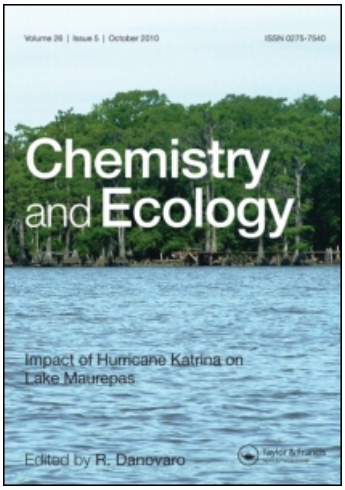

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GAS TRANSFER COEFFICIENT EVALUATION IN THE MEDITERRANEAN SEA USING BOMB PRODUCED RADIOCARBON

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A study on the carbon dioxide exchange at the water-air interface in the Western Mediterranean Sea was carried out. The attention was focused on the mean air-sea flux estimations by radiocarbon profiles and bomb ^{14}C concentration atmospheric data. Sampling techniques and analytical methods are reported; mass balance evaluations on data recorded during the MED'92 cruise are presented and discussed briefly.

KEY WORDS: Carbon dioxide, air/sea flux, Mediterranean Sea.

INTRODUCTION

ENEL (the Italian Electric Energy Board), ENEA (National Alternative Energies Board) and CISE have started a research programme in the marine environment, aimed to assess the carbon dioxide gas transfer coefficient in the Western Mediterranean area. Experimental activities were carried out on oceanographic ships during 1990–1993. The Mediterranean Sea is characterized by a complex structure; three main water masses, characterized by different salinity and temperature, are recognized: Surfacial or Atlantic Water, Intermediate or Levantine Water (LIW) and Deep Water (DW) (Ovchinnikov, 1983). Each water mass has a typical mean residence time (Table I). A carbon dioxide total global flux (F) [moles m^{-2} y^{-1}] approximate evaluation can be obtained from the equation that links total carbon amount in the atmosphere to the residence time, at the steady state: $F = N/\tau$ (Bolin, 1981). Assuming for N the preindustrial carbon value of 600 Gton, τ as 5.4 years (Munnich and Roether, 1967) and the global ocean surface of $3.62 \cdot 10^8$ km^2, a flux of 25 moles $m^{-2}y^{-1}$ is computed. The gas transfer coefficient, K_L [m d^{-1}], is obtained from the relation $K_L = F/C$, where C is the carbon dioxide concentration [ppm]. The total flux is substantially correlated to wind speed, sea state and surface roughness, so we can have a large spread of data, due to rapid fluctuations of meteorological parameters: for example Kelley and Gosink (1988) in different zones of the Arctic Sea found values ranging from 4.5 to 35.2 moles/ (m^2.year).

Table I Characteristics of Mediterranean waters.

	*Volume** [$km^3 \cdot 10^3$]	*Mean Res. Time** [*years*]	*Temperature*** [°C]	*Salinity*** [‰]
Mediterranean Sea	3842	95	–	–
Western Basin	1424	126	–	–
Eastern Basin	2291	80	–	–
Surfacial Water	343	8.5	13–25	35–38
Levantine Water	985	25.5	14.00	38.75
Deep Water	2514	61	12.74	38.44

* Ovchinnikov, 1983
** Andrie and Merlivat, 1988

RADIOCARBON METHOD

The nuclear weapon tests carried out by 1960 introduced a large amount of radiocarbon in the atmosphere and then into sea water by means of atmospheric carbon dioxide dissolution. The equilibrium between atmospheric and dissolved carbon dioxide requires times of the order of a year, depending on gas exchange coefficients, the height of the mixed layer, salinity and temperature (Najjar, 1992). Broecker (1980) stated that the equilibration time for bomb-produced isotopes is about ten times higher: in fact Figure 1 shows a 8–10 years gap between ^{14}C peak in the atmosphere and the peak in sea water.

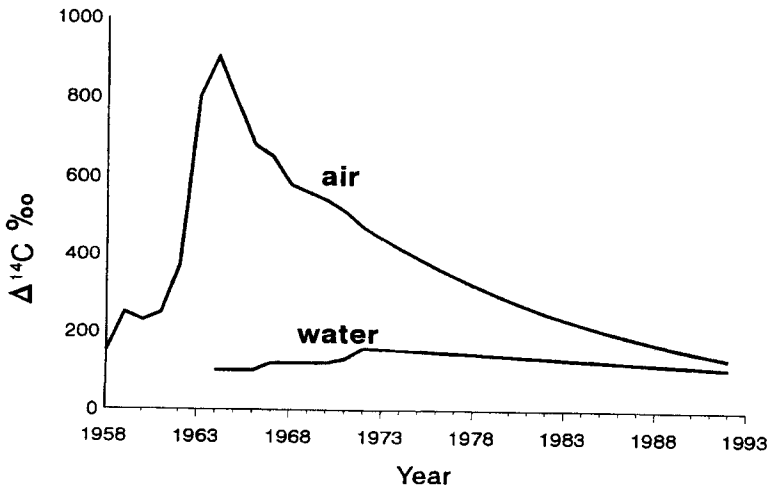

Figure 1 Water and air bomb-produced radiocarbon data.

The isotopic equilibrium time of $^{14}CO_2$ has to be taken into account, and it can be of the same order of magnitude as the surface water mean residence time (Broecker, 1980).

Total carbon dioxide flux computation can be obtained by ^{14}C mass balance, considering three different components: i) the total amount of radionuclide entered in the Mediterranean Sea with the Atlantic water; ii) the total amount of radionuclide effluent in Levantine water through the Gibraltar Strait; iii) the total amount exchanged with atmosphere:

$$F = \frac{K \cdot [C_{sup} \cdot V_{sup} - (C_{Atl} \cdot Q \cdot t - C_{Lev} \cdot V_{Lev} - C_{Prof} \cdot V_{Prof} - C_{Usc} \cdot Q \cdot t]}{A \cdot N \cdot t}$$

where F is the carbon dioxide total flux [moles $m^{-2} y^{-1}$]; K is the number of ^{14}C atoms, corresponding to a concentration of 1 Δ‰, per mole of carbon dioxide in a cubic metre of sea water. In the Mediterranean Sea, K corresponds to $1.63 \cdot 10^9$ atoms m^{-3}. C_{sup}, C_{Atl}, C_{Lev}, C_{Prof}, are the ^{14}C in Surfacial, Levantine, Deep and entering Atlantic water respectively: concentrations are expressed as Δ‰ with respect to the pre-bomb value. V_{Sup}, V_{Lev} and V_{Prof} are the corresponding total volumes (Table I). The term, t, is the elapsed time from the beginning of nuclear tests; C_{Usc} is the ^{14}C mean concentration in Levantine water, effluent from the Mediterranean basin and returned into the Atlantic Ocean during the considered integration time; Q is the flow rate of entering Atlantic water and effluent Levantine water = $40 \cdot 10^{12}$ $m^3 y^{-1}$. A is the Mediterranean surface water = $2.8 \cdot 10^{12}$ m^2. The term, N, is the ^{14}C atoms in 1 carbon mole, corresponding to the Δ‰ concentration in the atmosphere in the considered integration time, that is:

$$N = \int_0^t [(R'_a - R_a) - (R'_s - R_s)]\, dt$$

where R_a and R_s are ^{14}C pre-bomb concentrations in atmosphere and sea water respectively, whilst R'_a and R'_s are the measured values, in Δ‰.

During oceanographic cruises, performed in summer periods of 1991–1993 in selected areas of Western Mediterranean sea, vertical profiles of radiocarbon were determined as follows. Water samples of about 150 l were collected at different depths by using a Rosette sampler equipped with 12 Go-Flo bottles (30 litres each). Water samples were transferred in closed containers and preconcentrated on ship, by bubbling with nitrogen for 6 hours in the acidified samples (pH = 1). Carbon dioxide less nitrogen ($CO_2 - N$) removed was retained in a 2N KOH solution. In the laboratory the potassium hydroxide solutions were acidified and carbon dioxide was converted to benzene, following the procedure of Tamers (1975). Radiocarbon contents were measured accurately by low background liquid scintillation counting.

In computing total fluxes, two different sets of data were taken into account: concentration values obtained during GEOSECS Cruise 1978 reported by Stuiver and Ostlund (1983) in Ionian Sea (Table II) and the average values obtained during MED 92 (ENEA, 1993) on three different stations in the Western Mediterranean Sea by CISE (Table II). Considering a mean residence time of 8.5 and 25.5 year (Table I) for Atlantic and Levantine water respectively, in 1978, C_{Lev} can be considered negligible.

Applying a mass balance equation we are able to compute carbon dioxide total fluxes of 6.6 and 10.5 moles m^2 y^{-1} respectively, similar to those obtained by Cember

Table II ^{14}C concentration and volume values of Mediterranean water masses.

	GEOSECS 77–78(*)	*MED 92(**)*
Surfacial $\Delta^{14}C$ [‰](***)	140	160
Volume [$m^3 \cdot 10^{12}$]	343	343
Levantine $\Delta^{14}C$ [‰]	90	115
Volume [$m^3 \cdot 10^{12}$]	985	985
Deep $\Delta^{14}C$ [‰]	15	50
Volume [$m^3 \cdot 10^{12}$]	2514	2514
Atlantic $\Delta^{14}C$ [‰]	148	159
Volume [$m^3 \cdot 10^{12}$]	800	1360
Flux CO_2 [Moles m^2 y^{-1}]	6.6	10.5

(*) Stuiver and Ostlund data (1988)
(**) MED 92 average data (1992, ENEA)
(***) Expressed in Δ‰ over "pre bomb" value.

(1989) for Red Sea (8.5 moles m^2y^{-1}), but much lower than average values for Atlantic Ocean (about 20 moles m^2y^{-1}).

The carbon dioxide exchange coefficient evaluations derived from radiocarbon profiles are connected with large uncertainties, mostly due to the low representativity of the measuring stations with respect to the Mediterranean basin complicated morphology. The K_L values estimated by radiocarbon in sea water profiles give 2.0 m day^{-1} (ENEA 1993, MED 92) and 1.3 m day^{-1} (Stuiver and Ostlund, 1983). These values are much lower than the Atlantic ocean ones (3.8 m day^{-1}, Broecker and Peng, 1982); on the contrary they agree with the data estimated by Cember (1989) in Red Sea (about 8.5 m^2/year) and also with the values computed on the basis of wind velocity mean values, measured by meteorological satellites, as elaborated by Thomas and coworkers (Thomas *et al.*, 1988).

In any case we observe that the carbon dioxide transfer coefficients evaluated by present radiocarbon profiles in sea water are related with large errors due to the great radiocarbon amounts considered in the mass balance computation.

With regards to the Mediterranean Sea, to optimize flux evaluation the most interesting time period would be the decade immediately subsequent to the nuclear tests, since in these few years the bomb-produced ^{14}C detectable in surfacial Mediterranean water was due only to the "in situ" atmospheric exchange. It follows that marine organisms using carbon dioxide dissolved in sea water to build up their structure, living at that time and where age is easily estimated, can give an historical record of previous radiocarbon data. Annual coral rings were used widely in last few years for carbon dioxide exchange coefficient evaluations (Druffel and Linick, 1978; Toggweiler, 1983; Cember, 1989).

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