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A SIMPLE PROCEDURE FOR EVALUATING GLOBAL COSMOGENIC ^{14}C PRODUCTION IN THE ATMOSPHERE USING NEUTRON MONITOR DATA

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ABSTRACT. Radiocarbon (^{14}C) produced by cosmogenic processes in the atmosphere reacts rapidly with atomic oxygen to form ^{14}CO. The primary sink for this species is oxidation by the OH radical, the single most important oxidation mechanism for pollutants in the atmosphere. Hence, knowledge of the spatial and temporal distribution of ^{14}CO allows important inferences to be made about atmospheric transport processes and the distribution of OH. Because the chemical lifetime of ^{14}CO against OH attack is relatively short, 1–3 months, its distribution in the atmosphere should show modulations due to changes in ^{14}C production caused by variations in the solar cycle. In this work we present a simple methodology to provide a time series of global ^{14}C production to help interpret time series of atmospheric ^{14}CO measurements covering the whole of solar cycle 23. We use data from neutron monitors, a readily available proxy for global ^{14}C production, and show that an existing 6-year time series of ^{14}CO data from Baring Head, New Zealand, tracks changes in global ^{14}C production at the onset of solar cycle 23.

INTRODUCTION

Radiocarbon (^{14}C) analyses have played a major role in the interpretation of many aspects of earth system science both as a tracer and in radiocarbon dating studies. In the field of atmospheric chemistry, ^{14}C has been successfully used as a tracer to reveal the source strengths of the significant carbon containing trace gases as well as the dynamics of some aspects of atmospheric transport.

Atmospheric methane derived from contemporary organic material contains ^{14}C, whereas methane obtained from fossil sources contains essentially none. Thus, ^{14}C analyses can be used to separate biogenic and fossil sources of methane, providing an estimate of its "fossil fraction" (Lowe et al. 1988; Wahlen et al. 1989). Analyses of ^{14}C in atmospheric CO_2 have been used to examine cross-tropopause exchange and other aspects of atmospheric transport (Broecker 1994; Manning et al. 1990) as well as the rate of CO_2 absorption in the oceans (Broecker et al. 1995). More recently, measurements of ^{14}C in atmospheric carbon monoxide (CO) have been used to estimate the removal rate of CO from the atmosphere (Brenninkmeijer et al. 1992; Mak et al. 1994; Mak and Southon 1998; Quay et al. 1999).

The principal sink for ^{14}CO is atmospheric oxidation to $^{14}CO_2$ by the hydroxyl radical (OH), with a relatively short chemical lifetime of about 1–1.5 months in the tropics and mid latitudes of the summer hemisphere. OH is produced throughout the atmosphere by the reaction of $O(^1D)$ with water vapor, and has a maximum in the troposphere where lower photolytic production of $O(^1D)$ is more than compensated for by high water vapor levels. Because this production rate is dependent on the photolysis rate of $O(^1D)$ generation, it varies seasonally and is expected to be the principal driver of seasonal cycles in the abundance of atmospheric ^{14}CO. The chemical lifetime of ^{14}CO is comparable to seasonal changes in the production of OH but much shorter than atmospheric transport processes such as cross-tropopause exchange and inter-hemispheric transport. Thus the distribution of ^{14}CO in the atmosphere will be a function of the OH distribution, atmospheric transport and ^{14}C production processes. Hence, assuming that ^{14}CO transport and production processes are well known, the measured distribution of ^{14}CO could be used to infer the distribution of OH in the atmosphere.

Knowledge of the atmosphere's OH distribution is critical to an understanding of oxidation processes in atmospheric chemistry. It is the most significant oxidant in the atmosphere, and is responsible for controlling the atmospheric burdens of many industrial and agricultural pollutants, includ-

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ing volatile organic hydrocarbons, methane, CO as well as SO_2 and NO_x, the precursors of acid rain (Jacob 1999; Spivakovsky et al. 2000). Changes in OH abundance thus directly affect the oxidizing power of the atmosphere and have a wide range of implications for air pollution, aerosol formation, greenhouse radiative forcing and stratospheric ozone depletion (Thompson 1992). However, measurements of OH abundance are very difficult because its concentration is low and variable ($0–10^7$ molecules cm^{-3}), and direct determination usually involves sophisticated optical techniques working at the lower limits of their detection ranges (Brauers et al. 2001).

The global seasonality and distribution of OH have been predicted using photochemical models (e.g. Spivakovsky et al. 2000). These have been tested using observations of several chemical tracers that are oxidized by OH and have well known source functions, namely CH_3CCl_3 (Prinn et al. 1995), C_2H_6, HCFC-22, CH_2Cl_2 and ^{14}CO (Spivakovsky et al. 2000). Initially, ^{14}CO was considered to be a very promising tracer because of its relatively short chemical lifetime against OH and its known source function. However, interpretation of ^{14}CO data has proved difficult because of complex atmospheric transport processes that are not well understood (Spivakovsky et al. 2000). In particular, because at least half of ^{14}CO is produced in the stratosphere, the effect of cross-tropopause transport is a major uncertainty (Holton et al. 1995).

However, recent work by Jöckel et al. (2000) shows that a filter function derived using a 3-D transport model (including OH oxidation of ^{14}CO) may be used to define the atmospheric response time of ^{14}CO to changes in the total cosmogenic ^{14}CO source strength. Thus, the latitude response time and atmospheric lifetime of ^{14}CO can provide a test of the model's transport properties, particularly cross-tropopause exchange. Their work also suggests that a time series of ^{14}CO measurements could serve as a test for changes in atmospheric composition, in particular OH.

Because the atmospheric reservoir of CO is very small compared to methane and CO_2 (about 20,000 times smaller than CO_2) and its atmospheric lifetime is also short, we expect CO to be the only significant carbon-containing trace gas to track solar-cycle-driven variations in global ^{14}C production. A time series of ^{14}CO measurements made at Baring Head, New Zealand (41°S) is currently in preparation. The series covers the period 1989–2001 and overlaps most of solar cycle 23. To model the ^{14}CO data and test hypotheses of atmospheric transport and OH distributions, we require a time series of the global ^{14}C production during the same solar cycle.

There is extensive scientific literature covering the production of cosmogenic ^{14}C. However, we have not found published work that allows us to compare a time series of atmospheric ^{14}CO measurements directly with an equivalent time series of global ^{14}C production through a complete solar cycle. The main aim of this work is to present a simple methodology to provide a time series of global ^{14}C production to help interpret time series of atmospheric ^{14}CO measurements. Lingenfelter (1963) employed the monthly mean sunspot number as a proxy for solar modulation of ^{14}C production. We prefer to use neutron monitor data, as this is a much more direct proxy for the production process. As shown below, these data are readily available and provide extensive coverage over several solar cycles. In this paper we use previously published work on ^{14}C production and data from ground based neutron monitor records as a basis for calculating an updated global ^{14}C production rate time series covering 1989–2001.

Production of ^{14}C

The interaction of cosmic ray particles with the earth's atmosphere produces a cascade of secondary particles including neutrons that react with ^{14}N to produce ^{14}C. Most of this ^{14}C (>90%) reacts immediately with oxygen to form ^{14}CO (MacKay et al. 1963).

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$$^{14}N\ (n,p)\ \Rightarrow\ ^{14}C \quad (1)$$

$$^{14}C\ +\ O_2\ \Rightarrow\ ^{14}CO\ +\ O \quad (2)$$

This is followed by reaction with OH that removes ^{14}CO and produces $^{14}CO_2$

$$^{14}CO + OH\ \Rightarrow\ ^{14}CO_2 + H \quad (3)$$

which is subsequently absorbed by both the biosphere ("modern carbon") and the oceans. Thus, knowledge of ^{14}C production in the atmosphere and its temporal and spatial variations are a prerequisite to using atmospheric ^{14}CO measurements to infer atmospheric OH distributions.

The production of ^{14}C in the atmosphere from the interaction of neutrons and ^{14}N was first suggested over 60 years ago. This early work has been summarized by Lingenfelter (1963), who used diffusion theory to derive a global production rate of ^{14}C of 2.50 ± 0.50 atoms cm^{-2} sec^{-1} over a series of 10 solar cycles. Since then, a large number of papers on ^{14}C production have appeared in the literature including summaries and subsequent work by O'Brien (1979), Castagnoli and Lal (1980), and Masarik and Reedy (1995), and a summary of ^{14}C production data for use in ^{14}CO modeling work by Jöckel et al. (1999).

Most of the cosmic rays interacting with earth's atmosphere originate from outside the solar system, and are termed "galactic" cosmic rays. They approach the solar system from all directions and are considered to be temporally and spatially isotropic (at least over time scales of decades to centuries) with an average flux constant to within 10% over the last few million years (Vogt et al. 1990). However, the solar magnetic field in the heliosphere (extending to at least 10^{10} km from the sun) deflects some cosmic ray particles away from the earth. Variations in solar plasma output modulate the magnetic field of the heliosphere and thus the penetration of cosmic rays to the earth's atmosphere. When the sun's activity is high, only the more energetic part of the cosmic ray spectrum gets through to the earth, and hence fewer neutrons and less ^{14}C are produced. During the quiet sun the opposite is true. Of particular interest for the ^{14}CO work reported here are modulations in incident cosmic ray flux caused by the current solar cycle 23.

Solar Modulation Parameter

To determine the amount of ^{14}C produced by neutrons derived from cosmic rays, the solar modulation parameter (Φ) is critical (e.g. Castagnoli and Lal 1980). This indicates how much energy a cosmic ray particle must have to avoid being deflected by the heliospheric magnetic field during its traverse to earth, and is expressed in MeV. Masarik and Beer (1999) and others calculated global production and latitudinal dependence of ^{14}C as a function of this parameter.

Monitors at various locations on the earth's surface are used to determine neutron flux. The flux measured depends on the physical geometry of the counter, its altitude and geomagnetic latitude, and correlates with the flux of neutrons generated in the cosmic ray cascade processes in the upper atmosphere, e.g. Masarik and Beer (1999). Neutrons generated by solar proton events are included in the measured neutron flux, and therefore contribute to the inferred ^{14}C production.

The basis of the work reported here is to use time series of neutron flux data from ground based neutron monitors to determine the corresponding time series of Φ. This is then used to calculate global ^{14}C production as mentioned above. Masarik and Beer (1999) calculated Φ from neutron measurements made at Deep River, a neutron monitor site in Canada.

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In Figure 1A, we plot their annual Φ data versus annual averages of concurrent Deep River neutron data for 1953–1995 obtained from the website ftp://ftp.ngdc.noaa.gov/STP/SOLAR_DATA/COSMIC_RAYS. There is an excellent correlation; $r^2 = 0.984$ for a quadratic least squares fit, excluding the 3 years 1990–1992, which are clearly outliers.

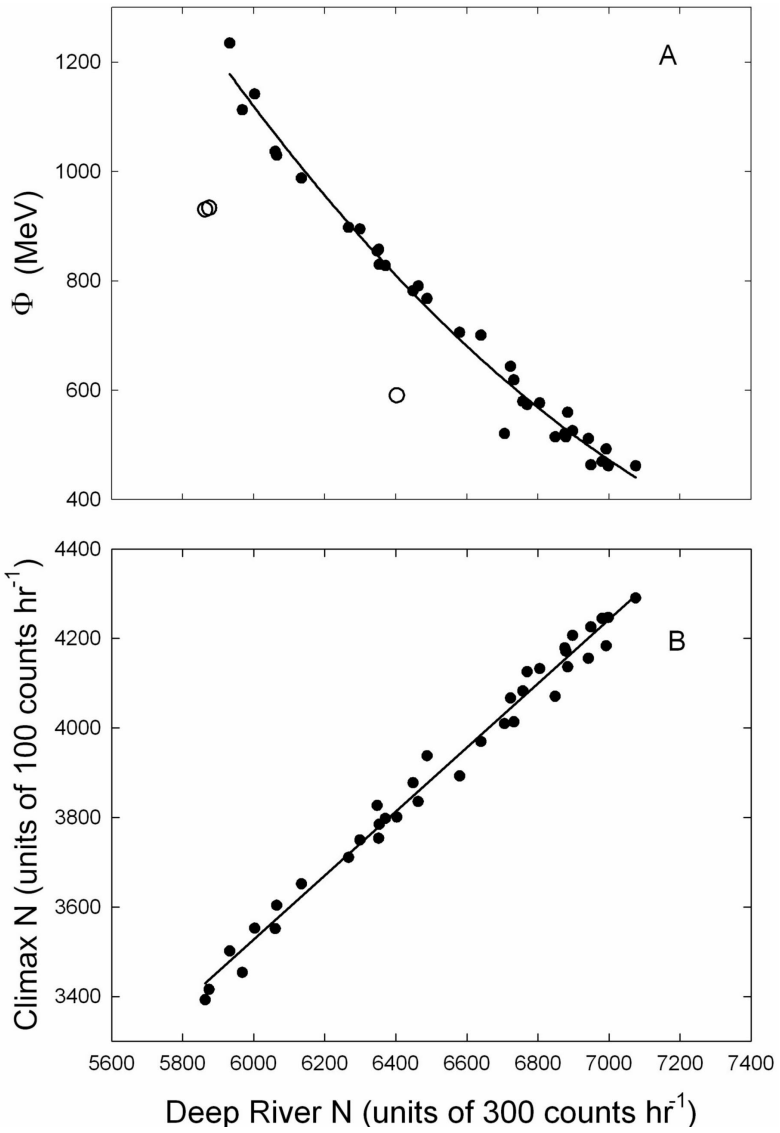

Figure 1 (A) Solar modulation parameter (Masarik and Beer 1999) versus Deep River neutron count rate. The full line is a quadratic least squares fit with $r^2 = 0.984$, excluding the points shown by open circles. (B) Climax neutron count rate versus Deep River neutron count rate. The full line is a linear least squares fit with $r^2 = 0.985$.

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To cover the complete solar cycle 23, and for future comparisons with ^{14}CO data, we need neutron data for the period 1989–2001. Unfortunately, the neutron monitor at Deep River was closed down in 1995. To bridge the gap we use neutron data from the Climax station in Colorado. Daily data updated each month are available from the website http://ulysses.uchicago.edu/NeutronMonitor. Because the two neutron monitor sites are at different altitudes and geomagnetic latitudes, and have counters with different geometries, we have tested the correlation of the data sets over the period 1958–1995. Figure 1B shows the comparison of Climax and Deep River neutron data for this period. The linear least squares fit shows excellent correlation ($r^2 = 0.985$) for the neutron measurements made at the two sites. Hence, we are justified in assigning yearly average Φ values derived from the Deep River neutron monitor record to corresponding yearly average Climax neutron monitor data. The resulting relationship for 1953–2000 is shown in Figure 2, excluding data for 1990–1992. It is well represented by the cubic least squares fitted function

$$\Phi = -22831 + 21.503\ N - 6.1312 \times 10^{-3}\ N^2 + 5.5673 \times 10^{-7}\ N^3 \qquad (4)$$

with $r^2 = 0.955$, N being the hourly Climax neutron count rate in units of 100 counts hr^{-1}.

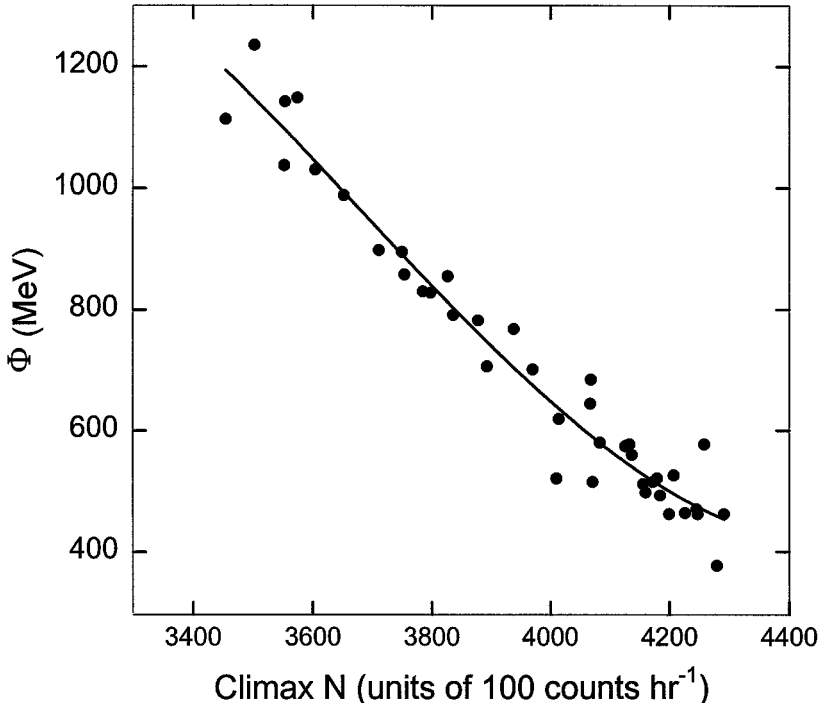

Figure 2 Solar modulation parameter Φ versus Climax neutron count rate. The full line is a cubic least squares fit with $r^2 = 0.955$. Data for the 3 years 1990–1992 have been excluded.

Global ^{14}C Production Rate

We take equation (4) to be a valid approximation to the general relationship between Φ and the Climax neutron count rate, so that we can use (4) to interpolate Φ values within the time period from which (4) is derived, and to extrapolate to times later than 1995. As an example, Figure 3A shows Φ versus time at two-weekly intervals over the period 1989–2001, generated from (4) using two-weekly means of the daily Climax neutron data.

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Masarik and Beer (1999) derived the following theoretically calculated relationship between global ^{14}C production rate P_g and Φ

$$P_g = 3.12 - 2.92 \times 10^{-3}\,\Phi + 2.01 \times 10^{-6}\,\Phi^2 - 6.45 \times 10^{-10}\,\Phi^3 \quad (5)$$

where P_g is in atoms $cm^{-2}\ sec^{-1}$ and Φ is in MeV. For comparison with Baring Head ^{14}CO data (see later), we require P_g at two-weekly intervals for the period 1989–2001. We therefore use the Φ values shown in Figure 3A to generate P_g values from (5) every two weeks, and the results are shown in Figure 3C. As expected, P_g shows an inverse relationship to the solar activity cycle, solar minimum occurring in mid-1996. Another more experimentally derived estimate for P_g is also plotted in Figure 3C using the following cubic function:

$$P_g = 4.03 - 4.67 \times 10^{-3}\,\Phi + 4.96 \times 10^{-6}\,\Phi^2 - 2.33 \times 10^{-9}\,\Phi^3 \quad (6)$$

This is derived from values for Φ = 0, 100, 450, and 1000 MeV for the present day geomagnetic field in Table 3 of Lal (1992). The two cubics show the same overall shape for ^{14}C production during the solar cycle but differ by about 0.6 atoms $cm^{-2}\ sec^{-1}$ during solar minimum. The large solar maximum fluctuations in P_g derived from (6) are artifacts of (6) being invalid for $\Phi > 1000$ MeV. The mean value of P_g from (5) over the 11 years 1990–2000 is 1.84 atoms $cm^{-2}\ sec^{-1}$, and the corresponding value from (6) is 2.28 atoms $cm^{-2}\ sec^{-1}$.

The 1996 solar minimum has a "flat-topped" maximum in neutron count rate and hence ^{14}C production rate. The next solar minimum should have a "peaked" maximum in neutron count rate, which may produce slightly different mean values of P_g. This occurs through the effect the 22-year solar magnetic field cycle (including a polarity reversal) has on cosmic ray transport in the heliosphere (Jokipii 1991).

Comparison ^{14}CO data are derived from measurements made on air samples collected at Baring Head during the period 1989–1994 (Moss et al. 1998), and are shown in Figure 3B. These data contain seasonal cycles with minima in summer and maxima in winter caused by annual variations in the mixing ratio of OH. To remove these cycles we place the original data into 26 bins per year, average them and use a spline routine to interpolate missing values. The resulting time series is then filtered using a 49-point smoother with a "Loess" fitting scheme (Cleveland et al. 1988) to remove the seasonal cycles and establish the secular trend in the original ^{14}CO data. This trend is shown in Figure 3C, and follows the ^{14}C trend closely. The ^{14}CO secular trend clearly shows the effect of changes in the solar cycle between 1989 and 1994, although the rapid variations in ^{14}C production near solar maximum (1990–1992) are not apparent in the smoothed ^{14}CO trend. This may be because the filter used to remove the OH seasonal cycles has also removed solar cycle variations with a similar period.

CONCLUSIONS

We have presented a simple procedure, based on the work of Masarik and Beer (1999), that generates time series of cosmogenic ^{14}C production from ground based neutron monitor data, for use in the analysis of measured ^{14}CO time series. A published 6-year record of ^{14}CO measured at Baring Head, New Zealand, clearly shows the effect of modulation of the cosmogenic production of ^{14}C by the solar cycle. Differences in the correlation between P_g and ^{14}CO concentrations will provide information on changes in the production of the atmospheric OH radical and/or changes in stratospheric/tropospheric exchange processes. A detailed assessment of the relationship between ^{14}C production and measured ^{14}CO, and the latter's potential to predict atmospheric OH trends, will require at least a full solar cycle of ^{14}CO data. This is beyond the scope of the present work, but such a study is currently in preparation.

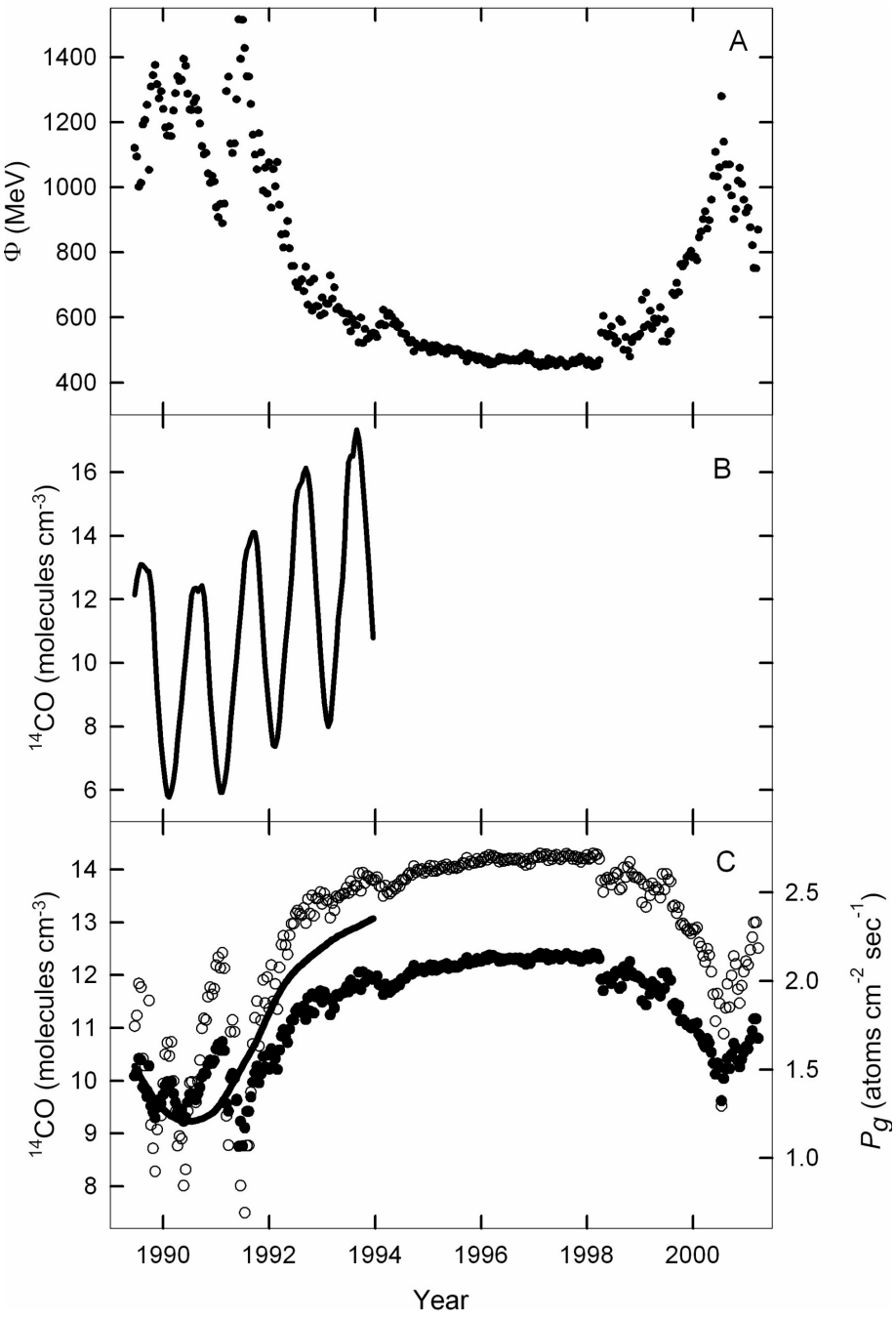

Figure 3 (A) Time variation of solar modulation parameter Φ using equation (4) evaluated at two-weekly intervals. The ordinate tick marks denote the beginning of the year. (B) Atmospheric ^{14}CO data from Baring Head, New Zealand, for the period 1989–1994, showing the effect of OH seasonal cycles. (C) Time variation of ^{14}C global production rate P_g using equation (5) (solid circles) and equation (6) (open circles). Also shown is the smoothed secular trend of ^{14}CO derived from the data in (B) by removing seasonal cycles (solid line).

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REFERENCES

Brauers T, Hausmann M, Bister A, Kraus A, Dorn HP. 2001. OH radicals in the boundary layer of the Atlantic Ocean 1. Measurements by long-path laser absorption spectroscopy. *Journal of Geophysical Research* 106:7399–414.

Brenninkmeijer CAM, Manning MR, Lowe DC, Wallace GW, Sparks RJ, Volz-Thomas A. 1992. Interhemispheric asymmetry in OH abundance inferred from measurements of atmospheric ^{14}CO. *Nature* 356:50–2.

Broecker WS. 1994. Stratospheric contribution to the global bomb radiocarbon inventory: Model versus observation. *Global Biogeochemical Cycles* 8:377–84.

Broecker WS, Sutherland S, Smethie W, Peng TS, Ostlund G. 1995. Oceanic radiocarbon: separation of the natural and bomb components. *Global Biogeochemical Cycles* 9:263–88.

Castagnoli G, Lal D. 1980. Solar modulation effects in terrestrial production of carbon-14. *Radiocarbon* 22(2):133–58.

Cleveland RB, Cleveland WS, McRae JE, Terpenning I. 1988. STL: a seasonal-trend decomposition procedure based on loess. *Journal of Official Statistics (Statistics Sweden)* 6:3–73.

Holton JR, Haynes PH, McIntyre ME, Douglass AR, Rood RB, Pfister L. 1995. Stratosphere-troposphere exchange. *Reviews of Geophysics* 33:403–39.

Jacob DJ. 1999. *Introduction to atmospheric chemistry.* Princeton: Princeton University Press.

Jöckel P, Brenninkmeijer CAM, Lawrence M. 2000. Atmospheric response time of cosmogenic ^{14}CO to changes in solar activity. *Journal of Geophysical Research* 105:6737–44.

Jöckel P, Lawrence MG, Brenninkmeijer CAM. 1999. Simulations of cosmogenic ^{14}CO using the three-dimensional model MATCH: effects of ^{14}C production distribution and the solar cycle. *Journal of Geophysical Research* 104:11,733–43.

Jokipii JR. 1991. Variations of the cosmic-ray flux with time. In: Sonett MS, Giampapa MS, Matthews MS, editors. *The sun in time.* Tucson: University of Arizona. p 205–220.

Lingenfelter RE. 1963. Production of carbon 14 by cosmic ray neutrons. *Reviews of Geophysics* 1: 35–55.

Lowe DC, Brenninkmeijer CAM, Manning MR, Sparks RJ, Wallace GW. 1988. Radiocarbon determination of atmospheric methane at Baring Head, New Zealand. *Nature* 372:522–5.

Lal D. 1992. Expected secular variation in the global terrestrial production rate of radiocarbon. In: Bard E, Broecker WS, editors. *The Last Deglaciation: absolute and radiocarbon chronologies.* NATO ASI series, Volume 12. Berlin: Springer-Verlag. p 113–26.

MacKay C, Pandow M, Wolfgang R. 1963. On the chemistry of natural radiocarbon. *Journal of Geophysical Research* 68:3929–31.

Mak JE, Brenninkmeijer CAM, Tamaresis J. 1994. Atmospheric ^{14}CO observations and their use in estimating carbon monoxide removal rates. *Journal of Geophysical Research* 99:22,915–22.

Mak JE, Southon JR. 1998. Assessment of tropical OH seasonality using atmospheric ^{14}CO measurements from Barbados. *Geophysical Research Letters* 25: 2801–4.

Manning MR, Lowe DC, Melhuish WH, Sparks RJ, Wallace GW, Brenninkmeijer CAM, McGill RC. 1990. The use of radiocarbon measurements in atmospheric studies. *Radiocarbon* 32(1):37–58.

Masarik J, Beer J. 1999. Simulation of particle fluxes and cosmogenic nuclide production in the Earth's atmosphere. *Journal of Geophysical Research* 104:12,099–111.

Masarik J, Reedy RC. 1995. Terrestrial cosmogenic-nuclide production systematics calculated from numerical simulations. *Earth and Planetary Science Letters* 136:381–95.

Moss R, Manning M, Lowe D, Ferretti D, Knobben R. 1998. Changes in atmospheric carbon monoxide in the Pacific region. In Clarkson TS, editor. *Workshop on the science of atmospheric trace gases, 1998.* NIWA Technical Report 15. Wellington, New Zealand. p 74–7.

O'Brien K. 1979. Secular variations in the prediction of cosmogenic isotopes in the earth's atmosphere. *Journal of Geophysical Research* 84:423–31.

Prinn RG, Weiss RF, Miller BR, Huang J, Alyea FN, Cunnold DM, Fraser PJ, Hartley DE, Simmonds PG. 1995. Atmospheric trends and lifetime of CH_3CCl_3 and global OH concentrations. *Science* 269:187–92.

Quay P, Stutsman J, Wilbur D, Snover A, Dlugokencky E, Brown T. 1999. The isotopic composition of atmospheric methane. *Global Biogeochemical Cycles* 13: 445–61.

Spivakovsky CM, Logan JA, Nontzka SA, Balkanski YJ, Foreman-Fowler M, Jones DBA, Horowitz LW, Fusco AC, Brenninkmeijer CAM, Prather MJ, Wofsy SC,

McElroy MB. 2000. Three-dimensional climatological distribution of tropospheric OH: update and evaluation. *Journal of Geophysical Research* 105:8931–80.

Thompson AM. 1992. The oxidizing capacity of the earth's atmosphere: probable past and future changes. *Science* 256: 1157–65.

Vogt S, Herzog GF, Reedy RC. 1990. Cosmogenic nuclides in extraterrestrial materials. *Reviews of Geophysics* 28:253–75.

Wahlen M, Tanaka N, Henry R, Deck B, Zeglen J, Vogel JS, Southon J, Shemesh A, Fairbanks A, Broecker W. 1989. Carbon-14 in methane sources and in atmospheric methane: The contribution from fossil carbon. *Science* 245:286–90.