



*Taihoru Nukurangi*

## **BARING HEAD**

# **Atmospheric Data Summary**

**Edited by: Antony Gomez**

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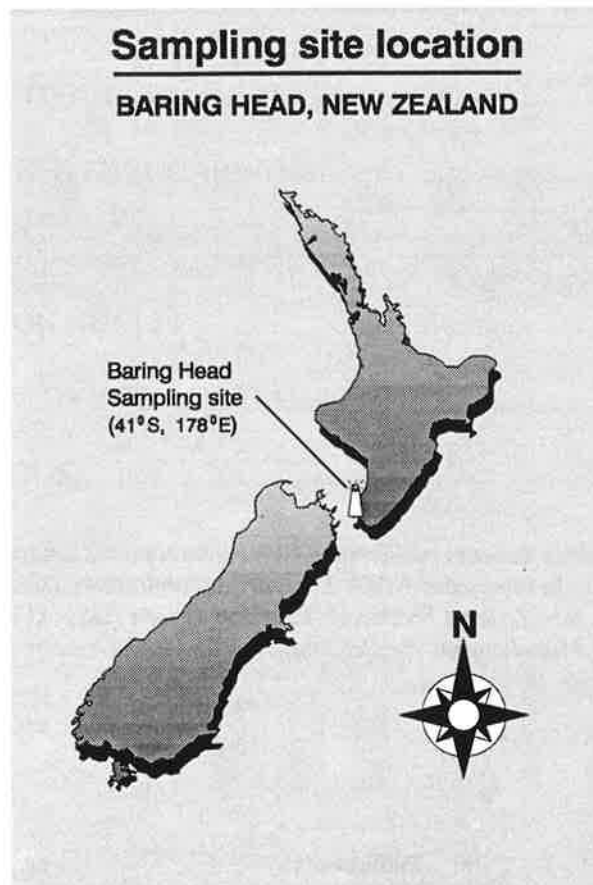
- 9 AUG 1996

PO Box 14-901  
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NIWA Science and Technology Series No. 39

# **BARING HEAD**

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**Edited by: Antony Gomez**

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**July 1996**

Cataloguing-in-publication

Gomez, A.J.

Baring Head Atmospheric Data Summary / A.J. Gomez. Wellington, NZ: National Institute of Water and Atmospheric Research Ltd., 1996. (NIWA science and technology series ; 39)

ISSN 1173-0382

ISBN 0-478-08385-8

The *NIWA Science and Technology Series* is published by NIWA (the National Institute of Water and Atmospheric Research Ltd.), New Zealand. It supersedes *NIWA Ecosystems Publications* (ISSN 1172-3726; published by NIWA Ecosystems, Hamilton), *New Zealand Freshwater Research Reports* (ISSN 1171-9842; published by NIWA Freshwater, Christchurch) and *Miscellaneous Publications, New Zealand Oceanographic Institute* (ISSN 0510-0054).

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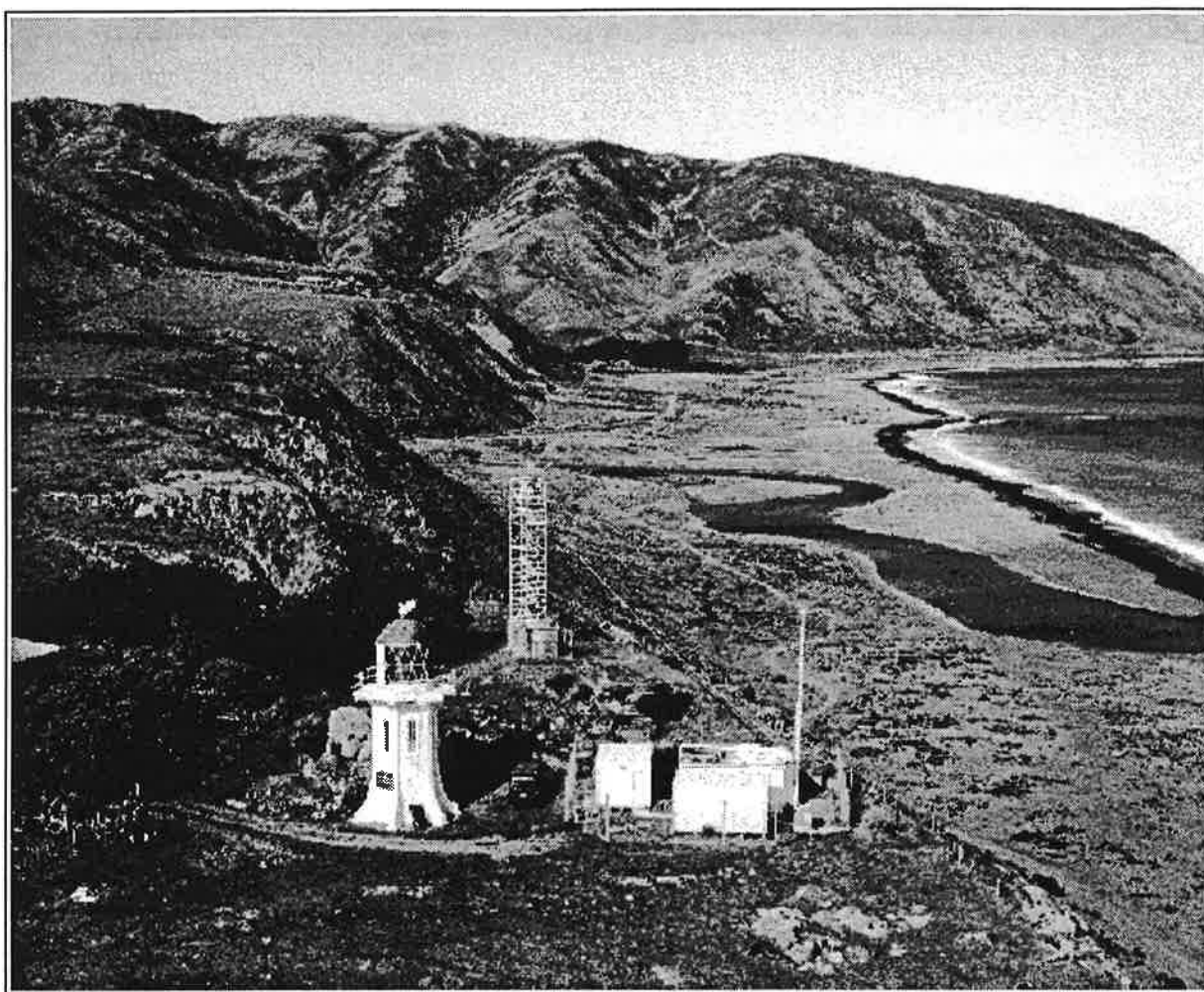
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## 1. INTRODUCTION

This report aims to bring together a brief summary of each of the various air sampling and monitoring activities taking place at the Baring Head atmospheric sampling station, in Wellington, New Zealand. The summaries have been provided by those involved in the collection and measurement of those individual species.

## 2. SITE DESCRIPTION



**Figure 1** The Baring Head atmospheric sampling station viewed from the west.

The Baring Head atmospheric sampling station is located at  $41^{\circ} 24.6' \text{ S}$ ,  $174^{\circ} 52.2' \text{ E}$  situated on a cliff top site 80 m above sea level on the south coast of the North Island of New Zealand. The site comprises of three buildings and a 12 m tower. Sample air lines are mounted up on the flagpole outside one of the buildings and air samples are taken through the air lines from inside the building. Equipment used to make continuous measurements of the air and record the local meteorology are housed within the buildings. Air lines are also mounted at the top of the tower

and flow into the buildings. A number of meteorological measuring devices are located at the top of the tower.

### 3. LOCAL METEOROLOGY

M J Harvey and S E Nichol

#### **Windspeed and direction:**

The frequency distribution of winds from all directions (Figure 2) and from the south (90° through 270°, Figure 3) are shown along with Weibull parameters for fitted Weibull distributions. The 1993 wind rose in Figure 4 is similar to that of 1991 and 1992 (Harvey, 1993). Storm force 10 and above winds comprised 1.1% of valid data..

#### **Back trajectories:**

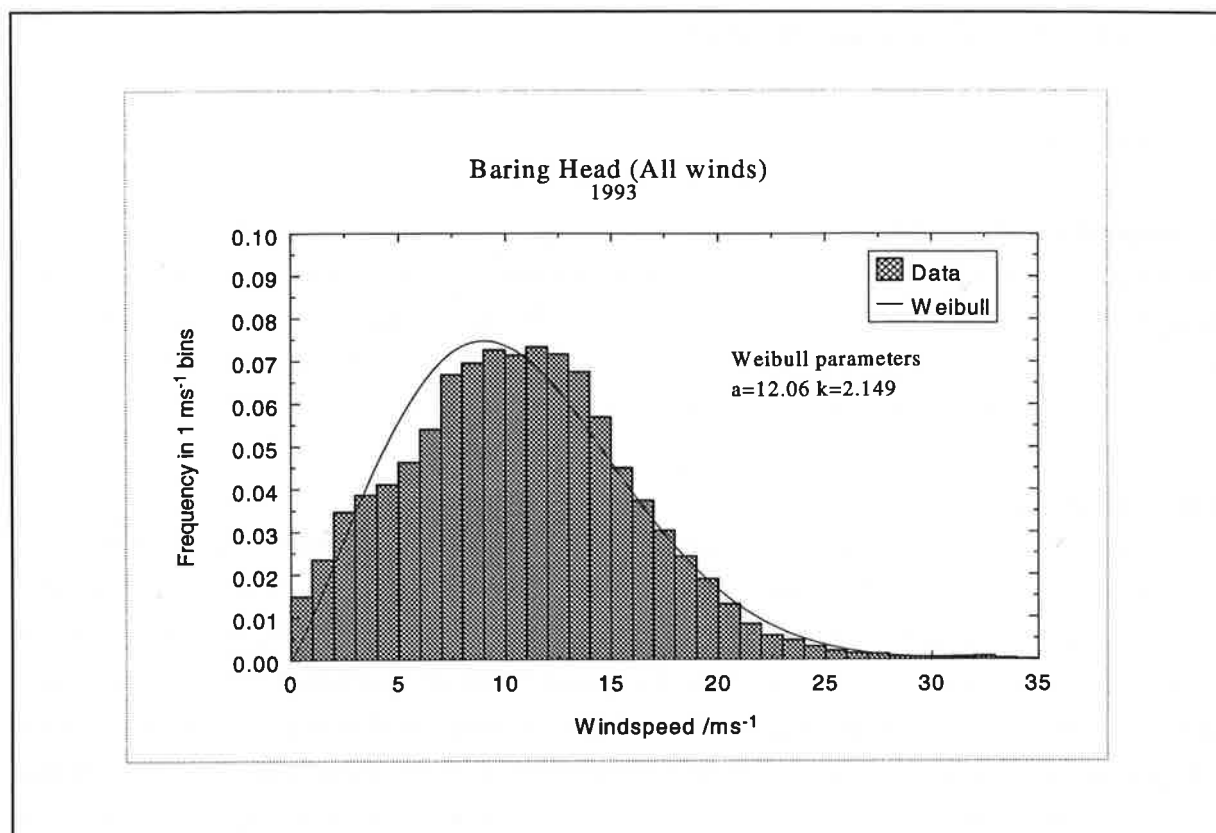
Four-day back trajectories are generated each day for midnight and midday at Baring Head. The endpoint pressure level for the trajectories is 950 hPa. The trajectories are generated from wind fields which are produced by the Meteorological Service of New Zealand and NIWA's numerical weather prediction analyses. The back trajectories are available from 1988 onwards. Cluster analysis is a technique which can be used to group similar trajectories into distinct transport regimes in order to determine an airflow climatology for a particular site (Moody and Galloway, 1986; Harris et al., 1992). Figure 5 shows the six cluster mean trajectories and their percentages for Baring Head for the period from 1988 to May 1993.

#### **Baseline Conditions:**

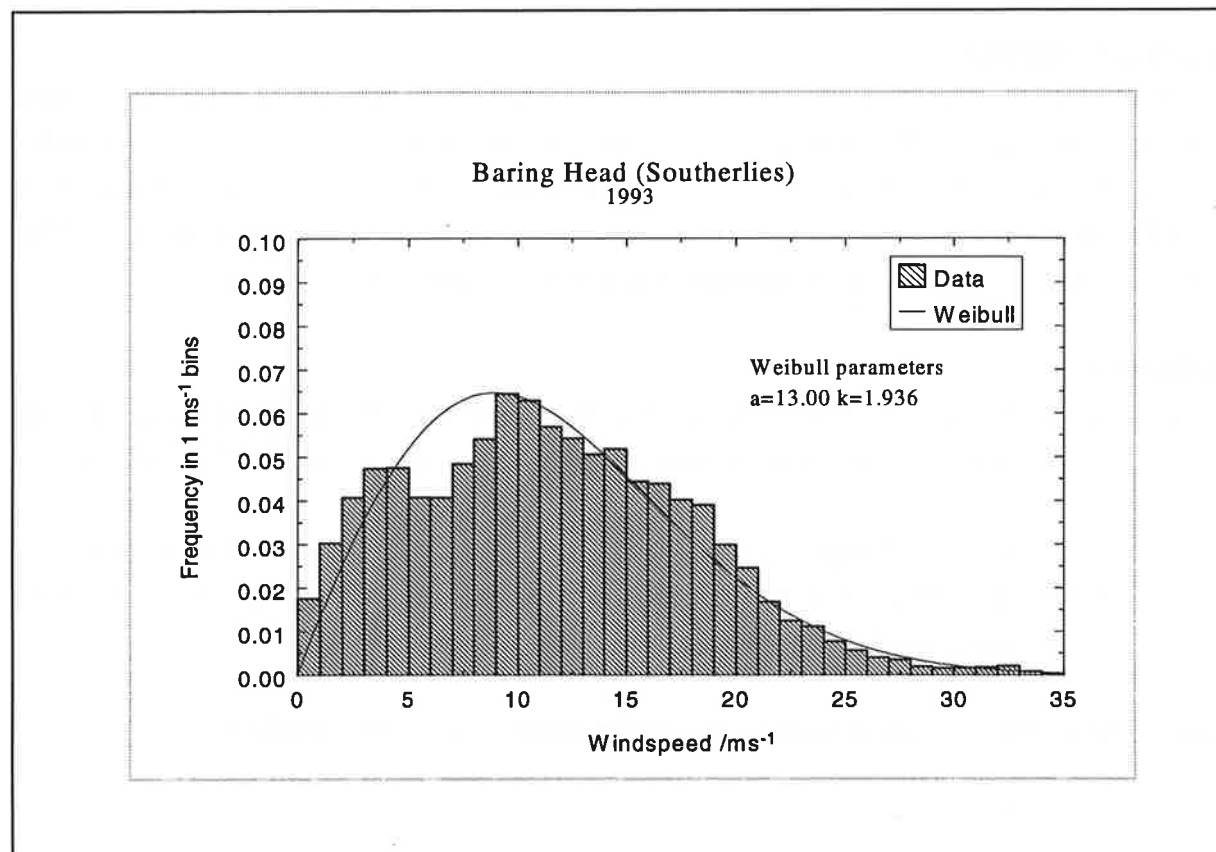
Baseline conditions are different for the different species measured and in most cases based solely on wind speed and direction. In most cases baseline samples are collected from a sector composed of pre-dominantly southerly winds. In the case of CO<sub>2</sub> it is based on the variation of the CO<sub>2</sub> measurement made being less than a given value for a defined time interval. This condition inevitably arises only in southerly winds and is called a steady interval.

#### **References:**

- Moody, J.L.; Galloway, J.N. (1988). Quantifying the relationship between atmospheric transport and the chemical composition of precipitation on Bermuda, *Tellus Ser. B*, 40, 463-479.
- Harris, J.M.; Tans, P.P.; Dlugokencky, E.J.; Masarie, K.A.; Lang, P.M.; Whittlestone, S.; Steele, L.P. (1992). Variations in atmospheric methane at Mauna Loa Observatory related to long-range transport, *J. Geophys. Res.*, 97, 6003-6010.
- Harvey, M.S. (1993). Wind at Baring Head, *NIWA Report, NIWA/Atmos/R/93-002*.



**Figure 2** Windspeed distribution for all winds at Baring Head.



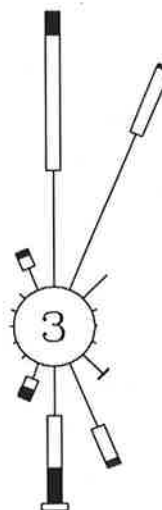
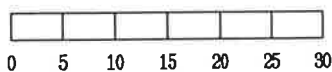
**Figure 3** Windspeed distribution for southerly winds at Baring Head.



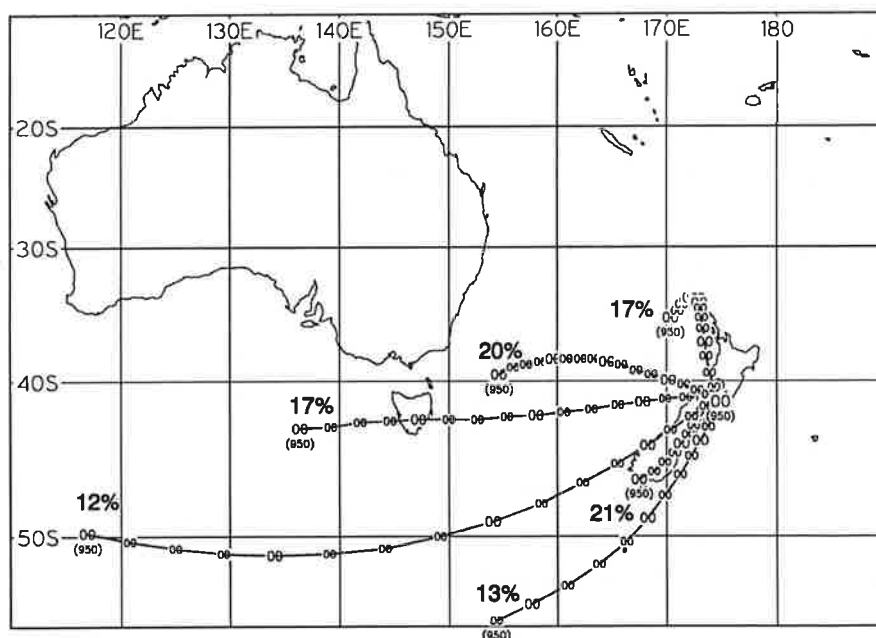
# Baring Head

1993

0.6-11.5 11.6-17.5 17.6-24.5 24.6 + m/s



**Figure 4** Wind rose diagram for Baring Head



**Figure 5** Cluster mean trajectories for Baring Head (1988-1993).

## 4. CARBON DIOXIDE - Continuous Measurement

M R Manning, A J Gomez, G W Brailsford, W J Ussler and K P Pohl

### Sampling and Measurement of CO<sub>2</sub>:

Determinations of atmospheric CO<sub>2</sub> mixing ratios are made using a Siemens Ultramat-3 non-dispersive infrared (NDIR) gas analyzer. The NDIR CO<sub>2</sub> analyzer is connected via a gas manifold consisting of stainless steel tubing and computer-controlled solenoid switches to 12 gas cylinders and 2 sample air lines that are continually purged. The NDIR analyzer compares ambient air CO<sub>2</sub> mixing ratios relative to known CO<sub>2</sub> mixing ratios in tanks of compressed reference gases. The analyzer operates in a differential mode, with a "zero" or baseline reference gas of CO<sub>2</sub> at ambient air levels flowing continuously through one cell of the analyzer at ~10 mL/min. Previously the baseline reference gas of CO<sub>2</sub> has had a mixing ratio 20 to 30 parts per million by volume (ppmv) below ambient CO<sub>2</sub> levels. When atmospheric CO<sub>2</sub> is measured a stainless steel bellows pump pulls air through the sample line at ~5 L/min. A small fraction of this (180 mL/min) is dried cryogenically to a temperature of approximately -70°C and passed through the sample cell of the CO<sub>2</sub> analyzer. Both the "zero" and sample gas are exhausted into the observatory building.

Operation of the analyzer system is controlled by a computer that switches a sample flow from one of the twelve reference calibration cylinders or one of the two sample air lines into the analyzer sample gas cell. For each calibration gas measurement, the computer monitors the analyzer voltage every second until the standard deviation of 60 consecutive values is below 0.02 ppmv. In some cases, stability is not reached within 5 min, so the computer repeats the previous gas followed by the gas that did not stabilise. All data for the 60 s of each calibration gas are recorded in a computer file, whether or not stability was achieved. CO<sub>2</sub>-in-natural-air mixtures prepared at Scripps Institution of Oceanography (SIO) and assigned a concentration on WMO standard scales are used for calibration.

A small amount of data are edited out from the record retrospectively where there is some evidence of malfunction. This is assisted by using at least one of the calibration gases as a *surveillance* gas and noting any periods where its apparent concentration differs from that assigned by SIO. A system of quality control is maintained on the calibration gases prior to any calculation being made of the CO<sub>2</sub> concentration in air. Data management procedures allow the choice of *surveillance* and *calibration* gases to be made retrospectively.

### Selection Criteria:

Baseline data are selected from the remaining data based on the steadiness of the CO<sub>2</sub> concentration. A baseline event or steady interval is normally defined as one in which the

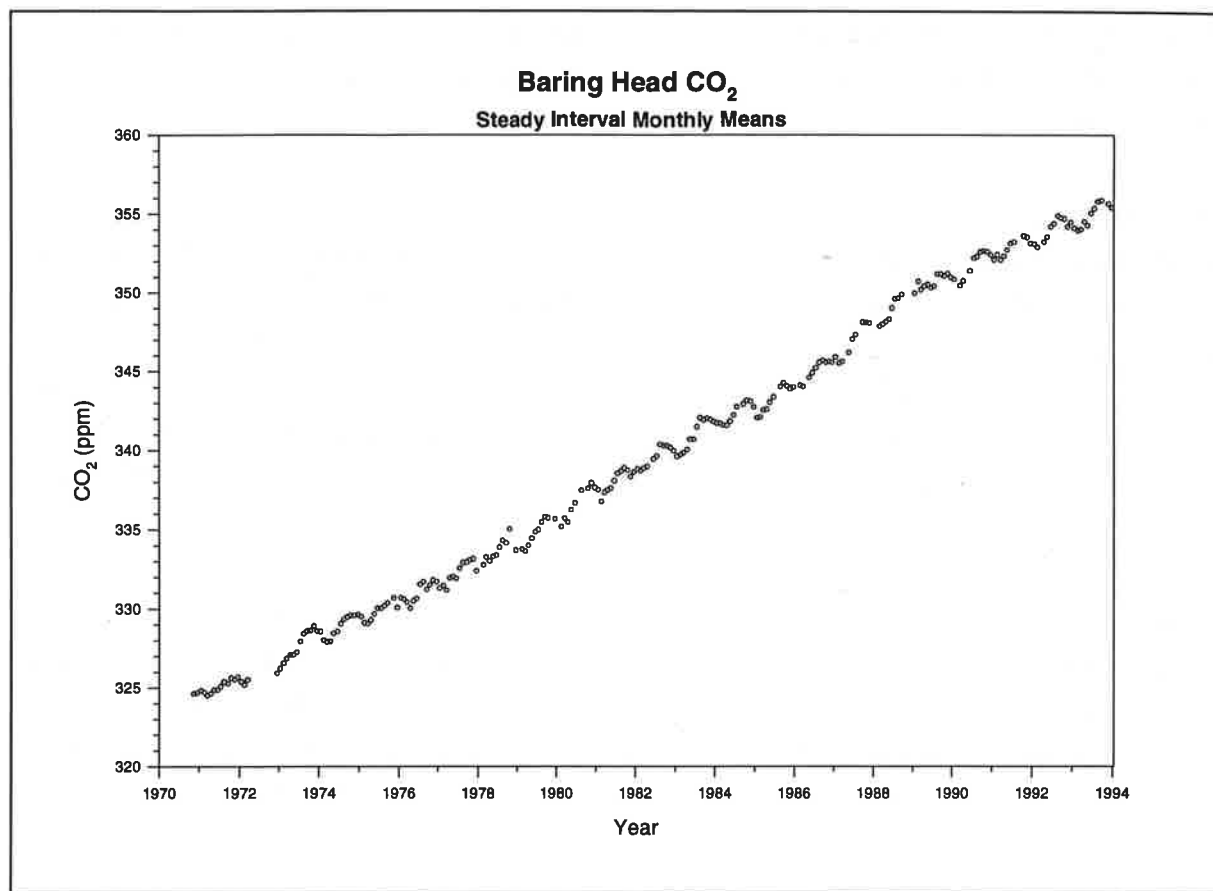
standard deviation of the minute-by-minute CO<sub>2</sub> concentrations is <0.1 ppmv for 6 or more hours. At Baring Head well mixed maritime air masses come from the southerly direction and inevitably all steady intervals occur in southerly wind conditions.

#### **Data Summary:**

The annual atmospheric CO<sub>2</sub> concentration at Baring Head rises between 0.7 and 2.5 ppmv per year. The monthly CO<sub>2</sub> record is typical of Southern Hemisphere sites: it shows a small seasonal cycle of approximately 1.0 ppmv peak to peak. Maxima occur from August to October, and minima occur from February to April. The CO<sub>2</sub> data is the longest continuous CO<sub>2</sub> record in the Southern Hemisphere beginning late 1970. It includes data measured at the Makara site from November 1970 to March 1972 before the Baring Head was established in December 1972.

#### **References:**

- Manning, M.R.; Gomez, A.J.; Pohl, K.P. (1994). Atmospheric CO<sub>2</sub> record from in situ measurements at Baring Head. pp 174-178. In *Trends '93: A compendium of data on global change, ORNL/CDIAC-65*, Eds: T.A. Boden, D.P. Kaiser, R.J. Sepanski and F.W. Stoess, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tenn, USA
- Manning, M.R.; Pohl, K.P.; Gomez, A.J. (1995). Status of the New Zealand CO<sub>2</sub> measurement programme. *Report of the Seventh WMO Meeting of Experts on Carbon Dioxide Concentration and Isotopic Measurement Techniques, Rome, Italy, 7 - 10 September 1993.* (Eds) G.I. Pearman and J.T. Peterson, WMO/TD-No 669, World Meteorological Organisation, Geneva.



**Figure 6** Monthly means of steady interval CO<sub>2</sub> concentrations at Baring Head.

## 5. CARBON DIOXIDE - Grab Sampling

M R Manning and W H Melhuish

### Sampling and Measurement of $^{13}\text{CO}_2$ :

Air samples are collected in pairs of 5 L evacuated glass flasks during southerly wind baseline conditions. The flasks are returned to the Scripps Institution of Oceanography for measurements of  $^{13}\text{CO}_2$  and  $\text{CO}_2$  concentrations.

### Sampling and Measurement of $^{14}\text{CO}_2$ :

Trays containing ~2 L of 5 normal NaOH carbonate-free solution are typically exposed for intervals of 1-2 weeks, and the atmospheric  $\text{CO}_2$  absorbed during that time is recovered by evolution using hydrochloric solution. The  $\text{CO}_2$  gas samples are measured using proportional gas counters. Considerable fractionation occurs during absorption into the NaOH solution, and the standard fractionation correction is used to determine a  $\Delta^{14}\text{C}$  value corrected to  $\delta^{13}\text{C} = -25$  per mil (‰).

### Data Summary:

These measurements of  $^{14}\text{C}$  in atmospheric  $\text{CO}_2$  at Wellington (Makara and Baring Head sites) constitute one of the longest isotopic records available, particularly from the Southern Hemisphere, and support the overall decline in atmospheric  $^{14}\text{CO}_2$  reported by others. The  $^{14}\text{C}$  record for Wellington in 1965 shows a peak occurring roughly 1 year later than that observed in the Northern Hemisphere. A seasonal component with a cycle of decreasing amplitude is present in the Wellington record. Up to 1980, the cycle had a maximum in March and a minimum in August along with a negative anomaly in December. The amplitude of the cycle for this period decreased steadily from a peak-to-peak range of 20 ‰ in 1966 to 3 ‰ in 1980. From 1980 onwards a new seasonal cycle emerged with an amplitude of ~5 ‰ having a maximum in July-August and a minimum in January.

### References:

- Manning, M.R.; Melhuish, W.H. (1994). Atmospheric  $\Delta^{14}\text{C}$  from Wellington. *pp 193-202. In: Trends '93: A compendium of data on global change, ORNL/CDIAC-65, Eds: T.A. Boden, D.P. Kaiser, R.J. Sepanski and F.W. Stoess, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, Oak Ridge, Tenn, USA*
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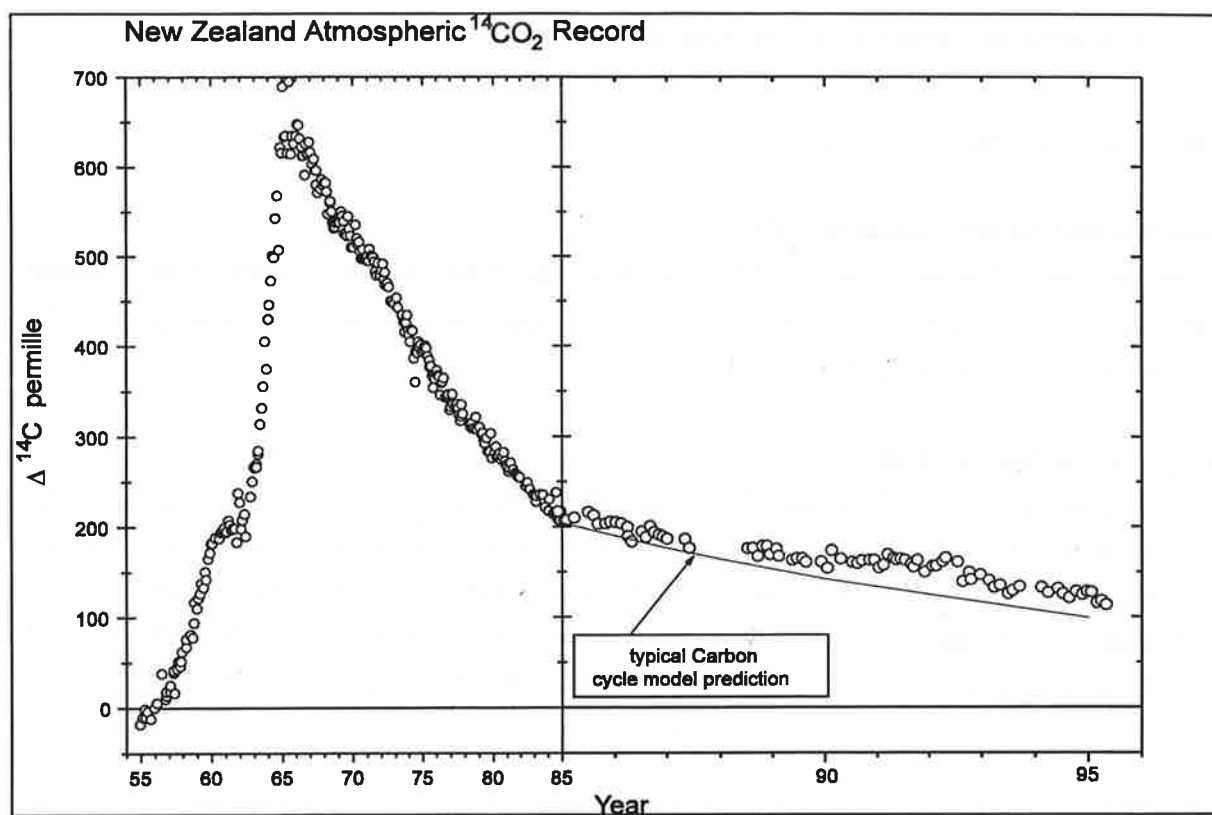


Figure 7  $^{14}\text{CO}_2$  measurements at Baring Head.

## 6. METHANE

D C Lowe, G W Brailsford, R C Moss and A M Bromley

### **Sampling procedure for CH<sub>4</sub>, <sup>13</sup>CH<sub>4</sub> and <sup>14</sup>CH<sub>4</sub>:**

For the methane isotopic analysis, dry whole air samples are collected in light gauge 22 and 70 L stainless steel tanks. Air is sampled through a 10 m long 12.5 mm o.d. stainless steel tube attached to the Baring Head sampling mast. The air is pumped from the mast to the tanks using a Thomas oil free compressor and dried using a 1 L stainless steel trap containing 3 mm 13X molecular sieve pellets. For <sup>13</sup>CH<sub>4</sub> analyses the 22 L tanks are pumped to 7 Bar and for <sup>14</sup>CH<sub>4</sub> and <sup>13</sup>CH<sub>4</sub> analyses the 70 L tanks are pumped to about 5 Bar. Methane concentration measurements are made on the same air samples and also on low pressure air samples collected in 2 L light gauge stainless steel cans using a rubber diaphragm pump through the same air line without drying.

### **Measurement procedure for CH<sub>4</sub>, <sup>13</sup>CH<sub>4</sub> and <sup>14</sup>CH<sub>4</sub>:**

For the isotopic analyses, methane in the air samples is quantitatively converted to CO<sub>2</sub> in the laboratory over a platinum catalyst after the removal of interfering species like CO<sub>2</sub>, N<sub>2</sub>O, CO and non-methane hydrocarbons (NMHC). This CO<sub>2</sub> is measured on a stable isotope ratio mass spectrometer for <sup>13</sup>C against an international light barium carbonate standard distributed by the IAEA in Vienna, Austria. <sup>14</sup>C is determined by converting the CO<sub>2</sub> to a graphite target and analysis by accelerator mass spectrometry versus international radiocarbon standards. Methane concentration is determined by gas chromatography fitted with flame ionisation detection and compared against standards purchased from NIST. The ratio of the NOAA/CMDL scale (an alternative standard) to the NIST scale is determined as 0.986.

Both the sampling and measurement procedures are fully described in Lowe et al (1991)

### **Selection Criteria:**

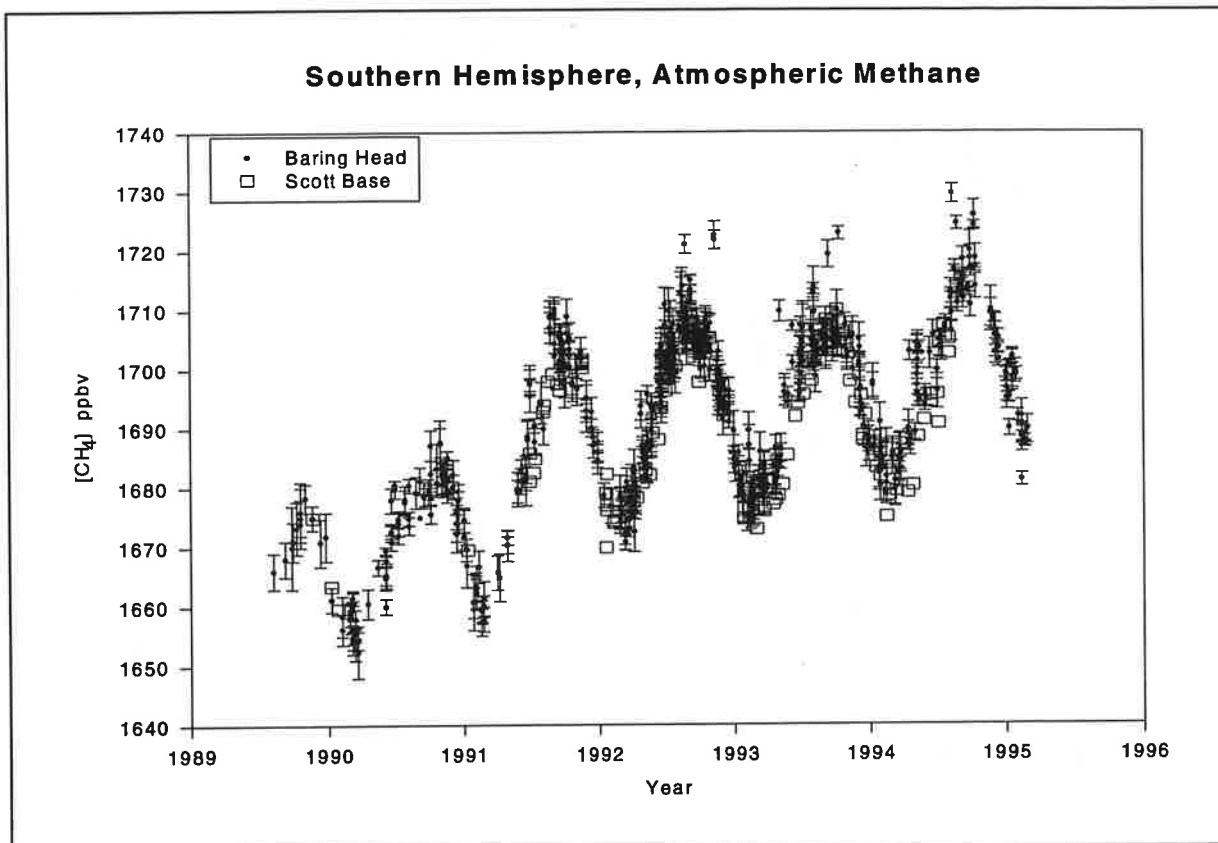
Air samples for methane isotopic and concentration analyses are usually collected during southerly baseline conditions at Baring Head. To determine the effect of local sources and sinks of methane in the Baring Head region, a limited number of air samples have been collected during north easterly conditions. For baseline studies of atmospheric methane in the south Pacific region, analyses are selected for wind directions between 50° and 350° and wind speeds of greater than 14 knots.

### **References:**

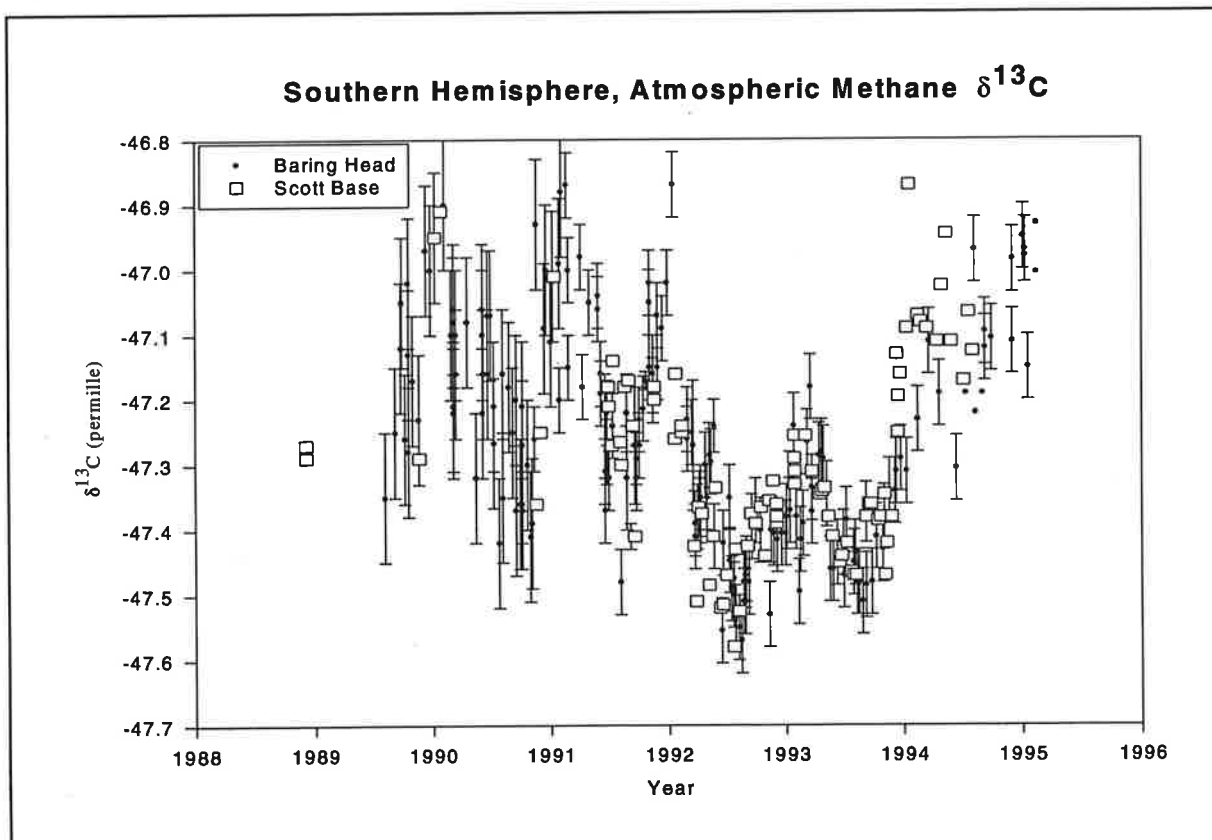
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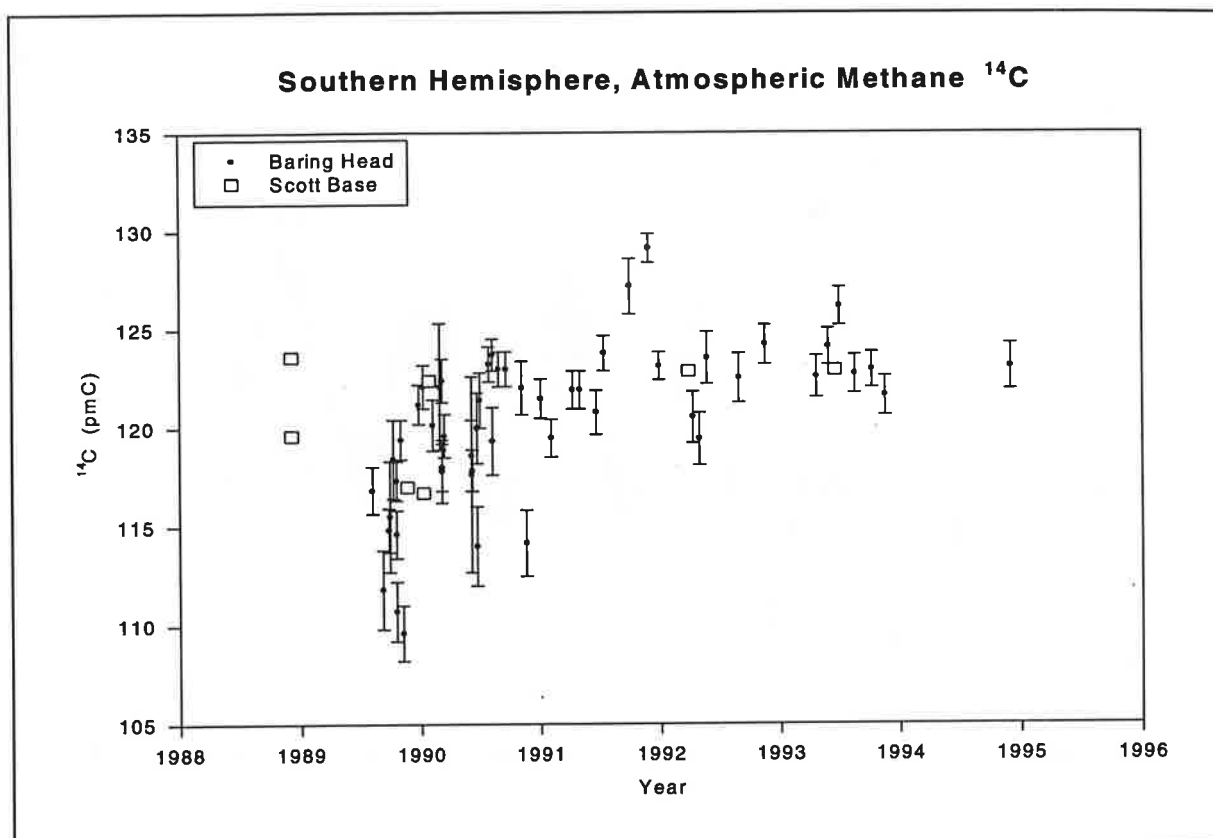




**Figure 8** Selected  $\text{CH}_4$  concentrations for Baring Head and Scott Base ( $78^\circ\text{S}$ ,  $167^\circ\text{E}$ ).



**Figure 9**  $\delta^{13}\text{CH}_4$  measurements for Baring Head and Scott Base ( $78^\circ\text{S}$ ,  $167^\circ\text{E}$ ).



## 7. CARBON MONOXIDE

C A M Brenninkmeijer, G W Brailsford, W Ussler, R Moss and P A Roberts

### Sampling Procedure:

Large whole air samples (1000 - 1200 L) are collected using KNF Neuberger membrane compressor by pressurising stainless steel cylinders to approx 250 psi. Recent sample collection has been aimed at southerly (on shore) winds and typically 25 samples are obtained spread fairly uniformly throughout a year.

### Measurement Procedure:

CO is extracted from the whole air samples by first removing CO<sub>2</sub> with very high efficiency cryogenic trapping, then oxidising the CO and removing the resulting CO<sub>2</sub> (Brenninkmeijer, 1993). As the extraction procedure is quantitative, a manometric measurement of the CO concentration can be obtained from pressure measurements of the extracted CO<sub>2</sub> in a calibrated volume. The CO-derived CO<sub>2</sub> is measured on a ratio isotope mass spectrometer for stable isotopes of <sup>13</sup>C and <sup>18</sup>O and then diluted with "dead" CO<sub>2</sub>, containing virtually no <sup>14</sup>C, to provide approximately 0.2 - 0.3 mg of carbon for <sup>14</sup>C measurement by accelerator mass spectrometry.

### Data Summary:

Figure 11 shows all data for CO concentration,  $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ , and <sup>14</sup>CO mixing ratio for the period July 1989 to June 1995. Solid circles represent air collected under baseline (southerly wind) conditions and open circles under non-baseline conditions. The solid lines show seasonal cycles estimated from the median values of baseline data collected over the entire period in given calendar months.

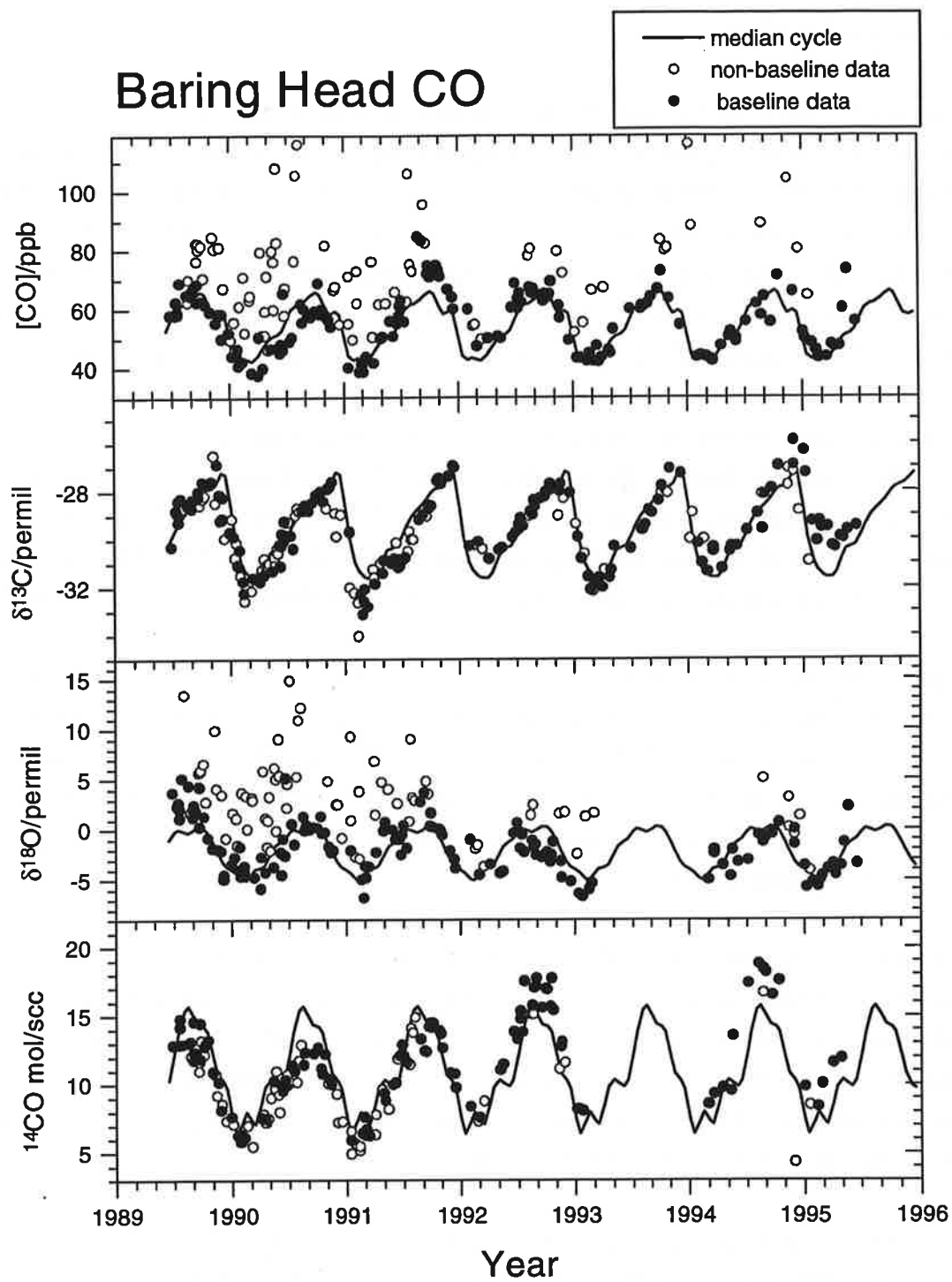
A positive anomaly in CO concentrations occurred in mid 1991 and continued into 1992. Otherwise these data support measurements at Cape Point, South Africa, in suggesting that there is no trend in CO concentration in the Southern Hemisphere. Both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  show large seasonal cycles. The cycle in  $\delta^{13}\text{C}$  has a different shape from that in concentration and highest <sup>13</sup>C enrichments occur 6 - 8 weeks after the maximum in concentration. <sup>14</sup>CO has shown an increase over the 1990 - 1995 period which is qualitatively consistent with the expected variation in <sup>14</sup>C production through the current (11-year) solar cycle.

### References:

Brenninkmeijer, C.A.M. (1993). Measurement of the abundance of <sup>14</sup>CO in the atmosphere and the <sup>13</sup>C/<sup>12</sup>C and <sup>18</sup>O/<sup>16</sup>O ratio of atmospheric CO with applications in New Zealand and Antarctica.. *J. Geophys Res*, 98:10,595-10,614

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**Figure 11** Concentration and isotope measurements for CO at Baring Head.

## 8. NON-METHANE HYDROCARBONS

T S Clarkson and R J Martin

### **Sampling and Measurement of Non-Methane Hydrocarbons (NMHCs):**

From December 1991 to September 1993 an automatic gas chromatograph system operated at Baring Head for a study of light hydrocarbons in clean air. During routine operation automated measurements were made at intervals of about 4 hours. A sample of two litres of ambient air was drawn through a cryogenic trap at liquid nitrogen temperature for preconcentration of the hydrocarbons within about an hour. Then the sample was heated to about 80°C and injected onto a 30m capillary column (GS-Q). The flow rate of the hydrogen carrier gas was 10 mL/min and the column temperature was programmed from 40 to 200°C after the C<sub>2</sub> compounds had passed through. This column has been effective for separating hydrocarbon compounds from C<sub>2</sub> to C<sub>8</sub>. With an FID detector, the separation was virtually identical to that described by Rudolph et al. (1990) for this column. In addition to the light alkanes and alkenes, the system was sensitive to benzene, toluene, xylenes, ethyl benzene and methyl chloride. Detection limits were about 2 parts per trillion (10<sup>12</sup>) (ppt) for benzene and up to 10 ppt for the lighter NMHCs.

In addition to the automated samples collected at Baring Head, we have collected flask samples at the same site since early 1993. Flasks used in most cases were 800 mL electropolished stainless steel canisters fitted with Nupro SS-4H4 valves for flow-through sample collection. Flask preparation was carried out at 100°C and involved flushing with dehumidified zero air followed by evacuation. These flasks were filled by flushing with ambient air and pumping to 38 psi above atmospheric pressure.

The flask samples have been analyzed on a different GC system, based on a Varian 2740-20, with a two stage cryogenic trapping and transfer system, developed from that described for light hydrocarbon analysis by Greenberg et al (1994). This system had a 0.08" i.d. 20 ft phenyl isocynate/ Porasil C column with 7 mL/min helium carrier used isothermally at 50°C which provided good separation for C<sub>2</sub> to C<sub>5</sub> alkanes and alkenes. Satisfactory separation of acetylene and methyl chloride was never achieved by this method.

Species for which time series data were obtained at Baring Head during 1992-1994 were: ethane, ethene, acetylene, propane, propene, n-butane, isobutane, n-pentane, isopentane, benzene, toluene, methyl chloride. See Figures 12-15.

### **Selection Criteria:**

We have developed time series of all data for these compounds and have determined the same time series selected for only southerly wind data. The criterion for a "southerly" is a wind

averaging over 10 knots and between 130° and 230° through the sampling time.

Here we present only concentration data in southerly air for ethane and propane, the longest lived NMHCs together with benzene and toluene, the only aromatic compounds detected in Baring Head air.

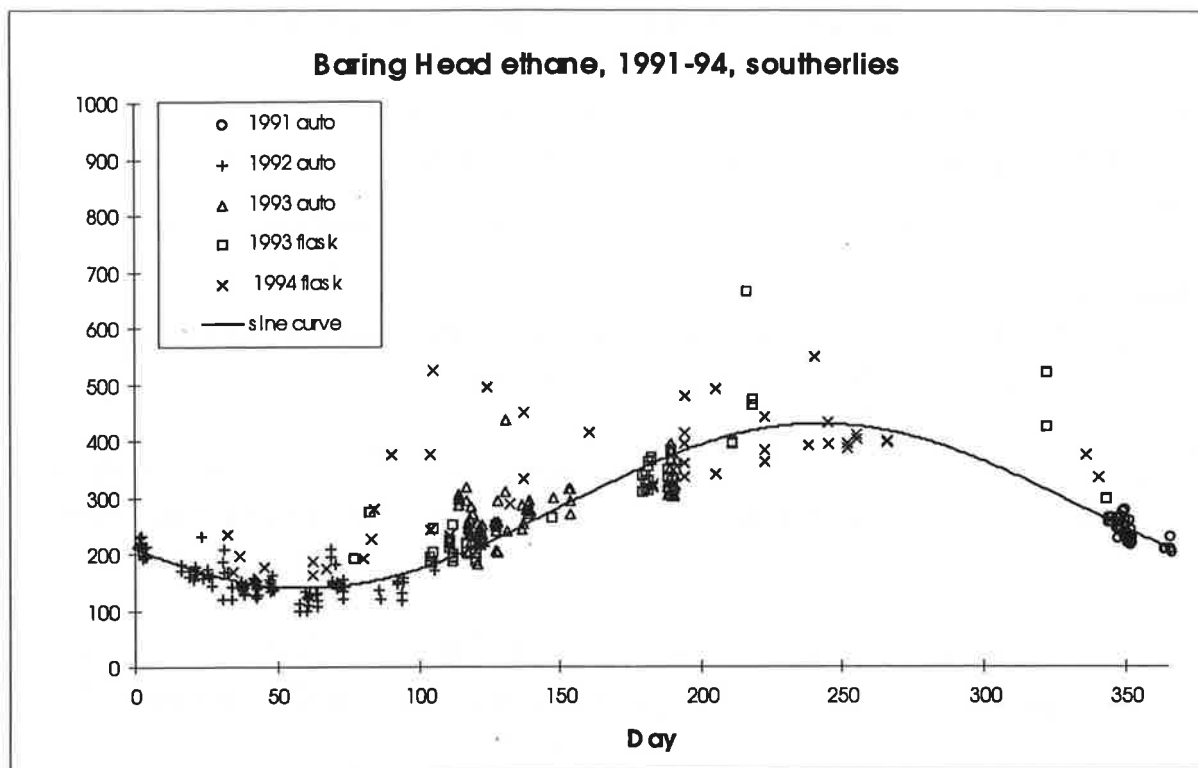
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Clarkson, T.S.; Martin R.J.; Rudolph, J.; Graham, B.W. (1996). Benzene and toluene in New Zealand Air. *Atmospheric Environment*, 30, 569-577.

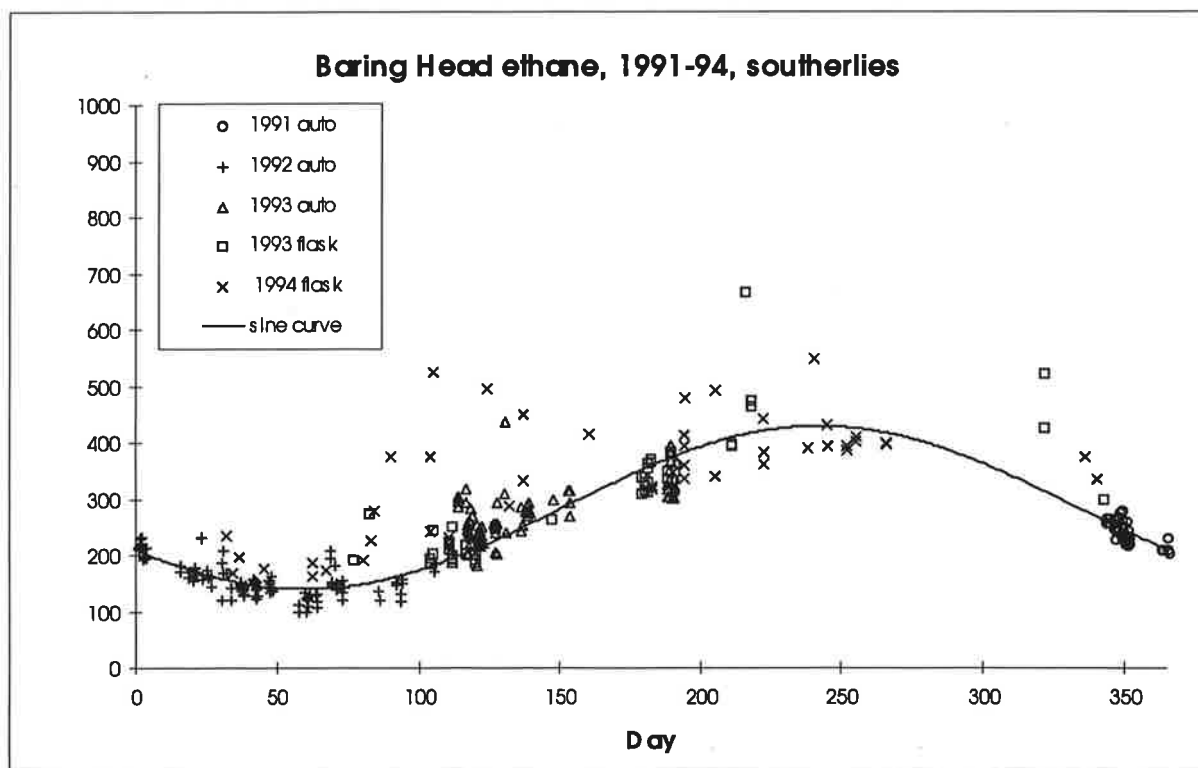
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Rudolph J.; Johnen F.J.; Khedim A.; Pilwat G. (1990). The use of automated on-line gas chromatography for the monitoring of organic trace gases in the atmosphere at low levels. *Intern. J. Environ. Anal. Chem.* 38, 143-155.

Greenberg J.P.; Lee B.; Helmig D.; Zimmerman P.R. (1994). Fully automated gas chromatograph-flame ionization detector system for the in situ determination of atmospheric non-methane hydrocarbons at low parts per trillion concentration. *Journal of Chromatography A* 676, 389-398.

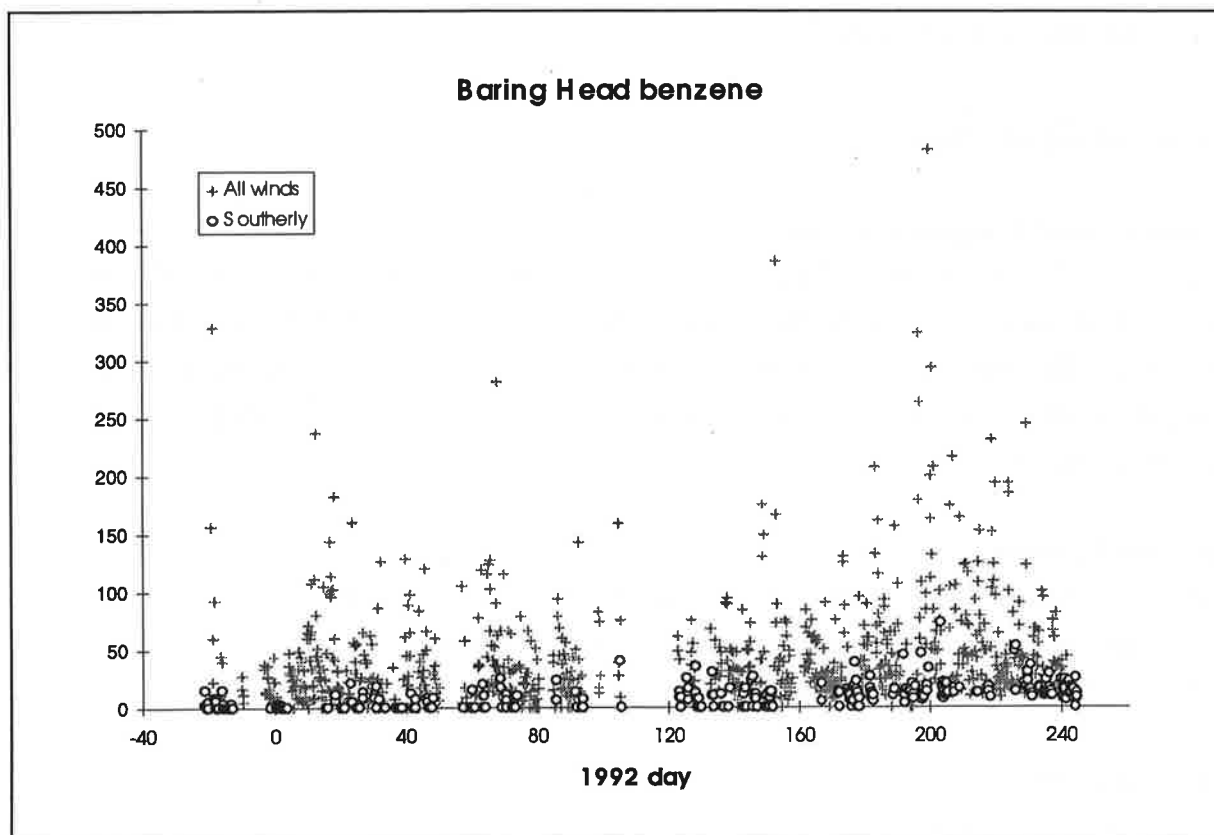


**Figure 12** Measurements of ethane concentrations (in ppt) at Baring Head.

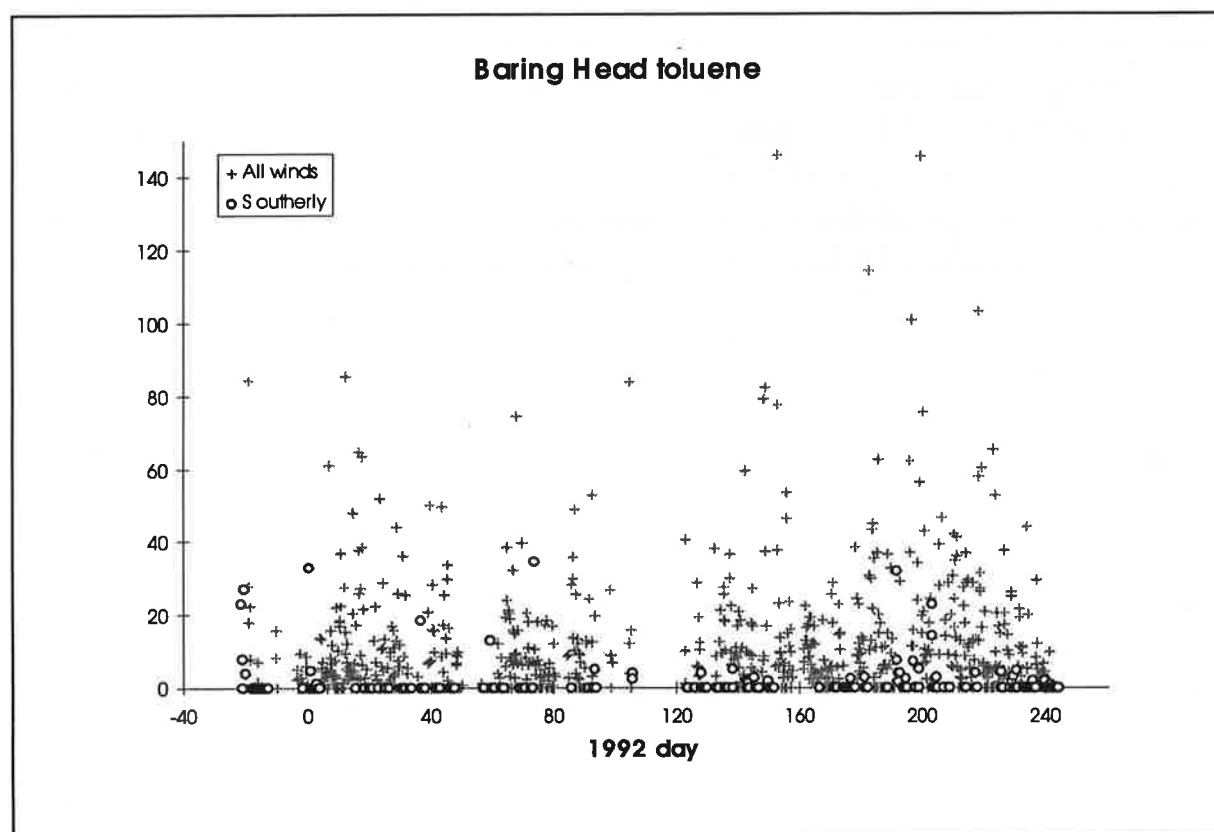


**Figure 13** Measurements of propane concentrations (in ppt) at Baring Head.





**Figure 14** Measurements of benzene concentrations (in ppt) at Baring Head.



**Figure 15** Measurements of toluene concentrations (in ppt) at Baring Head.

## 9. SURFACE OZONE

S E Nichol and M J Harvey

### **Sampling and Measurement of O<sub>3</sub>:**

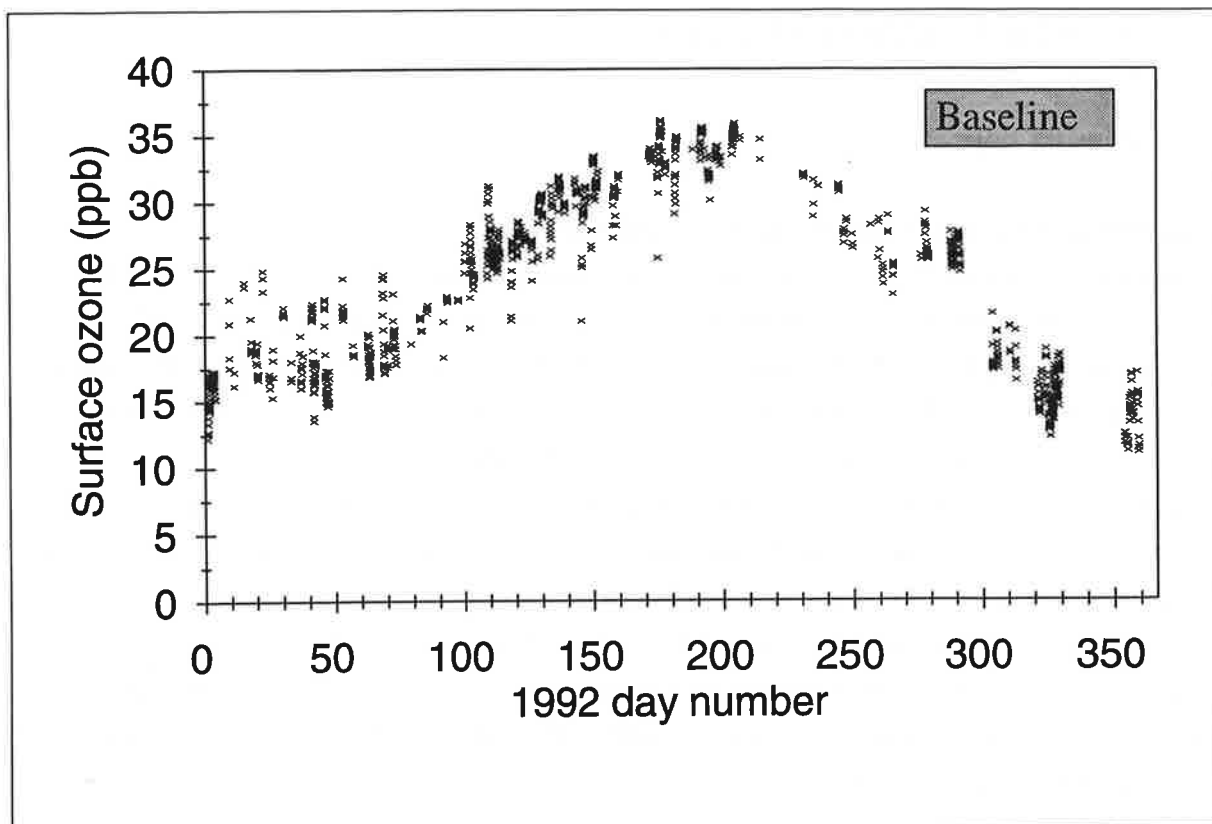
A Dasibi UV ozone monitor (Model 1003-PC) has been used to measure surface ozone at Baring Head since 1991. Air for these measurements is drawn from 5 metres above the ground through a dedicated teflon tube with a 0.5 µm teflon filter on the inlet to exclude aerosols. Sample readings are calculated every 30 seconds, with 10-minute averages being recorded on a Campbell Data Logger.

### **Selection Criteria:**

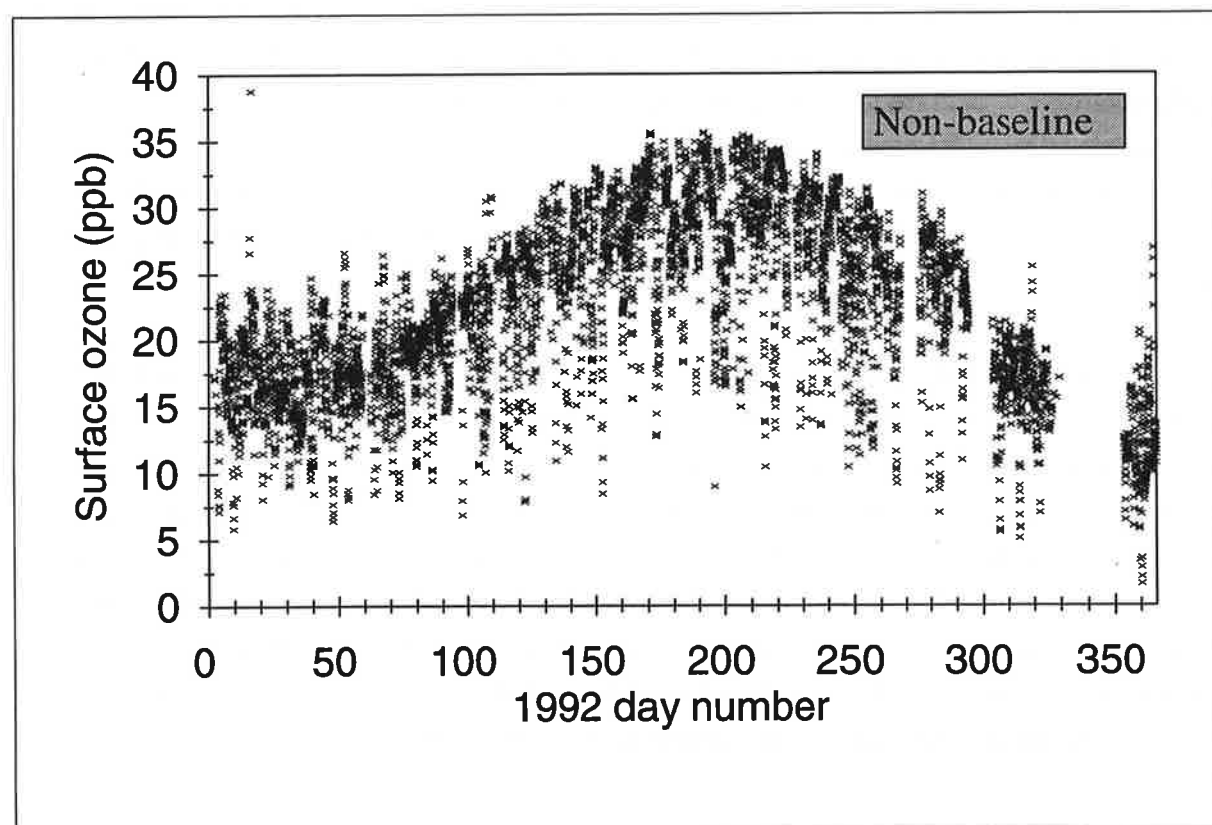
Figure 16 shows hourly surface ozone values for Baring Head for 1992, using baseline conditions (i.e. wind direction between 150° and 210°, and wind speed greater than 5 m/s). Figure 17 shows the non-baseline data for 1992.

### **Data Summary:**

There is a marked seasonal cycle, with minimum values during the summer (day 335 to 365, and day 1 to day 59) and maximum values in the winter (day 152 to 243). In baseline conditions there is a relatively narrow range of high ozone concentrations, since the southerly winds come from the ocean, where the ozone destruction processes are very slow i.e. deposition velocity is smaller than over land. The greatest surface ozone variability occurs with northerly winds and calm periods. This variability is caused by two effects: (1) northerly winds pass over the ground surface, which is an effective sink for ozone; the effectiveness of this sink diminishes with increasing windspeed; and (2) the urban centres to the north of Baring Head are sources of NO<sub>x</sub> and hydrocarbons, which are important precursors to ozone production.



**Figure 16** Hourly averages of baseline surface ozone at Baring Head for 1992.



**Figure 17** Hourly averages of non-baseline surface ozone at Baring Head for 1992.

## 10. CONDENSATION NUCLEI

M J Harvey, I S Boyd and C F Walker

### **Sampling and Measurement of Condensation Nuclei:**

Condensation nuclei (CN) were continuously monitored between 1992 day 128.58 and 1993 day 56.0 using a Environment One Model Rich 100 CN monitor measuring particles  $>2.5$  nm in diameter according to its specification. Two histograms are shown, one for "northerly" and one for southerly winds. The majority of observations in southerlies, Figure 18, (marine sector 134 to 280°) fall in the lowest category ( $<200$  cm<sup>-3</sup>) with exponential decrease in frequency with increase in concentration. In "northerlies", Figure 19, (terrestrial sector 280° through north to 134°) there is a much broader distribution (one tail normal). The highest concentration recorded in "northerly"/light wind conditions was around 50,000 cm<sup>-3</sup>. The concentration of CN in all winds typically follows the solar cycle with a peak in CN concentration around midday during steady wind conditions. The Environment One monitor makes a bulk measurement and is not accurate at low concentrations. There is not sufficient accuracy to determine any seasonal cycle in southerly unpolluted conditions.

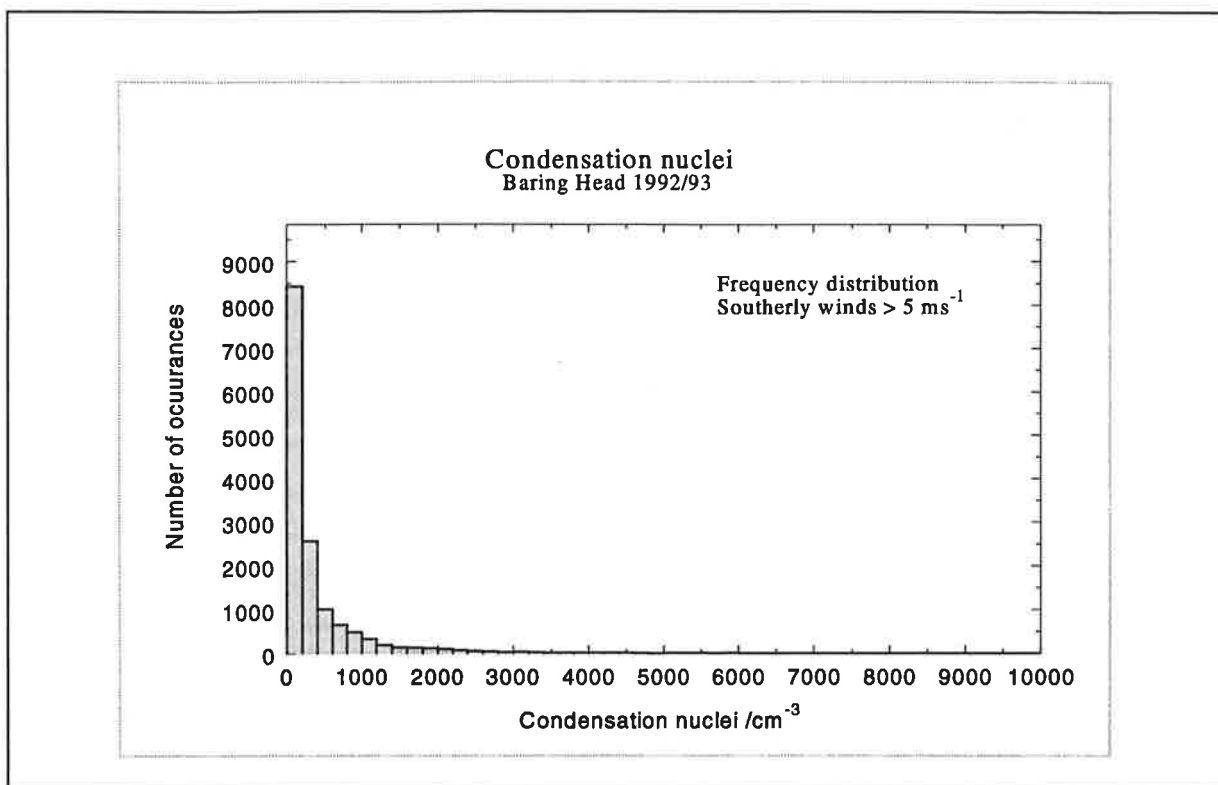
### **Aerosol chemistry:**

Analyses for aerosol sulphur components are shown in Figures 20 & 21 for data from 1991 to 1994. The figures show the concentration of airborne non-sea-salt sulphate (nssSO<sub>4</sub><sup>-</sup>) and methanesulphonic acid (MSA) for Baring Head and two other coastal sites: Leigh on the east coast north of Auckland (monitored by University of Auckland) and Karamea on the central west coast of the South Island. The solid line shows a "lowess" fit to all the data. Concentrations for nssSO<sub>4</sub><sup>-</sup> have been calculated using sodium as a conservative tracer of sea salt aerosol.

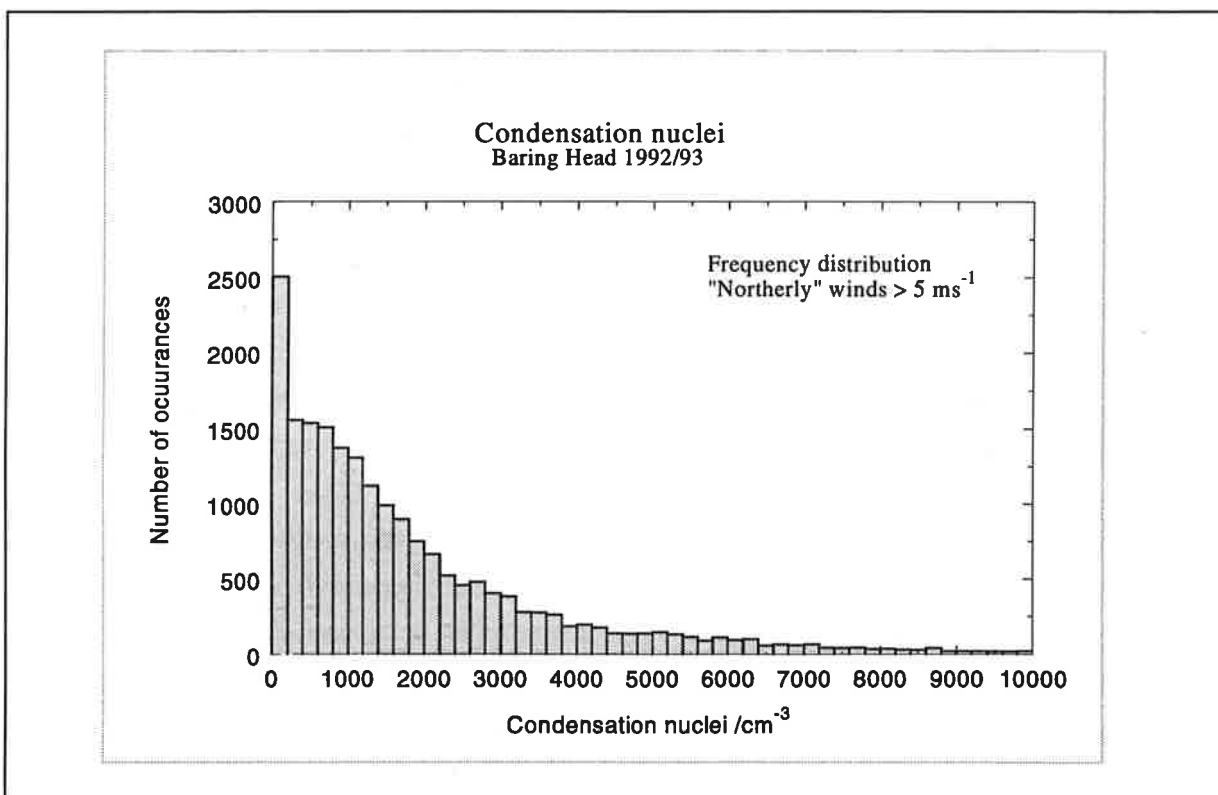
In unpolluted air at Baring Head, the major source of both nssSO<sub>4</sub><sup>-</sup> and the only source of MSA is thought to be the atmospheric oxidation of dimethylsulphide gas. The total atmospheric sulphate loading is about 1.2 µg/m<sup>3</sup> in onshore winds and 1.0 µg/m<sup>3</sup> in offshore winds. The order is reversed for nssSO<sub>4</sub><sup>-</sup> with an average concentration of 0.4 µg/m<sup>3</sup> and 0.6 µg/m<sup>3</sup> in offshore and onshore winds respectively. In onshore winds, there is evidence for a seasonal cycle in nssSO<sub>4</sub><sup>-</sup> and MSA concentrations rising around November and falling again in March. This cycle is likely to be associated with the seasonal cycle in dimethylsulphide precursor which has also been measured at this site. Similar trends in sulphur components have been observed at Leigh and Karamea where aerosol measurements have also been made.

**References:**

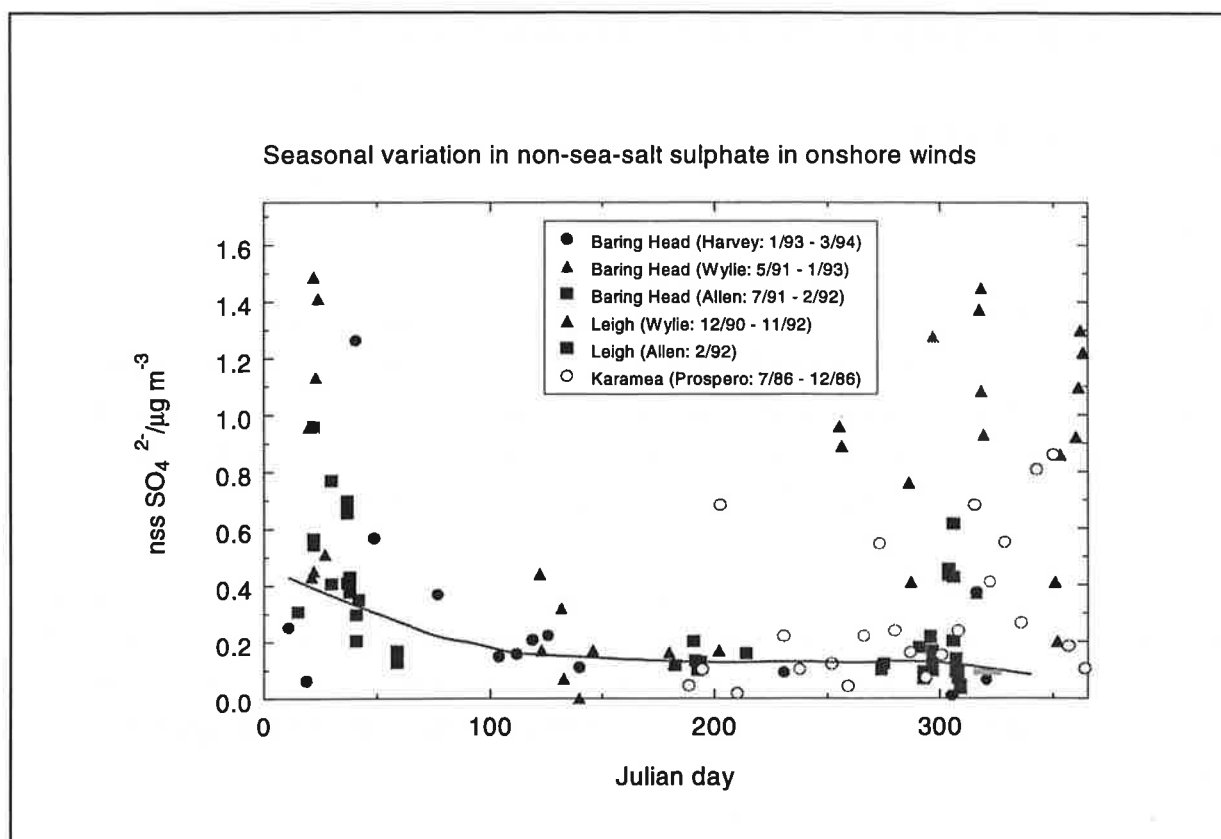
Walker, C.F.; Harvey, M.J.; Boyd, I.S. (In preparation). Comparison of background and urban aerosol chemistry in New Zealand.



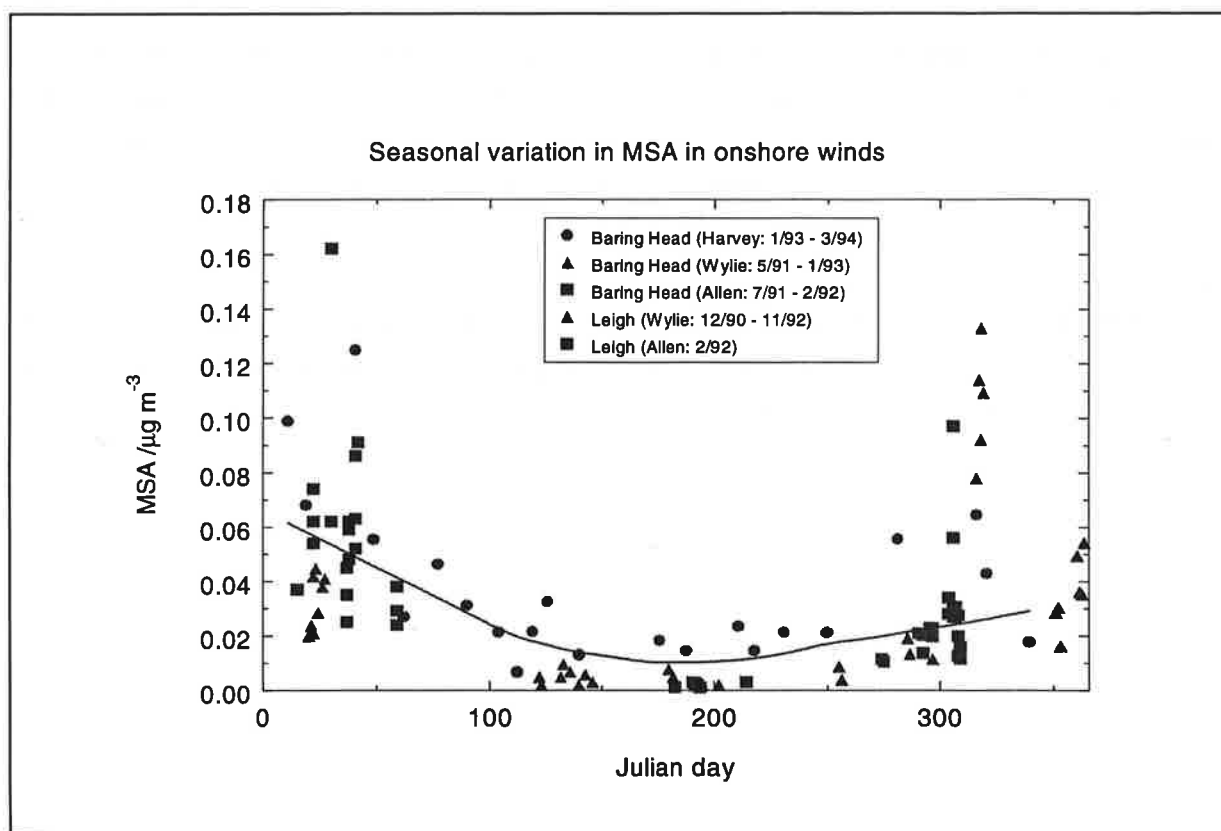
**Figure 18** Condensation nuclei measurements for southerly winds at Baring Head.



**Figure 19** Condensation nuclei measurements for northerly winds at Baring Head.



**Figure 20** Non-sea-salt sulphate measurements at Baring Head and two other sites in NZ.



**Figure 21** Methanesulphonic acid measurements at Baring Head and two other sites in NZ.

## 11. ATMOSPHERIC OXYGEN / NITROGEN RATIOS

G Brailsford and W Ussler

### Sampling and Measurement procedure for O<sub>2</sub>/N<sub>2</sub> ratios:

Measurement of O<sub>2</sub>/N<sub>2</sub> ratios in clean southern hemisphere marine air was started at Baring Head in 1991 in collaboration with the University of Rhode Island (Prof Michael Bender, Dr Taylor Ellis). Duplicate flask samples are collected during southerly winds. Air is pumped through a dry-ice trap to remove water vapour and a 2 L double ended glass flask fitted with Louwers-Hapert valves and viton O-ring seals. After flushing the flask the valves are closed.

Flask pairs are returned to URI for measurement using a mass-spectrometric isotope ratio method developed by Prof Bender and colleagues. This uses repeated measurements of the difference between mass 29 to mass 32 ratios in sample and standard air. Results are reported as the relative difference between sample and standard in parts per million (quoted as “per meg”). i.e.

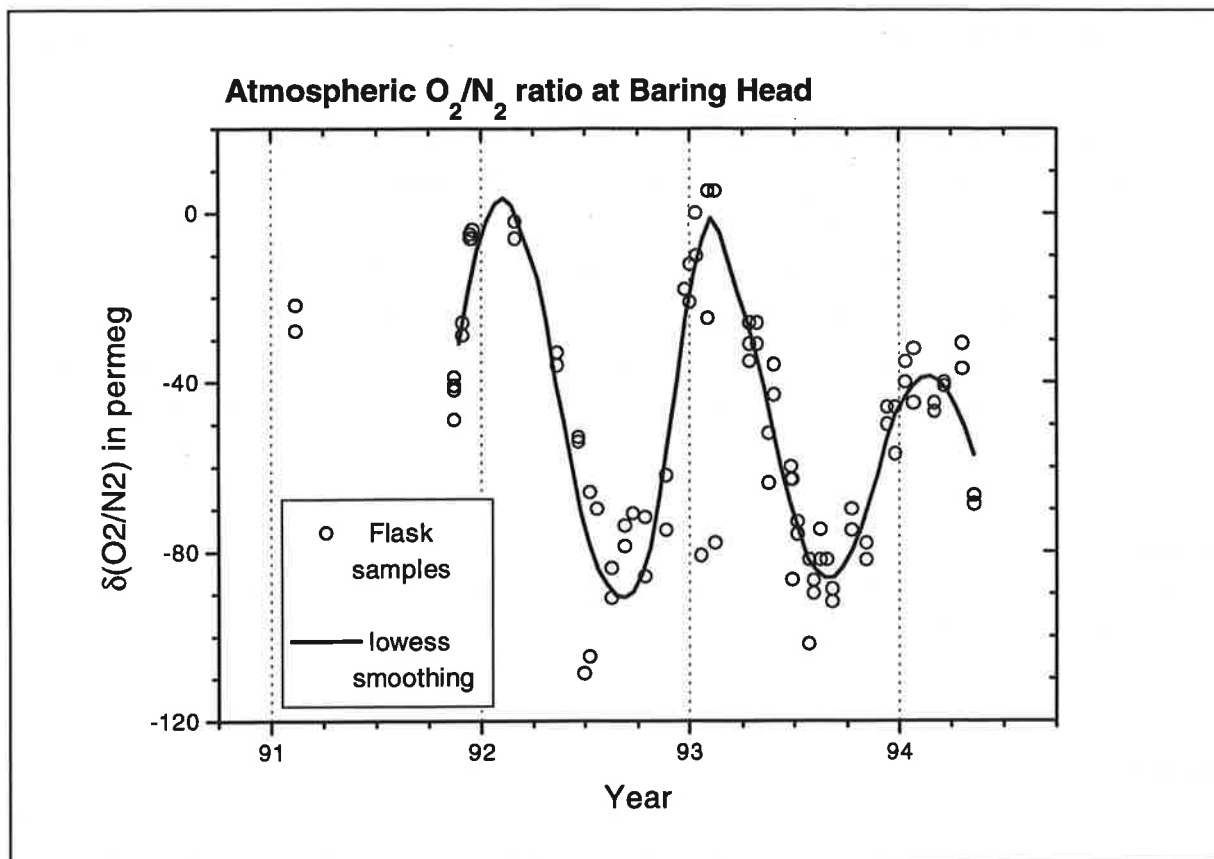
$$\delta(\text{O}_2/\text{N}_2) = [ (\text{O}_2/\text{N}_2)_{\text{sample}} / (\text{O}_2/\text{N}_2)_{\text{standard}} - 1 ] \times 10^6$$

Results for the period 1991 - mid 1994 are shown in Figure 22. The annual cycle of about 80 per meg in  $\delta\text{O}_2$  is due largely to the release of O<sub>2</sub> by marine photosynthesis in the southern oceans during the spring and summer. The apparent decline in O<sub>2</sub> levels is related to the ongoing combustion of fossil fuels. An analysis of the Baring Head data and comparison with a similar record from Cape Grim, Tasmania, is published in Bender et al (1996).

### References:

Bender, M.; Ellis, T.; Tans, P.; Francey, R.; Lowe, D. (1996). Variability in the O<sub>2</sub>/N<sub>2</sub> ratio of southern hemisphere air, 1991-1994: Implications for the carbon cycle. *Global Biogeochemical Cycles* 10: 9-21.





**Figure 22** Atmospheric O<sub>2</sub>/N<sub>2</sub> ratio at Baring Head.

## 12. MISCELLANEOUS

### ATMOSPHERIC RADIONUCLIDES

The work is carried out for the US Department of Energy. The remote atmospheric measurements program (RAMP) covers 41 sites globally. The sampling at Baring Head involves continuous sampling of atmospheric radionuclides onto filters that are sampled for the duration of a week. Monitoring started in 1987 at Lower Hutt and was shifted to Baring Head in August 1993. A sodium iodide detector is used to make measurements of short lived gamma ray emitters such as  $^7\text{Be}$ . The filters are then mailed to US DOE for further analysis using germanium detectors.

#### References:

Larsen, R.J.; Sanderson, C.G.; Kada, J. (1995). EML Surface air sampling program, 1990-1993  
*Data. EML-572*

### RADON

The radon detector at Baring Head was installed in October 1994, and re-calibrated in September 1995. Its design is similar to that reported by Whittlestone et al. 1994. The main features of the design are high sensitivity (0.2 counts/sec per  $\text{Bq/m}^3$ ), simplicity of construction and operation (no routine maintenance), and low power consumption (with appropriate choice of blowers, the instrument can operate on 40 watts).

This instrument operates continuously. Air is drawn through a filter into the delay chamber, which is 2000 L in volume, and vented to the atmosphere through a pipe which is painted black internally to prevent light from entering the chamber. The function of this "external" flow loop is to change the air with a residence time of less than half an hour. An internal blower circulates air inside the chamber through a fine screen which captures radon decay products. Alpha particles from the screen impinge on zinc sulphide, which is a scintillator. Light pulses from the ZnS are converted to electric pulses in a photomultiplier. After amplification, these signals are recorded on a data logger at half hour intervals. The response time of the detector is 45 minutes to 50% of maximum count.

#### References:

Whittlestone, S.; Zahorowski, W.; Wasiolek, P. (1994). High sensitivity two filter radon / thoron detectors with a wire or nylon screen as the second filter, *ANSTO/E718, ISSN 1030-7745, ISBN 0 642 59957 2*.

## **Appendix**

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University of Miami, Miami, USA.

University of Rhode Island, Kingston, USA.

University of Washington, Seattle, USA.

## Definitions:

|      |  |
|------|--|
| CMDL | Climate Monitoring and Diagnostics Laboratory, NOAA, Boulder, USA. |
| IAEA | International Atomic Energy Agency, Vienna, Austria.               |
| NIST | National Institute of Standards and Technology, USA.               |
| NOAA | National Oceanic and Atmospheric Administration, USA.              |
| SIO  | Scripps Institution of Oceanography, La Jolla, California, USA.    |
| WMO  | World Meteorological Organization.                                 |

|                                   |                         |
|-----------------------------------|-------------------------|
| CN                                | Condensation nuclei     |
| NDIR                              | Non-dispersive infrared |
| NMHC                              | Non-methane hydrocarbon |
| MSA                               | Methanesulphonic acid   |
| nss SO <sub>4</sub> <sup>2-</sup> | Non-sea-salt sulphate   |

|                       |   |
|-----------------------|---|
| $\delta^{13}\text{C}$ | deviation from standard $^{13}\text{C}/^{12}\text{C}$ ratio |
| $\delta^{13}\text{O}$ | deviation from standard $^{18}\text{O}/^{16}\text{O}$ ratio |
| $\Delta^{14}\text{C}$ | deviation from standard $^{14}\text{C}$ activity            |
| ‰                     | per mil (per thousand)                                      |