The Ocean in a High CO_2 World

An International Science Symposium.
May 10-12, 2004
UNESCO, Paris, France

Preliminary

Synthesis of *in-situ* Iron Enrichment Experiments

In the end when satisfied, then praise:

Phil Boyd, Ken Buesseler, Dorothee Bakker, Yann Bozec, Marie Boye, Kenneth Coale, Peter Croot, Etienne Hannon, Paul Harrison, William Hiscock, Ken Johnson, Patrick Laan, Christiane Lancelot, Maurice Levasseur, Adrian Marchetti, Jun Nishioka, Yukihiro Nojiri, Tim van Oijen, Ulf Riebesell, Sigenobu Takeda, Klaas Timmermans, Atsuhsi Tsuda, Marcel Veldhuis, Andy Watson, and many many others....

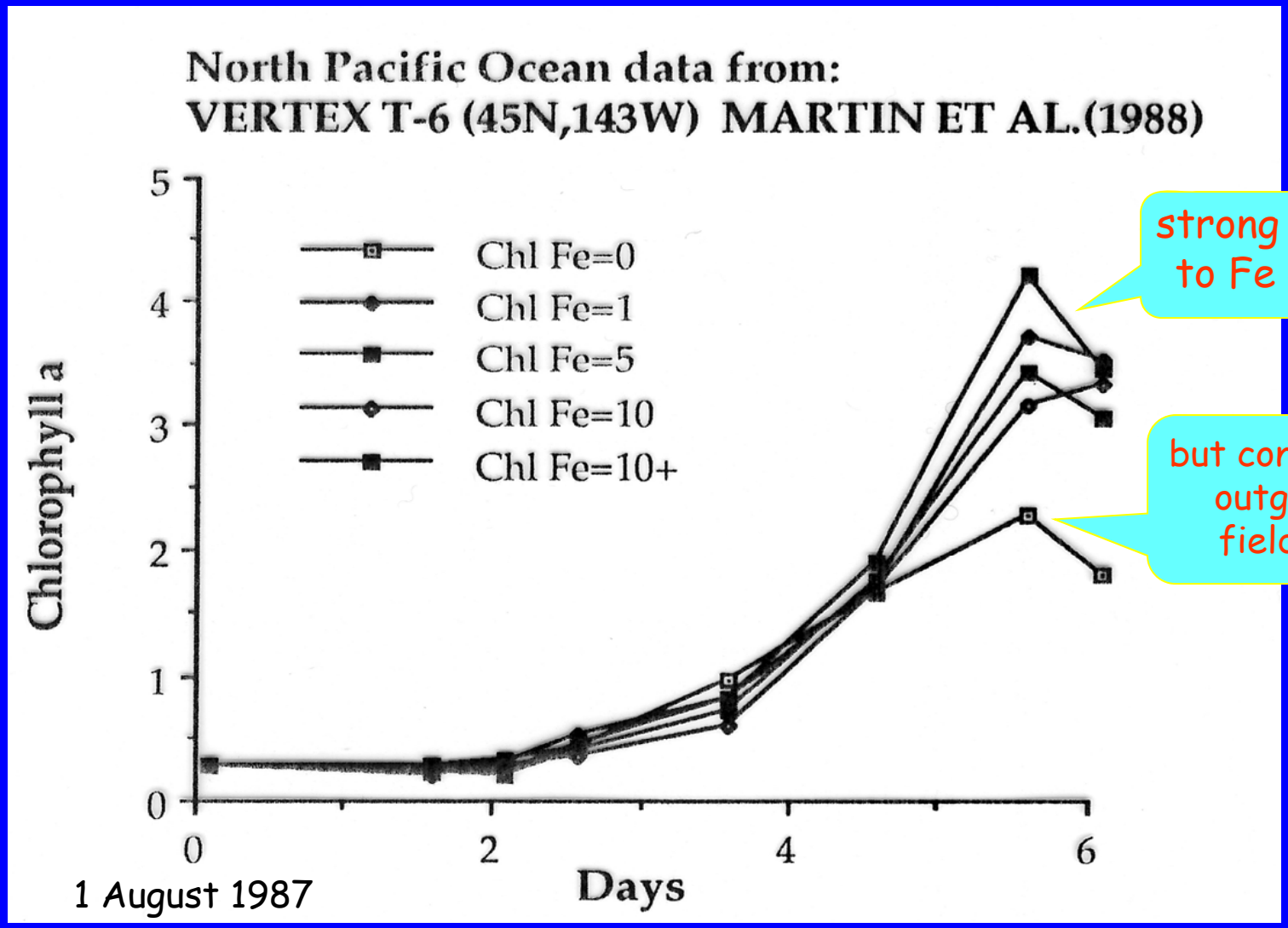
When disappointed with poor synthesis, blame:

Hein de Baar

Royal Netherlands Institute for Sea Research

NIOZ 1876

Subarctic North Pacific, August 1987



strong response to Fe addition

but control also outgrowing field value

....as shown in Paris by John Martin in September 1987

Contents

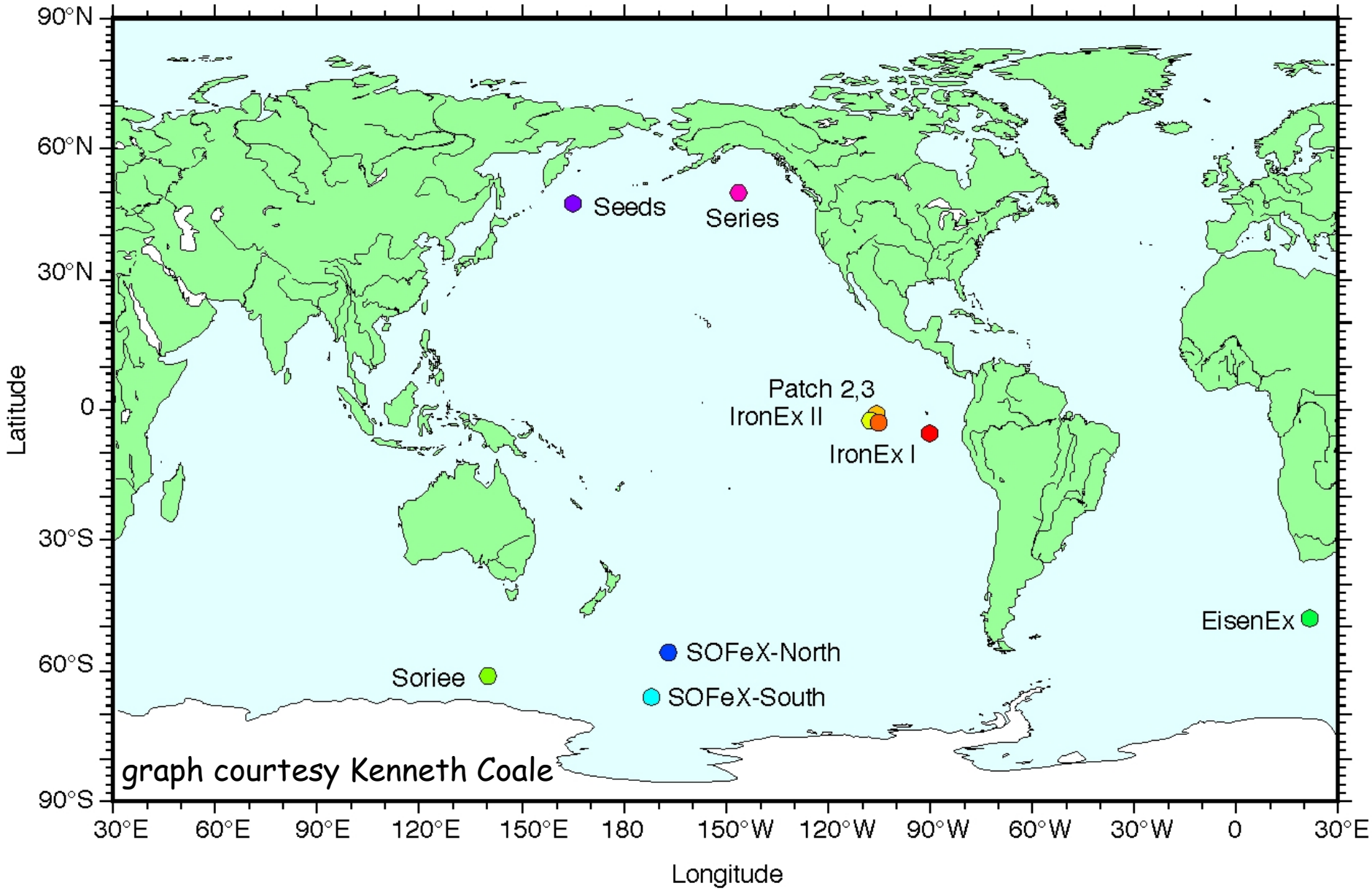
- Nine Experiments 1993-2004
- Light Limitation
  - Wind and Wind Mixed Layer
  - lateral patch dilution
  - temperature effects ?
- Big Diatoms
- Iron Chemistry
- Carbon Fluxes
- Summary & Discussion

Nine Ferrous Fertilizations

Experiment	Location	Month(s), Year
IronEx I	E Eq Pac	10-11, 1993
IronEx II	E Eq Pac (3)	5-6, 1995
SOIREE	Aust. Sect. SO 61°S	2, 1999
EisenEx	Atl. Sect. SO 48°S	12, 2000
SEEDS	NW Pac. 48.5°N	7, 2001
SOFeX North	Pac. Sect. SO, 56°S	1-2, 2002
SOFeX South	Pac. Sect. SO, 66°S	1-2, 2002
SERIES	N Pac., 50°N	6, 2002
Eifex	Atl. Sect. SO	2-3, 2004

Not shown:

GreenSea 1	Gulf of Mexico	1, 1998
GreenSea 2	Gulf of Mexico	5, 1998



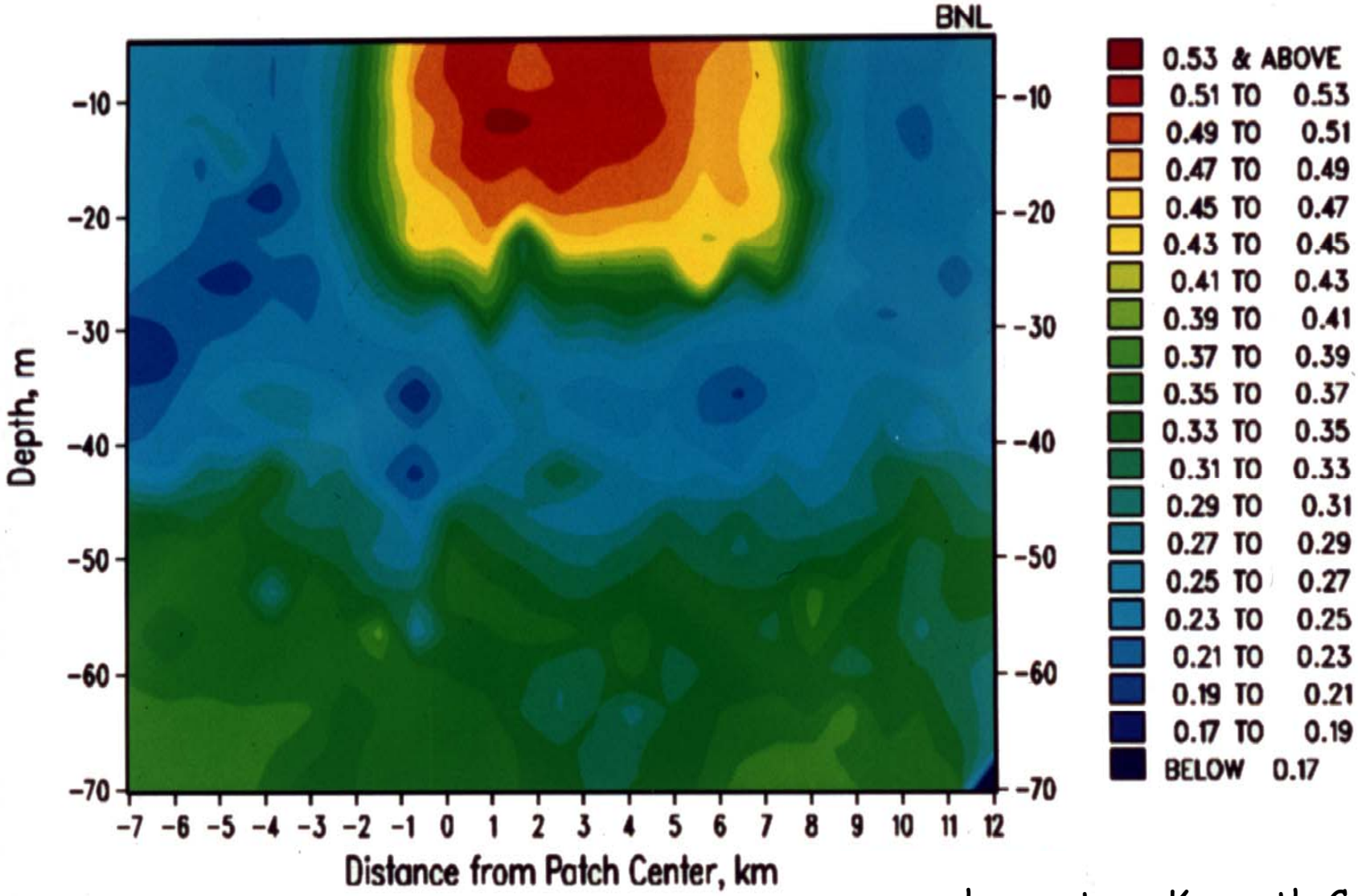
IronEx I ● IronEx II ● Control Expt. Patch 2 ● Control Expt. Patch 3 ● Soriee ●

EisenEx ● SOFeX-South ● SOFeX-North ● Seeds ● Series ●

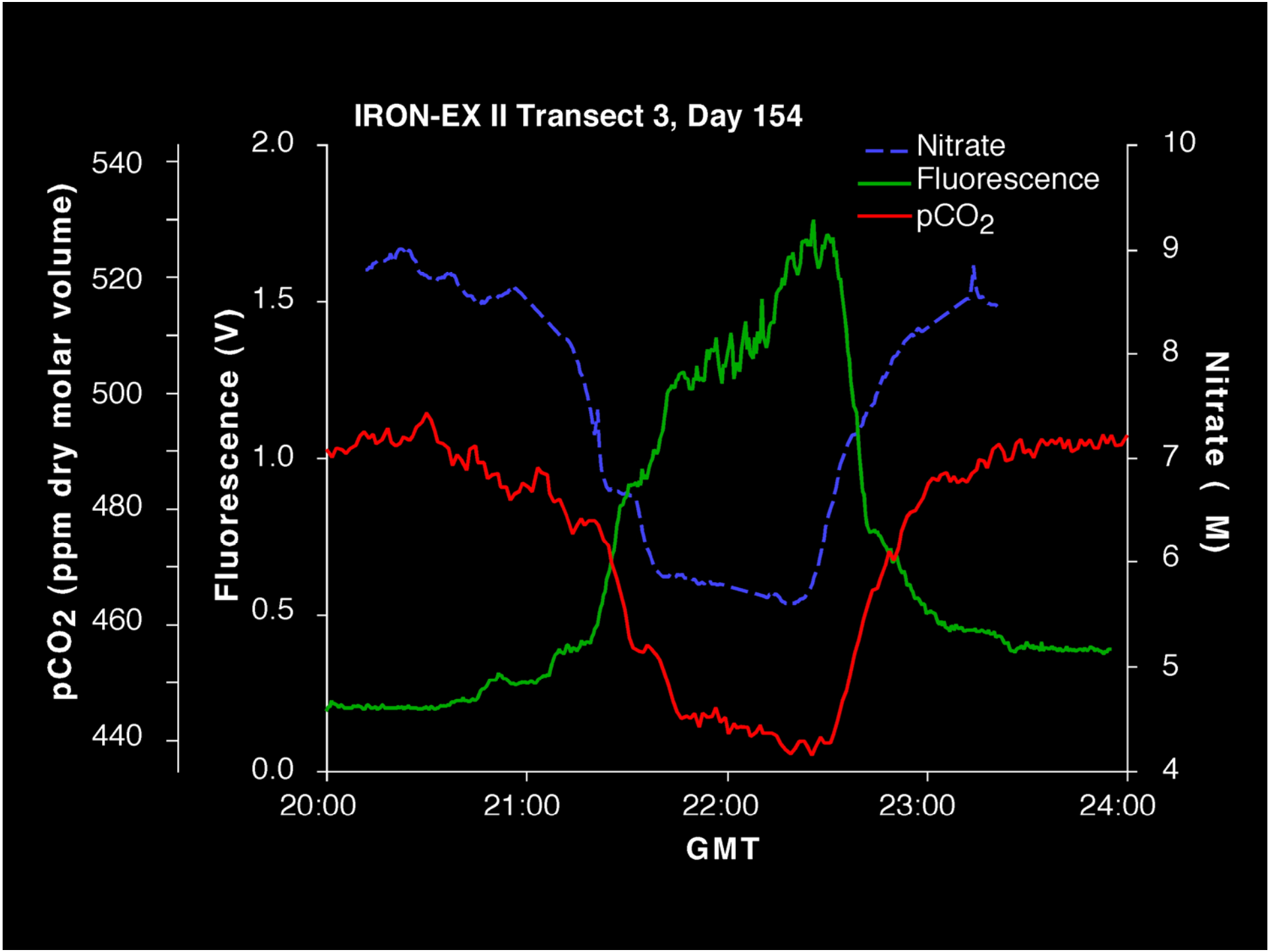
not yet shown: Eifex 2004 (Polarstern)

IronEx II Variable Fluorescence

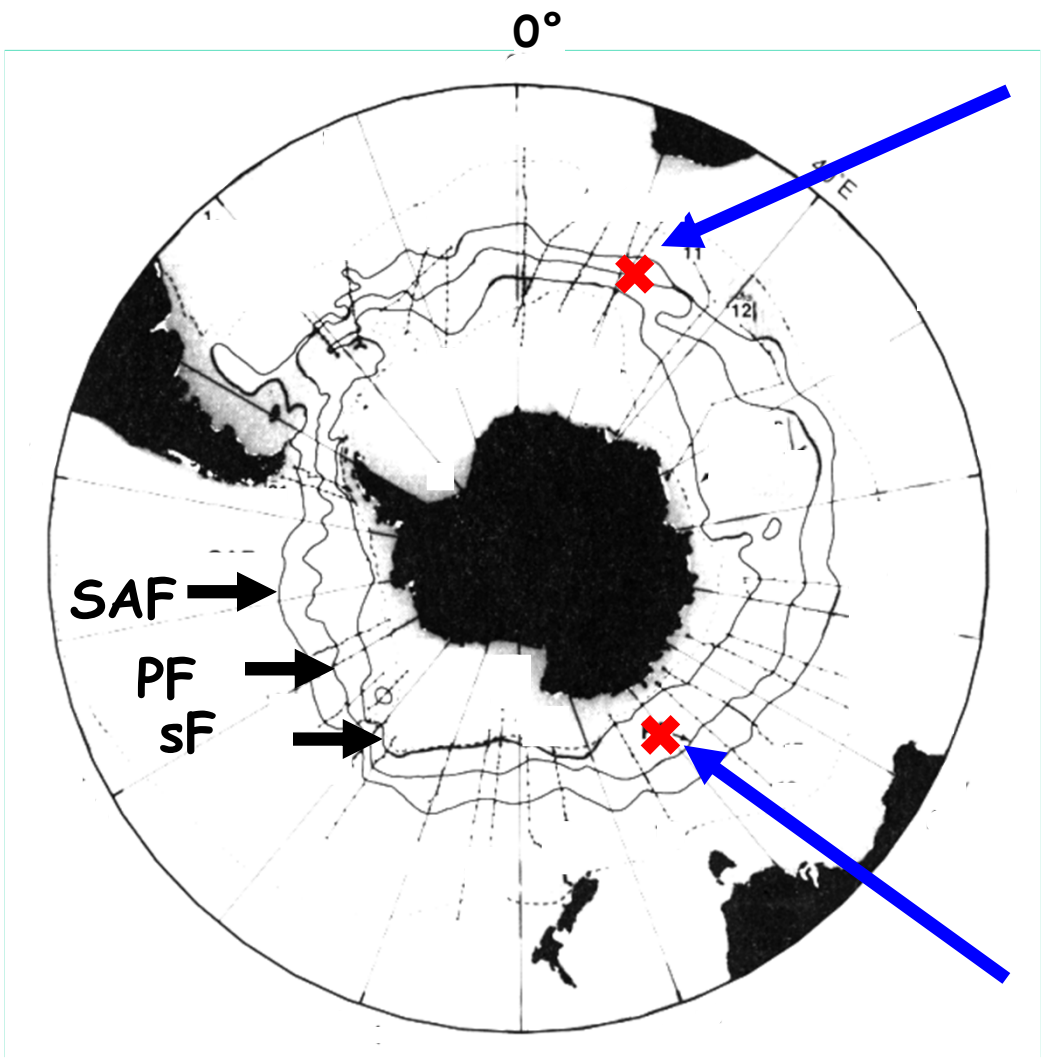
(Chlorophyll abundance)



graph courtesy Kenneth Coale


IRON-EX II Transect 3, Day 154
Nitrate
Fluorescence
pCO2
pCO2 (ppm dry molar volume)
540
520
500
480
460
440
Fluorescence (V)
2.0
1.5
1.0
0.5
0.0
Nitrate (M)
10
9
8
7
6
5
4
20:00
21:00
22:00
23:00
24:00
GMT

Southern Ocean

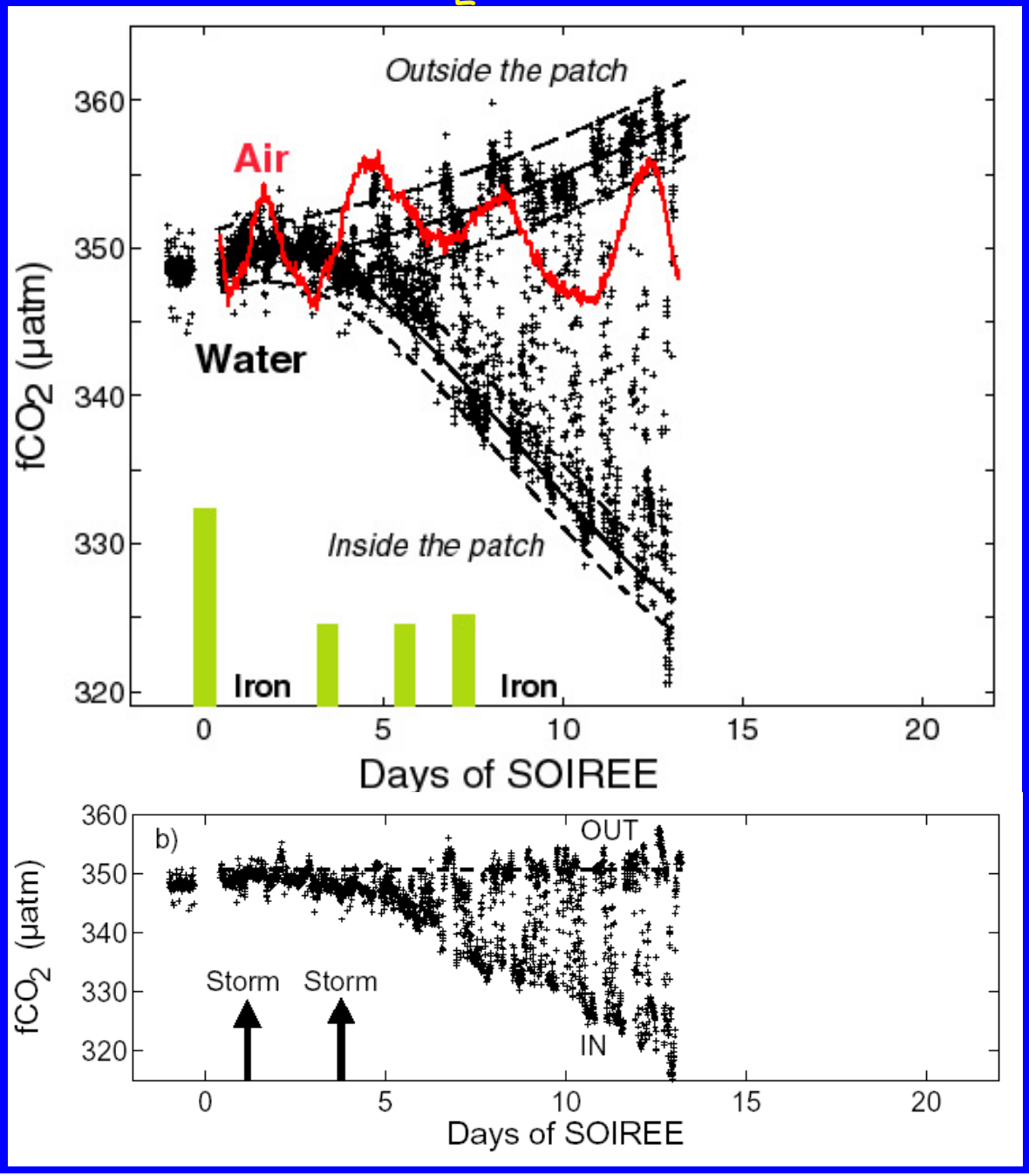


EisenEx
Nov 2000
PFZ

Feb 1999
South of PF

(slide by Dorothee Bakker after Orsi et al., 1995)

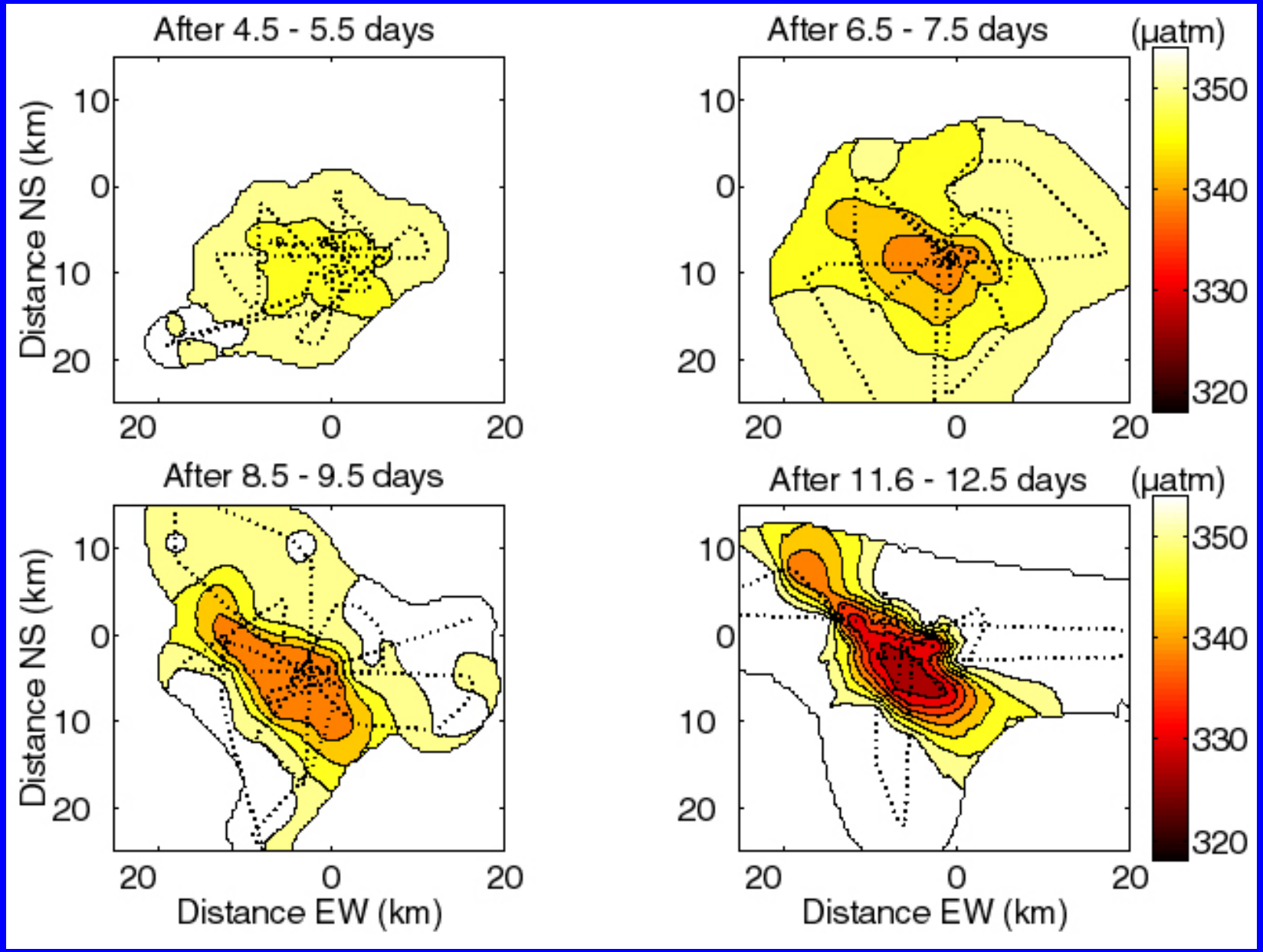
Surface water fCO_2 in SOIREE



Dorothee Bakker, Andy Watson, Cliff Law, 2001

normalized to standard atmospheric pressure and constant temperature

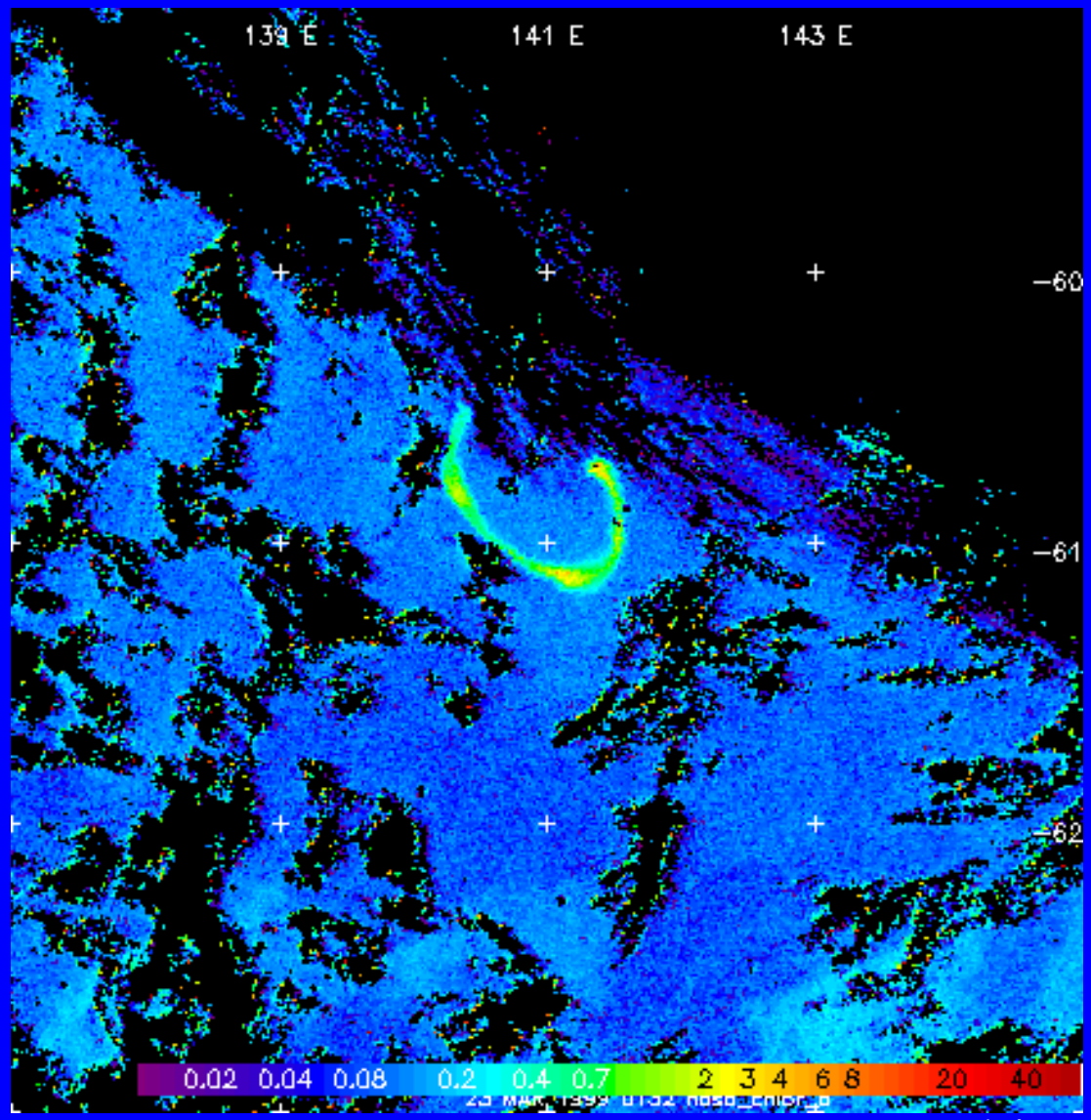
Surface water fCO_2 maps in SOIREE



(Bakker, Watson and Law, 2001)

data and slide by Dorothee Bakker

SOIREE
after 42 days

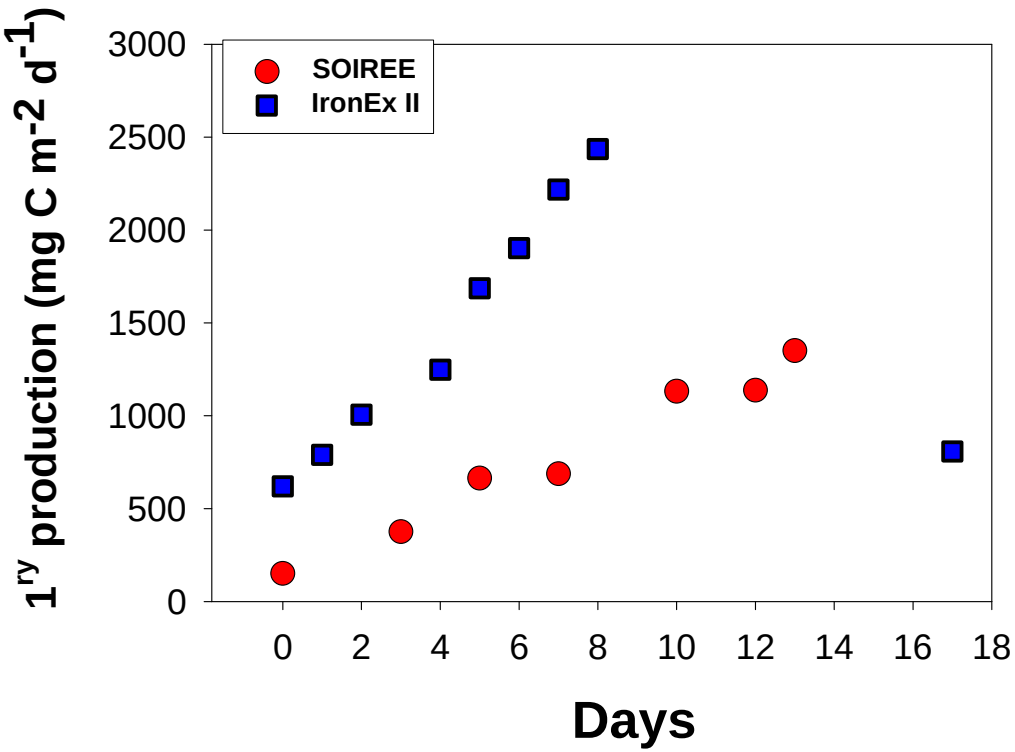


23 March 1999
(Abraham et al., 2000)

NASA SeaWiFS project, DAAC/GSFC, ©ORBIMAGE.

Ironex-2 (1995) and SOIREE (1999)

- **Ironex-2**
- East Equatorial Pacific
- T = 25 ^{0}C
- WML = 40m
- 17 days
- patch size
  - 72 km^2 to
  - 120 km^2



- **SOIREE**
- Southern Ocean
- T = 2 ^{0}C
- WML = 65 m
- 13 days
- Patch size
  - 50 km^2 to
  - 200 km^2

Ironex-2 much better growth in warmer, shallower, more confined patch

graph kindly provided by Phil Boyd

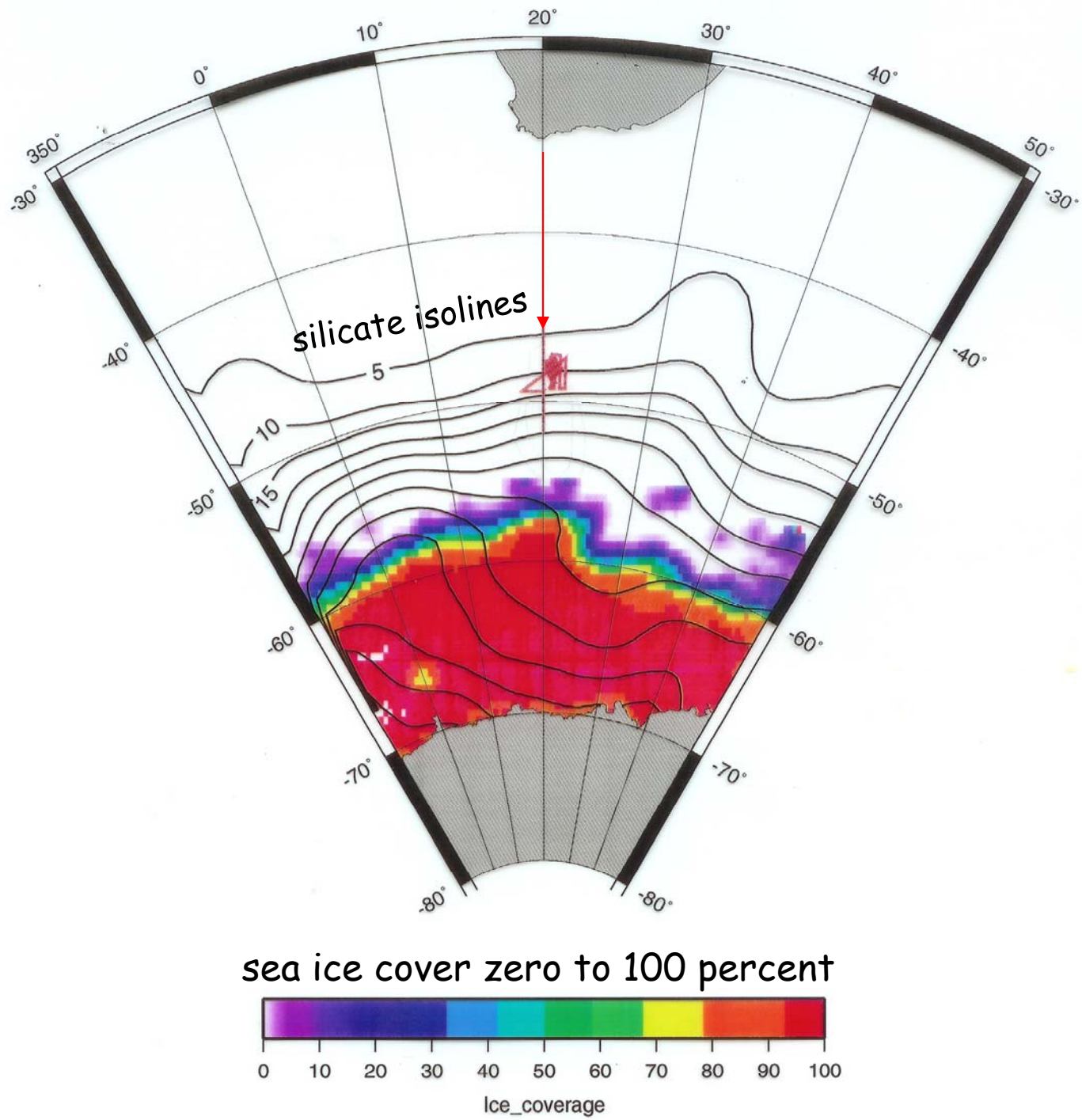
EISENEX

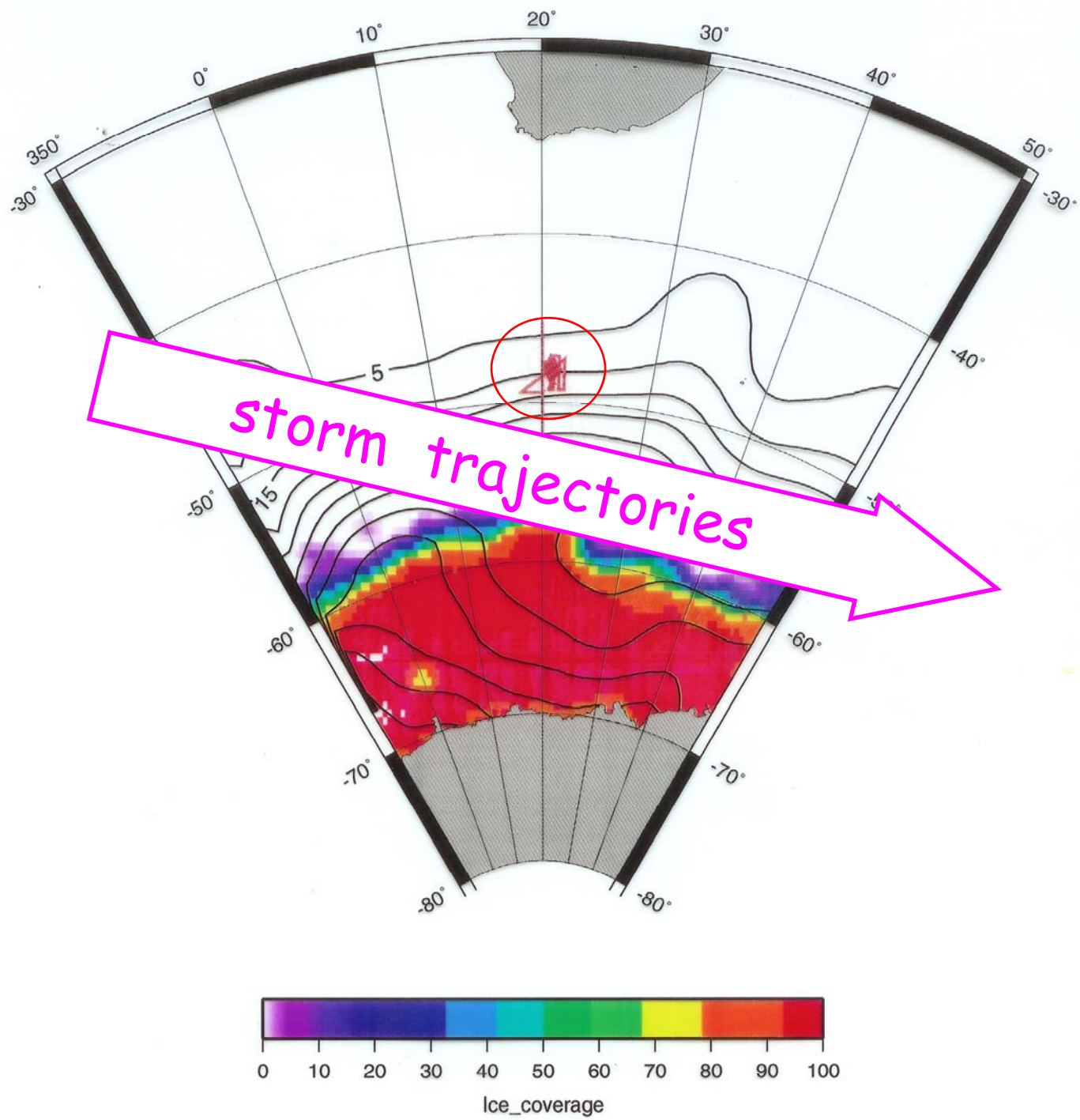
Polarstern
November
2000

early in austral
spring season

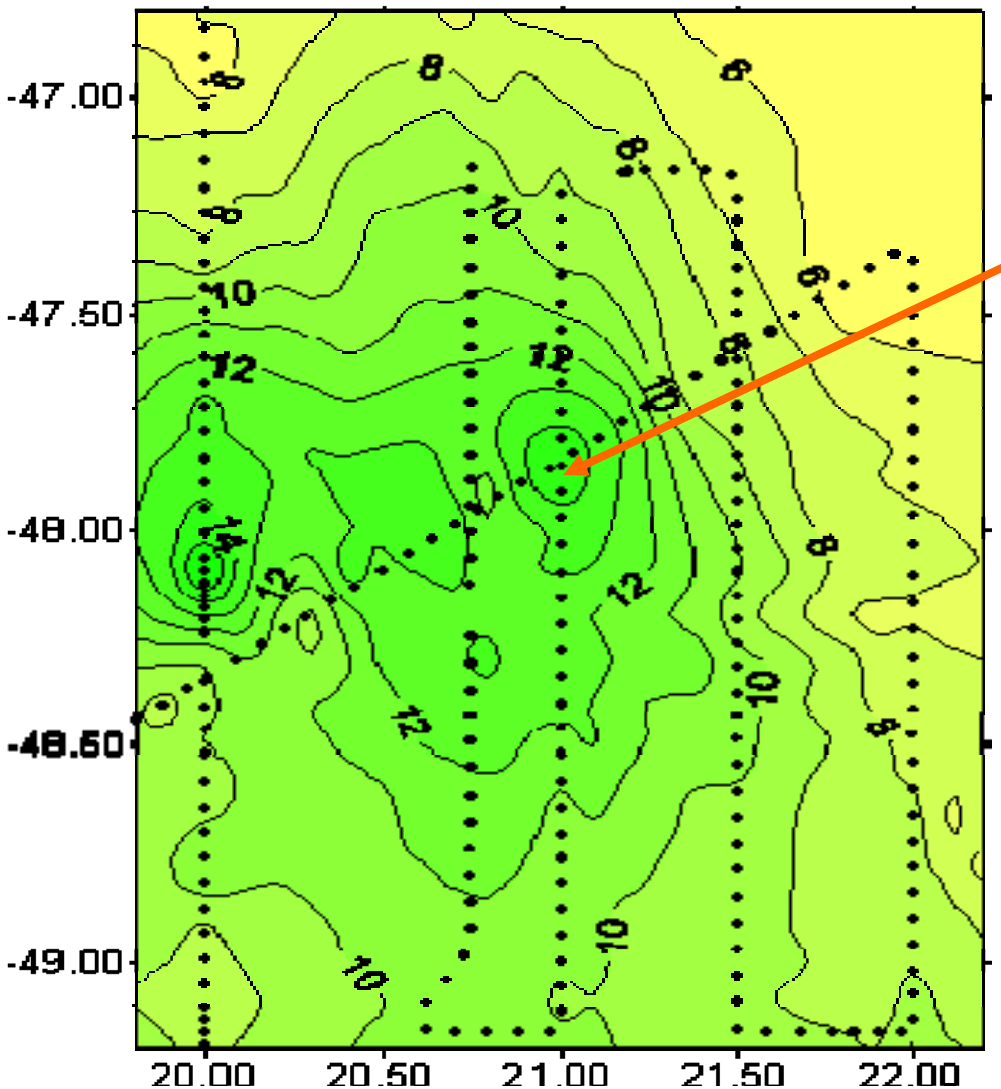
ice-free between
50 and 56 South
with
high Silicate
exceeding
15 mmol.m-3

However ....

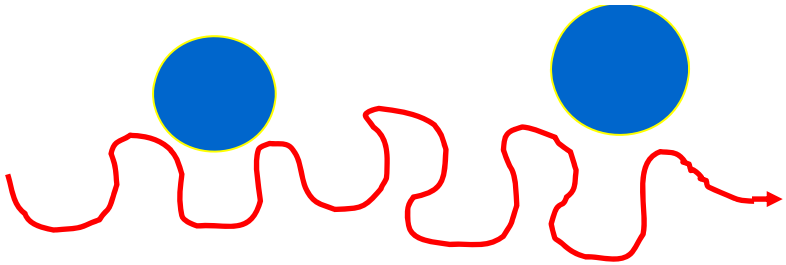



storm trajectories
20°
10°
30°
0°
40°
350°
50°
-30°
-30°
-40°
5
-50°
15
-60°
-60°
-70°
-70°
-80°
-80°
0
10
20
30
40
50
60
70
80
90
100
Ice_coverage

Silicate (µM) Grid



cold Antarctic eddy, high silicate;
but moved north
conveniently off storm trajectory



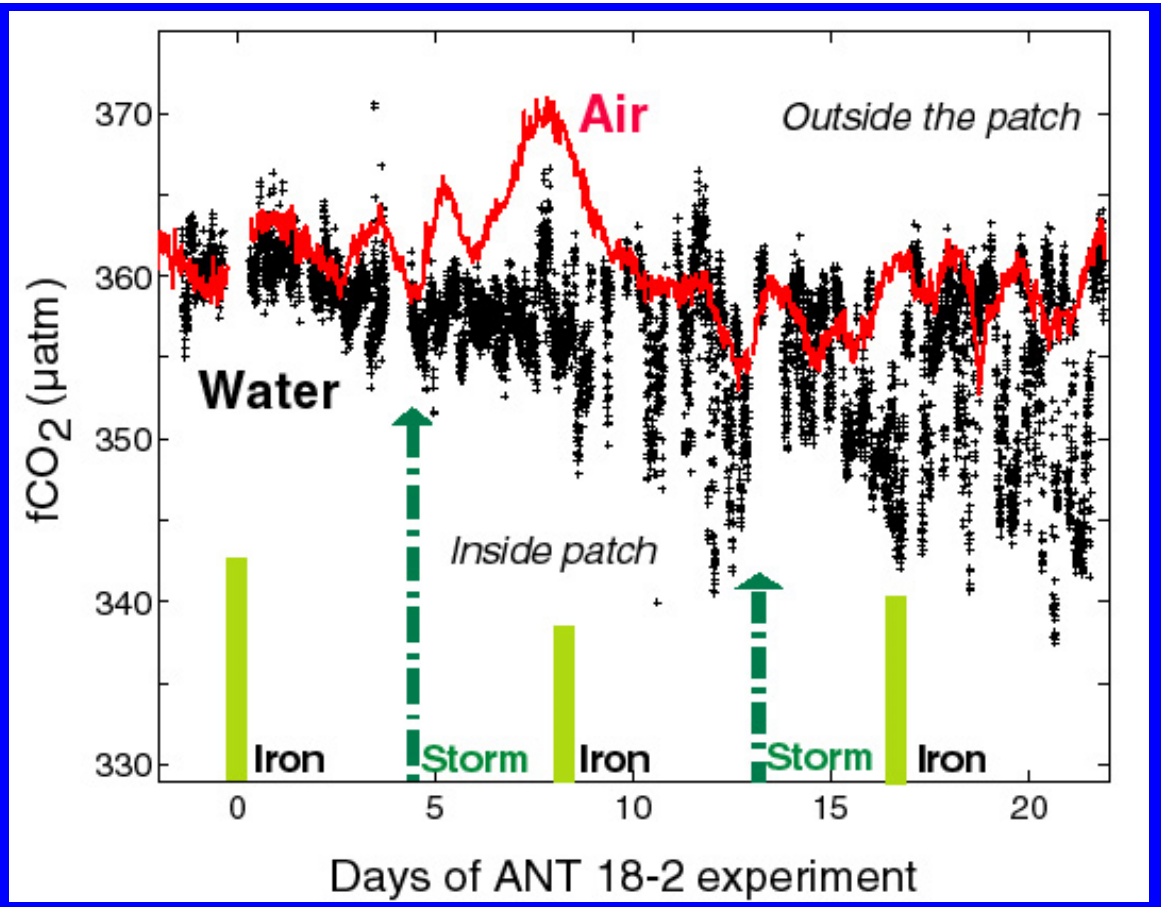
Polar Frontal jet

Flushing down the FeSO4 powder

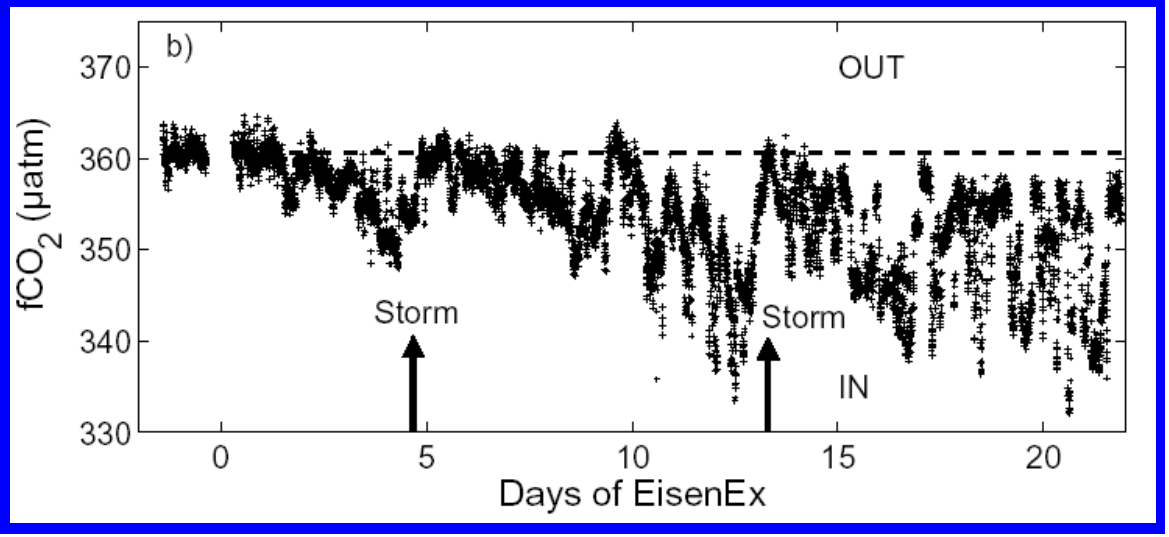
HCl
acid

down the drain

EISENEX
Surface water fCO2

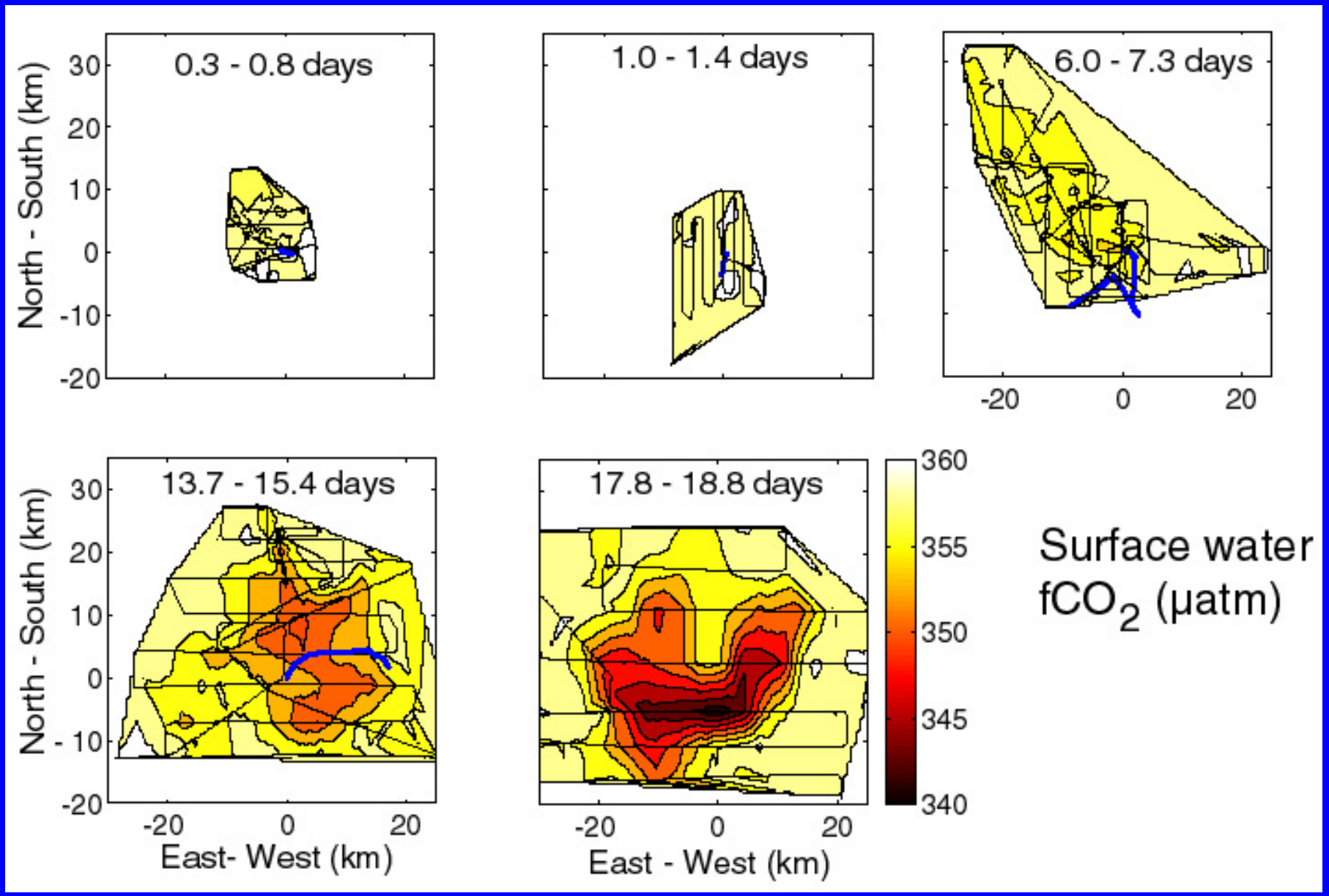


Dorothee Bakker et al, Deep-Sea Research, submitted



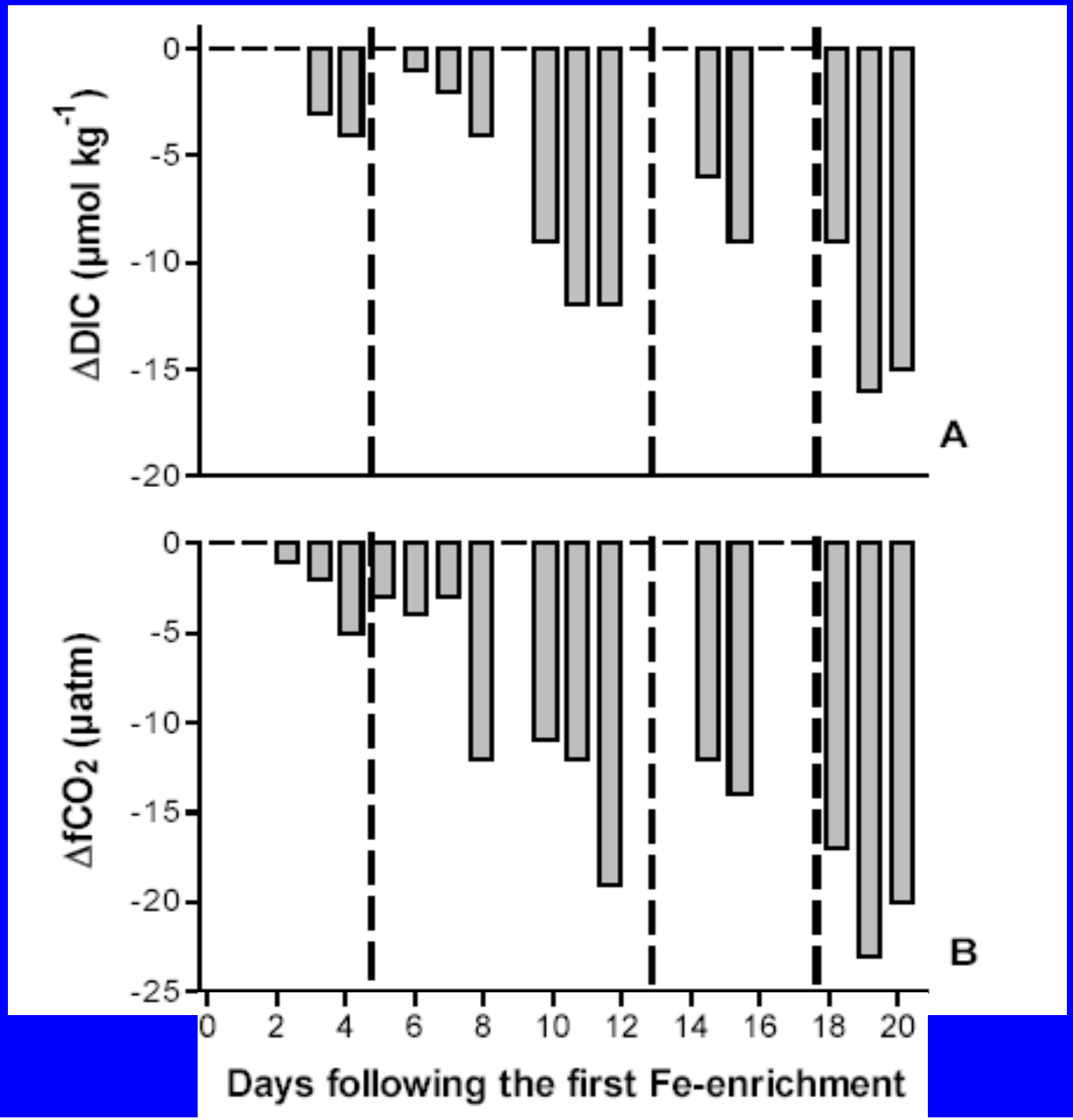
normalized to 4 ^{0}C and standard atmospheric pressure

Surface water fCO_2 maps in EisenEx



(Dorothee Bakker and Andy Watson, UEA)

Eisenex delta-DIC and delta-fCO2

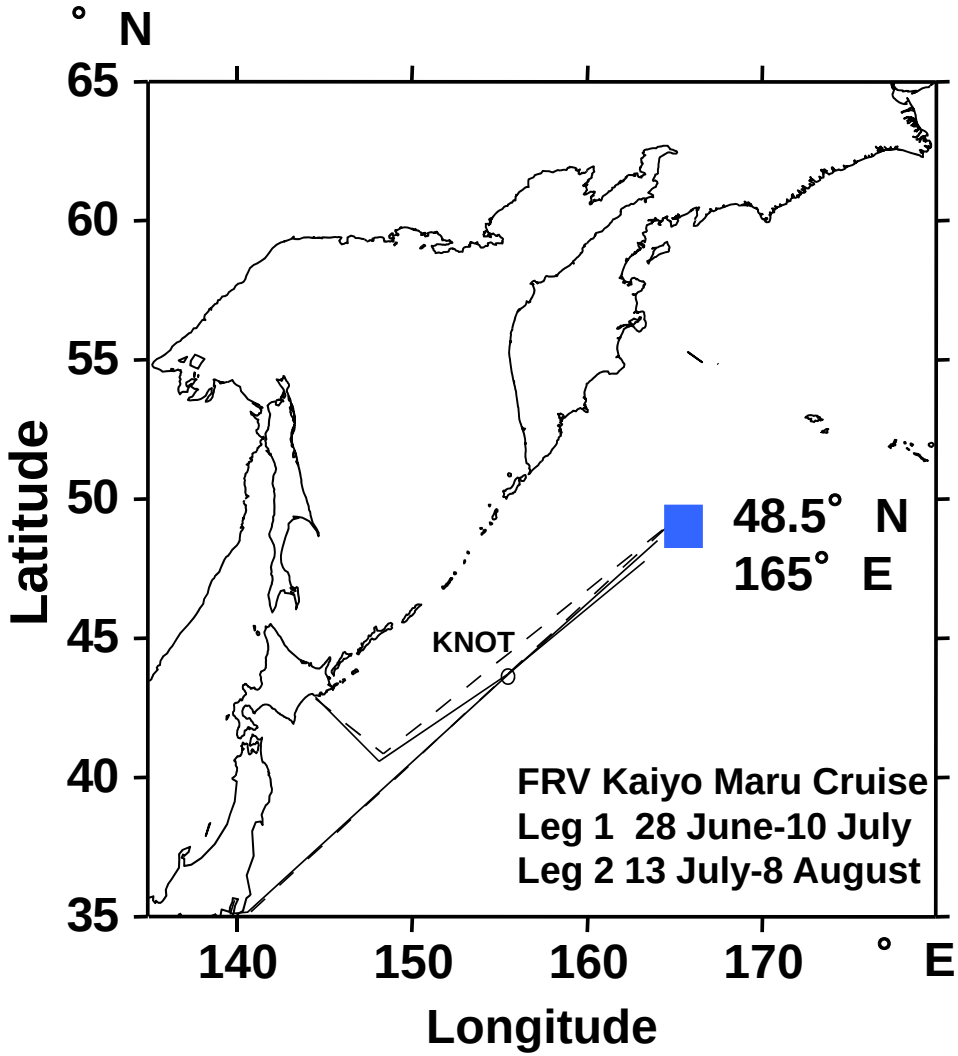


Bozec et al, Mar Chem, in press

Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study SEEDS

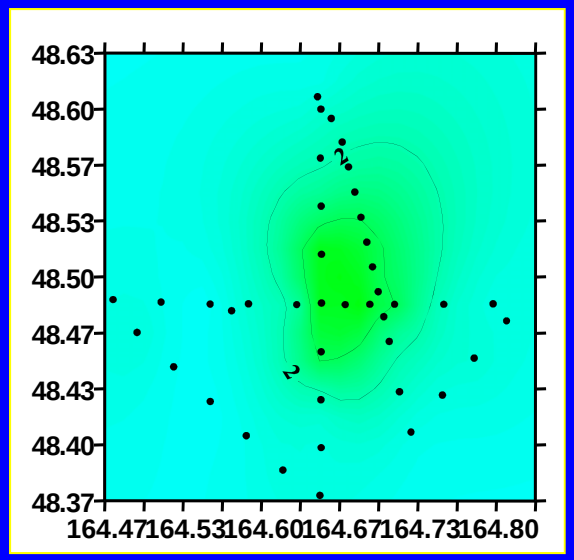
1 single Fe infusion
Fe = 5 nM at time zero

Kaiyo Maru at very calm sea

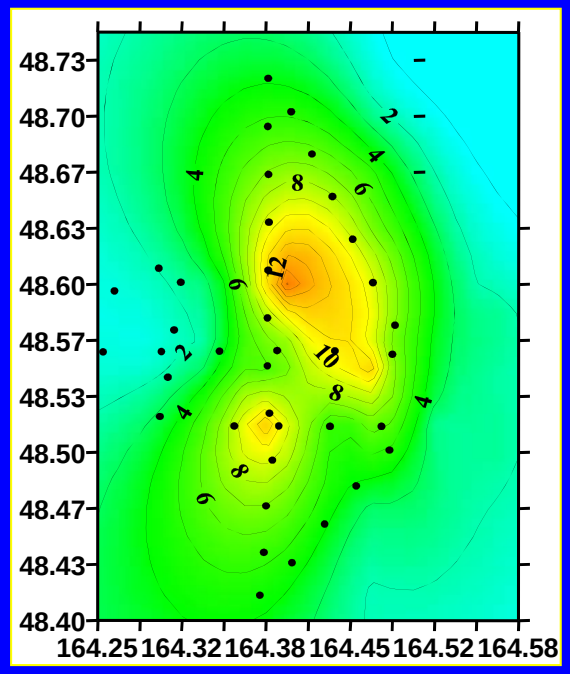


Contours of Chlorophyll *a* concentration

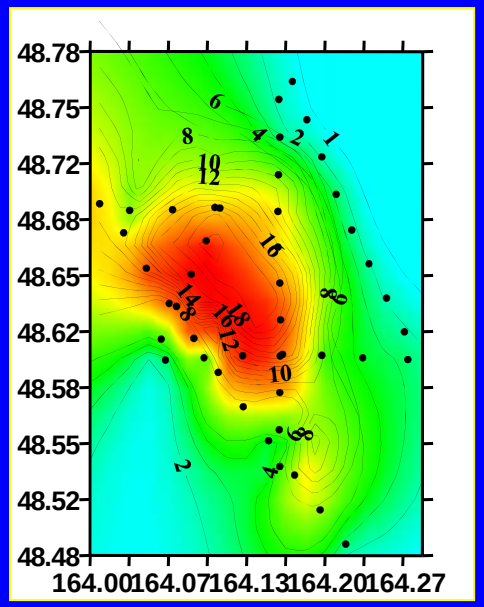
Day 6



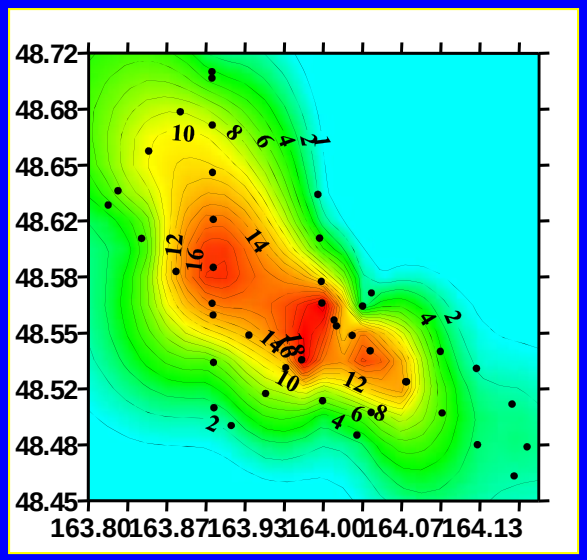
Day 8



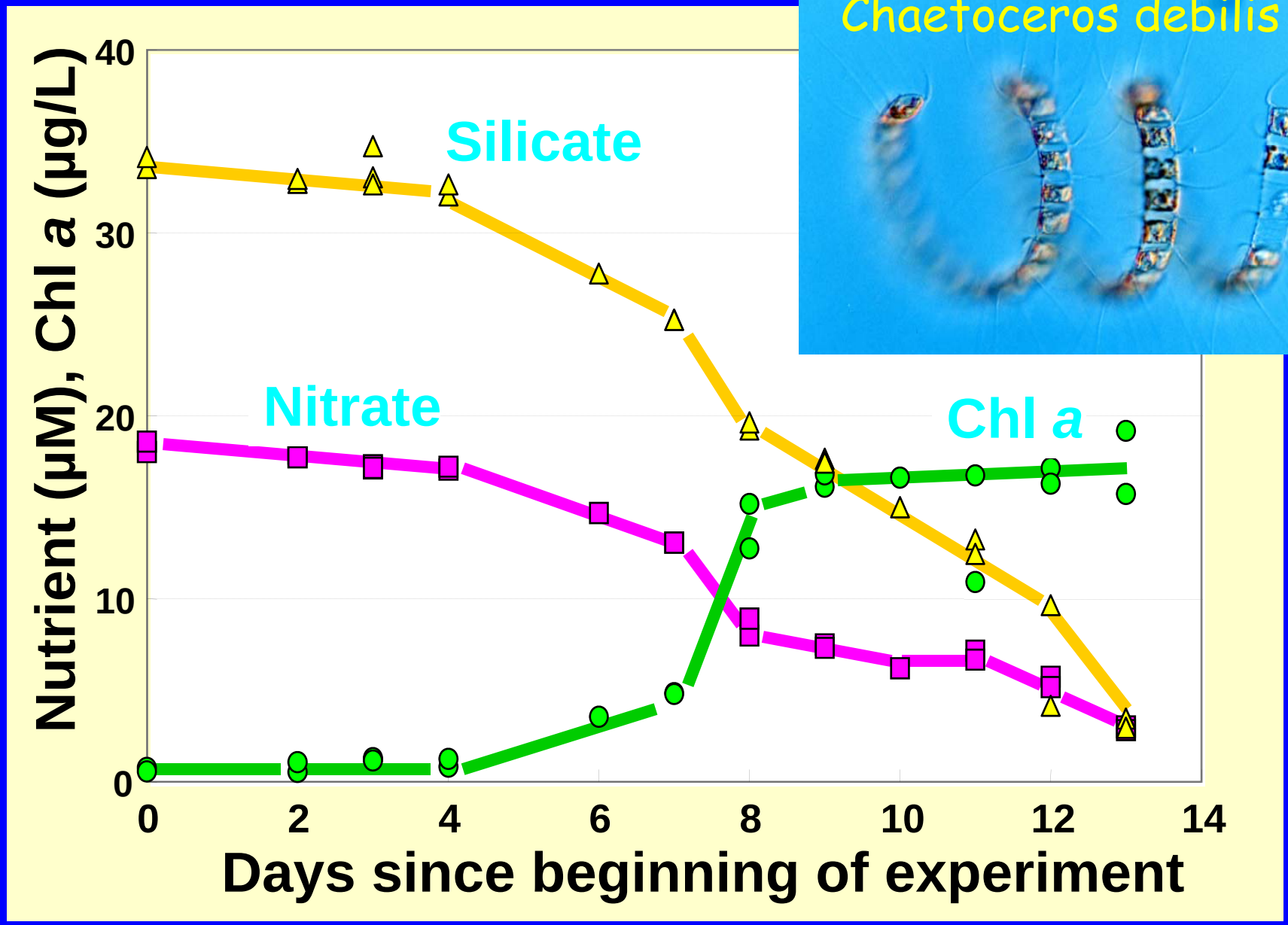
Day 10



Day 12

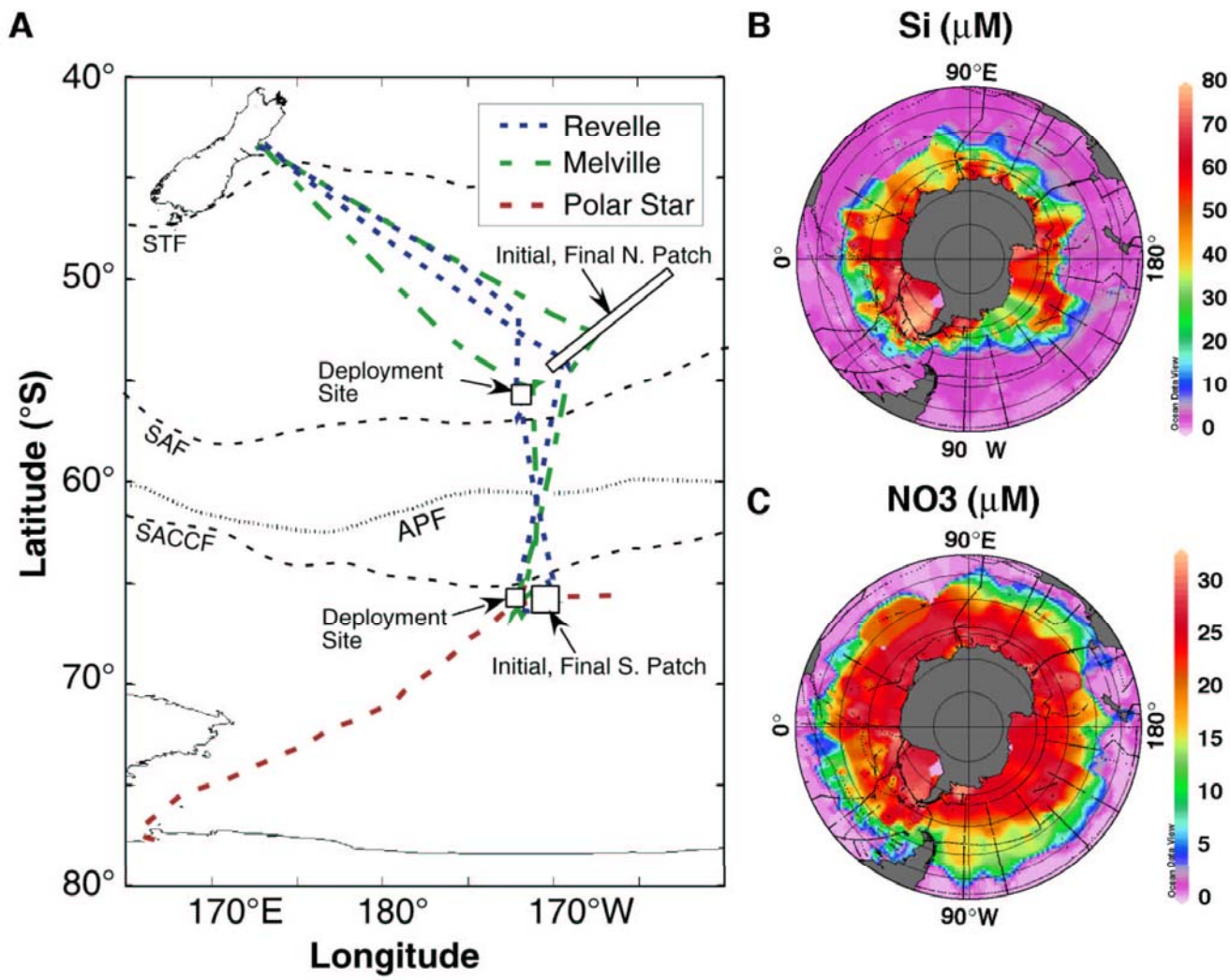


Time-series data of nutrients and Chl *a*



SOFEX 2002

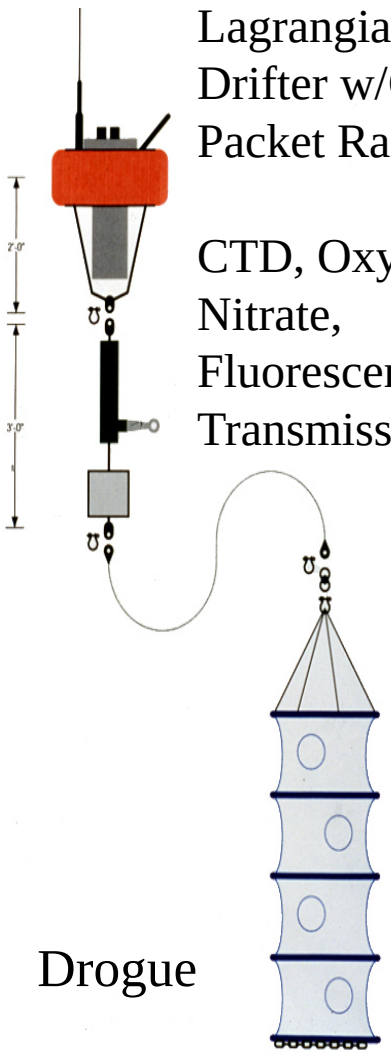
North and South Patches



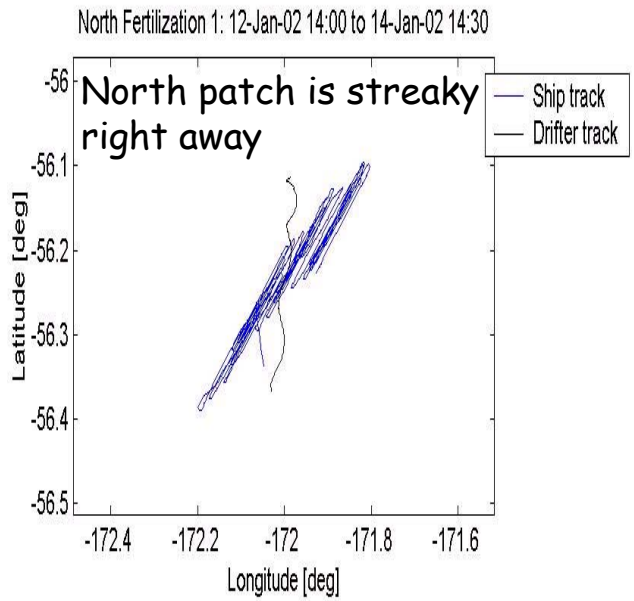
slide courtesy Ken Buesseler

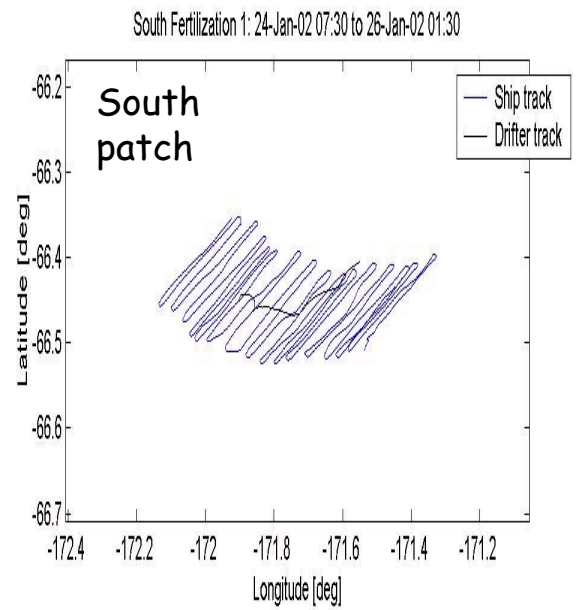
MBARI Lagrangian Drifter w/GPS, Packet Radio

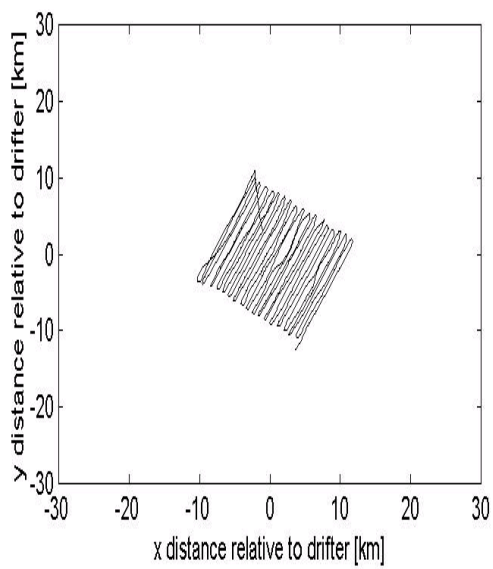
CTD, Oxygen Nitrate, Fluorescence, Transmissometer

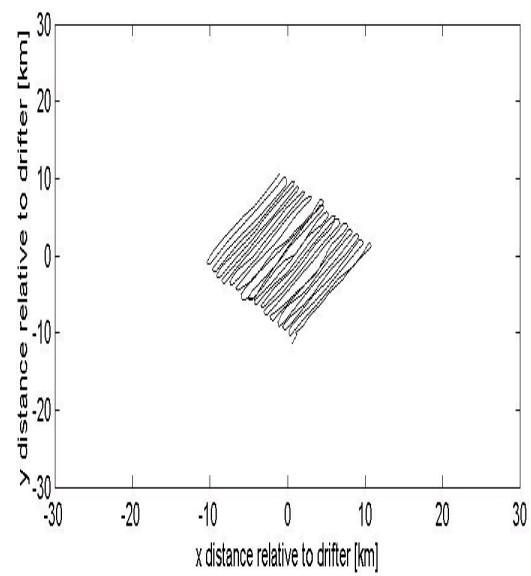


Drogue

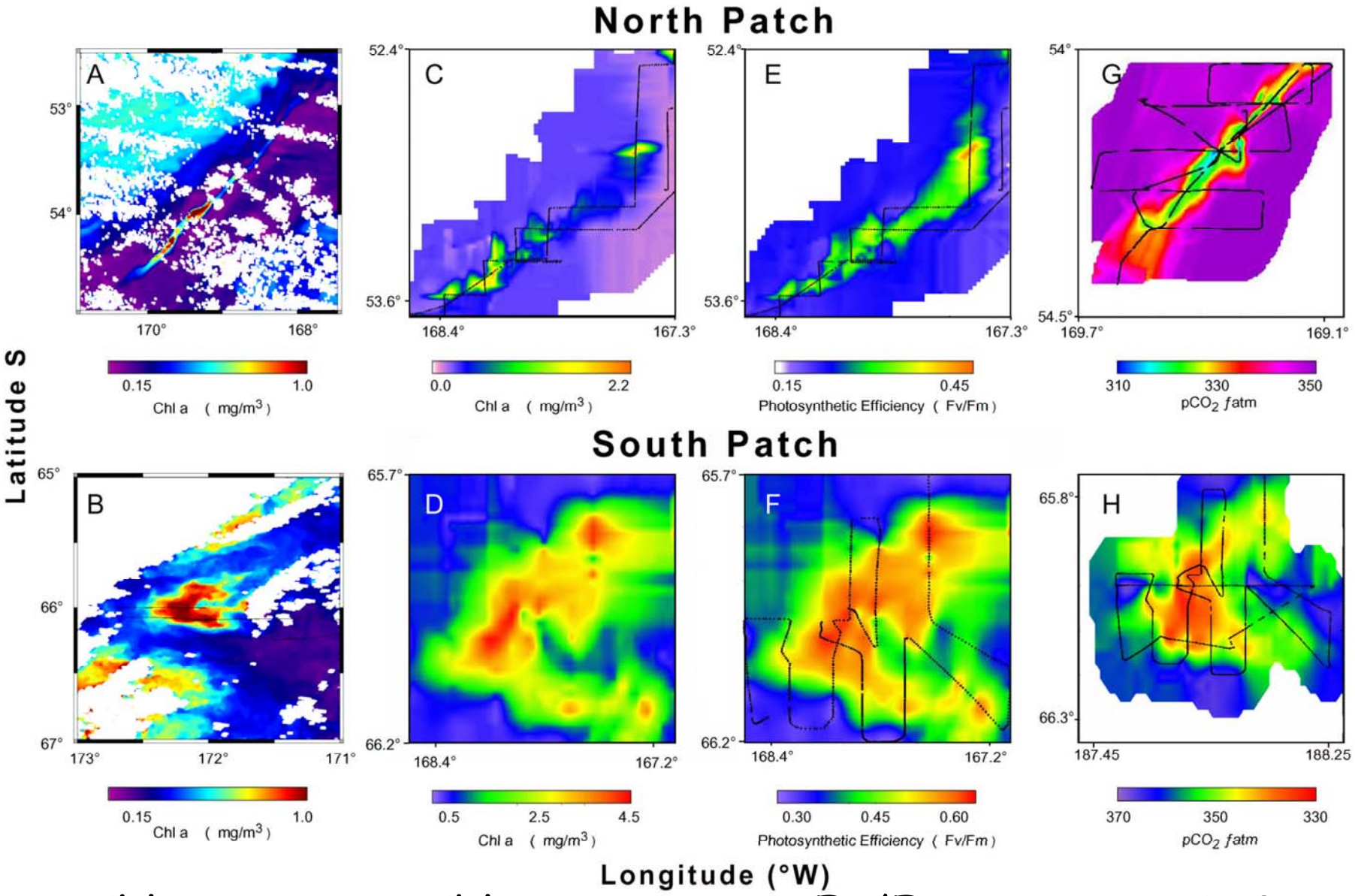






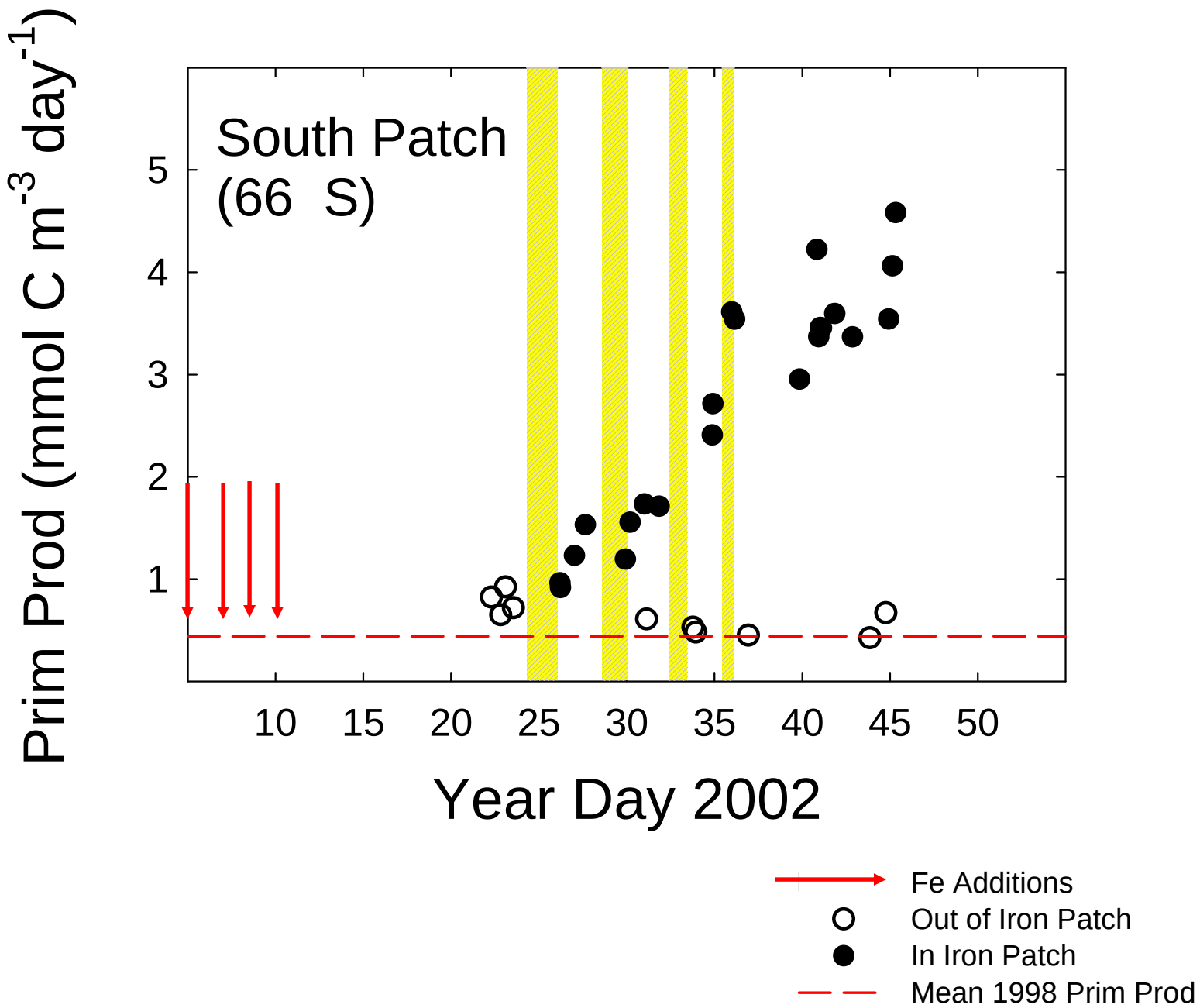


slide courtesy Kenneth Coale



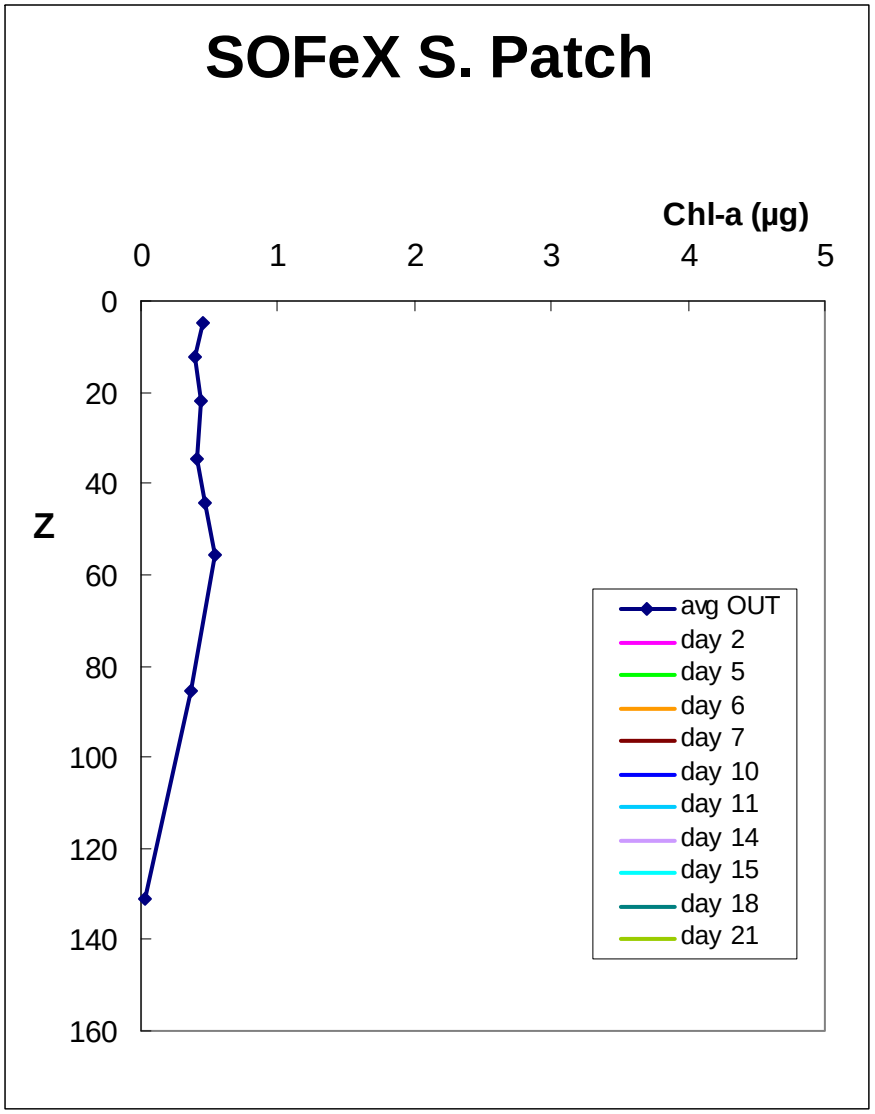
$Chl_{satellite}$ $Chl_{shipboard}$ Fv/Fm pCO2

slide courtesy Ken Buesseler

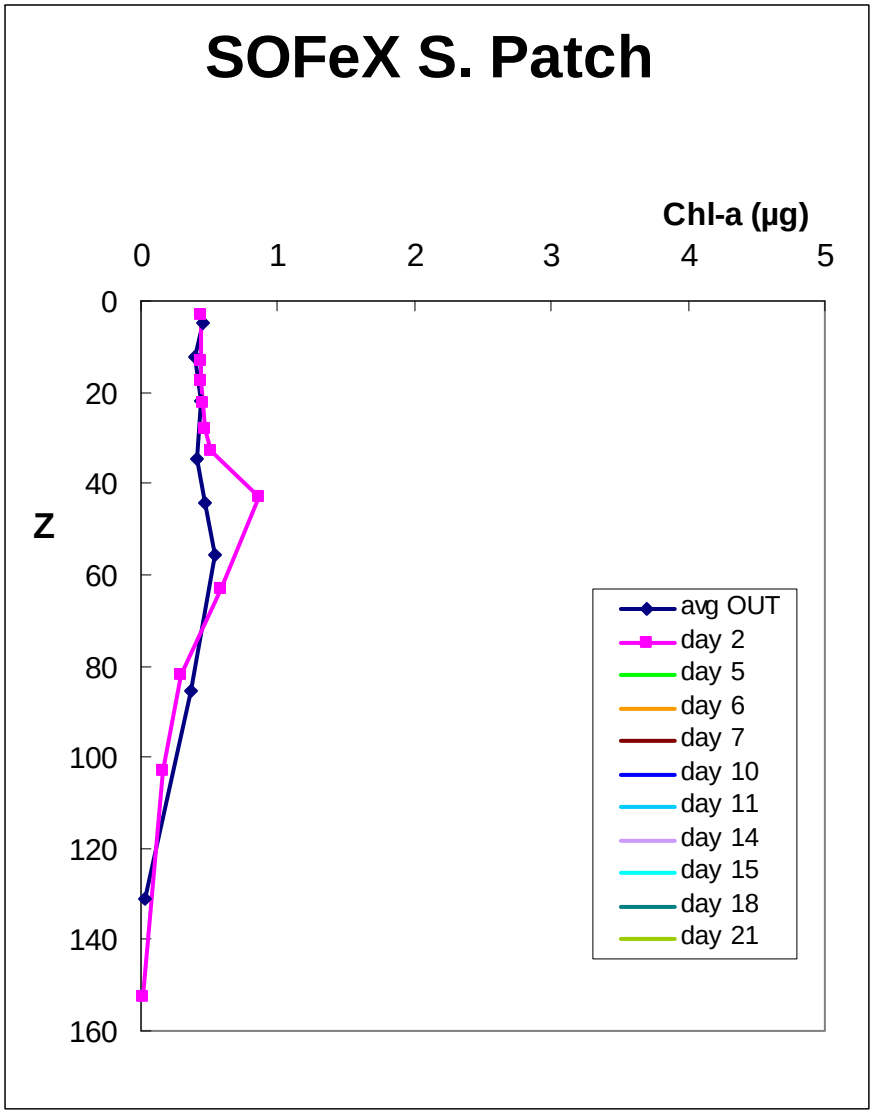

South Patch
(66 S)
Prim Prod (mmol C m-3 day-1)
Year Day 2002
1
2
3
4
5
10
15
20
25
30
35
40
45
50
Fe Additions
Out of Iron Patch
In Iron Patch
Mean 1998 Prim Prod

watch
Coale's
comic strip

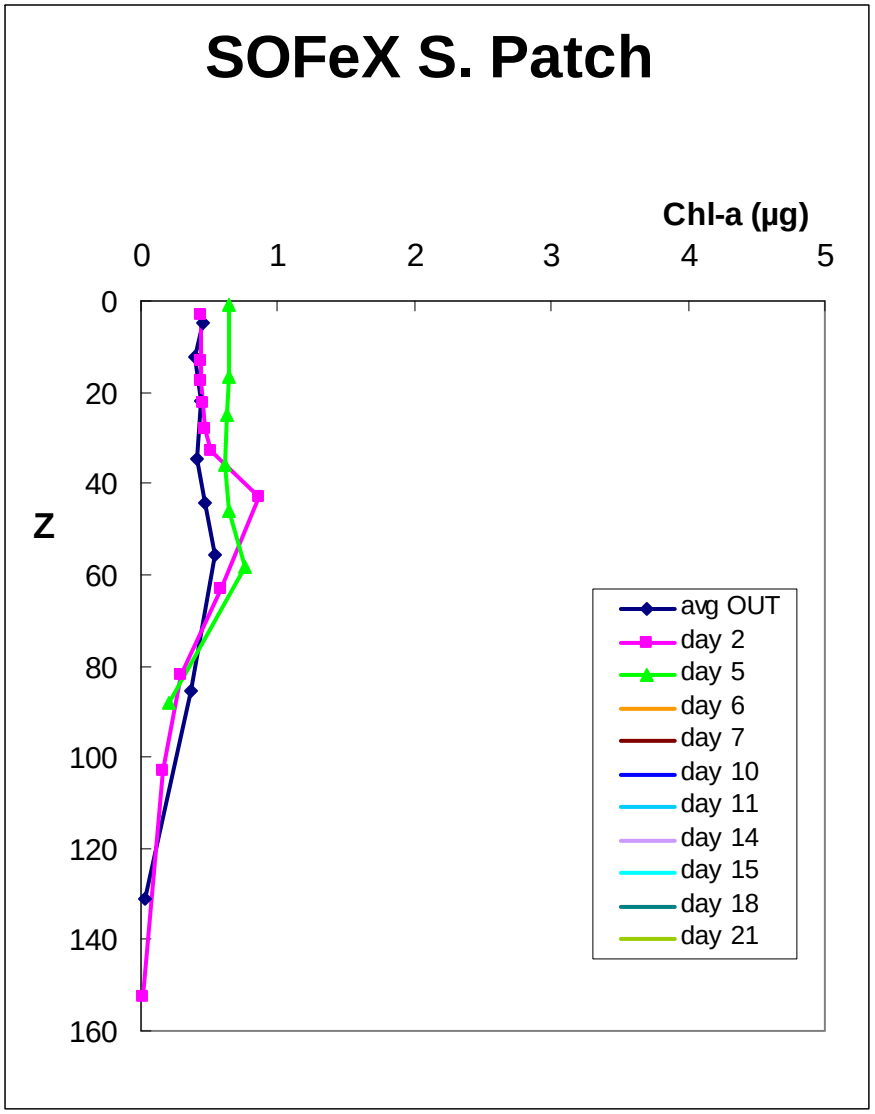
Chlorophyll Movie



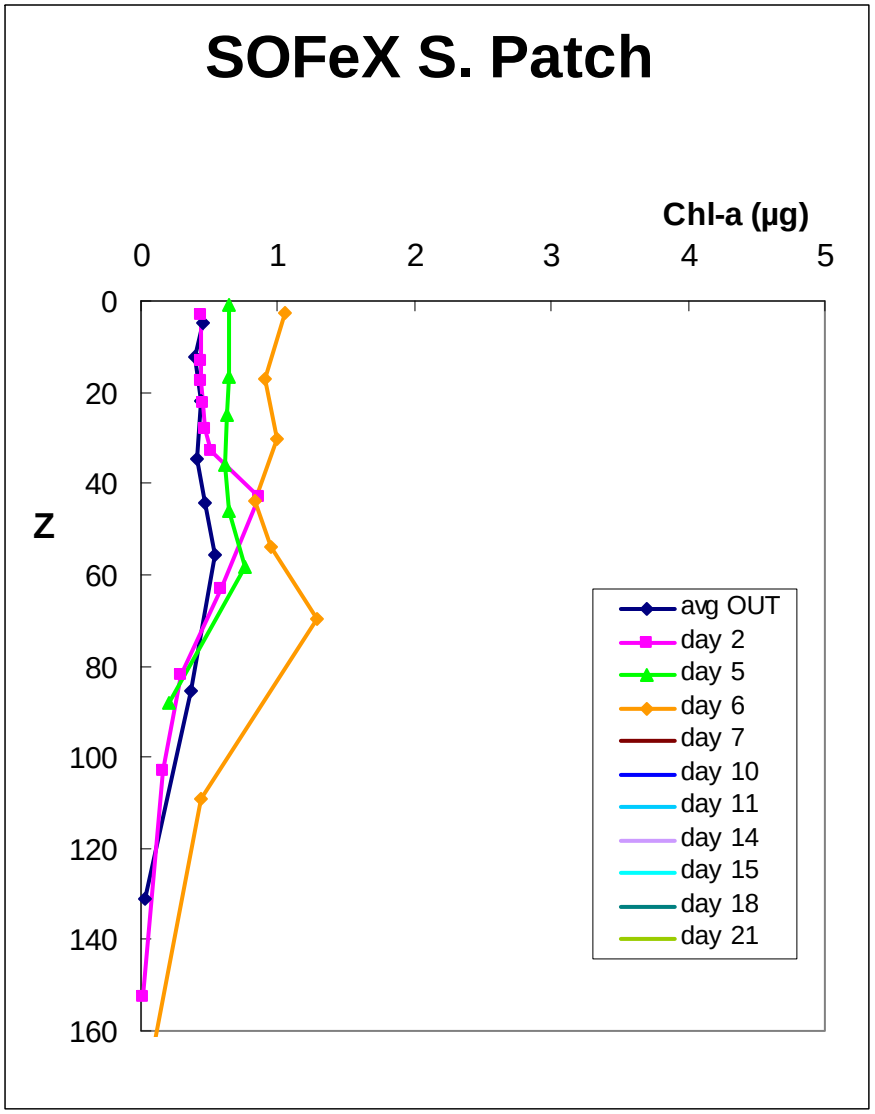
Chlorophyll Movie



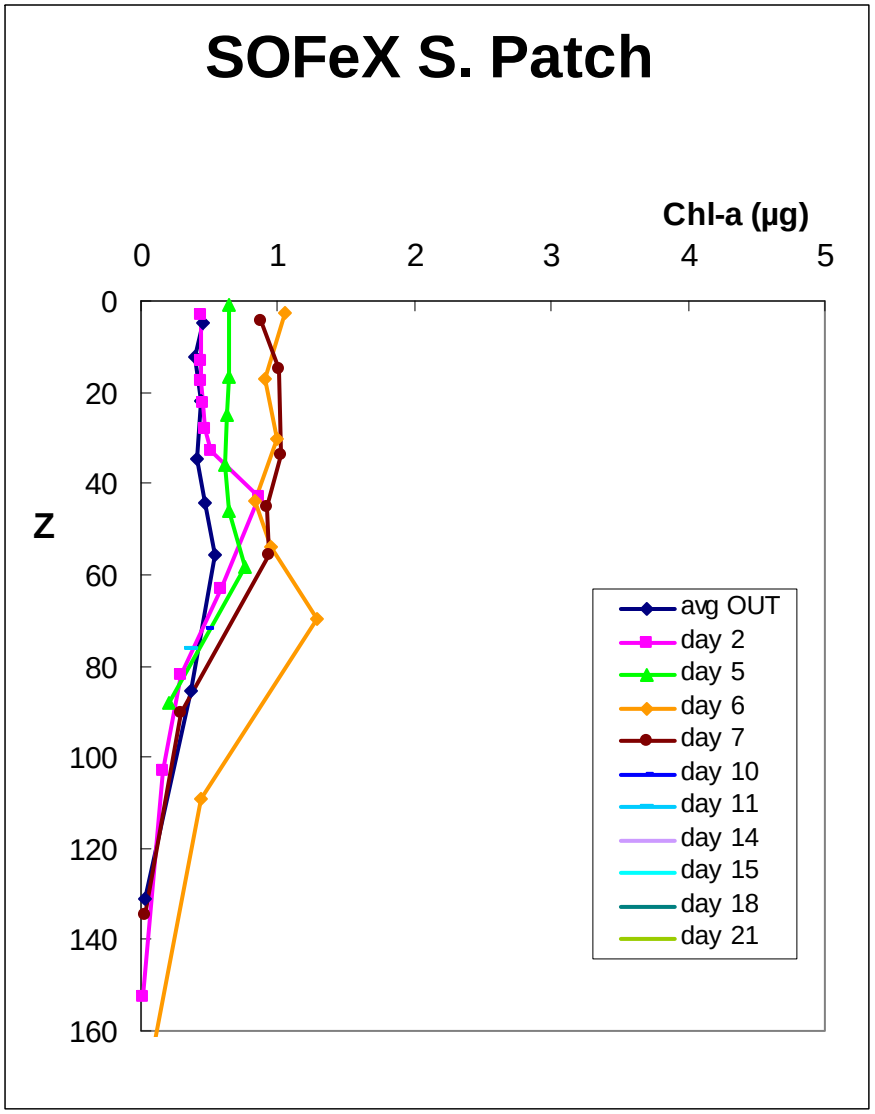
Chlorophyll Movie



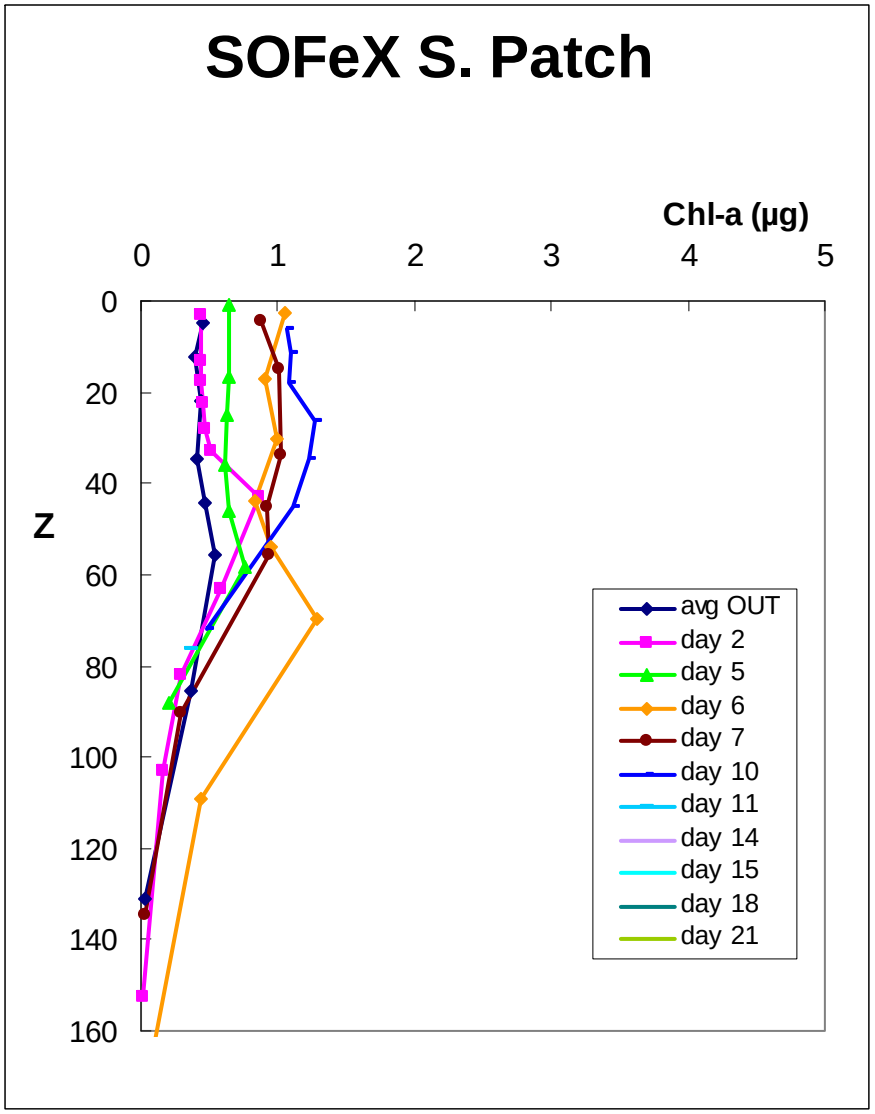
Chlorophyll Movie



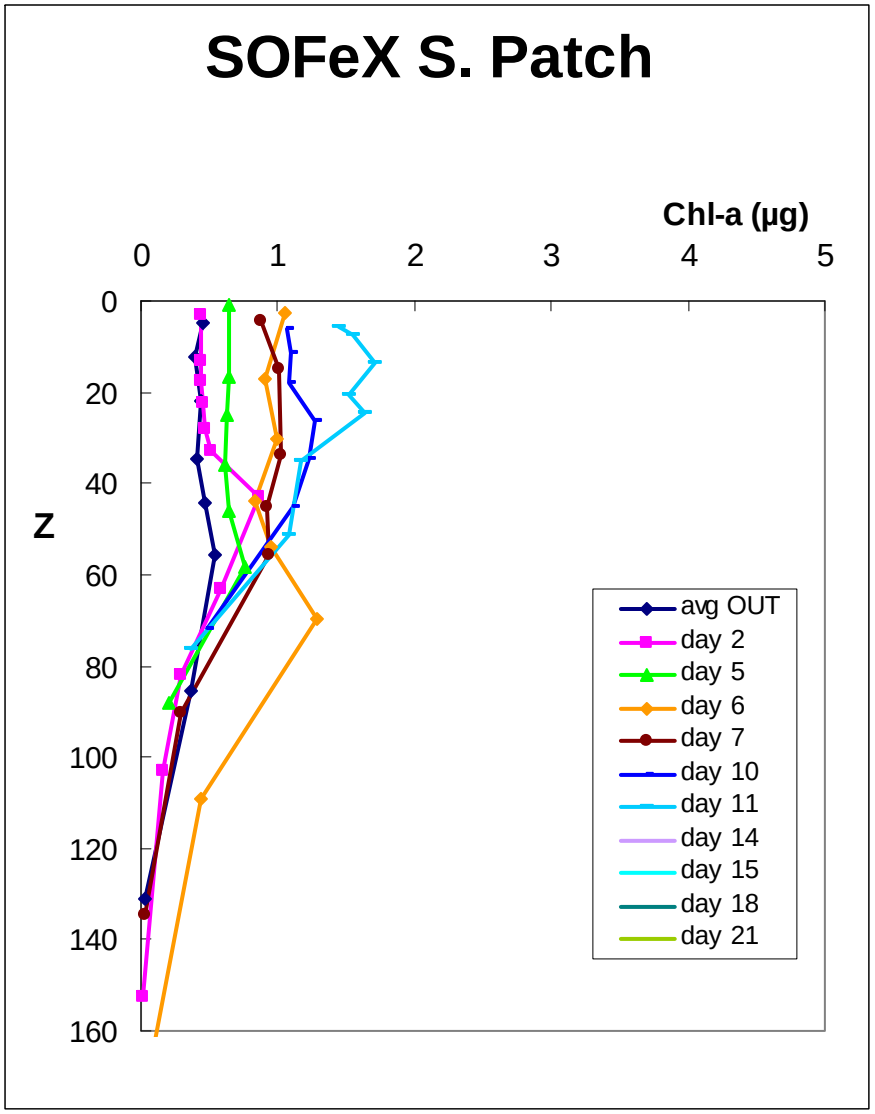
Chlorophyll Movie



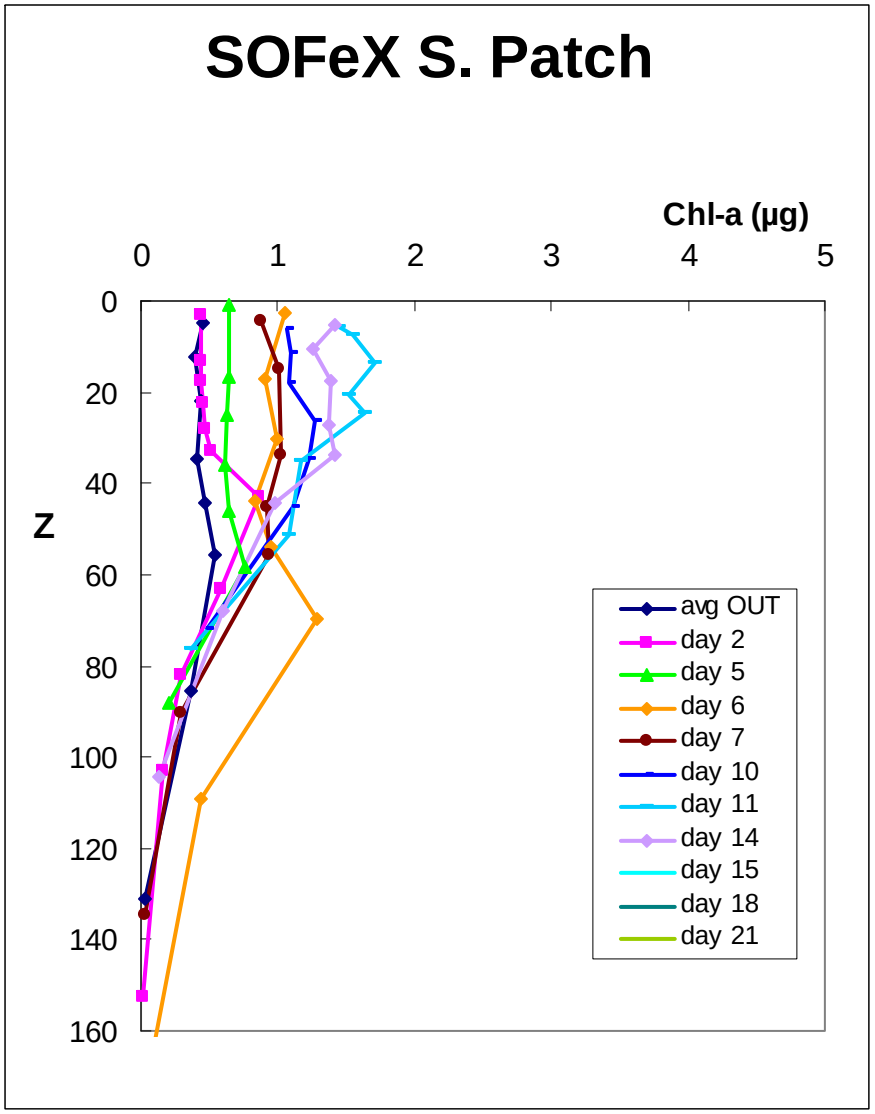
Chlorophyll Movie



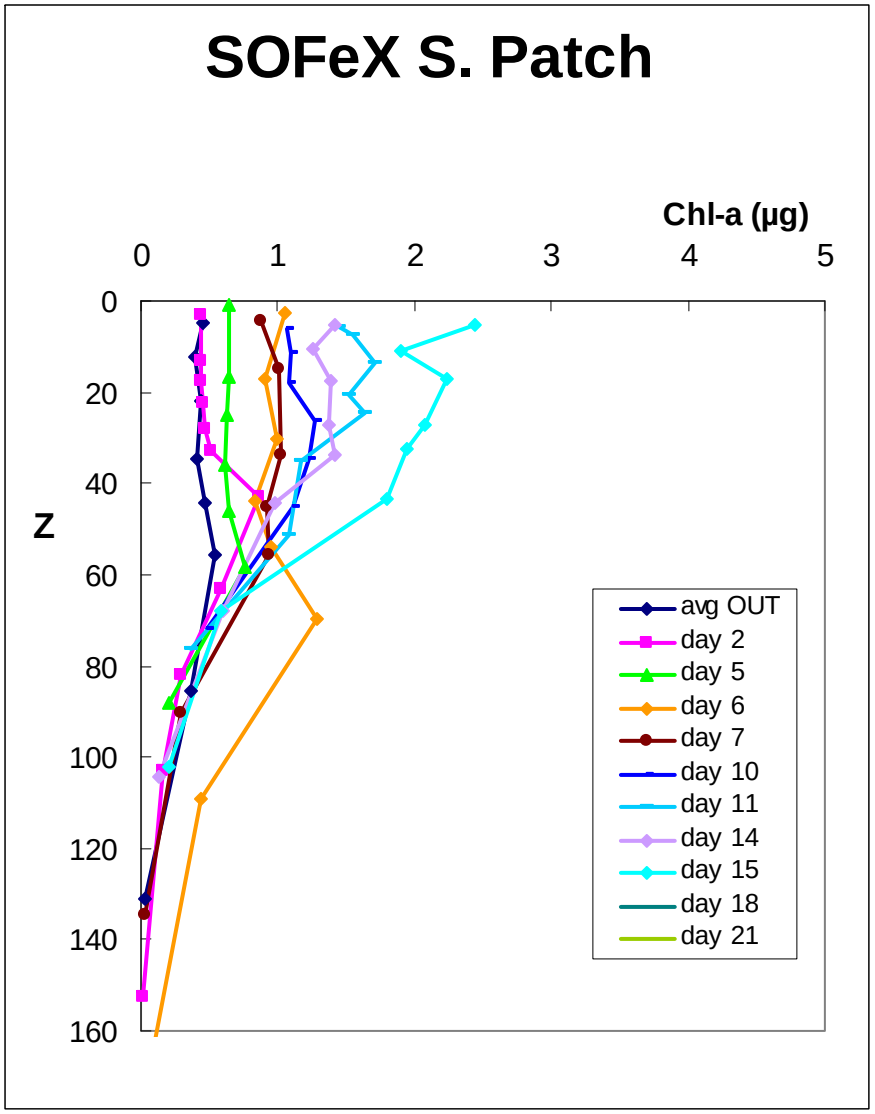
Chlorophyll Movie



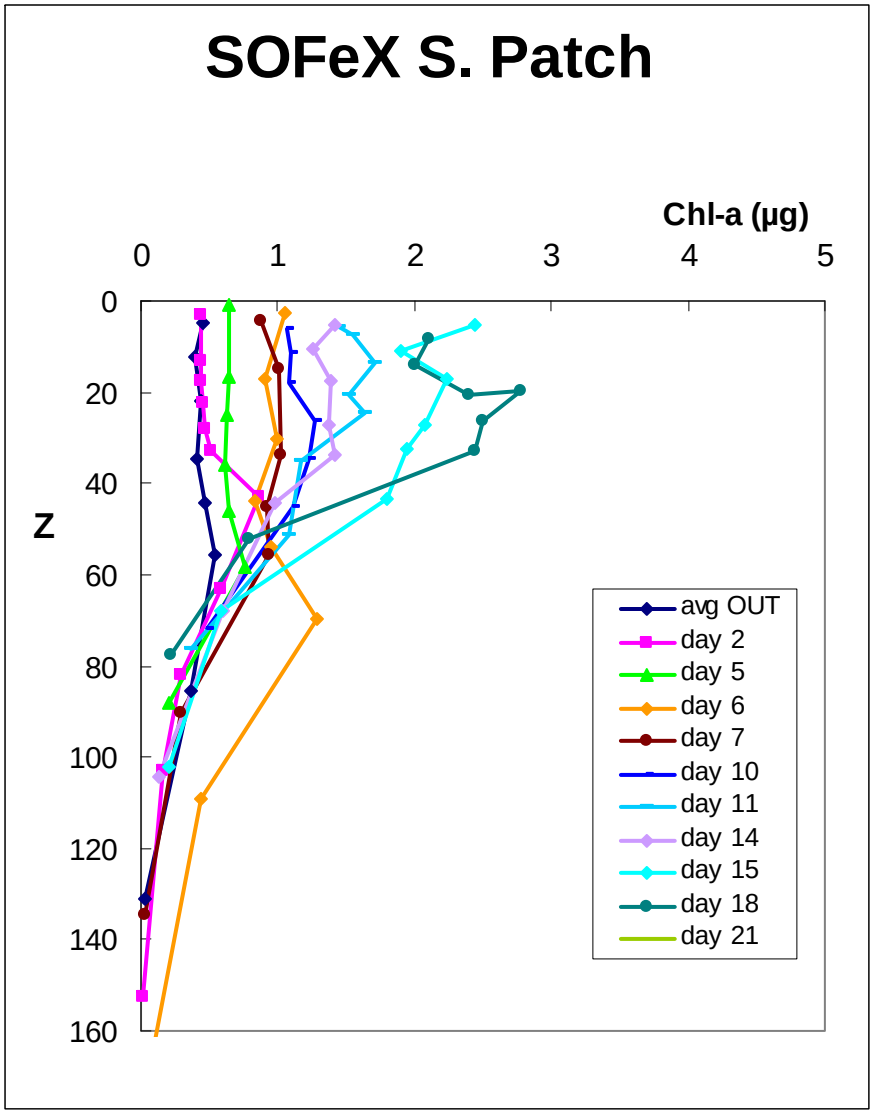
Chlorophyll Movie



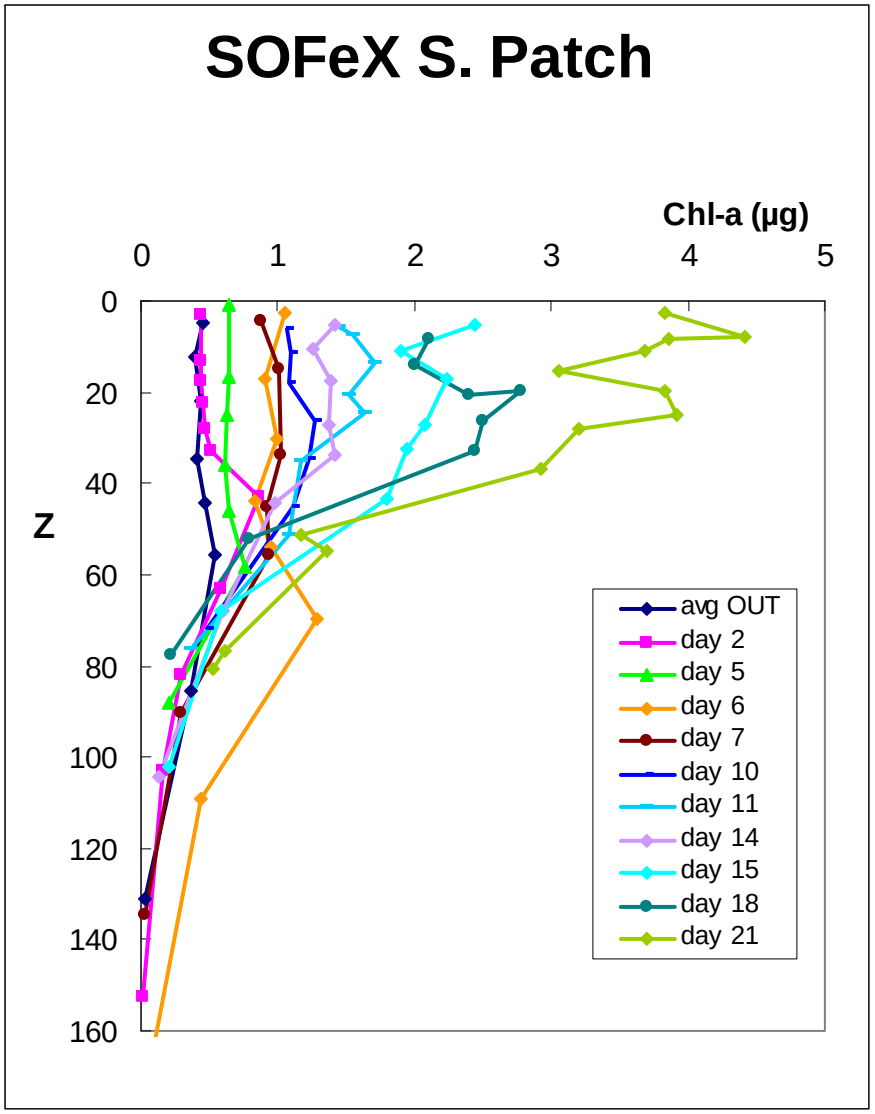
Chlorophyll Movie



Chlorophyll Movie



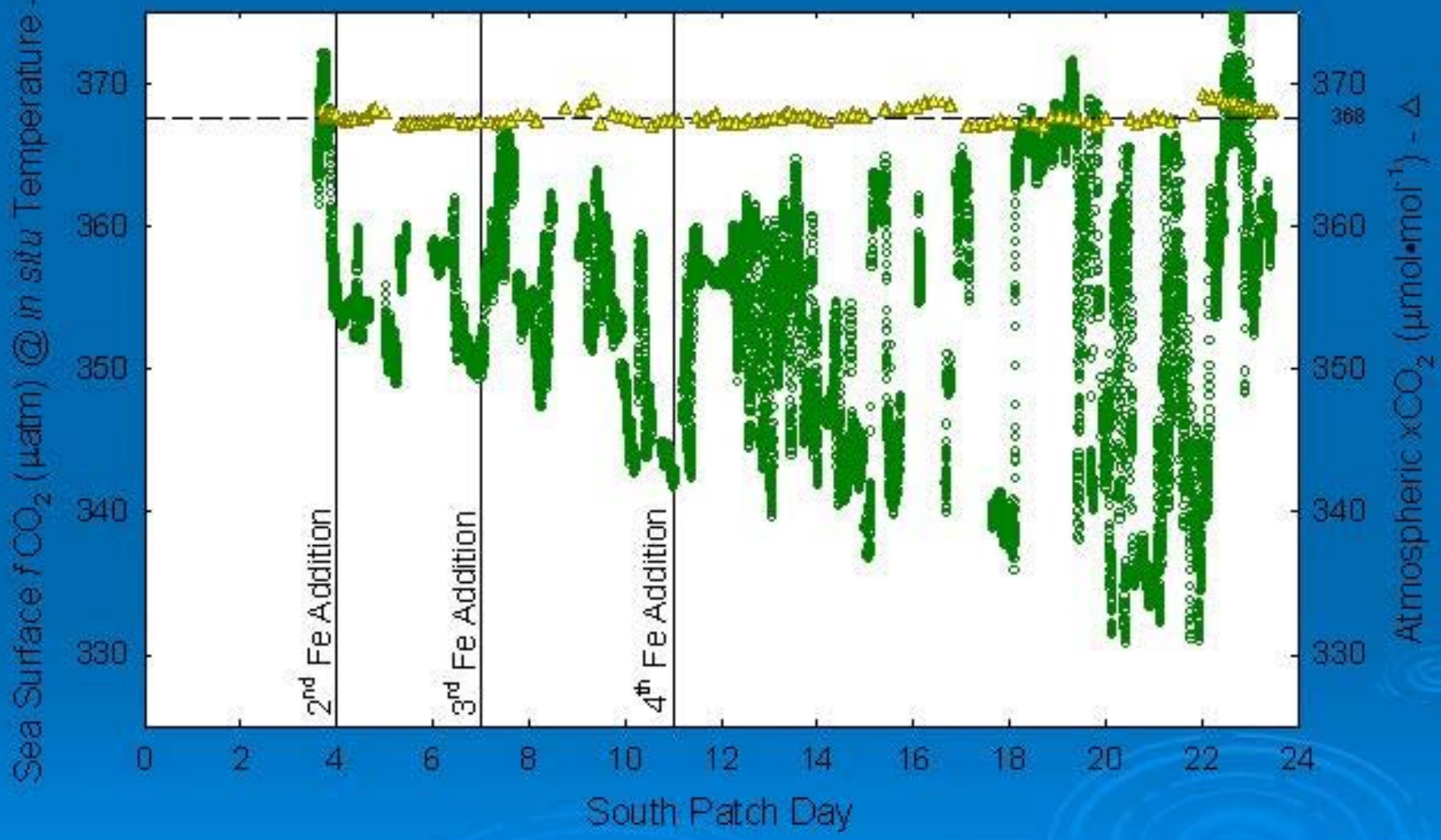
Chlorophyll Movie




044-0610
66.09.03
170.59.92
OUT
ST-34
043-050

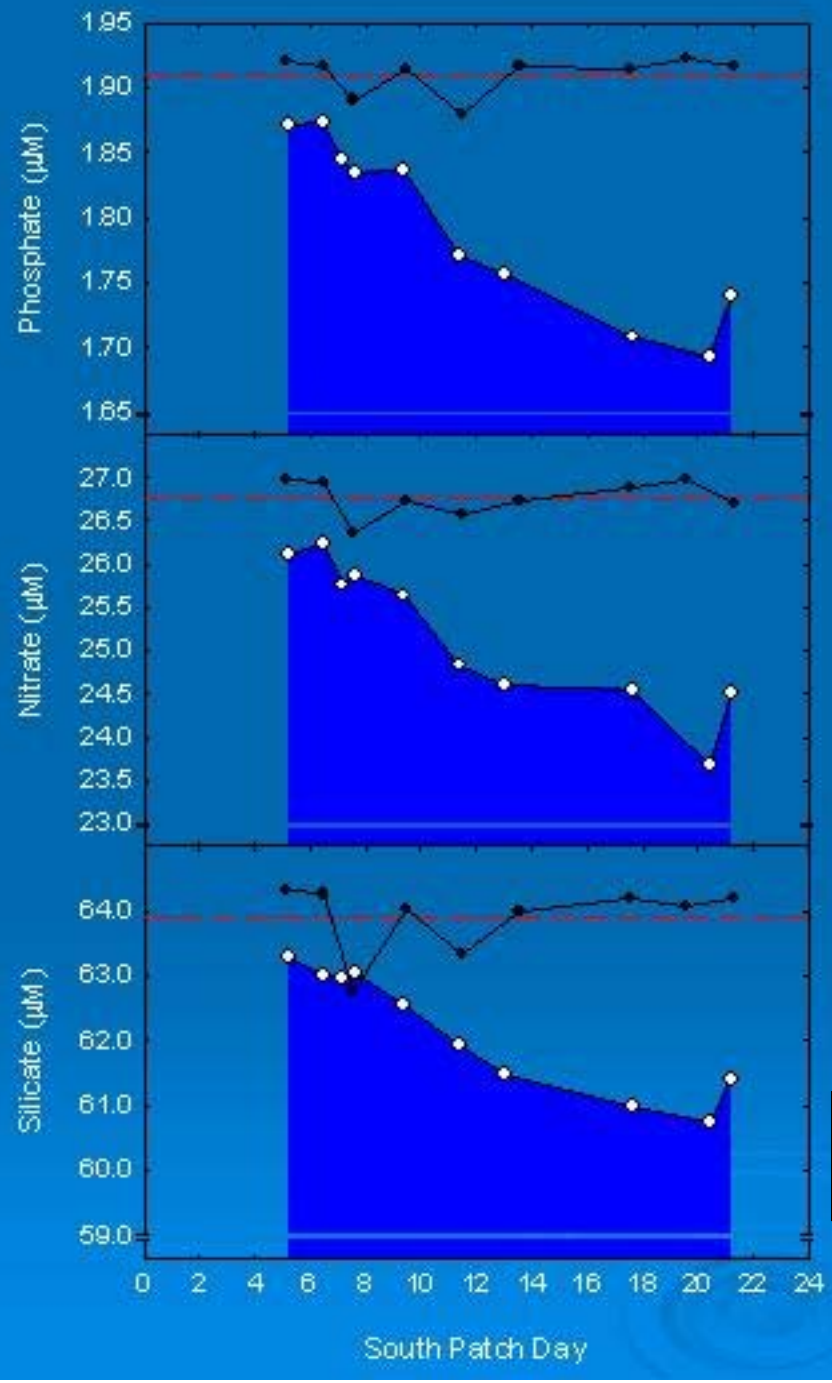
SOFEX South

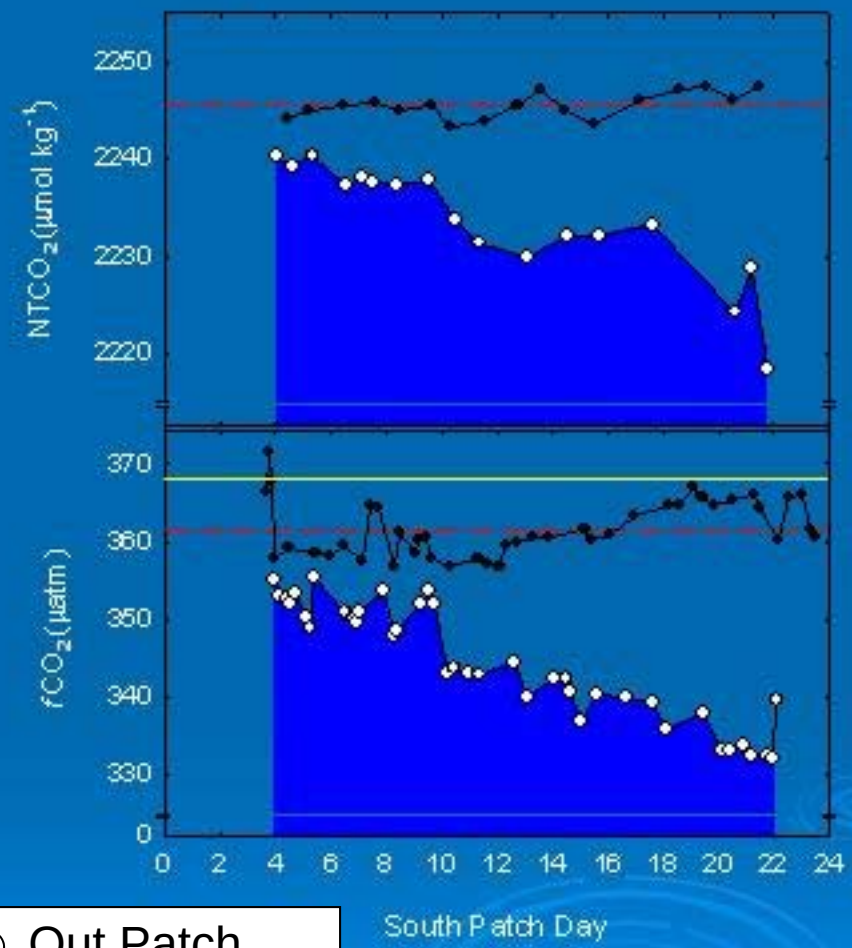
pCO2 in surface waters pCO2 in air



data and slide courtesy William Hiscock

South Patch – Time Series Response to Fe-enrichment



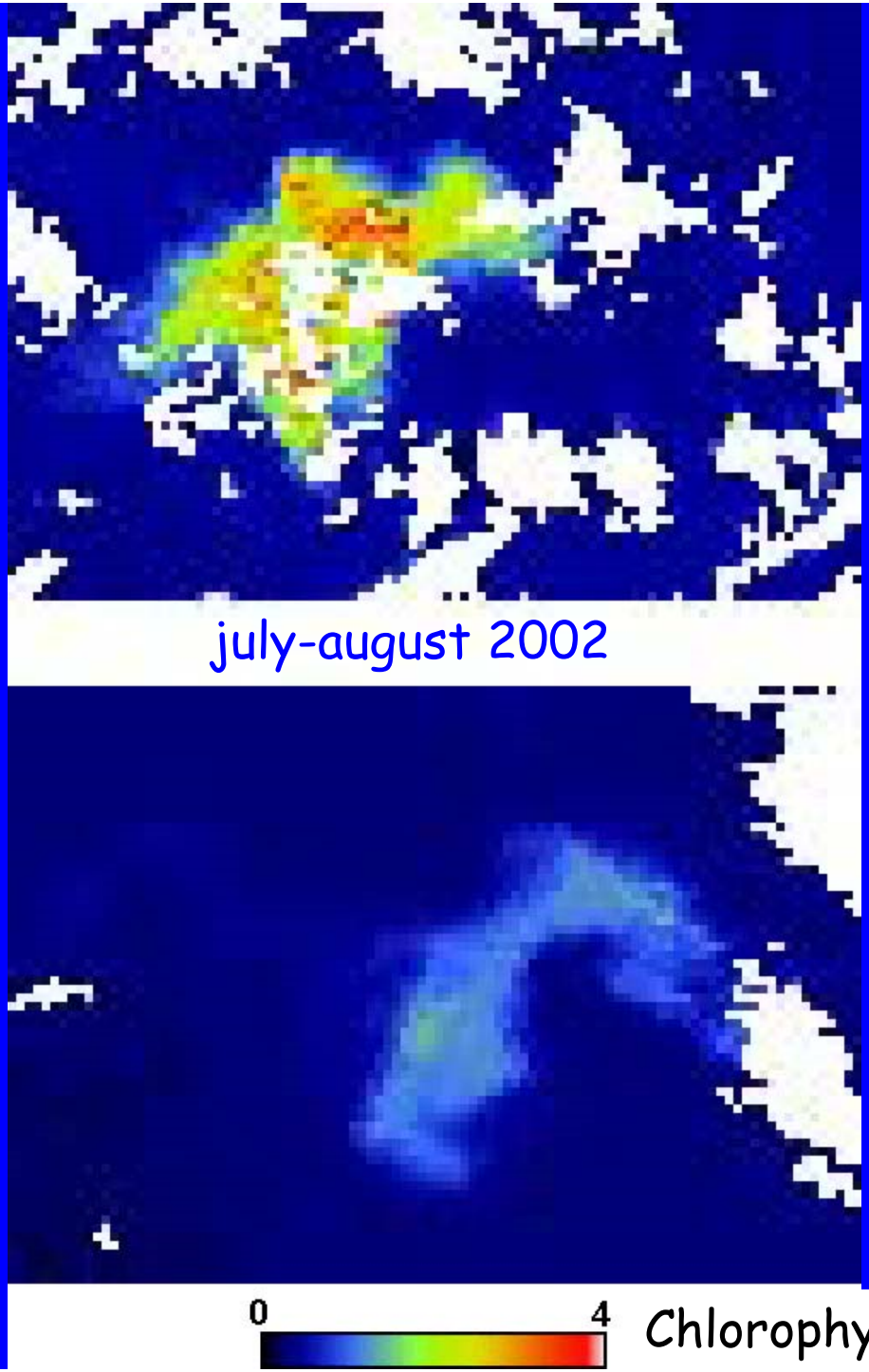


○ Out Patch
● In Patch

slide courtesy William Hiscock

SERIES:

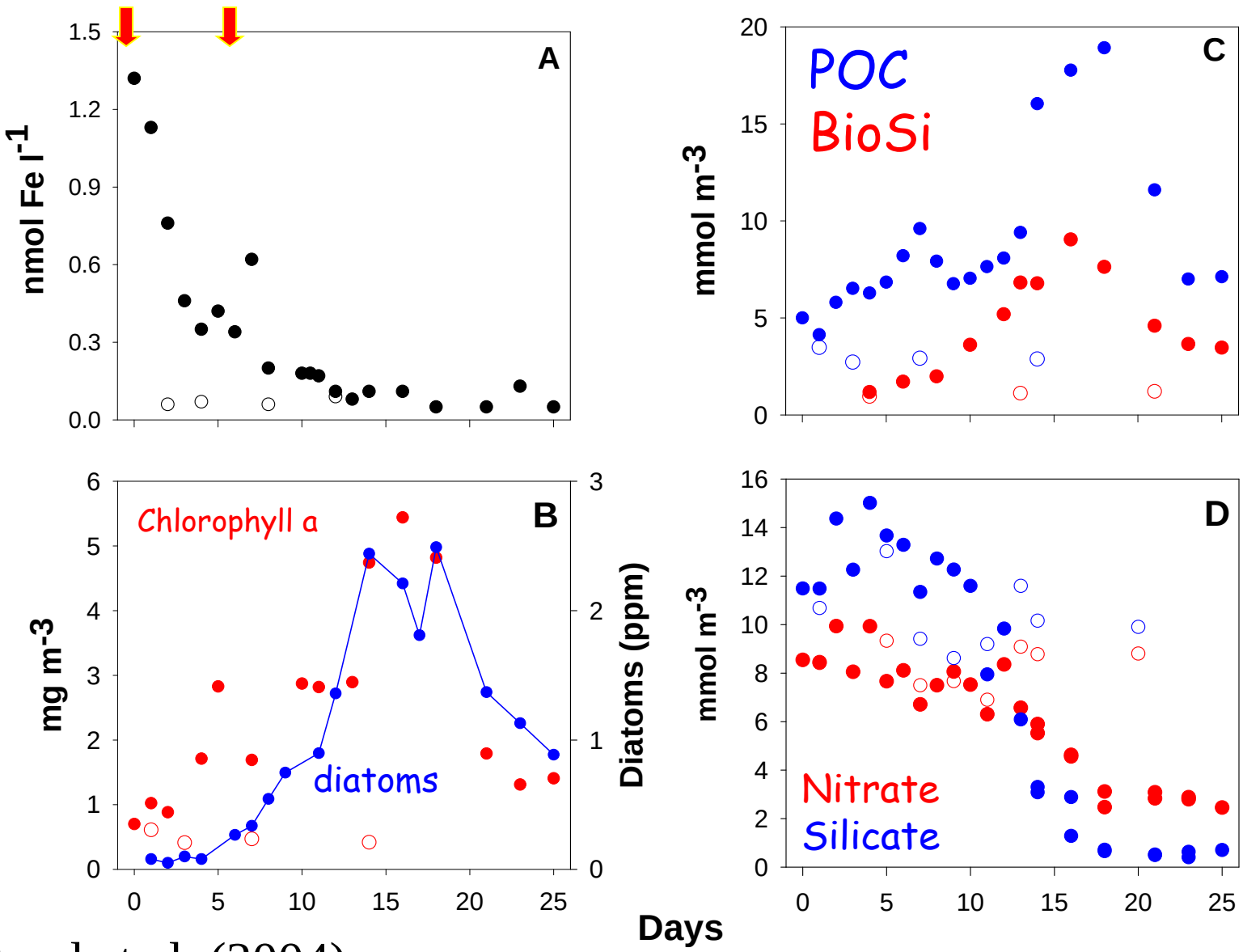
The decline and fate of an iron-induced subarctic bloom



SERIES bloom day 19

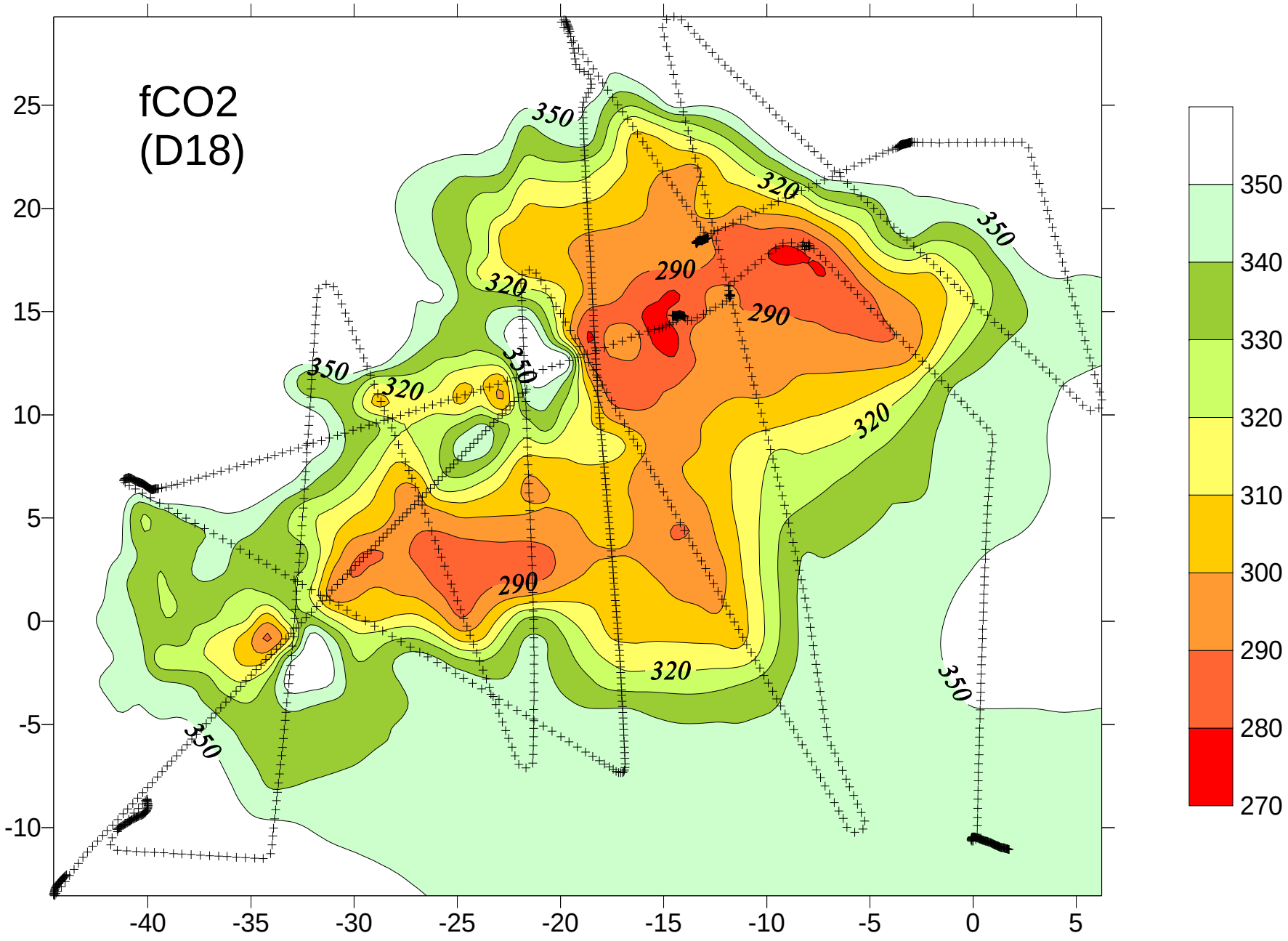
Bloom has declined on day 24

Boyd et al. (2004)



Boyd et al. (2004)

filled symbols is IN-PATCH
open symbols is OUT-PATCH



Boyd et et al. (2004)

SERIES 2002

three-ships experiment at peaceful Pacific

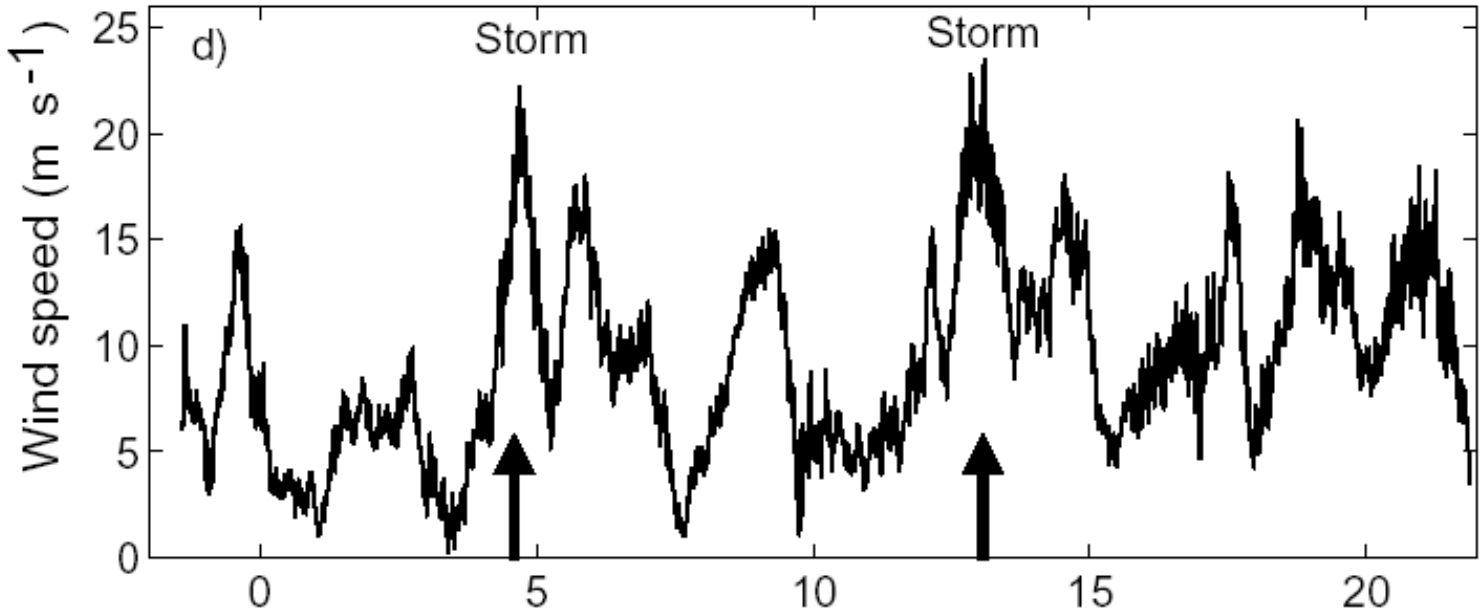
RV Kaiyo Maru seen from RV John P. Tully

photo courtesy F. Whitney

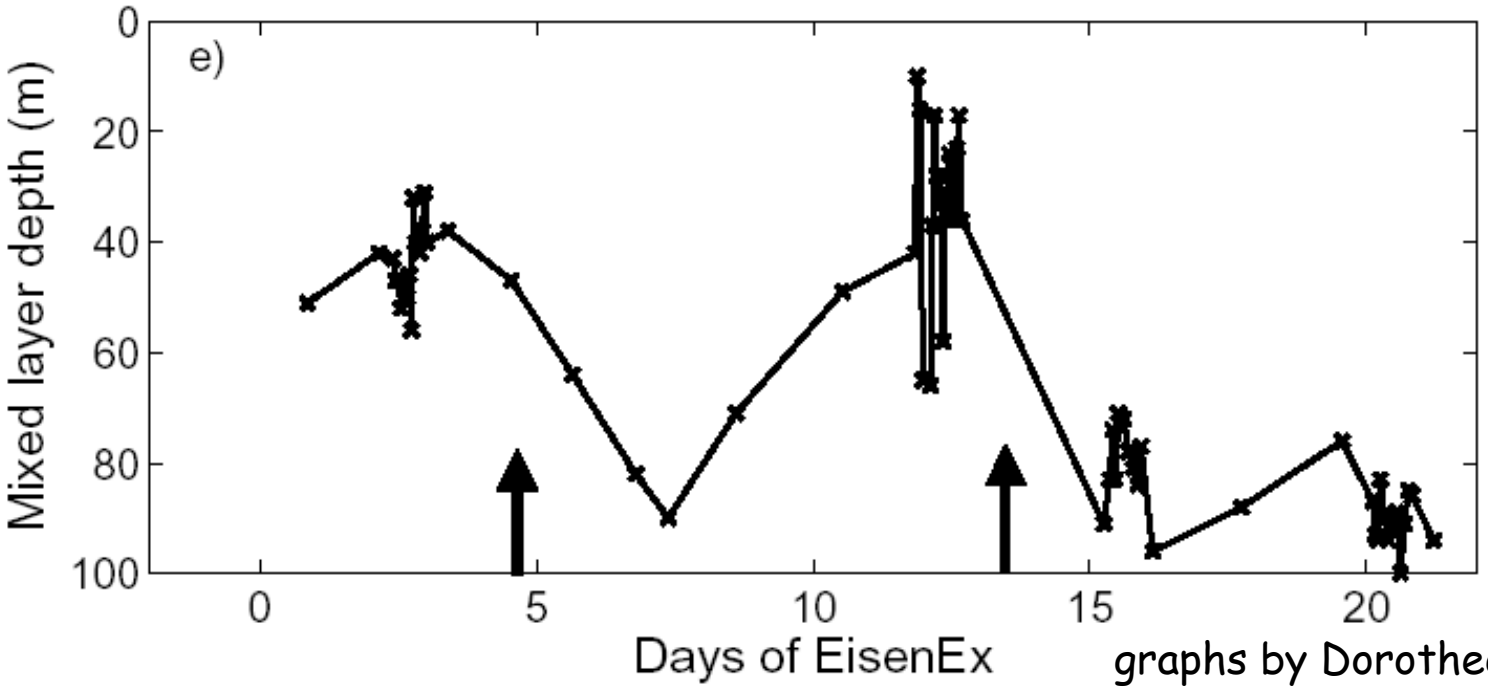

November 2000
RV Polarstern pumping iron
in the roaring forties
pump
hose
over
the stern

Light limitation

- Wind speed and Wind-Mixed-Layer depth
- Other forcings:
  - Photosynthetic Active Irradiance PAR
  - Temperature effects
  - Storm dilution effects, and shear stress
- Case study: EISENEX versus SEEDS

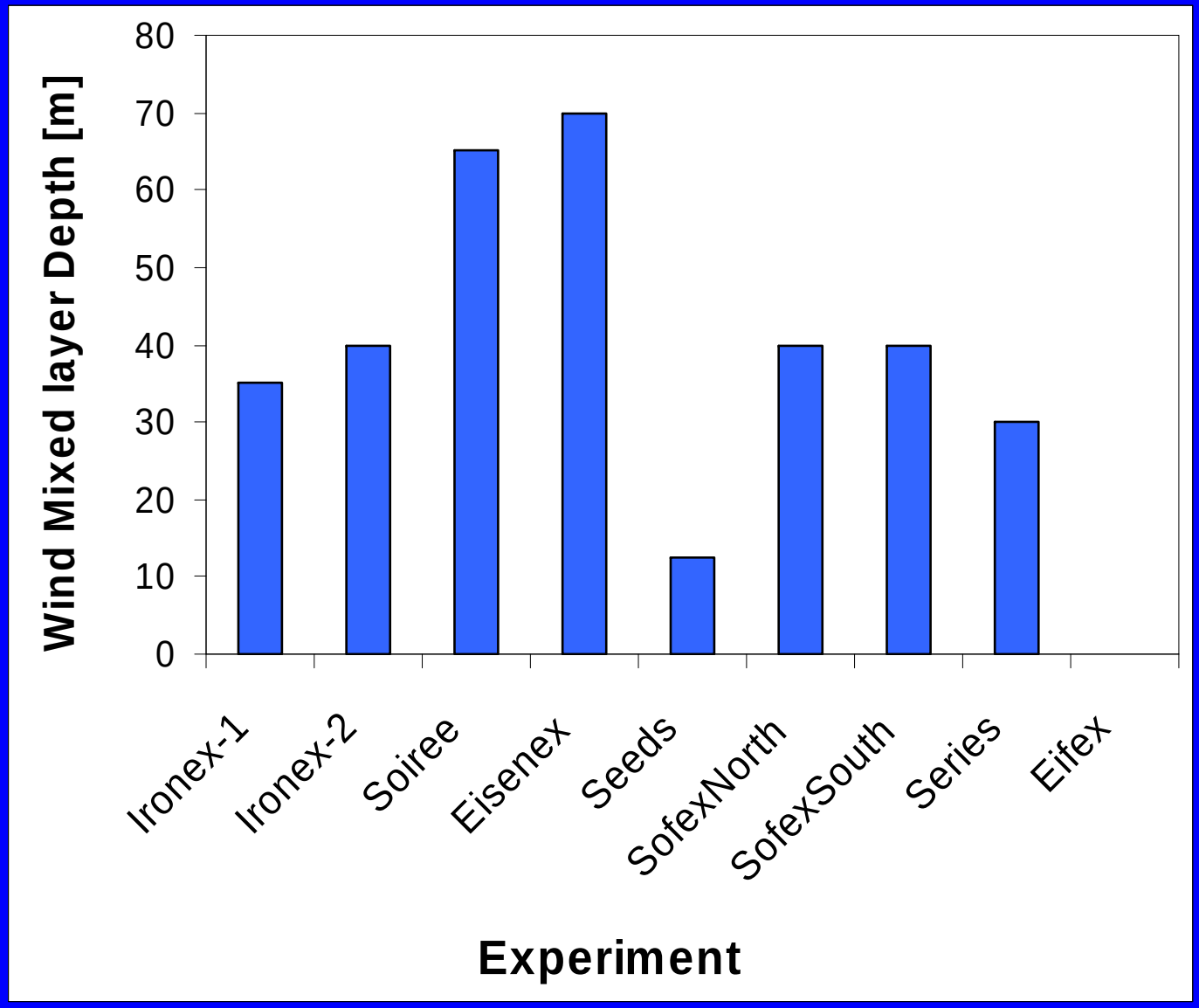


Eisenex had a lot of wind



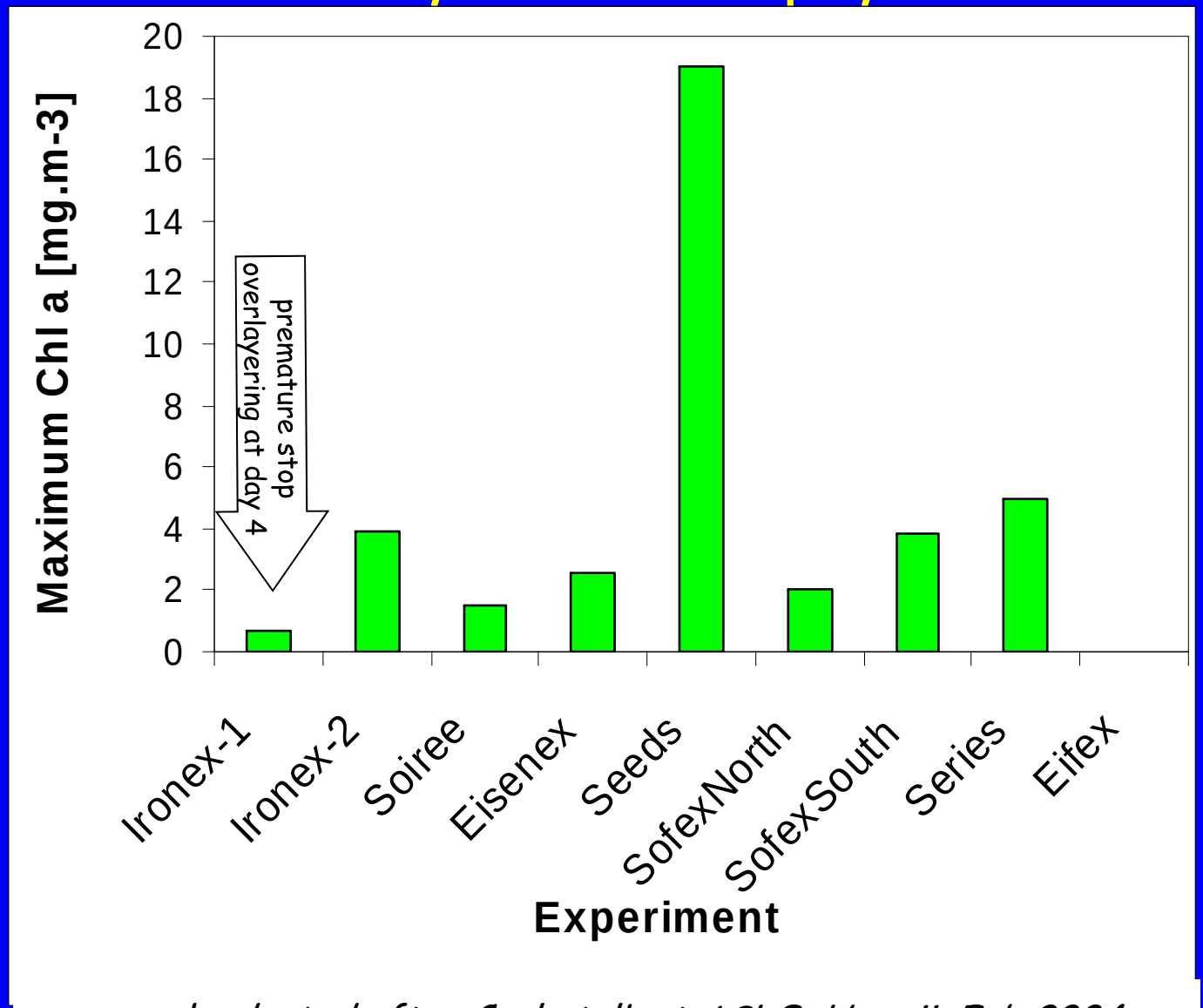
graphs by Dorothee Bakker

Depth of Wind Mixed Layer



Shallow 10-15 m at SEEDS versus deep 65-70 m at SOIREE, EISENEX

Indeed record yield Chlorophyll *a* in SEEDS

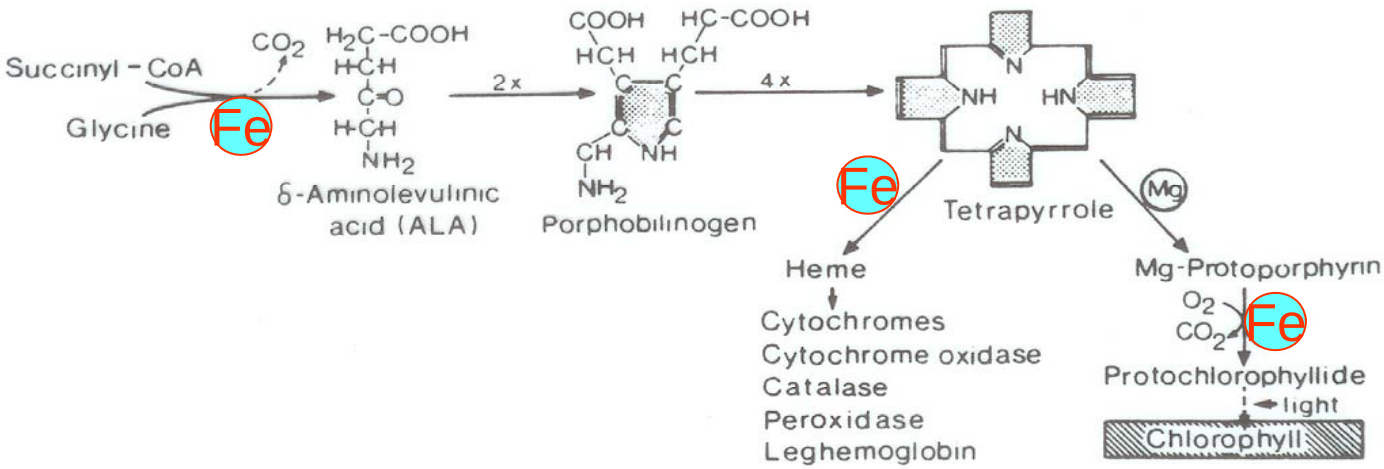


graph adapted after Coale talk at ASLO, Hawaii, Feb 2004

lowest yields at SOIREE and Eisenex where deepest Wind Mixed Layers

Chlorophyll *a* is NOT a reliable biomass indicator in Fe enrichments

- Chlorophyll *a* is nice and useful
- Synthesis pathway of Chl *a* requires iron Fe



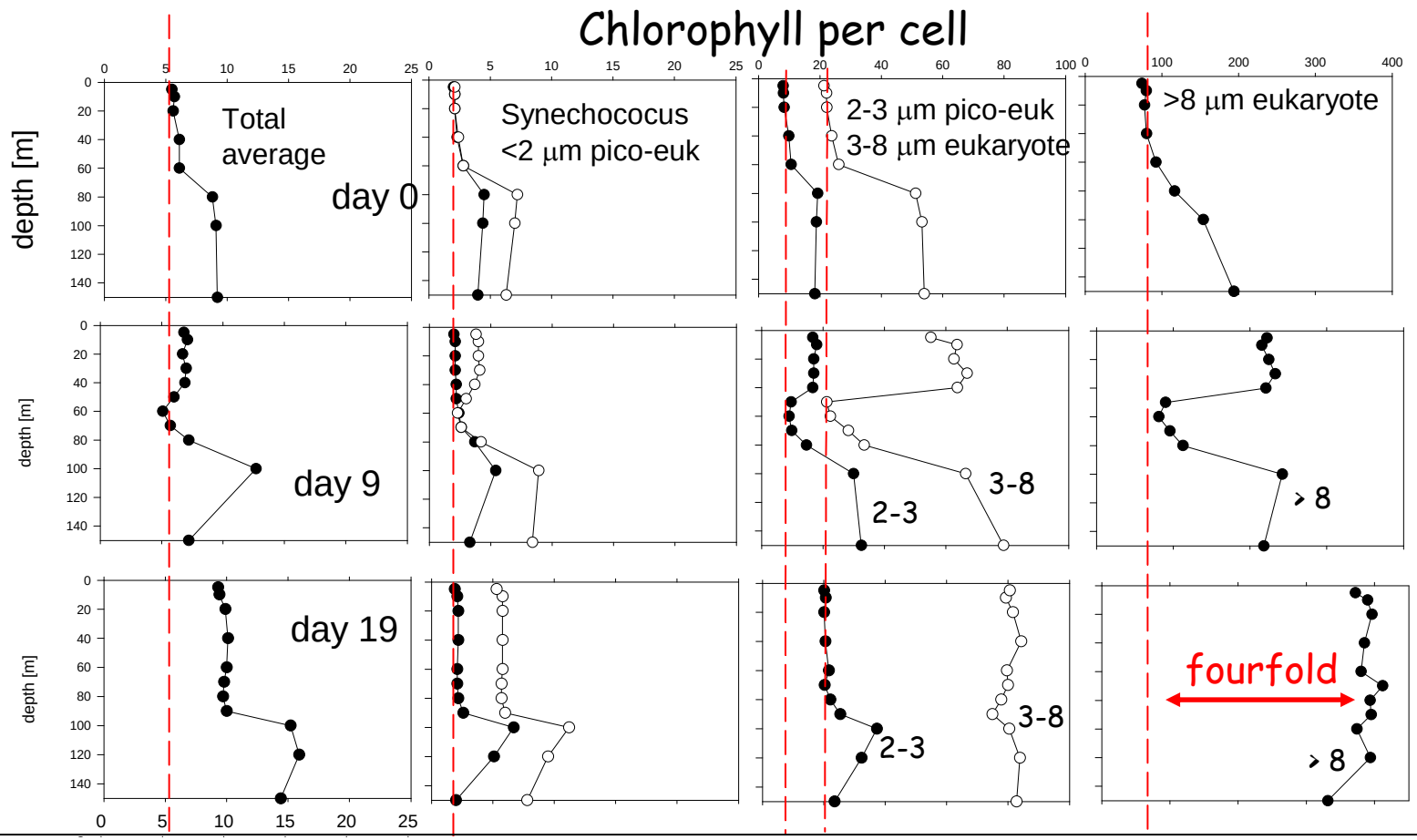
synthesis route of Chlorophyll a has several Fe-enzymes

Eisenex IN PATCH

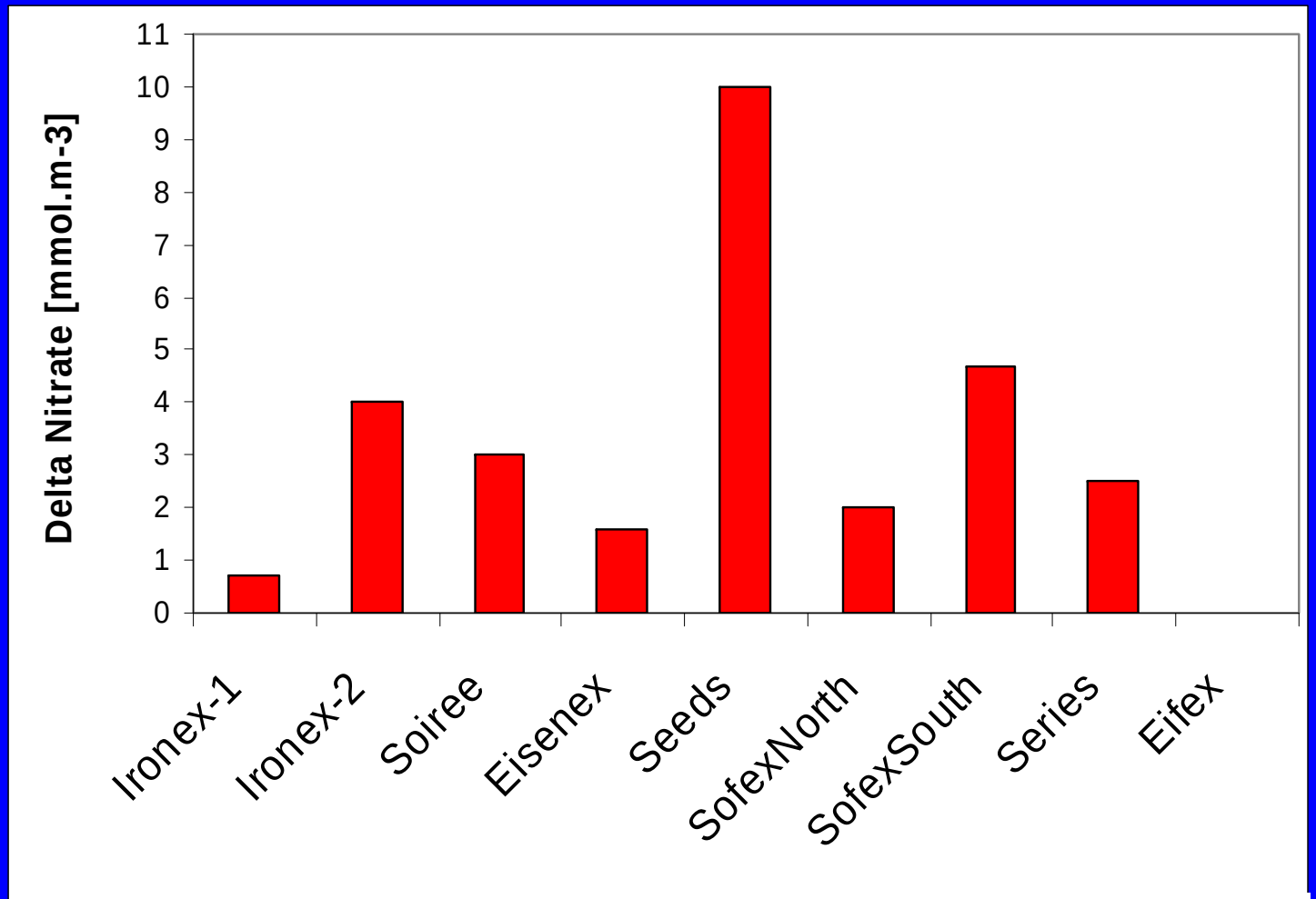
Total size class gets higher Chl/cell

strongest fourfold increase in the larger 3-8 micron and >8 micron cells (diatoms)

Veldhuis and Timmermans, submitted



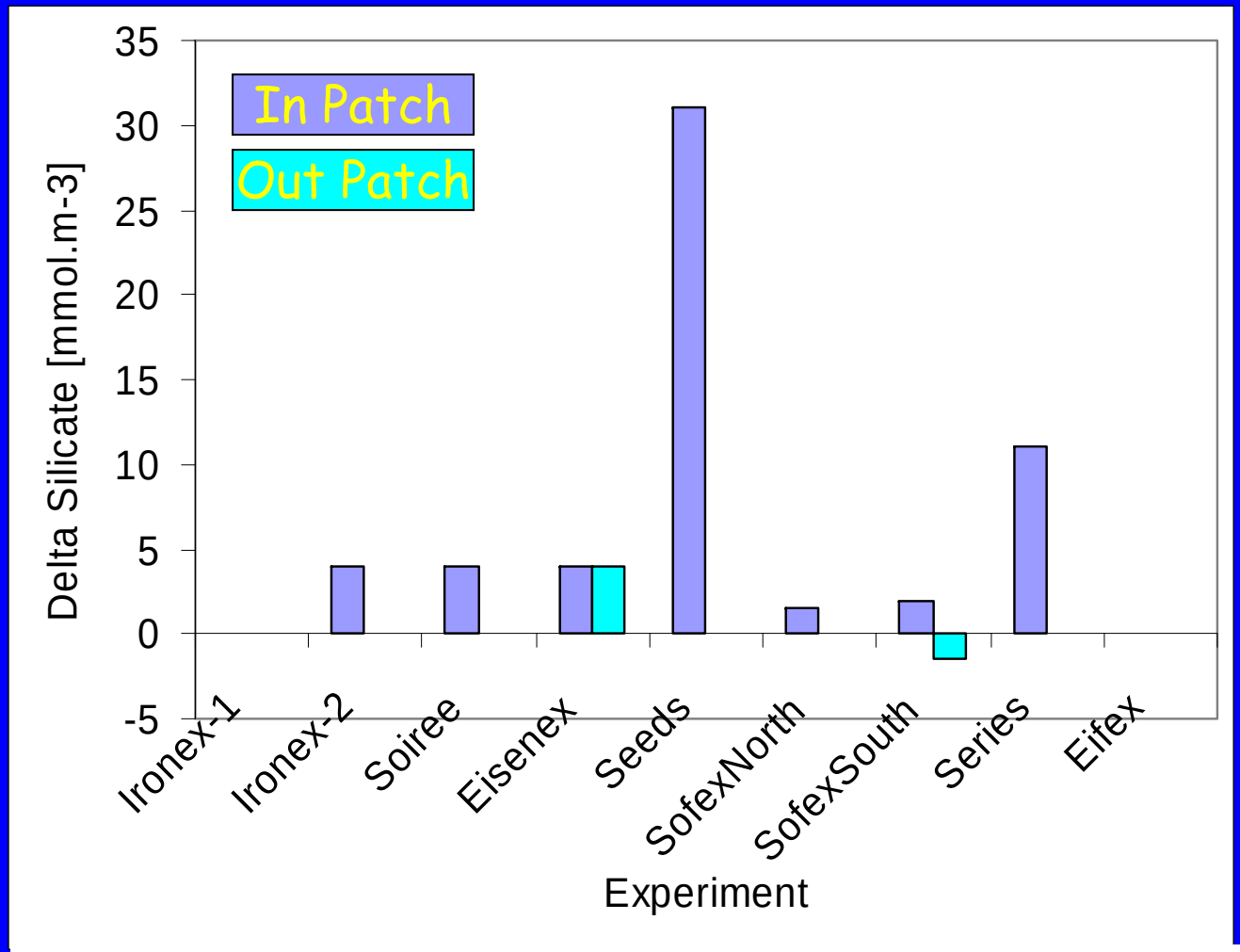
Nitrate removal as biomass indicator



graph adapted after Coale talk at ASLO, Hawaii, Feb 2004

Also highest at SEEDS and lowest at EISENEX
Ironex-2 and SofexSouth doing very well

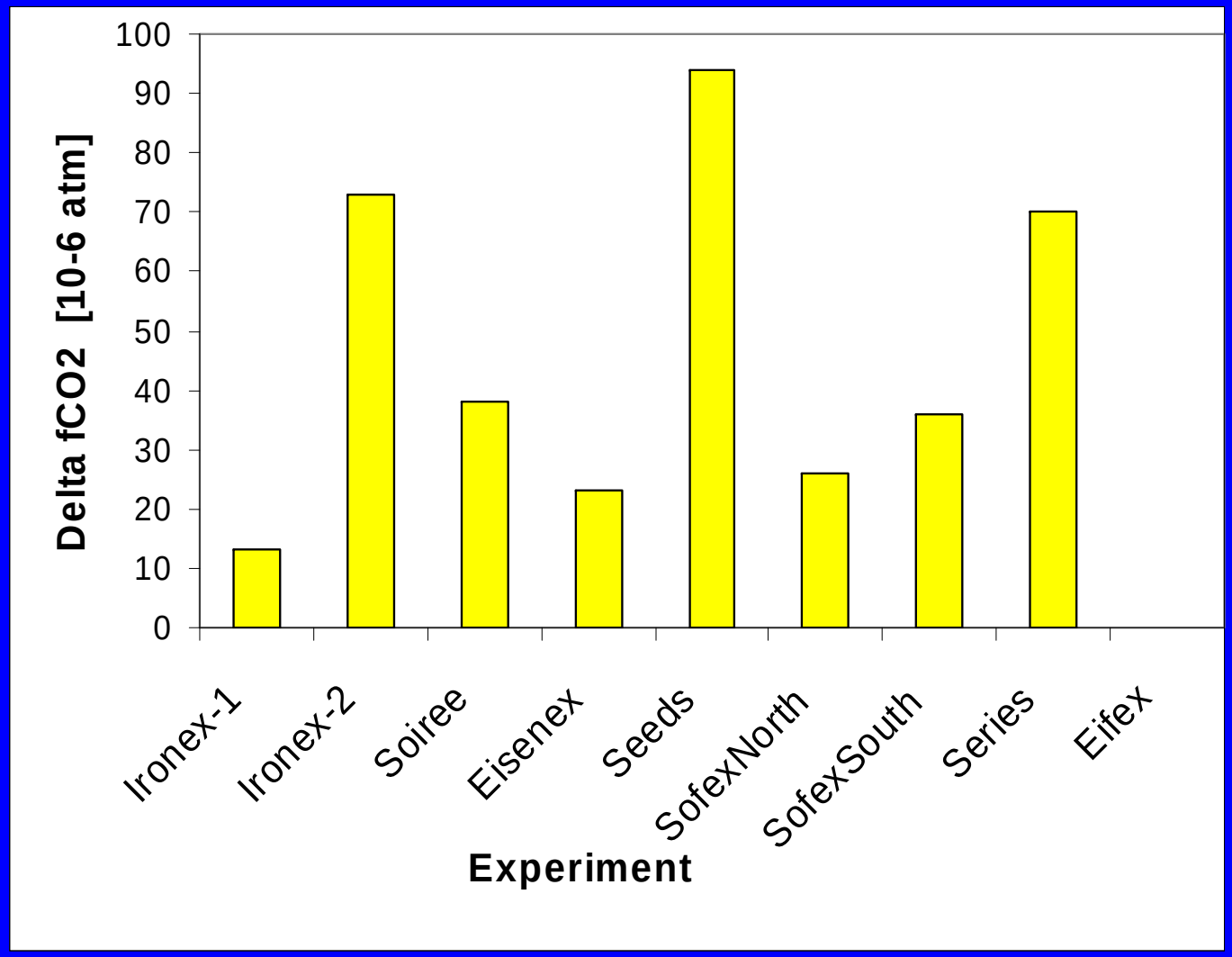
Removal of Silicate



Out Patch data found only for Eisenex and SofexSouth

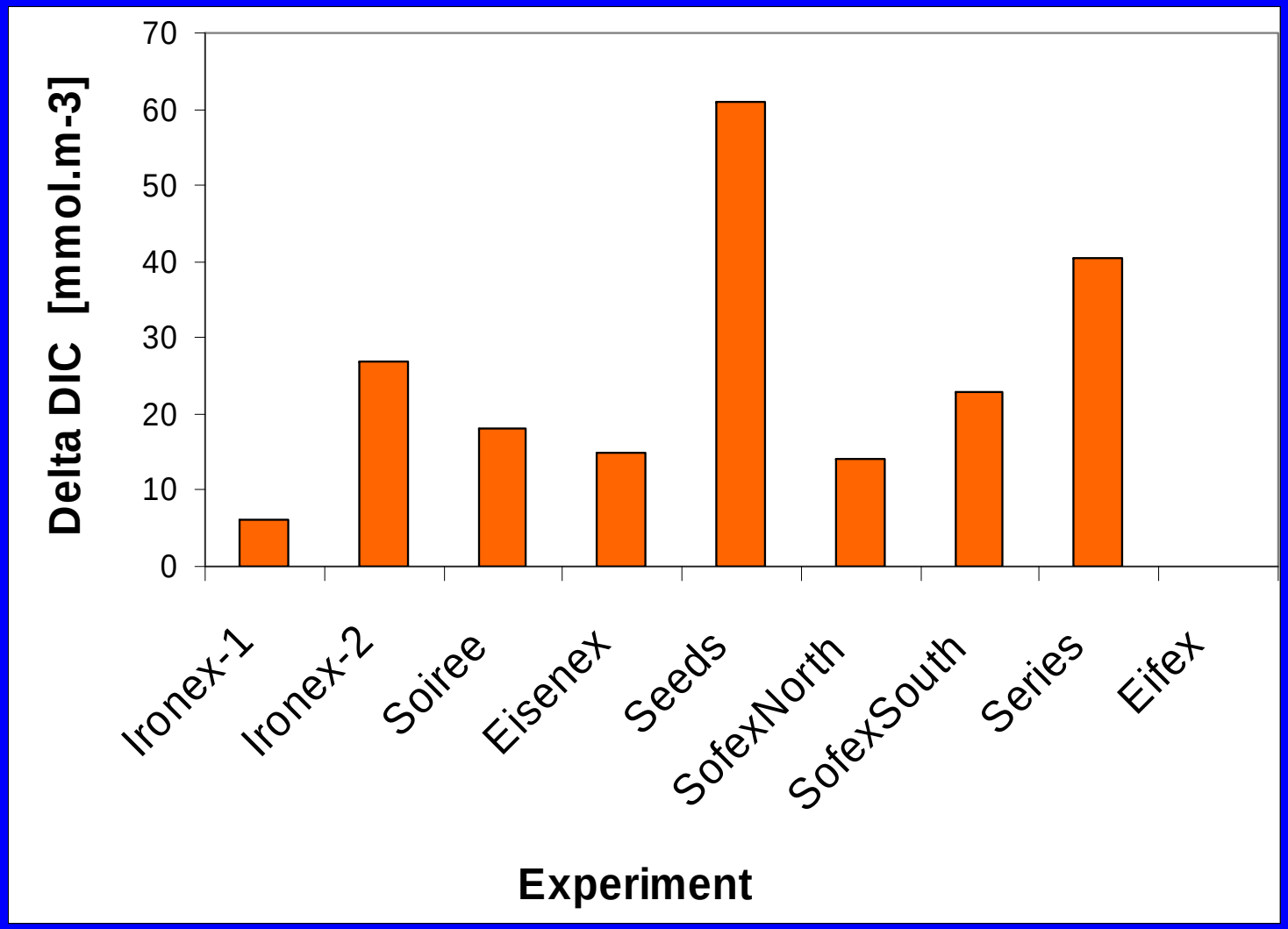
Eisenex Out-patch shows same Silicate removal (Bozec et al, in press)
SofexSouth Out-Patch shows Silicate mineralization increase

decrease of fCO_2



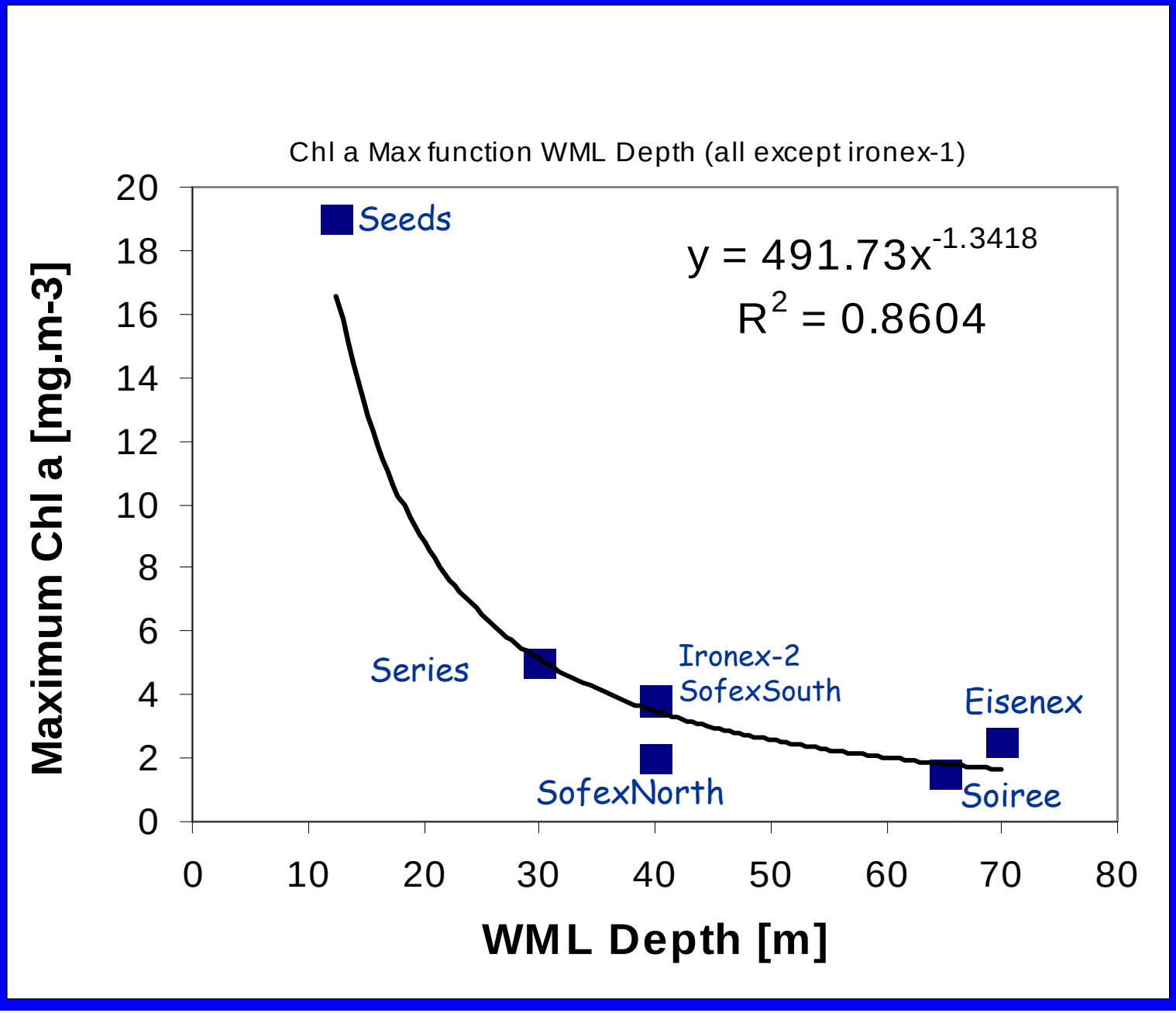
again most at SEEDS and least at EISENEX
Ironex-2 and SERIES coming close to SEEDS

Decrease of Dissolved Inorganic Carbon pool

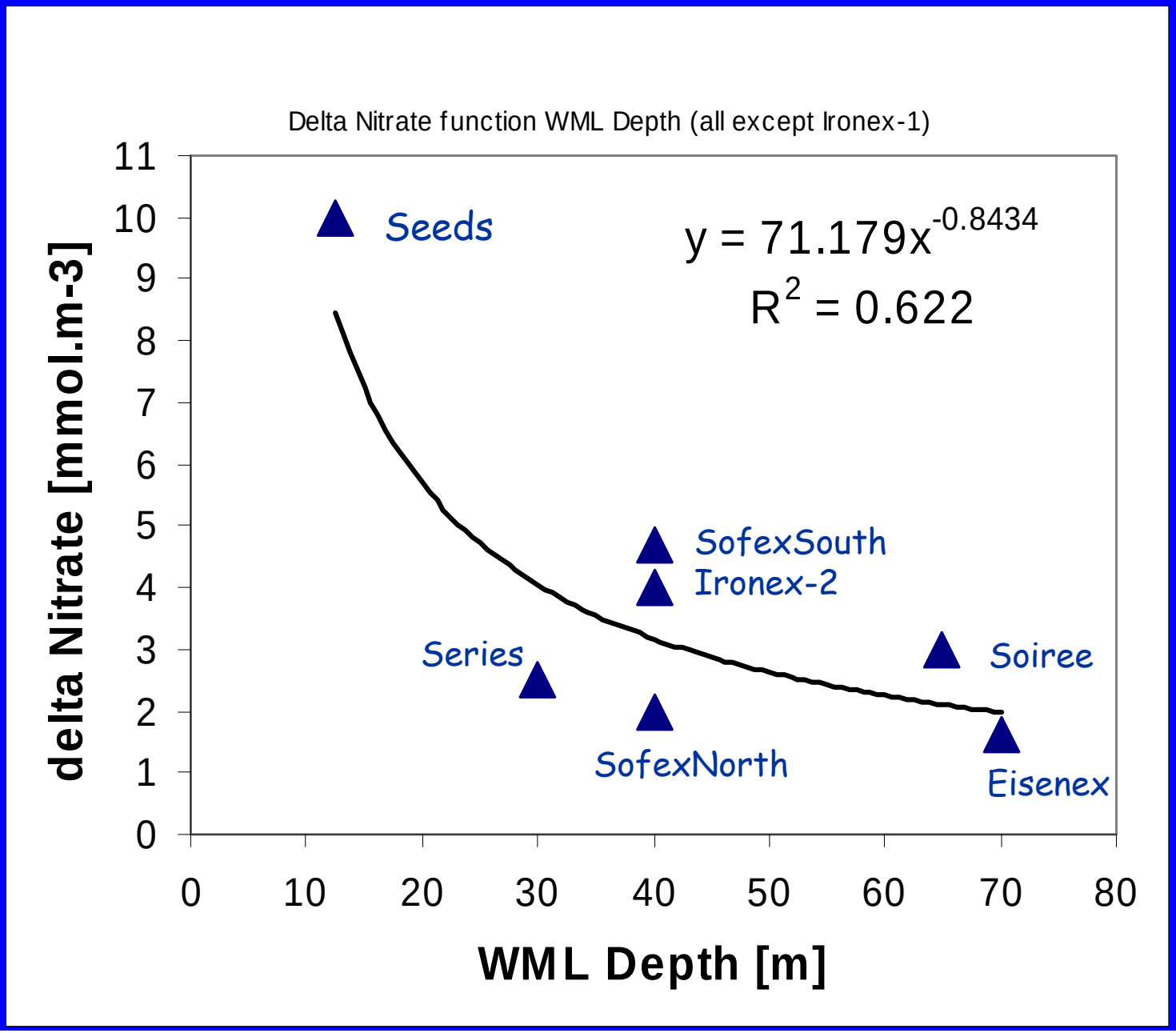


again SEEDS is leading, next SERIES
Ironex-2 and SofexSouth doing very well
SOIREE, EISENEX and SofexNorth in same league

Dominant forcing of Chlorophyll by WMLdepth

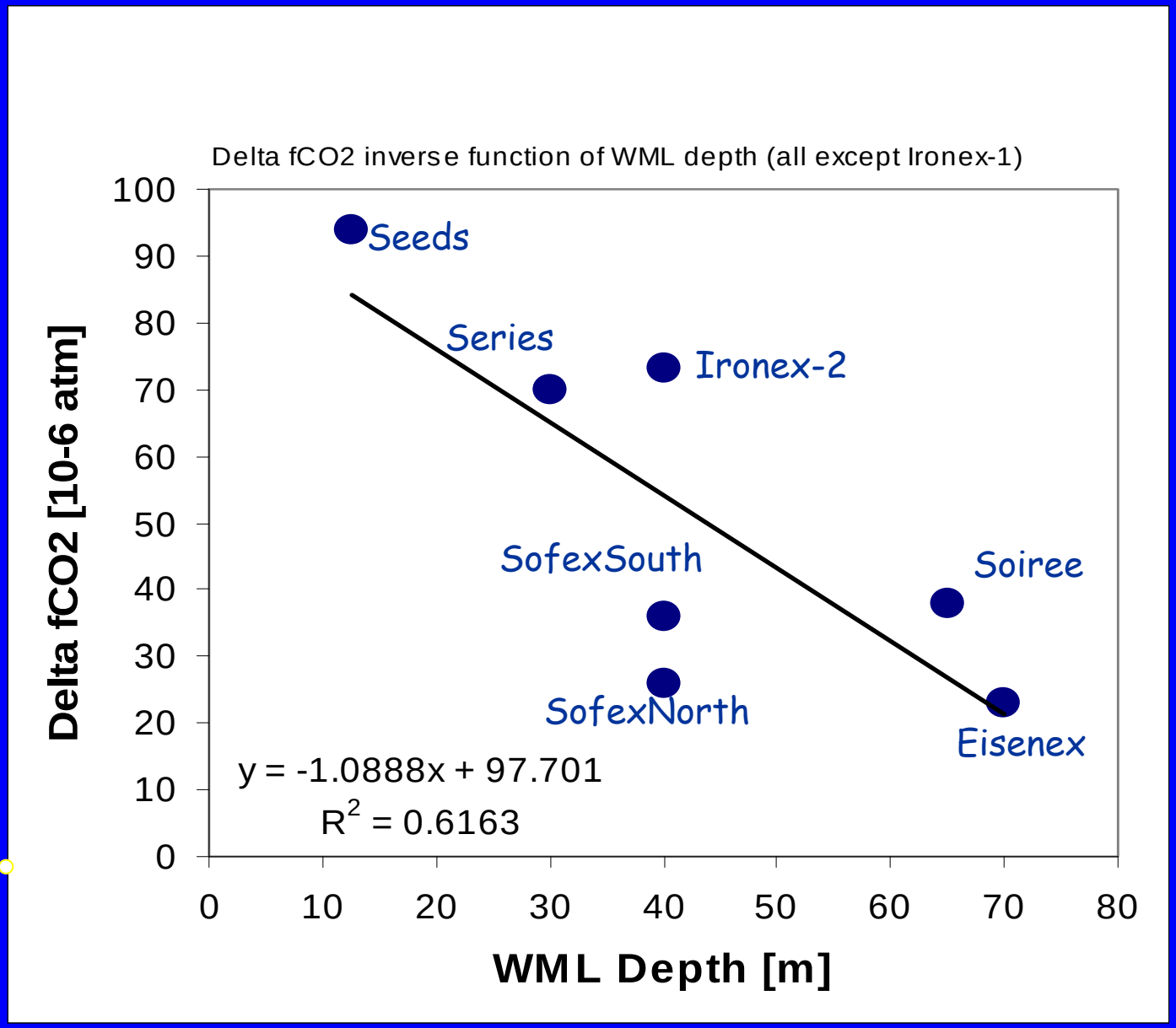


Similar trend for nitrate removal ?



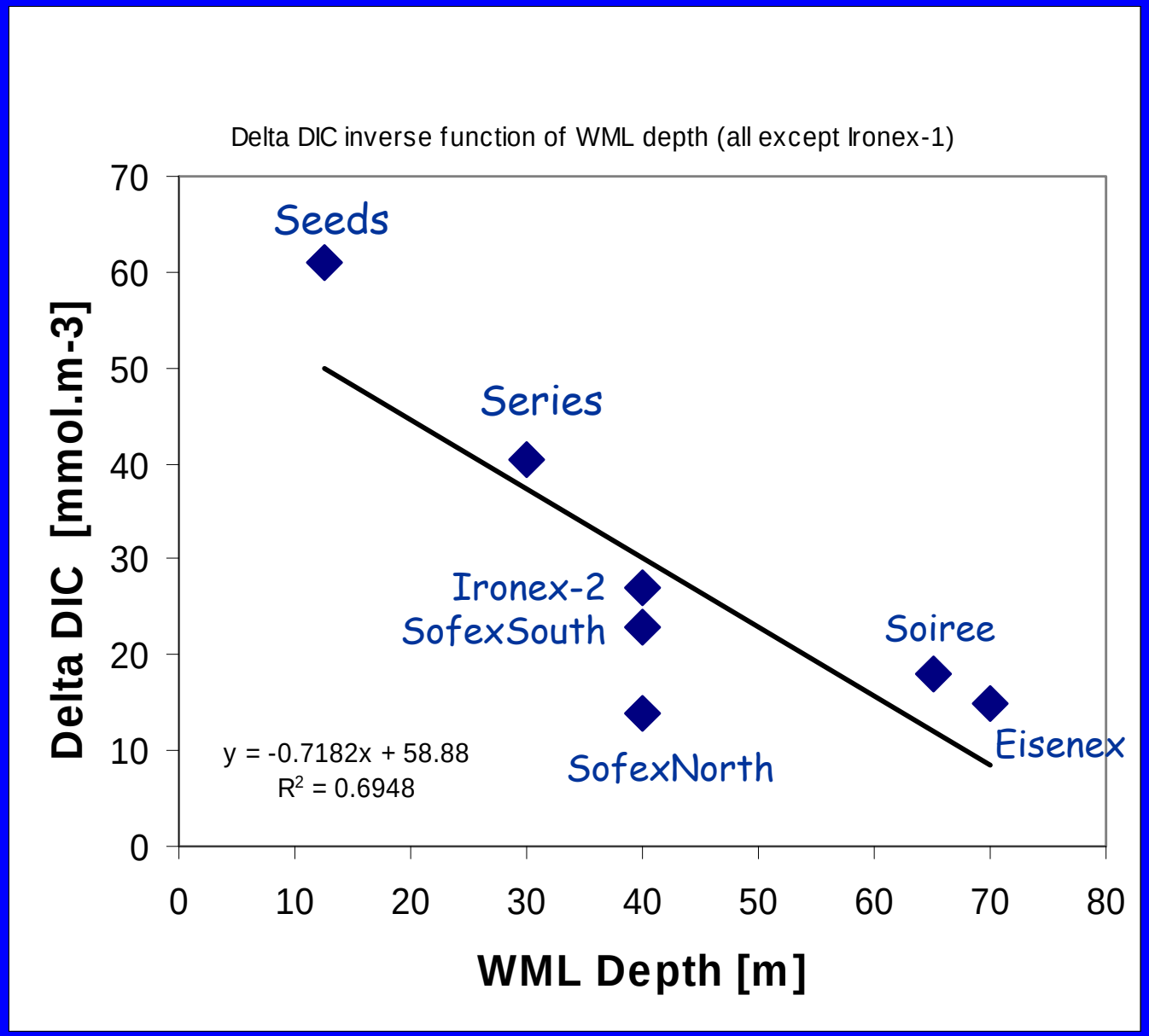
best CO_2 fixation at shallow WML depth

is R^2=0.62 still a real trend ?

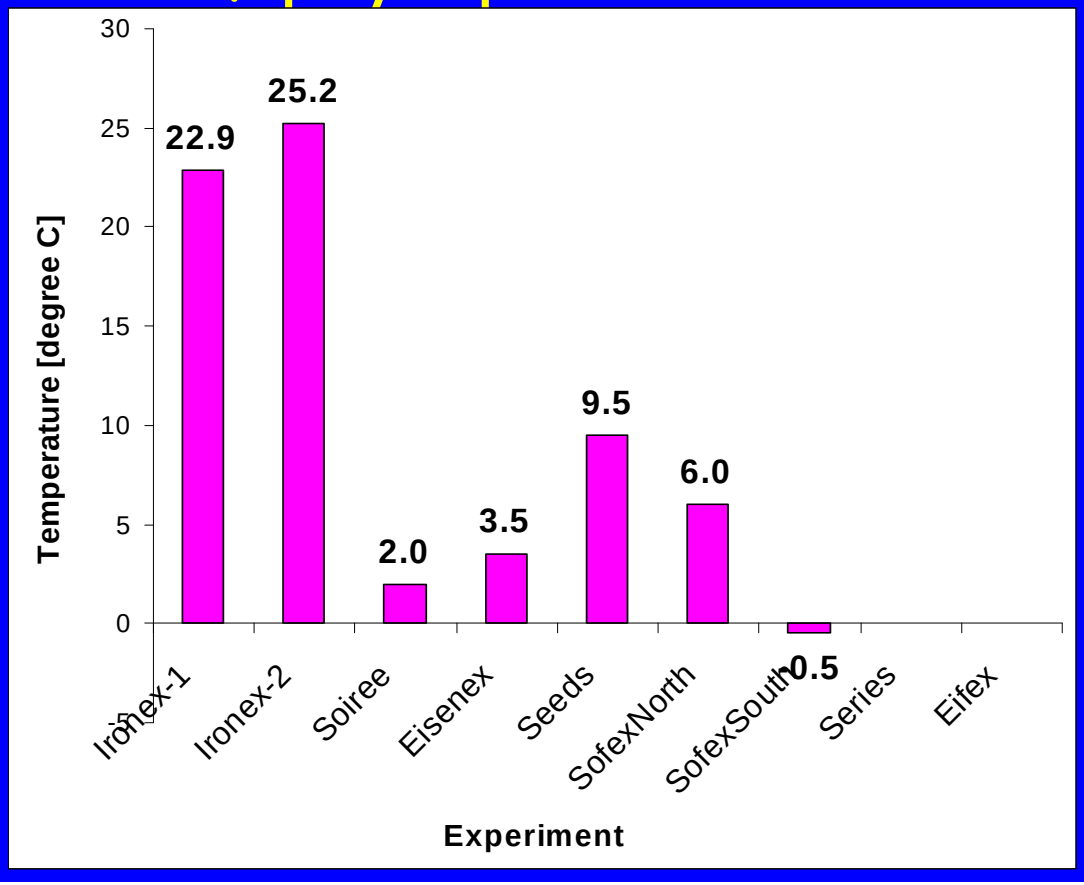


Most DIC uptake at shallow WML depth

is R^2=0.69
a
real trend ?

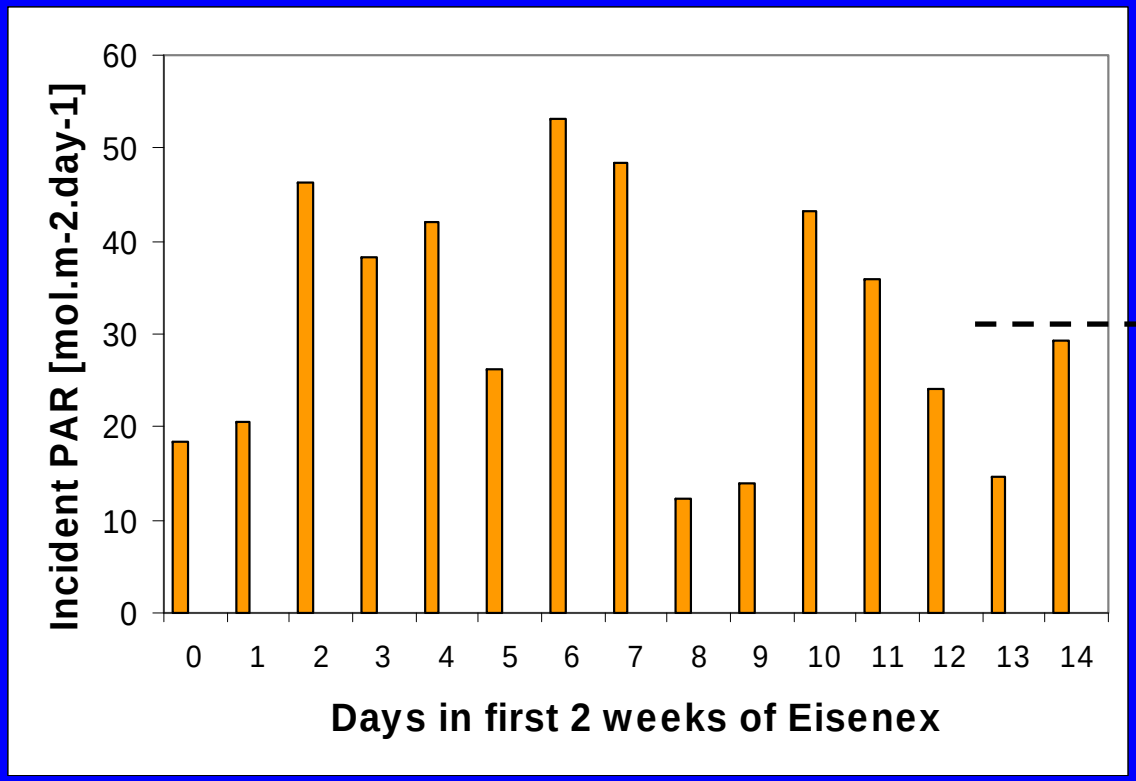


Temperature also affects optimum growth rates of phytoplankton cells



- factor 1.88 per 10 ^{0}C (Eppley, 1972)
- factor 2.08 per 10 ^{0}C (Goldman and Carpenter, 1974)
- Thus Ironex-1 & 2 should be about fourfold faster than SOIREE
- Thus SEEDS to be about one-and-half times faster than EISENEX
  - *Chaetoceros debilis* does 2.6 doublings per day in SEEDS

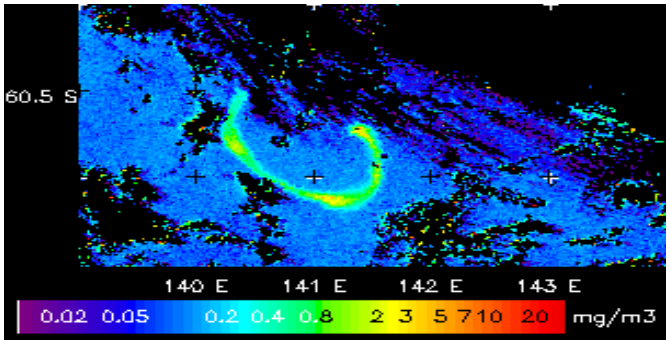
Irradiance at sea surface
(Photosynthetic Active Radiation PAR)



average PAR
31.1 $mol.m^{-2}.d^{-1}$

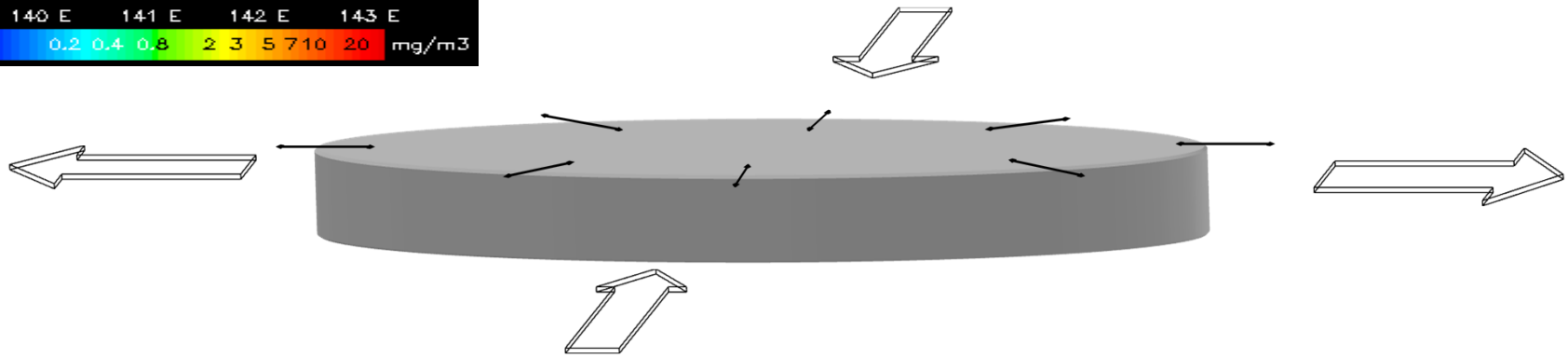
- each single experiment large daily variation
- large variation between experiments

Storm Dilution Effects



Why the exceptional longevity of SOIREE?

Fe Patch increased from 50 to 1100 km^2



Stretching via horizontal flows

Mixing of water by horizontal diffusion

slide courtesy Phil Boyd & Ed Abraham

IN: HNLC waters	OUT: Patch waters
hi Si	low Si
low Fe	hi Fe*
low diatoms	hi Chl a
low Chl a	hi diatoms

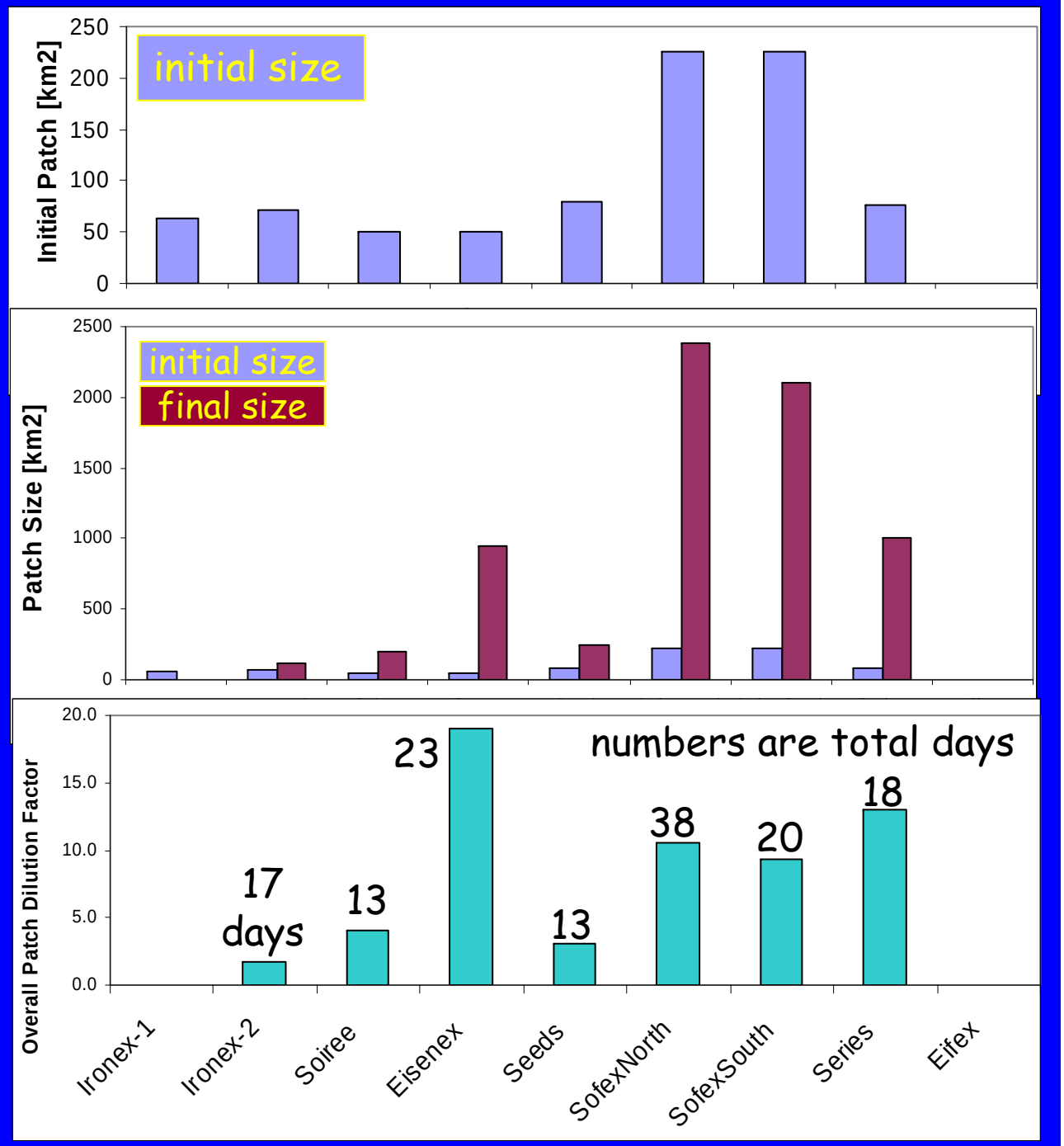
chemostat (Monod, Paris, 1942) for nutrients Si, N, P
in contrast the fertilizer Fe is washed out

wind speed

as well as

sheer stress of fronts and currents

cause high dilution factor of a patch



Ironex-2 and Seeds lowest dilution factor

Eisenex highest 19-fold dilution

Case Study: Linking Eisenex with Seeds

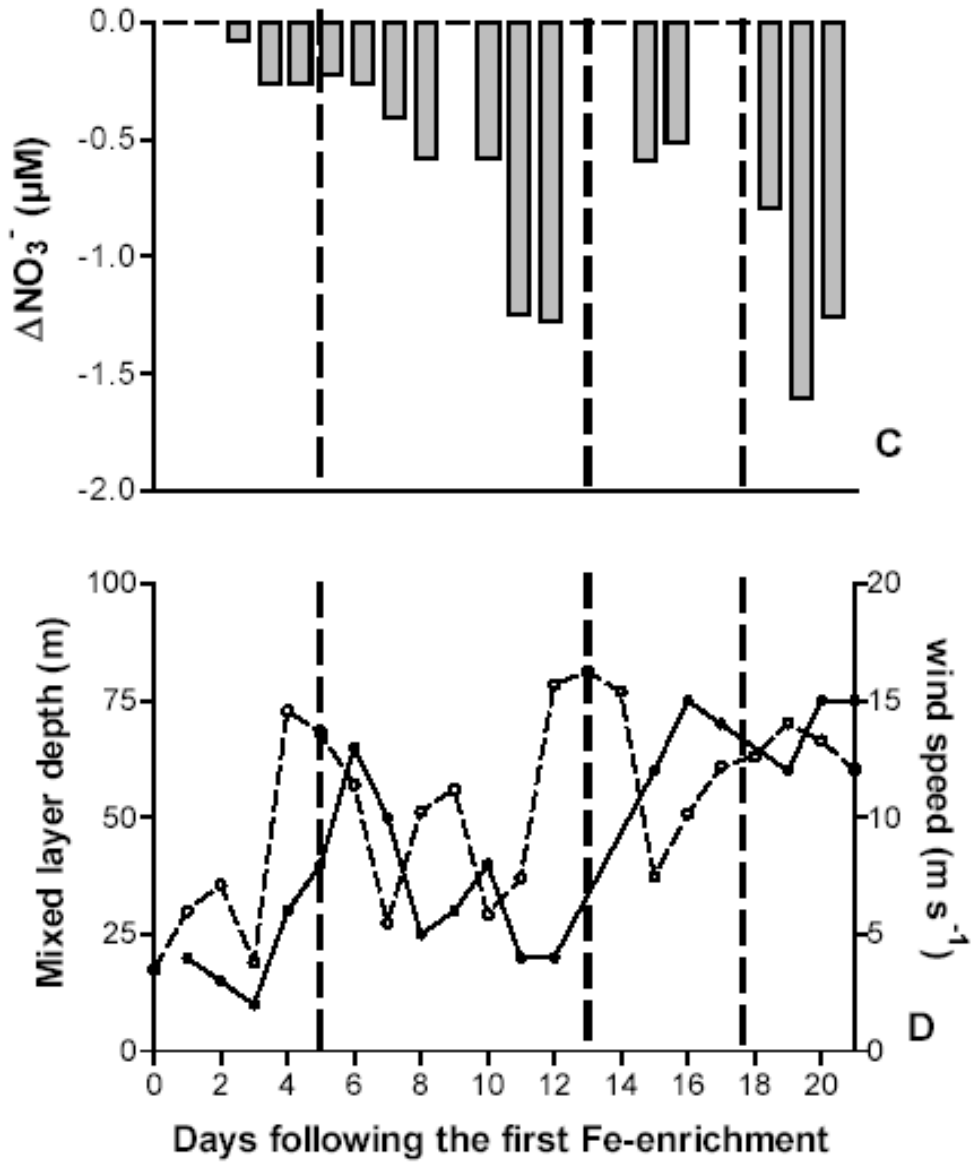
- 1) Eisenex *in situ* experiment
  - WML depth 25-110 m,
  - strong patch dilution,
  - variable PAR
- 2) Eisenex deck incubations
  - In-Patch versus Out-Patch water
  - simulated WML depth 8-16m
  - same variable PAR as *in situ* experiment
- 3) Eisenex bottle incubations
  - In-Patch versus Out-Patch water
  - artificial constant light in 12/12 day/night; simulated WML= 30m
- 4) Seeds *in situ* experiment
  - WML depth 10-15 m
  - modest patch dilution

1. Eisenex *in situ* experiment

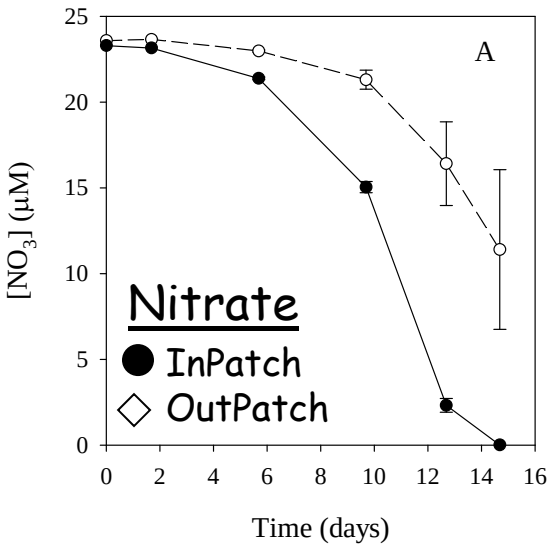
delta NO_3 =
1.6 mmol.m^{-3}
after 23 days

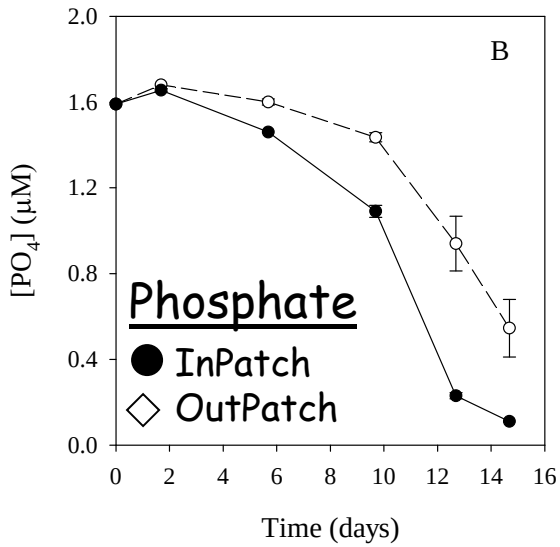
WML depth varies
between 10 and 100 m

patch dilution 19-fold

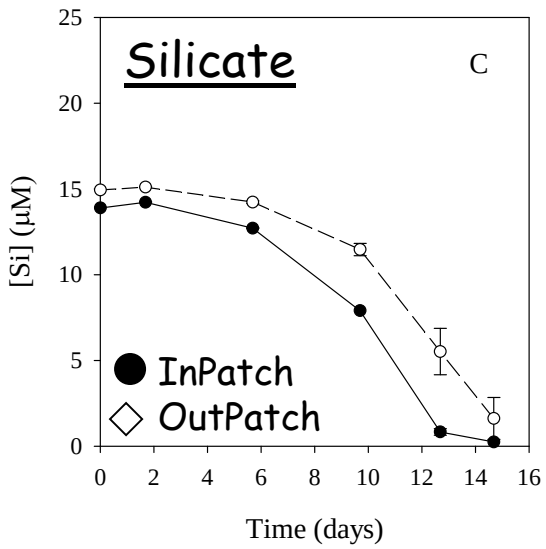


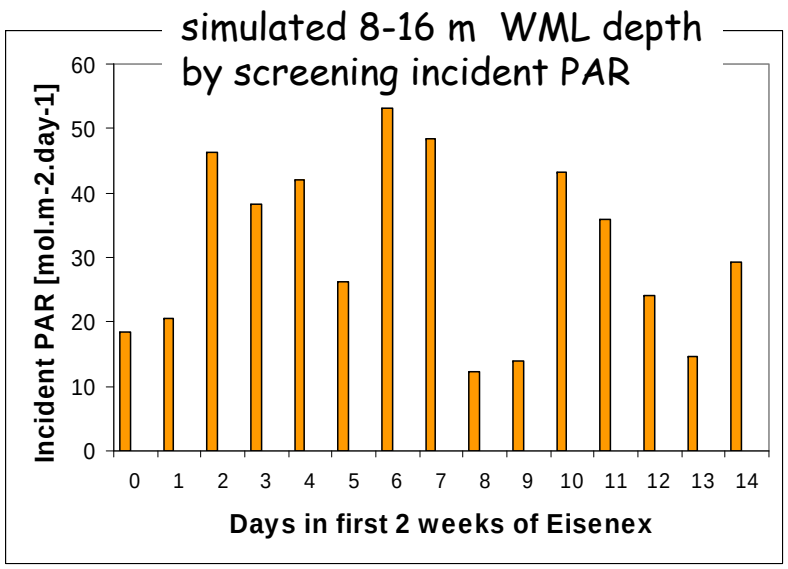
2. Eisenex deck incubations 20 Liters of
InPatch and OutPatch waters





- shallow WML = 8-16m
- no patch dilution
- all nutrients depleted in 12 days ! ! ! !
- delta NO3 = 21
- delta Si =13.5
- delta PO4 = 1.6

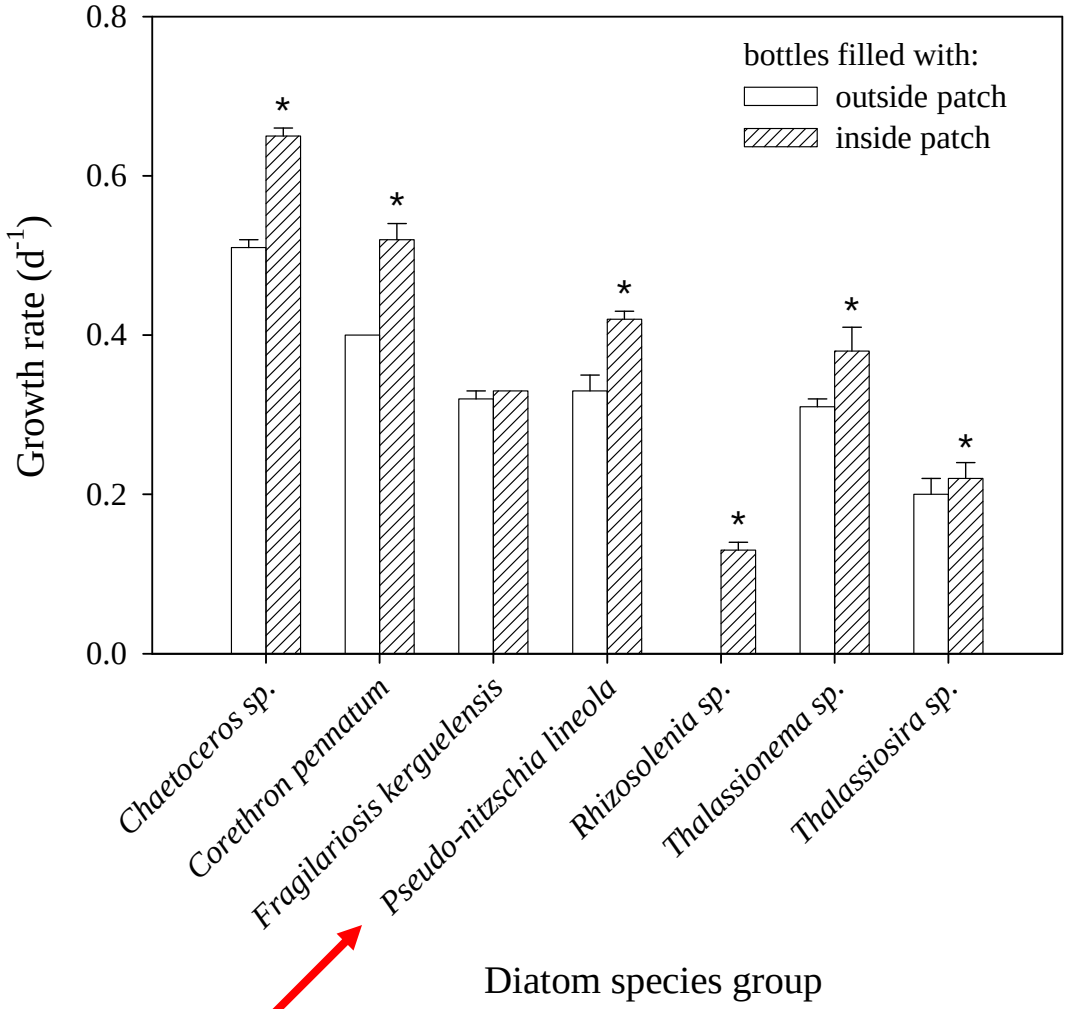




Data and Graphs by Tim van Oijen & Micha Rijkenberg

2. Eisenex deck incubations
Diatom growth rates

Typical Growth Rate 0.4 - 0.6 day^{-1}



* significant Fe stimulus

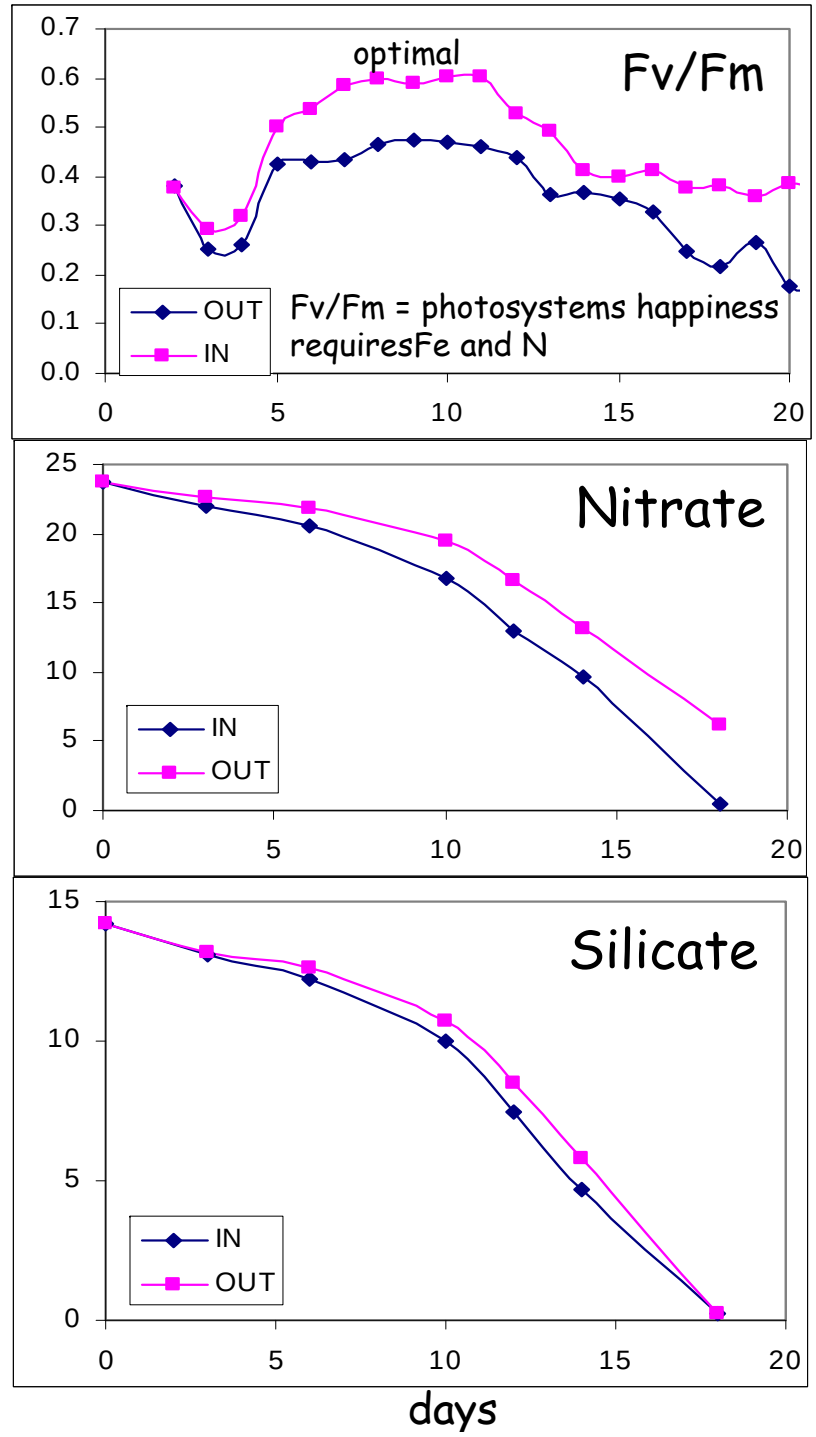
also dominant in *in-situ* patch

3. Eisenex bottle incubations with artificial light

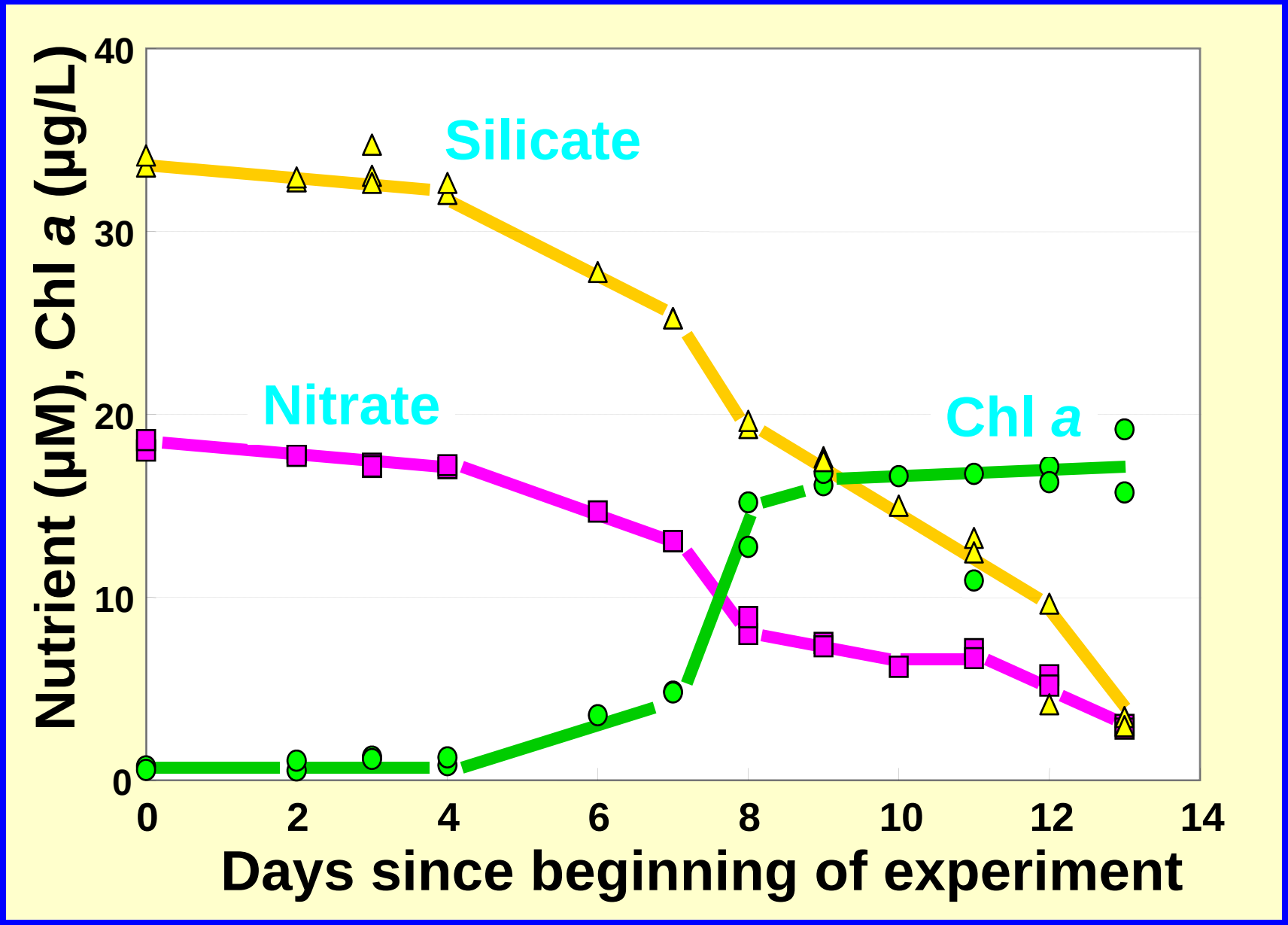
- 20 L water of In & Out Patch
- artificial light at 3.5 mol.m-^{2}d^{-1}
- simulated WML depth = ~30 m
- 12/12 hours light/dark cycle

- optimal Fv/Fm InPatch bottle
- fair Fv/Fm OutPatch bottle
  - drops in end due to lack of Fe and N
- delta NO3 = 24 after 18 days
- delta Si = 14.5 after 18 days

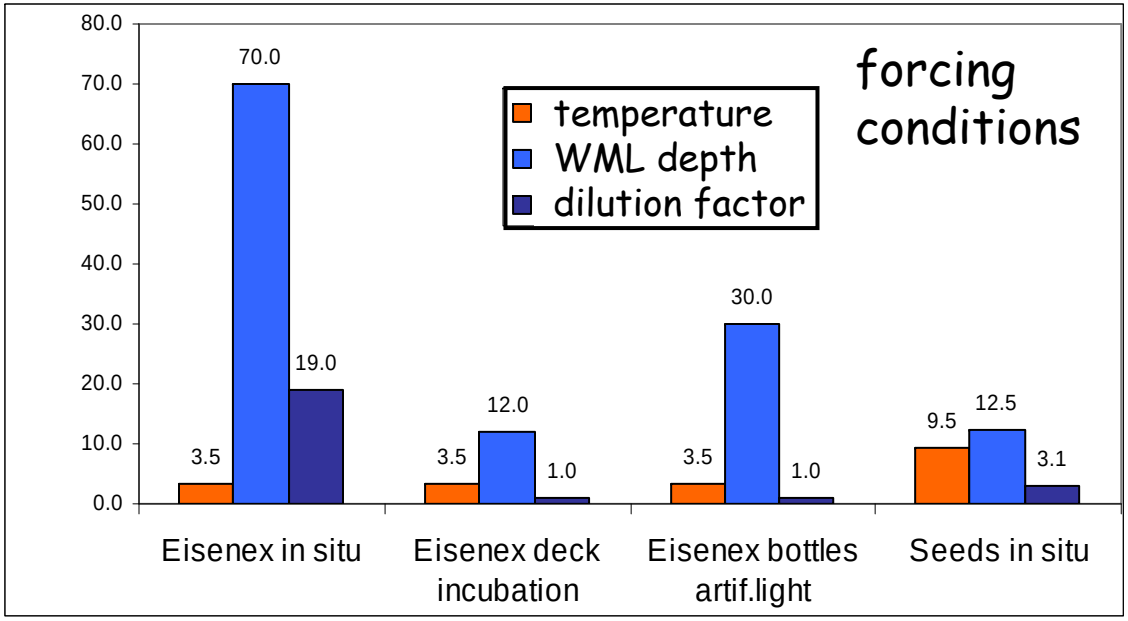
data and graphs by Klaas Timmermans

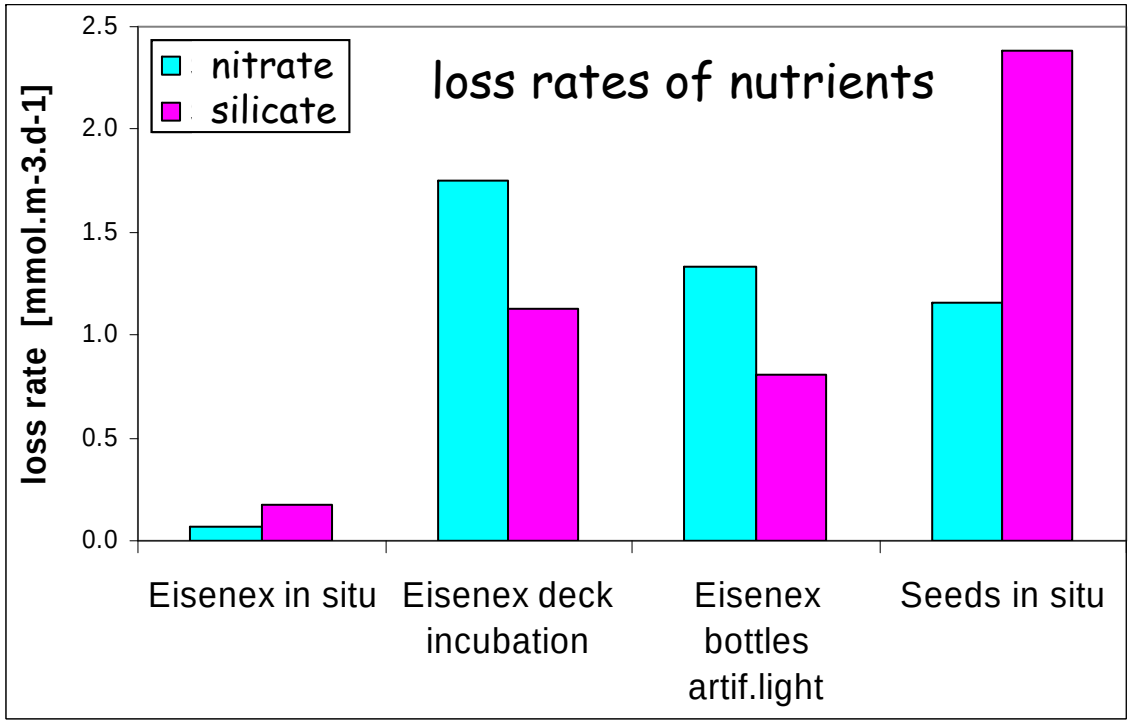


4. Seeds *in situ* Experiment



data and graph kindly provided by Tsuda et al.





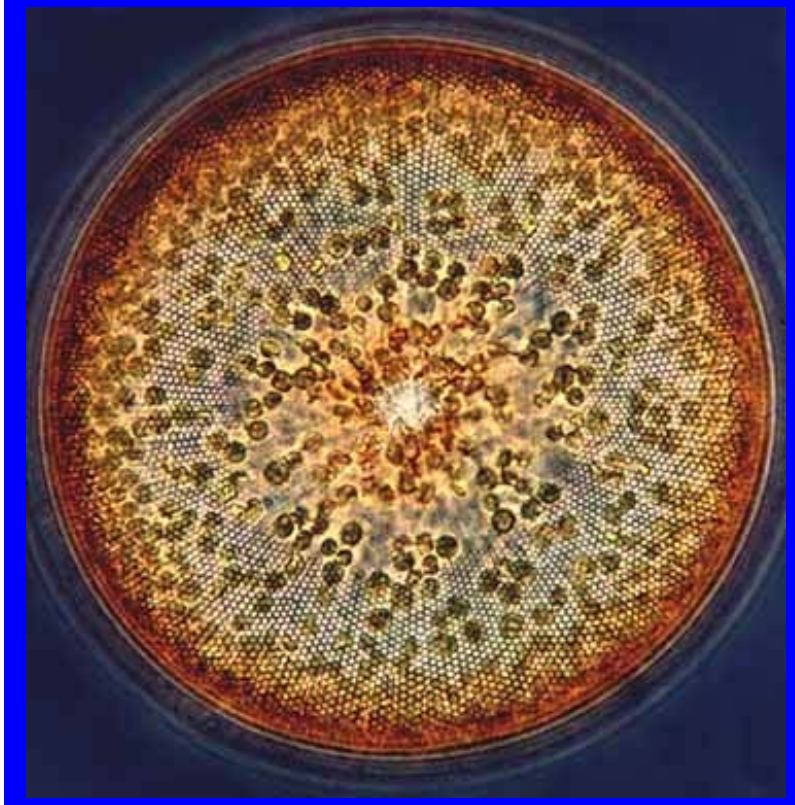
- **Conclusions**
- WML depth and dilution factor are dominant
- some effect of temperature
- NB SEEDS incident light still not taken into account

- **Future Work**
- ecosystem modeling
- day-to-day changes
- several depths throughout patch

diatoms optimal specific growth rates depend on temperature as well

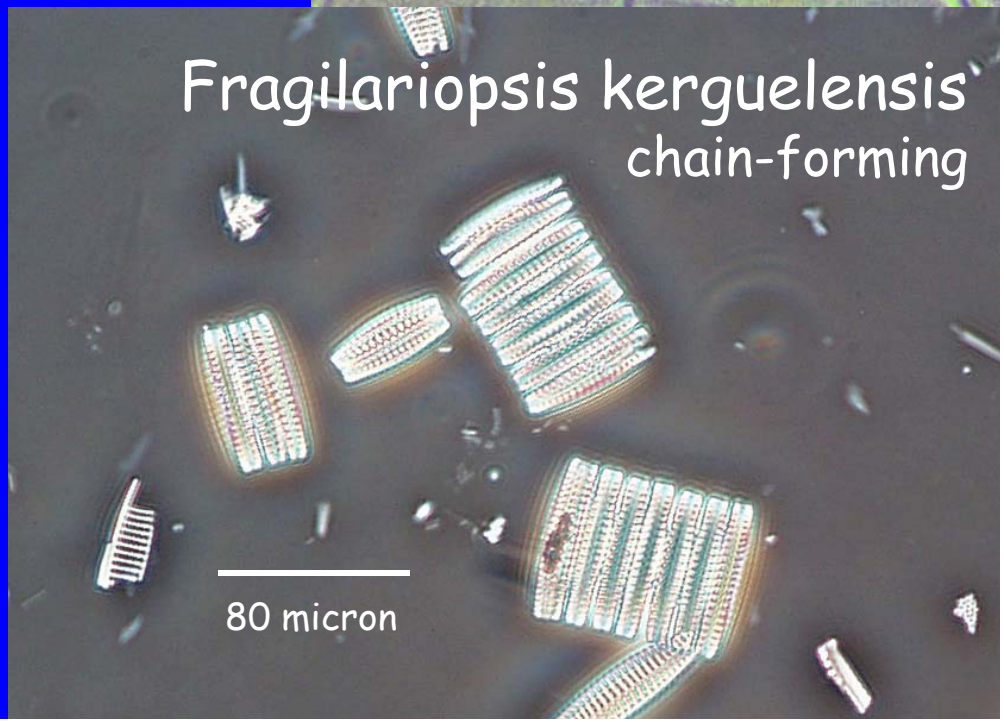
- Eisenex Southern Ocean at 3.5 ^0C
  - in deck incubators μ = 0.4 to 0.6 day^{-1}
- SEEDS *in situ* subarctic Pacific at 9.5 ^0C
  - Chaetoceros debilis μ = 1.79 day^{-1} !!!! from day 4 through day 7
  - slows down to μ = 0.42 day^{-1} in days 9 to 14

BIG DIATOMS

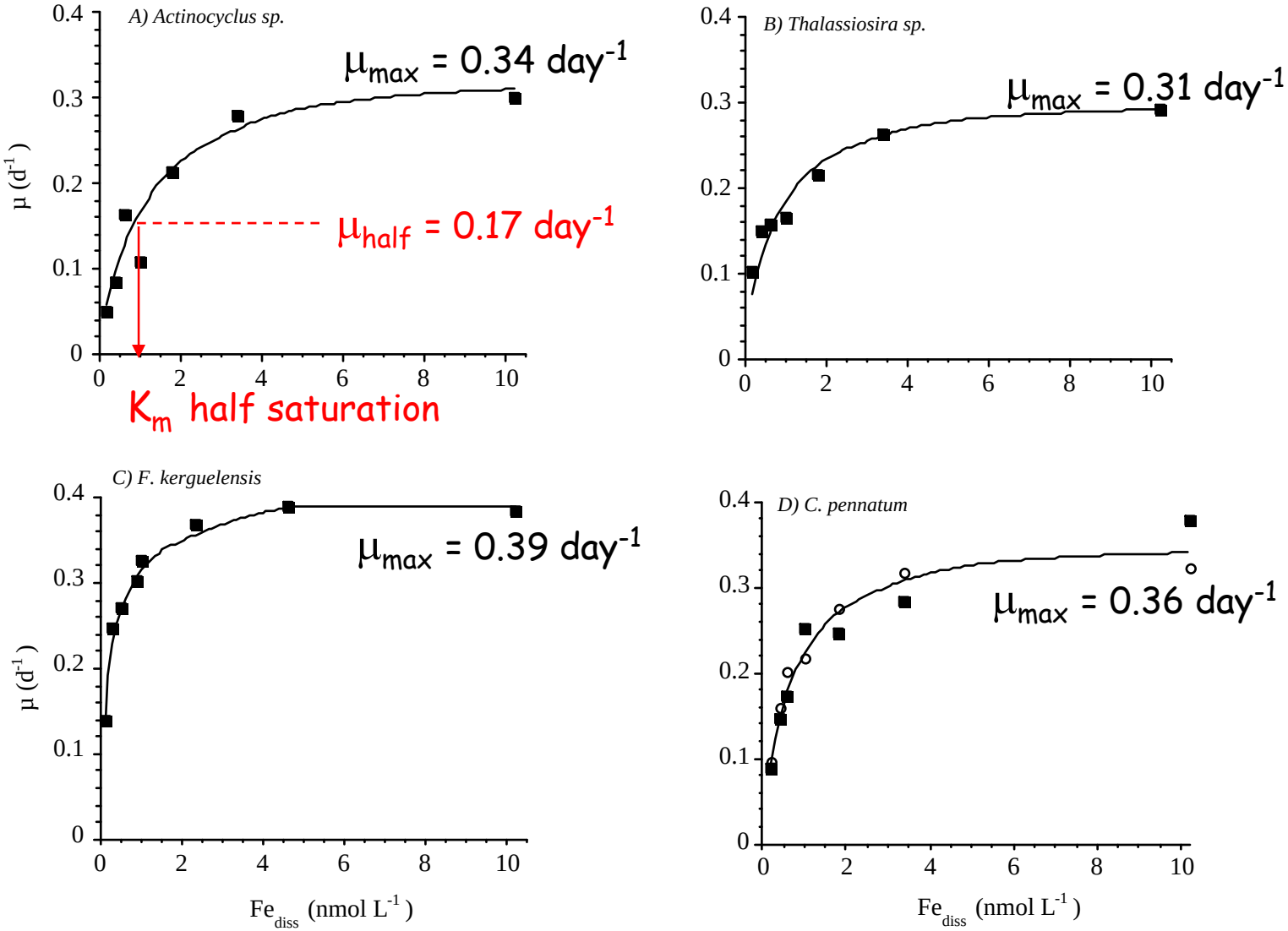


Actinocyclus

140 micron
diameter

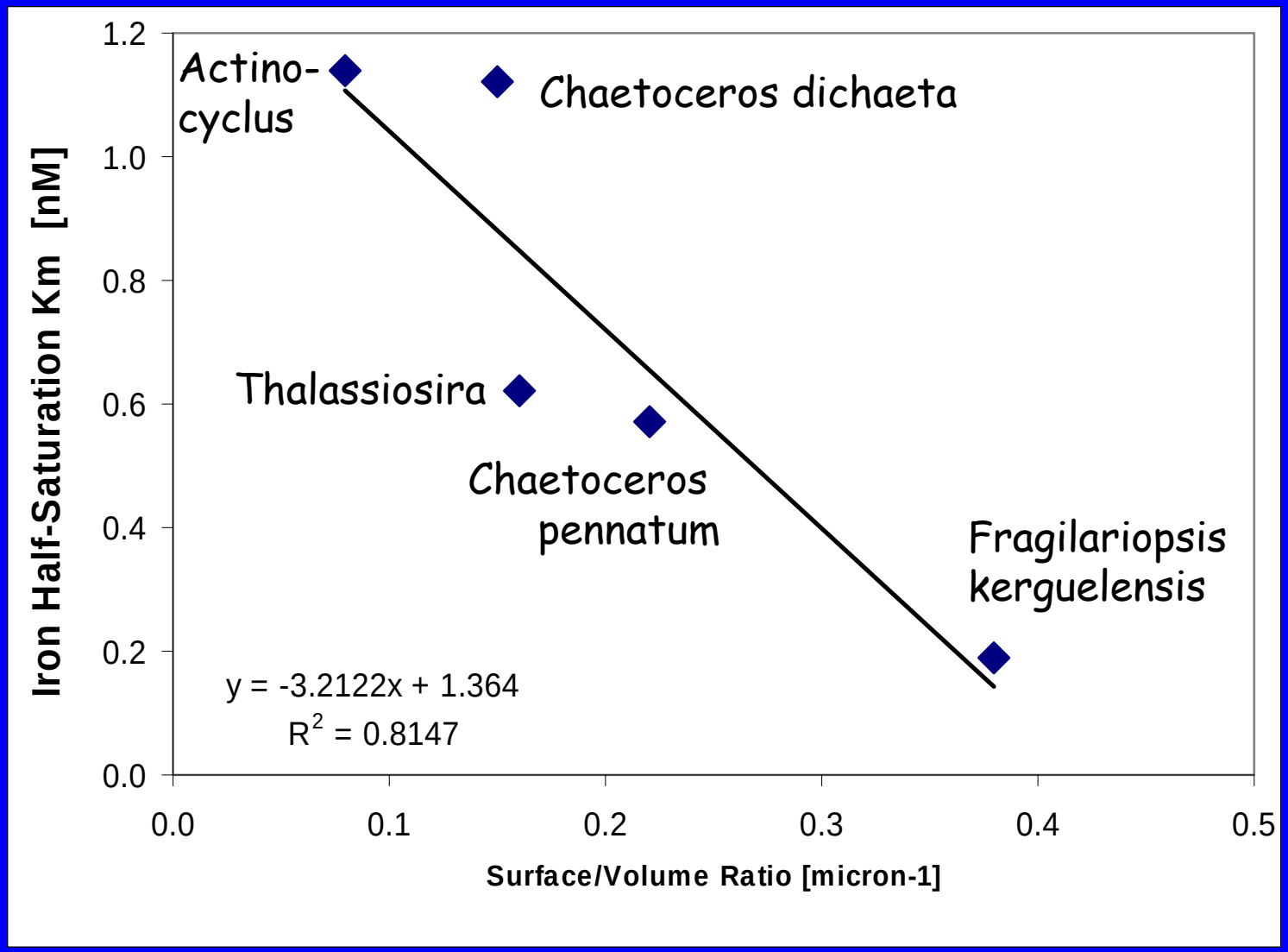


Monod growth curve for dissolved Fe [nM]
in pristine (EDTA-free) Antarctic seawater



Timmermans, VanderWagt and de Baar, 2004, L&O, in press

Bigger diatoms need higher ambient dissolved Fe



bigger diatoms need higher ambient dissolved Fe

Fe requirements large Antarctic diatoms

Big Diatom	Km
Actinocyclus	1.14 nM
Chaetoceros dichaeta	1.12 nM
Thalassiosira	0.62 nM
Chaetoceros pennatum	0.57 nM
Fragilariopsis kerguelensis	0.19 nM

- Need for optimal growth within Fe-fertilized patch

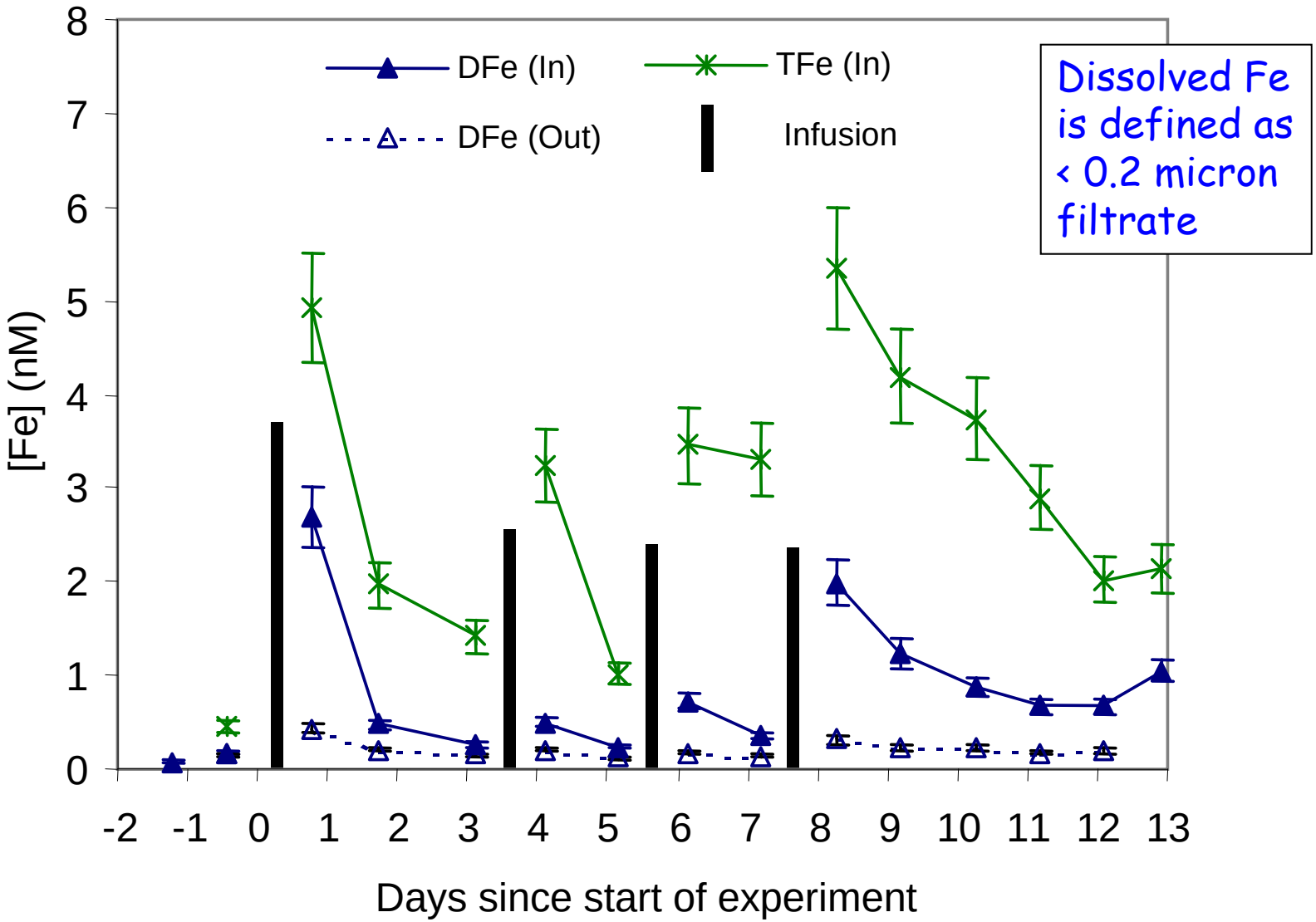
Fe [nM]	μmax
2.28 nM	0.34 d^{-1}
2.24 nM	0.62 d^{-1}
1.24 nM	0.31 d^{-1}
1.14 nM	0.36 d^{-1}
0.38 nM	0.39 d^{-1}

This is why the biggest diatoms still are rare in fertilization experiments

Dissolved Fe in SOIREE adequate to support dominant Fragilariopsis

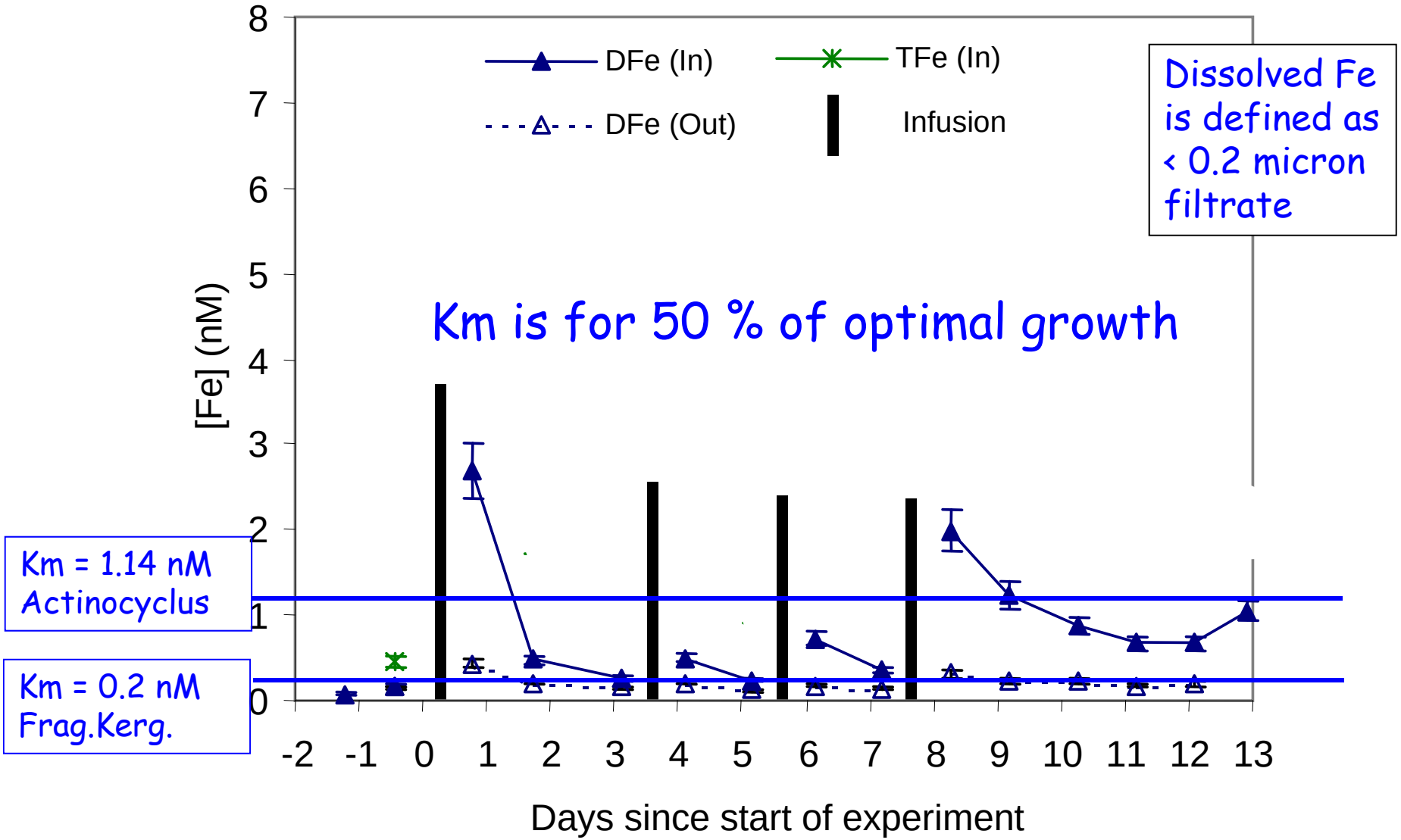
Dissolved Fe in EISENEX on average too low for Fragilariopsis:
smaller Pseudonitschzia eventually dominates EISENEX

IRON CHEMISTRY



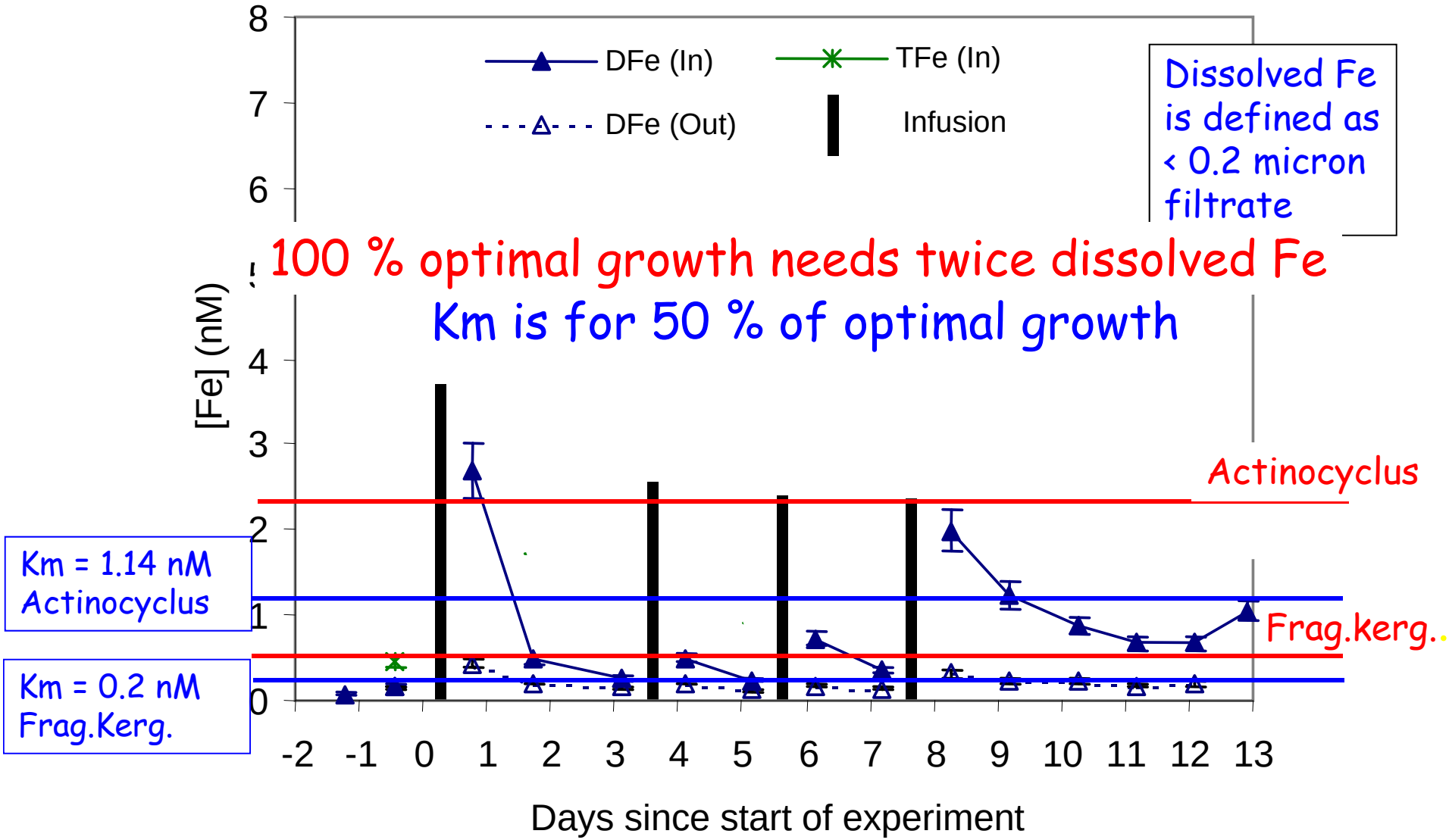
SOIREE experiment (Bowie et al., 2001, DRS II, 48, 2703

IRON CHEMISTRY



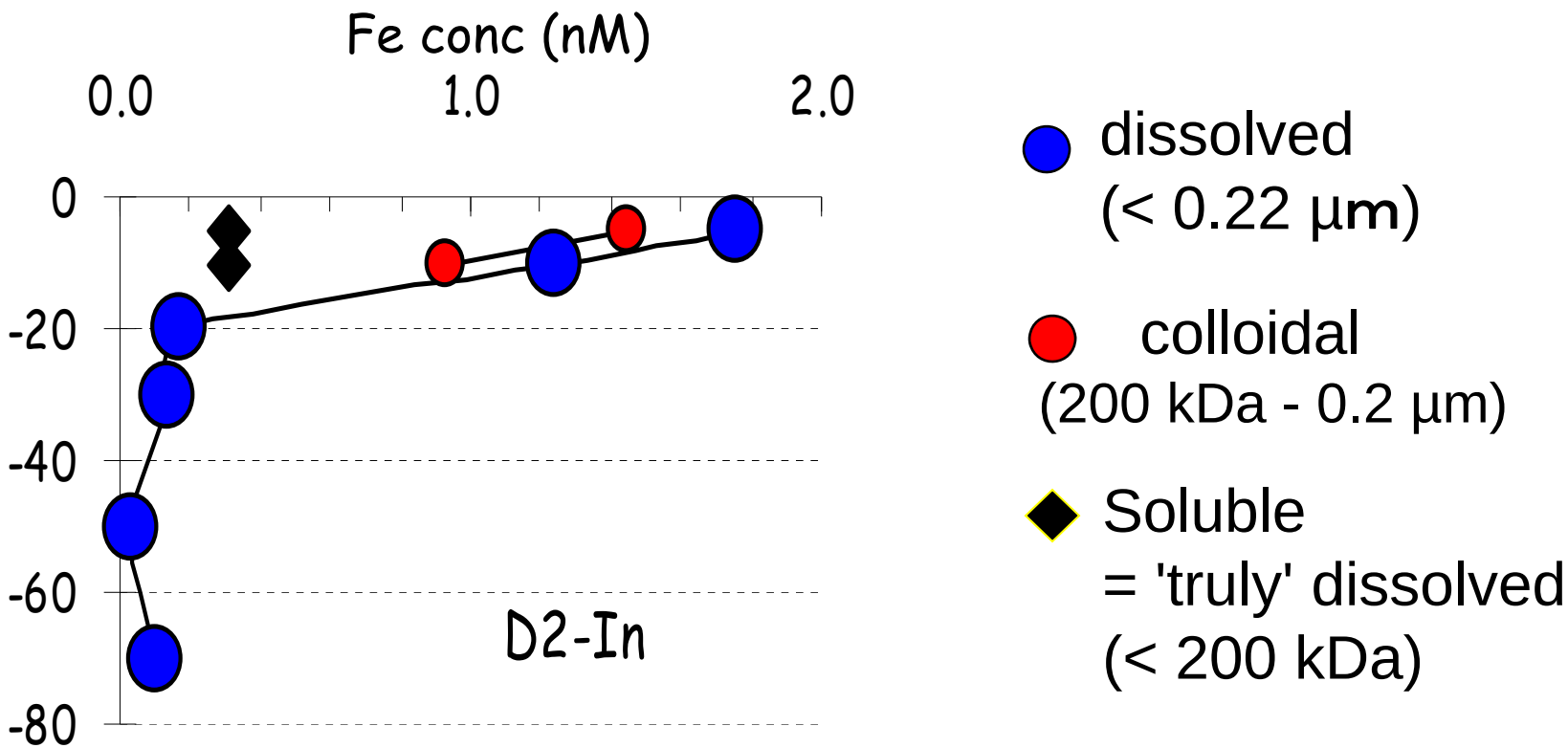
SOIREE experiment (Bowie et al., 2001, DRS II, 48, 2703

IRON CHEMISTRY



SOIREE experiment (Bowie et al., 2001, DRS II, 48, 2703

So-called dissolved Fe (<0.2 micron) in fact is colloids



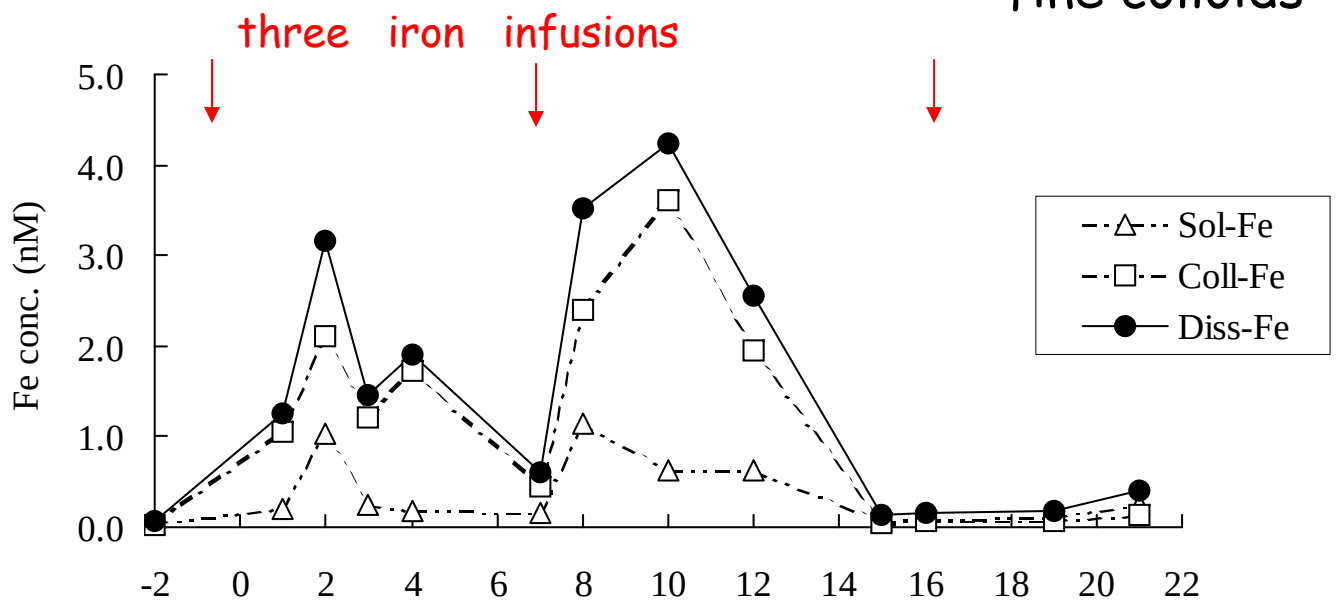
SEEDS, 2 days after Fe injection (data and graph Jun Nishioka)

EISENEX

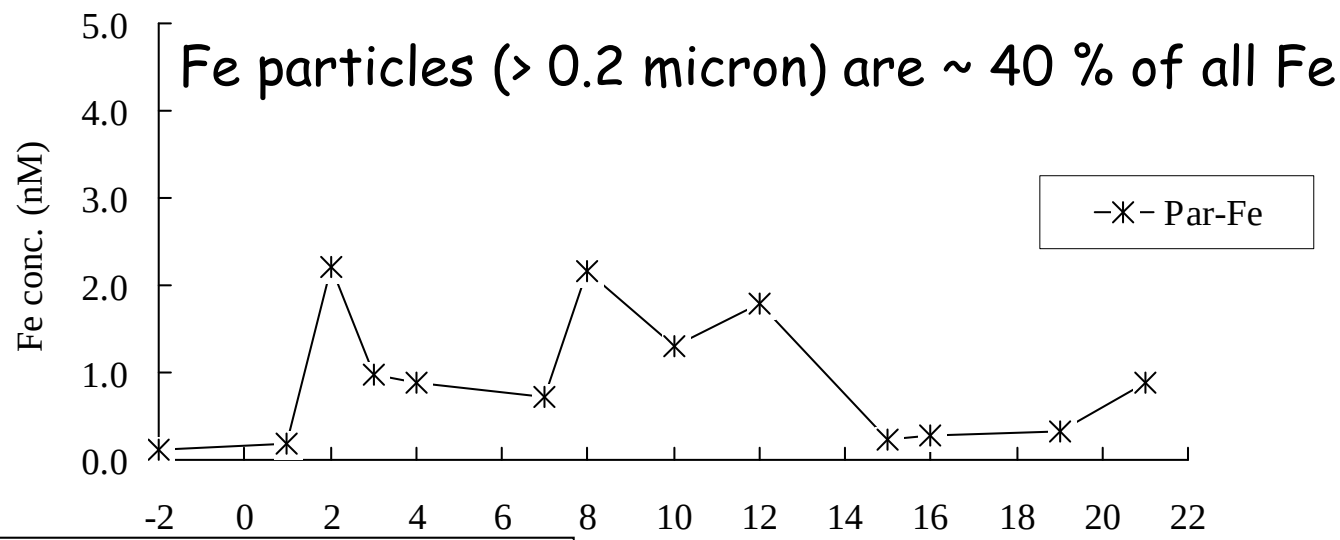
Within 24-48 hours almost all of the added dissolved reduced Fe(II) is converted by oxidation into colloids and larger particles

Thus the available Fe for uptake by diatoms is even less than was believed on basis of 'dissolved' < 0.2 micron fraction

76 % of < 0.2 micron filtered ('dissolved') in fact is fine colloids

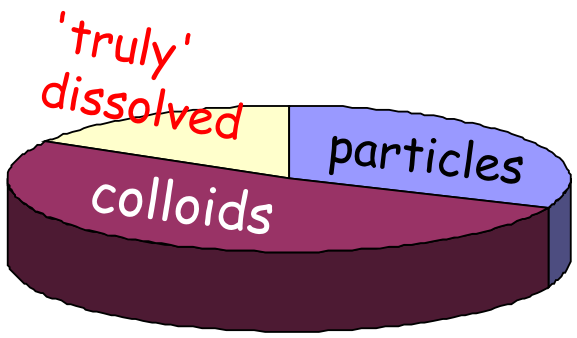


Fe particles (> 0.2 micron) are ~ 40 % of all Fe



Nishioka et al., accepted Mar Chem special issue

Fate of the Added Iron



EISENEX in-patch all 22 days

- only small portion of added Fe available for uptake by diatoms
- rapid removal of added Fe into colloids next into larger particles
- 'truly' dissolved Fe (< 200kDa) mostly organic ligands
- confirms that dissolved Fe does not belong in the ocean
  - which was the original problem anyway
- in-patch Fe chemistry deviates strongly from natural ocean
- tendency for new field studies of natural Fe gradients
  - FeCYCLE 2003; BICEP 2004 at Crozet; KEOPS 2005 at Kerguelen

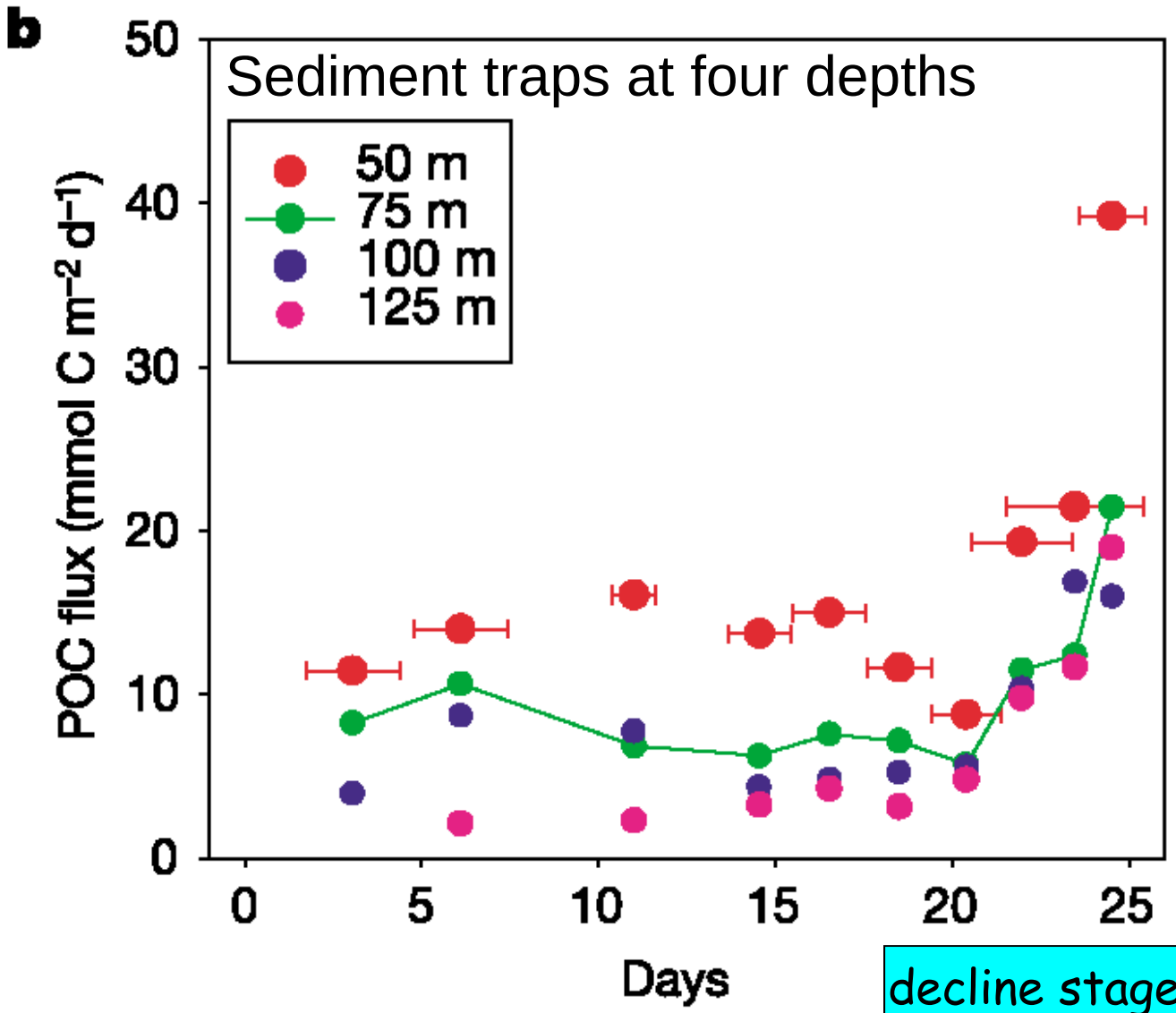
CARBON FLUXES

- Primary Production = CO2 Fixation
- Air/Sea Gas Exchange
- Delta-DIC Inventory (= TotalCO2)
- Delta-POC Inventory (Particulate Organic Carbon)
- Export Flux
  - direct evidence only at SERIES, SOFEX-South

- Combination of 8 different experiments still preliminary:
- Many inconsistencies and assumptions between experiments

Sources: Steinberg et al., 1998, MarChem; Tsuda et al 2003, Science; Riebesell et al, 2003, Science, in rejection; Boyd et al., 2004, Nature; Coale et al., 2004, Nature; Buesseler et al., 2004, Nature; Bozec et al., 2004, MarChem, in press; Coale, 2004 ASLO lecture at Hawaii; Bakker et al 2004, DSR submitted.

SERIES sediment trap fluxes

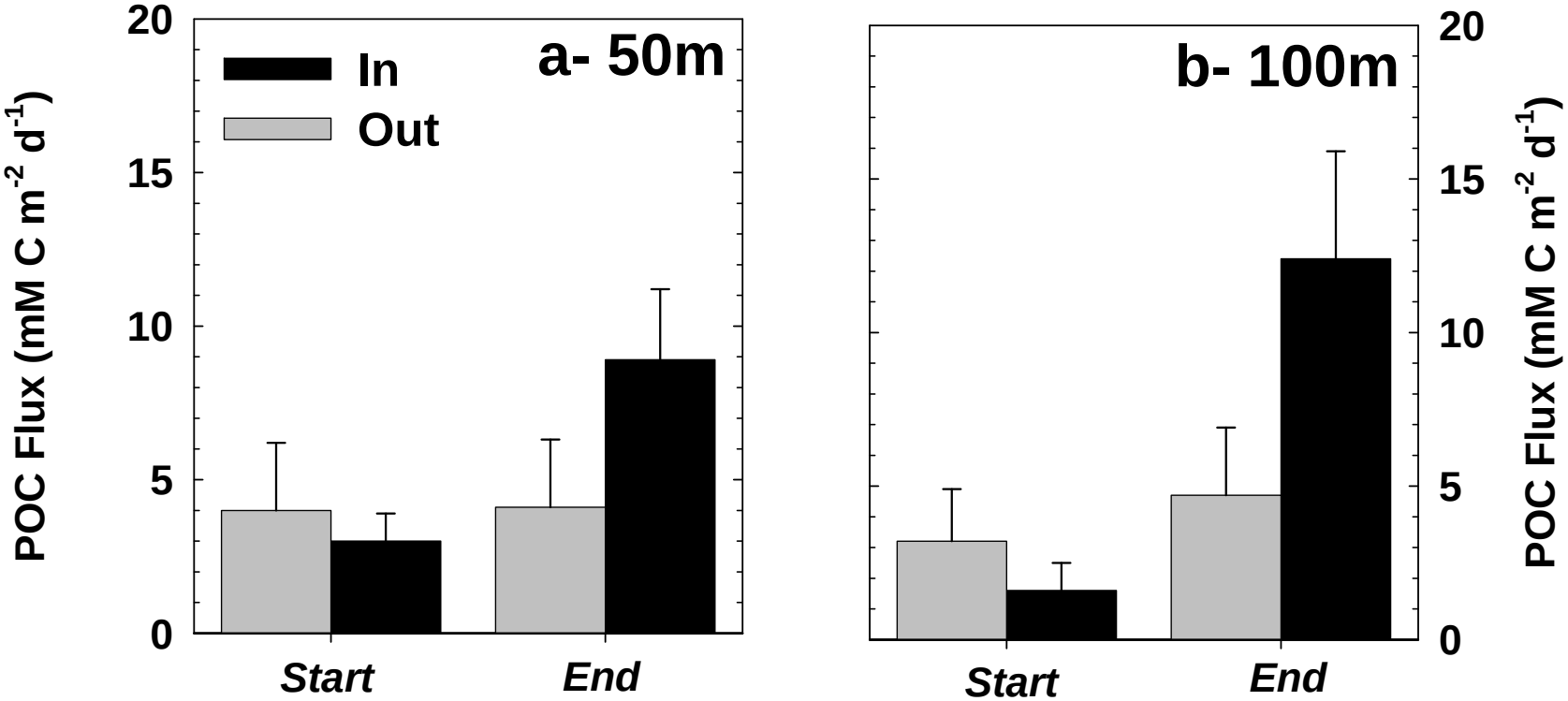


decline stage bloom

Boyd et al. (2004) Nature, 428, 549

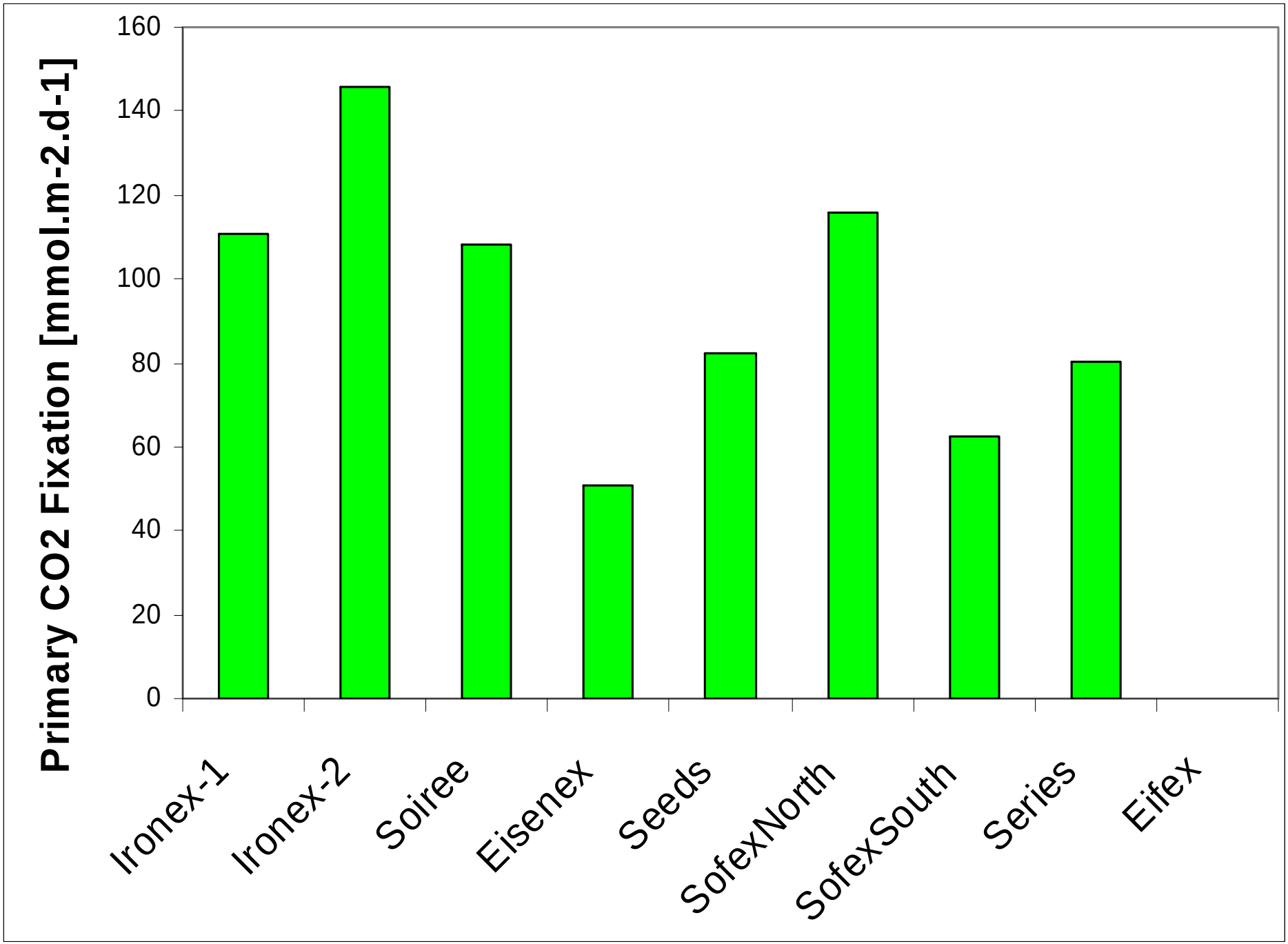
SOFEX-South Patch ^{234}Th deficiency method

Carbon flux = ^{234}Th flux • [POC/^{234}Th]

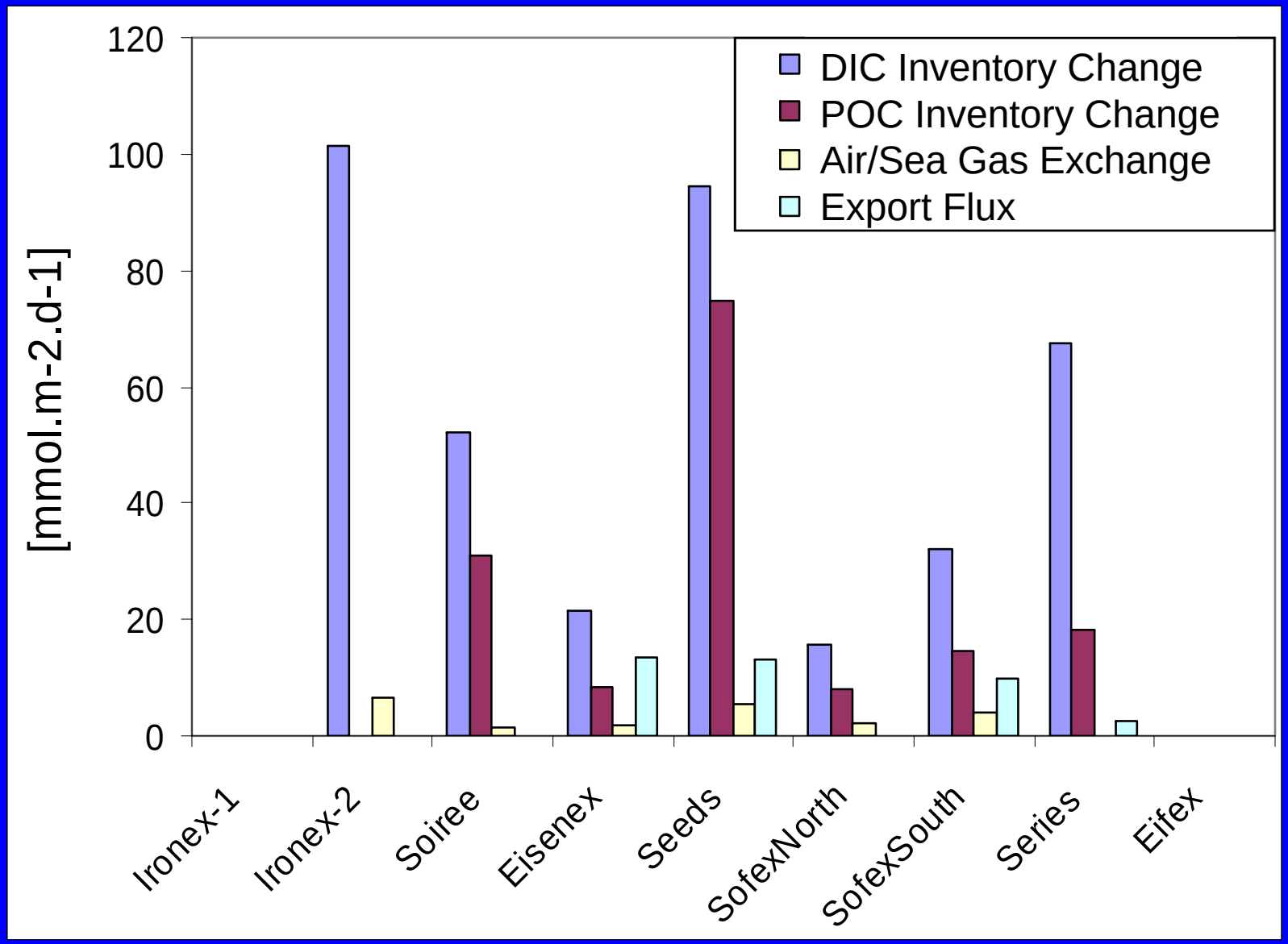


POC flux IN > OUT by end of 28 day SOFeX-South observations
- but not large relative to previous Southern Ocean blooms at this site

Buesseler et al. (2004) Science, 304, 414


Primary CO2 Fixation [mmol.m-2.d-1]
160
140
120
100
80
60
40
20
0
Ironex-1
Ironex-2
Soiree
Eisenex
Seeds
SofexNorth
SofexSouth
Series
Eifex

Rates of Change for Carbon Inventories and Fluxes



air/sea exchange negligible

export is small and debatable

Conclusions

- Light limitation by depth of Wind Mixed Layer nicely confirmed by 8 iron experiments
  - WML depth inversely related with Chlorophyll, ΔDIC, ΔNitrate
  - temperature, patch dilution, irradiance also play a role
- Shift-up to larger size classes diatoms
  - bigger diatom at higher dissolved Fe
  - difficult to maintain constant high dissolved Fe for largest diatoms
- Most added Fe rapidly lost into colloids and larger particles
  - only about 20 % is 'truly' dissolved (<200 kDa fraction)
- Carbon Inventories and Fluxes only Preliminary Comparison
  - gas exchange flux is negligible
  - export flux is proven in Series and Sofex-South
  - export flux is small and exact value debatable