

Communication

## Laser Photoacoustic Detection of CO<sub>2</sub> in Old Disc Tree-Rings

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**Abstract:** A homemade CO<sub>2</sub>-laser photoacoustic spectrometer has been used for monitoring CO<sub>2</sub> in gas samples extracted under vacuum from the wood of old spruce disc tree-rings for a ~60 year series. The experimental results show that (1) the CO<sub>2</sub> concentration exhibits annual trends correlated with an increase in atmospheric CO<sub>2</sub> in a number of cases; (2) at the time when the annual CO<sub>2</sub> trend changes from positive to negative, the annual tree-ring stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of CO<sub>2</sub> change as well; (3) the disc tree-ring widths are observed to decrease in most cases where the annual CO<sub>2</sub> increased; (4) simultaneously with the annual CO<sub>2</sub> variation, annual H<sub>2</sub>O distribution was detected in gas samples of the wood tree-rings of one spruce disc. The observed patterns of the annual CO<sub>2</sub> distribution in the disc tree-rings are assumed to be the evidence of the impact of the atmospheric CO<sub>2</sub> increase. In other words, a change in the concentration gradient between the stem and the atmospheric CO<sub>2</sub> may lead to a gradual CO<sub>2</sub> accumulation in the stem because of a decrease in the diffusion rate and to a change in the tree parameters.

**Keywords:** laser photoacoustic gas analysis; carbon dioxide; tree-rings; H<sub>2</sub>O

**Classification:** PACS: 42.62.Fi

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## 1. Introduction

It is recognized that due to a high CO<sub>2</sub> concentration in the stem of a living tree [1], an increase in the atmospheric CO<sub>2</sub> produce minor changes in the concentration gradient between the atmospheric and stem CO<sub>2</sub>. Thus an increase in the atmospheric CO<sub>2</sub> does not significantly affect the diffusion of CO<sub>2</sub> from the tree stem into the atmosphere. However, an annual change in the concentration gradient due to the increase in the atmospheric CO<sub>2</sub> does exist (and will exist in the future) and we believe that the dynamics of this process must be evident in the CO<sub>2</sub> concentration trend in the stem. We have hypothesized [2] that the wood of tree-rings of old tree discs where a large amount of CO<sub>2</sub> has been preserved [3] may contain this information, since gases involved in metabolism of a living tree in each of the years studied are sorbed by a capillary-porous system of the ring wood and may be preserved for a long time within stems. In this work, we report the results of a laser photoacoustic gas analysis of CO<sub>2</sub> present in gas samples extracted under vacuum from annual rings of 5 spruce discs for a ~60 year series, as well as results of correlation analysis of data versus the concentration of atmospheric CO<sub>2</sub>. Nowadays photoacoustic spectrometers based on different lasers are unique tools for gas testing [4–7], medical diagnostic by breath [8,9], *etc.*

## 2. Experimental Section

The concentration of CO<sub>2</sub> (extracted under vacuum) in the wood of tree-rings was measured on 5 spruce discs, collected 30 km away from Tomsk in 2004. The mean radius and height of the trees were ~26 cm and ~23 m, respectively, and the number of rings was ~85. All discs were stored under laboratory conditions until 2009, so the wood can be considered to be room-dried. The measurements were made using a homemade laser photoacoustic spectrometer with a computer-controlled tunable waveguide CO<sub>2</sub>-laser [10]. The detection limit of the spectrometer for a laser power of 70 mW was  $2 \times 10^{-5} \text{ cm}^{-1}$  and the measurement error was  $\pm 5\%$ . Before the measurements, the system was calibrated using a CO<sub>2</sub>/N<sub>2</sub> reference mixture. A maximum sensitivity of the photoacoustic detector was achieved for a total pressure of 100 Torr. All measurements were performed at this pressure. To prepare the samples for the analysis, the wood of 4 rings was planed down using special chisels. Then the samples were weighted (3–20 g) and placed in 4 sealed exposure chambers. The latter were evacuated down to a vacuum of ~0.1 Torr for 1 min for gas diffusion stimulation. Because the larger the sample amount, the higher the gas pressure P(total) and P(CO<sub>2</sub>), it follows that P(CO<sub>2</sub>): P(total) [ppm] = const, irrespective of the sample weight. Then the exposure chambers were allowed to stay for 40 min to ensure a maximum yield of gases sorbed by the wood. Next, an exposure chamber was connected to the evacuated photoacoustic detector so that the gas samples enter the detector and air was admitted to get a total pressure of 100 Torr. We have analyzed each ring gas sample at the same pressure (~6 Torr) and in the same volume (photoacoustic detector). The signal amplitudes  $U_m$  from the analyzed gas sample (100 + 6 Torr) and from air  $U_a$  (at 100 Torr) were recorded, and the difference  $\Delta U = U_m - U_a$  was determined automatically. Using a calibration curve, we determined a relative CO<sub>2</sub> content in the gas sample for each of 4 rings of the disc. Then, the wood of the next 4 rings was examined on CO<sub>2</sub> and so on. The absorption by the gas samples in a detector of laser radiation at 3 laser lines 10P (20, 16, 14) was found to be approximately equal. For our purposes,

use was made of an average value of absorption. The CO<sub>2</sub> measurements were made at laser lines that did not coincide with water lines at a gas sample pressure of 6–8 Torr. The absorption coefficients of H<sub>2</sub>O in the P10 (20, 16, 14) laser lines calculated by the line-by-line method [11] with spectroscopic database HITRAN 2008 [12] were 10<sup>2</sup>–10<sup>3</sup> times lower than the CO<sub>2</sub> absorption coefficient (at 1 atm). We believe that these measurements refer mostly to CO<sub>2</sub> in these lines, the water contribution is negligible small. The presence of water in the gas samples was detected from the signal in the CO<sub>2</sub> laser line 10R (20) whose frequency coincided with the H<sub>2</sub>O absorption line center.

H<sub>2</sub>O detection experiments were carried out using a classical drying method [13]: milled wood of the rings was placed into weighting bottles and that were allowed to stay in a thermostat 100–103 °C for two days and the difference in weights was then determined.

The tree-ring stable carbon isotope ratio ( $\delta^{13}\text{C}$ ) of CO<sub>2</sub> chemically extracted from the wood rings was analyzed by an automated measuring MI-1201V Mass Spectrometer and DELTA V Advantage. The samples were prepared using standard certified methods of chemical preparation of organic substances. The results were reduced to the PDB international standard of Vienna Pee Dee belemnite for C.

### 3. Results and Discussion

In our earlier work [2], the annual CO<sub>2</sub> distribution in the wood of tree-rings of old fir tree discs was reported for a 25-year series. It was found that in most cases, the CO<sub>2</sub> content in gas samples extracted under vacuum from the annual rings of the discs was higher than the atmospheric CO<sub>2</sub>. Moreover, an annual trend of the CO<sub>2</sub> concentration exists and in some cases, it correlates with atmospheric CO<sub>2</sub> (and O<sub>3</sub> [14]).

Measurements of CO<sub>2</sub> extracted under vacuum from the wood of the tree rings of 5 spruce discs were performed for a ~60 year series (1940–2004) using the homemade laser photoacoustic spectrometer.

#### 3.1. Correlation between Tree-Rings and Atmospheric CO<sub>2</sub>

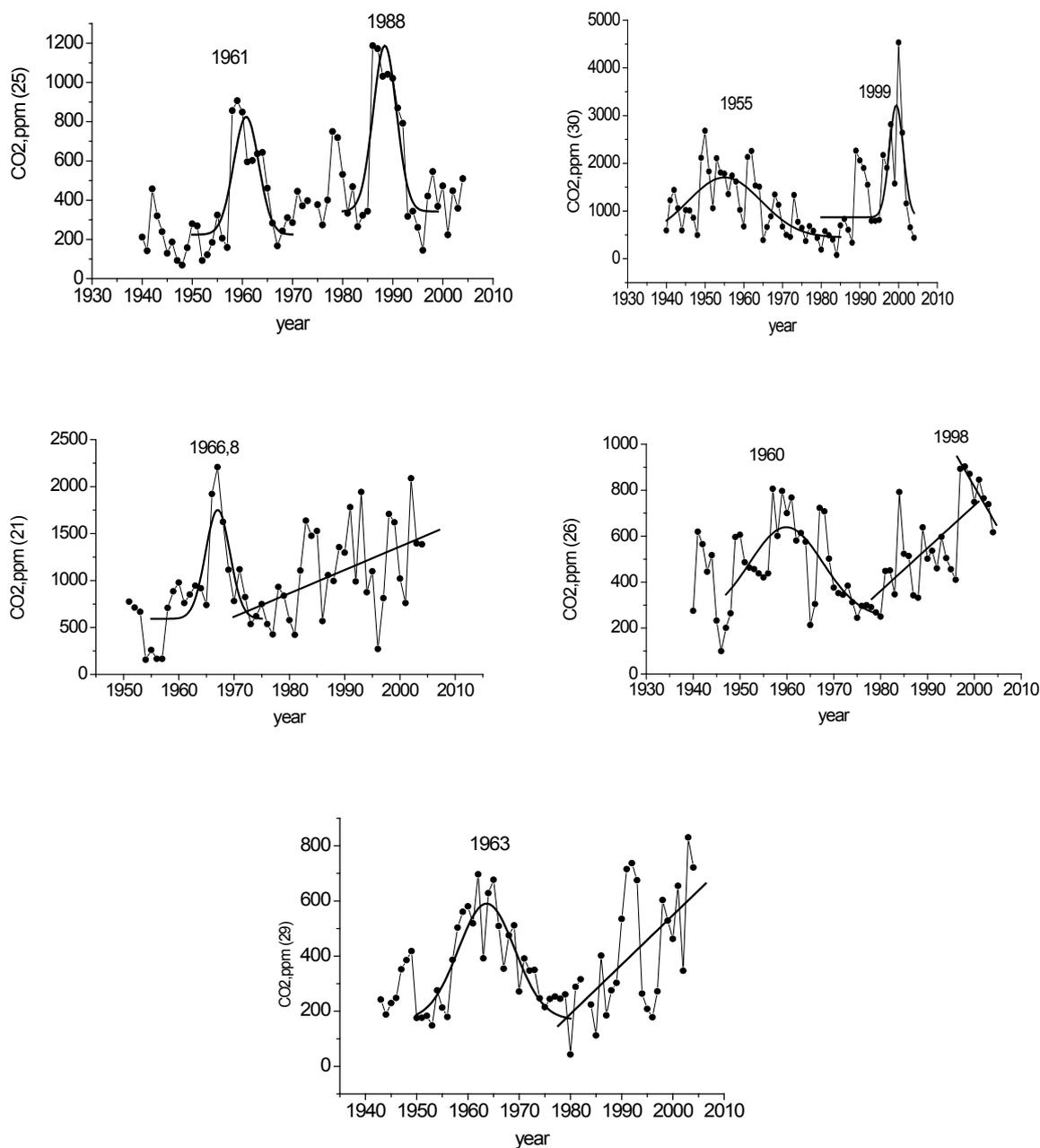
The measurements of the CO<sub>2</sub> content in the wood of the rings of 5 spruce discs revealed certain characteristic features: in all discs the first CO<sub>2</sub> concentration maximum in the tree-rings was roughly dated to the 1960s, whereas the second maximum observed in certain discs was dated to ~1988–1999 (Figure 1). Strong CO<sub>2</sub> fluctuations were caused by structural heterogeneity of the biological objects under study and partly by the difference in wood ring destruction during sample preparation. However, even for such a spread in the results, the tendency for the CO<sub>2</sub> growth in the discs is well pronounced.

We compared our CO<sub>2</sub> measurements in the tree-rings with the atmospheric CO<sub>2</sub>. To this end, all annual CO<sub>2</sub> trends were divided into annual sections and the years where CO<sub>2</sub> increased were compared with the those of Mauna Loa data on an increase in the atmospheric CO<sub>2</sub> (2008, <http://cdiac.ornl.gov/ftp/trends/co2/maunaloa.co2>). If a linear approximation could be used for our data and those of Mauna Loa, the correlation between them was determined using Origin software package and the correlation coefficients R and P values (probability that R is zero) were estimated.

The results of the correlation are presented in Table 1. Assuming the significance level of  $P \leq 0.05$ , we may conclude that the observed positive CO<sub>2</sub> trend in the disc tree rings for the above indicated CO<sub>2</sub> fluctuations correlate well with the increase in the atmospheric CO<sub>2</sub>. The change of the sign of the trend seen in the 1990s was observed by a number of investigators who carried out isotope analyses for

cellulose carbon in tree rings [15,16]. The decrease in the tree-ring  $\delta^{13}\text{C}$  was explained in the following way: “Tree-ring  $\delta^{13}\text{C}$  chronologies showing a decline over recent decades, that is not explained by a parallel change in the controlling climatic variables, have been reported from several areas, including the Swiss Alps, north-eastern France. McCarroll *et al.* (2009) suggest that this is threshold effect, with trees having reached the limits of physiological adaptation to increasing  $\text{CO}_2$  levels in the atmosphere” [17]. Conceivably, the change of the sign of the trend in the annual  $\text{CO}_2$  distribution (maximum) in the disc and cellulose carbon is due to general metabolic processes. We recorded another maximum as early as the 1960s. It is evident in Figure 1 that, for certain discs, the annual  $\text{CO}_2$  growth in the 1990s did not reach a maximum, probably due to tree growth conditions.

**Figure 1.** Annual trends of the  $\text{CO}_2$  concentration in spruce discs (No. 21, 25, 26, 29, 30) obtained with the use of a Gaussian approximation for identifying a maximum content.



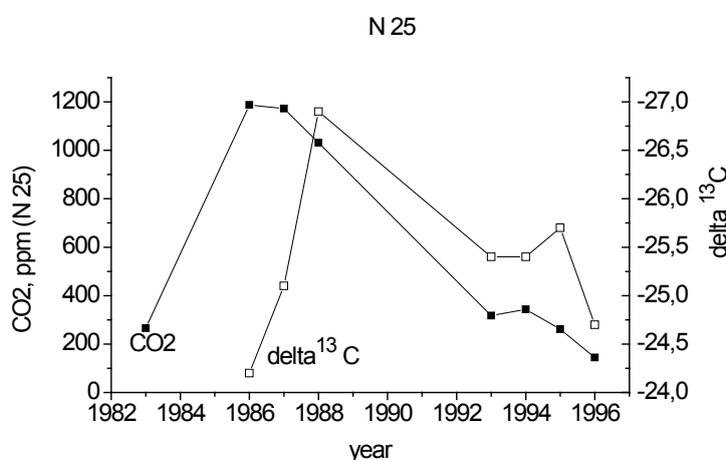
**Table 1.** Correlation between spruce disc and atmospheric CO<sub>2</sub>.

Spruce No.	Total number of tree rings	Time period	Correlation coefficients	Probability (that R=0)	N, number of measurements (data points)
			R	P	
21	~75	1970–2004	+0.5	0.00216	34
25	~90	1966–1993	+0.66	$1.9 \times 10^{-4}$	27
26	~80	1975–1997	+0.53	0.01	22
		1938–1960	+0.73	0.01	11
29	~80–90	1980–2004	+0.59	0.00261	24
30	~150	1988–2000	+0.69	$3.6 \times 10^{-4}$	22

### 3.2. The Sign of the CO<sub>2</sub> Trend Associated with a Change in Metabolic Processes

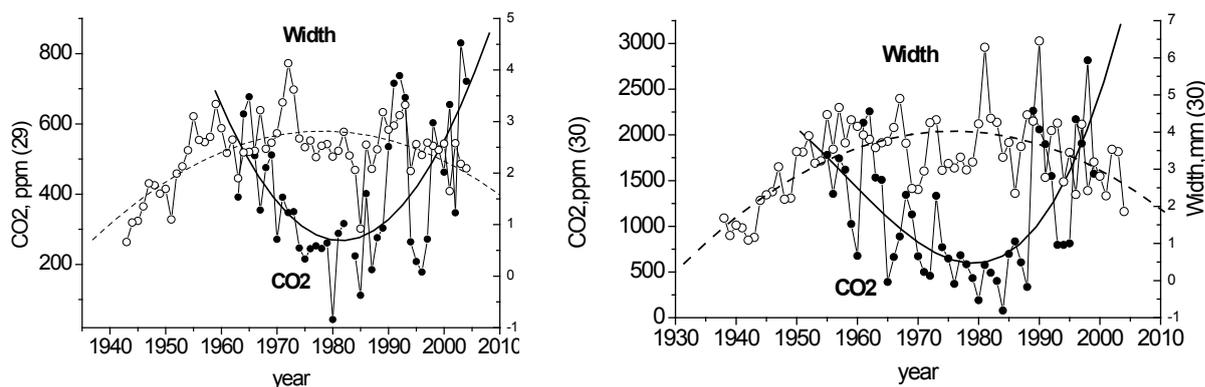
According to our earlier assumption [18], the change of the sign of the trend (*i.e.*, a decrease in the CO<sub>2</sub> concentration in the discs after its increase) is attributable to any change in metabolic processes. This assumption can be verified by analyzing the tree-ring stable carbon isotope ratios of CO<sub>2</sub> ( $\delta^{13}\text{C}$ ). It is known that terrestrial plants (C<sub>3</sub> type, including conifers) are characterized by a range of isotope compositions ( $\delta^{13}\text{C}$ ) from approximately  $-22\text{‰}$  to  $-32\text{‰}$ , while the isotope composition of the atmosphere is on average  $-7\text{‰}$  [19]. The results obtained from an investigation of ( $\delta^{13}\text{C}$ ) in the time period where the disc CO<sub>2</sub> (spruce 25) changes the sign are illustrated in Figure 2. It is obvious that CO<sub>2</sub> was formed by the tree itself. Stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of CO<sub>2</sub> changed as well, along with the annual CO<sub>2</sub> variations in the tree-rings.

**Figure 2.** Annual trend of the CO<sub>2</sub> concentration in a spruce disc (No. 25) and  $\delta^{13}\text{C}$  isotope composition (delta<sup>13</sup>C).



We compared our annual CO<sub>2</sub> distribution over spruce disc tree-rings with the ring widths. In most cases, the annual ring width narrows with increase in the annual CO<sub>2</sub> (Figure 3).

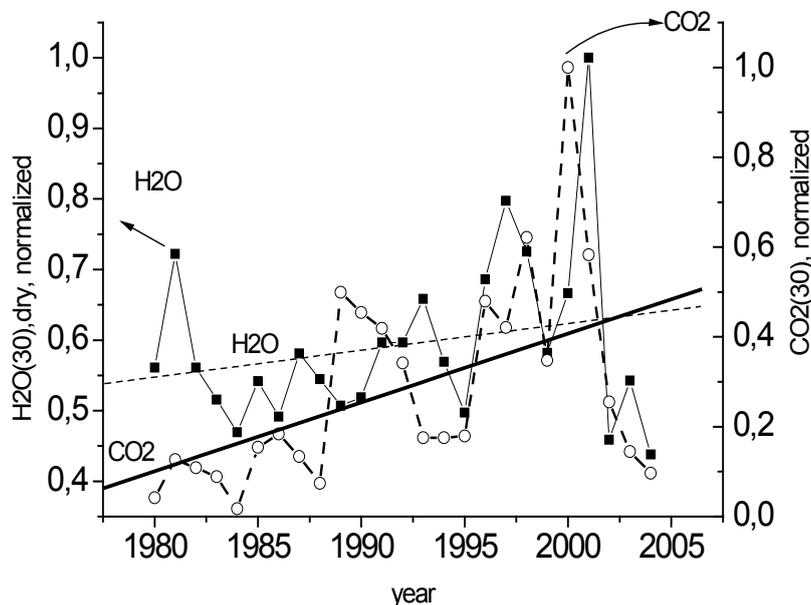
**Figure 3.** Annual trends of the tree-ring CO<sub>2</sub> concentration and widths of spruce discs (No. 29, 30).



### 3.3. Presence of CO<sub>2</sub> in Tree-Ring Water

Early in the experiment, it was assumed that CO<sub>2</sub> was sorbed only by the wood capillary-porous system. The results showed that tree-ring gas samples contained not only CO<sub>2</sub> but H<sub>2</sub>O as well. Figure 4 illustrates the annual CO<sub>2</sub> distribution (normalized to unity) measured by the photoacoustic method and the annual H<sub>2</sub>O distribution measured by the classical drying method in the tree-rings (disc 30). As seen from Figure 4, CO<sub>2</sub> and H<sub>2</sub>O demonstrate nearly identical trends. This leads us to suggest that CO<sub>2</sub> also exists in water solution. There are many papers concerning the moisture content in wood (see, e.g., [20,21]), but none of them considers annual H<sub>2</sub>O distribution in old disc tree-rings.

**Figure 4.** The tree-ring CO<sub>2</sub> and H<sub>2</sub>O concentrations (normalized to unity) of a spruce disc (No. 30) obtained by two methods.



#### 4. Conclusions

It is generally accepted that a long stay of tree discs under atmospheric conditions makes the stem-contained excess CO<sub>2</sub> to decrease down to the atmospheric CO<sub>2</sub> level due to diffusion processes. However, the results of our measurements of the CO<sub>2</sub> extracted under the vacuum from the wood of tree-rings of old discs by the photoacoustic method have shown that (1) in most cases, the relative CO<sub>2</sub> content in gas samples exceeds the atmospheric CO<sub>2</sub> concentration; (2) certain annual trends of the CO<sub>2</sub> concentration are observed; (3) the trend of the annual CO<sub>2</sub> concentration in the rings of spruce discs changes the sign (from positive to negative) and the tree-ring stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) change as well; and (4) in the time period where the CO<sub>2</sub> concentration in the wood of tree-rings increases, the ring widths change (they are generally narrowed).

It is our opinion, that the observed CO<sub>2</sub> trends are associated with the increase in the atmospheric CO<sub>2</sub> content: the permanent growth of the atmospheric CO<sub>2</sub> always decreases the CO<sub>2</sub> diffusion rate from the stem, thus resulting in CO<sub>2</sub> accumulation and, probably, in a change of certain internal metabolic processes. It is impossible to detect such a trend in a living tree, whereas the analysis of the wood sorbed gas can reveal its existence. We can also assume that the increased sorbed CO<sub>2</sub> concentration in the tree-rings may be attributed to the ring narrowing, which conceivably explains why the trees do not show large radial increment when the temperature and atmospheric CO<sub>2</sub> increase. The results obtained show that old discs contain valuable information that can be used for estimating the carbon budget in forests.

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