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The concentration of atmospheric carbon dioxide at Baring Head, New Zealand

By D. C. LOWE, *Institute of Nuclear Sciences, DSIR, Lower Hutt, New Zealand*, P. R. GUENTHER and C. D. KEELING, *Scripps Institution of Oceanography, California, U.S.A.*

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ABSTRACT

The concentration of atmospheric CO_2 has been measured at Baring Head, near Wellington, New Zealand, since December 1972. In the period January 1973 to January 1977, the CO_2 concentration was observed to rise by 4.6 p.p.m. Superimposed on the long-term increase was a seasonal oscillation with an amplitude of 1.1 p.p.m. having a maximum in October and a minimum in April. The oscillation was in phase with, and of nearly the same amplitude as, the seasonal oscillation observed at the South Pole. The mean CO_2 concentrations at Baring Head and the South Pole over the period January 1973 to January 1977, were almost the same, each being about 2 p.p.m. lower than at Mauna Loa in Hawaii for the same period.

The problem of intercomparison between different atmospheric CO_2 monitoring stations has been minimized by chemical analyses of all reference gases used at the stations. The reference gases were analysed both before and after use at the field stations by a single calibration laboratory at Scripps Institution of Oceanography.

1. Introduction

Atmospheric carbon dioxide plays a part in determining the earth's radiation balance. Several models have linked climatic change with the increasing CO_2 concentration of the atmosphere (Manabe and Wetherald, 1975; Augustsson and Ramanathan, 1976). However, observed global temperature changes evidently do not directly reflect the increasing concentration of atmospheric CO_2. Temperatures in the Northern Hemisphere have generally been declining since 1940 (Mitchell, 1975), whereas several Southern Hemisphere regions have undergone temperature increases since 1935 (Salinger and Gunn, 1975). Because many parameters are responsible for determining the temperature of the atmosphere, a direct causal link between atmospheric CO_2 increases and air temperature increases will be difficult to establish.

Several long-term atmospheric CO_2 monitoring projects are in current operation. The longest records have been obtained at Mauna Loa Observatory in Hawaii, 14 years through 1971 (Keeling et al., 1976a), the South Pole, 15 years through 1971 (Keeling et al., 1976b), and Barrow, Alaska, 1961–67 and 1969–present (Kelley, 1969).

For use in global CO_2 models, atmospheric CO_2 measurements need to be representative of large geographical regions and remote from local disturbing sources and sinks of CO_2. New Zealand, because of its geographical position, and topography, is potentially well situated for sampling air that is representative of large areas of the mid-southern latitudes. A CO_2 monitoring programme began at Makara on the west coast of the North Island of New Zealand in 1970 (Lowe, 1974) (Fig. 1). However, it was found that contamination due to local vegetation and smoke from a nearby village obscured the seasonal and secular trends of CO_2 concentration. In 1972, monitoring began at another site: Baring Head Lighthouse, situated on a south-eastern point of the North Island. This site is well exposed to air from the south. Typical wind trajectories, provided by the New Zealand Meteorological Service, show that air crossing the coastline at Baring Head has often passed well to the south of the South Island of New Zealand

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(Hunter, personal communication). The CO_2 concentration of this air is representative of a large part of the mid-south western Pacific. CO_2 measurements at Baring Head should therefore help to establish secular and seasonal trends of CO_2 in the middle latitudes of the Southern Hemisphere.

2. Sampling site

Baring Head is situated at 41.4° S, 174.9° E, on a south-eastern tip of the North Island of New Zealand (Fig. 1). New Zealand ranges from latitude 34° S to latitude 47° S, and is remote from all other major land masses except Australia. Despite its large latitude range, it is relatively small in area and experiences almost continuous oceanic weather with prevailing westerly winds. Near Baring Head, winds are strongly influenced by the funnelling action of the Cook Strait. When the unimpeded wind is from the west, the wind at Baring Head is from the north or north-west; when the unimpeded wind is from the south or south-west, the Baring Head wind will be from the south-east or south. These effects also occur at Kelburn, 17 m north-west of Baring Head, where 47% of the winds are from the north or north-west, and 29% from the south or south-east (Maunder, 1971). Since all northerly air at Baring Head is potentially contaminated by local sources and sinks of CO_2, only southerly air has been considered here for the purpose of long-term CO_2 monitoring.

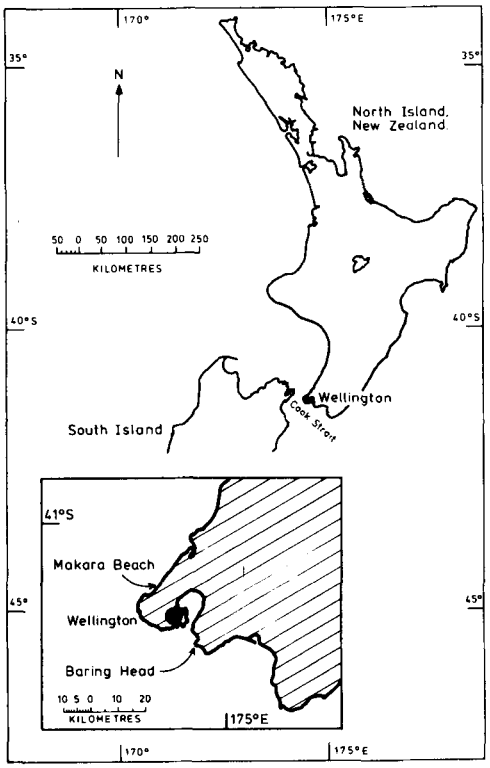

Fig. 1. Map of New Zealand showing the location of the Makara and Baring Head atmospheric CO_2 sampling sites.

The CO_2 sampling and analysis equipment is housed in a small concrete out-building of Baring Head Lighthouse Station (Fig. 2). The air-sampling intakes are located on a mast adjoining the out-building, at the brink of an 80 m high cliff directly overlooking the eastern part of the Cook Strait and the south-west Pacific Ocean. The only vegetation between the air intakes and the ocean are a few scattered flax bushes *Phormium tenax* on the cliff face, and a 20 m stretch of lupine bushes, *Lupinus sp.*, on the beach below the cliff. Southerly storms are frequent at the site, especially during the winter. A typical storm will last for 3 days, with wind velocities averaging 30 knots from the south and south-east, with gusts up to 80 knots. During these storms, hourly average concentrations of CO_2 often remain within a 0.3 p.p.m. range for 30 h or more.

3. Experimental procedures

3.1 The gas analysers

Continuous measurements of atmospheric CO_2 concentration in dry air are made with two non-dispersive infra-red (NDIR) gas analysers designed for monitoring flowing gas. A Hartmann and Braun URAS1 NDIR analyser has been used since the outset of the monitoring programme at Baring Head. In January 1976, a Hartmann and Braun URAS2T analyser was placed in series with the URAS1, thus providing two independent measurements of the same air stream.

To reduce water vapour interference to the NDIR CO_2 analysis, the air and reference gases used in the calibrating procedure are dried by passage through two stainless-steel cold traps in series maintained at approximately −40 °C by a freon refrigeration plant. At the exit of the final cold trap, both air and reference gas have the same

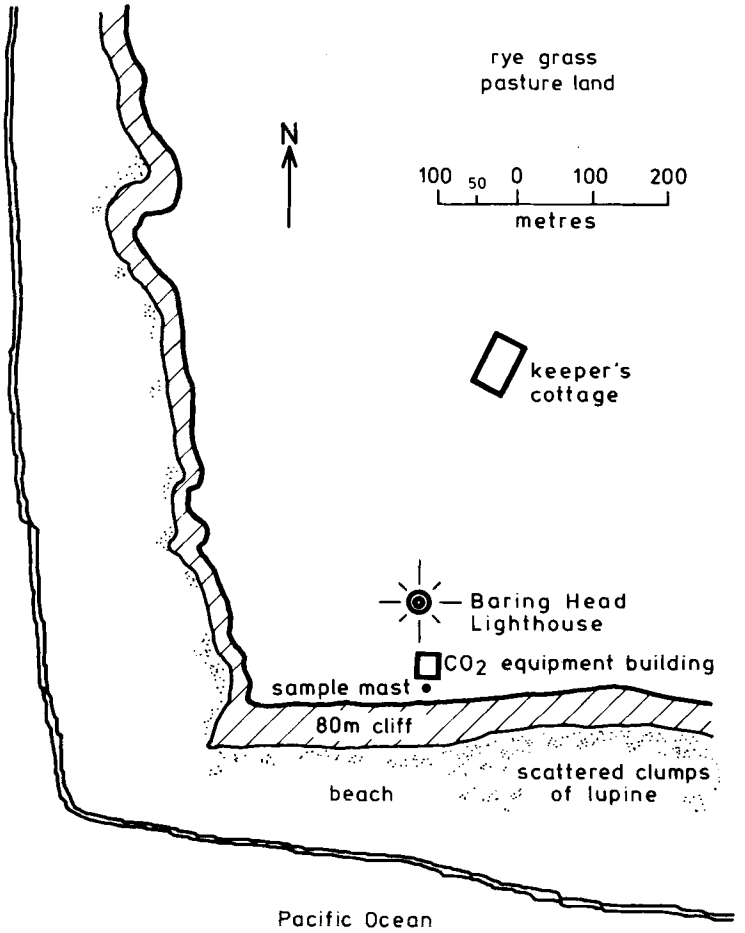

Fig. 2. Plan view of the Baring Head Lighthouse Station.

dew point of about −40 °C as determined by a dew-point hygrometer. The URAS1 NDIR analyser at Baring Head is about 100 times more sensitive to CO_2 than to water vapour. At a dew point of −40 °C, the residual water vapour in the analyser sample gas produces the same instrument response for both air and reference gas equivalent to about 1.5 p.p.m. of CO_2. Thus consistent results are obtained without removing all the water vapour. The precision (twice the standard deviation) in mutual comparisons of reference gases is about 0.2 p.p.m.

3.2. Air sampling system

A polyethylene air line and a stainless-steel air line have air sucked thorugh them at 2.5 l/m by separate neoprene rubber diaphragm pumps. Air from each air line is alternately flushed through the NDIR analysers at 0.5 l/m by the operation of gas solenoid valves. A micro-processor controlled sequencing system samples each air line for 27 min per hour, and a working reference gas for the remaining 6 min per hour. The polyethylene air line is protected against chafing and against possible deterioration from sunlight by a sheath of heavy opaque plastic hose. The polyethylene line is 6 mm inside diameter, 20 m long, and samples air 6 m above ground level and 3 m from the brink of the south-facing sea cliff (Fig. 2). The stainless-steel line is 5 mm inside diameter, 10 m long, and samples air from the same point as the polyethylene line. The polyethylene line has been in service

at Baring Head since the programme began. The stainless-steel line was installed in November 1976 as a check for possible contamination in the polyethylene line. However, after 15 months of parallel operation at various flow rates no systematic difference in CO_2 concentration has been detected between the air sampled from each of the two lines.

3.3. Calibration

The continuous measurement of atmospheric CO_2 by NDIR analysis requires regular comparisons of air against reference gas mixtures. Routine use and calibration of the Baring Head analysers is accomplished with a series of CO_2 in nitrogen reference gases, prepared by Scripps calibration laboratory and supplied in steel gas cylinders. The routine calibration techniques used at Baring Head are described elsewhere (Lowe, 1973; Lowe and Rowse, 1975).

To establish the relatively small seasonal and secular trends of atmospheric CO_2 in the Southern Hemisphere, precise calibration of the analysis equipment is required. Calibration systems for various NDIR analysers have been investigated by several workers (Keeling et al., 1976a; Bischof, 1977; Pearman, 1977; Bischof, 1975). In March 1975, a special meeting was held at La Jolla, California, by the World Meteorological Organisation (WMO). One of the aims of the meeting was to investigate various calibration systems and settle on a universal system so that atmospheric CO_2 measurements from different sites might be directly comparable.

The system chosen provisionally was a CO_2 in nitrogen reference gas procedure which we will refer to as the 1974 WMO manometric system. However, most published data which depend on gases from the WMO laboratory at Scripps Institution of Oceanography have so far been expressed in units of a scale which we will refer to as the "adjusted index scale". This system is directly related to the 1974 manometric system, but, because it is directly based on the NDIR measurements, is not subject to further adjustment when the WMO system is up-dated (Keeling et al., 1976a). The adjusted index scale has therefore been adopted for the data and plots of this paper. When the reference gases contain pure nitrogen as the carrier gas, the adjusted index scale, J, may be converted to the 1974 manometric system, X, in p.m.m. of CO_2 in dry air by use of the expression:

$$X = \sum_{n=0}^{3} C_n J_C^n$$

where $C_0 = 76.582$, $C_1 = 0.584910$, $C_2 = 3.1151 \times 10^{-4}$, $C_3 = 7.3225 \times 10^{-7}$, and $J_C = 1.012006\,[J - 0.005\Delta t]$ with Δt the number of months prior to July 1974. (Δt is negative after July 1974.) This expression is described in more detail elsewhere (Keeling et al., 1976a).

NDIR analysers are sensitive to oxygen in the sample gas stream because of an oxygen-induced pressure broadening effect on the CO_2 adsorption bands. The magnitude of the effect varies with the model of analyser used and even analysers of the same model number can show different effects. Thus calibration in the 1974 WMO scale alone is not sufficient for comparison of the results from different CO_2 monitoring stations. Account must also be taken of the effect of pressure broadening by oxygen on each analyser.

A preliminary investigation of the effect on the analysers at Baring Head was carried out in 1976 and 1977, using CO_2 in air reference gases prepared at the Scripps laboratory. For a given CO_2 in air concentration near 330 p.p.m., the URAS2T consistently read 0.9 p.p.m. CO_2 lower than the Scripps laboratory Applied Physics NDIR analyser. The URAS1 NDIR, however, consistently read within 0.1 p.p.m. of the Scripps NDIR. Hence the oxygen correction for the URAS1 will be assumed to be identical to that of the Scripps instrument, whereas the correction for the URAS2T will be assumed to be 0.9 p.p.m. lower in the region of 330 p.p.m. CO_2 in air. The mean difference between the URAS1 and URAS2T monthly means of steady intervals of CO_2 concentration at Baring Head over the 18-month period February 1976 to August 1977 was 1.0 p.p.m. in good agreement with the CO_2 in air reference gas tests. The comparability of measurements made at Baring Head and measurements made with the Scripps Applied Physics NDIR analyser have also been checked by using air samples collected in 2-l glass flasks. The Scripps NDIR analyses of seven samples collected at Baring Head during a southerly storm in July 1977 had a mean concentration of 328.39 p.p.m., $\sigma =$ 0.15 p.p.m. This is 0.05 p.p.m. higher than the

results of the on-site URAS1 analysis for the same period, showing good agreement of the two techniques.

3.4. Logging the data

Normally two alternations of air versus reference gas are obtained each hour, and registered on a recorder chart. The difference, in centimetres, between successive traces is read where the trace registers the change between air and reference gas. These differences are used with daily calibrations of the analysis system to produce hourly averages of the CO_2 concentration at Baring Head. For purposes of determining the secular and seasonal trends of CO_2, only the portions of the record taken during southerly winds are considered. Also, southerly air data are accepted only if the hourly averages of CO_2 concentration lie within a 0.3 p.p.m. concentration range for at least 6 h—we will refer to these as "steady intervals". These criteria reduce the number of days on which acceptable CO_2 data are logged to about 5 per month in the austral summer, and 15 per month in the austral winter months of May to October. Southerly winds and hence steady intervals are more frequent at Baring Head during the winter months.

The data selection process is illustrated in Fig. 3, which shows a typical portion of the record taken during a southerly storm in July 1976. Almost immediately after the onset of a southerly wind at Baring Head, the record becomes less variable, indicating that air well mixed with respect to CO_2 is reaching the station. Application of the steady interval criteria to the southerly air data results in the rejection of the first 2–3 h of a strong southerly, and also the rejection of weak and variable southerlies. This helps to ensure that the hourly average values selected during a southerly wind reflect the prevailing CO_2 concentration over the adjacent Pacific Ocean.

Steady intervals of CO_2 concentration were weighted according to their length and formed into monthly weighted means of CO_2 concentration. These are listed in Table 1 in units of the adjusted index scale with the total number of hours of steady data recorded each month. An approximate estimate of the variability of the record may be made by calculating the standard deviation of the differences between the monthly mean CO_2 concentrations of the URAS1 and URAS2T from Tables 1a and 1b. For the 14-month period February 1976 to March 1977, this

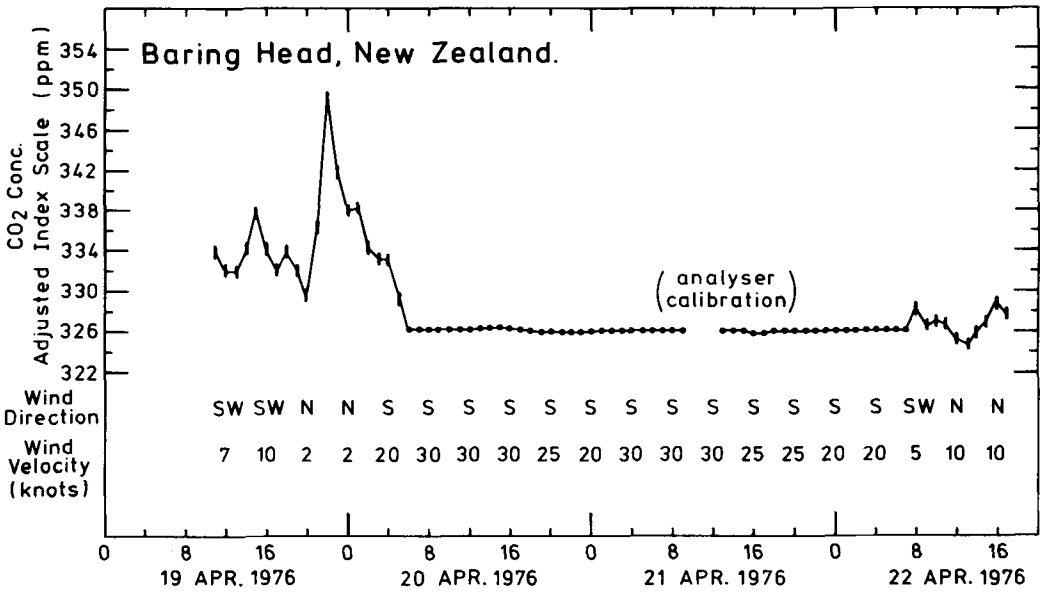

Fig. 3. Hourly average atmospheric CO_2 concentration at Baring Head during a typical southerly storm in 1976. Concentrations are plotted in the adjusted CO_2 index scale. Vertical bars indicate periods during which the record was variable, because of local contamination brought to the site by a northerly wind. The straight part of the record shows steady intervals of CO_2 concentration taken during a strong southerly wind.

Table 1a. *Monthly weighted mean concentration of atmospheric carbon dioxide, in adjusted index scale, based on steady intervals at Baring Head. Data recorded by URAS1 analyser, results of both air lines combined*

	1973		1974		1975		1976		1977	
Month	No. of hours	Adjusted CO_2 index	No. of hours	Adjusted CO_2 index	No. of hours	Adjusted CO_2 index	No. of hours	Adjusted CO_2 index	No. of hours	Adjusted CO_2 index
January	54	322.59	184	324.61	97	325.46	115	327.32	44	327.17
February	146	322.73	128	324.29	122	325.10	155	327.34	86	327.34
March	145	323.23	149	323.99	60	324.96	109	327.27	76	326.97
April	185	323.39	234	323.94	36	325.19	99	326.99		
May	54	323.51	69	324.45	70	325.56	120	327.34		
June	123	323.74	206	324.57	204	325.84	119	327.53		
July	310	324.05	173	325.07	181	325.93	164	327.83		
August	223	324.54	289	325.37	84	326.93	139	327.89		
September	62	324.66	318	325.48	66	327.27	168	327.89		
October	93	324.87	124	325.52	94	327.50	156	328.60		
November	92	324.77	101	325.60	120	327.47	142	328.16		
December	122	324.67	45	325.57	63	327.45	63	327.52		

Table 1b. *Monthly weighted mean concentration of atmospheric carbon dioxide, in adjusted index scale, based on steady intervals at Baring Head. Data recorded by URAS2T analyser, results of both air lines combined*

	1976		1977	
Month	No. of hours	Adjusted CO_2 index	No. of hours	Adjusted CO_2 index
January			44	325.94
February	155	326.46	86	326.02
March	109	326.29	76	325.84
April	99	325.97		
May	120	326.39		
June	119	326.38		
July	164	326.68		
August	139	327.24		
September	135	326.96		
October	156	327.39		
November	142	327.01		
December	63	326.26		

is 0.2 p.p.m. Annual means of the CO_2 concentration at Baring Head in both the adjusted index scale and the 1974 WMO manometric system are listed in Table 2.

Table 2. *Annual mean atmospheric carbon dioxide concentration at Baring Head in adjusted index and 1974 WMO manometric scales. Data recorded by URAS1 analyser, results of both air lines combined*

Year	Adjusted CO_2 index	1974 WMO manometric index
1973	323.90	327.50
1974	324.87	328.58
1975	326.22	330.05
1976	327.64	331.59

3.5. Computation of the data

Calculation of the air data is based on a method of mutual comparisons with reference gas mixtures prepared in the Scripps laboratory. The NDIR analysers are also automatically calibrated once daily at Baring Head with an hour-long series of comparisons of three reference gases. The URAS1 NDIR was found to be non-linear with respect to the adjusted index scale and account was taken of this in the analysis of the air data. The analysis of the non-linearity and the individual reference gas calibrations and atmospheric air measurements are too extensive to reproduce in this article. They have

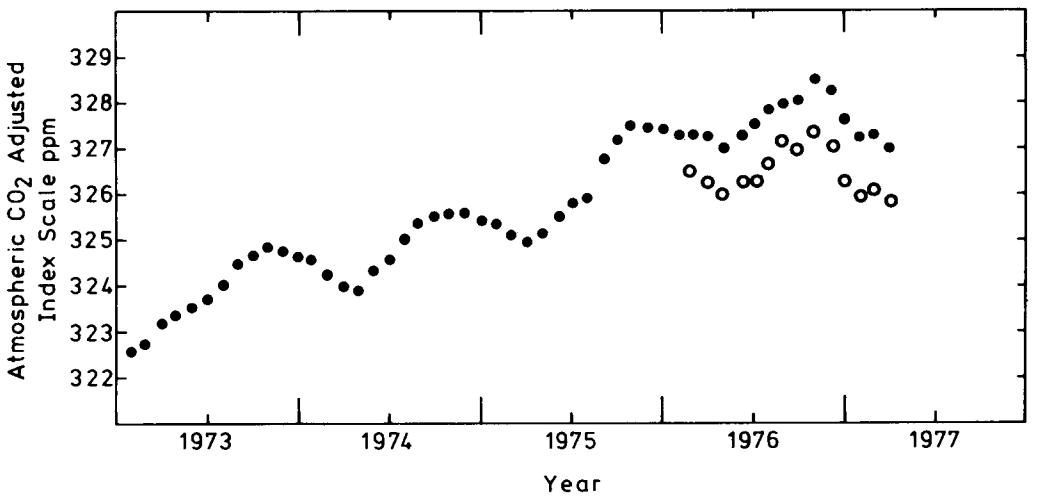

Fig. 4. Long-term variation of atmospheric CO_2 concentration at Baring Head during southerly winds. The solid points are observed monthly average concentrations recorded by a URAS1 NDIR. The circles are observed monthly average concentrations recorded by a URAS 2T NDIR.

been reported elsewhere (Lowe, Keeling and Guenther, 1978) and deposited with the National Auxiliary Publications Service of the American Society for Information Science.[1]

4. Discussion

Fig. 4 shows the mean monthly CO_2 concentration plotted for the period January 1973 to March 1977. During this period the mean annual CO_2 concentration increase was 1.15 p.p.m. Superimposed on this long-term increase was a seasonal oscillation with an amplitude of 1.1 p.p.m. peak to peak. Assuming a linear long-term increase of 1.15 p.p.m./year, the secular trend was removed from the data of Fig. 4 to produce the seasonal trend plotted in Fig. 5. Also plotted in Fig. 5 are similar data from Mauna Loa Observatory, Hawaii, and the South Pole, treated in the same way for the same period (Keeling, 1978). At Hawaii, the amplitude of the seasonal effect is 6 p.p.m. peak to peak (see Fig. 1), about five times greater than the amplitude observed at Baring Head and at the South Pole. The seasonal oscillation in CO_2 at Mauna Loa is attributed to seasonal variations in the growth rate of Northern Hemisphere plants (Keeling et al., 1976a). The Northern Hemisphere is 45% land, 55% ocean, and contains most of the earth's vegetation whose growth and CO_2 assimilation is likely to be seasonal. The Southern Hemisphere, however, is only 11% land and most of its vegetation is found in the tropical jungles of South America and Africa where seasonal variations in growth are small. Seasonal variations in CO_2 concentration due to changes in vegetative growth will therefore be considerably smaller in the Southern Hemisphere than in the Northern Hemisphere.

At Mauna Loa Observatory, the peak in the seasonal CO_2 concentration occurs in May. At this time, the CO_2 concentration begins to decline due to the rapid uptake of atmospheric CO_2 by Northern Hemisphere vegetative growth. At Baring Head, however, the maximum occurs in October which is one to two months earlier than expected for a change caused by spring growth in the Southern Hemisphere. Maximum spring growth in New Zealand, Australia, and southern South America, usually occurs in November (Troughton, 1978). About 70% of the earth's oceans lie in the Southern Hemisphere. Thus one would expect the

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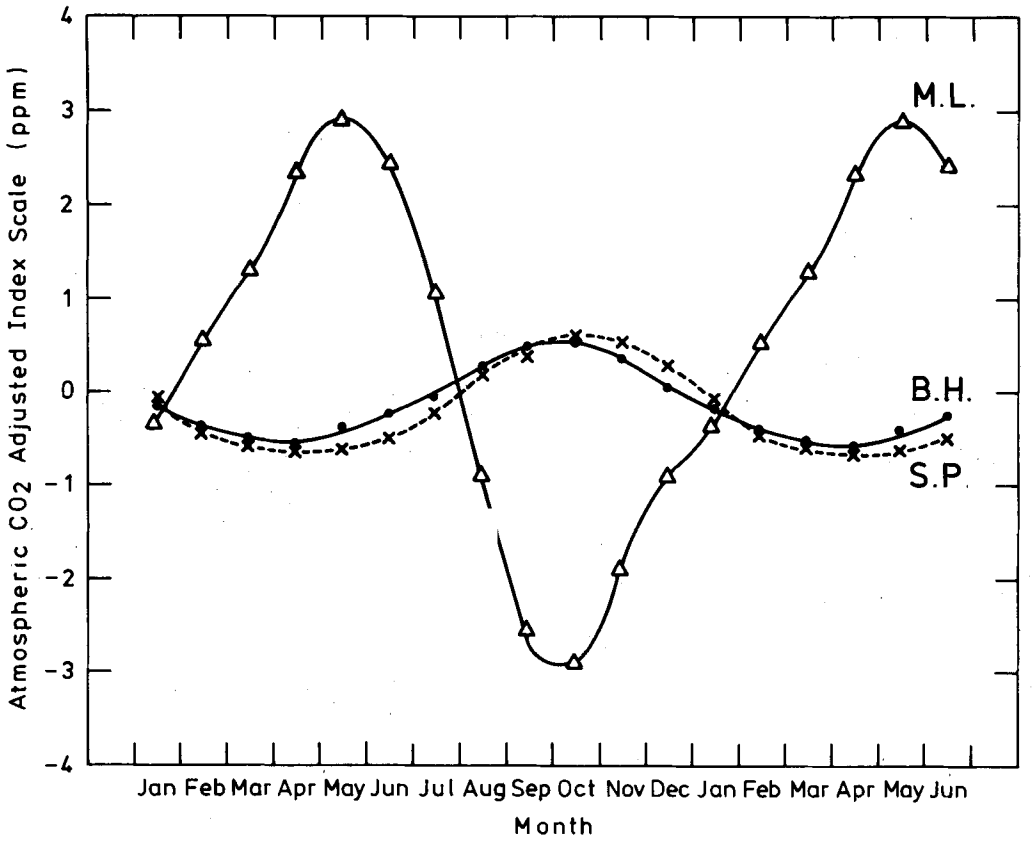

Fig. 5. Average seasonal variation of the atmospheric CO_2 concentration at Baring Head, Mauna Loa, and South Pole, from 1973 to 1976. The solid line (B.H.) indicates the Baring Head seasonal variation, the broken line (S.P.) the South Pole seasonal variation, and the triangles (M.L.) the Mauna Loa seasonal variation. The seasonal variation was computed for each station by removing a linear trend from the monthly averages of CO_2 concentration over the period January 1973 to December 1976. The resulting monthly averages were reduced to 12-monthly averages for the plot, by averaging each set of January, February, ... December. January–June values have been plotted twice to show the seasonal variation more clearly. The Mauna Loa and South Pole variations are computed from unpublished data.

CO_2 concentration at Baring Head to be more influenced by seasonal changes in oceanic CO_2 exchange, than the CO_2 concentration at Hawaii. However, the solubility of CO_2 in sea water increases as the temperature of the water decreases. Also surface sea-water temperatures near New Zealand are at their minimum in September, which is about the time of the observed seasonal maximum at Baring Head. The phase of the Baring Head seasonal oscillation cannot therefore be explained by seasonal changes in sea-surface temperature. It is possible, however, that part of the seasonal oscillation observed at Baring Head originates from the oscillation in the Northern Hemisphere. This oscillation would be considerably attenuated after crossing the inter-tropical convergence and would be delayed in phase (Bolin and Keeling, 1963).

In the four-year period 1973 to 1976, the average CO_2 concentration at Baring Head and the South Pole was almost the same indicating that the Southern Hemisphere is probably well mixed with respect to atmospheric CO_2. However, during the same four-year period, the average CO_2 concentration difference between the Mauna Loa station and the Baring Head and South Pole stations was about 2 p.p.m., demonstrating the existence of a large sink for atmospheric CO_2 in the

Southern Hemisphere. The oceans are probably a major sink for CO_2 (Bolin and Keeling, 1963). This suggests that the Southern Hemisphere, because of its larger ocean surface area, is a greater sink for CO_2 than the Northern Hemisphere. The oceans to the south of Baring Head constitute 40% of the Southern Hemisphere's ocean surface area, and probably form the greater part of the Southern Hemisphere's oceanic CO_2 sink. They are cold, and average surface wind velocities are high when compared with winds to the north of Baring Head. Laboratory experiments have shown that CO_2 transfer across an air–ocean interface is proportional to the square of surface wind velocity and inversely proportional to the temperature of the water (Kanwisher, 1963; Deacon, 1977).

Evidently several factors contribute to the seasonal oscillation observed at Baring Head. The oscillation is probably caused by a combination of Northern Hemisphere mixing and the Southern Hemisphere's spring growth and sea-surface CO_2 partial pressure changes.

It is planned that Baring Head will be maintained as a permanent monitoring station as part of the WMO international effort to determine future atmospheric CO_2 trends.

5. Acknowledgements

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КОНЦЕНТРАЦИЯ УГЛЕКИСЛОГО ГАЗА В АТМОСФЕРЕ В БЭРИНГ ХЭД, НОВАЯ ЗЕЛАНДИЯ

Начиная с декабря 1972 г. в Бэринг Хэд вблизи Веллингтона в Новой Зеландии измерялась концентрация CO_2 в атмосфере. За период с января 1973 г. по январь 1977 г. концентрация CO_2 выросла на $4.6 \cdot 10^{-6}$ по объему. На этот долгопериодный рост было наложено сезонное колебание с амплитудой $1.1 \cdot 10^{-6}$ с максимумом в октябре и минимумом в апреле. Это колебание было в фазе и с той же амплитудой, что и сезонное колебание, наблюдавшееся на Южном полюсе. Средние концентрации CO_2 в Бэринг Хэд и на Южном полюсе за период с января 1973 по январь 1977 гг. были почти одинаковыми и на $2 \cdot 10^{-6}$ ниже, чем в Мауна Лоа на о. Гавайи в то же время.

Проблема интеркалибровки между различными станциями, ведущими наблюдения за CO_2, была сведена к минимуму химическим анализом всех газов сравнения, используемых на этих станциях. Газы сравнения анализировались как до, так и после их использования на полевых станциях в одной и той же калибровочной лаборатории в Институте океанографии Скриппса.