

N₂ measurements by the gas tension method

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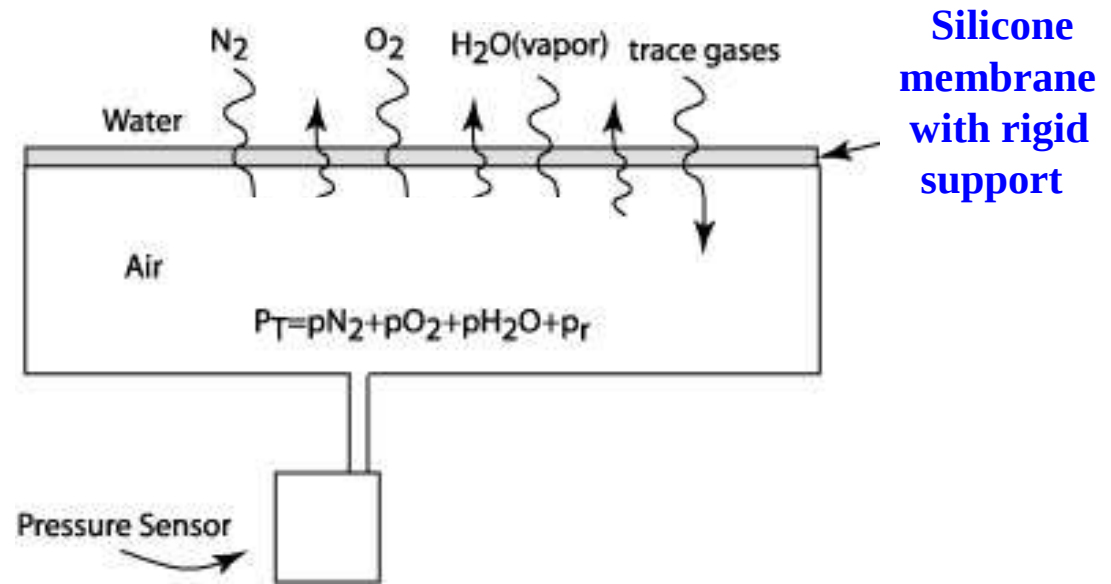
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Overview:

- 1.Measuring N₂ using gas tension method
- 2.Overview of the gas tension device (GTD)
- 3.Measurement errors
- 4.Some results from the field
- 5.Overview of pCO₂ sensor

1. Measuring N₂ using gas tension method



Gas tension (or total dissolved gas pressure) is:

$$P_T = pN_2 + pO_2 + pAr + pH_2O + pCO_2 + \dots$$

~78 %	~21 %	~1 %	1 to 5 %	usually negligible
‘GTD’	‘optode’ ‘SBE43’	‘assume’	‘TS’	

hence:

$$pN_2 \approx P_T - pO_2 - pAr - pH_2O$$

use:

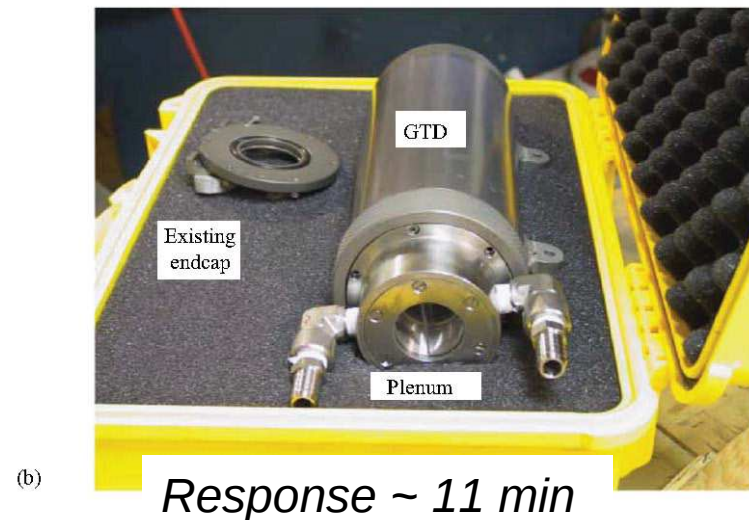
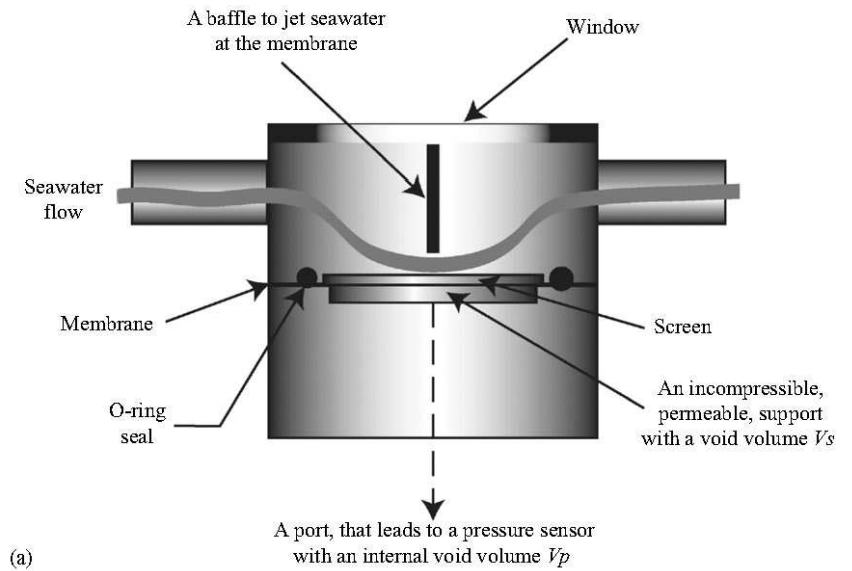
$$[Gas] = S_H(T,S) \times pGas \quad (\text{Henry's Law})$$

2. The gas tension device (GTD)

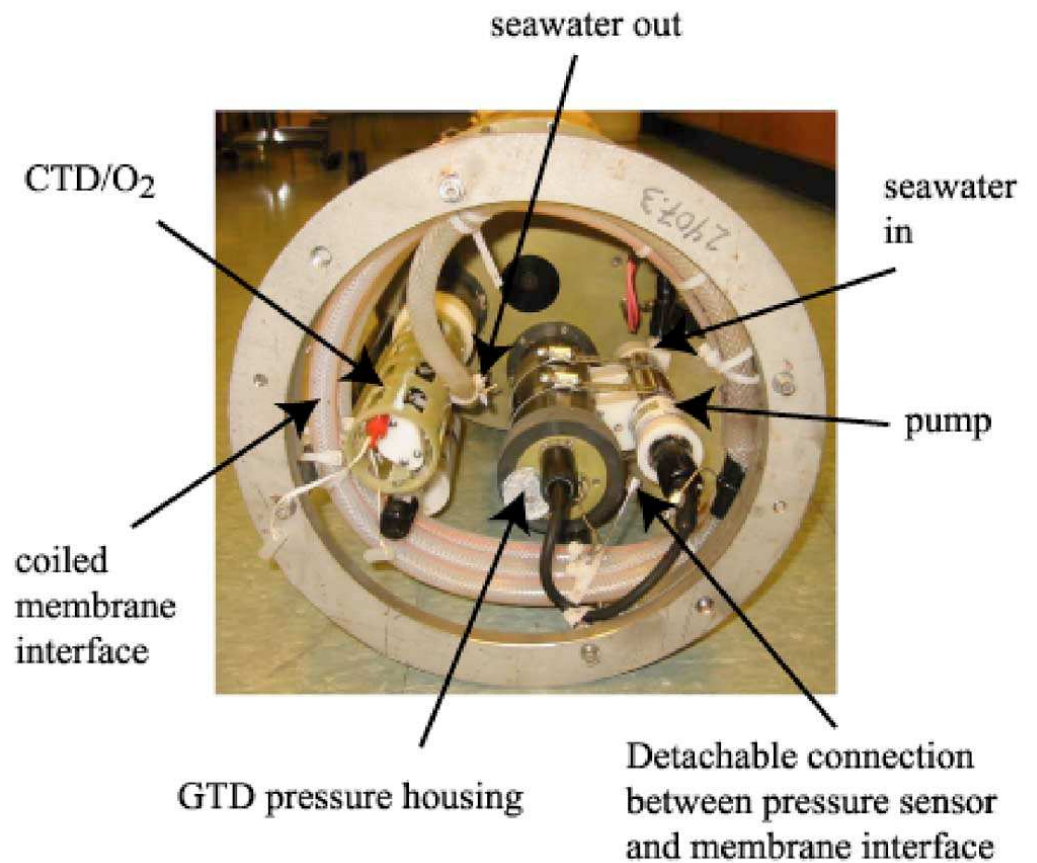
- Moored GTD



- Shipboard GTD



- Float GTD



$\tau \sim 2$ min at surface

$\tau \sim 10$ min at 60 m

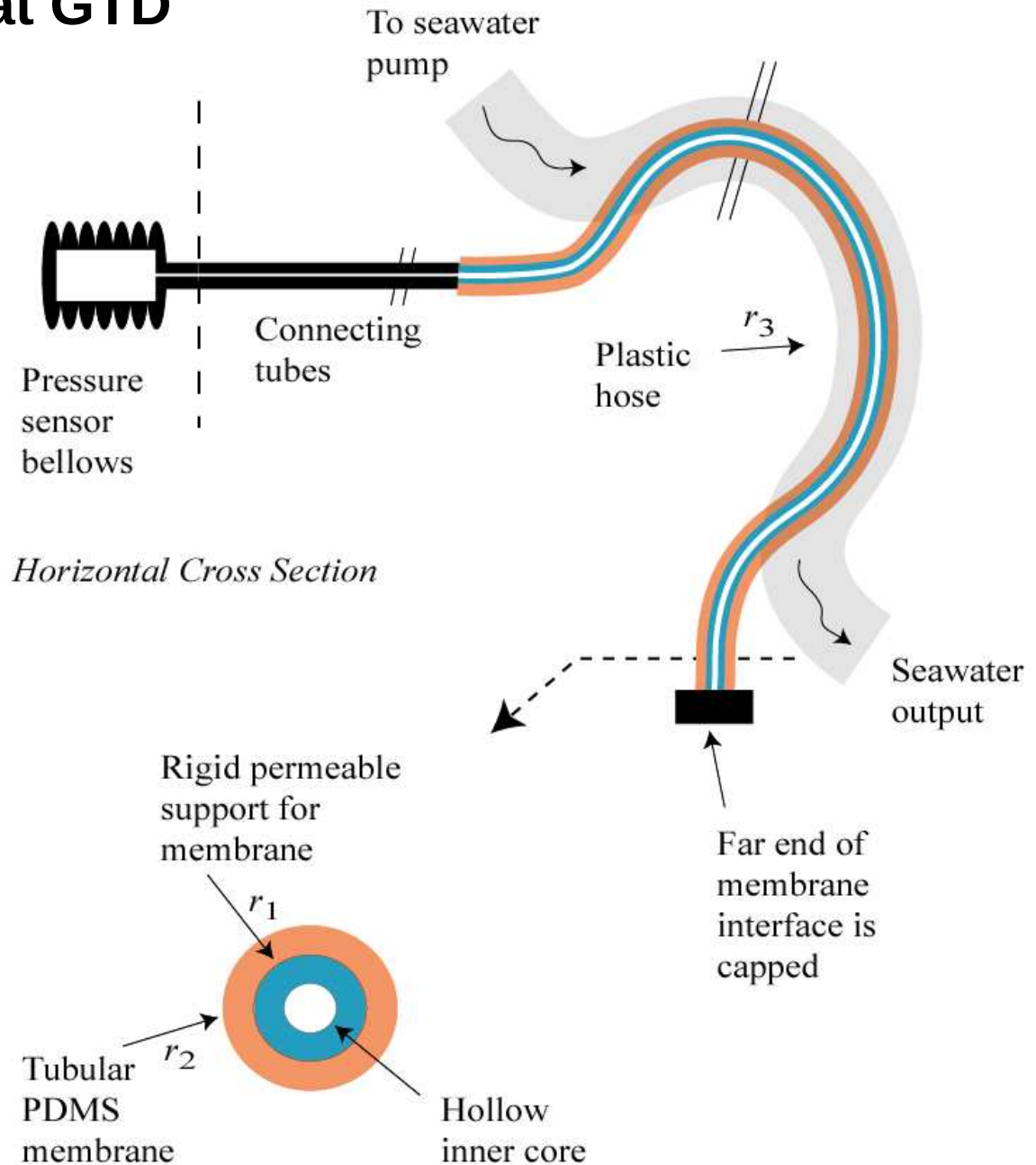
More details on float GTD

$\tau \sim 2$ min at surface
 $\tau \sim 10$ min at 60 m

Tank tests:

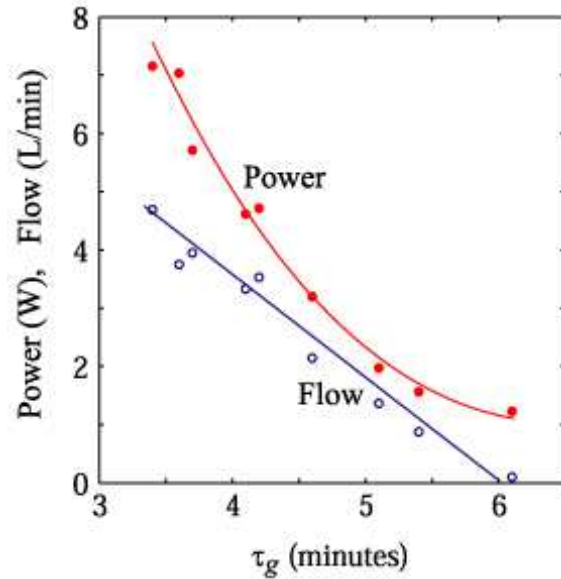
350 m (smaller HGTD)
1000m (larger CO₂)

Patented 2008
(Johnson & McNeil)



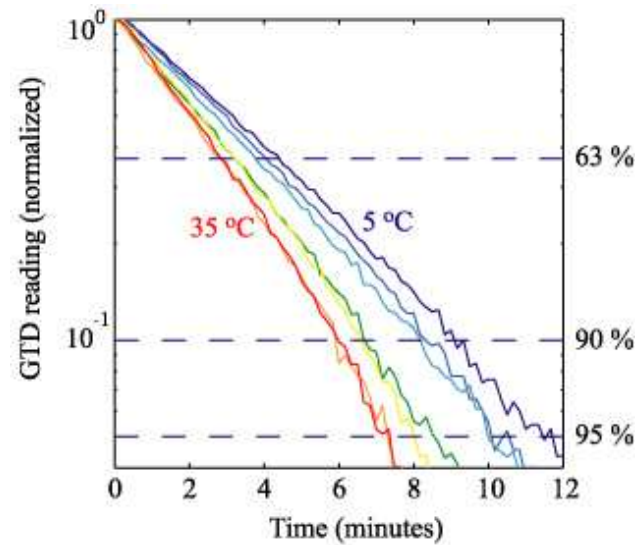
Equilibration time for float GTD

#1 pump speed



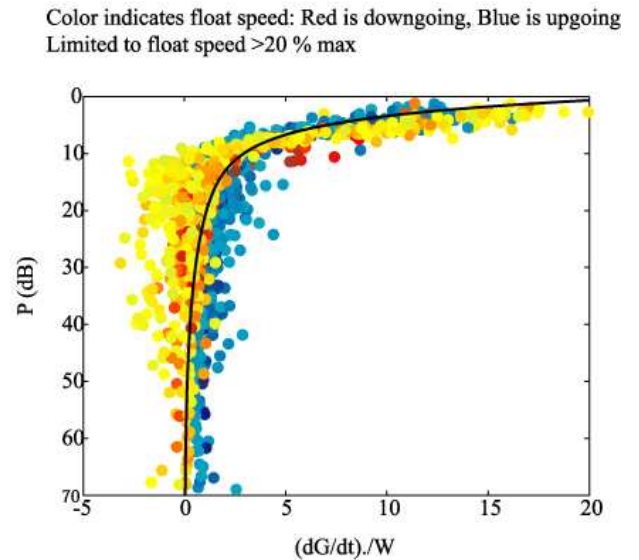
Pulse pumping is
2 times slower but 90%
more efficient!

#2 water temperature



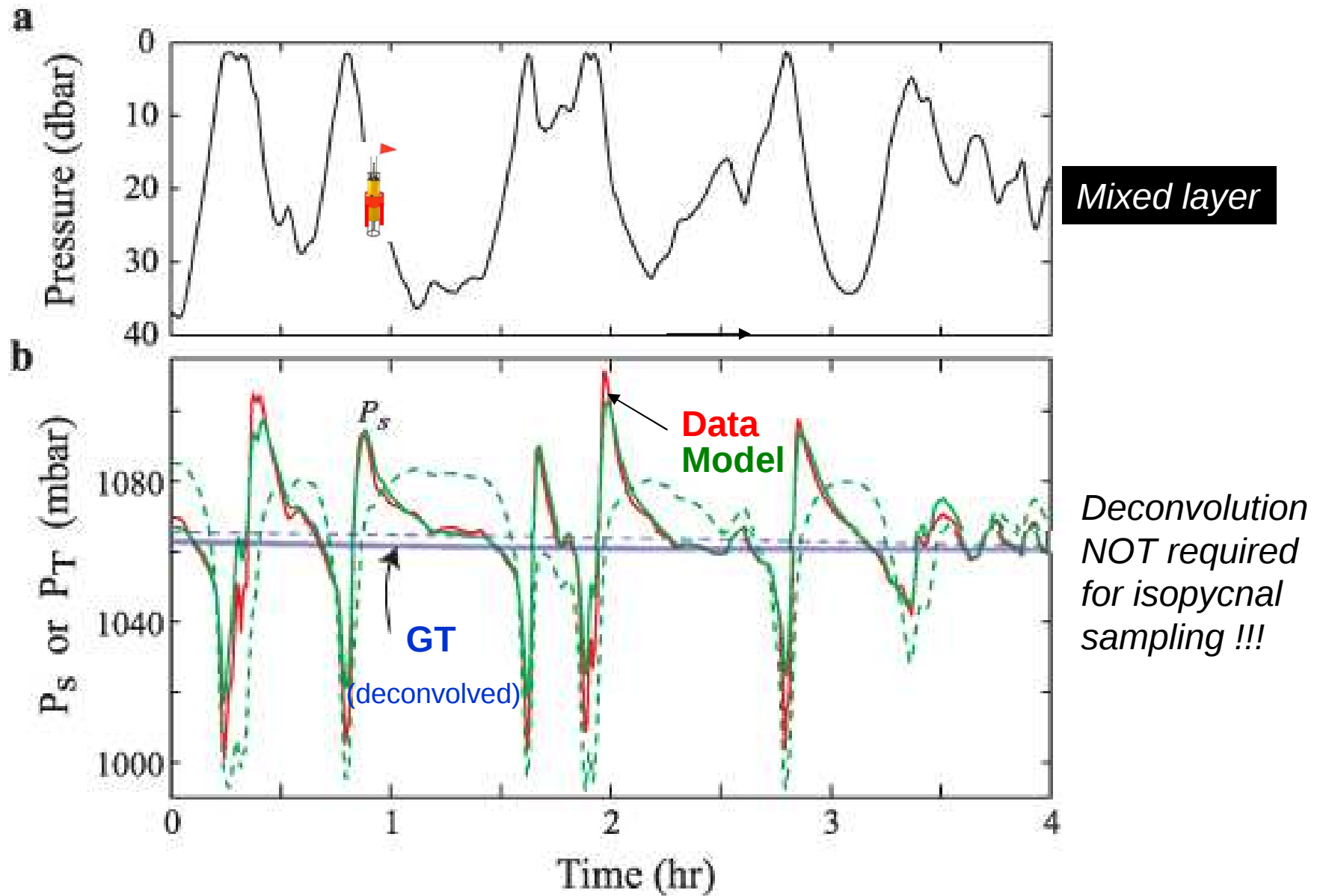
1.7 times faster at
35 °C than 5 °C

#3 hydrostatic pressure



Compressible
 $H < 10$ m

Dynamical response of float GTD



3. Measurement errors for N₂

1) Gas solubility coefficients, $S_H(T,S)$ - **big**

$$S_H(N_2) \sim 0.14\% \quad S_H(O_2) \sim 0.2\% \quad S_H(Ar) \sim 0.13\% \quad [\text{Hamme \& Emerson, 2004;} \\ \text{Garcia \& Gordon, 1992}]$$

2) Winklers - **big**

[O₂] ~ typical 0.5 %, at best 0.2%

NB: error on pN₂ is 0.14%, at best 0.06%

3) Assume Argon levels - **medium**

a) best use Ar sat = N₂ sat (recursive approach); within 2% at HOT/BATS
or b) Ar sat =100%, and conservatively within 10% equilibrium

NB: error on pN₂ is 0.03% for assumption (a), and 0.13% for assumption (b).

4) Gas tension - **small**

accuracy: ± 0.2 mbar or $\sim 0.02\%$

precision $\sim 0.00001\%$

drift $> 0.02\%$ per year !

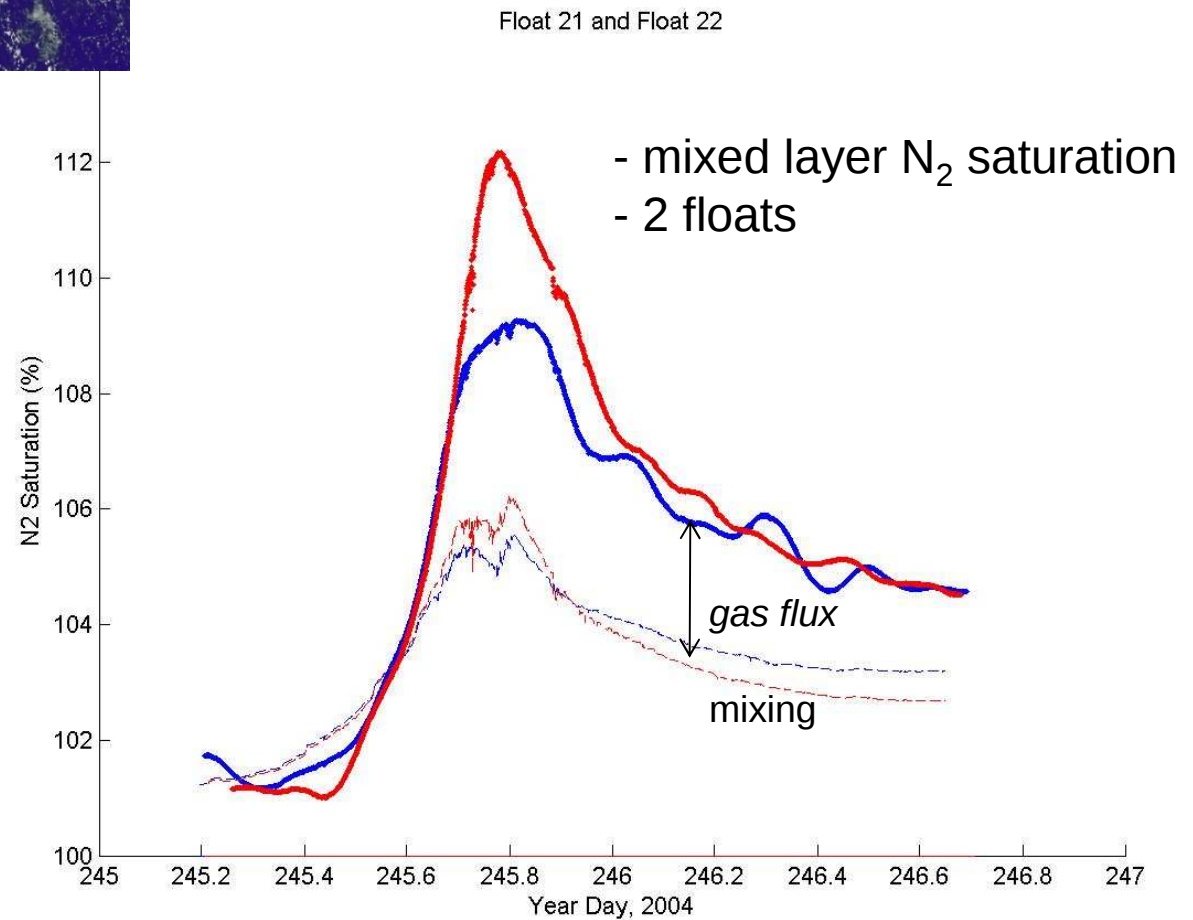
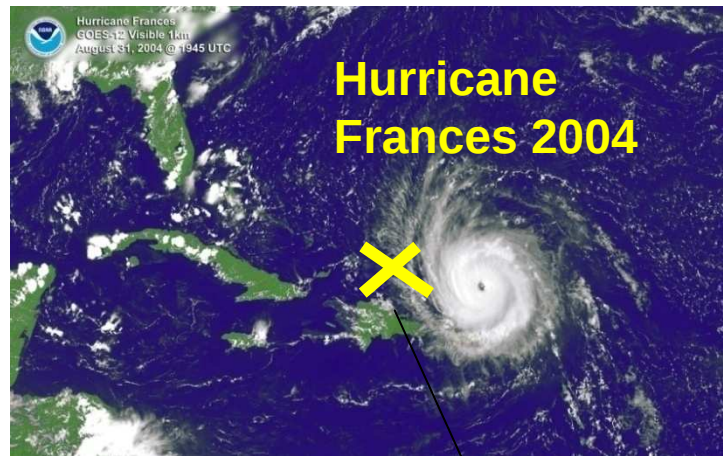
Reported T controlled water bath tracks air pressure to within $\pm 0.07\%$ over 8 days.

Minimum predicted error for $[N_2]$ is $\pm 0.25\%$
(requires careful Winklers and GTD equilibration)

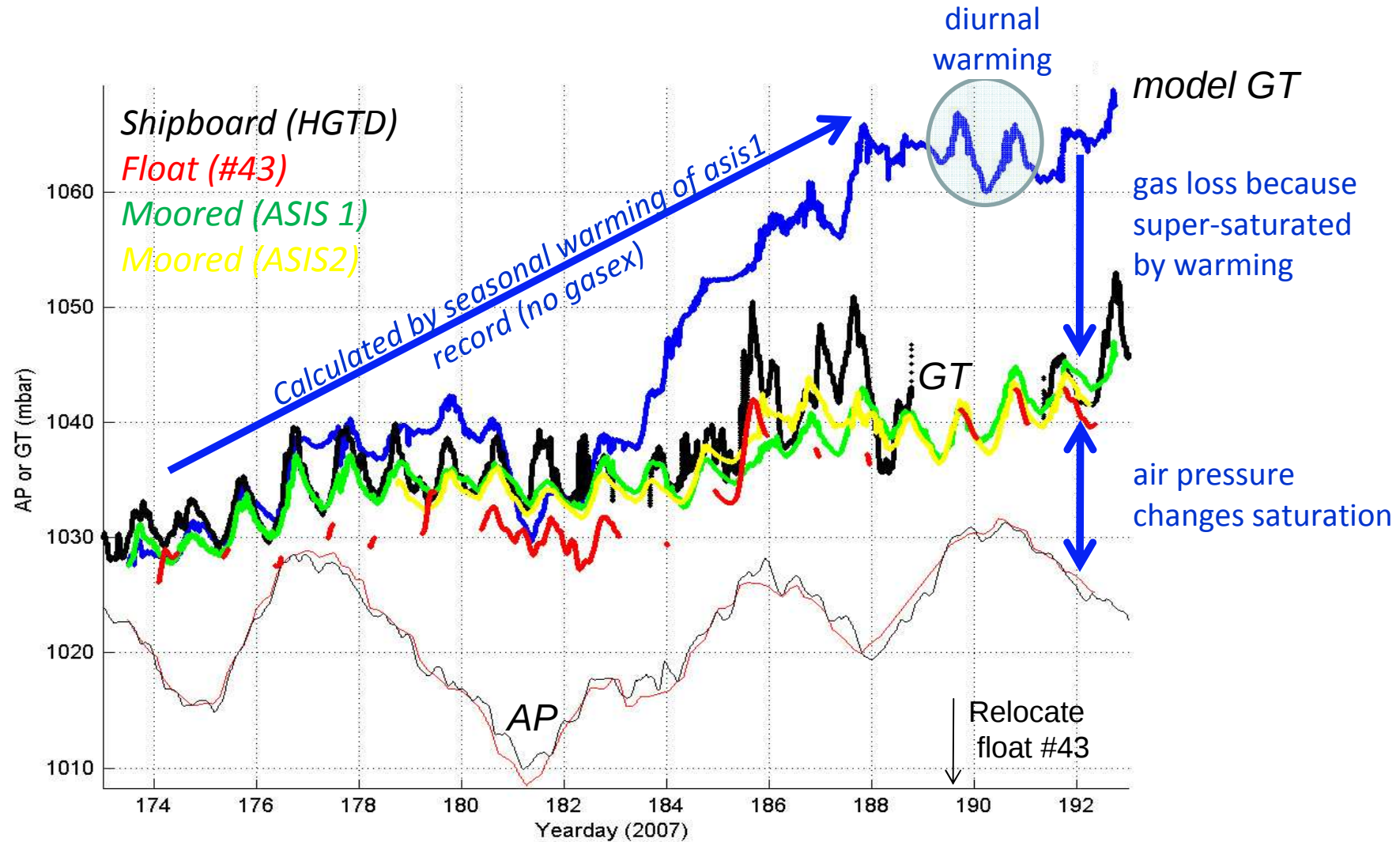
Mass-spec (MS) intercomparisons

- 😊 Time series: *Emerson et al.* [2002] made comparisons over 2 yrs at HOTS, reported pN_2 better than $\pm 0.5\%$
- 😞 Vertical profiles: McNeil et al. [2006] using floats at < 45m depth in Puget Sound showed GTD- N_2 up to 2.8% higher than MS- N_2 . Co-located sampling is hard to do, but this difference was large. Unresolved, needs more work!

4. Some results from the field



Sea surface gas tension during DOGEE-II (NE Atlantic off Portugal)

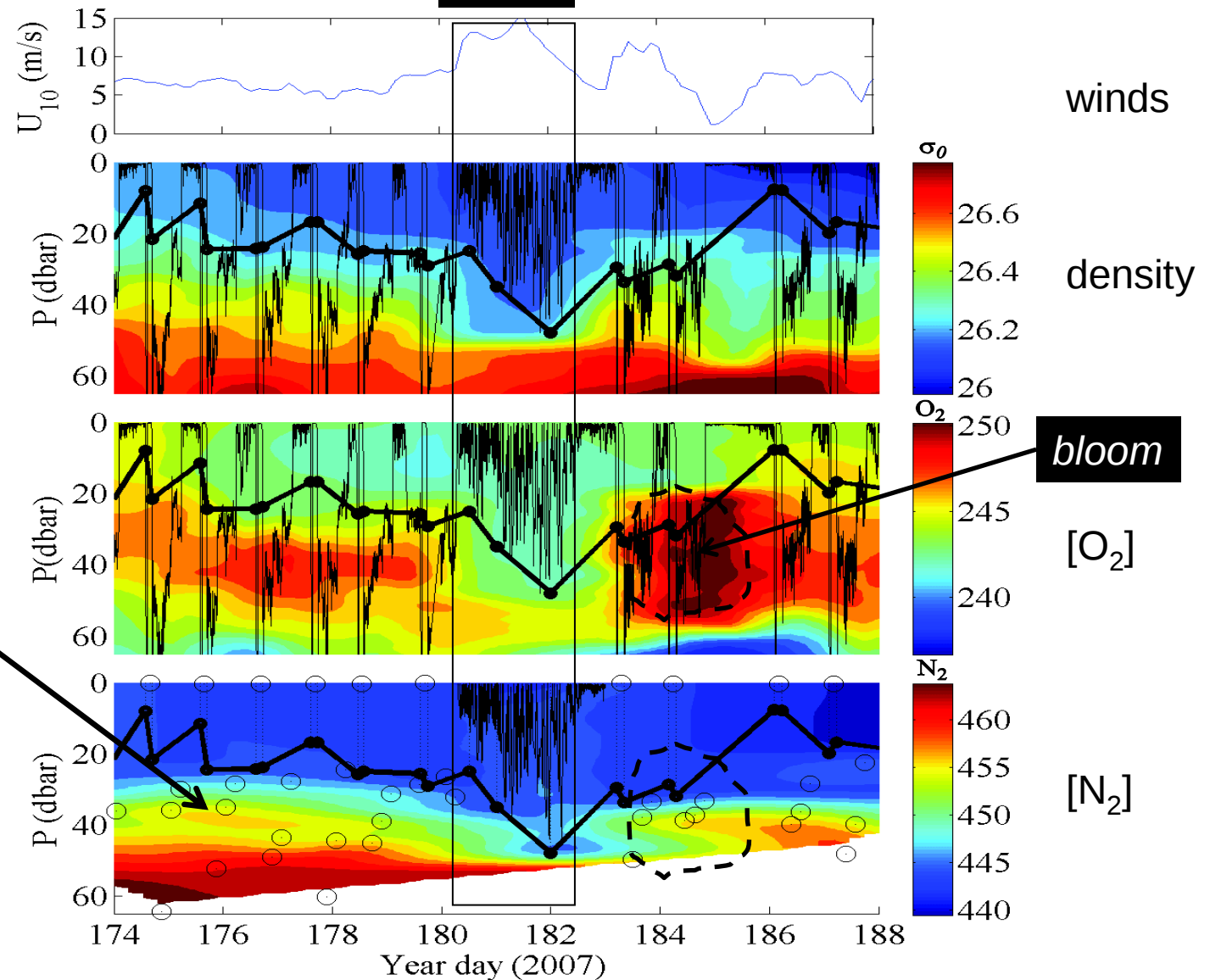


Collaborators: Eric D'Asaro (APL/UW) Rob Upstill-Godard,(UK) Phil Nightingale (UK) Will Drenan (U Miami)
Mike DeGrandpre (U. Montana)

DOGEE-II float data



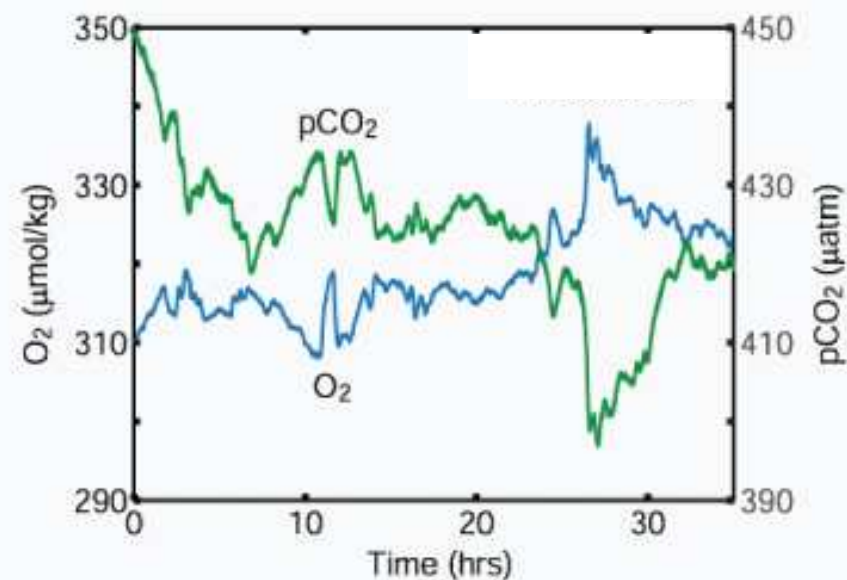
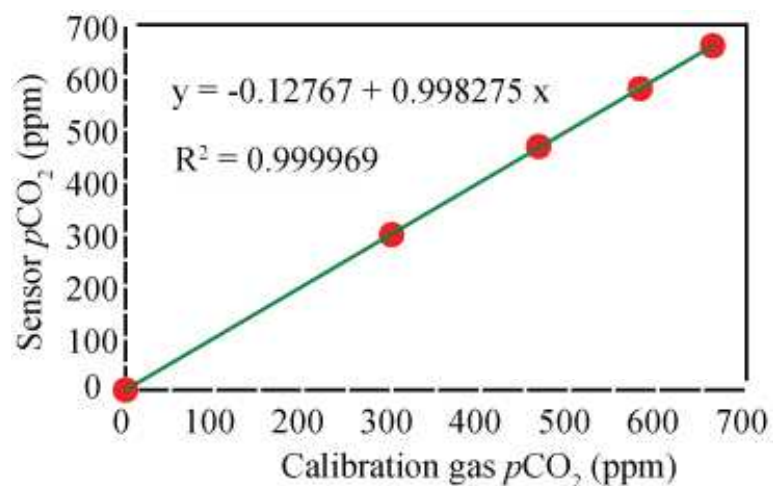
storm



1) Use isopycnal sampling for N_2 profiles.

2) Assuming N_2 is conservative in pycnocline (ie. linear $[N_2]$ versus density) can estimate precision of $[N_2]$ determinations to be $\pm 0.14\%$ (N=13).

5. New CO₂ sensor uses same patented membrane interface



response: 3+ minutes depth: 1000 m size: 17x33 cm power: 5+ Watts
 accuracy: $x\text{CO}_2 \pm 1$ ppm (approx) precision $x\text{CO}_2$: ± 0.01 ppm

6. Summary

- Measurements of N_2 provide information on gas exchange and productivity; complements O_2 as proxy for 'abiotic O_2 '
- Gas tension is very precise and stable (± 0.02 % per year), has been measured on ships, moorings, and profiling floats
- Estimate N_2 to better than $\pm 0.5\%$; needs good TS and O_2 (Winklers)
- Expect new low power float sensor suit to measure $O_2/N_2/CO_2/CH_4$

Dynamical Response of Profiling GTD

$$\frac{dP_M}{dt} = -(P_M - P_T) / \tau_g + w\beta_m(p)$$

$\tau_g(p)$ = equilibration time of GTD

$\beta_m(p)$ = isothermal compressibility of membrane (or $1/K_m$)

w = vertical velocity of float

P_M = measured pressure of GTD

P_T = true gas tension of the water

P = hydrostatic pressure

Forward Solution: use 'best guess' for $P_T(z)$, integrate then compare to P_M

Inverse Solution: solve directly for P_T