^{14}C in air over the Arabian Sea

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Global monitoring of radiocarbon in atmospheric CO_2 began during the mid fifties to determine the time scales of exchange of radiocarbon (and CO_2) between the atmosphere and other terrestrial reservoirs. The distribution of natural radiocarbon in the environment was perturbed significantly during the 1960s through injection of ^{14}C from nuclear weapon tests. This 'bomb ^{14}C' has proved to be an excellent tracer to characterize and quantify CO_2 exchange between various reservoirs. We have measured radiocarbon activity of marine air over the central and eastern Arabian sea during 1993–95. The mean $\Delta^{14}C$ values are 121 ± 6, 116 ± 6 and $105 \pm 5‰$ respectively for these three years. These values, in conjunction with those reported in the literature for troposphere for the decades of 60s through 80s, show that the ^{14}C activity in the tropospheric air has been decreasing exponentially with an e-folding time of ~ 16 years.

Cosmic ray-produced carbon-14 (half life = 5730 yr) is one of the commonly used geochronometers for dating events of the late Pleistocene[1,2]. Its production by the interaction of neutrons with atmospheric ^{14}N and its distribution among the various reservoirs of the earth, oceans, biosphere and atmosphere, is fairly well known[1,3–6]. It has been used successfully to determine the time scales of exchange of carbon between various earth surface reservoirs[7–8]. However, nuclear weapon tests[9], conducted during the late fifties and early sixties, resulted in the injection of considerable amounts of ^{14}C into the environment which increased its inventory in the atmosphere by about factor of two[8–12]. Though this has significantly perturbed the steady-state distribution of natural radiocarbon (i.e. cosmic ray produced) in the environment, it provided an additional means to assess more precisely the time scales of various processes associated with carbon exchange. The bomb radiocarbon activity in the atmosphere has been decreasing with time because of its exchange with other reservoirs. The measurements of atmospheric ^{14}C activity, begun in the early 1950s (ref. 13) have continued, at some location or the other over globe, during the past four decades. These measurements have provided valuable data on the rates of CO_2 exchange among various reservoirs[2,4]. In India, atmospheric ^{14}C measurements were made at a few stations, Gulmarg (34°N), Bombay (19°N) and Kodaikanal (~ 10°N) during 1963 and 1964 (ref. 8). As a part of our programme on studies of water circulation in seas around India using ^{14}C, atmospheric air was also sampled during the cruises, to measure its ^{14}C activity, the results of which are reported in this paper.

Atmospheric CO_2 samples were collected during three cruises, SK-83 in 1993 on board *ORV Sagar Kanya*, and in 1994 and 1995 on board *FORV Sagar Sampada* (see Figure 1 for sampling locations). All the three cruises were conducted during January–May. Atmospheric air was purged at the rate of 4–6 l/min through two 500 ml plastic bottles, each containing 250 ml of 2 N NaOH, using a small greaseless and oil-free air compressor when the ship was cruising. The NaOH solutions were sealed and brought to the laboratory and processed for their ^{14}C activity. The measurements were made within ~ 1 yr of collection. Typically 2–6 litres of CO_2 was recovered from each sample. A blank run of 250 ml of 2 N NaOH stored in the same type of sampling bottles for a period of one year, yielded 10 ml CO_2, which is < 0.5% of the sample volume. The CO_2 was converted to benzene following conventional procedures using a TASK benzene synthesizer. The ^{14}C activity in the benzene sample was analysed using a Packard Liquid Scintillation Counting System[14]. The system has a background count rate of 1.15 ± 0.01 counts per minute (cpm)[14]. This compares with sample count rates which ranged from 8.3 to 21.2 cpm. A small aliquot of the liberated CO_2 was used for $\delta^{13}C$ measurements[15].

The $\delta^{13}C$ values, in the trapped CO_2 ranged between –8.0 and –18.0‰, similar to or lower than that in atmospheric CO_2 (–7.7 to –9.6‰)[16]. The lower values are suggestive of fractionation during the trapping process. Some of the earlier measurements, which were based on trapping of CO_2 in $Ba(OH)_2$ and NaOH solutions kept in open trays[7–10], had also recorded similar low $\delta^{13}C$ values. The $\Delta^{14}C$ values (Table 1) are calculated from the measured $\delta^{13}C$ and ^{14}C activity based on standard equations[17,18].

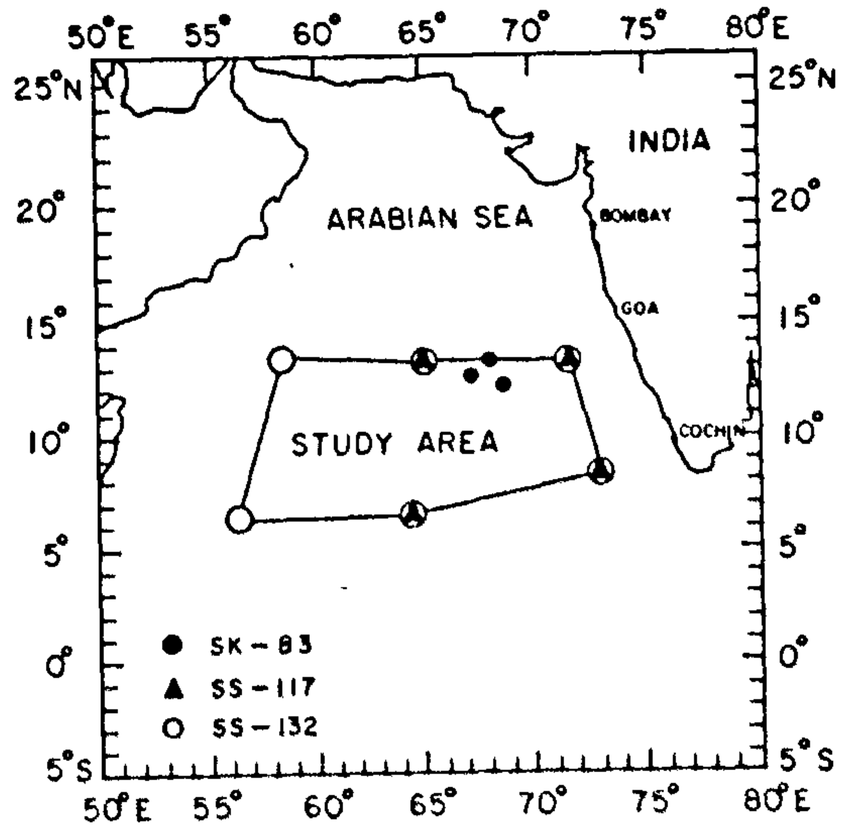

Figure 1. Cruise tracks in the Arabian Sea where CO_2 sampling of air over sea surface was done. Some of the stations occupied during SS-132 (open circles) and SS-117 (solid triangles) overlap. The sampling was done during 1993-95 (Table 1).

The locations of the samples along with their $\delta^{13}C$ and $\Delta^{14}C$ data are given in Table 1. The $\Delta^{14}C$ values of CO_2 in the air mass over the central and eastern Arabian Sea varied between 92‰ and 135‰. The four samples collected during SK-83 from very close locations (Figure 1) have yielded $\Delta^{14}C$ values which are in excellent agreement with each other, attesting to the reliability of the sampling procedures and measurements. The range in the $\Delta^{14}C$ values, 104 to 135‰ during SS-117 and 92 to 122‰ during SS-132 (Table 1) was significantly more than the typical uncertainties in the measurements (~ 6‰). The cause for this scatter is unclear, but may arise from variations in the mixing proportions of different sources of CO_2. It is interesting to note that the lowest value measured, viz. 92 ± 7‰ was in the sample A4 collected during the second week of May 1995 (Table 1), when strong premonsoonal winds prevailed and the sea state was at 6. Studies of geopotential anomaly[19] in the south-west coast of India (south of 10°N) show that upwelling in this region starts by March, intensifies through May–June and decays by July. It is possible that upwelling which brings to surface cooler deeper waters with higher ΣCO_2 and lower $\Delta^{14}C$ may liberate CO_2 to the atmosphere, diluting the atmospheric $\Delta^{14}C$. Rough calculation suggests that for a two-end member mixing, atmospheric CO_2 with $\Delta^{14}C \sim 110$‰ and oceanic CO_2 (upwelled from 200 m depth) with $\Delta^{14}C$ ~0‰, the fraction of oceanic CO_2 in the A4 sample would be ~ 15%. Earlier work[8] on $\Delta^{14}C$ in atmospheric samples from the coastal station of Bombay showed that during August, $\Delta^{14}C$ values were 641 and 657‰, about 100–150‰ lower compared to samples collected during November 1963 and 1964. Rozanski *et al.*[20] have recently reported $\Delta^{14}C$ values as low as 90‰ during Aug–Nov. 1992 at the high altitude (~ 3000 m amsl) coastal equatorial Pacific station, Aychapicho in Equador. These low values have been attributed to upwelling located in the eastern equatorial Pacific. The above hypothesis, though can be a likely explanation for the low $\Delta^{14}C$ of the A4 sample, the observation that during SK-83 sampling conducted during approximately the same time period as SS-132 (Table 1), did not have such low values, requires that the upwelling effects have to be very localized and time specific. Many more measurements are needed to validate this hypothesis and assess the role of upwelling in contributing to $\Delta^{14}C$ variations in the Arabian sea marine atmosphere.

The mean (arithmetic) $\Delta^{14}C$ measured in this study is plotted in Figure 2 (adapted from ref. 21), assuming that they represent the annual values for the years 1993–95. Figure 2 represents the temporal variation in atmospheric ^{14}C since 1954 (refs 10, 22–27). The measurements during 1954 are prenuclear $\Delta^{14}C$ values, which increased to ~ 1000‰ in the northern hemispheric troposphere and ~660‰ in its southern counterpart due to injection of ^{14}C by nuclear weapon tests conducted in the northern hemisphere between 1958 and 1963 (Figure 2). The ^{14}C measurements of tropospheric CO_2 from various locations, including those of the present study, show a steady decrease that appears exponential (Figure 2). The minor perturbations in the exponentially decreasing trend of ^{14}C activity are a result of small scale nuclear weapon testings[12]. The decrease in the atmospheric bomb ^{14}C results from its exchange with

Table 1. ^{14}C in surface air over the Arabian Sea

Sample code	Location		$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)
	From	To		
Cruise SK-83 (April–May 1993)				
83/A1	Goa	12°30′N 67°E	–*	124 ± 6
83/A2	12°30′N 67°E	13°N 68°E	–15.1	119 ± 5
83/A3	13°N 68°E	12°30′N 69°30′E	–15.3	119 ± 5
83/A4	13°N 68°E	12°30′N 69°30′E	–*	121 ± 8
			Mean =	121 ± 6†
Cruise SS-117 (January–February 1994)				
117/A1	Cochin	8°2′N 73°E	–*	104 ± 5
117/A2	8°2′N 73°E	12°58′N 64°49′E	–16.4	135 ± 5
117/A3	12°58′N 64°49′E	12°49′N 71°37′E	–14.6	109 ± 6
			Mean =	116 ± 6†
Cruise SS-132 (April–May 1995)				
132/A1	Cochin	12°58′N 64°29′E	–11.5	101 ± 5
132/A2	12°58′N 64°29′E	5°43′N 56°12′E	–18.0	122 ± 6
132/A3	5°43′N 56°12′E	6°11′N 64°25′E	–8.0	104 ± 5
132/A4	6°11′N 64°25′E	Cochin	–8.2	92 ± 7
			Mean =	105 ± 6†

*For these samples $\delta^{13}C$ was not measured, a value of –15‰ (mean of the four measured values during SK-83 and SS-117 cruises) is used to calculate $\Delta^{14}C$.
†Uncertainties given are the arithmetic mean of the standard deviations of individual measurements ($\pm \sigma$).

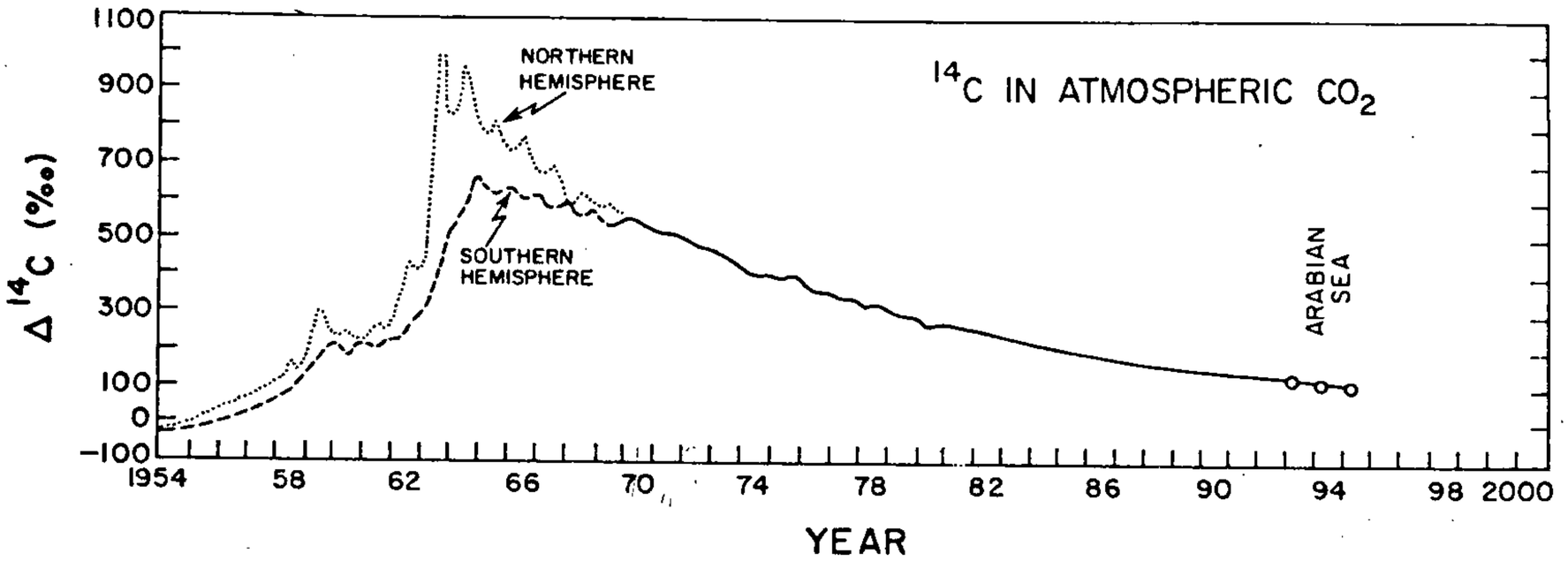

Figure 2. $\Delta^{14}C$ variations in tropospheric air since 1954 (figure modified from ref. 21 with additional data from refs. 24–28 for post 1980). Data collected during this study is plotted as open circles in the Figure. As evident, the Arabian Sea data falls in the general trend.

Table 2. Mean residence time of radiocarbon in the troposphere of the northern hemisphere

Year	$\Delta^{14}C$ (‰)†	ΔT (years)*		τ (years)**	
		1963	1970	1963	1970
1963	1000	0	–	–	–
1970	550	7	–	–	–
1993	121	30	23	15.3	16.5
1994	116	31	24	15.6	16.8
1995	105	32	25	15.4	16.6
1993–95‡	114	31	24	15.5	16.6

†From ref. 21 for 1963 and 1970.
*ΔT is the time elapsed since the base year, 1963 or 1970.
**Residence time calculated with respect to 1963 and 1970 after correcting for Suess effect.
‡Based on the mean of all measurements in Table 1.

other terrestrial reservoirs, oceans and the biosphere. In addition to this exchange, a small but finite decrease in the atmospheric ^{14}C also results from introduction of 'dead CO_2' (Suess effect) to the atmosphere through fossil fuel burning[5,13,26–28]. It is estimated that the rate of decrease of $\Delta^{14}C$ in atmospheric CO_2 due to Suess effect is about –6.8‰ per decade since 1937. Other factors that contribute to $\Delta^{14}C$ variations in the atmosphere are those connected with changes in ^{14}C production due to cosmic rays, however, these changes during the past ~ 50 years are not significant, only ~ 2‰ in $\Delta^{14}C$ (ref. 5).

The temporal variations in $\Delta^{14}C$ data in the atmosphere (Figure 2) allows one to calculate its removal time scale. Based on the observation that the $\Delta^{14}C$ decrease in the atmosphere follows an exponential trend (Figure 2), the mean-life or e-folding time for tropospheric radiocarbon is calculated to be ~ 15.5 years and ~ 16.6 years with respect to the base year 1963 and 1970 respectively after correcting for Suess effect, i.e. –0.68‰ per year (ref. 5, Table 2). The calculation is based on $\Delta^{14}C$ values of 1000 and 550‰ for 1963 and 1970 respectively, and assumes that the samples collected over the Arabian Sea during various periods (Table 1) represent the annual values for northern hemispheric air. The difference in the e-folding time of ~ 1 yr when calculated with respect to 1963 and 1970 as base years, is attributed to incomplete mixing of radiocarbon between the two hemispheres for a few years after the bomb tests. A similar value of ~ 17 years was deduced by Manning *et al.*[24] based on their data collected from New Zealand (south Pacific).

We report here the first measurements of radiocarbon in the air over the Arabian sea, covering a latitudinal range of 6°N–13°N and longitude of 56°E–74°E. The data are consistent with those expected for the exponentially decreasing trend of bomb radiocarbon in the atmosphere and yield a value of ~ 16 years for mean residence time of radiocarbon in the tropospheric air. The data also show signatures of contribution of CO_2 from the Arabian sea to the atmosphere during upwelling, but these need to be ascertained through more extensive measurements.

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