

# $^{14}\text{CO}_2$ in the Southern Hemisphere Atmosphere – the Rise and the Fall

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## Introduction

In the 1950s a group of NZ scientists had the foresight to establish an atmospheric monitoring programme for  $^{14}\text{CO}_2$  which has continued to the present day, and has involved many scientists and several institutions. The resulting 50-year record has provided valuable insight into the global carbon and radiocarbon cycles.

The radioactive isotope of carbon,  $^{14}\text{C}$ , is formed in the upper atmosphere (stratosphere) when incoming cosmic flux neutrons react with  $^{14}\text{N}$ . The  $^{14}\text{C}$  is then rapidly oxidised to  $^{14}\text{CO}_2$ , and is distributed throughout the natural carbon reservoirs via the carbon cycle, in particular the atmospheric, terrestrial, and oceanic reservoirs.  $^{14}\text{C}$  radioactively decays with a half-life of 5730 years. Before the industrial revolution in the mid-18<sup>th</sup> century the upper atmosphere production of  $^{14}\text{C}$  balanced the radioactive decay over the long term and the system was in an approximately steady state situation.

With the onset of industrialisation and changing land use in the mid-18<sup>th</sup> century the natural carbon cycle was perturbed. The burning of fossil fuels, such as coal, oil and gas, released carbon to the atmosphere that was previously locked up in relatively inaccessible reservoirs. Atmospheric levels of carbon dioxide have increased by more than 30% in the last 250 years due to human activities, and the anthropogenic  $\text{CO}_2$  has also entered the terrestrial and ocean reservoirs. Carbon dioxide released by fossil fuel combustion is devoid of  $^{14}\text{C}$ , so-called dead carbon, therefore the atmospheric  $^{14}\text{CO}_2$  is diluted and the ratio  $^{14}\text{C}:^{12}\text{C}$  decreases. This consequence is termed the *Suess effect* after Hans Eduard Suess who first described it.<sup>1</sup>

Fossil fuel burning, although not directly producing  $^{14}\text{CO}_2$ , decreases the proportion of  $^{14}\text{CO}_2$  in the atmosphere, therefore affecting the fluxes with the other reservoirs. During photosynthesis plant uptake reflects the atmospheric composition, so the fraction of  $^{14}\text{C}$  in the biomass decreases as the atmospheric ratio decreases. The increasing carbon dioxide in the atmosphere resulting from anthropogenic forcing has increased the  $\text{CO}_2$  flux into the oceans, leading to an increase in the total oceanic  $\text{CO}_2$ . This has only a minor effect on the  $^{14}\text{CO}_2$  flux.<sup>2</sup>

Atmospheric testing of thermonuclear bombs in the late 1950s produced neutrons around the fireballs of the explosions. Most of the detonations occurred in the northern hemisphere, at the surface or in the lower atmosphere (troposphere), but the fireballs were lifted into the stratosphere. The neutrons then reacted with  $^{14}\text{N}$  in the same

way as the neutrons of cosmic ray origin. The resulting  $^{14}\text{CO}_2$  is termed *bomb carbon* and produced a large spike in the atmospheric  $^{14}\text{CO}_2$  record and, subsequently, in that of other reservoirs as it exchanged with them. The majority of the atmospheric nuclear bomb testings ceased with the signing of the Test Ban Treaty of 1963. However France and China did not sign the treaty immediately but continued atmospheric nuclear bomb testing until 1968 and 1980, respectively. The global atmospheric  $^{14}\text{CO}_2$  concentration peaked in 1963, and then decreased with a half-life of 12.9 years as the bomb carbon was taken up by the terrestrial and oceanic reservoirs. Enhanced levels of  $^{14}\text{CO}_2$  are now evident in many other carbon pools, including the oceans,<sup>3</sup> tree rings,<sup>4,5</sup> corals,<sup>6</sup> and ice cores.<sup>7</sup> Over time ocean circulation processes have removed some of the bomb carbon away from the surface ocean. In areas of the ocean where downwelling occurs, such as the North Atlantic Ocean, bomb carbon has been found as deep as 3000 m. When these waters return to the surface, the recycled  $^{14}\text{C}$  leads to an increase in surface  $^{14}\text{C}$ , and a change in the atmosphere-ocean flux. The distribution of the bomb carbon concentration spike has proved a useful tracer for determining residence times and fluxes between carbon reservoirs, and for teasing out the various underlying processes. However, the large bomb spike has masked the effects of fossil fuel burning and changing land use on the  $^{14}\text{CO}_2$  distribution making it difficult to directly assess their impact.

Nuclear power stations produce  $^{14}\text{C}$  in the reactor, some of which can escape to the environment. Enhanced  $^{14}\text{CO}_2$  concentrations have been measured close to some reactors,<sup>8</sup> but the effect on the global inventory is small.

A test of global models of  $\text{CO}_2$  cycling in the oceans and biosphere is that they are able to reproduce the record of the rate at which the bomb carbon has been removed from the atmosphere.

## Methods

Regular measurements of atmospheric  $^{14}\text{CO}_2$  have been made at Wellington since 1954 (Fig. 1), and comprise the longest such time-series in the world. Initially the samples were collected at Makara, on the west coast near Wellington (41.25 °S, 174.69 °E, 280 m asl; 0), but in 1987 the sampling site was moved to Baring Head, at the entrance to Wellington Harbour, and now the site of a clean air atmospheric monitoring station operated by NIWA (41.41 °S, 174.87 °E, 80 m asl; 0). Samples are collected using static absorption of the  $\text{CO}_2$  into a solution of NaOH - a

vessel containing the NaOH solution is simply exposed to the overlying atmosphere for periods of one to two weeks. Back in the laboratory, an aliquot of the solution is acidified, and the released gas is collected and purified by cryogenic distillation. From 1954 until 1995 the  $^{14}\text{C}$  in the extracted carbon dioxide was measured by gas proportional counting, but since then accelerator mass spectrometry (AMS) has been used.



Fig. 1. Map of the southern North Island of NZ showing the location of Makara and Baring Head  $^{14}\text{CO}_2$  sampling sites.

The abundance of  $^{14}\text{CO}_2$  is generally expressed as a ratio of  $^{14}\text{C}$  to total carbon, and compared to a standard ratio of  $1.176 \times 10^{-12}$ , with corrections applied for fractionation and decay. The standard ratio is that which wood growing in 1950 would have been in the absence of the Suess Effect. The  $^{14}\text{C}$  level is reported as  $\Delta^{14}\text{C}$ , parts per thousand greater or less than the standard ratio.

## Results

The time series measurements are shown graphically in Fig. 2.  $\Delta^{14}\text{CO}_2$  increased from a background level of  $-10\text{‰}$  in 1955 to a peak of  $690\text{‰}$  in 1965 due to the input of bomb-derived  $^{14}\text{C}$ . The southern hemisphere peak occurred slightly later than that in the northern hemisphere<sup>9</sup> because the majority of the tests were conducted in the northern hemisphere atmosphere and it takes about a year for the atmosphere to mix. The concentration then decreased exponentially with a half-life of 12.9 years to the present day (2005) level of  $76\text{‰}$ . The decrease is due to the cessation of the majority of atmospheric nuclear bomb tests, oceanic and terrestrial uptake, fossil fuel dilution and atmospheric mixing processes.

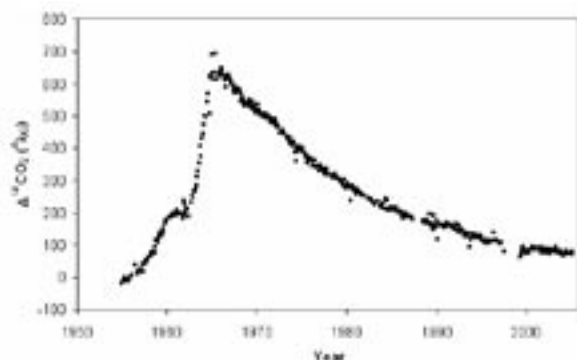


Fig. 2. Time series record of  $\Delta^{14}\text{CO}_2$  at Wellington, NZ.

The inventory of  $^{14}\text{CO}_2$  in the global troposphere (Fig. 3) was determined from  $\Delta^{14}\text{CO}_2$  measured at Wellington, and from the  $\text{CO}_2$  mixing ratio measured at Mauna Loa (Hawaii) for the period 1958 to 1970, and Wellington for the period 1970 until 2005. A troposphere:stratosphere ratio of 85:15, and an atmospheric  $\text{CO}_2$  burden of  $2.1276 \text{ PgC/ppmv}$  was used<sup>10</sup> to scale from the point measurements to the global tropospheric inventory. The calculated inventory is shown in Fig. 3. The maximum value of 580 RCU (1 RCU = 1 radiocarbon unit =  $10^{26} \times ^{14}\text{C}$  atoms) occurred in 1965, the values then decrease to 420 RCU in 1998. Fig. 3. also illustrates how the concentration of total  $\text{CO}_2$ , i.e. all carbon isotopes, expressed as a mixing ratio has increased from 316 ppmv in 1958 to 375 ppmv in 2005 due mostly to fossil fuel burning.

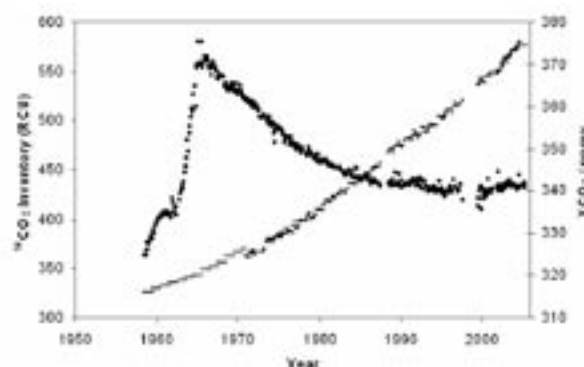


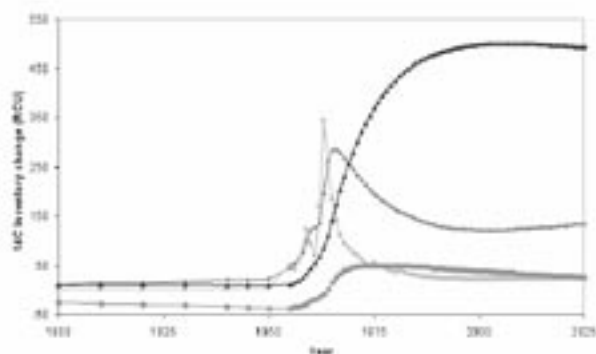
Fig. 3. Global tropospheric inventory of  $^{14}\text{CO}_2$  ( $\blacklozenge$  symbol, left-hand axis), and  $\text{XCO}_2$  ( $\text{—}$  symbol, right-hand axis).

The changes in the carbon inventories of the rapidly-changing reservoirs have been examined using the Enting-Lassey model.<sup>10,11</sup> In brief, this model considers the three carbon isotopes, including natural, fossil fuel, and bomb-derived carbon; and six reservoirs – the troposphere, stratosphere, short-lived biosphere, long-lived biosphere, surface ocean, and deep ocean. The model simultaneously determines fluxes and reservoir inventories, using various usage/emission histories and predictions, and was calibrated using spot observations. The model is described in detail in the cited references.<sup>10,11</sup>

Several model runs have been performed to examine the effects of varying cosmogenic  $^{14}\text{C}$  production, deep ocean diffusivity, fraction of photosynthesis fertilized by  $\text{CO}_2$ , the size of the long-lived biosphere, and the atmospheric  $\text{CO}_2$  turnover time. The E-L model output for the run in which the cosmogenic  $^{14}\text{C}$  production is tuned is shown in Fig. 4 where the outputs are given as changes in the inventory of the various reservoirs since 1750, and not absolute inventory size. This is because determination of the absolute inventory is almost impossible, and in large reservoirs such as the ocean the changes are small compared with the absolute value. All of the model runs produce similar outputs, varying only slightly in the magnitude and timing of the various events.

The  $^{14}\text{C}$  in the troposphere, stratosphere, and oceans slightly increase from 1900 to 1950 as  $^{14}\text{C}$  transfers from the biosphere as a result of deforestation and changing land use. In the 1950s the injection of bomb-carbon initially increases the stratospheric inventory, then is mixed into

the troposphere, and then exchanged into the oceans and biosphere. The tropospheric inventory change decreases exponentially from about 286 RCU in 1966 to 123 RCU in 1997. A broad minimum in the modeled tropospheric inventory is predicted to occur between 1999 and 2007, and this is to be followed by a gradual increase as the  $^{14}\text{C}$  is exchanged from the oceans back into the troposphere. The biosphere inventory continues to decline.



**Fig. 4.** The modeled change since pre-industrial times in the tropospheric, stratospheric, oceanic, and biospheric  $^{14}\text{C}$  inventories for the period 1750-2050.

We are now at the point in time when the observations will soon be able to tell us if the model predictions of an increase in atmospheric  $^{14}\text{CO}_2$ -content is indeed occurring. The 21<sup>st</sup> century then, could be the time when the oceans change from being a sink for atmospheric  $^{14}\text{C}$  to being a source, the first time this is known to have happened.

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