Ber. Inst. Erdwissenschaften K.-F.-Univ. Graz	Bd. 8	ISSN 1608-8166	Isotope Workshop Volume	Graz 2004

Carbon isotopic composition of atmospheric CO_2: contaminated and non-contaminated areas

Antonio Longinelli[1], Renzo Lenaz[2], Carlo Ori[2], Enrico Selmo[1], Federico Giglio[2]

[1]University of Parma, Department of Earth Sciences, Parco Area delle Scienze 157A, 43100 Parma ,Italy, e-mail: longi@unipr.it

[2]National Research Council (CNR), ISMAR, Area della Ricerca, Via Gobetti 101, 40129 Bologna, Italy

CO_2 is one of the primary agents of global climate changes. The increase of atmospheric CO_2 concentrations is essentially related to human-induced emissions and, particularly, to the burning of fossil fuel. Continuous records of CO_2 concentrations were repeatedly carried out along hemispheric courses from Italy to Antarctica by the use of a vessel of the Italian National Research Program in Antarctica. During these expeditions discrete air samples were collected in 4 liter Pyrex flasks in order to carry out precise carbon isotope analyses on atmospheric CO_2 from different areas including theoretically "clean" open ocean areas as well as highly polluted sections. Samples were collected during the 1998-'99 expedition as well as during the 2001-'02 and the 2003-'04 expeditions. The flasks were carefully evacuated to 10^{-3} mmHg , opened on the windward side of the ship 15 meters above sea level and closed after air collection by means of high vacuum greasless stopcocks. The flasks were then stored in wooden boxes kept at room temperature until the arrival of the ship at the final harbour in Italy.

The CO_2 samples were separated from other gases in the laboratory by means of a vacuum line by very slow pumping (about 6 ml/min) through a Swagelock microvalve and a liquid nitrogen cooled spiral trap. After pumping down the flask to about 10^{-3} mmHg the trap was isolated by means of high vacuum stopcocks and heated to about - 80°C by means of an ethyl-alcohol-liquid nitrogen slash. The evolving CO_2 was collected in a sample tube and measured in a Finnigan Delta S mass spectrometer against a standard CO_2 obtained from a very pure Carrara marble, calibrated against NBS-19 and NBS-20 international standards. The standard deviation of the carbon

isotope measurements ($\delta^{13}C$), tested on air samples collected with the same procedure and treated in the same way ranges from ± 0.02 to ±0.04 ‰ (1σ).

The data obtained show, as expected, a relatively large atmospheric pollution in the Mediterranean area and particularly in the Adriatic Sea and near the coast of Egypt. In the Mediterranean area South-Westerly winds tend to reduce the effect of atmospheric pollution even though, despite a large variability of CO_2 concentrations, these values are systematically higher (from a few ppmv to about 15 ppmv) than those measured in open ocean "clean" areas.

A marked pollution is apparent in the area of the Bab-el-Mandeb strait where the $\delta^{13}C$ was found more negative (up to about 2 ‰) than in the Southern Red Sea and in the Arabian Sea and Indian Ocean. This effect is likely related to the pollution caused by the oil refineries in the Gibuti area.

The concentration of atmospheric CO_2 over the "clean" Indian Ocean increased from 365 ppmv at the end of 1998 to 372 ppmv at the end of 2001 to 377 ppmv at the end of 2003. Simultaneously, the mean $\delta^{13}C$ value of atmospheric CO_2 over Indian Ocean decreased from -8.07 ‰ at the end of 1998 to -8.17 ‰ at the end of 2001.

The isotopic values of atmospheric CO_2 over the Mediterranean, Red Sea and Indian Ocean at the end of 2003 will be measured soon, the flask samples collected during the last expedition being expected at the Parma laboratory within the end of April.