ESTIMATING THE AMOUNT OF $^{14}$CO$_2$ IN THE ATMOSPHERE DURING THE HOLOCENE AND GLACIAL PERIODS

I Svetlik$^{1,2}$ • P P Povinec$^3$ • K Pachnerova Brabcova$^1$ • M Fejgl$^2$ • L Tomaskova$^1$ • K Turek$^1$

ABSTRACT. Radiocarbon has been used to define parameters for modeling past, recent, and future CO$_2$/carbon amounts in the atmosphere and in other environmental compartments. In the present paper, we estimate the amount of $^{14}$C in the atmosphere by calculating the molar activity of $^{14}$CO$_2$ (quantity of $^{14}$CO$_2$ molecules per mol of air). Data on the reconstruction of the past concentration of atmospheric CO$_2$ from Antarctic ice cores and $\Delta^{14}$C activities from the IntCal09 calibration curve were applied. The results obtained indicate that cosmogenic production had a dominant influence on the $^{14}$C amount in the atmosphere between 50 and 20 ka BP, when the CO$_2$ concentrations were relatively stable, with a slowly decreasing trend. The decreasing $^{14}$C activity ($\Delta^{14}$C) between 20 and 2 ka BP seems to be caused predominantly by a dilution of atmospheric $^{14}$CO$_2$ by input of CO$_2$ with a depleted amount of $^{14}$C (probably from deeper oceanic layers), which is evident from a comparison with the $\Delta^{14}$C and molar activity time series. A strong linear relation was found between the $^{14}$C activity and CO$_2$ concentration in the air for the period 20–2 ka BP, which confirms a dominant influence of atmospheric dilution of $^{14}$CO$_2$. The observed linear relation between the CO$_2$ and $\Delta^{14}$C levels persists even in the prevailing part of the Holocene. Likewise, the quantity of $^{14}$CO$_2$ in the atmosphere (calculated as molar activity) during the prevailing part of the deglacial period (20–11 ka BP) was surprisingly increasing, although a decreasing trend in the $^{14}$C cosmogenic production rate could be expected.

INTRODUCTION

The radioactive carbon isotope $^{14}$C originates naturally as a result of cosmic-ray interactions in the atmosphere. The $^{14}$C produced is subsequently oxidized to $^{14}$CO$_2$ and transferred from the atmosphere to other carbon sinks, especially to oceanic waters and terrestrial biota. The $^{14}$C or $^{14}$CO$_2$ can be released from both of these sinks back into the atmosphere. $^{14}$C can also be transferred to long-term sinks, e.g. peat bogs, swamps, organic compounds in soils or deep oceanic waters, and sediments. It is assumed that significant changes in temperature, ocean circulation patterns, or surface ventilation can increase the $^{14}$CO$_2$ (and CO$_2$) reflux back into the atmosphere.

Activity of atmospheric $^{14}$CO$_2$ increased significantly during the 1950s and 1960s due to nuclear weapons tests carried out in the atmosphere. The maximum was observed in the Northern Hemisphere in 1963, when it reached double the natural level caused by cosmogenic production. Over the subsequent years, the $^{14}$CO$_2$ activity has decreased quickly compared to the $^{14}$C half-life, and so by 1970 the “bomb effect” had been reduced by half (Meijer et al. 1995). The rate of the decrease proves that the $^{14}$C radioactive decay in the atmosphere affects the $^{14}$CO$_2$ levels only partially.

Due to the similar chemical and physical properties of CO$_2$ and $^{14}$CO$_2$, $^{14}$C can be used to define some parameters of models for simulation and prediction of CO$_2$/carbon transport to the atmosphere and to other carbon reservoirs. Up to now, many of the input parameters have been questioned, as well as their considerable uncertainties (Levin et al. 2008, 2010). Therefore, it would be beneficial to specify the long-term natural behavior of atmospheric $^{14}$CO$_2$ (in a horizon of thousands or tens of thousands of years). The main chemical form of $^{14}$C in the atmosphere is $^{14}$CO$_2$. Other chemical forms containing $^{14}$C (CO, CH$_4$, and other organic compounds) occur in concentrations at least 10$^3$ times smaller. During photosynthesis, $^{14}$CO$_2$ is captured by plants and thus becomes part of the

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food chain. It can be therefore assumed that $^{14}$C activity data used for $^{14}$C dating corrections of terrestrial samples corresponds to the atmospheric $^{14}$CO$_2$ activity during the same time periods.

**CALCULATION OF ATMOSPHERIC $^{14}$CO$_2$ MOLAR ACTIVITY**

The molar activity of $^{14}$CO$_2$ (quantity of $^{14}$CO$_2$ in 1 mole of the air) was calculated to estimate a total $^{14}$C amount in the atmosphere. Values of $\Delta ^{14}$C ($^{14}$C activity$^4$) were adopted from the $^{14}$C calibration curve IntCal09 (Figure 1) (Reimer et al. 2009). The values of $\Delta ^{14}$C correspond to the abundance of $^{14}$C in the carbon isotope mixture (Stuiver and Polach 1977). IntCal09 is applied world-wide for correction of natural $^{14}$C activity fluctuations in dating of terrestrial samples, and reaches up to 50,000 yr BP. IntCal09 data with time steps of 5 yr are available up to 11.2 ka BP, then the steps expand gradually up to 200 yr for the oldest values. Concentration of atmospheric CO$_2$ in available databases is reported in ppm$_V$ as a partial volume of CO$_2$. Several available reconstructions of CO$_2$ data extend to 50 ka BP (NOAA, http://www.ncdc.noaa.gov/paleo/icecore/icecore-varlist.html).

These time series were assembled on the basis of CO$_2$ analyses of several Antarctic ice cores (see Figure 1). Table 1 lists the ice cores used. The time intervals at which CO$_2$ concentration values are available are irregular. The $\Delta ^{14}$C values were calculated for years with known CO$_2$ concentrations using linear interpolation of the nearest IntCal09 timescale values; these calculations were made using MATLAB$^\text{®}$ software.

To estimate a past amount of $^{14}$CO$_2$ in the atmosphere, we calculated a parameter that depends only on the number of $^{14}$CO$_2$ molecules per unit of air. For such a purpose, weight, molar, or volume (vol-

$^4$The symbol $\Delta ^{14}$C instead of the term "$^{14}$C ($^{14}$CO$_2$) activity" is reported to prevent confusion with $^{14}$CO$_2$ molar activity.
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Table 1 Antarctic ice cores used in this study.

<table>
<thead>
<tr>
<th>Name</th>
<th>Time period/data</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPICA Dome C Ice Core</td>
<td>High-resolution Holocene and transition CO$_2$ data</td>
<td>Monnin et al. 2004</td>
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<tr>
<td>Dome C</td>
<td>0–22 kyr BP</td>
<td>Monnin et al. 2001</td>
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<tr>
<td>Vostok</td>
<td>0–440 kyr BP</td>
<td>Petit et al. 1999a</td>
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<tr>
<td>Taylor Dome</td>
<td>19–63 kyr BP</td>
<td>Indermühle et al. 1999a</td>
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<tr>
<td>EPICA Dome C Ice Core Termination I</td>
<td>$^{13}$CO$_2$ data</td>
<td>Lourantou et al. 2010</td>
</tr>
<tr>
<td>EPICA Dome C</td>
<td>Nitrous oxide, CO$_2$, and CH$_4$ data</td>
<td>Flückiger et al. 2002</td>
</tr>
<tr>
<td>EPICA Dronning Maud Land</td>
<td>CO$_2$ data for the last millennium</td>
<td>Siegenthaler et al. 2005</td>
</tr>
<tr>
<td>Law Dome Ice Core 2000-Year</td>
<td>CO$_2$, CH$_4$, and N$_2$O data</td>
<td>MacFarling et al. 2006</td>
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The molar activity of atmospheric $^{14}$CO$_2$ is not affected by the fossil CO$_2$ amount in the atmosphere (i.e. it is not dependent on the quantity of CO$_2$ molecules with stable carbon isotopes). The $^{14}$CO$_2$ “concentration” is calculated as a molar activity according to the following formula:

$$a_m = a_{std}(1+0.001\cdot\Delta^{14}C)\cdot M_C \cdot k \cdot c_{CO_2}$$

where $a_m$ is the atmospheric $^{14}$CO$_2$ molar activity (in Bq mol$^{-1}$), $a_{std}$ is the activity of the $^{14}$C standard (Bq g$^{-1}$ of the carbon isotope mixture, which is $\sim 0.226$ Bq g$^{-1}$), $\Delta^{14}C$ represents the $^{14}$C activity according to the IntCal09 calibration curve (%), $M_C$ is a carbon mass (12.01 g mol$^{-1}$), $c_{CO_2}$ is CO$_2$ concentration (ppmV), and $k$ (1.0092) is the ratio of molar volumes of air and CO$_2$, which are 22.47 and 22.26 10$^{-3}$ m$^3$ mol$^{-1}$, respectively (for 0 °C, 101.325 kPa). If the global air content in the atmosphere (number of air moles) is assumed to be stable, the total amount of $^{14}$CO$_2$ molecules in the atmosphere is proportional to the calculated molar activity. The $^{14}$CO$_2$ content in the atmosphere is given by the input rate (cosmogenic production of $^{14}$C and a $^{14}$CO$_2$ reflux from the other carbon reservoirs to the atmosphere) and the output rate (transfer of $^{14}$CO$_2$ from the atmosphere to other carbon sinks). The $^{14}$CO$_2$ activity decrease due to radioactive decay in the atmosphere is negligible because of the long half-life of $^{14}$C, and a relatively short residence time. If the clear fossil ($^{14}$C-free) CO$_2$ is released into the atmosphere, it leads to a decrease of $\Delta^{14}$C values due to a dilution (i.e. the $^{14}$C abundance in the carbon isotopic mixture of atmospheric CO$_2$ is decreased), but without changes in $^{14}$CO$_2$ molar activity (i.e. the number of $^{14}$CO$_2$ molecules per mole of air remains the same). If the CO$_2$ (and $^{14}$CO$_2$) residence time in the atmosphere increases (e.g. as a result of a shift in atmospheric/oceanic carbon distribution), then both the CO$_2$ concentration and $^{14}$CO$_2$ amount (molar activity) will also increase in the atmosphere.

RESULTS AND DISCUSSION

It is apparent from Figure 2 that the $\Delta^{14}$C ($^{14}$CO$_2$ activity) and the $^{14}$CO$_2$ molar activity time series between 50 and 20 ka BP follow similar trends. The CO$_2$ concentration was relatively stable at that time, without abrupt changes, and with only a slightly decreasing trend (Figure 1). For this reason, the $^{14}$CO$_2$ activities seem to be influenced mainly by changes in the cosmogenic production rates during this period.

If we compare the calculated $^{14}$CO$_2$ molar activities with the $^{10}$Be production during the period 50–20 ka BP, both time series show similar trends (Figure 3). The parameter “$^{10}$Be cosmogenic produc-

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5 This is also evident from a sharp decrease in atmospheric $^{14}$CO$_2$ activity during the 1960s (Meijer et al. 1995).
tion” was corrected for $^{10}$Be redeposition; it also contains data from a few deep oceanic sediments sampled at geographically distant areas (Frank et al. 2007). The time series called “global $^{10}$Be production rate” contains data obtained entirely from the Atlantic sedimentary sequences with an average sedimentation rate larger than 10 cm per 1000 yr, to minimize influence of postdepositional processes and to obtain a better time resolution. The $^{230}$Th ex normalization has been included with the aim to reduce a (climate-induced) oceanic transport signal, as discussed by Christl et al. (2010).

A different situation can be observed for the younger period up to 20 ka BP. The $\Delta ^{14}$C and atmospheric $^{14}$CO$_2$ molar activity time-series trends are considerably different. If we compare CO$_2$ concentrations and $\Delta ^{14}$C, apparent “mirroring” of both time series can be observed for the prevailing part of this period (see Figure 1). In the period 20–2 ka BP, a surprisingly high anti-correlation (i.e., relation where $\Delta ^{14}$C is decreasing with increasing concentration of CO$_2$) of 93.1% between $\Delta ^{14}$C values and CO$_2$ concentration was found (Figure 4). High anti-correlations were also found for the periods 20–10 ka BP (93.3%) and 10–2 ka BP (76.6%). Therefore, in the period ~20–2 ka BP, the $\Delta ^{14}$C time component seems to be influenced mainly by intake of the CO$_2$ with a depleted amount of $^{14}$CO$_2$. A decreased abundance of $^{14}$CO$_2$ in the CO$_2$ input to the atmosphere can be probably explained by an extended residence time (comparable to the $^{14}$C half-life) in long-term carbon sinks, e.g. CO$_2$ from deep oceanic waters (Schmittner 2003).

The molar activities of $^{14}$CO$_2$ increased slowly in the period approximately 20–11 ka BP, which corresponds to the ingrowth in the amount of $^{14}$CO$_2$ in the atmosphere, although the activities of atmospheric $^{14}$CO$_2$ ($\Delta ^{14}$C) decreased (see Figures 2 and 3). Timescales of $^{10}$Be (“$^{10}$Be cosmogenic production” and “global $^{10}$Be production rate”) show a systematic decrease during this period, which probably also implies decreasing cosmogenic production of $^{14}$C. Hence, growth in the atmospheric $^{14}$CO$_2$ content during this period could be explained by (1) increased CO$_2$ residence time in the atmosphere and (2) partial (although depleted) $^{14}$CO$_2$ content in CO$_2$ released from long-term carbon sinks.
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![Figure 3](image)

Figure 3  Comparison of calculated 14CO₂ molar activities (triangles) and 10Be time series: (a) 10Be cosmogenic production (black line) (Frank et al. 1997); (b) global 10Be production rate (gray line) with broken lines representing uncertainties (Christl et al. 2010), where 0 and 1 values correspond to production of 1.5 \(10^9\) and 1.9 \(10^9\) atoms cm\(^{-2}\) ka\(^{-1}\), respectively (M Christl, personal communication, 2013).

![Figure 4](image)

Figure 4  Anti-correlation of 14C activity (Reimer et al. 2009) and CO₂ concentration from 20 to 2 ka BP (CO₂ data: Indermühle et al. 1999a,b; Petit et al. 1999a; Smith et al. 1999; Monnin et al. 2001, 2004; Flückiger et al. 2002; Siegenthaler et al. 2005; MacFarling et al. 2006; Lourantou et al. 2010).

\[ y = -4,3323x + 1230,6 \]

\[ R^2 = 0,9311 \]
The observed interval of the strong relation between Δ14C and CO2 includes the time intervals connected with a distinct rise in CO2 and Δ14C drops in the Heinrich Stadial 1 “Mystery Interval,” about 17.5–14.5 ka BP, and the Younger Dryas, about 13–11 ka BP (Broecker and Barker 2007; Broecker 2009; Cléroux et al. 2011). Nevertheless, according to our data, this relation seems to continue until ~2 ka BP in the Holocene. The Southern Ocean, where carbon was detained in the reservoir of abyssal water, is usually proposed as a dominant source of CO2 with a depleted amount of 14C, but other possibilities have also been proposed (Butzin et al. 2005, 2012; Broecker and Barker 2007; Marchitto et al. 2007; Anderson et al. 2009; Broecker 2009; Stott et al. 2009; Basak et al. 2010; Bryan et al. 2010; Skinner et al. 2010; Cléroux et al. 2011; Lund et al. 2011; Sortor and Lund 2011; Menviel et al. 2012; Roth and Joos 2012; Schmitt et al. 2012).

A gradual warming arises during the period of the Late Glacial, and associated changes due to oceanic relations can be estimated in the range between 20.8 and 17 ka BP (Stott et al. 2007; Tachikawa et al. 2009), which also can be seen from reconstructed temperature curves (Figure 5). Two time series of proxy data were used for this purpose: (1) temperature reconstruction based on the Antarctica Vostok ice core, corresponding to the area of disposable CO2 reconstructions; (2) temperature reconstruction based on the Greenland GISP2 ice core, with available analogous polar data from the Northern Hemisphere (Jouzel et al. 1987, 1993, 1996; Petit et al. 1999b; Alley 2000). Warming continued until approximately 10 ka BP and was accompanied by a gradual decrease in 14CO2 activity and by an ingrowth of CO2 concentration. As previously mentioned, the observed decrease in atmospheric 14CO2 activity was probably caused by inputs of CO2 with depleted amounts of 14C in the carbon isotopic mixture, which is also indicated by the “mirrored” relation between CO2 and Δ14C during this period (Figure 1).

The period 17–10 ka BP includes a large gradual increase in temperatures and CO2 concentrations. Nevertheless, 1 exception can be observed during the Younger Dryas and Allerød. The CO2 concentration increased sharply at ~14.0 ka BP and remained relatively stable until 12.2 ka BP. It must be
pointed out that only CO₂ time series from Antarctic ice cores were available. Hence, the Vostok ice core records were preferred to compare temperature headway. The uniform temperature increase terminates at ~14.0 ka BP, and a sharp cooling period followed for the next 500 yr. In the subsequent period, only fine temperature fluctuations can be observed until 12.3 ka BP, when gradually both the temperature and CO₂ increases resumed. According to the Greenland GISP2 ice-core data, the temperature time series shows a disruption in the increase of the earlier period at ~14.5 ka BP, and gradual warming was recovered starting at ~11.9 ka BP (see Figure 5). Activity of ¹⁴C (Δ¹⁴C values) decreases until 14.2 ka BP, followed by moderate, irregular growth from 13.9 ka BP. Retrieval of systematic decreasing ¹⁴CO₂ activity can be observed from 12.4 ka BP. However, the ¹⁴CO₂ quantity in the atmosphere (molar activity of ¹⁴CO₂) was rising since 17 ka BP until 11.1 ka BP, when maximal values are observed. From the perspective of ¹⁴CO₂ molar activity, the period 14.4–14.0 ka BP is connected only with several slightly decreased values, although other parameters show significant changes at this time (see Figures 1, 5). The increasing amount of ¹⁴CO₂ in the atmosphere reached its maximum value (~11.1 ka BP) when the increase in CO₂ concentration decelerated.

A remarkable change in trends also can be observed for the temperature time series at 11.1 ka BP (Figures 1, 5). Both time series of ¹⁰Be are connected generally with a uniform decrease during the 17–11 ka BP interval. Only the time series “cosmogenic production of ¹⁰Be” reflects a sharp decrease since 14 ka BP of several hundred of years’ duration (Figure 3). The period of the maximal amount of ¹⁴CO₂ in the atmosphere can be connected mainly with CO₂ inflow, as is evident from the series of trends and local extremes presented above. From this point of view, it seems again that limitation of CO₂ input also caused a decrease in ¹⁴CO₂ input. Hence, the CO₂ input from long-term carbon sinks seems to contain a significant amount of ¹⁴CO₂, although depleted. The direct influence of cosmogenic ¹⁴C production on the culminating amount of ¹⁴CO₂ in the atmosphere during this period was not confirmed by the ¹⁰Be time series. A connection between the amount of ¹⁴CO₂ in the atmosphere and other parameters was not observed, which could be due in part to uncertainties in the age calibration of other parameters, particularly applied temperature curves. The sharp temperature decrease at the end of the Allerød and the stagnation of relatively low temperatures in the Younger Dryas are exceptions during the Late Glacial, which can be characterized by a gradual warming in general. A strong temperature decrease in the late Allerød, lasting several hundred years, is the youngest “cooling” period. Various records of ¹⁴C activity are available for that time.

Better knowledge of CO₂ and ¹⁴CO₂ transport during this anomalous period could improve the possibility of carbon transport modeling under conditions different from gradual temperature increase, which could also enhance the tools for validation of prediction models. A verification of the course of the atmospheric CO₂ time series for Northern Hemisphere localities, and its comparison with northern and southern polar temperature curves, would be an important asset to this purpose (Bianchi and Gersonde 2002; Schulz and Paul 2004). Likewise, the improvement of time resolution and reduction of uncertainties in the time positions of the extremes during this relatively short period (14–11 ka BP at minimum) would be a benefit. A comparison with cosmogenic production of other radionuclides (namely, ¹⁰Be, and ³⁶Cl or ²⁶Al when available) could also facilitate more precise studies of this interesting, unique period.

Long-term trends are not observed in both temperature time series since the beginning of the Holocene (10 ka BP; see Figure 5). In the period 10–7 ka BP, both concentrations of CO₂ and activities of ¹⁴C (Δ¹⁴C values) were relatively stable. During 7–2 ka BP, CO₂ concentration increased gradually, in addition to implying ¹⁴C activities, as indicated by a continuation of the “mirroring effect” of both parameters with a high correlation for this period (76.6%; see Figure 1). Hence, it can be assumed that releases of CO₂ with partly depleted amounts of ¹⁴CO₂ (from long-term carbon
sinks) also continued at that time. The “mirroring effect” of CO₂ concentrations and ¹⁴C activity history is restricted approximately to 2 ka BP. Hereafter, the obtained (anti) correlation of both time series is not statistically significant (2.4%). This implies that the changes in ¹⁴C activity (Δ¹⁴C) younger than 2 ka BP are not significantly influenced by effect of ¹⁴CO₂ atmospheric dilution caused by releases of CO₂ with depleted amounts of ¹⁴C into the atmosphere, as discussed above.

**CONCLUSIONS**

In the time interval from 50 to 20 ka BP, the cosmogenic production of ¹⁴C seems to have a dominant influence on the ¹⁴CO₂ amount in the atmosphere, when the concentrations of atmospheric CO₂ were relatively stable with a slowly decreasing trend. Likewise, the curves of ¹⁰Be production seem to have a similar shape as well as calculated molar activity (estimated ¹⁴CO₂ amount in the atmosphere) for this period. High anti-correlation (93.1%) was found for the CO₂ concentration and Δ¹⁴C values from 20 to 2 ka BP. The decrease in Δ¹⁴C levels seems to be caused by atmospheric dilution of ¹⁴CO₂ by inputs of CO₂ with depleted amounts of ¹⁴C from deeper oceanic layers, as a result of gradually increasing temperature. The interval of strong relation between CO₂ and Δ¹⁴C covers periods of the Heinrich Stadial 1 “Mystery Interval” (~17.5−14.5 ka BP) and Younger Dryas (~13−11 ka BP) where rapid rises in CO₂ concentrations and drops in Δ¹⁴C activity were observed. Likewise, this relation continues until the prevailing part of the Holocene. The observed quantity of ¹⁴CO₂ in the atmosphere (calculated as molar activity) appears to show an increasing trend during the deglacial period, in the interval 20–11 ka BP, with only fine variations, although the opposite trend is evident for the ¹⁰Be time series. During the last 2000 yr, the anticorrelation between the CO₂ and Δ¹⁴C was not significant (2.4%).

It would be interesting to compare a time component of ¹⁴CO₂ molar activity with a calibrated time series for other cosmogenic radionuclides, e.g. ²⁶Al and ³⁶Cl, when such data become available. Extending the CO₂ concentration time series with gas-age calibrated data from Greenland ice cores, if available, could also verify our conclusions.

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