AGU PUBLICATIONS

Geophysical Research Letters

RESEARCH LETTER
10.1002/2015GL066921

Measurements and modeling of contemporary radiocarbon in the stratosphere

A. M. Kanu[1,2], L. L. Comfort[1], T. P. Guilderson[3], P. J. Cameron-Smith[2], D. J. Bergmann[2], E. L. Atlas[4], S. Schauffler[5], and K. A. Boering[1,6]

[1]Department of Chemistry, University of California, Berkeley, California, USA, [2]Atmospheric, Earth and Energy Division, Lawrence Livermore National Laboratory, Livermore, California, USA, [3]Center for Accelerator Mass Spectrometry, Lawrence Livermore National Laboratory, Livermore, California, USA, [4]Department of Atmospheric Sciences, University of Miami, Miami, Florida, USA, [5]Atmospheric Chemistry Observations and Modeling Laboratory, National Center for Atmospheric Research, Boulder, Colorado, USA, [6]Department of Earth and Planetary Science, University of California, Berkeley, California, USA

Key Points:
- Stratospheric ^{14}C is governed by cosmogenic production, transport, and stratosphere-troposphere exchange
- Global annual mean ^{14}C production rate and net flux to the troposphere are determined empirically
- ^{14}C is a sensitive tracer of stratospheric transport and residence times

Supporting Information:
- Tables S1 and S2

Correspondence to:
K. A. Boering,
boering@berkeley.edu

Citation:
Kanu, A. M., L. L. Comfort, T. P. Guilderson, P. J. Cameron-Smith, D. J. Bergmann, E. L. Atlas, S. Schauffler, and K. A. Boering (2016), Measurements and modeling of contemporary radiocarbon in the stratosphere, *Geophys. Res. Lett.*, *43*, 1399–1406, doi:10.1002/2015GL066921.

Received 6 NOV 2015
Accepted 27 JAN 2016
Accepted article online 29 JAN 2016
Published online 13 FEB 2016

Abstract Measurements of the ^{14}C content of carbon dioxide in air collected by high-altitude balloon flights in 2003–2005 reveal the contemporary radiocarbon distribution in the northern midlatitude stratosphere, four decades after the Limited Test Ban Treaty restricted atmospheric testing of nuclear weapons. Comparisons with results from a 3-D chemical-transport model show that the $^{14}CO_2$ distribution is now largely governed by the altitude/latitude dependence of the natural cosmogenic production rate, stratospheric transport, and propagation into the stratosphere of the decreasing radiocarbon trend in tropospheric CO_2 due to fossil fuel combustion. From the observed correlation of $^{14}CO_2$ with N_2O mixing ratios, an annual global mean net flux of $^{14}CO_2$ to the troposphere of $1.6(\pm0.4)\times10^{17}$‰ mol CO_2 yr^{-1} and a global production rate of $2.2(\pm0.6)\times10^{26}$ atoms ^{14}C yr^{-1} are empirically derived. The results also indicate that contemporary $^{14}CO_2$ observations provide highly sensitive diagnostics for stratospheric transport and residence times in models.

1. Introduction

Carbon-14 is produced in the stratosphere and upper troposphere by nuclear reactions of atmospheric nitrogen with thermal neutrons produced naturally by cosmic rays and by atmospheric nuclear weapons testing primarily in the 1950s and 1960s. The radiocarbon atoms are then rapidly (<3 months) oxidized to CO and then CO_2, an inert gas which circulates throughout the stratosphere and troposphere; at Earth's surface $^{14}CO_2$ can enter the oceanic and terrestrial carbon reservoirs. Because its production and redistribution in the Earth system are unlike any other gas, $^{14}CO_2$ is a unique geophysical and biogeochemical tracer. For example, measurements of the decay of the bomb radiocarbon signal yielded insight into the stratospheric circulation that is independent of chemistry occurring there [e.g., *Hall and Waugh*, 2000; *Jackman et al.*, 1991; *Johnston*, 1989; *Kinnison et al.*, 1994; *Park et al.*, 1999; *Prather and Remsberg*, 1993], unlike most other tracers. Likewise, its partitioning between the atmosphere, oceans, soils, plants, and other carbon reservoirs, as well as its absence in fossil fuel-derived CO_2 [*Suess*, 1955], has been used to quantify the inventories, residence times, and gross fluxes of carbon in and between these reservoirs [e.g., *Braziunas et al.*, 1995; *Broecker and Peng*, 1994; *Caldeira et al.*, 1998; *Guilderson et al.*, 2000; *Levin et al.*, 2003; *Randerson et al.*, 2002; *Trumbore*, 2000]. However, only 14 measurements of stratospheric $^{14}CO_2$ [*Nakamura et al.*, 1994] have been made since 1974—that is, since the atmospheric circulation has purged the stratosphere of the large amounts of ^{14}C originally deposited there by nuclear weapons testing. Moreover, no stratospheric radiocarbon data sets have yet included simultaneous measurements of other long-lived tracers, which has hampered interpretation and comparison with global-scale models by exploiting the correlations between long-lived tracers [e.g., *Boering et al.*, 1996; *Plumb*, 2007; *Plumb and Ko*, 1992]. Despite the promise outlined by, e.g., *Johnston* [1989] and *Levin and Hesshaimer* [2000], this lack of data (and unwarranted lack of confidence in the stratospheric bomb era $^{14}CO_2$ data [*Hesshaimer and Levin*, 2000]) has limited the use of $^{14}CO_2$ as a stratospheric tracer, as well as for assessment of models of the cosmogenic ^{14}C production rate and transport to the troposphere needed for carbon cycle studies. The latter assessments are particularly needed now that the natural cosmogenic production rate and the rates and details of radiocarbon transport to the troposphere are playing an increasingly important role relative to the bomb radiocarbon input in studies of surface radiocarbon and its redistribution there [e.g., *Graven et al.*, 2012a; *Levin et al.*, 2010; *Randerson et al.*, 2002] and the use of atmospheric observations to infer regional anthropogenic emissions [e.g., *Graven et al.*, 2012b; *Levin et al.*, 2010; *Randerson et al.*, 2002; *Riley et al.*, 2008].

Here we present measurements of stratospheric $^{14}CO_2$ from whole air samples collected by high-altitude balloon flights in 2003–2005 for which measurements of other long-lived tracers were also made, including nitrous oxide (N_2O). We use these new measurements and comparisons with a 3-D global chemical transport model to (1) show current levels of $^{14}CO_2$ in the middle and lower stratosphere and the dominant processes controlling its distribution and variations, (2) empirically estimate the annual global mean net flux of stratospheric radiocarbon to the troposphere and the global radiocarbon production rate, and (3) demonstrate that $^{14}CO_2$ observations can be used as a sensitive diagnostic for stratospheric transport and residence times in models.

2. Methods

A cryogenic whole air sampler (CWAS) [*Froidevaux et al.*, 2006; *Lueb et al.*, 1975] was flown by high-altitude balloons launched from Fort Sumner, New Mexico (34.47°N, 104.24°W) on 5 October 2003, 29 September 2004, and 1 October 2005. The CWAS consists of a manifold of 26 electropolished, 800 mL stainless steel canisters, which are immersed in liquid neon to serve as a cryopump when each motor-driven canister valve is actuated. Airflow into the canisters was monitored by pressure changes in the manifold, and the canisters were filled to pressures of 1690–2140 kPa (1 psi = 6895 Pa). Samples were collected between 15.3 and 33.3 km altitude. The mixing ratios (mole fractions) of a number of trace gases in the canisters were then measured at the University of Miami or National Center for Atmospheric Research, including N_2O and CH_4 using an HP5890 II+ series GC and NIST-traceable standards to precisions of 0.1% and 0.3%, respectively. Aliquots of a total of 59 samples from these three flights were transferred to 1.6 L electropolished stainless steel canisters and shipped to UC Berkeley, where the CO_2 in the samples was cryogenically collected and purified using a series of five traps immersed in LN_2 and/or LN_2/ethanol slushes at -75°C, and then flame-sealed in glass ampoules. Samples were subsequently split into two or three aliquots of 20 to 30 micromoles of CO_2 each for separate analyses of radiocarbon and, for some samples, $\delta^{13}C$, $\delta^{17}O$, and $\delta^{18}O$. For the ^{14}C analyses, using methods similar to *Graven et al.* [2012a], the CO_2 samples were graphitized and then analyzed by accelerator mass spectrometry. Measurements are reported as $\Delta^{14}C$ for geochemical samples [*Stuiver and Polach*, 1977] (corrected assuming $\delta^{13}C$ of -8‰ V-PBD) with a precision of 2‰ (1σ) or better.

To gain a global perspective on the measurements, $^{14}CO_2$ and N_2O were simulated using the Lawrence Livermore National Laboratory's (LLNL) 3-D global chemical-transport model IMPACT (Integrated Massively Parallel Atmospheric Chemical Transport). IMPACT is based on an operator-split method of emissions, advection, diffusion, deposition, convection, gravitational settling, photolysis, and chemistry, and can be run using either input meteorological fields from a general circulation model (GCM) or assimilated data [*Rotman et al.*, 2004]. Unless otherwise noted, all the model results reported here were generated using (1) meteorological data from the MACCM3 climate model at 4° × 5° latitude-longitude horizontal resolution, with 52 levels in the vertical from the ground to 0.006 mbar; meteorological data for the period 1 January to 31 December 1997 were used for every model year [*Rotman et al.*, 2004]; (2) cosmogenic radiocarbon production rates as a function of latitude, longitude, and altitude from the formulation of *Koch and Rind* [1998], based in turn on *Lal and Peters* [1967] and *Lingenfelter* [1963], interpolated bilinearly onto the IMPACT grid; and (3) prescribed surface boundary conditions for $\Delta^{14}C$ of CO_2 from a linear fit to observations at La Jolla, CA (32.87°N, 117.25° W) from June 1992 to February 2007 [*Graven et al.*, 2012a], for CO_2 mixing ratios from an average [*Boering et al.*, 1996] of observations at Mauna Loa and American Samoa from July 1976 to March 2010 from the Global Monitoring Division of NOAA's Earth System Research Laboratory (http://www.esrl.noaa.gov/gmd/ccgg/), and for N_2O mixing ratios from mean surface observations from 20°S to 20°N from 1977 to 2007 from the World Data Center for Greenhouse Gases (http://ds.data.jma.go.jp/gmd/wdcgg/). For simulating stratospheric N_2O, three reactions were included: $N_2O + h\nu \rightarrow N_2 + O(^1D)$, $N_2O + O(^1D) \rightarrow N_2 + O_2$, and $N_2O + O(^1D) \rightarrow 2NO$. The model was run from 1962 to 2012, which includes 20 years of spin-up needed for the model atmosphere to lose memory of the initial model conditions chosen.

To test the sensitivity of modeled $\Delta^{14}C$ of CO_2 to solar cycle variations in the ^{14}C production rate, an upper limit was estimated here by assuming that the largest local variation in the solar-cycle-dependent ^{14}C production rate of 10% [*Jockel et al.*, 1999] is applicable globally and then modulating the 3-D production rates with a sinusoid of amplitude 10% and periodicity of 11 years. Finally, to test the sensitivity of $\Delta^{14}C$ of CO_2 to meteorology, we also used meteorological fields from the FVCCM (Finite Volume Community Climate Model) and FVDAS (Finite Volume Data Assimilation System) at 4×5 horizontal resolution with 28 levels in the vertical from the ground to 0.656 mbar for 1 July 1999 to 30 June 2000 [e.g., *Schoeberl et al.*, 2003] in separate model runs. The MACCM3, FVCCM, and FVDAS meteorologies used here are known to have significant differences in their residual circulations and, hence, result in significant differences in stratospheric mean ages of air [e.g., *Schoeberl et al.*, 2003].

3. Results and Discussion

Vertical profiles of $\Delta^{14}C$ of CO_2 and of N_2O are shown in Figures 1a and 1b. In general, values for $\Delta^{14}C$ increase with altitude, as expected for a long-lived tracer with a stratospheric source and tropospheric sink, with a leveling off at ~24 km and above. The main excursions away from this trend with altitude observed at 34°N for any given balloon flight are consistent with filaments of air from higher or lower latitudes moving into the balloon flight path. For example, in 2003, older, photochemically aged air from higher latitudes with much lower values of N_2O was sampled between 19 and 22 km, with correspondingly higher values of $\Delta^{14}C$. This interpretation is consistent with the model results, which show large variations in $\Delta^{14}C$ with latitude for a given altitude, with older air at higher latitudes having significantly larger $\Delta^{14}C$ values (Figure 1a). Similarly, in 2004, the profiles are influenced by higher-latitude air with higher $\Delta^{14}C$/lower N_2O values up to ~22 km and then again above 28 km; and in 2005, higher $\Delta^{14}C$/lower N_2O air from higher latitudes is apparent at ~24 km, while lower $\Delta^{14}C$/higher N_2O air from lower latitudes is apparent above ~28 km. Indeed, the variability due to these filaments is largely smoothed out by plotting $\Delta^{14}C$ versus N_2O (Figure 1c) in which the data follow a tighter relationship, as expected when two tracers that are long-lived with respect to quasi-horizontal transport and mixing are plotted against each other [e.g., *Plumb*, 2007; *Plumb and Ko*, 1992]. In these $\Delta^{14}C:N_2O$ scatterplots, $\Delta^{14}C$ increases as N_2O decreases down to ~200 ppb (nmol/mol) and then levels off for $N_2O < 200$ ppb. In other words, $\Delta^{14}C$ increases with increasing mean age up to a mean age of roughly 4 years [*Boering et al.*, 1996] and then levels off. The model results predict a small decrease in $\Delta^{14}C$ (<5‰) for this higher-altitude extratropical air, although the filaments of air influencing the balloon profiles make it difficult to test this particular model prediction.

After considering the impact of filaments of air from higher or lower latitudes, the next identifiable influence on the stratospheric $^{14}CO_2$ profiles and their correlation with N_2O from year to year is the propagation of the trend in $\Delta^{14}C$ of tropospheric CO_2 into the stratosphere. $\Delta^{14}C$ of tropospheric CO_2 is decreasing by 7 to 12‰ yr^{-1} [e.g., *Graven et al.*, 2012a; *Levin et al.*, 2010], due solely since 1990 to the burning of fossil fuel [*Levin et al.*, 2010], which, because of its age, has no ^{14}C [*Suess*, 1955]. Thus, in general, $\Delta^{14}C$ of stratospheric CO_2 is lower in 2004 than 2003 and lower in 2005 than 2004. Although the filaments of older or younger air from higher or lower latitudes, respectively, make a precise determination of the difference from year to year due to the tropospheric trend difficult, the decreases of ~10‰ and 7‰ between 2003 and 2004 and between 2004 and 2005, respectively (calculated as the differences between linear fits to the 2003–2005 data for N_2O between 120 and 200 ppb) are consistent with observed tropospheric trends and with model predictions of a 5‰ decrease at 34°N. Decreases of ~5 to 7‰ between 2004 and 2005 are also apparent in Figure 2, which shows $\Delta^{14}C$ versus N_2O for $250 < N_2O < 320$ ppb and are similar to IMPACT model predictions of 5‰ decreases at these lower altitudes. Comparison of these measurements with $^{14}CO_2$ measured on 14 samples collected by balloon over Japan in September 1989 and July 1990 [*Nakamura et al.*, 1992, 1994] show that these trends also extend to longer timescales, with average decreases of ~8 to 10‰ yr^{-1} between 1989/1990 and 2003–2005 for all samples collected above 21 km.

In addition to the propagation of the decreasing tropospheric trend and to differences due to regional and relatively small-scale filaments of air encountered in the balloon flights, it is also possible that variations in $\Delta^{14}C$ for the 2003–2005 data sets could arise from the time dependence of the radiocarbon production rates due to modulation of the cosmic ray flux by the 11 year cycle in solar activity [e.g., *Jockel et al.*, 2000]. Inputting an estimated upper limit to the solar cycle modulation (see section 2) into the model, however, resulted in much smaller variations in $\Delta^{14}C$ than either of the other two effects above—less than 2‰ for $250 < N_2O < 320$ ppb (not shown). While more realistic variations can be input into global models [e.g.,

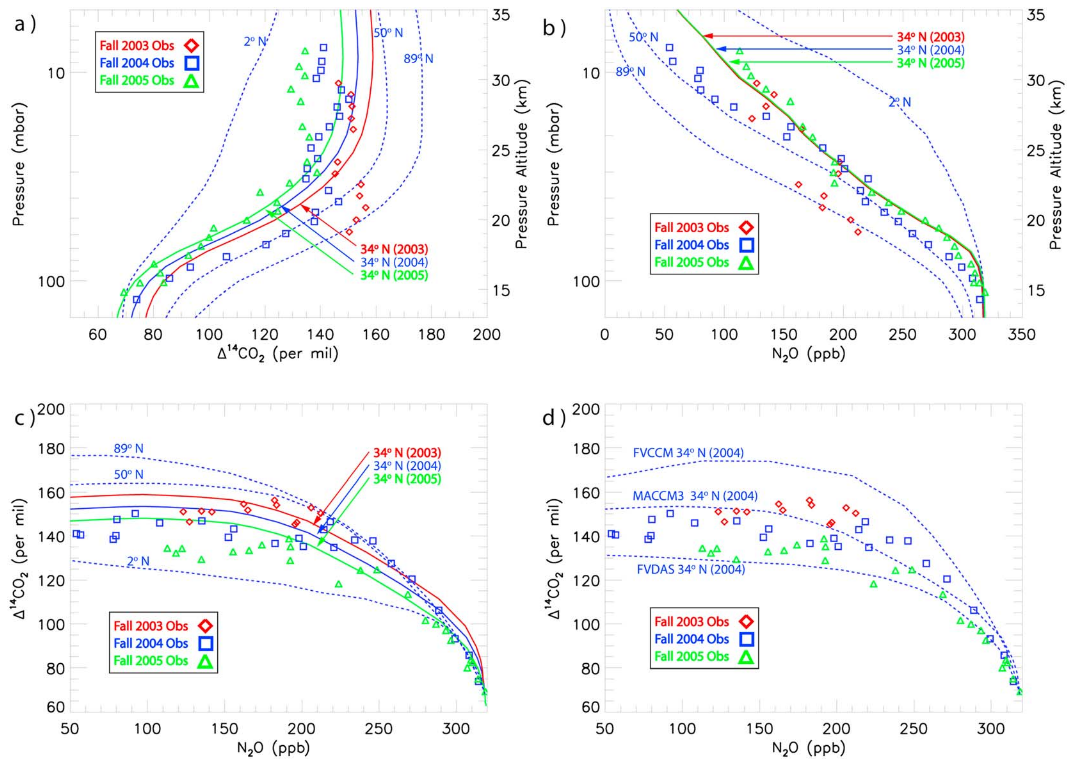

Figure 1. (a) $\Delta^{14}C$ of CO_2 and (b) N_2O versus pressure (mbar) and pressure altitude (km) for samples collected from the Cryogenic Whole Air Sampler (CWAS) at 34°N over Fort Sumner, NM (symbols) for single flights in 2003–2005, along with IMPACT model results using meteorological fields from MACCM3 for 34 N (solid lines, color coded by year) and at the additional latitudes indicated for 2004 (dashed lines). $\Delta^{14}C$ of CO_2 versus N_2O from the CWAS samples (symbols) along with model results for different latitudes (c) using MACCM3 and (d) using the FVDAS, MACCM3, FVCCM meteorologies at 34°N.

Jockel et al., 2000], we expect the year-to-year variation due to the solar cycle between 2003 and 2005 to be only a small fraction of that due to propagation of the tropospheric trend and, to first order, can be neglected.

Importantly, the correlation of $\Delta^{14}C$ with N_2O also allows empirical estimates of (1) the global net isoflux between the stratosphere and troposphere and (2) the global $\Delta^{14}C$ production rate to be made. *Plumb and Ko* [1992] showed that the slope of the compact relationship between two tracers that are in slope equilibrium (that is, are long-lived with respect to vertical and quasi-horizontal transport) is equal to the ratio of their net vertical fluxes. Since N_2O is destroyed only in the stratosphere, the global net vertical flux of N_2O is simply the global N_2O loss rate, known independently to be 4.50×10^{11}(±25%) mol N_2O yr^{-1} [*Minschwaner et al*., 1993; *Prather and Ehhalt*, 2001]. Thus, the global net vertical flux for other species of interest can be estimated from the value of the slope of their correlations with N_2O, an approach used previously to estimate global cross-tropopause fluxes of O_3 [*McLinden et al*., 2000; *Murphy and Fahey*, 1994], nitrogen oxides [*Murphy and Fahey*, 1994; *Olsen et al*., 2001], meteoritic material [*Cziczo et al*., 2001], and N_2O and CO_2 isotopologues [*Luz et al*., 1999; *Park et al*., 2004]; since air is returning to the troposphere from the lower stratosphere, observations for N_2O mixing ratios >250 ppb are generally used.

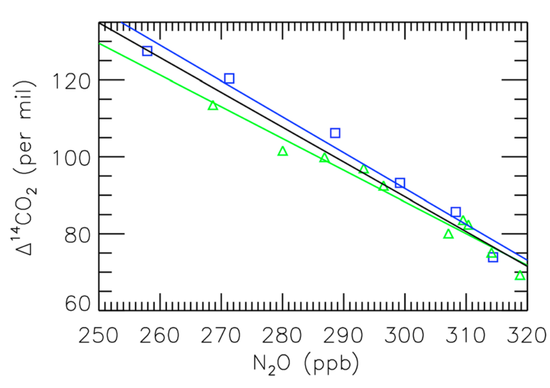

Figure 2. $\Delta^{14}C$ versus N_2O for $N_2O > 250$ ppb (nmol/mol) for the data in Figure 1; also shown are the Williamson-York bivariate fits [*Cantrell*, 2008] for 2004 (blue line; $m = -0.93 \pm 0.07$), 2005 (green line; $m = -0.82 \pm 0.06$), and the combined 2004/2005 data set (black line; $m = -0.90 \pm 0.05$), yielding a global ^{14}C production rate of 2.30, 2.04, and 2.24×10^{26} atoms yr^{-1}, respectively, with uncertainties of ±30% (1σ), using equation (2).

Table 1. Comparison of Global ^{14}C Production Rates

Global Mean ^{14}C Production Rate (10^{26} atoms ^{14}C yr^{-1})	Time Period	Solar Max, Solar Min Production Rate (10^{26} atoms ^{14}C yr^{-1})	Study
2.2 (±0.6)	~2002–2005 (mid-Solar Cycle 23)	--	This work (Empirically-derived from $^{14}C:N_2O$ observations)[a]
1.8–2.4[b]	--	2.1, 2.4[c]	This work (Derived from IMPACT model results for ^{14}C and N_2O)[a]
2.33	--	--	This work (Global mean production rate in the IMPACT model)[d]
4.0(±0.8)	1867–1963	3.3, 4.2	*Lingenfelter* [1963] (calculated)
2.9			*Suess* [1965] (^{14}C inventory)
3.7(±0.4)	1964–1976	3.1, 4.2	*Light et al.* [1973] (calculated)
3.2			*Damon et al.* [1978] (^{14}C inventory)
2.9		2.6, 3.1	*O' Brien* [1979] (calculated)
3.3(±0.3)	1953–1995	2.7–3.9	*Masarik and Beer* [1999] (calculated)
2.96 or 3.68[e]	1989–2001	~2.2, 3.5 or 2.4, 4.3	*Lowe and Allan* [2002] (calculated)
2.1			*Levin et al.* [2010] (^{14}C inventory)
2.64	1951–2010	1.8, 3.5	*Kovaltsov et al.* [2012] (calculated)

[a]Using the relationship between ^{14}C and N_2O in the lower stratosphere (see text).
[b]Including model results for 34° and 50°N.
[c]Estimate of upper (2.2 + 10%) and lower (2.2 − 5%) limit to Plumb and Ko-based method using IMPACT model results with a 10% solar cycle variation in ^{14}C production rate everywhere extrapolating from the empirical production rate from 2004/2005.
[d]Total ^{14}C content in the atmosphere in the IMPACT model after 1 year with the planetary boundary layer sink turned off, using the *Koch and Rind* [1998] implementation of ^{14}C rates from *Lal and Peters* [1967].
[e]Value depends on the functional form of the relationship between the solar modulation parameter, Φ, and the ^{14}C yield.

Indeed, model results in Figure 1c show that we expect that the $\Delta^{14}C:N_2O$ relationship is quite compact and nearly global for $N_2O > 250$ ppb (except for the deep tropics) and hence that the Plumb and Ko approach for $N_2O > 250$ ppb is likely to provide a reasonable approximation for the stratospheric radiocarbon production rate. From the data in Figure 2, we can estimate a global net vertical $\Delta^{14}C$ flux between the stratosphere and troposphere using equation (1), based on *Luz et al.* [1999] and *Park et al.* [2004]:

$$\text{Global Net } \Delta^{14}\text{C flux} = MF_{air}[CO_2]_{strat}\left[m\cdot\left(-\frac{(L+G_{strat})}{MF_{air}}\right)+\Delta^{14}C_{trop}\right] - MF_{air}[CO_2]_{trop}\left[\Delta^{14}C_{trop}\right] \quad (1)$$

where MF_{air} is the air mass flux between the stratosphere and troposphere in mol air yr^{-1}; $[CO_2]_{trop}$ and $[CO_2]_{strat}$ are the CO_2 mixing ratios for air entering and leaving the stratosphere, respectively; m is the slope of the stratospheric $\Delta^{14}C$: N_2O correlation for N_2O >250 ppb, L is the global loss and G_{strat} is the net stratospheric growth rate of N_2O (4.5×10^{11} and 1.10×10^{10} mol N_2O yr^{-1}, respectively), and $\Delta^{14}C_{trop}$ is the tropospheric $\Delta^{14}C$ value in per mil. Furthermore, since $[CO_2]_{strat} = [CO_2]_{trop}$ to within 1%, equation (1) simplifies to equation (2).

$$\text{Global Net } \Delta^{14}\text{C flux} = [CO_2](m[-(L+G_{strat})]) \quad (2)$$

Using air mass fluxes from *Appenzeller et al.* [1996] or *Holton* [1990] and corresponding CO_2 mixing ratios in equation (1) or simply using equation (2) yields a global net $\Delta^{14}C$ flux of 1.6×10^{17}‰ mol CO_2 yr^{-1} (±30%, 1σ); see Table S1 in the supporting information. (Note that large differences in assumed air mass fluxes largely cancel out in isotope flux calculations [e.g., *Luz et al.*, 1999].)

Next, we note that the annually averaged global net vertical $\Delta^{14}C$ flux from equation (1) or (2) is equivalent to the annually averaged stratospheric ^{14}C production rate. Assuming a stratospheric-to-total ^{14}C production ratio of 0.5 [*Masarik and Beer*, 1999] and multiplying by Avogadro's number, the Modern Standard ratio of mass 14 to mass 12 abundances of carbon (1.176×10^{-12}) and 0.001 to convert from per mil to ^{14}C atoms yields a global ^{14}C production rate of $2.2\pm0.6\times10^{26}$ atoms ^{14}C yr^{-1}. This is the first completely empirical estimate of the global annual mean ^{14}C production rate that does not rely on estimates of reservoir sizes and exchange rates. It falls at the low end of the range in estimates from previous studies (Table 1), independently continuing the general downward trend of all the estimates. It is also lower than recent calculations by *Kovaltsov et al.* [2012] using updated galactic cosmic ray energy spectra for α particles and heavier nuclei which they assert explains the reduction relative to the many earlier calculations. Our stated 1σ uncertainty of 30% includes summing the uncertainties in the N_2O loss rate (25%) and the Williamson-York iterative bivariate fit [*Cantrell*, 2008] to the $^{14}CO_2$:N_2O correlation (~5%), as well as considering small differences between using the 2004, 2005, or the combined data set (Table S1), or using a lower cutoff of 250 versus 280 ppb N_2O. Not included are possible systematic errors that could result from assuming that (1) the Plumb and Ko method is globally applicable based on midlatitude measurements, (2) the stratospheric-to-total ^{14}C production ratio is 0.5, and (3) the loss of stratospheric ^{14}CO to the troposphere before oxidation to $^{14}CO_2$ is small. For (1), we believe that the Plumb and Ko method is reasonably sound since the global production rate in the IMPACT model can be retrieved using the modeled $^{14}CO_2$:N_2O correlations (but with some uncertainty due to sparse model points for $N_2O > 250$ ppb); see Table 1. For (2), if the true stratospheric-to-total production ratio is as high as 0.65 [*Masarik and Beer*, 1999], our estimated global ^{14}C production rate would be even lower by 20%. For (3), we used ^{14}CO observations from 1993 [*Brenninkmeijer et al.*, 1995] to estimate a conservative upper bound for a low bias in our global ^{14}C production rate due to ^{14}CO loss to the troposphere of $<5\%$. In addition, we note that sunspot number was a maximum in 2001 and a minimum in 2008 [*Gray et al*., 2010]; thus, the 2004 and 2005 data likely represent midsolar cycle ^{14}C production rates, integrated over the midlatitude stratospheric age spectrum for $N_2O > 250$ ppb (with a mean age ≤ 2 years [*Andrews et al*., 2001]). Our simplified solar cycle model results suggest an upper limit less than ~10% higher and a lower limit ~5% lower than the production rate estimated from the 2004/2005 observations (Table 1). Given that the uncertainty in the N_2O loss rate is a constant systematic rather than random error, such a solar cycle variation may be detectable from additional ^{14}C and N_2O measurements that span a solar cycle, while reduction in the N_2O loss rate uncertainty could narrow the overall uncertainty in the absolute global ^{14}C production rate.

Finally, Figure 1d shows that using different meteorological inputs in the same model yields very large differences in predicted $^{14}CO_2$ levels. The model results using MACCM3 meteorology simulate the $\Delta^{14}C$ observations well, and this meteorology is known to produce mean ages that are in generally good agreement with observations [e.g., *Strahan et al*., 2011]. In contrast, the FVCCM and FVDAS meteorologies used here are known [*Schoeberl et al*., 2003] to produce larger and smaller mean ages, respectively. The predicted $^{14}CO_2$ levels using these met fields also follow this order: too high for a residual circulation that is likely too slow and too low for a residual circulation that is too fast. These results demonstrate that contemporary radiocarbon measurements and their modeling provide important new constraints on stratospheric transport into, within, and out of the stratosphere and can serve as a sensitive new model diagnostic. Such constraints are greatly needed to accurately predict the timing of the recovery of the ozone layer as climate changes and to determine whether the stratospheric circulation is speeding up as the climate is warming. For example, a combination of mean age estimates from earlier tracer observations [*Engel et al*., 2009; *Stiller et al*., 2012] suggests that there has been no change in mean age over the past 30 years (at least at altitudes of 25–30 km at midlatitudes and to within the uncertainties), while models suggest it should have decreased significantly due to both ozone depletion and radiative forcing [e.g., *Butchart et al*., 2010; *Li et al*., 2012] and there appear to have been significant increases in tropical upwelling [*Kawatani and Hamilton*, 2013; *Randel et al*., 2006]. If tropical upwelling has increased but mean ages have not, then to reconcile both there must be a faster circulation in the lower stratosphere than in the middle stratosphere (and/or more air recirculating back into the tropics via the lower stratosphere or the upper troposphere) [e.g., *Bonisch et al*., 2011]. Stratospheric radiocarbon, which is expected to be a tracer of stratospheric residence times [e.g., *Hall and Waugh*, 2000], may best test these features of the stratospheric circulation and how they may be changing over time and whether models are capturing the most important circulation features (and their sensitivity to climate) or not. Validation of stratospheric $\Delta^{14}C$ levels and reliable fluxes of $\Delta^{14}C$ to the troposphere in models will also reduce uncertainties in carbon cycle studies that aim to partition radiocarbon signals at the surface between the atmosphere, oceans, terrestrial biosphere and human influences such as fossil fuel burning for which a higher temporal and spatial resolution of flux to the troposphere is needed beyond the annual mean estimate we provide here.

4. Conclusions

Measurements of radiocarbon ($\Delta^{14}C$ of CO_2) and N_2O mixing ratios from 59 whole air samples collected in 2003–2005 between 15 and 33 km at ~34°N, and their comparison with model simulations using a 3-D

CTM, show that contemporary stratospheric radiocarbon levels are governed by cosmogenic production and stratospheric transport, as well as by propagation of the decreasing $\Delta^{14}C$ trend in tropospheric CO_2. From the correlation of $\Delta^{14}C$ of CO_2 with N_2O, coupled with independent knowledge of the N_2O loss rate, the global net vertical ^{14}C isoflux to the troposphere and the global production rate were empirically estimated for 2004–2005, with the global production rate falling at the low end of estimates and calculations from previous studies. In addition to the entirely empirical net isoflux and global production rate for ^{14}C useful for carbon cycle studies, our work indicates that stratospheric $^{14}CO_2$ can provide new diagnostics for mean ages and residence times in stratospheric models.

Acknowledgments

We thank Rich Lueb and Roger Hendershot for development and deployment of the Cryosampler and X. Zhu and L. Pope for laboratory assistance. We gratefully acknowledge support from NASA UARP (NNX13AH10G and NNX09AJ95G to K.A.B. and NNX13AH20G and NNX12AH02G to E.L.A.); UC Lab Fees LF-09-118804 to K.A.B. and P.C.S.; UC IGPP/LLNL 07-GS-019 to K.A.B. and T.G; NOAA Climate Program Office (NA05OAR4311166 to T.G.), and to the Lawrence Scholar's Program for A.K.; portions of this work were performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory (W-7405-Eng-48 and DE-AC52-07NA27344 by A.K., T.G., P.C., and D.B.).
All measurements are available in the supporting information.

References

Andrews, A. E., et al. (2001), Mean ages of stratospheric air derived from in situ observations of CO_2, CH_4, and N_2O, *J. Geophys. Res.*, *106*(D23), 32,295–32,314, doi:10.1029/2001JD000465.

Appenzeller, C., J. R. Holton, and K. H. Rosenlof (1996), Seasonal variation of mass transport across the tropopause, *J. Geophys. Res.*, *101*(D10), 15,071–15,078, doi:10.1029/96JD00821.

Boering, K. A., S. C. Wofsy, B. C. Daube, H. R. Schneider, M. Loewenstein, and J. R. Podolske (1996), Stratospheric mean ages and transport rates from observations of carbon dioxide and nitrous oxide, *Science*, *274*(5291), 1340–1343, doi:10.1126/science.274.5291.1340.

Bonisch, H., A. Engel, T. Birner, P. Hoor, D. W. Tarasick, and E. A. Ray (2011), On the structural changes in the Brewer-Dobson circulation after 2000, *Atmos. Chem. Phys.*, *11*(8), 3937–3948, doi:10.5194/acp-11-3937-2011.

Braziunas, T. F., I. Y. Fung, and M. Stuiver (1995), The preindustrial atmospheric $^{14}CO_2$ latitudinal gradient as related to exchanges among atmospheric, oceanic, and terrestrial reservoirs, *Global Biogeochem. Cycles*, *9*, 565–584, doi:10.1029/95GB01725.

Brenninkmeijer, C. A. M., D. C. Lowe, M. R. Manning, R. J. Sparks, and P. F. J. van Velthoven (1995), The ^{13}C, ^{14}C, and ^{18}O isotopic composition of CO, CH_4, and CO_2 in the higher southern latitudes lower stratosphere, *J. Geophys. Res.*, *100*(D12), 26,163–26,172, doi:10.1029/95JD02528.

Broecker, W. S., and T. H. Peng (1994), Stratospheric contribution to the global bomb radiocarbon inventory: Model versus observation, *Global Biogeochem. Cycles*, *8*(3), 377–384, doi:10.1029/94GB00680.

Butchart, N., et al. (2010), Chemistry-climate model simulations of twenty-first century stratospheric climate and circulation changes, *J. Clim.*, *23*(20), 5349–5374, doi:10.1175/2010JCLI3404.1.

Caldeira, K., G. H. Rau, and P. B. Duffy (1998), Predicted net efflux of radiocarbon from the ocean and increase in atmospheric radiocarbon content, *Geophys. Res. Lett.*, *25*(20), 3811–3814, doi:10.1029/1998GL900010.

Cantrell, C. A. (2008), Technical note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, *Atmos. Chem. Phys.*, *8*(17), 5477–5487, doi:10.5194/acp-8-5477-2008.

Cziczo, D. J., D. S. Thomson, and D. M. Murphy (2001), Ablation, flux, and atmospheric implications of meteors inferred from stratospheric aerosol, *Science*, *291*(5509), 1772–1775, doi:10.1126/science.1057737.

Damon, P. E., J. C. Lerman, and A. Long (1978), Temporal fluctuations of atmospheric ^{14}C: Causal factors and implications, *Annu. Rev. Earth Planet. Sci.*, *6*(1), 457–494, doi:10.1146/annurev.ea.06.050178.002325.

Engel, A., et al. (2009), Age of stratospheric air unchanged within uncertainties over the past 30 years, *Nat. Geosci.*, *2*(1), 28–31, doi:10.1038/ngeo388.

Froidevaux, L., et al. (2006), Early validation analyses of atmospheric profiles from EOS MLS on the Aura satellite, *IEEE Trans. Geosci. Remote Sens.*, *44*(5), 1106–1121, doi:10.1109/TGRS.2006.864366.

Graven, H. D., T. P. Guilderson, and R. F. Keeling (2012a), Observations of radiocarbon in CO_2 at La Jolla, California, USA 1992–2007: Analysis of the long-term trend, *J. Geophys. Res.*, *117*, D02302, doi:10.1029/2011JD016533.

Graven, H. D., T. P. Guilderson, and R. F. Keeling (2012b), Observations of radiocarbon in CO_2 at seven global sampling sites in the Scripps flask network: Analysis of spatial gradients and seasonal cycles, *J. Geophys. Res.*, *117*, D02303, doi:10.1029/2011JD016535.

Gray, L. J., et al. (2010), Solar influences on climate, *Rev. Geophys.*, *48*, RG4001, doi:10.1029/2009RG000282.

Guilderson, T. P., K. Caldeira, and P. B. Duffy (2000), Radiocarbon as a diagnostic tracer in ocean and carbon cycle modeling, *Global Biogeochem. Cycles*, *14*(3), 887–902, doi:10.1029/1999GB001192.

Hall, T. M., and D. W. Waugh (2000), Stratospheric residence time and its relationship to mean age, *J. Geophys. Res.*, *105*(D5), 6773–6782, doi:10.1029/1999JD901096.

Hesshaimer, V., and I. Levin (2000), Revision of the stratospheric bomb $^{14}CO_2$ inventory, *J. Geophys. Res.*, *105*(D9), 11,641–11,658, doi:10.1029/1999JD901134.

Holton, J. R. (1990), On the global exchange of mass between the stratosphere and the troposphere, *J. Atmos. Sci.*, *47*, 392–395, doi:10.1175/1520-0469(1990)047<0392:OTGEOM>2.0.CO;2.

Jackman, C. H., A. R. Douglass, K. F. Brueske, and S. A. Klein (1991), The influence of dynamics on two-dimensional model results: Simulations of ^{14}C and stratospheric aircraft NO_x injections, *J. Geophys. Res.*, *96*, 22,559–22,572, doi:10.1029/91JD02510.

Jockel, P., M. G. Lawrence, and C. A. M. Brenninkmeijer (1999), Simulations of cosmogenic ^{14}CO using the three-dimensional atmospheric model MATCH: Effects of ^{14}C production distribution and the solar cycle, *J. Geophys. Res.*, *104*(D9), 11,733–11,743, doi:10.1029/1999JD900061.

Jockel, P., C. A. M. Brenninkmeijer, and M. G. Lawrence (2000), Atmospheric response time of cosmogenic ^{14}CO to changes in solar activity, *J. Geophys. Res.*, *105*(D5), 6737–6744, doi:10.1029/1999JD901140.

Johnston, H. S. (1989), Evaluation of excess carbon 14 and strontium 90 data for suitability to test two-dimensional stratospheric models, *J. Geophys. Res.*, *94*(D15), 18,485–18,493, doi:10.1029/JD094iD15p18485.

Kawatani, Y., and K. Hamilton (2013), Weakened stratospheric quasibiennial oscillation driven by increased tropical mean upwelling, *Nature*, *497*(7450), 478–481, doi:10.1038/nature12140.

Kinnison, D. E., H. S. Johnston, and D. J. Wuebbles (1994), Model study of atmospheric transport using carbon 14 and strontium 90 as inert tracers, *J. Geophys. Res.*, *99*(D10), 20,647–20,664, doi:10.1029/94JD01822.

Koch, D., and D. Rind (1998), Beryllium 10/beryllium 7 as a tracer of stratospheric transport, *J. Geophys. Res.*, *103*(D4), 3907–3917, doi:10.1029/97JD03117.

Kovaltsov, G. A., A. Mishev, and I. G. Usoskin (2012), A new model of cosmogenic production of radiocarbon 14C in the atmosphere, *Earth Planet. Sci. Lett.*, *337*, 114–120, doi:10.1016/j.epsl.2012.05.036.

Lal, D., and B. Peters (1967), Cosmic Ray produced radioactivity on the Earth, in *Kosmische Strahlung II/Cosmic Rays II*, edited by K. Sitte, pp. 551–612 , Springer, Berlin Heidelberg.

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

Levin, I., B. Kromer, M. Schmidt, and H. Sartorius (2003), A novel approach for independent budgeting of fossil fuel CO_2 over Europe by $^{14}CO_2$ observations, *Geophys. Res. Lett.*, *30*(23), 2194, doi:10.1029/2003GL018477.

Levin, I., T. Naegler, B. Kromer, M. Diehl, R. J. Francey, A. J. Gomez-Pelaez, L. P. Steele, D. Wagenbach, R. Weller, and D. E. Worthy (2010), Observations and modelling of the global distribution and long-term trend of atmospheric 14CO(2), *Tellus Ser. B-Chem. Phys. Meteorol.*, *62*(1), 26–46, doi:10.1111/j.1600-0889.2009.00446.x.

Li, F., D. W. Waugh, A. R. Douglass, P. A. Newman, S. E. Strahan, J. Ma, J. E. Nielsen, and Q. Liang (2012), Long-term changes in stratospheric age spectra in the 21st century in the Goddard Earth Observing System Chemistry-Climate Model (GEOSCCM), *J. Geophys. Res.*, *117*, D20119, doi:10.1029/2012JD017905.

Light, E. S., M. Merker, H. J. Verschell, R. B. Mendell, and S. A. Korff (1973), Time dependent worldwide distribution of atmospheric neutrons and of their products: 2 Calculation, *J. Geophys. Res.*, *78*(16), 2741–2762, doi:10.1029/JA078i016p02741.

Lingenfelter, R. E. (1963), Production of carbon 14 by cosmic-ray neutrons, *Revi. Geophys.*, *1*(1), 35–55, doi:10.1029/RG001i001p00035.

Lowe, D. C., and W. Allan (2002), A simple procedure for evaluating global cosmogenic C-14 production in the atmosphere using neutron monitor data, *Radiocarbon*, *44*(1), 149–157.

Lueb, R. A., D. H. Ehhalt, and L. E. Heidt (1975), Balloon-borne low temperature air sampler, *Rev. Sci. Instrum.*, *46*(6), 702–705, doi:10.1063/1.1134292.

Luz, B., E. Barkan, M. L. Bender, M. H. Thiemens, and K. A. Boering (1999), Triple-isotope composition of atmospheric oxygen as a tracer of biosphere productivity, *Nature*, *400*(6744), 547–550, doi:10.1038/22987.

Masarik, J., and J. Beer (1999), Simulation of particle fluxes and cosmogenic nuclide production in the Earth's atmosphere, *J. Geophys. Res.*, *104*(D10), 12,099–12,111, doi:10.1029/1998JD200091.

McLinden, C. A., S. C. Olsen, B. Hannegan, O. Wild, M. J. Prather, and J. Sundet (2000), Stratospheric ozone in 3-D models: A simple chemistry and the cross-tropopause flux, *J. Geophys. Res.*, *105*(D11), 14,653–14,665, doi:10.1029/2000JD900124.

Minschwaner, K., R. J. Salawitch, and M. B. McElroy (1993), Absorption of solar radiation by O_2: Implications for O_3 and lifetimes of N_2O, $CFCl_3$, and CF_2Cl_2, *J. Geophys. Res.*, *98*(D6), 10,543–510,561, doi:10.1029/93JD00223.

Murphy, D. M., and D. W. Fahey (1994), An estimate of the flux of stratospheric reactive nitrogen and ozone into the troposphere, *J. Geophys. Res.*, *99*(D3), 5325–5332, doi:10.1029/93JD03558.

Nakamura, T., T. Nakazawa, N. Nakai, H. Kitagawa, H. Honda, T. Itoh, T. Machida, and E. Matsumoto (1992), Measurement of C-14 concentration of stratospheric CO_2 by accelerator mass spectrometry, *Radiocarbon*, *34*(3), 745–752.

Nakamura, T., T. Nakazawa, H. Honda, H. Kitagawa, T. Machida, A. Ikeda, and E. Matsumoto (1994), Seasonal variation in C-14 concentrations of stratospheric CO_2 measured with accelerator mass spectrometry, *Nucl. Instrum. Methods Phys. Res*, *92*(1–4), 413–416, doi:10.1016/0168-583x(94)96045-3.

O'Brien, K. (1979), Secular variations in the production of cosmogenic isotopes in the Earth's atmosphere, *J. Geophys. Res.*, *84*(A2), 423–431, doi:10.1029/JA084iA02p00423.

Olsen, S. C., C. A. McLinden, and M. J. Prather (2001), Stratospheric N_2O-NO_y system: Testing uncertainties in a 3-dimensional framework, *J. Geophys. Res.*, *106*(D23), 28,771–28,784, doi:10.1029/2001JD000559.

Park, J., M. K. W. Ko, C. H. Jackman, R. A. Plumb, and K. H. Sage (1999), Report of the 1998 Models and Measurements II Workshop, *NASA Ref. Publ.*, *NASA/TM-1999-209554*.

Park, S., E. L. Atlas, and K. A. Boering (2004), Measurements of N_2O isotopologues in the stratosphere: Influence of transport on the apparent enrichment factors and the isotopologue fluxes to the troposphere, *J. Geophys. Res.*, *109*, D01305, doi:10.1029/2003JD003731.

Plumb, R. A. (2007), Tracer interrelationships in the stratosphere, *Rev. Geophys.*, *45*, RG4005, doi:10.1029/2005RG000179.

Plumb, R. A., and M. K. W. Ko (1992), Interrelationships between mixing ratios of long-lived stratospheric constituents, *J. Geophys. Res.*, *97*, 10,145–10,156, doi:10.1029/92JD00450.

Prather, M. J., and D. H. Ehhalt (2001), Atmospheric chemistry and greenhouse gases, in *Climate Change 2001: The Scientific Basis, Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J. T. Houghton, Cambridge Univ. Press, Cambridge, U. K., and New York.

Prather, M. J., and E. Remsberg (1993), The atmospheric effects of stratospheric aircraft: Report of the 1992 Models and Measurements Workshop, NASA Ref. Publ. 1291.

Randel, W. J., F. Wu, H. Vomel, G. E. Nedoluha, and P. Forster (2006), Decreases in stratospheric water vapor after 2001: Links to changes in the tropical tropopause and the Brewer-Dobson circulation, *J. Geophys. Res.*, *111*, D12312, doi:10.1029/2005JD006744.

Randerson, J. T., I. G. Enting, E. A. G. Schuur, K. Caldeira, and I. Y. Fung (2002), Seasonal and latitudinal variability of troposphere Delta(CO2)-C-14: Post bomb contributions from fossil fuels, oceans, the stratosphere, and the terrestrial biosphere, *Global Biogeochem. Cycles*, *16*(4), 1112, doi:10.1029/2002GB001876.

Riley, W. J., D. Y. Hsueh, J. T. Randerson, M. L. Fischer, J. G. Hatch, D. E. Pataki, W. Wang, and M. L. Goulden (2008), Where do fossil fuel carbon dioxide emissions from California go? An analysis based on radiocarbon observations and an atmospheric transport model, *J. Geophys. Res.*, *113*, G04002, doi:10.1029/2007JG000625.

Rotman, D. A., et al. (2004), IMPACT, the LLNL 3-D global atmospheric chemical transport model for the combined troposphere and stratosphere: Model description and analysis of ozone and other trace gases, *J. Geophys. Res.*, *109*, D04303, doi:10.1029/2002JD003155.

Schoeberl, M. R., A. R. Douglass, Z. X. Zhu, and S. Pawson (2003), A comparison of the lower stratospheric age spectra derived from a general circulation model and two data assimilation systems, *J. Geophys. Res.*, *108*, 4113, doi:10.1029/2002JD002652.

Stiller, G. P., et al. (2012), Observed temporal evolution of global mean age of stratospheric air for the 2002 to 2010 period, *Atmos. Chem. Phys.*, *12*(7), 3311–3331, doi:10.5194/acp-12-3311-2012.

Strahan, S. E., et al. (2011), Using transport diagnostics to understand chemistry climate model ozone simulations, *J. Geophys. Res.*, *116*, D17302, doi:10.1029/2010JD015360.

Stuiver, M., and H. A. Polach (1977), Reporting of C-14 data—Discussion, *Radiocarbon*, *19*(3), 355–363.

Suess, H. E. (1955), Radiocarbon concentration in modern wood, *Science*, *122*, 415–417, doi:10.1126/science.122.3166.415-a.

Suess, H. E. (1965), Secular variations of cosmic-ray-produced carbon 14 in atmosphere and their interpretations, *J. Geophys. Res.*, *70*(23), 5937–5952, doi:10.1029/JZ070i023p05937.

Trumbore, S. (2000), Age of soil organic matter and soil respiration: Radiocarbon constraints on belowground C dynamics, *Ecol. Appl.*, *10*(2), 399–411, doi:10.1890/1051-0761(2000)010[0399:AOSOMA]2.0.CO;2.