# Possible Forcing of the Greenhouse Phenomenon Under Stress of Plants and Soil Caused by Atmospheric Pollutants

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## Introduction

Plant biosystems take an active part in planetary biochemical cycles and may affect chemical and physical characteristics of the earth's atmosphere. To estimate the long-term variation in concentration levels of  $CO_2$  and other gases contributing to the greenhouse effect, the biospheric-atmospheric exchange specificity must be investigated under controllable stress actions, such as superconcentration of atmospheric pollutants in industrial regions, for example. The response of plant biosystems to natural and anthropogenic stressors can be manifested by activation of respiration processes, which, as a rule, is accompanied by an increase of the  $CO_2$ -evolution (Mokronosov and Kovaleva 1989, Nichiporovich 1990, Moldau 1993).

The elevated concentration of the atmospheric  $O_3$  and pollutants such as  $C_xH_y$  and  $CO_x$  are the subjects of our prime interest. So, we will discuss a diagnostic potentiality of the absorption spectroscopy instrumentation for estimating the kinetics of the  $CO_2$  evolution by different plants exposed to polluted atmosphere action.

Infrared (IR) gas analyzers with broadband thermal sources of radiation for detecting a particular gas (Moldau 1993) are designed for industrial purposes and do not allow simultaneous measurements of other atmospheric constituents emitted during the gas exchange processes, e.g., ethylene ( $\tilde{N}_2 I_4$ ) taking part in the hormone balance, or ammonia (NI<sub>3</sub>), characterizing the protein metabolism. That is why the monitoring of the above-mentioned gases, as well as of other volatile matters (metabolites), is performed by biochemistry testing methods (Polevoi 1982).

Methods and technologies of the laser photoacoustic (PA) spectroscopy have been developed at the Institute of Atmospheric Optics SB RAS during the preceding 25 years. They enable highly sensitive investigations of plant gas exchange kinetics, including simultaneous measurements of CO<sub>2</sub>,  $C_2H_4$ , NH<sub>3</sub>, H<sub>2</sub>O, and O<sub>3</sub> concentrations under different

atmospheric conditions, and dose impacts of contaminating gases and aerosols on plants (N'Soukpoe-Kossi and Leblane 1990).

This paper describes some results of a series of experiments on the kinetics of carbon dioxide emission by herbs and leaves of various trees, in the case of enhanced  $C_2H_4$ , CO, and  $O_3$  concentrations. All measurements have been performed using the PA spectrometer with a frequency tunable  $CO_2$  laser.

# Experimental Method and Equipment

The method of the laser PA spectroscopy is based on the PA effect, i.e., acoustic waves generation in a substance absorbing the laser radiation. When the modulated laser radiation passes through a PA cell filled with a gas mixture under study, the molecules absorbing the light are excited, and then they relax with emission or without it. The radiationless relaxation results in a gas heating, which, in turn, generates a pressure wave in the closed volume of the PA cell. The pressure pulse is recorded with a sensitive microphone and the microphone electrical signal can be processed using standard instruments for measuring pulse and periodic electric signals (Antipov et al. 1984).

For the multicomponent gas mixture, the amplitude  $U(\lambda_i)$  of the electric signal on the microphone output (PA signal) is described by the expression

$$U(\lambda_{i}) = \left(\sum_{j=1}^{m} k_{ij} x_{j} + \beta(\lambda_{i})\right) \cdot \alpha \cdot W(\lambda_{i}), i = 1, ... n$$
(1)

where  $\lambda_i$  is the wavelength of laser radiation;  $W(\lambda_i)$  is the radiation power at the same wavelength;  $\alpha = f(P)$  is the sensitivity of a PA detector; P is the total gas pressure in the PA cell;  $k_{ij}$  is the absorption coefficient of the j-th gas at

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wavelength  $\lambda_i$ ;  $x_j$  is the j-th gas concentration, and  $\beta(\lambda_i)$  is the background absorption, which, as a rule, is determined by the laser radiation absorption on the windows of the PA cell (Antipov et al. 1984)

The use of the  $CO_2$ -laser in the PA gas analyzer is preferable in treating such components of the plant gas exchange cycle as  $CO_2$ ,  $C_2H_4$ , and  $NH_3$ , since all these molecules have strong vibrational-rotational absorption lines within the  $CO_2$  laser generation band.

The PA gas analyzer, based on a discrete frequency tunable continuous wave CO<sub>2</sub> laser, has been used to observe the kinetics of CO<sub>2</sub> emitted by plants (Ageev et al. 1996, Zigrist et al. 1994). This gas analyzer uses a commercial CO<sub>2</sub> laser. A diffraction grating (100°lines/mm) and a 100% reflecting mirror were used for the wavelength tuning. The mirror was adjusted so that the first-order reflected radiation should fall back on the diffraction grating and then back to a spherical mirror (with 100% reflectivity) tightly welded to the laser gas-discharge tube. The radiation was emitted through the zeroth order of the grating diffraction. The laser wavelength was tuned by turning the plane mirror. PA spectrometer with the CO<sub>2</sub> laser provides the measurements of the following concentrations: for CO<sub>2</sub> ~ 10<sup>4</sup> ppb, C<sub>2</sub>H<sub>4</sub> ~ 1-5 ppb, NH<sub>3</sub> ~ 1 ppb, and CH<sub>4</sub> ~ 200 ppb.

Because of the high chemical activity of the ozone, the development of the method of creation and control of  $O_3$  content in the  $O_3$ -air mixture requires particular attention. So, an experimental setup consisting of a  $O_3$  generator, analyzer of  $O_3$  concentration, and the fumigation chamber was constructed. Under exposure to a mercury lamp, a flow of the air enriched with  $O_3$  was created within the generator and then it entered the fumigation chamber with experimental plants. The  $O_3$  concentration was measured by a spectrophotometrical method from the attenuation of mercury lamp radiation at 254 µm wavelength. A detailed description of the  $O_3$ -analyzer provides a detection of  $O_3$  in the air at its concentration  $\geq 0.05$  ppm.

# **Results and Discussion**

Ethylene is a gas of environmental interest because it is the only gaseous hormone regulating physiological processes at all stages of plant development. Moreover, the ethylene is one of the hydrocarbons polluting the atmosphere due to the activity of oil-chemical enterprises. We have investigated the action of ethylene high concentration on the kinetics of  $CO_2$  evolution by pea seedlings. Initially, the seedlings were placed into the air medium with a fixed ethylene concentration (48 h in the dark), then they were put in an

exposure chamber with pure air at standard temperature and pressure. After that, we measured the  $CO_2$  evolution by the tested plants and by the controlled ones. The latter have not been affected by the ethylene influence. The ethylene effect on the tested plants results in a double increase of  $CO_2$  evolution (see Figure 1). Available data (Warman and Theophanes 1988) confirm the activation of the plants' respiration under an exogenously applied ethylene.



Figure 1. Influence of exogenously applied ethylene on  $CO_2$  evolution by pea seedlings.

We also studied the influence of another important atmospheric pollutant, the CO, on the plants' respiration. Barley seedlings were used as the tested objects at 66 hours of exposure time. The experiment did not reveal any explicit changes in  $CO_2$  evolution at moderate CO concentration. Moreover, the tested group of plants exposed to the air with maximum CO concentration of 3640 ppm (in the course of the given experiment) exhibited a decrease in  $CO_2$  emission.

In conclusion, we present the data on influence of elevated  $O_3$  concentration on  $CO_2$  evolution by plants. The objects of investigation were ozone-fumigated plants: 1) 9-day-old pea seedlings, and 2) needles of 4- to 5-year-old pine seedlings. The plants were fumigated with  $O_3$  extreme concentration (at roughly 8 mg/m<sup>3</sup>) for 1, 3, and 6 hours. Then ozone-treated material was put into clean exposure chambers with the air at 101 kPa. All experimental results on  $CO_2$  evolution by the pea seedlings fall on the same line (Figure 2). So we can state that we worked beyond the threshold of the plants' sensitivity to  $O_3$ .

Measurements of  $CO_2$  evolution by buds and needles after 6 hours of ozone fumigation were made for four types of pine seedlings (Figure 3).



**Figure 2**. Temporal dependence of CO<sub>2</sub> evolution by pea seedlings. t-duration of stay the plants in exposure chambers.  $\bullet - 1, \times - 3$ , and - 6 hours of O<sub>3</sub> fumigation; - control plants.



**Figure 3**.  $CO_2$  evolution by needles of fast (1 and 3) and slow (2 and 4) pine seedlings for Altai (1 and 2) and Tomsk region (3 and 4),  $\blacksquare$  - control,  $\Box$  - experiment.

Preliminary results show an interesting feature:  $O_3$  causes the inhibition of  $CO_2$  evolution by buds (in comparison with control), whereas for needles the opposite result was obtained.

We also have estimated the  $CO_2$  evolution by soil samples inside the exposure chambers. We can also detect  $CO_2$ evolution by soil, but significantly less than  $CO_2$  evolution by tested plants.

# **Concluding Remarks**

The presented results show that the laser PA gas-analysis instrumentation allows one to determine the kinetics of the plants'  $CO_2$  evolution under exposure to elevated concentration of pollutants. The following obtained data demonstrate that practically all kinds of actions cause an increase of  $CO_2$  evolution:

- The increase of C<sub>2</sub>H<sub>4</sub> concentration in the air on the tested plants results in a double increase of CO<sub>2</sub> evolution in darkness.
- After 6 hours of O<sub>3</sub> fumigation, measurements of CO<sub>2</sub> evolution in Siberian pine needles show an increase of about 50% or more.

The discovered specificity of the plant response to the stressors' action may be used in a selection of the most resistant species. To clarify the stressors' action mechanisms and to obtain the quantitative relations between characteristics of stressors and intensity of  $CO_2$  evolution, it is necessary to study the correlations of  $CO_2$  kinetics and biochemical processes inside the plant tissue. The study of the gas-exchange exposed to the action of several stressors is now of prime interest, because the result of integrated action can differ principally from that of only one stressor action. The experimental gas-exchange data accumulation will permit a creation of a database for simulation of atmospheric-biospheric interaction in concrete ecologo-climatic situations.

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