N_2 measurements by the gas tension method

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Overview:

1. Measuring N_2 using gas tension method

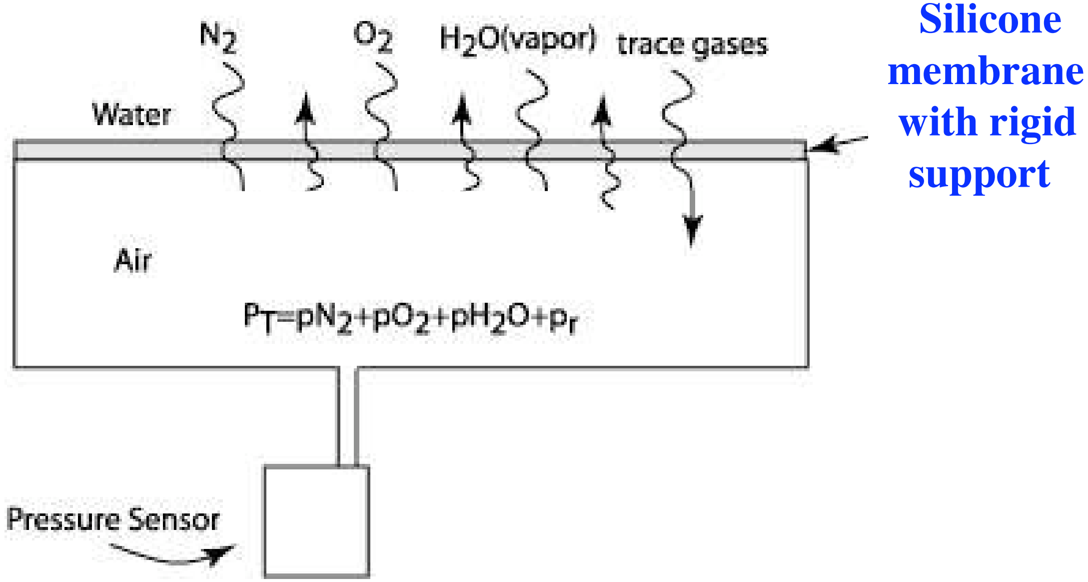
2. Overview of the gas tension device (GTD)

3. Measurement errors

4. Some results from the field

5. Overview of pCO_2 sensor

1. Measuring N_2 using gas tension method



Gas tension (or total dissolved gas pressure) is:

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

	pN_2	pO_2	pAr	pH_2O	pCO_2
	~78 %	**~21 %**	~1 %	1 to 5 %	usually negligible
	'GTD'	***'optode'*** ***'SBE43'***		***'assume'***	***'TS'***

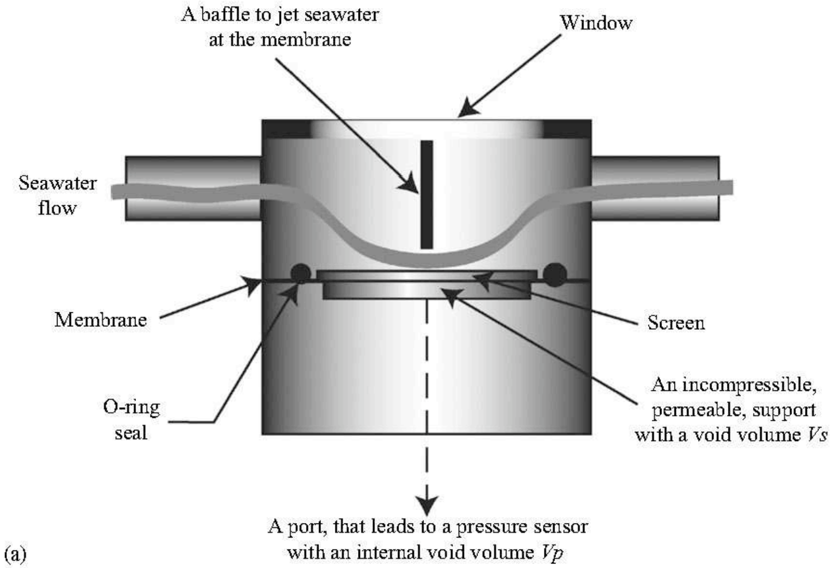
hence: $$pN_2 \approx P_T - pO_2 - pAr - pH_2O$$

use: $$[Gas] = S_H(T,S) \times pGas$$ (Henry's Law)

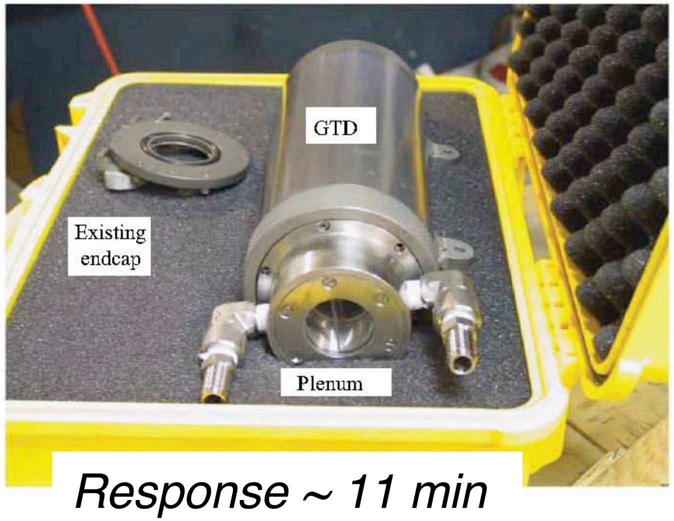
2. The gas tension device (GTD)

- Moored GTD

- Shipboard GTD

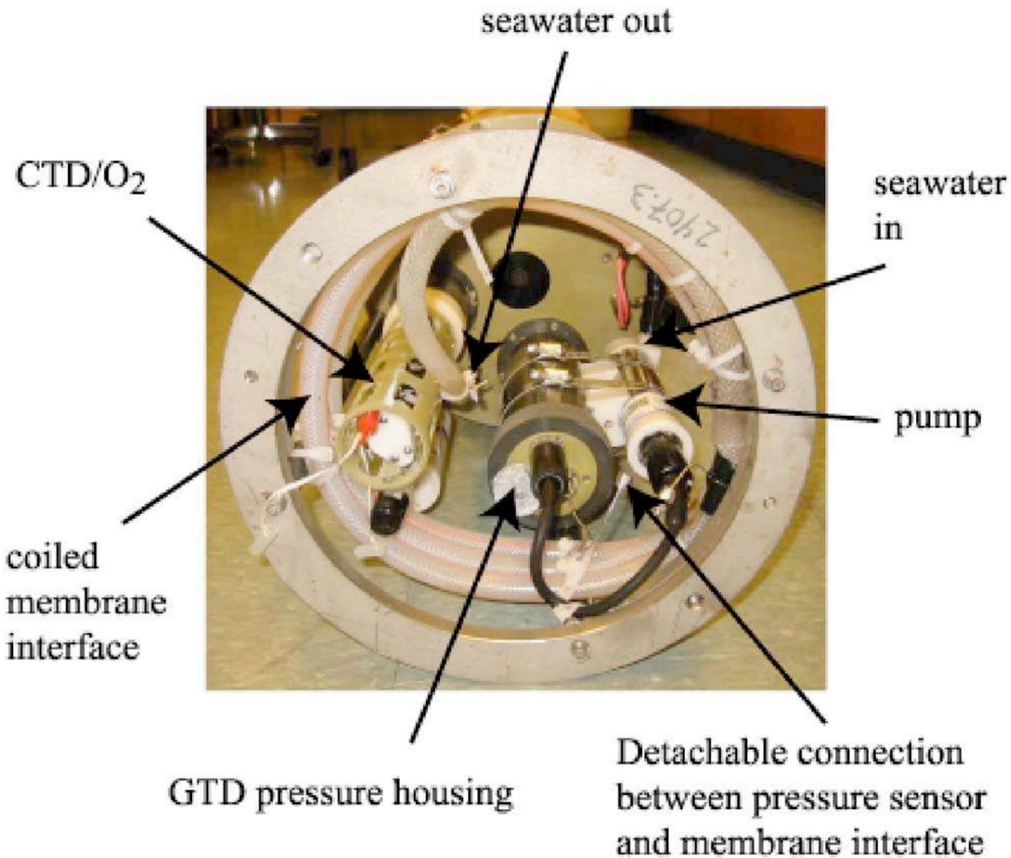


(a)



(b)

- Float GTD



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

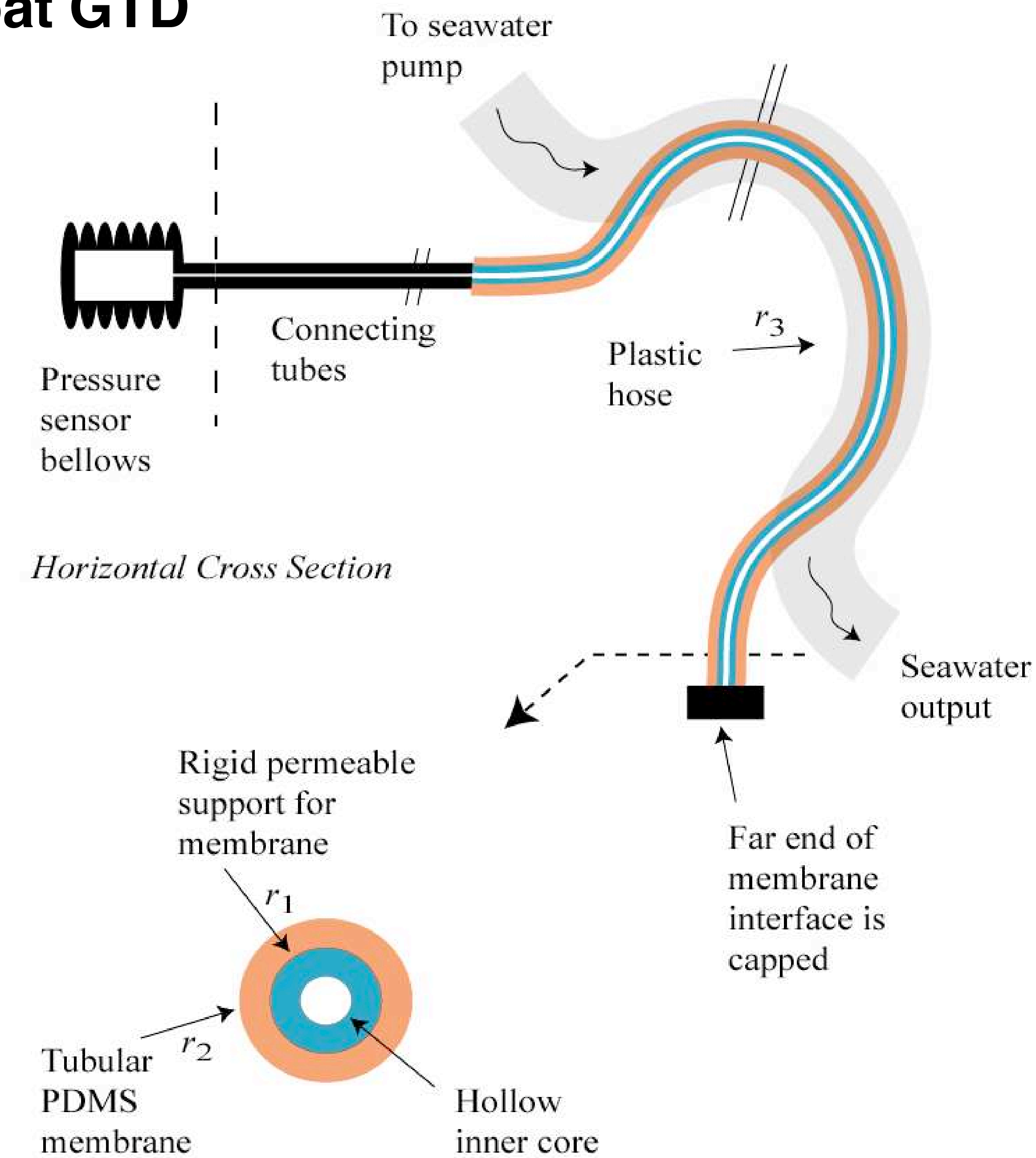
More details on float GTD

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

Tank tests:

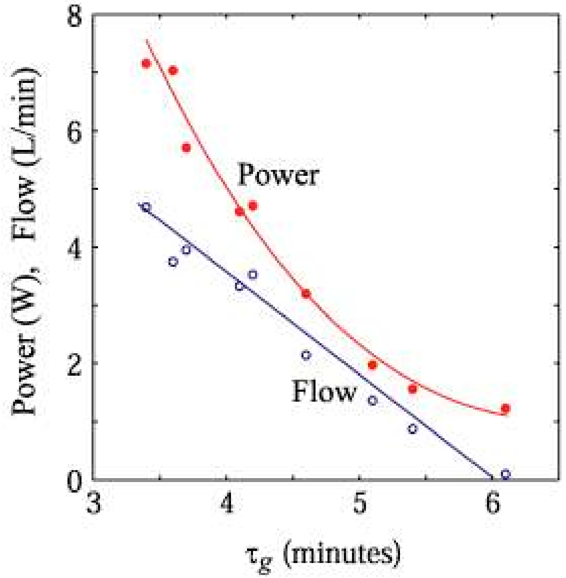
350 m (smaller HGTD)
1000m (larger CO_2)

Patented 2008
(Johnson & McNeil)



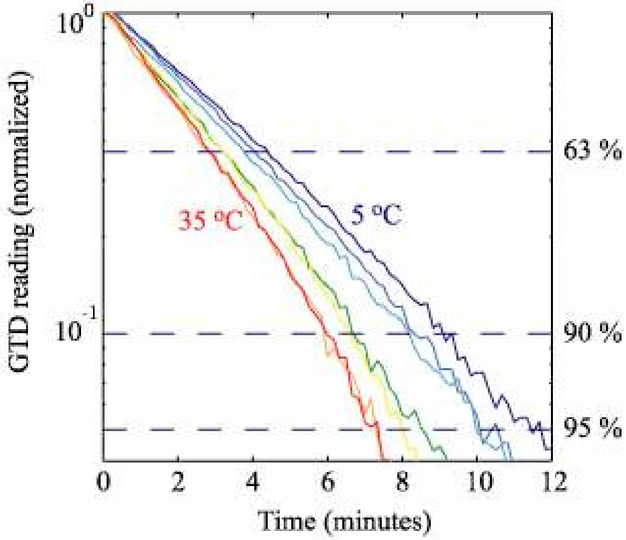
Equilibration time for float GTD

#1 pump speed



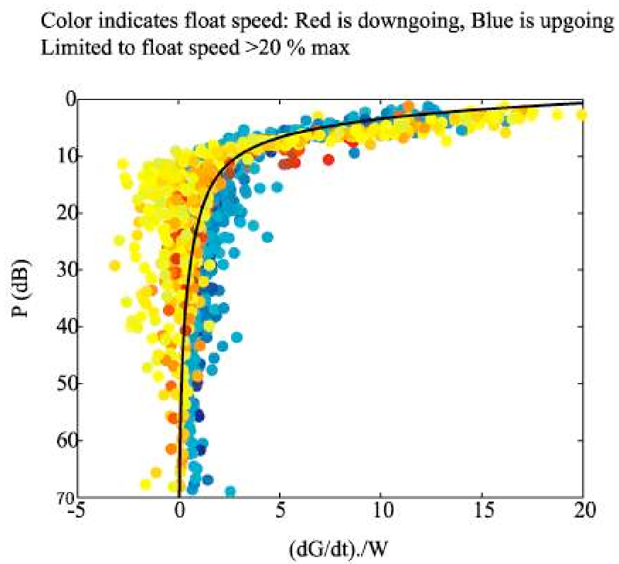
Pulse pumping is
2 times slower but 90%
more efficient!

#2 water temperature



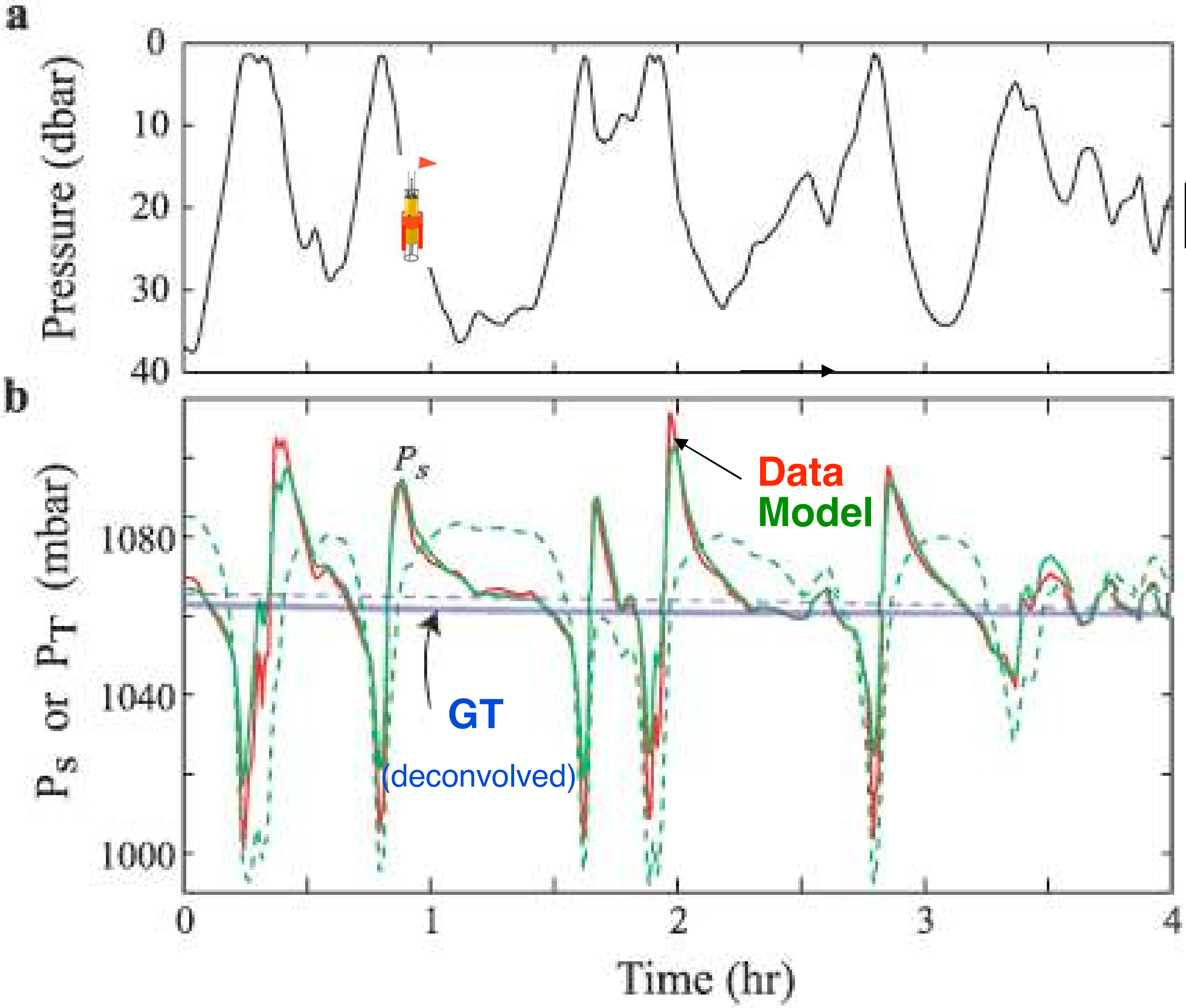
1.7 times faster at
35 °C than 5 °C

#3 hydrostatic pressure



Compressible
H < 10 m

Dynamical response of float GTD



Mixed layer

Deconvolution NOT required for isopycnal sampling !!!

3. Measurement errors for N_2

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

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

2) Winklers - big

$[O_2] \sim$ typical 0.5 %, at best 0.2%
NB: error on pN_2 is 0.14%, at best 0.06%

3) Assume Argon levels - medium
a) best use Ar sat = N_2 sat (recursive approach); within 2% at HOT/BATS
or b) Ar sat =100%, and conservatively within 10% equilibrium

NB: error on pN_2 is 0.03% for assumption (a), and 0.13% for assumption (b).

4) Gas tension - small

accuracy: ± 0.2 mbar or ~ 0.02% precision ~ 0.00001%
drift > 0.02% per year !
Reported T controlled water bath tracks air pressure to within ± 0.07% over 8 days.

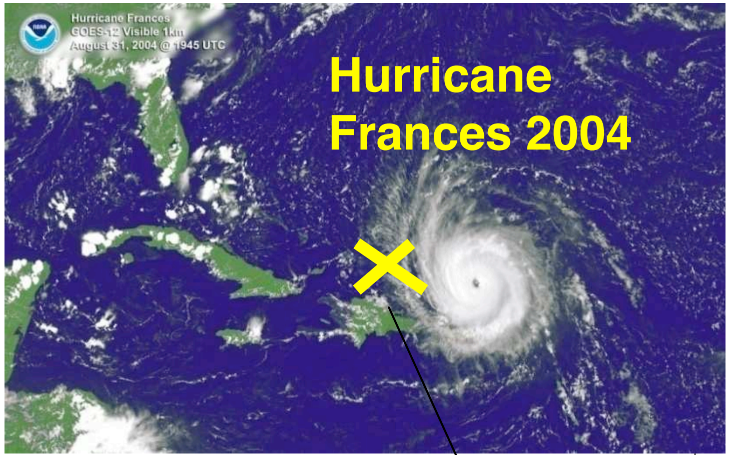
Minimum predicted error for [N_2] is **± 0.25%**
(requires careful Winklers and GTD equilibration)

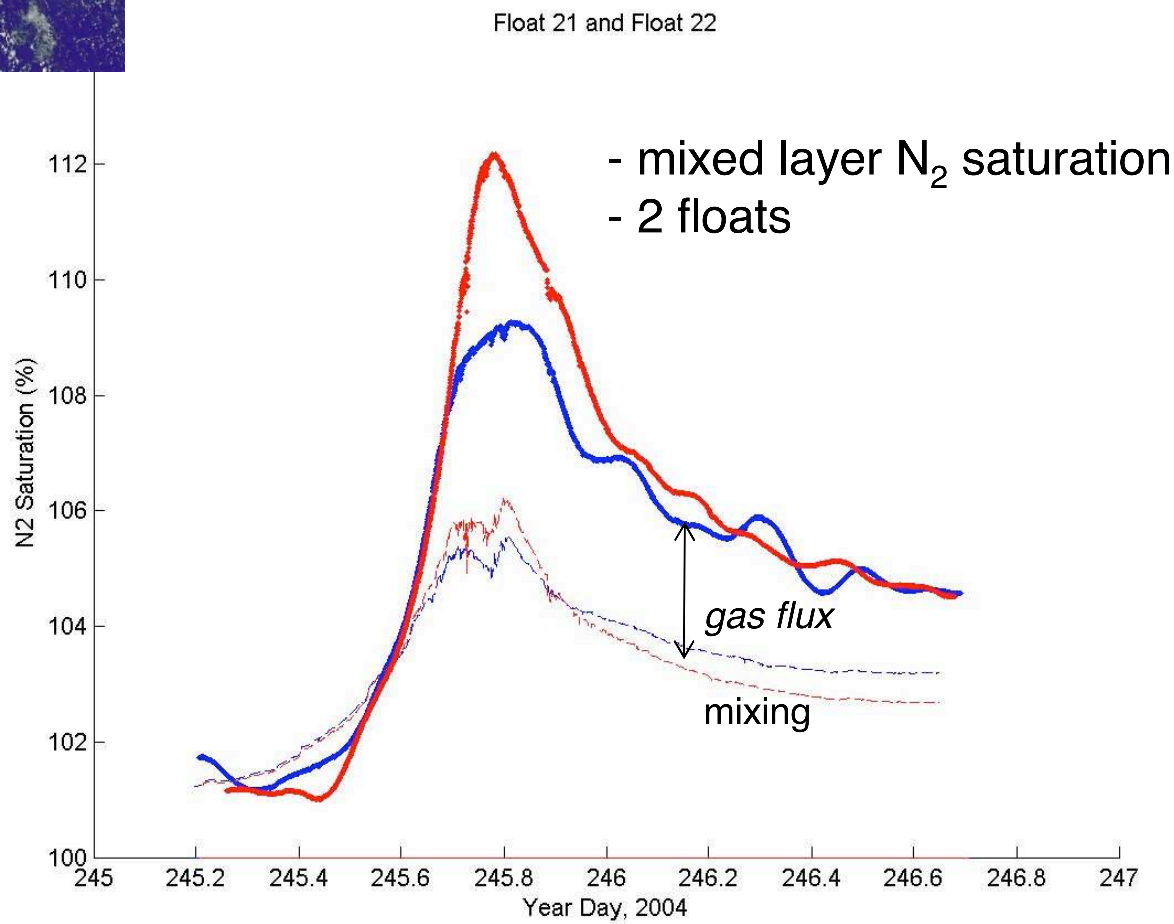
Mass-spec (MS) intercomparisons

Time series: *Emerson et al.* [2002] made comparisons over 2 yrs at HOTS, reported pN_2 better than **± 0.5%**

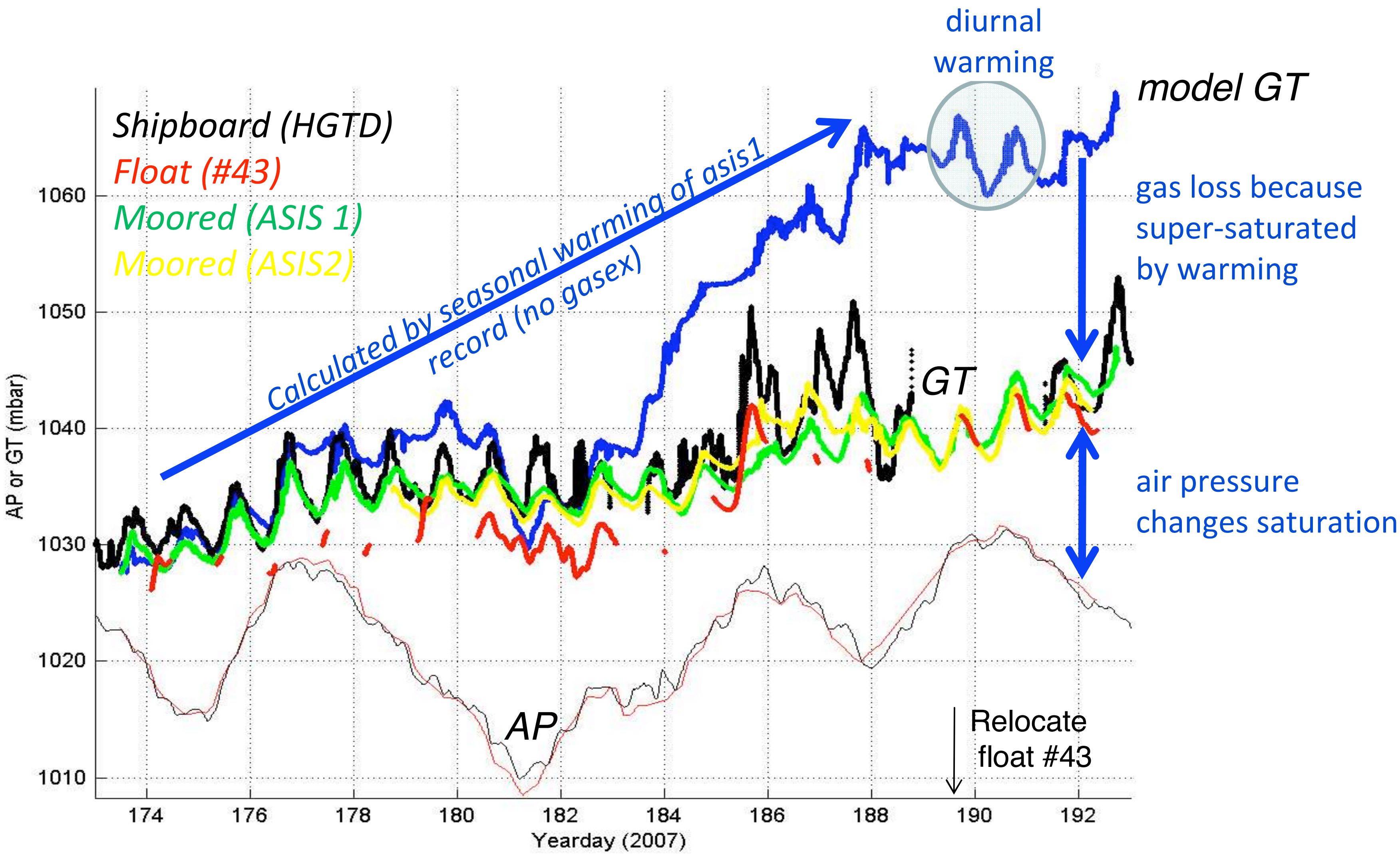
Vertical profiles: McNeil et al. [2006] using floats at < 45m depth in Puget Sound showed GTD-N_2 up to 2.8% higher than MS-N_2. Co-located sampling is hard to do, but this difference was large. Unresolved, needs more work!

4. Some results from the field



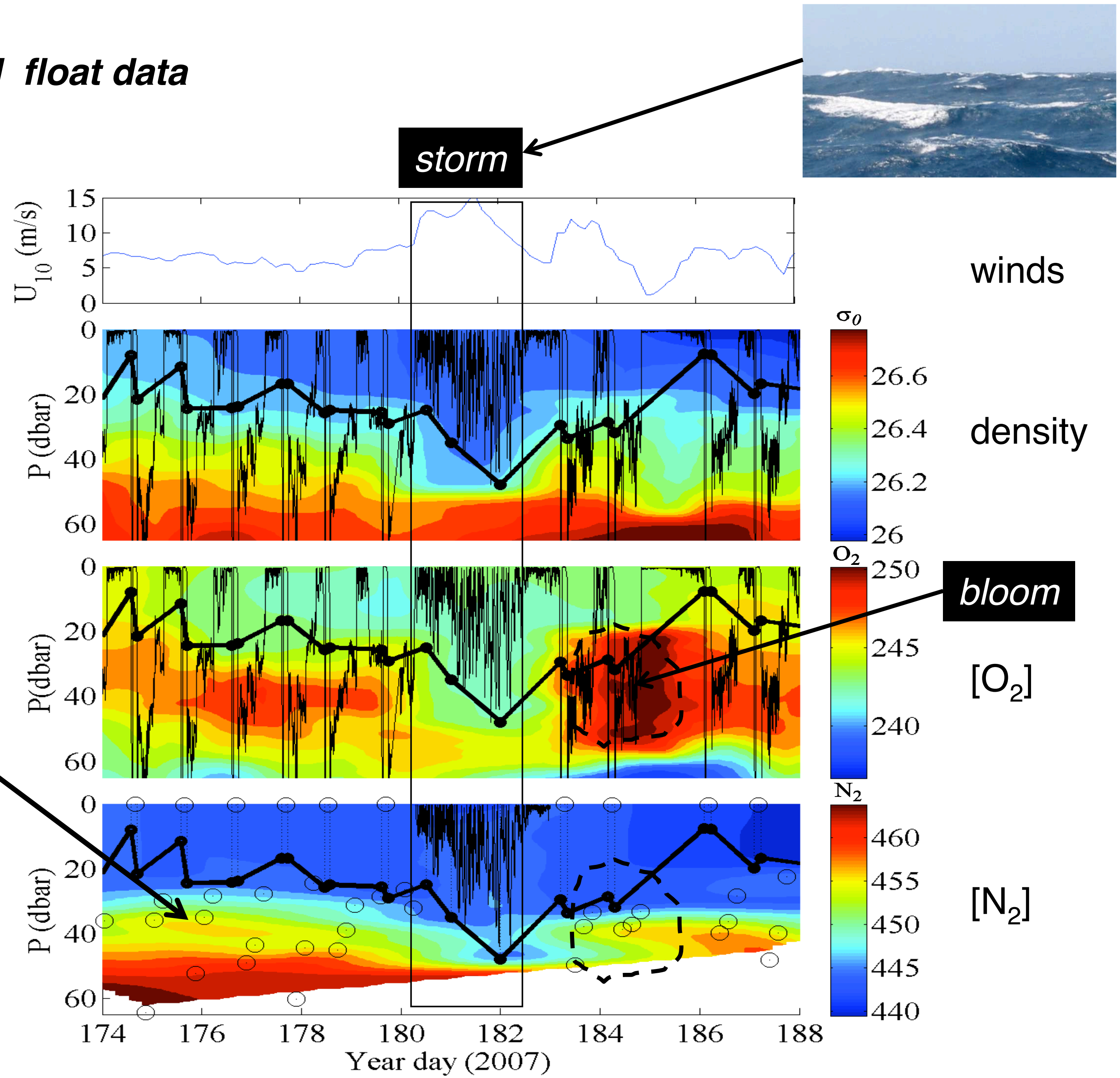


Sea surface gas tension during DOGEE-II (NE Atlantic off Portugal)



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

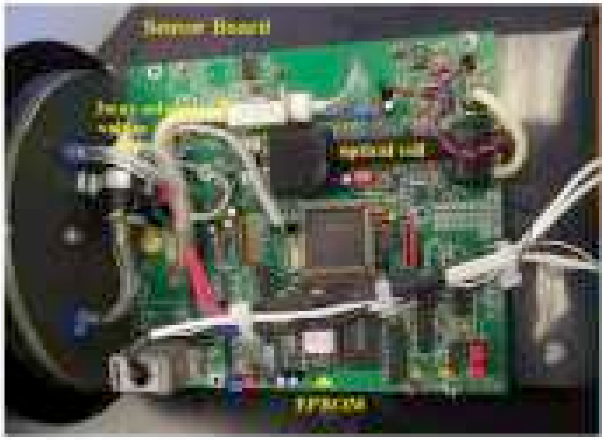
DOGEE-II float data

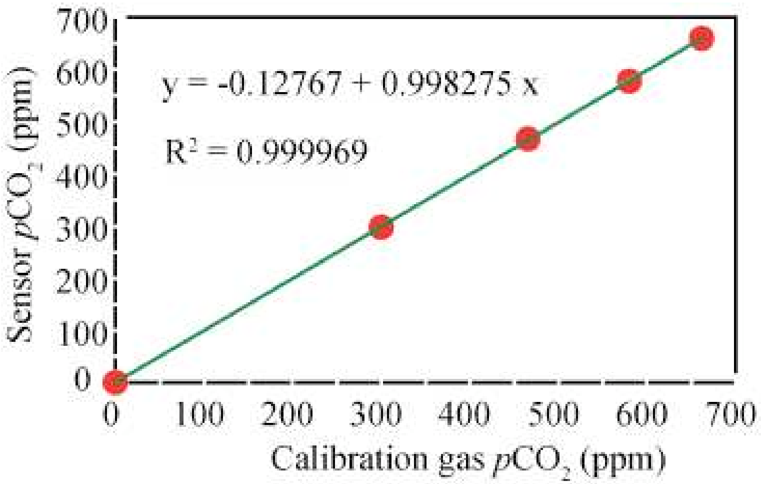


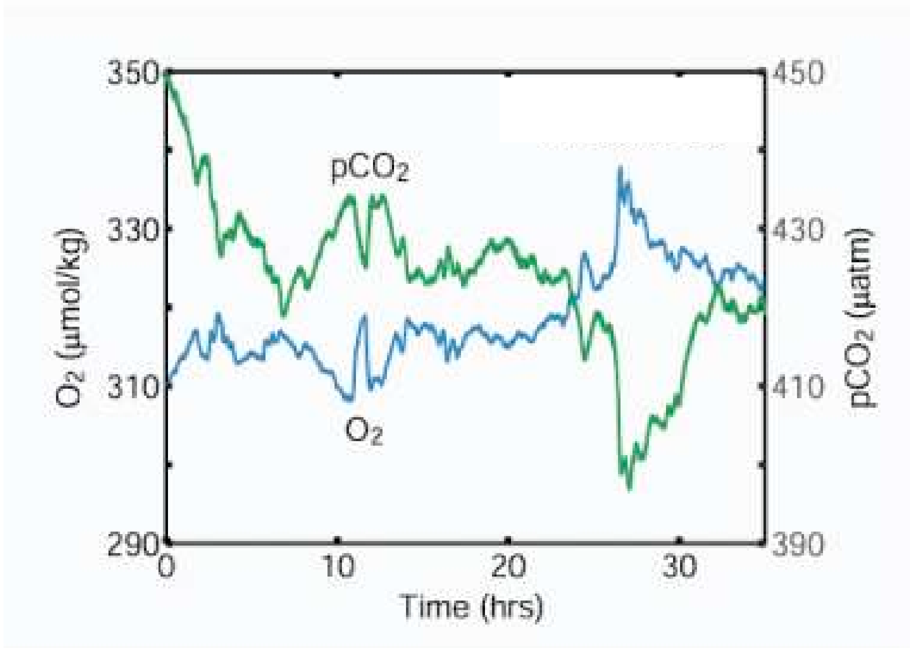
1) Use isopycnal sampling for N_2 profiles.

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

5. New CO_2 sensor uses same patented membrane interface







response: 3^{+} minutes depth: 1000 m size: 17x33 cm power: 5^{+} Watts

accuracy: xCO_2 ± 1 ppm (approx) precision xCO_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 ± 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