Partial pressure and air–sea flux of CO₂ in the Northeast Atlantic during September 1995

R.S. Keir*, G. Rehder¹, M. Frankignoullé

*GEOMAR, Wischhofstraße 1-3, D-24148 Kiel, Germany
¹Mécanique des Fluides Géophysiques, Unité d’Océanographie Chimique (B5), Université de Liège, B-4000 Sart Tilman, Belgium

Abstract

Previous work has shown that during early summer, the partial pressure of CO₂ ($p_{CO_2}$) in surface waters north of about 45°N in the Atlantic exhibits widespread undersaturation. In many areas, this follows after a “spring bloom” of phytoplankton, at which time, nutrient concentrations and $p_{CO_2}$ decrease sharply from their winter surface values. As part of OMEX I, the late summer distribution of surface water $p_{CO_2}$ was surveyed in the northeastern Atlantic on cruises of R/V Poseidon and R/V Belgica in 1995. The pattern of the surface distribution of the sea–air $p_{CO_2}$ difference ($\Delta p_{CO_2}$) measured on these ship surveys was generally in accord with that observed in this area in early to mid-summer of 1981. The greatest CO₂ undersaturation ($-95\mu atm$) during our surveys was observed near the west coast of Iceland, with $\Delta p_{CO_2}$ increasing to about $-60\mu atm$ away from the coast. In shelf waters south of Ireland, the $p_{CO_2}$ was relatively higher than in surface waters of the open ocean adjacent to the Celtic Shelf margin, but the Celtic Shelf waters were still undersaturated relative to the atmospheric CO₂ concentration. Because of the variation of wind speed, the synoptic distribution of air–sea CO₂ flux, derived from the transfer velocity and $\Delta p_{CO_2}$, does not resemble the distribution of $\Delta p_{CO_2}$ itself. The sharp increase in wind speed at about 53°N, 20°W during the R/V Poseidon survey produces an order of magnitude rise in the estimated air–sea flux of CO₂, to a level of about 10–14 mol m⁻² a⁻¹. The overall synoptic picture appears to be one of moving centers of higher air–sea fluxes that occur where storms pass over regions of surface water $p_{CO_2}$ undersaturation. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

As part of the Ocean Margin EXchange project (OMEX), surveys of the distribution of surface water and air CO₂ partial pressures were conducted in the northeastern Atlantic. The open...
northern Atlantic appears to be a natural sink for atmospheric CO$_2$ because of the cooling of poleward-transported surface water, which subsequently sinks and forms deep water (Volk and Liu, 1988; Keir, 1993). However, the process is complicated by a very strong seasonal oscillation in surface water partial pressure (pCO$_2$) due to variation in the biological pump (Takahashi et al., 1985, 1993). During the spring phytoplankton bloom, the CO$_2$ partial pressure decreases sharply in the mixed layer, which becomes highly undersaturated with respect to atmospheric CO$_2$. In the following months, the mixed layer pCO$_2$ increases only slowly, apparently due to warming and later vertical mixing as well as uptake from the atmosphere. As a result, low pCO$_2$ tends to persist in the northern Atlantic in summer, when surface water temperatures are relatively warmer, and higher pCO$_2$ prevails in winter, when temperatures are cold but total CO$_2$ and nutrient concentrations are higher in the surface due to convection and vertical mixing.

It appears that undersaturation of the surface water is widespread in the northern Atlantic in summer. This was indicated by measurements on discrete samples during the transient tracers in the ocean (TTO) survey in 1981 (Takahashi et al., 1993). Subsequent higher resolution surveys using continuous underway equilibrator methods confirm this picture (see Takahashi et al., 1995; Lefèvre, 1997 for summaries). Equilibrator studies along 20°W between 50°N and 60°N indicate that the spring drawdown in surface pCO$_2$ is time-transgressive (Watson et al., 1991; Schneider et al., 1992; Schneider and Morlang, 1995). At 50°N, the decrease in pCO$_2$ begins in late April or early May, whereas at 60°N, most of the pCO$_2$ decrease appears to occur at the end of May to early June. Thus, during the early phase of the spring bloom, only a weak undersaturation may occur at 60°N, 20°W, with the surface water pCO$_2$ decreasing southward (Watson et al., 1991). By summer, the northward migration of the bloom results in the entire region being significantly undersaturated relative to atmospheric CO$_2$.

Our pCO$_2$ surveys were conducted on R/V Poseidon and R/V Belgica in September 1995, in the northeast Atlantic roughly between Iceland and the Iberian margin, including the shelf waters of the Celtic Sea. This gives a quasi-synoptic picture of the late summer situation, which we compare to the distribution observed 14 years earlier, derived from TTO. Fig. 1 indicates the cruise tracks of our surveys in relationship to the summer 1981 distribution of the sea-to-air pCO$_2$ difference, ΔpCO$_2$ (Takahashi et al., 1993). The TTO measurements were made one or two months earlier in the season than our surveys, from late June to early July, south of 60°N along the R/V Poseidon line and during the second week of August, west of Iceland.

2. Methods

2.1. CO$_2$ partial pressure

Continuous underway measurements were made on R/V Poseidon and R/V Belgica using two different designs of CO$_2$ equilibrator. Both consist of a continuous flow of seawater through a gas–liquid exchanger in which a closed loop of air is circulated. In both systems, the mole fraction of CO$_2$ in dry gas was measured using a single standard gas calibration. The two systems have been calibrated in subsequent work using two standard gases. These calibrations show that the response of both systems are linear in the range of at least 330–400 ppmV. The equilibrator used on R/V Poseidon consists of bubble exchange with seawater in a lower chamber followed by
further exchange of the air, as it continues upward into a glass column with the counter current flow of seawater down the inner wall of column (Körtzinger et al., 1996). A small volume of air is periodically shunted out of the loop into a gas chromatograph where the CO$_2$ is catalytically

Fig. 1. Ship tracks of R/V Poseidon (Cruise P211, 31 August to 11 September) and R/V Belgica (Cruise BG95/21-22, 13–27 September). Contours show the distribution of air–sea pCO$_2$ difference in μatm during late June to early August 1981, as given by Takahashi et al. (1993). Negative values indicate the surface ocean is undersaturated with respect to atmospheric CO$_2$. The diamonds indicate TTO stations that are within about 140 km of the R/V Poseidon track.
converted to methane, which is measured by flame-ionization detection. A mixture of 361.1 ppmV CO₂ in natural air (Deuste Steiniger GmbH) was used for calibration. The gas chromatograph cycles automatically through a series of gas inputs from the equilibrator, the standard gas, and air from outside the ship for atmospheric measurements. The intake for the atmospheric samples was located forward over the bridge. The sequence of measurements was set to produce a measurement of equilibrator gas every 20 min and an air sample every 40 min. The reproducibility of calibration gas measurements was ±1.8 ppmV. The system is described in more detail in Rehder (1996) and Rehder and Suess (2001).

The equilibrator used on R/V Belgica consists of a Plexiglas cylinder (height: 80 cm, diameter: 10 cm) filled with marbles to increase the exchange surface area (Frankignoulle et al., 2001). Seawater flows through the equilibrator from the top to the bottom at a rate of 3 l/min, and air in the closed loop circulates countercurrent to the water at a similar flow rate up the column. The CO₂ concentration in the circulating air is measured every minute with an infra-red spectrophotometer (Li-Cor 6262). The system was calibrated with a certified dry mixture of 350 ±1 ppmV CO₂ in nitrogen, provided by Air Liquide Belgium. Based on the deviation from the zero intercept in pure N₂ gas, the estimated precision is ±1 ppmV for the Li-Cor.

CO₂ partial pressures in the surface water and in air were calculated assuming 100% saturation for the water vapor pressure (P_vap) according to \( p_{CO_2} = X_{CO_2}(P_{tot} - P_{vap}) \), where \( P_{tot} \) is the total gas pressure and \( X_{CO_2} \) the measured mole fraction of CO₂ in the dry gas sample. The seawater \( p_{CO_2} \) values were then corrected for the temperature difference between the in situ seawater and water in the equilibrator using the algorithms of Takahashi et al. (1993) for R/V Poseidon data and Copin-Montégut (1988) for R/V Belgica data. The temperature difference between the equilibrator and in situ surface water was always less than 1°C due to the rapid throughflow rates, and in this temperature range, the correction from either of these algorithms is small and consistent with the other.

2.2. Flux estimation from \( \Delta p_{CO_2} \) and wind speed

The net flux of CO₂ across the interface is estimated according to the product of the dissolved aqueous CO₂ concentration difference across a thin layer at the sea surface and a transfer velocity, \( k \). The concentration difference is taken to be proportional to the CO₂ partial pressure difference (\( \Delta p_{CO_2} \)) between the atmosphere and the bulk seawater in the surface mixed layer, and this difference is directly observed. The air-to-sea flux, \( F_{as} \), is then given by \( F_{as} = k \Delta p_{CO_2} \), where \( k \) is the CO₂ solubility in seawater at a given temperature and salinity.

The transfer velocity, \( k \), is inversely related to the resistance of the gas molecules to transport across the air–sea interface. The transfer velocity cannot be observed directly, but it is known from wave tank experiments that this quantity increases with wind shear at the surface as well as other physical properties such as water turbulence. For the purpose of estimating the local net CO₂ flux, an empirical relation between wind speed and the transfer velocity is employed. This relationship is derived in principle from the shape of transfer velocity versus wind speed in laboratory experiments together with calibration to field observations. Several of these relationships are summarized by Wanninkhof (1992), who also discusses in detail the factors involved. Additional functions have been put forward since then, most recently by Wanninkhof and McGillic (1999), who suggest a cubic relationship between the transfer velocity and wind...
speed. In this work, we have calculated the net air–sea CO\textsubscript{2} flux according to the widely used Wanninkhof (1992) relationship between short-term wind speed and transfer velocity. This relationship is calibrated to the radiocarbon-determined CO\textsubscript{2} exchange fluxes both in the global ocean and in the Red Sea together with an estimate of the effect of variance around the long-term average wind speed. Fig. 1 of Wanninkhof and McGillis (1999) shows that the different algorithms diverge in their estimate of the transfer velocity at high wind speeds, differing by more than a factor of three at wind speeds around 20 m s\textsuperscript{–1}. The transfer velocity predicted by the Wanninkhof (1992) relationship at higher wind speeds is in between his more recent estimate and, for example, the Liss and Merlivat (1986) relationship, which appears to give a better fit to a number of radon measurements and dual tracer data.

3. Distribution of surface pCO\textsubscript{2}

The distribution of sea–air ΔpCO\textsubscript{2} disequilibrium along the track of the R/V Poseidon is shown in Figs. 2 and 3. In comparing our results to the earlier TTO data, we have not attempted to correct the ΔpCO\textsubscript{2} between 1981 and 1995 for any effects of the rise in atmospheric CO\textsubscript{2} concentration, which is about 20 ppmV during this time interval. As discussed by Takahashi et al. (1995), the CO\textsubscript{2} partial pressure in low-latitude surface waters is expected to nearly keep up with the rise in atmospheric CO\textsubscript{2}, and ΔpCO\textsubscript{2} in these waters should be almost independent of anthropogenic effects. However, in high-latitude regions where deep mixing and deep water formation occur, the lag in the surface water pCO\textsubscript{2} rise as compared to the atmosphere could be considerable. The effect of such a lag would be to increase the undersaturation of the surface water over time, in the extreme case by as much as about −19 μatm in the 14-year interval if the surface water pCO\textsubscript{2} simply did not increase at all in response to the atmosphere. The actual effect is likely quite a bit less because the vertical overturn is diluted by the northward horizontal transport of low-latitude surface water to high latitudes. Since it is not possible to quantitatively estimate the anthropogenic effect along the cruise track, we simply compare the ΔpCO\textsubscript{2} found at the two time periods. In principle, this represents the sum of natural and anthropogenic effects.

In general, the distribution of sea–air CO\textsubscript{2} disequilibrium that we observed in September 1995 is similar to the pattern observed during the late June to early August period in 1981. South of 60°N to about 50°N, 15°W, the track of R/V Poseidon ran approximately parallel to the ΔpCO\textsubscript{2} isolines in the summer of 1981 (Fig. 1). We observed an approximately constant ΔpCO\textsubscript{2} of about −55 μatm in this general region, between 63°N and 53°N (Fig. 2a). This is slightly more undersaturated than indicated by the TTO map (−45 μatm, Fig. 1). Southward and eastward of 50°N, 15°W, the sea–air pCO\textsubscript{2} disequilibrium diminishes in summer according to the TTO map (Fig. 1), and our observations are in agreement with this pattern (Fig. 2a). Southeastwards from 44.5°N, 12°W and then southwards along the Iberian coast, the horizontal gradient in ΔpCO\textsubscript{2} that we observed appears to be greater than observed during TTO. Off of Cape Finisterre (43°N), the ΔpCO\textsubscript{2} measured on R/V Poseidon had already risen to 0 μatm, and by 38.5°N off of Lisbon, we measured an oversaturation of about +20 μatm. These values appear to be systematically higher than observed in late June of 1981 (Fig. 1), but qualitatively, the distribution is similar.

On the R/V Poseidon track to the west of Iceland at about 64°N, we observed a roughly constant ΔpCO\textsubscript{2} of about −60 μatm west of 26°W (Fig. 3a). This is consistent with the TTO
picture (Fig. 1) and with the compilation shown in Takahashi et al. (1995). In September 1995, the surface water $pCO_2$ decreased to the east of 26°W, and the largest $\Delta pCO_2$ ($\sim 95 \mu atm$) was observed near Iceland. This may be due to a late summer phytoplankton bloom in this area.

One other consideration in comparing the $\Delta pCO_2$ distributions is how similar the distribution of water masses may have been at the two different times, particularly in regard to sea-surface temperature. In Fig. 2c, we compare the near-surface temperatures at individual TTO stations within 140 km of the R/V Poseidon track (see Fig. 1) with the ship's thermosalinograph temperature record. This comparison indicates that at the ends of the north-south line, the surface
Fig. 3. (a) Air–sea $\Delta pCO_2$ difference versus longitude westward from Iceland (segment A–B shown in Fig. 1). (b) Net air–sea CO$_2$ flux, calculated from $\Delta pCO_2$ and wind speed on this segment.
temperatures were similar, whereas in the middle, especially between 45°N and 50°N, the surface temperatures were warmer by 2–3°C in early September 1995 than in early July 1981. Despite the somewhat warmer temperatures around 50°N, the ΔpCO₂ in July 1981 and September 1995 appears to be similar.

It is interesting to compare the pattern of the temperature increase from north to south (Fig. 2c) observed on R/V Poseidon to that of the increase in ΔpCO₂ (Fig. 2a). Since the atmospheric CO₂ varies relatively little, the increase in ΔpCO₂ mainly reflects the increase in surface water pCO₂. If this increase were mainly due to the temperature effect on CO₂ solubility under conditions of constant total dissolved inorganic carbon and alkalinity, the pattern of the pCO₂ and temperature increases would be similar. Although the overall magnitude of the ΔpCO₂ increase from north to south (80 μatm in Fig. 2a) roughly corresponds to the decrease in solubility due to the observed 10°C increase in sea-surface temperature (Fig. 2c), the patterns of these two increases are not the same. The temperature increase “precedes” the pCO₂ increase as one proceeds southwards, the former increase mostly occurring between 62°N and 53°N and the latter from about 53°N to the end of the line at 39°N. This may be due to relatively greater net biological production during the previous months in the latitudes around 50°N than to the north or south.

At about 50°N, the TTO data indicate an eastward increase in pCO₂, starting from about 17°W to the shelf margin (Fig. 1). We observed a similar horizontal gradient in this area; in addition, our observations on R/V Belgica extend eastward over the Celtic Shelf. Although there is significant small scale variability in the pCO₂ of the shelf waters, the general picture is that on the Celtic Shelf, the pCO₂ is relatively constant between about 320 and 335 μatm, and the decrease in pCO₂ to the west begins roughly at the shelf edge (Fig. 4). West of about 7°W, the profile of pCO₂ along about 49.8°N that we observed in September 1995 is quite similar to the distribution observed by Körtzinger (1995) along a similar track in mid-October, 1994 (Fig. 5). It appears that

![Fig. 4. Distribution of CO₂ partial pressure at OMEX I area (Celtic Shelf margin). Color scale shows the pCO₂ along the ship tracks in μatm. The contours show the general distribution as interpreted from this data. The shelf edge is indicated by the 200 m isobath.](image-url)
the $p$CO$_2$ of these shelf waters in late summer/early fall is somewhat higher than in the open ocean to the west, but still undersaturated relative to an uncontaminated atmospheric CO$_2$ mole fraction (354 ppmV). The actual atmospheric CO$_2$ concentration in the Celtic Shelf region may be influenced by industrial production on land and thus vary according to the wind direction, as indicated by the CO$_2$ higher values observed by Körtzinger (1995). Recent work indicates that surface waters on the Celtic and Armorican shelves undergo a significant seasonal oscillation, with the $p$CO$_2$ rising to near equilibrium with the atmospheric mixing ratio in winter (Frankignoulle and Borges, in press). At the time of our surveys in September 1995, the relatively constant $p$CO$_2$ in the shelf waters was bounded on the east by quite high $p$CO$_2$ (400 µatm) in the waters near Brittany (Fig. 4). This is consistent with previous observations which indicate that high CO$_2$ partial pressures appear throughout most of the English Channel in September (Frankignoulle et al., 1996) and October (Körtzinger, 1995).

4. $\Delta p$CO$_2$-based air–sea flux distribution

Surface water $\Delta p$CO$_2$ and the net air–sea flux derived from this quantity and transfer velocity for the R/V Poseidon cruise are compared in Figs. 2 and 3. Due to the large variation of the wind speed during the cruise, the variation in the estimated net CO$_2$ flux does not follow the pattern of the $\Delta p$CO$_2$ distribution. This is particularly noticeable at 52°N on the north-south leg (Figs. 2a and b), where the ship approached a strong low pressure centered over the Celtic Shelf and the wind speed increased sharply. Here, the air-to-sea flux is calculated to increase to about 14 mol m$^{-2}$ a$^{-1}$ according to the Wanninkhof (1992) short-term relation. This is about five times greater than the air–sea flux one would expect from “average winds” and the observed $\Delta p$CO$_2$ of about −50 µatm in the area: using the global average air–sea exchange flux of CO$_2$ of 20 mol m$^{-2}$ a$^{-1}$ (Broecker et al., 1986) and an atmospheric $p$CO$_2$ of about 350 µatm, one obtains $50/350 \times 20 = 3$ mol m$^{-2}$ a$^{-1}$ for the latter value. At the other extreme, in areas to the west of

Fig. 5. East-west CO$_2$ partial pressure in µatm along about 49.8°N. Black line shows data from R/V Belgica along the northernmost line shown in Fig. 4. Points are data from R/V Poseidon, in the segment between 50°N and 47.5°N on the line shown in Fig. 4. The gray line shows data from October 1994, taken on R/V Meteor on an east-west line similar to that of R/V Belgica (Körtzinger, 1995).
Iceland, the net air–sea flux estimated from the transfer velocity practically vanishes due to the light winds, despite considerable undersaturation of the surface water (Fig. 3b). The dissimilarities in the patterns of $\Delta p_{CO2}$ and estimated air–sea CO2 fluxes, shown in Figs. 2 and 3, indicate that on a short-period time-scale of days or perhaps weeks, the frequency and path of storms through regions of CO2 disequilibrium between the sea and air may determine the strength of sea surface sources and sinks.

5. Conclusions

From a comparison of our results to the earlier TTO measurements, it appears the general pattern of CO2 undersaturation is a persistent seasonal feature into the late summer of the northeastern Atlantic. At the OMEX I site in late summer, surface waters appear to be moderately undersaturated over the Celtic Shelf, and the $p_{CO2}$ decreases to the west of the shelf edge. It appears that in regions where disequilibrium between atmospheric and surface water $p_{CO2}$ exists, the pattern of wind speed distribution rather than the magnitude of the $\Delta p_{CO2}$ may be the important factor in determining the horizontal distribution of sea surface sources and sinks on short time scales.

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References


