

Laser Photoacoustic Method for Disc Tree-Ring Gas Analysis

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Abstract A laser photoacoustic gas analysis was used to study the annual CO₂ and H₂O trends in tree rings and their comparison with the tree ring width of dry discs was made. The measurements show that 1) the CO₂ concentration in gas samples vacuum-extracted from annual tree rings correlates with atmospheric CO₂ rise in certain cases; approximately 4-year cycles in CO₂ distribution were readily fixed; 2) for the Scots pine discs, years with small tree ring width are characterized by high CO₂ concentration, while those with large tree ring width are associated with small CO₂ concentration. Abrupt changes in atmospheric conditions are assumed to favour increased amplitudes of one of natural cycles of annual CO₂.

Keywords CO₂, annual tree rings, laser photoacoustic method

1. Introduction

Current period is extremely interesting from the viewpoint of studying the effect of sharply changing atmospheric conditions on plants: changes in CO₂ in the atmosphere and those in the C isotope ratio in CO₂ are likely to affect plant photosynthesis and to give rise to changes in certain plant parameters as a response to stress.

Tree rings are generally considered as records of past climatic conditions and environmental changes[1]. However, researchers encounter some problems in studying the effect of atmospheric CO₂ rise on the plants or in estimating the internal and external CO₂ release by stems[2]. The atmospheric CO₂ rise and climate warming are expected to enhance the annual growth of tree ring widths, which is not the case, however. In particular, Schweingruber[3] wrote, that: "... the fact remains that none of the many studies from the northern and southern hemisphere show for the last 500 years an unexplainable growth increase that is clearly symptomatic of the modern climate change or of CO₂- fertilization". As Gedalof and Berg have noted in their work[4], a direct CO₂ fertilization effect is traceable in as little as 20 % of the areas around the globe.

The atmospheric CO₂ concentration (0.04%) is known to be lower than the CO₂ content in stems, where it may be as high as 20% and more. Except for gas-phase CO₂, a large amount of CO₂ in stems is dissolved in xylem sap. Most CO₂ within stems originates from respiring cells in stems

and roots. It is well established now that a large amount of respired CO₂ is transported upward in a transpiration stream, and some portion of CO₂ is fixed in green woody tissues/leaves before it can diffuse to the atmosphere[5]. At the same time, the vacuum method used in our investigations for gas sample extraction from the annual ring wood showed that a certain amount of CO₂ remained in dry old discs and exhibited a specific annual distribution. We have hypothesized that this distribution is the result of atmospheric parameter changes: atmospheric CO₂ rise alters the annual concentration gradient between the atmospheric and stem-contained CO₂. Hence, the dynamics of this process is likely to cause the annual CO₂ changes in stems. There are many papers aimed at estimating the CO₂ release to the atmosphere by stems, however, to our knowledge, none of them deals with annual CO₂ trend estimations inside stems.

Using our laser photoacoustic spectrometer with a tunable CO₂ laser, it is possible to trace the annual CO₂ trend in discs and to characterize the H₂O distribution over tree rings. The water content in discs of living trees has been studied by different methods (e.g., by computer X-ray tomography[6]). However, we are not aware of any attempts to characterize the annual water distribution over rings in dry discs. It should be noted that the method suggested here was tested not only on dry discs, i.e., those stored under laboratory conditions for a few years, but on a disc of a living tree as well.

A laser photoacoustic analysis based on different laser sources is a modern gas-detection tool used successfully in many applications for a long time[7-13]. We were the first to use this method for measuring the annual CO₂ content and determining the H₂O trends in disc rings of some coniferous trees. A plausible explanation of small tree ring

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growth appears to be stress situation (atmospheric CO₂ rise and C isotope ratio change) leading to a CO₂ accumulation inside stems due to “possible shifts in respiration”[14].

This work compares measurements of the CO₂ content in annual tree rings of dry discs of the Siberian stone pine, Scots pine, and living Scots pine. A correlation between the CO₂ content measurements and atmospheric CO₂ rise is analyzed, the characteristics of the annual H₂O distribution over disc tree rings are presented, and the carbon isotope content of CO₂ desorbed from tree rings of discs is estimated.

The measurement results can be used by dendrochronologists, dendroecologists, and those dealing with carbon budget and carbon dioxide flux estimation between terrestrial ecosystems and the atmosphere. Hopefully, they will increase the reliability of tree ring data as proxies for environmental conditions.

2. Material and Methods

The CO₂ content in gas samples extracted under vacuum from tree rings was measured in a Siberian stone pine dry disc, two Scots pine dry discs and a newly sawed Scots pine disc. The Siberian stone pine disc was sawed at a height of 1.5 m, and two Scots pine dry discs (No.6 and No.12) were sawed at a height of 60 cm and 1.4 m above the ground, respectively. The newly sawed Scots pine disc (pine 2011) was sawed from a pine tree broken by the wind in the spring of 2011 at a height of 70 – 80cm above the ground. All discs were sawed near Tomsk (West Siberia, Russia). The dry discs were stored from 6 months to a few years under laboratory conditions, so the wood material can be considered to be room-dried. The time series studied spanned 100 years for the Siberian stone pine, 104 and 90 years for two dry Scots pine discs and 55 years for the newly sawed pine disc.

The measurements were performed using a computer-controlled laser photoacoustic (PA) spectrometer with a frequency-tunable waveguide CO₂ laser[15]. PA spectroscopic methods offer essential advances in pollutant gas monitoring[7–9,16–18]. The PA signal originates from the non-radiative de-excitation of the energy absorbed by gas in optical transitions, the absorbed power is determined directly via heat, and sound is generated in a gas sample. The acoustic waves are then measured by a cell microphone. Therefore, the PA spectrum can be correlated with optical absorption spectra of the sample[18]. Once the system is calibrated, i.e., the absorption in gases with known concentrations is measured and the calibration coefficient is found, the absorbing component concentration in the gas sample studied is determined.

The spectrometer setup (Fig.1) and measurement procedure were standard for PA gas absorption measurements. The sealed-off RF-excited waveguide CO₂ laser with computer controlled tuning frequency and stabilization to the centre of the line chosen was used as a light source[15]. It

was found experimentally that such lasers have a high constructive rigidity and low sensitivity to external mechanical impacts. A gold-coated reflecting grating with a period of 150 mm⁻¹ is used as a back laser mirror.

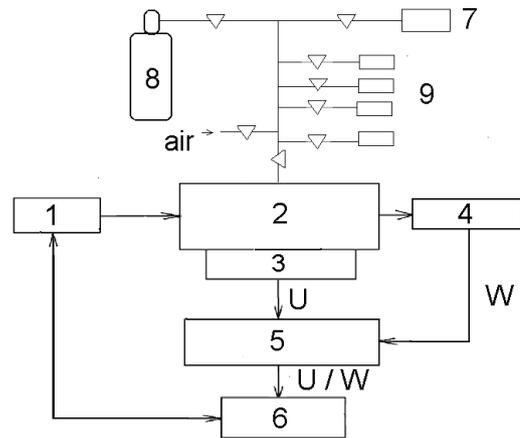


Figure 1. Block-diagram of the PA-Laser spectrometer: 1— a CO₂ Laser, 2—a photoacoustic cell, 3—a microphone, 4 — a photodetector, 5 — a system for measuring and recording electric signals, 6 — a computer, 7— a pump, 8— CO₂/N₂ reference mixture, 9 — exposure chambers

The laser emits more than 70 lines within a tuning spectral range of 9.2 – 10.8 μm with an output power of 0.3 — 3 W in a single-mode single-frequency regime. Laser radiation is modulated via amplitude modulation of a pump power high-frequency (RF-) generator. An attenuator (Ge or BaF₂) is placed in front of a PA-cell so that the modulated CO₂ laser radiation is ~ 70 mW before passing through the cell. A nonresonance photoacoustic detector is used for measuring the absorption photoacoustic signal U. A detector made from stainless steel consists of a cylindrical gas PA-cell (Ø10×100 mm) (2) and is connected to a microphone cell (3), where a homemade plane capacitor microphone is placed. BaF₂ windows are mounted at both ends of the PA-cell. Low (123 Hz) modulation frequency of radiation is selected to increase the signal-to-noise ratio of the PA-detector[16]. Another photoacoustic detector (4) is used to measure the laser power W. The photodetector design is similar to the gas PA-cell, except that the chamber with a nonselective absorber (blackened metal foil) is used instead of a gas. The photoacoustic detector signals U and W are amplified by wideband amplifiers and fed into the measuring and recording system based on a computer sound card. Laser line tuning, detector signal recording and preliminary processing (averaging, ratio determination) are performed by means of special software.

The measurement results are stored in a file containing the values of $A = U/W$ for the corresponding laser lines, yielding an analog of the absorption spectrum in the sample. Information about the spectrum is displayed on a computer monitor to visualize the spectrometer data.

The system is pre-calibrated using a CO₂/N₂ reference mixture containing a known amount of CO₂. The PA cell is filled with the reference mixture of CO₂ concentration, and the values of $A=U/W$ and CO₂ concentration in the mixture

used are compared for selected laser lines. The ultimate absorption coefficient sensitivity of the spectrometer used was $2 \cdot 10^{-5} \text{ cm}^{-1}$ for a laser power of 70 mW, and the calibration measurement error did not exceed $\pm 5\%$.

Gas samples were prepared in the following way. The wood of tree rings was placed in four sealed exposure chambers pumped out for a short time to stimulate sorbed gas diffusion, and 20 minutes later the measurements were performed[19].

In all measurements, the gas samples from each exposure chamber (at a pressure of $\sim 800 - 1100 \text{ Pa}$) were admitted to an evacuated PA cell to which air was added to get a total pressure of 13300 Pa in the cell so that a maximum sensitivity of the PA cell was reached. Every **A_{ring}** measurement series in the wood-extracted sample studied was accompanied by measurements of background air absorption **A_{air}**. The information-bearing value was **DA = A_{ring} - A_{air}** from which the relative CO₂ concentration in the sample was determined using a calibration curve. Signals were recorded from four tunable CO₂ laser lines: 10 P (20, 16, 14) (coinciding with CO₂ absorption lines) and 10 R (20) (coinciding with an H₂O vapor absorption line). The H₂O absorption coefficients in the 10P (20, 16, 14) lines was much lower than the CO₂ absorption coefficients in these lines[20]. Thus, H₂O is considered to make a minor contribution to the CO₂ absorption in the 10 P (20, 16, 14) lines under our experimental conditions. Measurements in 10 P (14) were made to detect a possible appearance of the signal from ethylene, whose absorption coefficient in 10 P (14) is 10^3 times higher than that of CO₂.

To verify the fact that CO₂ in the samples studied was generated by the tree itself and not supplied from the atmosphere, an isotope analysis of the carbon ($\delta^{13}\text{C}$) CO₂ for a few rings was performed. Terrestrial plants (C₃ type, including conifers) are known to be characterized by a range of carbon isotope compositions ($\delta^{13}\text{C}$) from approximately -22 ‰ to -32 ‰ , whereas the atmospheric carbon isotope composition is on average -8.07 ‰ [21] with respect to standard Pee Dee belemnite (PDB)[22]:

$$\delta^{13}\text{C}, (\text{‰}) = [(R_{\text{sample}} / R_{\text{standard}}) - 1] \cdot 1000 \quad (1)$$

To study the isotope composition, CO₂ was desorbed from a tree ring in a nitrogen atmosphere at $T = 80^\circ\text{C}$. The stable carbon isotope ratio ($\delta^{13}\text{C}$) of the wood CO₂ was measured at Laboratory of Isotopic Methods of Tomsk Branch of FSUB SRIGGMR (Certificate No. ROSS RU 001 517930), using a DELTA V Advantage mass spectrometer, to within ± 0.5 for a confidence probability of 0.95.

The tree ring widths were measured on disc surfaces by a LINTAB measuring system within an accuracy of 0.01 mm.

3. Results

3.1. Temporal Variations of Signals

We have performed a preliminary analysis of the gas re-absorption rate from a sample and its possible reciprocal sorption by the wood in exposure chambers. To this end,

four exposure chambers filled with wood material, approximately homogeneous and equal in mass, were simultaneously subjected to short-term pumping-out, and during a certain time were under vacuum. Figure 2 presents normalized results of the signal variations with time for different CO₂ laser lines for these four exposure chambers.

The H₂O signal in short-term vacuum peaked within approximately 25 min, and then reabsorption began. In the other three lines, where the CO₂ signal was recorded, it reached its maximum only within $\sim 2.5 \text{ h}$, and then the re-absorption started again. While the values of the CO₂ absorption coefficients in the laser lines were very close, there was a marked difference between the gas sample absorption at the same wavelength. This is evidence of an organic wood material inhomogeneity in different exposure chambers.

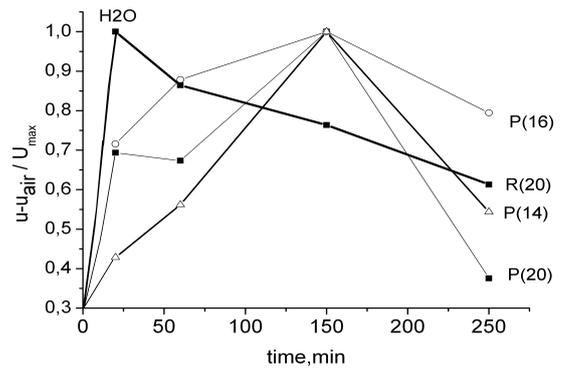


Figure 2. Temporal variations of signals from components reabsorbed from a disc at four CO₂ laser lines

3.1. Measurements of CO₂ Content in Disc Tree Rings

The measured relative tree ring CO₂ concentrations in the disc gas samples studied are shown in Figures 4, 5, 6, 7 and 8. The trends in carbon isotope composition $\delta^{13}\text{C}$ and atmospheric CO₂ (curve 1)[21] and NOAA data (curve 2) are illustrated in Fig. 3.

The annual CO₂ variations and annual behavior of the tree ring width of spruce[23] are also shown in Figure 8 for comparison. It is evident from Figs 4 – 8 that the CO₂ concentration in the tree rings is higher than the atmospheric CO₂ and that a noticeable annual trend in CO₂ exists. A comparison of the data for the Siberian stone pine ring widths and annual concentration of CO₂ extracted from tree rings shows that a rapid rise of the CO₂ content occurred after 1960, when the tree ring widths were minimal (Fig. 4). At the same time, the CO₂ concentration in dry discs of the Scots pine (Figs 5 and 6) increased up to 1960 (the data were taken as averages over 3 spectral lines), and then the CO₂ concentration decreased drastically down to a constant level of 1000 ppm (pine 12) or showed a slow rise (pine 6). Figures 5 and 6 for the Scots pine demonstrate the main tendencies in the CO₂ distribution over rings: 1) all data on the annual CO₂ concentration for pine up to 1960 exhibit distinct cycles with ~ 4 -year period; 2) the tree ring widths and CO₂ concentration in the Scots pine discs (Nos. 6 and 12) vary, roughly speaking, in “antiphase”: years with small

tree ring widths show high CO₂ concentrations, and vice versa.

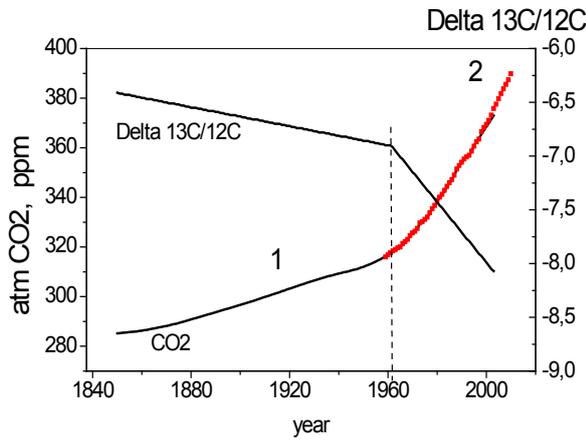


Figure 3. Trends in the stable carbon isotope ratio $\delta^{13}\text{C}$ (delta 13C) and atmospheric CO₂[21] (curve 1) and NOAA data (curve 2) [ftp://ftp.cmdl.noaa.gov/ccg/co2/trends/co2_annmean_mlo.txt].

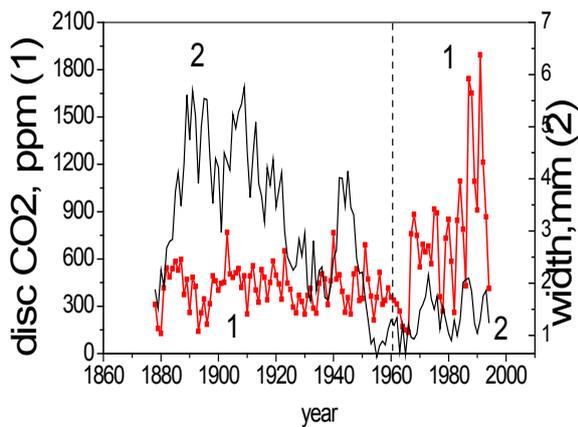


Figure 4. Annual variations in the tree ring CO₂ content (curve 1) and width (curve 2) in a Siberian stone pine disc

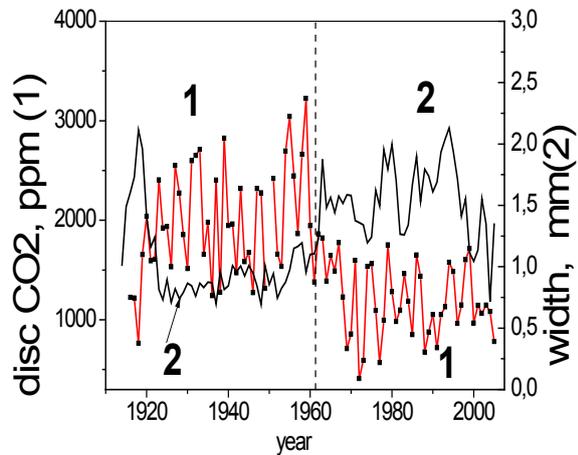


Figure 5. Annual variations in the tree ring CO₂ content (curve 1) and width (curve 2) in a Scots pine disc No. 6

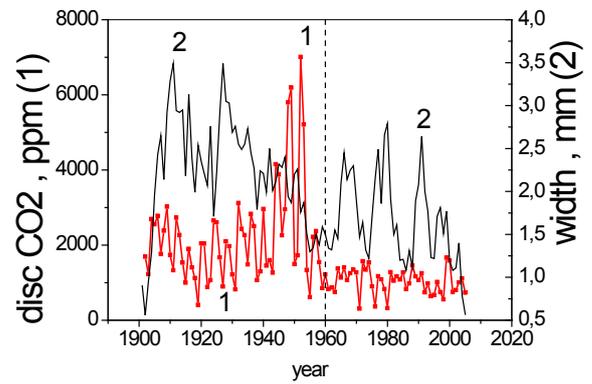


Figure 6. Annual variations in the tree ring CO₂ content (curve 1) and width (curve 2) in a Scots pine disc No. 12

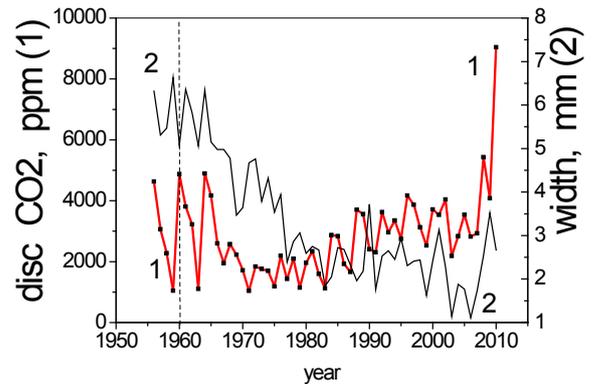


Figure 7. Annual variations in the tree ring CO₂ content (curve 1) and width (curve 2) in newly sawed Scots pine disc (pine-2011)

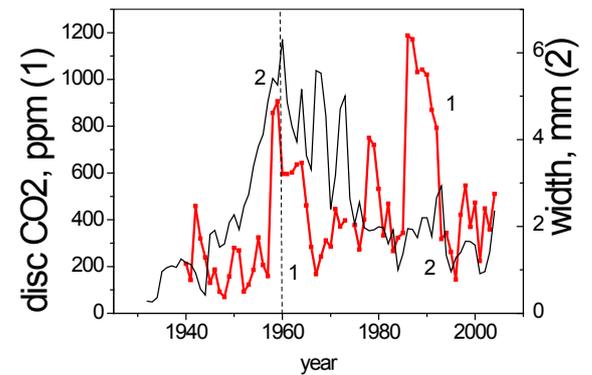


Figure 8. Annual variations in the tree ring CO₂ content (curve 1) and width (curve 2) in spruce No. 25

For a newly-sawed Scots pine disc (Fig. 7), the CO₂ concentration was high in wide tree rings of the early growth stage between 1956 and 1965 (positive coefficient correlation $R=0.45$, $P=0.0449$, $N=20$). On the contrary, in 1970 – 2010, the CO₂ annual content increased, whereas the tree ring width decreased in the pine studied ($R = -0.34$, $P=0.002751$, $N=41$). Thus, all discs show CO₂ rise, with the CO₂ concentration reaching 3000 – 8000 ppm in the Scots pine discs around 1960. The data on the CO₂ distribution in

the spruce tree rings (Fig. 8) also show a maximum around 1960. Notably, there is a second maximum of the CO₂ content (identified with a Voigt fit).

In our earlier work[24], we found a correlation between the annual trend in CO₂ in fir tree discs and total stratospheric ozone concentration for the growing period after 1980. However, the observed increase in the CO₂ concentration in the tree rings is attributable to atmospheric CO₂ rise [25]. A comparison of the tree ring CO₂ data obtained with those on the trend in the atmospheric CO₂ for Mauna Loa (2008, <http://cdiac.ornl.gov/ftp/trends/co2/maunaloa.co2>) and NOAA results showed their correlation: positive correlation coefficients varied in the range $R = 0.5 - 0.73$ ($P = 0.002 - 0.01$) for all spruce discs[23], and a significant correlation of the coefficient $R = 0.63$ ($P < 0.0001$) was found for the Siberian stone pine. A comparison of the trend in CO₂ for the Scots pine discs with atmospheric CO₂ showed a weak positive correlation between them until 1960 ($R = 0.39$, $P = 0.0081$ for pine No. 6 and $R = 0.40$, $P = 0.00321$ for pine No. 12), but an insignificant correlation was established after 1960. However, a slight CO₂ rise in the disc tree rings of pine No. 6 was observed. For the living tree disc (pine-2011), there was a weak correlation between the tree ring CO₂ and atmospheric CO₂ rise in 1959 – 2010: $R = 0.46$, $P = 5.35863 \cdot 10^{-4}$. Comparison of the CO₂ measurements for all discs of different conifers shows that sudden changes in the atmospheric conditions (Fig. 3) intensify one of the cyclic processes (e.g., with the 30-year period, see Figure 8), whose first maximum appears in the 1960s (Fourier analysis has shown the presence of harmonic oscillations with periods of 2, 4, 16.5, 23.5 and 29 years in the tree ring CO₂ distributions[19]). There is no second maximum for dry discs of the Scots pine. This may be due to CO₂ actively accumulated around the first maximum somewhere around 1960. For the pine-2011 disc, CO₂ was found to rise after 1970, supposedly, indicating the development of the second maximum

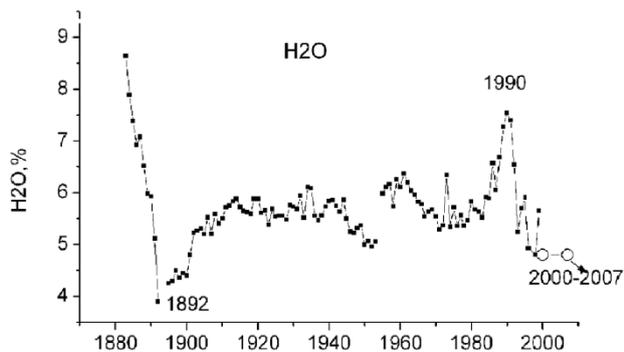


Figure 9. Variation of water content in Siberian stone pine tree rings

3.2. Trend in H₂O in Disc Tree Rings

Results on the annual water content in Siberian stone pine rings obtained by the classical method of sample drying up to a perfectly dry state are presented in Fig. 9. Data for 1954 are excluded because of a high water content due

to increased resin concentration. The tree rings for recent years also contain a lot of resin. It was shown that there existed a weak correlation between water content in the Siberian stone pine disc and summer precipitations during 1896 – 1960 ($R = 0.20$; $P = 0.10926$). A high correlation ($R = -0.88$, $P = 8.69396 \cdot 10^{-4}$) exists between the water content in disc rings and the ring width in the beginning of the tree growth (1883 – 1896), and a weak correlation for other years ($R = -0.41$, $P < 0.0001$, $N = 103$).

CO₂ in plant tissues is known to exist both in gaseous and liquid phases[2]. Tuning of the CO₂ laser line allows for detection of water vapour extracted simultaneously with CO₂ from the tree rings under vacuum with the use of the 10R(20) laser line whose frequency coincides with the H₂O absorption line center. Variations in signals ΔA characterizing the CO₂ laser absorption by H₂O desorbed from the tree rings for the Siberian stone pine disc and Scots pine disc (No. 6) are illustrated in Fig. 10 (a, b). Approximately 4-year cycles are readily seen. At the same time, certain long-period cycles were detected as well. Long-period cycles were roughly estimated using polynomial fits: the oscillation periods were 25 – 30 years for the Siberian stone pine and 29 – 30 years for pine. For the pine-2011 disc, a significant positive correlation was established between CO₂ and H₂O signals ($R = 0.88$, $P < 0.0001$, $N = 55$), suggesting that most of CO₂ extracted from the pine-2011 disc tree rings is dissolved in water.

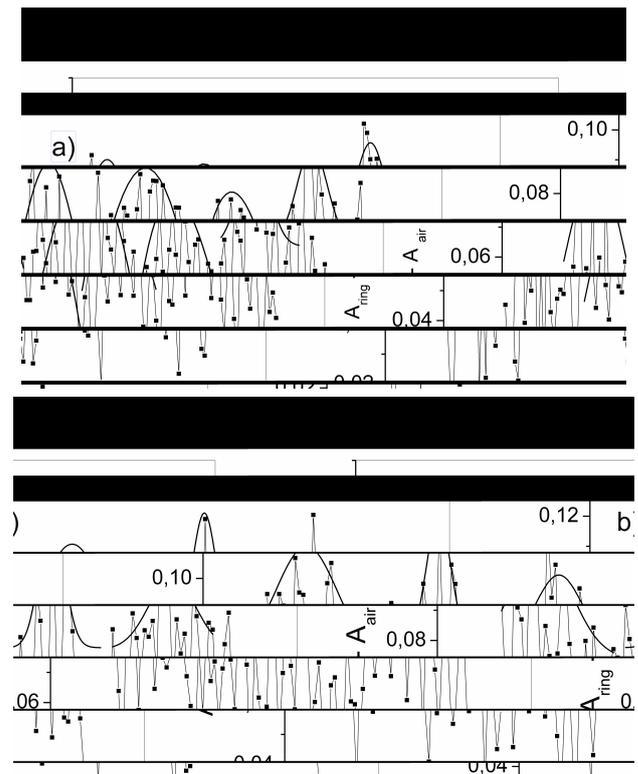


Figure 10 (a,b). Periodic variations of H₂O signals for annual tree rings of (a) Siberian stone pine and (b) Scots pine discs. Fitting is used for cycle detection

In contrast to the experiment where the water amount in tree rings was determined through the total drying for 48 h

up to a perfectly dry state, in the case at hand we detected free water, that easily diffused into the exposure chamber during 20 min due to a decrease in the pressure.

3.3. Variations of the Carbon Isotope Composition of CO₂ ($\delta^{13}\text{C}$)

Measurements of the carbon isotope composition of desorbed CO₂ from the Siberian stone pine and Scots pine tree rings show variations of $\delta^{13}\text{C}$ in the samples studied, on the average, in the (-22.1) — (-36.6) ‰ range, thus strongly indicating generation of the desorbed tree-ring CO₂ by the trees themselves. Measurements of the carbon isotope composition of CO₂ desorbed from stone pine disc tree rings show that the carbon isotope composition changes practically immediately with CO₂ content rise in the sample: the higher is the CO₂ concentration in the sample, the lighter is its isotope composition, and vice versa (Fig. 11). Moreover, the carbon isotope composition of CO₂ desorbed from the Siberian stone pine tree rings dated to the 1990s (-36.6 ‰) turned out to be lighter than that dated to the 1920s (-26.5 ‰) (Fig. 12). A similar tendency was noted for Scots pine No12 (-25.4 ‰ in 1930 and -34.8 in 1969). This seems to be primarily due to age-related changes in biochemical reactions and in the associated processes of fractionating of the carbon isotopes [22,26–29].

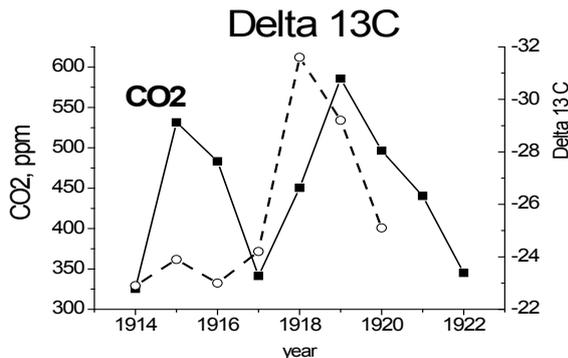


Figure 11. Variations of the carbon isotope composition of CO₂ and CO₂ content (ppm) in tree rings of the Siberian stone pine disc

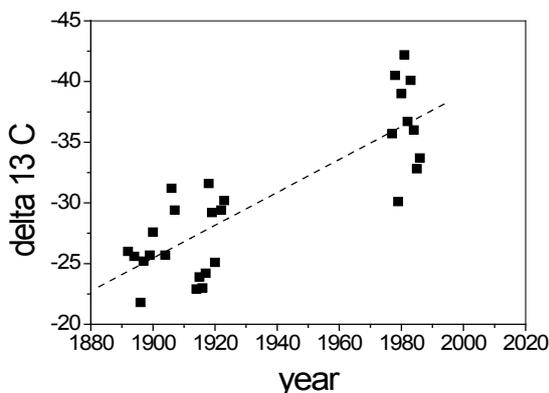


Figure 12. Variation of the isotope composition of the carbon of CO₂ in gas samples of the 1920s and 1990s in tree rings of the Siberian stone pine disc

4. Conclusions

Our studies of the annual CO₂ and H₂O content in disc tree rings by the laser photoacoustic method suggest the following conclusions:

1) disc tree rings contain a certain amount of tree-produced CO₂ whose concentration is higher than that of atmospheric CO₂, that does not diffuse to the atmosphere;

2) the annual increase of the disc CO₂ content correlates with atmospheric CO₂ rise in certain cases;

3) based on a comparison of the CO₂ data for all tree-ring discs, we can assume that changes in atmospheric conditions (rapid CO₂ rise and carbon isotope ¹³C/¹²C ratio variations) favour increased amplitudes of one of the natural cycles of the annual CO₂ tree ring distribution in the stem whose first maximum lies somewhere in 1960. Naturally, the energy lost to maintain this process results in a smaller ring width;

4) if our assumption that the CO₂ diffusion rate from the stem changes with atmospheric CO₂ rise is correct, care should be taken in performing experiments on growing chambers where the effect of an excess CO₂ content on plants is modeled. This is due to the fact that in some cases, the excess CO₂ influences the tree ring width. It would be interesting to monitor the annual CO₂ distribution and tree ring width in discs of this kind.

Thus, the use of the laser photoacoustic method provides a unique opportunity for studying the multiyear time series of the CO₂ and H₂O contents in conifer disc tree rings and obtaining valuable information on their relation to atmospheric parameters.

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