Environmental Safety for Chernozem Soil Fertilized with Phosphogypsum and Ash for Spring Wheat Cultivation in North Kazakhstan

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Abstract. Currently, year by year the industrial waste stockpiles increase, but at the same time its recycling is not more than 10-15% of the production. There are several methods of recycling of such waste as phosphogypsum and ash, among which one of the perspective directions is considered using them in agriculture as fertilizer and ameliorator. The limiting factor of their widespread use in agriculture is the presence of heavy metals and radionuclides in them. This article presents data about environmental safety of using phosphogypsum and ash for cultivation spring wheat on the chernozem soils of Northern Kazakhstan. According to the results of research, using phosphogypsum and ash doesn't give negative impact on the environment, the presence of heavy metals and radionuclides in the soil and grain do not exceed the maximum allowable concentrations.

1 Introduction

The accumulation of industrial waste is a global environmental problem. Industrial waste, the production of which is growing every year, includes ash and phosphogypsum. The accumulation of ash adversely affects the environment, it occupies large areas, due to its sparseness it is hard for transporting, light particles are carried by wind and pollute nearby water courses and land and cause damage to the local population's health by penetrating into the body through the respiratory system[1].

Annual production of ash and its utilization varies greatly in different countries. Annual production of ash in China is about100 million tons, 75 million tons in USA, 40in Germany, the UK and Canada and15 and 6 million tons respectively. If the disposal of ash and in China and the USA is 38.45, and 65% of the annual production, in Germany, England and Canada they utilized 85, 50and 75% of the annual production of ash[2].

Phosphogypsum is a by-product of the production of phosphate fertilizers [3]. The chemical composition of phosphogypsum is represented by CaO, sulfates (such as SO3), SiO2, Al2O3, Fe2O3, P2O5, and F, contains heavy metals such as lead, cadmium, chromium, mercury and selenium [4] Only 15% of the total production of phosphogypsum

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in the world is used mainly in the construction and agricultural sectors. The remaining 85% are not recycled, and of course it causes great harm to the environment, occupies vast areas, polluting the environment with chemicals and radiation.
One of the promising areas of application of industrial wastes is their using as fertilizer or ameliorator. Phosphogypsum in agriculture is used to improve soil structure and increase productivity [5], reducing erosion and increasing soil available presence of S and P forms [6].

In turn, the using of ash for various crops helps not only to increase concentration of such elements required for plants such as K, Na, Ca, and Mg, but also reduce the presence of heavy metals such as Mo, Se, Al [7]. Ash adding helps to reduce the presence of heavy metals in plant tissues such as Cd, Cu, Cr; The researchers attribute this to improving reaction of the soil environment [8].

In Kazakhstan, the annual output of ash and ash mixtures from the combustion of coal is about 19 million tons, and in the ash dumps, nowadays, there has been accumulated more than 300 million tons of waste, the volume of their use does not exceed 10% in our country. [9]. Only in Akmola region as a result of TPP and boiler rooms work in 2011, according to the Department of Natural Resources and Environmental Control ,there was formed 599, 372 thousand tons of ashes representing 29% of the total volume of the produced ones in Northern Kazakhstan (202 457.6 thousand tons) [10]. In general, in Northern Kazakhstan, according to the Department of Natural Resources and Environmental Control of Akmola, Kostanai, Pavlodar and North Kazakhstan regions, there were formed 202.5 millions of tons of ash waste, the amount of formation of phosphogypsum only in Stepnogorsk is 9 million tons [11].

That means, in the country for a long time there is an acute issue of utilization of stockpiled ash and phosphogypsum. However, despite the above mentioned numerous studies demonstrating the possibilities and prospects for the use of phosphogypsum and ash in agriculture [5-8], information about the studies on phosphogypsum and ash in Northern Kazakhstan is very small. It is also necessary to take into account the fact that a number of foreign scientists have warned about the dangers of the use of phosphogypsum because of the presence of toxic metals and radionuclides, which, as a result of steeping can contaminate the soil and plants [12,13]. In addition, Page's studies show that the use of ash increases the presence of boron, which in turn inhibits microbial activity [14].

Thus, for the use of phosphogypsum and ash as fertilizer a thorough research about the environmental safety of industrial waste in soil and climatic conditions of Northern Kazakhstan is necessary. On this basis, field experiments and laboratory studies have been conducted to study the use of ash and phosphogypsum as the fertilizers on chernozem soils. The results of the environmental impact on the safety of industrial waste are presented in this article.

2 Material and Methods

The experiments were conducted on the experimental field of LPO "North-Kazakhstan Research Institute of Agriculture", Chaglinka village, Akmola region (53 ° 10 '9.12 "N, 69 ° 7' 37.57" E 53.1692 °, 69.127103 °), during 2014 -2015. Spring wheat of local selection "Astana" was cultivated in the experiment and zonal cultivation technology was used. Soil from the experimental area - ordinary black loam moderately low humus content. Ashes for the experiments were taken from gold shaft district in Kokshetau and pre-sowing treatment for 10 days before planting was done. Phosphogypsum was taken from dumps LPO "Kazphosphate" Stepnogorsk. Experiments have been carried down according to systematic method in triplicate. The scheme of experiments with ash includes 6 following options: (1) control, (2) superphosphate (3) Ashes from 0.2 t / ha (4) Ashes from 0.3 t / ha (5) Ashes from 0.4 t / ha (6) ash and 0.5 t / ha. The scheme of experiments with

phosphogypsum is also presented in six options: (1) control, (2), superphosphate (3) phosphogypsum 1 t / ha (4) phosphogypsum 2 t / ha (5) phosphogypsum 3 t / ha (6) and phosphogypsum 4 t / ha.

The determination of zinc, copper, lead and cadmium in soil and plant samples was conducted on atomic absorption spectrometry (AA 6200, Japan) in atomic adsorption mode. The definition of the presence of mobile forms of heavy metals in soil samples was carried out in 0.1N HNO3 extract; and the determination of heavy metals in plant samples was performed after mineralization by dry ashing to constant weight.

Results and their discussion

Among the pollutants on the scale and effects of pollution on biological objects, heavy metals take special place. In principle, many of them are essential for living organisms, but as a result of intensive atmospheric dispersion in the biosphere and a significant concentration in the soil, it becomes toxic to biota.

Migration and accumulation of contaminants such as heavy metals and radionuclides by the complex is closely related with the processes as leaching, capillaries size, sorption, pH, humidity of the root system and etc. [15,16].

It is also known that heavy metals are found in nature, in the soil organic material, clay, in the Fe or Mn oxides, carbonates, etc., without disturbing the ecological balance [17-19].

It is known that, the term "maximum permissible concentration" (MPC) is used to assess major environmental soil pollution standards, such as contained element in the soil, which for constant contact or interaction for a certain period of time has no effect on the animals, plants, microorganisms and humans.

According to modern conception, the MPC of chemical substances in the soil is a complex indicator of harmless to human of chemicals in the soil, as used in its justification criteria reflect the impact of the possible ways of contacting elements on the environment, soil biological activity and its self-purification processes.

The laboratory tests confirm the sanitary and environmental safety of introducing ash into spring wheat on chernozem soils of Northern Kazakhstan. The use of different doses of ash entering from 0.2 to 0.4 tons / ha does not exceed MPC of heavy metals in the soil and wheat grain (Table 1).

According to the research, during the year of application of ashes the excess of Pb in the soil was observed on all variants of the experiment and ranged from 4.08 (Ashes from 0.4 t / ha) to 4.51 mg / kg (Ashes from 0.2 t / ha) that exceed the control at 3.65 and 4.08 mg / kg respectively. However, it did not affect the content of Pb in the grain of wheat, where there was noted a slight excess - in the range 0.03-0.1 mg / kg. Noteworthy is the fact that in the following year after the introduction of ash, Pb content in soil was reduced by half, and Pb content in the grain and does less control. We suppose that this is due to the improvement of soil reaction and absorption ability stipulated with the introduction of ash, that is confirmed by Petruzelli's data[8].

Significant increase of Cu and Zn content was not observed in the grains. The highest rate of Cu in 2014 noted at the option Ashes 0.3 t / ha (4.8 mg / kg) and the excess Zn in the form of ash 0.5 t / ha (10.7 mg / kg) does not exceed the maximum permissible concentration. In 2015, the content of these elements in wheat grains did not differ from the control variant. However, there was a significant excess of Cu and Zn in the soil of the ash entering year and in subsequent years. Compared with the control, an increase in the content of Cu to various doses of ash entering varied slightly and averaged 5.2 mg / 2014 and 1.47 to 2015. Content of Zn is also increased in 2014 and in 2015 and the total amount was 17.08 mg / kg and 3.75 mg / kg, respectively. This is largely due to the high content of these elements in the chemical composition of the ash. It is necessary to point out that both Zn, and Cu are also trace elements, essential for the normal growth and development of plants [20]. Thus, we can conclude that the introduction of ash improves soil nutrient regime, since the use of ash does not exceed the maximum permissible concentration.

Table 1. The effect of dose application of ash on the content of heavy metals in the soil and in grain of spring wheat, mg / kg.

Experiment variants	Pb		Cd		Cu		Zn	
	2014y.	2015y.	2014y.	2015y	2014y.	2015y.	2014y.	2015y.
Soil*								
Control	0.43	0.47	0.0	0.078	0.5	0.21	0.12	0.93
P20	0.50	2.13	0.0	0.038	0.32	1.24	0.38	1.82
Ash 0,2 [t/ha]	4.51	0.84	1.7	0.054	5.1	1.26	17.0	3.28
Ash 0,3 [t/ha]	4.20	1.84	1.5	0.071	5.4	1.84	17.2	3.95
Ash 0,4 [t/ha]	4.08	2.86	1.2	0.042	5.7	1.68	17.1	4.68
Ash 0,5 [t/ha]	4.12	2.74	1.3	0.028	5.9	1.89	17.8	4.75
Wheat**								
Control	0.25	0.44	0	0	0.09	1.6	7.7	6.3
P20	0.28	0.46	0	0	0.16	1.9	3.5	2.8
Ash 0,2 [t/ha]	0.14	0.094	0	0	4.2	0.35	8.8	1.8
Ash 0,3 [t/ha]	0.28	0.091	0	0	4.8	0.95	9.2	2.0
Ash 0,4 [t/ha]	0.31	0.06	0	0	2.8	0.87	10.1	2.3
Ash 0,5 [t/ha]	0.35	0.13	0	0	0.87	0.76	10.7	2.7
MPC*	Pb – 32		Cd –3,0		Cu – 33		Zn – 23	
MPC**	Pb – 0.50		Cd – 0.10		Cu – 10		Zn – 50	

The excess of Cd to within a 2.7-4.71 mg / kg observed in the soil in the year ash was added, while the content was not found in the wheat grain. The following year as compared to the control, there was not exceeding the level of Cd, in any of the variants of the experiment.

As a result, despite a slight excess on the deposit options ash content of mobile heavy metals did not exceed the maximum allowable concentrations or in the soil or in the grain of wheat. The results of our study are confirmed by the experience of foreign scientists. In the experiments made by Nileshusing of ash did not exceed Cd and Pb in the grain of wheat, beans and mung slightly (within MPC) exceeding Zn [21] content.

As mentioned above, one of the problems hindering its widespread in agriculture is the content of radioactive Radium and radon. However, according to Mays and Mortved, introduction of 112t / ha phosphogypsum containing 25 pCi 226Ra in loamy soils helped to grow such cereals successfully(maize, spring wheat) and oilseeds (safflower). As they note, the application rate of 112 t / ha application rate exceeds the plaster under the peanuts more than 200 times, but it was not observed any negative effect on the excess of the radioactivity of any grain or in the soil [22].

At the same time some scientists warn about the dangers of the use of phosphogypsum because of the content of toxic metals and radionuclides, that as a result of leaching can contaminate the soil and plants [12,13].

Our studies have shown that the use of phosphogypsum in doses of 1-4 t / ha contributed to a slight increase in the content of heavy metals in soil and wheat grain, but did not exceed the maximum allowable concentrations (Table 2). According to Table 2, in the year of application of phosphogypsum as compared to the control there was no excess of heavy metals in the soil in all experimental variants. However, in the following year noted an excess of Cu Zn and Pb. Partly, it can be explained by poor solubility of phosphogypsum in soil, and therefore in the second year the strong aftereffect of phosphogypsum was observed. Comparing different doses of phosphogypsum application, an excess of the highest Pb, Zn and Cu are found to form phosphogypsum 4t / ha; in comparison with the control, excess Pb in this embodiment made - 2.55 mg / kg: Zn 4.58 mg / kg and Cu 3.93 mg / kg. However, these data, is the greatest indicator of increasing data content items, are within the acceptable concentrations.

Regarding the impact of phosphogypsum for heavy metal content in the grain must be noted that the application rates of phosphogypsum had not significant impact on their content, except Zn, the content of which in the wheat grain in 2014 exceeded the control on an average of 4.18-6.88 mg / kg . However, already in the following year the Zn content in the wheat grain has come back to normal, and all indicators do not exceed their maximum allowable concentrations.

O. V. Dubravina notes that introduction of phosphogypsum at the norm of 3 t/hectare doesn't cause accumulation in the soil of heavy metals, but increases in the humus of the Kamennaya steppe the presence of P2O5 on 5.6 mg/kg of the soil [23].

N. A. Protasova, N. S. Gorbunova claim that prolonged using of phosphogypsum and composts on its basis doesn't lead to essential change of HM presence in the plain chernozem soil and agricultural production, thanks to high buffering and ecological stability of humus [24].

Table 2. Influence of application of phosphogypsum on the presence of heavy metals in the soil and in a grain of a spring wheat, mg/kg.

Experience options	Pb		Cd		Cu		Zn	
	2014	**2015**	**2014**	**2015**	**2014**	**2015**	**2014**	**2015**
Soil*								
Control	0.48	0.41	0.00	0.052	0.7	0.27	0.13	0.8
P20	0.52	2.28	0.00	0.034	0.5	1.8	0.35	1.74
Phosphogypsum1 [t/hectare]	0.44	1.27	0.00	0.061	0.8	2.3	0.02	3.8
Phosphogypsum 2 [t/hectare]	0.45	1.82	0.00	0.037	0.7	2.5	0.03	4.1
Phosphogypsum 3 [t/hectare]	0.41	1.93	0.00	0.083	0.6	3.2	0.02	4.8
Phosphogypsum 4 [t/hectare]	0.42	2.96	0.00	0.054	0.6	4.2	0.02	5.38
Grain**								
Control	0.28	0.34	0	0	0.12	1.8	7.3	6.0
P20	0.23	0.45	0	0	1.9	1.4	3.6	3.0
Phosphogypsum1 [t/hectare]	0.08	0.043	0	0	0.84	2.8	4.2	8.5
Phosphogypsum 2 [t/hectare]	0.09	0.045	0	0	4.3	1.2	5.0	9.3
Phosphogypsum 3 [t/hectare]	0.10	0.17	0	0	6.8	0.9	6.1	9.4
Phosphogypsum 4 [t/hectare]	0.12	0.16	0	0.033	7.0	1.1	7.2	10.1
MPC*	Pb – 32		Cd –3,0		Cu – 33		Zn – 23	
MPC**	Pb – 0,50		Cd – 0,10		Cu – 10		Zn – 50	

3 Conclusion

Researches have shown ecological safety of application of waste of the local industry as fertilizer on black soils of Northern Kazakhstan. Introduction of doses of phosphogypsum

till 4/t and ash till 0.4 t/hectare hasn't exceeded maximum-permissible concentrations of heavy metals and radionuclides in the plain chernozem soil and in a grain of a spring wheat.

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