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Dissolved Carbon Dioxide in Tropical East Atlantic Surface Waters

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Abstract - Variability of dissolved inorganic carbon (DIC) and the fugacity of carbon dioxide ($f\text{CO}_2$) is discussed for tropical East Atlantic surface waters in October–November 1993 and May–June 1994. High precipitation associated with the Intertropical Convergence Zone, river input and equatorial upwelling affected the content of DIC and $f\text{CO}_2$ of these tropical surface waters. Individual hydrographic regions had a characteristic CO_2 -chemistry. © 1999

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1 Introduction

Air-sea exchange of carbon dioxide (CO_2), F , is driven by a concentration difference of CO_2 across the air-water interface (Liss and Slater, 1974):

$$F = k_w ([\text{CO}_{2\text{T}}]_{\text{bulk}} - K'_0 f\text{CO}_{2\text{air}}) \quad (1)$$

As the fugacity of CO_2 in marine air ($f\text{CO}_{2\text{air}}$) is relatively constant, the exchange is mainly determined by changes in the transfer velocity (k_w), the solubility of CO_2 (K'_0) and the concentration of dissolved CO_2 in bulk surface water, $[\text{CO}_{2\text{T}}]_{\text{bulk}}$.

Variability of dissolved inorganic carbon (DIC) and $f\text{CO}_2$ are investigated for tropical East Atlantic surface-waters. The data were obtained during the southward cruise ANT XI/1 in October–November 1993 and the northward cruise ANT XI/5 in May–June 1994 at R.V. *Polarstern* (Fig. 1). During ANT XI/1 an eastward excursion was made towards the mouth of the Congo River.

2 Methods

Water from 12 m depth was introduced into an equilibrator. Samples from the headspace of the equilibrator and marine air collected at 30 m above sea level were dried with silicagel. Every 18 minutes a gas chromatograph analysed the CO_2 -content of three calibration gases, marine air and the headspace of the equilibrator. Calibration gases (BOC, UK) had been calibrated against NOAA certified standard gas mixtures. A correction was made for the temperature difference between *in situ* seawater and water in the equilibrator (Copin-Montégut, 1988, 1989).

The DIC-content of water from 12 m depth was measured every 10 minutes by a coulometer (Stoll, 1994) adapted for semi-continuous operation. The coulometer was calibrated every three days against standards provided by Dr. A.G. Dickson (DOE, 1994). Recovery was 98.7 % to 98.8 %.

Temperature and salinity of water at 12 m depth were recorded by the ship's online data acquisition system. Air temperature, humidity and atmospheric pressure were determined at 25 m above sea level.

3 Results

A maximum of surface water temperature was observed north of the equator and in the region of the Congo outflow (XI/1) (Fig. 2a). Temperatures between 10° and 20° latitude were lower in spring than in autumn.

Salinity, DIC and $f\text{CO}_2$ had relatively low values in a 'Low Salinity Region' (LSR) for 2.0°–10.0°N (XI/1) and 0.6°–8.0°N (XI/5) (Fig. 2). The region with low salinity shifted towards the equator between cruises. Within the LSR at 5.22°N 16.45°W salinity increased from the sea surface to 40 m depth, while temperature remained constant (XI/5) (Fig. 3).

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Fig. 1. Cruise tracks of the southward cruise ANT XI/1 in October–November 1993 and of the northward cruise ANT XI/5 in May–June 1994 at R.V. *Polarstern*.

A minimum of surface water temperature, a maximum of salinity and DIC, slightly elevated nitrate contents and fluorescence were encountered at 0.3° – 2.0° S in October–November 1993 and at 0.6° N– 2.0° S in May–June 1994 (Fig. 2) and indicated recent or active equatorial upwelling.

Surface water salinity, DIC and $f\text{CO}_2$ were highly variable for 0° – 5° S in the Gulf of Guinea during ANT XI/1, probably as the result of coastal and equatorial upwelling and westward advection of river water along the South Equatorial Current (Dessier and Donguy, 1994). Low salinity and DIC delineated the Congo outflow for 4.7° – 8.5° S (XI/1).

4 Discussion

The temperature maximum north of the equator agrees with seasonal temperature charts (Philander, 1986; Peterson and Stramma, 1991; Reid, 1994) and with the mean position of the thermal equator within the Inter-tropical Convergence Zone (ITCZ) (Tchernia, 1980; Tomczak and Godfrey, 1994). High salinity of (sub-)tropical surface water reflects high evaporation along the North and South Equatorial Currents (NEC, SEC) (Tomczak and Godfrey, 1994).

High rainfall related to the ITCZ results in low surface water salinity north of the equator (Dessier and Donguy, 1994). The displacement of the LSR between cruises is related to the southward shift of the ITCZ in northern winter, which precedes the southward movement of the region with low surface salinity by two months (Dessier and Donguy, 1994). The gradual increase of salinity from

Fig. 2. The latitudinal distribution of (a) surface water temperature, (b) salinity, (c) dissolved inorganic carbon (DIC) and (d) the difference in $f\text{CO}_2$ between surface water and marine air, $\delta f\text{CO}_2(\text{w-a})$, for the cruises ANT XI/1 in October–November 1993 (thick line) and ANT XI/5 in May–June 1994 (thin line). The abbreviations are: ED – Equatorial Divergence, LSR – Low Salinity Region.

Fig. 3. Vertical profiles of (a) water temperature and (b) salinity at 5.22°N 16.45°W on 1 June 1994 (ANT XI/5).

Fig. 4. (a) The surface-water content of dissolved inorganic carbon (DIC) as a function of salinity for 20°N to 20°S during ANT XI/1. (b) Linear regression lines between surface water DIC and salinity for the northern ($\square$) and southern ($\blacksquare$) edge of the Low Salinity Region and for the Congo outflow (open triangles) (after Bakker *et al.*, 1999).

0 to 40 m depth at 5.22°N 16.45°W (XI/5) supports the theory of progressive dilution of surface water by rainwater in the absence of wind mixing. It is unlikely that the North Equatorial Countercurrent (NECC) has advected low salinity water from the Amazon outflow as far east as 24°W (Dessier and Donguy, 1994). In June–August 1986

similar strong salinity gradients occurred between surface water with high salinity (> 36.2) in the Guinea Dome (10°–14°N 25°W, 12°N 22°W) and water with low salinity (< 35.4) towards the south in the NECC (Oudot, 1989). Regional salinity charts indicate a latitudinal band of low salinity water north of the equator in the East Atlantic

Table 1. Linear regression between dissolved inorganic carbon (DIC) and salinity (S) in surface water with the equation $DIC = aS + b$ for the northern and the southern edge of the Low Salinity Region and the Congo outflow during ANT XI/1 (after Bakker *et al.*, 1999). Symbols indicate the correlation coefficient (*r*), the standard deviation (σ_{a-1}) and the number of data points (#).

Latitude	a	b	r	σ_{a-1}	#
	($\mu\text{mol kg}^{-1}$)	($\mu\text{mol kg}^{-1}$)		($\mu\text{mol kg}^{-1}$)	
7.5°N - 15.0°N	99.3	-1575	0.97	8.6	254
1.0°S - 4.0°N	95.5	-1415	0.99	5.5	208
5.0°S - 10.0°S	54.0	109	0.96	14.1	149

Ocean, but do not suggest the observed strong horizontal salinity gradients on its edges.

Dilution of (sub-)tropical seawater with a salinity of 36.1 with rainwater to a salinity of 35.1 decreases DIC by 55 to 64 $\mu\text{mol kg}^{-1}$ and $f\text{CO}_2$ by 14 to 18 μatm (Bakker *et al.*, 1999). The calculated decrease of $f\text{CO}_2$ by dilution with rainwater is counteracted by a simultaneous increase of temperature by 1.9°C for the LSR. Observed DIC and $f\text{CO}_2$ are well below estimated values for conservative mixing of adjacent (sub-)tropical surface water and rainwater (Bakker *et al.*, 1999).

Two mixing lines with the equations:

$$DIC = 99.3 S - 1575 \quad (2)$$

$$DIC = 95.5 S - 1415 \quad (3)$$

can be distinguished between surface water in the Low Salinity Region and adjacent (sub-)tropical water with high salinity (Table 1). Both the negative offset on the y-axis of these mixing lines and the low observed values of $f\text{CO}_2$ and DIC in the LSR relative to values calculated for conservative mixing indicate that either adjacent (sub-)tropical surface water is not the seawater endmember involved in the mixing with rainwater or that an additional process has changed DIC and $f\text{CO}_2$. Upwelling at the equator or in the divergence between the NECC and the NEC may have increased DIC and $f\text{CO}_2$ of the high salinity water after the mixing took place. Biological uptake of CO_2 may have decreased DIC and $f\text{CO}_2$ in the LSR. Although the observed fluorescence was low, ocean colour observations indicate seasonal algal blooms at 5°-10°N (Longhurst, 1993).

Surface water with low salinity and $f\text{CO}_2$ was previously encountered at 4°-6°N 17°W-20°W in June-July 1986 in the convergence between the NECC and SEC (Oudot and Andrié, 1989). Other observations of low salinity water with low $f\text{CO}_2$ were made in October 1995 by Lefèvre *et al.* (1998), who ascribed the low $f\text{CO}_2$ to high precipitation and biological uptake of CO_2 .

Similar to our measurements mean surface water $f\text{CO}_2$ at 22°W was lower for 0°-5°N than for 0°-5°S in January-February 1983-84 and July-August 1982-84 (Andrié and Oudot, 1989). Andrié and Oudot (1989) conclude that high $f\text{CO}_2$ south of the equator results both from equatorial upwelling south of the equator (Keeling, 1968) and subsequent warming of the water in the westward flow of the SEC. The decrease of DIC and $f\text{CO}_2$ by high precipitation and biological uptake of CO_2 north of the equator contributes to meridional differences of DIC and $f\text{CO}_2$.

A mixing line with the equation:

$$DIC = 54.0 S + 109 \quad (4)$$

can be distinguished between water in the Congo outflow and adjacent surface water (Fig. 4, Table 1). The equation suggests that Congo water has an average DIC-content of 109 $\mu\text{mol kg}^{-1}$, neglecting DIC-changes after the water entered the ocean.

The latitudinal distribution of DIC was closely related to that of salinity. An eventual effect of temperature on DIC was overshadowed by strong salinity changes in the (sub-)tropical surface waters. Rainfall, evaporation, equatorial upwelling and biological uptake of CO_2 affected $f\text{CO}_2$ and DIC of tropical surface waters. These processes, which are governed by ocean circulation and the tropical climate system, leave such a strong imprint on surface-water CO_2 -chemistry that individual hydrographic regions have specific CO_2 -characteristics.

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