ATMOSPHERIC \(^{14}\)CO\(_2\) VARIATIONS IN THE EQUATORIAL REGION

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ABSTRACT. We present here first results of \(^{14}\)CO\(_2\) monitoring at two sampling sites in the equatorial region of the South American continent (station Aychapicho, Ecuador and station Llano del Hato, Venezuela). We also include the data for two other stations representing undisturbed marine atmosphere at mid-latitudes of both hemispheres, far from large continental sources and sinks of CO\(_2\) (station Izana, Tenerife, Spain and station Cape Grim, Tasmania). Between 1991 and 1993, \(^{14}\)CO\(_2\) levels in the tropical troposphere were generally higher by 2-5\% when compared to mid-latitudes of both hemispheres. This apparent maximum of \(^{14}\)C in the tropics can be explained by two major factors: 1) emissions of \(^{14}\)C-free fossil fuel CO\(_2\), restricted mainly to mid-latitudes of the northern hemisphere; and 2) \(^{14}\)C depletion due to gas exchange with circumpolar Antarctic upwelling water, influencing mainly mid- and high southern latitudes. The \(^\Delta^{14}\)C record so far available for the Aychapicho station provides direct evidence for a regional reduction of atmospheric \(^{14}\)CO\(_2\) levels due to gas exchange with \(^{14}\)C-depleted equatorial surface ocean in the upwelling regions and dilution with the \(^{14}\)C-depleted CO\(_2\) released in these areas. Recurrent ENSO events, turning on and off the \(^{14}\)C-depleted CO\(_2\) source in the tropical Pacific, lead to relatively large temporal variations of the atmospheric \(^{14}\)C level in this region.

INTRODUCTION

The less abundant isotopes of carbon (\(^{14}\)C, \(^{13}\)C) have proved to be tracers well suited to studying the global carbon cycle. They provide additional constraints to current models of the carbon cycle and help to identify the nature of atmospheric sources and sinks (Francey et al. 1993; Hesshaimer, Heimann and Levin 1994).

The \(^{14}\)C activity in atmospheric CO\(_2\) is controlled by four main sources: 1) natural \(^{14}\)C produced by interactions of cosmic rays in the upper atmosphere; 2) the bomb \(^{14}\)C originally introduced into the stratosphere but subsequently stored in the ocean and in the biosphere; 3) \(^{14}\)C released by nuclear power plants; and 4) fossil-fuel CO\(_2\), acting as a "\(^{14}\)C-free dilutant". Because these sources are not globally uniform, and some of them show significant seasonal variations, spatial and temporal variations of the \(^{14}\)CO\(_2\) level are observed in the atmosphere.

Information on spatial and temporal changes in atmospheric \(^{14}\)CO\(_2\) concentration has been obtained from regular monitoring over the past three decades at mid- and high latitudes in both hemispheres (Levin et al. 1992). The data reveal a generally decreasing trend of \(^{14}\)CO\(_2\), with superimposed seasonal fluctuations as well as substantial changes in the interhemispheric gradient. Until now, no systematic observations of \(^{14}\)CO\(_2\) have been made in the tropics.

We present here first results of \(^{14}\)CO\(_2\) monitoring at two sampling sites in the equatorial region of the South American continent: 1) station Aychapicho, Ecuador (0.11°S, 78.85°W) 2996 m asl, ca. 250 km from the Pacific coast; and 2) station Llano del Hato, Venezuela (8°N, 72°W) 3600 m asl, located in the Cordillera de Mérida. Regular sampling began in April 1991 at Llano del Hato and in June 1992 at Aychapicho. Both stations are located in remote areas, far from local sources of anthropogenic CO\(_2\) (cf. Fig. 1).

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METHODS

The same sampling technique, based on dynamic absorption of atmospheric CO\textsubscript{2} in a concentrated alkaline solution (Levin, Münnich and Weiss 1980), was used at both sampling sites. Air was pumped continuously through a rotating glass tube (Rasching tube) filled with CO\textsubscript{2}-free sodium hydroxide solution to assure complete absorption of atmospheric CO\textsubscript{2}. In general, two-week composite samples were collected and the volume of the pumped air measured for each sample. Alkali solution was shipped back to the analyzing laboratories (Heidelberg and Vienna) where the sample CO\textsubscript{2} was extracted by adding an inorganic acid. The 14C activity was measured in both laboratories by gas proportional counting. The $^{13}$C/$^{12}$C ratios in the collected samples were measured by mass spectrometry from small aliquots of the CO\textsubscript{2} gas and used primarily for correction of the 14C results for possible fractionation effects during sampling and analysis.

All 14CO\textsubscript{2} activities are expressed as the per mil deviation ($\Delta^{14}$C) from 95% of the NBS oxalic acid activity corrected for decay (Stuiver and Polach 1977). The $^{13}$C/$^{12}$C ratios are expressed as the per mil deviation ($\delta^{13}$C) from the V-PDB standard (Coplen 1994). To obtain a direct comparison with plant material, the 14CO\textsubscript{2} activities are normalized to correspond with a $\delta^{13}$C = -25‰ using the mean $\delta^{13}$C value of all samples collected at the given station for the entire observation period. The 1-σ precision of a single $\Delta^{14}$CO\textsubscript{2} analysis is typically ±3‰ and ±6‰ for Llano del Hato and Aychapicho, respectively.

RESULTS AND DISCUSSION

Figure 2 shows the $\Delta^{14}$C results obtained from Llano del Hato and Aychapicho, in direct comparison with similar data from two other stations representing undisturbed marine atmosphere at mid-latitudes of both hemispheres, far from large continental sources and sinks of CO\textsubscript{2}: Izaña (28°N, 16°W, 2367 m asl) and Cape Grim (41°S, 145°E, 95 m asl). Results for Izaña are available only until the end of 1992. The Llano del Hato station reveals relatively small variations of $\Delta^{14}$C and, except for the summer months (July–September), the level is slightly higher than at the maritime baseline station Izaña (Table 1). During the period of parallel observations, the Llano del Hato $\Delta^{14}$C level is significantly higher than at Cape Grim (by 5.5‰), suggesting a broad maximum of $\Delta^{14}$C in low latitudes.
Atmospheric $^{14}$CO$_2$ Variations in the Equatorial Region

Fig. 2. Atmospheric $^{14}$CO$_2$ levels monitored at four stations shown in Figure 1, which represent the tropical region and mid-latitudes of both hemispheres: Llano del Hato, Venezuela (8°N, 72°W, 3600 m asl), Aychapicho, Ecuador (0.11°S, 78.85°W, 2996 m asl), Izaña, Tenerife, Spain (28°N, 16°W, 2376 m asl) and Cape Grim, Tasmania (41°S, 145°E, 95 m asl)

Table 1. Quarterly mean $\Delta ^{14}$C of atmospheric CO$_2$ between April 1991 and December 1993 for three baseline stations: Izaña (28°N, 16°W, 2376 m asl), Llano del Hato (8°N, 72°W, 3600 m asl) and Cape Grim (41°S, 145°E, 95 m asl) and the coastal Pacific station Aychapicho (0.11°S, 78.85°W, 2996 m asl). Deviations from the $^{14}$CO$_2$ level recorded at Llano del Hato are reported in parentheses.

<table>
<thead>
<tr>
<th>Period</th>
<th>Llano del Hato</th>
<th>Aychapicho</th>
<th>Izaña</th>
<th>Cape Grim</th>
</tr>
</thead>
<tbody>
<tr>
<td>April–June 1991</td>
<td>144.5</td>
<td>--</td>
<td>143.0 (−1.5)</td>
<td>139.6 (−4.9)</td>
</tr>
<tr>
<td>July–September 1991</td>
<td>144.2</td>
<td>--</td>
<td>147.5 (+3.3)</td>
<td>140.3 (−3.9)</td>
</tr>
<tr>
<td>October–December 1991</td>
<td>145.6</td>
<td>--</td>
<td>142.6 (−3.0)</td>
<td>136.5 (−9.1)</td>
</tr>
<tr>
<td>January–March 1992</td>
<td>139.1</td>
<td>--</td>
<td>136.9 (−2.2)</td>
<td>134.5 (−4.6)</td>
</tr>
<tr>
<td>April–June 1992</td>
<td>138.4</td>
<td>--</td>
<td>136.4 (−2.0)</td>
<td>133.8 (−4.6)</td>
</tr>
<tr>
<td>July–September 1992</td>
<td>138.0</td>
<td>125.3 (−12.7)</td>
<td>139.1 (+1.1)</td>
<td>132.8 (−5.2)</td>
</tr>
<tr>
<td>October–December 1992</td>
<td>139.2</td>
<td>130.5 (−8.7)</td>
<td>137.9 (−1.3)</td>
<td>130.4 (−8.8)</td>
</tr>
<tr>
<td>January–March 1993</td>
<td>133.1</td>
<td>130.9 (−2.2)</td>
<td>--</td>
<td>127.7 (−5.4)</td>
</tr>
<tr>
<td>April–June 1993</td>
<td>130.9</td>
<td>117.0 (−13.9)</td>
<td>--</td>
<td>128.3 (−2.6)</td>
</tr>
<tr>
<td>July–September 1993</td>
<td>--</td>
<td>118.6</td>
<td>--</td>
<td>127.9</td>
</tr>
<tr>
<td>October–December 1993</td>
<td>--</td>
<td>119.4</td>
<td>--</td>
<td>121.9</td>
</tr>
</tbody>
</table>
The Aychapicho $\Delta^{14}C$ record reveals a distinct minimum between August and October 1992. The decrease of $^{14}C$ concentration during this time period is substantial: from ca. 135% in June and July 1992, in good agreement with Llano del Hato, to 100% by the end of August and only 90% at the beginning of October. In November 1992 the $^{14}C$ concentration returned to the level observed at Llano del Hato. From April to June 1993 another negative $\Delta^{14}C$ anomaly is observed at Aychapicho. In general, the Aychapicho $\Delta^{14}C$ level is substantially more variable than that observed for Llano del Hato.

The anomalous $\Delta^{14}C$ values observed at Aychapicho station between August and October 1992 are most probably associated with the upwelling activity of the Pacific Ocean off the coast of Ecuador and Peru. This region is known for intense upwelling, with excess partial pressure of CO$_2$ reaching 80 $\mu$atm (Broecker and Peng 1982). It extends roughly from the equator to 15°S and between 80°W and 90°W (region Niño 1+2). Another region of intense upwelling is located in the eastern equatorial Pacific, roughly between 130°W and 180°W (Broecker and Peng 1982; Lefevre and Dandonneau 1992; Wong et al. 1993).

Owing to relatively large excess partial pressures of CO$_2$ persisting in the surface waters, the upwelling regions are considered an important net source of atmospheric CO$_2$. The available estimates of CO$_2$ evasion rates from the entire tropical Pacific range between 0.6 and 0.8 Gt C per year (Wong et al. 1993). Freely et al. (1993) showed that the CO$_2$ flux is higher in the eastern Pacific, south of the equator, mainly due to higher wind speeds in this region.

The $^{14}C$ content of the CO$_2$ being released to the atmosphere in the upwelling regions was not measured directly. It can, however, be estimated from the available data on the $\Delta^{14}C$ of surface ocean waters (Broecker et al. 1985). Unfortunately, no such data are available for the upwelling region off the coast of Ecuador and Peru (region Niño 1+2). An assessment of the $^{14}C$ level in surface ocean water in this region can be obtained from $^{14}C$ analyses of banded corals. Analyses performed by Druffel and Suess (1983) on corals originating from Galapagos Islands showed that the $\Delta^{14}C$ level in corals that grew ca. 1975 in Galapagos waters was only +20‰, as compared with +160‰ recorded in Florida corals and ca. +380‰ in the tropical atmosphere. One may expect, therefore, that under normal upwelling conditions, the Pacific Ocean off the coast of Ecuador and Peru is significantly depleted in $^{14}C$ when compared to the atmosphere. For 1978, Druffel and Suess (1983) estimated the difference between $\Delta^{14}C$ values in the atmosphere and those in the surface water around Galapagos Islands to be close to 350‰. For the 1990s, we estimate this disequilibrium to be at least 200‰.

The El Niño/Southern Oscillation (ENSO) events, large-scale irregular fluctuations of the coupled ocean-atmosphere system of the equatorial Pacific, generate a distinctive pattern of environmental anomalies that recur every 2–7 yr (Enfield 1989). The events are known to be associated with significant changes of sea surface temperature (SST), upwelling rates and biological activities in the Pacific waters (Wong et al. 1993; Freely et al. 1993). Also, atmospheric circulation in the region changes dramatically during these events. All these changes modulate the rates of exchange of CO$_2$ between the ocean and the atmosphere. Suppressed upwelling and reduced biological activity of surface seawater result in a significant reduction in, or even disappearance of, the net CO$_2$ source from the tropical Pacific Ocean during ENSO events (Wong et al. 1993).

During spring 1992 a moderate ENSO event developed in the eastern equatorial Pacific. Figure 3C shows the record of monthly mean SST anomaly for the region Niño 1+2 during 1992 and 1993, calculated as the deviation from the long-term average (WMO 1994). The record reveals a maximum positive anomaly in May 1992. During the following months, the SST was dropping rapidly, reaching lower than normal temperature in August 1992. Between September 1992 and May 1993 there were signs of returning to ENSO conditions, which lessened again toward the end of 1993.
Fig. 3. Record of (A) $\Delta^{14}C$ and (B) $\delta^{13}C$ of atmospheric CO$_2$ collected at the Aychapicho, Ecuador station ($0.11^\circ$S, 78.85$^\circ$W, 2996 m asl). Data points represent two-week composite samples. (C) Record of monthly mean SST anomaly off the coast of Peru and Ecuador during 1992 and 1993 (WMO 1994). The record can be considered a proxy indicator of the intensity of upwelling: high positive anomaly indicates occurrence of the ENSO event and suppressed upwelling in the eastern Pacific.
The record of SST anomalies shown in Figure 3C can be considered a proxy indicator of the intensity of upwelling off the coast of Ecuador and Peru: a high positive anomaly indicates occurrence of the ENSO event and suppressed upwelling. It is noteworthy that the negative SST anomaly in August 1992, indicating intense upwelling rates, coincides with the onset of the period of anomalously low $\Delta^{14}C$ values recorded at Aychapicho station (Fig. 3A). Presumably, atmospheric circulation during that period favored the advection of maritime air masses with reduced $^{14}C$ levels due to equilibration with $^{14}C$-depleted surface water and/or the direct emission of $^{14}CO_{2}$ from the upwelling regions toward the sampling site.

Although an interpretation of the $^{13}C$ record for Aychapicho station (Fig. 3B) can be no more than qualitative, owing to fractionation effects associated with the partial crystallization of carbonate in the Rasching tube during sample transfer, it nevertheless indicates that an anthropogenic origin can be ruled out for the major negative anomaly in $\Delta^{14}C$ observed at Aychapicho between August and October 1992. A two-component mixing model suggests that admixture of only 4% of pure fossil-fuel $CO_{2}$ ($\Delta^{14}C = -1000/o; \delta^{13}C = -25/o$) would reduce the atmospheric $\Delta^{14}C$ level to the observed 90/o. However, at the same time, the $\delta^{13}C$ value of the mixture should become more negative by ca. 0.7/o. Figure 3B reveals an opposite effect: the samples collected between August and October 1992 tend to be more enriched in $\delta^{13}C$, if compared to the period of suppressed upwelling.

Jirikowic and Kalin (1993) suggested that a decrease of atmospheric $^{14}C$ due to dilution of atmospheric $^{14}CO_{2}$ by $^{14}C$-depleted $CO_{2}$ released from the ocean in upwelling areas is an explanation for regional differences in atmospheric $^{14}C$ activity archived in tree-ring cellulose. The fact that $\Delta^{14}C$ from tree-ring series obtained from Washington State differs systematically from similar, intercalibrated measurements from Arizona, was attributed to the relative proximity of the Northern Pacific upwelling region. Atmospheric circulation brings $^{14}C$-depleted air masses from the upwelling region to the Washington site during the spring high-growth period.

CONCLUSION

Between 1991 and 1993, $\Delta^{14}C$ in atmospheric $^{14}CO_{2}$ of the tropics was generally higher by 2–5/o when compared to mid-latitudes in both hemispheres. This apparent maximum of $\Delta^{14}C$ in the tropics can be explained by two major factors: emission of $^{14}C$-free fossil-fuel $CO_{2}$, restricted mainly to the northern hemisphere, and $^{14}C$ depletion due to gas exchange with circumpolar Antarctic upwelling water, influencing mainly mid- and high southern latitudes.

The $\Delta^{14}C$ record so far available from the Aychapicho station provides for the first time direct evidence for regional reduction of atmospheric $^{14}CO_{2}$ levels due to gas exchange with $^{14}C$-depleted equatorial surface ocean in the upwelling regions. The ENSO events, turning on and off the $^{14}C$-depleted $CO_{2}$ “source” in the tropical Pacific, may lead to relatively large variations of atmospheric $^{14}C$ levels in this region.

This study is still at a preliminary stage. Ongoing isotope monitoring at the Llano del Hato station should provide further information on the evolution of atmospheric $^{14}CO_{2}$ levels in the tropics. Further, the data being gathered at the Aychapicho station should allow a more detailed investigation of the regional disturbances of atmospheric $^{14}CO_{2}$ levels due to the proximity to upwelling regions of the Pacific Ocean.
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