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The current status of atmospheric trace gas research in New Zealand

Martin R. Manning

National Science Strategy Committee for Climate Change The Royal Society of New Zealand

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prepared for the National Science Strategy Committee for Climate Change by

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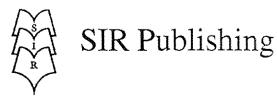
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Foreword

In late 1991 the Minister of Research, Science and Technology established the National Science Strategy Committee for Climate Change to advise him on the needs and the level of expenditure for climate change research in New Zealand. The Committee also advises on priorities and is required to promote coordination, both between research groups and between scientists and the user community.

As a means of promoting coordination and to help in selecting priorities the NSS Committee, through The Royal Society of New Zealand, is publishing a series of information papers on topics of key importance to atmosphere and climate change.

They both outline the background in particular research areas and point out the present New Zealand contributions. The New Zealand research groups are listed and further research needs are indicated.

By widely distributing these information papers it is hoped that New Zealand research workers and the public will be better informed; also that research groups not currently involved in the particular field may see where their expertise and equipment may be able to contribute usefully.

The Committee is greatly indebted to the authors of the papers who have written them during a very busy period in New Zealand Science reorganisation.

A. J. Ellis Convener NSS Committee for Climate Change

June 1994

National Science Strategy Committee for Climate Change

Terms of reference

- i to develop overall goals and a broad strategic framework for the NSS topic by consultation with end-users and science providers;
- to develop, in consultation with all interested parties, a portfolio of scientific research programmes which will meet the objectives of the NSS;
- actively promote knowledge of, and access to, information of common interest to those engaged in research and to end users in the NSS topic area;
- iv to provide advice to funding agencies on the priority and integration of research proposals in the NSS topic area;
- v to provide advice to the Ministry of Research, Science and Technology on any proposal to Government from a government department for new research funding on the NSS topic;
- vi to provide advice to the Ministry of Research, Science and Technology on the overall level of funding appropriate for scientific research programmes included in the NSS research portfolio;
- vii to provide on-going advice to the Ministry of Research, Science and Technology and to participating agencies in the NSS topic programme (both funders and providers) on the effective coordination and implementation of the NSS itself;
- viii to provide advice on the establishment and maintenance of links within the international climate change programme, with particular emphasis on joint and/or complimentary activity with overseas funding agencies and with reference to the World Climate Research Programme and the International Geosphere-Biosphere Programme;
- ix to provide a major statement on climate change research, including overall funding levels, priorities within the programme and the identification of key research programmes; in time for this material

to be used in developing the first long term five year priority statement, ie by 31 March 1992;

- to widely consult the user community and to be aware of private sector programmes;
- xi to provide advice on the monitoring needs of climate change science.

Committee members

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The Royal Society of New Zealand has objects and functions consistent with its role as New Zealand's national academy of sciences, a federation of scientific and technological societies, an association for the advancement of science and technology and the regional body adhering to the International Council of Scientific Unions. The Society is charged with the statutory responsibility to promote scientific and technological endeavour and achievement, and to inform the Crown on science and technology. Established in 1867 as *The New Zealand Institute*, the Society is a Crown Agency incorporated under *The Royal Society of New Zealand Act*, 1965. It comprises Fellows, branches, constituent scientific societies, scientists, technologists, technicians and lay members.

Background

Our planet is surrounded by a thin film of gases, called the atmosphere. The density of these gases decreases exponentially with altitude, but if all this gaseous matter were at the same density as it is at the Earth's surface, it would form a layer about 8 km thick. The mass of the atmosphere is a little less than 1 millionth of the total mass of the planet, but its geophysical significance is extraordinary.

Earth is distinguished from the other planets in our Solar System by the presence of liquid water, relatively small temperature variations, and complex organic molecules supporting a diversity of life forms. All these features depend on our atmosphere. Atmospheric gases remove highly energetic (UV) radiation that can disrupt organic molecules essential for life. They trap lower energy (IR) radiation so raising the Earth's surface temperature by about 30°C. Rapid transport of water and heat through the atmosphere reduces and smooths out temperature variations. Finally the direct transport of matter in the atmosphere plays a key role in global biogeochemical cycles, not the least of which is the provision of O_2 (oxygen) for animals and CO₂ (carbon dioxide) for plants.

For about a century, scientists have become increasingly aware of the complex role played by the atmosphere and its interactions with the oceans and biosphere. At the same time, human activity has altered the composition of the atmosphere and some of its properties. In the 19th century it became clear that smoke and particles from industrial emissions could damage human health. Today, although many countries enforce air quality regulations, our large cities often experience unsafe O_3 (ozone) or CO (carbon monoxide) levels.

Apart from the more visible and obvious effects of air pollution in urban areas, the most remote parts of the atmosphere are also being changed. In particular the long lived greenhouse gas CO_2 has increased by about 25% over the last 200 years due to burning of fossil fuels and deforestation. CFCs which do not occur naturally, and were originally hailed as safe because of their chemical inertness, are now known to alter the chemistry responsible for maintaining the ozone layer in the lower stratosphere. Understanding the role of trace gases and the consequences of changing

them is becoming more urgent as the capacity of humans to modify the atmosphere increases.

To express the composition of the atmosphere in consistent terms, the relative amounts of different gases are normally given as volume mixing ratios in dry air, often called concentrations. This is because water vapour is present in highly variable amounts up to 3% by volume in the tropics. The dominant gases in dry air are N₂ (nitrogen) (78.08%), O₂ (oxygen) (20.95%), and Ar (Argon) (0.94%). The concentrations of these gases undergo only very small relative changes. The remaining 0.04% of dry air is made up of many trace gases, the dominant one being CO₂ at about 0.035%. We normally cite trace gas mixing ratios (concentrations) in parts per million (ppm), parts per billion (ppb) or parts per trillion (ppt).

The concentrations of trace gases can vary considerably with geographic location, altitude, and in time. Such variations are due to the combined effects of transport and the distribution of the corresponding sources (production processes) and sinks (removal processes). A common misunderstanding is that heavier gas molecules tend to settle near the Earth's surface. In fact, physical mixing in the atmosphere completely dominates gravitational fractionation of gases at altitudes below about 100 km.

Arrhenius (1896) was apparently the first to recognize the significance of changes in atmospheric composition. He realised that the "greenhouse effect", which raises the surface temperature of the Earth through absorption of infra-red radiation, could be increased by increasing concentrations of CO_2 from the burning of fossil fuels. The complexity of the issues surrounding atmospheric trace gases is highlighted by the fact that scientists are still trying to develop more reliable estimates of this effect.

Although several attempts were made prior to 1950 to measure atmospheric trace gases, it is only in the last 30 years that we have had sufficiently precise techniques to directly observe changes in CO_2 and the rarer gases. One of the outstanding achievements in environmental science in this century has been to extend these contemporary measurements back in time by analysing the composition of air trapped in bubbles in ice. In this way we have built up a fascinating picture of changes in atmospheric composition closely correlated with temperature and climate changes over the last 100,000 years.

Both ice-core and contemporary measurements of trace gases show that there have been many modifications of atmospheric components by human activity over the last 200 years. The effects of increasing CO₂, CFCs and urban air pollution have already been mentioned. More generally we are concerned that human emissions of trace gases may alter the natural chemistry of the atmosphere (see e.g. Crutzen and Zimmerman, 1991). Emission of reactive gases such as CO (carbon monoxide) has probably depleted the oxidizing power of the atmosphere, leading to slower removal rates for a wide class of pollutants. Increasing levels of the greenhouse gas CH_4 (methane) are due at least in part to this change in the ability of the atmosphere to oxidise and remove pollutants.

At no stage in the Earth's history has the atmosphere been in the state it is now. Thus we cannot use historical evidence as a guide for predicting the future. Instead we must learn to understand the chemical, physical and biological processes that add, modify and remove atmospheric trace gases. Synthesising this understanding has to be done with the aid of models of atmospheric chemistry and transport. While such models are not as complex as the general circulation models of atmospheric thermodynamics used in climate change studies, they are similar in several respects and do require significant computing resources.

A good summary of current activities and priorities in international studies of trace gases is given in the summary of the International Global Atmospheric Chemistry Programme (IGAC) (Galbally, 1989).

This review will be limited to trace gases in the troposphere. The troposphere is the well mixed lower part of the atmosphere, which contains about 85% of its mass, and extends to between 7 and 11 km depending on latitude. Separate papers in this series have addressed the issue of increasing UV radiation due to ozone depletion occurring above the troposphere, and the role of aerosols.

Current observations and interpretations

Present observation programmes are determined partly by our assessment of which are the most important trace gases, but also by technical limitations in our measurement ability. It would be very valuable to measure directly many highly reactive, and hence very short lived, species such as the OH radical. However, these occur at such low concentrations, and require such sophisticated instrumentation for reliable measurement, that few measurement programmes exist in the world and these are restricted in extent.

A wide range of physical chemistry techniques are used to measure trace gases. The predominant technique is gas phase chromatography, used to separate different gas species, followed by a detection step using ionization, thermal or electrical properties of the gas to obtain quantitative concentrations. Absorption of radiation can be used to measure trace gases without separating them from air. For example $\rm CO_2$ can be measured very precisely from its infra-red absorption properties, provided the air is first dried. A wide range of trace gas species can be measured using tuneable diode laser techniques but these are not yet available in New Zealand.

Because of strong interest in the sources and sinks of trace gases, the measurement of isotope ratios (the ratio of heavy to light molecules having the same chemical formula) is an extremely valuable adjunct to concentration measurements. For example, different sources of CH_4 have different characteristic ratios of $^{13}C/^{12}C$, $^{14}C/^{12}C$ and $^{2}H/H$. The ratios observed in atmospheric methane can therefore be used to place constraints on the relative mix of its sources. Isotope ratios are measured mainly for C, H and O in trace gases, with some work done on N and S isotopes.

Table 1 lists some of the trace gases being monitored globally and shows typical concentrations in clean air and their average growth rate over recent decades where known.

This table does not give an exhaustive list of trace gases that are important in the atmosphere. Many species which are known to be important are still not sufficiently well measured that we can quote global average concentrations or growth rates. Table 1 Typical concentrations and growth rates for some trace gases.

Concentration Average growth rate Comments					
CO2	355 ppm	0.4 % yr ⁻¹	major greenhouse gas		
CH ₄	1.72 ppm	0.7 % yr ⁻¹	important greenhouse gas, growth rate ha declined since 1989		
N ₂ O	310 ppb	0.25 % yr ⁻¹	important greenhouse gas		
CO	50 – 200 ppb	?	increasing in Northern Hemisphere 1% yr ⁻¹		
O3	10 – 100 ppb	?	increasing in Northern Hemisphere		
(tropospheric)					
NOx	highly variable	?	increasing in Northern Hemisphere		
C_2H_6	400 – 1000 ppt	?	increasing in Northern Hemispher 1% yr ⁻¹		
Ozone depleter	s				
CFC-11	255 ppt	4 % yr ⁻¹	•		
CFC12	450 ppt	4 % yr ⁻¹	*		
CH ₃ CCl ₃	150 ppt	3 % yr ⁻¹	*		
CCl₄	110 ppt	1 % yr ⁻¹	*		
CFC-113	64 ppt	10 % yr ⁻¹	*		
CBrF ₃	2 ppt	15 % yr ⁻¹			
CBrClF ₂	2 ppt	10 % yr ⁻¹			

*growth rates decreasing due to adherence to Montreal Protocol

DMS (dimethylsulphide, CH_3SCH_3) is important because it oxidises to form SO_2 which is a precursor for cloud condensation nuclei. DMS produced by marine biota is a major contributor to atmospheric sulphur, particularly in the Southern Hemisphere. It has been suggested that changes in DMS production can lead to changes in cloud cover and that this could be a negative feedback on global temperature changes (Charlsson et al, 1987).

There are other greenhouse gases such as hydrogenated chlorofluorocarbons (HCFCs) which are now being used as replacements for CFCs and are increasing in the atmosphere. A wide range of volatile organic compounds (VOCs) including non-methane hydrocarbons mentioned above are emitted to the atmosphere and have local effects on atmospheric chemistry and air quality.

Anthropogenic activity is increasing the diversity of chemical species in the atmosphere faster than our measurement programmes are able to track them or their effects. An exhaustive list of all important trace gas species is beyond the scope of this paper.

The sources of most trace gases are generally not well known. CFCs and other synthetic gases, that do not occur at all in nature, form an exception and generally the sources of these gases can be inferred with reasonable accuracy from industry statistics. On the other hand, gases such as N_2O have a wide range of natural, agricultural and industrial sources some of which (e.g. nitrification and de-nitrification in soils) are affected by many factors. The development of global emission inventories is a key component of IGAC.

Removal rates of many trace gases are also not well known. Many species are oxidized in the atmosphere and a proper understanding of oxidation mechanisms and rates is central to determining trace gas removal. The atmosphere is an oxidising environment because of the large amount of oxygen it contains. However, at ambient temperatures molecular oxygen itself is not a major oxidant. Much more powerful oxidants, such as O_3 and the OH radical, are produced from oxygen by photochemistry which is driven in turn by ultra-violet radiation from the sun. This photochemistry and the competition between formation and removal of highly reactive species must be understood in order to determine oxidation rates in the atmosphere.

 $\rm CO_2$ is not removed by chemical reactions in the atmosphere and is an end point in the oxidation process for species such as CO and CH₄. Rather, CO₂ is removed by dissolution in the surface oceans and uptake by plant photosynthesis. Approxmately 30% of the CO₂ in the atmosphere is cycled through the oceans and biosphere by this uptake and a closely matching release back to the atmosphere. Ice core data indicate that atmospheric CO₂ has been in a relatively stable dynamic equilibrium with the biosphere and oceans for 10,000 years since the last ice-age.

This equilibrium has recently been disturbed through addition of excess CO_2 to the atmosphere from fossil fuel burning and as a result of deforestation and land use change. The excess atmospheric CO_2 is removed

on a variety of time scales as the other geophysical reservoirs of carbon, such as the oceans, re-adjust to the atmospheric perturbation. Understanding CO_2 removal rates in order to predict future greenhouse warming effects, depends on an understanding of the global carbon cycle on time scales of up to 1000 years.

Sources of trace gas are often highly variable from point to point and it is difficult to integrate results from process studies at the level of a smokestack or plot of land to form regional or global scale emission rates. Even where good data are available for surface fluxes, large scale averages can only be determined to a factor of about 1.5 (Moore *et al*, 1993). Because of this many of our estimates of trace gas fluxes are inferred from observed atmospheric concentrations. On the global scale such estimates are reasonably robust. If we can estimate the average removal rate and the total atmospheric inventory of a trace gas, then the total source strength can be estimated as that which balances the removal rate and observed change in inventory.

More generally, if a specific source of a trace gas is significant, then it will normally produce a corresponding signature in the concentration distribution in the atmosphere from which we may be able to infer the strength and distribution of the source. Estimating sources from the concentration gradients they produce is known as the "inverse problem" in geophysics. In practice it requires very precise concentration measurements carefully distributed relative to the source.

Increasingly trace gas measurement programmes are being designed to determine sources and sinks. For example the WMO CO_2 Experts Group has set as a goal for the international CO_2 measurement network the determination of large scale sources and sinks to within 0.5 PgC/yr (1 Pg = 10^{15} g). Particularly in the USA and Australia, measurement of vertical concentration profiles from high towers and by aircraft sampling is being used in conjunction with meso-scale atmospheric transport models of the boundary layer to infer surface fluxes.

Determining trace gas sources and sinks is made more difficult by the fact that these are continually changing. In addition to seasonal cycles there are often significant changes from year to year. For example, current

anthropogenic emissions of CO_2 amount to about 6 PgC/yr, while the nett uptake of excess CO_2 by marine and terrestrial systems varies between 1 and 5 PgC/yr. Over the last 3 to 4 years we have observed a reduction in the growth rate of CO_2 due to a succession of years of high uptake.

The growth rate of CH_4 has been observed to decrease dramatically over the last 5 years to practically zero in 1993. A unique record of isotope measurements in CH_4 from Baring Head shows a reduction in isotopically heavy methane sources over this period and clearly indicates a change in sources rather than sinks.

Understanding these varying trace gas fluxes and their relationship with natural cycles, climate variations, and changes in anthropogenic activity, require consistent long term records.

Although O_2 is not a trace gas, recent developments have allowed us to measure small variations in its concentration with very high precision (Keeling and Shertz, 1992). O_2 is released by photosynthesis and consumed by respiration or combustion in the reverse manner to corresponding changes in CO_2 . Thus we observe a decreasing trend and a seasonal cycle in O_2 anticorrelated with those of CO_2 . Excess atmospheric CO_2 taken up by the biosphere leads to an increase in atmospheric O_2 , whereas that taken up by dissolution in the oceans does not. Because of this O_2 measurements are now seen as an important way of resolving ambiguities in the global carbon cycle.

Marine biota fix carbon from dissolved CO_2 in the surface oceans releasing O_2 in the process. Seasonal cycles in marine production affect surface concentrations of both CO_2 and O_2 which affect atmospheric exchange and produce signals in the corresponding atmospheric concentrations. In the case of CO_2 the signal in the atmosphere is heavily damped due to the large amount of carbon in the surface ocean and buffering reactions connecting dissolved CO_2 and the seasonal cycles we can now measure for O_2 can be used to infer marine productivity averaged over large ocean regions.

Generally the trace gases that are significant for reasons of air quality and human health are short lived in the atmosphere and are not transported far from their sources. Although many industrial emissions, e.g. solvents, are of concern, the ubiquitous source of air pollution is the motor vehicle. CO from vehicle exhaust can become a problem in some urban areas, but a more serious problem is usually the production of O_3 as the indirect product of chemical reactions triggered by vehicle emissions of hydrocarbons and oxides of nitrogen. In the USA, O_3 is implicated as a major cause of human respiratory problems and as a major cause of crop loss due to damage to plant leaf physiology. The costs of air pollution in the USA alone are measured in billions of dollars per year.

Significance for New Zealand

For most trace gases the bulk of emissions occur in the Northern Hemisphere. Typically there is a nett release in the Northern Hemisphere and a nett removal in the Southern Hemisphere. The time taken for gases to exchange between the hemispheres is about 1 year and this means that shorter lived species do not penetrate into the Southern Hemisphere significantly.

For CO_2 we now believe that, prior to human impacts, there was a nett uptake by oceans in the Northern Hemisphere and a nett release from oceans in the Southern Hemisphere. There was a southwards oceanborne flux of carbon balanced by a northwards flux in the atmosphere. Anthropogenic emissions of CO_2 in the Northern Hemisphere have reversed the nett flux in the atmosphere and forced a nett flux into the oceans in both hemispheres. In order to predict future CO_2 levels it is important to understand whether this reversal of the natural flux from ocean to atmosphere in the Southern Hemisphere will increase or decrease. Although the surface oceans adjust to the atmospheric CO_2 concentration on time scales of about 7 years, long term removal of excess atmospheric CO_2 depends on how quickly dissolved CO_2 can be transported into the deep ocean. The dominant pathways to the deep oceans are in the high latitude regions such as the Antarctic circum-polar current, and understanding these regions is particularly important.

The New Zealand record of CO_2 from Baring Head is the longest

continuous record of this greenhouse gas in the Southern Hemisphere and when compared with data at other sites helps to quantify CO_2 sinks in our region. Recent analysis of the New Zealand data has shown a strong correlation between the CO_2 growth rate and the Southern Oscillation Index which in turn is directly related to El Nino / La Nina ocean cycles (Manning, *et al*, 1993). This type of data record is needed to validate new and improving models of atmosphere ocean exchange of CO_2 and hence improve our ability to predict future global concentrations.

Measurement of the background concentrations of other trace gases in the New Zealand region makes a similar contribution to global scale studies of their source and sink budgets. Southerly winds arriving in New Zealand bring with them large well mixed air masses typical of the Southern Ocean region around 55°S. By comparing levels of trace gases here with levels in the Northern Hemisphere we provide much basic data for global trace gas budgets. This is particularly true for CH_4 and the most extensive record of isotope measurements in CH_4 is that from Baring Head.

Short lived gases such as NMHCs (non-methane hydrocarbons) and NO_x (reactive oxides of nitrogen) when produced in the Northern Hemisphere are largely removed before they penetrate into the Southern Hemisphere. This isolates us from much of the modification to atmospheric chemistry occurring due to anthropogenic activity in the Northern Hemisphere. However, the study of atmospheric chemistry in the Southern Hemisphere is still important for two reasons.

Firstly we can observe air closer to pre-industrial conditions and hence provide a baseline for understanding changes that have already occurred in the Northern Hemisphere. Secondly, the Southern Hemisphere atmosphere is exposed to increasing gas emissions from the rapidly developing economies in South East Asia. Already more tropical biomass burning occurs in the Southern Hemisphere than the Northern Hemisphere. Emissions of NO_x , SO_2 (sulphur dioxide) and similar industrial pollutants from SE Asia are predicted to increase several fold over the next few decades. As few detailed studies of atmospheric chemistry have addressed issues specific to the tropical regions we are unsure of the impact this will have. Studies of isotope ratios of CH_4 and CO in New Zealand suggest that at some times of the year significant amounts of these gases in our region have come from agricultural and forest burning activities in the tropics. As CO is a short lived species an understanding of the behaviour of this gas in our region will lay the basis for determining the impact of future tropical emissions. So far our research on CO and its isotopes suggests that oxidation rates are higher in the Southern Hemisphere than predicted by atmospheric chemistry models and so far we have not seen any increase in concentrations of CO.

New Zealand recognizes a responsibility to study and protect the Antarctic environment and this includes the Antarctic atmosphere. Of particular interest is the fact that, during the polar winter, photochemistry and the oxidation mechanisms it drives are absent for long periods. In the Arctic this allows high levels of pollutants to build up during winter as industrial emissions are transported slowly into the polar region, become trapped by the zonal wind patterns, and are not removed by the oxidation that occurs at lower latitudes. In principle a similar problem could occur in the Antarctic although the tropospheric air circulation patterns are rather different. Some of our trace gas programmes have been extended into the Antarctic region to determine the extent of winter-time build up of CO and NMHCs.

Although urban pollution is not a major problem in New Zealand, we cannot afford to be complacent about this issue. By the standards of Europe or North America we have as yet little or no regulatory control of industrial and vehicle emissions. Our relatively unpolluted environment results solely from our low population density. Major industrial sites and our larger urban areas do create locally elevated levels of some atmospheric pollutants and if these are not controlled there will be impacts on health and environment.

A summary of current New Zealand research

Several New Zealand research groups measure trace gases in the atmosphere as part of process studies. For example Landcare Research has

an extensive programme studying uptake and release of CO_2 by forest and soil systems and measurement of CO_2 fluxes over small areas is part of this work. Because of the very wide range of such process studies I have not attempted to summarize this type of work here.

Only three New Zealand groups regularly measure trace gases in the lower atmosphere. These are:

NIWA (National Institute of Water & Atmospheric Research Limited) Atmospheric Division

This operates several Foundation for Research, Science and Technology (FRST) funded research programmes making trace gas measurements in clean air. The main species covered are:

 CO_2 : has been measured continuously at Baring Head since 1972; (¹⁴C in CO_2 has been measured in the Wellington region since 1954). Measurements are also made on flask samples from Raoul Island in collaboration with Department of Conservation and Scripps Institution of Oceanography, USA.

 CH_4 : ¹⁴C and ¹³C isotopes have been measured in air samples collected at Baring Head since 1986; concentrations have been measured since 1989. Measurements have been extended to Antarctic supply flights and to sites north of Auckland. Samples from North West USA are measured for interhemispheric comparison in collaboration with overseas collaborators.

CO: Concentrations, ¹⁴C, ¹³C, and ¹⁸O isotopes have been measured in air samples collected at Baring Head since 1989. The measurement programme has been extended to Antarctic supply flights, Scott Base (fortnightly), and to samples from Germany and the USA in conjunction with overseas collaborators.

C2 – C4 Alkanes and alkenes: have been measured continuously at Baring Head since 1989. In 1993 the sampling frequency has been dropped.

O3 (tropospheric): has been measured at Baring Head since 1991.

NOx: has been measured at Lauder, Otago, using both absorption and

chemiluminescent techniques, but this programme is not currently operating.

For more information on the NIWA programmes contact Dr Martin Manning, NIWA Atmospheric Division.

ESR (Institute of Environmental Science & Research Limited)

This operates an urban air quality monitoring programme funded by the Department of Health which makes continual routine measurements of CO, SO_2 , and NO_x at Auckland and Christchurch.

Some of the data from this programme is reported to the World Health Organization as part of the Global Environmental Monitoring Programme, and much is also reported to the OECD via Ministry for the Environment. For further information on this work contact Dr Bruce Graham, ESR, Auckland.

Auckland University Chemistry Department

This operates an atmospheric sulphur cycle research programme from University funding which measures DMS in conjunction with sulphur measurements on aerosols. A recent PhD thesis (Wylie, 1993) presents a large amount of such data for sites at Leigh, Baring Head, and McDonald's Beach, Antarctica. For further information on this work contact the Auckland University Chemistry Department.

Research gaps and problems - basic science

New Zealand has a small skill base and limited equipment for work in atmospheric chemistry. Many individual universities in the USA have more atmospheric chemists and greater equipment resources than the whole of New Zealand, but have a narrower range of research interests.

Through the 1980s atmospheric chemistry was the fastest growing area of science in the USA and many European countries. Some growth did occur in New Zealand in the late 80s, but this area of science is not identified as a separate discipline to the extent it is in most OECD

countries. Output area 33 of the Public Good Science Fund includes atmospheric chemistry, meteorological research and "climate change". The latter topic has included studies of terrestrial and marine systems that have the potential to alter the climate.

The wide range of research topics covered in Output area 33 could be used to develop broad inter-disciplinary approaches to climate research. However, such an approach has been constrained by the small amount of funding available for the area in relation to the potential for research work. The effect then, of the wide ranging definition of Output area 33, has been to cause a certain amount of insecurity for all areas of research covered.

This situation has been addressed by the recent FRST research strategy on Climate and Atmosphere. This review identifies core areas of atmospheric research and suggests funding levels for these over 5 years. The review also signals that "non-atmospheric" research should be funded from Output area 33 only to the extent that it studies processes that "affect the atmosphere".

This shift in emphasis towards the atmosphere and away from the more general climate context puts long term atmospheric research programmes on a surer footing. However, there remains the issue of planning interdisciplinary climate research, which needs to involve many research groups, and matching this to the present funding systems. There would appear to be a continuing role for the NSS Climate Change Committee in this regard.

In considering New Zealand trace gas research, it is appropriate to bear in mind the proximity of a larger atmospheric chemistry community in Australia. Australia is in a better position to support a wider range of measurements and interpretation, and the New Zealand role should be to complement that in important areas, and to focus on issues specific to our own region.

With this aspect in mind some specific areas where New Zealand's trace gas research effort should be focussed are:

The ocean is a dominant source and/or sink for many trace gases in

the Southern Hemisphere. The development of research programmes that measure air – sea trace gas exchange in our region is proceeding rather slowly. Key species for this research in New Zealand would include DMS, for its potential role in cloud formation, and CO_2 studied in conjunction with marine carbon cycle processes. We should also study the isotopic signatures of CH_4 and CO from the oceans. In these areas New Zealand's strength in marine biology would complement broadly related research in Australia. One problem we have in this respect is the purely administrative one of funding such programmes which fall between outputs 32 and 33 in the Public Good Science Funding system.

- It is essential that trace gas programmes aimed at global budget issues remain closely intercalibrated with leading groups in other countries if their data are to be valuable. For example, a significant difference in CO₂ concentrations has been observed between Baring Head and Cape Grim, Tasmania, which, if real, implies a strong regional sink for CO₂. However, scientists in both countries are reluctant to use this as hard evidence for such a sink because of uncertainty in the relative calibration of our instruments. The WMO is promoting better inter-calibrations of global networks and we should strongly support such work.
- The small resource base of scientists and equipment means that development into new areas is very slow. We would be unable to respond quickly if new problems of national importance were identified. One way of alleviating this problem might be to develop ongoing programmes using visiting overseas scientists and science teams to work in the New Zealand region on a regular basis, as a way of importing a wider range of skills.
- Our ability to interpret trace gas data is limited by lack of experienced staff and computer facilities in the field of chemical tracer modelling. The required models are significantly simpler than general circulation models of the atmosphere, although similar in some respects, and they could be established in New Zealand at quite a small cost.

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- An area of special expertise in trace gas research in New Zealand is the measurement of carbon isotope ratios, particularly 14 C in CO₂, CH₄ and CO. The combination of accelerator mass spectrometry and trace gas studies has been developed further in New Zealand than anywhere else and has earned international recognition. The separation of isotope facilities into one Crown Research Institute and atmospheric research into another has raised questions as to the long term viability of this work.
- New techniques for determining surface fluxes of trace gases from measurement of vertical concentration gradients are now sufficiently developed that we should use them in New Zealand. In particular, programmes should be considered that will produce better estimates of emissions of N_2O and CH_4 averaged over large regions.

Research gaps and problems – policy related research

Another type of research gap is emerging in trace gas studies in New Zealand. This is in the area of policy-related research. Emissions of trace gases are becoming matters of national policy. The Framework Convention for Climate Change (FCCC) requires signatory countries to report national inventories of greenhouse gas emissions and corresponding sinks. The OECD has developed basic protocols for this purpose, but also allows for a hierarchy of "comparable" protocols.

In order that developing countries can conform to reporting requirements the basic protocols depend heavily on use of pre-existing national statistics (e.g. the amount of gasoline purchased) and average conversion factors (e.g. the amount of CO_2 emitted per litre of gasoline used). Both the methodology and the conversion factors to be used will be set externally to the reporting country, and may not reflect local departures from "average" behaviour. At the top of the methods hierarchy will be assessments of emissions or sinks based on detailed measurements in the reporting country and careful consideration of any compensating factors.

New Zealand emissions of CH₄ from livestock, and of N₂O from agricultural

processes, may well not conform to "average" behaviour in those countries where detailed studies have been made.

New Zealand appears to have significant potential for sequestering carbon from the atmosphere into expanding forests. This type of carbon sink is explicitly recognized by the FCCC and can be taken into account in our national emissions inventory. Scientists in this country have already played a major role in defining the best methods for assessing forest carbon sinks. However, there remain unresolved issues, particularly in relation to changes in soil carbon, shifting climate zones, and the CO_2 fertilization effect.

Such issues require country specific studies of actual sources and sinks, and the processes that cause them, from a policy perspective that is usually somewhat different from the perspective of basic research. There is a similar need to review methodologies used by the International Negotiating Committee to ensure that they are relevant to New Zealand.

A case in point is the Global Warming Potential (GWP) for CH₄. The GWP figure gives a ratio of the relative climate forcing of 1 kg of CH4 to that for 1 kg of CO2 over some time horizon, typically 100 years. New Zealand has high per capita CH₄ emissions arising primarily from livestock. Such agricultural emissions derive their carbon from recent atmospheric CO2 and act to temporarily displace CO2 from the atmosphere. (To oversimplify slightly: the grass is formed from CO2 and could either die leading to direct recycling of CO2 by respiration, or be eaten by the animal leading to CH4 which is then oxidised slowly to CO2 in the atmosphere.) Thus a case can be made for a lower GWP for agricultural emissions of CH_4 than, for example, for fossil fuel emissions of CH_4 . This issue was debated briefly at an IPCC Working Group I meeting prior to publication of the IPCC 1992 report, but the IPCC have not commented formally on such modifications to GWP figures. In the context of international negotiations on greenhouse gas controls it is probably not in the interests of most OECD countries to promote separate GWPs for agricultural CH₄ emissions. It certainly is in New Zealand's interests to have this matter well researched in the scientific literature.

Some New Zealand scientists have looked at these issues briefly but

usually as an adjunct to other basic research work. The present lack of policy related research in New Zealand is not due to a lack of scientific expertise. Instead it stems from difficulties in agreeing on and managing the boundary between public good science, funded by FRST, and operational research, traditionally funded by Government Ministries and Departments. In contrast, our nearest geographic and cultural neighbour, Australia, has less problem in merging policy related research with basic science (e.g. through the National Greenhouse Advisory Committee).

An implication of the Resource Management Act is that control of sources and sinks of trace gases in New Zealand is largely delegated to Regional Authorities. However, for generic issues a more coordinated approach is required to identify key issues for policy purposes and manage the funding of these. If this is to be done properly it may well require some shifts in and re-development of the present scientific resource base. For example, although we have several internationally recognized experts on CH_4 , we do not at present have an atmospheric chemistry model capable of estimating the GWP for this gas.

In the area of urban air quality it is not yet clear how Regional Authorities will respond to new responsibilities under the Resource Management Act. One issue is the extent to which air quality assessment will be properly standardized throughout the country. As yet we do not have serious problems with air quality and in principle it would be relatively easy to bring together the resources to do the relevant monitoring and assessments. However, complementary resources are spread thinly across different organizations and it is not clear whether competition or collaboration will occur or how this will affect the quality and efficiency of the work.

Policy related research is not just "window dressing" for our commitments under the FCCC. Countries with greater technical expertise in studying atmospheric trace gases will be able to identify more precisely their actual emissions and removal processes. This will allow them to make better cost/benefit decisions on mitigation practices, and will alert them earlier to opportunities for mitigation and adaptation. This technology is becoming increasingly important as we move globally towards management of the atmosphere.

Research priorities - basic science

By way of summary the following research priorities for trace gas research in New Zealand in the next 5 to 10 years are suggested:

- Studies of the exchange of gases between oceans and atmosphere, particularly CO₂ and DMS, but also CH₄, CO, and NMHCs. This work should be coordinated with marine carbon cycle studies.
- Maintenance of existing programmes contributing to global budgets of CO_2 , CH_4 and CO, and inter-calibration with leading groups in other countries.
- Studies of precursors to cloud condensation nuclei and the relationship between cloud radiative properties and trace gases, particularly sulphur species.
- Studies of atmospheric oxidation processes in the Southern Hemisphere through a coordinated programme of measurements and modelling. The more urgent requirements are for computer modelling, and obtaining local NO_x measurements, e.g. through collaboration with an overseas agency.
- Establishment of 3-dimensional chemical tracer models for the interpretation of inter-annual variations in trace gas observations.
- Resolution of anomalies in the budget for CO in the Southern Hemisphere.
- (longer term) Assessment of the impact of future tropical emissions on background air quality in the New Zealand region.
- Development of improved atmospheric chemistry and meso-scale transport modelling facilities to enable specific air quality and air pollution problems to be assessed quickly for accurate impact assessment of pollutant releases.

Progress can be made in many of these areas by importing existing techniques from other countries and improving the local skill base. Most if not all of the above work should be closely co-ordinated with comparable research in Australia. Atmospheric scientists in both our countries

acknowledge that there are efficiencies to be gained by combining resources, but we still have not done this to the extent that we could.

Research priorities - policy related research

In the area of policy related research, it appears that the initial problems to be overcome are structural. Some of the issues that need to be addressed are:

- Developing better mechanisms for coordinating policy related and basic science research on trace gases and enabling the development of new science resources to study policy related issues.
- Scientific studies of specific trace gases for which the OECD emissions inventory methods may be suspect or require modification due to local factors. The most important such species is expected to be N_2O , but consideration should also be given to local studies of livestock CH_4 emissions.
- Scientific studies of carbon sequestration in New Zealand forests and soils.
- Scientific reviews of other aspects of methods adopted by the IPCC, and the INC, where local factors may need to be taken into account (e.g. use of different GWP figures for different sources of CH_4).
- Establishment of standardised high quality protocols for the assessment and monitoring of air quality, for use throughout New Zealand.

In the area of policy related research there is an overall requirement to adapt techniques developed in other countries on the basis of a sound understanding of the issues involved.

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