Article

We Need to Know More about Atmospheric Chemistry

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About the Author

Martin Manning, BSc, MSc (Hons.), PhD (McMaster), ONZM, has been involved with climate change science for the past thirty years. After gaining his PhD degree from McMaster University in Canada he worked as a theoretical nuclear physicist in that country, in the UK and NZ, where he moved into climate change research. At NIWA he led research programs covering atmospheric chemistry and the carbon cycle for some ten years and represented NZ on the Intergovernmental Panel on Climate Change (IPCC). This led to his spending five years in Colorado managing the recent IPCC assessment of the physical science of climate change prior to that organization being awarded the 2007 Nobel Peace Prize. He has been involved in World Meteorological Organisation committees, and a member of the Scientific Steering Committee of the International Global Atmospheric Chemistry. He returned to NZ in early 2008 to become Director of Victoria University's Climate Change Research Institute, with responsibility for the interdisciplinary climate change study. He gained national honours in 2008, being made an Officer of the New Zealand Order of Merit.

Introduction

Our understanding of global environmental change has gone through many stages of steady accumulation of information followed by sudden realisation that things are happening more rapidly or more extensively than expected. Here I want to argue that it is now becoming important to carry out research that will anticipate potentially serious changes in atmospheric chemistry to a greater extent than we have done so far.

The most recent example of our starting to understand that global changes can be more rapid than was initially expected has come from observations of accelerating changes in the Greenland and Antarctic ice sheets. In 2006, when I was heavily involved along with other lead authors in finalising the Fourth Assessment of Climate Change for the Intergovernmental Panel on Climate Change (IPCC), it had become clear that the observed increasing rates of sea level rise and melting of glaciers and ice sheets were starting to look inconsistent with projections for future sea level rise.

Because there was a lack of scientific literature covering what these new rates of change could mean for this century, all we could do was to include a statement about sea level having been higher by about 6 m the last time that the Earth became significantly warmer than it was now.[1] A major advance in our understanding of sea level rise came soon afterwards with a much better explanation of the changes that had occurred since 1961.[2] This showed that not only could the entire rise be attributed to the effects of climate change, but that about 60% was now due to the widespread melting of glaciers and the accelerating loss of major ice sheets. It contrasted very strongly with the previous climate model projections for future sea level rise that had been based on assumptions that, even by 2100, only about 20–25% of sea level rise would be due to ice sheet and glacier loss.

While a better understanding of future sea level rise is clearly very important, my reason for raising this now is to argue that a much better understanding of the stability and possible trends in atmospheric chemistry can be even more important. Evidence coming from paleoclimatic studies has shown that the Earth can have abrupt changes involving a wide range of interconnected biogeochemical and physical processes, but the extent to which past changes have been related to structural changes in atmospheric chemistry is not yet clear. Furthermore, the increasing emission of new chemical species into the atmosphere means that its composition is already significantly different from what it has been at any time in the past.

Much of our understanding of atmospheric chemistry has come from research on the greenhouse gases that drive climate change, and the need to quantify their sources and removal rates. In particular, this applies to atmospheric oxidation, the basis for which has only been understood for the last forty years and which is still open to significant questions about its trends and even its stability.

Climate change scientists now expect that the environmental changes that will occur over this century, and beyond, may well cross thresholds and enter into some new states for biological and physical systems. If this were to become the case for atmospheric chemistry as well, it opens up major reasons for concern, and recent research on some trace gas species suggests that global average oxidation rates are varying and that there have also been some sudden temporary changes occurring over large regions.

To set the context for atmospheric chemistry being a key factor when considering the implications of global change, the following section provides a short sum-

mary of the history that lies behind this field. It covers what have been two major *surprises* for scientists, both of which have meant that atmospheric changes were more serious than originally expected. This is followed by a section describing the new way for measuring atmospheric oxidation rates developed in New Zealand that has now shown evidence for some significant variations. Then I link this to a comparison of the different processes that remove greenhouse gases from the atmosphere and show why atmospheric chemistry is the most important of these. My final comments raise the potential for changes in atmospheric chemistry that are being driven by human activities to create a divergence between air quality in the Northern and Southern Hemispheres. This shows that, ironically, the predominance of emissions in the Northern Hemisphere could possibly lead to worse implications for the Southern Hemisphere.

A Short History of Atmospheric Chemistry

Understanding the greenhouse effect, which determines the Earth's surface temperature, resulted from research that identified CO_2 as a trace gas which, along with water vapour, absorbed outgoing infrared radiation.[3] By the end of the 19th century, Svante Arrhenius had estimated that a global warming of about 4 °C would arise from a doubling of atmospheric CO_2 concentrations.[4] However, he did not expect that to occur for thousands of years, probably because he won the 1903 Nobel Prize in chemistry for his work on electrolytic dissociation that was closely related to the solubility of gases like CO_2. So, initially, there was a general view that the CO_2 being emitted into the atmosphere by combustion of fossil fuels, was being taken up predominantly in the oceans.

Fifty years later, scientists studying ocean chemistry realised that carbonate in sea water is subject to a strong buffering process, which prevents much of the CO_2 that was being added to the atmosphere from being absorbed into the oceans.[5] At the same time, some early developments of the new radiocarbon dating technique were discovering that the carbon in the atmosphere was getting *older* to an extent that could only be explained by fossil fuel CO_2 accumulating in the atmosphere. NZ's Athol Rafter played a lead role in this, and it was quickly followed by Dave Keeling in San Diego developing new methods for accurately tracking the changes in atmospheric CO_2 concentrations.[6]

The initial use of radiocarbon (^{14}C) as a way of distinguishing between natural fluxes of CO_2 and fossil fuel emissions quickly became pre-empted by the development of nuclear weapons testing in the late 1950s. That led to a doubling of the total amount of ^{14}C in the atmosphere in the early 1960s followed by a slow decrease as the atmospheric CO_2 was steadily exchanged with the biosphere and oceans.[7] However, the growing use of radiocarbon dating to determine the age of wood samples from the past also led to more focus on the natural source of ^{14}C, which is due to the effects of cosmic rays penetrating into the stratosphere and upper troposphere.

It was discovered that most of the ^{14}C atoms produced by cosmic rays very rapidly become carbon monoxide (^{14}CO)

due to atomic collisions, and are then oxidised again to form $^{14}CO_2$ much more slowly over several months.[8] This means that the natural source of ^{14}CO produces a tracer for the atmospheric oxidation rate that is not directly affected by nuclear weapons testing. The use of this tracer for atmospheric chemistry is taken up in the next section, but a broader picture has to be covered first.

Understanding the atmospheric chemistry for CO came a few years later. Bernard Weinstock, who was on the scientific research staff of the Ford Motor company, produced the first quantitative budget for the production and removal of CO and this was complemented by some more detailed analyses of its sources.[9] But these studies of CO led to questions about both its lifetime and the nature of atmospheric oxidation processes.

A fundamental step forward was to recognise that oxidation in the atmosphere was driven, not by oxygen (O_2) or ozone (O_3) directly, but by a very short lived by-product of photochemistry, the hydroxyl radical (•OH).[10] This growing recognition of the importance of atmospheric chemistry was also leading to more detailed studies of methane (CH_4), which was discovered as an atmospheric trace gas in 1948, but for which the first detailed coverage of its sources and removal processes did not occur until the early 1970s.[11] While CH_4 was initially studied in relation to atmospheric chemistry, it was then realised that the increases in its atmospheric concentrations were causing the second largest contribution to changes in the greenhouse effect.[12]

Further major advances in this area came from the development of techniques to extract air that had been trapped as bubbles in Antarctic and Greenland ice cores thousands of years ago, and to then measure its chemical composition accurately. This showed that atmospheric CH_4 concentrations had more than doubled when going from the ice ages to the warmer interglacial periods.[13] But its concentration had now become more than twice as large again than it had been in those previous warm periods between the ice ages. So the completely new composition of our atmosphere has become recognised in stages.

In parallel with these rapid developments in understanding of atmospheric CO and CH_4, there was also recognition that the release of chlorofluorocarbons (CFCs) from several sources was making significant changes to atmospheric chemistry in the stratosphere. A short paper by Molina and Rowland in 1974 was based on laboratory analysis and not on direct measurements in the atmosphere; nevertheless its abstract clearly stated that *Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.*[14] Once again, this became recognised as yet another significant contribution to the increasing greenhouse effect and climate change.[15] These rapid developments also involved Paul Crutzen who had unravelled links between CFC chemistry and the nitrogen oxides and, with Molina and Rowland, shared the 1995 Nobel Prize in chemistry, the first time that prize had been awarded for work on environmental chemistry.

Thomas Midgely, who developed the efficient techniques for commercial production of CFCs, had promoted the value of these synthetic and new compounds in the 1920s on the basis that they were not toxic in the way that all the other alternative refrigerants were. The discovery, fifty years later, that their effects on stratospheric ozone could lead to an increase in skin cancer and eye cataracts showed that the effects of changes in the chemistry of our environment can be both subtle and significant, and are something that has to be considered more carefully.

Rapid developments in atmospheric chemistry during the 1970s led to the construction of detailed models aimed at quantifying the chemical interactions between many of the key species.[16] It led to recognition also of major structural differences in stratospheric and tropospheric chemistry.[17] But a key question was still how to determine the oxidation rates that were predominantly due to •OH, which has an average lifetime of only about one second. Furthermore, because this highly reactive radical is produced by solar ultraviolet (UV) radiation, and then reacts with a wide range of species very quickly, its atmospheric concentration fluctuates dramatically from day to night or even when clouds block the incoming UV radiation.

Quantifying the atmospheric oxidation rates, and testing computer models that simulate the underlying processes, has led to a growing reliance on the use of diagnostic species. In this context a one-page paper by James Lovelock developed the approach of using 1,1,1-trichlorethane (also referred to as methyl chloroform - MCF) as an indicator because it was realised that its sources were all anthropogenic and its removal was predominantly due to •OH.[18] This has led to a carefully planned measurement and analysis strategy that has been very productive in quantifying oxidation rates.

By 1979, there was enough information from MCF measurements to produce new estimates of the concentrations of •OH radicals based on measurements.[19] This immediately challenged the atmospheric chemistry modelling of that time, which had estimated much larger oxidation rates. It opened up also a new question because the tropospheric oxidation rate appeared to be significantly larger in the northern hemisphere than in the southern hemisphere. Was that right? Was it due to the higher levels of many anthropogenic trace gases that had been emitted primarily in the northern hemisphere? Or was it due to natural causes? It was clear that there were still major questions about the structure of atmospheric chemistry to be answered.

The need to dig deeper led to development of global networks that measure a range of trace gases in more detail. Ron Prinn, who did his MSc in chemistry at Auckland University and then moved to the Massachusetts Institute of Technology, had started by investigating the chemistry of atmospheres on other planets, but became heavily involved in the development of atmospheric chemistry models for this planet. He developed, and ran, a global atmospheric monitoring network that is still a major source of information on the continuing changes in atmospheric chemistry.[20]

Over the last thirty years, many research groups have contributed to a consolidation of our understanding of atmospheric chemistry following the rapid developments of the 1970s. A simple summary of current understanding of the dominant processes controlling •OH is shown in Fig. 1. There have been several independent estimates of the average atmospheric concentration of •OH and a general agreement that this is about 10^6 molecules/mL, although strong seasonal and diurnal cycles modulate this average value considerably. Atmospheric chemistry models have been constructed that are consistent with much of the available data and also with some direct estimates of •OH concentration, but there are still major questions about how these concentrations may change over time.[21]
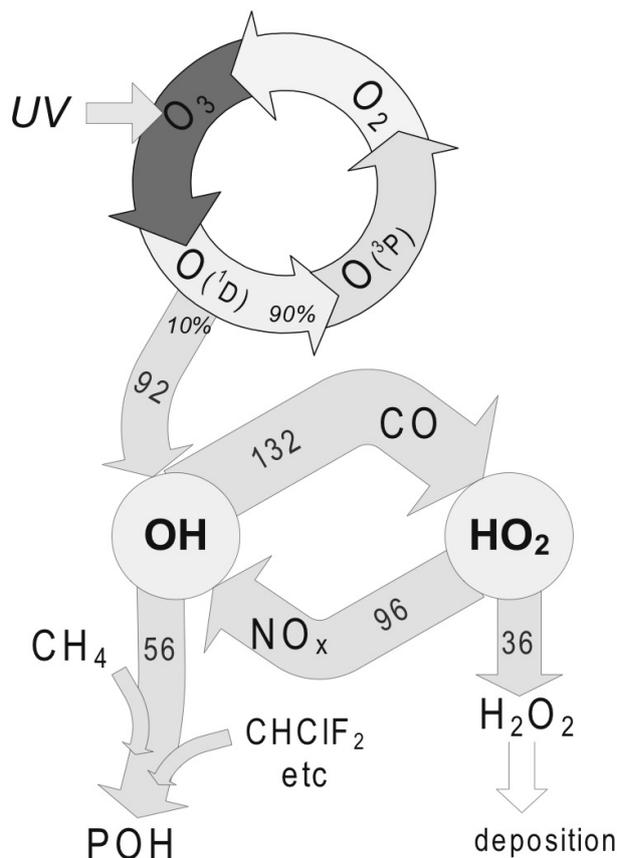

Fig. 1. Representation of •OH chemistry in clean air with values taken from ref. 22. Absorption of UV by O_3 is the initial driver with about 10% of activated oxygen species diverted to •OH through interactions with H_2O; •OH and HO_2 control most of the removal of other species by atmospheric chemistry; POH denotes *partially oxidized hydrocarbons* and the values given within the arrows are in units of Tmol/yr.

An excellent and broad review of our present understanding of •OH has summarised the evidence which shows that, in recent decades, its global average concentration does not appear to have changed substantially, but it was pointed out that this is remarkable given the large increase in CH_4, CO and other trace gases that react with •OH.[23] Lelieveld *et al.* concluded that there had been a balance between significant increases in •OH concentrations over land and smaller decreases over the more extensive oceans, resulting in a net global balance between two types of change driving •OH in opposite directions. But this raises the question as to whether one of these two counteracting drivers may reach a limit leading to signifi-

cant subsequent changes in atmospheric oxidation rates.

While detailed understanding of atmospheric chemistry clearly has clearly progressed very much in the last thirty years, I want to end this section with a note of caution. In 1985, three scientists from the British Antarctic Survey published the paper that revealed their discovery of the Antarctic Ozone hole.[24] The first two sentences in the abstract of this paper set out the sharp contrast between what was coming from the current detailed models of the stratospheric chemistry for ozone depletion, versus the new observations of dramatic and much larger changes that were being seen over the Antarctic. The observed changes had been so unexpected and so large that some US scientists who had also been making measurements of stratospheric ozone in the Antarctic had assumed that the very anomalous values starting to appear in the month of October were just an instrumental malfunction. They were not.

The 1995 Nobel Prize in chemistry was awarded for major advances in our understanding of stratospheric chemistry, but the range of processes that were involved had taken some time to be identified. As when Svante Arrhenius had first studied the implications of CO_2 increasing in the atmosphere, a growing understanding of environmental chemistry had again revealed that the changes could occur much more quickly than was initially expected, even when the initial research had been carried out by some of the world's best scientists.

New Issues with Atmospheric Oxidation Rates

As noted above, it was recognised in the early 1960s that production of ^{14}C in the atmosphere led to the formation of ^{14}CO which was then oxidised by •OH to form $^{14}CO_2$ over some months. This led to a growing interest in measuring ^{14}CO directly but, given that the atmospheric concentration of CO in clean air is less than 100 ppb and the fraction of carbon in the form of ^{14}C is of the order of 10^{-11}, the fraction of ^{14}CO molecules in the atmosphere is around 10^{-18}, or just 10 molecules/mL of air at standard pressure. This is about 100,000 times smaller than the concentration of •OH which is known to be very difficult to measure. However, there are two reasons why accurate measurements of ^{14}CO are possible. The first is that this atmospheric species can be preserved for a long time in large air samples that are collected and then held in high quality containers. The second is that radiocarbon dating was already being used to measure $^{14}C/^{12}C$ ratios of about 10^{-12}. The difficulties, however, were the need to collect enough atmospheric CO in a large air sample and then separate it from the CO_2 and CH_4, which both have much higher concentrations and quite different $^{14}C/^{12}C$ ratios. This challenging measurement was first made in the late 1970s by Andreas Volz who was able to establish both an initial global average concentration for ^{14}CO and also identify a strong seasonal cycle in the mid-latitudes, expected because of the seasonal cycle in •OH concentrations.[25] However, Volz used a traditional carbon dating technique so this was an extremely difficult measurement to make and its use did not continue.

During the 1980s there was a growing development of accelerator mass spectrometry as a method to provide new isotopic information for atmospheric chemistry on very small samples and much of this started up in New Zealand. In DSIR, Dave Lowe led the development of these new measurements of $^{14}C/^{12}C$ in trace gases and produced the first clear observational estimates of how much of the CH_4 that was accumulating in the atmosphere was due to fossil fuel sources.[26] Carl Brenninkmeijer then moved on to the issue of measuring ^{14}CO by using closely related techniques and developing ways of handling the gas with much lower atmospheric concentrations.[27] These measurements have continued in NZ for over twenty years and were extended into Scott Base, Antarctica, for much of that time. A wider range of measurements became available through aircraft sample collection, developed by John Mak, and the techniques became extended into the Northern Hemisphere as other groups adopted similar approaches.[28] This also led to interpretation of the data using models of atmospheric chemistry.[29]

Continued analysis of ^{14}CO measurements has to take account of an eleven year solar cycle that strongly modulates the production rate of ^{14}C by cosmic rays. After we had data extending beyond one solar cycle, it became possible to compare periods when the production rates had been very similar and to ensure that this cycle in production could be separated from detecting any trend in the rate of removal by •OH.[30] But when this was done it revealed some new features. Thus, Fig. 2 shows the residual in ^{14}CO concentration after taking account of the changes in ^{14}C production rate together with the annual cycle in atmospheric oxidation rate, which explain most of the variations in concentration.[30,31] There is some spread in these results, but there are also patterns of consistency between the two locations, which are about 4,000 km apart. Because there are different delays between sample collection at the two sites and the subsequent laboratory measurement, the similar patterns of behaviour at the two sites excludes variations that might be caused by some systematic laboratory problems for what is a very challenging measurement. Planning for our ^{14}CO measurement programme in New Zealand put a high priority on doing measurements frequently because this is a short-lived tracer that can respond rapidly to changes in atmospheric transport or chemistry. Monitoring of the longer-lived species like MCF can only show much slower responses to changes in •OH and averaged over a much wider area.

The ^{14}CO tracer for atmospheric oxidation shows two anomalous events in our thirteen year record. Marker A in Fig. 2 shows the time of the Mt. Pinatubo eruption in June 1991, which is known to have caused significant changes in atmospheric composition in both the stratosphere and troposphere. Marker B shows an abrupt increase in ^{14}CO that followed soon afterwards and then died away more slowly. This is consistent with some other analyses of changes in atmospheric composition following the Pinatubo eruption, but the ^{14}CO data indicate that there was a reduction in atmospheric oxidation rates by up to 20% over a wide area. The ^{14}CO that is being measured has come down from the upper troposphere, rather than the

equatorial region where Mt. Pinatubo is located. So the observed change is being driven by a reduction in •OH in the New Zealand region caused by the transport of trace gases that leads to a delay between the eruption and this observed effect. Similarly, marker C shows the period in 1997 when major and extensive fires occurred in Indonesia. Marker D then indicates the subsequent period when a consequent reduction in oxidation rates of up to 20% occurred again and took more than a year to recover. The ^{14}CO data shown here have been corrected for simultaneous increases in the CO concentration and so this represents a change in the removal rate for the cosmogenically produced tracer.
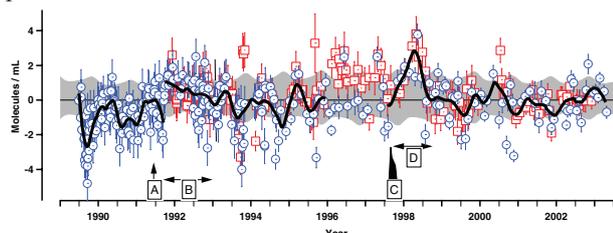

Fig. 2. Blue and red data points are the anomaly in ^{14}CO concentration (molecules/mL) at Baring Head, NZ, and Scott Base, Antarctica, over the period 1989 to 2003, after taking account of expected variations in ^{14}C production due to changes in the solar cycle as well as the seasonal cycle in removal rate by •OH – see refs 30 and 31; the black line is a smooth curve during the periods when there was no significant difference between the two sites and the grey band shows the magnitude of variations that would be expected for a 10% change in •OH; the events labelled A-D are described in the text.

Other studies have looked at specific aspects of the change in atmospheric composition that are linked to these events but, while some model-based estimates show changes in oxidation rates, these have not been large enough to explain the observed ^{14}CO changes.[32] A possible reason for this is that the full range of processes that control •OH may not have been included in those model calculations.

There is another implication of the data shown in Fig. 2, which is that the 1991 event may have led to a step up in ^{14}CO concentration, implying a step down in atmospheric oxidation rates, after which there was never a complete recovery. This has to be treated with caution though, because it was only after late 1991 that we had measurements taking place in both NZ and Antarctica and from then on it was the close agreement between these sites that enabled more reliable identification of systematic changes in atmospheric chemistry over a wide region.

The results coming from ^{14}CO measurements in both hemispheres have been analysed using global models that cover atmospheric oxidation rates as well as transport. A key issue in this respect is the need to explain a smaller difference in ^{14}CO between NZ and Antarctica than exists across the same latitude range in the Northern Hemisphere: some initial analyses had expected more symmetry between the two hemispheres.[33] A more recent analysis has suggested this can be explained by modifying the spatial distribution of ^{14}C production, which is an area of continuing uncertainty.[34] However, this ability to adjust models to explain observations shows that there are still some significant uncertainties, rather than clear

explanations. In my view, there is still a major question as to whether different ^{14}CO distributions in the two hemispheres reflect some differences in atmospheric chemistry.

A result that can be related to this has come from extensive measurements of the $^{13}C/^{12}C$ ratio for CH_4 in NZ and the South Pacific region. Analyses of the data combining the effects of atmospheric chemistry and transport have shown growing evidence that some removal of CH_4 is due to reaction with chlorine.[35] Recently, this proposed explanation of the CH_4 isotopic data in the Pacific region has become reflected in new northern hemisphere studies which also suggest a larger role for chlorine in tropospheric chemistry in the marine environment than had been expected.[36]

Atmospheric Oxidation is the Major Control on Climate Change

While there are still significant questions about atmospheric chemistry, I would like to now summarise the importance of this, and particularly of •OH, from a broader environmental perspective. This will consider the implications for climate change, but it should also be recognised that changes in atmospheric chemistry can have a much wider relevance.

Much of our understanding of changes in greenhouse gases is often expressed simply as the net change in concentration that is occurring in a year. However, a proper comparison of the different gases has to consider the full range of natural processes that are removing them from the atmosphere and the ways in which these processes may change in the future. For this reason, it is important to consider the gross fluxes into and out of the atmosphere rather than just the net result. The flux into the atmosphere is dominated by anthropogenic activity, and the flux out is the critical aspect of natural responses mitigating that activity.

In the case of the global carbon cycle, about 28% of atmospheric CO_2 undergoes exchange with other reservoirs in the biosphere and oceans each year.[37] So, while the addition of a little more than 1% of atmospheric CO_2 each year due to the use of fossil fuels is a driver for climate change, it is also very necessary to understand how the global cycle will respond in future. Similarly, for the other greenhouse gases, it is important to consider the natural removal processes and their potential for future changes. In the case of CH_4, the net annual changes in concentration are very small, but this is because the emissions are very close to the removal rate of about 10% each year. As the greenhouse effect is more sensitive to changes in CH_4 than in CO_2, this means that the removal process for CH_4 is playing a larger role in limiting climate change than the carbon cycle.

This type of comparison of the removal processes that are currently compensating for emissions was put together recently by expressing the removal rates of all the different gases in terms of the consequent rate of reduction in radiative forcing.[38] This also leads to a grouping of the drivers of climate change according to the natural processes that

are controlling them and this is shown in Fig. 3. The key factor emerging from this comparison is that atmospheric oxidation by •OH is playing a bigger role in reducing the forcing of climate change than the global carbon cycle and that this has been the case for the last fifty years.
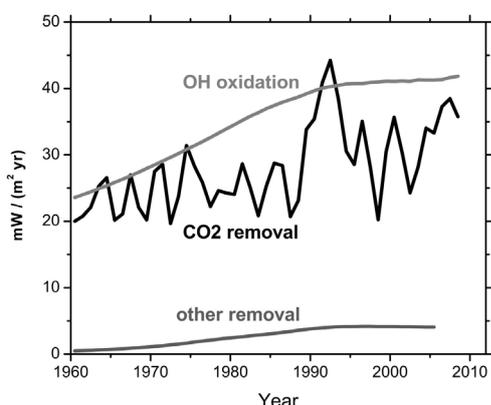

Fig. 3. Radiative forcing removal rates that show the nine greenhouse gases with the largest contributions grouped according to the removal process as follows: oxidation by •OH, removal of CO_2 by vegetation and oceans, and all other removal processes – see ref 38.

The slight upturn in the role of •OH in the last three years is partly due to an increase in atmospheric CH_4 concentration, for reasons that are still not fully understood, and partly because of a continuing increase in the fluorohydrocarbon HCFC-22 ($CHClF_2$). This also shows that when the role of different greenhouse gases is considered in the context of a growing reliance on natural removal processes, then HCFC-22 is now the third most important gas, not N_2O as it seems if one only looks at the net changes rather than the actual processes.

The importance of •OH (and the closely associated atmospheric chemistry) in controlling climate change clearly needs a much more thorough level of understanding. Current scientific literature generally shows that the potential increases in concentrations of many trace gas species are expected to decrease •OH but, in contrast to that, higher levels of tropospheric ozone and of atmospheric water vapour due to warming are both expected to increase •OH.[39] There is also a need to consider wider ranging chains of interactions - a recent study has linked the increase in stratospheric N_2O to a reduction in ozone that increases UV radiation into the troposphere and so the concentration of •OH.[40]

As noted earlier, the amount of information on past trends in •OH is very limited, but there are several reasons for expecting it to have decreased since the 18th century. That was reinforced recently by analysis of sulfate in Antarctic ice cores and shows evidence for significant increases in the concentrations of O_3 and H_2O_2 over the last 150 years, which implies that there will also have been a reduction in •OH.[41]

Much of what has been covered here is consistent with the summary provided by Lelieveld *et al.*, which suggested an increasing difference between •OH concentrations over land and ocean due to systematic differences in the

changes that are occurring there.[23] As shown in Fig. 1, increases in NO_x that can be linked to fuel combustion and agricultural emissions, tend to increase the production of •OH. However, NO_x is a very short-lived species and so its influence on atmospheric chemistry stays close to its sources over land.

Thinking About the Future

The fact that •OH is predominant in mitigating anthropogenic climate change, shows the seriousness of being able to project how it is likely evolve in the future. So far, our history shows that we have learned about some of the critical features in atmospheric chemistry after major changes have started to take place. We are modifying a complex non-linear system that we still do not understand in detail, and there may be a potential for abrupt changes if some trigger points are reached.

While it appears that counteracting drivers of change in •OH have been globally balanced over recent decades, the key issue is whether this may change in future and whether our current knowledge is adequate for determining that. As noted above, there are reasons for expecting the drivers for change in •OH to be different over land and ocean. However, rapid mixing within the troposphere will tend to merge these two trends within each hemisphere, so it becomes more an issue of differences between the two hemispheres.

The predominant emissions that are leading to changes in atmospheric chemistry are located in the Northern Hemisphere and this means that the Southern Hemisphere is more likely to show effects that are dominated by the longer-lived species. CO lasts for 2–3 months in the troposphere, so its effect on depleting •OH can be expected to propagate much more widely than the counteracting effect of NO_x. That could lead to CO being a more significant factor in the Southern Hemisphere. However, because the CO lifetime is short compared to the interhemispheric mixing time of about one year, its flux from the Northern to Southern Hemispheres is small. A bigger issue could emerge from the very different ratio of land to ocean areas in the two hemispheres and this again suggests that CO depletion of •OH is more likely to become dominant in the Southern Hemisphere.

To set a broader context for these issues, one of the major advances in understanding global change was a paper by Roger Revelle and Hans Suess in 1957 that built on earlier work done in New Zealand by Athol Rafter.[5] At that stage, the potential CO_2 changes that were being recognised were described as *a large scale geophysical experiment of a kind that could not have happened in the past nor be reproduced in the future*. Unfortunately, I now have to disagree – we could reproduce this type of *experiment* with anthropogenic changes in atmospheric chemistry.

Understanding future stability is not easy in the context of atmospheric chemistry, and in this context I want to cite Nobel Prize Laureate, Sherwood Rowland who, soon after being awarded his 1995 prize, was invited to give an overview lecture in Brisbane at an international conference on environmental science. He then had a session

with a small group of us in which he summarised what he saw as the serious issues in atmospheric chemistry. To my surprise, he spent much of his time talking about the importance of our measurements of [14]CO in NZ because these could unravel much more information about changes in atmospheric oxidation rates. But when I then asked Rowland if we could identify just a few key components of atmospheric chemistry so as to focus our limited research funding, he came back firmly saying that we had to treat this as an area where very minor trace species could play major roles in our atmosphere and that we must not assume that we knew what those all were.

There is a wide range of new species being added to the atmosphere and this short summary has not covered any of the growing recognition that aerosol chemistry is another key factor in all of this as well. It has to be recognised that chemistry plays a major role in our atmosphere and that it is now in a completely new state that has never existed before. The complexity of atmospheric chemistry, and the number of factors that it is already responding to, means that we should neither take it for granted nor assume that we can just extrapolate past trends. Instead, we now have to dig much deeper and develop a clear basis for understanding its resilience to global change.

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