

## THE USE OF RADIOCARBON MEASUREMENTS IN ATMOSPHERIC STUDIES<sup>1</sup>

M R MANNING, D C LOWE, W H MELHUISE, R J SPARKS, GAVIN WALLACE,  
C A M BRENNINKMEIJER and R C MCGILL

Institute of Nuclear Sciences, Department of Scientific and Industrial Research  
Lower Hutt, New Zealand

**ABSTRACT.**  $^{14}\text{C}$  measured in trace gases in clean air helps to determine the sources of such gases, their long-range transport in the atmosphere, and their exchange with other carbon cycle reservoirs. In order to separate sources, transport and exchange, it is necessary to interpret measurements using models of these processes. We present atmospheric  $^{14}\text{CO}_2$  measurements made in New Zealand since 1954 and at various Pacific Ocean sites for shorter periods. We analyze these for latitudinal and seasonal variation, the latter being consistent with a seasonally varying exchange rate between the stratosphere and troposphere. The observed seasonal cycle does not agree with that predicted by a zonally averaged global circulation model. We discuss recent accelerator mass spectrometry measurements of atmospheric  $^{14}\text{CH}_4$  and the problems involved in determining the fossil fuel methane source. Current data imply a fossil carbon contribution of ca 25%, and the major sources of uncertainty in this number are the uncertainty in the nuclear power source of  $^{14}\text{CH}_4$ , and in the measured value for  $\delta^{14}\text{C}$  in atmospheric methane.

### INTRODUCTION

Trace gases in the atmosphere play a crucial role in determining our environment. Greenhouse gases in the troposphere determine the earth's temperature through selective absorption of infra-red radiation. Ozone in the stratosphere filters out ultra-violet radiation that would destroy complex organic molecules essential for life. Because the amounts of these gases are small and the balance of processes maintaining them complex, they are a potentially fragile part of our environment.

Many of the trace gases that must be studied in relation to changes in climate and atmospheric chemistry contain carbon. For these gases, isotopic measurements are directly relevant in determining sources and sinks, because sources will have different isotopic composition and sinks will involve fractionation. The importance of carbon isotope measurements in building global budgets for gases such as  $\text{CO}_2$  (Keeling, Mook & Tans 1979; Peng *et al* 1983),  $\text{CH}_4$  (Ehhalt 1973) and CO (Stevens *et al* 1972) has been recognized for some time.

The atmospheric concentration of gases with lifetimes of the order of minutes or less is determined by local atmospheric chemistry and the presence or absence of light. For gases with lifetimes of many years, concentrations are relatively homogeneous due to atmospheric mixing. Between these extremes there are atmospheric species with intermediate lifetimes, the concentration of which depends on both atmospheric transport and the distribution of sources and sinks. To understand the varying concentrations of such species, we must combine quantitative information on advection and diffusion in the atmosphere with information on the spatial distribution of sources and sinks. This is a difficult task, but holds the prospect that we may determine a consistent picture of all the processes involved.

Each of the gases  $\text{CO}_2$ ,  $\text{CH}_4$  and CO is a candidate for study using a detailed physical and chemical model of the atmosphere. Extensive modeling of the annual cycle of  $\text{CO}_2$  concentrations (Trabalka 1985; Heimann & Keeling 1986) has shown that even though this gas has a lifetime in the atmosphere of many years, the latitudinal and seasonal variation of its concentration yields information on long-range atmospheric transport.

$\text{CH}_4$  has a lifetime similar to that of  $\text{CO}_2$ , but is a complementary tracer of atmospheric transport because the distribution of its sinks is quite different. While the sinks for  $\text{CO}_2$  are all at the surface, the dominant sink of  $\text{CH}_4$  is through reaction with the OH radical distributed throughout the atmosphere. The OH radical is produced photolytically in the troposphere and its maximum diurnal concentration, and therefore the sink strength for  $\text{CH}_4$ , varies considerably with latitude, altitude and season (Logan *et al* 1981).

Reaction with the OH radical is also the major sink for CO (Volz, Ehhalt & Derwent 1981), so CO has a sink structure similar to  $\text{CH}_4$ . As the lifetime of CO ( $\approx 4$  months) is shorter than the time required to mix throughout the troposphere, this gas does not become

<sup>1</sup> This paper was presented at the 13th International Radiocarbon Conference, June 20–25, 1988 in Dubrovnik, Yugoslavia.

fully dispersed from its sources. In regions where the mean transit time for CO arrival from a source is of the order of its lifetime, we can expect significant variation in concentrations as a result of transient changes in atmospheric transport.

The natural cosmogenic formation of  $^{14}\text{C}$  in the stratosphere (Lal & Peters 1962) leads to both  $^{14}\text{CO}$  and  $^{14}\text{CO}_2$ . As this  $^{14}\text{C}$  production is greatest in the stratosphere, we expect a natural vertical gradient in atmospheric  $^{14}\text{C}$ . Human intervention through nuclear weapons testing, which put  $^{14}\text{C}$  in the stratosphere, and release of fossil carbon from the surface has enhanced this natural gradient. Relatively rapid mixing in the troposphere can be expected to dissipate this gradient at lower altitudes, but across the tropopause and in the stratosphere it will persist.

Thus,  $^{14}\text{C}$  is a useful tracer of transport in the atmosphere, and particularly of vertical transport. The longer-lived species such as  $^{14}\text{CO}_2$  and  $^{14}\text{CH}_4$  provide information on the longer time scales associated with stratosphere to troposphere and interhemispheric exchange, whereas  $^{14}\text{CO}$  can provide information on the shorter time-scale movements associated with transport within a hemisphere.

We show here that the seasonal component of a 32-yr atmospheric  $^{14}\text{CO}_2$  record can be used to infer stratospheric residence times for  $\text{CO}_2$ . Our data are compared with a two-dimensional model of atmospheric transport and discrepancies are shown which imply either deficiencies in present modeling of vertical transport, or the presence of complex sources and sinks of  $^{14}\text{C}$  or both. We also show how measurements of  $^{14}\text{CH}_4$  can identify the relative strengths of fossil and modern sources of methane, and can set limits on the production of this species from nuclear power plants.

#### MEASUREMENTS OF ATMOSPHERIC $^{14}\text{CO}_2$ IN THE SOUTH PACIFIC

Measurements of  $^{14}\text{C}$  in atmospheric  $\text{CO}_2$  at Wellington, New Zealand and at other South Pacific sites ranging from the Antarctic to the Equator, were initiated by T A Rafter and G J Fergusson in the early 1950s. Early results and procedures are reported elsewhere (Rafter 1955; Rafter & Fergusson 1959; Rafter & O'Brien 1970). Our data report the results of this program up to May 1987.

The sampling procedures used to obtain nearly all the data are described by Rafter and Fergusson (1959). Trays containing ca 2L of 5 normal NaOH carbonate-free solution are exposed for intervals of 1–2 weeks, and the atmospheric  $\text{CO}_2$  absorbed during that time is recovered by acid evolution. Considerable fractionation occurs during absorption into the NaOH solution, and the standard fractionation correction (Stuiver & Polach 1977) is used to determine a  $\Delta^{14}\text{C}$  value corrected to  $\delta^{13}\text{C} = -25\text{‰}$ .

A few early measurements were made by bubbling air through columns of NaOH for several hours. These samples can be readily identified in the data as their  $\delta^{13}\text{C}$  value is much higher (*ie*, closer to the ambient air value). Also, some samples reported here were taken using BaOH solution or with extended tray exposure times. These variations in procedures do not appear to affect the results.

Table 1 lists the Wellington data for the period, Dec 1954–May 1987, and data for shorter periods at six other sites. Dates refer to the mid-point of the sampling interval, and an asterisk denotes a sample for which contamination is known or suspected. Figures 1A, B show the data after discarding these suspect cases.

Low latitudinal gradients are to be expected in the South Pacific, as the sources of  $^{14}\text{CO}_2$  are far from the sampling sites and  $\text{CO}_2$  has a mean lifetime in the atmosphere which is long compared to the time required for tropospheric mixing. This is borne out by our data which show only small variations between sites. Quantifying these differences is made difficult by the noise level, which appears to exceed the error due to counting statistics, and by the sparsity of data from different sites for common times.

Table 2 summarizes the station differences relative to the Wellington station, using months where data are common to both. This suggests that  $^{14}\text{C}$  levels in atmospheric  $\text{CO}_2$  were slightly higher in the Equatorial Pacific than at mid-southern latitudes, and were

TABLE 1  
Radiocarbon measurements of South Pacific air

Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number	Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number
<i>Tarawa, Kiribati, 1.5° N, 173.0° E</i>				750105	-21.3	391.3±3.5	NZ4101
660805	-21.6	645.7±3.6	NZ2448	750204	-18.6	376.4±3.3	NZ4102
661004	-20.9	636.6±3.8	NZ2449	750605	-22.4	415.5±3.7	NZ4079
661205	-21.2	649.3±3.8	NZ2452	750707	-20.8	401.3±3.3	NZ3829
670205	-21.5	611.6±3.9	NZ2466	750826	-22.3	390.6±3.3	NZ4141
670605	-20.9	612.7±3.8	NZ2482	750904	-23.2	358.9±3.2	NZ4142
670805	-19.5	600.2±3.8	NZ2481	751014	-22.8	363.4±3.3	NZ4299
670905	-19.3	605.6±3.9	NZ2498	751104	-23.1	366.6±3.3	NZ4300
671005	-19.5	597.8±3.8	NZ2485	751204	-22.7	360.4±3.3	NZ5646
671205	-19.4	594.8±3.8	NZ2484	760104	-22.6	371.7±3.3	NZ5647
680305	-19.3	576.1±3.8	NZ2506	760204	-22.3	354.9±3.3	NZ5648
680405	-20.5	574.8±3.8	NZ2507	760304	-22.2	353.4±3.3	NZ5649
680505	-20.1	567.2±3.8	NZ2508	760404	-21.2	357.4±3.3	NZ5650
680605	-20.2	574.0±3.8	NZ2509	760504	-21.7	348.6±3.7	NZ5651
680705	-22.8	594.6±6.0	NZ2723	760612	-20.6	357.8±5.3	NZ5692
680805	-21.9	557.5±3.5	NZ2721	760706	-20.6	353.3±3.3	NZ5693
680830	-20.7	593.8±6.0	NZ2722	760813	-21.6	352.0±3.7	NZ5694
680906	-22.6	542.2±3.9	NZ3474	770812	-16.9	348.4±3.3	NZ5695
680927	-21.1	553.4±3.9	NZ3479	<i>Funafuti, Tuvalu, 8.5° S, 179.2° E</i>			
681025	-21.0	564.1±5.9	NZ2724	660805	-21.6	650.8±3.8	NZ2446
681205	-19.4	554.9±3.8	NZ2557	661005	-21.8	638.5±3.8	NZ2447
690105	-20.3	548.8±3.8	NZ2558	661204	-21.9	619.9±3.8	NZ2450
690305	-21.5	559.1±3.8	NZ2559	670205	-22.3	636.6±3.8	NZ2465
690505	-20.6	545.2±3.8	NZ2563	670505	-20.5	609.9±3.8	NZ2474
690705	-18.9	536.7±4.0	NZ2569	670605	-21.1	612.8±3.9	NZ2475
690905	-18.7	519.4±3.6	NZ2568	670805	-19.8	596.9±4.5	NZ2476
691105	-20.6	529.6±3.9	NZ2579	671005	-20.7	598.9±3.8	NZ2483
700105	-22.4	533.0±3.8	NZ2578	671205	-21.8	582.7±4.5	NZ2486
700305	-21.5	513.6±3.9	NZ2596	671205	-21.8	586.2±4.5	NZ2489
700505	-19.9	510.3±3.9	NZ2597	680305	-20.2	563.6±3.8	NZ2510
700706	-21.8	507.4±3.9	NZ2608	680405	-21.0	596.6±3.9	NZ2511
700905	-21.5	514.0±3.9	NZ2609	680505	-21.7	561.1±3.8	NZ2512
701105	-23.1	507.4±3.9	NZ2626	680602	-19.5	551.4±3.8	NZ2513
710105	-23.3	507.6±3.9	NZ2627	680804	-20.7	549.8±3.9	NZ2525
710306	-22.8	502.7±3.9	NZ2628	680830	-22.3	556.4±3.9	NZ2526
710507	-22.7	486.5±3.9	NZ2630	680906	-18.3	544.0±4.0	NZ2527
710704	-21.5	486.3±3.7	NZ2655	680927	-21.1	570.2±5.1	NZ2725
710904	-21.2	492.0±3.5	NZ2654	681205	-21.0	553.7±3.8	NZ2536
711104	-23.5	506.2±3.9	NZ2656	690105	-18.7	552.6±3.8	NZ2537
721006	-21.3	460.5±3.6	NZ4095	690305	-20.7	552.8±3.8	NZ2554
721104	-21.9	463.6±3.3	NZ4096	690505	-21.4	535.9±3.9	NZ2561
721204	-20.5	455.9±3.6	NZ4097	690705	-20.8	529.1±3.9	NZ2565
730104	-22.8	442.8±3.3	NZ4098	690905	-21.2	518.6±3.9	NZ2574
730205	-22.9	444.8±3.7	NZ2685	691105	-21.1	517.4±3.9	NZ2575
730405	-22.7	438.1±3.3	NZ2686	700105	-21.1	513.5±3.9	NZ2577
730504	-22.3	452.7±3.7	NZ2687	700304	-20.6	527.0±3.9	NZ2580
740804	-21.3	401.8±3.3	NZ4080	700505	-21.2	523.5±3.9	NZ2594
740904	-22.5	405.4±3.7	NZ4081	700705	-21.1	504.5±3.9	NZ2595
741109	-21.5	394.2±3.6	NZ4099	701005	-22.3	516.8±3.9	NZ2615
741204	-21.8	393.9±3.6	NZ4100	701205	-21.9	517.1±3.9	NZ2616

TABLE 1 (continued)

Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number	Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number
710205	-22.2	502.6±3.9	NZ2632	650813	-22.3	640.1±3.8	NZ2047
710305	-24.2	504.3±3.5	NZ2633	650924	-22.9	654.6±3.9	NZ2036
710505	-22.4	512.8±4.0	NZ2634	651105	-23.9	653.2±3.8	NZ2041
710705	-22.7	498.7±3.6	NZ2637	660106	-22.0	666.5±3.8	NZ2039
710905	-23.0	496.2±3.9	NZ2648	660204	-23.4	644.9±3.8	NZ2042
711105	-22.5	487.4±3.5	NZ2649	660305	-21.8	635.4±3.8	NZ2040
720106	-22.2	490.0±3.6	NZ2674	660605	-23.2	649.0±3.6	NZ2044
720305	-20.8	487.9±3.6	NZ2083	660705	-23.3	622.5±3.8	NZ2048
Suva, Fiji, 18.1°S, 178.4°E				660805	-24.3	626.4±3.9	NZ2043
580402	-9.0	74.5±3.8	NZ2000	660905	-23.0	625.8±3.8	NZ2049
580407	-25.0	68.4±3.8	NZ2001	661205	-21.4	636.3±3.8	NZ2046
580510	-9.0	71.4±3.3	NZ2002	670220	-20.7	616.5±3.8	NZ2050
580510	-25.0	69.0±4.7	NZ2003	670714	-22.4	593.1±3.8	NZ2051
581104	-25.0	117.1±4.6	NZ2005	670804	-22.4	587.2±3.9	NZ2052
590228	-23.6	124.1±4.6	NZ2007	671006	-21.9	584.9±3.9	NZ2054
590703	-24.5	151.3±4.1	NZ2004	671205	-21.1	567.9±3.7	NZ2053
590922	-22.3	180.4±4.5	NZ2006	680205	-20.8	573.6±3.8	NZ2055
600122	-22.1	189.8±4.5	NZ2009	680415	-20.3	567.3±3.8	NZ2056
600414	-21.1	185.1±4.5	NZ2008	680604	-19.6	553.7±3.9	NZ2057
600902	-22.7	197.0±4.5	NZ2010	680805	-21.5	549.3±3.6	NZ2058
600929	-24.6	202.3±4.5	NZ2012	680906	-21.9	545.4±3.6	NZ2059
610120	-23.7	196.5±4.5	NZ2011	681005	-20.0	549.4±5.0	NZ2093
610301	-21.2	196.8±4.2	NZ2034	681105	-21.7	556.5±3.9	NZ2060
610414	-22.9	192.9±5.0	R00945	681205	-21.4	530.4±3.8	NZ2061
610708	-22.1	196.5±5.0	NZ2013	690105	-20.7	542.4±3.9	NZ2062
610818	-23.1	207.2±4.2	NZ2033	690307	-20.0	546.9±3.8	NZ2063
610929	-23.7	180.8±5.0	NZ2015	690505	-18.6	531.5±3.6	NZ2064
611110	-23.5	183.5±6.8	R00997	690706	-20.2	533.8±3.6	NZ2065
611219	-24.7	198.2±4.9	NZ2014	690905	-22.1	541.9±3.9	NZ2066
620119	-21.7	214.4±4.2	NZ2032	691107	-22.4	531.0±3.9	NZ2067
620301	-23.2	208.3±5.0	NZ2016	700109	-21.8	521.7±3.9	NZ2068
620301	-23.2	233.0±9.4	NZ2092	700306	-22.1	525.8±3.9	NZ2069
620412	-21.8	223.5±5.3	NZ2021	700509	-21.6	536.0±3.9	NZ2070
620412	-21.8	234.4±4.3	NZ2020	700705	-21.6	514.3±3.9	NZ2071
620706	-26.5	238.9±5.9	NZ2091	700905	-22.1	504.5±3.9	NZ2073
620927	-24.5	259.3±3.9	NZ2019	701106	-22.3	506.4±3.9	NZ2072
630117	-19.8	289.0±4.8	NZ2017	710108	-21.6	512.1±3.9	NZ2074
630705	-21.7	380.5±4.1	NZ2022	710305	-20.6	498.6±3.9	NZ2075
630917	-22.7	417.6±4.1	NZ2038	710509	-22.0	492.3±3.9	NZ2076
630927	-26.8	413.5±4.1	NZ2037	710710	-22.5	486.9±4.0	NZ2077
631220	-21.6	497.0±3.4	NZ2024	710905	-23.2	494.6±3.6	NZ2078
640116	-21.9	490.7±4.0	NZ2025	711105	-21.5	498.4±3.9	NZ2079
640409	-21.9	545.6±3.5	NZ2026	711205	-21.1	491.4±3.6	NZ2087
640522	-23.2	548.7±3.5	NZ2027	720106	-21.4	488.6±3.3	NZ2088
640702	-26.1	580.4±4.0	NZ2028	720305	-28.8	501.5±3.6	NZ2080
640925	-22.6	630.1±3.9	NZ2029	720505	-21.1	474.3±3.6	NZ2081
641217	-22.7	644.4±3.7	NZ2030	720704	-24.5	496.5±6.7	NZ2094
650115	-19.6	654.5±3.8	NZ2045	720705	-24.6	473.9±3.3	NZ2082
650408	-20.2	643.0±3.9	NZ2031	720805	-20.2	473.4±5.1	NZ2096
650701	-22.9	647.8±3.9	NZ2035	721005	-24.1	468.8±3.3	NZ2084
				730108	-18.4	458.4±4.6	NZ2095

TABLE 1 (continued)

Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number	Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number
730205	-21.1	451.3±3.7	NZ2085	660905	-28.0	631.6±3.8	NZ2456
730406	-20.4	444.6±3.3	NZ2086	661005	-23.1	614.3±3.8	NZ2455
730605	-23.0	433.6±3.3	NZ2090	661205	-20.5	602.8±3.8	NZ2457
730805	-23.9	456.2±3.7	NZ2089	670205	-16.1	592.4±3.8	NZ2470
731005	-23.9	423.1±3.3	NZ4053	670606	-20.3	501.3±4.5	NZ2473
731126	-22.5	430.7±7.4	NZ3816	670705	-19.5	516.3±3.9	NZ2497
731207	-21.3	456.5±3.3	NZ4054	670805	-20.8	535.3±3.6	NZ2472
740106	-20.9	427.3±3.7	NZ4055	670905	-21.5	575.3±3.9	NZ2496
740319	-22.4	409.8±3.7	NZ4059	680205	-20.2	561.1±3.9	NZ2500
740405	-21.6	415.2±3.7	NZ4060	680405	-19.4	562.3±3.9	NZ2501
740505	-21.4	416.1±4.4	NZ3847	680605	-21.0	529.1±3.9	NZ2517
740607	-21.4	403.8±3.7	NZ4061	680704	-22.5	517.8±3.9	NZ3468
750307	-21.6	392.6±3.3	NZ4103	680804	-20.3	503.5±3.9	NZ2519
750404	-21.8	384.1±3.3	NZ4104	680828	-20.2	533.1±3.9	NZ2518
750504	-19.7	379.0±3.3	NZ4105	680905	-25.0	531.7±3.9	NZ2533
750608	-22.0	389.3±3.7	NZ4106	680926	-21.7	509.7±3.9	NZ2534
<i>Melbourne, Australia, 37.8° S, 144.9° E</i>				681003	-19.8	515.9±3.9	NZ3495
581104	-23.6	76.5±4.0	NZ2311	681031	-22.8	521.8±3.9	NZ3480
590229	-24.6	103.3±3.8	NZ2312	681107	-22.3	535.0±3.9	NZ3482
590703	-25.1	101.5±4.6	NZ2318	681205	-19.7	512.7±3.9	NZ2532
590926	-25.2	136.6±4.5	NZ2319	690105	-19.5	534.8±3.8	NZ2555
600122	-22.4	161.5±4.5	NZ2330	690305	-19.3	532.6±3.9	NZ2556
600415	-21.4	182.1±4.5	NZ2331	690505	-19.7	496.6±3.9	NZ2562
600708	-23.0	155.1±4.6	NZ2335	690705	-20.6	496.3±3.4	NZ2581
600930	-21.0	173.0±4.5	NZ2337	690906	-20.6	488.3±3.9	NZ2586
601112	-23.5	181.7±4.5	NZ2342	691104	-19.0	507.0±3.9	NZ2588
610120	-22.5	188.8±4.5	NZ2343	700105	-18.0	515.8±3.9	NZ2587
610929	-20.7	183.2±4.0	NZ2357	700305	-19.4	509.0±3.9	NZ2620
611219	-19.0	185.2±4.0	NZ2358	700505	-20.0	486.7±3.9	NZ2621
620413	-21.3	198.6±4.0	NZ2359	700701	-20.3	475.6±3.9	NZ2622
620928	-22.5	221.8±5.2	NZ3580	700905	-19.7	486.5±3.9	NZ3547
630118	-18.2	240.9±4.1	NZ2366	701104	-20.3	480.3±3.5	NZ3548
630705	-21.0	282.3±3.9	NZ2388	710105	-19.2	484.6±3.9	NZ2625
630926	-20.5	348.9±3.8	NZ2385	710604	-17.9	433.1±3.9	NZ2650
631219	-19.4	411.5±3.8	NZ2386	710804	-18.8	463.6±3.5	NZ2651
640116	-21.6	436.8±3.8	NZ2387	711004	-19.6	462.3±3.9	NZ2652
640410	-19.7	486.6±4.0	NZ2397	711204	-18.4	470.5±3.5	NZ2653
640702	-20.3	512.0±4.0	NZ2398	720604	-18.8	398.1±6.7	NZ2733
640925	-20.2	560.3±3.9	NZ2400	<i>Wellington, New Zealand, 41.3° S, 174.8° E</i>			
641218	-20.5	574.4±3.9	NZ2399	541215	-9.4	-17.7±7.6	NZ2100
650115	-20.6	609.3±3.8	NZ2459	550222	-9.4	-10.1±7.7	NZ2099
650409	-20.1	608.0±3.9	NZ2422	550414	-9.4	-1.4±7.6	NZ2098
650520	-19.8	589.8±3.8	NZ2460	550510	-24.9	-10.3±7.8	NZ2097
651001	-20.9	612.5±3.8	NZ2423	550615	-9.4	-4.1±5.9	NZ2102
651105	-20.9	620.7±3.8	NZ2430	550907	-8.8	-11.9±4.0	NZ2103
651205	-20.1	516.9±3.9	NZ2461	551215	-8.8	0.1±5.4	NZ2104
660107	-20.2	610.2±3.8	NZ2424	560219	-8.8	5.6±3.9	NZ2105
660305	-21.1	614.0±3.8	NZ2438	560615	-25.0	37.9±4.8	NZ2107
660505	-22.8	614.9±3.8	NZ2437	560925	-25.8	10.1±4.8	NZ2108
660605	-20.5	587.3±3.9	NZ2440	561021	-9.0	13.6±4.7	NZ2110

TABLE 1 (continued)

Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number		Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number
561022	-9.2	18.1±4.7	NZ2109		630118	-25.9	265.5±3.9	NZ2154
570127	-9.0	18.3±3.7	NZ2111		630301	-23.6	269.7±3.9	NZ2156
570127	-10.1	24.9±3.7	NZ2112		630301	-23.6	266.4±3.8	NZ2159
570428	-10.6	39.0±4.7	NZ2113		630414	-23.5	280.9±3.8	NZ2160
570428	-9.8	41.5±4.7	NZ2114		630414	-23.5	284.3±3.9	NZ2157
570522	-24.8	16.6±4.8	NZ2115		630526	-24.2	313.2±4.1	NZ2163
570723	-9.4	44.9±3.9	NZ2120		630706	-24.7	331.1±4.1	NZ2161
570723	-9.6	43.4±3.9	NZ2118		630817	-24.7	355.6±4.3	NZ2162
570827	-24.8	51.4±4.0	NZ2116		630929	-23.7	405.2±3.8	NZ2164
571009	-12.5	46.3±5.1	NZ2122		631110	-24.7	374.8±4.1	NZ2165
571106	-9.7	51.6±4.7	NZ2124		631220	-24.7	429.5±3.8	NZ2166
571126	-8.8	62.0±4.6	NZ2123		640117	-23.1	445.7±3.8	NZ2167
580318	-9.4	67.5±4.0	NZ2126		640301	-22.8	472.5±4.0	NZ2168
580318	-10.1	76.2±4.0	NZ2125		640411	-23.7	500.3±4.0	NZ2169
580704	-25.0	81.1±3.8	NZ2128		640523	-25.9	498.3±3.9	NZ2170
580828	-25.0	77.8±3.8	NZ2127		640703	-24.7	542.4±3.7	NZ2171
580929	-24.8	93.9±3.5	NZ2129		640815	-24.6	567.4±4.0	NZ2173
581009	-24.6	116.9±4.6	NZ2130		641003	-25.4	507.0±3.9	NZ2172
581223	-25.0	110.1±3.8	NZ2131		641106	-24.7	621.9±3.9	NZ2174
590117	-25.0	121.1±3.8	NZ2132		641217	-19.9	615.7±3.9	NZ2175
590302	-25.0	126.0±4.6	NZ2133		650115	-22.0	689.4±7.5	NZ2271
590411	-25.1	137.2±3.8	NZ2134		650227	-23.6	633.6±3.9	NZ2176
590601	-25.9	132.8±3.8	NZ2136		650408	-23.9	634.1±3.9	NZ2178
590713	-25.2	150.1±3.8	NZ2135		650521	-21.4	615.2±3.8	NZ2177
590813	-25.0	141.8±4.5	NZ2137		650702	-25.7	694.5±3.9	NZ2180
591001	-26.4	164.6±4.5	NZ2138		650813	-23.9	614.1±3.9	NZ2179
591119	-24.5	171.4±4.5	NZ2139		650924	-25.2	634.2±4.0	NZ2181
591219	-25.0	181.7±4.5	NZ2140		651106	-18.1	625.7±4.0	NZ2182
600121	-25.2	181.8±4.5	NZ2141		651224	-24.9	634.4±3.9	NZ2183
600414	-23.4	187.9±4.5	NZ2142		660204	-24.6	647.3±3.9	NZ2184
600714	-24.0	187.4±4.5	NZ2143		660308	-26.4	646.5±3.9	NZ2185
600901	-22.8	193.7±4.5	NZ2145		660402	-23.9	631.8±3.6	NZ2186
600929	-22.5	195.9±4.5	NZ2144		660520	-26.1	622.1±3.8	NZ2189
601113	-26.4	198.4±4.5	NZ2147		660610	-25.0	612.4±4.2	NZ2188
601219	-24.5	193.7±4.5	NZ2146		660706	-23.2	612.2±4.4	NZ2187
610120	-25.5	194.9±4.5	NZ2148		660819	-24.8	590.8±3.9	NZ2190
610310	-24.9	207.1±5.1	NZ2149		660909	-26.8	625.2±3.8	NZ2191
610414	-25.0	201.9±4.5	NZ2150		661007	-23.8	614.8±3.9	NZ2192
610526	-26.3	196.7±4.5	NZ2151		661105	-25.1	614.9±4.2	NZ2193
610706	-25.1	198.3±9.5	NZ2263		661211	-24.8	627.8±3.9	NZ2194
610819	-25.3	197.9±6.3	NZ2262		670109	-24.6	616.4±3.9	NZ2195
611003	-24.7	182.8±5.0	NZ2152		670224	-23.0	602.9±4.4	NZ2196
611111	-23.8	237.2±9.4	NZ2264		670408	-23.4	609.0±3.8	NZ2197
611219	-25.1	227.3±9.4	NZ2265		670506	-23.7	596.5±3.8	NZ2198
620119	-24.6	197.4±5.0	NZ2268		670610	-23.7	580.0±6.3	NZ2272
620302	-23.4	207.3±7.5	NZ2266		670610	-23.7	595.9±5.4	NZ2273
620425	-24.5	214.3±5.1	NZ2267		670719	-24.4	571.3±3.8	NZ2199
620525	-24.5	189.4±9.5	NZ2269		671006	-23.1	575.1±3.8	NZ2200
620928	-24.5	233.5±4.4	NZ2155		671110	-25.7	586.0±5.2	NZ2274
621109	-24.0	250.4±5.9	NZ2270		671209	-24.4	579.6±3.9	NZ2201
621220	-28.4	266.6±3.9	NZ2153		680113	-23.9	583.0±3.9	NZ2202

TABLE 1 (continued)

Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number	Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number
680211	-24.5	582.5±3.9	NZ2203	720317	-22.5	474.8±7.4	NZ2282
680311	-22.5	572.8±3.6	NZ2204	720331	-23.8	482.4±3.6	NZ2250
680406	-23.9	547.6±3.7	NZ2205	720420	-22.6	468.1±3.6	NZ2254
680531	-24.8	560.5±3.9	NZ2206	720504	-23.0	469.5±5.1	NZ2286
680607	-24.6	561.7±3.9	NZ2207	720610	-24.4	470.1±5.1	NZ2287
680705	-26.3	550.4±3.9	NZ2208	720707	-24.0	465.9±5.1	NZ2288
680809	-24.7	538.1±3.9	NZ2209	720901	-24.7	450.3±5.1	NZ2289
680830	-23.8	535.5±3.8	NZ2210	721007	-24.4	449.9±6.7	NZ2283
680906	-23.7	531.5±3.9	NZ2211	721208	-24.9	447.3±4.7	NZ2285
681004	-24.6	532.8±3.9	NZ2212	730210	-24.3	453.9±5.1	NZ2291
681018	-24.7	537.6±3.9	NZ2213	730309	-23.6	442.8±3.3	NZ2255
681102	-25.3	541.9±3.9	NZ3470	730706	-24.7	435.0±3.7	NZ2256
681108	-26.9	541.2±3.9	NZ2214	730811	-24.5	427.1±3.3	NZ2257
681206	-23.8	539.6±3.9	NZ2215	730907	-24.4	415.9±3.7	NZ2258
690110	-24.3	539.1±3.9	NZ2217	731006	-24.1	426.0±3.3	NZ2259
690207	-23.1	537.7±3.8	NZ2216	731109	-23.4	434.3±3.7	NZ2260
690308	-23.3	550.4±3.8	NZ2218	731207	-23.3	417.2±3.2	NZ2261
690413	-23.4	545.4±3.8	NZ2222	740111	-23.2	412.8±3.5	NZ3565
690502	-23.1	530.4±4.0	NZ2220	740201	-23.0	405.1±3.3	NZ3566
690509	-22.8	539.6±3.9	NZ2221	740308	-22.2	418.5±3.3	NZ3567
690607	-23.4	525.2±4.2	NZ2223	740404	-23.0	417.2±3.3	NZ3568
690711	-23.2	526.3±3.9	NZ2219	740510	-23.3	386.8±3.3	NZ3572
690809	-23.0	522.8±3.9	NZ2224	740607	-23.3	359.7±3.3	NZ4052
690905	-23.5	544.9±3.8	NZ2225	740706	-23.3	394.5±3.3	NZ4057
691010	-25.2	531.2±3.9	NZ2226	740807	-24.8	392.3±3.7	NZ4058
691103	-23.2	523.0±3.9	NZ2227	740906	-23.4	405.0±3.3	NZ4062
691205	-22.5	510.2±3.9	NZ2228	741005	-23.2	398.7±4.7	NZ3848
700109	-22.5	510.2±3.9	NZ2229	741108	-22.8	401.7±3.3	NZ4065
700306	-22.5	535.3±3.9	NZ2230	741208	-23.4	393.7±3.3	NZ4074
700410	-22.1	520.4±3.9	NZ2232	750110	-22.2	396.3±3.3	NZ4076
700509	-22.4	513.5±3.9	NZ2231	750207	-23.4	399.0±3.7	NZ4078
700606	-23.3	516.2±3.9	NZ2233	750307	-23.3	400.6±3.3	NZ4083
700710	-23.8	505.9±3.9	NZ2234	750405	-23.4	397.7±3.3	NZ4088
700807	-23.6	497.4±3.5	NZ2235	750510	-23.2	389.1±3.7	NZ4090
700911	-24.5	508.0±3.9	NZ2236	750620	-23.9	384.5±3.3	NZ4092
701010	-24.3	498.6±3.9	NZ2237	750709	-23.1	377.3±3.3	NZ4094
701106	-23.3	497.6±4.0	NZ2238	750810	-24.9	378.1±3.7	NZ4108
701223	-22.7	495.6±3.9	NZ2239	750912	-26.2	367.5±3.7	NZ4110
710110	-22.3	500.6±3.9	NZ2240	751003	-23.6	354.0±8.8	NZ4121
710205	-23.8	494.7±3.7	NZ2241	751010	-22.4	365.3±3.3	NZ4119
710305	-24.6	508.3±3.9	NZ2242	751115	-23.0	363.8±3.7	NZ4122
710409	-24.8	501.0±3.9	NZ2243	751205	-23.6	370.8±3.7	NZ4124
710507	-24.9	499.7±3.9	NZ2244	760113	-23.8	373.4±3.7	NZ4126
710611	-24.6	499.0±3.9	NZ2245	760206	-24.3	368.1±3.3	NZ4135
710709	-25.9	494.2±4.1	NZ2246	760306	-23.7	366.7±3.1	NZ4137
710808	-23.5	483.3±4.0	NZ2248	760410	-23.0	346.1±3.3	NZ4145
710910	-24.5	478.8±4.5	NZ2247	760510	-22.9	359.6±3.3	NZ4140
711010	-24.0	492.5±3.9	NZ2249	760606	-25.0	360.9±3.4	NZ4144
711203	-24.8	479.3±3.9	NZ2251	760704	-22.2	365.0±5.0	NZ4302
720109	-23.9	484.5±3.6	NZ2252	760815	-23.9	343.3±3.7	NZ5659
720206	-24.7	491.6±4.0	NZ2253	761011	-22.9	344.2±5.1	NZ5673

TABLE 1 (continued)

Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number	Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number
761104	-25.3	346.5±3.3	NZ5675	811203	-25.4	254.8±3.2	NZ6067
761210	-23.6	329.6±3.7	NZ5678	820402	-25.4	* 385.6±3.7	NZ6432
770103	-24.5	332.9±3.7	NZ5679	820509	-23.5	245.2±3.2	NZ6449
770211	-24.3	347.0±5.3	NZ5688	820605	-25.0	248.5±3.2	NZ6450
770311	-24.7	335.4±4.5	NZ5690	820708	-23.3	249.2±3.8	NZ6451
770506	-24.8	332.9±3.3	NZ5697	820902	-25.8	241.3±3.2	NZ6459
770612	-24.1	335.6±4.7	NZ5699	821206	-25.2	235.5±3.4	NZ6523
770715	-22.4	331.5±3.7	NZ5900	830117	-24.1	233.6±3.7	NZ6527
770813	-24.1	323.6±3.3	NZ5702	830207	-24.9	227.4±3.7	NZ6528
770909	-24.8	317.6±3.3	NZ5707	830306	-25.8	233.9±3.3	NZ6529
771001	-28.1	335.1±3.4	NZ5730	830519	-2.2	* 398.4±15.5	NZ6623
771007	-24.2	322.0±3.7	NZ5731	830607	-25.2	235.6±3.7	NZ6530
771111	-23.4	325.0±3.7	NZ5732	830819	-25.0	235.0±3.7	NZ6538
780502	-24.6	314.6±3.7	NZ5866	831015	-24.9	221.2±3.7	NZ6539
780611	-25.8	310.4±3.7	NZ5867	831029	-7.3	* 290.0±9.6	NZ6624
780630	-25.9	314.8±3.7	NZ5868	840115	-25.0	217.5±3.3	NZ6540
780804	-25.2	308.8±3.2	NZ5869	840205	-24.2	230.3±3.8	NZ6549
780908	-18.0	309.0±5.1	NZ5870	840508	-25.3	214.0±3.8	NZ6816
781007	-25.5	321.3±8.9	NZ5871	840610	-25.9	* 244.8±4.5	NZ6815
781110	-25.4	308.1±3.3	NZ5872	840709	-25.3	214.5±3.8	NZ6817
790112	-24.9	310.2±3.3	NZ5910	840803	-26.4	238.0±4.4	NZ6807
790317	-24.7	302.8±3.3	NZ5911	840910	-25.4	208.1±3.5	NZ6820
790407	-25.3	304.2±3.7	NZ5912	841111	-25.4	206.9±2.7	NZ6821
790509	-24.9	296.2±3.2	NZ5913	841202	-26.4	216.8±3.3	NZ6831
790603	-24.5	292.3±3.3	NZ5914	850202	-26.5	206.9±3.3	NZ6847
790710	-24.9	298.6±3.8	NZ5915	850324	-25.4	209.8±3.8	NZ6858
790812	-25.4	284.0±3.8	NZ5916	850706	-27.2	218.0±8.0	NZ7257
791005	-25.3	282.9±3.7	NZ5956	850809	-25.7	213.0±6.0	NZ7277
791103	-25.2	303.5±3.8	NZ5957	850909	-25.8	204.0±6.0	NZ7272
791209	-24.3	276.4±3.3	NZ5958	851102	-26.0	203.4±4.2	NZ7408
800212	-25.3	282.3±3.3	NZ5959	851202	-26.6	205.1±4.2	NZ7409
800308	-25.1	289.0±3.8	NZ5960	860110	-23.7	204.0±4.0	NZ7264
800404	-24.8	277.6±3.3	NZ5961	860214	-26.0	207.0±5.0	NZ7286
800508	-23.7	279.4±3.3	NZ5969	860331	-26.0	199.0±5.0	NZ7382
800616	-23.5	* 239.1±7.9	NZ5971	860502	-23.5	184.0±7.0	NZ7417
800706	-25.4	281.5±3.7	NZ6008	860712	-25.8	194.5±4.2	NZ7410
800801	-25.0	274.3±3.7	NZ6009	860810	-26.5	188.3±3.7	NZ7412
800905	-24.8	278.1±3.3	NZ6010	860907	-26.1	200.8±3.7	NZ7413
801009	-25.5	282.7±3.7	NZ6011	861005	-26.0	194.0±4.0	NZ7430
801111	-25.6	272.9±3.2	NZ6012	861108	-25.5	191.0±4.0	NZ7431
801204	-25.4	268.6±3.4	NZ6013	861207	-25.6	189.0±4.0	NZ7432
810110	-24.7	266.0±3.7	NZ6014	870103	-25.5	185.0±4.0	NZ7454
810206	-25.4	260.9±3.7	NZ6015	870405	-25.6	189.0±5.6	NZ7395
810312	-24.0	264.1±4.7	NZ6016	870510	-25.5	190.0±4.2	NZ7455
810410	-25.2	270.9±3.3	NZ6017	870609	-25.8	176.2±4.6	NZ7456
810507	-24.5	* 352.2±3.3	NZ6421	<i>Campbell Is, New Zealand, 52.5° S, 169.2° E</i>			
810606	-26.2	263.3±3.7	NZ6062	700105	-25.2	501.6±3.9	NZ2600
810809	-26.1	259.5±3.3	NZ6063	700305	-23.7	511.0±3.9	NZ2601
810904	-25.1	258.0±5.1	NZ6064	700504	-24.4	512.5±3.9	NZ2604
811002	-26.0	256.8±3.3	NZ6065	700710	-25.2	496.7±3.9	NZ2607
811101	-25.4	254.7±3.7	NZ6066				



TABLE 1 (continued)

Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number
700904	-25.6	486.7±3.6	NZ2662
701104	-24.9	482.6±3.9	NZ2663
710106	-24.3	494.0±3.9	NZ2664
710307	-23.3	504.6±3.9	NZ2665
710404	-18.3	506.1±3.9	NZ2666
710704	-25.2	489.9±3.7	NZ2667
710904	-26.1	483.7±5.2	NZ2742
730105	-26.2	453.9±5.2	NZ2743
731008	-22.7	409.8±3.7	NZ2690
731108	-25.2	406.4±3.3	NZ2691
731206	-26.1	403.3±3.3	NZ2692
740115	-24.8	404.8±3.3	NZ2693
740304	-25.4	411.5±3.7	NZ4066
740404	-25.1	403.2±3.3	NZ4067
740506	-26.1	412.2±3.7	NZ4068
740607	-25.9	408.4±3.3	NZ4069
740706	-25.9	401.1±3.7	NZ4070
740804	-24.8	402.8±3.7	NZ4071
740904	-25.4	397.2±3.7	NZ4072
740908	-26.6	400.4±3.7	NZ4084
741004	-25.2	420.2±3.2	NZ5644
741104	-24.1	402.2±3.3	NZ4086
741208	-22.9	393.5±7.4	NZ3835
750112	-23.3	393.7±5.1	NZ4127
750204	-24.4	374.5±4.6	NZ4128
750313	-24.3	389.3±3.7	NZ4111
750417	-25.7	395.3±5.1	NZ4112
750506	-25.2	385.1±5.5	NZ4113
750608	-25.4	400.4±5.8	NZ4114
750707	-26.1	368.4±3.3	NZ4115
750813	-25.1	359.7±3.7	NZ4116
750908	-22.7	359.9±3.2	NZ4117
751008	-26.8	373.2±3.3	NZ4129
751105	-25.1	368.9±3.7	NZ4130
751204	-25.9	364.0±3.3	NZ4131
760104	-24.7	370.4±3.3	NZ4132
760204	-25.4	363.8±3.7	NZ4133
760304	-25.3	353.6±3.7	NZ5666
760406	-25.3	362.1±3.3	NZ5667
760504	-24.3	352.5±3.2	NZ5668
760604	-25.5	350.2±3.5	NZ5669
760704	-24.8	351.4±3.3	NZ5670
760803	-25.2	344.0±3.3	NZ5671
760904	-25.3	343.0±3.2	NZ5681
761004	-24.9	330.4±3.2	NZ5682
761104	-25.3	333.3±3.7	NZ5683
761204	-25.2	342.0±3.3	NZ5684
770104	-24.3	337.7±3.3	NZ5685
770204	-23.5	334.3±3.7	NZ5686

Date	$\delta^{13}\text{C}$ ‰	$\Delta^{14}\text{C}$ ‰	Lab number
<i>Scott Base, Antarctica, 77.9° S, 166.7° E</i>			
611105	-26.1	195.7±6.4	NZ2695
611230	-25.6	196.7±9.6	NZ3577
620207	-27.7	180.3±9.9	NZ3575
620228	-27.4	203.2±6.3	NZ3573
621201	-32.3	251.5±3.9	NZ2373
630107	-29.1	255.8±4.1	NZ2374
660102	-26.1	622.0±3.8	NZ2426
660124	-23.1	635.2±3.9	NZ2417
660205	-23.8	622.5±3.8	NZ2427
660217	-14.9	633.3±3.6	NZ2418
671202	-23.4	573.8±3.9	NZ2493
671229	-24.6	577.6±3.9	NZ2494
680129	-21.3	539.3±5.2	NZ2715
680212	-17.6	573.6±3.9	NZ2495
681121	-23.2	539.1±3.8	NZ2547
681216	-25.0	542.3±3.9	NZ2548
690110	-24.6	545.1±3.8	NZ2549
690208	-26.3	542.4±3.9	NZ2550
691106	-19.4	556.6±8.8	NZ2729
691227	-19.2	476.1±7.3	NZ2730
700116	-16.4	492.4±7.3	NZ2731
710408	-22.9	496.2±3.5	NZ2658
710420	-24.5	497.3±3.9	NZ2657
710714	-24.5	479.5±3.6	NZ2659
711112	-27.8	477.7±4.0	NZ2661
711218	-26.5	477.5±4.0	NZ2660
730215	-20.5	447.3±3.7	NZ2682
730412	-23.6	433.7±5.2	NZ2747
730914	-25.0	432.4±4.5	NZ2750
731019	-20.3	438.0±6.8	N

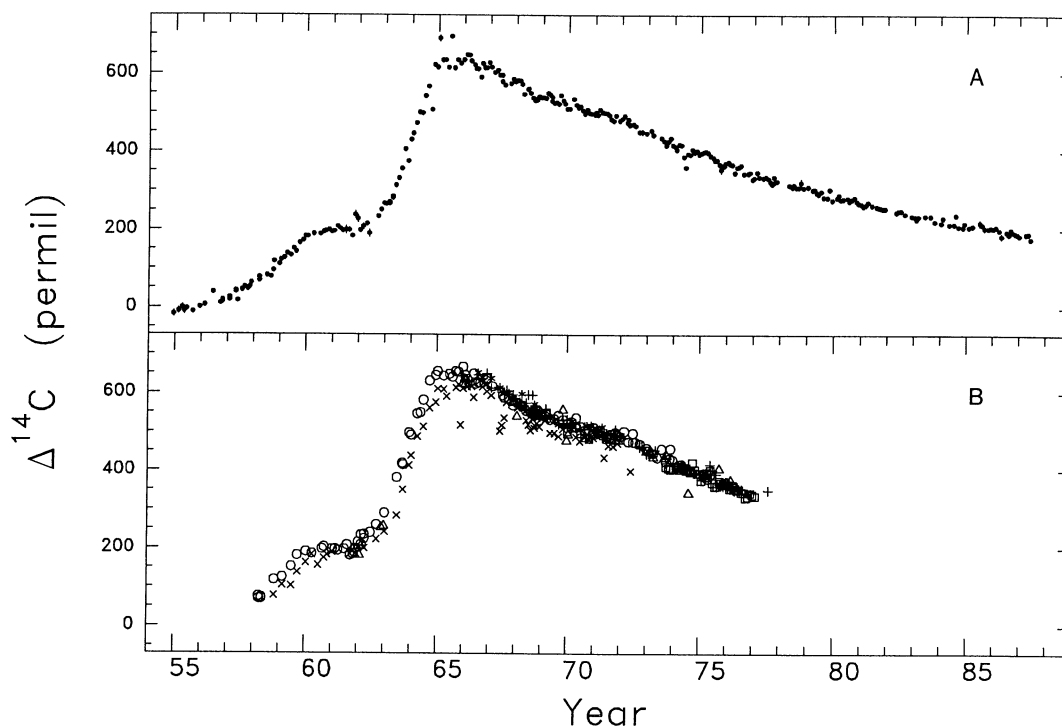


Fig 1.  $\Delta^{14}\text{C}$  values measured in atmospheric  $\text{CO}_2$  at (A) Wellington, New Zealand and (B) other sites in the South Pacific, 1954–1987. Symbols used in (B) are: + Tarawa Is, 1.5°N; \* Funafuti, 8.5°S; O Suva, 18.1°S; x Melbourne, 37.8°S; □ Campbell Is, 52.5°S; and △ Scott Base, 77.9°S.

slightly lower at higher latitudes during 1966–1976. The data from Melbourne are ca 25‰ lower than the Wellington data, and as pointed out by Rafter and O'Brien (1970), this is likely to be due to a local effect of fossil-fuel carbon at the monitoring site which was a rooftop in the center of Melbourne city.

The  $^{14}\text{C}$  record for the South Pacific in Figures 1 A, B clearly shows a peak in 1965 occurring a little over one year later than that observed in the Northern Hemisphere (Nydal & Lovseth 1983; Levin *et al* 1985). Although Northern Hemisphere surface measurements of  $^{14}\text{CO}_2$  were higher than those reported here in the mid-1960s, this difference had disappeared by 1968. From 1980 onwards, the Southern Hemisphere  $\Delta^{14}\text{C}$  values appear slightly higher than those measured in Europe. This is consistent with a regional “Suess” effect influencing the European data. The continuing fall of excess  $^{14}\text{CO}_2$  has a 1/e time of ca 17 yr.

TABLE 2

$\Delta^{14}\text{C}$  for South Pacific sites relative to Wellington statistics of differences in data for the same month

Site	No of common months	Median difference	Mean difference	Standard deviation about mean
Tarawa, 1.5°N	58	8.7	7.3	16.2
Funafuti, 8.5°S	34	8.6	10.2	17.0
Suva, 18.1°S	86	8.7	8.7	20.3
Melbourne, 37.8°S	60	-22.3	-27.0	23.4
Campbell Is, 52.5°S	50	-6.4	-3.5	13.9
Scott Base, 77.9°S	29	-4.5	-6.6	21.1

The seasonal structure in the region of the peak Southern Hemisphere values is much less pronounced than for Northern Hemisphere data. This, together with the later arrival of the peak in the Southern Hemisphere, is consistent with the fact that most of the release of  $^{14}\text{C}$  from nuclear weapons testing occurred in the Northern Hemisphere. Further, it is well established (Telegadas 1971) that most of the  $^{14}\text{C}$  inventory produced by nuclear tests was located in the stratosphere by the mid-1960s. Figure 2 shows this stratification of the  $^{14}\text{C}$  inventory between the stratosphere and troposphere by comparing surface data (Levin *et al* 1985; this work), with tropospheric and stratospheric data (Telegadas 1971).

#### ANALYSIS OF $^{14}\text{CO}_2$ DATA

We average all the data (usually just one value) available for Wellington in each month in order to obtain a time series spanning 391 months with 104 missing values. The missing data are fairly evenly distributed through the record and so are unlikely to bias the following analysis.

In order to extract a seasonal component, we must determine a smooth trend in the data about which the seasonal variation occurs. There are many procedures for doing this (eg, Cleveland Freeny & Graedel 1983; Enting 1987). The methods used here are based on "loess" smoothing (Cleveland 1979) and the "STL" procedure for seasonal and trend decomposition (Cleveland & McRae 1989).

Loess smoothing determines a smoothed value at each point in the series from a window of a fixed number of nearest neighbors. The smoothed value is determined by fitting a straight line to the data window using weights that decrease with distance from the subject point. Both loess smoothing and the STL procedure are robust with respect to outliers, *ie*,

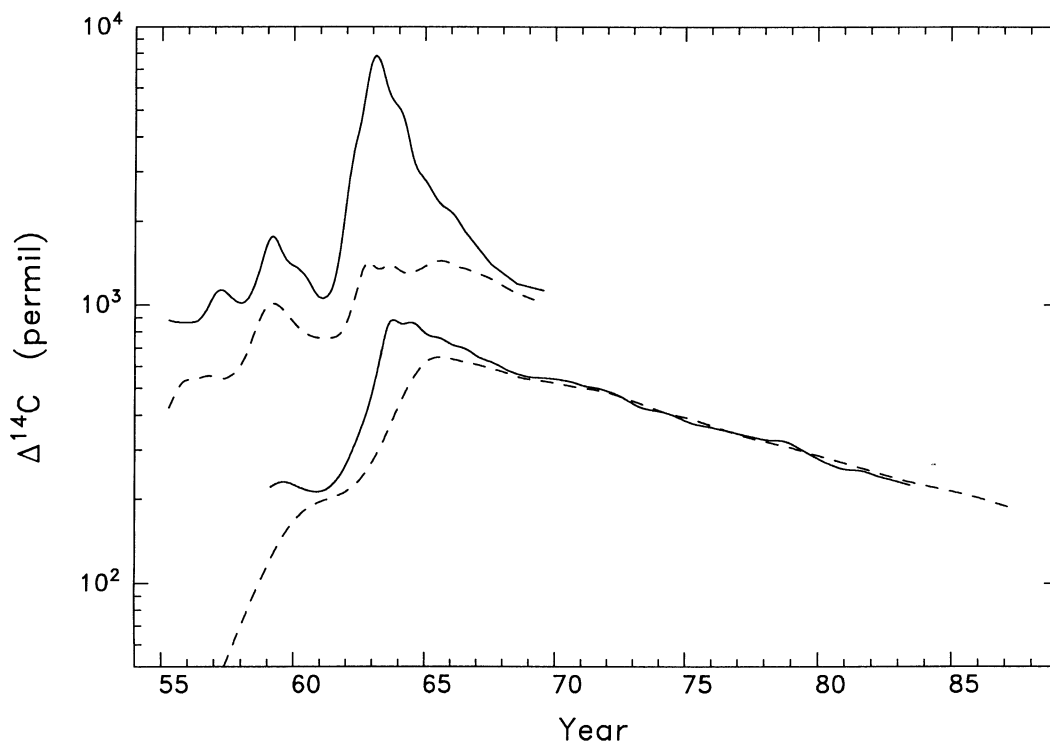


Fig 2.  $\Delta^{14}\text{C}$  values in the stratosphere and at the earth's surface shown as smooth spline curves fitted to available data; the upper two curves are for the stratosphere and the lower two for the surface; — denotes Northern Hemisphere and — — Southern Hemisphere. Based on stratospheric data from Telegadas (1971), Northern Hemisphere surface data from Levin *et al* (1985) and Southern Hemisphere surface data from this work.

outlier points are identified by an initial calculation, their weights are reduced and the calculation repeated. The STL procedure determines the seasonal and trend components simultaneously with a consistent philosophy of the structure of each. The trend component is determined by loess smoothing of the data minus the seasonal component, the latter being determined for each calendar month by loess smoothing of the data minus the trend component. STL allows arbitrary variation of the seasonal component from month to month within the year (in contrast to band pass filtering methods) but ensures small variation in the seasonal cycle from year to year.

There are inherent difficulties in separating seasonal and trend components for both the rapid rise in  $\Delta^{14}\text{C}$  values during the early 1960s and the following decay. Further, the relative distribution of  $^{14}\text{C}$  throughout the atmosphere may have been significantly altered by the very large tests of the early 1960s. Thus, in order to determine a consistent and slowly varying seasonal component, we have limited the analysis to 1966 onwards.

The STL procedure does not allow for missing data, so missing values have been interpolated by fitting a Reinsch (1967) spline to the data, and adjusting the tension of the spline so that the number of sign changes in residuals agrees with that expected for a random sequence. We have tried alternative procedures for interpolating missing data which do not significantly affect the results. Figures 3A, B, C, show the trend, seasonal and remainder components. The seasonal component shows a cycle of decreasing amplitude with some evidence of a phase change in the latter part of the record.

Up to 1980, the cycle has a maximum in March and a minimum in August; a negative anomaly occurs in December. The amplitude of the cycle decreases steadily from a peak-to-peak range of 20‰ in 1966 to 3‰ in 1980. From 1966–1975, while the shape of the cycle is roughly constant, the amplitude decays exponentially with a  $1/e$  time of 12 yr. From 1980 onwards, a different cycle emerges with an amplitude of ca 5‰, a maximum in July–August

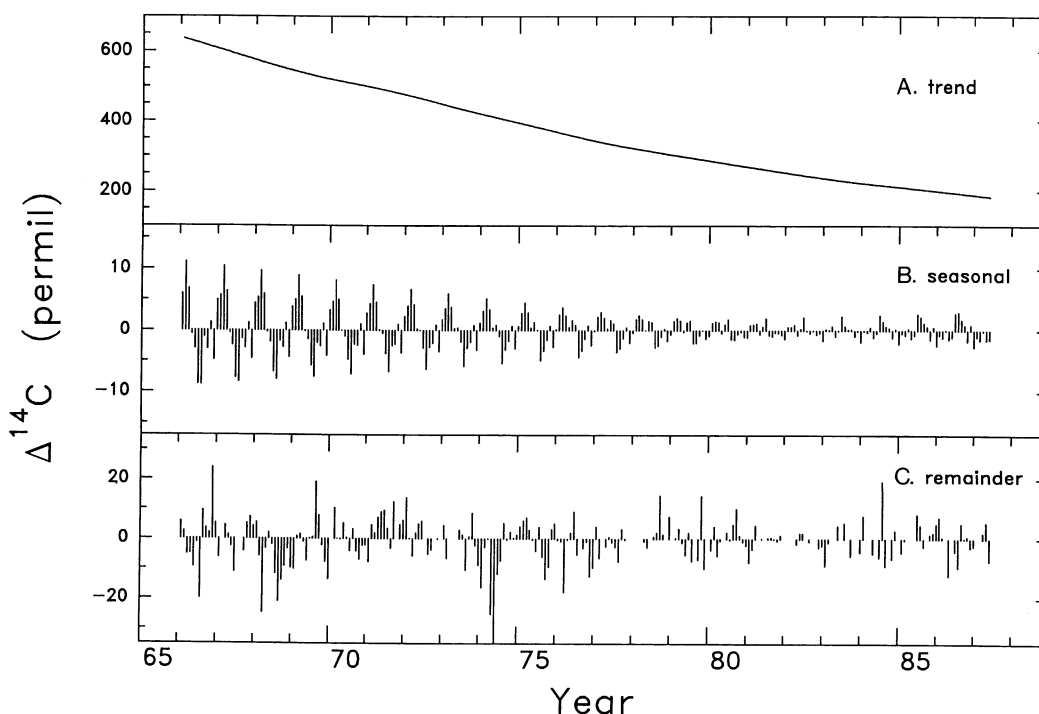


Fig 3. The (A) smooth trend, (B) seasonal and (C) remainder components of the Wellington  $\Delta^{14}\text{C}$  data record determined by the STL procedure as discussed in the text.

and minimum in January. If present, this would have been masked in the earlier part of the record by the larger decaying cycle.

A direct indication of the change in the seasonal cycle can be seen by plotting the differences of the original data from a smooth trend, against a calendar month. Figures 4A, B show such “month-plots” of differences from the smooth trend, in the periods 1966–1977 and 1981–1987. Horizontal bars show the mid-mean (mean of values between the upper and lower quartiles) of all data for a given month. Individual data values are shown by a spike from the mid-mean for the corresponding month. The contrast in the annual cycle for these two periods confirms that the change in the seasonal cycle is not an artifact of the interpolation or outlier rejection techniques used with the STL procedure.

Finally, we note that the seasonal cycles at the other South Pacific sites are not well determined by our data, and for some months the differences between sites are large compared with errors due to counting statistics. These appear often enough to suggest that regional variations in  $^{14}\text{CO}_2$  may be as large as 20‰.

#### INTERPRETATION OF $^{14}\text{CO}_2$ SEASONAL AND TREND VARIATION

The overall decline in atmospheric  $^{14}\text{CO}_2$  has been studied extensively in many analyses of the global carbon cycle (Oeschger *et al* 1975; Enting & Pearman 1983). This decline is predominantly determined by the rate of exchange of carbon between the atmosphere and the ocean, and is one of the best determinants of that exchange rate.

Although the seasonal cycle in atmospheric  $^{14}\text{CO}_2$  has not been well researched, seasonal cycles in other “bomb”-produced radionuclides, particularly  $^{90}\text{Sr}$  and  $^3\text{H}$ , are influenced by seasonal changes in transport of stratospheric air into the troposphere. The transport of gaseous tracers such as  $^{14}\text{CO}_2$  is by advection and diffusion, whereas for other radionuclides particulate deposition and rainout phenomena are dominant (Sarmiento & Gwinn 1986; Schell, Sauzay & Payne 1974). Thus, differences between the seasonal cycle of  $^{14}\text{CO}_2$  and other fallout species are expected.

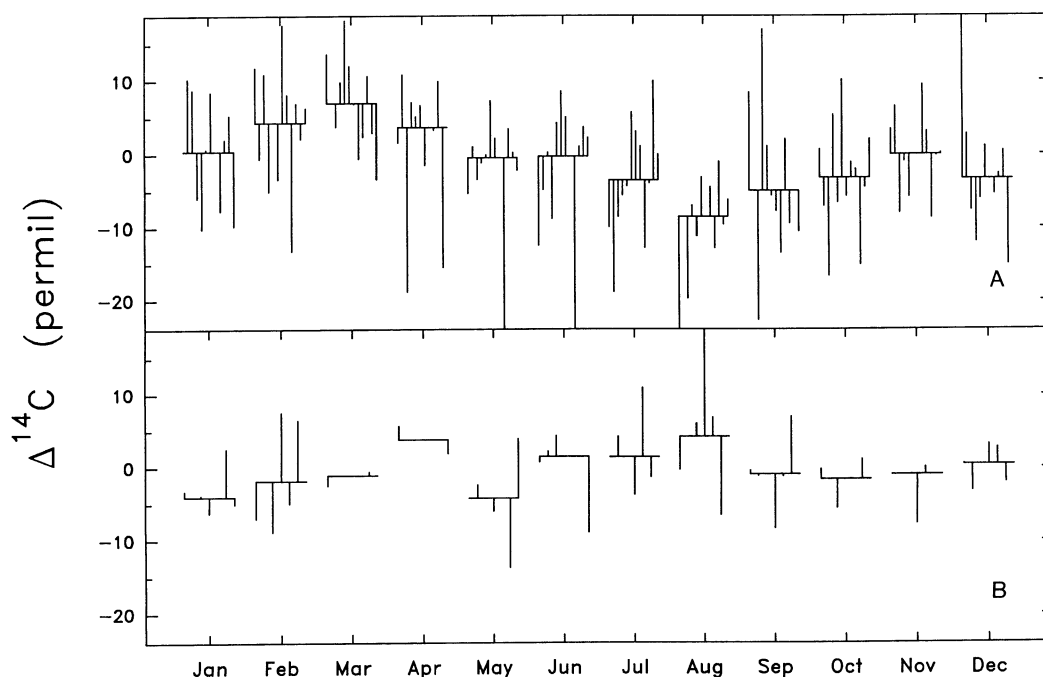


Fig 4. Seasonal cycles of differences between  $\Delta^{14}\text{C}$  data and their smooth trend. Data are grouped by calendar month and shown as spikes from the mid-mean, (A) for period 1966–1977 and (B) for period 1981–1987.

Factors other than transport from the stratosphere also contribute to seasonal variation in  $^{14}\text{CO}_2$ . Levin (1985) reports variations at a European site due to seasonal changes in the release of fossil-fuel  $\text{CO}_2$ , and at an Antarctic site due to seasonal changes in ocean-atmosphere exchange.

The seasonal cycle from 1966 to 1980 is consistent with a seasonal variation in the transfer of “bomb”  $^{14}\text{CO}_2$  from the stratosphere to the troposphere. The decay in the amplitude of this cycle is then explained by the depletion of the stratospheric inventory. Because mixing within the Southern Hemisphere troposphere occurs within a few months, we assume that the amplitude of the seasonal component seen at the surface is proportional to the amount of  $^{14}\text{CO}_2$  transferred from stratosphere to troposphere in the previous few months. If this is assumed to be proportional to the  $^{14}\text{CO}_2$  inventory in the stratosphere, modulated by the seasonally varying exchange rate, then the 12-yr decay time of the seasonal cycle is equal to the mean residence time for stratospheric  $\text{CO}_2$ .

This estimate of stratospheric mean residence time is longer than the value of 7.0 yr (half-life of 58 months) derived by Telegadas (1971) from measurements of  $^{14}\text{C}$  in the stratosphere up to 1969. This earlier data may reflect a residence time for just the lower part of the stratosphere. The value derived here is closer to an alternative estimate of 10 yr for the mean residence time of air in the stratosphere based on energy and mass flux (Walker 1977).

#### COMPARISON OF $^{14}\text{CO}_2$ DATA WITH ATMOSPHERIC TRANSPORT MODELS

Modeling of tracer transport in the atmosphere due to advection and diffusion has progressed considerably in recent years (Mahlman, Levy & Moxim 1980; Golombek & Prinn 1986). Models that incorporate consistent global circulation and realistic (if approximate) climatology can now be used to predict tracer concentrations. This approach is preferable to inferring atmospheric transport from tracer data alone.

We now present some results using a two-dimensional model for atmospheric transport (Plumb & Mahlman 1987; Plumb & McConalogue 1988) which is a zonally averaged version of a larger three-dimensional global circulation model (GCM) (Mahlman & Moxim 1978). The zonally averaged version gives the same net tracer transport as the three-dimensional model, but requires much less computer time. A resolution of  $2.4^\circ$  in latitude and 10 vertical levels extending to the 10mBar level (33km) are used.

The vertical diffusion coefficients at the lowest two layers were increased to  $8\text{m}^2\text{s}^{-1}$  (bottom level) and  $6\text{m}^2\text{s}^{-1}$  (next lowest level), based on other work using this model for determining seasonal variation of atmospheric  $\text{CO}_2$  concentrations (Plumb, pers commun). Otherwise the fields determining atmospheric transport are as determined from the three-dimensional GCM.

To relate our South Pacific  $^{14}\text{CO}_2$  data with this model, it was run from an initial condition where a tracer is injected instantaneously with uniform concentration throughout the lower three grid layers of the stratosphere representing pressure levels 110, 65 and 38mbar. The only sink for the tracer is at the surface, where there is a uniform sink strength set to give approximately the observed overall decay rate from 1966 onwards. Figure 5 shows the tracer concentration at  $45^\circ\text{S}$  predicted by the model. Note that results for the first two years are sensitive to the artificial initial conditions. Figure 6 shows a month plot, in the same format as Figure 4A, of the seasonal component of this predicted time series, extracted using the STL procedure after removal of the first two years of data.

There is a significant discrepancy in phase between the predicted seasonal cycle in Figure 6 and the observed one in Figure 4A. The model predicts that the concentration of a tracer injected into the stratosphere will peak in September and reach a minimum in January, almost totally out of phase with the observed result. This implies that either the seasonality of vertical transport in the model is incorrect or the observed seasonal cycle in  $^{14}\text{CO}_2$  is determined by effects other than seasonality in transport from the stratosphere.

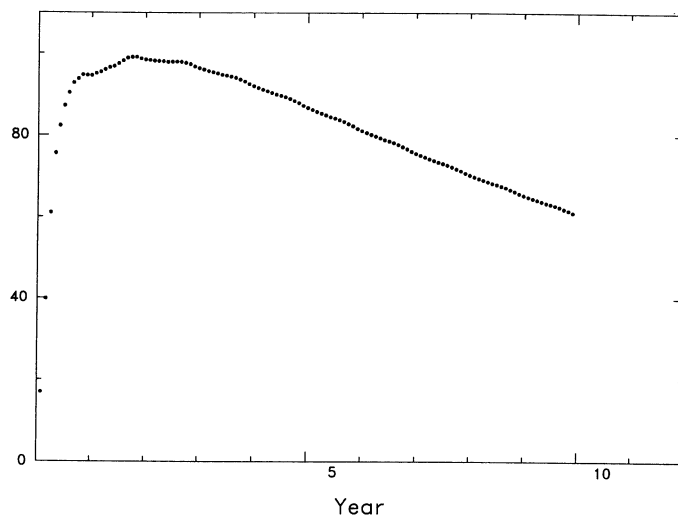


Fig 5. Predicted concentration of tracer at 45°S after a stratospheric injection in the two-dimensional model discussed in the text. The units on the vertical axis are arbitrary.

The seasonal cycles for  $^{90}\text{Sr}$  and  $^3\text{H}$  in the Southern Hemisphere (Taylor 1968) are different from that given here for  $^{14}\text{CO}_2$ . As already mentioned, different transport effects determine the concentration of these isotopes observed at the surface.  $^{90}\text{Sr}$  is deposited by aerosols with tropospheric lifetimes on the order of weeks, so its annual cycle at the surface closely follows variations in input from the stratosphere. In contrast, variations in the long-lived  $^{14}\text{CO}_2$  should lag behind, and in fact be almost completely out of phase with their input from the stratosphere. Comparing Taylor's results with ours shows the  $^{14}\text{CO}_2$  cycle lags by ca 5 months, much as expected. As the  $^{90}\text{Sr}$  and  $^{14}\text{CO}_2$  data support one another, we believe that the annual cycle in transport between the stratosphere and the troposphere as used in the zonally averaged GFDL model is incorrect.

#### $^{14}\text{CH}_4$ MEASUREMENTS IN THE SOUTH PACIFIC

There are many known sources of atmospheric methane (Khalil & Rasmussen 1983). The major sources appear to be biogenic, such as ruminant animals and rice paddies, in which methane is produced by anaerobic bacteria. Further, atmospheric methane concentra-

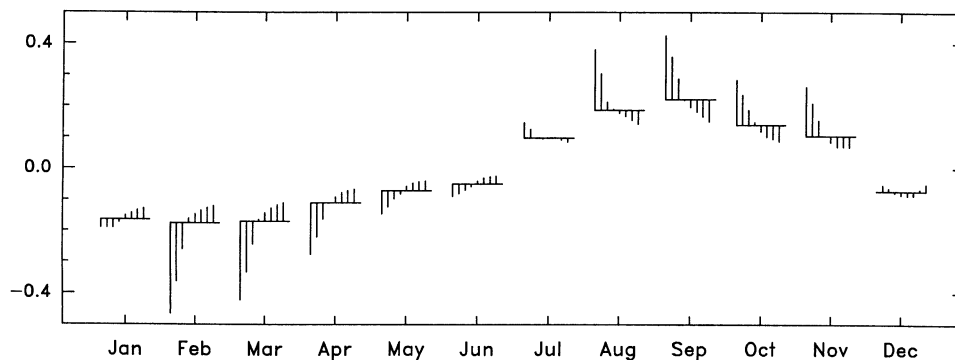


Fig 6. The seasonal cycle in the predicted concentration of tracer at 45°S after a stratospheric injection in the two-dimensional model discussed in the text. The format is as used in Figure 4 and the units on the vertical axis are arbitrary.

tions have been increasing at ca 1%/a over recent decades, suggesting an increasing source strength.

Measurement of  $^{14}\text{C}$  in atmospheric methane provides a way to determine the relative amount of methane released from fossil fuel and primordial methane sources (Ehhalt 1973). Lowe *et al* (1988) recently reported Accelerator Mass Spectrometry (AMS) measurements from the South Pacific which showed lower ( $^{14}\text{C}/^{12}\text{C}$ ) ratios than anticipated, and indicated a significant (25–35%) component of recently released methane has been of fossil origin. Carbon isotope measurements of atmospheric methane from clean air, extending those given by Lowe *et al* and using the same sampling techniques, are shown in Table 3. We include 7 new measurements and omit 2 reported earlier which do not meet stricter consistency criteria now imposed on our AMS data to screen out unsatisfactory graphite targets.

All reported methane samples were taken at Baring Head (41°S, 175°E) near Wellington, New Zealand, under baseline conditions, *ie*, periods of strong onshore winds and while simultaneously measured  $\text{CO}_2$  concentrations indicate well-mixed air. The sample mean and standard deviation for  $\delta^{14}\text{C}$  values in Table 3 is  $+78 \pm 94\text{‰}$ . The sample standard deviation is higher than the mean error associated with the AMS measurement, and this indicates some noise due to sampling and  $\text{CH}_4$  extraction procedures.

An improved atmospheric methane sampling method is being developed in which sampled air is pumped through a molecular sieve into 67L stainless steel tanks to a pressure of ca 120 psi. Methane is subsequently extracted in the laboratory by oxidation to, and collection of  $\text{CO}_2$ , after use of a high-efficiency cryogenic trap to remove any residual  $\text{CO}_2$  and water vapor in the tanks.

In the next two sections, we indicate the nature of the constraints placed on methane sources by the isotope ratios of atmospheric methane. The analysis is based on a very simple model of methane sources, which classifies these as either “modern” or “fossil” and uses average values for the isotope ratios of each. Allowance is also made for  $^{14}\text{CH}_4$  from nuclear power plants. A more realistic model would incorporate sources of intermediate age, such as

TABLE 3  
Carbon isotopic composition of atmospheric methane collected at Baring Head, New Zealand, under baseline conditions

Date coll	$\delta^{13}\text{C}$ (‰)	pMC % mod	$\delta^{14}\text{C}$ (‰)	Lab no.
870312	$-47.24 \pm 0.05$	$102.7 \pm 5.4$	$-19 \pm 52$	NZA-47
870316	$-47.03 \pm 0.05$	$106.8 \pm 3.3$	$+20 \pm 32$	NZA-62
870317	$-48.90 \pm 0.05$	$102.3 \pm 5.7$	$-27 \pm 54$	NZA 46
870410	$-46.10 \pm 0.05$	$106.7 \pm 2.6$	$+21 \pm 25$	NZA 52
870616	$-45.68 \pm 0.05$	$105.4 \pm 5.2$	$+10 \pm 50$	NZA105
870619	$-45.57 \pm 0.05$	$104.0 \pm 4.5$	$-3 \pm 43$	NZA117
870626	$-45.96 \pm 0.05$	$109.5 \pm 3.6$	$+48 \pm 34$	NZA119
870626	$-48.59 \pm 0.05$	$129.1 \pm 6.5$	$+229 \pm 62$	NZA135
870626	$-46.37 \pm 0.05$	$111.2 \pm 5.8$	$+64 \pm 55$	NZA142
870702	$-45.80 \pm 0.05$	$131.3 \pm 5.4$	$+258 \pm 52$	NZA143
870715	$-42.57 \pm 0.05$	$122.4 \pm 4.7$	$+180 \pm 45$	NZA201
870723	$-46.62 \pm 0.05$	$105.8 \pm 10.0$	$+12 \pm 96$	NZA128
870812	$-45.05 \pm 0.05$	$118.7 \pm 7.9$	$+138 \pm 76$	NZA150
870923	-40.	$122.7 \pm 4.4$	$+189 \pm 42$	NZA225
871117	$-46.9 \pm 0.05$	$115.9 \pm 4.8$	$+107 \pm 46$	NZA226
880317	$-45.9 \pm 0.05$	$119.7 \pm 9.0$	$+146 \pm 87$	NZA273
880412	$-43.9 \pm 0.05$	$97.8 \pm 2.7$	$-60 \pm 26$	NZA297
880513	$-43.79 \pm 0.05$	$113.6 \pm 4.8$	$+93 \pm 46$	NZA305



swamps, and use direct isotope measurements of a range of sources with appropriate source strengths. However, the simpler analysis gives an upper estimate for the proportion of methane derived from fossil fuel, and demonstrates the sensitivity of such estimates to some general parameters of atmospheric transport and chemistry.

#### A TWO BOX ATMOSPHERE MODEL FOR CH<sub>4</sub> ISOTOPES

To interpret the <sup>14</sup>CH<sub>4</sub> data above, we use a model treating the two hemispheres as well-mixed boxes with mass balanced exchange and consider the inventories of CH<sub>4</sub>, <sup>13</sup>CH<sub>4</sub> and <sup>14</sup>CH<sub>4</sub> separately. The changes in inventories are related to fluxes by

$$\begin{aligned}\frac{d}{dt} C_h &= Q_h - k (C_h - C_{h'}) - \lambda C_h \\ \frac{d}{dt} {}^{13}C_h &= {}^{13}Q_h - k ({}^{13}C_h - {}^{13}C_{h'}) - \epsilon \lambda {}^{13}C_h \\ \frac{d}{dt} {}^{14}C_h &= {}^{14}Q_h - k ({}^{14}C_h - {}^{14}C_{h'}) - \epsilon^2 \lambda {}^{14}C_h\end{aligned}\quad (1)$$

where:

$h$	labels the hemisphere S or N;
$h'$	labels the alternate hemisphere;
$C_h, {}^{13}C_h$ and ${}^{14}C_h$	are the inventories of CH <sub>4</sub> , <sup>13</sup> CH <sub>4</sub> and <sup>14</sup> CH <sub>4</sub> in hemisphere h;
$Q_h, {}^{13}Q_h$ and ${}^{14}Q_h$	are the source fluxes of CH <sub>4</sub> , <sup>13</sup> CH <sub>4</sub> and <sup>14</sup> CH <sub>4</sub> into hemisphere h;
$k$	is the inter-hemispheric fractional exchange coefficient, taken to be (2 yr) <sup>-1</sup> ;
$\lambda$	is the inverse mean life of CH <sub>4</sub> , taken to be (9.6 yr) <sup>-1</sup> following Prinn <i>et al</i> (1987). Note that the small difference between the mean life of <sup>12</sup> CH <sub>4</sub> and CH <sub>4</sub> is ignored here;
$\epsilon$	is the kinetic isotope effect coefficient, taken to be $0.990 \pm 0.007$ following Davidson <i>et al</i> (1987) ( $k_{13}/k_{12}$ in their notation).

The solution of these equations can be written as

$$\begin{aligned}C_N(t) + C_S(t) &= \int_{-\infty}^t e^{\lambda(x-t)} (Q_N(x) + Q_S(x)) dx \\ C_N(t) - C_S(t) &= \int_{-\infty}^t e^{\lambda(2k+\lambda)(x-t)} (Q_N(x) - Q_S(x)) dx\end{aligned}\quad (2)$$

with similar equations for <sup>13</sup>C and <sup>14</sup>C.

The inventories are sensitive to the source flux terms Q only over the last few mean lifetimes of CH<sub>4</sub>, *ie*, over the last few decades. For the recent past, we assume that the total CH<sub>4</sub> source flux has increased exponentially at 1%/a and further that the regional distribution of fluxes has remained constant. Then

$$\begin{aligned}Q_N(x) + Q_S(x) &= Q_{\text{tot}} e^{\mu(x-1987)} \\ Q_N(x) - Q_S(x) &= \Delta Q_{\text{tot}} e^{\mu(x-1987)}\end{aligned}\quad (3)$$

where:

$Q_{\text{tot}}$	is the total CH <sub>4</sub> release/a in 1987;
$\Delta Q_{\text{tot}}$	is the excess release in the Northern Hemisphere over the Southern Hemisphere;
$\mu$	is the exponential increase rate, taken as 0.01.

Evaluating the appropriate integrals in equation (2) we have for the total CH<sub>4</sub> inventories:

$$\begin{aligned} C_N(t) + C_S(t) &= \frac{Q_{\text{tot}}}{\lambda + \mu} e^{\mu(t-1987)} \\ C_N(t) - C_S(t) &= \frac{\Delta Q_{\text{tot}}}{2k + \lambda + \mu} e^{\mu(t-1987)}. \end{aligned} \quad (4)$$

Assuming, in 1987, a mean atmospheric CH<sub>4</sub> concentration of 1670 ppb, and an interhemispheric difference of 90 ppb (Steele *et al* 1987; Fraser *et al* 1986), an atmospheric mass of  $1.82 \times 10^{20}$  moles, and values of  $\lambda$ ,  $\mu$  and  $k$  already quoted, we have

$$Q_{\text{tot}} = 3.47 \times 10^{13} \text{ moles/a}$$

$$\Delta Q_{\text{tot}} = 0.91 \times 10^{13} \text{ moles/a.}$$

To determine the inventories of <sup>13</sup>CH<sub>4</sub> and <sup>14</sup>CH<sub>4</sub>, we assume that the CH<sub>4</sub> source can be separated into fossil and modern carbon components each having different isotope ratios, which together with the relative proportions of the two sources, have not changed in recent decades. Then

$$^{13}Q_h(t) = (1 + \alpha \, ^{13}\delta_{\text{fos}} + (1 - \alpha) \, ^{13}\delta_{\text{mod}}) \, ^{13}R_0 Q_h(t) \quad (5)$$

where:

- $\alpha$  is the fossil carbon fraction of the total CH<sub>4</sub> source
- $^{13}R_0$  is the (<sup>13</sup>C/<sup>12</sup>C) ratio of the PDB standard
- $^{13}\delta_{\text{fos}}$  is the  $\delta^{13}\text{C}_{\text{PDB}}$  of the fossil carbon CH<sub>4</sub> source
- $^{13}\delta_{\text{mod}}$  is the  $\delta^{13}\text{C}_{\text{PDB}}$  of the modern carbon CH<sub>4</sub> source.

The inventories resulting from these fluxes are given by

$$\begin{aligned} ^{13}C_N(t) + ^{13}C_S(t) &= (1 + \alpha \, ^{13}\delta_{\text{fos}} + (1 - \alpha) \, ^{13}\delta_{\text{mod}}) \, ^{13}R_0 \frac{Q_{\text{tot}}}{\epsilon\lambda + \mu} e^{\mu(t-1987)} \\ ^{13}C_N(t) - ^{13}C_S(t) &= (1 + \alpha \, ^{13}\delta_{\text{fos}} + (1 - \alpha) \, ^{13}\delta_{\text{mod}}) \, ^{13}R_0 \frac{\Delta Q_{\text{tot}}}{2k + \epsilon\lambda + \mu} e^{\mu(t-1987)}. \end{aligned} \quad (6)$$

Turning next to <sup>14</sup>CH<sub>4</sub>, note that the fossil carbon source has no contribution to  $Q_h$ , but that a nuclear power source (Povinec, Chudy & Sivo 1986) must be considered even though this is a negligible source of total CH<sub>4</sub>. Thus

$$\begin{aligned} ^{14}Q_N(t) &= (1 - \alpha) (1 + ^{14}\delta_{\text{mod}}(t)) \, ^{14}R_0 Q_N(t) + ^{14}Q_{\text{Nuc}}(t) \\ ^{14}Q_S(t) &= (1 - \alpha) (1 + ^{14}\delta_{\text{mod}}(t)) \, ^{14}R_0 Q_S(t) \end{aligned} \quad (7)$$

where:

- $^{14}\delta_{\text{mod}}(t)$  is the mean  $\delta^{14}\text{C}$  of the modern carbon source
- $^{14}R_0$  is the (<sup>14</sup>C/<sup>12</sup>C) ratio of the modern <sup>14</sup>C standard (0.95 NBS oxalic acid), taken to be  $1.176 \times 10^{-12}$  following Karleen *et al* (1964) and
- $^{14}Q_{\text{Nuc}}(t)$  is the nuclear power source term.

This leads to

$$\begin{aligned}
 {}^{14}C_N(t) + {}^{14}C_S(t) &= \int_{-\infty}^t e^{\epsilon^2 \lambda (x-t)} [(1 - \alpha) (1 + {}^{14}\delta_{\text{mod}}) {}^{14}R_0 Q_{\text{tot}} e^{\mu(x-1987)} + {}^{14}Q_{\text{Nuc}}(x)] dx \\
 {}^{14}C_N(t) - {}^{14}C_S(t) &= \int_{-\infty}^t e^{(2k+\epsilon^2 \lambda)(x-t)} [(1 - \alpha) \\
 &\quad \cdot (1 + {}^{14}\delta_{\text{mod}}) {}^{14}R_0 \Delta Q_{\text{tot}} e^{\mu(x-1987)} + {}^{14}Q_{\text{Nuc}}(x)] dx. \quad (8)
 \end{aligned}$$

The value of  ${}^{14}\delta_{\text{mod}}(t)$  has changed with time due to changes in the  $\delta^{14}\text{C}$  of atmospheric  $\text{CO}_2$  which provides the carbon from which the modern  $\text{CH}_4$  is derived. We assume a residence time of one year between carbon photosynthesis and methane production, and correct for fractionation to  $\delta^{13}\text{C}$  of  $-65\text{‰}$  (note this is the inferred value of  $\delta^{13}\text{C}$  for the modern carbon  $\text{CH}_4$  source—see below). Thus

$$(1 + {}^{14}\delta_{\text{mod}}(t)) = \left( \frac{1 - 65\text{‰}}{1 - 25\text{‰}} \right)^2 (1 + \Delta^{14}\text{C}_{\text{atm}}(t - 1)) \quad (9)$$

where  $\Delta^{14}\text{C}_{\text{atm}}(t)$  is the atmospheric  $\Delta^{14}\text{C}$  value for time  $t$ . In order to estimate this last term, we use an average of the atmospheric  ${}^{14}\text{C}$  data of Levin *et al* (1985) representing the Northern Hemisphere, and the atmospheric  ${}^{14}\text{C}$  data given here representing the Southern Hemisphere. Where the Northern Hemisphere data is missing we assume it is the same as the Southern Hemisphere, and prior to 1955 we assume a constant value of  $-20\text{‰}$ . The lower limit of the integration range in equation (8) is taken as 1940, as the integrands become negligible prior to this. Numerical integration then produces

$$\begin{aligned}
 \int_{-\infty}^{1987} (1 + {}^{14}\delta_{\text{mod}}) e^{(\epsilon^2 \lambda + \mu)(x-1987)} dx &= 10.718 \\
 \int_{-\infty}^{1987} (1 + {}^{14}\delta_{\text{mod}}) e^{(2k+\epsilon^2 \lambda + \mu)(x-1987)} dx &= 1.0037. \quad (10)
 \end{aligned}$$

Levin (pers commun) has estimated the nuclear power term  $Q_{\text{Nuc}}(t)$  and we use her estimates here. In 1987 the estimated release rate is 1100 Ci/a, corresponding to 17.6 moles of  ${}^{14}\text{CH}_4/\text{a}$ . This is more conveniently expressed as  $0.43 {}^{14}R_0 Q_{\text{tot}}$ , based on the value of  $Q_{\text{tot}}$  given above. Using Levin's exponential growth rates, we have

$$\begin{aligned}
 Q_{\text{Nuc}}(t) &= 0.43 {}^{14}R_0 Q_{\text{tot}} e^{0.16(t-1987)}, \text{ for } t = 1975 \text{ to } 1987, \\
 Q_{\text{Nuc}}(t) &= 0.063 {}^{14}R_0 Q_{\text{tot}} e^{0.26(t-1975)}, \text{ for } t = 1969 \text{ to } 1975 \text{ and} \\
 Q_{\text{Nuc}}(t) &= 0, \text{ for } t \leq 1969. \quad (11)
 \end{aligned}$$

The integrals in equation (8) involving  $Q_{\text{Nuc}}$  can now be evaluated as

$$\begin{aligned}
 \int_{-\infty}^{1987} e^{\epsilon^2 \lambda (x-1987)} Q_{\text{Nuc}}(x) dx &= 1.6153 {}^{14}R_0 Q_{\text{tot}} \\
 \int_{-\infty}^{1987} e^{(2k+\epsilon^2 \lambda)(x-1987)} Q_{\text{Nuc}}(x) dx &= 0.3407 {}^{14}R_0 Q_{\text{tot}}. \quad (12)
 \end{aligned}$$

#### INTERPRETATION OF ${}^{14}\text{CH}_4$ DATA

We can now calculate  $\alpha$ , the fossil carbon fraction, from observed  $\delta^{14}\text{C}$  values for atmospheric  $\text{CH}_4$ . To summarize, values of  $k$ ,  $\lambda$ ,  $\mu$ , and mean hemispheric  $\text{CH}_4$  concentrations are used to estimate  $Q_{\text{tot}}$  and  $\Delta Q_{\text{tot}}$ ; then estimates of  $\epsilon$ ,  ${}^{14}\delta_{\text{mod}}(t)$  and  ${}^{14}Q_{\text{Nuc}}(t)$  are used to calculate the hemispheric  ${}^{14}\text{CH}_4$  inventories relative to the total  $\text{CH}_4$  inventory in terms of

an unknown  $\alpha$ . Finally, we relate the inventory ratio to the observed  $\delta^{14}\text{C}$  using

$$\frac{{}^{14}\text{C}_S}{\text{C}_S} = {}^{14}\text{R}_0 (1 + \delta^{14}\text{C}_{\text{obs}}) \quad (13)$$

giving an equation which is solved for  $\alpha$ . With the parameters values given above, this leads to

$$1.226 (1 - \alpha) + 0.150 = (1 + \delta^{14}\text{C}_{\text{obs}})$$

where 1.226 is the value of  $(1 + \delta^{14}\text{C})$  that would arise if the only source was from modern carbon, and 0.150 is the shift due to the nuclear power source. From these values we have  $\alpha = 0.243$ .

Consistency of the  ${}^{13}\text{CH}_4$  and  ${}^{14}\text{CH}_4$  budgets is now considered. Equation 6 predicts a slight difference in the  $\delta^{13}\text{C}$  values of  $\text{CH}_4$  for the two hemispheres. This arises because the larger source term in the Northern Hemisphere leads to a net export of aged (and, due to the kinetic oxidation effect, heavier)  $\text{CH}_4$  to the Southern Hemisphere. Ignoring this very small effect, we have

$$1 + \delta^{13}\text{C}_{\text{obs}} \approx \frac{\lambda + \mu}{\epsilon\lambda + \mu} (1 + \alpha {}^{13}\delta_{\text{fos}} + (1 - \alpha) {}^{13}\delta_{\text{mod}})$$

or, to a good approximation

$$\delta^{13}\text{C}_{\text{obs}} \approx \alpha {}^{13}\delta_{\text{fos}} + (1 - \alpha) {}^{13}\delta_{\text{mod}} + 9\text{‰}. \quad (14)$$

If the fossil  $\text{CH}_4$  source is assumed to be entirely from fossil fuels then the value of  ${}^{13}\delta_{\text{fos}}$  should be ca  $-30\text{‰}$  and, in order to explain  $\delta^{13}\text{C}_{\text{obs}} = -47\text{‰}$ , we must have  ${}^{13}\delta_{\text{mod}} \approx -65\text{‰}$ . Although this inferred value is slightly lighter than that used in other  $\text{CH}_4$  budgets (eg, Tyler, Blake & Rowland 1987; Stevens & Engelkemeir 1988), it is well within the range of  $\delta^{13}\text{C}$  values of the known sources of modern carbon  $\text{CH}_4$ . Equation 13, based on observed  ${}^{14}\text{C}$  values, gives a more reliable estimate of  $\alpha$  than Equation 14, based on  ${}^{13}\text{C}$  values, because of the considerable uncertainty in  ${}^{13}\delta_{\text{mod}}$  in the latter. Thus, we have used equation 13 to determine  $\alpha$  and equation 14 to check consistency.

To estimate the sensitivity of  $\alpha$  to the parameters of this two-box model, we consider the effect of making variations in these parameters of the order of their uncertainties. This leads to

parameters as described above	$\alpha = 0.243$
k changed from $(2 \text{ yr})^{-1}$ to $(1 \text{ yr})^{-1}$	$\alpha = 0.255$
$\lambda$ changed from $(9.6 \text{ yr})^{-1}$ to $(8.6 \text{ yr})^{-1}$	$\alpha = 0.252$
$\epsilon$ changed from 0.990 to 0.997	$\alpha = 0.233$
$Q_{\text{Nuc}}$ reduced to half equation (11)	$\alpha = 0.182$
$\delta^{14}\text{C}_{\text{obs}}$ changed from $+78\text{‰}$ to $+172\text{‰}$	$\alpha = 0.166$

This shows that  $\alpha$  is not very sensitive to the methane lifetime estimate, the kinetic isotope effect or the inter-hemispheric exchange time. Yet it is sensitive to the magnitude of the nuclear power source term, and to the value of  ${}^{14}\delta_{\text{obs}}$ . The estimated growth rate of  $17\%/a$  in the total nuclear power  ${}^{14}\text{CH}_4$  should cause a significant increase in the  $\delta^{14}\text{C}$  of atmospheric  $\text{CH}_4$ . The figures used in the previous section imply an increase in the Southern Hemisphere of ca  $25\text{‰}/a$  and, provided the fossil carbon fraction  $\alpha$  is not also increasing, this should be clearly measurable after 2 to 3 years of measurements.

A more detailed calculation of the transport of methane between the hemispheres has been carried out using the zonally averaged atmospheric transport model already described.

When the model is run with a northern mid-latitude tracer source and a uniformly distributed sink corresponding to a tracer lifetime of 10 yr, the difference between the predicted values of the tracer concentrations at 45°N and 45°S corresponds to a 2.5-yr inter-hemispheric exchange time. This supports the value of  $k$  used above.

#### CONCLUSION

Our 32-yr record of atmospheric  $^{14}\text{CO}_2$  measurements in the South Pacific covers nearly all the period in which atmospheric  $^{14}\text{C}$  has been influenced by nuclear weapons testing, and begins with  $\Delta^{14}\text{C}$  values below zero. Since 1966 the decrease of this “bomb” carbon in the atmosphere has roughly followed an exponential decay with a  $1/e$  time of 17 yr. From 1966–1977, the  $^{14}\text{CO}_2$  data show a small latitudinal variation, and a definite seasonal cycle peaking in February. This seasonal cycle in  $^{14}\text{CO}_2$  is believed due to seasonal changes in the rate of transport of “bomb” carbon from the stratosphere and is consistent with the cycle of other fallout products. The cycle decayed in amplitude with a  $1/e$  time of 12 yr, which is inferred to be the mean residence time for  $\text{CO}_2$  in the stratosphere.

A two-dimensional model of atmospheric transport based on a three dimensional general circulation model predicts a seasonal cycle in the arrival of a tracer injected into the stratosphere, but the phase of the predicted cycle disagrees with that observed for  $^{14}\text{CO}_2$ . It would seem that stratosphere-to-troposphere transport is not estimated correctly in the model.

An analysis of  $^{14}\text{CH}_4$  data has shown how these can be used to estimate the fraction of atmospheric methane derived from fossil carbon. A major uncertainty in this estimate appears to be the contribution of nuclear power plants to  $^{14}\text{CH}_4$  in the atmosphere. However, comparable measurements in both hemispheres over a number of years should enable the nuclear power source of  $\text{CH}_4$  to be better determined.

#### ACKNOWLEDGMENTS

The atmospheric  $^{14}\text{CO}_2$  data presented here are the result of the work of many people. We wish to acknowledge the contribution of M K Burr, who was responsible for maintaining our gas counters for much of the period covered. Sampling at the Wellington site was done by the staff of the New Zealand Post Office Makara radio station; at the South Pacific island sites, by meteorological observers from the New Zealand Meteorological Service; at Scott Base, by staff of the Antarctic division, DSIR, and at Melbourne, by E D Gill of the National Museum of Victoria. We are grateful for the assistance of all these people.

R A Plumb kindly provided the source code and transport coefficients for the zonally averaged model of atmospheric transport, and his support and guidance in the use of this model are much appreciated. We would also like to thank W S Cleveland for supplying code for his STL procedure. Finally, we would like to pay tribute to T A Rafter, who had the foresight to begin measurements of atmospheric  $^{14}\text{CO}_2$  in New Zealand, and who recognized the importance of extending these to other South Pacific sites many years ago.

#### REFERENCES

- Cleveland, W S 1979 Robust locally weighted regression and smoothing scatterplots. *Jour Am Statistical Assoc* 74: 829–836.
- Cleveland, W S, Freeny, E and Graedel, T E 1983 The seasonal component of atmospheric  $\text{CO}_2$ : Information from new approaches to the decomposition of seasonal time series. *Jour Geophys Research* 88: 10934–10946.
- Cleveland, W S and McRae, J E 1989 The use of loess and STL in the analysis of atmospheric  $\text{CO}_2$  and related data. In Elliott, W P, ed, The statistical treatment of  $\text{CO}_2$  data records. *NOAA Tech Memo ERL ARL-173*, Silver Spring, Maryland.
- Davidson, J A, Cantrell, C A, Tyler, S C, Shetter, R E, Cicerone, R J and Calvert, J G 1987 Carbon kinetic isotope effect in the reaction of  $\text{CH}_4$  with  $\text{HO}$ . *Jour Geophys Research* 92: 2195–2199.
- Ehhalt, D H 1973 Methane in the atmosphere. In Carbon and the biosphere. *Brookhaven symposium in biology*, 24th, Proc. Upton, New York, USAEC, CONF-720510.
- Enting, I G 1987 On the use of smoothing splines to filter  $\text{CO}_2$  data. *Jour Geophys Research* 92: 10977–10984.
- Enting, I G and Pearman, G I 1983 Refinements to a one-dimensional carbon cycle model. *CSIRO Div Atmos Research tech paper* 3.
- Fraser, P J, Hyson, P, Rasmussen, R A, Crawford, A J and Khalil, M A K 1986 Methane, carbon monoxide and methylchloroform in the Southern Hemisphere. *Jour Atmos Chem* 4: 3–42.

- Colombek, A and Prinn, R G 1986 A global three-dimensional model of the circulation and chemistry of  $\text{CFCl}_3$ ,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{CCl}_4$ , and  $\text{N}_2\text{O}$ . *Jour Geophys Research* 91: 3985–4001.
- Heimann, M and Keeling, C D 1986 Meridional eddy diffusion model of the transport of atmospheric carbon dioxide, 1. Seasonal carbon cycle over the tropical Pacific ocean. *Jour Geophys Research* 91: 7765–7781.
- Karlen, I, Olsson, I, U, Kallberg, P and Kilicci, S 1964 Absolute determination of the activity of two  $^{14}\text{C}$  dating standards. *Arkiv Geofysik* 4: 465–471.
- Keeling, C D, Mook, W G and Tans, P P 1979 Recent trends in the  $^{13}\text{C}/^{12}\text{C}$  ratio of atmospheric carbon dioxide. *Nature* 277: 121–123.
- Khalil, M A K and Rasmussen, R A 1983 Sources, sinks and seasonal cycles of atmospheric methane. *Jour Geophys Research* 88: 5131–5144.
- Lal, D and Peters, B 1962 Cosmic ray produced isotopes and their application to problems in geophysics. *Progress in elementary particle and cosmic ray physics*. Amsterdam, North Holland 6: 1–74.
- Levin, I (ms) 1985 Atmospheric  $\text{CO}_2$  in continental Europe—An alternative approach to clean air  $\text{CO}_2$  data. Paper presented at IAMAP mtg, Atmospheric carbon dioxide its sources, sinks, and global transport, Kandersteg, Switzerland.
- Levin, I, Kromer, B, Schoch-Fischer, H, Bruns, M, Münnich, M, Berdau, D, Vogel, J C and Münnich, K O 1985, 25 years of tropospheric  $^{14}\text{C}$  observations in central Europe. *Radiocarbon* 27(1): 1–19.
- Logan, J A, Prather, M J, Wofsy, S C and McElroy, M B 1981 Tropospheric chemistry: A global perspective. *Jour Geophys Research* 86: 7210–7254.
- Lowe, D C, Brenninkmeijer, C A M, Manning, M R, Sparks, R and Wallace, G 1988 Radiocarbon determination of atmospheric methane at Baring Head, New Zealand. *Nature* 332: 522–525.
- Mahlman, J D, Levy, H and Moxim, W J 1980 Three dimensional tracer structure and behaviour as simulated in two ozone precursor experiments. *Jour Atmos Sci* 37: 655–685.
- Mahlman, J D and Moxim, W J 1978 Tracer simulation using a global general circulation model: results from a midlatitude instantaneous source experiment. *Jour Atmos Sci* 35: 1340–1374.
- Nydal, R and Lovseth, K 1983 Tracing bomb  $^{14}\text{C}$  in the atmosphere 1962–1980. *Jour Geophys Research* 88: 3621–3642.
- Oeschger, H, Siegenthaler, U, Schotterer, U and Gugelmann, A 1975 A box diffusion model to study the carbon dioxide exchange in nature. *Tellus* 27: 168–192.
- Peng, T-H, Broecker, W S, Freyer, H D and Trumbore, S 1983 A deconvolution of the tree ring based  $\delta^{13}\text{C}$  record. *Jour Geophys Research* 88: 3609–3620.
- Plumb, R A and Mahlman, J D 1987 The zonally averaged transport characteristics of the GFDL general circulation /transport model. *Jour Atmos Sci* 4: 298–326.
- Plumb, R A and McConalogue, D D 1988 On the meridional structure of long-lived tropospheric constituents. *Jour Geophys Research* 93: 15,897–15,913.
- Povinec, P, Chudy, M and Sivo, A 1986 Anthropogenic radiocarbon: past present and future. In Stuiver, M and Kra, R S, eds, Internatl  $^{14}\text{C}$  conf, 12th, Proc. *Radiocarbon* 28(2A): 668–672.
- Prinn, R, Cunnold, D, Rasmussen, R, Simmonds, P, Alyea, F, Crawford, A, Fraser, P and Rosen, R 1987 Atmospheric trends in methylchloroform and the global average for the hydroxyl radical. *Science* 238: 945–950.
- Rafter, T A 1955  $^{14}\text{C}$  variations in nature and the effect on radiocarbon dating. *New Zealand Jour Sci Tech* 37: 20–38.
- Rafter, T A and Fergusson, G J 1959 Atmospheric radiocarbon as a tracer in geophysical circulation problems. In *United Nations peaceful uses of atomic energy*, Internatl conf, 2nd, Proc. London, Pergamon Press.
- Rafter, T A and O'Brien, B J 1970 Exchange rates between the atmosphere and the ocean as shown by recent  $\text{C}14$  measurements in the south Pacific. In Olsson, I U, ed, *Radiocarbon variations and absolute chronology*, Nobel symposium, 12th, Proc. Stockholm, Almqvist & Wiksell.
- Reinsch, C M 1967 Smoothing by spline functions. *Num Math* 10: 177–183.
- Sarmiento, J L and Gwinn, E 1986 Strontium 90 fallout prediction. *Jour Geophys Research* 91: 7631–7646.
- Schell, W R, Sauzay, G and Payne, B R 1974 World distribution of environmental tritium. In *Physical behaviour of radioactive contaminants in the atmosphere*, IAEA and WMO symposium, Proc. Vienna, IAEA-STI/PUB/354, IAEA.
- Steele, L P, Fraser, P J, Rasmussen, R A, Khalil, M A K, Conway, T J, Crawford, A J, Gammon, R H, Masarie, K A and Thoning, K W 1987 The global distribution of methane in the troposphere. *Jour Atmos Chem* 5: 125–171.
- Stevens, C M and Engelkemeir, A 1988 Stable carbon isotopic composition of methane from some natural and anthropogenic sources. *Jour Geophys Research* 93: 725–733.
- Stevens, C M, Krout, L, Walling, D and Venters, A 1972 The isotopic composition of atmospheric carbon monoxide. *Earth Planetary Sci Letters* 16: 147–165.
- Stuiver, M and Polach, H A 1977 Discussion: Reporting of  $^{14}\text{C}$  data. *Radiocarbon* 19(3): 355–363.
- Taylor, C B 1968 A comparison of tritium and strontium-90 fallout in the southern hemisphere. *Tellus* 20: 559–576.
- Telegadas, K 1971 The seasonal atmospheric distribution and inventories of excess carbon-14 from March 1955 to July 1969. *US Atomic Energy Comm rept HASL-243*.
- Trabalka, J R, ed 1985 Atmospheric carbon dioxide and the global carbon cycle. *US Dept Energy rept DOE/ER-0239*.
- Tyler, S C, Blake, D R and Rowland, F S 1987  $^{13}\text{C}/^{12}\text{C}$  ratio in methane from the flooded Amazon forest. *Jour Geophys Research* 92: 1044–1048.
- Volz, A, Ehhalt, D H and Derwent, R G 1981 Seasonal and latitudinal variation of  $^{14}\text{CO}$  and the tropospheric concentration of OH radicals. *Jour Geophys Research* 86: 5163–5171.
- Walker, J C G 1977 *Evolution of the atmosphere*. New York, MacMillan.