RACIONAMENTO ECOLÓGICO DE DOSES DE UMA PREPARAÇÃO CONTENDO CARBONO DE MÚLTIPLOS COMPONENTES ATRAVÉS DE CONTEÚDO DE METAIS PESADOS E ATIVIDADE MICROBIOLÓGICA DO SOLO

ECOLOGICAL RATIONING OF DOSES OF A MULTICOMPONENT CARBON-CONTAINING PREPARATION THROUGH HEAVY METAL CONTENT AND SOIL MICROBIOLOGICAL ACTIVITY

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RESUMO

O artigo trata dos resultados da regulação ecológica de doses introduzidas em uma preparação multicomponente contendo carbono para a queima de metais pesados e a atividade microbológica do solo. A relevância da pesquisa está baseada, por um lado, na degradação global, degaseificação e redução da fertilidade do solo. Por outro lado, é o acúmulo global de resíduos de produção e consumo. O objetivo deste estudo foi avaliar o efeito de doses do produto das cinzas, escórias e negro de carbono sobre o pH, teor de metais pesados e a atividade microbológica do chernossolo no cultivo de trigo de primavera. Os experimentos foram conduzidos em uma zona murada do norte do Cazaquistão. O pH do solo foi determinado por um método potenciométrico; a atividade microbológica do solo pela aplicação de floe; a microflora foi explicada pela semeadura da suspensão do solo em meio nutriente sólido e os metais pesados foram determinados por voltametria por decapagem. Bactérias utilizando compostos orgânicos de nitrogênio; microrganismos que consomem nitrogênio mineral; oligonitrófilos; bactérias que mobilizam fosfatos minerais; microrganismos destruidores de celulose; nitrificação; e cogumelos foram estudados. Observou-se que a preparação estudada contribui para a neutralização do solo e a ativação de processos microbiológicos. De acordo com as evidências, pode-se verificar que a preparação de cinzas e negro de carbono afeta ambigualmente o número de microrganismos. Observou-se um aumento no número de bactérias amonizantes, agentes nitrificantes e no coeficiente de transformação da matéria orgânica, bem como um aumento na disponibilidade de solo com nitrogênio facilmente hidrolisado. O teor de metais pesados não excedeu a concentração máxima admissível. Assim, o uso de um produto à base de cinzas, escórias e negro de fumo para fertilizar solos negros da terra nas culturas de trigo da primavera é ambientalmente seguro.

Palavras-chave: *chernossolo comum, metais pesados, trigo de primavera, extrato aquoso de pH, microorganismos.*

ABSTRACT

The article deals with the results of environmental regulation of doses introduced into a multicomponent carbon-containing preparation for the burning of heavy metals and the microbiological activity of the soil. The relevance of the research is based on, on the one hand, in global degradation, degasification and reduction of soil fertility. On the other hand, it is the worldwide accumulation of production and consumption waste. This study aimed to assess the effect of doses of the product from ash, slag, and carbon black on pH, heavy metal content, and microbiological activity of ordinary chernozem soil for cultivating spring wheat. The experiments were conducted in a walled-zone of Northern Kazakhstan. Soil pH was determined by a potentiometric method, the application of floe discovered the microbiological activity of the soil, the microflora was accounted for by sowing the soil suspension on solid nutrient media, and heavy metals were determined by stripping voltammetry. Bacteria utilizing organic nitrogen compounds; microorganisms consuming mineral nitrogen; oligonitrophils; bacteria mobilizing mineral phosphates; cellulose-destroying microorganisms; nitrification and mushrooms were studied. The studied preparation was observed to contribute to the neutralization of the soil, and the activation of

microbiological processes. According to the evidence, it can be verified that the preparation of ash and carbon black ambiguously affects the number of microorganisms. An increase in the number of ammonifying bacteria, nitrifying agents and the coefficient of transformation of organic matter, as well as an increase in the availability of soil with easily hydrolyzed nitrogen, were noted. The content of heavy metals did not exceed the maximum permissible concentration. Thus, the use of a product based on ash, slag, and carbon black to fertilize black earth soils on spring wheat crops are environmentally safe.

Keywords: *Ordinary chernozem soil, heavy metals, spring wheat, aqueous extract pH, microorganisms.*

1. INTRODUCTION:

Currently, coal is one of the primary sources of energy for most countries worldwide. Long-term use of coal leads to the accumulation of its residues in the form of ash and slag in significant quantities. The combustion of coal, peat and their mixtures for energy purposes (VNITSSMV and NITSPURO, 2011) generate ash and slag waste (ASW).

Vast quantities of ASW accumulate in the dumps that occupy large areas of land and their maintenance requires significant expenses. For example, the stock of accumulated ASW in the Akmola region is about 599.2 thousand tons, of which 423.4 thousand tons of ASW was generated by industrial, and suburban and residential sectors contributed the remaining. These wastes are stored around the city on unique ash dumps, occupy vast territories and exert a negative impact on the soil and water bodies (Khusainov, 2001).

Nevertheless, ash and slag are valuable and can be effectively used as secondary raw materials. According to Maiti and Prasad (2016) (2016), different countries have extensive experience in using them in various sectors of the economy. In 2012, in India it was used 63% of the total accumulated ash and slag, in China was 67% (2010), in the USA was 38.4% (2011), in EU countries was 32% (2010) and in Germany was 91.4% (2010). 2.5% ash and slag is used in agriculture as a fertilizer.

In the Republic of Kazakhstan, the utilization of ash and slag requires an operational solution because currently, only about 10-15% of the ASW of enterprises is recycled to produce cement, cinder blocks, and other building materials. An integrated approach to the processing of ASW can give a significant boost to the economy of Kazakhstan. Therefore, it is necessary to develop industrial technologies for the use of ASW, as well as to develop a set of marketing measures to promote ASW-based products.

Ash and slag are waste of the fifth hazard class, i.e., almost safe and quite useful in the

production of building materials, in construction of roads, and recultivation of disturbed lands (Dik and Soboleva, 2006). Among other things, ash and slag can be sources of valuable rare-earth elements, as well as oxides of silicon, aluminum, and iron. One of the possible ways to solve the issue of ASW from heat power stations is to use it as a fertilizer for agriculture (Berezin *et al.*, 2012).

The use of ASW to preserve soil fertility holds promise in agriculture because besides enhancing soil fertility, it solves the problems of utilization of local waste produced (Satybaldin, 2001). However, many scientists believe that this type of trash can be toxic to the environment and their use as a fertilizer is associated with the danger of soil contamination with heavy metals, changes in the pH of the environment, as well as a decline in soil microbiological activity (Cruz-Paredes *et al.*, 2017; Korcak, 2001; and others).

Therefore, the development of measures for the use of ASW as fertilizer should be accompanied by an assessment and prediction of the soil chemical composition and plants growing on it, as well as associated microbiological activity as a valuable bioindicator of the soil condition. Also, there is a need for scientific substantiation of the used ASW doses as fertilizer on specific soils for certain crops.

This article assessed the environmental impact of the application of ash, slag, and carbon black preparation as a fertilizer for soft spring wheat on chernozem soil in Northern Kazakhstan. The Objectives of this study were:

- to evaluate the effect of ash, slag, and carbon black preparation in different doses on the acidity of black earth soils;
- to establish the impact of the preparation in varying doses on the microbiological activity of black earth soils;
- to carry out environmental rationing of preparation doses on the heavy metals content in the soil.

This study is the first to assess the chernozem soil of Northern Kazakhstan in terms of ash, slag and carbon black preparations in

different doses on the response of the soil environment and the microbiological activity of the soil, as well as the ecological rationing on the heavy metals content in the soil. The use of ash, slag, and carbon black preparations to fertilize chernozem soils will improve soil fertility by enriching it with carbon and microelements for better spring wheat productivity, neutralize the soil environment and activate microbiological processes in the soil.

2. MATERIALS AND METHODS:

Chernozem soil, the preparation of ashes and carbon black, and spring soft wheat variety (*Shortandinskaya 95*, improved). *AgroBionov* preparation was used in powder form, which includes low-calcium ash of Ekibastuz coal, and carbon black. Chemical composition of fly ash from Ekibastuz coal deposits consisted of SiO₂, 62.9%; Fe₂O₃, 6.35%; Al₂O₃, 26.35%; CaO, 1.9%; MgO, 0.9%; SO₃, 1.2%; Na₂O, 0.23%. Macro - and microelement composition of ash consisted of elements in descending order as K > Fe > Al > Mg > Ca > Mn > Sr > Pb > Co > Zn > Cu > Sn > As > Ni > Cd > Hg. Technical carbon consists of more than 99% carbon (Sarsenova, 2013).

The experiment was conducted as per the guidelines of the educational research and production center, "Elite" of Kokshetau State University named after S. Ualikhanov.

The field under investigation is located 32 km north of Kokshetau. The soil cover of the experimental plot is ordinary chernozem soil, with medium carbonate and heavy loamy composition. The arable layer of soil contains 3.96% humus, and the soil solution is slightly alkaline (pH - 7.9).

The easily hydrolyzed nitrogen and mobile phosphorus contents were estimated to be 46 mg·kg⁻¹ and 17 mg·kg⁻¹, respectively. The degree of availability of easily hydrolyzed nitrogen, according to Tyurin and Kononova, was estimated to be medium, and mobile phosphorus according to Machigin was estimated to be low. The heavy metal content before sowing did not exceed the permissible concentration.

The experiment was carried out four sets as follows:

- control without fertilizer applications;
- P16 (1/10 of the estimated dose), as the background;
- on the mineral background, agrobiont preparation was applied in doses of 100, 200, 300, 400, 500 kg·hectare⁻¹ as the primary

treatment before sowing. The plot area was 125 m² (5 x 25 m), and the reference area was 100 m² (4 x 25 m).

The experiment used soft spring wheat of Shortandinskaya 95 variety with an improved medium-late type of ripening and a vegetation period of 95-100 days. This variety has a complex of economically valuable traits, such as high-yield, drought-resistance, resistance to diseases and pests.

The agroclimatic zoning experimental field belongs to a slightly moist, moderately warm zone. According to long-term average data, the hydrothermal coefficient is 0.8-1.0; the sum of active temperatures above 10 °C - 2200-2500 °C; the length of the growing season is 135-140 days. Under the conditions of 2018, the average daily temperature during the growing season (May-October) was 15.1 °C, compared with the long-term average daily temperature (16.22 °C) lower than by 1.12 °C. During the growing season, 242 mm of atmospheric precipitation fell, which is 31 mm more than the average long-term data (211 mm).

In the experiments, observations, counts, and analyses were carried out after collecting the soil samples from the 0-20 cm layer according to GOST 28168-89 before sowing during the tillering stages and full ripeness of soft spring wheat.

The pH of the aqueous extract of the soil samples (GOST 26423-85, GOST 26483-85, GOST 26490-85) (Gosstandart of the USSR, 2011, 1985a, 1985b) was determined by a potentiometric method. The content of heavy metals was determined by stripping voltammetry at the National Center of Examination of the Regional Public Health Department, Ministry of Health, Republic of Kazakhstan, Akmola region (GOST 50686-94, GOST 50683-94) (Gosstandart of the USSR, 1994a, 1994b).

The number of soil microorganisms was accounted for by sowing soil suspension on solid nutrient media, meat-peptone agar (MPA) for bacteria utilizing organic nitrogen compounds, starch ammonia agar (SAA) for microorganisms consuming mineral nitrogen, Mishustina's medium for oligonitrophilia, Muromtsev-Gerretsen medium for bacteria mobilizing mineral phosphates, Getchinson medium for cellulose-degrading microorganisms, water agar with the addition of double ammonium-magnesium salt of phosphoric acid for nitrifying agents, Czapek's medium, acidified with magnesium phosphoric acid for nitrifying agents (Aristovskaya *et al.*, 1962).

Statistical analyses of the results were carried out using Microsoft Excel.

3. RESULTS AND DISCUSSION:

The results of our study show that the preparation (drug) in different doses significantly changed the response of 0-40 cm of the soil layer. Furthermore, an increase in the preparation dose from 100 to 500 kg·hectare⁻¹, led to a decrease in the pH from 7.5 to 7.1, while the control pH remained at 7.9.

A correlation was found between the pH of the aqueous extract and the doses of the applied preparation (correlation coefficient $r = -0.76$). That is, the studied development reduced the pH from slightly alkaline to neutral, which can be explained by the chemical composition of the preparation (Figure 1).

The evaluation of microbiological diversity showed that the number of microorganisms ranged from 515.3 to 580.1 million CFU·g⁻¹ of soil. In terms of ecological-trophic groups, the proportion of bacteria per MPA of the total number in the control was 9.69%, the background of + 100 kg·hectare⁻¹ was 14.29%, the microorganisms on SAA were 10.99% and 12.27%, oligonitrophils were respectively 39%, 71%, and 35.03%, phosphate-mobilizing 39.59% and 38.39%, cellulose-destroying 0.02%, respectively.

The above data indicates that with the use of the preparation, a tendency towards slight redistribution of the primary groups of agronomically essential microorganisms in the chernozem soil was observed.

Besides the analyses of relative microbial ratios, the absolute value of the number of bacteria is of particular interest. Figures 2 and 3 show the effect of the preparation at a dose of 100 kg·hectare⁻¹ on the number of microorganisms.

The obtained data indicate that the preparation of ash, slag, and carbon black ambiguously affects the number of microorganisms in the soil. A comparative analysis shows that the total number of microorganisms in the fertilized variant is less than in control by an average of 11.8%. Also, a decrease in oligonitrophils, phosphate-mobilizing, and cellulose-degrading microbes were observed by 21.6%, 13.8%, and 38%, respectively. At the same time, compared to the control, the number of ammonifying bacteria and nitrifying agents increased by 23.6% and 77.2%, respectively, which contributed to the improved nitrogen dietary

regime of spring wheat.

The studied preparation did not contribute to increase in the number of phosphorus-mobilizing microorganisms and, consequently, improve the dietary phosphorus regime of spring wheat. Therefore, phosphorus fertilizers were applied in the background at the rate of P₁₆. The drug mineralization coefficient of the variant P₁₆+100 kg·hectare⁻¹ was estimated to be lower than that of the control by 23.9% (Table 1).

The transformation ratio of organic matter (PM) was calculated as the product of the ratio MPA/SAA * (MPA + SAA).

In our studies, we evaluated heavy metals that are the primary group of environmental pollutants (Table 2).

The results of laboratory studies show that the introduction of the product from ash, slag, and carbon black does not contribute to excess of heavy metals in the soil maximum permissible concentration (MPC) for the studied elements, although it was accompanied by an increase in Pb and Zn content by the harvest period with increasing dose of the preparation (Figure 4 and Figure 5). The most significant accumulation of Pb was noted after the introduction of the preparation in doses of 400 and 500 kg·hectare⁻¹, which exceeded the levels estimated in control by 321.4% and 357.1%, respectively.

In a comparative assessment of heavy metal content in soil samples taken in summer and autumn periods, the lead content in all variants increased by the harvest period. For other elements, an absolute dependence could not be established. Thus, the zinc content in the fall compared with summer samples of the control and the background decreased by 45.6% and 52.7%, respectively. Contrarily, an increase from 166.7% to 363.6% in the Zn content, was observed in the variants after the use of the preparation. The highest values were noted for the options "background + 100 kg·hectare⁻¹" and "background + 400 kg·hectare⁻¹", while the Zn content exceeded that of the control by 378.4%.

When using the drug at a dose of 100 kg/ha against the background of phosphorus fertilizer at a dose of 16 kg/ha of the active substance, due to the activation of microbiological processes in the soil and increasing the availability of its easily hydrolyzed nitrogen, the yield of spring wheat increased by 21.8% and amounted to 1.43 t/ha (control 1.19 t/ha).

The influence of ash and slag on the physical, chemical and biological properties of the

soil has been comprehensively studied by scientists from India, China, and Poland (Ciecko *et al.*, 2009; Ferreira *et al.*, 2003; Fulekar, 1993; Gracia *et al.*, 1995; Kalra *et al.*, 1997; Lai *et al.*, 1999; Menon *et al.*, 1993; Pandey and Singh, 2010; Phung *et al.*, 1979; Ram and Masto, 2010; Singh *et al.*, 2010; Vincini *et al.*, 1994; Właśniewski, 2009).

While conducting the current study, we paid particular attention to changing the soil environment under the influence of the preparation of ash, slag, and carbon black, since there is no consensus on this issue in the scientific literature. Several scientists (Etiégni and Campbell, 1991; Ohno and Susan Erich, 1990) note that ASW significantly affects soil acidity. For example, the studies of Adriano *et al.* (1980) and El-Mogazi *et al.* (1988) show that modeling the interacting processes of ash and slag with the soil changed its acidity to a value close to neutral. The authors indicated that in the variants with a more massive amount of ash and slag, the pH of the salt changed towards alkalinity. Scientists believe that the introduction of ash and residue into the soil changes the acidity of the soil rather quickly, in the very first year of application. Such a change in acidity can be explained by the easily accessible, high calcium content in ash and slag. Moreover, ash can loosen the soil and change its structure; therefore, the determination of soil pH is a crucial stage of field research.

The product of ash, slag, and carbon black in this study had a positive effect on soil acidity. Ash is highly alkaline and thus neutralizes excess soil acidity (Asmare and Markku, 2016; Sheoran *et al.*, 2014). Moreover, the use of fly ash improves the soil pH and also increases the content of organic carbon and organic matter (Sarangi *et al.*, 2001). Similar results were obtained in studies by Buddhe *et al.* (2014), where a close correlation (-0.83) was established between the doses of ash and slag and the pH value, which enabled the authors to conclude about the positive effect of ash on the pH of the soil environment. The economic role of ash in neutralizing the soil environment has also been emphasized, which makes it possible to use unproductive, empty acidic lands in rural and forest areas after ash and slag reclamation (Saraswat and Chaudhary, 2014).

Changes in the combination of factors that reflect the agrochemical characteristics of the soil under the influence of the preparation can affect the biological activity of the soil. Therefore, the use of the preparation of ash, slag, and carbon black as fertilizer must be assessed for its effect on the microbiota of ordinary chernozem soil, more so,

because there are very few similar, available studies.

When assessing the impact of fertilizers on the soil microbiota, determining the number of microorganisms of various ecological-trophic groups and the nature of changes (increase or decrease), it is not always possible to consider these changes as a uniquely positive or negative phenomenon.

Studies on microorganisms through environmental parameters make it possible to reproduce the biological reactions of organisms under different geochemical conditions and to get answers to unclear questions that arise when studying organisms in their natural environment (Koval'skiy, 1974).

Adriano *et al.* (1978), J. W. C. Wong, and M. H. Wong (1990), and Saffigna *et al.* (1989) report that ash reduces soil microbiological activity. On the contrary, Schutter and Fuhrmann (2001) state that ash increases microbial activity.

The extent of microbiological processes in the soil is determined not only by the number of microorganisms but primarily by their activity. In this regard, it is vital to study the effect of the applied mineral fertilizers on the rate of the essential microbiological processes in the soil. Studies (Kalra *et al.*, 1997) showed that a 5% concentration of fly ash in soil increased microbial activity, while the addition of more significant amounts of fly ash inhibited biological processes. However, research conducted by Vincini *et al.* (1994) showed that the concentration of FA in soil higher than 10% still enhanced microbial activity in the soil.

To assess the activity of microbiological processes, we calculated coefficients reflecting the dominant activity of a particular group of microflora. Microorganisms using mineral forms of nitrogen (growing on SAA) indicate the coefficient of mineralization (ratio SAA/MPA).

A higher coefficient of mineralization (>1), indicates better immobilization processes, which may be due to either a very high supply of ammonia nitrogen in the soil (this may be due to robust ammonifiers) or with organic matter deficient in nitrogen (straw, bark, etc.).

In agrocenosis, too high the Mishustin coefficient (>3-5) may indirectly indicate an increase in the rate of decomposition of humus, a specific soil organic matter (Kazeev *et al.*, 2016).

According to Mukha (1980), the PM value indicates the directionality of the microbiological

transformation process of plant residues either towards the synthesis of humic substances or towards mineralization of organic matter. Therefore, it reflects the potential intensity of accumulation of humic substances in the soil (Korobova, 2013). This may be because the studied preparation contributes, at least, to the preservation of humus in the soil.

Pollution due to heavy metals is one of the possible aspects of the impact of ASW on the environment. According to many studies, in ASW, heat from power plants, several times higher than the original coal, can increase the content of toxic (Be, Hg, As, F), and potentially toxic (Mn, Pb, V, Ni, Co, Cr, Cd, Se) elements (Mjajina, 2004).

The presence of calcium, magnesium, zinc, iron, and other elements makes fly ash a source of trace elements when used as a fertilizer. Its use helps to increase crop yields from 15 to 200% or higher (Kumar, 2009).

Along with the study of soil fertility, there is interest in the effects of heavy metals on soil and plants, since elements such as Fe, Mn, Cu, Zn, and Mo are vital for plants, animals, and humans. Being trace elements, they also have a dual effect on the soil-plant system, and their insufficient content in the soil leads to a slowdown in the growth and development of plants, while, their excess may cause inhibition of plant growth and chemical pollution of the soil. However, heavy metals do not harm plants if the concentration of their available forms in the soil does not exceed the MPC. The application of fly ash for soil fertilization is associated with plant growth and yield increase (Ajaz and Tiyaqi, 2003; Iyer and Scott, 2001; Khan and Khan, 1996; Singh and Agrawal, 2010; Singh *et al.*, 2010).

Jacek Antonkiewicz and Robert Pelka (2014) assessed the ash and slag deposits and observed that the content of heavy metals did not exceed the MAC. Likewise, Mukhanbet *et al.* (2016) indicated that when ash and slag were introduced at a dose of 400 kg·hectare⁻¹, the heavy metal content in the chernozem soil of northern Kazakhstan did not exceed the MPC.

As trace elements, Zn and Cu are crucial for average growth and development of plants (Zacccone *et al.*, 2007). Thus, both their abundance and scarcity in the soil are dangerous. Therefore, the excess of these heavy metals compared to that in control, in this case, cannot be definitively considered as pollution.

4. CONCLUSIONS:

In modern times, intensive development of industrial activity, energy, housing, and communal complex, lead to the generation of large volumes of waste, including ash and slag waste. They can be used efficiently, in particular, to improve soil fertility and the productivity of the plants cultivated on them. Studies have shown the possibility of effective use of the preparation based on ash and black carbon as a fertilizer on ordinary chernozem soil in Northern Kazakhstan. In particular, the increase in soil fertility was associated with a change in pH to neutral and an increase in the number of ammonifying bacteria and nitrifiers, which facilitate the improvement of the nitrogen regime of spring wheat. Lastly, the heavy metal content did not exceed the MPC.

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Table 1. The Effect of the Drug on the Orientation of Soil-Microbiological Processes

Variant	Number of microorganisms		SAA/MPA	MPA+SAA	MPA/SAA	PM
	in MPA million CFU.g ⁻¹	on SAA million CFU.g ⁻¹				
Control	56.2	63.7	1.13	119.9	0.88	105.5
Field + 100	73.6	63.2	0.86	136.8	1.16	158.7

Table 2. Effect of ash, slag and carbon black preparation on heavy metal content in the soil (mg.kg⁻¹)

Variants	Pb		Cd		Zn		Cu		As	
	summer	autumn	summer	autumn	summer	autumn	summer	autumn	summer	autumn
MPC	32		0.5		23		33		2.0	
Control	0.49	0.56	0	0	0.68	0.37	0	0	0	0.016
P ₁₆ - field	0.44	1.2	0	0.01	0.72	0.34	0	0	0	0
Field + 100, kg.ha ⁻¹	0.69	1.1	0	0.03	0.87	1.4	0.07	0.04	0	0
Field + 200, kg.ha ⁻¹	-	1.1	-	0	-	0.57	-	0	-	0
Field + 300, kg.ha ⁻¹	0.52	1.3	0	0.02	0.33	1.2	0.09	0.14	0.01	0.003
Field + 400, kg.ha ⁻¹	-	1.8	-	0	-	1.4	-	0	-	0
Field + 500, kg.ha ⁻¹	0.72	2.0	0	0	0.6	1.0	0.07	0	0	0

Figure 1. Effect of the Ash, Slag, and Carbon Black Preparation on the PH of the Aqueous Extract of Ordinary Chernozem Soil and on Spring Wheat Crops

Figure 2. Effect of the Preparation of Ash, Slag, and Carbon Black on the Number of Microorganisms in Ordinary Chernozem Soil

Figure 3. Effect of the Preparation of Ash, Slag, and Carbon Black on the Number of Cellulose-Degrading, Nitrifying Bacteria, and Fungi in Ordinary Chernozem Soil

Figure 4. The Content of Pb in the Soil

Figure 5. The Content of Zn in the Soil