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RECONSTRUCTION OF PAST CO_2 CONCENTRATION AT A NATURAL CO_2 VENT SITE USING RADIOCARBON DATING OF TREE RINGS

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ABSTRACT. Total CO_2 exposure levels in a naturally enriched site (Lajatico, Italy) were reconstructed using radiocarbon analysis by accelerator mass spectrometry combined with dendrochronological analysis on wood cores extracted from trees grown in the fossil CO_2 source proximity. Over 3 decades (1964–1998), the data show a mean CO_2 concentration in the atmosphere of 650 ppm, about twice the current concentration in atmosphere, with a maximum around 1980.

INTRODUCTION

Anthropogenic activities are altering Earth's principal climate parameters, resulting in the complex process commonly referred to as global climate change (Intergovernmental Panel on Climate Change [IPCC] 2001). This phenomenon is promoted by the increase of atmospheric CO_2 concentrations and other greenhouse gases (i.e. CH_4, N_2O) (Milich 1999). Alteration of the global carbon cycle, for which CO_2 represents the principal gaseous mean of exchange, promotes different responses within the compartments where changes take place. Among these, the autotrophic component of the terrestrial biosphere reacts to this disturbance as a sink, removing a greater amount of CO_2 from the atmosphere and sequestering it into its biomass and residues with long residence times (Comins and McMurtrie 1993; Levy et al. 2004). To study the responses of terrestrial ecosystems to elevated atmospheric CO_2, a great number of experiments have been performed with different techniques to simulate atmospheric carbon dioxide enrichment. The most important approaches, in order of decreasing disturbance to the ecosystems, are the closed chambers (Cotrufo et al. 1998), the open top chambers (Finnan et al. 2002; DeAngelis and Scarascia-Mugnozza 1998), and the FACE systems (Miglietta et al. 2001; Hendrey et al. 1999). An important alternative to these "artificial" methods is offered by the fossil vents of CO_2 which create a "zero impact" atmospheric enrichment for the ecosystems that grow in the vicinity (van Gardingen et al. 1995; Miglietta et al. 1998). The activity of the geological source of carbon dioxide increases CO_2 levels in its proximity, providing a powerful tool to understand the effects of carbon dioxide on fertilization, with minor manipulation and disturbance, on a longer time scale than the simulations mentioned above. The growth rates of different tree species in the CO_2-enriched areas show different physiological responses (Jones et al. 1995; Schwantz and Polle 1988; Tognetti et al. 1999). All the experiments conducted at these sites assume that the levels of exposure to the CO_2 have been constant during the growth of the plants (constant exposure hypothesis). However, only brief CO_2 monitoring campaigns using infrared gas analysis (IRGA) instrumentations have been performed over the last few decades (Tognetti et al. 1999, 2000; Miglietta et al. 1993).

In these sites, total exposure is due to 2 different CO_2 sources: the background atmosphere and the fossil source emissions, strongly differentiated in terms of ^{14}C content.

Since the beginning of nuclear weapons testing in 1955, the atmospheric CO_2 radiocarbon content is characterized by an enrichment with a peak corresponding to 1964 ($\Delta^{14}C \cong 1000‰$ in the North-

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ern Hemisphere), followed by an exponential decrease due to biosystem and ocean uptake and the CO_2 dilution coming from fossil fuel use (Burchuladze et al. 1989). The ^{14}C content of CO_2 from the fossil source can be assumed equal to zero because of the geological age (>>50 kyr) of the parent material where the fossil emission originates (fossil emission hypothesis).

The woody species, with their characteristic stem anatomy due to cambial activity, preserve in every growth ring a record of the CO_2 isotopic content used during the photosynthesis assimilation (Cherubini 2000). Therefore, an important goal is to validate the constant exposure hypothesis discussed above, historically reconstructing the total CO_2 exposure levels in the naturally enriched site. This approach is achievable with the combination of dendrochronological analyses and ultrasensitive ^{14}C determination, resolving an isotopic mass balance equation for the amount of ^{14}C in each growth ring of woody species exposed to natural fossil vents of CO_2.

MATERIALS AND METHODS

Site Description

The naturally enriched site of I Borboi near Lajatico, Pisa, Italy (lat 43°26′N, long 10°42′E) was studied. The enriched area, with an extension of about 0.7 ha, is characterized by dry, hot summers and wet, mild winters, with a mean annual temperature of 13.7 °C (max 33°C, min –4°C) and an annual mean precipitation of 882 mm (values coming from the Salina meteorological station, about 12 km from Lajatico and referring to the period from 1958–1995).

The Lajatico vegetation is a coppice dominated by evergreen and deciduous woody species such as *Quercus ilex* L., *Q. pubescens* Willd., *Arbutus unedo* L., and isolated individuals of *Q. cerris* L., *Fraxinus ornus* L., *Smilax aspera* L., *Cystus scoparius* L., *Cistus salvifolius* L., *Spartium junceum*, *Pistacia lentiscus* L., and *Phillyrea latifolia* L. The soil where the vegetation develops is a non-calcareous, brown, loamy, clayey soil developed from a calcareous marl parent material.

The emission (about 98% of CO_2 and 0.04×10^{-6} of H_2S) originates from a fossil source situated at the bottom of a northfacing aspect slope (20%) at 210 m asl. Also, seasonal vents located along narrow creeks contribute to the total release of CO_2 arising from the decomposition of carbonate parent material.

In the last decade, the CO_2 mole fraction has been monitored by periodic measuring campaigns performed with portable infrared gas analyzer systems and absorptive diffusion tubes. From these measurements, it has been deduced that in the vent area, the level of CO_2 exposure is approximately 700 ppm, with short-term variations between 500 and 1000 ppm depending on meteorological conditions (Tognetti et al. 2000; Raiesi 1998).

Sampling

On 10 April 2003, by means of a corer (8 mm diameter, 40 cm length), an individual *Q. pubescens* tree growing about 20 m from the source was sampled. The choice of this species has been dictated by previous evidence showing a lack of false-ring formation in trees at the same site (Cherubini et al. 2003). From this tree, 3 cores (at a mean height of 1 m) were sampled with the aim to reach the center of the stem in order to extract the oldest rings. After extraction, all the cores were preserved in HCl pre-cleaned Pyrex™ tubes.

To test the fossil emission hypothesis, during the core sampling, 2 L of the gas emitted from the source was collected using a Pyrex gas container (flask). The flask, previously evacuated using a

high vacuum system and connected to a tube, was fixed near the mouth of the fossil source, with the tube inside. The emission collection was performed, generating a flow inside the flask, by means of a field dry pump system for a total of about 3 hr.

Sample Preparation

Each core was dried within the glass tubes for about 48 hr at 80 °C. Each dried core was examined with a 20× stereoscope and dendrochronologically dated. Subsequently, the cores were split in single-year fractions (annual tree rings), with the exception of the 1970–1978 and 1980–1987 segments forming, because of the limited thickness of each annual tree ring, 2 multiyear pools. From each annual tree ring, only the latewood fraction was analyzed in order to avoid bias due to the usage of previous year carbon pool to synthesize the earlywood (Hill et al. 1995). Every ring also underwent chemical pretreatment to extract the alphacellulose wood fraction. This pretreatment followed the modified protocol of Green (1963), which can be summarized in the following phases:

1. HCl (4% water solution) treatment for 1 hr at 80 °C;
2. Sodium chlorite ($NaClO_2$) powder (15 g) and acetic acid (CH_3COOH 100%) in a water (2 L) solution treatment;
3. NaOH (4% water solution) treatment for 1 hr at 80 °C;
4. HCl (4% water solution) treatment for an 1 hr at 80 °C.

In order to obtain a neutral pH for the solution, before each phase samples were rinsed with distilled water. The principal process of phase 2 is lignin oxidation (Robertson et al. 2001) and lasts for 3 to 6 hr depending on the wood characteristics, with a mass yield that may vary within the 25–40% range. The extracted α-cellulose (residual of lignin oxidation) was dried at 40 °C and pyrolized in a quartz tube under a gaseous nitrogen (N_2) flow at 600 °C.

In order to obtain graphite for AMS analysis, the residual of the previous treatment was initially oxidized (900 °C) to CO_2 in a static vacuum combustion chamber, and then reduced to graphite in a 15-mL graphitization chamber following the standard iron-hydrogen procedure of Vogel et al. (1987). The graphite normally produced in this reaction (which lasts about 4 hr) develops itself on the iron powder catalyst (Φ_p = 200 mesh). The gaseous sample extracted from the fossil vent was purified to CO_2 on a cryogenic vacuum line (Bertolini T, Rubino M, Lubritto C, D'Onofrio A, Marzaioli F, Passariello I, Terrasi F, unpublished data) and directly reduced to graphite using the same procedure discussed above.

The graphite, together with silver powder, was pressed in a copper lab code-marked cylinder to be used like cathode in the source of the Bochum Universität Accelerator Mass Spectrometry system (Lubritto et al. 2004). The residual graphite was used to determine its $\delta^{13}C$ by means of an elemental analyzer (Thermo Flash EA 1112™) coupled with a conventional mass spectrometer (Thermo Delta Plus™).

Calculation Model

Assuming an instant mixing phenomenon between gaseous volumes (V) with CO_2 concentration (C) emitted from the source (s) and the ambient atmosphere CO_2 (a), the air (t) in the vent neighborhood is characterized by:

Total CO_2 concentration:
$$C_t = \frac{V_a C_a + V_s C_s}{V_a + V_s}$$

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Radiocarbon isotopic ratio ($^{14}C/^{12}C$): $R_t = \dfrac{R_a V_a C_a + R_s V_s C_s}{V_a C_a + V_s C_s}$

Defining the volumetric atmospheric fraction $X = V_a/(V_a+V_s)$ and molar CO_2 atmospheric fraction $Y = V_a C_a/(V_a C_a+V_s C_s)$, one can write:

$$C_t = X C_a + (1 - X)C_s \tag{1}$$

$$R_t = Y R_a + (1 - Y)R_s \tag{2}$$

Assuming a fossil CO_2 emission ($R_s = 0$) in Equation 2, the molar CO_2 atmospheric fraction Y can be written as

$$Y = R_t / Ra \tag{3}$$

By substituting the relationship between X and Y

$$X = 1/\left[1 + \frac{C_a(1 - Y)}{C_s Y}\right]$$

in Equation 1, the expressions of total CO_2 exposure concentration (C_t) and X fraction become:

$$C_t = C_a/\left[Y + \frac{C_a}{C_s}(1 - Y)\right] \tag{4}$$

$$X = 1/\left[1 + \frac{C_a(1 - Y)}{C_s Y}\right] \tag{5}$$

Knowing the CO_2 atmospheric concentration (C_a), C_t can be calculated from Equation 4, assuming C_s is equal to 98% and obtaining Y from Equation 3. Moreover, by assuming constant mean mixing conditions during the investigated time interval, the achievement of the CO_2 fraction derived from the fossil source (1–X), depending on the vent emission rate, is possible.

The methods to reconstruct the isotopic content of past atmospheres through the study of tree rings are well known (Cherubini 2000). Annually resolved tree rings permit determination of mean annual C_t and (1–X).

According to the definitions given above, C_a is obtained from an atmospheric CO_2 concentration report (IPCC 2001), and Y is measured by the ratio, for the same reference year, between percent of modern carbon (pMC) of an annual tree ring grown in the Lajatico site and that of the atmosphere coming from an atmospheric ^{14}C database (Nydal and Lövseth 1993).

RESULTS AND DISCUSSION

The effective ^{14}C depletion of the CO_2 emission was tested by measuring its cryogenically purified $^{14}CO_2$ pMC. The result of this measurement (1.3 ± 0.2 pMC) was in agreement with the fossil emission hypothesis, confirming the effective ^{14}C absence of the emission, and is compatible with the other graphite blank (1.1 ± 0.1 pMC).

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For each ring, the pMC was measured (R_t) and $\delta^{13}C$-corrected to account for fractionation effects. The results, summarized in Table 1, can be compared with the Nydal and Lövseth atmospheric ^{14}C database (R_a) (Nydal and Lövseth 1993). The effect of the fossil source ^{14}C dilution on the atmospheric bomb-enriched background atmosphere is clearly seen by the comparison of R_t with R_a. From this data, together with the CO_2 annual mean concentrations derived from IPCC (2001) (C_a), we calculated the total CO_2 exposure level (C_t) and the (1–X) values over the last 3 decades. As shown in Figure 1, the C_t and source activities within the period of investigation (1964–1998) are not constant around their mean values (651 ± 20 and 320 ± 21 ppm, respectively).

Table 1 Measured data from Lajatico tree rings and literature data (R_a and C_a) for the C_t and (1–X) calculations (errors in parentheses).

Year	$\delta^{13}C$ of tree rings (‰)	R_t (%)	R_a (%)	C_a (ppm)	C_t (ppm)	(1–X) (ppm)[a]
1963	–29.2 (0.2)	98 (2)	186 (1)	318.8 (0.3)	607 (13)	294 (13)
1968	–34.3 (0.2)	85 (1)	157 (1)	323.0 (0.3)	597 (7)	280 (7)
1970–78	–31.7 (0.2)	72 (1)	142 (1)	328.5 (0.8)	649 (10)	327 (10)
1979	–30.8 (0.2)	59 (1)	131 (1)	334.9 (0.5)	736 (8)	410 (9)
1980–87	–31.0 (0.2)	59 (1)	122 (1)	341.6 (0.9)	705 (13)	371 (14)
1988	–29.7 (0.2)	62 (1)	117 (1)	348.5 (0.5)	656 (9)	314 (9)
1998	–30.1 (0.2)	65 (1)	109 (1)	363.5 (0.6)	608 (9)	249 (9)

[a]The (1–X) decimal fraction is multiplied by 10^6 and is reported as ppm volume mixing ratio.

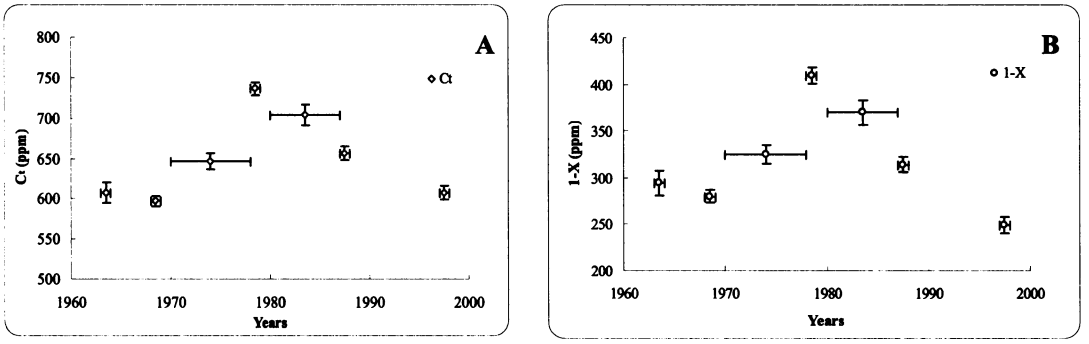

Figure 1 Graphical time trends of total CO_2 mean concentration (C_t) in (A) and (1–X) in (B) obtained from ^{14}C determination of tree rings.

Our results indicate a wiggle in the total exposition level, probably due to an increase of the source activity (about 65% with respect of the basal value) in the 1980s. This pulse, of about 100 ppm (in comparison to the mean value) in its maximum (1979), is characterized by a regular rise starting after 1968 and a regular decrease ending in 1998. For this period, the Lajatico plant community has experienced a non-constant enrichment of CO_2, as confirmed by the χ^2 test ($\nu = 6$, $\chi^2 = 25.78$, $p[\chi^2] = 0.02\%$) conducted on a constant exposure hypothesis (H_0) of 651 ppm (mean value). The ecophysiological effects of this pulse are actually not well known, and a great number of experiments still need to be carried out to characterize the effects of this long-term non-constant exposure on a plant community.

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CONCLUSIONS

We have shown how the AMS ^{14}C determination on tree rings, compared with atmospheric ^{14}C records, can provide a valid method to reconstruct the past CO_2 content of naturally enriched local atmospheres. This result is useful to the global change biological scientific community and also to geochemistry applications (Hoefs 1997).

It is possible to achieve a high sensitivity in the C_t and $(1–X)$ determinations because of the strong differences in terms of ^{14}C content of the sources contributing to the total CO_2 exposure in the Lajatico enriched site. The small mass required (a few milligrams) for an AMS determination permitted non-destructive sampling, preserving the sampled individual for other and/or further analyses.

The period to which this kind of analysis can be extended is limited by the availability of old trees on the site and, by means of wiggle matching (Bronk Ramsey 2001), to a few generations of individuals.

Over 34 years (1964–1998), the Lajatico enriched atmosphere has maintained its CO_2 concentration levels around an average value of 652 ppm, with a variation amplitude of 139 ppm (max 736, min 597). All the C_t values are largely included in the variation range of the latest IRGA campaigns, as discussed in the Site Description section (Tognetti et al. 2000), but they indicate to the scientific community a need to revise the constant exposure hypothesis within the period of our investigation.

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