Excess Nitrogen Gas in Oxygen Deficient Zones

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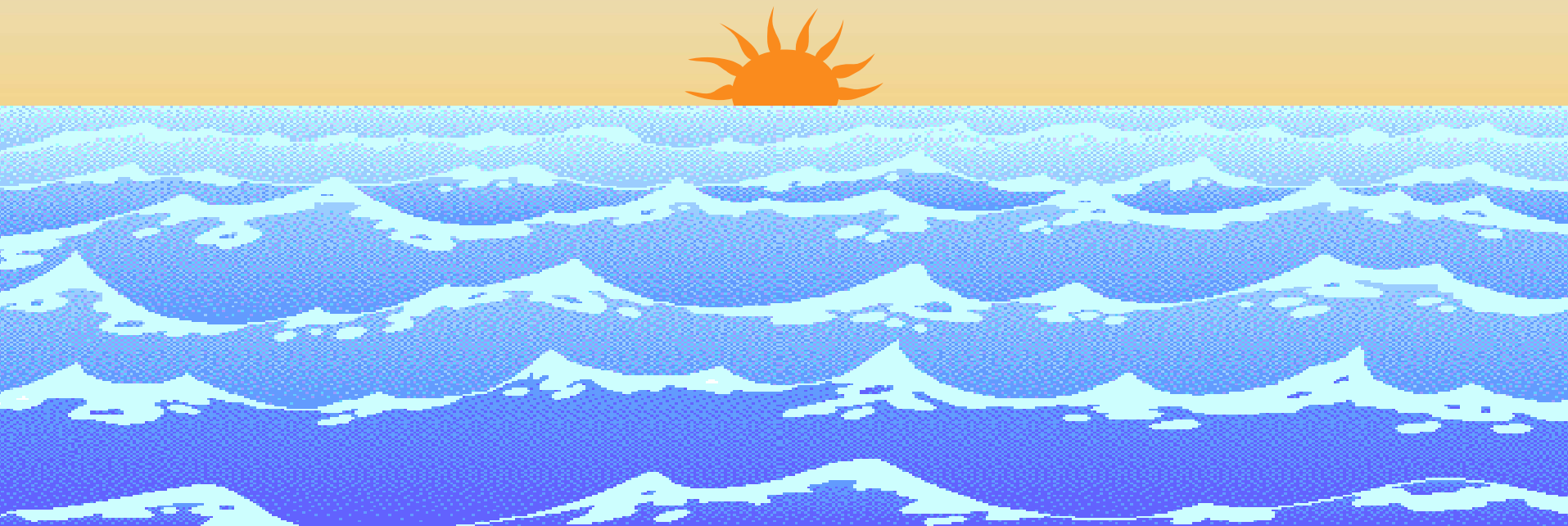


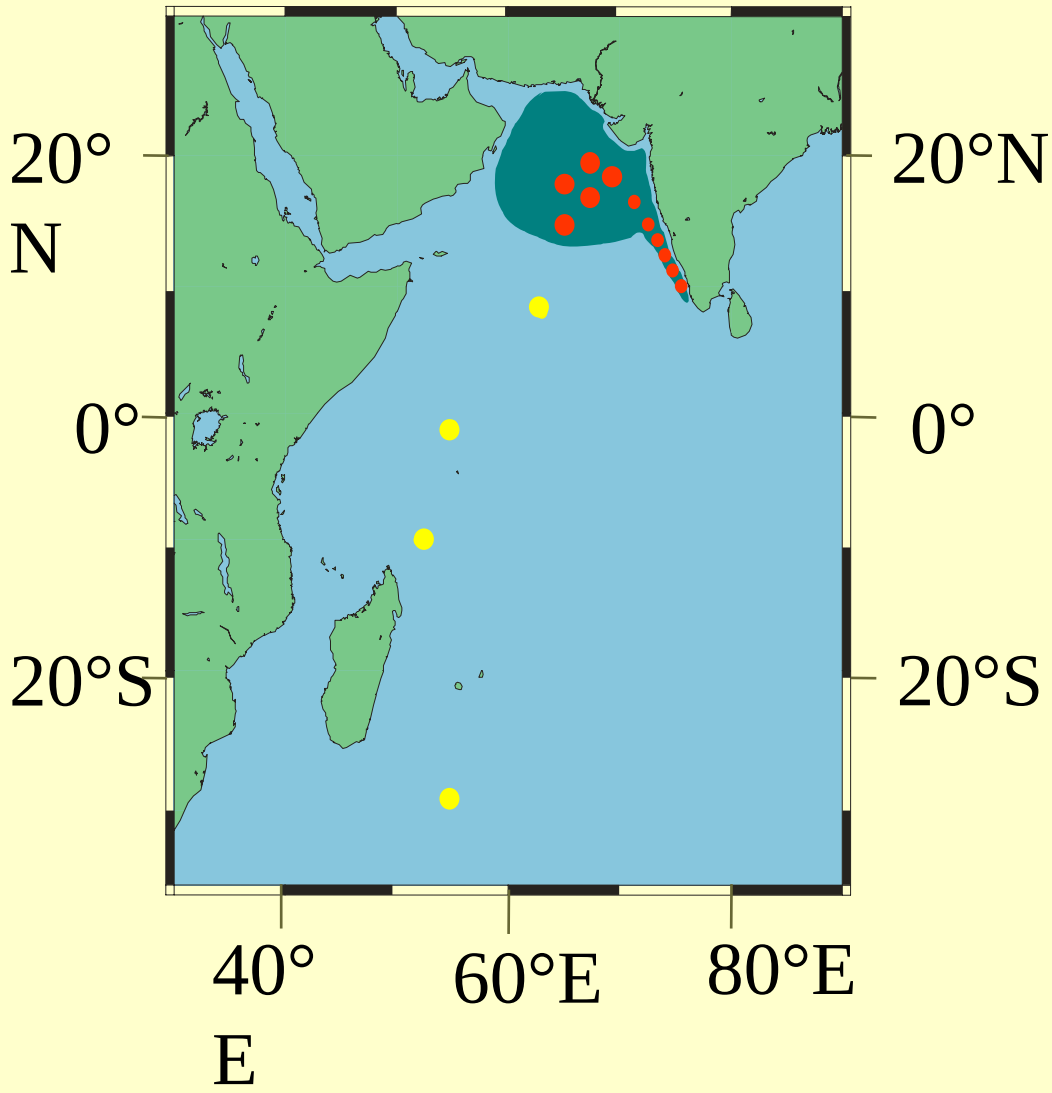
The amount of denitrification in the major ODZ of the oceans is rarely directly measured. It is almost always estimated from RKR stoichiometry (nitrate deficit (N_{def}) or N).*

There are less than a handfull of direct rate measurements

Goal:

Measure the excess N_2 gas produced by denitrification using IRMS.

Old Arabian Sea Sampling Sites



Units Of Measurement

$(N/Ar)_n = (N/Ar)_{sample} / (N/Ar)_{atm\ eq}$

Where:

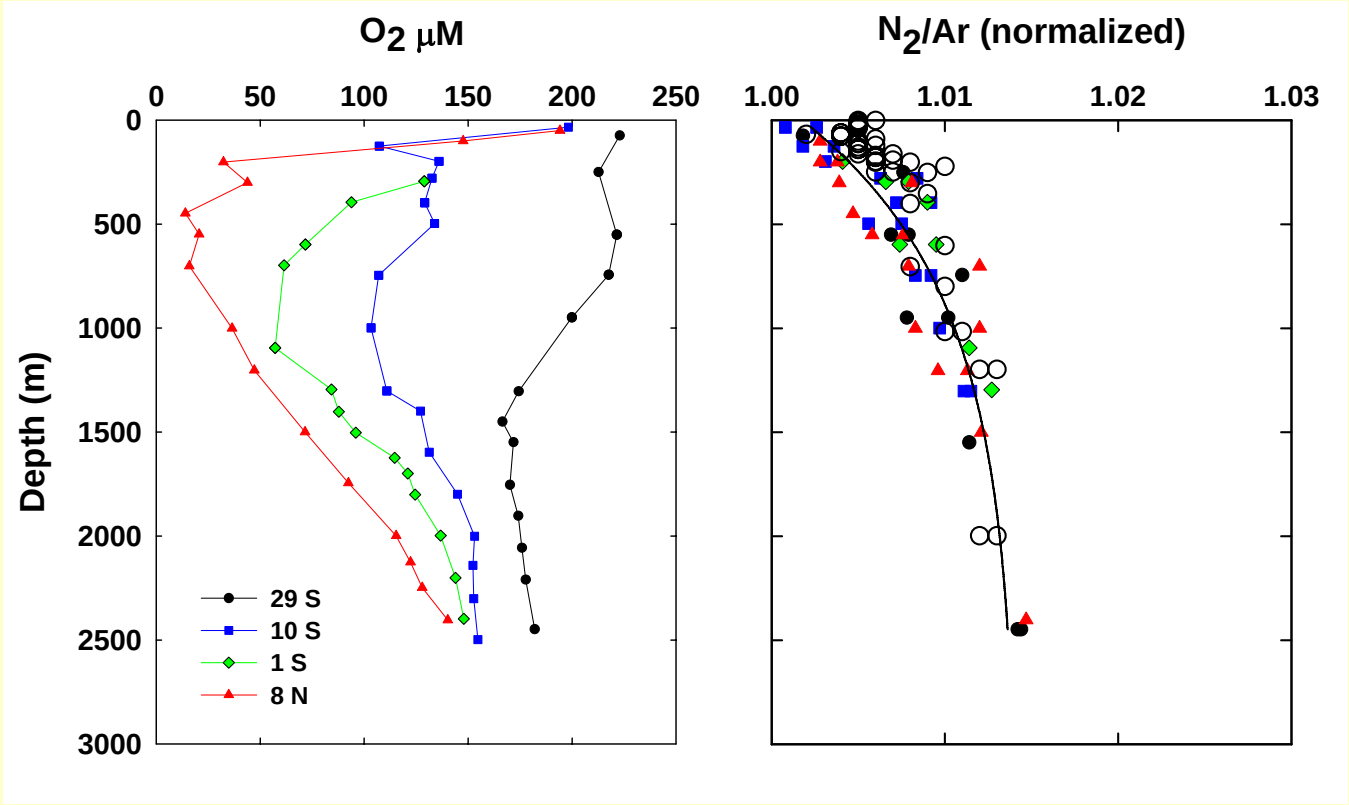
$(N/Ar)_n$ = Normalized N/Ar ratio

$(N/Ar)_{sample}$ = Sample N/Ar ratio

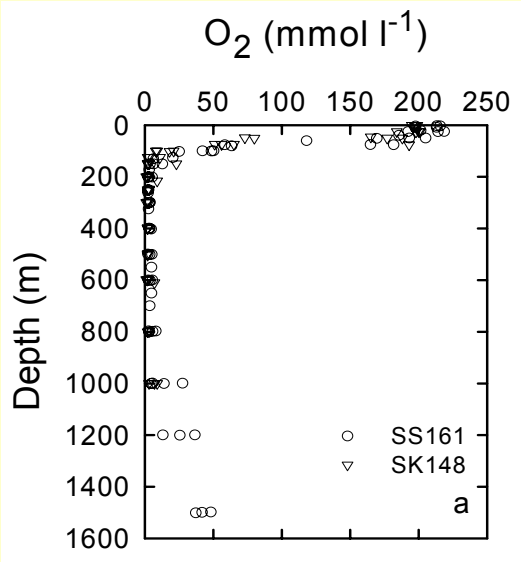
$(N/Ar)_{atm\ eq}$ = Atmospheric equilibrium N/Ar ratio

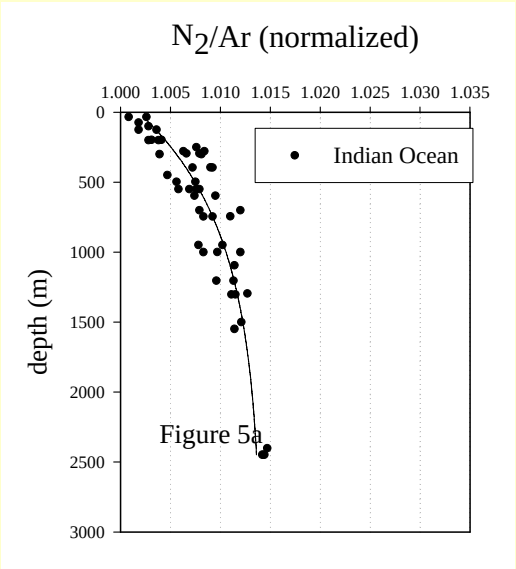
i.e. *$(N/Ar)_n$ is the fractional deviation from atmospheric equilibrium*

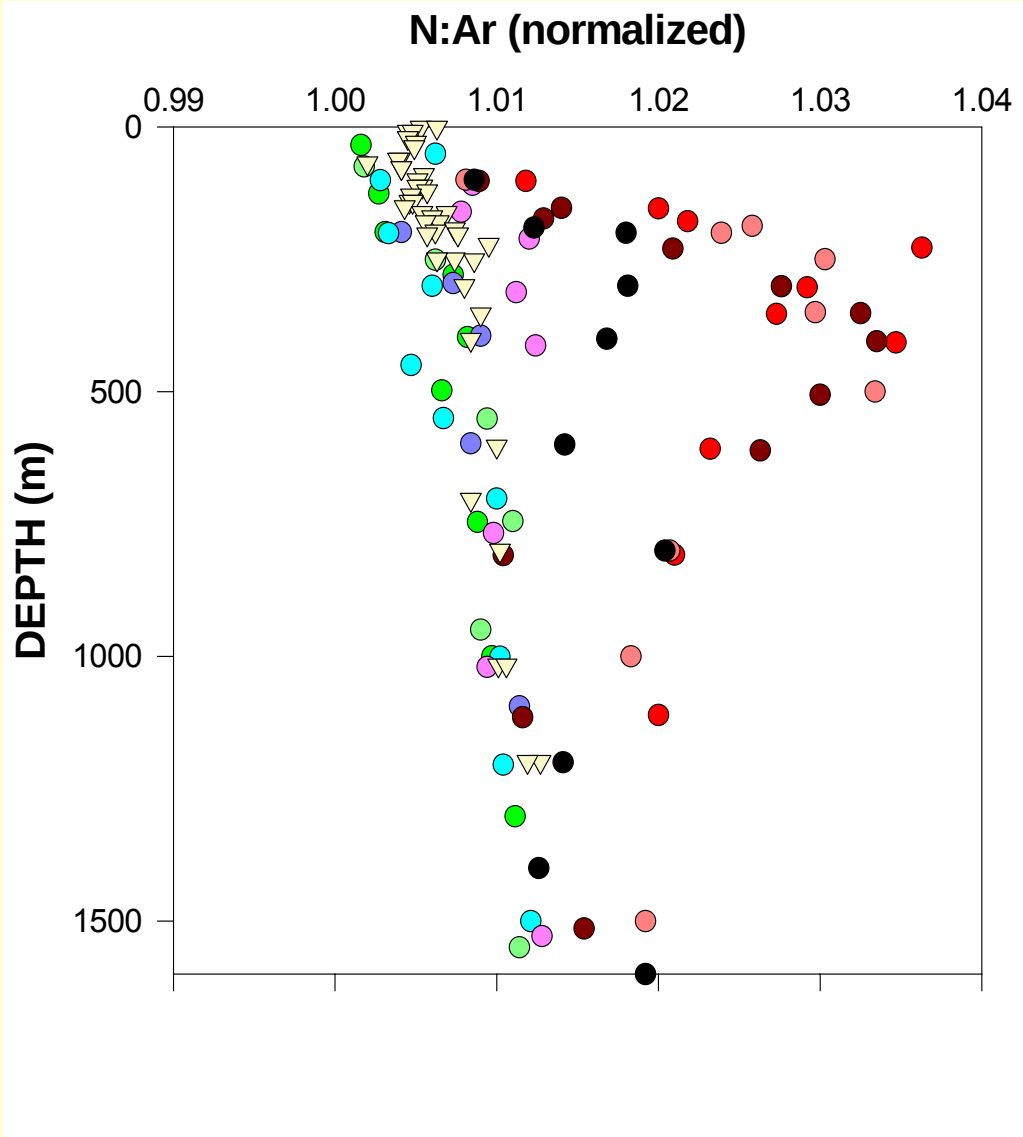
WOCE
I5
outside
ODZ



WOCE outside ODZ plus Arabian Sea ODZ

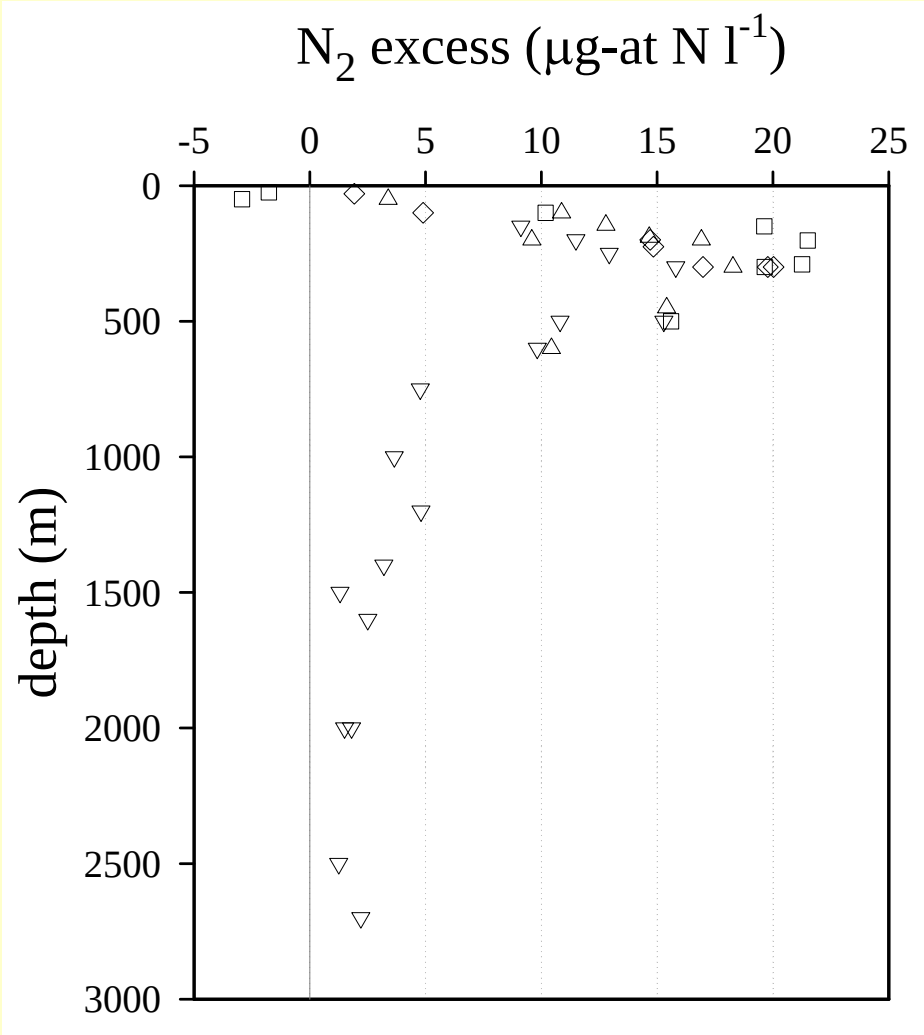




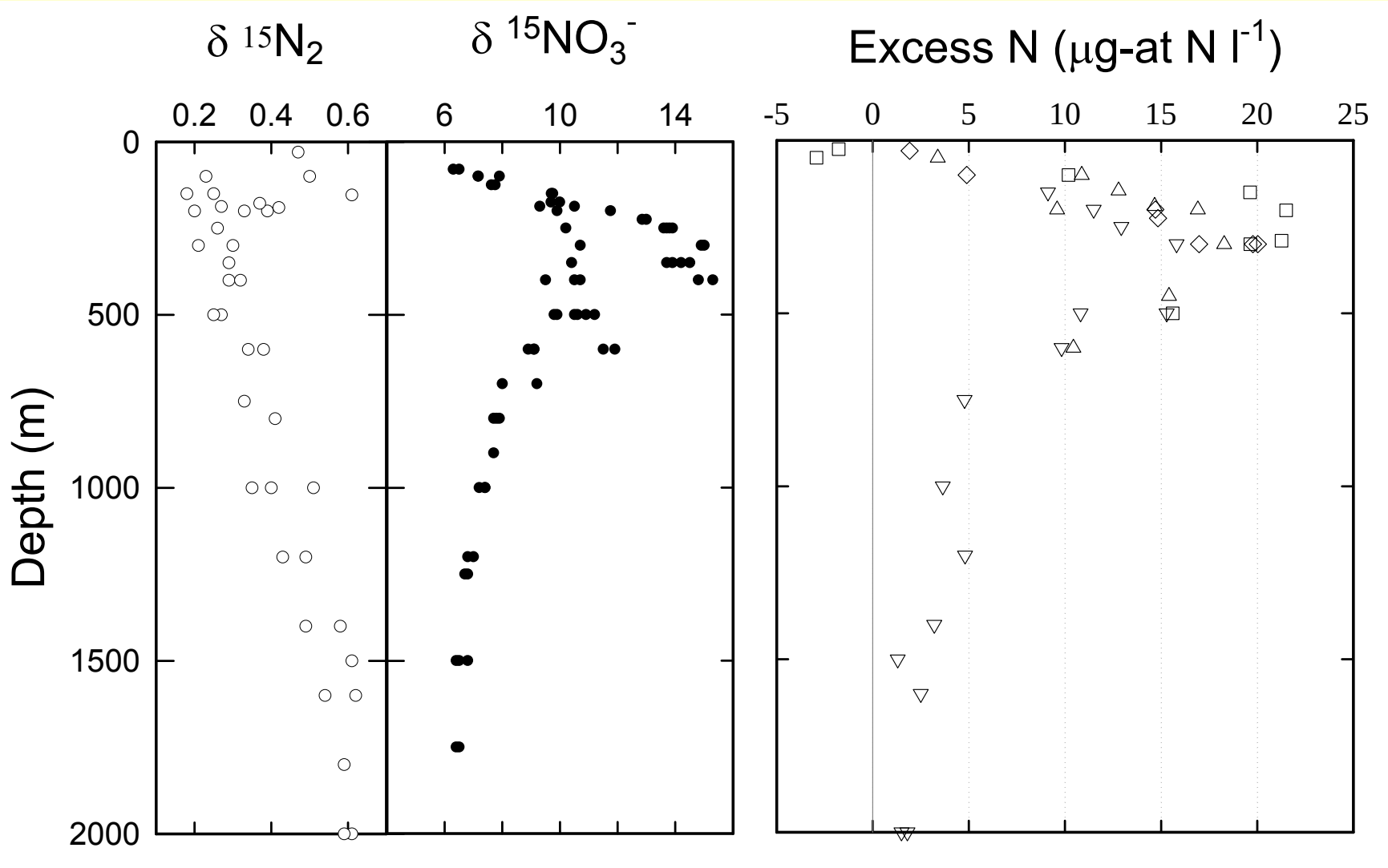


Conversion to $N_{2excess}$

$$N_2excess = [(N/Ar)_{nODZ} - (N/Ar)_{nWOCE}] * N_{2(s,t)}$$



Does this make sense?

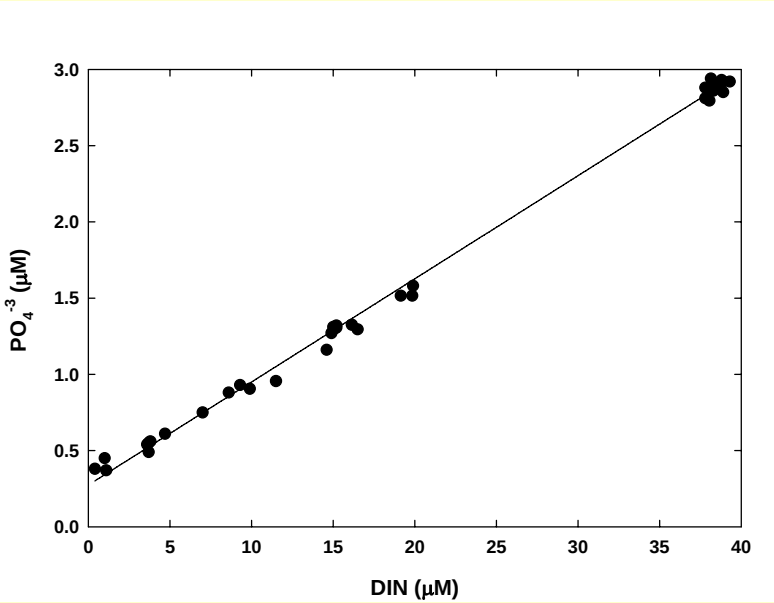


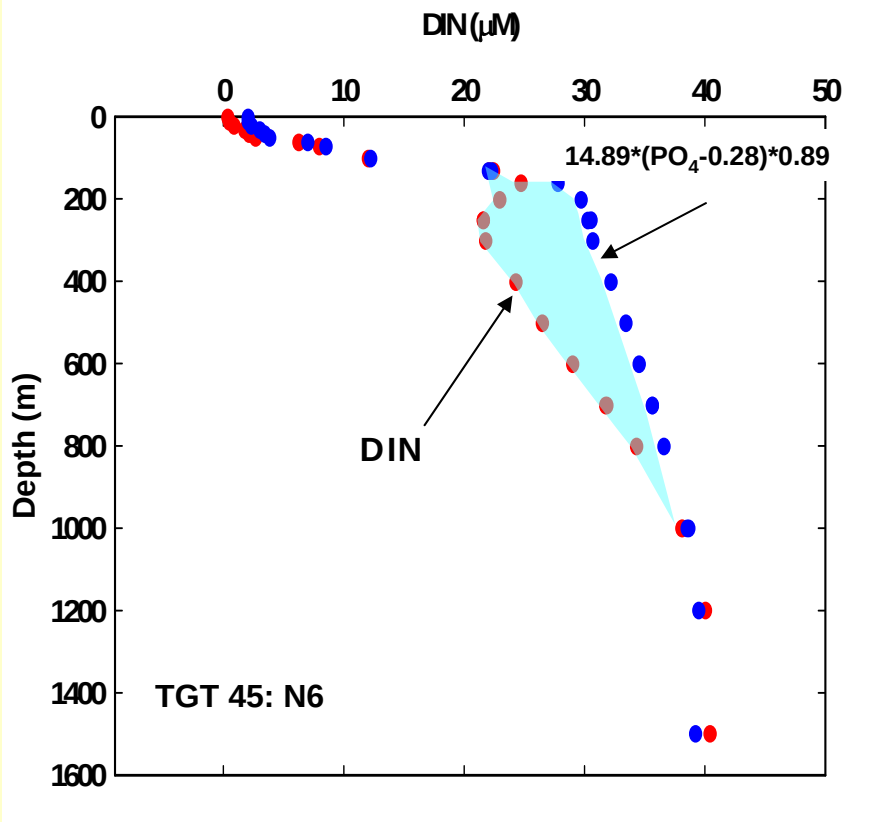
What is the NO_3 deficit ?

- N*= (N – 16*P) + 2.9 ; negative N* is denitrification, but N* is for Global Ocean

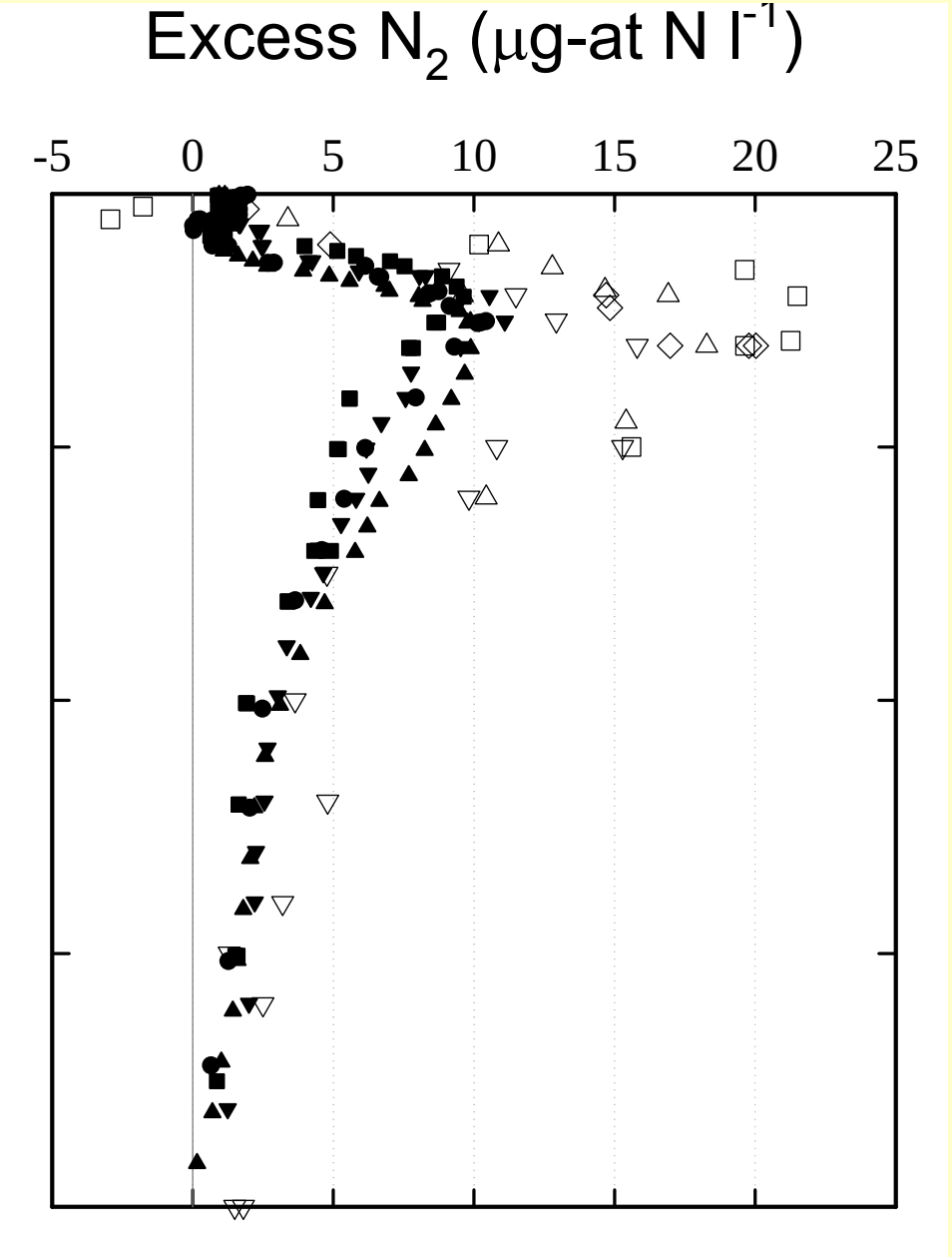
$N_{def} = [14.89*(P – 0.28)-N] \times 0.86$

(Codispoti et al., 2002)

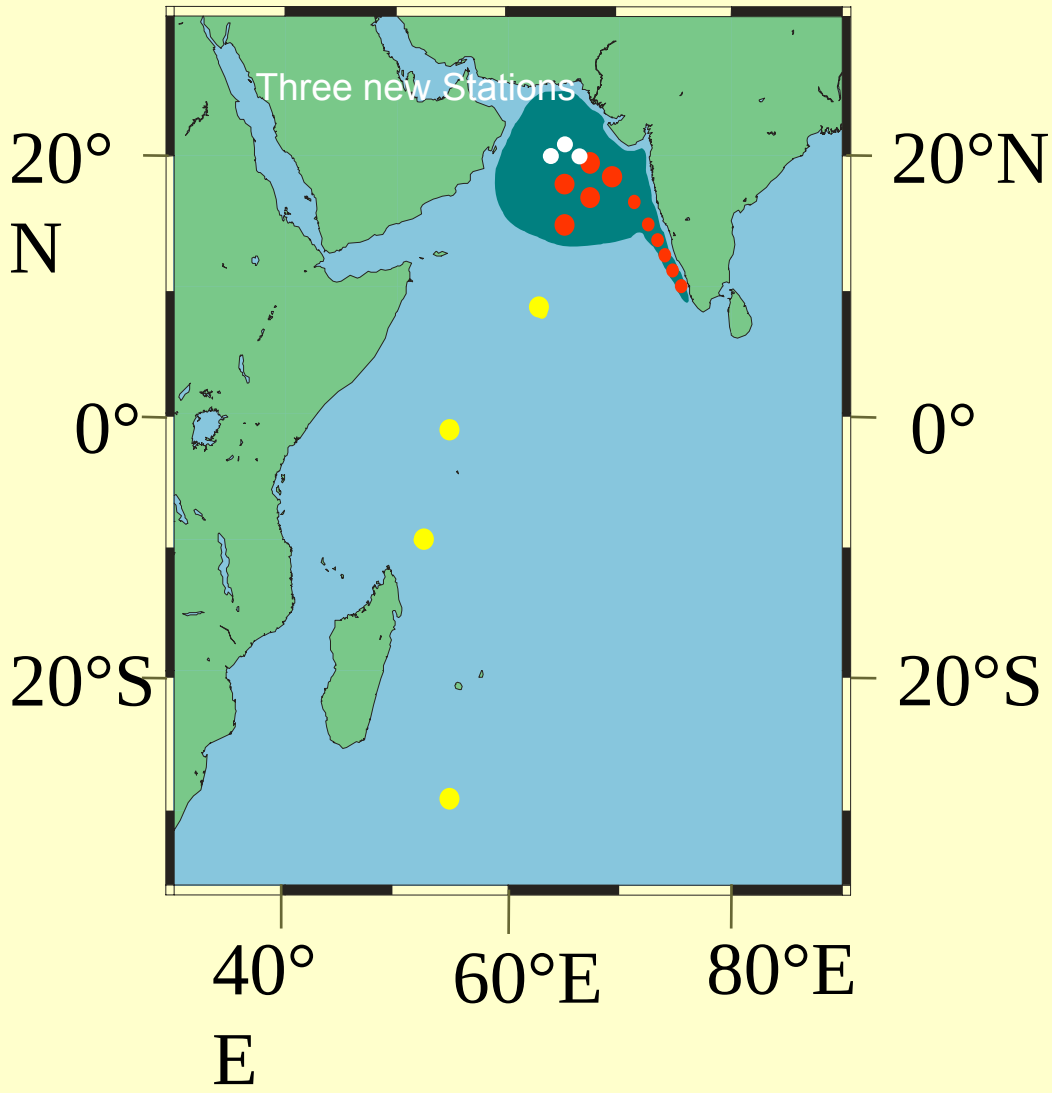




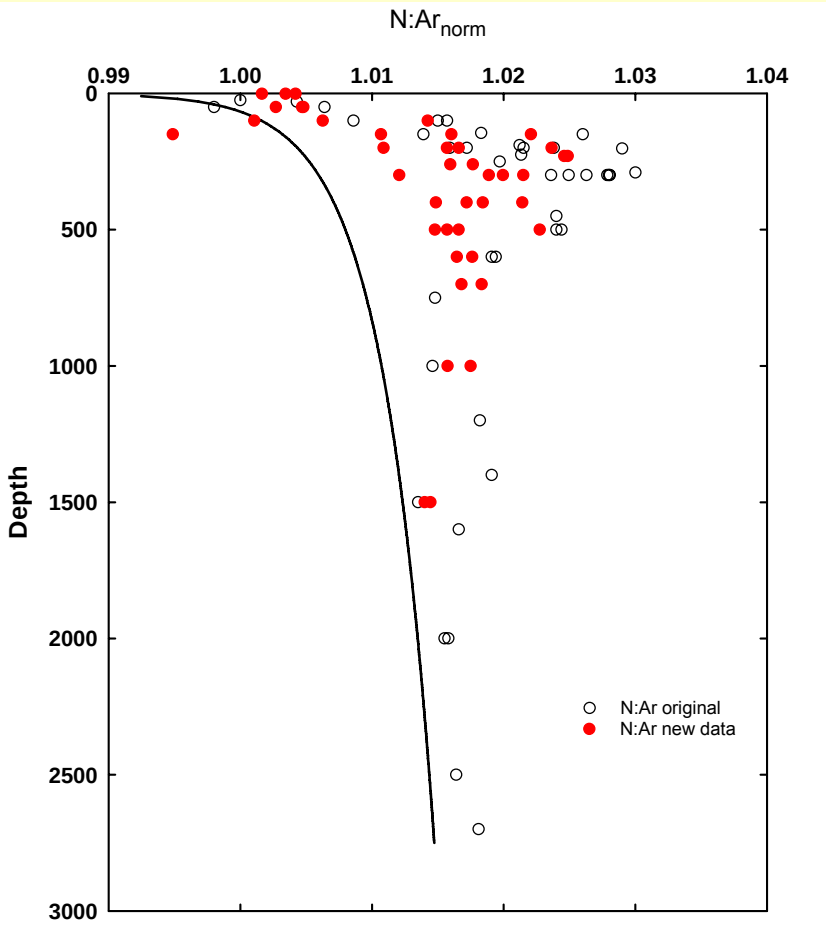
N_{def} vs. $N_{2excess}$

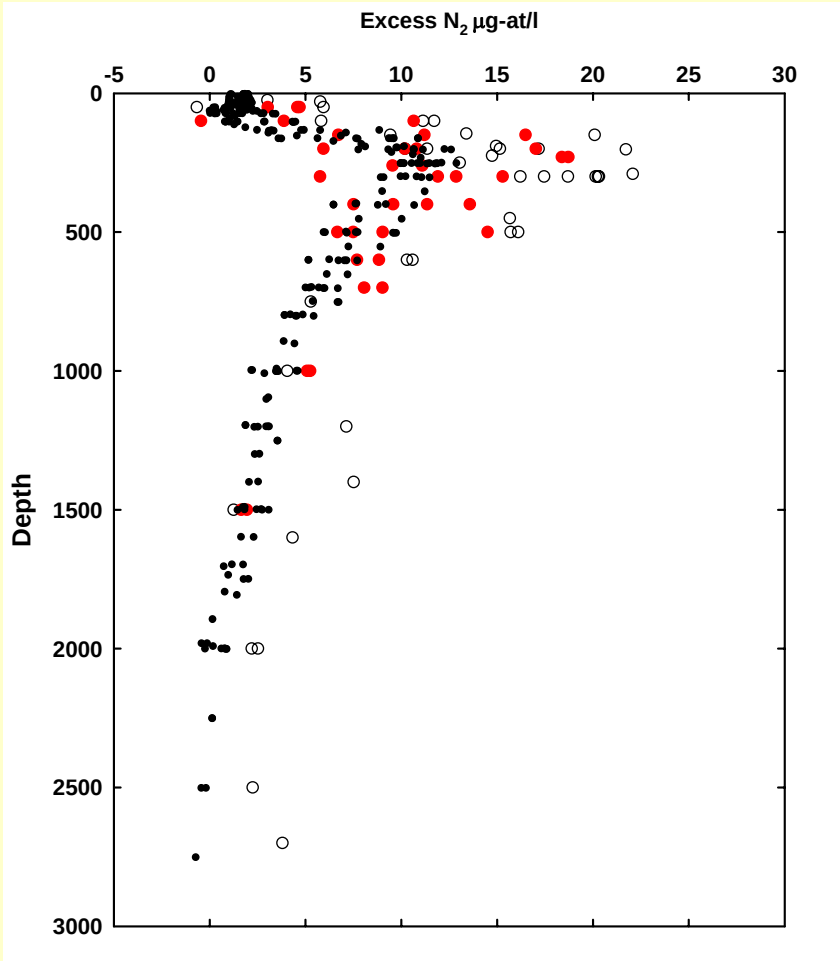


New Arabian Sea Sampling Sites



- New Arabian Sea Data

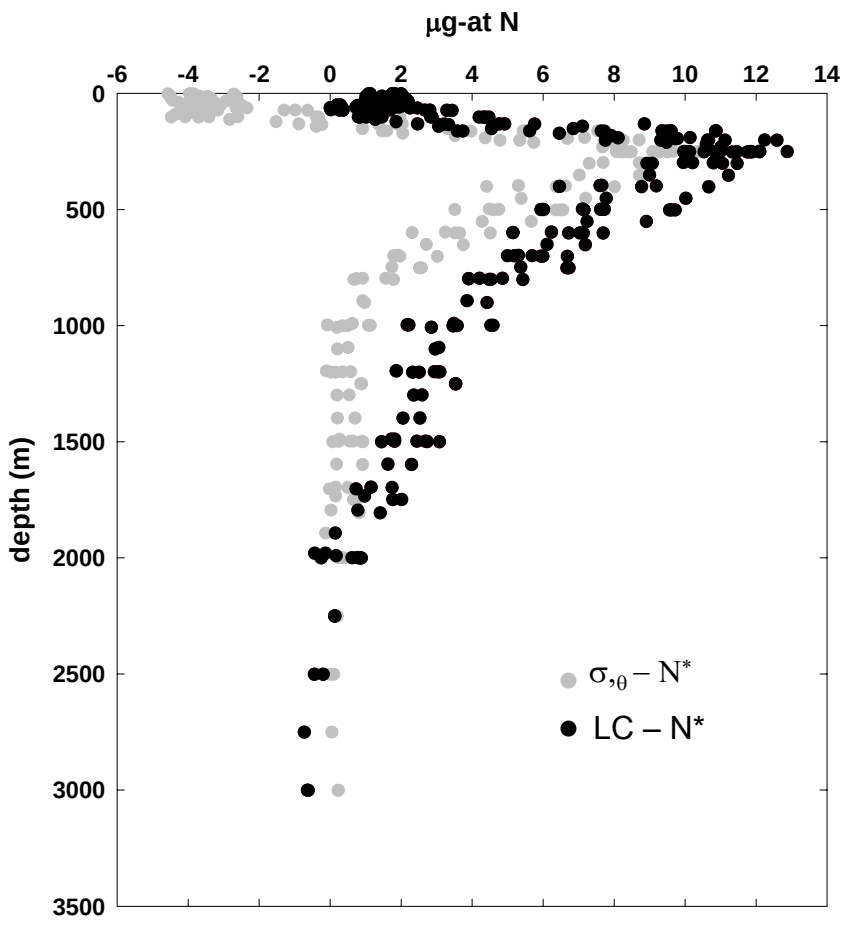


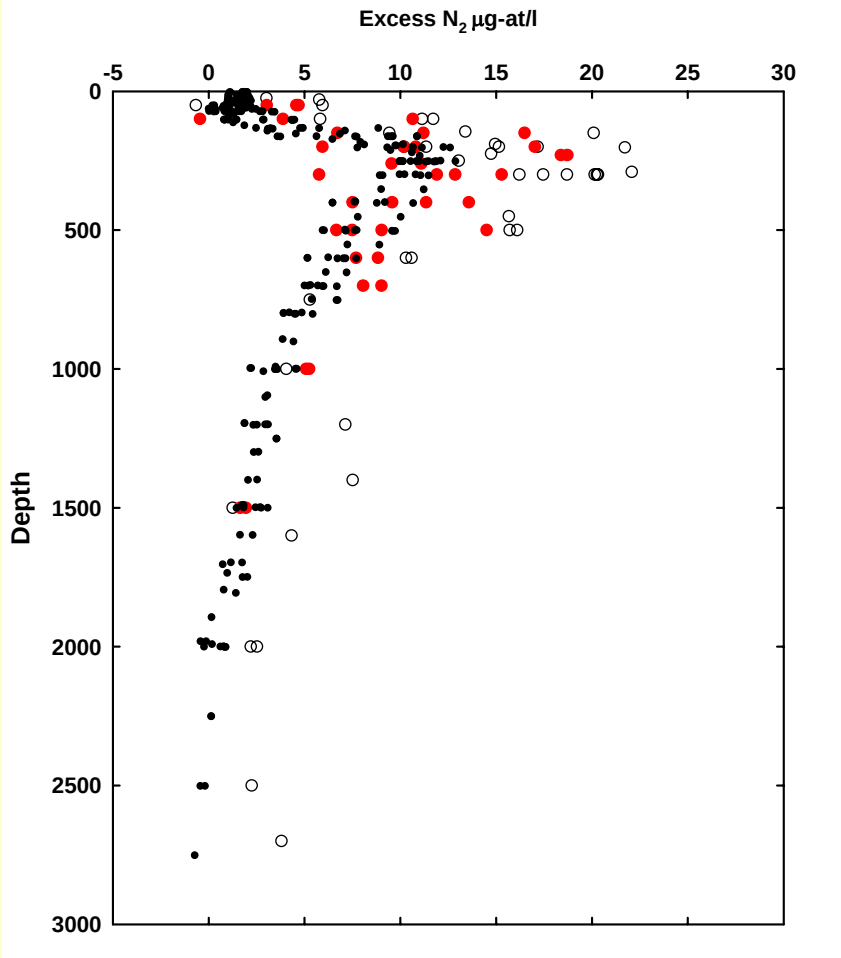


What does it all Mean ?

$\int(\sigma,\theta - N*)dz$ = 60 gN/M2

$\int(LC - N^*)dz$ = 123 gN/M2





How do we rationalize?

- Organic ammine (H_2O column anammox) ?
- Non Redfield ?
- MnO_2, IO_3 ?
- Sediments and sedimentary anammox ?
- N_2 Fixation ?

Non-RKR OM (Van Mooy et al., 2002)

- RKR org + 84.8 NO_3 -> 106 CO_2 + 16 NH_3 +PO_4 + 42.4 N_2
- 16NH_3 + 16NO_2 -> 16 N_2 (The annamox reaction)

Organic ammine (H_2O column anammox)

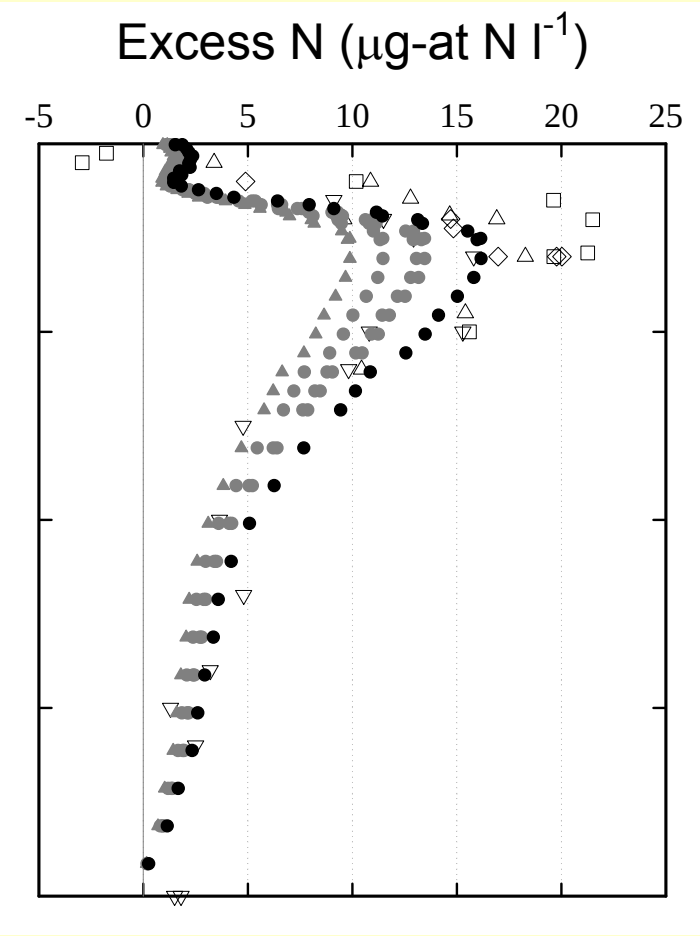
- Van Mooy et al. observed preferential oxidation of proteins in ODZ of ETNP
- Assumed ideal protien
- $C_{61}H_{97}O_{20}N_{16}$ + 50 NO_3 -> CO_2 + 33N_2

MnO_2, IO_3?

- MNO_2 and IO_3 will catlyze N_2 Production

Sedimentary denitrification and anammox

- Assume $5*10^{11}$ m^2 margin sediment in contact with the ODZ
- Assume same carbon oxidation rate as Mexico ODZ
- Assume sulfate reduction & $S^{=}$ is reoxidized by NO_3



$$(CH_2O)106(NH_3)_{16}(PO_4) + 53\ H_2SO_4 \rightarrow 106\ CO_2 + 16\ NH_3 + 53\ H_2S + 106\ H_2O + PO_4$$

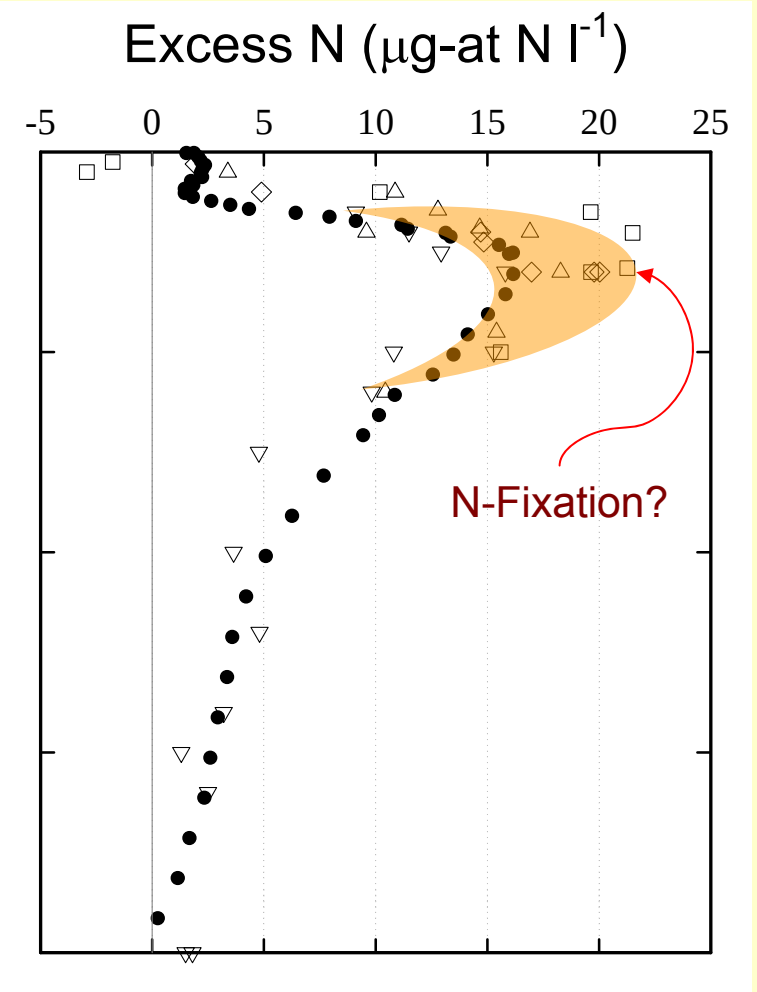
$$53\ H_2S + 53HNO_3 + 53H_2O \rightarrow 53H_2SO_4 + 53\ NH_3$$

$$16\ NH_3 + 53\ NH_3\ 53HNO_2 \rightarrow 69\ N_2 + 138\ H_2O$$

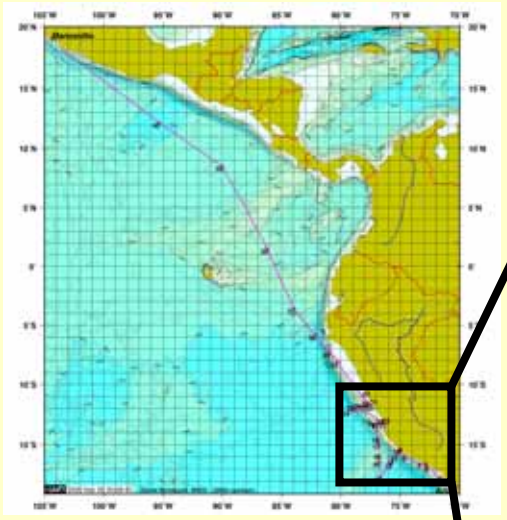
$$(CH_2O)106(NH_3)_{16}(PO_4) + 53\ HNO_3 + 69\ HNO_2 \rightarrow 106\ CO_2 + 69\ N_2 + 191\ H_2O + PO_4$$

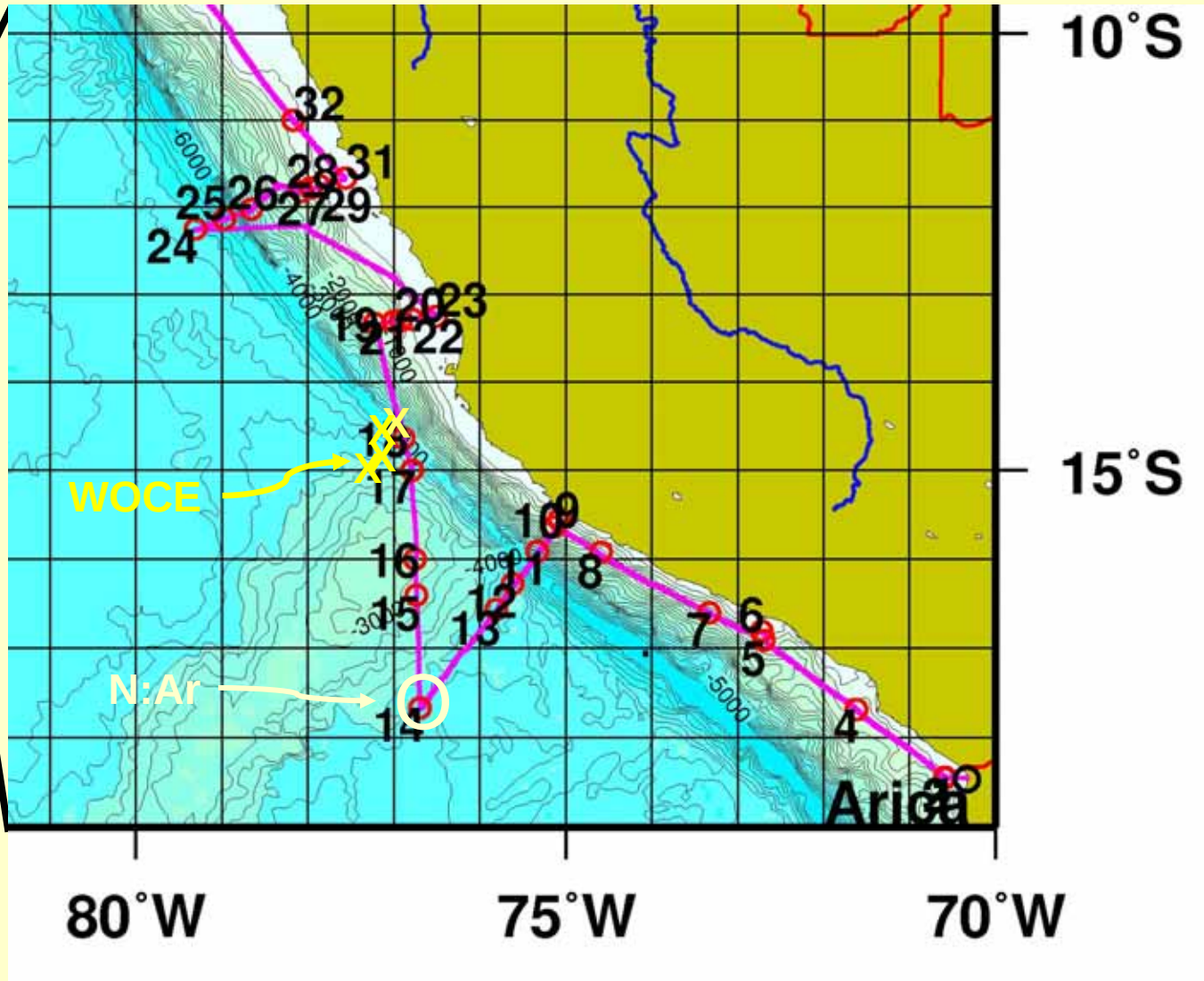
Is there a Nitrogen Fixation signal ?

- Community N:P may be > 20
- Brandes and Devol estimate 20% of PPR is supported by N-fixation
- N:P Export at HOT may be 40



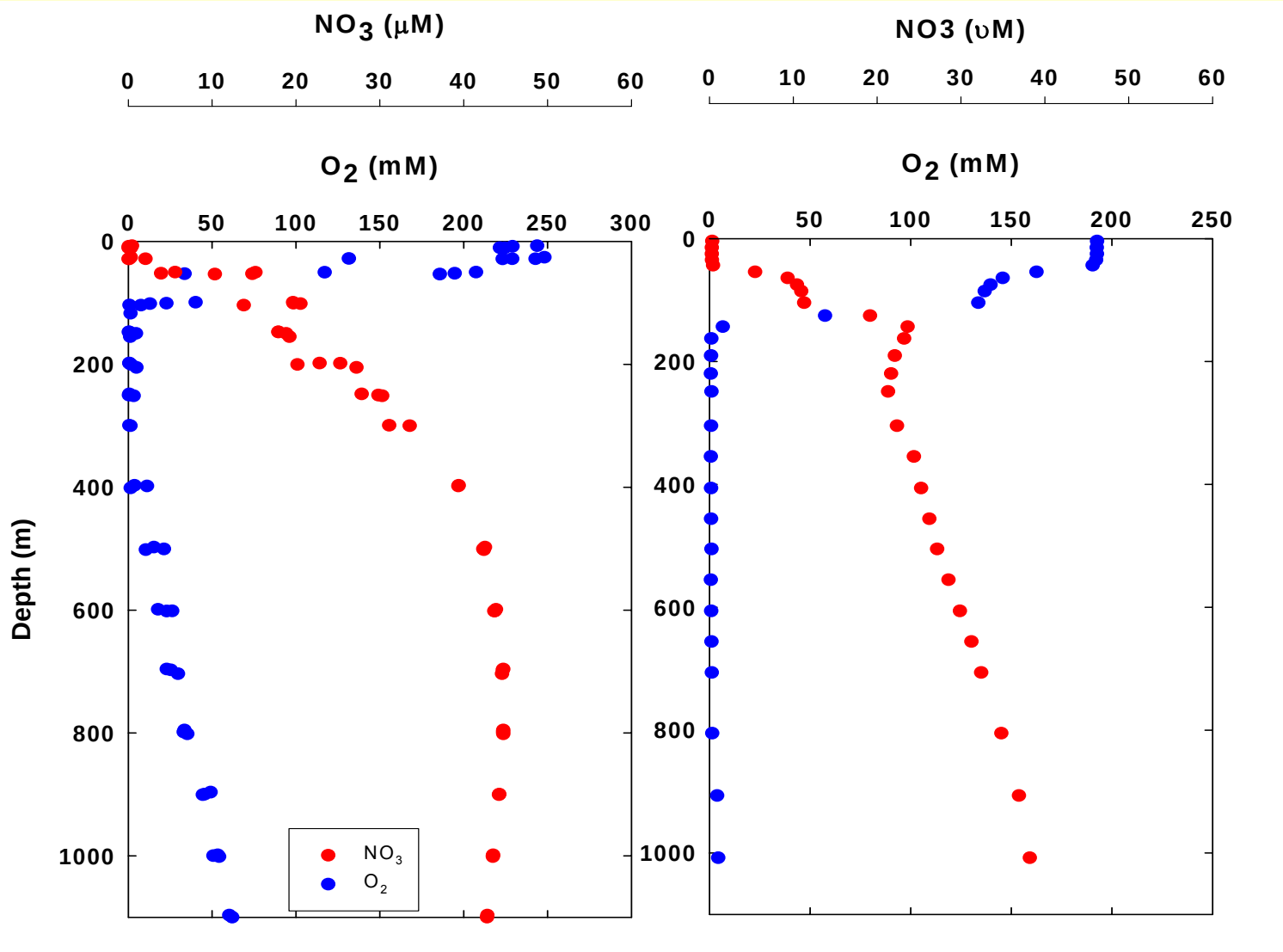
Peru Cruise – Oct 2005



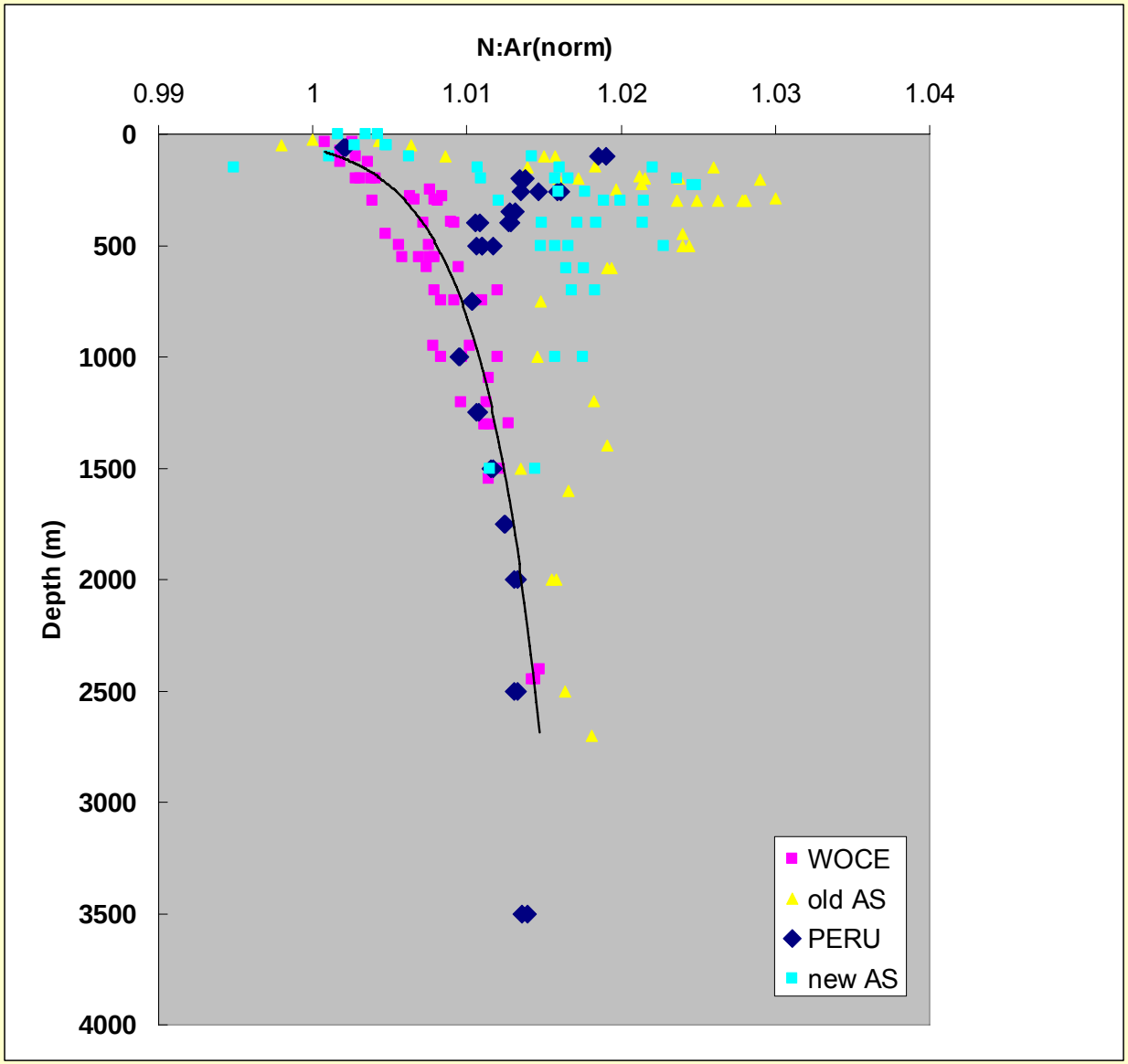


ETSP

Arabian Sea

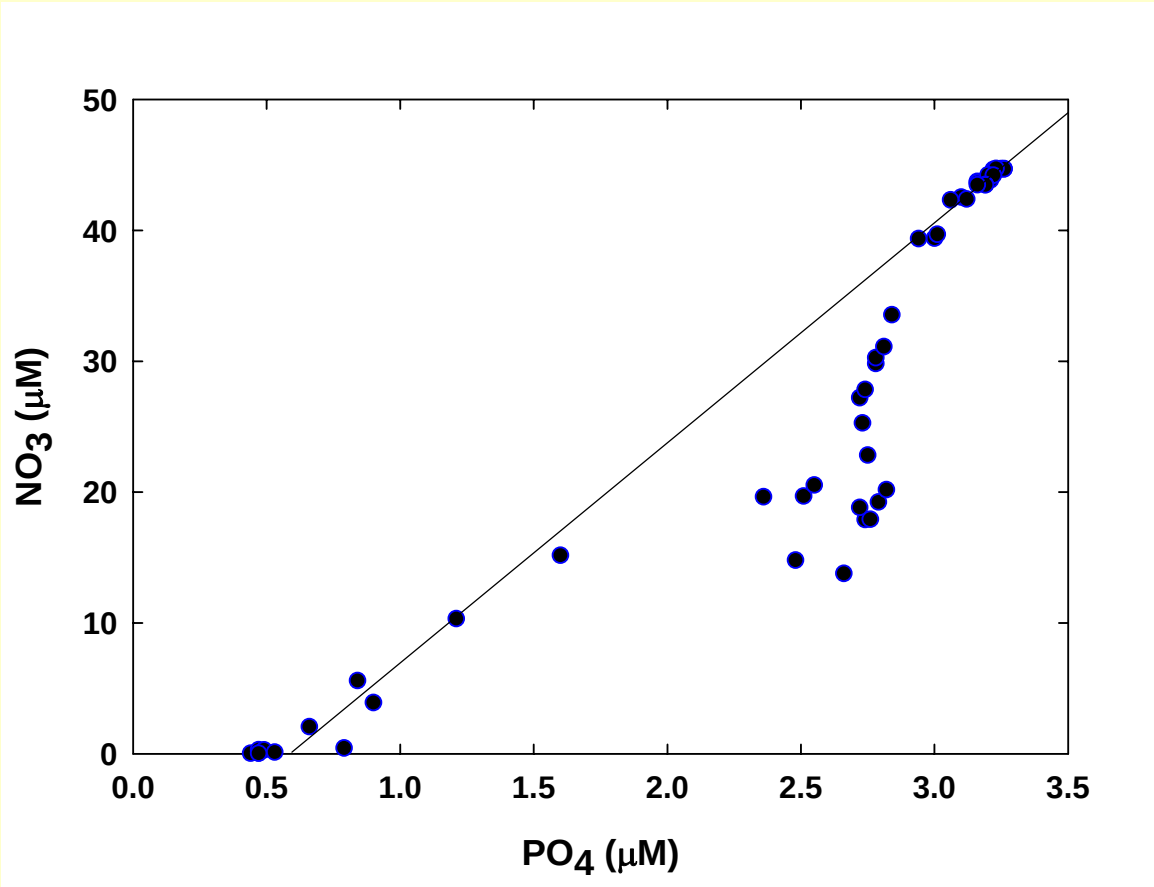


Comparison of N:Ar Values between ETSP and Arabian Sea

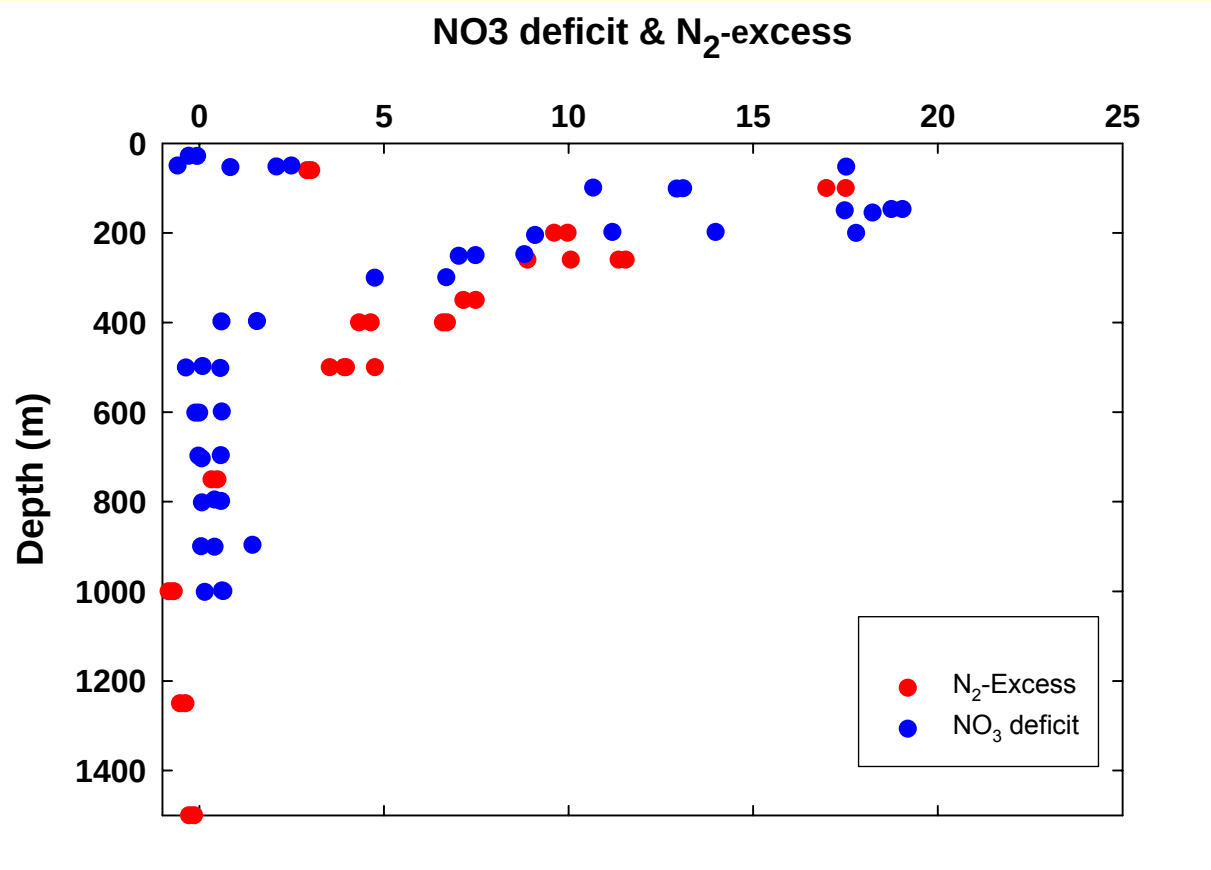


N-deficit equation for ETSP

$$N_{def} = \{16.7*(PO_4-0.6)-DIN\}*0.89$$



ETSP


NO3 deficit & N2-excess
0
5
10
15
20
25
0
200
400
600
800
1000
1200
1400
Depth (m)
N2-Excess
NO3 deficit

Summary and Conclusions

- N_2 concentration measuresd in the Arabian Sea and eastern tropical South Pacific show N_2 supersaturation in the ODZ.
- Arabian Sea excess N_2 is greater than NO_3 deficit, while in the ETSP they are about equal.
- It is suggested that the extra N_2 in the arabian sea is due to nitrogen fixation in the surface waters resulting in a non-Redfieldian organic matter flux into the ODZ. Alternatly,water column anammox and sedimentary N cycling may be important contributors to the excess N_2 in the Arabian Sea.

Future research questions

- How important is water-column anammox) ?
- Does denitrification follow RKR stoichiometry ?
- Are MnO_2, IO_3 interactions with the N cycle important pathways of N_2 production?
- Do sedimentary signals contribute to chemical distributions in the central Arabian Sea ?
- Does newly fixed nitrogen (N_2 Fixation) contribute to the N_2 excess in the ODZ?

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Issues with stoichiometrically based methods (NO, N_2 production)

- based on uncertain stoichiometric calculations
- rate calculation is dependent on residence time
- may not account for organic N ($R\text{-}NH_3$) to N_2
- wide range in estimated rates

Sampling Method