

Review

**Biogeochemical Technologies for Managing CO<sub>2</sub> Flows in Agroecosystems**Vladimir Bashkin <sup>1,\*</sup>, Andrey Alekseev <sup>1</sup>, Boris Levin <sup>2</sup>, Evgenia Mescherova <sup>2</sup>

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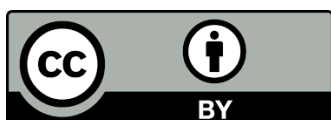
\* **Correspondence:** Vladimir N. Bashkin; E-Mail: [vladimirbashkin@yandex.ru](mailto:vladimirbashkin@yandex.ru)**Academic Editor:** Daniel M. Alongi**Special Issue:** [Agricultural Greenhouse Gas Emissions and Carbon Management](#)*Adv Environ Eng Res*

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The review article discusses the application of biogeochemical technologies aimed at restoring biogeochemical cycles in agroecosystems, primarily in the microbial link regulating CO<sub>2</sub> flows. The factors of management this microbial link when applying mineral and organic fertilizers are shown. The processes of mineralization of soil organic matter and methods of controlling soil's conjugate carbon- and nitrogen-mineralizing ability are considered. The changes in the productivity of agricultural ecosystems under conditions of increasing concentration of carbon dioxide in the atmosphere and soil air are considered. Various agrotechnological techniques are considered, including using zero tillage, organic fertilizers of various nature, and various meliorants, including phosphogypsum. Examples of recultivation of disturbed and polluted soils, waterlogged and/or over-drained soils are given and the impact on CO<sub>2</sub> fluxes is estimated. Based on numerous data, it is concluded that agroecosystems in most cases are a net source of CO<sub>2</sub>, and sequestration occurs only when agricultural land is transferred to fallow lands and at afforestation. At the same time, techniques aimed at reducing CO<sub>2</sub> fluxes using fertilizers in the "production–application" cycle are evaluated. A set of biogeochemical



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technologies aimed at assessing and stabilizing the microbial link of the biogeochemical cycle in agroecosystems is presented. Examples of the use of these technologies for regulating CO<sub>2</sub> emissions in agroecosystems are given. Using one of the biogeochemical technologies, the almost 5-fold decrease in the rate of CO<sub>2</sub> flows during the reclamation of disturbed tundra ecosystems is shown. Adopting agricultural low carbon technologies (ALCTs) cannot yet testify to their applicability to ensure both food and environmental safety. It is necessary to further develop and use biogeochemical technologies to restore biogeochemical cycles in agroecosystems, primarily in the microbial link regulating CO<sub>2</sub> flows.

### **Keywords**

Agroecosystems; CO<sub>2</sub> flows; microbocenoses; regulating factors; fertilizers; biogeochemical technologies

## **1. Introduction**

The beginning of the current century was marked by the aggravation of global changes in the natural environment and climate, leading to alterations of biogeochemical cycles of carbon and nitrogen, an increase in concentrations of "greenhouse" gases in the atmosphere, loss of biodiversity and ecosystem stability, deterioration of soil quality and health [1-10].

Such ecological disturbances, in turn, radically change the biogeochemical processes and the cycle of elements both for the agroecosystem as a whole and only the soil profile, affecting, first of all, the soil biota. Changes occur both at the macro scale (the root system of plants, and soil animals) and in the community of soil microorganisms that carry out oppositely directed processes of formation and decomposition of soil organic matter. The imbalance of these processes leads to a change in soil humus reserves and an increase in greenhouse gas emissions into the atmosphere [11]. Cultivated crops in agroecosystems result from the net primary production of photosynthesis, which then becomes a source of CO<sub>2</sub> during decomposition [12, 13].

The organic carbon remaining after microbial decomposition of net primary products is transformed into the formed biomass; the proportion of carbon returned to the arable land is limited and does not compensate for the carbon costs of soil organic matter for microbial respiration during soil cultivation, including mineralization. As a result, agriculture is a source of CO<sub>2</sub> [14-16].

There is a widespread decrease in soil organic content during their long-term agricultural use. First, this is explained by the fact that the formation of biomass of crops occurs due to the elements released during the mineralization of organic substances, and their replenishment in soils by applying mineral fertilizers only partially compensates for the removal of nutrients with the harvest. Secondly, the removal of agricultural products leads to an almost ubiquitous negative carbon balance in the soils of agroecosystems. There are also known methods of replenishing the carbon mass by introducing organic fertilizers of various nature into the soil: manure, waste from the food, woodworking and chemical industries, municipal sewage sludge, various spropels and peats. Several agrotechnologies allow for maintaining and replenishing the stock of organic matter in soils: minimal treatment (no-tillage), plowing of legumes and siderates, various specialized crop rotations, and afforestation [17].

However, these techniques are insufficient in modern conditions, when carbon dioxide accumulates in the atmosphere due to natural and anthropogenic processes. According to some estimates, carbon dioxide intake into the atmosphere from the planet's agricultural lands is about 10% of its share formed by burning fossil fuels [7, 14].

Consequently, regulation of the composition of organic matter in soils is required, and this process is still far from being characterized both qualitatively and/or quantitatively; the role of combined application of mineral and organic fertilizers (including "green" fertilizers) in the formation of a carbon-absorbing pool of soil organic matter is not clear. There is no unambiguous quantitative parameterization of runoff and CO<sub>2</sub> emission in the soil-plant-atmosphere system, especially in a changing climate. There is also no clear idea of the parameters of the biogeochemical carbon cycle in specific agroecosystems, primarily in its microbial link.

At the same time, it is known that microbial biomass is the key to estimating the fluxes of CO<sub>2</sub> and NO<sub>x</sub>. There are also serious disturbances in the biogeochemical cycles of N and C in agroecosystems.

Therefore, it is necessary to manage microbial processes in agricultural soils. This is of particular importance in the conditions of modern agriculture, aimed at obtaining maximum production, and in which the role of soil is often reduced to a substrate that provides mechanical fixation of plant roots and regulates the water-air regime. To obtain high yields, constantly increasing doses of mineral fertilizers are applied. Under these conditions, the microbial link of the biogeochemical cycle of the main biophilic (nutrient) elements, primarily carbon and nitrogen, changes significantly compared to natural parameters, the microbiocenosis is simplified, the relationships between different types of microbes and their functions are destroyed. The closure of the biogeochemical cycles of elements is altered; they turn into agrogeochemical ones with the release, in particular, of greenhouse gases into the atmosphere – CO<sub>2</sub> and NO<sub>x</sub> [18, 19].

Therefore, new technological approaches to managing CO<sub>2</sub> emissions from agroecosystems are needed. One such campaign is the development of nature-like biogeochemical technologies. Biogeochemical engineering and biogeochemical technologies aim at restoring biogeochemical cycles. We need to consider the applicability of such technologies for controlling CO<sub>2</sub> flows in agricultural systems.

Therefore, the purpose of this review was to consider various factors related to the management of CO<sub>2</sub> emissions in agroecosystems, including targeted management of the soil microbiome using biogeochemical technologies.

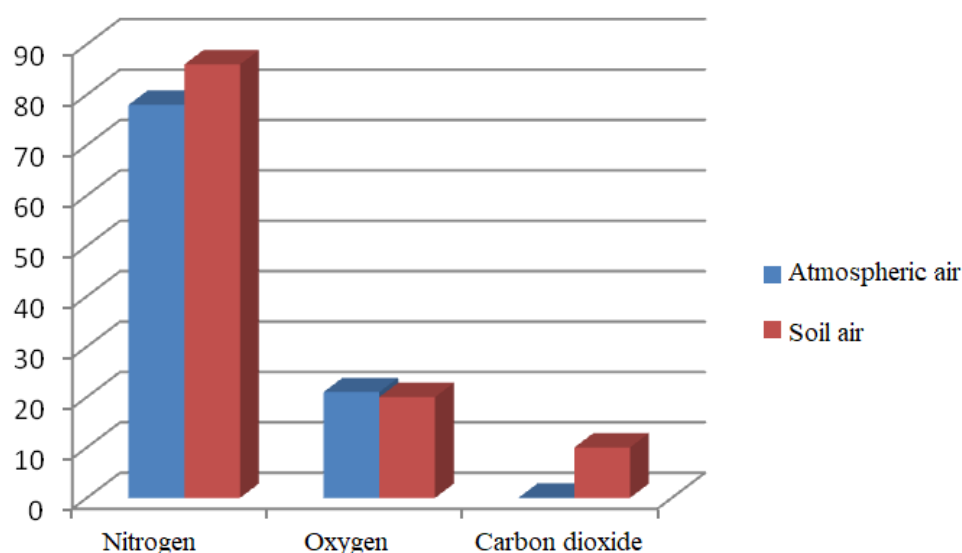
## **2. Management Factors**

### **2.1 Application of Fertilizers**

#### **2.1.1 Management of the Processes of Mineralization of Soil Organic Matter**

The emission by soils and the runoff in them of CO<sub>2</sub>, as well as CH<sub>4</sub> and N<sub>2</sub>O (greenhouse gases, GHG) is the result of various microbiological processes, which, in turn, depend on factors that determine the growth and development conditions of microorganisms. The behavior of CO<sub>2</sub> (CH<sub>4</sub> and N<sub>2</sub>O) may vary depending on the soil, its physicochemical parameters, soil temperature and humidity, density, organic matter content, etc. The main factors influencing the intensity of GHG emission by soils or their absorption include the temperature and humidity of the soil cover. Carbon

dioxide in soil air is hundreds of times higher than in atmospheric air; oxygen is 10-20% lower (Figure 1).



**Figure 1** Main components of atmospheric and soil air, (%) (constructed according to data from [19]).

In arable soils, the concentration of  $\text{CO}_2$  is only 1-2%. When applying fresh organic fertilizers, the carbon dioxide content increases to 2, sometimes up to 9-12%. Carbon dioxide emission into the atmosphere depends on the type of soil type, organic matter content, humidity and temperature [20]. Soil air provides plants with  $\text{CO}_2$ , based on its constant exchange with atmospheric air. 10-15% of the composition of soil air is renewed per day [21]. At the same time, in agroecosystems, soil air composition is partly regulated by organic matter.

It was shown that in the organic matter (OM) of the chernozem soil on the variants with the use of mineral fertilizers there was more hard-to-mineralize carbon than on the control, but 1.1-2.2 times less than on the corresponding backgrounds with manure. The revealed features of the structure of the active pool of organic matter could be due to at least two reasons. Firstly, more intensive mineralization and stabilization of fresh organic matter in the soil of the agroecosystem compared to the fallow land, and secondly, insufficient and unstable return of fresh organic matter to the soil, the predominance of low-quality material with a wide C: N ratio in its composition, which prevented the development of fast-growing microorganisms and the accumulation of microbial biomass in the soil. The actual carbon content of microbial biomass ( $C_{mb}$ ) in the control soil and with the use of fertilizers was only 0.4—0.6% of the  $C_{org}$  with minor differences between the variants and was 4.7-7.3 times lower than in the soil of the fallow land site. The increased values of the metabolic coefficient  $c/\text{CO}_2$  in the soil of the experimental variants and especially when applying mineral fertilizers indicate an unfavorable ecological and physiological state of soil microorganisms, which are forced to consume carbon mainly from newly received sources, maintaining the content of organic matter and its quality. Since plant residues mineralize to  $\text{CO}_2$  faster and more than fresh or composted manure, organic carbon accumulation in the soil decreases in the following row: composted manure > fresh manure > straw > green mass of plants. At the same time, the biomass

of microorganisms grown on easily recyclable organic substrates is transformed faster and more efficiently into humic substances [22, 23]. The authors suggested that the organic matter of the soil, formed mainly from plant residues, is more aromatic and, consequently, stable compared to the organic matter formed from manure. The use of mineral fertilizers against the background of manure application either did not cause a significant increase in the mineralization of organic matter and its loss, or the number of plant residues entering the soil in fertilizer variants exceeded mineralization losses.

The overall amount of CO<sub>2</sub> released in various variants (n = 48) significantly correlated with the total losses of soil nitrogen and fertilizer ( $r = 0.578$ ), as well as with the content of mineral nitrogen in the soil ( $r = -0.427$ ). The parabolic function accurately described the dynamics of net mineralization of nitrogen in soils with plants under control and when applying nitrogen fertilizer [24].

## **2.2 Plant & Microbial Productivity Management**

The ever-increasing concentration of CO<sub>2</sub> in the atmosphere has a direct impact not only on the Earth's climate, but also on the primary bio-productivity of terrestrial ecosystems. In turn, changes in plant productivity and some of their physiological processes can lead to changes in the structure and functioning of both natural and managed plant communities and affect the subsurface carbon balance [14].

The primary productivity of plants directly depends on the assimilation of CO<sub>2</sub> by leaves and the absorption of nutrients by roots. An increased concentration of carbon dioxide potentially increases C3 plant photosynthesis and growth, but the realization of this potential depends on other nutrients and moisture availability. The data obtained in field experiments show an ambiguous reaction of wild and agricultural plant species to an increased concentration of CO<sub>2</sub>. Nevertheless, in most experiments, the responsiveness of plants to an increased concentration of CO<sub>2</sub> was positive – the increase in crop yield was from 30 to 50%, and the productivity of some woody species increased by 100-300% [25].

In a detailed review by Curtis and Wang [25], more than 500 reports on the effect of increased CO<sub>2</sub> concentration on the biomass of woody plants were summarized. The variability of the size of the CO<sub>2</sub> effect was considered in connection with the interaction with other factors. The total biomass and net assimilation of CO<sub>2</sub> by tree crops increased significantly from doubling the atmospheric concentration of CO<sub>2</sub>, regardless of growing conditions. In another review conducted by Rogers et al. [26], it was shown that in the overwhelming number of experiments, an increase in dry mass (by 100-200%) and root length (by 110%) was observed with an increase in atmospheric CO<sub>2</sub> concentration regardless of climatic conditions. Moreover, the increase in dry weight was almost entirely due to the growth of small roots. Nevertheless, there are contradictory data, especially on the ratio of roots and stems, the volume of roots, and their length. The spread of data may be caused by experimental conditions, since the increase in underground biomass strongly depends on the absorption capacity of the root system, which, in turn, is controlled by the soil volume per plant.

A positive reaction of plants to an increased concentration of CO<sub>2</sub> is possible provided there is no shortage of other major nutrients in soils (nitrogen, phosphorus, potassium). Despite extensive information on the effects of increased CO<sub>2</sub> concentration on plant growth, there is very limited

information regarding its effect on the rhizosphere and soil processes. An increased concentration of CO<sub>2</sub> in the atmosphere can increase the rhizosphere's carbon content due to increased root secretions of plants, which affects the number and activity of fungi, and bacteria, including nitrogen-fixing species.

In [27], a study was conducted on the effects of high concentrations of atmospheric carbon dioxide (400, 800, and 1200 ppm) on the growth of poplar deltoids (*Populus deltoides*). The work was carried out on the basis of the closed system Biosphere 2 (Arizona, USA). Studies have shown that the increasing concentration of carbon dioxide in the atmosphere can be considered a factor of atmospheric fertilizer, contributing to increased plant productivity. In the experiment, the deltoid poplar's largest total mass was formed when the concentration of CO<sub>2</sub> in the atmosphere doubled in comparison with the modern one. The tripling of the CO<sub>2</sub> concentration did not cause a further increase in plant productivity. The growth of plant biomass at twice the concentration of CO<sub>2</sub> in the atmosphere was carried out to a greater extent at the expense of the aboveground part, whereas at triple – the proportion of roots in the total mass of plants increases. An increase in CO<sub>2</sub> in the atmosphere from 400 to 800, and 1200 ppm enhanced the mineralization processes of organic residues in soils under trees. The emission intensity increased in 400, 800, and 1200 ppm CO<sub>2</sub> concentrations in the model atmospheric air.

The content of microbial biomass in the soil under the influence of high concentrations of atmospheric carbon dioxide increased. The largest amount of C<sub>mb</sub> was in the variant with a tripled concentration of CO<sub>2</sub> (75.1 mg/100 g), and the smallest – at normal concentration (53.7 mg/100 g). A decrease in the metabolic efficiency of soil microorganisms accompanied the increase in the concentration of CO<sub>2</sub> in the atmosphere. The metabolic coefficient of C–CO<sub>2</sub>/C<sub>mb</sub> was 2.35, 2.43, and 3.07 for biomes of 400, 800, and 1200 ppm.

Currently, satellite data is the most reliable for spatial objects. The satellite images demonstrate an increase in the leaf surface on an almost global scale [28]. It is possible to distinguish both direct factors related to anthropogenic land use management and indirect factors (such as climate change, an increase in the CO<sub>2</sub> content in the atmosphere, greater nitrogen deposition with precipitation and dry precipitation, less degradation of various ecosystems, and/or their faster recovery). Assessing these factors, it can be concluded that climate change and the impact of CO<sub>2</sub> fertilization are the main ones. It is important to note that the new satellite data (2000–2017) demonstrate distinct patterns. The greatest increase in the degree of greening is manifested in China and India, although it generally extends to arable land worldwide. The authors note that China accounts for 25% of the global net increase in leaf surface area. At the same time, it should be borne in mind that these ecosystems occupy only 6.6% of the global vegetation area. Forests (42%) and arable lands (32%) are among the most important ecosystems in which greening is manifested in China, and in India this is due to arable lands (82%) with a significantly lower contribution of forests (4.4%).

As noted [28], significant efforts are being made in China to preserve and expand areas of forests. This primarily aims to mitigate the effects of land degradation, air pollution and climate change. Moreover, since the beginning of this millennium, food production in China and India has increased by more than a third, which was facilitated by an increase in acreage, the use of multiple crops, increased use of fertilizers and irrigation. Such results indicate that this direct factor is a key driver of the "greening of the Earth," a process that accounts for more than a third, and possibly more, of the observed net increase in the area of green foliage cover. The authors emphasize the need for a realistic representation of the practice of human land use in Earth models as a system in which the

factors of greening due to the increasing concentration of CO<sub>2</sub> in the atmosphere should be taken into account.

A study by European authors [29] also assessed factors associated with an increase in the productivity of agroecosystems in conditions of increased CO<sub>2</sub> fluxes, primarily due to agriculture. Agriculture largely contributes to the increase in greenhouse gas flows into the atmosphere, so there is often a dilemma – either an increase in production, or an increase in environmental concerns about sustainable development. In these conditions, the search for palliative solutions is necessary. The authors assessed the impact of greenhouse gases on grain crops in EU countries. The aim of the study was to climate change, greenhouse gas emissions and grain production. They assessed the relationship between greenhouse gas emissions and grain production in the European Union, with the exception of Malta, in the period 2000-2016. The results showed a positive impact of greenhouse gas emissions in agriculture and fertilizer consumption in the previous year on grain production in the following year. This means that the increase in greenhouse gas emissions has led to an increase in grain production. This result should be considered when characterizing the parameters of sustainable agriculture.

The data obtained suggest that the steady emerging trend of increasing the concentration of CO<sub>2</sub> in the atmosphere as a result of human economic activity not only does not hurt the plant communities of the Earth but also contributes to an increase in their photosynthetic productivity. The increased carbon dioxide assimilation by plants with an increase in its concentration in the atmosphere can be considered as an additional CO<sub>2</sub> sink. The size of this sink is still difficult to estimate. However, it can be predicted that the productive activity in general on the globe will increase. However, the respiratory activity of not only plants, but also soil microorganisms will also increase. Whether carbon storage will increase in the form of biome products with long residence times of carbon is a question to which there is no answer yet [14].

### ***2.3 Management of the Carbon- and Nitrogen-mineralizing Ability of the Soil under the Influence of Mineral (Nitrogen, Phosphorus) and Organic Fertilizers***

Despite decades of research, accurate assessment of carbon and nitrogen mineralization, a microbiological process, remains difficult [6]. As noted above, mineralization indicators depend on soil properties, the quantity and quality of organic substances and climatic factors [30-32]. For example, studies using <sup>15</sup>N indicators show that N mineralized from soil organic matter (SOM) usually provides >50% of the N absorbed by corn during the growing season, despite the large use of N-fertilizers [33].

Evaluating the results of the determination of nitrogen mineralization obtained by various methods, it should be emphasized that along with taking into account a number of factors that determine the mineralization of carbon and nitrogen in the soil, one of the most important is not taken into account, namely the impact of the applied mineral nitrogen fertilizers on this process. Although various techniques and methods have been developed that allow either calculating or determining analytically, for example, using labeled nitrogen fertilizers, this effect, however, in the practice of assessing the effectiveness of nitrogen use, as well as the diagnosis of both nitrogen nutrition and total mineralization, they have not been put into practice. Therefore, it was necessary to develop a fairly simple, but at the same time informative method for determining the nitrogen mineralizing ability of soils.

Methodologically, this method is based on the following approaches. The assessment of the nitrogen mineralizing ability of the soil, which is the most important criterion for the degree of severity of the agrogeochemical nitrogen cycle, can be performed based on a method for determining the mineralized nitrogen of the soil, equivalent in availability to nitrogen fertilizers, carried out under composting conditions of samples with increasing doses of nitrogen fertilizers. Composting of soil samples is carried out under optimal conditions of temperature (18-28°C) and humidity (60% WHC) for four weeks with a set of (4-6) doses of nitrogen fertilizers equivalent to those planned for various crops. The value of the nitrogen mineralizing capacity of the soil is determined by finding the first derivative of the quadratic regression equation describing the accumulation of available nitrogen (nitrates and exchangeable ammonium) in the soil, depending on the doses of nitrogen fertilizers applied. You can also use the method of solving this equation by finding its roots. The influence of the growing season's hydrothermal conditions is considered using long-term meteorological forecasts or based on long-term average data for a specific region. This accounting is carried out using corrections to the rate of accumulation of available nitrogen in the soil during composting, depending on temperature and humidity conditions.

Using a mathematical expression of the dependence of the accumulation of available nitrogen in the soil during composting on the doses of nitrogen fertilizers, it is possible to estimate the nitrogen mineralizing ability of the soil. This will include all potentially available soil organic nitrogen capable of mineralization during the predicted growing season [34].

The justification of the proposed method for determining the nitrogen mineralizing ability is associated with the assessment of the so-called "priming effect" or "extra"-N values, which characterizes the degree of increased mineralization of nitrogen and carbon compounds of the soil by microflora when nitrogen fertilizers are applied [11, 30-35]. Therefore, at any given time, the value of the nitrogen mineralizing ability will be proportional to the value of "extra"-N. The values of "extra"-N found in the soil in the form of available nitrogen compounds after composting it in plastic bags will reflect the actual ability of the soil to mineralize organic nitrogen components.

When determining this value according to the proposed method, an assessment of the actual nitrogen mineralizing ability of soils is given, i.e., the one that may occur during the next predicted growing season. This differs from the nitrogen mineralizing potential when potentially mineralized nitrogen is determined. Therefore, the values estimated by the proposed method will be mostly smaller.

Thus, the nitrogen mineralizing ability of gray forest soil was evaluated in a multifactorial experiment. In this experiment, the influence of three types of tillage was evaluated - dump-based plow, surface-based milling and combined (surface + free loosening); three fertilizer modes - without fertilizer, the optimal rate (60 kg N/ha for barley and 90 kg N/ha for winter wheat and a high rate (120 kg N/ha + 20 t/ha of manure for barley and 120 kg N/ha + 40 t/ha of manure for winter wheat). The AMC values were estimated for 0-20 and 20-40 cm soil layers.

Gray forest soil's nitrogen mineralizing ability (NMA) in the upper soil layer (0-20 cm) was usually higher than in the underlying layer of 20-40 cm, reaching 180 kg N/ha when applying organic fertilizers together with mineral fertilizers. The minimum values were noted when using dump plowing on variants without fertilizers – up to 10 kgN/ha. It should be noted that introducing a high dose of nitrogen and manure shifted the maximum value to the lower layer, which was most pronounced on variants with minimal tillage.

The study of the type of cultivated crop and, accordingly, the degree of soil fertilization was also carried out on leached heavy loamy chernozem and sod-podzolic sandy loam soil. The NMA value in virgin chernozem was higher than in virgin sod-podzolic soil. The application of organic fertilizers for industrial crops, such as potatoes and hemp, as well as for corn and winter wheat (40-100 t/ha of cattle manure) led to an increase in the nitrogen–mineralizing ability of both chernozem and sod-podzolic soil. The cultivation of barley in grain crop rotation on chernozem without fertilizers was accompanied by a decrease in the ability of the soil to mineralize nitrogen compared to the virgin difference by two times (115 and 66 kgN/ha). On the contrary, the cultivation of perennial grasses increased the NMA values on both types of soils, and in relative terms, this increase was large on sod-podzolic soil [34].

The potential mineralization capacity of leached chernozem's organic matter was studied with field crops fertilization systems, including increasing doses of manure (5 and 10 t/ha) and mineral fertilizers (N52P48K50 and N114P96K94, as well as a fallow land. At the same time, the cumulative production of C-CO<sub>2</sub> by soils (the method of membrane samplers) during the experiment exceeded its emission (the method of insulators) by 11.6 times under plants and by eight times per pair with a significant closeness of the relationship between these indicators ( $r = 0.730$ ). The release of C-CO<sub>2</sub> estimated by both methods characterized the differences between soils in total and microbial carbon content increased in the presence of plants. The introduction of nitrogen fertilizers stimulated them. The rate constant of mineralization ( $k$ ), day<sup>-1</sup>, varied from 0.005-0.006 when applying manure to 0.014-0.019 with additional mineral fertilizers. At the same time, despite the maximum reserves of potentially mineralized carbon, the values of the mineralization rate constant in the fallow land were 0.009.

The production and emission of C-CO<sub>2</sub> correlated in dynamics with the net mobilization of soil nitrogen ( $r = 0.845$ - $0.976$  and  $r = 0.905$ - $0.942$ , respectively). 40-80 units of C-CO<sub>2</sub> were produced per unit of net mobilized nitrogen in the soil and 4-8 units of C-CO<sub>2</sub> were released into the atmosphere [22].

The intensity of the release of CO<sub>2</sub> by the soil over a long period of incubation under constant conditions gives an idea of the availability of carbon to microorganisms as a source of nutrition and energy. During the initial nine days, the highest rate of release of C-CO<sub>2</sub> was characteristic for the soil on the variants with the use of mineral fertilizers and manure (10 t/ha) and reached 4-5 mg C-CO<sub>2</sub>/100 g of soil per day. Slightly less carbon dioxide was formed in the soil with only manure – up to 3 mg C-CO<sub>2</sub>/100 g of soil per day. The intensity of C-CO<sub>2</sub> production in the soil with applying 5 t/ha of manure with mineral fertilizers was also slightly higher than in control. In the future, the formation of carbon dioxide occurred at a constant rate. At the same time, it was lower in the soil of variants with mineral fertilizers than in the corresponding backgrounds without their use. The rate of production of C-CO<sub>2</sub> by the soil of the fallow land in comparison with the experimental variants was significantly higher throughout the studied period, by the end of observations it gradually decreased to <1 mg C-CO<sub>2</sub>/100 g of soil per day.

The size of the total production of C-CO<sub>2</sub> by the soil of the evaluated variants for 125 days of the experiment reached 200-300 mg of C-CO<sub>2</sub>/100 g of soil in fallow land, on variants with the use of manure at doses of 5-10 t/ha – 60-80 mg of C-CO<sub>2</sub>/100 g of soil, and with the combined use of manure and mineral fertilizers decreased to 40–60 mg of C-CO<sub>2</sub>/100 g of soil. Smaller values were shown when applying increased doses. By approximating the curves of cumulative production of CO<sub>2</sub> during incubation with a one-component first-order kinetics equation, it is possible to

determine the content of potentially mineralized carbon ( $C_{pm}$ ) in leached chernozem with different fertilization systems of field crops.

The soil of the experimental variants contained 2.2-5.2 times less potentially mineralized carbon,  $C_{pm}$ , than for fallow land. Agrogenic depletion of leached chernozem with potentially mineralized carbon was significantly higher than total organic carbon. The share of potentially mineralized carbon in the soil of the fallow land was 5.2% of the  $C_{org}$ , on non-manured control - 1.5%. The use of organic fertilizers once every five years at doses of 25 and 50 t/ha (5 and 10 t/ha of crop rotation arable land) led to a 1.9 and 2.4 times increase in the availability of leached chernozem  $C_{pm}$  compared with the control. The share of  $C_{pm}$  in the soil of these variants reached 2.7 and 3.2% of  $C_{org}$ . The application of mineral fertilizers on the background of manure caused a decrease in the content of  $C_{pm}$ . Especially low availability of  $C_{pm}$  was created when applying mineral fertilizers on the 10 Mg ha<sup>-1</sup> background of manure, which is why its share in the total  $C_{org}$  was even less than in control [36].

### 3. Application of Various Agricultural Technologies and Meliorants

The analysis of own and literature data allows us to estimate the possibilities of arable soils for sequestration of atmospheric CO<sub>2</sub> using modern agricultural technologies based on mineral fertilizers and minimizing tillage. Due to the increase in yield and, accordingly, the number of plant residues, these technologies provide a relatively small absolute increase in  $C_{org}$  in the upper layer of the soil – up to 0.1% C. Approximate estimates show that for forest-steppe chernozems, this is no more than 10% of the amount of  $C_{org}$  that they lost after plowing before reaching the C equilibrium stage. There are at least two reasons that do not allow using agricultural technologies to restore most of the organic matter lost by virgin soils. The first is associated with a sharp, three-fold or more, decrease in the intake of plant matter in arable soils in comparison with their virgin counterparts. As a result, easily mineralized fractions of organic matter are lost, which is most noticeable by the change in the content of detritus or more mass in the soil. The second reason for arable soils' insufficient carbon sequestering ability is their weak ability to firmly fix freshly formed humus substances. Such fixation protects humus substances from further mineralization by soil microorganisms. It is shown that with the annual introduction of labeled <sup>14</sup>C plant residues by the fifth year of the experiment, the increase in carbon in the soil stopped due to the establishment of an equilibrium between the processes of mineralization and fixation of labeled <sup>14</sup>C compounds in the soil. The ability to firmly fix freshly formed humus substances is an exceptional feature of virgin (fallow) soils [37].

Thus, based on the kinetics ( $k$ ) of the turnover rate of soil organic matter, as well as on the quantitative assessment of C sources in the soils of various chronological sequences and paired plots in Russia and the United States, nonlinear indicators of the turnover of soil carbon stocks after the cultivation of natural pastures and subsequent afforestation of arable land were obtained. It is shown that the rate of reduction of C content in soils within 250 years after the transition from natural pastures to permanent arable lands is 0.010 year<sup>-1</sup>. At the same time, after settlement, the content of C in the soil occurred faster ( $k$  - 0.055 year<sup>-1</sup>). This tree-C contribution reached 22 Mg C ha<sup>-1</sup> 70 years after tree planting [17].

Consequently, arable lands can play a significant role in the sequestration of atmospheric CO<sub>2</sub> only after their transfer to the fallow lands. However, for obvious reasons, such a method of

sequestration of CO<sub>2</sub> can be used on a very limited scale, mainly on land that, for one reason or another, is impractical to use for crop production. It should also be emphasized that the increase in organic matter in the soil occurs only during the first 20-30 years, and then this indicator stabilizes [38]. As already noted, the efficiency of CO<sub>2</sub> sequestration in the soil depends on the composition of organic matter of plant origin used as organic fertilizers. By changing the composition of these fertilizers depending on the soil, it is possible to estimate both the size of the stabilization of the soil organic matter (SOM) and the possible sequestration of GHG. Accordingly, the effect of organic fertilizer (compost from bird droppings), mineral fertilizer (rock phosphate) and their mixtures on the redistribution of organic matter transport from plants and their subsequent inclusion in the SOM composition was investigated [38]. It was revealed that the addition of compost from bird droppings and its mixture with rock phosphate led to an increase in the biomass of roots and a greater transfer of organic carbon from the roots to active pools in comparison with the use of only rock phosphate. The soil fertilized with compost from bird droppings had a higher microbial biomass content than the soil with only the introduction of mineral fertilizer. At the same time, according to the authors, the revealed differences in the dynamics of the formation of POM can be explained by the influence of sources of phosphorus fertilizers on the processes of stabilization of SOC [39]. Thus, organic and mineral phosphorus fertilizers can have the opposite effect on the flow of organic carbon from the plant to the soil, particularly on the redistribution of rhizospheric organic matter into labile or stable SOC fractions. Using phosphogypsum as a source of phosphorus in experiments with its long-term surface application in combination with lime in agricultural systems with no-tillage, the effects of this practice on the net assimilation of CO<sub>2</sub>, the activity of antioxidant enzymes and sucrose synthesis, as well as corn grain yield during the dry winter period were evaluated. The combination of lime and phosphogypsum enhanced root development at a greater depth and improved the nutrition of corn plants. These combined effects increased the concentration of photosynthetic pigments and gas exchange even in drought conditions. The net rate of photosynthesis was maximal with the joint application of lime and phosphogypsum and reached 30-40 mmol C-CO<sub>2</sub> m<sup>-2</sup> s<sup>-1</sup>. [40].

Improving the use of phosphorus from phosphogypsum is possible when it is combined with residual waste during water treatment. This can lead to both an improvement in the physical properties of the soil and an increase in the yield of agricultural plants. At the same time, it is important to have balanced nitrogen nutrition. The results obtained in such an experiment showed that the carbon content in the soil microbial biomass, the release of CO<sub>2</sub> and dehydrogenase activity significantly increased with the addition of the studied substances. The most significant indicator was dehydrogenase activity. Microbial biomass was maximal with the introduction of phosphogypsum, and the rate of CO<sub>2</sub> release with the joint application of phosphogypsum and nitrogen fertilizer. At the same time, in the variant with the introduction of nitrogen alone, the CO<sub>2</sub> emission rate was the lowest. Various combinations of nitrogen fertilizer with phosphogypsum and water treatment waste increased the emission rate by 9-26% [41].

The composition of the microbial community can be changed under the influence of various factors. Among these factors, various fertilizers and meliorants play a dominant role in agroecosystems. In [42], the effect of superphosphate (SPP) and phosphogypsum (PPG) on the succession of bacterial and fungal communities were evaluated. Changes in molecular ecological networks have also been investigated. When SP and PPG were added during composting, there were positive changes in the richness and diversity of bacteria. At the same time, this effect was

negative in the case of mushrooms. Microbial diversity and saturation were higher when superphosphate was added than phosphogypsum. The dominant genera comprised *Turicibacter*, *Bacillus*, *norank\_o\_SBR1031*, *Thermobifida*, *norank\_f\_Limnochordaceae*, *Truepera*, *Thermopolyspora*, *Mycothermus*, *Dipodascus*, *Thermomyces*, and *unclassified\_p\_Ascomycota*.

#### 4. Recultivation of Disturbed and Polluted Soils

##### 4.1 Recultivation of Disturbed Soils of Tundra Pastures

The Yamalo-Nenets Autonomous District (Russia) has huge reserves of natural gas in the country and the largest number of domestic deer. At the same time, the degradation of natural tundra ecosystems occurs during the extraction of hydrocarbons (oil and gas) and during overgrazing of deer. It should be emphasized that pasture degradation occurs on a much larger scale during reindeer's overgrazing. As a result, the integrity of tundra soils is altered since they are partially or completely deprived of vegetation cover and organogenic layer. Then comes the period of their destruction under the influence of wind, which leads to the formation of sandy outcrops. And these processes significantly exceed the losses of pastures during the industrial development of territories. At the same time, the natural restoration of knocked-out deer pastures may take several decades. Consequently, timely reclamation of tundra soils disturbed by the extraction and transportation of hydrocarbon raw materials and irrational grazing of reindeer herds, becomes extremely urgent to prevent their irrevocable "desertification."

This problem can be solved effectively with the help of innovative biogeochemical reclamation technology, which provides a nature-like approach to restoring the fertility of disturbed and polluted tundra soils. According to the conceptual model of this technology, in disturbed soils, firstly, we have to consider their granulometric composition or total moisture capacity. Then, the local peat must be applied, estimating its composition, best suited for this particular site [43-45]. This is followed by sowing seeds and growing a mixture of perennial grasses on this site using potassium humate obtained from selected local peat as a stimulant for the growth and development of these plants. This classic natural process is guaranteed to be completed with the desired result thanks to the developed technologies that consider regional natural and climatic features with a focus on the natural parameters of a particular recultivated area. The applied biogeochemical technology includes a strictly defined sequence of operations performed in three stages [44]. The first stage: a) on a large-scale map of the territory with a scale of 1:200,000 and larger, intended for soil reclamation, separate areas with disturbed soils are identified with the measurement of their areas, and also the locations of peat deposits are determined, selecting the peat, which can potentially be used for reclamation; b) averaged representative samples of soil and peat (from a layer of 0-6 cm) are taken from these sites and deposits, respectively, to determine the granulometric composition and/or the total moisture capacity of the soil, and for the purpose of subsequent selection of the deposit, – peat must be taken from it, which is best suited for recultivation of this particular site; c) the granulometric composition of the soil is determined in the case of reclamation of disturbed soils in areas with undulating relief and heterogeneous soil cover; d) the total moisture capacity of the soil is determined in the case of reclamation of disturbed soils in areas with flat or poorly divided relief and monotonous soil cover. The most important thing at this stage is that most of the results are obtained in the laboratory, for ex., during winter, no more than 30 days. Second stage: a) based on the selected ratio peat: soil, the mass of peat embedded in the 0-6 cm layer of disturbed soil,

and the mass of the disturbed soil itself in the 0-6 cm layer, based on the area of the recultivated area are calculated; b) the prepared peat mass is preliminarily brought to a crumbly state by air drying, this is necessary for the convenience of its uniform distribution over the entire area of the recultivated area and its further embedding in a layer of disturbed soil; c) peat embedding, by the calculated dose, is carried out in a 0-6 cm layer of disturbed soil of the site; d) after a mixture of perennial grasses is sown according to the principle of "tinning," i.e., creating a continuous grass cover on the site, using appropriate technologies and equipment. As part of grass mixtures formed from perennial grasses can be brome (*Bromus inermis*), Siberian wild boar (*Elymus sibiricus*), fescue (*Festuca pratensis*), red fescue (*Festuca Rubra*), bluegrass meadow (*Poa pratensis*), timothy grass (*Phleum pratense*) and other species that allow obtaining dense grass and dense grass turf on the recultivated site.

The third stage: a) to improve the sowing properties of seeds, to regulate the condition of plants at various stages of their growth and development, in the process of forming their productivity, as well as to increase the resistance of plants to adverse environmental influences, a potassium humate preparation is used, which is used in certain doses for soaking seeds before sowing, root dressing and non-root dressing (spraying) during the growing season, using appropriate technology and techniques [44]; b) the preparation of potassium humate is isolated originally from local, specially selected peat of the Yamalo-Nenets Autonomous District, optimally corresponding to the recultivated area. Humic acids are extracted from this peat. Their purification is carried out according to all the rules for producing chemically clean substances that practically do not affect the molecular structures of humic acids. This guarantees the receipt of a stable preparation of potassium humate; c) further care of vegetation in the recultivated area is carried out using appropriate technologies and equipment; d) the effectiveness of recultivation of disturbed soils using peat and potassium humate is evaluated in general, based on the results of a comparative analysis of two key indicators of fertility restoration – the activity of the enzyme dehydrogenase and the biomass of a mixture of perennial grasses obtained on disturbed and recultivated soils. The high efficiency of the innovative biogeochemical technology of recultivation of disturbed tundra soils was confirmed by the assessment of the restoration of soil fertility on the Taz Peninsula in the abnormally hot and dry summer of 2016 in the Yamal-Nenets Autonomous District. So, already during 2 weeks of observation, the activity of the enzyme dehydrogenase in recultivated soil increased by 50 times, and the biomass of a mixture of perennial grasses on recultivated soil increased by 50% relative to disturbed soil, indicating a great potential for restoring soil fertility by this method.

Restoring these disturbed tundra pastures also dramatically reduces carbon dioxide emissions (Table 1).

**Table 1** Carbon dioxide fluxes from disturbed and recultivated tundra soil in reindeer pastures.

Soil	Maximal rate of emission, mkmol CO <sub>2</sub> m <sup>-2</sup> h <sup>-1</sup>	Total daily emission, g CO <sub>2</sub> m <sup>-2</sup> d <sup>-1</sup>	Changing CO <sub>2</sub> balance, mkmol CO <sub>2</sub> m <sup>-2</sup> d <sup>-1</sup>	Total respiration of ecosystem, mkmol CO <sub>2</sub> m <sup>-2</sup> d <sup>-1</sup>
disturbed	0.21	1.02	0.12	0.62
recultivated	0.04	0.21	0.19	0.19

These changes reflect the restoration of the temperature regime during the reclamation of pastures, which contributes to less mineralization of organic matter (peat material) and fewer CO<sub>2</sub> emissions.

It should be emphasized that these tundra soils are used for pastures in permafrost areas, which are among the major components of the global carbon cycle. In case of predicted climate change, they may be a significant source of greenhouse gases emission. A four-year-long transplantation experiment (translocation of soil cores 20 cm high and 10 cm in diameter) with the peat horizon of soils was arranged to assess the temperature sensitivity of CO<sub>2</sub> efflux of palsa peatland soils in the north of Western Siberia. An average 7°C increase in temperature caused positive feedback (30–70%) of transplanted soils' CO<sub>2</sub> efflux values compared to control. Temperature dependence of transplanted soils CO<sub>2</sub> efflux had the highest value ( $R^2 = 0.8$ ) in the first two years due to maximum contrast of temperature conditions between sites and decreased in the last two years. On the contrary, the temperature sensitivity of transplanted soils' CO<sub>2</sub> efflux showed a high value during most years ( $Q_{10} = 3–6$ ), thus indicating the increased rate of organic matter decomposition in peatland soils of permafrost area for an extended period (4 years) [46].

#### 4.2 Recultivation of Contaminated Soils

As was shown, the total emission of CO<sub>2</sub> from soils in agroecosystems is determined by the influence of a complex of environmental factors on the totality of soil's biological and physico-chemical processes. It is quite difficult to identify the influence of soil pollution on their background. Operational monitoring has shown that aerotechnogenic soil pollution by chemical emissions increases the mineralization of organic matter in soils. Gaseous carbon losses are higher in soils of light mechanical composition with low humus content. So, if in non-polluted gray forest soil, carbon losses in steam totaled 6.5% over three years, and in polluted - 9.3%, then in alluvial soil, they reached 18.5%. In sod-meadow soil, characterized by favorable properties and high buffering to pollution, losses were less (7.2%). The CO<sub>2</sub> emission during the growing season in the control uncontaminated gray forest soil was 131.0 g/m<sup>2</sup>, and in the case of its contamination with fluorides, only 123.3 g/m<sup>2</sup>. In polluted alluvial soil, these values decreased to 109.8 g/m<sup>2</sup>, but at the same time increased to 150.1 g/m<sup>2</sup> in sod-meadow soil, despite its contamination. Experiments show an inverse relationship between the intensity of gaseous carbon losses and the humus resource in polluted soils, which is consistent with the ideas about the resistance of soil organic matter to mineralization [47].

The intensification of mineralization processes in polluted soils is confirmed by studies of nitrogen balance and circulation using the isotope <sup>15</sup>N. The change in the relative content of C-biomass indicates an increase in the ability of organic substances in polluted alluvial and gray forest

soils. The changes are probably related to non-specific adaptive reactions of the soil microbial complex under pollution conditions [11]. The intensification of mineralization processes may be due to an increase in the proportion of fungi in the microbial community. According to numerous data, they are more resistant to contamination than bacteria and actinomycetes. The entry of organic substances of technogenic origin into the soil could also affect the intensification of mineralization processes, due to the "seed effect". For example, increased CO<sub>2</sub> emissions from soils at low concentrations of benzo (a)pyrene is known [48]. Complex soil pollution affects biological, physical, and chemical processes. It is known that with technogenic soil contamination with fluorides, organic compounds and other pollutants, the destruction of organomineral complexes associated with the peptization of colloids is possible. As a result, humus degradation and deterioration of the structure of arable soils occur.

However, in conditions of high soil pollution, as a rule, suppression of mineralization of organic substances and reduction of CO<sub>2</sub> emissions are observed. This was established at the end of the last century [49-53].

In the conditions of the continental climate of Siberia, the largest part of carbon dioxide from soils in agroecosystems enters the atmosphere during the frost-free period. Emissions in winter do not exceed 1-2% of the total annual production of CO<sub>2</sub>. The observations show that in the Baikal region (Russia) conditions, the total emission of CO<sub>2</sub> from soils during the growing season is 80-90% of the annual flow. Taking this into account, it is possible to give an approximate estimate of the intake of CO<sub>2</sub> from soils in agroecosystems and compare it with direct anthropogenic emissions. According to the authors' calculations [47], the total emission of CO<sub>2</sub> from soils in agroecosystems in the impacted area of local pollution of Sayanskkhimprom JSC reaches 48 thousand tons per year, which is 6.6 times higher than industrial emissions.

The soil microbial complex, thanks to the developed mechanisms of maintaining homeostasis (a numerically and species-redundant microbial pool, polyfunctionality, duplication and reversibility of microbiological processes, etc.), dynamically react to changes in environmental factors. The set of reactions that support the functional stability of the system under external influences is considered an adaptation. There is a direct relationship between the content of C-biomass and the ability of the microbial complex to adapt. The greater the number and biomass of microorganisms, the higher the community's ability to survive in adverse conditions.

At the same time, the negative effect of soil pollution corresponding to the "acceptable" value is manifested in a decrease in the stability of the soil microbial complex, especially in soils with a low humus resource. The increase in energy consumption, as a result of adaptation to changing environmental conditions at the scale of the cell, population and microbial community, contributes to increased mineralization, CO<sub>2</sub> emission and a decrease in the resource of organic matter in soils.

Recultivation of soils contaminated with TM is possible using various technologies, for example, peat and organic compost [54]. Compost or composting has been widely investigated under the background of heavy metal pollution of agricultural soils and the rapid growth of organic wastes. Compost is rich in nutrients, humic matter, and microorganisms; it may be added to agricultural soil as a fertilizer to improve soil fertility and promote the growth of crops and microorganisms, and as a soil amendment to relieve heavy metal pollution.

As noted above, the rate of nitrogen (re)immobilization is associated with microbial biomass formation. However, due to high lability, let's consider that the synthesis of newly formed substances is accompanied by more active mineralization. There may not be a significant

accumulation of them in the soil. The decrease in nitrogen (re)immobilization noted in polluted soils is partly due not to the inhibition of processes, but, probably, to the increased recirculation of newly formed substances. The active involvement of neoplasms in mineralization-immobilization processes depends on the increased demand of the microbial complex in the substrate under stress. As a result, only a part of the newly formed carbon- and nitrogen-containing substances participate in resynthesis. The other part (possibly a large one) is exposed to atmospheric emission.

Using soil remediation technology by plowing siderates increased CO<sub>2</sub> emissions in field experiments on gray forest medium loamy soil of southern Siberia, Russia. During the growing season (May-September), 1.3-1.6 times more CO<sub>2</sub> was volatilized from the soil in the variant with siderates compared to traditional treatment, which can be explained by the intensive mineralization of fresh organic matter [55].

Thus, regional features of soils and hydrothermal conditions, along with anthropogenic and technogenic effects on agroecosystems, affect the emission of CO<sub>2</sub>. Its increase in technogenically polluted soils is associated with increased mineralization of organic matter, which can lead to degradation and a decrease in the humus resource. It can be assumed that under pollution conditions, the increase in carbon losses depends on changes in the metabolism of soil microorganisms.

#### **4.3 Recultivation of Waterlogged and/or Over-dried Soils**

In several regions with excessive moisture, peat extraction is carried out by draining peat bogs. When using residual peat deposits (peat thickness 1-1.5 m) after drainage, plowing and tilling as haymaking, it is important to estimate the size of CO<sub>2</sub> emissions. In [56], CO<sub>2</sub> fluxes were measured using dynamic cameras: with undisturbed vegetation, NEE (Net ecosystem exchange) was measured as the flow of CO<sub>2</sub> between the ecosystem and the atmosphere (per unit area of soil, g CO<sub>2</sub>·m<sup>-2</sup>·h<sup>-1</sup>) and Reco (Ecosystem respiration) as the flow of CO<sub>2</sub> from the ecosystem to the atmosphere, determined by the respiration of roots and aboveground parts of plants, as well as soil heterotrophs (per unit area of soil, g CO<sub>2</sub>·m<sup>-2</sup>·h<sup>-1</sup>), and when it is removed — Rsoil (Soil respiration) as the flow of CO<sub>2</sub> from the soil into the atmosphere, determined by the respiration of plant roots and soil heterotrophs (per unit area of soil, g CO<sub>2</sub>·m<sup>-2</sup>·h<sup>-1</sup>). To simulate CO<sub>2</sub> fluxes, their relationship with soil and air temperature, the depth of soil and groundwater, photosynthetically active radiation, and underground and aboveground phytomass of plants were used. Parameterization of the models was carried out, taking into account the stability of the coefficients estimated by the statistical modeling method (bootstrap). Numerical experiments have been conducted to assess the effect of different modes of haymaking on NEE. It was found that the total for the season (from May 15 to September 30) NEE did not significantly differ in the haymaking without mowing (K0) and fallow land, amounting to 4.5 ± 1.0 and 6.2 ± 1.4 tons S·ha<sup>-1</sup>·season<sup>-1</sup>, respectively. Thus, both objects are a source of carbon dioxide in the atmosphere. A single mowing of hay in a season (K1) leads to an increase in NEE to 6.5 ± 0.9, and a double (K2) — to 7.5 ± 1.4 t·ha<sup>-1</sup>·season<sup>-1</sup>. Both at K1 and K2, carbon losses increase slightly in comparison with K0 and turn out to be close in comparison with the fallow land. At the same time, the carbon accumulated by plants is partially converted during mowing into agricultural products (the value of the mown phytomass for K1 and K2 is 0.8 ± 0.1 and 1.4 ± 0.1 t·ha<sup>-1</sup>·season<sup>-1</sup>), while a significant part of it returns to the atmosphere during the dying and subsequent decomposition of plants.

Based on the data of field measurements of CO<sub>2</sub> fluxes, the simulation results showed that with extensive use (without fertilization, irrigation, grass sowing, etc.), the CO<sub>2</sub> balance of hayfields would differ slightly from fallow peat bogs, especially taking into account the plant phytomass withdrawn during haymaking. Unused hayfields on drained peatlands are a source of CO<sub>2</sub> into the atmosphere, and their return to agricultural circulation can translate part of the "useless" CO<sub>2</sub> emissions into agricultural products.

It was also noted that the moistening of dried and thawing of frozen soils led to a sharp, short-term increase in the release rate of C-CO<sub>2</sub> by 2.7—12.4 and 1.6-2.7 times, respectively, compared with constant incubation conditions. As the soil was depleted by potentially mineralized organic matter, the intensity of C-CO<sub>2</sub> pulses initiated by disruptive influences decreased. Cumulative extra production of C-CO<sub>2</sub> by soils of natural lands for six cycles amounted to 21-40% about variants with constant incubation conditions. The content of potentially mineralized organic matter in soils repeatedly subjected to drying-moistening—freezing—thawing decreased 1.6—4.4 times compared to soils without disturbing effects, and the rate constants of mineralization decreased 1.9—3.6 times. It is emphasized that the cumulative effect of drying—moistening—freezing—thawing cycles is manifested not so much in a decrease in the total content of C<sub>org</sub> from the soil, as in a decrease in the mineralization potential of soil organic matter [57].

In general, it can be concluded that for modeling CO<sub>2</sub> fluxes in agricultural systems, successfully applied:

- balance approach – to determine the dynamics of CO<sub>2</sub> in terrestrial ecosystems at various scales [58];
- cartographic method – overlapping of different types of maps to integrate CO<sub>2</sub> fluxes in arable soils [59, 60];
- geoinformation analysis – to assess CO<sub>2</sub> uptake by forests and potential carbon stock in vegetation cover [61];
- regression dependences of CO<sub>2</sub> emissions on hydrothermal or soil-climatic parameters of the environment [62, 63].

When modeling the biogeochemical carbon cycle using mathematical methods, several challenges arise: multiple calculation methods; high requirements for input data; limited availability of input information; the need to take into account climate change; errors in describing the functional dependence of CO<sub>2</sub> emissions on temperature. All these factors are characterized by high uncertainty and often low spatial availability. Quantitative parametrization of various links of the biogeochemical carbon cycle is important and necessary. At the same time, it is necessary to describe the dual role of soil in the processes of greenhouse gas emission and absorption quantitatively. There is still no strict quantitative assessment of the parameters of the interaction of carbon and nitrogen cycles; there are no significant criteria for dividing the soil organic carbon pool into fractions. This is especially true of the ratio of microbial and root respiration. However, one can hope that further development of the obtained biogeochemical models will help to better assess the most important blocks: greenhouse gas flows, the influence of climatic and anthropogenic factors, and GHG flow management strategies [64].

## 5. Green Agricultural Production and Its Achievability Using Environmentally Friendly Fertilizers and Biogeochemical Technologies

### 5.1 Fertilizer Production

In producing mineral fertilizers, emissions of various gases, primarily CO<sub>2</sub>, are inevitable. Since production is at the beginning of the "fertilizer-harvest" chain, it is important to evaluate this about a specific producer. Thus, the company PJSC "Phosargo", one of the world's leading fertilizers, pays great attention to production aimed at minimizing specific and total CO<sub>2</sub> emissions into the atmosphere (Table 2). The calculation of specific greenhouse gas emissions is carried out by arithmetically dividing the values of gross greenhouse gas emissions (coverage 1) by the values of indicators of manufactured and semi-finished products. A program has been adopted to achieve the target values, reducing the marks by 2028. The target value of specific greenhouse gas emissions (coverage 1) will be 109.1 kg in CO<sub>2</sub>-eq./t, which is 30.9% lower than the base level of 2018.

**Table 2** Gross and specific greenhouse gas emissions of coverage 1 and 2 in the Phosagro Group as a whole by year (2018-2021) and planned for 2028, thousand tons of CO<sub>2</sub>-eq.

Indicator	2018	2019	2020	2021	2028
Gross greenhouse gas emissions: coverage 1, thousand tons	4 855,3	4 656,3	4 739,4	4 675,8	4 175,5
Gross greenhouse gas emissions: coverage 2, thousand tons	924,1	967,0	978,3	893,3	794,7
Specific greenhouse gas emissions of coverage 1, kg/t	158,0	143,3	140,1	132,7	109,1

For emissions of coverage 1 (direct emissions) and 2 (indirect emissions), scientifically based emission targets are established by international requirements. The total value of the scientifically based target values of greenhouse gas emissions of coverages 1 and 2 in 2028 will be (coverage 1 – 4175.6 and coverage 2 – 794.7) a total of 5,134,898 tons of CO<sub>2</sub>-eq., which is 14% (or 835,914 tons of CO<sub>2</sub>-eq.) lower than the baseline [65, 66].

At the same time, gross emissions in 2021 of coverages 1 and 2 totaled 5,569,1 thousand tons of CO<sub>2</sub>-eq for PJSC "Phosargo". As already noted above (see section 4.2), industrial emissions for the territory of Russia are significantly lower than CO<sub>2</sub> emissions from soils. Thus, the assessment of soil respiration in Russia gave the total amount of CO<sub>2</sub> emissions; the soil cover of Russia is responsible for about 9 billion tons during the growing season [67]. Later estimates [15] showed that the arable lands of Russia for the period 1990-2016 represented a net source of C-CO<sub>2</sub> in the amount of 21-27 (on average 24.5) million tons of C-CO<sub>2</sub>/year, or about 95 million tons of CO<sub>2</sub> to date.

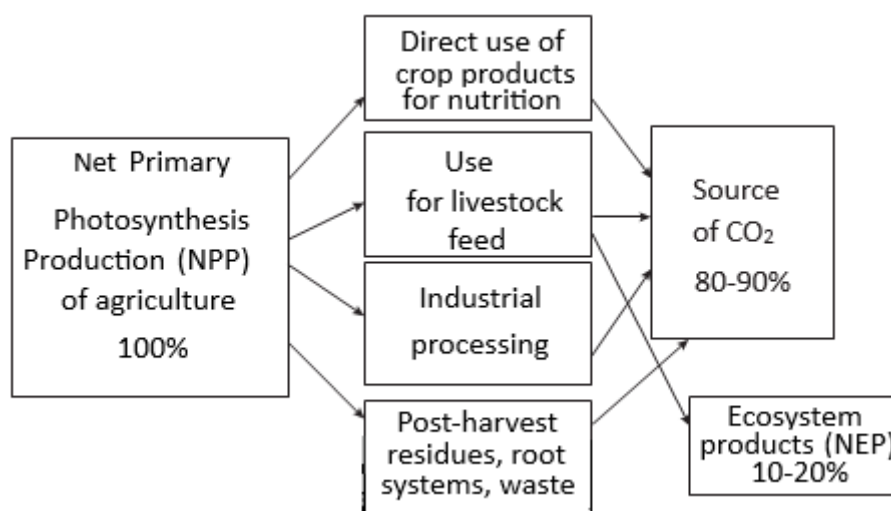
In recent years, there has been a tendency in the literature to evaluate the entire life cycle of a product, including its "carbon footprint". At the same time, several companies producing mineral fertilizers announced the creation of production facilities for the production of completely "green" fertilizers. It was assumed that all the energy used in this production process would be obtained from renewable energy sources. However, the energy crisis has led to a significant adjustment of such plans. Therefore, it seems logical to show the preserved plans of individual companies, for

example, PJSC Phosagro, regarding the reduction of CO<sub>2</sub> emissions. Along with the environmental consequences, this will also contribute to energy conservation.

Similar studies have been conducted in several other regions, particularly in various provinces of China. It is shown that economic growth, financial opportunities and energy intensity have an inverse U-shaped nonlinear effect on CO<sub>2</sub> emissions. At the same time, the mechanisms of influence of these three influencing factors are different, and the corresponding state regulation should be adapted to these parameters. For example, the impact of urbanization on CO<sub>2</sub> emissions shows a soft “M-shaped” picture, and there is an inverse “N-shaped” nonlinear relationship between trade openness and CO<sub>2</sub> emissions. Therefore, environmental regulations should consider differentiated emission reduction policies at different stages [68, 69].

## 5.2 Cultivation of Agricultural Products

A feature of agricultural production is that all manufactured products are net primary photosynthetic products (NPP), quickly disposed of and become a source of CO<sub>2</sub> (Figure 2).



**Figure 2** The fate of agricultural products [15].

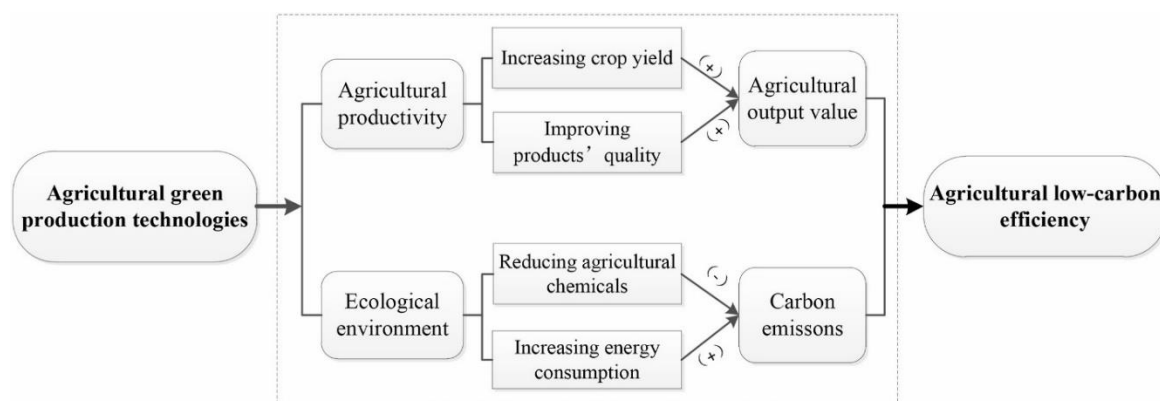
Organic carbon remaining after microbial decomposition of NPP passes into the category of ecosystem products (NEP). The value of NEP is a hard-to-determine value in agricultural production conditions. Unidirectional biogeochemical flows of substances prevail in the modern agro-industrial complex. The harvested crop (NPP) is processed and used as food, animal feed, or raw materials for industry. And production waste (except manure) practically does not return to the fields and soils. The share of organic carbon returned to the fields with manure is limited and does not compensate for the carbon costs of soil organic matter for microbial respiration in soil cultivation. In agroecosystems, clean ecosystem products are very small and practically do not compensate for the carbon consumption of biome products for mineralization. As a result, agricultural production is a net source of CO<sub>2</sub> [15].

At the same time, the observed quantitative changes in the stocks of SOS are still very insignificant. However, their importance should not be underestimated. This can manifest to the greatest extent when monitoring soil lands adjacent to dairy and meat farms. As a typical example, data on the inventory of SOC stocks with ten-year intervals performed in Sweden can be cited [70].

Soil monitoring data included topsoil samples from two cadastral intervals (2001-2007 and 2011-2017) obtained at reference points on 159 dairy farms, 86 meat farms, 318 arable farms, and 13 pig farms. Analysis of the results showed that the SOC content on dairy farms (3.0%) was significantly higher than on arable farms (2.3%) and pig farms (2.4%), but did not differ significantly from meat farms (3.1%). SOC stocks in the upper 20 cm increased significantly on dairy, meat and arable farms by 0.38, 0.14 and 0.21 Mg/ha<sup>-1</sup> year<sup>-1</sup>, respectively, from 2001-2007 to 2011-2017. For dairy farms, this corresponded to 1.4 Mg CO<sub>2</sub> ha<sup>-1</sup> and approximately 0.22 kg CO<sub>2</sub> kg<sup>-1</sup> of milk. Even taking into account the need for additional correction factors, for example, to account for the carbon footprint of the energy used, it can be concluded that these SOC changes can significantly impact CO<sub>2</sub> emissions and assessments of the environmental sustainability of dairy farming.

### 5.3 Agricultural Green Production Technologies

Pathways from agricultural green production technologies to low-carbon efficiency are shown in the Figure 3.



**Figure 3** Pathways from agricultural green production technologies to low-carbon efficiency [71].

Within the framework of the possibility of switching to low-carbon technologies for growing grain crops, the effectiveness of this approach was evaluated using the Tobit model with random effects [72]. From 2000 to 2017, the average estimates of using and adapting such technologies for mainland China amounted to no more than 20%, mainly in the northeast and northwest. It should also be emphasized that due to the growth of agricultural production, there was an increase in carbon emissions. At the same time, the efficiency of low-carbon technologies tended to decrease. It is shown that deep tillage using fertilizers and water-saving irrigation lead to both an increase in grain production and an increase in CO<sub>2</sub> emissions at the regional and national scales.

At the same time, it has been established that the introduction of these technologies has not only an economic, but also a social component. Thus, assessing low-carbon technologies in rice cultivation depends on the farmer's experience, gender, education, access to agricultural information, knowledge sharing and the availability of mobile networks and mail servers. Using the example of 1115 farms, it is shown that almost 95% of farmers used at least one low-carbon technology. The majority agreed with the observed changes in local weather parameters (52.74% of respondents), particularly with irregular precipitation (52.56%) over the past year. Most farmers

also agreed with the statement that agricultural production contributes to climate variability (26.73% fully agreed, and 40.54% agreed with this statement) [73].

In addition, environmental management and, particularly the management of greenhouse gas flows, requires the development of appropriate environmental regulations. These standards are directly related to the parameters of energy efficiency, both in producing and evaluating their logistics. To achieve them, it is important to assess both environmental challenges and energy costs. This can be achieved by applying quantile regression, which makes it possible to assess the comprehensive influence of explanatory variables on dependent variables, including maximum, minimum and median. This approach has been successfully used for 30 provinces in China. Based on data from 2005 to 2019, quantile regression methods were used to model the impact of environmental regulations on CO<sub>2</sub> emissions and energy efficiency [74-76].

Consequently, such regulatory measures and low-carbohydrate agricultural technologies should consider the specifics of local features of agricultural production, in particular, various geographical, climatic and socio-economic factors. This will make it possible to form a regionally differentiated system of low-carbon agricultural technologies and appropriate management and support measures. Such a system, including various low-carbon technologies and measures to support them on a national and regional scale, will allow farmers to make informed decisions [77].

Among such technologies, biotechnological techniques aimed at using compost from green and wood residues can also be considered. For example, siderates' plowing contributes to agriculture's sustainability and the restoration of biogeochemical cycles in agroecosystems. Organic farming allows you to regulate the soil microbiome. However, the response of soil microbial communities to various fertilization regimes on a regional scale is uncertain [78-92].

Composting agricultural waste is a fairly common technique in low-carbon technologies. However, its widespread use is limited by several technological approaches; in particular, the composting process is very time-consuming and, at the same time, the final product, as a rule, has a low nutrient content compared to mineral fertilizers. This is especially true of nitrogen. Nevertheless, several complex technological techniques have been developed to improve the composting process and increase the nitrogen content in organic fertilizers. Thus, in work [88], the study of the complex use of biochar and specific microorganisms was carried out. This accelerates the composting process, accumulates available forms of nitrogen and generally improves the quality of compostable products.

Such campaigns can generally contribute to the biologization of agriculture, within which one or another replacement of chemical N-fertilizers with bio-organic fertilizers is possible. However, this requires studying the combined use of compost, bio-coal and N-fixing bacteria in agroecosystems.

In addition, the biologization of agriculture, or in other words, the development of organic systems of agricultural technology, does not contribute to the required increase in agricultural productivity. However, its environmental benefits are beyond doubt. One of the possible ways to eliminate these limitations is the management of the soil microbiome, which plays a crucial role in the soil system [92, 93].

Thus, one of the possibilities for managing the soil microbiome is the regulation of intra-soil carbon fluxes. This can contribute to both an increase in plant yield and the restoration of soil health [94]. We must develop nature-like technologies to manage biogeochemical cycles and nitrogen, phosphorus and/or water flows. This will make it possible to maintain a continuous flow of soluble carbon underground to ensure the vital activity of soil microorganisms.

### 5.4 Biogeochemical Technologies for Managing Microbioms and CO<sub>2</sub> Flows in Agroecosystems

Various biogeochemical technologies are based on the principles of management of microbial communities in soils. The main strategies of microorganisms in the soil can be conditionally characterized as r-species — with low efficiency of substrate use, growing rapidly on readily available compounds, and K-strategies — slowly but effectively mineralizing hard-to-reach carbon (including humic substances). It is shown that the predominance of species with an r- or K-strategy in the microbial community determines the rates of growth processes, and the competitive relationships of microorganisms with different growth strategies underlie the emission mechanisms, sequestration and turnover of soil carbon. The impact of such stressful environmental factors as increased carbon dioxide content leads to an increase in the proportion of rapidly growing microorganisms in the community. On the contrary, in case of heavy metal contamination and moisture deficiency, microorganisms with a K-strategy gain an ecological advantage. An increase in pollution leads to a significant decrease in the maximum specific growth rate and the dominance of microorganisms with a K-strategy in microbial communities of technogenically polluted soils. In general, the change of the dominant ecological strategy of the soil microbial community is a mechanism of adaptation of soil microorganisms to changes in the ecological situation [11].

The biogeochemical technologies presented in Table 3 regulate the efficiency of the microbial link of biogeochemical cycles in agroecosystems. As a rule, these technologies include using various mineral and organic fertilizers, meliorants and agricultural waste. The problem of elaboration and implementation of innovative, feasible, ecologically friendly nature-like technologies aiming at an increase in carbon (C) stock and a significant reduction in greenhouse gas (GG) emission from all agricultural areas, including those under rice cultivation, is critically important.

In particular, in field tests conducted in Hunan Province, China, carbon dioxide (CO<sub>2</sub>) sequestration by roots of rice plants was evaluated as influenced by silicon (Si) fertilizers. The amount of additional CO<sub>2</sub> sequestered depended on the content of plant-available Si in agrochemicals, the frequency, and duration of their application, and the granulometric composition of soil [95].

**Table 3** Technologies for managing the microbial link of biogeochemical cycles in agroecosystems.

Technology	Technological principles	Reference
Method of sample preparation for nitrogen isotope analysis.	Estimation of isotopic parameters of microbial mineralization	Copyright certificate of the USSR, 1982, No. 1043565. [96]
Method for determining the nitrogen mineralizing ability of soils.	Assessment of the mineralizing capacity of soils	Copyright certificate of the USSR, 1983, No 1206703. [97]
A method for assessing the biodegradation of pesticides.	Assessment of recovery of native microflora	Copyright certificate of the

A method for assessing soil purification from pesticide residues.	Rehabilitation of contaminated soils	USSR, 1991, No. 5005241. [98] Copyright certificate of the USSR, 1994, No. 1836636. [99] Copyright certificate of the USSR, 1995, No. 1753415. [100]
A method for predicting the behavior of nitrogen in agroecosystems.	Assessment of the mineralizing capacity of soils	
Biogeochemical monitoring and evaluation of the modes of functioning of agroecosystems on technogenically polluted soils.	Rehabilitation of contaminated soils	[47]
A method for monitoring the purification of soils contaminated with hydrocarbons and the neutralization of hydrocarbon sludge by analyzing the activity of catalase.	Rehabilitation of contaminated soils	RF Patent for invention No. 2387995, 2010. [101]
A method for monitoring the purification of soils contaminated with hydrocarbons and the neutralization of hydrocarbon sludge by analyzing the activity of dehydrogenase.	Restoration of the microbial link of the biogeochemical cycle during the reclamation of contaminated soils	RF Patent for invention No. 2387996, 2010. [102]
A method for monitoring the effectiveness of recultivation of disturbed tundra soils of various granulometric composition by analyzing the activity of dehydrogenase	Restoration of the microbial link of the biogeochemical cycle during the reclamation of disturbed tundra soils	RF Patent for invention No. 2491137, 2013. [103]
A method for evaluating the effectiveness of recultivation by peat of disturbed tundra soils with different water holding capacity.	Restoration of the microbial link of the biogeochemical cycle during the reclamation of disturbed tundra soils	RF Patent for invention No. 2611159, 2017. [104]
A method for obtaining potassium humate from local tariffs of the Yamalo-Nenets Autonomous District	Restoration of the microbial link of the biogeochemical cycle during the reclamation of disturbed tundra soils	RF Patent for invention No. 2610956, 2017. [105]
A method for evaluating the effectiveness of recultivation of disturbed tundra soils by introducing local peat and potassium humate.	Restoration of the microbial link of the biogeochemical cycle during the reclamation of disturbed tundra soils	RF Patent for invention No. 2611165, 2017. [106]

A method for diagnosing chronic and accidental contamination of soils with heavy metals by analyzing the activity of the enzyme dehydrogenase.	Restoration of the microbial link of the biogeochemical cycle during the reclamation of contaminated soils	RF Patent for invention No. 2617533, 2017. [107]
A method of biochemical control of the effectiveness of recultivation of disturbed and polluted tundra soils.	Restoration of the microbial link of the biogeochemical cycle during the reclamation of disturbed tundra soils	RF Patent for invention No. 2672490, 2018. [108]
A method for identifying the source and time of contamination of the environment and human biological substrates with the pesticide DDT in the regions of the Far North.	Restoration of the microbial link of the biogeochemical cycle during the reclamation of contaminated soils	RF Patent for invention No. 2701554, 2019. [109]
A method for identifying microbial contamination of the aquatic environment by analyzing the activity of the enzyme dehydrogenase.	Assessment of restoration of native microflora in case of pollution of aquatic ecosystems	RF Patent for invention No. 2735756, 2020. [110]
Lime and phosphogypsum amendment	Restoration of the microbial link of the biogeochemical cycle during the reclamation of degraded soils Innovative, feasible, ecologically friendly nature-like technologies aiming at an increase in carbon stock and significant reduction in greenhouse gas emission from all agricultural areas, including those under rice cultivation, by silicon application	[40]
Carbon sequestration by rice roots under silicon fertilization		[95]

The data obtained evidence of the potential of Si fertilizers to promote the process of C sequestration and reduction in GG emission under rice cultivation. Their application increased rice yield by 12,1 to 71,2% and the CO<sub>2</sub> fixation by root system by 0,95 to 14,9 t/ ha over one season. Returning C to soil and fertility reproduction could be provided via enhanced plant root system development and increased root debris after harvesting. Agrochemicals containing silicon available for plants should be included in the technology for implementing agricultural crops' 4R-STRATEGY of mineral nutrition.

It should be emphasized that the list of biogeochemical technologies presented in Table 3 is far from exhaustive. This may also include various approaches that contribute to the restoration of native microflora, for example, when agricultural soils are contaminated with heavy metals and petroleum products [111], as well as other techniques and methods aimed at regulating the biogeochemical structure of agroecosystems as a whole.

Therefore, it is necessary to monitor all the components of the biogeochemical cycles of carbon and nitrogen, from the microbial link to humans as the closing food trophic chains. It is important to understand and evaluate the economic and social dimensions of both CO<sub>2</sub> emissions into the

atmosphere and the impact of elevated concentrations of this gas on human health. The approaches used in the economic assessment of industrial gas emissions on human health in various provinces of China deserve attention here [112].

## 6. Conclusions

Analysis of modern literature shows that agroecosystems in most cases are a source of CO<sub>2</sub>, and sequestration occurs only when agricultural land is transferred to fallow lands. The microbial link of biogeochemical cycles in agroecosystems is responsible for CO<sub>2</sub> emission, sequestration and transformation of carbon compounds in soils. Among the management factors of this microbial link, the following can be noted:

- application of mineral and organic fertilizers;
- orientation of the processes of mineralization of soil organic matter and methods of controlling the conjugate carbon- and nitrogen-mineralizing ability of soils;
- changes in the productivity of agricultural ecosystems under conditions of increasing carbon dioxide concentrations in the atmosphere and soil air;
- agrotechnological techniques, including the use of zero tillage, organic fertilizers of various nature, as well as various meliorants, including phosphogypsum;
- reclamation of disturbed and polluted soils, waterlogged and/or over-dried soils, affecting CO<sub>2</sub> flows.

At the same time, techniques aimed at reducing CO<sub>2</sub> fluxes with the use of fertilizers in the "production – application" cycle are evaluated. The existing practice of adoption of agricultural low carbon technologies (ALCTs) cannot yet testify to their applicability to ensure both food and environmental safety. It is necessary to further develop and use biogeochemical technologies to restore biogeochemical cycles in agroecosystems, primarily in the microbial link regulating CO<sub>2</sub> flows.

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## Author Contributions

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The authors have declared that no competing interests exist.

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