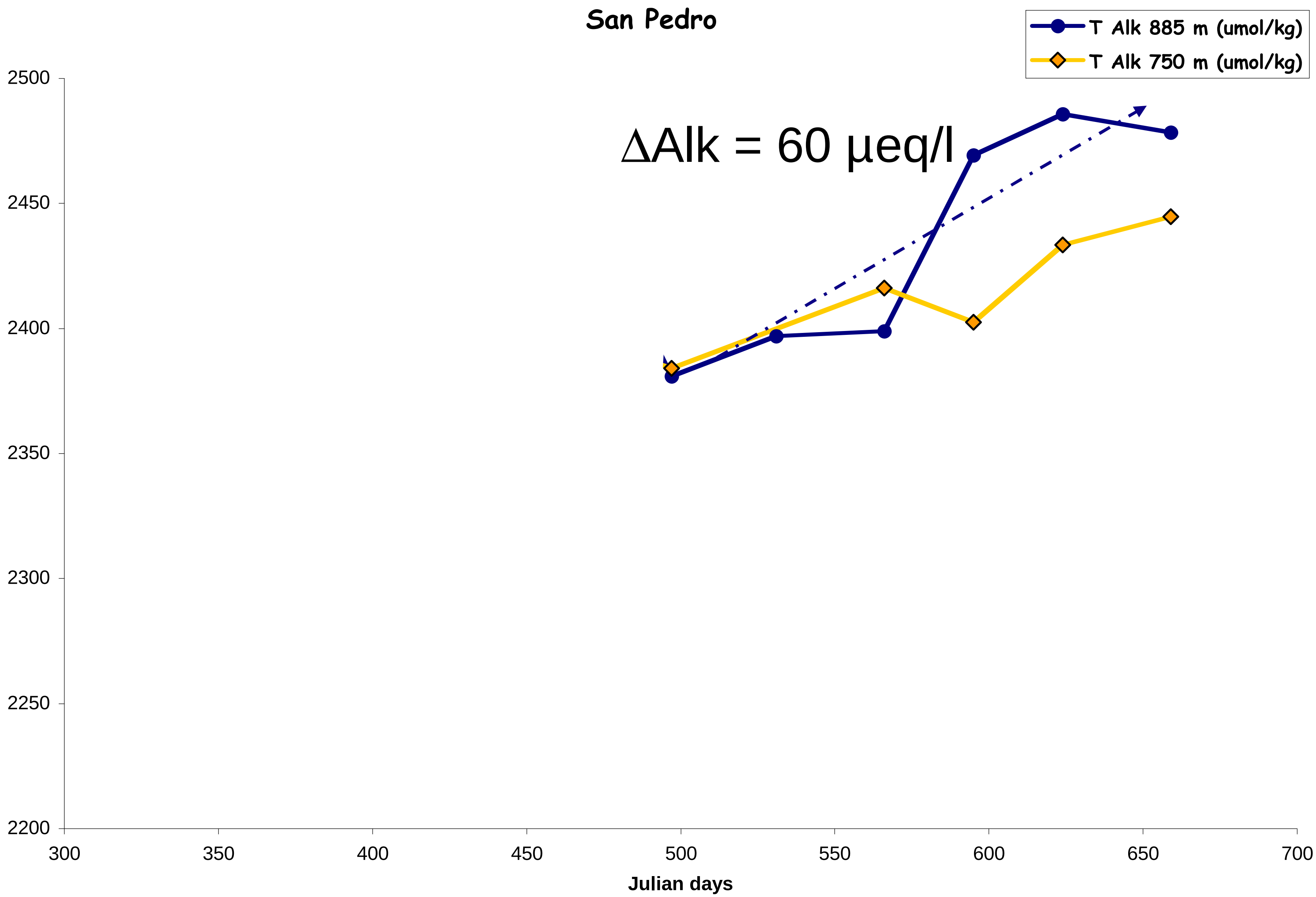

San Pedro
Nitrate (uM)
Julian days
42
40
38
36
34
32
30
12
10
8
6
4
2
0
0
100
200
300
400
500
600
700
Oxygen
Nitrate
NO3 885
Oxygen 885
2004

‘Flushing Events’




San Pedro
Nitrate (uM)
42
40
38
36
34
32
30
12
10
8
6
4
2
0
0
100
200
300
400
500
600
700
Julian days
Δoxygen/Δtime vs. time
Δnitrate/Δtime vs. time
NO3 885
Oxygen 885


San Pedro
ΔTCO2 = 40 μM
ΔO2 = 3 μM
Oxygen 885
TCO2 885 mM
Julian days
TCO2 (umol/kg)
0
2
4
6
8
10
12
0
100
200
300
400
500
600
700
2300
2320
2340
2360
2380
2400
2420
2440


San Pedro
T Alk 885 m (umol/kg)
T Alk 750 m (umol/kg)
ΔAlk = 60 μeq/l
2500
2450
2400
2350
2300
2250
2200
300
350
400
450
500
550
600
650
700
Julian days

TCO2 mass balance

ΔTCO2 = 40 μM

ΔO2 = 3 μM

ΔNO3 = 4 μM

ΔAlk = 60 μeq/l = 30 μM CO3

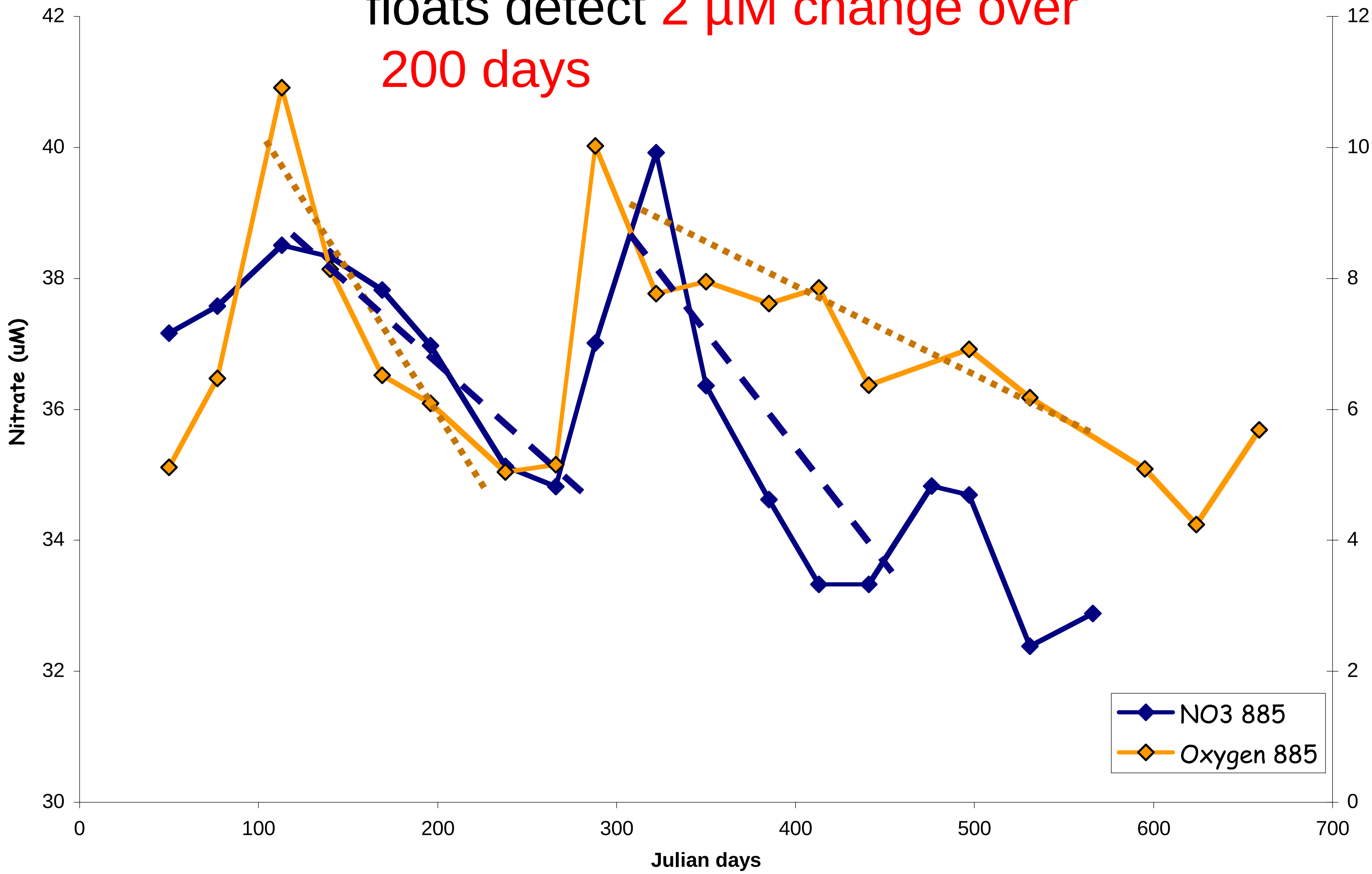
40 ~ 3 + 4 + 30

Therefore

$CaCO_3$ dissolution in water column

These zones may be important carbonate filters

Δnitrate/Δtime = 4 μM/200 days
1/2 to 2/3 signal is from benthic uptake--
floats detect 2 μM change over
200 days



Denitrification Rates

40 µM in 200 days
  40-120 m, 20°C (Richards and Broenkow, 1971)

2 µM in 200 days (Here)

Similar rates found in OMZ waters (B. Ward et al.)

Signal is large enough to be seen by float nitrate detectors
Only true, in situ, rate determination

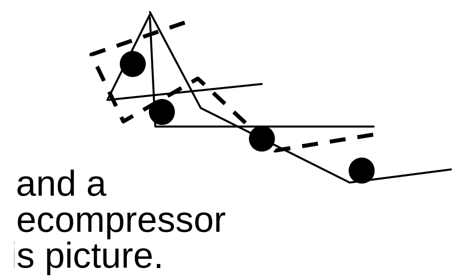
Mid-American Denitrification Experiment = MAD-EX

3 Gliders (O2, optics) ——

4 Floats (O2, nitrate, optics) ●

Oxygen (µM)

1 Cruise - - - -



O2/Ar

18O

Traps

C Explorers

N2 profiles (MIMS)

GTD

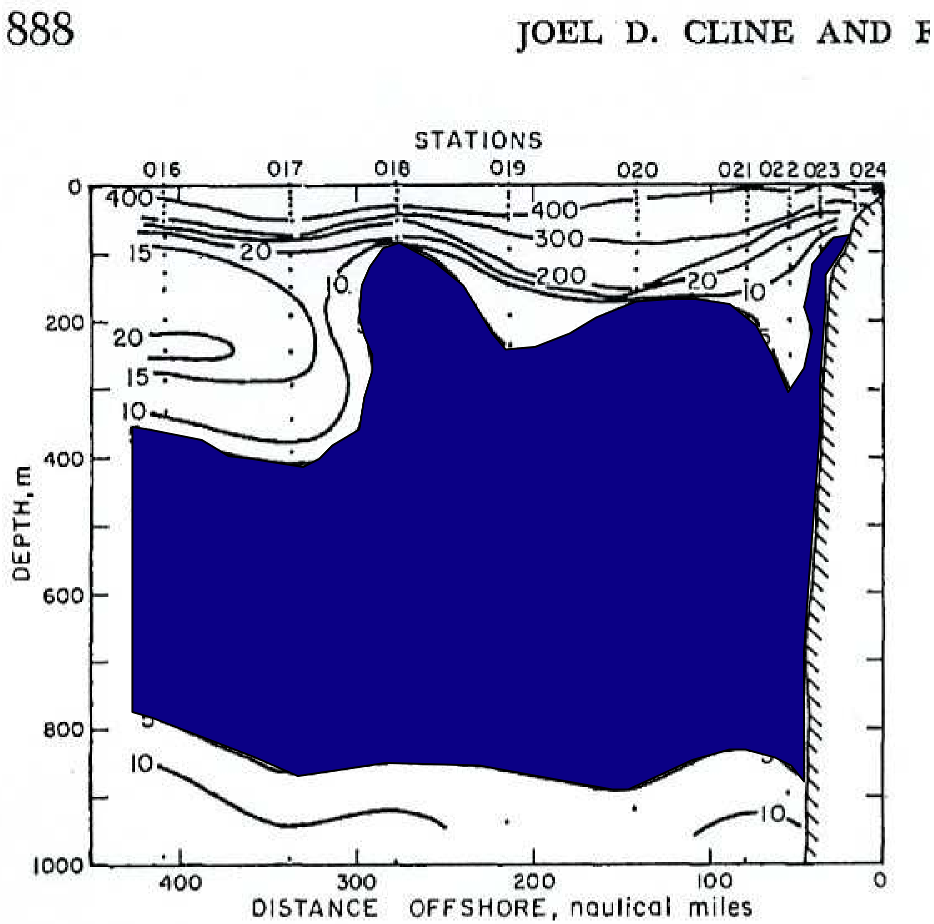
N isotopes

N2O profiles

N2 fixation

Stramma et al. 2008

E. Boss measuring blooms



Some Unique Deliverables:

-Dynamic variability in the depth of the very low oxygen water (internal waves?, >200 m)

-High resolution imaging of POC production, oxygen consumption

-Rates of water col. denitrification

-Low oxygen water/sunlight
= N2 fixation via anaerobic phototrophs (purple non-sulfur bacteria---distinctive pigments)!?

-Important Greenhouse gas flux

Floats and Gliders
essential to successful study of N transformation processes and rates

Thanks

Meeting organizers
MBARI
NSF
Other sponsors

Inorganic oxidation of ammonia is thermodynamically possible, but we have no evidence suggesting its occurrence. One such reaction might be the van Slyke reaction:

$$NH_4^+ + NO_2^- = N_2 + 2H_2O, \quad (11)$$

but the rate of reaction is not known. In the absence of a suitable catalyst and at low temperatures, this reaction is presumably slow; its probable significance is further diminished by the preferential extraction of both NO_2^- and NH_4^+ by organisms for growth.

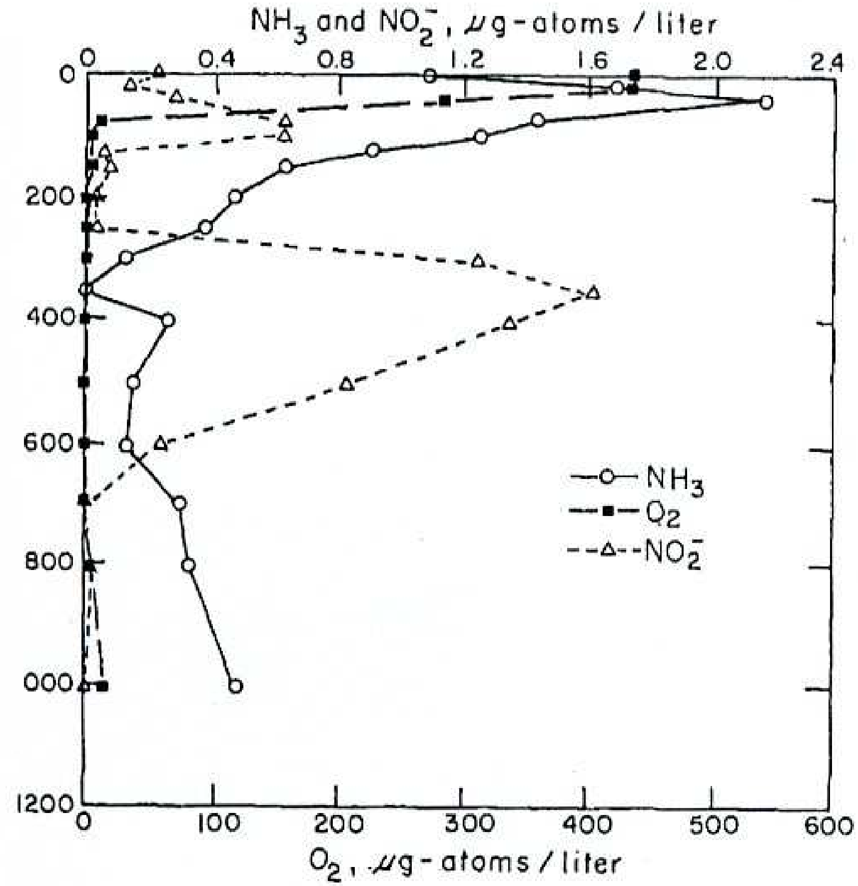


FIG. 9. Ammonia, oxygen, and nitrite concentrations at station 028, PONCHO (TT-026). Note the near-zero oxygen gradient between 100 and 800 m.

Cline and Richards, 1972

Calculations

ΔTCO2 = 40 µM

ΔO2 = 3 µM= 3 µM TCO2

ΔNO3 = 3 µM=4 µM TCO3

40-7 = 33

ΔAlk = 60 µeq/l = 30 µM CO3

In 200 days over 100 m

0.150 nmoles/cm3 day

0.15e8 nmoles/m2day

=15 mmol/m2d of carbonate dissol in deep water

Nitrate uptake

1.5 mmol/m2day

Sediments = 1

Water column =0.5

‘Finding of anammox in the absence of denitrification raises serious challenges to our understanding of organic matter cycling.’

B. Ward et al. 2007

1 sample every 2 m captures detail in NO_2^- profile

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

85 m

112 m

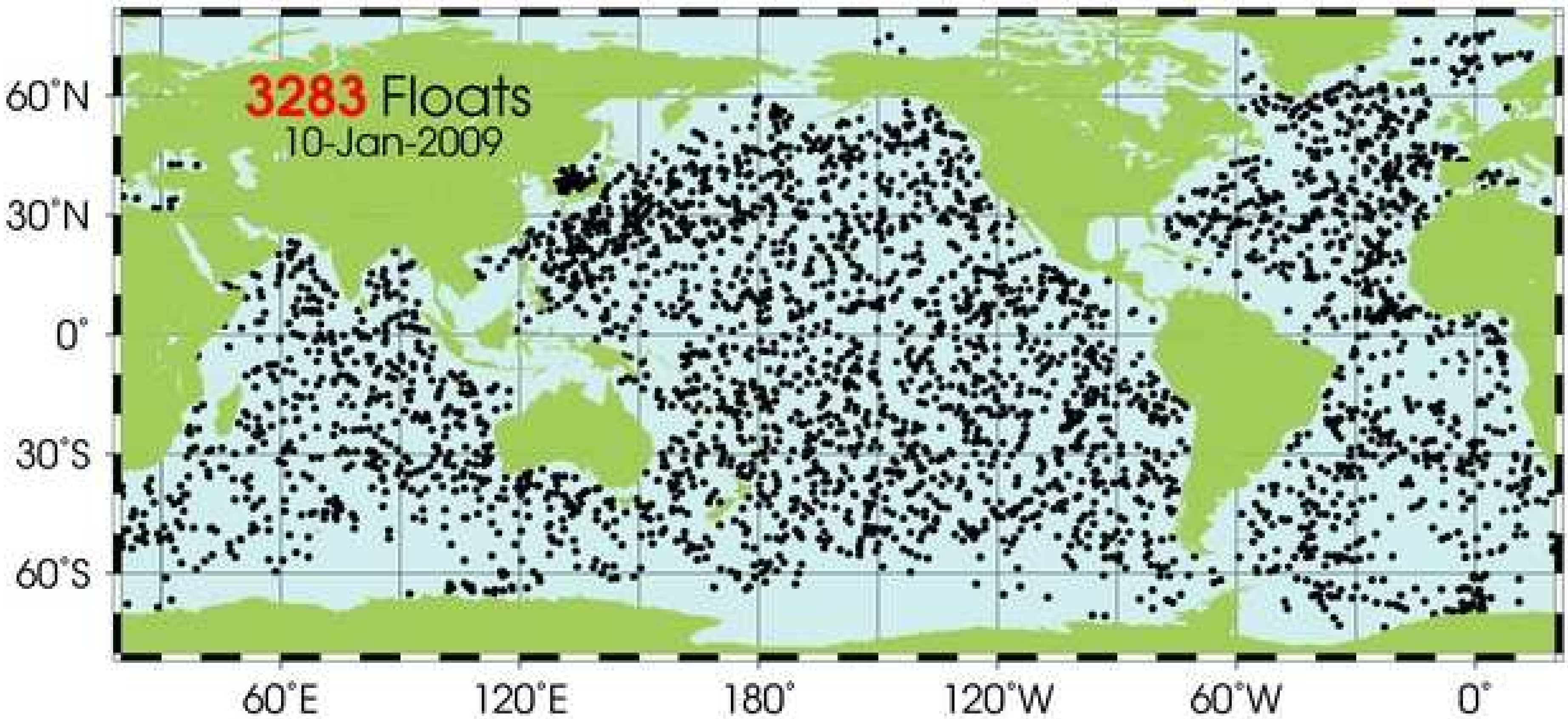
Fuchsman et al.

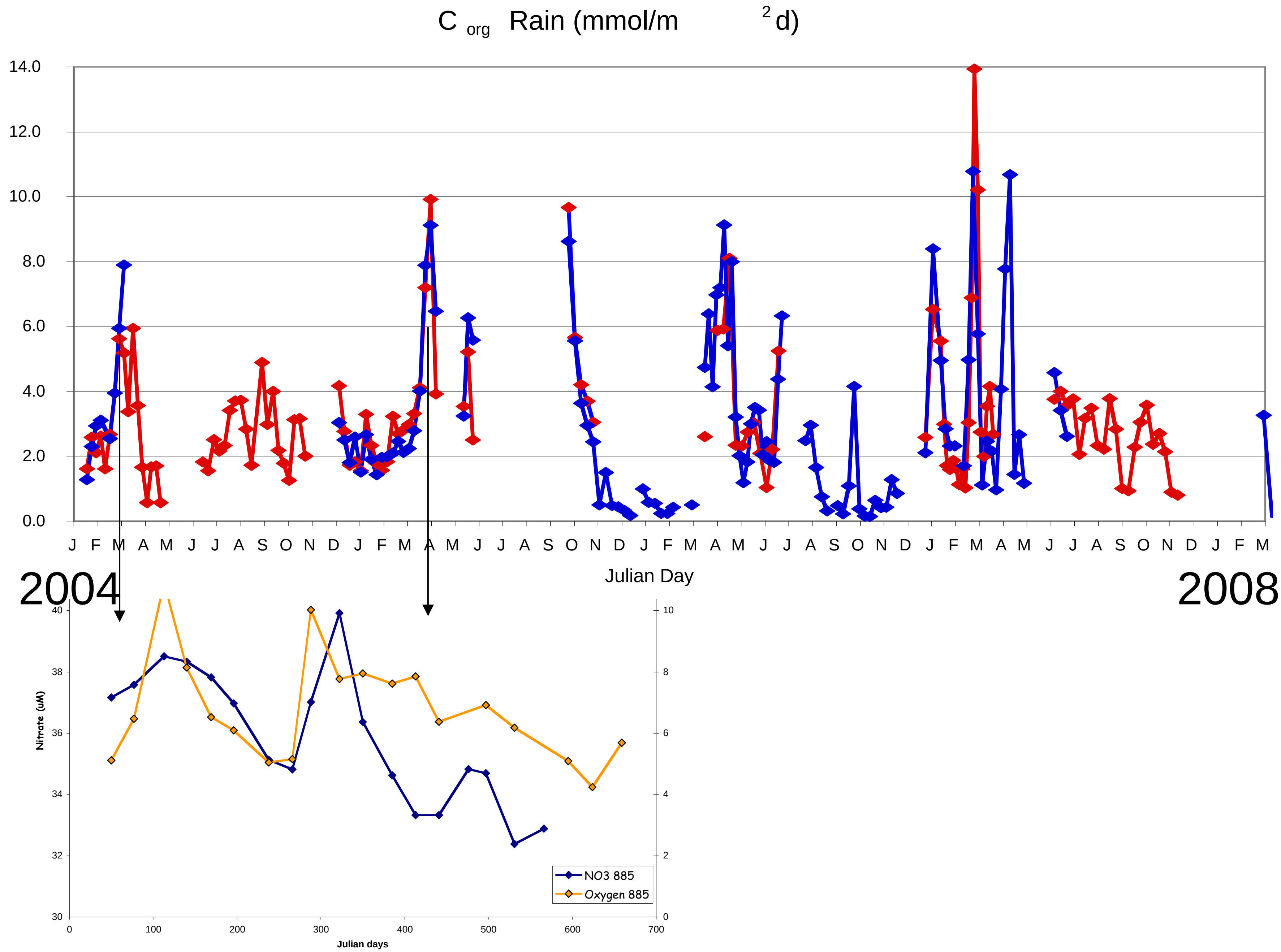
1 sample every 3 m captures detail in N_2 profile

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

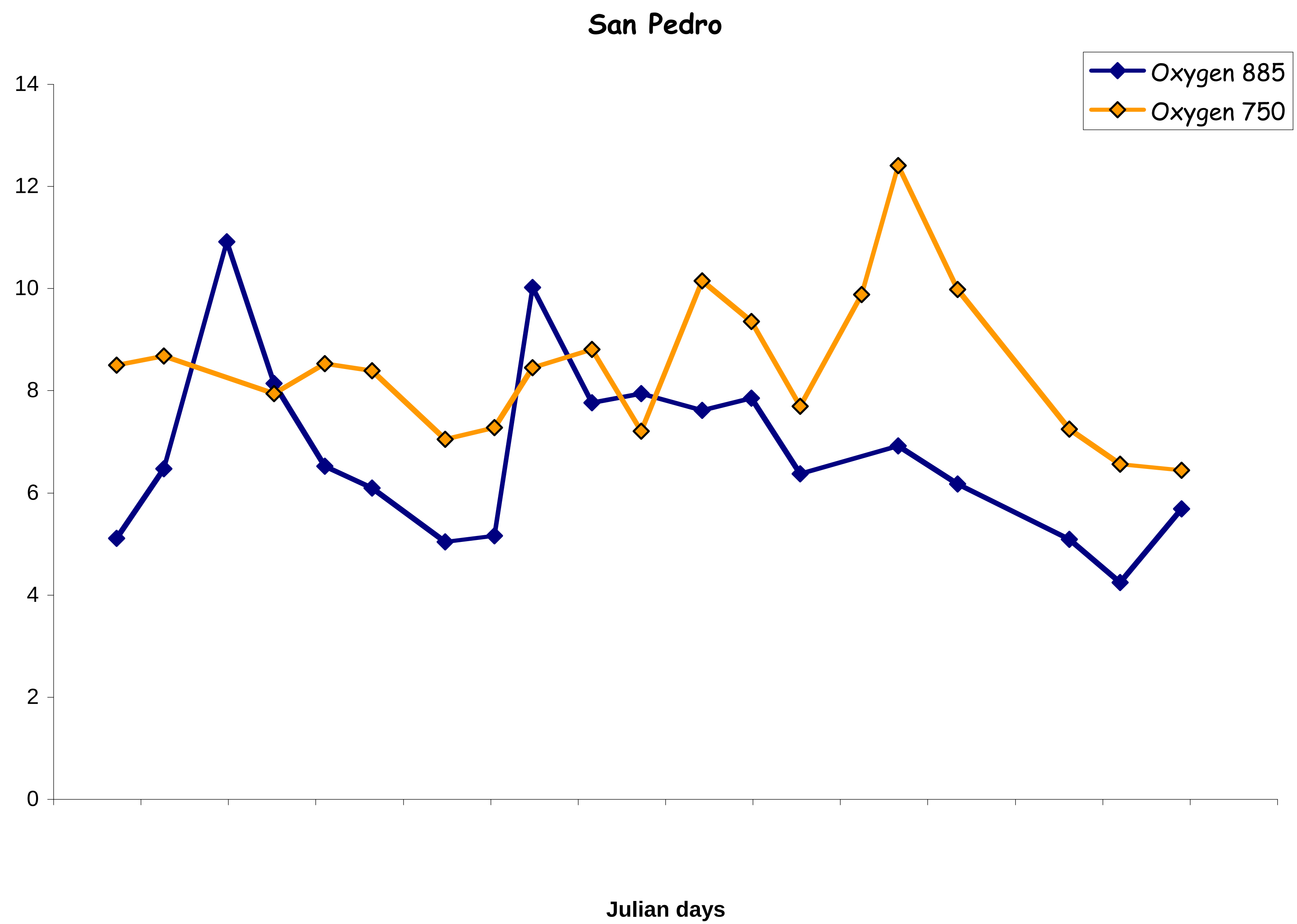
QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

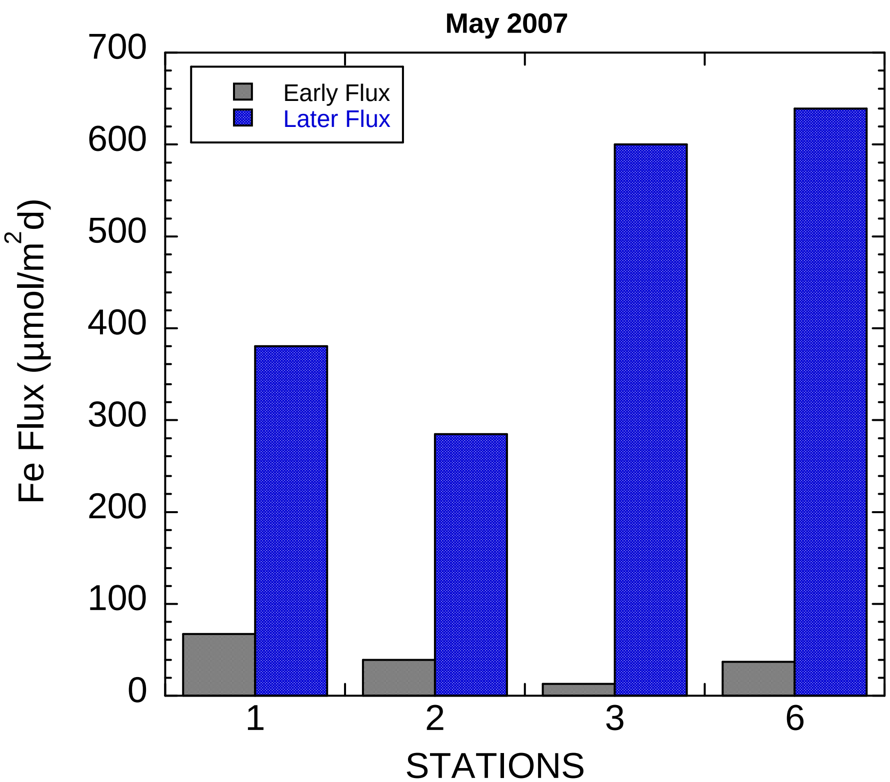
Fuchsman et al.

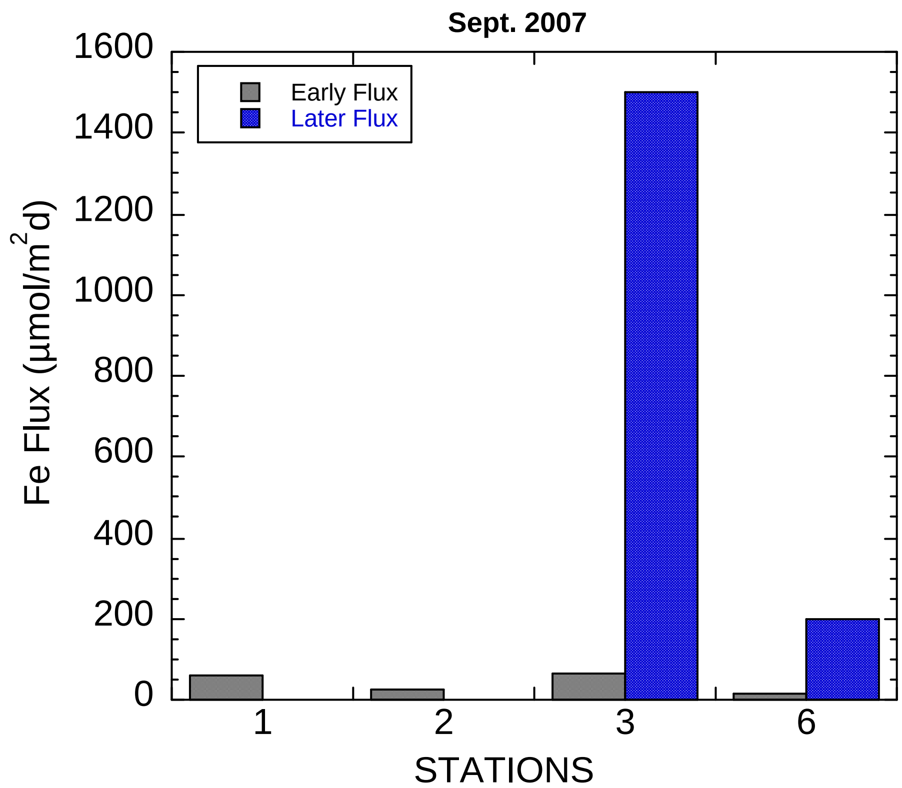

3283 Floats
10-Jan-2009
60°N
30°N
0°
30°S
60°S
60°E
120°E
180°
120°W
60°W
0°



C org Rain (mmol/m 2 d)
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M
Julian Day
2004
2008
40
38
36
34
32
30
Nitrate (uM)
10
8
6
4
2
0
0 100 200 300 400 500 600 700
Julian days
NO3 885
Oxygen 885

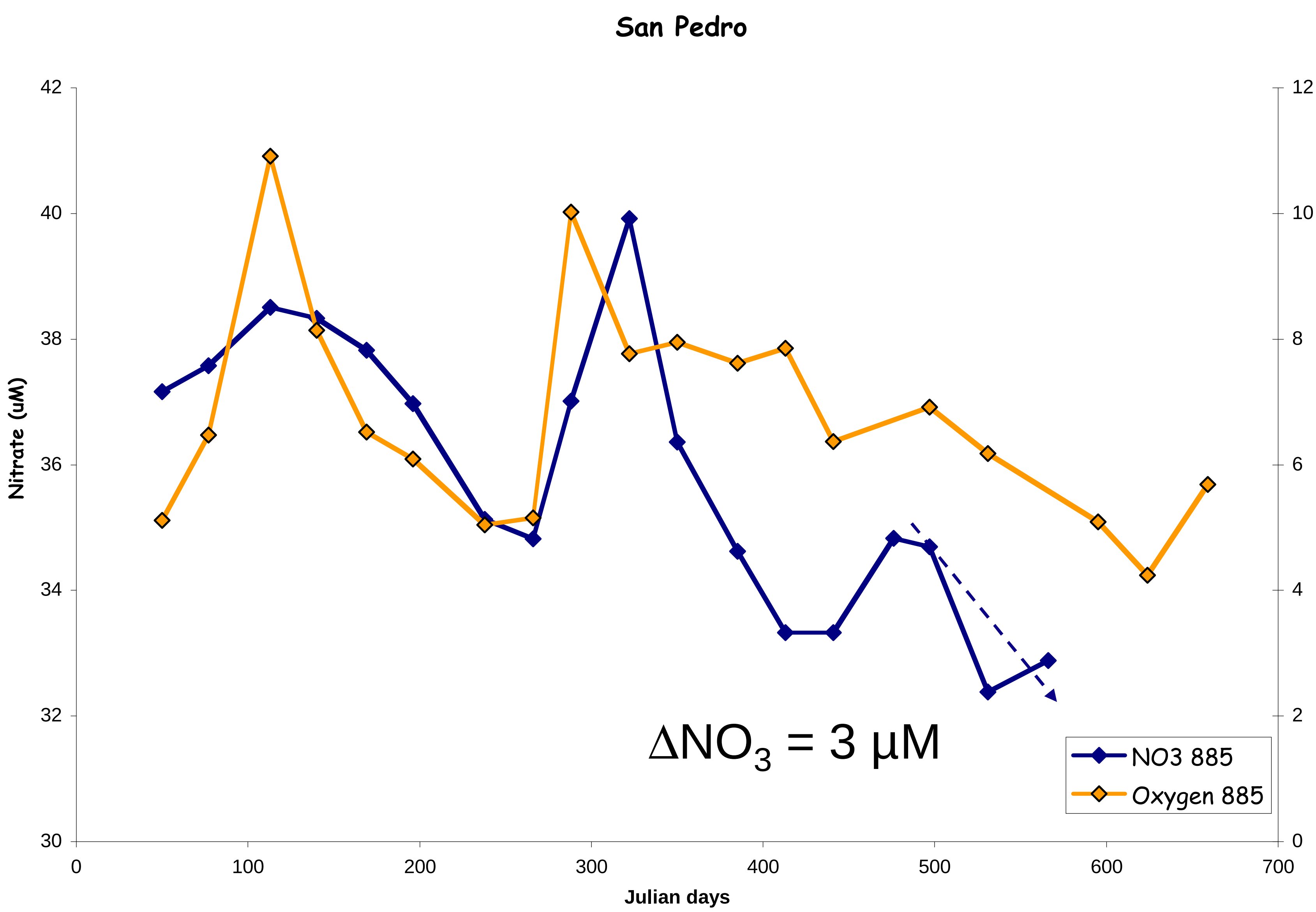

San Pedro
Oxygen 885
Oxygen 750
14
12
10
8
6
4
2
0
Julian days


May 2007
Early Flux
Later Flux
Fe Flux (µmol/m2d)
700
600
500
400
300
200
100
0
1
2
3
6
STATIONS


Sept. 2007
Early Flux
Later Flux
Fe Flux (µmol/m2d)
1600
1400
1200
1000
800
600
400
200
0
1
2
3
6
STATIONS

Intrusion of low oxygen water onto shelf will generate a burst of Fe into water column
(enough to support PP at a rate of 20 molesC/m^2day!!)

Builds a positive feedback into Hypoxic Zone troubles



San Pedro
Nitrate (uM)
Julian days
42
40
38
36
34
32
30
12
10
8
6
4
2
0
0
100
200
300
400
500
600
700
ΔNO3 = 3 µM
NO3 885
Oxygen 885