Seasonal Dynamics of Carbon-Containing Compounds under Different Effects of Natural and Anthropogenic Factors

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Abstract. It was found that the processes of exchange of carbon compounds between the soil and the atmosphere are characterized by high variation in different periods of the annual cycle. It has been proved that CO2 emission, as well as the release and absorption of methane from the soil, is the main expenditure item in the balance of organic matter, which significantly affects the fertility and the level of productivity of agrobiocenoses. Soil fertility management and carbon gas cycle processes largely overlap. With an increase in the content of organic carbon from 0.55 to 0.98%, the loss of carbon dioxin and the absorption of methane compounds increase 1.5–4.3 times. A weak correlation was established between the release of carbon dioxin and the degree of soil cultivation (Kendall coefficient r = 0.23 at p = 0.05), seasonal dynamics of soil moisture r = 0.23 at p = 0.05) and a strong one (r = 0.87 at p = 0.0002) with methane release / uptake dynamics. The same relationship was found between the dynamics of carbon dioxide release and the temperature of the soil layer 0–5 (Pearson's coefficient r = 0.82–0.84 at p = 0.003–0.04), and 0–20 cm (r = 0.68–0.71 at p = 0.003–0.006).

1. Introduction
The release of carbon dioxide (C – CO2), and the release / uptake of methane (C – CH4) are essential for the composition of the atmosphere and global climate change [1, 2]. At the same time, the cultivated areas of the soil are absorbers of atmospheric carbon. Arable land is the object of research, since it occupies about 10% of the land area and the main role belongs to natural fertility and the content of organic matter, depending on the cultivated field crops [3, 4, 5].

The amount of carbon dioxide absorbed by soils varies according to the growing season of plants, from the number of formed roots and vegetative mass, the content of mycorrhiza, as well as from weather conditions [6, 7, 8]. Soil respiration throughout the year is directly or indirectly controlled by soil temperature and moisture, as evidenced by a frequently found correlation with these variables. In the course of year-round field observations, it was found that CO2 emission from soddy-slightly podzolic and gray forest soils occurs not only in the warm season, but also in the winter months, albeit at a slower rate [8, 9].

Soils of the earth's surface act as both a biogenic source and an absorber of methane at the same time. In identical soils, typical conditions may develop when methane will be released or absorbed. This
phenomenon is associated with the alternation of aerobiosis and anaerobicity, when the arable horizon is improved due to the accumulation of humus.

2. Materials and methods

The aim of the study is to assess the dynamics of the exchange of carbon-containing gases between sod-podzolic soil of varying degrees of cultivation and the atmosphere in the seasonal cycle from the level of fertility of the soddy-podzolic soil and environmental factors. Field measurements were carried out in the Long-term field experiment of the RSAU-Moscow Agricultural Academy in 2016–2017, laid down in 1912 by Professor A.G. Doyarenko on the initiative of Academician D.N. Pryanishnikov.

The soil of the studied plots was diagnosed as agrosod-podzolic gley on layered moraine sediments. The granulometric composition of the upper horizon is light loamy.

Studies to evaluate flows of carbon-containing gases were carried out in the 105-year-old fallow field in variants with different degrees of cultivation of the soil: degraded with an organic carbon content of 0.55%, poorly cultivated – 0.68, and well cultivated – 0.95%.

To measure soil respiration and methane flux, studies were carried out during 2016–2017, a static chamber method was used, the principle of operation of which is to isolate a small volume of the atmosphere in contact with the soil with the help of a sealed chamber. The chamber method allows one to measure gas exchange between soil and atmosphere in the field with high spatial resolution [10, 11].

In the case of carbon dioxide, the method allows one to assess the following main indicators characterizing the biological processes of the carbon cycle, carried out by autotrophic and heterotrophic components of the ecosystem:

– net exchange of CO\(_2\) between ecosystem and atmosphere – measured by transparent chambers.
– the daily respiration of the ecosystem – opaque chambers that ensure the “shutdown” of photosynthesis in the daytime.
– soil respiration, including respiration of underground plant organs and oxidation of organic matter by soil microorganisms. These indicators characterize the main biological processes of the carbon cycle, carried out by autotrophic and heterotrophic components of the ecosystem.

The volume fraction of carbon dioxide and methane in the samples was determined on a “Kristall 2000M” gas chromatograph with a flame ionization detector. Analyzed sample volume is 1 ml. Column Hayesep Q 80/100 mesh, 2m. Analysis mode for CH\(_4\) determination: column temperature 65 °C, detector temperature 160 °C, carrier gas (helium) flow rate 35 ml / min, hydrogen flow rate 30 ml / min, air flow rate 300 ml/min. Analysis mode for CO\(_2\) determination: column temperature 80 °C, methanator temperature 350 ° C, other parameters are the same as for CH\(_4\) measurement.

The indicator characterizing the transfer of gaseous matter between the soil and a well-mixed, biologically inert atmosphere is the surface density \(q\). Density of gas flow between soil and atmosphere \(q\) (mg C – CO\(_2\)) per 1 m\(^2\) per hour) was calculated using the least squares method, based on the assumption that it is constant during the exposure of the camera, according to the formula:

\[
q = \frac{dc}{dt} \times \frac{M}{V_m} \times \frac{V}{S}
\]

where: \(dc/dt\) (ppm/h) - rate of change in the volume fraction of gas in the chamber, \(M = 12\ g/mol\) – molar mass of carbon, \(V_m = 22.4\ l/mol\) – molar volume, \(V\) (m\(^3\)) – chamber volume, \(S\) (m\(^2\)) – soil area under the chamber.

Simultaneously with the measurement of the gas flow, observations were made of the environmental factors affecting the gas exchange between the soil and the atmosphere. The temperature was measured during the exposure of the camera at depths of 5 and 20 cm using temperature sensors Thermochron Button DS1921. Moisture content was determined gravimetrically. All determinations were repeated 6 times, which made it possible to calculate standard errors using the bootstrap method.
3. Research results

The use of soil for arable land leads to a change in the structure of the microbial community, a decrease in the total biomass of microorganisms and the number of active biomass, which is clearly consistent with the values of greenhouse gas fluxes: a more biogenic soil gives a greater emission of carbon dioxide and methane [15, 16]. Research has shown that CO$_2$ emission largely depended on hydrothermal conditions, as well as the characteristics of the functioning of microbial communities: the maximum release of CO$_2$, regardless of the level of organic carbon content, was observed at the stage of stable functioning of agrobiocenoses (first decade of August) under optimal conditions of the hydrothermal regime (table 1).

| The degree of soil cultivation | formation (09.06.2016) | sustainable functioning (09.08.2016) | deceleration (04.10.2016) |
|-------------------------------|------------------------|--------------------------------------|-------------------------|
| Degraded                     | 18.0 x 10$^4$          | 82.5 x 10$^4$                       | 34.0 x 10$^4$           |
| Poorly cultivated            | 22.5 x 10$^4$          | 78.0 x 10$^4$                       | 37.0 x 10$^4$           |
| Well cultivated              | 29.0 x 10$^4$          | 121.0 x 10$^4$                      | 62.5 x 10$^4$           |
| HCP$_{0.5}$                  | 2.70                   | 15.0                                 | 9.10                    |

The total number and ratio of various groups of microorganisms in the structure of the microbial community changes not only with prolonged (more than 100 years) exposure to natural and anthropogenic factors, but also in the annual cycle at different stages of the functioning of agrobiocenoses. The total number of microorganisms increased by the time the stable functioning of agrobiocenoses was achieved and decreased by the stage of deceleration due to a decrease in soil temperature and an increase in soil moisture.

So the flow of carbon dioxide in variants with different degrees of soil cultivation at the stage of sustainable functioning of agrobiocenoses (09.08.2016) was 29.6 mg C-CO$_2$ m$^{-2}$ h$^{-1}$ on degraded soil, 90.1 on poorly cultivated and 105.1 mg C-CO$_2$ m$^{-2}$ h$^{-1}$ on well cultivated soil. Minimum value (0.2 – 0.3 mg C-CO$_2$ m$^{-2}$ h$^{-1}$) of CO$_2$ flows was observed in winter, regardless of the degree of soil cultivation. This was facilitated by low temperatures and poor permeability of the frozen soil for gaseous substances, as well as a slowdown in the intensity of the functioning of the soil biota. In the spring period (04.05.2017), the emission of carbon dioxide in all studied variants increased, following the warming up of the soil and an increase in the activity of soil microorganisms (table 2). Consequently, the curve of the seasonal dynamics of CO$_2$ emission has a unimodal character with a maximum during the period of stable functioning of agrobiocenoses.

| Dates of determination | Degraded Value | Degraded p | Poorly cultivated Value | Poorly cultivated p | Well cultivated Value | Well cultivated p |
|------------------------|----------------|------------|-------------------------|---------------------|-----------------------|-------------------|
| 09.06.2016             | 16.0           | 1.01       | 20.4                    | 2.11                | 45.1                  | 11.63             |
| 28.06.2016             | 14.3           | 1.11       | 25.0                    | 3.51                | 57.1                  | 1434              |
| 09.08.2016             | 29.6           | 15.61      | 90.1                    | 29.22               | 105.1                 | 21.03             |
| 04.10.2016             | 23.6           | 10.51      | 33.2                    | 15.64               | 48.6                  | 12.11             |
| 08.02.2017             | 0.2            | 0.11       | 0.5                     | 0.12                | 0.3                   | 0.11              |
| 05.04.2017             | 1.4            | 0.42       | 5.5                     | 1.22                | 16.7                  | 1.42              |
The absorption of CH$_4$ by the soil most actively occurs at a temperature of 20–22 °C and slows down when it rises to 30 °C and decreases to 0 °C. Our studies confirmed the established regularities and showed that the maximum absorption of CH$_4$ was also observed during this period and reached (−7.4 μg C-CH$_4$ m$^{-2}$h$^{-1}$) on degraded, less (−5.7 μg C-CH$_4$ m$^{-2}$ h$^{-1}$) – on poorly cultivated. On the variant with well cultivated soil the maximum was observed on 28.06.2016 and reached (−4.3 μg C-CH$_4$ m$^{-2}$ h$^{-1}$) (table 3).

| Dates of determination | Degraded | Poorly cultivated | Well cultivated |
|------------------------|----------|------------------|-----------------|
|                        | Value    | p    | Value    | p    | Value    | p    |
| 09.06.2016             | -1.8     | 0.22 | -1.5     | 0.22 | -1.9     | 0.55 |
| 28.06.2016             | -3.4     | 0.62 | -4.5     | 0.74 | -4.3     | 0.45 |
| 09.08.2016             | -7.4     | 1.01 | -5.7     | 2.03 | -4.6     | 2.12 |
| 04.10.2016             | 0.3      | 0.03 | -0.3     | 0.22 | +0.1     | 0.02 |
| 08.02.2017             | +0.4     | 0.21 | +0.6     | 0.11 | +0.8     | 0.23 |
| 05.04.2017             | -0.4     | 0.22 | -0.3     | 0.12 | -0.2     | 0.11 |

In the autumn period, the rate of methane absorption significantly decreased, which is associated with a decrease in soil temperature, an increase in moisture and an increase in the solubility of methane in soil moisture and, accordingly, a decrease in its availability for microorganisms.

In winter, the release of methane was noted, which amounted to 0.4 C-CH$_4$ μg m$^{-2}$ h$^{-1}$ on degraded soil, 0.6 C-CH$_4$ μg m$^{-2}$ h$^{-1}$ on poorly cultivated soil, and 0.8 μg C-CH$_4$ m$^{-2}$ h$^{-1}$ on plots with well-cultivated soil, which is associated with the low activity of bacterial oxidation of methane by methanotrophs. In the spring, methane again began to be absorbed by the soil, which is associated with an increase in temperature and activation of the vital activity of methanotrophic bacteria.

In the course of the research, correlations were established between the dynamics of changes in the flow of carbon-containing gases with the moisture content of the arable layer and the temperature of the layer of 0–5 cm and 0–22 cm.

Correlation analysis between moisture values and CO$_2$ fluxes was carried out for each option separately. According to the results of the assessment of soil respiration by the release of C-CO$_2$ mg m$^{-2}$ h$^{-1}$, the following regularities were revealed: in areas with degraded soils, a weak positive correlation was established ($r = 0.09$ at significance level 0.7), which indicates that changes in dioxide fluxes at a low level of soil fertility are chaotic; on plots with poorly and well cultivated soils, the correlation dependence was also weak ($r = 0.09$ at $p = 0.7 -- 0.15$) and ($r = 0.18$ at $p = 0.15$) respectively, that is, the revealed relationship between the two indicators is not reliable, and therefore the value of the carbon dioxide flux was determined by other parameters of the state of the soil.

Methane is one of the most important microcomponents of the atmosphere, largely determining the process of global climate change. The main biological source and sink of methane in the biosphere are the processes of microbial transformation of methane in soils. The amount of methane flux from soils into the atmosphere is mainly determined by the occurrence of two oppositely directed microbial processes – the release and absorption of methane by methanogenic and methanotrophic bacteria.

According to the laws of biochemical kinetics, microbial methane oxidation, which is a determining factor in the amount of CH$_4$ absorption, is influenced by various factors, including soil moisture and soil temperature.

Our studies have confirmed the author's opinion that soil moisture influences the methane flux much more significantly than the CO$_2$ emission. The average correlation was established for the variant with degraded soils ($r = 0.47$, while the level of significance is 0.058). On poorly cultivated and well cultivated soils, the relationship between CH$_4$ fluxes and its moisture content was significant: the
correlation coefficient in this case was 0.54 and 0.56, and the significance level was 0.023 and 0.06, respectively (figure 1).

![Figure 1. Dependence of methane flux on soil moisture.](Image)

The response of biochemical processes to temperature changes in the soil is characterized by the temperature coefficient \( Q_{10} \). It represents an increase or decrease in the rate of CO\(_2\) release from the soil, respectively, with an increase or decrease in its temperature by 10\(^\circ\)C. Our studies have confirmed these patterns (table 4).

The highest level of carbon dioxide emission and methane absorption was noted at the optimum soil temperature, both in the surface and in the topsoil, which was within 24–25 \(^\circ\)C. Further, it was found that the dynamics of carbon dioxide emission and methane absorption has a clearly pronounced seasonal character and is closely related to the activity of soil microorganisms.

Thus, in the initial period, when the soil warmed up to a temperature of 12–14 \(^\circ\)C, the emission of carbon dioxide on average for the studied variants was 26.5 mg C-CO\(_2\) m\(^{-2}\) h\(^{-1}\). As the soil warms up and the conditions for the vital activity of soil microorganisms, actively participating in the decomposition of organic matter, are optimized, the release of carbon dioxide increases to 57.2 mg C-CO\(_2\) m\(^{-2}\) h\(^{-1}\).

A decrease in soil temperature in the autumn and winter periods slows down the processes of CO\(_2\) release, the value of which at a temperature of 12 \(^\circ\)C is 23.6, at a temperature of 6 \(^\circ\)C, it decreases to 10.7, and at zero soil temperature it drops to 0.2 mg C-CO\(_2\) m\(^{-2}\) h\(^{-1}\), that is, the process of gas exchange between the soil and the atmosphere practically stops.

The same relationships were noted when measuring the absorption of CH\(_4\) by the soil during the warm growing season, with a decrease in temperature in the autumn and winter periods, on the contrary, its release was noted.
Table 4. Dynamics of changes in the flows of carbon-containing gases at different humus content and soil temperature during the study period.

| Dates of determination | Level of cultivation | Soil temperature T, °C in layer 0–20 cm | Flow of CO₂, mg C-CO₂ m⁻² h⁻¹ | Flow of CH₄, μg C-CH₄ m⁻² l⁻¹ |
|------------------------|----------------------|------------------------------------------|---------------------------------|---------------------------------|
| 09.06.2016             | Degraded             | 12.9                                     | 16.0                            | -1.8                            |
|                        | Well cultivated      |                                          | 45.1                            | -1.9                            |
| 28.06.2016             | Degraded             | 22.6                                     | 14.3                            | -3.4                            |
|                        | Poorly cultivated    |                                          | 25.0                            | -4.5                            |
|                        | Well cultivated      |                                          | 57.1                            | -4.3                            |
| 09.08.2016             | Degraded             | 20.3                                     | 29.6                            | -7.4                            |
|                        | Poorly cultivated    |                                          | 90.1                            | -5.7                            |
|                        | Well cultivated      |                                          | 105.1                           | -1.9                            |
| 04.10.2016             | Degraded             | 12.5                                     | 23.6                            | -0.3                            |
|                        | Poorly cultivated    |                                          | 33.2                            | -0.3                            |
|                        | Well cultivated      |                                          | 48.6                            | 0.1                             |
| 08.02.2017             | Degraded             | 0.5                                      | 0.2                             | 0.4                             |
|                        | Poorly cultivated    |                                          | 0.5                             | 0.6                             |
|                        | Well cultivated      |                                          | -0.3                            | 0.8                             |
| 05.04.2017             | Degraded             | 3.9                                      | 1.4                             | -0.4                            |
|                        | Poorly cultivated    |                                          | 5.5                             | -0.3                            |
|                        | Well cultivated      |                                          | 10.7                            | -0.4                            |

Statistical processing of the data obtained between the emission of carbon dioxide and the temperature of the arable layer is shown in figure 2. It was found that there is a strong correlation between these indicators with a correlation coefficient of more than 0.71. At the same time, a more significant relationship between them was established for variants with a higher content of organic matter, and a weaker one – for degraded soils.

Figure 2. Dependence of carbon dioxide emission on the temperature of the arable soil layer.
4. Conclusion
The relationship between these indicators in the 0–20 cm layer was weaker due to the change in temperature fluctuations in this layer during the period of determination of these indicators and a slower gas exchange due to the high density of the soil, especially in the options without fertilization and lower organic matter content. The strong relationship of these indicators allows predicting carbon losses both during the growing season and during cold periods of the year.

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