Anthropogenic fossil carbon dioxide and claims of its dominance and role in global warming

by Kenneth Skrable, George Chabot, and Clayton French July 5, 2020

Table of Contents

	Pag	ge
Abstr	act	1
1. Int	troduction	2
2. Dis	scussion	3
2.1 2.1.1	Definitions of quantities in Table 1 Definitions of symbols and abbreviations for input data	33
2.1.2 2.2.	Summary of methodology and equations used to calculate the anthropogenic-fossil and non-fossil components of annual mean arthur dioxide	3
2.3 2.3.1	Equations used to calculate the values of the d13C and D14C statistics reported by NOAA \dots Equations for d13C and ratio R_{S13}	4 5 5
2.3.2 2.4 2.5	Equations for D14C, ratio R_{S14} , and specific activity, $S(t)$ Niwot Ridge annual mean CO_2 quantities for changes in the d13C and D14C statistics Niwot Ridge specific activity. $S(t)$ of 14C in $C(t)$ in 1750 through 2020	5 7 9
2.6 2.7	Niwot Ridge $\langle S(t) \rangle$, $\langle C_F(t) \rangle$, and $100 \langle C_F(t) \rangle / C(0)$ 1 Plots of d13C and the CO ₂ and other quantities in report, "State of the Climate 2014"	10 10
2.8 3 Co	Plot of the D14C statistic from the NOAA website	13 14
4. Re	ferences	15
Table	es and Figures	16
Table Figur	c 1. Niwot Ridge annual mean CO2 quantities for changes in the d13C and D14C statistics 1 re 1.1. Niwot Ridge d13C versus $C_F(t)$	17 18
Figur Figur Figur	e 1.2. Niwot Ridge S(t) versus $C_F(t)$	18 18 18
Table Figur	2. Niwot Ridge specific activity of 14C in C(t) in 1750 through 2020	19 19
Table Figur	$ s 3. Niwot Ridge , , and 100 /C(0)$	20 20

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Kenneth Skrable¹, George Chabot, and Clayton French

Abstract- This paper exemplifies and emphasizes portions of our essay^[1] titled, "Anthropogenic Fossil and Non Fossil Components of Mauna Loa and Niwot Ridge Annual Mean Carbon Dioxide". Annual mean values of the D14C statistic associated with the total annual mean mole fraction, C(t), in 2004 through 2012 at NOAA's observatory in Niwot Ridge, Colorado are used to calculate values of the 14C specific activity S(t) in C(t). Values of C(t) and S(t) and their initial values of C(0) and S(0) in 1750, then are used to calculate the anthropogenic-fossil component, $C_{F}(t)$, and the non fossil component, $C_{NF}(t)$, present in C(t) at t years after 1750. Values of the d13C, D14C, and S(t) statistics have been used to detect changes in $C_{\rm F}(t)$, but only two of these are successfully used for this purpose. The d13C and D14C statistics have been used/misused by some members of the scientific community as a means to validate fossil fuels as the major source of increases in atmospheric CO_2 . The S(t) statistic is a critical quantity in our methodology for determining the value of $C_{\rm F}(t)$. It is demonstrated that the rapid decreases in the values of d13C and D14C in plots arise from the fact that the magnitudes and slopes of their underlying relative deviations from a standard are multiplied by a factor of 1,000 when they are expressed in the unit of per mil, which is represented by the symbol *‰*. It also is demonstrated that the steep slopes in plots of values of the d13C and D14C statistics from one year to the next are not directly related to the value of $C_{\rm F}(t)$, which only varies each year with the specific activity, S(t), in C(t). Plots of values for the d13C and D14C statistics presented at the NOAA, Wikipedia, and other websites, likely have misled persons in the public, government, and scientific communities throughout the world to believe that elevated levels of anthropogenic-fossil CO₂ have caused global warming. This false belief has severe potential societal implications and presses the need for very costly remedial actions that are misdirected, presently unnecessary, and completely ineffective in curbing global warming.

Table 1 and plots in four figures of the annual mean CO_2 quantities, which account for changes in the d13C and D14C statistics in 2004 through 2012, provide the data used in the evaluation of the efficacy of the three statistics for the detection of increases in $C_F(t)$ each year. The sensitivities of the d13C, D14C, and S(t) statistics for the detection of an increase of 1 ppm in the annual mean amount of $C_F(t)$ are respectively: -0.0214‰ per ppm, -3.4063‰ per ppm, and -0.0468 dpm/gC per ppm. The relative sensitivities of D14C/d13C and of D14C/S(t) are, respectively, 159‰ per ‰ of d13C and 72.8‰ per dpm/gC of S(t) for the plots of the statistics versus $C_F(t)$ and versus time t in years since 1750.

For the change of d13C of -6.5‰ in 1750 to a value of -8.5‰ in 2020, which corresponds to a relative change of 30.77%, the change in the value of R_{S13} for the (13C/12C) ratio is from 0.01116 in 1750 to 0.01114 in 2020, which corresponds to a relative change of only -0.20%. This change in the d13C statistic bears no relationship to the changes in the anthropogenic component, $C_F(t)$, in the total carbon dioxide. Calculations in section 2.4 indicate that d13C* in C(t) in 2012 would have had to have been -12.8‰ if the fossil component $C_F(t)$ were to have represented 30% of C(t) instead of its actual value of 9.51%. This d13C* value of -12.8‰ for C(t) is much lower than the current value of d13C of -8.5‰ listed in Table 1 for 2020, and it negates claims and inferences that most of the CO₂ added to the atmosphere over the past 200 years or so has been the anthropogenic-fossil component.

The expected values of $\langle C_F(t) \rangle$, in Table 3 and Figure 3 are: 0.38 ppm in 1800, 3.92 ppm in 1950, 9.23 ppm in 1975, 23.45 ppm in 2000, and 51.07 ppm in 2020. These values of $\langle C_F(t) \rangle$ are discussed in the evaluation of plots of d13C and CO₂ in a report titled, "State of the Climate 2014", in section 2.7. Our data for the anthropogenic-fossil component, $C_F(t)$, and the non fossil component, $C_{NF}(t)$, contradict the claims that the atmospheric increase in carbon dioxide is dominated by fossil fuel emissions as implied in a plot of D14C and accompanying text in a NOAA website article discussed in section 2.8.

¹University of Massachusetts Lowell, 1 University Avenue, Lowell, MA

The authors declare no conflicts of interest. For correspondence, Email: skrablekw@aol.com

1. Introduction

Since the start of the industrial revolution in 1750 and the onset of the use of fossil fuels in vehicles and power plants, atmospheric concentrations of CO_2 began to increase along with increases in temperatures. Atmospheric measurements of the total CO_2 were not available until 1959 at the Mauna Loa, Hawaii observatory of the *National Oceanic and Atmospheric Administration* (NOAA), which has provided the longest record of atmospheric measurements of the total CO_2 , which is designated in this paper by the symbol C(t), where t represents the number of years since 1750. Based on our knowledge, the anthropogenic-fossil component, $C_F(t)$, and non fossil component, $C_{NF}(t)$, in C(t) have never been estimated by NOAA at its observatories or at any other observatory from atmospheric measurements of CO_2 . Despite this fact, claims by NOAA and others in sections 2.7 and 2.8 that most or all of the increase in C(t) since 1800, mostly from estimates of compressed snow and/or ice cores in Antarctica until 1959, has been due to the anthropogenic-fossil component, $C_F(t)$.

Other atmospheric measurements of C(t) began in 2003 at the NOAA observatory in Niwot Ridge, Colorado, including measurements of the three isotopes of carbon: 12C, 13C, and 14C. Carbon-14 is a radioactive isotope of carbon having a half-life of 5,730 years. Carbon-14 atoms have been produced at essentially a constant rate in the atmosphere by interactions of cosmic rays, and they have reached an essentially constant steady state activity, i.e. disintegration rate, in the total world environment. The age of fossil fuels is much longer than the 5,730 y half-life of the 14C isotope; consequently, fossil fuels are devoid of the 14C isotope. When the anthropogenic-fossil component of CO₂ is released to the atmosphere, the specific activity, S(t) in C(t), of 14C decreases. The ratio R_{S13} of the (13C/12C) atoms and the ratio R_{S14} of the (14C/12C) atoms at Niwot Ridge are used to calculate, respectively, two statistics designated as d13C and D14C, both of which are said to decrease when the anthropogenic-fossil component, $C_{\rm E}(t)$, increases in the atmosphere. Both statistics represent 1,000 times the deviations of their ratios from that of a standard divided by their respective standard ratios when expressed in per mil given by the symbol *‰*. This magnification increases their underlying relative deviations and slopes in plots by a factor 1,000. The steep slopes in plots likely have led persons throughout the world to falsely conclude that the anthropogenic component has dominated the increase of CO_2 and caused global warming. These false conclusions have severe potential societal implications that press the need for very costly remedial actions that are misdirected, presently unnecessary, and completely ineffective in curbing global warming.

Values of the D14C statistic in C(t) at NOAA's observatory in Niwot Ridge, Colorado in 2004 through 2012 are used to calculate values of the annual mean 14C specific activity, S(t), at t years after 1750. The values of C(t) and S(t) are compared to our chosen initial values in 1750 for C(0) and S(0) of, respectively, 280 ppm and 16.33 dpm/gC. This comparison is used in the calculation of annual mean values of the anthropogenic-fossil component, $C_F(t)$, and the non fossil component, $C_{NF}(t)$, present in C(t), as well as the annual changes, $DC_{NF}(t)$, in the non fossil component. The annual change, $DC_{NF}(t)$, is associated with exchanges of CO₂ among its reservoirs. These values of the CO₂ quantities are used to evaluate the efficacy of the d13C, D14C, and S(t) statistics for the detection of changes in $C_F(t)$. The first two of the statistics, d13C and D14C, have been used/misused by some members of the scientific community as a means to validate fossil fuels as the major source of increases in atmospheric CO₂. The S(t) statistic is the critical quantity in our methodology for determining the anthropogenic-fossil component, $C_F(t)$, which is demonstrated to be independent of C(t) and d13C. The slopes of the linear plots of values of the three statistics versus the value of $C_F(t)$ represent their sensitivities for detecting an increase of 1 ppm in $C_F(t)$. Their relative sensitivities are given by the ratios of their slopes.

The values of all components of CO_2 and the three statistics in Table 1 are used in section 2.7 to evaluate plots of d13C and CO_2 in a report titled, "State of the Climate 2014". Our data for the anthropogenic-fossil component, $C_F(t)$, and the non fossil component, $C_{NF}(t)$, contradict the claims that the atmospheric increase in carbon dioxide is dominated by fossil fuel emissions as implied in a plot of D14C and accompanying text in a NOAA website article discussed in section 2.8.

2. Discussion

2.1 Definitions of quantities in Table 1

Table 1 provides Niwot Ridge annual mean CO₂ quantities in 2004 through 2012, including the d13C statistic (i.e., δ^{13} C) and the D14C statistic (i.e., Δ^{14} C) and their effects on changes in other quantities. The lower case letter d placed before a symbol for a quantity represents the lower case Greek symbol delta (δ), and the upper case letter D represents the upper case Greek symbol Delta (Δ). The word delta represents the change or difference of a quantity from some reference quantity. Table contents and the four plots of quantities listed in the table are discussed below the table. Input data are listed at the top of the table and highlighted in yellow, and their symbols and abbreviations are defined:

2.1.1 Definitions of symbols and abbreviations for input data

- $C(0) \equiv$ initial total CO₂ concentration in the atmosphere in ppm at t = 0 in 1750, which is considered as the non fossil component, $C_{NF}(0)$, at the beginning of the industrial revolution even though this value also includes fossil components from natural sources.
- S(0) = initial specific activity of 14C (i.e., carbon-14 or ¹⁴C), dpm/gC present in C(0) in 1750.
- At. Wt. 13C = atomic weight of 13C.
- At. Wt. 12C = atomic weight of 12C.

 $R_{std13} \equiv ratio$, (13C/12C), of the number of 13C atoms to the number of 12C atoms in the standard.

 $R_{std14} \equiv ratio$, (14C/12C), of the number of 14C atoms to the number of 12C atoms in the standard.

2.1.2 Definitions and abbreviations for annual mean quantities of CO₂ at time t years after 1750:

Symbols and abbreviations are listed at the top of columns numbered (1) through (16) in Table 1, and these numbers are used for the equations used to calculate annual mean quantities in those columns. Definitions are listed sequentially along with some of the equations and/or their section numbers:

- (1) t = time in years since 1750 at the beginning of the industrial revolution = (Year of Mean 1750).
- (2) $C(t) \equiv$ the total annual mean mole fraction in ppm of CO₂ calculated from a file provided by NOAA.
- (3) D14C ≡ annual mean value of Delta 14C present in C(t) calculated from the same file in (2) by Equation (3) in section 2.3.2.
- (4) $F_d \equiv$ decay factor of 14C calculated from time t for C(t) to the time t of 200 years for a standard in 1950 and calculated by Equation 4 listed at the top of Table 1.
- (5) d13C = delta 13C value at time t estimated from a plot provided by NOAA and calculated by Equation (5) listed at the top of Table 1, except for years 1750 and 2020 as explained in the notes below the table.
- (6) $F_{13} =$ factor in equation for D14C calculated by Equation (6) listed at the top of Table 1.
- (7) $R_{S13} \equiv$ annual mean ratio, (13C/12C), of the number of 13C atoms to the number of 12C atoms in C(t) calculated by Equation (7) listed at the top of Table 1 and in section 2.3.1.
- (8) AB13 = % abundance of 13C in C(t) calculated by Equation (8) listed at the top of Table 1.
- (9) AB12 = % abundance of 12C in C(t) calculated by Equation (9) listed at the top of Table 1.
- (10) At. Wt. C = atomic weight of carbon in C(t) = 0.01 (AB13)(At. Wt. 13C) + 0.01(AB12)(At. Wt. 12C).
- (11) k = factor used to convert ratio, R_{S14}, of (14C/12C) in C(t) to its specific activity, S(t), and calculated by Equation (11) listed at the top of Table 1.
- (12) $R_{s_{14}} \equiv$ annual mean ratio, (14C/12C), of the number of 14C atoms to the number of 12C atoms in C(t) calculated by Equation (12) listed at the top of Table 1 and in section 2.3.2.
- (13) $S(t) \equiv$ annual mean specific activity of 14C in C(t) calculated by the product, kR_{S14}, of the factor k and the ratio R_{S14} discussed in section 2.3.2.

- (14) $C_F(t) \equiv$ annual mean anthropogenic-fossil component in C(t) calculated by Equation (14) in section 2.2: $C_F(t) = [(S(0)/S(t)) 1]C(0)$ for values of C(0) and S(0) listed at the top of Table 1.
- (15) $C_{NF}(t) \equiv$ annual mean non fossil component present in C(t) calculated by Equation (15) in section 2.2: $C_{NF}(t) = C(t) C_F(t)$.
- (16) $DC_{NF}(t) =$ annual change in the non fossil component due to the redistribution of CO₂ among its reservoirs, which may be positive or negative in the year since 1750. It is calculated by Equation (16) in section 2.2: $DC_{NF}(t) = C_{NF}(t) C(0)$.

2.2. Summary of methodology and equations used to calculate the anthropogenic-fossil and non fossil components of annual mean carbon dioxide

The basis of the methodology used for the estimation of the annual mean quantities of the anthropogenic-fossil component, $C_F(t)$, and the non fossil component, $C_{NF}(t)$, present each year in the total carbon dioxide, C(t), measured by NOAA for the Niwot Ridge and Mauna Loa observatory beginning in 1959 is summarized as follows. All calculated annual mean quantities present each year in the atmosphere automatically include any redistribution of CO₂ with its exchange reservoirs, the oceans and terrestrial biosphere. Based on our knowledge, the components of CO₂ have never been estimated by NOAA at its observatories or at any other observatory from atmospheric measurements of CO₂.

The methodology relies on two accepted facts: (1) the initial total mole fraction C(0), of 280 ppm before 1750 has been essentially constant for several thousand years^[2] before 1750 and (2) the production rate of 14C atoms in the atmosphere has been essentially constant for at least fifteen thousand years^[3]. Therefore, the steady state activity of 14C per unit volume of the atmosphere also would have been constant except for the redistribution of CO₂ in the atmosphere in each year with other CO₂ reservoirs. The product C(t)S(t) is proportional to the activity per unit volume of the atmosphere, which varies each year depending on whether there is a net input or output, DC_{NF}(t), of non-anthropogenic-fossil CO₂ in the atmosphere because it contains no activity of 14C. Also, the 14C specific activity, S(t), (i.e., the activity in *disintegrations per minute* (dpm) per gram of total carbon, abbreviated as dpm/gC) would have remained constant at its initial value, S(0)^[4, 5, 6], of 16.33 dpm/gC in 1750 except for the dilution of S(0) by the anthropogenic-fossil component, C_F(t), present in the atmosphere each year. This dilution effect is noted as the Suess effect^[7] discussed at the link: https://en.wikipedia.org/wiki/Suess effect.

Two pathways can be used to estimate $DC_{NF}(t)$, $C_{NF}(t)$, and $C_{F}(t)$:

Pathway 1: The statement for the change, $DC_{NF}(t)S(t)$, of the 14C activity per unit volume of the atmosphere at time t is: $DC_{NF}(t)S(t) = C(t)S(t) - C(0)S(0)$, which yields Eq. (1a) through Eq. (3a):

Eq. (1a):
$$DC_{NF}(t) = [C(t)S(t) - C(0)S(0)]/S(t) \rightarrow$$

Eq. (2a): $C_{NF}(t) = C(0) + DC_{NF}(t) \rightarrow$ Eq. (3a): $C_{F}(t) = C(t) - C_{NF}(t)$.

Pathway 2: Eq. (1a) above gives an expression for the specific activity: $S(t) = C(0)S(0)/[C(t) - DC_{NF}(t)]$, which reduces to: $S(t) = C(0)S(0)/[C(0) + C_F(t)]$, and which yields alternative equations for $C_F(t)$ and the other two quantities in Pathway (1) above:

Eq. (14):
$$C_F(t) = [(S(0)/S(t)) - 1]C(0) \rightarrow Eq. (15): C_{NF}(t) = C(t) - C_F(t) \rightarrow Eq. (16): DC_{NF}(t) = C_{NF}(t) - C(0).$$

The equation numbers above for Pathway 2 as well as those in the following sections are the numbers heading the columns in Table 1. The equation for $C_F(t)$ is independent of $DC_{NF}(t)$, C(t), and d13C. It can be used to estimate the anthropogenic-fossil component, $C_F(t)$, from 1750 to today as indicated in Table 3 and Figure 3. The equations in Pathway 2 are used in Table 1 to calculate $C_F(t)$, $C_{NF}(t)$, and $DC_{NF}(t)$.

2.3 Equations used to calculate the values of the d13C and D14C statistics reported by NOAA

Equations are used to calculate values of the d13C and D14C statistics reported by NOAA in the common unit of per mil (‰). These values are used in their plots to depict trends in the anthropogenic-fossil component, and they are given as follows.

2.3.1 Equations for d13C and ratio R_{S13}

The annual mean values of the d13C statistic listed in column (5) obtained from a NOAA file are calculated by an equation containing the annual mean atom ratios, (13C/12C), in C(t) and in a standard:

$$dI3C = \left(\frac{\left(\frac{13C}{12C}\right)_{sample}}{\left(\frac{13C}{12C}\right)_{standard}} - 1\right) 1,000\% = \left(\frac{R_{SI3}}{R_{stdI3}} - 1\right) 1,000\% = \left(\frac{R_{SI3} - R_{stdI3}}{R_{stdI3}}\right) 1,000\%, \quad (5)$$

which latter expression shows that the d13C statistic is actually a relative delta value multiplied by 1,000‰ and not simply the annual mean ratio, R_{S13} of (13C/12C) atoms in C(t).

When plots of the d13C statistic are made over time, the rate of change of the d13C statistic relative to that for the ratio R_{S13} is given by a constant representing their relative sensitivities:

$$\frac{\frac{d}{dt}(d13C)}{\frac{d}{dt}(R_{S13})} = \frac{d(d13C)}{d(R_{S13})} = \frac{1,000\%}{R_{std13}} = \frac{1,000\%}{0.011237} = 88,992\% \text{ of } d13C \text{ per unit } (13C/12C) \text{ ratio; also,}$$
$$\frac{d(R_{S13})}{\frac{d(R_{S13})}{d(d13C)}} = \frac{R_{std13}}{1,000\%} = \frac{0.011237}{1,000\%} = 0.000011237 \text{ (}13C/12C) \text{ ratio per } \% \text{ of } d13C.$$

Thus, a change of 1‰ in the d13C statistic causes only a very small change of 0.000011237 in the annual mean value of the R_{S13} ratio. The magnification of 1,000 in the slopes of plots of d13C has caused many persons to falsely conclude that the rapid decrease in the d13C values means that the increase in C(t) since 1800 is due mostly or entirely to the increase of the anthropogenic-fossil component, $C_F(t)$. Scientists or others who provide such plots in publications like those at the NOAA and Wikipedia websites should caution readers of this situation, but they have not done so. Other processes, such as large fires and decay of material that made up the terrestrial biosphere can reduce the (13C/12C) ratio because of the lower abundance of 13C resulting from isotope fractionation effects associated with plant uptakes of CO₂.

The annual mean ratio, R_{S13} , of (13C/12C) atoms measured in C(t) are obtained by Equation (5):

$$R_{SI3} = (1 + 0.001 \, dI3C) R_{stdI3}, \text{ which}$$
⁽⁷⁾

are slightly smaller than that of the standard ratio, R_{std13} , as indicated by the listed values in column (7) of Table 1. Thus, it appears that changes in the d13C values from 2004 to 2012 make very small changes in the ratios, R_{s13} , of (13C/12C) atoms in C(t). The slope of a plot of R_{s13} versus d13C values is 0.001 R_{std13} , which equals (0.001)(0.011237) or 0.000011237 (13C/12C) ratio per ‰ of d13C, which explains why the ratio, R_{s13} , is insensitive to even large changes in the d13C statistic.

2.3.2 Equations for D14C, ratio R_{S14}, and specific activity, S(t)

Much of the discussion and conclusions in section 2.3.1 above for d13C and R_{s13} apply to D14C. The factor F_d in column (4) of Table 1 is added to the equations in section 2.3.1 to account for the decay

of 14C atoms from the year of the annual mean value for C(t) and its D14C statistic to the year 1950 for the standard. The factor F_{13} in column (6) of Table 1 is added to account for the fractionation of 13C and 14C atoms between the atmosphere and its exchange reservoirs. The equation revised from Equation (5) for d13C yields the annual mean value of the D14C statistic calculated from a file provided by NOAA:

$$D14C = \left(\frac{R_{S14}F_dF_{13}}{R_{std14}} - 1\right) 1,000\% = \left(\frac{R_{S14}F_dF_{13} - R_{std14}}{R_{std14}}\right) 1,000\%.$$
(3)

The latter expression shows that the D14C statistic also is a relative delta value multiplied by 1,000‰. The factors F_d and F_{13} in Table 1 change very little from 2004 to 2012, and the first expression for D14C is approximated by a general linear equation of D14C versus R_{S14} multiplied by 1,000‰: $y \cong (Ax + B)1,000\%$, where y is D14C; A is (F_dF_{13}/R_{std14}) , which is the slope of the linear equation before multiplying by 1,000; x is R_{S14} ; and B is -1 and the y intercept of the underlying linear equation. Thus, a plot of values of the D14C statistic when expressed in per mil (‰) versus R_{S14} has the slope A and the y intercept, -1, multiplied by a factor of 1,000 in this underlying linear equation. Very much the same considerations that apply in the discussion of the factor of 1,000 magnification involved with the use and presentation of the d13C also apply in regard to D14C. Similar considerations to those for d13C also apply to D14C regarding fires and decay of organic materials, which result in some reduction in both the value of D14C and the specific activity, S(t), calculated from the value of D14C. Fossil fuels have an R_{S14} value of zero; therefore, fossil-based CO₂ has a D14C value of -1,000‰.

The ratio R_{514} of (14C/12C) atoms in C(t) at t years after 1750 is obtained by Equation (3) above:

$$R_{SI4} = (1 + 0.001DI4C) \frac{R_{stdI4}}{F_d F_{13}}.$$
 (12)

It should be noted that this ratio R_{S14} is the annual mean value in C(t) and in D14C in the year of the measurement and not the year 1950 for the standard ratio, R_{std14} . Thus, R_{S14} is independent of all three factors to the right of the bracketed expression for R_{S14} , as well as the d13C statistic in Equation (6) for the F_{13} factor listed at the top of Table 1. As noted in Equation (13) below, R_{S14} is used to calculate the specific activity, S(t), which then yields values for $C_F(t)$, $C_{NF}(t)$, and $DC_{NF}(t)$ in, respectively, columns headed by numbers, (14), (15), and (16) in Table 1. Therefore, S(t), $C_F(t)$, $C_{NF}(t)$, and $DC_{NF}(t)$ are independent of the value of d13C, except as noted below.

The above Equation (12) for R_{S14} when multiplied by the factor k in column (11) of Table 1 yields the specific activity, S(t), in column (13):

$$S(t) = kR_{SI4} = k(1 + 0.001D14C)\frac{R_{std14}}{F_dF_{13}} = (1 + 0.001D14C)\frac{S_{std14}}{F_dF_{13}},$$
 (13)

where $S_{std14} = 13.41$ dpm/gC based on the product, k R_{std14} , of the k value of $1.140x10^{13}$ dpm/gC per unit (14C/12C) ratio listed in all applicable rows for column (11) and the ratio, R_{std14} , of 1.176E-12 listed at the top of Table 1. The value of 2.920E7 listed in row 23 for the difference of the k value in 2012 and the k value in 2004, indicates a very slight increase in the k value occurs as a result of an increase in the percent abundance, AB12, of 12C atoms and a decrease in the atomic weight of carbon, At. Wt. C, in Equation (11) listed at the top of Table 1 used to calculate the factor k in column (11). These very slight changes result from decreases in values of the d13C statistic listed in column (5) and the consequent decreases in values for the percent abundance, AB13, of 13C atoms in column (8). Such small changes have no practical significance on the values of the specific activity, S(t), listed in column (13) as well as on the values of the anthropogenic-fossil component, $C_F(t)$, non fossil component, $C_{NF}(t)$, and annual change, $DC_{NF}(t)$, in the non fossil component listed respectively in columns, (14), (15), and (16).

The last expression in Equation (13) approximates a linear equation for S(t) versus D14C whose rate of change in plots over time is its slope approximated by 0.001 S_{std14}/F_dF_{13} times the slope of D14C in its plot over time. The ratio of the D14C slope to the S(t) slope is the relative sensitivity of the D14C statistic to that of the S(t) statistic for detecting increases of the anthropogenic-fossil component, $C_F(t)$. This relative sensitivity of D14C to S(t) is approximated by 1000 F_dF_{13}/S_{std14} , which is equal to (1000)(0.9930)(0.9964)/(13.41)‰ per dpm/gC or 73.8‰ per dpm/gC of S(t), which is based on average values for F_d and F_{13} in Table 1. This value of 73.8‰ per dpm/gC compares to a value of 72.8‰ per dpm/gC calculated in both Figure 1.3 and Figure 1.4 from the ratio of the slopes of the plots for D14C and S(t) versus, respectively, $C_F(t)$ and t.

By Equation (14) in section 2.2, the equation for S(t) can be expressed directly in terms of $C_F(t)$:

$$S(t) = C0)S(0)/[C_F(t) + C(0)], (17)$$

which is a non-linear equation. A plot of S(t) versus $C_F(t)$ has the slope $dS(t)/dC_F(t)$:

$$dS(t)/dC_{F}(t) = -C(0)S(0)/[C(0) + C_{F}(t)]^{2} = -S(t)/[C(0) + C_{F}(t)], (18)$$

which is the sensitivity each year of S(t) for detecting an increase of 1 ppm in $C_F(t)$.

When the expression for S(t) in Equation (13) above is set equal to that for S(t) in Equation (17): $(1 + 0.001 \text{ D}14\text{C})\text{S}_{\text{std}14}/\text{F}_{d}\text{F}_{13} = \text{C0}\text{S}(0)/[\text{C}_{\text{F}}(t) + \text{C}(0)]$, then D14C can be expressed in terms of C_F(t):

$$D14C = 1,000\% \left[-1 + C(0)S(0)F_{13}F_{d}/S_{std14}(C_F(t) + C(0))\right], (19)$$

which also is a non-linear equation versus $C_F(t)$. A plot of D14C versus $C_F(t)$ has the slope dD14C/dC_F(t):

$$dD14C/dC_{F}(t) = -1,000\% C(0)S(0)F_{13}F_{d}/S_{std14}[C_{F}(t) + C(0)]^{2} = -1,000 R_{S14}F_{13}F_{d}/R_{std14}[C_{F}(t) + C(0)], (20)$$

which is the sensitivity each year of D14C for detecting an increase of 1 ppm in $C_{\rm F}(t)$.

The above equations make very clear that the use of the per mil unit of expression for D14C causes its slopes in linear or non-linear plots versus $C_F(t)$ to be a factor 1,000 times larger than they otherwise would be without this factor. This factor 1,000 also applies to plots of D14C versus time t and versus S(t) but not versus d13C because plots of d13C in the common unit of per mil versus other quantities have this same 1,000 factor magnification in its slopes.

2.4 Niwot Ridge annual mean CO₂ quantities for changes in the d13C and D14C statistics

This section describes annual mean CO_2 quantities listed in Table 1 accounting for changes in the d13C and D14C statistics. The following facts are important to recognize for quantities listed in Table 1:

- (1) The values of the d13C and D14C statistics are values reported for the year of the measurements of their respective atom ratios, R_{S13} of (13C/12C) and R_{S14} of (14C/12C), adjusted by applicable factors, prior to calculating the relative deviations from their respective standard atom ratios, R_{Std13} of (13C/12C) and R_{Std14} of (14C/12C), in a 1950 standard, which then is multiplied by 1,000‰ when each statistic is expressed in the common unit of per mil. Thus, all reported values of the two statistics represent their relative changes from their 1950 standards, multiplied by 1,000‰.
- (2) The values of all other CO_2 quantities listed in Table 1, except for $DC_{NF}(t)$, represent annual mean quantities present in the year of their measurements in relationship to initial values of C(0) and S(0) present in 1750 at the beginning of the industrial revolution. Their annual mean values automatically account for any redistribution of CO_2 among its reservoirs.

Sections 2.3.1 and 2.3.2 above provide, respectively, the d13C and D14C definitive equations, their applications, and their limitations for the detection of an addition of 1 ppm to the annual mean anthropogenic-fossil component of CO_2 , which represents the sensitivity of each statistic. In this regard, we are considering the term sensitivity to represent the output of one quantity for a unit input of another quantity.

Certain results in Table 1 are described below with respect to their locations indicated by letter designations for columns and number designations for rows in the Excel sheet used to generate the table. The number of digits for quantities in cells of the Excel sheet is more than shown in those cells; therefore, the reader will not be able to verify all listed quantities in the copy of the Excel table. With respect to the increases in the total carbon dioxide, C(t), in column C, it is noted that the annual mean value for the anthropogenic-fossil component, $C_F(t)$, in column O present each year also is the change, $DC_F(t)$, from the value of zero in 1750. Also, the annual change in the non fossil component, $DC_{NF}(t)$, in column Q represents the change from the initial value, C(0), of 280 ppm in 1750, which also is considered as the initial non-anthropogenic-fossil component, $C_{NF}(0)$.

Values of d13C in column F may have a significant effect on the values of quantities listed only in columns G through L. The ratio of the d13C value of -8.287‰ in 2012 to its value of -8.074‰ in 2004 is listed in cell F21 as 1.026, which corresponds to a relative change of 2.64% listed in cell F22. All of the 2012 to 2004 quantity ratios, in row 21, in the six columns, G through L, are 1.000. Except for the first three quantities in columns G through I, the relative changes in row 22 of the other three quantities in columns J through L are 0.00%. Those in columns G through I in row 22 are, respectively, only 0.04% for the F_{13} factor, - 0.02% for the R_{S13} ratio of (13C/12C), and -0.02% for the AB 13C, all of which are much less the relative change of 2.64% for d13C in cell F22. For the change of d13C of -6.5% in 1750 to a value of -8.5% in 2020, which corresponds to a relative change of 30.77% in cell F27, the change in the value of R_{S13} for the (13C/12C) atom ratios in column H is from 0.01116 in 1750 to 0.01114 in 2020, which corresponds to a relative change of only -0.20%. These results indicate that the relative changes of d13C from 2004 to 2012 and from 1750 to 2020 do not cause a significant practical change of consequence in any of the quantities listed in the six columns, G through L, of rows 21 through 27. Except for the slight changes in the value of the factor k in column L, the changes in the d13C statistic since the start of the industrial revolution are otherwise unrelated to the changes in the anthropogenic component, $C_F(t)$, in the total carbon dioxide.

The above analysis of the d13C statistic demonstrates that it is not a very sensitive indicator for the detection of small changes in the fossil contribution to atmospheric CO_2 . If the atmosphere were to contain the very significant fractions of fossil-derived CO_2 that have been declared or inferred by many climatologists and involved groups, then the d13C values would have to be appreciably more negative than they have been in modern times. For example, NOAA has accepted a value of -28‰ for the d13C_F value for fossil fuels^[9], but the d13C_{NF} value for the non fossil component is not listed. Table 1 values in 2012 are listed: total carbon dioxide, C(t), of 394.83 ppm; anthropogenic-fossil component, C_F(t), of 37.55 ppm; non fossil component, C_{NF}(t), of 357.28 ppm; and d13C of -8.287‰ for C(t). The value of d13C for C(t) equals the weighted mean value expected from C_F(t), designated by d13C_F, and from C_{NF}(t), designated by d13C_{NF}, which is calculated as follows.

 $\begin{aligned} d13C &= (d13C_F)C_F(t)/C(t) + (d13C_{NF})C_{NF}(t)/C(t), \text{ or } \\ d13C_{NF} &= [(d13C)C(t) - (d13C_F)C_F(t)]/C_{NF}(t), \text{ or } \\ d13C_{NF} &= [(-8.287\%))(394.83 \text{ ppm}) - (-28\%) (37.55 \text{ ppm})]/(357.28 \text{ ppm}) = -6.215\%. \end{aligned}$

If we assumed, instead, that the fossil CO₂ represented 30% of the total CO₂, rather than the 9.51% in the above example for 2012, and used this value of -6.215‰ for the non-fossil contribution, $d_{13C_{NF}}$, we would obtain a value, designated as d_{13C} , for C(t) in 2012:

$$d13C^* = 0.3(-28\%) + (0.7)(-6.215\%) = -12.8\%$$

This d13C* value of -12.8‰ for C(t) in 2012 is much lower than the current d13C value of -8.5‰ listed in Table 1 for 2020, and it negates claims and inferences that most of the CO_2 added to the atmosphere over the past 200 years or so has been the anthropogenic-fossil component.

Changes in the D14C statistic in column D from 2004 to 2012 affect the changes in columns M through Q. No changes in the listed values of the factor k in column L occur from 1750 to 2020. The ratio R_{\$14} of (14C/12C) in column M decreases from 1.304E-12 in 2004 to 1.263E-12 in 2012, which corresponds to a relative change of -3.20% as a result of the increases of C_F(t) in column O. Values for S(t) decrease from 14.88 in 2004 to 14.40 in 2012, which corresponds to the same relative change of -3.20% as that for R_{S14}. The anthropogenic-fossil component, C_F(t), in column O increases from 27.39 ppm in 2004 to 37.55 ppm in 2012, which corresponds to a relative change of 37.11%. In 2020, the value of $C_F(t)$ is 48.11 ppm. The non fossil component, $C_{NF}(t)$, increases from 350.58 ppm in 2004 to 357.28 ppm in 2012, which corresponds to a relative change of 1.91%. The value of the annual change, $DC_{NF}(t)$, in the non fossil component since 1750 increases from 70.58 ppm in 2004 to 77.28 ppm in 2012, which corresponds to a relative change of 9.50%. Thus, over the period from 2004 to 2012, the increase in C(t) is dominated by the anthropogenic-fossil component, $C_{\rm F}(t)$. The value of DC_{NF}(t) in 2020 is 83.25 ppm, which indicates that it has continued to increase along with increases in the anthropogenicfossil component, $C_F(t)$. The value of 48.11 ppm for $C_F(t)$, i.e., $DC_F(t)$, in 2020 when added to the value of 83.25 ppm for $DC_{NF}(t)$ in 2020 yields the change, DC(t), of 131.36 ppm in C(t) in cell C26 since 1750. Thus, over the period from 1750 to 2020, the non fossil component, $C_{NF}(t)$, dominates the increase in C(t).

In Figure 1.4, all plots over the period from 2004 to 2012 of quantities are well represented by their linear equations, whose slopes represent the rates of change in each quantity versus t. The quantities $C_{NF}(t)$ and $DC_{NF}(t)$ have the same slope of 0.8343 ppm y⁻¹, which when added to that for $C_F(t)$ of 1.2372 ppm y⁻¹ yields the slope for C(t) of 2.0715 ppm y⁻¹. Thus, $C_F(t)$ represents 59.72% and $DC_{NF}(t)$ represents 40.28% of the rate of change and of the total increase of CO_2 from 2004 to 2012. As a consequence, the proportion of $C_F(t)$ in C(t) increases in each year, and it will eventually become the dominant component of C(t). This situation is reflected by the convergence of the trend lines for $C_F(t)$ and $DC_{NF}(t)$ and by the divergence of the trend lines of C(t) and $C_{NF}(t)$ in their plots. However, the value of $DC_{NF}(t)$ will eventually become negative in the next glacial period when average temperatures decrease again as they have done over all of the previous glacial-interglacial periods in the last 800,000 years^[10].

As indicated in the text below the table and the equations listed in Figures 1.2 and 1.3, the S(t) and D14C have non linear equations with respect to $C_F(t)$. As a consequence, their slopes and therefore sensitivities in their plots versus $C_F(t)$ have slight changes from one year to the next. There is no known relationship between d13C and $C_F(t)$, and the correlation shown in the plot of d13C versus $C_F(t)$ in Figure 1.1 may be coincidental. Based on the assumption of linear relationships of each statistic with $C_F(t)$, the sensitivities of d13C, S(t), and D14C for the detection of the addition of 1 ppm to the anthropogenic-fossil component $C_F(t)$ are given by their linear slopes. Their relative sensitivities are given by the ratio of their slopes. It should be noted that the relative sensitivity of D14C to d13C is 159 and that of D14C to S(t) is 72.8‰ per dpm/gC of S(t) in both Figure 1.3 versus $C_F(t)$ and Figure 1.4 versus t.

2.5 Niwot Ridge specific activity, S(t), of 14C in C(t) in 1750 through 2020

Table 2 and Figure 2 contain eighteen input specific activities, S(t), from 1750 to 2020 that are used to obtain expected specific activities, $\langle S(t) \rangle$, from 1750 to 2020 based on an equation for an approximation fitting function. The description of the eighteen input specific activities and the process used to obtain the parameter values in the equation for the approximation fitting function are described in the text below the table and figure, which lists the equation for calculating the expected specific activities, $\langle S(t) \rangle$, in each annual mean total mole fraction, C(t), present each year. As indicated in the text, the values of the eighteen points for the input specific activities, S(t), and the values calculated for the expected specific activities, $\langle S(t) \rangle$, in the blue line from the equation for the approximation fitting function provide a realistic representation of the expected initial small decreases and later more significant decreases in the specific activities expected after the start of the industrial revolution in 1750 and the increased burning of fossil fuels each year.

2.6 Niwot Ridge <S(t)>, <C_F(t)>, and 100 <C_F(t)>/C(0)

This section discusses calculations in Table 3 and plots in Figure 3 of expected values in 1750 to 2020 of annual mean quantities of the specific activity, $\langle S(t) \rangle$ in C(t), the anthropogenic-fossil component, $\langle C_F(t) \rangle$ in C(t), and 100 times the ratio of $\langle C_F(t) \rangle / C(0)$ based on the equation for the approximation fitting function discussed in section 2.5 above. As indicated in the discussion below the table and figure, the quantities are based on the fact that the expected anthropogenic-fossil mole fractions, $\langle C_F(t) \rangle$, present in 1750 through 2020 vary only with changes in the expected specific activities, $\langle S(t) \rangle$, in the total mole fractions, C(t). Values for $\langle C_F(t) \rangle$ are calculated by Equation (14) listed in sections 2.1.2 and 2.2: $\langle C_F(t) \rangle = [(S(0)/\langle S(t) \rangle) - 1]C(0)$. The initial value in 1750 of the total mole fraction, C(0), is 280 ppm, which also is considered as the initial value, $C_{NF}(0)$, of the non fossil component. Its specific activity, S(0), is 16.33 dpm/gC. Particular values of $\langle C_F(t) \rangle$ of interest are discussed as follows.

The expected value, $\langle C_F(t) \rangle$, is 51.07 ppm in 2020 based on an $\langle S(t) \rangle$ value of 13.81 dpm/gC. These values compare to a $C_F(t)$ value of 48.11 ppm and S(t) value of 13.94 dpm/gC listed in Table 1. The slight discrepancy in $C_F(t)$ and $\langle C_F(t) \rangle$ is due to differences in the specific activities. In Table 1, the total mole fraction, C(t), in 2020 has a value of 411.36 ppm and the non fossil component, $C_{NF}(t)$, has a value of 363.25 ppm. Thus, in 2020, the anthropogenic-fossil component, $C_F(t)$, of 48.11 ppm represents 11.7% and the non fossil component, $C_{NF}(t)$, represents 88.3% of the total mole fraction, C(t).

It is stated in the publication, The Carbon Cycle and Atmospheric CarbonDioxide^[11]:

"Before the Industrial Era, circa 1750, atmospheric carbon dioxide (CO_2) concentration was 280 ± 10 ppm for several thousand years. It has risen continuously since then, reaching 367 ppm in 1999."

As noted later in discussions of plots of total CO₂ provided by others, atmospheric CO₂ remained at 280 ppm in 1800 when it then took a dramatic increase that continues today. In 2000, the value of the non fossil component, $C_{NF}(t)$, is calculated as 344 ppm from the difference, $(C(t) - C_F(t))$, of C(t) of 367 ppm listed in the quote above for 1999 and $< C_F(t) >$ of 23.45 ppm listed in Table 3. In 1800, the value of the non fossil component, $C_{NF}(t)$, is calculated as 279.62 ppm from the difference, $C(t) - C_F(t)$, for C(t) of 280 ppm listed in the quote above and for $< C_F(t) >$ of 0.38 ppm listed in Table 3, which also represents the change, $DC_F(t)$, in the anthropogenic-fossil component since 1750. The change, $DC_{NF}(t)$ in 1800, in the non fossil component is calculated from the difference, $C_{NF}(t) - C(0)$, of (279.62 - 280) ppm or -0.38 ppm, due to the annual redistribution in 1800 of CO₂ in its reservoirs. Thus, the total change in C(t) in 1800 since 1750 is the sum, ($DC_F(t) + DC_{NF}(t)$), of (0.38 - 0.38) ppm or zero. After 1800, both the anthropogenic-fossil components of CO₂ continue to increase, but the increase, ($DC_F(t) + DC_{NF}(t)$), in the total mole fraction, C(t), each year is dominated by the non fossil component. We believe the value of $DC_{NF}(t)$ is dominated by net releases of CO₂ from the oceans as a result of the temperature increases in recent years caused by the increased solar radiation^[12], which the earth is currently experiencing.

2.7 Plots of d13C and the CO₂ and other quantities in report, "State of the Climate 2014"

The report^[13], "State of the Climate 2014", is from the Australian Government, Bureau of Meteorology and the *Commonwealth Scientific and Industrial Research Organization* (CSIRO). The following text and figures between the two horizontal dashed lines below have been copied directly from the report with no changes in the text or figure except for format changes. The three figures are similar to those in the paper, "A revised 1000 year atmospheric d13C-CO₂ record from Law Dome and South Pole, Antarctica", published in the Journal of Geophysical Research (JGR)^[14].

Greenhouse gases

Carbon dioxide emissions

Global anthropogenic CO_2 emissions into the atmosphere in 2013 are estimated to be 38.8 billion tonnes of CO_2 (10.6 billion tonnes of carbon), the highest in history and about 46 per cent higher than in 1990. Global CO_2 emissions from the use of fossil fuel are estimated to have increased in 2013 by 2.1 per cent compared with the average of 3.1 per cent per year from 2000 to 2012.

Since the industrial revolution more than two centuries ago, about 30 per cent of the anthropogenic CO_2 emissions have been taken up by the ocean and about 30 per cent by land vegetation. The remaining 40 per cent of emissions have led to an increase in the concentration of CO_2 in the atmosphere.

The origin of CO_2 in the atmosphere can be determined by examining the different types (isotopes) of carbon in air samples. This identifies the additional CO_2 as coming from human activities, mainly the burning of fossil fuel, and not from natural sources. Most of the CO_2 emissions from human activities are from fossil-fuel combustion and land-use change (top graph). Emissions are expressed in gigatonnes of carbon (C) per year. A gigatonne is equal to 1 billion tonnes. One tonne of carbon (C) equals 3.67 tonnes of carbon dioxide (CO_2). CO_2 emissions from human activities have been taken up by the ocean (middle graph, in blue, where negative values are uptake), by land vegetation (middle



graph, in gold), or remain in the atmosphere. There has been an increase in the atmospheric concentration of CO_2 (bottom graph, in red), as identified by the trend in the ratio of different types (isotopes) of carbon in atmospheric CO_2 (bottom graph, in black, from the year 1000). CO_2 and the carbon-13 isotope ratio in CO_2 ($\delta^{13}C$) are measured from air in Antarctic ice and firm (compacted snow) samples from the Australian Antarctic Science Program, and at Cape Grim -(northwest Tasmania).

Our conclusions regarding the plots in the three figures of the report from CSIRO have serious conflicts with those of the authors of the report. These conflicts are based on (1) contradictions in the report itself; (2) our calculations of $C_F(t)$ and $C_{NF}(t)$ present in the total carbon dioxide, C(t); and (3) changes in the d13C and the D14C statistics associated with each annual mean value of C(t) in 2004 through 2012 at the NOAA observatory in Niwot Ridge, Colorado. Tables, figures, and sections of text in our paper are referenced in our comments about these conflicts. It is important to recognize that our calculations of the annual mean values of the anthropogenic-fossil and non fossil components of the total CO₂ automatically account for any exchanges in CO₂ among its reservoirs. They are based on atmospheric measurements of the total mole fraction, C(t), and its specific activity, S(t), at time t years after 1750 in comparison to the initial values C(0) of 280 ppm and its specific activity S(0) of 16.33 dpm/gC in 1750. The authors of the CSIRO report have not provided any estimates of the components of CO₂ present each year in the atmosphere. They assume from their plots of values of the total CO₂ and of the d13C statistic in the third figure above that essentially all of the increase in the total CO₂ beginning in 1800 until today has been due to the anthropogenic-fossil component, C_F(t). They also imply in the last sentence above containing the phrase, "carbon-13 isotope ratio in CO_2 (d13C)", that the (13C/12C) atom ratio is the same as the d13C statistic, which is a very misleading inference that is wrong in many ways.

In the first figure above, the emission rate of fossil-based carbon did not exceed 1 Gt/y until about 1930 when the rate slowly started to take a dramatic increase reaching about 9.5 Gt/y in about 2012. Despite this observation, the atmospheric CO₂ in the third figure above begins to dramatically increase in 1800, which is 130 years previous to the beginning in 1930 of significant emissions greater than 1 Gt/y of anthropogenic-fossil CO₂. This 130 year time conflict for the beginning in 1930 of the release of significant anthropogenic-fossil-based carbon to the atmosphere and the beginning of the significant increase of CO₂ in 1800 is bewildering. It is concluded that the increases of atmospheric CO₂ after 1800 must have been due primarily to increasing net inputs, DC_{NF}(t), of non fossil CO₂ from the oceans due to temperature increases, not fossil CO₂ from the burning of fossil fuels. This conclusion is consistent with and confirmed by values of the annual mean anthropogenic component, $\langle C_F(t) \rangle$, in 1750 to 2020 that are summarized in Table 3 and Figure 3.

Our calculations of the changes in 1800 of the anthropogenic-fossil component, $DC_F(t)$, and of the non fossil component, $DC_{NF}(t)$, are, respectively, + 0.38 ppm and - 0.38 ppm, which corresponds to a total non fossil component, $C_{NF}(t)$ of (280 - 0.38) ppm or 279.62 ppm present in 1800, which when added to the fossil component, $C_F(t)$, of 0.38 ppm equals the total CO_2 , C(t), of 280 ppm in the plot of the third figure above. These results, discussed in section 2.6, are based on data in Table 3 and the plots in Figure 3, and they are consistent with data plotted in the first and third figure above. Based on data for Niwot Ridge in Table 1, the increases from 1750 projected to 2020 are 48.11 ppm for $DC_F(t)$ and 83.25 ppm for $DC_{NF}(t)$. These increases correspond to a total increase, DC(t), of 131.36 ppm and total mole fraction, C(t), of 411.36 ppm calculated from the sum of 280 ppm for C(0) in 1750 and 131.36 ppm for DC(t). Thus, in 2020 the anthropogenic-fossil component, $C_F(t)$, is 11.7%, and the non fossil component is 88.3% of the total C(t) of 411.36 ppm.

The plot by the authors in the above cited report of values of the total mole fraction, C(t), along with its d13C statistic, i.e. δ^{13} C, in the third figure, is apparently intended to convince the reader that essentially all of the increase in C(t) is from the anthropogenic component, C_F(t), which they claim in their text for the figure:

"The origin of CO_2 in the atmosphere can be determined by examining the different types (isotopes) of carbon in air samples. This identifies the additional CO_2 as coming from human activities, mainly the burning of fossil fuel, and not from natural sources."

This claim by the authors has no foundation. It is disputed by our analysis of the underlying equation for the d13C statistic in section 2.3.1, the values of quantities in columns F through L in rows 21 through 27 in Table 1 that might be affected by changes in values of the d13C statistic from one year to the next, and the sensitivities and relative sensitivities of the d13C, D14C, and S(t) statistics for the detection of changes in the anthropogenic-fossil component, $C_F(t)$. It is a clear example of the misuse of the d13C statistic as a means to validate fossil fuels as the major source of increases in atmospheric CO₂.

If the atmosphere did contain the very significant fractions of fossil-derived CO_2 declared or inferred by many climatologists and involved groups, then d13C values would have had to have been appreciably more negative than they have been in modern times. This expectation for a much smaller d13C value has been demonstrated by the calculation in section 2.4, which predicts a value for d13C* of -12.8‰ for a fossil component of 30% of the total CO_2 in 2012 instead of the actual value of 9.51%. This d13C* value of -12.8‰ for C(t) in 2012 is much lower than the current value of -8.5‰ listed in Table 1 for 2020, and it negates claims and inferences that most of the CO_2 added to the atmosphere over the past 200 years or so has been the anthropogenic-fossil component.

It has been demonstrated that the dramatic decrease of values for the d13C statistic in the last figure above is essentially unrelated to the increase in the anthropogenic-fossil component of CO₂. This demonstration rests solely on the inherent insensitivity of the d13C statistic for detecting changes in the (13C/12C) atom ratios, which is unrelated to our methodology and our estimates of the annual mean anthropogenic-fossil component, $C_F(t)$, present each year. The plot of the d13C statistic in the same figure with the plot of the total CO₂ by the authors evidently has the intended purpose to convince the reader that all of the observed increase in CO₂ since 1800 has been due to the anthropogenic-fossil component.

2.8 Plot of the D14C statistic from the NOAA website

The NOAA website^[16] describes the use of the D14C statistic (i.e., Δ^{14} C) for detecting trends of anthropogenic-fossil CO₂ in the atmosphere as depicted in the figure to the right copied from the site. The caption in the figure and the following text copied from the NOAA website provide a description of the figure and plot of D14C values:

"¹⁴C is the isotope NOAA scientists use to understand fossil fuel CO₂ emissions. You can see how Δ^{14} C values have decreased since 2003 in the background air at Niwot Ridge: The steady downward trend in Δ^{14} C of background air shows that the additional carbon dioxide added to the atmosphere must have a lower Δ^{14} C value than what is already in the atmosphere. Well, we know that fossil fuels have a Δ^{14} C signal of -1000‰, but that all other sources have a signal that is very close to that of ambient air (approximately +45‰ in 2010, actually). Therefore, when CO₂ from fossil fuels enter the atmosphere, the Δ 14C value in the atmosphere goes down. We can precisely calculate how much the Δ^{14} C value in the atmosphere goes down when fossil fuel CO₂ is added. It turns out to be about a 3‰ decrease in Δ^{14} C for every 1 ppm of fossil fuel CO₂ added to the atmosphere."



"The trend in Δ^{14} C of the clean background air at Niwot Ridge. This graph shows all samples, since 2003, of air that has come from the undeveloped Rocky Mountains."

Annual mean values of the D14C statistic are listed in Table 1, and they are discussed below the table and in sections 2.3.2 and 2.4. Figure 1.4 contains a plot of the annual mean values of D14C in 2004 through 2012 for Niwot Ridge. Sensitivities and relative sensitivities for d13C, D14C, and S(t) are shown in Figures 1.1 through 1.4. The sensitivity of D14C in Figure 1.3 for detecting an increase of 1 ppm in fossil CO₂ is -3.4063‰ per ppm, which compares to -3‰ per ppm in the NOAA quote above. The relative sensitivity of D14C/d13C is 159‰ per ‰ of d13C, and the relative sensitivity of D14C/S(t) is 72.8‰ per dpm/gC of S(t), which are the same values listed in Figure 1.4 for plots of the three statistics versus time t in years since 1750. In Equation (3) for D14C in section 2.3.2, fossil fuels have an R_{S14} value of zero; therefore, fossil-based CO₂ has a D14C value of -1,000‰ as indicated in the quote above.

The following NOAA statement^[17] includes the claim: "By studying how the concentration of ¹⁴C has changed in the atmosphere, scientists have determined that the atmospheric increase in carbon dioxide is dominated by fossil fuel emissions". This claim is not true for several reasons. This statement has no foundation, and it is not supported by our calculations of the annual mean values for the anthropogenicfossil component, $C_{\text{E}}(t)$, and the non fossil component, $C_{\text{NE}}(t)$, present in C(t) in Table 1. NOAA does use the sensitive D14C statistic to detect increasing trends of fossil fuel CO₂, but the value of this statistic does not tell "how the concentration of ¹⁴C has changed in the atmosphere". The concentration of 14C per unit volume of the atmosphere does not change with the addition of fossil fuel emissions. Only the specific activity, S(t), and the D14C statistic change, i.e., they decrease as more fossil fuel CO₂ emissions are added to the atmosphere. Although D14C is a very sensitive statistic for detecting increases in the fossil component, $C_{\rm F}(t)$, its amount and change from one year to the next do not represent the amount of the anthropogenic component, $C_F(t)$, present in each year. Its enhanced sensitivity when expressed in per mil (‰) causes an increase in the slope by a factor 1,000 in a plot of values of the relative deviations of its (14C/12C) atom ratios, R_{S14} , from its standard ratio, R_{std14} , like the plot from the NOAA site above. This 1,000 factor magnification in its slope may well have caused persons to falsely conclude that the increase of CO₂ has been dominated by increases of the anthropogenic-fossil component.

The D14C statistic is 159 times more sensitive than the d13C statistic for the detection of changes in the anthropogenic-fossil component from one year to the next in air samples at Niwot Ridge. We have demonstrated that the steep decrease in the d13C statistic in the third figure in section 2.7 above is

essentially unrelated to changes in the anthropogenic-fossil component. The samples discussed in section 2.7 above and taken over the last thousand years to establish values quoted as, " CO_2 and the carbon-13 isotope ratio in CO_2 ($\delta^{13}C$) from air in Antarctic ice and firn (compacted snow) samples from the Australian Antarctic Science Program, and at Cape Grim -(northwest Tasmania)," also would contain 14C atoms, which have a half-life of 5,730 years. Analyses for the 14C isotope, perhaps, could have been used to estimate values of the D14C statistic, yet such measurements are not mentioned in the report, "State of the Climate 2014".

3. Conclusions

Based on the discussion and results, we conclude:

- Plots of the d13C and D14C statistics are expressed in per mil (‰), which effectively causes increases by a factor of 1,000 in the magnitudes of the respective differences in the (13C/12C) and the (14C/12C) atom ratios of air samples and their respective standards relative to those standards, with a similar magnification of the slopes associated with plots of these relative differences. This 1,000 factor magnification likely has led persons to falsely conclude that most or all of the increase in CO₂ since 1800 has been due to the use of fossil fuels.
- Large changes in the d13C statistic make very little change in the ratio R_{S13} of (13C/12C) atoms in C(t), and the steep slopes of values of the d13C statistic in plots bear no practical significance to the increase in the anthropogenic-fossil component in the atmosphere from 1750 to 2020.
- The sensitivities of the d13C, D14C, and S(t) statistics for the detection of an increase of 1 ppm in the anthropogenic-fossil component are, respectively, -0.0214‰ per ppm, -3.4063‰ per ppm, and -0.0468 dpm/gC per ppm. A value of -3‰ per ppm for D14C is reported by NOAA^[17] for 2010. The relative sensitivity of S(t)/d13C is 2.19 dpm/gC per ‰ of d13C. The relative sensitivity of D14C/S(t) is 72.8‰ per dpm/gC of S(t) and that for D14C/d13C is 159‰ per ‰ of d13C, which are the same values calculated in Figure 1.4 from the slopes of the plots of D14C, d13C, and S(t) versus the time t.
- Projected quantities in 2020 for the atmospheric components of the total mole fraction C(t) of 411.36 ppm at Niwot Ridge are: 48.11 ppm for the anthropogenic-fossil component, $C_F(t)$, and 363.25 ppm for the non fossil component, $C_{NF}(t)$, which equals the sum of 280 ppm in 1750 and the annual change, $DC_{NF}(t)$, of +83.25 ppm in the non fossil component from inputs of CO₂ into the atmosphere from its exchange reservoirs. We believe the value of $DC_{NF}(t)$ is dominated by net releases of CO₂ from the oceans as a result of the temperature increases in recent years caused by the increased solar radiation^[18], which the earth is currently experiencing.
- In 2012, if the value of the fossil component, C_F(t), were assumed to represent 30% of the total CO₂, instead of the actual value of 9.51%, then the d13C* value would have had to have been -12.8‰. This d13C* value of -12.8‰ for C(t) is much lower than the current d13C value of -8.5‰ listed in Table 1 for 2020, and it negates claims and inferences that most of the CO₂ added to the atmosphere over the past 200 years or so has been the anthropogenic-fossil component.
- Based on the 130 year time conflict for the beginning in 1930 of the release of significant anthropogenic-fossil-based carbon to the atmosphere and the beginning of significant increases of CO₂ in 1800, it is concluded that the increases of atmospheric CO₂ after 1800 must have been due primarily to increasing net inputs, DC_{NF}(t), of non fossil CO₂ from the oceans due to temperature increases, not fossil CO₂ from the burning of fossil fuels.
- Values of the anthropogenic-fossil and non fossil components of CO₂ are needed for verifying past and current models used for predicting anthropogenic climate change and global warming as well as for making timely choices for sources of heating, electric power generation, and transportation. The assumption that most or all of the increase in CO₂ since 1800 has been from the use of fossil fuels since 1750 is not settled science. If it were assumed to be settled science, then concerns might trigger very costly drastic actions to curb the use of fossil fuels in vehicles and power plants, which would be misdirected, presently unnecessary, and completely ineffective in curbing global warming.

4. References

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Tables and Figures

	Α	В	С	D	E	F	G	Н	I	J	К	L	М	N	0	Р	Q
1		Table 1. Niwot Ridge annual mean CO ₂ quantities for changes in the d13C and D14C statistics															
2																	
3		C(0) =	280	ppm.	S(0) =	16.33	dpm/gC.	A	t. Wt. 13C =	13.0034	g/mole. A	t. Wt. 12C =	12	g/mole.	*		
4		$K_{std13} = U.U11237 (13U/12U) Talio. K_{std14} = 1.1/bE-12 (14U/12U) Talio. (5) 013U = -U.U2bb^TC - 1.318. (6) F_{13} = (0.975/(1+0.001*d13C))^{-}.$ 7) Sample P = (1+0.001*d13C)*P = (1-0.001*b14C)*P = (E *E = (4) E = EVD/(1/b/2)/E720)*(200 +1) for t upper ofter 17E0.															
5	(7) Samp	(1) Sample $n_{S13} = (1 + 0.001 + 0.1001 + 0.101 + 0.011 + 0$															
6	(8) AB13,	% 13C = 100)*R _{S13} /(1+R _{S13})	. (9) AB12,	% 12C = 100	/(1+R _{S13}).			(11) k =	1.385E+12	*(AB12)/(At.	Wt. C) in units of	dpm/gC per ι	init ratio of	14C/12C	•	
8	Year	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15}	(16)
9	of	Time t	C(t)	D14C	F _d	d13C	F ₁₃	R ₅₁₃	AB13	AB12	At. Wt. C	k	R ₅₁₄	S(t)	C _F (t)	C _{NF} (t)	DC _{NF} (t)
10	Mean	(v)	(mgg)	(‰)	factor	(‰)	factor	(13C/12C)	(%)	(%)	(g/mole)	(See Ea. 11)	(14C/12C)	(dpm/gC)	(maa)	(maa)	(maa)
11	2004	254	377.97	64.61	0.9935	-8.074	0.9662	0.01115	1.1023	98.8977	12.0111	1.140E+13	1.304E-12	14.88	27.39	350.58	70.58
12	2005	255	380.63	58.21	0.9934	-8.101	0.9662	0.01115	1.1023	98.8977	12.0111	1.140E+13	1.297E-12	14.79	29.23	351.41	71.41
13	2006	256	382.96	55.57	0.9932	-8.128	0.9663	0.01115	1.1023	98.8977	12.0111	1.140E+13	1.293E-12	14.75	29.98	352.99	72.99
14	2007	257	383.90	50.91	0.9931	-8.154	0.9663	0.01115	1.1023	98.8977	12.0111	1.140E+13	1.288E-12	14.69	31.33	352.57	72.57
15	2008	258	386.60	46.93	0.9930	-8.181	0.9664	0.01115	1.1022	98.8978	12.0111	1.140E+13	1.283E-12	14.63	32.49	354.10	74.10
16	2009	259	388.14	43.22	0.9929	-8.207	0.9664	0.01114	1.1022	98.8978	12.0111	1.140E+13	1.279E-12	14.58	33.58	354.56	74.56
17	2010	260	390.51	38.88	0.9928	-8.234	0.9665	0.01114	1.1022	98.8978	12.0111	1.140E+13	1.273E-12	14.52	34.87	355.64	75.64
18	2011	261	393.13	33.77	0.9926	-8.261	0.9665	0.01114	1.1021	98.8979	12.0111	1.140E+13	1.267E-12	14.45	36.41	356.72	76.72
19	2012	262	394.83	29.99	0.9925	-8.287	0.9666	0.01114	1.1021	98.8979	12.0111	1.140E+13	1.263E-12	14.40	37.55	357.28	77.28
20		Average:	386.52	46.90	0.9930	-8.181	0.9664	0.01115	1.1022	98.8978	12.0111	1.140E+13	1.283E-12	14.63	32.54	353.98	73.98
21	Row	19/Row 11:	1.045	0.464	0.999	1.026	1.000	1.000	1.000	1.000	1.000	1.000	0.968	0.968	1.371	1.019	1.095
22	Relative	% Change:	4.46	-53.59	-0.10	2.64	0.04	-0.02	-0.02	0.00	0.00	0.00	-3.20	-3.20	37.11	1.91	9.50
23	Row 2	19 - Row 11:	16.86	-34.63	0.00	-2.13E-01	4.15E-04	-2.39E-06	-2.34E-04	2.34E-04	-2.35E-06	2.920E+07	-4.174E-14	-0.48	10.16	6.70	6.70
24	1750	0	280	-	-	-6.5	0.9631	0.01116	1.1041	98.8959	12.0111	1.140E+13	-	16.33	0	280	0
25	2020	270	411.36	-3.696	0.9916	-8.5	0.9670	0.01114	1.1019	98.8981	12.0111	1.140E+13	1.222E-12	13.94	48.11	363.25	83.25
26	Row 2	25 - Row 24:	131.36	-	-	-2.00E+00	3.89E-03	-2.25E-05	-2.20E-03	2.20E-03	-2.21E-05	2.74E+08	-	-2.39	48.11	83.25	83.25
27	Relative	% Change:	46.91	-	-	30.77	0.40	-0.20	-0.20	0.00	0.00	0.00	-	-14.66	-	29.73	-
29	Notes: T	he heading	s of columns	are numb	ered (1) th	rough (16),	and some of	f these numl	bers are list	ted with the	equations at t	he top of the tab	le and in Figu	re 1.4. Lett	er design	ations for c	olumns
30	and number designations for rows are used to describe the locations of data in this table. Abbreviations and symbols for all quantities are defined in section 2.1 along with equations for quantities																
31	not show	vn in the ta	ble. The calc	ulations in	the table a	account for	changes in t	he values of	d13C and	of D14C from	n one year to t	he next. Solid ver	rtical lines are	used to se	parate co	lumns of d	ata relating
32	to chang	ges in only t	he d13C stat	istic or in c	only the D1	4C statistic	as indicated	below. Inpu	ıt data at tl	ne top of the	table are high	nlighted in yellow	. The table co	ntains calc	ulations o	of annual m	ean values
33	of CO ₂ q	uantities in	2004 throug	gh 2012 in 1	respectively	y row 11 th	rough row 1	9 at the Niw	ot Ridge, C	olorado obs	ervatory of NC	DAA, and in 1750	and 2020 in, r	espectively	, row 24	and row 25	5. In rows
34	11 through 19 for, respectively, 2004 through 2012, the input annual mean C(t) and D14C values in respectively columns C and D are those calculated from a file ^[8] provided by NOAA. which are used														h are used		
35	to calcul	ate all quar	ntities in colu	imns M thr	ough Q. Va	alues for C(t) and D14C	for 2020 are	based on I	inear extrap	olations using	equations listed	for, respective	ely, plot (2)	and plot	(3) in Figur	e 1.4.
36	Values f	or the d13C	statistic exp	ressed in p	er mil by t	he symbol 🤅	‰ are calcul	ated by an e	quation: d	13C = -0.026	6 t - 1.318. Pa	rameter values fo	or this equatio	n have bee	n estima	ted from a	plot in a
37	file prov	ided by NO	AA for ice co	re measure	ements in A	Antarctica. I	or 2004 thr	ough 2012, a	average val	ues of quant	ities are listed	l in row 20. Ratio	s of values for	quantities	in 2012 t	o those in	2004 are
38	listed in	row 21. Re	lative % char	nges of qua	ntities fron	n 2004 to 2	012 are liste	d in row 22.	Values in 2	2012 minus v	alues in 2004	are listed in row	23. Values of	quantities l	isted for	1750 and 2	020 are
39	calculate	ed from d13	BC values of,	respective	ly, -6.5‰ a	nd -8.5‰ e	stimated fro	om the plot p	provided by	/ NOAA. Qua	ntities in row	24 through row 2	7 apply only t	o these d1	3C values	and only f	or
40	quantiti	es in colum	ns G through	i column L.	Quantities	in 2020 mi	nus those in	1750 are lis	ted in row	26. Relative	% changes of	quantites in 2020	from those in	n 1750 are	listed in r	ow 27. Pro	vided there
41	is an uno	derlying rela	ationship, e.	g. an equat	ion, betwe	en a statist	ic and the ar	nthropogenio	c-fossil com	nponent, C _F (t	;), the slope of	a plot of that sta	itistic versus C	C _F (t) repres	ents its se	ensitivity fo	r the
42	detectio	n of 1 ppm	of C _F (t); othe	erwise, any	apparent	correlation	in the plot n	nay just be c	oincidenta	l. The S(t) sta	tistic is calcul	ated from the D1	4C statistic an	d both stat	istics hav	e equation	s relating
43	them to	C _F (t). There	e is no such r	elationship	between o	d13C and C _I	(t). Based o	n the assum	ption there	are relation	ships of each	statistic with C _F (t)), the sensitivi	ties of d13	C, S(t), an	d D14C are	e given as
44	follows.	The sensitiv	vity of S(t) in	Figure 1.2	is -0.0468	dpm/gC pe	r ppm of C _F (1	:). The sensit	ivity of d13	BC in Figure 1	L.1 is -0.0214%	‰ per ppm of C _F (t	:). The sensitiv	ity of D140	C in Figure	e 1.3 is -3.4	063‰ per
45	ppm of (ppm of C _r (t). A value of -3‰ per ppm is reported by NOAA ^[15] . The ratio of the slope of one statistic to that of another statistic represents their relative sensitivities for the detection of increases in													eases in		
40	the anthropogenic fossil component. The relative sensitivity of S(t)/d13C in Figure 1.2 is 2.19 dpm/gC per % of d13C. In Figure 1.3, the relative sensitivity of D14C/S(t) is 72.8% per dpm/gC and that																
47	for D14C/d13C is 159, which are the same values listed in Figure 1.4 calculated from the slopes of the plots of D14C, d13C, and S(t) versus the time t since 1750.																
49																	
50	17																
51									-								
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The blue trend line in the figure is obtained from an equation for an approximation fitting function for the eighteen input specific activities, S(t). This equation is used to estimate the annual mean expected specific activities, S(t), listed here and in Table 3 in 2004 through 2020 for the Niwot Ridge site. The S(t) values for each year are used in Table 3 along with the initial total mole fraction, C(0), of 280 ppm and its expected specific, <S(0), of 16.33 dpm/gC in 1750 in the estimation of the expected anthropogenic fossil mole fractions, $<C_F(t)$, present each year after 1750, the assumed start of the industrial revolution and burning of fossil fuels. *The second through the eighth S(t) values in this table are estimates chosen to yield a fit that would not deviate significantly from the points for other input S(t) values in the table and plot, most importantly our chosen value, S(0), of 16.33 dpm/gC in year 1750 and the value of 14.91 dpm/gC for S(254 y) in 2004. Except for our chosen S(0) value, these input S(t) values and others in 2005 through 2012 have been calculated from the same linear fit equation in Figure 1.4 given: S(t) = y = -0.0579 x + 29.574. **The input S(t) value for 2020 is set equal to the expected <S(t)> value. The eighteen points and the blue line in the figure provide a realistic representation of the expected initial small decreases and later more significant decreases in the specific activities expected after the start of the industrial revolution in 1750 and the increased burning of fossil fuels each year. The origin of the value chosen for S(0) is discussed in another document of work in progress by the authors^[1].

Table 3. Niwot Ridge $\langle S(t) \rangle$, $\langle C_F(t) \rangle$, and $100 \langle C_F(t) \rangle / C(0)$



The solid blue trend line in this Figure 3 is obtained from the equation for the approximation fitting function listed in Figure 2 from the eighteen input S(t) values in Table 2, which are shown as solid points for plots of all quantities in the figure above. The equation is used to estimate the expected specific activities, $\langle S(t) \rangle$, in this table in 1750 through 2020. The expected anthropogenic mole fractions, $\langle C_F(t) \rangle$, in the table are calculated by the equation: $\langle C_F(t) \rangle = [(S(0)/\langle S(t) \rangle) - 1]C(0)]$ listed in sections 2.1.2 and 2.2. The initial values in 1750 for the total mole fraction, C(0), of 280 ppm and its specific activity, S(0), of 16.33 dpm/gC are listed at the top of the table. The value of 100 times the ratio of $\langle C_F(t) \rangle/C(0)$ are listed in the last column above. See discussion below Table 2 and Figure 2 for the process used to obtain the equation for the approximation fitting function.