Environmental safety and efficacy of ordinary chernozem fertilization with “Agrobionov” preparation under barley crops

A T Khusainov, M K Syrlybayev and A S Ayapbergenova

Sh. Ualikhanov Kokshetau State University, 76, Abay Street, Kokshetau, 020000, Republic of Kazakhstan

E-mail: abil_tokan@mail.ru

Abstract. An intensive decrease in soil fertility is observed in the Republic of Kazakhstan. The main reason is the low volumes of mineral fertilizers, only 6-8 kg per hectare of arable land. Traditional mineral fertilizers are inaccessible due to high prices. Therefore, there is a need to search for alternative types of fertilizers. Barley is the main grain crop from the group of “brown” breads used for fodder and food purposes. An important reserve for barley yield increase is the use of fertilizers. This publication presents the results of research work on the environmental safety and effectiveness of the use of the “Agrobionov” preparation, produced from local, affordable, cheap industrial waste - ash and carbon black for soils fertilizing under barley crops. The content of heavy metals and radionuclides was determined by the method of inverse voltammetry (GOST 50686-94, GOST 50683-94), the grain yield was recorded by the direct combining method, the statistical processing of the crop was carried out according to the Fisher method as adapted by Dospekhov, the yield data is 100% pure and 15% standard humidity. The results of the study showed that the use of the “Agrobionov” preparation for chernozem soils fertilizing under barley crops is environmentally safe and gives an economic effect. The content of heavy metals and radionuclides in the soil and grain of barley does not exceed the maximum permissible concentrations (MPC) and tentatively permissible norms (TPN). Barley grain productivity increases, costs for its production decrease.

1. Introduction
An intensive decrease in soil fertility is observed in the Republic of Kazakhstan. The main reason is the low volume of application of mineral fertilizers, only 6-8 kg per hectare of arable land [1]. For most agroformations, traditional mineral fertilizers are inaccessible due to high prices. Therefore, there is a need to search for alternative types of fertilizers [2].

This publication presents the research results on environmental safety, economic efficiency and economic feasibility of the “Agrobionov” preparation use for ordinary chernozem fertilization under barley crops.

The “Agrobionov” preparation consists of 67% ash and slag. The experience of ash and slag use for soils fertilizing for various crops is known in world science and practice.

Deborah Schönegger et al indicate that fly ash contains important macronutrients such as P, K, Mg, Ca, S and trace elements, including Fe, Mn, Zn and Cu can provide the soil with a sufficient amount of mineral nutrients, including those available for plants. The use of ash in agriculture is a promising
alternative. Therefore, the authors propose to introduce fly ash into the soil, which improves the nutritional regime of the soil and crop yields [3].

ManishaBasu, et al. note that a high concentration of elements (K, Na, Zn, Ca, Mg and Fe) increases the yield of many crops [4].

Ewa Ociepa, et al used a mixture of wastewater to fertilize the soil, waste fractions of lignite, brown coal ash enriched with mineral potash fertilizer. The first year yield was 1.6, and the third year yield - 2.7 times higher when fertilizing the soil with the test mixture, compared with the control [5]. Our experience also proves that the introduction of the “Agrobionov” preparation, consisting of a mixture of ash and nanocarbon, contributed to an increase in barley yield.

The above sources show that the use of ash-and-slag waste to increase soil fertility and crop yields is a promising direction, since, along with the food problem, it also allows solving environmental problems of recycling local production waste [6]. Our studies have also shown the high efficiency of the “Agrobionov” use for chernozem soils fertilizing under barley crops. The improvement of water-physical, agrochemical, biological properties of the soil and the increase of barley productivity [15].

At the same time, a number of scientists believe that ash-and-slag can be toxic to the environment and their use as a fertilizer pollutes the soil with heavy metals as well as changes the reaction of the soil environment and suppresses the microbiological activity of the soil [7].

This publication presents the research results on the environmental safety and the use effectiveness of the “Agrobionov” preparation, produced from local, affordable, cheap industrial waste (ash and carbon black) for fertilizing soils under barley crops.

The research purpose is to study the environmental safety, economic efficiency and economic feasibility of the “Agrobionov” preparation use for ordinary chernozem fertilization under barley crops.

Research Objectives are:
- to conduct environmental standardization of the heavy metals and radionuclides content in ordinary chernozem and barley grain at various doses of the “Agrobionov” preparation.
- to study the doses effect of the “Agrobionov” preparation on the productivity of barley grain.
- to make a comparative analysis of the costs for traditional mineral fertilizers applying and for the “Agrobionov” preparation under barley crops.

2. Research Objects and Methods

Research Objects are common chernozem and spring barley cultivar “Astan-2000”. The research Subject is “Agrobionov” preparation, which includes fly ash of coal from the Ekibastuz coal field and carbon black – waste from a tire factory. Ash-and-slag has the following chemical composition: SiO\textsubscript{2} - 62.9%, Fe\textsubscript{2}O\textsubscript{3} - 6.35%, Al\textsubscript{2}O\textsubscript{3} - 26.35%, CaO - 1.9% MgO - 0.9%, SO\textsubscript{3} - 1.2%, Na\textsubscript{2}O - 0.23%. Carbon black is 99% carbon. The preparation has a powder form [8].

The research was conducted at the experimental field of the Educational-Scientific-Production Center “Elite” of Sh. Ualikhanov Kokshetau State University, near the city of Kokshetau, the Republic of Kazakhstan. Soil is ordinary chernozem, carbonate, medium-power, low humus, heavy loam. The content of humus is 3.8%, easily hydrolyzable nitrogen is 46.0 mg/kg, mobile phosphorus is 17.0 mg/kg and exchange potassium is 582 mg/kg in the soil layer of 0-40 cm. The availability of easily hydrolyzable nitrogen (according to Tyurin’s and Kononova’s classification) is average, mobile phosphorus is low and exchangeable potassium is high (according to Machigin’s classification). The reaction of the soil solution is slightly alkaline; the pH of the aqueous extract is 7.8.

The field experience “Environmental assessment of the “Agrobionov” preparation doses on ordinary chernozem under barley crops” started in 2018 according to the following scheme: 1) control - without fertilizer; 2) 1/10 P of the estimated dose (ground); 3) ground + preparation 100 kg/ha; 4) ground + 200 kg/ha; 5) ground + 300 kg/ha; 6) ground + 400 kg/ha; 7) ground + preparation 500 kg/ha. The repetition of the experiment is 4-times, the plot area is 125 sq.m., the record area is 100 sq.m. In 2019, the second start of experience was carried out according to the same scheme. The total estimated dose of mineral fertilizers on the first start was 161 kg/ha, on the second start - 110 kg/ha.
In the experiments, the content of heavy metals and radionuclides was determined by the method of inversion voltammetry (GOST 50686-94, GOST 50683-94), the grain yield was recorded by the direct combining method, the statistical processing of the crop was carried out according to the Fisher method as adapted by Dospekhov, the yield data are brought to 100% purity and 15% standard humidity.

3. Results and discussion
The results of laboratory studies showed that in the options where the Agrobionov preparation was applied, the lead content increased in the soil, depending on the dose, to 2.10-2.60 mg/kg (0.56 mg/kg in the control), but did not exceed the maximum permissible concentration (MPC 32 mg/kg). The content of cadmium, arsenic and mercury in the soil was below threshold. On fertilized options, the zinc content in the soil was at the control level or even lower - 0.20-0.40 mg/kg (0.37 mg/kg in the control). Copper content was not found in the control, but on fertilized options, its presence increased to 0.20-0.64 mg/kg, moreover, with an increase in the preparation dose from 100 to 500 kg/ha, the copper content decreased from 0.64 to 0.20 mg/kg (table 1).

The lead content in the barley grain in the control was 0.32 mg/kg; with an increase in the preparation dose from 100 to 500 kg/ha, there was a tendency to increase the lead content in barley grain from 0.33 to 0.47 mg/kg, but still these indicators were below the MPC value of 0.5 mg/kg. The content of cadmium, zinc, arsenic and mercury in barley grain was below threshold.

Table 1. The doses effect of the “Agrobionov” preparation on heavy metals content in the soil and grain of barley.

| No. | Option          | Object  | Heavy metals content, mg/kg |
|-----|----------------|---------|-----------------------------|
|     |                | Soil    | Pb  | Cd  | Zn  | Cu  | Ar  | Hg  |
| 1   | Control without fertilizer | Soil    | 0.56 | 0.00 | 0.37 | 0.00 | 0.0 | 0.00 |
|     |                | Grain   | 0.32 | 0.00 | 0.00 | 0.00 | 0.0 | 0.00 |
| 2   | 1/10 P - ground preparation 100 kg/ha | Soil    | 0.54 | 0.00 | 0.40 | 0.20 | 0.0 | 0.00 |
|     |                | Grain   | 0.32 | 0.00 | 0.00 | 0.00 | 0.0 | 0.00 |
| 3   | Ground preparation 100 kg/ha | Soil    | 2.60 | 0.00 | 0.39 | 0.64 | 0.0 | 0.00 |
|     |                | Grain   | 0.33 | 0.00 | 0.00 | 0.00 | 0.0 | 0.00 |
| 4   | Ground preparation 200 kg/ha | Soil    | 2.50 | 0.00 | 0.37 | 0.46 | 0.0 | 0.00 |
|     |                | Grain   | 0.36 | 0.00 | 0.00 | 0.00 | 0.0 | 0.00 |
| 5   | Ground preparation 300 kg/ha | Soil    | 2.40 | 0.00 | 0.35 | 0.48 | 0.0 | 0.00 |
|     |                | Grain   | 0.37 | 0.00 | 0.00 | 0.00 | 0.0 | 0.00 |
| 6   | Ground preparation 400 kg/ha | Soil    | 2.10 | 0.00 | 0.31 | 0.21 | 0.0 | 0.00 |
|     |                | Grain   | 0.37 | 0.00 | 0.00 | 0.00 | 0.0 | 0.00 |
| 7   | Ground preparation 500 kg/ha | Soil    | 2.30 | 0.00 | 0.20 | 0.20 | 0.0 | 0.00 |
|     |                | Grain   | 0.47 | 0.00 | 0.00 | 0.00 | 0.0 | 0.00 |
| MPC |                | Soil    | 32.0 | n/s | n/s | n/s | n/s | n/s |
|     |                | Grain   | 0.50 | 0.03 | n/s | 0.03 | 0.2 | 0.02 |

*n/s = not standardized

L.N. Skipin, A.A. Weimer, E.V. Zakharova, E.V. Gaevaya (2014) studied the content of heavy metals in the soils of the Tyumen region farms that have different levels of chemicalization. The results of the author’s studies showed that with a high level of chemization in the Zavodoukovskoye experimental industrial complex, MPCs in terms of cadmium content exceeded by 2% of the area of...
arable land. The presence of other heavy metals, regardless of the degree of chemization, did not exceed the MPC level. Based on experimental data, the authors conclude that it is possible to use high doses of fertilizers in all farms of the region [9]. Currently, pollution of soils with heavy metals is practically non-existent in Northern Kazakhstan, since the level of mineral fertilizers application is very low. A.T. Khussainov’s research found only local soil pollution with heavy metals in the territories near uranium mining enterprises [10].

Mehbub Alam, Zavar Hussein, et al. found that soils with a high content of heavy metals negatively affect the growth and yield of garden radish, while the application of organic fertilizers reduced the availability of heavy metals, increased the growth of garden radish and minimized the risk to human health. Among organic fertilizers, vermicompost was more effective and reduced the absorption of Cd, Cr, Pb, and Mn by 32.5, 50.25, 44.50, and 42.25%, respectively, and enriched radish growth [11]. In our experience, the source of the organic basis is carbon present in the Agrobionov preparation.

Ning et al. indicate that overuse of mineral fertilizers founded a potential risk to soil quality. The use of organic additives and the reduction of inorganic fertilizers are economically feasible and environmentally sound approaches to the development of sustainable agriculture [12]. In our experience, we bring only 1/10 of the required amount of mineral fertilizers.

Our research has shown that with an increase in the preparation dose from 100 to 500 kg/ha, the strontium-137 content in the soil increased from 2.2 to 10.7 Bq/kg (4.8 Bq/kg in the control). The radium-226 content also increased to 21.0-30.3 Bq/kg (20.4 Bq/kg in the control). In fertilized options, the content of thorium-232 in the soil was even lower than the control option — 31.2–46.5 Bq/kg (in the control — 54.2 Bq/kg). In terms of potassium-40 content, fertilized options also did not differ significantly from the control. Strontium-90 in the soil was not found at all. The specific effective radioactivity in the control was 145 Bq/kg, and in fertilized options it was lower than in the control one - 102-129 Bq/kg (Table 2).

### Table 2. The doses effect of the “Agrobionov” preparation on the radionuclides content in ordinary chernozem

| No. | Option                  | Radionuclides content, Bq/kg | SERA*       |
|-----|-------------------------|-----------------------------|-------------|
|     |                         | Cs-137 Ra-226 Th-232 K-40 Sr-90 |             |
| 1   | Control - no fertilizer | 4.8±12.5 20.4±21.7 54.2±26.8 603.0±267 | - 145±48 |
| 2   | 1/10 - P – ground       | 7.1±11.9 8.9±19.1 37.4±23.4 559.0±247 | - 108±42 |
| 3   | Ground + preparation 100 kg/ha | 2.2±11.4 21.0±20.1 33.9±23.0 567.0±249 | - 116±42 |
| 4   | Ground+ preparation 200 kg/ha | 2.2±12.9 29.2±21.8 32.3±23.8 608.0±264 | - 126±45 |
| 5   | Ground+ preparation 300 kg/ha | 2.3±12.5 30.3±22.9 31.2±23.6 494.0±254 | - 102±45 |
| 6   | Ground+ preparation 400 kg/ha | 7.21±9.26 24.8±16.4 46.5±19.7 488.0±197 | - 129±35 |
| 7   | Ground+ preparation 500 kg/ha | 10.7±11.8 21.5±19.3 38.8±22.6 556.0±239 | - 122±41 |

* SERA - specific effective radiation activity

On fertilized options, the content of cesium-137, radium-226, thorium-232 and potassium-40 in barley grain was not found. The presence of cesium-137 was detected within 1.89 Bq/kg in the control option. The content of strontium-90 in the options with the preparation introduction, depending on the dose, was 0.0-5.3 Bq/kg, and did not exceed the control option - 5.2 Bq/kg (Fig. 1).

Soil contamination with radionuclides is possible as a result of the phosphate fertilizers application into the soil, often containing uranium isotopes [13]. (http://biofile.ru/geo/8145.html - source). In our
experience, with the use of phosphorus fertilizer at a dose of 14 kg/ha of the active substance, an increase in the content of cesium-137 was noted, but the content of radium-226, thorium-232 and potassium-40 decreased.

P. Shahul Hameed, G. Sankaran Pillai, R. Mathiyarasu claim that the application of phosphorus fertilizers increased the level of $^{238}$U in the soil [14]. However, the average value of Ra-226 did not significantly change and did not exceed the permissible limit of 370 Bq/kg; therefore, cultivated soils do not pose a radiological risk. In our experience, the radium content is incomparably lower - 20 Bq/kg. That is, the use of the “Agrobionov” preparation does not pose a radiological hazard.

![Figure 1. The doses effect of the “Agrobionov” preparation on the content of radionuclides in barley grain](image)

| No. | Option                  | 2018, t/ha | 2019, t/ha | Average, t/ha | Increase in control |
|-----|-------------------------|------------|------------|----------------|---------------------|
| 1   | Control – no fertilizer | 1.38       | 0.75       | 1.06           | -                   |
| 2   | 1/10 P₂O₅, ground      | 1.40       | 0.93       | 1.16           | 0.10               | 9.4                |
| 3   | Ground+100 kg/ha preparation | 1.88 | 1.04 | 1.46 | 0.40 | 37.7 |
| 4   | Ground+200 kg/ha preparation | 1.79 | 1.00 | 1.40 | 0.34 | 32.1 |
| 5   | Ground+300 kg/ha preparation | 1.84 | 1.10 | 1.47 | 0.41 | 38.7 |
| 6   | Ground+400 kg/ha preparation | 1.90 | 1.01 | 1.45 | 0.39 | 36.8 |
| 7   | Ground+500 kg/ha preparation | 1.92 | 0.92 | 1.42 | 0.36 | 34.0 |
|     | LSD₀.₀₅                 | 0.08       | 0.10       | 0.09           | -                   |

In the experiments of 2018 and 2019 of the start, the barley grain yield in the control was 1.38 and 0.75 t/ha. In 1/10 option of the estimated fertilizer dose (ground), the yield increase was not significant. On other fertilized options, depending on the preparation dose, a reliable yield increase was obtained in 2018 from 0.41 to 0.54 t/ha (29.7-39.1%) and in 2019 from 0.17 to 0.35 t/ha (22.7-46.7%). On average, over two years, the increase caused by the use of the “Agrobionov” preparation
amounted to 0.10-0.41 t/ha or 28.3-38.7%. Doses of the preparation did not have a significant effect on the value of the barley crop (table 3).

Mineral fertilizers in the market of Kazakhstan, for example superphosphate, have a high cost and are practically not affordable to small and medium-size farms. The cost of double granular superphosphate in the wholesale market is 140 KZT/kg; at a dose of 20 kg/ha, application costs will amount to 15,000 KZT/ha, while the cost of ash-and-slag at a dose of 100 kg/ha is 2,700 KZT/ha, that is 5.5 times cheaper. Buying activity in the fertilizer market of the Republic of Kazakhstan is characterized by an increase in supply; a high demand for fertilizers among farmers, there is an annual decrease in the volume of fertilizer purchases and a decrease in purchasing activity within the entire market. This is primarily due to rising fertilizer prices, transportation costs associated with the delivery of products (in view of the remoteness of production from markets) and poor government support. For this reason, the demand for fertilizers within the Republic of Kazakhstan remains at a very low level [15].

The research carried out confirmed the market and consumer attractiveness of the fertilizer product based on ash-and-slag, subject to the economic viability of the application, environmental safety, the lack of fertilizer production based on ash-and-slag waste. It seems advisable to start production of this fertilizer within Northern Kazakhstan and bring this product to the market of the Republic.

4. Conclusion
In modern conditions, there is a decrease in soil fertility, to a greater extent due to the insufficient use of organic fertilizers. To increase effective soil fertility, it is advisable and economically justified to use local industrial waste as fertilizer. The research has shown environmental safety and high efficiency of the “Agrobionov” preparation, produced on the basis of ash and carbon black, as a fertilizer of ordinary chernozem in the conditions of Northern Kazakhstan. The content of heavy metals and radionuclides in the soil and in barley grain did not exceed the maximum permissible concentrations. Barley productivity increased by 32.1-38.7%, the fertilizer application costs decreased by 5.5 times. An economically viable dose is 1/10 of the calculated dose of phosphate fertilizers + 100 kg/ha of the “Agrobionov” preparation.

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