

The role of background observations of atmospheric composition at Cape Grim

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Background observations of the composition of the atmosphere are contributing to a wide range of scientific studies including climate and the influence of man, long-range atmospheric transport and deposition of materials, and the natural biogeochemical cycling of elements. The field is relatively new and the frontiers involve the development of observational technology, data selection procedures and a theoretical basis, including the interactions of chemistry, air-surface exchanges and atmospheric dynamics. This paper presents a brief summary of the history, philosophy and measurement program at the newly-opened Australian background observatory at Cape Grim, Tasmania. Selected data sets are used to illustrate the integral role the observations play in atmospheric composition research.

Introduction

The decade of the 1960s saw a rapid development of environmental awareness throughout much of the western world, with concomitant demands for scientific knowledge to support the requirements of environmental impact assessments. What started as research into the urban environment grew to include the possible effects natural and anthropogenic compounds in the atmosphere may have on global climate. Atmospheric scientists were asked to assess the significance of such potential hazards as ozone and climatic changes resulting from the effects of supersonic aircraft exhaust gases or spray-can propellants, and also the climatic effects of higher than average volcanic activity that occurred in the early 1970s. While the number of potential problems identified has been quite large, the growing concentration of carbon dioxide in the atmosphere, and its possible effects on climate and vegetation, has become the most widely recognised problem of this kind.

Amongst atmospheric scientists it is not unusual for cynical reference to be made to newly identified compounds of potential importance as 'the pollutant of the month'. Undoubtedly, the rush of doomsday threats coupled with the highly qualified statements scientists have had to make have been detrimental to the general image of this area of science in the public eye.

What appears to be poorly appreciated is the elementary state of this area of science. The past decade or so has made us very aware of how little we know about the global distribution of trace constituents in the atmosphere. When faced with issues such as the spray-can propellant/ozone problem, crash programs of observations, laboratory experiments and theoretical modelling were needed. It is my contention that what is needed is a serious attempt to establish a sound basis for

this area of science so that pronouncements can be made on the recognised issues, and in the future we will be more able to assess proposed problems without recourse to crash reviews and hand-waving science. In particular in this paper it is argued that an essential part of a burgeoning field such as this, is a comprehensive observational data base to serve as guidance in the development of laboratory experimentation and adequate theory.

A national background observatory

In 1971, C. H. B. Priestley and I. E. Galbally from the CSIRO Division of Meteorological (now Atmospheric) Physics and S. Twomey from Cloud Physics considered the need for southern hemisphere observations in studying the composition of background air. The following year the United Nations Conference on Human Environment in Stockholm, recommended that all member nations be encouraged to assist in the establishment of a global network of atmospheric observatories highlighting, in particular, the relationship of these stations to climate change research.

During the following three years, through the initiative of Dr C. H. B. Priestley and Dr W. J. Gibbs (Bureau of Meteorology), an Australian project was formulated which was supported by the Australian Government. The background observing station was to be part of an international commitment to the United Nations Global Environment Monitoring System, of which the Background Atmospheric Pollution Monitoring Network coordinated by the World Meteorological Organization, was a part.

Extensive field surveys were performed in Tasmania by CSIRO and the Departments of

Table 1. Summary of the measurement program at the Australian Cape Grim Atmospheric Observatory.

<i>Measurement</i>	<i>Purpose/Relevance</i>
<u>Gases</u>	
Carbon Dioxide Isotopic forms of CO ₂ Carbon monoxide Methane	¹² CO ₂ , ¹³ CO ₂ , ¹⁴ CO ₂ CO CH ₄
Nitrous oxide Nitrogen dioxide Nitric oxide Ozone	N ₂ O NO ₂ NO O ₃
Trichlorofluoromethane Dichlorodifluoromethane Methyl chloroform Carbon tetrachloride	CCl ₃ F CCl ₂ F ₂ CH ₃ CCl ₃ CCl ₄
<u>Aerosols</u>	
Total particle concentrations	Direct effect on interception of incoming solar radiation and outgoing solar and terrestrial radiation; effect on cloud formation and type.
Condensation nuclei Ice nuclei	Measure of 'pollution' level and indicator of scattering potential.
Particle size distribution	Factors influencing cloud amount and cloud type.
Particle chemical composition	Identification of numbers in size range of significance to cloud formation, etc.
<u>Solar radiation</u>	
Beam Global Diffuse Turbidity	Source identification and particle behaviour.
Influence of atmospheric composition on amount and quality of solar energy reaching earth's surface.	
Together the resultant effect of atmospheric composition on the transmission of radiation through the atmosphere as a measure of input on energy budget.	

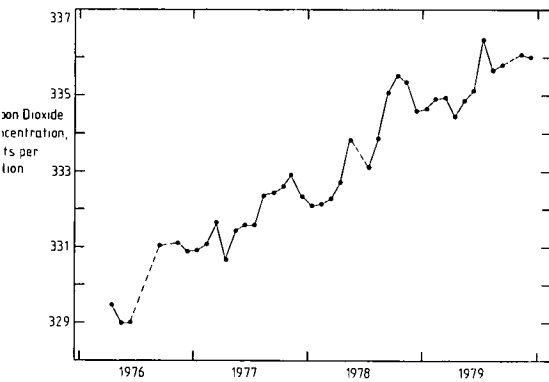
<i>Measurement</i>		<i>Purpose/Relevance</i>
Global UV Global erythema UV		Stability of ozone layer and potential biological effects of ultraviolet radiation.
<u>Precipitation chemistry</u>		Influenced by the integrated effects of the composition of the atmosphere through which rain has fallen. Indicator of long-range transport, source of aerosols, contribution of rain to elements supplied to soils, etc. Removal of soluble materials from the atmosphere.
Acidity Alkalinity	pH	Identification of acid rain conditions, measure of total dissolved salts.
Sulphate	SO ₄ ^{- -}	Sulphur cycle, large scale transport of pollutants.
Nitrate Ammonium	NO ₃ ⁻ NH ₄ ⁺	Nitrogen cycle.
Chloride Sodium Magnesium	Cl ⁻ Na ⁺ Mg ⁺⁺	Indicators of oceanic origin.
Calcium Potassium	Ca ⁺⁺ K ⁺	Indicators of terrestrial origin.
<u>Support observations</u>		Assist in the identification of air mass types, explaining time variability of composition measurements.
Radon	²²² Rn	Indicator of terrestrial/oceanic origin of air mass.
Dry bulb temperature Wet bulb temperature Pressure Wind speed Wind direction Air mass trajectories		Establishing air mass characteristics and changes for interpretation of composition data. Indicating vertical and horizontal space scales to be related to observations and establishing selection criteria.
Precipitation		Estimating total element precipitation rates.

gases individually and collectively play a role in the so-called planetary 'green-house' effect and thus in the determination of climate.

The most significant of these other gases is carbon dioxide. Measured with high precision since 1958, it is the observed increases in this gas that have caused wide-spread interest in the carbon cycle in recent years (see for example Williams 1978; Pearman 1980; Pittock et al. 1981). The observations at Cape Grim support those at other baseline stations, namely a rise of just over 1 ppmv per year (see Fig. 2). These observations complement those made in the CSIRO aircraft program (Beardsmore et al.

1978) and at the other baseline stations, providing details of the vertical and horizontal distribution of the gas as a function of time. Through the use of estimated rates of vertical mixing and, more recently, global transport simulation models, the data have been used to establish the net fluxes of carbon dioxide through the global atmosphere (Pearman et al. 1981). With improvements in the network of observations, greater precision through improved data selection procedures and better models of the atmospheric dynamics, the regional features of the global carbon cycle will be quantitatively defined.

Fig. 2 Monthly mean carbon dioxide concentration in the background atmosphere as observed at Cape Grim.

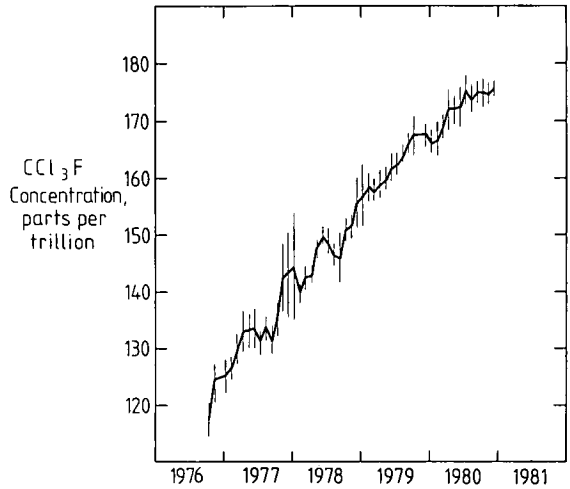


Ozone (O₃) in the troposphere is at lower concentrations than in the stratosphere, and yet due to the higher pressure is the next most significant gas in terms of infrared absorption. Northern hemisphere observations have indicated a rise in concentration of tropospheric ozone of about 1 per cent per year (Liu et al. 1980). This change is presently related to the oxidation of anthropogenic carbon monoxide and hydrocarbons and the effects of oxides of nitrogen emitted from aircraft and other combustion sources (Pittock et al. 1981). Further confirmation of this interpretation will come if southern hemisphere troposphere ozone can be shown to be unchanging through observations such as those in progress at Cape Grim.

In 1974, Molina and Rowland (1974) proposed that certain man-made halocarbons, in particular the chlorofluoromethanes CCl₃F (Freon 11) and CCl₂F₂ (Freon 12), would photodissociate in the stratosphere releasing chlorine and catalyse the destruction of ozone. Subsequently, measurement programs were established to determine how much of these gases remained in the atmosphere. It should be emphasized that until the 1970s these gases had not been detected in the atmosphere as a suitable measurement technique did not exist. The Cape Grim record for CCl₃F (Fig. 3) is the most comprehensive made at a background station anywhere in the world. Used in conjunction with the other stations it has led to a clear picture of the global distribution of the gas. Assuming that the release statistics are not significantly in error, we are now in a position to say that the residence time of the gas in the atmosphere is long, approximately 50 years, and that there are no significant natural sources or sinks apart from stratospheric photolysis (Hyson et al. 1980). Present-day levels reflect almost all the mass of the gas ever released by man except for the small loss due to photodissociation.

While the rising levels of chlorofluoromethanes were initially considered important because of the potential effect on ozone in the stratosphere, CCl₃F and CCl₂F₂ are strong absorbers of infrared radiation in the atmospheric window (9 to 15 μm)

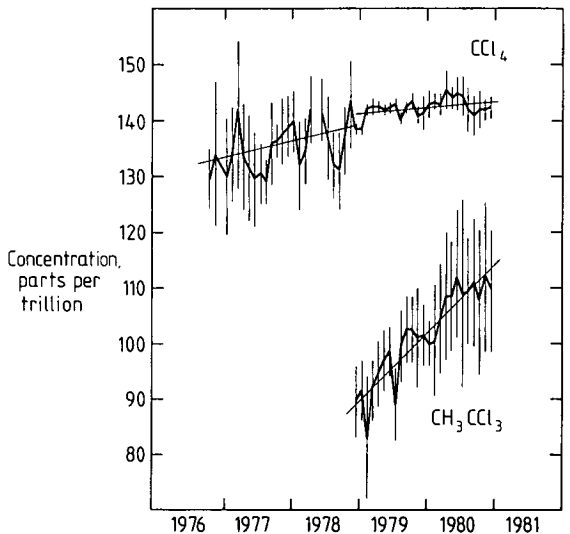
Fig. 3 Monthly mean CCl₃F (Freon 11) concentration at Cape Grim (from Baseline 1981).



and may contribute to the atmospheric greenhouse effect. A 20-fold increase in CCl₃F, for example, is calculated to have the equivalent greenhouse effect as about a 10 per cent increase of carbon dioxide (i.e. ~0.3°C global mean surface warming; see Pittock et al. 1981).

The observational program has revealed levels of other chlorinated species. These include CCl₂F₂ (Freon 12; Baseline 1981), CHClF₂ (Freon 22; Khalil and Rasmussen 1981), CH₃CCl₃ (methyl chloroform; Baseline 1981), and CCl₄ (carbon tetrachloride; Baseline 1981; see Fig. 4). CH₃CCl₃ is a degreasing solvent which is becoming widely used in industry. If current rates of increase were to continue, then in less than 20 years CH₃CCl₃ levels might potentially rival those of CCl₃F or CCl₂F₂ as a source of chlorine in the stratosphere despite the

Fig. 4 The atmospheric trend in CH₃CCl₃ (methyl chloroform) and CCl₄ (carbon tetrachloride) observed at Cape Grim (from Baseline 1981).



fact that its residence time is comparatively short (~10 years). At present it is not possible to infer the complete budget of CCl_4 . Large uncertainties exist as to the actual global release by man (Galbally 1976) and whether or not CCl_4 is generated in the atmosphere *in situ* (Lovelock and Simmonds 1980). The trends observed at Cape Grim do, however, suggest that the global source strength of CCl_4 is significantly greater than previously estimated by inventory techniques (Fraser, personal communication).

Methane (CH_4) and nitrous oxide (N_2O) are two other important radiatively active gases in the atmosphere. Isolated measurements of methane over the past decade or so have suggested, yet not conclusively, that the gas might be accumulating in the atmosphere. Measurements on air samples archived from Cape Grim, and more recently on grab samples collected routinely, have shown that methane is increasing at present at a rate of about 1 per cent per year (Fraser et al. 1981). This is supported by similar observations at Cape Meares in the northern hemisphere (Fig. 5). The interhemispheric differences in the absolute concentration and rate of increase, and the slight suggestion of some seasonality in the record provide some clues as to the cause of the increase. Wastage in the winning and use of fossil fuels or changes in the global biosphere are potential candidates.

Observations of nitrous oxide at Cape Grim have not indicated any significant trend within the natural variability and measurement noise of the data (Baseline 1981; Fig. 6). This contrasts with the recent suggestion of an upward trend made by Weiss (1981). This difference perhaps reflects the difficulty of making measurements at the parts per billion level to better than 1 per cent precision. Samples of Cape Grim air, collected over the past few years and retained in special containers, are being re-analysed for N_2O using a new higher precision instrument (Galbally and Roy, personal communication). This should lead to a more precise definition of the trend of N_2O at Cape Grim.

With the possible exception of nitrous oxide, many of the infrared absorbing gases are accumulating in the atmosphere (CO_2 , CCl_3F , CCl_2F_2 , CHClF_2 , CH_3CCl_3 , CH_4). Any consideration of the future climatic response to changing atmospheric composition must be cognizant of the combined effect of all of these compounds.

Transport of compounds

Individual components of the atmosphere can be used as tracers of the general dynamical mixing processes. Classically, gases such as water vapour, ozone and $^{14}\text{CO}_2$, together with volcanic particulate matter and nuclear bomb debris, have been utilised in this way. The suitability of these components is influenced by their chemical stability and surface exchange rates. Some gases, for example the highly

Fig. 5 The increase of CH_4 (methane) observed at Cape Grim and Cape Meares (after Fraser et al. 1981).

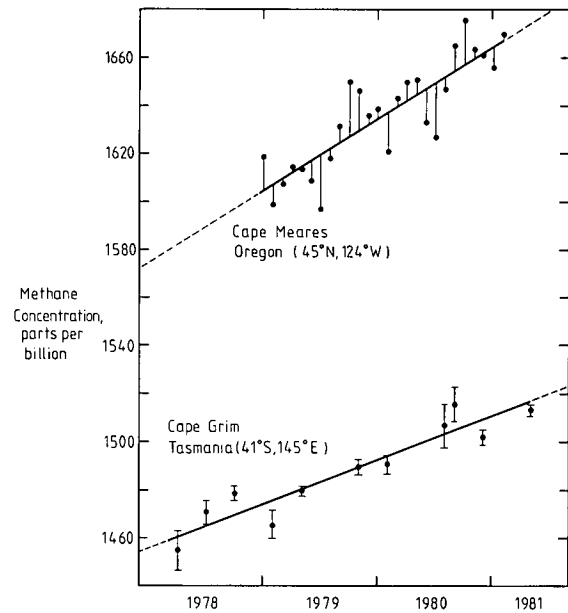
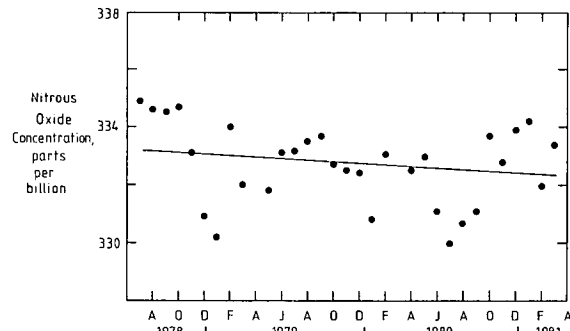


Fig. 6 Atmospheric observations of nitrous oxide (N_2O) at Cape Grim (from Baseline 1981).



stable CCl_3F , are especially suitable for tracer work.

Cape Grim CCl_3F data can be used to illustrate two examples of such tracer studies. Firstly, Cape Grim is remote from any significant sources of CCl_3F . However, on a few rare occasions significant deviations of concentration from the steadily rising background concentration, have indicated the arrival of air at the station which has passed over a significant source. Such a situation was reported by Fraser and Pearman (1978) when trajectory studies confirmed that the air mass had previously traversed the Melbourne metropolitan area (Fig. 7), more than 300 km away.

On a global scale, CCl_3F concentrations are shown to be ~9 per cent lower at Cape Grim than at northern hemisphere background stations. This difference, when coupled with known release rates (primarily northern hemispheric) and the rates of concentration increase, indicate the large-scale

Fig. 7 Calculated surface air-mass trajectory describing movement of air arriving at Cape Grim on 23 June 1977, a day when CCl_3F concentrations were unusually high (after Fraser and Pearman 1978).

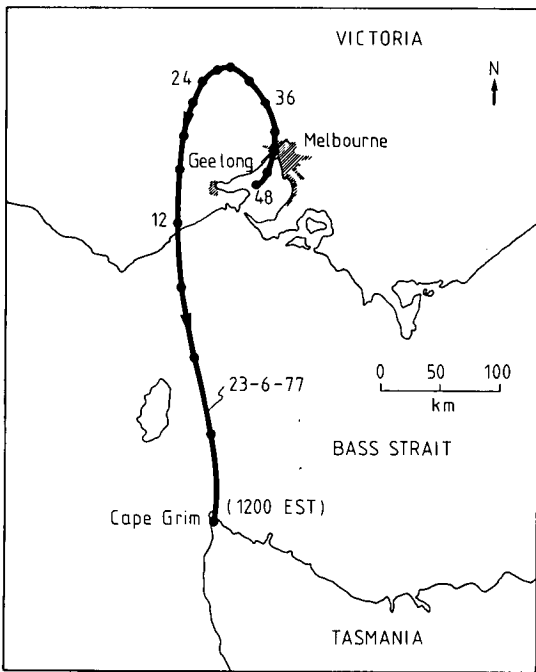
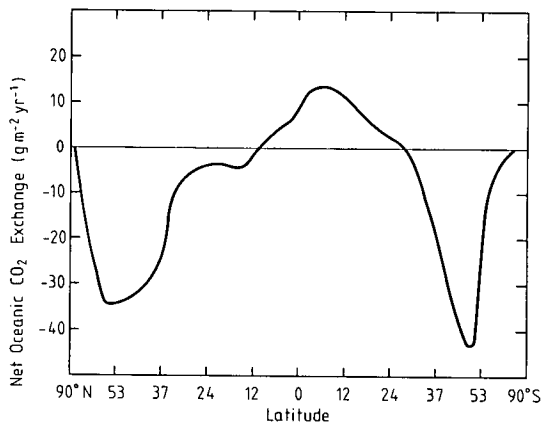


Fig. 8 Estimated present annual net carbon dioxide exchange (mass of carbon) between the atmosphere and oceans, based on theoretical simulations of atmospheric transport and ocean uptake, validated with background concentration observations (after Pearman et al. 1981).



Although in its early stages of development, this study has used the data to verify the 2-dimensional model of the global carbon cycle and quantitatively establish the rates of air-ocean carbon dioxide exchange as a function of latitude (Pearman et al. 1981; Fig. 8). The seasonality of carbon dioxide concentration at a number of observatories has been used to establish the meridional variations of net ecosystems production as a function of season (Pearman and Hyson 1980) and lead to the conclusion that the seasonal turn-over of carbon by the temperate biosphere of the northern hemisphere appears to have increased slightly over the past two decades (Pearman and Hyson 1981). These studies are illustrative of the kind of uses planned for the data being presently accumulated.

A key uncertainty in the understanding of the global carbon cycle, and hence our ability to predict future carbon dioxide levels, is the role of deforestation as a source of atmospheric carbon dioxide. The magnitude of this contribution will be

atmospheric mixing rates. Such information has been used to tune a global diffusion simulation model (Hyson et al. 1980) which is then used to study the behaviour of other gases such as carbon dioxide (Pearman and Hyson 1980; Pearman et al. 1981). The CCl_3F data imply an interhemispheric mixing time (pole to pole) of 9 to 10 months.

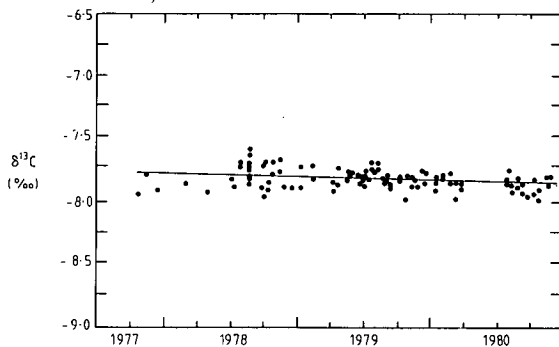
Other data from Cape Grim (e.g. radon, particle numbers, particle composition) have yet to be fully utilised as indicators of long-range transport in the southern hemisphere. The whole question of the sources of particulate and precipitation fall-out of key elements and their transoceanic transport is an exciting and promising challenge for the near future.

Cycling of elements

The corollary of the previous section is that, given that the capacity of the atmosphere to transport materials is known, then when dealing with a conservative species, the surface exchanges of that species can be deduced from the observed atmospheric distribution. For many compounds, the current state of knowledge concerning the sources and sinks is so rudimentary that even relatively poor knowledge of atmospheric mixing rates on a global scale is sufficient to establish at least the order of the large-scale fluxes.

Cape Grim data have been combined with that of the CSIRO aircraft sampling network (Beardsmore 1980) and data from other observatories to establish a global mean distribution of carbon dioxide.

Fig. 9 The trend in normalised carbon-13 to carbon-12 ratio ($\delta^{13}\text{C}$) of atmospheric carbon dioxide observed at Cape Grim (from Goodman 1980 and Baseline 1981).



determinate once the rate of change of the stable carbon isotopic composition of atmospheric carbon dioxide is established (Pearman 1980). This results from the fact that both fossil fuels and biospheric carbon contain less of the heavier isotope ^{13}C than the atmosphere. The changes that need to be measured in the ^{13}C to ^{12}C ratio for this purpose are very subtle (of order one part in 100 000 per year). Measurements thus far at Cape Grim are not that conclusive, but given two or three years more data the trend should be well established (Goodman 1980; Fig. 9).

Conclusions

The composition of the large-scale atmosphere is receiving a growing level of attention and the field is rapidly developing. This development reflects a greater appreciation that the chemistry of the atmosphere is as important as the physical characteristics which are generally regarded as characterising the climate and human environment.

The science involves the consideration of interactions of chemistry, atmospheric dynamics and air-surface exchange phenomena. The complexity is such that good observations are necessary to aid the development of a sound theoretical basis for the subject. These observations are themselves demanding of modern technology and scientific methodologies.

The Australian background atmospheric observatory at Cape Grim is an excellent facility, which reflects the wide objectives of atmospheric composition data collection and the high standards required to make the endeavour a success. Every effort should be made to ensure that the nature of the station reflects the philosophy on which the station was planned and established. In this way, maximum return for effort will be assured by way of the national and international use of data resulting in scientific advancement to the credit of Australia.

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