Correcting an Error in Some Interpretations of Atmospheric ^{14}C Data

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Key Point

- A simple mistake in interpreting data collected by others has led several authors to unconventional conclusions about human responsibility for atmospheric CO_2 increases.
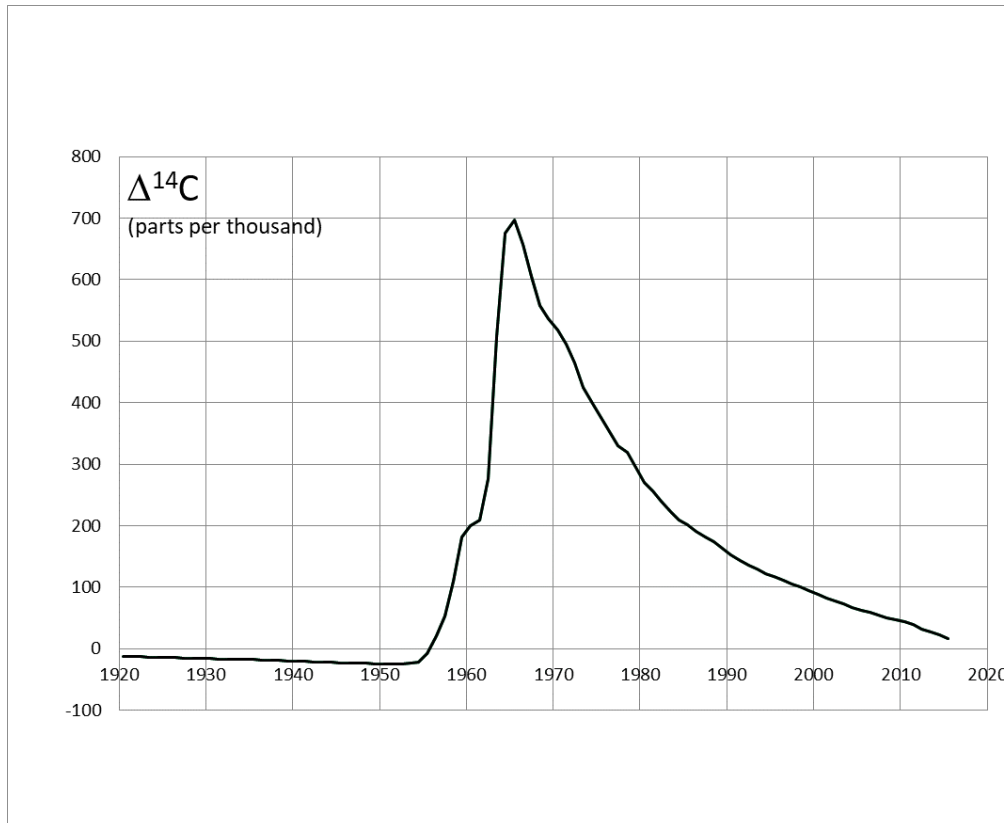
Abstract: A misunderstanding of the definition of the variable " $\Delta\ ^{14}C$ ", commonly used in radiocarbon dating and tracing applications to quantify ^{14}C levels, has led at least three authors from other fields to reach wrong conclusions about the fate of carbon introduced into the atmosphere. Models motivated by the mistake are excluded by the very same ^{14}C data, properly interpreted.

1. The Error Explained

The success of radiocarbon dating is predicated on an at least approximately stable abundance ratio between ^{14}C and the other carbon isotopes in the natural environment for tens of thousands of years. (See for example Caldeira, et al. (1998.)) Natural ^{14}C is produced in the upper atmosphere from cosmic ray generated neutrons interacting with nitrogen. $^{14}CO_2$ is ultimately formed and distributed throughout the biosphere. A balance between the production of ^{14}C and its radioactive decay (half-life of ~5730 years) maintained ^{14}C at approximately 1 part per trillion of the total atmospheric carbon through about 1950. But the balance was upset when atmospheric nuclear weapon testing nearly doubled the atmospheric ^{14}C content, during the decade beginning about 1955. While this will complicate future radiocarbon dating applications, several groups saw an opportunity to use the imbalance to study and refine models of carbon transport. (Caldeira, et al, 1998) (Turnbull et al.2009) (Levin and Hasshaimer, 2000) As a result, the recovery of the ^{14}C/C_{total} abundance ratio since 1965 is well documented (Turnbull et al, 2017) (Hua et al., 2013) (Graven et al., 2017).

The data is generally presented as a plot of "$\Delta\ ^{14}$C" versus time, for example as shown in Figure 1. But $\Delta\ ^{14}$C is a variable that caters to the interests of the ^{14}C community and that is where the problem begins. $\Delta\ ^{14}C$ is the fractional deviation of an isotope abundance ratio from a standard (see further discussion in Section 2). But Essenhigh(2009), Harde(2017)(2019), and Berry(2019) mistakenly interpreted $\Delta\ ^{14}C$ as the fractional deviation of ^{14}C *concentration* (say in grams/liter, or ppmv) from its pre-bomb test value. Looking at plots similar to Figure 1, the three authors erroneously, and apparently independently, concluded that after atmospheric nuclear testing ceased, the "pulse" of extra ^{14}C introduced by the tests exponentially disappeared from the atmosphere with a time constant of approximately 16 years. They reasoned that

anthropogenic carbon from fossil fuel burning would behave similarly, and ultimately concluded that human activity was not a major contributor to increasing atmospheric CO_2. Essenhigh's analysis was roundly criticized by Cawley (2011), and Harde's by Kohler et al.(2017), on other grounds which will not be reviewed here. But neither Cawley nor Kohler call attention to the misinterpretation of "$\Delta\ ^{14}C$" by Essenhigh and Harde, the error which apparently misled them and later Berry.

Figure 1:. Atmospheric nuclear testing in the 1950's and '60's increased $\Delta\ ^{14}C$ by about 70% (700ppt). The recovery following cessation of testing is well described by an exponential decay towards 0 with a time constant of about 16 years. The above plot is an attempt at a global average for this variable, with northern hemisphere, southern hemisphere, and tropical data for each year from (Graven 2017) weighted equally.

2. Definitions of $\Delta\ ^{14}C$

^{14}C dating measurements use isotope abundance ratios rather than absolute concentrations both because they are easier to measure and because they contain the information needed for dating. The ^{14}C concentration in a sample by itself is impossible to interpret, unless the concentration of other carbon isotopes is also known. When a sample of biological origin was alive, exchanging carbon with the atmosphere, isotope ratios in the organism presumably matched those in the atmosphere at that time (ignoring fractionation). After the organism died and became isolated from the atmosphere, the slow radioactive decay of ^{14}C changed the isotope

ratio, since the ^{12}C content was stable. Thus knowing the current isotope ratio, and the half-life of ^{14}C, enables an estimate of the sample's age. Similarly, in tracing flows of carbon, gradients in the more accurately known isotope ratios are the standard tool. That isotope ratios are usually, though not always, the quantities of interest is so ingrained that papers presenting ^{14}C data often do not explicitly define $\Delta\ ^{14}C$. No doubt the fact that $\Delta\ ^{14}C$ is dimensionless also contributed to its misinterpretation by some interested instead in following the ^{14}C concentration.

Several reviews of standard ^{14}C protocols are available (Turnbull et al.2009) (Stenstrom et al.2011) (Stuiver and Polach 1977). The definition of "$\Delta\ ^{14}C$" is not identical in all of them, because a convenient operational choice depends on the technology used for the measurement. But all compare the ^{14}C content with other carbon in the sample and measure the deviation from a standard in parts per thousand as follows:

$$\Delta\ ^{14}C = 1000\times\left[\frac{A_{measured}}{A_{standard}} - 1\right] \tag{1}$$

The quantity "$A_{measured}$" can be the specific activity of a sample, i.e. Becquerels per kg of carbon (which depends on ^{14}C/C_{total}) (Stenstrom et al.2011), or Becquerels per liter of Oxalic acid (Stuiver and Polach 1977) (which, since the fraction of carbon in Oxalic acid is fixed, also reduces to a measure of ^{14}C/C_{total}). $A_{measured}$ can also be a direct measurement of ^{14}C/^{13}C (or ^{14}C/^{12}C) by an accelerator mass spectrometer (Turnbull et al. 2009). The quantity "$A_{standard}$" must of course be in the same units as $A_{measured}$ and is established by convention. Examples are $A_{standard}$=226 Bq/kgC (Stuiver and Polach 1977) and $A_{standard} = 1.176x10^{-12}$ mol^{14}C/molC (Turnbull et al. 2009). These choices make atmospheric $\Delta\ ^{14}C$ near zero, but slightly negative, just prior to the bomb tests. Corrections for the fractionation of isotopes during sample preparation or in biological processes are important considerations in making different measurement technologies give consistent results, and complicate this simplified overview. But as these corrections are much smaller than the error being addressed, there is no need to elaborate further here.
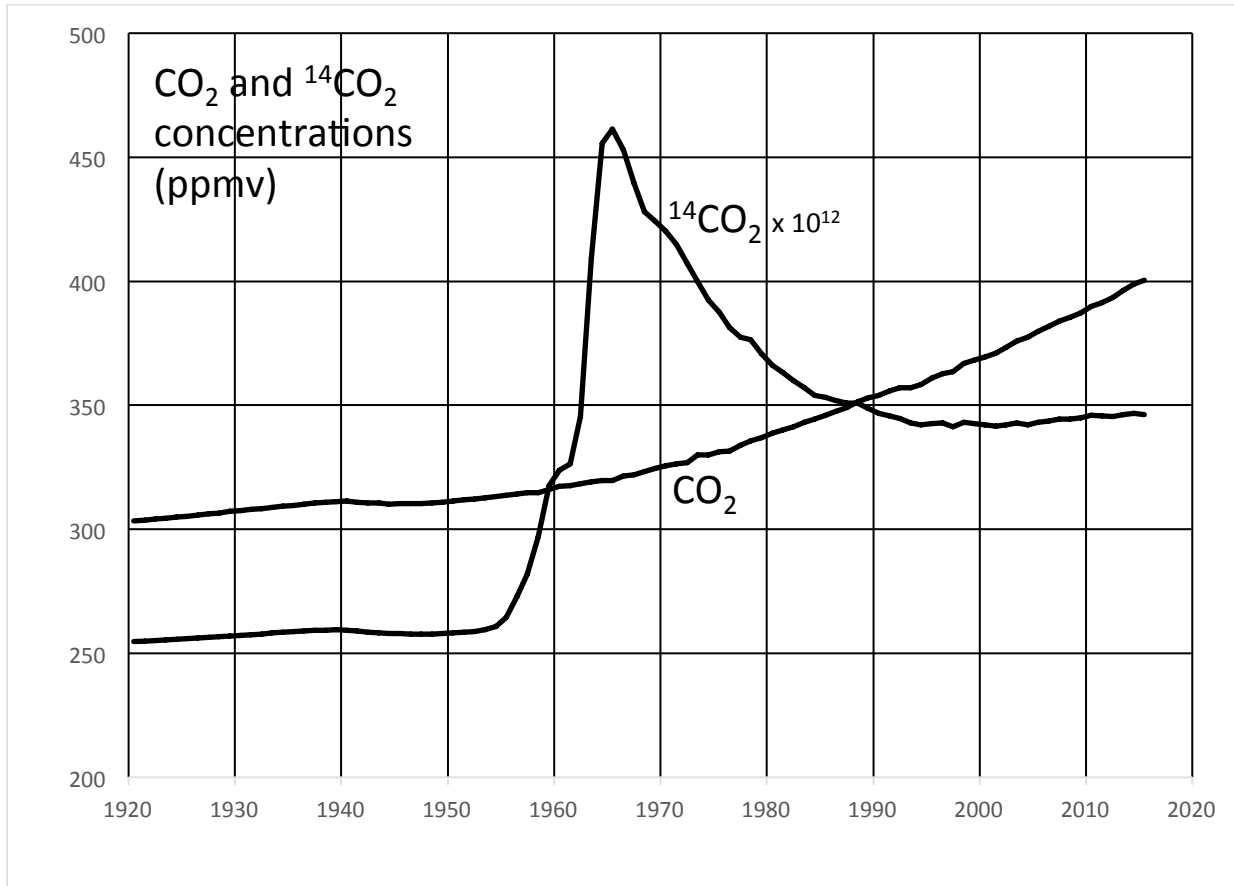
In a dating measurement the ^{14}C changes, making $\Delta\ ^{14}C$ change, while the ^{12}C is fixed. But if this variable is used in atmospheric studies of ^{14}C changes with a baseline of ~60 years, not only the ^{14}C is changing. The time dependence of $\Delta\ ^{14}C$ now reflects changes in the concentration of all the carbon as well as ^{14}C concentration changes. For example, as $\Delta\ ^{14}C$ approaches 0 in 2020, this does NOT mean that ^{14}C *concentrations* have nearly returned to 1955 values. It means that *the isotope abundance ratio* has nearly returned to its previous value. Therefore, since atmospheric ^{12}CO$_2$ has increased by about 30% since 1955, the ^{14}C concentration remains well above its pre-bomb test value.

3. Finding the true ^{14}C concentration

It is of course possible to determine the true ^{14}C concentration as a function of time (call it ^{14}C(t)), from $\Delta\ ^{14}C$ if we also know how the concentration of the rest of the carbon varies with time. (Call that function C(t)). Rearranging equation 1, making A=^{14}C/C, and explicitly identifying the time dependent factors gives

$$^{14}C(t) = C(t) \times \frac{^{14}C_{std}}{C_{std}} \times \left[1 + .001 \times \Delta\,^{14}C(t)\right] \qquad (2)$$

To estimate C(t), we use the Mauna Loa trend data, which has the seasonal variation filtered out, for 1958 and after, and ice core data for the years before (World Data Centre for Greenhouse Gasses (http://gaw.kishou.go.jp/)). This familiar curve is shown in Figure 2. Also shown in Figure 2 is our estimate of the global average ^{14}C concentration over the last century, computed from this C(t), the Figure 1 data for $\Delta\,^{14}C$, and $^{14}C_{std}/C_{std} = 1.176 \times 10^{-12}$ mol^{14}C/molC. While plots of $\Delta\,^{14}C$ through the bomb test period appear frequently in the literature, plots of ^{14}C concentration are surprisingly scarce and qualitatively different. The concentration curve shown should be taken as global average *data* derived from the isotope ratio measurements with minimal model assumptions.

Figure 2 The atmospheric concentration of CO_2 and $^{14}CO_2$ in the last century. The CO_2 follows the familiar "Keeling curve". The $^{14}CO_2$ concentration is multiplied by a factor of 1 trillion. ^{14}C concentration in 2020 is about 30% higher than before the atmospheric nuclear testing. But the isope ratio in 2020 is not far from its 1920 value, as can be ascertained from either this figure or Figure 1.

4. Discussion:

      4.1   Essenhigh(2009), Harde(2017)(2019), and Berry(2019) mistook the isotope ratio curve (Figure 1) for the ^{14}C concentration curve of Figure 2. Essenhigh labels an axis "^{14}C concentration" for a plot that is clearly of $\Delta\,^{14}C$. Both Harde and Berry have asserted that $\Delta\,^{14}C$ is equivalent to concentration (personal communications.) The isotope ratio curve shown in Figure 1, interpreted as a concentration curve, invites a single time constant model for absorption of atmospheric ^{14}C by terrestrial or oceanic sinks. All three authors fit the isotope ratio data to a simple exponential, assumed this was the concentration, and produced "alternative carbon cycle" models. But single time constant models are excluded by the true concentration curve shown in Figure 2, which is derived from the same data, properly interpreted.

      4.2   The imbalance in ^{14}C concentration between the atmosphere and other carbon sinks equilibrated on a couple of decade time scale. This implies exchange of atmospheric ^{14}C with terrestrial or oceanic ^{12}C on a relatively short time scale, but not the "absorption" that the errant papers claim.

      4.3   The data show that ^{14}C concentration in the atmosphere is now actually *increasing*. This at first sight seems to contradict the "Suess effect" (Suess 1955). Since fossil fuel emissions are largely ^{14}C free, the carbon having been in the ground much longer than the ^{14}C lifetime, one expects the ^{14}C/^{12}C ratio to fall as ^{14}C in the carbon cycle is diluted, and this is evident in Figure 1 data prior to 1950. However the observed increase in the *concentration*, not the ratio, around the year 2000 was predicted by Caldeira, et al (1998). They found that new ^{12}C from fossil fuels displaces ^{14}C in terrestrial and oceanic sinks and competes with the continued influx of cosmic ray generated ^{14}C for places in those sinks. In other words, higher atmospheric carbon concentrations are now required to move carbon to the terrestrial and oceanic sinks. Caldeira's analysis predicts that $\Delta\,^{14}C$ will ultimately again go negative from the Suess effect, even as the ^{14}C concentration continues to rise.

      ^{14}C studies indeed give valuable insights into the carbon cycle when the variables are properly understood. In particular they show that the discussed "alternative carbon cycle" models are incompatible with the data that motivated them. These models have little standing in the scientific community, but continue to attract some lay support. That the basic error discussed herein can persist over a decade and be repeated suggests dysfunctional communications between two sides of an important public debate.

References

Berry, E. X. (2019). Human CO_2 emissions have little effect on atmospheric CO_2. *International Journal of Atmospheric and Oceanic Sciences,* 3(1), 13-26. doi: 10.11648/j.ijaos.20190301.13

Caldeira, K., Raul,G. H., and Duffy,P. B. (1998). Predicted net efflux of radiocarbon from the ocean and increase in atmospheric radiocarbon content. *Geophysical Research Letters*, 25(20), 3811-3814.

Cawley, G. C. (2011). On the atmospheric residence time of anthropogenically sourced CO_2. *Energy Fuels* 25, 5503–5513, http://dx.doi.org/10.1021/ef200914u.

Essenhigh, R. H. (2009). Potential dependence of global warming on the residence time (RT) in the atmosphere of anthropogenically sourced carbon dioxide. *Energy & Fuels*, 23, 2773−2784.

Graven, H., Allison, C. E., Etheridge, D. M., Hammer, S., Keeling, R. F., Levin, I., et al. (2017) Compiled records of carbon isotopes in atmospheric CO_2 for historical simulations in CMIP6, *Geosci. Model Dev.,* 10, 4405–4417, https://doi.org/10.5194/gmd-10-4405-2017.

Harde, H.(2017). Scrutinizing the carbon cycle and CO_2 residence time in the atmosphere. *Global and Planetary Change*, 152,19-26.

Harde, H. (2019). What humans contribute to atmospheric CO2: Comparison of carbon cycle models with observations. *Earth Sciences*. 8(3), 139-159. doi: 10.11648/j.earth.20190803.13

Hua, Q., Barbetti, M., Rakowski, A. Z. (2013). Atmospheric radiocarbon for the period 1950–2010. *Radiocarbon*, 55, pp. 2059–2072. https://doi.org/10.2458/azu_js_rc.v55i2.16177

Koehler, P., Hauck, J., Volker, C, .Wolf-Gladrow, D. A., Butzin, M, Halpern, J. B. et al.(2017) Comment on "Scrutinizing the carbon cycle and CO_2 residence time in the atmosphere by H. Harde". *Global and Planetary Change*. 164, 67-71.

Levin, I. and Hesshaimer, V. (2000). Radiocarbon: A unique tracer of global carbon cycle dynamics., *Radiocarbon*, 42(1), 69–80.

Stenstrom, K. E., Skog, G., Gerogiadou, Genberg. J., Johansson, A. (2011). A guide to radiocarbon units and calculations. Lund University, LUNFD6(NFFR-3111)/1-17/(2011). https://www.hic.ch.ntu.edu.tw/AMS/A%20guide%20to%20radiocarbon%20units%20and%20calculations.pdf

Stuiver, M. and Polach, H.(1977). Discussion: Reporting of ^{14}C data". *Radiocarbon,* 19(3), 355-363. https://journals.uair.arizona.edu/index.php/radiocarbon/article/viewFile/493/498

Suess, H. E. (1955), Radiocarbon concentration in modern wood", *Science*, 122, 415-417.

Turnbull, J., Rayne, P., Miller, J., Naegler, T., Ciais, P., Cozic, A. (2009). On the use of [14]CO_2 as a tracer for fossil fuel CO_2: Quantifying uncertainties using an atmospheric transport model., *Journal of Geophysical Research*, 114, D22302. https://doi.org/10.1029/2009JD012308

Turnbull, J. C., Mikaloff Fletcher, S. E., Ansell, I., Brailsford, G. W, Moss, R. C., Norris, M.W, et al. (2017). Sixty years of radiocarbon dioxide measurements at Wellington, New Zealand: 1954–2014. *Atmos. Chem. Phys*., 17, 14771–14784. https://doi.org/10.5194/acp-17-14771-2017.