OCEANIC pH:
FROM MONTHLY TO HIGH RESOLUTION DETERMINATION

Melchor González Dávila
Department of Chemistry, Faculty of Marine Sciences,
University of Las Palmas G.C., 35017 Spain.
mgonzalez@dqui.ulpgc.es

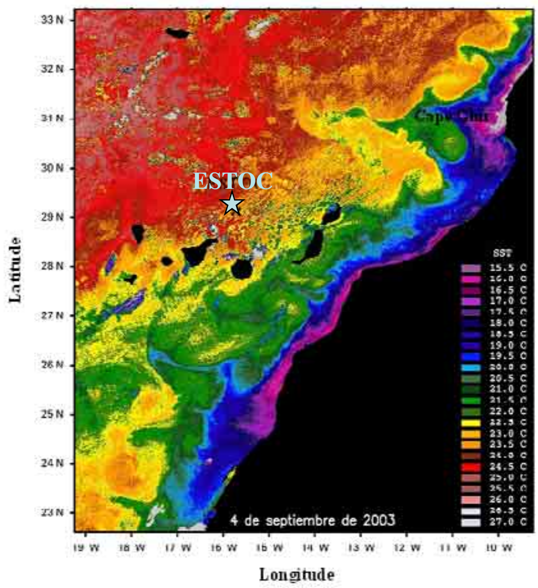
Contributing: J. Magdalena Santana-Casiano

Solution pH is widely conceptualized as a master variable in the regulation of natural aqueous systems.

Key feature in:

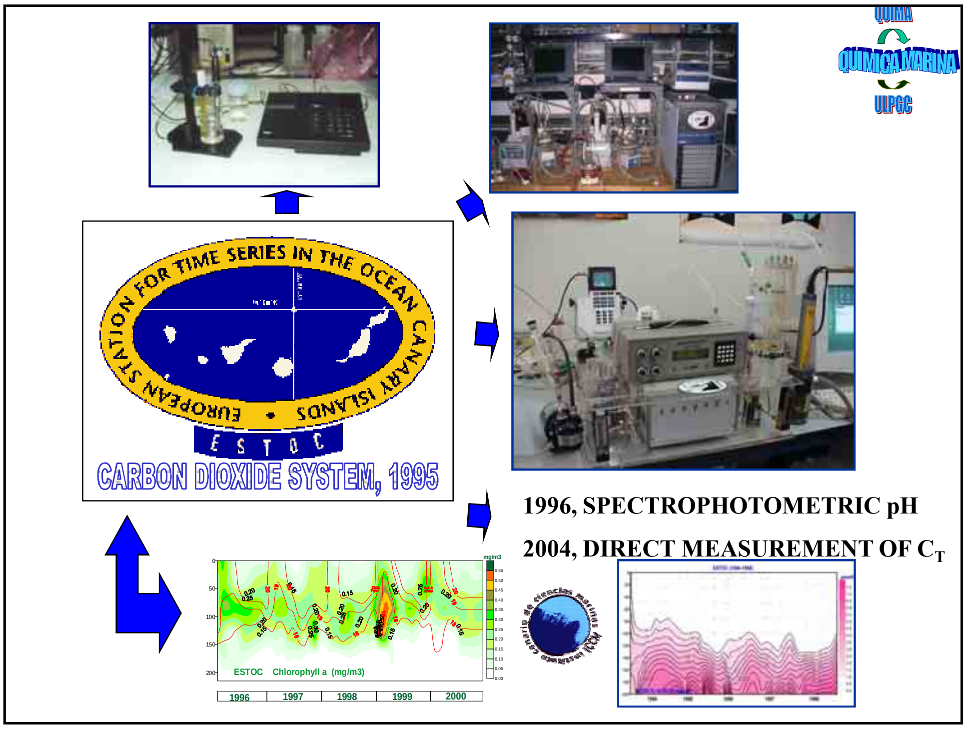
1. **Descriptive models of carbonate system chemistry**
2. **Trace metal speciation and bioavailability**
3. **Oxidation-reduction equilibria and kinetics**
4. **Biologically induced carbon system transformations**
5. **The aqueous interactions and transformations of minerals**

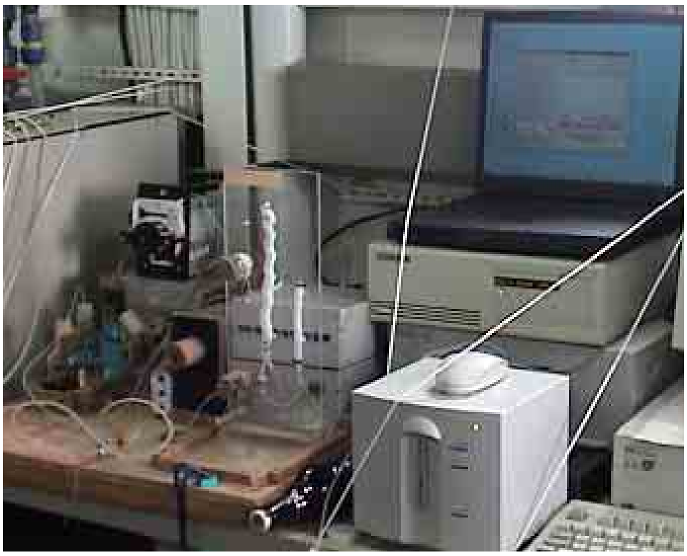
The importance of pH in investigations of terrestrial and oceanic biogeochemistry has necessitated improvements in not only the quality of measurements (precision and accuracy) but also in the spatial and temporal resolution of measurements in the field.



The ESTOC site (29º10’N, 15º30’W) is located in a strategic situation in the Canary Current, in the transitional zone between the North-West African coastal upwelling region, and the open ocean oligotrophic waters of the North East Atlantic subtropical gyre

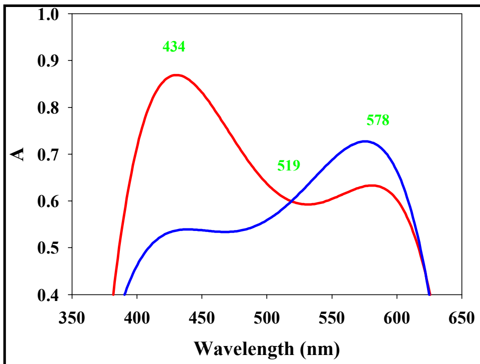
Carbonate system determination started on October 1995.

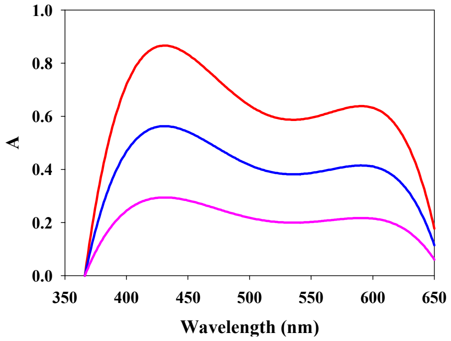


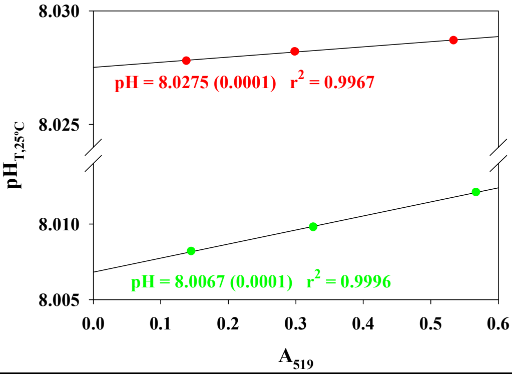


Spectrophotometric system for discrete and continuous mode pH determination developed in our lab following Bellerby et al. (1995) and mCP dye after Clayton and Byrne (1993).

A stopped-flow protocol was used to analyse seawater previously thermostated to 25ºC for a blank determination at 750 nm, 578 nm and 434 nm. We use a fourth λ = 519 nm, the isosbestic point.

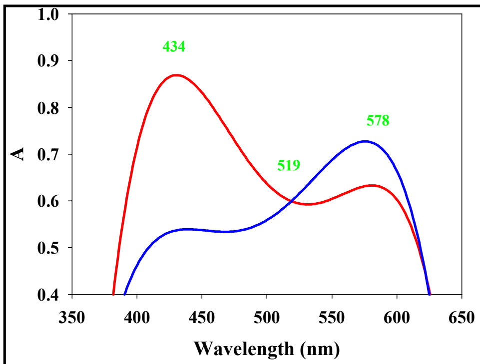


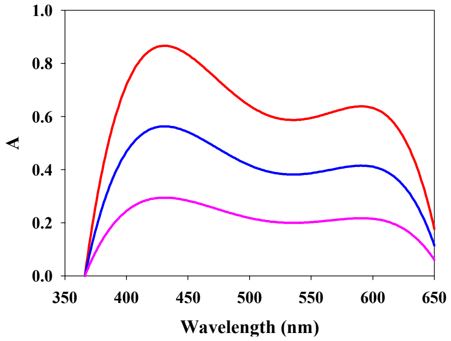


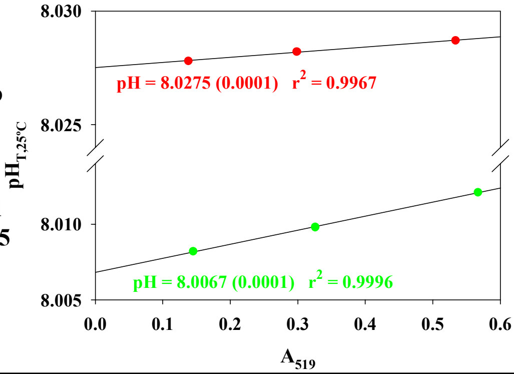


The flow is restarted, the indicator injection valve switched on to inject 10 µl dye through a mixing coil. Three photometric measurements were carried out for each injection after mixing along the coil in order to remove all dye effect from the seawater pHt measurement.

González-Dávila et al., GBC 2003







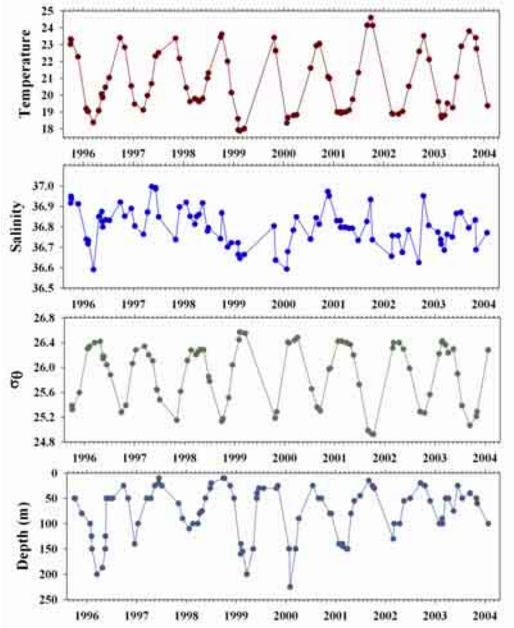
$A_{519} = [HL^-]\,{}^{519}\varepsilon_{HL}b + [L^=]\,{}^{519}\varepsilon_{L}b$

$A_{519} = ([HL]+[L])\,{}^{519}\varepsilon_{HL}b = [HL]_T\,{}^{519}\varepsilon_{HL}b$

$[HL]_T \ \alpha\ A_{519}$

Repeatedly, seawater measurements of different CRM samples (batches #35 and #42) give a standard deviation of ± 0.0015 (n = 59).

Inter-annual variability of hydrographic properties



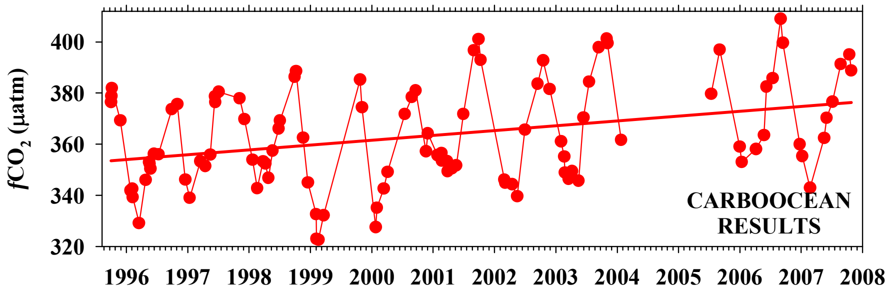
Seasonal oscillation 4º-6ºC
From 18ºC to 24ºC

Salinity range 36.6 – 37.0

Potential density 25.0 - 26.4

The MLD fluctuated between 120 m (1998, 2003) and 200 m (1996, 1999, 2000)

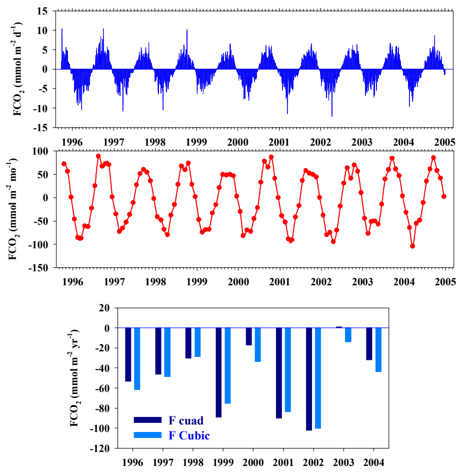
Inter-annual variability of *f*CO_2



$fCO_2 = -2924.72 + 1.546\ t + 9.535\ SST – 2.253\ \sin(2\pi(t-1995))$ $R^2 = 0.89$

Seawater *f*CO_2	**Seasonal variability: 60 - 70 µatm.** **Minimum values (320 -330 µatm) in Winter** **Maximum values (390 – 400 µatm) in Summer** **Average annual increase of 1.55 ± 0.43 µatm yr^{-1}.**
Atmospheric *f*CO_2	**Seasonal variability 7 µatm** **Average annual increase of 1.6 ±0.7 µatm yr^{-1}.**

Fluxes of CO_2



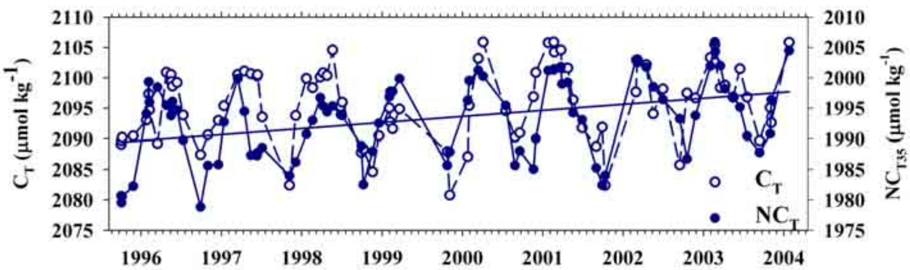
The seasonal oscillation in seawater fCO_2

CO_2 oversaturated
from June to November
acting as a source
The maximum outgassing rate took place between September-October when ΔfCO_2 and wind speed were at a maximum.

CO_2 under-saturated
from December to May,
acting as a sink of CO_2
Maximum rate of ingassing between March and April.

The area acted as a very small sink of CO_2 of 51 ± 36 mmol m^{-2} yr^{-1}

Inter-annual variability of C_T

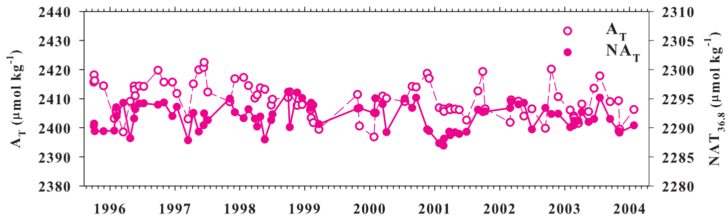


C_T Seasonal variability of 20 - 30 µmol kg^{-1}, with the lowest values in October and maximum values between April-May. The mean value was 2096 ± 6 µmol kg^{-1}.

$NC_{T,35}$, showed a seasonal variability of 30 µmol kg^{-1}
The annual variability of C_T at the ESTOC site was inversely related to SST changes, changes in biological production and gas exchange processes in the area.

NC_T increased, over the years of the study, at a rate of 0.99 µmol kg^{-1}yr^{-1}

Inter-annual variability of A_T

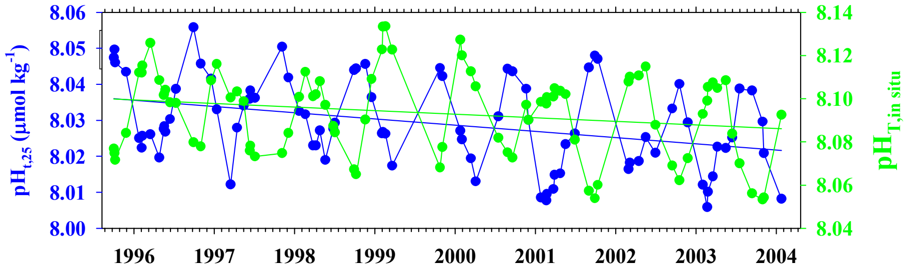


Surface alkalinity variability of 25 µmol kg^{-1} closely linked to salinity

$NA_{T,\ 36.8}$, relatively constant value of 2409.7 ± 2.4 µmol kg^{-1}

$NA_{T,35}$, gave a value of 2291.8 ± 2.2 µmol kg^{-1}, which coincides with the mean $NA_{T,\ 35}$ value of 2291 ± 4 µmol kg^{-1} in the North Atlantic (*Millero et al*., 1998).

Inter-annual variability of pH

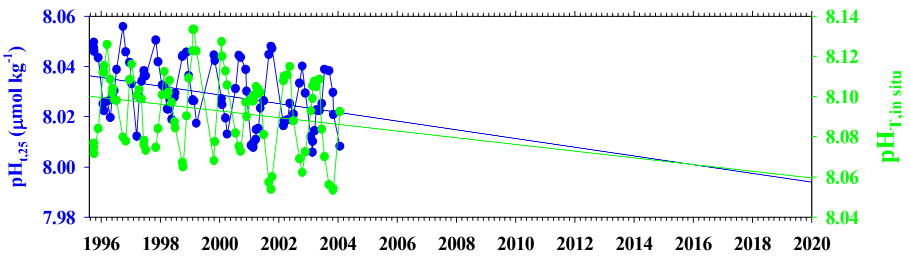


Surface pH_T seasonal variability **0.03 – 0.04 pH units.**
0.04 – 0.06 pH units

The lowest values were observed during Winter convective mix, increasing during the Summer stratification period until October.

The most important feature observed is the decrease in surface seawater pH at a rate of 0.0017 ± 0.0004 pH units yr^{-1}, related to the increased pressure of CO_2.

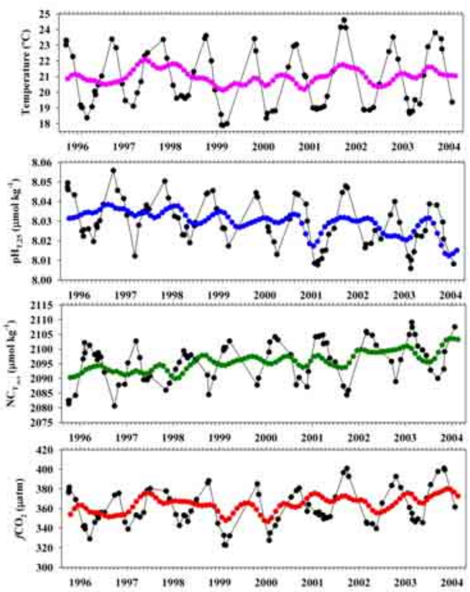
Inter-annual variability of pH



Surface pH_T seasonal variability 0.03 – 0.04 pH units.
0.04 – 0.06 pH units

At 1996, pH in sea surface water varied between 8.02 to 8.06 (8.08 to 8.12 in situ pH). In a scenario similar to that during 1995-2005 decade and after 25 years, sea surface pH at 25ºC will reach an average value slightly over 7.99 varying seasonally from 8.01 to 7.97, valid when hydrographic and biogeochemical conditions keeps the same trends as 1995 decade.

Inter-annual trends of CO_2 variables in ESTOC



Santana-Casiano et al., GBC 2007

The seasonal oscillation observed in the time series were treated mathematically, after decomposing the series by trend, seasonal components and errors, using harmonic functions, and taking into account serial correlations modeled after a second-order autoregresive process (AR(2))

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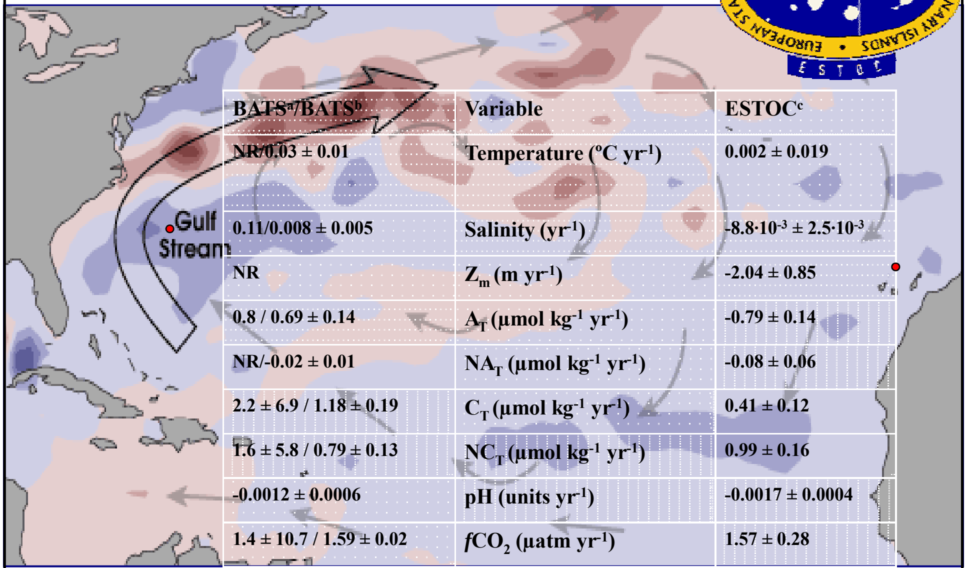
SPSS program and the routine trend cycle were used in order to remove the seasonal variability and to obtain the de-trended data.

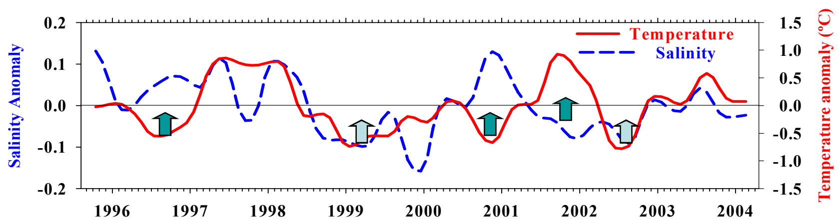
Inter-annual trends



BATS[a]/BATS[b]	Variable	ESTOC[c]
NR/0.03 ± 0.01	Temperature (ºC yr^{-1})	0.002 ± 0.019
0.11/0.008 ± 0.005	Salinity (yr^{-1})	$-8.8 \cdot 10^{-3} \pm 2.5 \cdot 10^{-3}$
NR	Z_m (m yr^{-1})	-2.04 ± 0.85
0.8 / 0.69 ± 0.14	A_T (µmol kg^{-1} yr^{-1})	-0.79 ± 0.14
NR/-0.02 ± 0.01	NA_T (µmol kg^{-1} yr^{-1})	-0.08 ± 0.06
2.2 ± 6.9 / 1.18 ± 0.19	C_T (µmol kg^{-1} yr^{-1})	0.41 ± 0.12
1.6 ± 5.8 / 0.79 ± 0.13	NC_T (µmol kg^{-1} yr^{-1})	0.99 ± 0.16
-0.0012 ± 0.0006	pH (units yr^{-1})	-0.0017 ± 0.0004
1.4 ± 10.7 / 1.59 ± 0.02	fCO_2 (µatm yr^{-1})	1.57 ± 0.28

[a] BATS data from *Bates* [2001]
[b] BATS and Hydrostation S from *Bates* [2005] and *Gruber et al.* [2002]
[c] ESTOC data from *Santana-Casiano et al.* [2007]

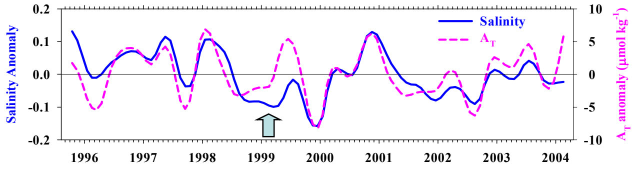
Time series of surface seawater anomalies at ESTOC



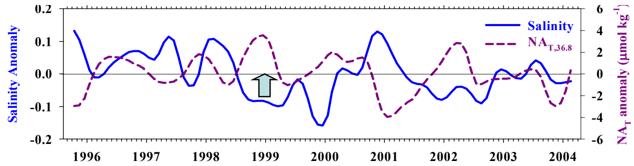
First scenario periods with cooler and fresher waters during 1999 and 2002

Second scenario periods with inverse relationships between temperature and salinity during the Autumn of 1996, 2000 and 2001

First scenario periods with cooler and fresher waters



A_T anomaly is strongly correlated with the salinity anomalies (0.704).

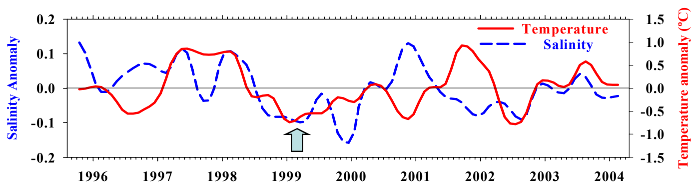


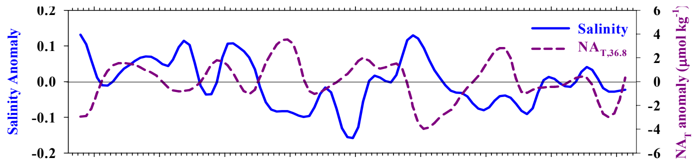
$NA_{T,36.8}$ is inversely correlated with salinity (-0.357).

This negative coefficient indicated the presence of fresher water in ESTOC with higher NA_T water.

Upwelled subsurface water presented higher NA_T due to the dissolution of calcium carbonate at depths.

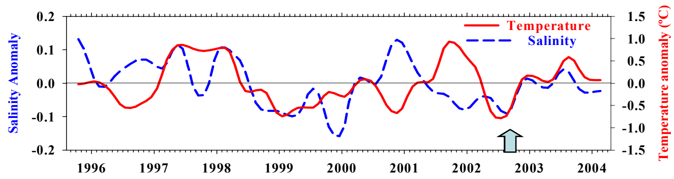
First scenario periods with cooler and fresher waters

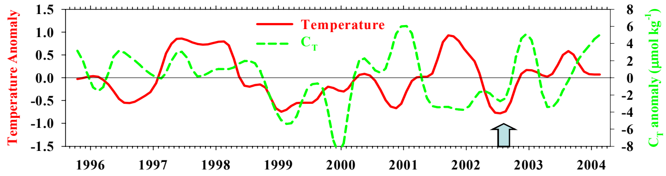




Winter 1999 — **Anomalous cold convective Wintertime periods (0.7ºC in 1999)**
Anomalous fresh waters
A deeper mixed-layer (60 m over the mean)

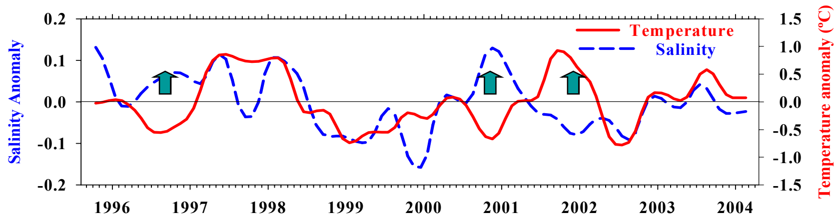
First scenario periods with cooler and fresher waters





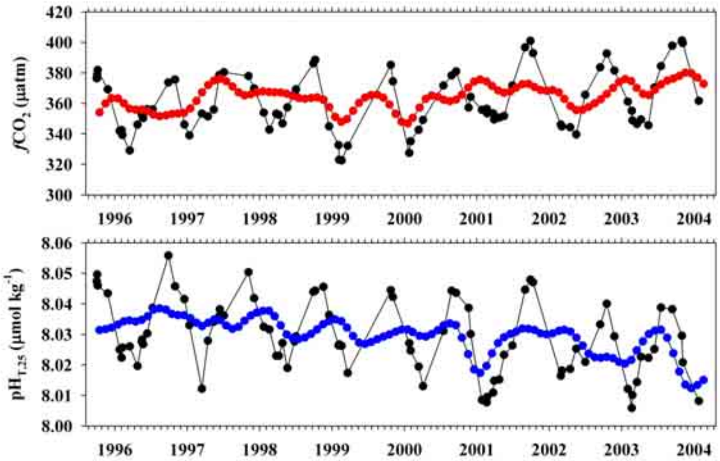
Summer 2002 **Temperatures 0.8ºC colder**
0.09 less saline waters
C_T lower than the mean.

Second scenario periods with inverse relationships between temperature and salinity



The negatively correlated temperature and salinity anomalies observed during the Autumn of 1996, 2000 and 2001. Variations in the position of the Azores Front.

The oceanic response to NAO forcing in the Eastern Atlantic Ocean is produced with a delay of around three years, in line with previous studies (Siedler et al., 2005). SST and mixed-layer depth anomalies at the ESTOC have been found to be significantly correlated to the NAO.

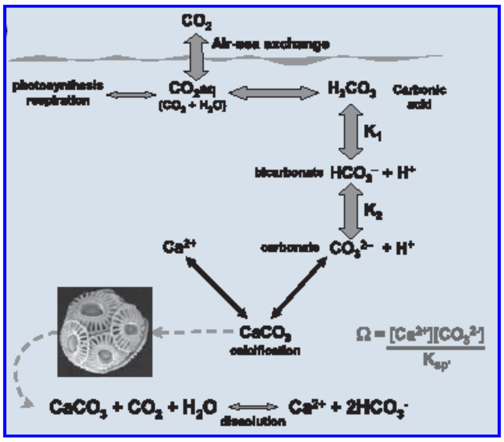


↑ fCO_2 ➡ ↓ pH ➡ ↑ C_T

⬇

$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$ $H^+ + CO_3^{2-} \rightarrow HCO_3^-$

$CO_2 + CO_3^{2-} + H_2O \rightarrow 2\ HCO_3^-$ $CO_2 + CaCO_3 + H_2O \rightarrow 2\ HCO_3^- + Ca^{2+}$

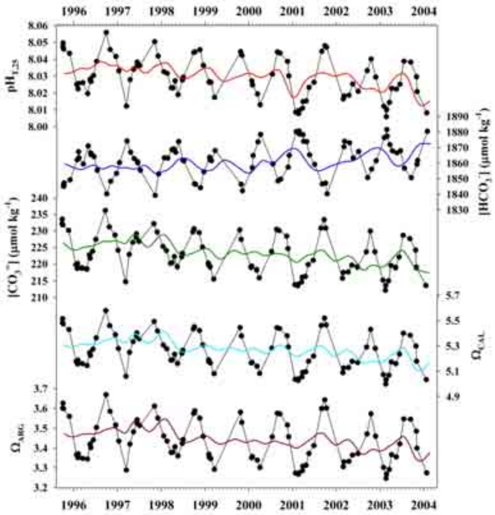


Kleypas et al., 2006

$\uparrow fCO_2$ → $\downarrow$ pH → $\uparrow C_T$

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad H^+ + CO_3^{2-} \rightarrow HCO_3^-$$

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2\ HCO_3^- \qquad CO_2 + CaCO_3 + H_2O \rightarrow 2\ HCO_3^- + Ca^{2+}$$



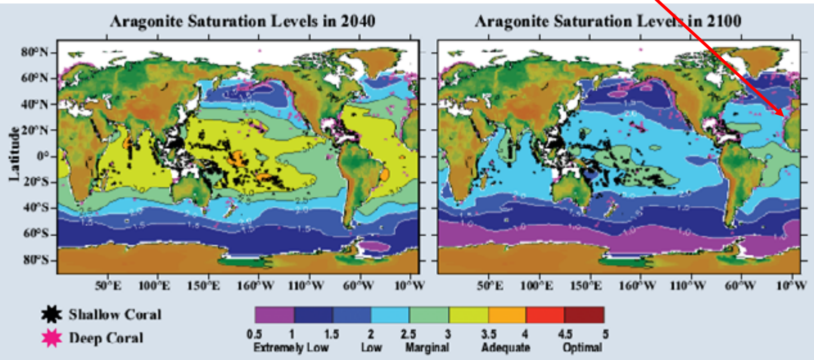
1.24 ± 0.16 µmol kg^{-1} yr^{-1}

-0.89 ± 0.06 µmol kg^{-1} yr^{-1}

-0.018 ± 0.006 unit yr^{-1}

-0.012 ± 0.004 unit yr^{-1}

ESTOC	Ωcalcite = 5.2	Ωaragonite = 3.4
IPCC scenarios	(-0.018 ± 0.006 unit yr^{-1})	(-0.012 ± 0.004 unit yr^{-1})
IS92a (788 ppmv, 2100)	Ωcalcite = 2.97	Ωaragonite = 1.93
S650 (563 ppmv, 2100)	Ωcalcite = 3.81	Ωaragonite = 2.48



Estimated aragonite saturation states of the surface ocean for the years 1765, 1995, 2040, and 2100 (Feely *et al.*, 2006) based on the modeling results of Orr *et al.* (2005) and a Business-As-Usual CO_2 emissions scenario. The distributions of deep-sea coral banks are from Guinotte *et al.* (2006).

WHAT DOES ESTOC REVEAL?

Surface pH_T interannual trend -0.0017 pH units yr^{-1}

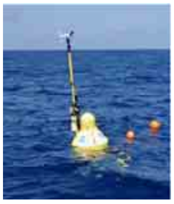
Surface pH_T seasonal variability 0.03 – 0.04 pH units. (25ºC)
0.04 – 0.06 pH units. (in situ)

Change in pH in the first 500 m. 0.20 – 0.25 pH units. (25ºC)
0.10 – 0.15 pH units. (in situ)

WHAT ABOUT DAILY CHANGES?

AUTONOMOUS INDICATOR-BASED pH SENSOR FOR SEAWATER APPLICATIONS

Develop an autonomous system for long-term in situ applications

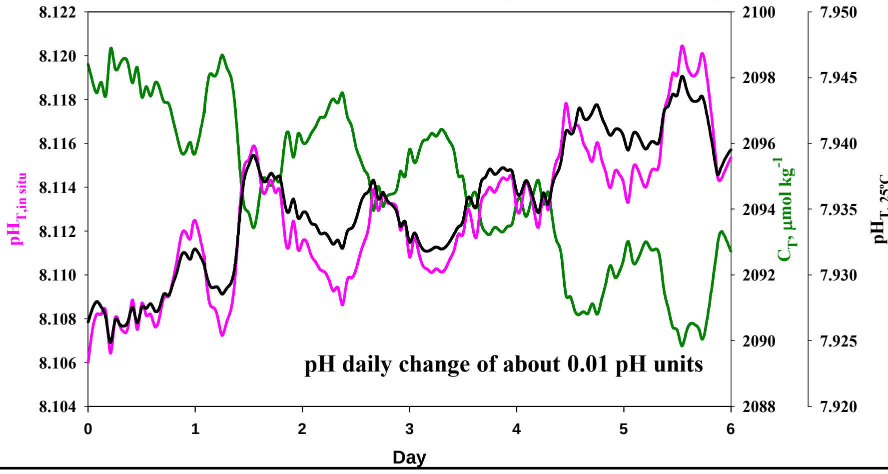


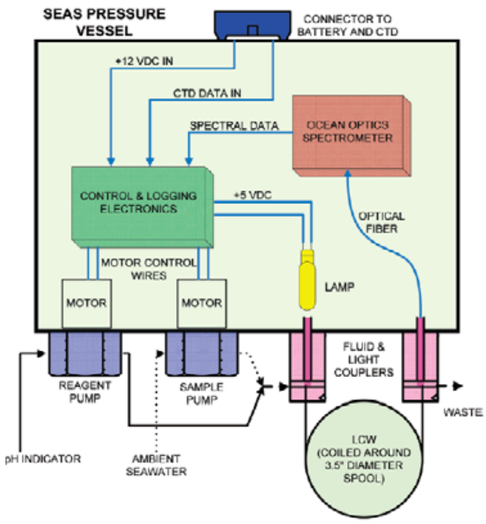
Carioca Buoys, xCO_2 and pH sensors

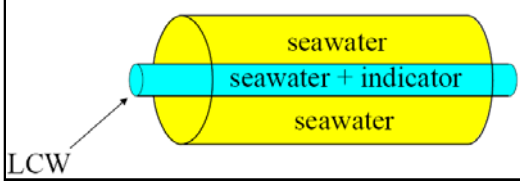
From Merlivat and colleagues, Martec Company

French POMME project, Azores area

Merlivat, González-Dávila et al., JGR Submitted

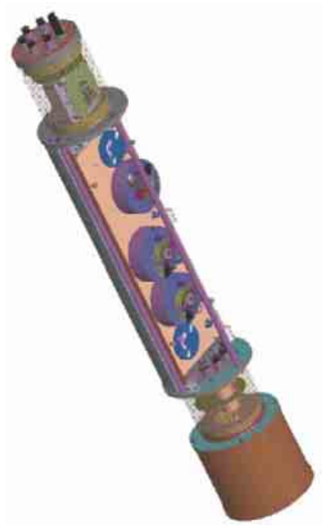




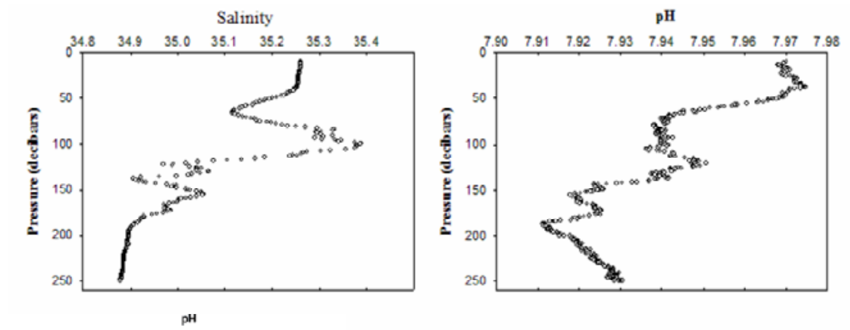


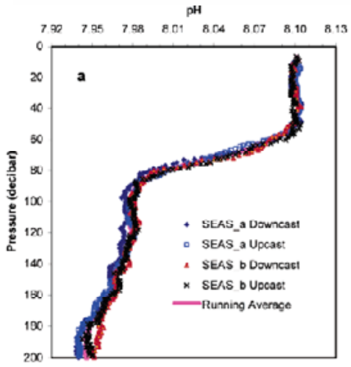
SEAS (spectrophotometric elemental analysis system)

Liu et al., 2006; Byrne et al., 2007



in situ **precision was ±0.0014**





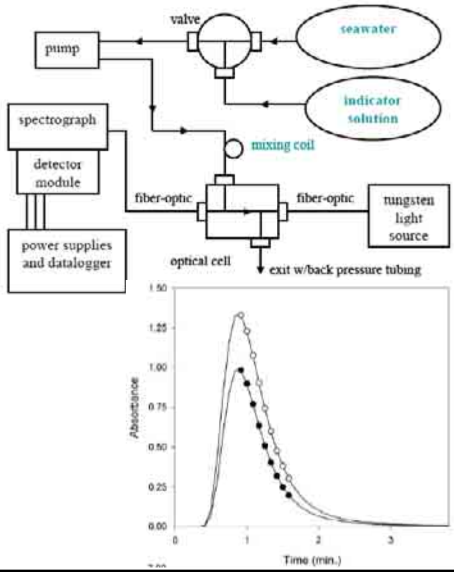
The pH changes in the first 200 m over 0.06 pH units (Equatorial Pacific, 2003)

Reaching 0.15 pH units in the Gulf of Mexico (Liu et al., 2006)

The Submersible Autonomous Moored Instrument for pH, or SAMI-pH

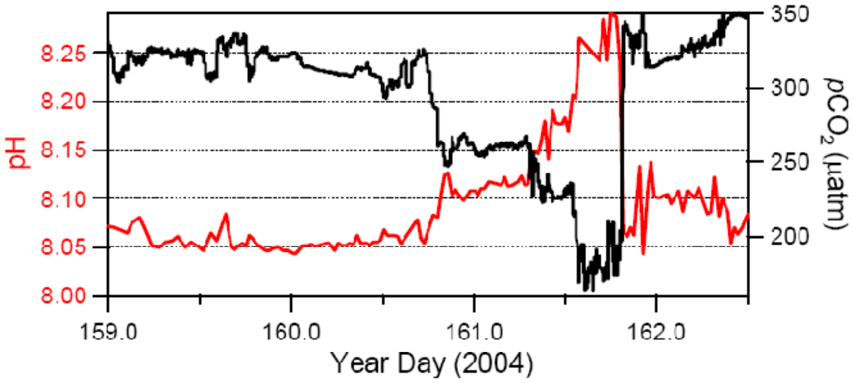
SAMI-pH

Manufactured by Sunburst Sensors



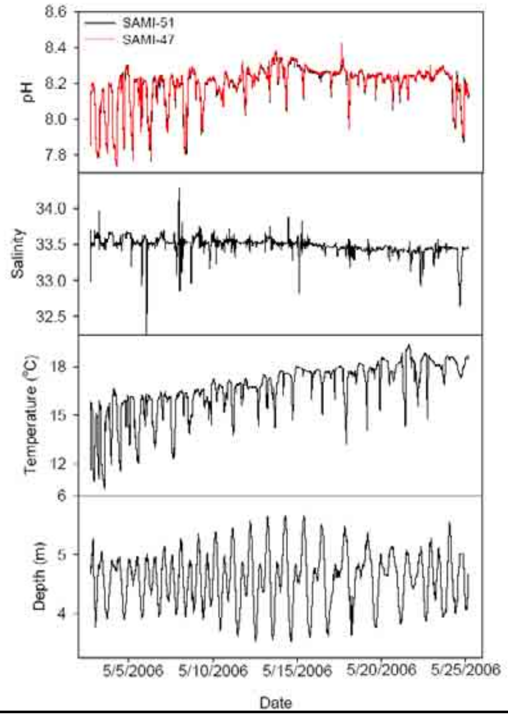
SAMI-pH sensor cell

Siedel et al., Mar. Chem. 2007



SAMI sensor in the Labrador Sea. The change of pH reached 0.25 units together with a decrease in pCO$_2$ over 150 µatm.

DeGrandpre, WHOI 2005



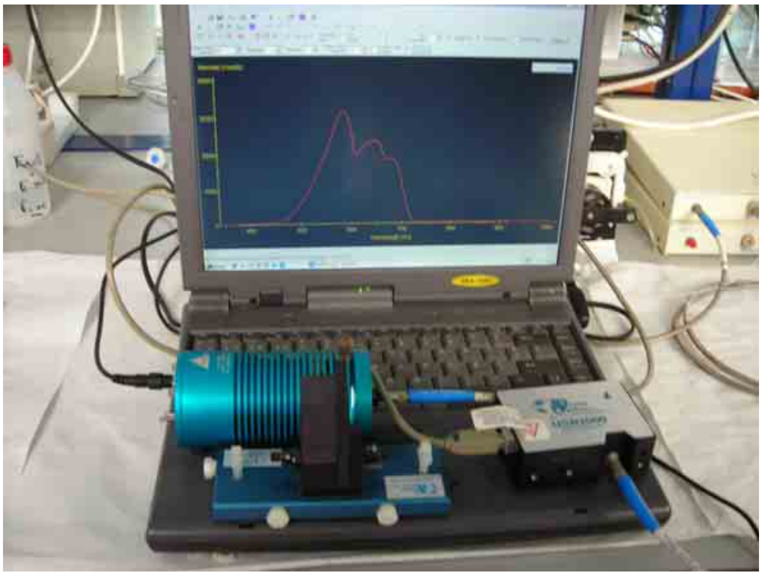
pH ranged from 8.42 to 7.74 with changes as large as 0.6 pH units over diurnal and tidal cycles.

Large lateral and vertical temperature gradients was confirmed. Temperature changes >6ºC were observed during tidal oscillations.

In-situ measurement capabilities are approaching the quality of laboratory measurements.

Siedel et al., Mar. Chem. 2007

EUROSites will include in a new ESTOC buoy a CARIOCA-pCO_2 sensor and a new pH spectrophotometric sensor developed by our group.



González Dávila et al., 2008