# Ship-board report on atmospheric CO<sub>2</sub> concentrations recorded on continuous from mediterranean sea to antarctica

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Summary. — We present the results obtained from continuous measurements performed during two cruises with hemispherical courses. In this way, we obtained the latitudinal trend of  $\mathrm{CO}_2$  in continuity of space and time along two hemispheric courses in 1994-95 and 1996-97 from Europe to Antarctica. The results are compared with measurements from the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostic Laboratory (CMDL) cooperative air sampling network. The fitting of data recorded on board with the historical data sets recorded at Palmer Station is also presented, highlighting the current annual increase in atmospheric  $\mathrm{CO}_2$  concentrations.

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## 1. - Introduction

Fifty-five percent of the change in radiative forcing caused by greenhouse gas emissions from 1980 to 1990 is due to the anthropogenic increase in atmospheric carbon dioxide [1]. The decline in the growth or stabilization of some greenhouse gases more recently observed in the atmosphere underlines the importance of  $\mathrm{CO}_2$  as a primary agent of global climate change [2]. However, the incomplete understanding of the variability of the global carbon budget makes it difficult to predict future levels of atmospheric  $\mathrm{CO}_2$ . From the 1970s on, high-precision measurements of air collected in glass flasks from large global networks have documented the increase in atmospheric  $\mathrm{CO}_2$  and the variability in its long-term growth [3, 4]. These observations are often used with 2- and 3-dimensional transport models to derive plausible distributions of the sources and sinks of  $\mathrm{CO}_2$ . The present knowledge of carbon dioxide concentration values and the possible distribution of sources, sinks and trends is usually determined

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from the weekly collection of air samples in glass flasks over a global network of sites since the 1970s. Up to the 1990s, such measurements constituted the most accurate data available [3, 4]. In spite of the importance of the rise in atmospheric  $CO_2$  expected to lead the global climatic change, after thirty years of measurements in air and oceans, the variations of the global atmospheric  $CO_2$  budget remain uncertain [5]. Nevertheless, any geographical distribution of  $CO_2$  is reflected in the spatial and temporal variations of  $CO_2$  concentration patterns in the atmosphere.

Numerical models of atmospheric transport can simulate these patterns and test hypotheses of the atmospheric CO<sub>2</sub> budget. However, the sparseness of sampling sites and the lack of temporal continuity among measurements at different locations are serious obstacles to this approach. The numerical forecasting models developed in the '70s and '80s [6, 7] demonstrated that climatic changes are amplified in remote areas, such as the polar regions. Later on, the simulations based on a coupled ocean model established that such amplifications are weaker than previously assumed. Hence, the need to verify these models by means of direct measurements performed not only in polar regions, but in surrounding oceanic areas. This is also necessary in order to verify the extension of the phenomena observed at the poles and the likelihood of their reaching intermediate latitudes. Recently, results obtained from direct measurements performed on board twice a day during cruises of limited shipping routes have been presented [8-12]. Continuous measurements along these two routes of hemispheric extension can now be used to further constrain models by providing the longitudinal and latitudinal gradient in oceanic areas.

We were able to take advantage of two cruises organized by the Italian national research program in Antarctica (PNRA):

- the EOLO 94 cruise with the ship R/V OGS EXPLORA bound for the Belling-shausen Sea through the Mediterranean Sea and North and South Atlantic ocean.
- the EOLO 96 cruise with the M/N ITALICA carrying instrumentation and supplies to the Ross Sea Italian Base through the Mediterranean Sea, Red Sea, Indian Ocean and the Southern Ocean.

We used these two opportunities to carry out tropospheric  $\mathrm{O}_3$  and  $\mathrm{CO}_2$  measurements and dust sampling.

The present paper compares the data of CO<sub>2</sub> concentration obtained during the two cruises with available measurements on the same days at Mt. Cimone (Italy), Seychelles Islands and the Jubany Station (Antarctica).

Moreover, a comparison of February means obtained from data recorded during the route in circum-Antarctic seas with the corresponding means at Palmer Station and South Pole Station allows us to assess the annual increase in the carbon dioxide concentration from 1968 in this area.

Finally, we compare data obtained on these cruises with values extracted at similar times and latitudes from a marine boundary layer (MBL) reference surface constructed using measurements from the NOAA CMDL cooperative air sampling network [13].

## 2. - Measurement methodology

The measurements were carried out with a Siemens Ultramat 5E analyzer set up for a marine use [14]. During the cruise EOLO 94 on the R/V OGS EXPLORA, the air

inlet was mounted over the bows, ten meters above sea level. In the EOLO 96 cruise on the M/N ITALICA, it was mounted on the upper deck (15 m above sea level). The inlet was protected from airborne particles and salt spray by two WHATMAN filters.

The pipe connecting the inlet to the measurement equipment was made from polyethylene, proven to be physically and chemically inert to  $\mathrm{CO}_2$  by experiments carried out at the Mt. Cimone Observatory. A single piece was employed in order to avoid leaks; the line was wrapped in a thermal insulating strip in order to avoid light and warming from the sun. The WMO-X93 scale was used and calibrations were performed with two working standards (345 ppm and 375 ppm), whose  $\mathrm{CO}_2$  concentration was determined at Mt. Cimone Observatory, a baseline site of the Italian Meteorological Service, with comparison against primary standards normally used at the site itself: these standards were tested in the Round-Robin intercomparison organized by the NOAA in April 1996.

The values measured using the working standards were almost always equal to the assumed concentration or different by no more than a decimal unit (0.1 ppm) even 24 hours after the last true calibration; the tests were usually carried out at least twice a day.

The meteorological monitoring system logged the wind direction (relative to the ship's axis) permitting us to flag as "suspect" those measurements made when the inlet was downwind from the ship's funnel within a selected angle.

## 3. - Data processing

The on-board data logger sampled the CO<sub>2</sub> concentration every 4 seconds and recorded 10 minutes means.

It should be noted that, in the first days of the EOLO 94 cruise, the data logger was unable to sample the decimal figures of the CO<sub>2</sub> measurements.

We processed the raw  $CO_2$  trying to eliminate data affected by anthropogenic influence in order to obtain a clean air selection conforming to the following criteria (fig. 1,2):

- Removal of the values measured when the inlet was downwind from the ship funnel within an angle of  $\pm$  60° from the ship axis.
- Removal of the EOLO 94 values recorded in proximity of South America (20–50 nm from the coast), when the true wind was blowing from the continent (from a latitude of  $-30^{\circ}$  to  $-60^{\circ}$  we accepted winds from 150° to 210°; at latitudes less than  $-60^{\circ}$  we accepted winds from 0° to 210°).

For the EOLO 94 cruise about 2000 values were rejected out of 5000 (70% below  $35^{\circ}$  S).

For the EOLO 96 cruise about 500 values were rejected out of 7500 (60% below  $40^{\circ}$  S).

– The use of a filter for the concentration values with the purpose of obtaining the steady-state criteria proposed by Thoning [15] for processing the Mauna Loa  $\rm CO_2$  hourly data. We computed the moving average of the previous hour and eliminated measurements differing by more than 0.5 ppm; special care was taken with the "first" data of a series; a data set starts after a calibration, a change of the humidity trap, some time downwind from the funnel or when the filter itself erases more than 40 minutes of data.

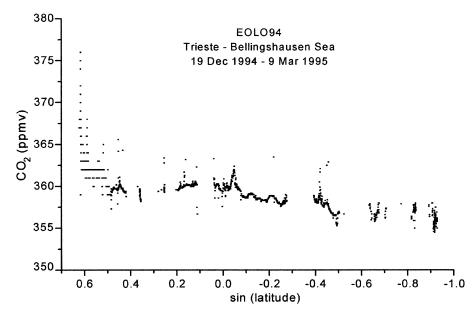


Fig. 1. – Latitudinal distribution of EOLO 94  $\mathrm{CO}_2$  concentration.

For the EOLO 94 cruise about 700 values were filtered out, evenly spaced in latitude.

For the EOLO 96 cruise about 3000 values were rejected (50% below 60°S).

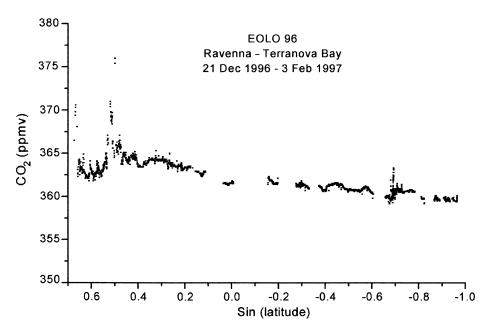


Fig. 2. – Latitudinal distribution of EOLO 96  $\mathrm{CO}_2$  concentrations.

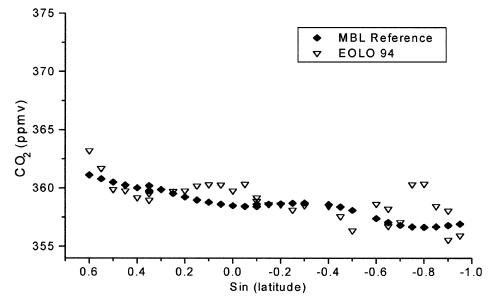


Fig. 3. – EOLO 94  $\mathrm{CO}_2$  concentrations against the MBL reference.

– In order to relate our measurements to the CMDL-MBL data [13], we computed the mean of the data sharing the same  $0.05 \sin$  (latitude) interval and the same "week" (7.6041 days). The time and latitude intervals are the same used in computing the MBL (fig. 3, 4).

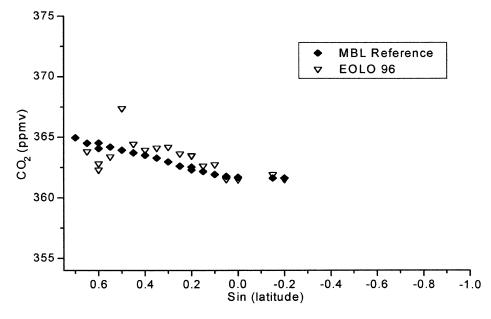


Fig. 4. – EOLO 96  $\mathrm{CO}_2$  concentrations against the MBL reference.

### 4. - Discussion

In order to assess the quality of the data, we compared measurements obtained on board the ships with those available to us recorded at the same time at different stations using daily means:

- 1) With respect to Mt. Cimone  $\mathrm{CO}_2$  data [16,17] the cruise values present a smoothed trend typical of a well-mixed marine site showing a mean difference of about 2.7 ppm in the Western Mediterranean Sea (EOLO 94) and about 1.4 ppm in the Eastern Mediterranean Sea.
- 2) The mean difference of data recorded on board compared to those of the Jubany station [18] is 0.7 ppm in the EOLO 94 cruise at a latitude below 55°S and same longitude (65°–75°W); in the EOLO 96 cruise the mean difference is 0.6 ppm at a latitude below 55°S and a longitude around 170°W (more than 100° from Jubany).

The difference between average data recorded in February both on board during EOLO 94 and EOLO 96 cruises in the Antarctic seas and at Palmer Station was 2.5 ppm and the rise was consistent with the value estimated in past records for the same stations.

- 3) We related our February mean with the historical trends at Palmer Station [4,5] (fig. 5); the trend seems to show an annual increase of more than 1.6 ppm/year, normally indicated as global increase [19].
- 4) Seychelles: only one flask was available in January 1997: the comparison of this sample analysis (361.9 ppm) agrees with the  $CO_2$  concentration measured on the same day at sea (361.5 ppm).

We also compared our data with the CMDL-MBL weekly interpolated values (see data processing). This distribution is computed from sparse data and is independent of circulation models or specific hypotheses on CO<sub>2</sub> sources and sinks whose latitude the authors try to determine.

We also see some differences probably due to local gradients, such as the one

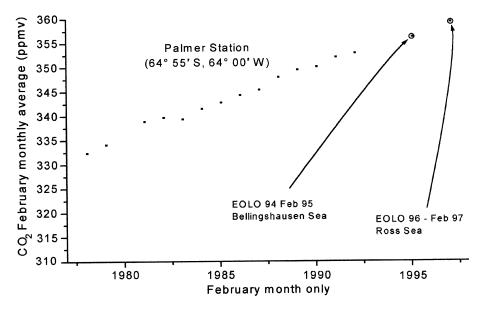


Fig. 5. – Palmer Station: historical CO<sub>2</sub> February means.

existing in the Mediterranean region which was evidenced by Mt. Cimone  $\mathrm{CO}_2$  data [16]. In this regard, the significant difference in longitude is relevant, bearing in mind that the MBL deal with  $\mathrm{CO}_2$  data collected mostly in the Pacific Ocean. The MBL curve presents a smoothed trend of the experimental  $\mathrm{CO}_2$  data collected during the two cruises. Typical, for example, is the positive disagreement in the equatorial belt between 0.2 and - 0.1 sin (lat) in the EOLO 94 cruise (fig. 3) in the Atlantic Ocean off central Africa and Southern America. The EOLO 96 data show a similar difference at a higher latitude between 0.4 and 0.1 sin (lat) (fig. 4). The filtered  $\mathrm{CO}_2$  data reveal another significant positive disagreement between - 0.6 and - 0.9 sin (lat), during EOLO 94 (fig. 3).

Overall, the difference between the meridian weekly  $CO_2$  distributions computed using all the CMDL-MBL sites in a local strategy (far sites weigh less) and the ship data measured on the same days seems to be less than 1 ppm.

### 5. - Conclusions

The activity exposed above was supported by the National Programme of Research in Antarctica (PNRA) and the data were carried out during a survey of unusual hemispheric extension by direct and continuous measurements of CO<sub>2</sub> concentration.

The most important aim in measuring a CO<sub>2</sub> latitudinal distribution is to obtain an idea of the trend and magnitude of the major sources and sinks of this gas, gaining further insight into the global carbon cycle.

The results, compared with values recorded at different stations, confirm the validity of the measurement system that worked without interruption from Europe to Antarctica twice on two different ship-boardings.

The criteria adopted for the data selection could permit the presentation of a steady concentration well representative of background data. The distribution obtained with  $\mathrm{CO}_2$  in continuous measurements is particularly important because we have a latitudinal distribution of data.

The other important consideration is that the measurements have been obtained at sea, where carbon dioxide measurements are rarer and sparse.

We set up a filter for the concentration values with the purpose of obtaining steadystate data working on the steadiness of the data themselves.

Although the routes for the different years are not the same, we obtained concentration values at the same latitudes, that differ only in the annual increase in the Antarctic regions.

The good quality of the data was validated by means of comparisons with simultaneous measurements taken at other stations.

The historical February means taken at the Palmer and South Pole Station, together with our February means, allowed us to estimate the current annual increase in the southern hemisphere as being higher than 1.6 ppm/year.

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