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Climate Change Science:

Human influence on the atmosphere



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Introduction – the “natural greenhouse effect”

Natural greenhouse gases like water vapor and carbon dioxide keep the Earth warmer than it would otherwise be. They allow energy from the sun to reach the surface but then absorb some of the longer wave radiation as it passes from the ground back through the atmosphere into space, in much the same way as actual greenhouse glass lets sunlight in but retains the heat inside the building. This effect is illustrated in Figure 1. The global average temperature is around +15°C thanks to this atmospheric “blanket”, which covers us to a height of about 100 km. If there were no greenhouse gases in the atmosphere the average temperature would be much colder and around -18°C.

The “enhanced greenhouse effect”

The enhanced greenhouse effect refers to the additional energy that is trapped when further greenhouse gases are added to the atmosphere due to human activities. These gases are sometimes referred to as ‘anthropogenic greenhouse gases’ and the most important are carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and the chlorofluorocarbon CFC-12. (Panel 1).

Of greatest concern is carbon dioxide and methane and in this “Alpha” we show how research at New Zealand’s National Institute of Water and Atmospheric Research (NIWA) contributes to our understanding of the global processes that determine the variations of these two greenhouse gases.

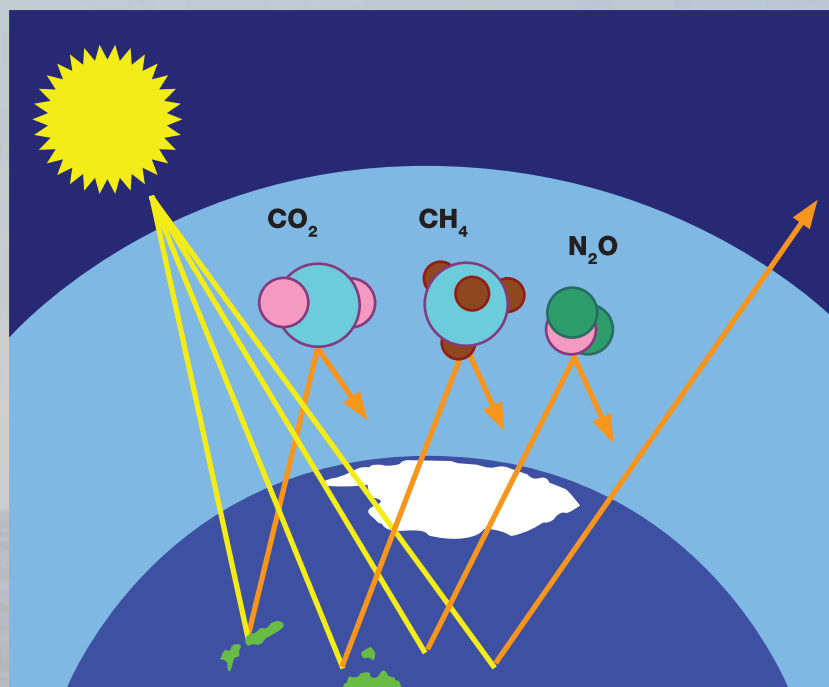


Fig. 1 Greenhouse gases trap outgoing infra-red radiation, causing the lower atmosphere and the Earth's surface to warm up. Source NIWA

PANEL 1 What do we know about the main anthropogenic greenhouse gases?

The table below outlines some key statistics regarding the major greenhouse gases in the Earth's atmosphere. Concentration is quoted in parts per billion or ppb, i.e. the number of molecules of the gas in every billion molecules of air. Mean lifetime gives an indication of how long, on average, a molecule of gas could be expected to remain in the atmosphere before being removed by natural processes. Global warming potential is a measure of the radiative forcing effect of 1 tonne of the gas in the atmosphere compared to the effect of 1 tonne of carbon dioxide, over a 100 year period.

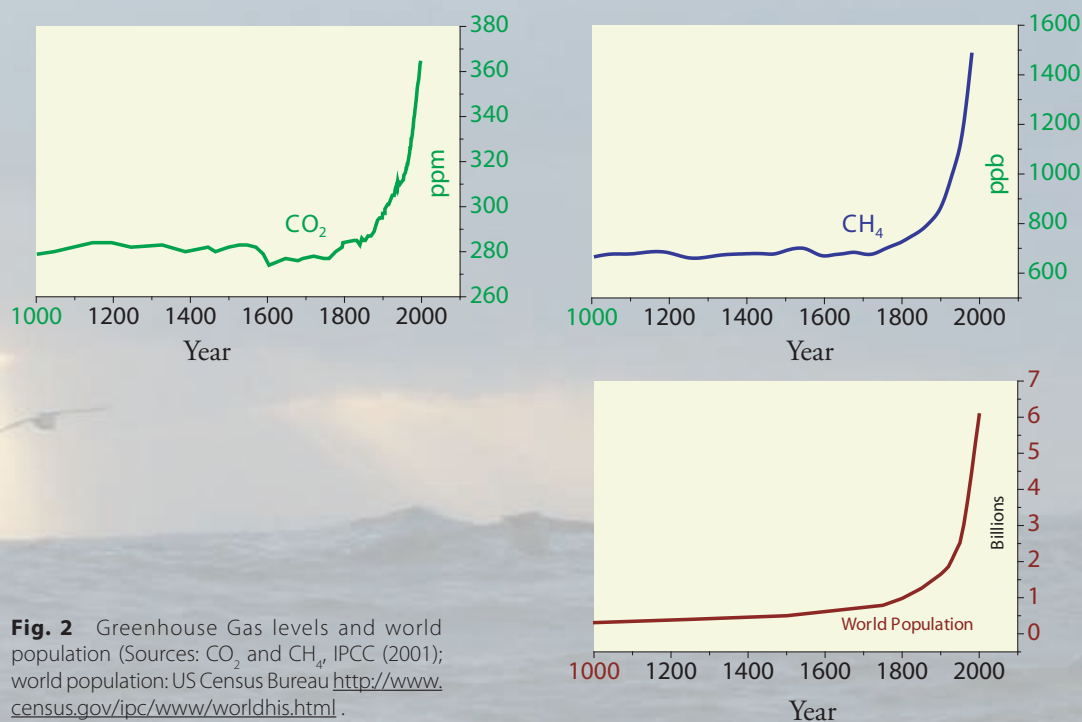
Species	Concentration ppb (2004)	Mean Lifetime (years)	Global Warming Potential (over 100 years)
CO ₂	~380000	150*	1
CH ₄	~1780	12	23
CFC-12	~0.54	100	10720
N ₂ O	~319	114	296

Source IPCC Third Assessment report.

* Surface-atmosphere exchange of CO₂ can occur rapidly. The mean lifetime describes the time taken for recovery to a prior concentration following addition of a pulse of CO₂ to the atmosphere.

How are greenhouse gas concentrations changing?

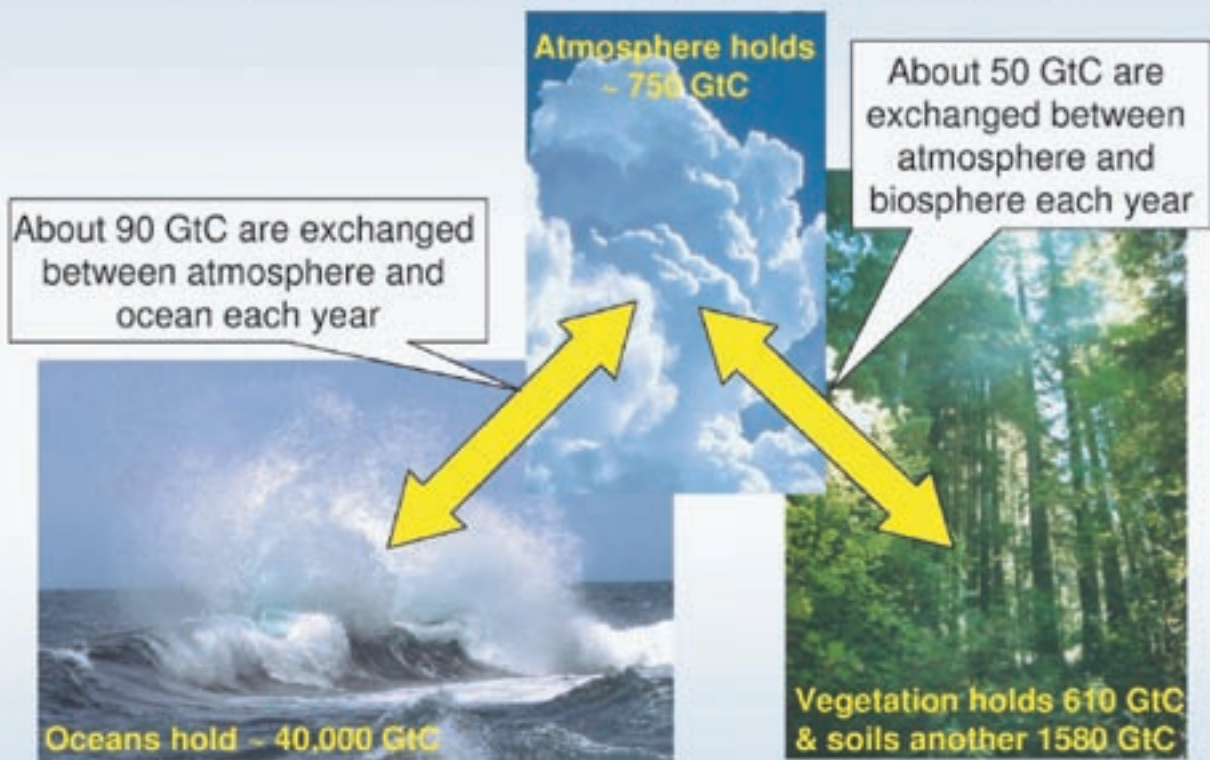
Figure 2 shows how these gas concentrations have increased, together with the world's population since pre industrial times. These graphs suggest a close connection between world population and greenhouse gas levels.



Where is the evidence for human impact?

In addition to looking at how the concentration of greenhouse gases have changed over time, we need to understand how carbon moves between reservoirs of the global carbon cycle.

The natural carbon cycle in balance



Note: 1 GtC = 1 billion tonnes of carbon

Fig. 3 The Natural Carbon Cycle

The Global Carbon Cycle and How Humans have influenced it.

Carbon is stored and exchanged between different 'reservoirs': the oceans, the atmosphere and the biosphere. The vast majority of the carbon on Earth is contained within the world's oceans. Much smaller amounts are found in soils, vegetation and in the atmosphere. Figure 3 outlines the amounts of carbon that cycles between these 'reservoirs' each year due to natural processes, on a global scale.

Human activities have altered this balance, mainly through the burning of fossil fuels that were previously locked away in the geological reservoir and through deforestation. Significant amounts of carbon are being emitted into the atmosphere from these processes. Figure 4 outlines the amounts of carbon involved.

How do we know that only about half of the carbon dioxide generated by fossil fuel burning goes into the atmosphere?

Measurements of the amount of CO_2 in the atmosphere are made at various sites around the globe and using intercalibrated techniques. At NIWA's Atmospheric Research Station at Baring Head on Wellington's south coast, an infra-red analyzer is used to monitor CO_2 levels in the atmosphere on a continuous basis (Figure 5). The concentration is found to be stable in southerly conditions at this site, which is when the air is blowing off the sea and is representative of the air over the Southern Hemisphere. Similar measurements are made at Mauna Loa, Hawaii, which give an indication of carbon dioxide levels in the Northern Hemisphere.

Industry and governmental records of global fossil fuel usage are well documented. Combining this information from around the world, together with an estimation of how much land has been cleared by deforestation, shows that approximately 500 billion tonnes of carbon has been released into the atmosphere since the mid 19th century. This amount of carbon should have increased the atmospheric mixing ratio or mole fraction of carbon dioxide to close to 500 ppm (parts per million). Currently carbon dioxide is at around 380 ppm, indicating that the rest has been reabsorbed by processes occurring at the Earth's surface. The ocean and the terrestrial biosphere are major sinks but they are not able to absorb CO_2 as fast as we are producing it.

Changing the carbon balance

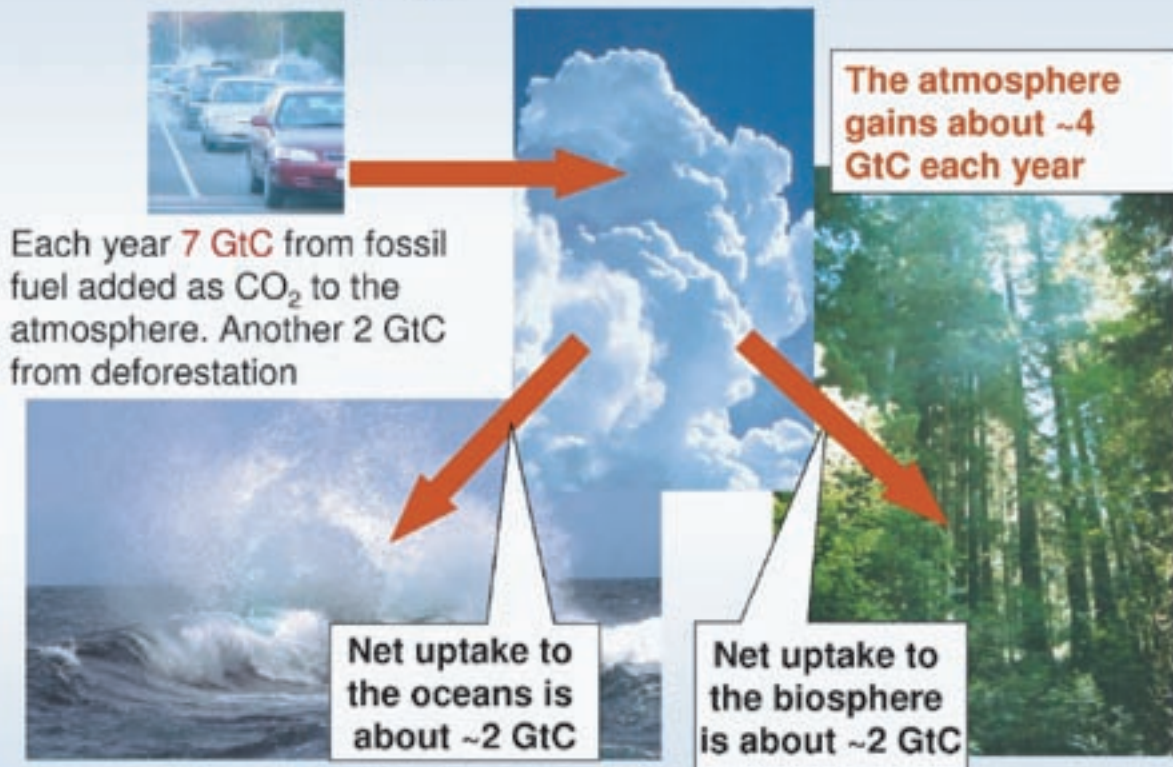


Fig. 4 Although a combination of fossil fuel burning and deforestation add around 9 billion tonnes of carbon to the atmosphere, nearly half of this is absorbed by the oceans and the terrestrial biosphere, in roughly equal proportions. The net result is that around 4 billion tonnes of carbon are added to the atmosphere each year.

Where is the evidence that holds humans responsible?

To unravel this complex picture, a combination of techniques are used, including: records of global fossil fuel usage, measurements of the carbon isotopes ^{14}C , ^{13}C , and ^{12}C in CO_2 (see Panel 2) and measurements of the concentration of atmospheric CO_2 and O_2 . The isotope measurements allow scientists to determine what kind of source greenhouse gases came from as they were emitted into the atmosphere – for example isotope measurements indicate that most carbon dioxide that has gone into the atmosphere since the industrial revolution has come from the burning of fossil fuels. Scientists at NIWA, New Zealand, are at the cutting edge of atmospheric stable isotope analysis work.

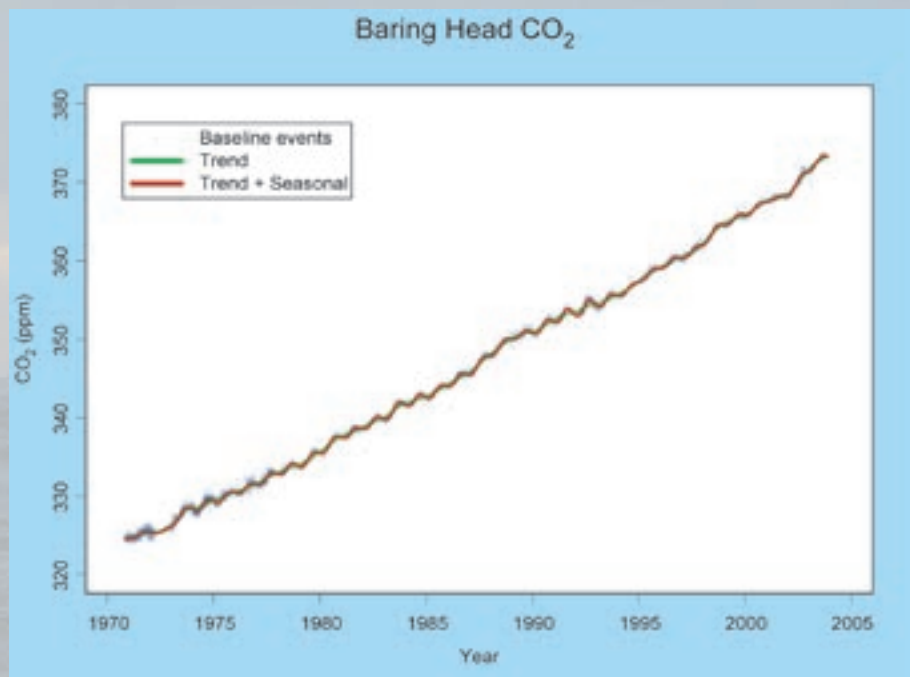
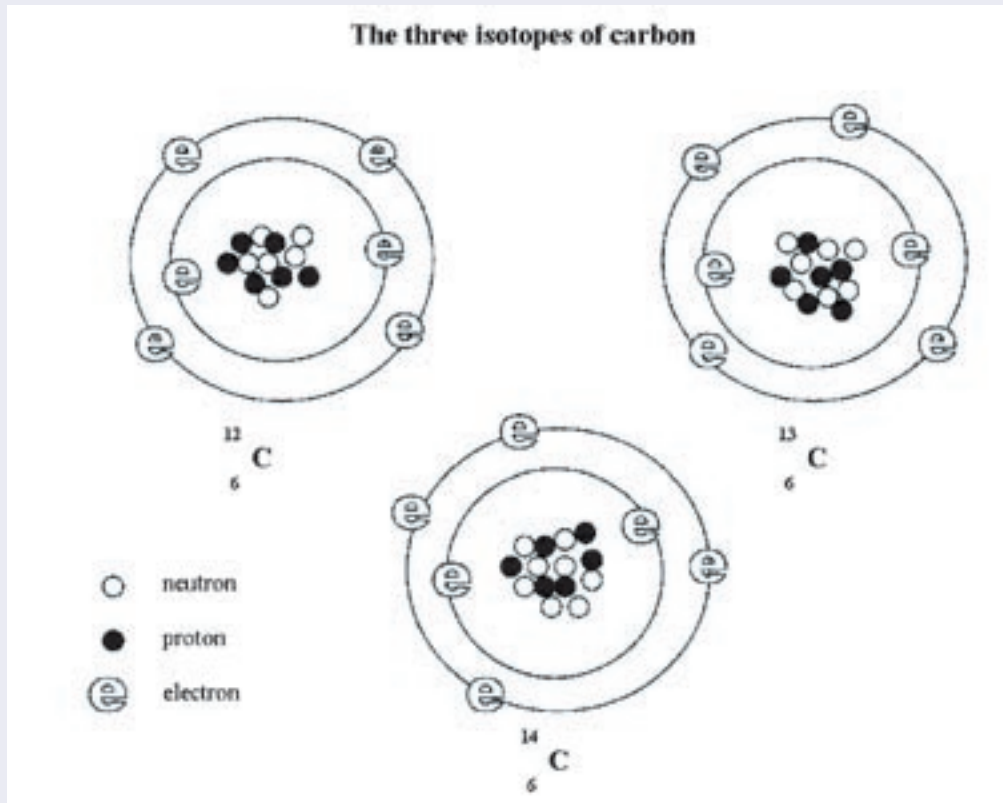


Fig. 5 Time series of carbon dioxide measured at Baring Head near Wellington (NIWA). Baseline events are periods in which analysed air is representative of the Southern Hemisphere. The trend is a long-term fit to the data and indicates the steady growth of atmospheric CO_2 due to human activities. The "Trend + Seasonal" line includes the annual cycling of CO_2 through the biosphere due to photosynthesis and respiration.

Isotopes

Isotopes are atoms of the same element with the same number of protons but different numbers of neutrons. Carbon for example is composed of three different isotopes: ^{12}C , ^{13}C , and ^{14}C . ^{12}C is the most common. ^{12}C and ^{13}C are stable isotopes, which together account for almost 100% of all carbon atoms. However, ^{14}C accounts for a tiny proportion, on average, around 1 in a trillion carbon atoms. ^{14}C is unstable; it is radioactive and decays according to the following equation:



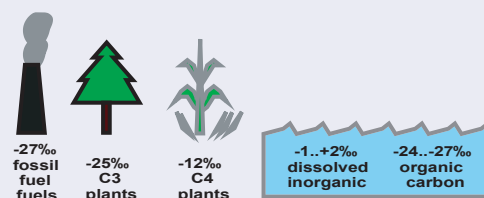
The isotope ^{14}C and its rate of decay is used extensively by archaeologists for “carbon dating”. However, the half life for the decay of ^{14}C is 5730 years; therefore in records of atmospheric ^{14}C over the last 50 years its radioactive decay does not change its atmospheric concentration significantly. CO_2 and CH_4 that have originated from different sources contain differing amounts of the isotopes ^{12}C and ^{13}C . Scientists refer to these measurements as ‘isotopic signatures’. The isotopic signatures of carbon in CO_2 and CH_4 samples provide an invaluable tool for tracing the source of these compounds. Additionally, information on biological and physical processes can be obtained from observing “fractionation” i.e., differences in the rates of uptake or release of ^{13}C compared to ^{12}C .

Isotope notation:

Isotopic composition is measured as the ratio of $^{13}\text{C}/^{12}\text{C}$ and is referred to as $\delta^{13}\text{C}$. The agreed international reference standards report isotopic values relative to a standard, which is a limestone rock from South Carolina in the USA, called “Pee Dee Belemnite”.

In a sample, as the relative amount of ^{13}C increases (is enriched), $\delta^{13}\text{C}$ increases; as the relative amount of ^{13}C decreases (is depleted) $\delta^{13}\text{C}$ decreases. Examples of typical isotopic signatures for carbon originating from various sources are given below. The unit is ‘per mille’ or ‘per one thousand’, ‰.

Source signatures for $\delta^{13}\text{CO}_2$ in natural carbon pools (See also Figure 10).



Carbon isotope signatures in atmospheric carbon dioxide

There are fundamental differences in the way different isotopes of carbon are exchanged between the reservoirs of the active carbon cycle. During photosynthesis, plants discriminate against carbon dioxide containing the heavy isotope of carbon, i.e. $^{13}\text{CO}_2$. In simple terms, plants absorb carbon dioxide molecules containing the slightly lighter ^{12}C atom more readily compared with those containing the heavier ^{13}C atom because this requires marginally less energy. This means that plant carbon contains less ^{13}C than atmospheric CO_2 . The process of photosynthesis therefore results in a slight enrichment of ^{13}C in the atmosphere.

Fossil fuels are derived from ancient plants. This means that plants and fossil fuels have roughly the same $^{13}\text{C}/^{12}\text{C}$ ratio or $\delta^{13}\text{C}$. As CO_2 from fossil fuel combustion is released into, and mixes with, the atmosphere, $^{13}\text{CO}_2$ in the atmosphere decreases. Because of the huge significance of this source of CO_2 , the fossil fuel signature is clearly visible in atmospheric observations and this is illustrated in Figure 6.

In the oceans, uptake of CO_2 discriminates far less against ^{13}C . This is because carbon dioxide that is taken up by the ocean is simply dissolved in the sea water, which is a physical process that does not dissolve $^{13}\text{CO}_2$ to any lesser extent than $^{12}\text{CO}_2$. Photosynthesis by marine plankton has minimal impact on global atmospheric values of ^{13}C . Oceanic carbon is therefore only slightly 'heavier' than atmospheric carbon.

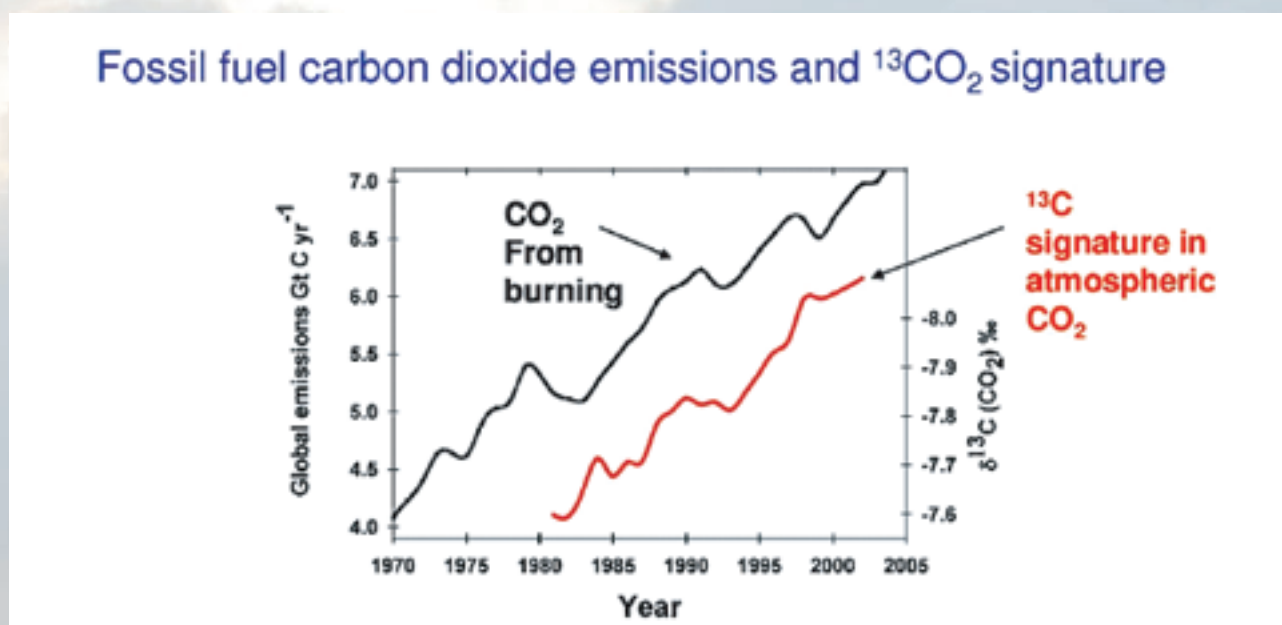


Fig. 6 Fossil fuel carbon dioxide emissions and the $^{13}\text{CO}_2$ signature of atmospheric carbon dioxide. The black line indicates an estimate of the amount of carbon that has been emitted into the atmosphere due to the combustion of fossil fuels each year since 1970. The red line is a record, from measurements of actual samples, of the $^{13}\text{C}/^{12}\text{C}$ isotope ratio, or $\delta^{13}\text{C}$, in atmospheric CO_2 over the last 20 years or so. Note that the vertical scale is inverted; in other words the atmosphere is gradually becoming more and more depleted in ^{13}C because ^{13}C depleted carbon from fossil fuel combustion is being constantly added. It can be seen quite clearly that there are similarities in the trends of the two lines, indicating that the observed decline in atmospheric $^{13}\text{C}/^{12}\text{C}$ ratio is related to fossil fuel combustion. Note, 1 Gt C is a Giga tonne of carbon (1 billion tonnes).

Measurements of ^{13}C in atmospheric CO_2 therefore help to differentiate between the two major carbon sinks, namely the ocean and the terrestrial biosphere. To make these measurements, however, a wide variety of sampling sites are needed together with a large amount of high precision CO_2 stable isotope data.

Another tool for differentiating between ocean and biosphere sinks of CO_2 is the measurement of the concentration of O_2 in the atmosphere. Burning of fossil fuels requires O_2 . For every CO_2 molecule that is produced one oxygen molecule is used up. The concentration of O_2 in the atmosphere is decreasing as a result. Uptake of CO_2 by the ocean does not involve any change in the atmospheric concentration of oxygen whereas when plants absorb CO_2 , oxygen is released during photosynthesis.

To learn more about the relationships between greenhouse gases and climate, and to what extent humans have affected this relationship, scientists are investigating historical greenhouse gas variations. The causes of change can be investigated, for instance through comparison of the current $\delta^{13}\text{C}$ in atmospheric CO_2 with the historic records. This perspective can determine whether or not current observations are just a temporary "blip" or a significant departure from the long term mean level.

How do we obtain information from the past – The use of proxies

Tree ring data

Over the last few decades, isotope geochemists have worked with tree ring experts to produce a time series, a so called dendrochronology. This technique makes use of the fact that trees grow one growth ring each year (see Fig. 7). During photosynthesis, trees take up carbon from the atmosphere and lay it down as plant organic matter in the annual growth rings. This provides a “snapshot” of the atmospheric composition at that time. The tree rings have a slightly different isotopic composition compared with the atmosphere because of the process of photosynthesis favoring ^{12}C . However, this can be taken into account when the data is processed. Tree rings have been used in this way to show that $\delta^{13}\text{C}$ in atmospheric CO_2 is now lower than it has been at any time in the last 10,000 years. Additionally, tree ring records show also that around 1850, $\delta^{13}\text{C}$ in atmospheric CO_2 began to drop, coinciding with the start of the industrial revolution when the atmospheric carbon dioxide concentration began to rise sharply.

Use of ice cores in trace gas analysis

Ice core research provides scientists with a powerful tool in analysing the past climate. In Antarctica, the recently drilled EPICA ice core provides over 650,000 years worth of temperature, atmospheric carbon dioxide and methane data (it may even reach 900,000 years, but analysis is not yet complete). (See Figure 8).

The correlations between past temperatures and methane and carbon dioxide concentrations are striking. For example, a rising temperature trend is matched by a rising trend in carbon dioxide and methane levels. At times when temperature has fallen, so have carbon dioxide and methane levels. Due to dating uncertainties, in some periods it is not well known if temperature increases came before carbon dioxide increases or the other way around. Scientists are trying to answer these kinds of questions with better analysis tools and new ice core analyses.

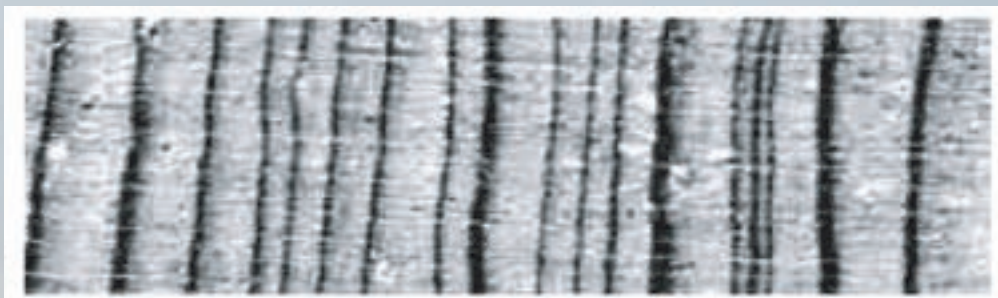


Fig. 7 Conifer wood showing annual tree rings

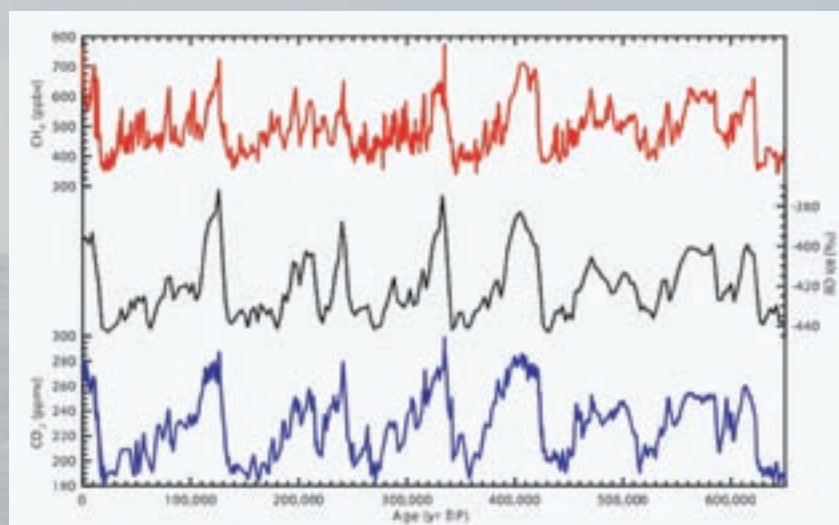


Fig. 8 Records from the EPICA Ice Core, Antarctica. (after Siegenthaler et al., Science, 2005, improved by T. Stocker). The progression of the Earth's climate through ice ages (generally lasting about 100,000 years) and “interglacial” periods, which are considerably shorter, can be seen in this record. (The last ice age ended around 12,000 years ago.). The black line shows a proxy for the air temperature, δD , variations of the amount of deuterium or ^2H found in water molecules, locked up as ice.

How do Scientists measure the age of the ice samples and reconstruct surface air temperatures?

In glacial regions, each year's snowfall buries the previous year's snowfall. The compounds contained in the snow are buried along with it. By drilling down through an ice sheet, and analysing the snow from greater and greater depths, a history of the compounds can be obtained. Snow that is buried more than about 80 metres deep (this varies depending on conditions at the site) turns into ice because of the weight of the snow above it. Trapped in the ice are small bubbles of air. This ancient air can be analysed to give information about the composition of the atmosphere at the time the ice was originally formed. The ice itself can be melted, and the substances in the meltwater are used to determine the age of the ice and the temperature of the air when the ice fell as snow.

One way to work out the age of the ice is to study the oscillations of the temperature-sensitive $^{18}\text{O}/^{16}\text{O}$ or $\delta^{18}\text{O}$ isotope signature in the ice itself. These oscillations relate to the air temperature at the time that the ice was formed. In summer, with warmer temperatures and a higher proportion of H_2^{18}O molecules in the atmosphere from increased evaporation, snow that falls therefore has a higher proportion of these heavier -isotope containing molecules. In winter, snow contains a lower proportion of H_2^{18}O . This effect produces oscillations of H_2^{18}O content on a seasonal basis and allows ice core dating to be carried out by counting the oscillations. This effect is illustrated in Figure 9. Additionally, these variations in H_2^{18}O in the ice allow an approximate air temperature to be estimated for the time that the snow fell. The isotope signature for hydrogen in water molecules, (i.e. the ratio of "heavy hydrogen" to normal hydrogen $2\text{H}/1\text{H}$ or δD) behaves in a similar way and can also be used to study past temperatures.



Photo 1 Top: View down a bore hole, left after an ice core has been drilled out, Law Dome, Antarctica 2004 Source: NIWA. Below: Trapped air bubbles within the ice core, Photo CSIRO.

What other forms of evidence or 'fingerprints' do scientists use when analyzing ice cores?

"Reference horizons", or specific past events, are an important aspect of ice core dating. They are particularly important in areas where snow accumulation is low and stratigraphic methods of counting the years are not so accurate. An example is the eruption of the volcano *Tambora* on the island of Sumbawa in Indonesia in 1815, which injected 114 million tonnes of sulfur dioxide into the stratosphere. Some of this sulfur dioxide returned to the troposphere and was washed out in precipitation. A layer of high sulfur dioxide concentration in the polar ice resulted from this event and can be detected by measuring the electrical conductivity of the core.

A full understanding results from use of multiple chemical tracers. For instance, hydrogen peroxide and the sodium ion Na^+ show a clear seasonal pattern. Hydrogen peroxide is five times higher in summer than in winter (caused by enhanced photochemistry), while Na^+ is higher in winter, due to marine air masses with high levels of sea salt. These seasonal variations can be used to "count" years and to determine the age of the ice core. For very old ice cores, radioactive isotopes are used to determine the age of sections of cores, such as ^{210}Pb , ^{10}Be , ^{14}C , and ^{36}Cl .

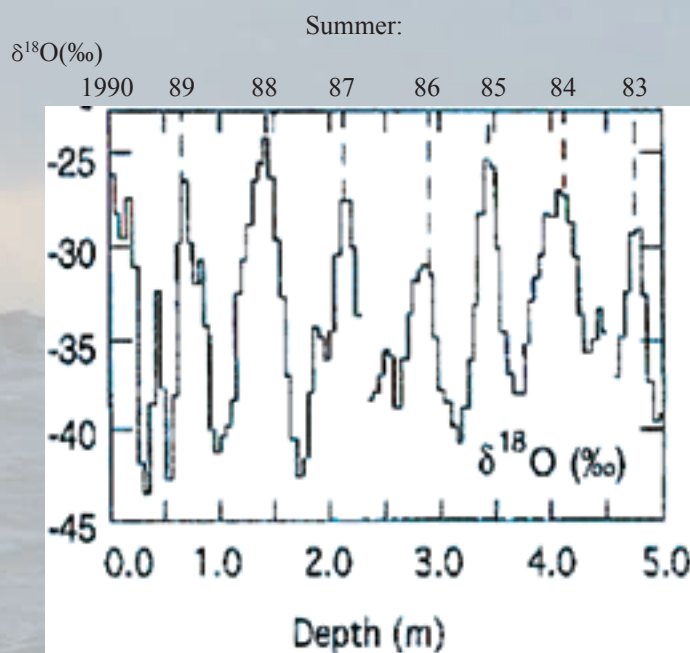


Fig. 9 A record of $\delta^{18}\text{O}$, which relates to the amount of the isotope ^{18}O found in ice (H_2^{18}O) in an Antarctic ice core. The same "δ" notation as for ^{13}C is used here for ^{18}O (see panel 2). The peaks occur during the summer and the troughs during the winter (Legrand et al 1997)

Methane research

Methane is the second most important anthropogenic greenhouse gas. When compared with carbon dioxide, 1 tonne of methane released into the atmosphere has the same warming effect as 23 tonnes of carbon dioxide, over a time frame of 100 years. (This is known as the global warming potential – Panel 1). Since about 1750, the concentration of methane in the Earth's atmosphere has almost trebled. NIWA scientists have been carrying out detailed measurements of methane since 1989. Examples include measuring methane emitted directly from ruminant animals, (for example sheep and cows), long-term changes in Southern Hemisphere methane as measured at Baring Head near Wellington, and using air trapped in ice to study methane levels in past environments.

The methane source types and isotopic compositions

Methane is emitted to the atmosphere from a wide range of naturally occurring sources and human activities (Figure 10). Of the total amount of methane that is annually emitted to the Earth's atmosphere (about 600 million tonnes per year at present) about one third of this amount is from natural sources and the other two thirds is from anthropogenic sources. Changes in atmospheric $\delta^{13}\text{CH}_4$ (i.e. the relative amounts of the ^{12}C and ^{13}C isotopes in atmospheric methane) allow the contributions from each of these source types to be deduced.

In Figure 11, a 2,000-year record of methane concentrations and the carbon isotopic composition of atmospheric methane is shown. For analysis this ancient air is sampled from ice cores drilled in Law Dome, Antarctica. Methods to extract ancient air from ice core samples either involve (i) melting to release the air from the bubbles or (ii) grating to cut and break the air bubbles. Subsequently the air is generally trapped in a container at low temperature so that the air sample can be transported to different instruments for analysis (although sometimes the air is passed directly from the melter/grater to the analysis instrument)

Identified methane sources		Natural	Human	$\delta^{13}\text{CH}_4$
Anaerobic	Wetlands (bogs & swamps)	✓	✓	-60
	Ruminant animals (e.g. wild animals, sheep, cattle)	✓	✓	
	Termites	✓		
	Landfills		✓	
	Rice agriculture		✓	
Aerobic	Plants	✓	✓	-50
Fossil	Energy generation (e.g. coal mining, oil & gas burning)		✓	-40
	Oceanic & geologic	✓		
Burning	Biomass burning (e.g. forest & grasslands)	✓	✓	-20

Fig. 10 The individual methane source components can be grouped into four general categories based on their isotopic composition. Anaerobically produced methane originates from bacteria that thrive in oxygen-free environments. Aerobically produced methane from plants was only discovered in 2005 and is not yet understood well enough to be considered fully at the time of writing. Natural fossil emissions are very small compared to those from human activities. Land use change is responsible for most burning, though climate also plays a role.

These isotope measurements allow determination of the individual source component variations through time (Figure 12) and reveal two important findings.

The methane source variations over the past 2000 years reveal important findings.

First, in the more recent part of the record, the isotope measurements verify that the reason atmospheric methane concentrations almost tripled over the past 250 years was due to increasing emissions from the following human activities; ruminant animals, rice agriculture, deforestation, and fossil fuel mining and combustion.

Second, prior to the industrial revolution about 250 years ago, the isotopes point to elevated levels of vegetation fires that substantially decrease between about 1000 and 300 years ago. Natural climate variability explains about half of the decrease in fires, with more wildfires and less wetland emissions during warm-dry climates compared to cool-wet climates. However, climate could not solely explain the observations, and the other half of the decrease in methane emissions from fires was likely to be caused by changes in anthropogenic fire emissions. Between 0–1500 AD, the indigenous population of the Americas burnt huge fires for agriculture and hunting. But after European explorers arrived, the indigenous population was plagued by new diseases and their population fell by as much as 90%. Methane emitted from their fires therefore is likely to have plummeted and thus played an important role in global methane isotope variations.

These measurements allow scientists to make predictions about how methane emissions from wildfires are likely to be higher during warm-dry intervals and may vary with future climate change. These results also highlight how humans have affected the Earth's atmospheric composition for long periods of time, even before the industrial revolution. Our agricultural methods clearly impact on atmospheric composition, yet natural greenhouse gas emissions are also closely related to climatic change.

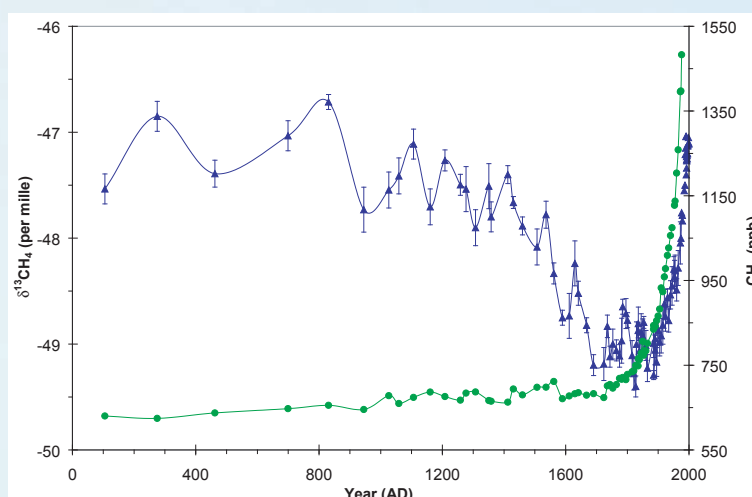


Fig. 11 The 2,000-year Law Dome record of $\delta^{13}\text{CH}_4$ (δ blue line) and CH_4 concentration (• green line). Between 1000–1700 AD $\delta^{13}\text{CH}_4$ undergoes a large 2‰ depletion, while CH_4 varies by less than 55 ppb. (NIWA)

Summary

Measurements of greenhouse gases in the Earth's atmosphere have provided clear evidence that, over the last few centuries, human activities have altered the chemical and radiative balance of the atmosphere. Greenhouse gases are now generally accepted to be influencing the Earth's climate and climate change is a hot topic in today's media. The science behind this media debate has been summarized by the Royal Society in its Gamma Series (Wood, 2005). We know a great deal about current and past greenhouse gas variations (see below) and the challenge now is to better predict future changes.

- The concentrations of greenhouse gases in the Earth's atmosphere are currently increasing.
- The global records of fossil fuel use correlate well with the observed increase in atmospheric CO_2 amount.
- The isotopic composition of CO_2 provides evidence that fossil fuels are the main source responsible for atmospheric CO_2 increases.
- The isotopic composition of CH_4 provides evidence that agriculture and fossil fuels are the main sources responsible for atmospheric CH_4 increases.
- Past atmospheres have been analysed from air trapped in polar ice and from the use of proxy materials such as tree rings and there is even evidence of human impact on the atmosphere even in pre-industrial times.

Understanding the effects of our use of the Earth's resources and how greenhouse gases and climate may change in the future is one of the greatest challenges facing humankind today – yet one of the most important tasks.

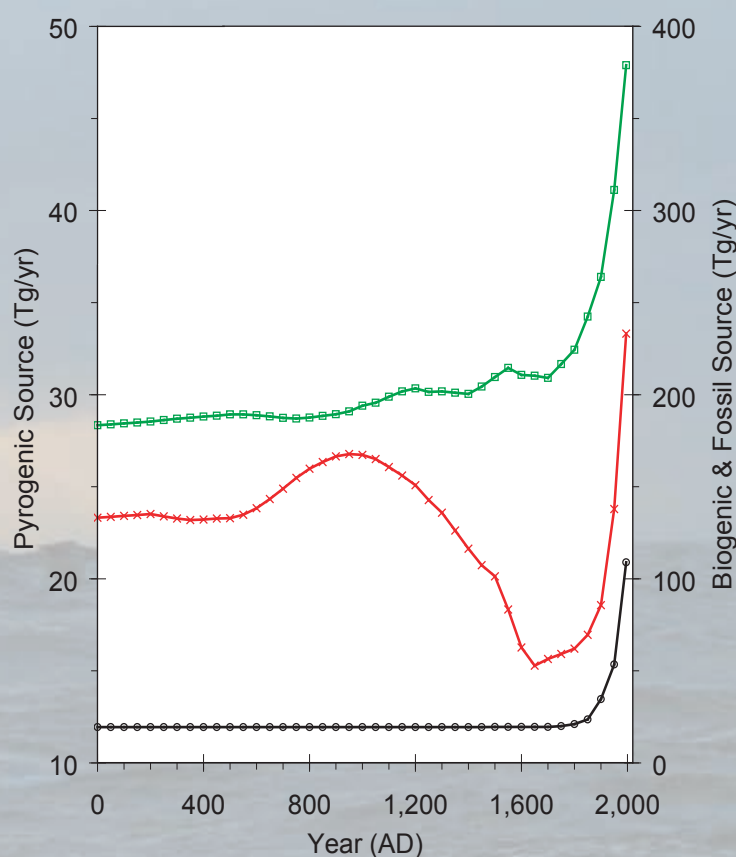


Fig. 12 The individual methane source component variations deduced from the methane isotope data. The black curve ● is the fossil sources, which are assumed to be constant prior to the industrial period. The green curve ■ is the anaerobic biogenic sources, The red curve × is the biomass burning emissions from fires, which vary greatly. (NIWA)

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- <http://www.chemistryinquiry.com>

To see clips of NIWA atmospheric scientists talking about their careers and an explanation of how greenhouse gases are monitored using gas chromatography, visit http://www.biotechlearn.org.nz/multimedia/hotshots_student_videos/wellington_girls_college_niwa_hotshots

Acknowledgements:

Co – authored: Phil Kendon, Upper Hutt College 05NZSMTTF, Dr. Mike Harvey, NIWA, Wellington, Dr. Dominic Ferretti, NIWA, Wellington, Dr. Katja Riedel, NIWA, Wellington

Editor: Jessie McKenzie RSNZ

Reviewed by: Dr Suzanne Boniface, Queen Margaret College, 05 New Zealand Sciences Mathematics and Technology Teacher Fellow

Design and Layout: Robert Lomas RSNZ

Cover Design: Erika Mackay, NIWA.

The work of the NIWA gas laboratory described in this Alpha is supported by the Foundation for Research, Science and Technology through research contract CO1×0204 “Drivers and Mitigation of Global Change”

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ISSN 0111 1957

2007.

Cover: The Baring Head Atmospheric Research Station operated by NIWA on rugged south coast of the North Island has contributed since 1970 to the Global Atmospheric Watch of greenhouse gases with high precision measurements. This Alpha describes how the isotopic composition of these gases is used to unravel the contribution of the various sources and sinks as represented by the pictograms of fossil fuel combustion, forests, other vegetation and the oceans.