The Marine Nitrogen Cycle Experiments

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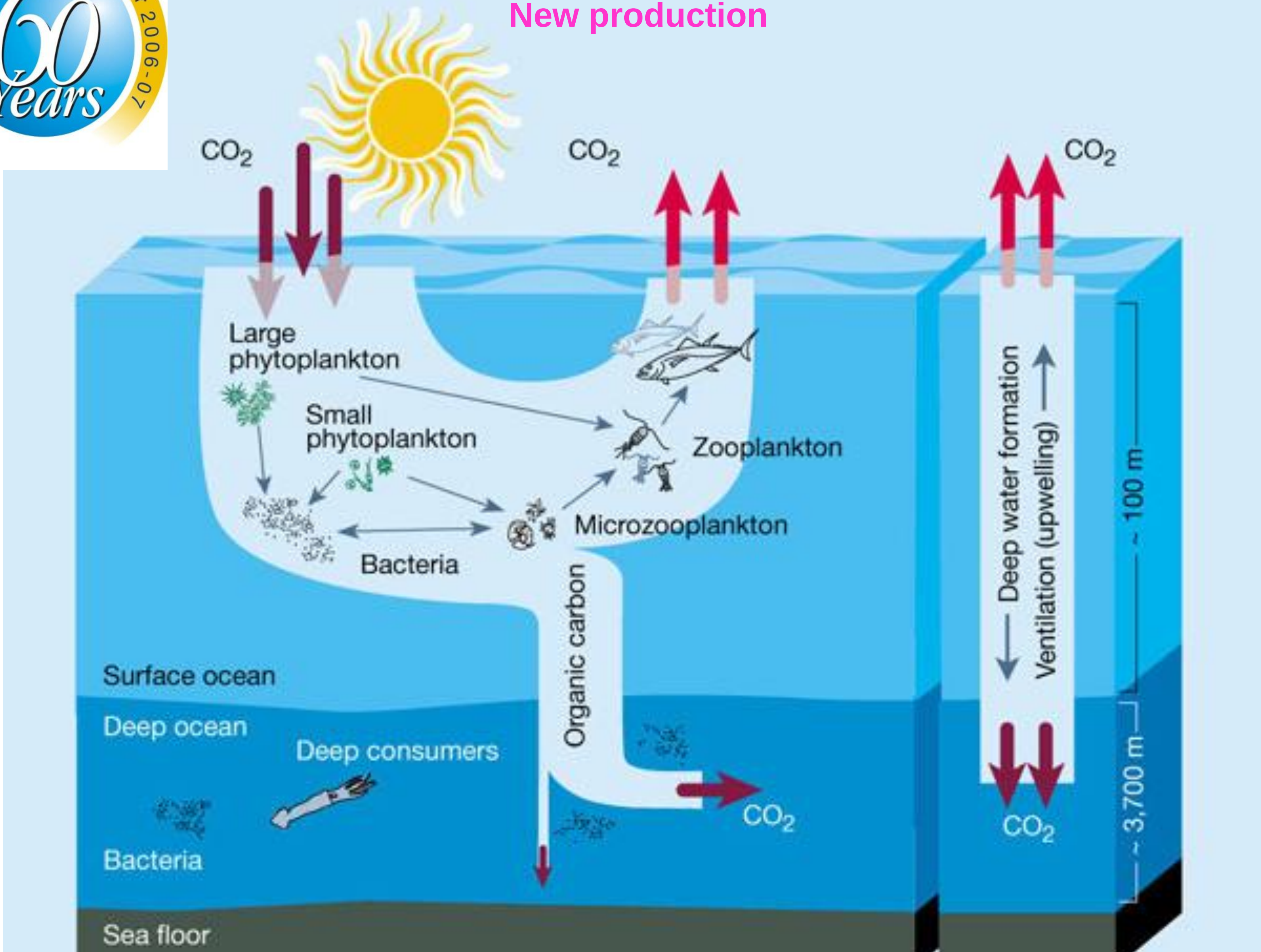
Solubility, Biological Pumps & New production

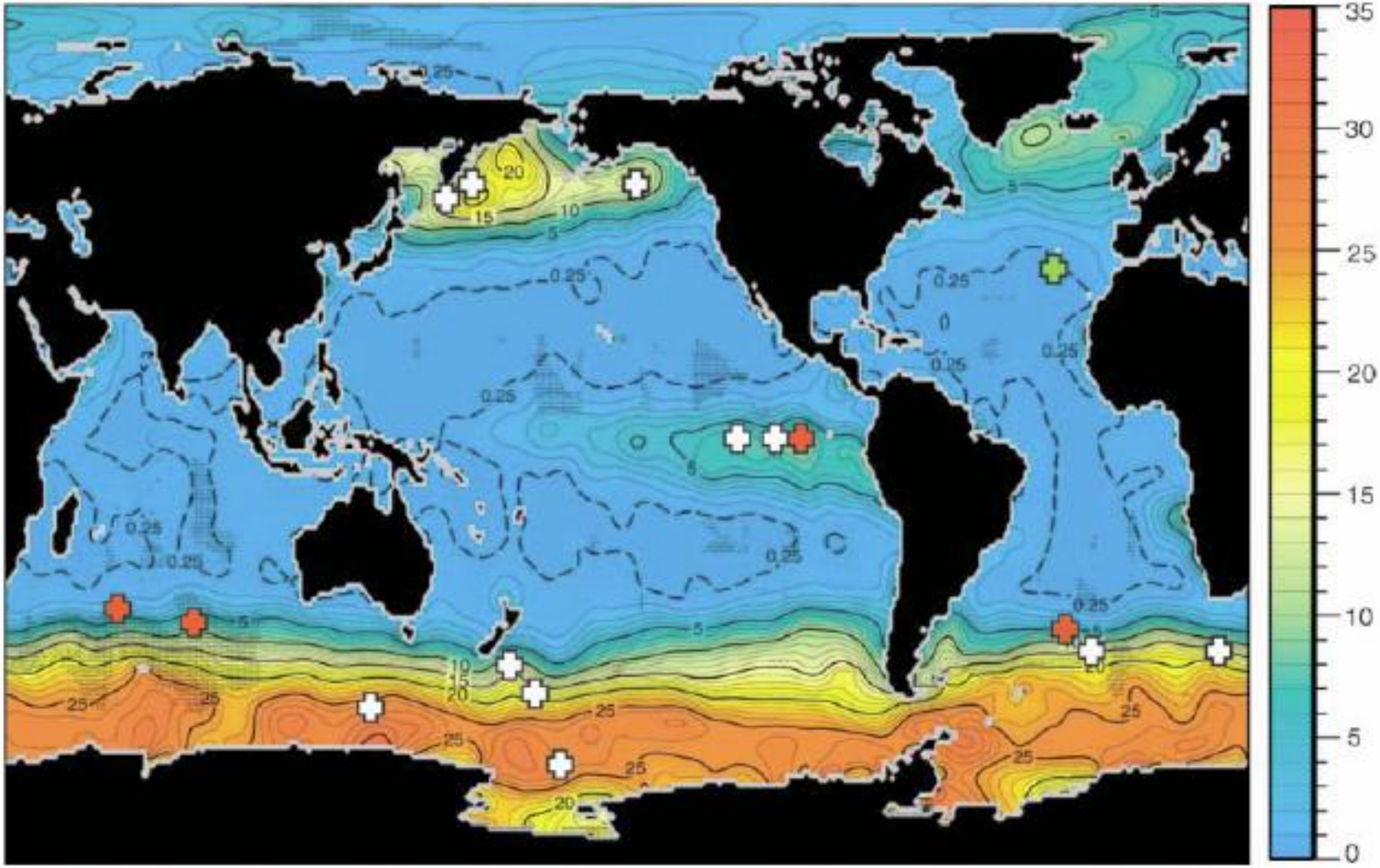


Redfield Ratio

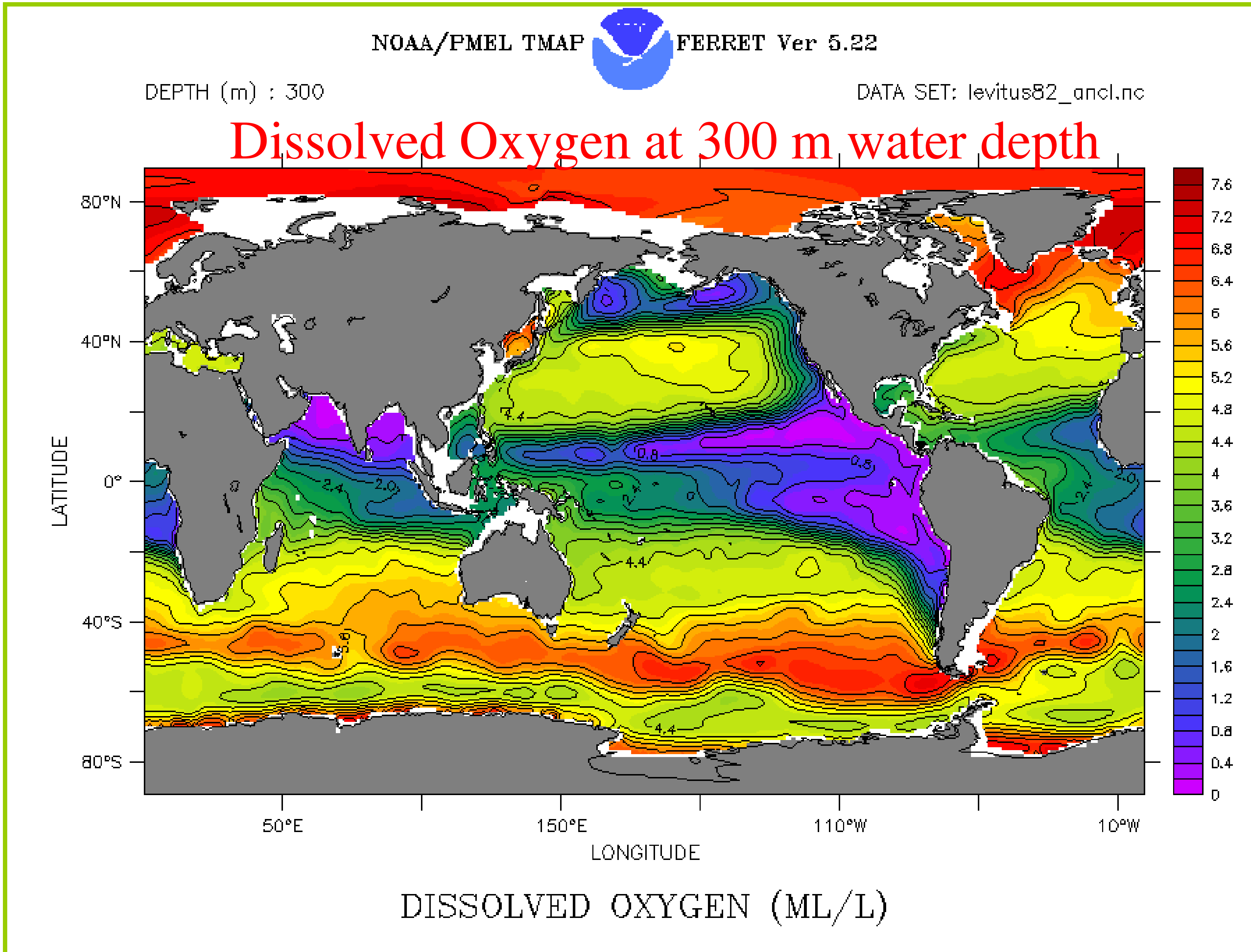
Generally referred to as Redfield ratios (Redfield *et al*., 1963). The same ratios approximately hold good for plankton and seawater (dissolved forms) but with some variations in time and space in the ocean.

$$106CO_2 + 16HNO_3 + H_3PO_4 + 122H_2O + \text{Trace elements} \rightarrow C_{106}H_{263}O_{110}N_{16}P + 138O_2$$

Nitrogen limitation in the oceans



Dissolved Oxygen at 300 m water depth



Levitus Data

N amounts in global reservoirs

Reservoirs	*Amount (Tg N)*	*% of total*
Atmospheric N_2	3.95×10^9	79.5
Sedimentary rocks	9.99×10^8	20.1
Ocean (N_2)	2.0×10^7	0.4
Ocean (NO_3^-)	5.7×10^5	$\sim 10^{-2}$
Soil organics	1.9×10^5	$\sim 10^{-2}$
Land biota	1.0×10^4	$\sim 10^{-3}$
Marine biota	500	$\sim 10^{-5}$

Source : J.N. Galloway, 2004

Natural abundance of isotopes

Element	Isotope	Abundance	Ratio measured	Reference standard
Hydrogen	^{1}H	99.984	$^{2}H/^{1}H$ (D/H)	VSMOW[a]
	^{2}H (D)[b]	0.0156		
Carbon	^{12}C	98.982	$^{13}C/^{12}C$	PDB[c]
	^{13}C	1.108		
Nitrogen	^{14}N	99.630	$^{15}N/^{14}N$	N_2-atm[d]
	^{15}N	0.366		
Oxygen	^{16}O	99.763	$^{18}O/^{16}O$	VSMOW, PDB[e]
	^{17}O	0.0375	$^{18}O/^{17}O$[f]	VSMOW
	^{18}O	0.1995		
Sulfur	^{32}S	95.02	$^{34}S/^{32}S$	CDT[g]
	^{33}S	0.756		
	^{34}S	4.210		
	^{36}S	0.014		

Natural Abundance Terminology

- Isotopic Ratio

$$R = \frac{\text{Abundance of Rare Isotope}}{\text{Abundance of Common Isotope}}$$

  - 13C/12C, D/H, 18O/16O, 15N/14N

- Delta notation

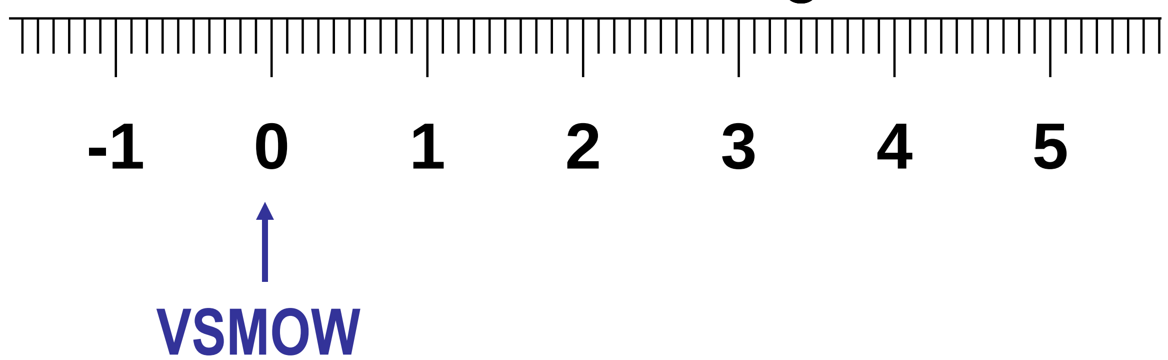
$$\delta = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \cdot 1000$$

  - Units (‰) Parts per thousand or “per mil”

δ Notations, ‰

$$\delta^{18}O = \left(\frac{\left(\frac{^{18}O}{^{16}O}\right)_{SAMPLE} - \left(\frac{^{18}O}{^{16}O}\right)_{VSMOW}}{\left(\frac{^{18}O}{^{16}O}\right)_{VSMOW}} \right) X\ 1000$$

Lower $\frac{^{18}O}{^{16}O}$ $\longleftarrow$ $\delta^{18}O$ $\longrightarrow$ Higher $\frac{^{18}O}{^{16}O}$



Different Oxic conditions

- **Hypoxic (non-reducing, nitrite [NO_2^-] ~0, O_2 ~ 4.4 µM)**
- **Suboxic (denitrifying NO_3^-,NO_2^- > 0, $0<O_2<4.4$ µM)**
- **Anoxic (Sulphate reducing; NO_3^-,NO_2^- ,O_2~ 0)**

Source: Naqvi et al., 2000

N-Cycle

(i) ***Nitrogen fixation*** **– conversion of atmospheric N_2 to organic N.**

$$N_2 + 8H^+ \rightarrow 2NH_3 + H_2$$

high energy is required to break the triple bond of N_2 – 226 kcal/mol

(ii) ***Ammonium assimilation*** **– NH_3 or NH_4^+ is taken up by an organism to become part of its biomass.**

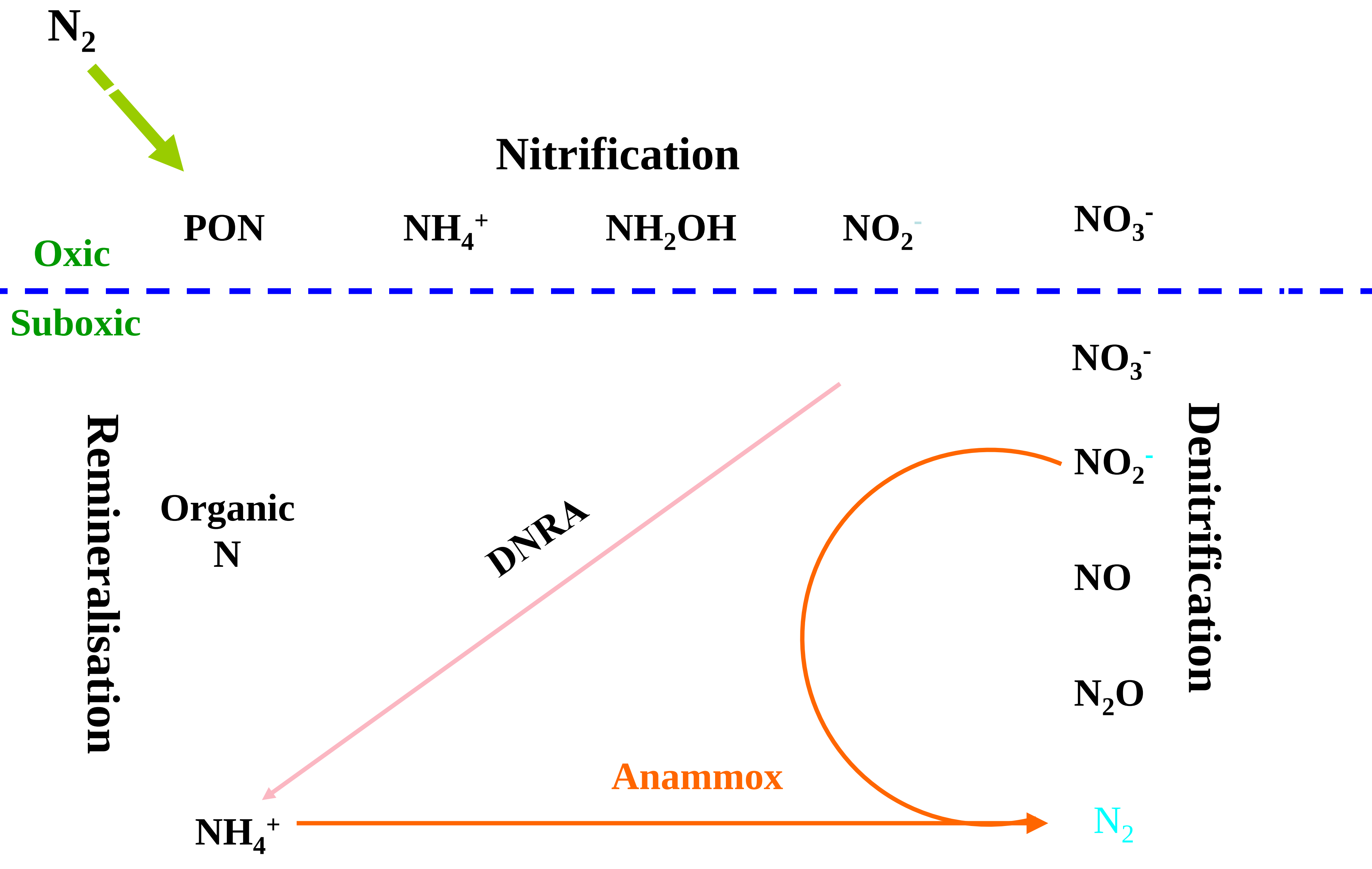
(iii) Nitrification **– Oxidation of NH_3 or NH_4^+ to nitrate or nitrite by an organism, as means of producing energy.**

$$NH_4^+ + 3/2O_2 \rightarrow NO_2^- + H_2O + 2H^+ \qquad \Delta G = -290\ kJ/mol$$

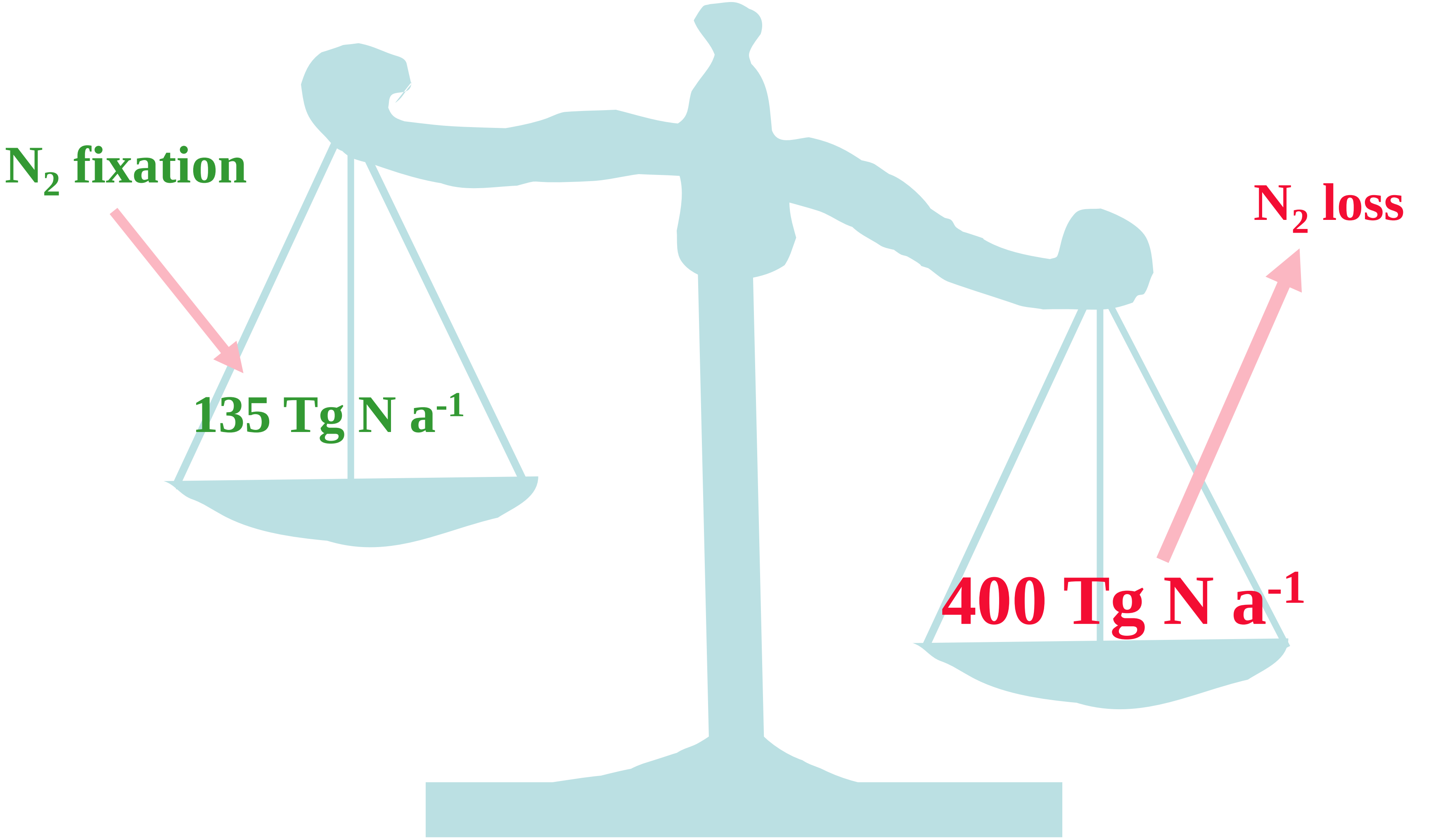
$$NO_2^- + 1/2O_2 \rightarrow NO_3^- \qquad \Delta G = -82\ kJ/mol$$

(iv) Assimilatory nitrate reduction **– is the uptake of nitrate by an organism and incorporation as biomass through nitrate reduction.**

The Marine Nitrogen Cycle



Global Marine Nitrogen Imbalance



Sources and Sinks

Reactive nitrogen budget

Loss by denitrification, and anammox

Gain by rivers, aerosols, and fixation by Diazatrophs (equivalents of legumes on land) capable of fixing atmospheric nitrogen (Nitrogen reductase)

Major Questions Addressed

1. **How much nitrogen and carbon is fixed during a *Trichodesmium* bloom period in the Arabian Sea? Is nitrogen cycle in balance in the Arabian Sea?**

2. **Does nitrogen fixation occur in sediments, if yes then how much? Is it significant?**

3. **Can we quantify theoretically the amount of external nitrogen inputs in the denitrification zones of the Arabian Sea?**

5.. **Does nitrogen through aerosol deposition significantly contribute to new production in the northern Indian Ocean?**

6. How much nitrogen from Indian rivers reaches to the Arabian Sea and Bay of Bengal? Is this contribution significant to new production?

Experimental procedure for N_2 fixation

Water sampling

Uptake Calculation

Tracer Addition

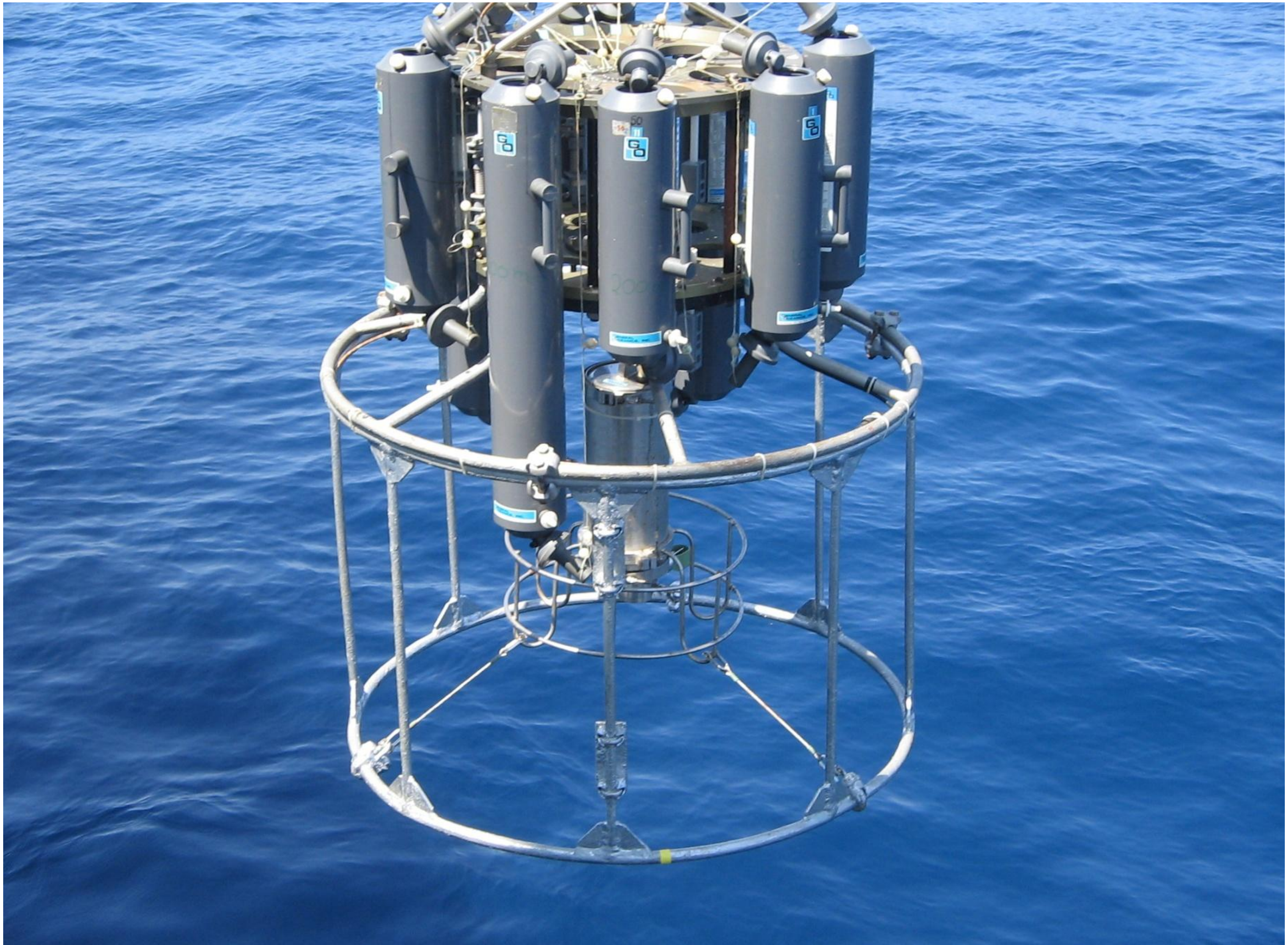
Analysis

Incubation

Filtration

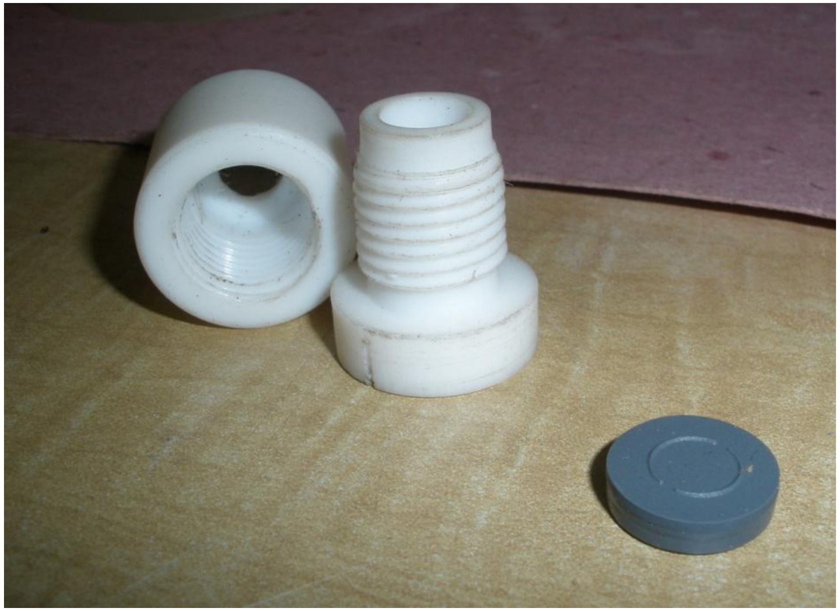
Preservation

Rosette Sampler



Students working on the deck

Methodology developed for N_2 fixation in water column



Filtration onboard ship

N_2- fixation calculation

Specific uptake rate

$$V(T^{-1}) = \left(\frac{1}{t}\right)\left(\frac{A_{PN_f} - A_{PN_0}}{A_{N_2} - A_{PN_0}}\right)$$

Volumetric rate of N_2 fixation

$$\rho \approx V[PN]_f$$

A_{N2} = ^{15}N enrichment of N_2 available for fixation

A_{PN0} = ^{15}N enrichment of PON at the start of experiment

A_{PNf} = ^{15}N enrichment of PON at the end of experiment

t = time of incubation (~4 hrs)

$[PN]_0$ = concentration of PON at the start of the experiment

$[PN]_f$ = concentration of PON at the end of the experiment

A_{N2} calculation *i.e.* estimation ^{15}N enrichment of N_2 available for fixation

$$A_{N_2} = \frac{\left({}^{15}N_{tracer} \times \text{tracer conc} + {}^{15}N_{natural} * \text{ambient conc}\right)}{(\text{tracer conc} + \text{ambient conc})}$$

Table 5. Solubility of nitrogen from moist air at one atmosphere total pressure in (ml/l).

T(°C)	SALINITY IN PERMIL 0	10	20	30	34	35	36	38	40
-1	—	—	16.28	15.10	14.65	14.54	14.44	14.22	14.01
0	18.42	17.10	15.87	14.73	14.30	14.19	14.09	13.88	13.67
1	17.95	16.67	15.48	14.38	13.96	13.86	13.75	13.55	13.35
2	17.50	16.26	15.11	14.04	13.64	13.54	13.44	13.24	13.05
3	17.07	15.87	14.75	13.72	13.32	13.23	13.13	12.94	12.76
4	16.65	15.49	14.41	13.41	13.03	12.93	12.84	12.66	12.47
5	16.26	15.13	14.09	13.11	12.74	12.65	12.56	12.38	12.21
6	15.88	14.79	13.77	12.83	12.47	12.38	12.29	12.12	11.95
8	15.16	14.14	13.18	12.29	11.95	11.87	11.79	11.62	11.46
10	14.51	13.54	12.64	11.80	11.48	11.40	11.32	11.17	11.01
12	13.90	12.99	12.14	11.34	11.04	10.96	10.89	10.74	10.60
14	13.34	12.48	11.67	10.92	10.63	10.56	10.49	10.35	10.21
16	12.83	12.01	11.24	10.53	10.25	10.19	10.12	9.99	9.86
18	12.35	11.57	10.84	10.16	9.90	9.84	9.77	9.65	9.52
20	11.90	11.16	10.47	9.82	9.57	9.51	9.45	9.33	9.21
22	11.48	10.78	10.12	9.50	9.26	9.21	9.15	9.03	8.92
24	11.09	10.42	9.79	9.20	8.98	8.92	8.87	8.76	8.65
26	10.73	10.09	9.49	8.92	8.71	8.65	8.60	8.50	8.39
28	10.38	9.77	9.20	8.66	8.45	8.40	8.35	8.25	8.15
30	10.06	9.48	8.93	8.41	8.21	8.16	8.12	8.02	7.92
32	9.76	9.20	8.67	8.18	7.99	7.94	7.89	7.80	7.71
34	9.48	8.94	8.43	7.96	7.77	7.73	7.68	7.59	7.51
36	9.21	8.69	8.20	7.75	7.57	7.53	7.48	7.40	7.31
38	8.95	8.46	7.99	7.55	7.38	7.33	7.29	7.21	7.13
40	8.71	8.23	7.78	7.36	7.19	7.15	7.11	7.03	6.95

Stable Isotope Mass Spectrometer for measuring 13C and 15N isotopes

Error Analysis

Sources of error in this case

(i) Incubation time 2-3%

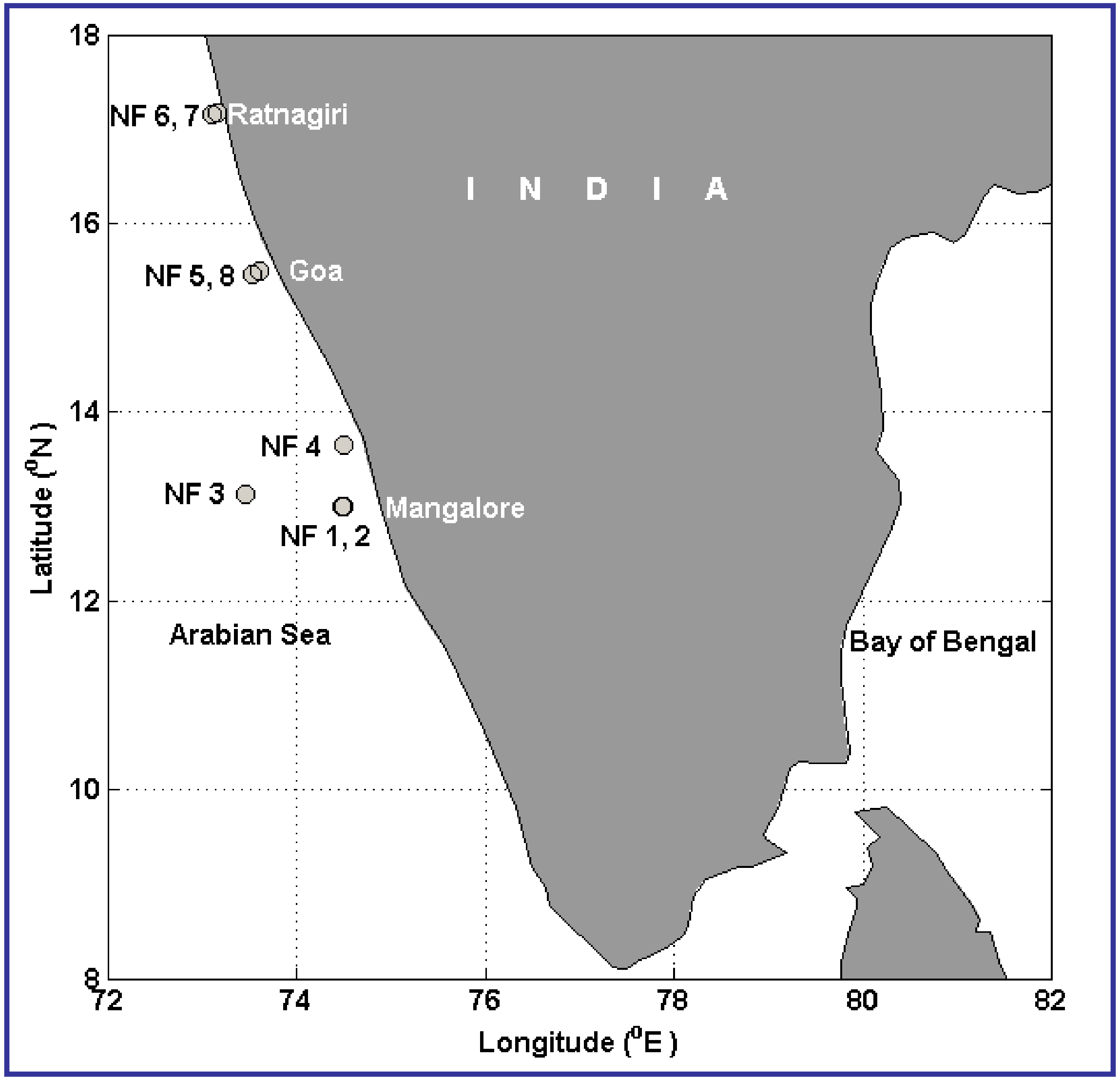
(ii) Isotopic composition of PON (A_{PN0} and A_{PNf}) ±0.2 ‰,

(iii) A_{N2} – 3%

(iv) PON concentration 4%

So maximum error in V ±6 % and in ρ ± 10.0%

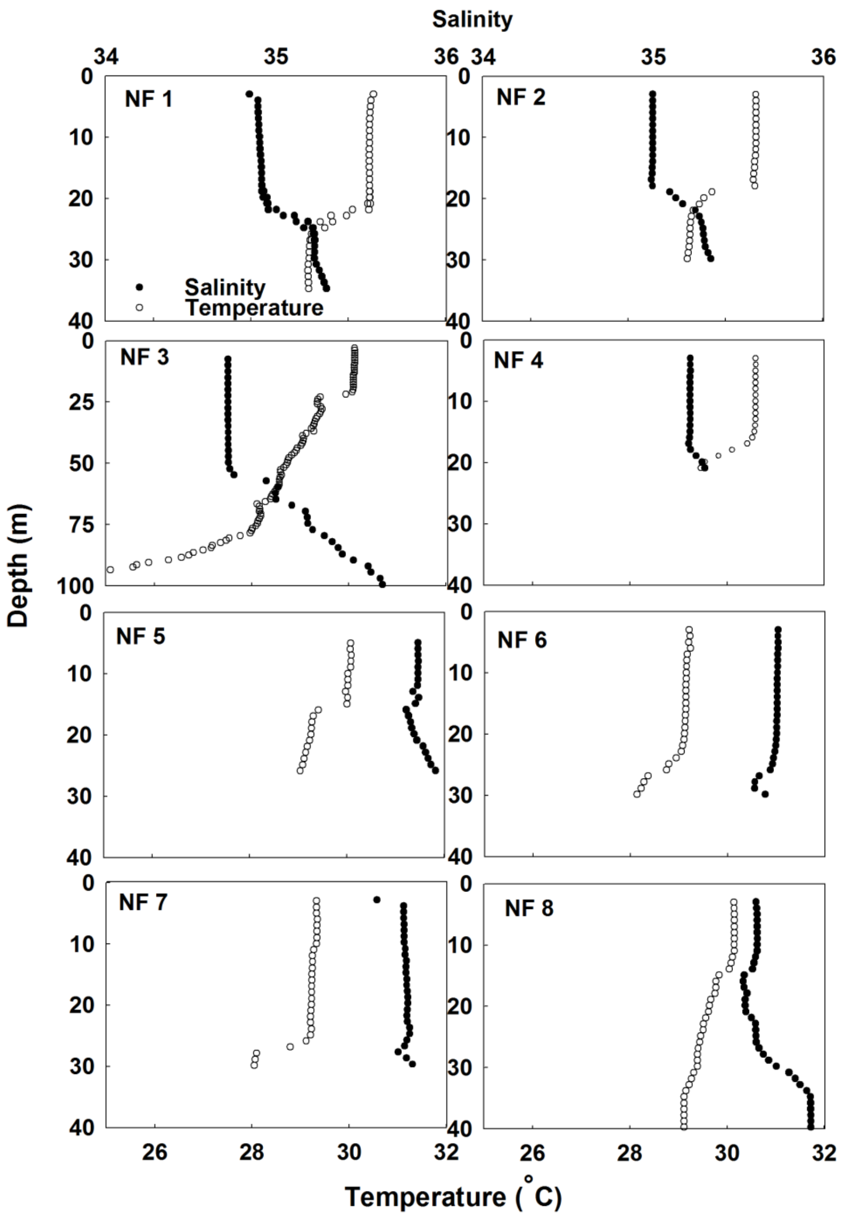
N_2 fixation in the Arabian Sea

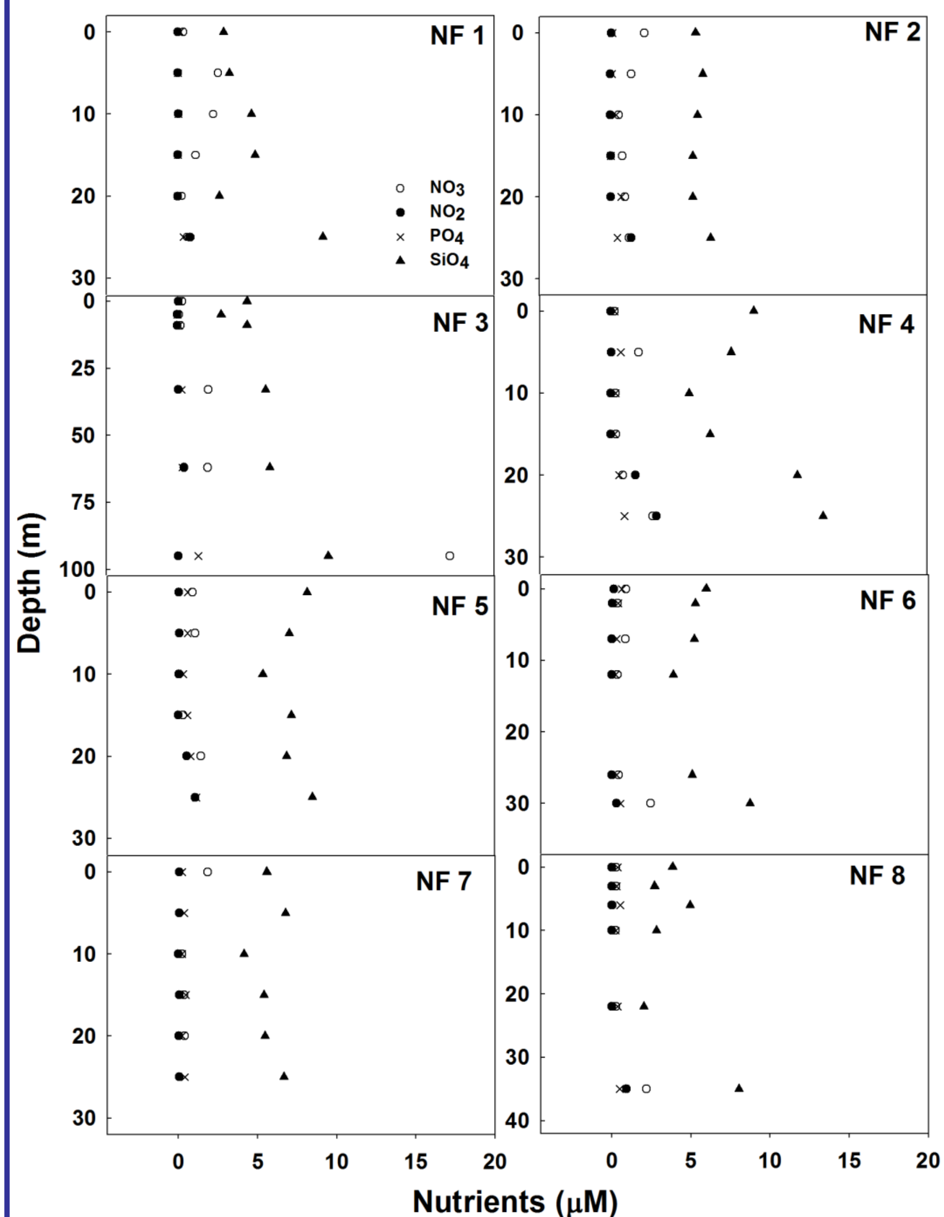


Sampling Locations

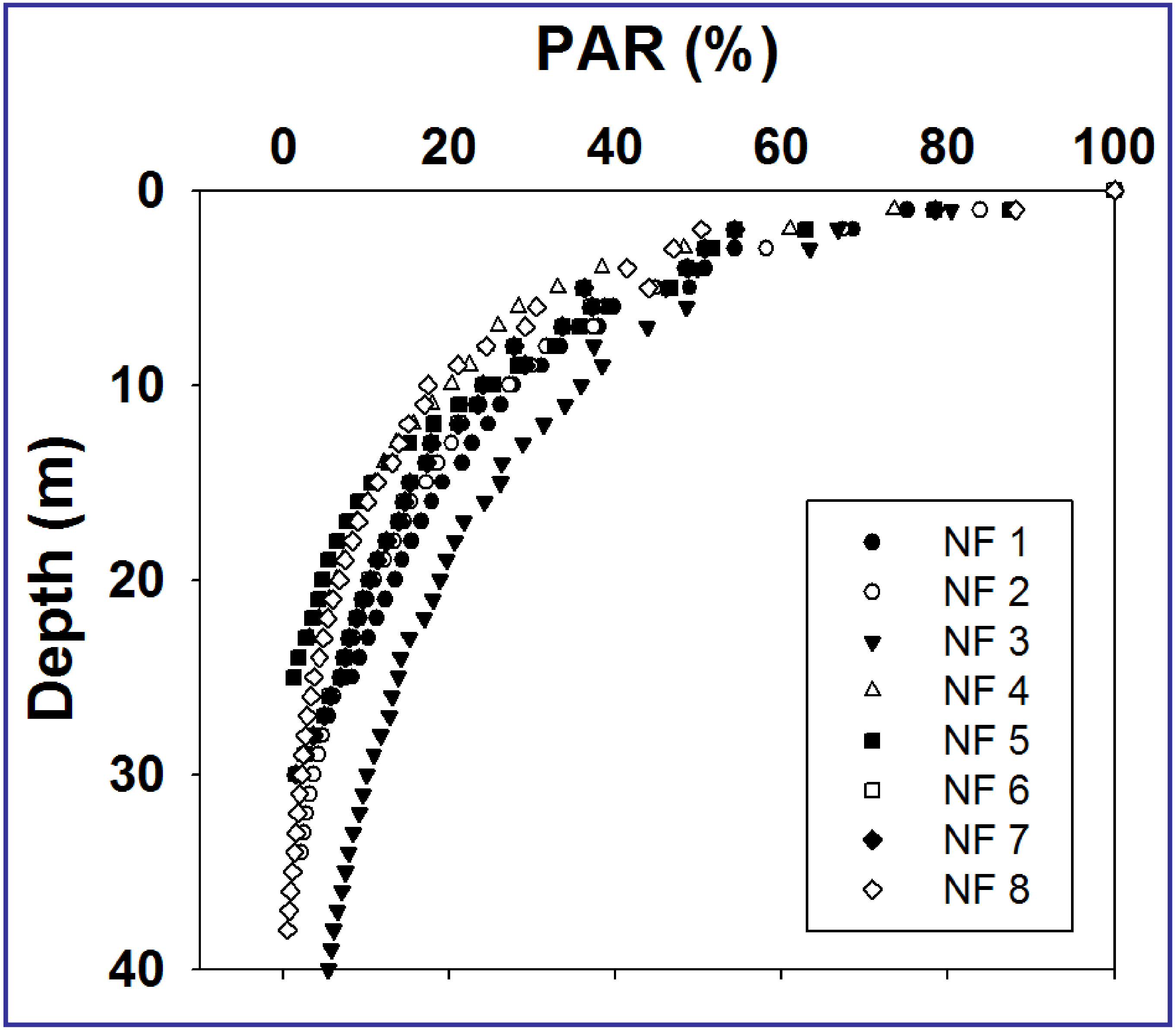
Study the *Trichodesmium* bloom in the Arabian Sea

Physical and chemical properties

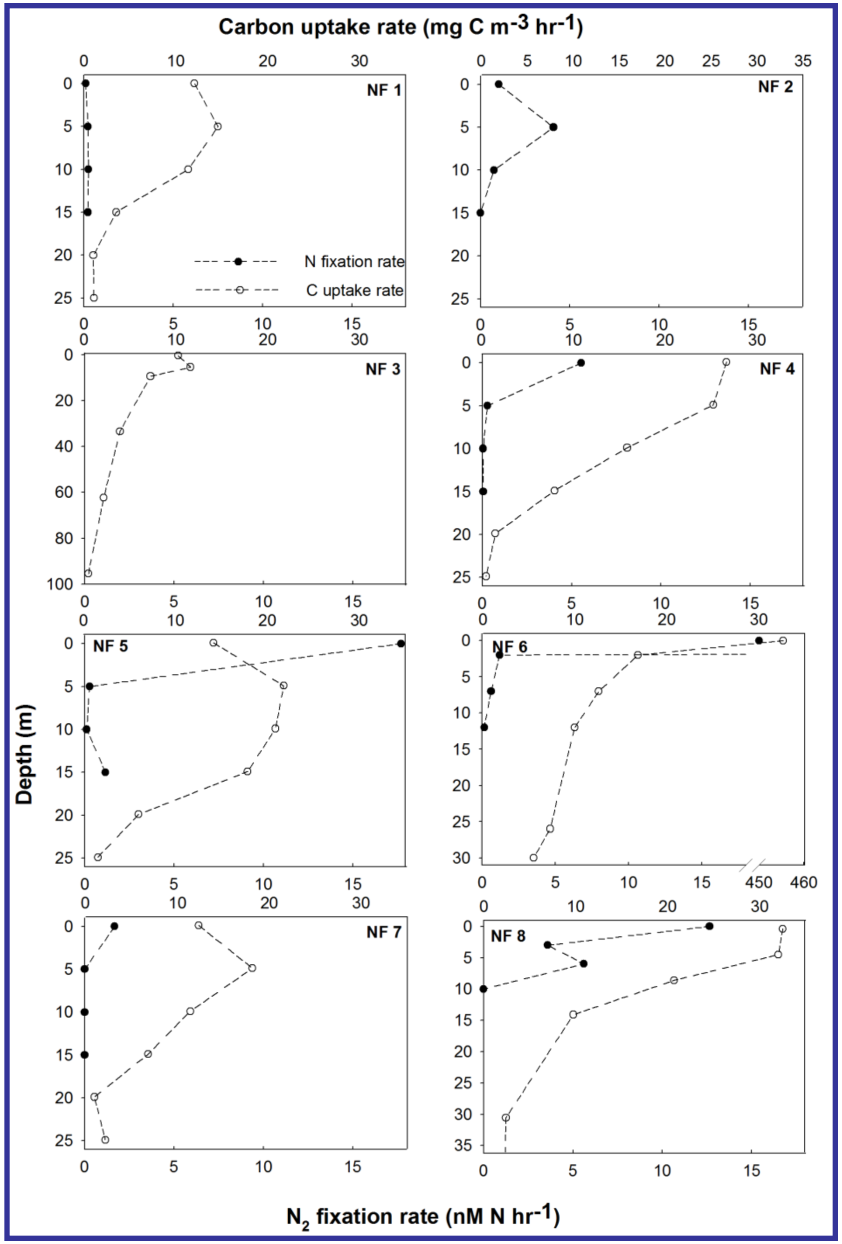




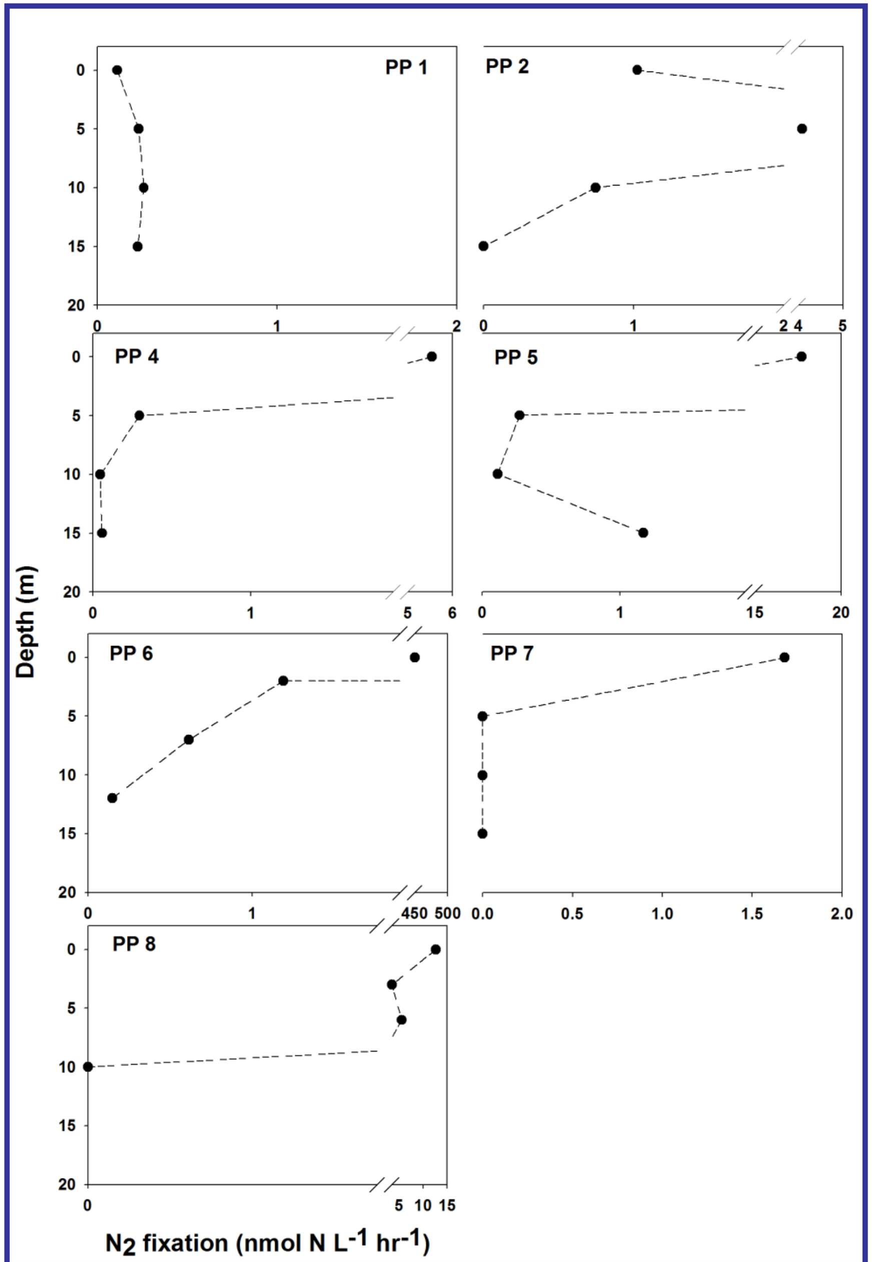
Light properties



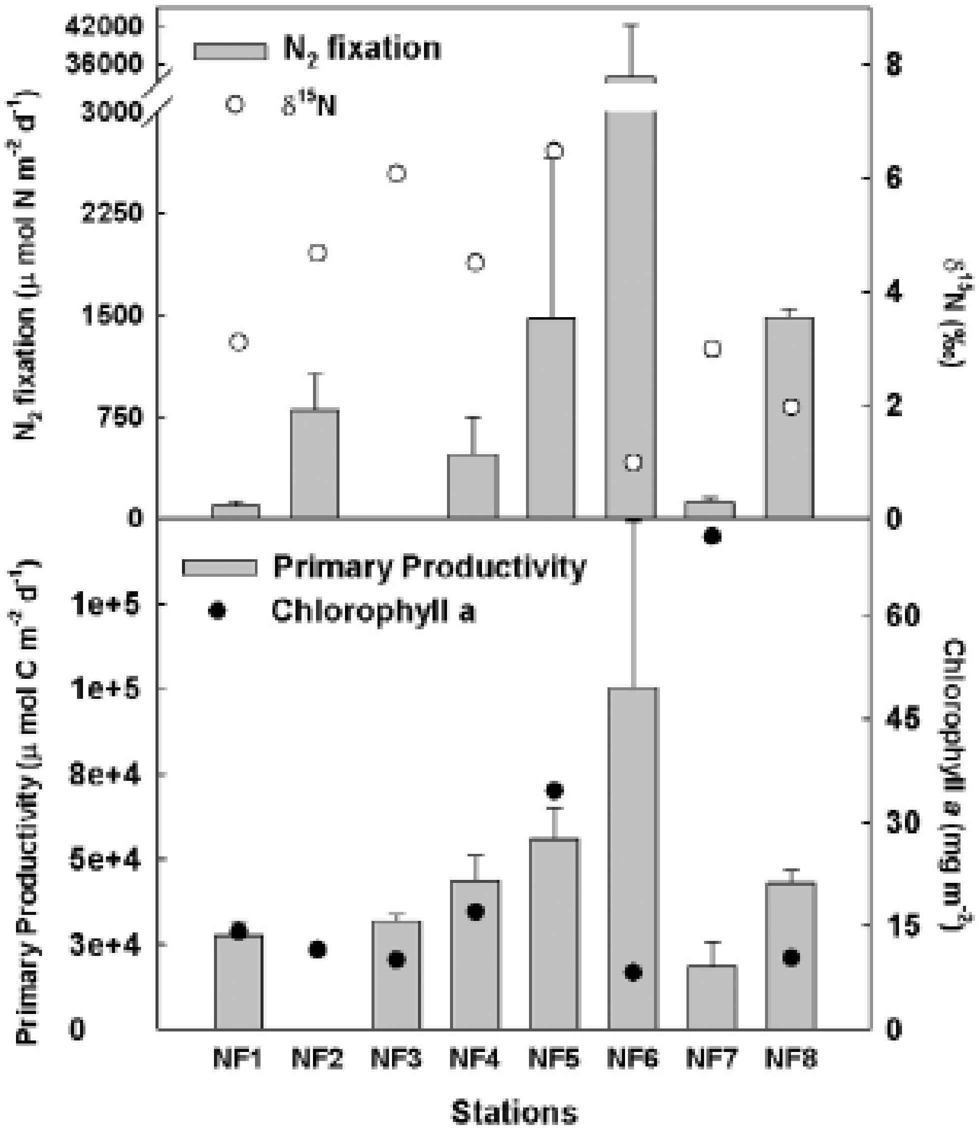
Depth profile of N_2 fixation and primary productivity



Depth profile of N_2 fixation



Integrated N_2 fixation and primary productivity



Gandhi et al 2011 Global Biogeochemical Cycles,25, GB4014

Summary of N_2 fixation in the Arabian Sea

1. N_2 fixation was measured during a bloom period for the in the NE Arabian Sea using a new technique.
2. We have estimated that 22.5 Tg y^{-1} nitrogen is fixed in the Arabian Sea, which is ~11% of global nitrogen fixation in the 2% of the global ocean area and much higher than previous indirect estimations.
3. There is no significant correlation between N_2 fixation and primary productivity.

Developments in the N-Cycle of Arabian Sea: Results from the present study

Nitrogen Fluxes (Tg N a^{-1})

Processes	Earlier Estimations	Present Estimations
Atmospheric deposition	1.6	1.2
N_2 fixation	3.3	22.5
Rivers	1.2	0.1
Other processes (non-photic)	?	?
Denitrification	- 33	?
Anammox	?	?