

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

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**ABSTRACT.** <sup>14</sup>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 <sup>14</sup>CO<sub>2</sub> 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 <sup>14</sup>CH<sub>4</sub> 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 <sup>14</sup>CH<sub>4</sub>, and in the measured value for δ<sup>14</sup>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 CO<sub>2</sub> (Keeling, Mook & Tans 1979; Peng *et al* 1983), CH<sub>4</sub> (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 CO<sub>2</sub>, CH<sub>4</sub> and CO is a candidate for study using a detailed physical and chemical model of the atmosphere. Extensive modeling of the annual cycle of CO<sub>2</sub> 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.

CH<sub>4</sub> has a lifetime similar to that of CO<sub>2</sub>, but is a complementary tracer of atmospheric transport because the distribution of its sinks is quite different. While the sinks for CO<sub>2</sub> are all at the surface, the dominant sink of CH<sub>4</sub> 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 CH<sub>4</sub>, 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 CH<sub>4</sub>. As the lifetime of CO (≈4 months) is shorter than the time required to mix throughout the troposphere, this gas does not become

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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 I  
 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>							
660805	-21.6	645.7±3.6	NZ2448	750105	-21.3	391.3±3.5	NZ4101
661004	-20.9	636.6±3.8	NZ2449	750204	-18.6	376.4±3.3	NZ4102
661205	-21.2	649.3±3.8	NZ2452	750605	-22.4	415.5±3.7	NZ4079
670205	-21.5	611.6±3.9	NZ2466	750707	-20.8	401.3±3.3	NZ3829
670605	-20.9	612.7±3.8	NZ2482	750826	-22.3	390.6±3.3	NZ4141
670805	-19.5	600.2±3.8	NZ2481	750904	-23.2	358.9±3.2	NZ4142
670905	-19.3	605.6±3.9	NZ2498	751014	-22.8	363.4±3.3	NZ4299
671005	-19.5	597.8±3.8	NZ2485	751104	-23.1	366.6±3.3	NZ4300
671205	-19.4	594.8±3.8	NZ2484	751204	-22.7	360.4±3.3	NZ5646
680305	-19.3	576.1±3.8	NZ2506	760104	-22.6	371.7±3.3	NZ5647
680405	-20.5	574.8±3.8	NZ2507	760204	-22.3	354.9±3.3	NZ5648
680505	-20.1	567.2±3.8	NZ2508	760304	-22.2	353.4±3.3	NZ5649
680605	-20.2	574.0±3.8	NZ2509	760404	-21.2	357.4±3.3	NZ5650
680705	-22.8	594.6±6.0	NZ2723	760504	-21.7	348.6±3.7	NZ5651
680805	-21.9	557.5±3.5	NZ2721	760612	-20.6	357.8±5.3	NZ5692
680830	-20.7	593.8±6.0	NZ2722	760706	-20.6	353.3±3.3	NZ5693
680906	-22.6	542.2±3.9	NZ3474	760813	-21.6	352.0±3.7	NZ5694
680927	-21.1	553.4±3.9	NZ3479	770812	-16.9	348.4±3.3	NZ5695
681025	-21.0	564.1±5.9	NZ2724	<i>Funafuti, Tuvalu, 8.5° S, 179.2° E</i>			
681205	-19.4	554.9±3.8	NZ2557	660805	-21.6	650.8±3.8	NZ2446
690105	-20.3	548.8±3.8	NZ2558	661005	-21.8	638.5±3.8	NZ2447
690305	-21.5	559.1±3.8	NZ2559	661204	-21.9	619.9±3.8	NZ2450
690505	-20.6	545.2±3.8	NZ2563	670205	-22.3	636.6±3.8	NZ2465
690705	-18.9	536.7±4.0	NZ2569	670505	-20.5	609.9±3.8	NZ2474
690905	-18.7	519.4±3.6	NZ2568	670605	-21.1	612.8±3.9	NZ2475
691105	-20.6	529.6±3.9	NZ2579	670805	-19.8	596.9±4.5	NZ2476
700105	-22.4	533.0±3.8	NZ2578	671005	-20.7	598.9±3.8	NZ2483
700305	-21.5	513.6±3.9	NZ2596	671205	-21.8	582.7±4.5	NZ2486
700505	-19.9	510.3±3.9	NZ2597	671205	-21.8	586.2±4.5	NZ2489
700706	-21.8	507.4±3.9	NZ2608	680305	-20.2	563.6±3.8	NZ2510
700905	-21.5	514.0±3.9	NZ2609	680405	-21.0	596.6±3.9	NZ2511
701105	-23.1	507.4±3.9	NZ2626	680505	-21.7	561.1±3.8	NZ2512
710105	-23.3	507.6±3.9	NZ2627	680602	-19.5	551.4±3.8	NZ2513
710306	-22.8	502.7±3.9	NZ2628	680804	-20.7	549.8±3.9	NZ2525
710507	-22.7	486.5±3.9	NZ2630	680830	-22.3	556.4±3.9	NZ2526
710704	-21.5	486.3±3.7	NZ2655	680906	-18.3	544.0±4.0	NZ2527
710904	-21.2	492.0±3.5	NZ2654	680927	-21.1	570.2±5.1	NZ2725
711104	-23.5	506.2±3.9	NZ2656	681205	-21.0	553.7±3.8	NZ2536
721006	-21.3	460.5±3.6	NZ4095	690105	-18.7	552.6±3.8	NZ2537
721104	-21.9	463.6±3.3	NZ4096	690305	-20.7	552.8±3.8	NZ2554
721204	-20.5	455.9±3.6	NZ4097	690505	-21.4	535.9±3.9	NZ2561
730104	-22.8	442.8±3.3	NZ4098	690705	-20.8	529.1±3.9	NZ2565
730205	-22.9	444.8±3.7	NZ2685	690905	-21.2	518.6±3.9	NZ2574
730405	-22.7	438.1±3.3	NZ2686	691105	-21.1	517.4±3.9	NZ2575
730504	-22.3	452.7±3.7	NZ2687	700105	-21.1	513.5±3.9	NZ2577
740804	-21.3	401.8±3.3	NZ4080	700304	-20.6	527.0±3.9	NZ2580
740904	-22.5	405.4±3.7	NZ4081	700505	-21.2	523.5±3.9	NZ2594
741109	-21.5	394.2±3.6	NZ4099	700705	-21.1	504.5±3.9	NZ2595
741204	-21.8	393.9±3.6	NZ4100	701005	-22.3	516.8±3.9	NZ2615
				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							
580402	-9.0	74.5±3.8	NZ2000	660805	-24.3	626.4±3.9	NZ2043
580407	-25.0	68.4±3.8	NZ2001	660905	-23.0	625.8±3.8	NZ2049
580510	-9.0	71.4±3.3	NZ2002	661205	-21.4	636.3±3.8	NZ2046
580510	-25.0	69.0±4.7	NZ2003	670220	-20.7	616.5±3.8	NZ2050
581104	-25.0	117.1±4.6	NZ2005	670714	-22.4	593.1±3.8	NZ2051
590228	-23.6	124.1±4.6	NZ2007	670804	-22.4	587.2±3.9	NZ2052
590703	-24.5	151.3±4.1	NZ2004	671006	-21.9	584.9±3.9	NZ2054
590922	-22.3	180.4±4.5	NZ2006	671205	-21.1	567.9±3.7	NZ2053
600122	-22.1	189.8±4.5	NZ2009	680205	-20.8	573.6±3.8	NZ2055
600414	-21.1	185.1±4.5	NZ2008	680415	-20.3	567.3±3.8	NZ2056
600902	-22.7	197.0±4.5	NZ2010	680604	-19.6	553.7±3.9	NZ2057
600929	-24.6	202.3±4.5	NZ2012	680805	-21.5	549.3±3.6	NZ2058
610120	-23.7	196.5±4.5	NZ2011	680906	-21.9	545.4±3.6	NZ2059
610301	-21.2	196.8±4.2	NZ2034	681005	-20.0	549.4±5.0	NZ2093
610414	-22.9	192.9±5.0	R00945	681105	-21.7	556.5±3.9	NZ2060
610708	-22.1	196.5±5.0	NZ2013	681205	-21.4	530.4±3.8	NZ2061
610818	-23.1	207.2±4.2	NZ2033	690105	-20.7	542.4±3.9	NZ2062
610929	-23.7	180.8±5.0	NZ2015	690307	-20.0	546.9±3.8	NZ2063
611110	-23.5	183.5±6.8	R00997	690505	-18.6	531.5±3.6	NZ2064
611219	-24.7	198.2±4.9	NZ2014	690706	-20.2	533.8±3.6	NZ2065
620119	-21.7	214.4±4.2	NZ2032	690905	-22.1	541.9±3.9	NZ2066
620301	-23.2	208.3±5.0	NZ2016	691107	-22.4	531.0±3.9	NZ2067
620301	-23.2	233.0±9.4	NZ2092	700109	-21.8	521.7±3.9	NZ2068
620412	-21.8	223.5±5.3	NZ2021	700306	-22.1	525.8±3.9	NZ2069
620412	-21.8	234.4±4.3	NZ2020	700509	-21.6	536.0±3.9	NZ2070
620706	-26.5	238.9±5.9	NZ2091	700705	-21.6	514.3±3.9	NZ2071
620927	-24.5	259.3±3.9	NZ2019	700905	-22.1	504.5±3.9	NZ2073
630117	-19.8	289.0±4.8	NZ2017	701106	-22.3	506.4±3.9	NZ2072
630705	-21.7	380.5±4.1	NZ2022	710108	-21.6	512.1±3.9	NZ2074
630917	-22.7	417.6±4.1	NZ2038	710305	-20.6	498.6±3.9	NZ2075
630927	-26.8	413.5±4.1	NZ2037	710509	-22.0	492.3±3.9	NZ2076
631220	-21.6	497.0±3.4	NZ2024	710710	-22.5	486.9±4.0	NZ2077
640116	-21.9	490.7±4.0	NZ2025	710905	-23.2	494.6±3.6	NZ2078
640409	-21.9	545.6±3.5	NZ2026	711105	-21.5	498.4±3.9	NZ2079
640522	-23.2	548.7±3.5	NZ2027	711205	-21.1	491.4±3.6	NZ2087
640702	-26.1	580.4±4.0	NZ2028	720106	-21.4	488.6±3.3	NZ2088
640925	-22.6	630.1±3.9	NZ2029	720305	-28.8	501.5±3.6	NZ2080
641217	-22.7	644.4±3.7	NZ2030	720505	-21.1	474.3±3.6	NZ2081
650115	-19.6	654.5±3.8	NZ2045	720704	-24.5	496.5±6.7	NZ2094
650408	-20.2	643.0±3.9	NZ2031	720705	-24.6	473.9±3.3	NZ2082
650701	-22.9	647.8±3.9	NZ2035	720805	-20.2	473.4±5.1	NZ2096
				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 I (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
700904	-25.6	486.7±3.6	NZ2662	<i>Scott Base, Antarctica, 77.9° S, 166.7° E</i>			
701104	-24.9	482.6±3.9	NZ2663	611105	-26.1	195.7±6.4	NZ2695
710106	-24.3	494.0±3.9	NZ2664	611230	-25.6	196.7±9.6	NZ3577
710307	-23.3	504.6±3.9	NZ2665	620207	-27.7	180.3±9.9	NZ3575
710404	-18.3	506.1±3.9	NZ2666	620228	-27.4	203.2±6.3	NZ3573
710704	-25.2	489.9±3.7	NZ2667	621201	-32.3	251.5±3.9	NZ2373
710904	-26.1	483.7±5.2	NZ2742	630107	-29.1	255.8±4.1	NZ2374
730105	-26.2	453.9±5.2	NZ2743	660102	-26.1	622.0±3.8	NZ2426
731008	-22.7	409.8±3.7	NZ2690	660124	-23.1	635.2±3.9	NZ2417
731108	-25.2	406.4±3.3	NZ2691	660205	-23.8	622.5±3.8	NZ2427
731206	-26.1	403.3±3.3	NZ2692	660217	-14.9	633.3±3.6	NZ2418
740115	-24.8	404.8±3.3	NZ2693	671202	-23.4	573.8±3.9	NZ2493
740304	-25.4	411.5±3.7	NZ4066	671229	-24.6	577.6±3.9	NZ2494
740404	-25.1	403.2±3.3	NZ4067	680129	-21.3	539.3±5.2	NZ2715
740506	-26.1	412.2±3.7	NZ4068	680212	-17.6	573.6±3.9	NZ2495
740607	-25.9	408.4±3.3	NZ4069	681121	-23.2	539.1±3.8	NZ2547
740706	-25.9	401.1±3.7	NZ4070	681216	-25.0	542.3±3.9	NZ2548
740804	-24.8	402.8±3.7	NZ4071	690110	-24.6	545.1±3.8	NZ2549
740904	-25.4	397.2±3.7	NZ4072	690208	-26.3	542.4±3.9	NZ2550
740908	-26.6	400.4±3.7	NZ4084	691106	-19.4	556.6±8.8	NZ2729
741004	-25.2	420.2±3.2	NZ5644	691227	-19.2	476.1±7.3	NZ2730
741104	-24.1	402.2±3.3	NZ4086	700116	-16.4	492.4±7.3	NZ2731
741208	-22.9	393.5±7.4	NZ3835	710408	-22.9	496.2±3.5	NZ2658
750112	-23.3	393.7±5.1	NZ4127	710420	-24.5	497.3±3.9	NZ2657
750204	-24.4	374.5±4.6	NZ4128	710714	-24.5	479.5±3.6	NZ2659
750313	-24.3	389.3±3.7	NZ4111	711112	-27.8	477.7±4.0	NZ2661
750417	-25.7	395.3±5.1	NZ4112	711218	-26.5	477.5±4.0	NZ2660
750506	-25.2	385.1±5.5	NZ4113	730215	-20.5	447.3±3.7	NZ2682
750608	-25.4	400.4±5.8	NZ4114	730412	-23.6	433.7±5.2	NZ2747
750707	-26.1	368.4±3.3	NZ4115	730914	-25.0	432.4±4.5	NZ2750
750813	-25.1	359.7±3.7	NZ4116	731019	-20.3	438.0±6.8	NZ2738
750908	-22.7	359.9±3.2	NZ4117	740423	-22.6	406.7±5.2	NZ3849
751008	-26.8	373.2±3.3	NZ4129	740513	-18.2	400.1±6.9	NZ3825
751105	-25.1	368.9±3.7	NZ4130	740816	-19.0	340.8±8.7	NZ3826
751204	-25.9	364.0±3.3	NZ4131	751008	-16.6	403.8±5.2	NZ3850
760104	-24.7	370.4±3.3	NZ4132	751123	-26.1	361.7±3.3	NZ5660
760204	-25.4	363.8±3.7	NZ4133	751230	-25.6	361.6±3.3	NZ5661
760304	-25.3	353.6±3.7	NZ5666	760130	-25.5	368.9±3.3	NZ5662
760406	-25.3	362.1±3.3	NZ5667	760316	-22.4	374.0±5.1	NZ5663
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				

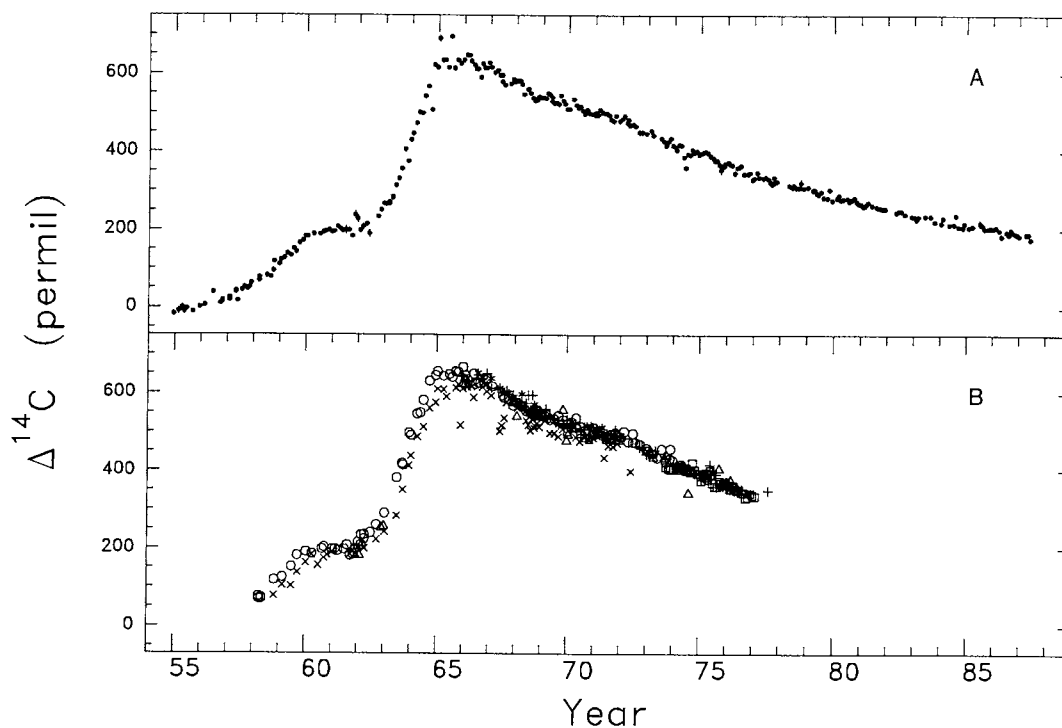


Fig 1.  $\Delta^{14}\text{C}$  values measured in atmospheric  $\text{CO}_2$  at (A) Wellington, New Zealand and (B) other sites in the South Pacific, 1954–1987. Symbols used in (B) are: + Tarawa Is, 1.5°N; \* Funafuti, 8.5°S; O Suva, 18.1°S; x Melbourne, 37.8°S; □ Campbell Is, 52.5°S; and  $\Delta$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

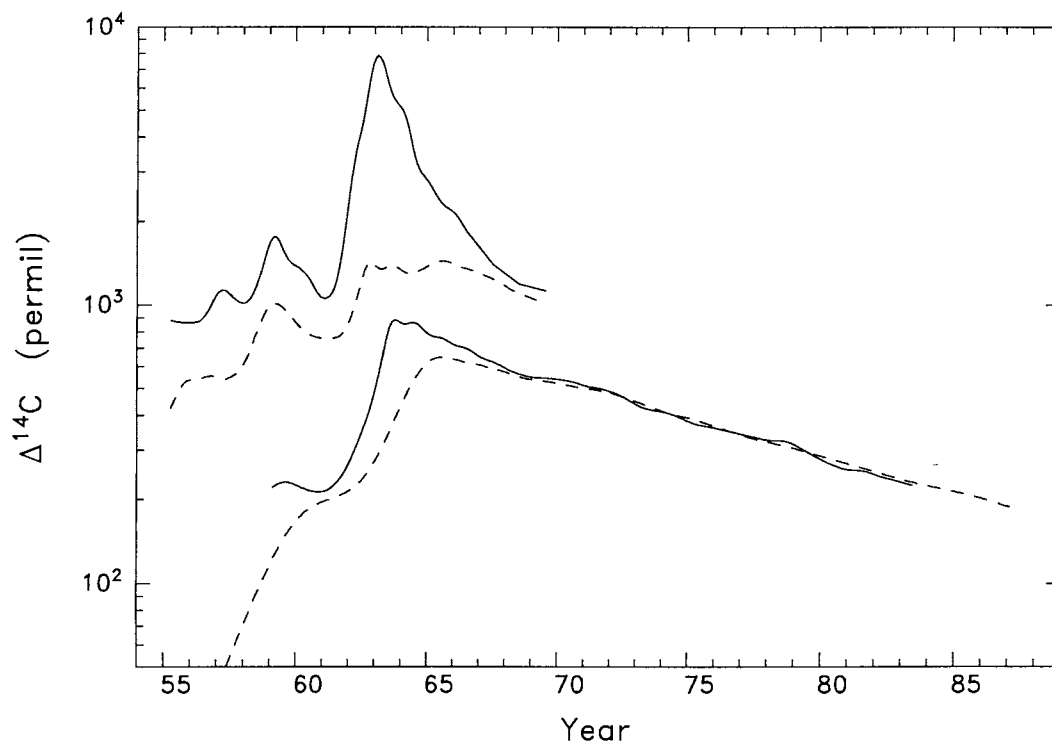


Fig 2.  $\Delta^{14}\text{C}$  values in the stratosphere and at the earth's surface shown as smooth spline curves fitted to available data; the upper two curves are for the stratosphere and the lower two for the surface; — denotes Northern Hemisphere and - - - Southern Hemisphere. Based on stratospheric 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

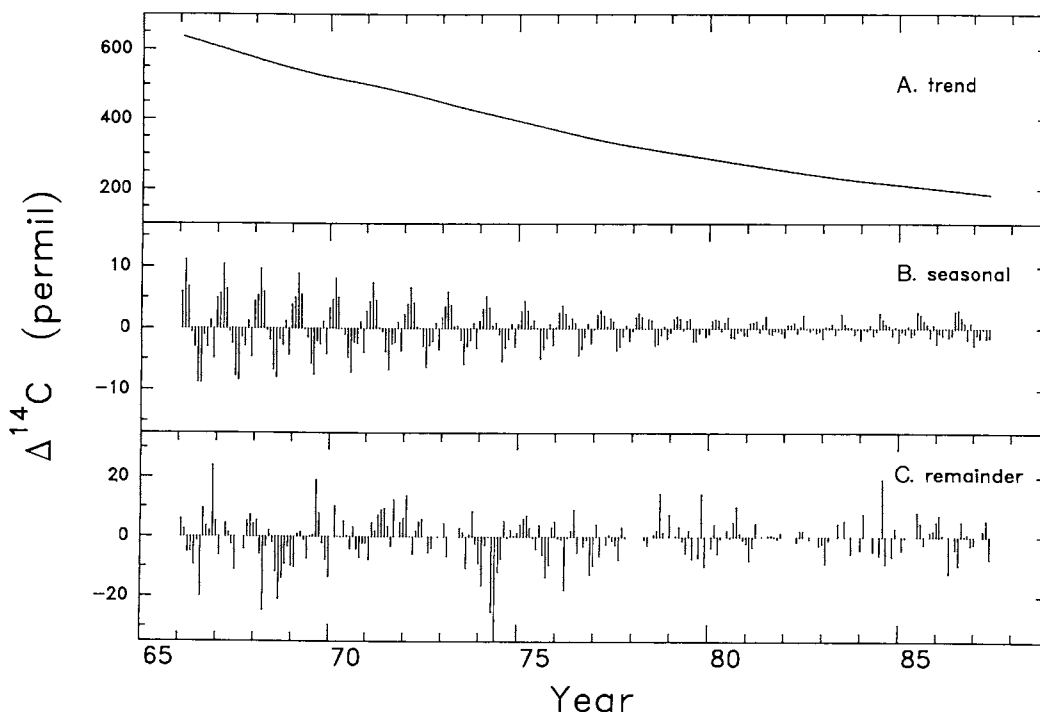


Fig 3. The (A) smooth trend, (B) seasonal and (C) remainder components of the Wellington  $\Delta^{14}\text{C}$  data record determined by the STL procedure as discussed in the text.

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.

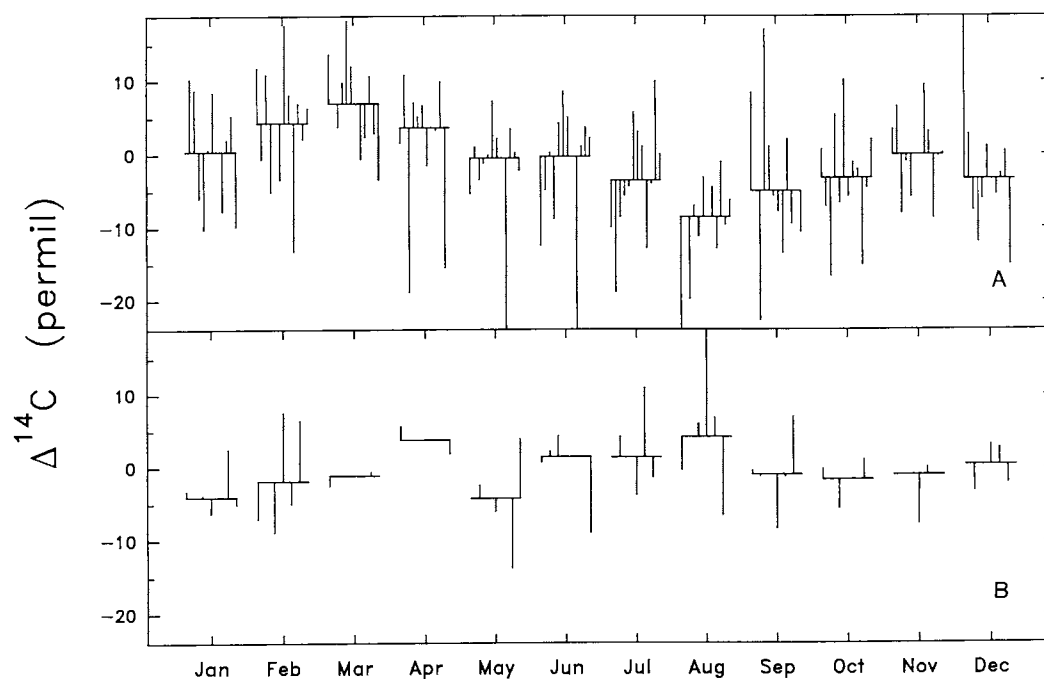


Fig 4. Seasonal cycles of differences between  $\Delta^{14}\text{C}$  data and their smooth trend. Data are grouped by calendar month and shown as spikes from the mid-mean, (A) for period 1966–1977 and (B) for period 1981–1987.

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.

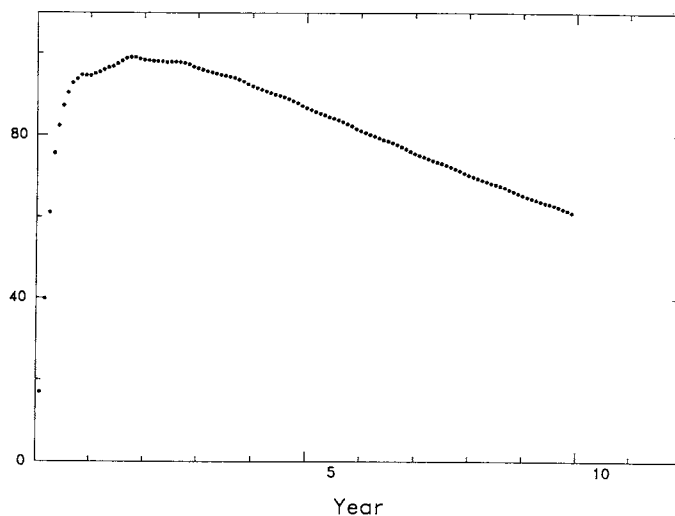


Fig 5. Predicted concentration of tracer at 45°S after a stratospheric injection in the two-dimensional model discussed in the text. The units on the vertical axis are arbitrary.

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-

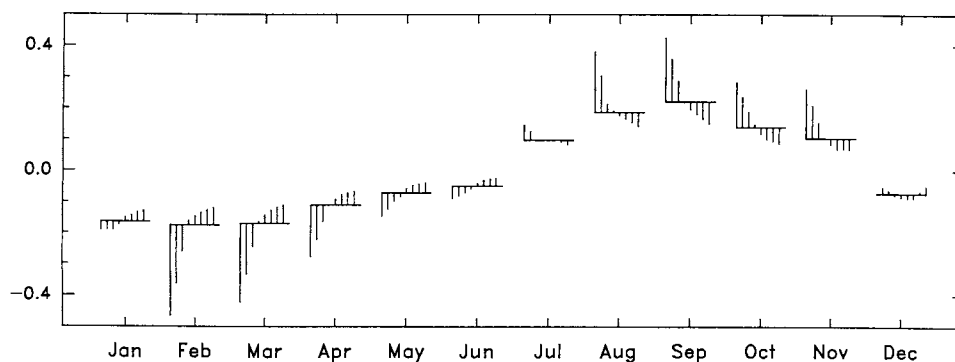


Fig 6. The seasonal cycle in the predicted concentration of tracer at 45°S after a stratospheric injection in the two-dimensional model discussed in the text. The format is as used in Figure 4 and the units on the vertical axis are arbitrary.

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 *et al* (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 *et al* (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%/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.

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