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# On the influence of interseasonal sea surface temperature on surface water *p*CO<sub>2</sub> at 49.0°N/16.5°W and 56.5°N/52.6°W in the North Atlantic Ocean

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The sea surface temperature (SST) and partial pressure of carbon dioxide ( $pCO_2$ ) derived from hourly *in situ* measurements at Northwest (56.5°N, 52.6°W) and Northeast (49.0°N, 16.5°W) subpolar sites of the Atlantic Ocean from 2003 – 2005 were employed to investigate the seasonal  $pCO_2$ –SST relationship. The results indicate weak to moderately strong significant negative relationships (r = -0.04 to -0.89, p<0.0001) and (r = -0.56 to -0.97, p<0.0001) between SST and  $pCO_2$  for the Northeast and Northwest observed data respectively. At the Northwestern site, the variation in surface water  $pCO_2$  might be partly controlled by the seasonal change in SST as well as biological activities and other physical processes. The variability in  $pCO_2$  distribution at the Northeastern oceanographic site were attributed principally to mixing and stratification processes during the autumn and spring seasons, while the  $pCO_2$ –SST interrelationship obtained during summertime suggested that  $pCO_2$  variability could have been induced mainly by thermodynamic effects.

**Key words:** Sea surface temperature,  $pCO_2$ , temperature effects, temperature anomalies, North Atlantic Ocean.

# INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) dominance in the atmosphere (mainly from anthropogenic sources) over other greenhouse gases has resulted in increasing pCO<sub>2</sub> in the surface ocean leading to measurably decreased pH (ocean acidification) (Canadell et al., 2007; Hopkins et al., 2010; Keeling and Whorf, 2005; Levine et al., 2008; Sabine and Feely, 2007). The world oceans are major natural sinks of atmospheric CO<sub>2</sub>. However, the North Atlantic Ocean is generally regarded as a primary gate for CO<sub>2</sub> entering the global ocean due to its subpolar climate.

In the open ocean, it has been established that significant correlation exists between surface water  $pCO_2$ 

and sea surface temperature (SST). However, the sea surface pCO<sub>2</sub>-SST relationships are primarily governed by a combination of processes, such as biological activity, transport-upwelling physical of nutrients. and thermodynamics (e.g. temperature effects on CO<sub>2</sub> dissociation and solubility) (Körtzinger et al., 2008a, b; Chen et al., 2007). Takahashi et al. (2002, 2009) have elucidated the mechanism and the role of thermodynamic effects on the uptake of  $CO_2$  by the global oceans. Recently, several studies have reported the low uptake of  $pCO_2$  in the North Atlantic Ocean suggesting a gradual weakening of an active carbon storehouse (Corbière et

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**Figure 1.** Map of the North Atlantic Ocean showing the Porcupine Abyssal Plain (49.0°N, 16.5°W) and Labrador Sea (56.5°N, 52.5°W) mooring sites.

al., 2007; Omar and Olsen, 2006; Schuster and Watson, 2007; Schuster et al., 2009; Ullman et al., 2009). The phenomenal  $CO_2$  low uptake is due to several factors including rising sea surface temperatures (Corbière et al., 2007), deep convection and re-stratification periods (Körtzinger et al., 2008a, b; Straneo, 2006) and variations in biological productivity (Behrenfeld et al., 2006; Lefèvre et al., 2004).

The role of temperature-controlled and biological processes in regulating ocean pCO<sub>2</sub> have been intensively investigated and reported (Feely et al., 2002; Friederich et al., 2008; Körtzinger et al., 2008a; Takahashi et al., 1993; 2002; Watson et al., 1991). According to Shim et al. (2007), the temporal change in surface water temperature could be a major factor that drives a seasonal variation in surface  $pCO_2$ . However, thermodynamic effect is caused by the dependence of CO<sub>2</sub> solubility and dissociation constants on temperature (Rangama et al., 2005). Many global biogeochemical cycles (notably  $CO_2$  and  $CH_4$  cycles), mediated by processes are highly biological dependent on temperature. The solubility of CO<sub>2</sub> and the dissociation of carbonic acid in seawater are moderated by temperature. It has been established that as temperature decreases the solubility of gases increases; this infers greater gas solubility for seawater in high latitudes. In this paper, observed data from two North Atlantic time series sites are employed in an attempt to assess the interseasonal sea surface temperature variations and anomalies at the eastern and western basins of the North Atlantic Ocean, and examine its effect on seasonal pCO<sub>2</sub> distribution at

these sites.

# **Description of mooring stations**

The Porcupine Abyssal Plain (PAP) observatory (Figure 1), located in the Northeast Atlantic oceanographic region is a major long-term ocean observatory operated since 1989 for international and interdisciplinary scientific research and monitoring, which are focused on physicalbiogeochemical observations. It is approximately 4800 m deep and is geographically positioned between the North Atlantic Current (NAC) and Azores Current (AC), and lies south of the main stream of the NAC, where it is subject to return flows from the West and Northwest. It is also characterized by significant presence of mesoscale eddies and deep winter mixing with strong interannual variability between 300 and 800 m (Longhurst, 2007). On the other hand, the K1 Central Labrador Sea (K1 CELAS) mooring site (Figure 1) is a deep-water formation oceanographic site of research importance that examines complex oceanic processes from surface waters to the seafloor by recording biological, chemical and physical parameters, as well as investigations of trends and variability in deep convection activity (Avsic et al., 2006).

#### METHODS AND DATA ANALYSIS

Detailed sampling and analytical procedures for SST and  $pCO_2$  data generation at the KI CELAS and PAP observatories have been

Table 1. SST and pCO<sub>2</sub> measurements, depths and time intervals at PAP and K1 CELAS stations.

Parameter	Depths measured (m)	Sensor employed	Sampling interval
Dissolved carbon dioxide	30, 40, 60, 75, 90, 110, 130, 150	Sunburst SAMI	1 h (PAP2 and K1), 2 h (PAP3, PAP4)
Temperature	0, 250, 300, 1000	MicroCat	15 min (PAP2, PAP3, PAP4), 12 h (K1)

Table 2. Geographical coordinates of PAP and K1 CELAS observatory mooring stations.

Mooring identifier	Mooring coordinates	Deployment cruise / date	Recovery cruise / date	Duration (days)	Total number of measurements
PAP-2	49.0°N 16.5°W	RV Poseidon 300 / 13-Jul-2003	RV Poseidon 306 / 03- Nov-2003	113	2679
PAP-3	49.0°N 16.5°W	Poseidon 306 / 18-Nov-2003	RSS-Charles Darwin 158 / 20-Jun-2004	213	2519
PAP-4	49.0°N 16.5°W	RSS Charles Darwin 158 / 23- Jun-2004	RSS Discovery 295 / 18-March-2005	267	6353
K1 CELAS	56.5°N, 52.5°W	15-Sept -2004	21-July-2005	310	7404



**Figure 2.** Monthly variation  $pCO_2$  and SST at PAP and K1 CELAS observatories Atmospheric CO<sub>2</sub> (cyan) is obtained from Mauna, Loa.

reported previously (Körtzinger et al., 2008a, b). These involved measurements of  $pCO_2$  with an autonomous sensor (SAMI-CO<sub>2</sub>, Sunburst Sensors LLC, Missoula, Montana, United States), while temperature measurements were carried out with an SBE-37 MicroCAT recorder (Sea-Bird Electronics Inc., Bellevue, Washington, United States). The data used in this study were obtained during three consecutive deployments between July 2003 and July 2005 for the PAP and K1 CELAS mooring stations. Details of mooring coordinates, nominal depth of deployment of sensors used, sampling interval, deployment and recovery dates, parameters measured and the total number of observational data successfully recovered are presented in Tables 1 and 2.

# **RESULTS AND DISCUSSION**

#### Distribution of surface water pCO<sub>2</sub> and SST

The distributions of sea surface temperature and  $pCO_2$  for the PAP-2 to PAP-4 deployments at the PAP and K1 CELAS time series observatories together with the atmospheric CO<sub>2</sub> are shown in Figure 2. The  $pCO_2$  distribution across the spatial gradients at both the eastern (PAP) and western (K1 CELAS) sites of the



**Figure 3.** (a) Monthly SST anomalies (°C) at the K1 Central Labrador Sea (CELAS) and Porcupine Abyssal Plain (PAP) sites between July 2003 – July 2005, (b) Monthly anomalies of  $pCO_2$  against SST monthly anomalies at the PAP site for fall/winter period (transparent red triangles) and the spring/summer period (black triangles), (c) Monthly anomalies of  $pCO_2$  against SST at the K1 CELAS site for the fall/winter period (transparent red triangles) and spring/summer period (red riangles).

subpolar North Atlantic Ocean showed distinct and consistent seasonal variability. The surface water  $pCO_2$  cycle is characteristically marked by a minimum and maximum  $pCO_2$  distribution pattern for the summertime and wintertime, respectively. It is also well depicted in Figure 2 that the  $pCO_2$  distribution patterns at both oceanographic sites are in antiphase to the temperature signal.

#### SST anomalies

The PAP and K1 CELAS monthly anomalies of SST

derived as a difference between monthly averages and the long-term mean temperatures of each oceanographic station are presented here. Negative SST anomalies (>2.5°C) were generally observed during late fall through the wintertime into springtime, whereas positive SST anomalies (<3.2°C) characterized the summertime at all the PAP sites (Figure 3a). A similar trend was observed for the K1 Central Labrador Sea data although with a relatively smaller but significant negative SST anomaly of approximately 1.36°C and high SST positive anomaly of 3.6°C (Figure 3a).

A comparison of the monthly anomalies of observed  $pCO_2$  with respect to SST anomalies at both sites are

shown in Figure 3b and c. For pCO<sub>2</sub> anomalies calculated based on average monthly observations at the PAP and CELAS sites indicate positive anomalies of K1 approximately 38 and 25 µatm respectively. These positive deviations coincided with the highest SST positive anomaly obtained for the PAP observations during spring/summer period (black triangles) Figure 3b, while it corresponded with the lowest SST negative anomaly for the K1 CELAS observed data during fall/winter period (transparent red triangles) Figure 3c. This implies that a positive  $pCO_2$ -SST relationship exists for the observed data obtained from the PAP time series site, while an inverse correlation may be established for K1 CELAS site. However, it should be noted that the pCO<sub>2</sub>-SST anomalies comparison did not suggest a clear and consistent relationship especially for the PAP location. For instance, positive pCO<sub>2</sub> deviations derived for summer and early fall of 2003 (July - October) coincided with positive SST anomalies, whereas the SST anomalies indicated an opposite behavior with marked negative  $pCO_2$  anomalies during the same period in 2004 (corresponding to 3<sup>rd</sup> PAP deployment) (Figure 3b). This variation might be attributed to thermodynamic effect or other physical processes such as mixing and stratification that might have resulted in negative pCO<sub>2</sub> anomalies with corresponding positive SST anomalies. Moreover, for the winter / springtime, positive pCO<sub>2</sub> anomalies at the PAP site are generally associated with significant negative SST anomalies which suggest biologically driven  $pCO_2$ variability. Negative SST anomalies are usually associated with enhanced nutrient and dissolved inorganic carbon (DIC) inputs, which could invariably lead to increase in primary productivity (Borges et al., 2007; Boyd et al., 2001).

#### Dependence of surface water pCO<sub>2</sub> on temperature

# Correlation between pCO<sub>2</sub> and SST

The Pearson correlation analysis were carried out to establish the inter-annual / inter-seasonal relationships between observed  $pCO_2$  and SST data obtained from the PAP and K1 CELAS sites. More so, given the large number of data, the interseasonal test of linear fits between  $pCO_2$  and SST were evaluated based on average monthly data collated from hourly measurements. The derived linear fits generally indicated strong but negative correlations between  $pCO_2$  and SST.

#### Correlation between pCO<sub>2</sub> and SST at PAP site

Figures 4a, b and c show the results of fitting linear model to describe the relationship of observed PAP site  $pCO_2$  as a function of sea surface temperature for the second (PAP2), third (PAP3), and forth (PAP4) deployments on an annual timescale.

A better mechanistic understanding of how changes in SST and other processes may have influenced sea surface pCO<sub>2</sub> was evaluated using seasonal observed data during each deployment. Sea surface pCO2-SST correlations generally showed negative correlations between these two variables ( $r^2 = 25.85$ , 74.13, 5.75, p < 0.0001) (Figures 4a to c) at the PAP site suggesting that SST had a non-dominance influence on  $pCO_2$  variability. This also suggests that a large part of the observed variation may be attributed to non thermal processes such as the enhanced biological activity associated with physical transport - upwelling of nutrient enriched water into the euphotic zone, mixing or stratification. This argument is supported by the derived pCO2-SST correlations for summer - fall 2003 observed data that characteristically indicated a strong influence of SST on  $pCO_2$  variability (Table 3). It should be noted however, that changes in sea surface temperature principally influenced the surface water  $pCO_2$  cycle at the PAP site during deployments in 2004 to 2005, with insignificant biological effect except during wintertime. In general, the correlations between temperature and pCO<sub>2</sub> based on observed data suggest that pCO<sub>2</sub> seawater patterns in the Northeast subpolar Atlantic Ocean is due to the counteracting effects of temperature, mixing and strong to moderate biological production. This observation is consistent with earlier reports by Körtzinger et al. (2008a) and Takahashi et al. (2002, 2009).

# Inter-relationship between pCO<sub>2</sub> and SST at Labrador sea site

Figure 5a and b illustrate the relationships of  $pCO_2$  as a function of SST during the period. A closer inspection of the derived linear fits reveal that the sea surface  $pCO_2$ -SST correlations were characteristically more variable and generally depicted the irrefutable effect of temperature and biology on  $pCO_2$ , although it is clear that the  $pCO_2$  cycle is strongly governed by thermodynamic forcing than biological effect. The  $pCO_2$ -SST correlation obtained for observed data during the deployment in 2004 indicated that there is a good linear relationship between sea surface  $pCO_2$  and in-situ SST (Table 3).

A similar relationship was found for sea surface  $pCO_2$ -SST correlations obtained for 2005 K1 deployment, but with a moderately strong relationship ( $r^2 = 0.53$ , p<0.0000) (Figure 5b). On an annual to seasonal timescale, the distribution pattern in surface seawater  $pCO_2$  might not be controlled by a seasonal change in temperature only but also by biology as well as mixing within the subsurface and stratification of the epipelagic zone of the K1 CELAS site (Körtzinger et al., 2008b).

However, it is obvious that the thermodynamic effects and other physical processes are the dominating variability driver compared to weak biology signature at



**Figure 4.** Distributions of  $pCO_2$  as a function of SST during PAP2 (a), PAP3, (b) and PAP4 (c) deployments.

Table 3. PAP and K1 CELAS seasonal pCO<sub>2</sub> distributions as a function of SST.

Time series location	Season	Correlation equation for <i>p</i> CO <sub>2</sub> (µatm)/SST (°C)	Correlation Coefficient (r)	Coefficient of determination (R <sup>2</sup> ) %
РАР	Summer (July-August) 2003	<i>p</i> CO <sub>2</sub> = -23.49×SST + 645.54	-0.80	64.28
	Fall 2003	$pCO_2 = -7.09 \times SST + 427.26$	-0.66	43.48
	Winter 2004	<i>p</i> CO <sub>2</sub> = -11.88 × SST + 469.58	-0.72	51.29
	Spring 2004	<i>p</i> CO <sub>2</sub> = -24.97 × SST + 615.49	-0.60	35.45
	Summer 2004	<i>p</i> CO <sub>2</sub> = -12.30 × SST + 430.95	-0.87	75.37
	Fall 2004	$pCO_2 = -8.52 \times SST + 374.36$	-0.89	79.49
	Winter 2005	<i>p</i> CO <sub>2</sub> = -26.65 × SST + 616.52	-0.85	71.69
	March (Early Spring) 2005	<i>p</i> CO <sub>2</sub> = -1.65× SST + 308.19	-0.04	0.16
	Fall 2004	<i>p</i> CO <sub>2</sub> = -9.65×SST + 395.45	-0.97	93.87
	Winter 2005	<i>p</i> CO <sub>2</sub> = -27.00×SST + 462.18	-0.81	65.27
K1 CELAS	Spring 2005	<i>p</i> CO <sub>2</sub> = -49.69×SST + 543.54	-0.87	75.74
	Summer (July-August) 2005	<i>p</i> CO <sub>2</sub> = -11.54×SST + 399.29	-0.56	31.18



**Figure 5.** Distributions of  $pCO_2$  as a function of SST at the Northwest Labrador Sea in 2004 (a), and 2005 (b) K1 deployments.

this subpolar NW Atlantic site. A comparison of the seasonal sea surface pCO2-SST correlations at the K1 CELAS site also reveal significant but negative correlations between these two parameters during autumn 2004 and spring 2005. This implies that other physical processes such as turbulence, mixing and stratification primarily govern the variability in  $pCO_2$ distribution. On the other hand, the  $pCO_2$ -SST correlation obtained for summer 2005 indicates a positively correlation significant implying that mainly thermodynamic effects induce pCO<sub>2</sub> variability. A summary of pCO<sub>2</sub>-SST relationships at both the Northeast and Northwest sites of the Atlantic Ocean is presented in Table 3.

# **CONCLUDING REMARKS**

This study has demonstrated that the surface water pCO<sub>2</sub>

distribution across the spatial gradients over a seasonal timescale at both the eastern (PAP) and western (K1 CELAS) basins of the subpolar North Atlantic Ocean is relatively consistent, however with distinct seasonal large variability. At the PAP site, consistent undersaturation of oceanic surface water was observed relative to the atmospheric CO<sub>2</sub>, while a similar trend occurred over the western area at the K1 CELAS location but with some degree of supersaturation between February and March 2005. On a seasonal timescale, the surface water  $pCO_2$ cycle is characteristically marked by minimum and maximum  $pCO_2$  distribution pattern for the summertime and wintertime respectively. It is obvious that the  $pCO_2$ distribution pattern in the NE PAP and NW CELAS sites of the subpolar North Atlantic were in antiphase to the temperature signal. Investigation of sea surface pCO2-SST correlations generally indicated moderate to strong but negative correlations between  $pCO_2$  and SST. Thus we conclude that the variation in surface ocean  $pCO_2$ 

may not be controlled by change in sea surface temperature only, but by biological activities and other physical processes. In the Northeastern basin, the variability in  $pCO_2$  distribution is primarily governed by other physical processes such as mixing and stratification during the autumn and springtime, while the  $pCO_2$ -SST relationship obtained for summertime indicates that  $pCO_2$ variability is induced mainly by thermodynamic effects.

# **Conflict of Interest**

The authors have not declared any conflict of interest.

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