Organic matter mineralization of larch bark and compositions based on it

A S Babur¹, O A Ulyanova², M S Butenko¹, V N Zhulanova³ and O V Martynova²

¹Siberian federal university, Krasnoyarsk, Russia
²Krasnoyarsk state agrarian university, Krasnoyarsk, Russia
³Tuva state university, Kyzyl, Russia

E-mail: ababur@sfu-kras.ru

Abstract. The process of organic matter mineralization in fertilizer mixtures consisting of larch bark and mineral additives was studied in order to optimize the timing of composting and preparation of high-quality fertilizers. The main factors affecting the process of bark mineralization are the reaction of the medium (pH), the ratio of C:N, mineral additives. The process of larch bark mineralization and compositions based on it is described by the equation of the first order. The calculated decomposition constants of fertilizer compositions exceeded the control by 2-3, 2 times depending on the variant of the experiment.

1. Introduction

The Russian Federation is a continent, given that the area and diversity of natural and climatic zones make it economically advantageous to bring the production of fertilizers directly to the regional agro-industrial complex using the availability of local raw materials. In this regard, there was interest in using of local mineral raw materials and industrial waste suitable for the preparation of fertilizers based on them. In the Krasnoyarsk territory with its rich forest potential, developed woodworking industry there are about 500 thousand tons of tree bark annually, which accumulate in dumps, occupy huge areas and pollute the environment. Meanwhile, tree bark contains valuable biogenic elements in its composition and is promising potential raw material resource for the production of fertilizers [1, 2]. Bark is large-tonnage waste of production and has high humus-forming potential. It is promising to use vermiculite as a component for fertilizer compositions and natural sorbents, which enhances the agrochemical effect of fertilizers [3]. The ease of chemical exchange processes and selectivity of sorption determine the uniqueness of the expanded vermiculite. It has high moisture capacity. When it is wet, vermiculite retains water five times its own weight. At the same time vermiculite using does not weigh down the soil, but allows it to be easily aerated, while providing good supply of moisture. Having in its composition various chemical elements (magnesium, potassium, calcium, manganese, iron, silicon, etc.), it serves as an active biogenic stimulator for plant growth. Despite the uniqueness of this mineral raw material, its agrochemical efficiency has not yet been sufficiently studied in the region. The proven vermiculite reserves of the Tatarskoye deposit, located in the Severo Yeniseysky district of the Krasnoyarsk territory are 2.3 million tons, and the forecast resources are about 5.0 million tons. In addition to vermiculite the Tatarskoye deposit produces phosphate ores, which are stored in a special dump. Their resources are huge and amount to 12 million tons. A rational scheme for phosphate ores utilization has not yet been developed [4]. At the same time soils of Siberian agrocenoses are in urgent need of phosphorus introduction, as about 34 % of arable soils in the
Krasnoyarsk territory have low and very low content of mobile phosphorus [5]. Therefore, the available local resources of phosphate ores are of particular importance, which can solve the problem of phosphorus availability in the soils of the region.

The above suggests that the composition, properties, reserves, cheapness and availability of wood bark, vermiculite, and phosphate ores determine them as promising components for the preparation of new fertilizer compositions (FC), the transformation of which has not yet been studied. This hinders the development of technologies for the integrated processing of waste in the wood processing enterprises using local minerals. In this regard, this study is aimed at the processing of large-capacity waste (bark) of forest processing enterprises and the using of local agro-ores in order to prepare promising organic fertilizers based on them and optimize the preparation time. To do this, it is necessary to study the mineralization of bark organic matter and fertilizer compositions based on it.

2. Methods and results
The objects of the study were larch bark-waste of the Yeniseysky sawmill, urea (N m), phosphorus flour (Pf) and vermiculite (V) of the Tatarskoye deposit, geographically located in the Krasnoyarsk territory, and organomineral compositions based on them. The research was carried out in the model experiment. The scheme of experience included the following options: 1. Bark (B) – control; 2. B + Nm; 3. B + Nm + Pf 1 % (Pf 1); 4. B + Nm + Pf 3 % (Pf 3); 5. B + Nm + Pf 1 + V; 6. B + Pf 1 + V; 7. B + Nm + V. Preparation of fertilizer compositions was carried out by composting for 180 days. As nitrogen-containing additive urea was used in amount of 1.5 % of nitrogen, and as phosphorus-containing additive phosphorus flour was used in doses of 1 and 3 % of the active substance per dry mass of bark. Also, vermiculite was introduced into the bark in amount of 10 % of its mass.

Mineralization of organic matter was determined by CO₂ releasing by the absorption method modified by I. N. Sharkov [6]. The total production of carbon dioxide from bark and compositions in the form of C-CO₂ during the observation period was performed by linear interpolation. To describe the process of organic matter mineralization exponential decomposition function was used, first proposed by H. Jenny, S. Gessel and F. Bingham [7] and examined in detail by J. Olson [8]. These authors showed that the decomposition process of organic compounds obeys the first-order reaction equation: dC/dT = -kC₀, where C₀ and C are the substrate concentrations at the beginning and end of the measurement period, T is the time and k is the substrate decomposition rate constant measured in units (hour, day, year).

Larch bark contains in its composition all the main elements of mineral nutrition, which become available to plants in the process of its mineralization. The bark is enriched with carbon, calcium, magnesium and other elements. The disadvantage of larch bark is the acidic reaction of the medium (pH 4.1), low nitrogen content (0.29 %) compared to high carbon content (49.8 %), hence the ratio of carbon to nitrogen is high -172. To eliminate these shortcomings it is necessary to conduct composting with additives that reduce the C:N ratio and neutralize the acidic pH of the original bark.

The most important indicator determining the intensity of organic matter mineralization in the bark is the rate of carbon dioxide production. The minimum intensity of CO₂ releasing from larch bark was observed at the control of 16 g m⁻² d⁻¹(fig 1). The limiting factor that reduces carbon dioxide releasing at the control is the acidic pH of the bark and low availability of mineral nutrition elements. Other factors restraining its decomposition are the bark enrichment with polyphenols, lignin, tannins, as the data of other authors evidenced [9]. The mineral additives introduction of urea, vermiculite, phosphorus flour into larch bark contributed to the neutralization of excess acidity, which stimulated the activity of microorganisms and, apparently, led to increasing the process of mineralization in 1.1-1.3 times during the first 60 days of composting, depending on the variant of the experiment.

By the 3rd month end of composting there was decreasing in the carbon dioxide releasing in all variants of the experiment, but options number 3 and number 4 were statistically different from the control for this indicator, where in the compositions phosphoric flour and urea were present together as additives, which were sources of mineral nutrition for microorganisms. In dynamics, as easily available food for microorganisms was consumed by the end of the 4th month of composting and in
the future carbon dioxide emissions decreased to the level of the control variant.

Figure 1. Dynamics of carbon dioxide production, g С∙m⁻²d⁻¹.

According to the equation proposed by the authors [7, 8], we calculated the rate constants of decomposition in larch bark and compositions based on it at different times of composting. The minimum decomposition constants of organic matter were noted in the control variant, as well as in the variant No. 6, due to the absence of a nitrogen component inhibiting the mineralization process. As can be seen from the table 1, up to 55-62 % of the organic matter in larch bark is mineralized from the total semi-annual emission of carbon dioxide depending on the variant of the experiment for the first 3 months of composting.

Table 1. Dynamics of mineralization rate in organic matter of larch bark and compositions based on it.

| № | Options         | 0-90 | 90-180 | 0-180 |
|---|-----------------|------|--------|-------|
|   | C               | k    | C      | k     |
| 1 | Bark (B) - control | 1136 | 0,24   | 848   | 0,03 |
|   | 57              | 43   | 100    |
| 2 | B +Nₘ            | 1294 | 0,27   | 867   | 0,30 |
|   | 60              | 40   | 100    |
| 3 | B+ Nₘ+P₁        | 1357 | 0,38   | 890   | 0,43 |
|   | 60              | 40   | 100    |
| 4 | B+ Nₘ+P₃        | 1372 | 0,26   | 826   | 0,36 |
|   | 62              | 38   | 100    |
| 5 | B+ Nₘ+P₁+V      | 1292 | 0,20   | 935   | 0,44 |
|   | 58              | 42   | 100    |
| 6 | B+ P₁+V         | 1279 | 0,13   | 952   | 0,04 |
|   | 57              | 43   | 100    |
| 7 | B+ Nₘ+V         | 1277 | 0,31   | 1036  | 0,46 |
|   | 55              | 45   | 100    |

Note. C - quantity of C-CO₂: in numerator - in g m⁻², in denominator - % of total emission for half a year, k - constant of mineralization rate, day⁻¹.

The combined presence of nitrogen and phosphorous flour in the 3-month composition stimulated the activity of microorganisms, which contributed to the maximum value of the decomposition constant in variant No. 3-0.38.
In the dynamics of the control variant the decomposition constant of organic matter remained at the same level, in the studied variants of the experiment it increased by 2-3, 2 times by the end of 180-day composting.

3. Conclusion
Thus, it is shown the possibility of larch bark processing with additives of phosphorous flour and vermiculite into fertilizer compositions, which are in dire need for agriculture. Mineralization processes occur with minimal intensity in the variant with larch bark. Adding of mineral fertilizers, phosphorus flour, vermiculite to the bark enhances mineralization flow. The process of larch bark mineralization and compositions based on it is described by the equation of the first order. The calculated decomposition constants exceeded the control by 2-3, 2 times depending on the variant of the experiment. The decomposition constants of larch bark and fertilizer compositions based on it vary from 0.063 to 0.088. The decomposition constants of bark and compositions based on it correlate with the indices C:N (r = 0.75-0.80), C: ash (r = 0.83-0.86).

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