International Journal of Agriculture Innovations and Research
Volume 4, Issue 5, ISSN (Online) 2319-1473
Manuscript Processing Details (dd/mm/yyyy) :
Received : 15/03/2016 | Accepted on : 04/04/2016 | Published : 12/05/2016

Characteristics of Changes in the Content of Copper, Zinc, Cobalt and Cadmium in Soils of Northern Kazakhstan in the Long-term Application of Fertilizers

G. Churkina, K. Kunanbayev, Zh. Kaskarbayev, N. Zueva,
G. Akhmetova, Y. Nazdrachev, L. Zhloba

Abstract – **One of the sources of trace elements in soil and heavy metals is long-term application of mineral fertilizers. The effects of prolonged exposure to fertilizer N-20, P-20 kg/ha (P- superphosphate, N-ammonium nitrate, NP- nitroammophos) on the accumulation of trace elements and heavy metals were determined in flax crops in 4 field flax-wheat rotationon southern calcareous black soil. Annual application of mineral fertilizers does not currently increase the maximum permissible values of mobile forms of copper and zinc. This is partially explained by the weak migration of these elements in a neutral and a slightly alkaline reaction of a solution of southern black soils. However, these results suggest that a systematic, long-term fertilizer application contributes to the accumulation of cadmium.**

Keywords – **Mineral Fertilizers, Mobile Forms of Copper, Zinc, Cobalt, Cadmium, Flax Seeds.**

I. Introduction

With the development of virgin soil in Northern Kazakhstan on millions of hectares of arable land, there was intense anthropogenic impact on the soil, hitherto unknown in world practice.Within a decade, the natural steppe biogeocenoses were turned into agrocenosises focused on the cultivation of spring cereals. Anunduly high proportion of arable land in some areas of Northern Kazakhstan has led to the loss of soil fertility and wheat yield on cultivated lands. The content of humus is the main indicator of soil fertility, decreased by 20-30% [1]. The need to increase the productivity of crops has increased the need for fertilizers as a source of various nutrients for plants and soil properties, particularly nitrogen, phosphorus and potassium [2]. All these elements belong to the group of macronutrients, since they are absorbed by plants in considerable quantities.Mineral fertilizers are fast and highly effective means to increase yields and improve soil fertility. At the same time, the use of phosphorus fertilizers can lead to the accumulation of heavy metals including cadmium in soil and plants [3] – [4]. This is due to the fact that mineral fertilizers are composed of salts of heavy metals in the form of ballast.Long-term use of fertilizers may increase the content of heavy metals [5] – [6]. The aim of this research was to study the processes of heavy metals accumulation with prolonged use of mineral fertilizers in the black soils of Northern Kazakhstan.

II. Material and Method

The experimental fields of the A.I. Barayev Scientific Production Center for Grain Farming are located on the southern calcareous black soil of Northern Kazakhstan. The steppe zone of Northern Kazakhstan is characterized by a continental and arid climatewith erratic alternation of wet and dry years. This area has a deficit of moisture for arable crops with a mean annual rainfall of only 321 mm. In the arid steppe, distribution of precipitation over different periods of the year has considerable importance. The soil condition is typical for the prevailing weather. The humus depth is an average of 50 cm and the soils characteristically have a high carbonate content of up to 5%. Organic matter varies from 3- 5%, nitrogen is 0.3% and phosphorus is 0.1%; the soil is slightly alkaline (pH 7-7.9). In terms of absorption, calcium (80%) and magnesium (11%) were predominated. Mobile phosphorus is determined by the Machigin method with a CINAO modification (extraction with 1% solution of ammonium carbonate). The organic matter was determined by the CINAO method, which involves carbon oxidation containing humus substances to CO_2 through a potassium dichromate solution $K_2Cr_2O_7$ and subsequent determination of trivalent chromium equivalent to the content of the organic substance. The concentration of these indicators was determined by absorbance in a spectrophotometer (Cary 50, Varian, Australia). Nitrate content was determined by the ionometrical method (NSS 26951-86) with a Sartorius PP 50(Germany). In experimental trials the mineral fertilizers have been applied more than ten years and were introduced at the rate N-20, P-20 kg/ha (P – superphosphate, N – ammoniumnitrate, NP –nitroammophos). Phosphorus and nitrogen fertilizers were applied in rows with crops of flax (in the last ten days of May) with zero technology.

In field experiments studies were made of the regularities of content changes in mobile forms of microelements in the southern calcareous black soil of Northern Kazakhstan under the influence of different types of nitrogen and phosphorus fertilizers in control variants with and withoutfertilizer.Contentof copper (Cu), Zinc (Zn), cobalt (Co), cadmium (Cd) in the soil and in the plants weredetermined by atomic - absorption spectroscopy AA - 140 (Varian, Australia).

Statistical analysis of the research results was carried out by using statistical software Agros 2.11. (Novosibirsk, Russia). The differences between averages were determined using the Tukey's test, at P < 0.05. The experiments were repeated three times. The size of each plot was 4 × 40 meters. Sampling was carried out in June at the depth of 0 - 20 cm.

III. Result and Discussion

Research was conducted to assess the influence of long-term application of nitrogen-phosphorus fertilizer on heavy metals accumulation and trace elements on the southern calcareous black soils of Northern Kazakhstan under different climatic conditions in the period 2012-2014. Research results for 2012 showed that the copper (Cu) content in the soil is studied less than its clarke element and indicates the scattering of elements related to the lithosphere (Table I).

Table I - Concentration trace element in soil, 2012 year

Element	Clarke value	Limit	Control	P_2	N_4	N_4 P_2	NP	$LSD_{(0.05)}$
Cu, mg/kg	18.0	6.0	5.01	5.00	5.04	4.88	5.14	ns
Co, mg/kg	-	5.0	2.49	1.95	1.69	1.98	2.42	0.34
Zn, mg/kg	37.0	23.0	5.18	5.49	5.48	5.26	5.39	ns
Cd, mg/kg	0.3	1.0	0.27	0.30	0.26	0.26	0.23	ns
NO_3, mg/kg			31.05	54.60	29.25	53.6	39.35	3.66
P_2O_5 mg/kg			26.40	52.15	33.10	39.8	39.45	8.50
C_t, %			3.02	2.92	2.81	2.76	2.64	ns

ns – not significant

Comparative analysis between the control variant and the variant with fertilizer showed no significant differences in copper between them. In the experiments we have also noted the absence of excess maximum allowable concentrations (MPC). The content of mobile zinc in black soils ranged from 0.12 to 20.0 mg/kg soil. Background element zinc content reaches 37.0 mg/kg. At the same time, the content of mobile zinc was significantly lower than the soil clarke, which indicates the scattering of soil trace elements in the lithosphere. Having high carbonate content in the soil, pH >7 slows the mobility and solubility of zinc in the soil content[7] – [8] state that there is no direct correlation between the dose of phosphorus fertilization and zinc content; this explains the rather low levels of zinc in the soil. Insufficiency and elevated concentrations of cobalt in soils through the food chain can cause endemic diseases in humans and animals [9] – [10]. Cobalt is one of the active elements and it is always contained in the body of animals and plants. Studies on black soils of Northern Kazakhstan have shown that the highest cobalt content was in the control variant and a variant with fertilizer (nitroammophos). In the version with superphosphate, ammonium nitrate and mixtures of Co were significantly lower. This feature could occur due to the difference between the field soils, since the diversity in *in situ* source rock largely determines the fluctuations in the content of cobalt in soils. The element cadmium, which enters the soil with superphosphate, is an impurity. The content of cadmium in black soils in 2012 was at the level of the soil clarke. However, its content does not exceed the MPC; thus pollution by cadmium in the soil did not occur, and the slightly alkaline reaction of the soil solution indicates an inactive state of sorbed Cd in the soil. The lack of significant differences between the variants confirms the assumption that the content of cadmium in the first year of studies is part of the background and appears to have a natural origin. Thus, the application of nitrogen and phosphate fertilizers in the first year of studies did not cause significant changes in the content of cadmium and was five times less than the maximum allowable concentration, which is consistent with a number of authors [4], [11] – [12]. reported that concentration of heavy metal has recommended to exposure limits for non-contaminated soil by increasing level of cadmium. The findings are consistent with existing research with increasing pH bioavailability of trace elements zinc and lead decreased. Thus, in 2012 in the first year of the study, cases of heavy metal accumulation in the soil have not been observed.

Trace elements are closely related to the components of the soil and organic matter as a result of redox processes [13]. Contents of macronutrients in soil varied depending on fertilizer options. Thus, the highest content of available nitrogen and phosphorus was fixed to the variant with superphosphate, as well as with the variant with nitroammophos and superphosphate. The content of organic matter was in the range of 2.64 to 3.02%. Studies in 2013 made it possible to clarify, supplement and confirm the results of previous studies; the copper content in the control version and versions with fertilizer was on the same level, as evidenced by the absence of significant differences between the variants (Table II).

International Journal of Agriculture Innovations and Research
Volume 4, Issue 5, ISSN (Online) 2319-1473

Table II - Concentration of trace element in soil in 2013

Element	Clarke value	Limit	Control	P_2	N_4	N_4 P_2	NP	$LSD_{(0.05)}$
Cu, mg/kg	18.0	6.0	4.89	4.95	4.92	4.95	5.90	ns
Co, mg/kg	-	5.0	9.03	8.26	7.54	6.89	6.61	0.40
Zn, mg/kg	37.0	23.0	5.69	5.94	5.85	6.26	4.96	0.79
Cd, mg/kg	0.3	1.0	0.33	0.26	0.24	0.31	0.54	ns
NO_3, mg/kg			27.7	27.65	65.20	29.5	18.7	2.98
P_2O_5, mg/kg			23.7	22.85	20.50	18.0	17.35	2.87

ns – not significant

At the same time we have marked differences in the content of zinc with the nitroammophos variants on average 0.8 mg/kg less than other samples, fertilizers and the controlvariant. The cobalt content in all variants exceeds the soil clarke by 1.61-4.03 mg/kg. In the samples with fertilizers, there were not any regular changes in the cobalt content to record,compare to other type of fertilizers. Apparently, the change in the content of this trace element is to a greater extent dependent on water than on fertilizer application rates. In the version with nitroammophos we observed an excess of Cd 0.24, compared with soilclarke. Since the content of cadmium in phosphorous fertilizers can vary within different limits, we can observe an increase of the element [14] – [15]. High levels of nitrate were observed in the form of ammonium nitrate. Nevertheless, the use of the compound fertilizer nitroammophos did not lead to an increase in the content of available nitrogen and phosphorous in soil. In general, the provision of macro-gradation nitrogen and phosphorus in the fertilized variants was average. In 2014, significant differences in control options and options with fertilizers were not detected among the trace amounts of copper and zinc (Table III).

Table III - Concentration of trace element in soil in2014

Element	Clarke value	Limit	Control	P_2	N_4	N_4 P_2	NP	$LSD_{(0.05)}$
Cu, mg/kg	18.0	6.0	5.52	5.76	5.61	5.74	5.90	ns
Co, mg/kg	ns	5.0	3.82	4.00	3.56	4.21	6.05	0.54
Zn, mg/kg	37.0	23.0	3.68	3.98	3.68	3.61	4.67	ns
Cd, mg/kg	0.3	1.0	0.36	0.54	0.49	0.50	0.54	ns
K_2O, mg/kg			551.50	523.50	461.50	468.0	523.0	22.86
NO_3, mg/kg			22.4	22.0	56.10	25.55	14.25	1.79
P_2O_5, mg/kg			17.5	23.75	11.40	15.35	18.15	1.16
C_t, mg/kg			3.12	3.12	2.70	2.96	3.00	0.27

ns – not significant

At the same time the increase of cobalt content was noted on the options using a mixture of fertilizer: ammonium nitrate and superphosphate, as well as the use of nitroammophos compared to the control. In general, the cobalt content in the soils under the influence of phosphate fertilizers decreased from 2013 to 2014. The nature of this phosphorus fertilizers effect on the trace elements content in the soil, apparently, lies in the partial binding of metal cations and hydrophosphate ions in elements transition in less mobile and inaccessible to plants condition [16].

In 2014 the cadmium content of all the options exceeded the content of clarke soil Cd. This is due to the accumulation of heavy metals in soil. The trend of increased cadmium in the soil may be related to the use of mineral fertilizers in 2012, and its accumulation in the soil. This is consistent with the opinion of some authors, indicating that the increase in number of trace elements in soils may occur under the influence of long-term use only fertilizers [17]. Among the movable elements we noted high potassium content, which is a characteristic feature of the southern calcareous black soils. Nitrate on the options ranged from low supply on the version with nitroammophos to high on a variant with ammonium nitrate. At the same time supply of mobile phosphorus was the average for all variants including control without fertilizer. Provision of organic material for all variants was average. Analysing the average data for the three years of research, accumulation of elements copper and cadmium may be noted (Table IV).

Table IV – Concentration of trace element in soil, 2012 – 2014

Year	Nutrient			
	Cu	Co	Zn	C
	mg/kg			
2012	4.97	1.87	5.41	0.27
2013	4.95	7.56	6.02	0.27
2014	5.76	3.92	3.76	0.51
$LSD_{(0.05)}$ for years	0.50	0.38	0.34	0.10

IV. Conclusion

The cobalt content varied widely, from the smallest number in 2012, with a gradual increase in 2013-2014. The opposite dynamics are observed with zinc content by years of research, which may be related to the removal of Zn from the soil by plants, and migration into the underlying layers due to water runoff. A summary of factual data shows that fertilizers practically do not change the pH and have no appreciable effect on the changes in the content and mobility of trace elements in the topsoil.

V. Acknowledgment

Article is made within the framework of the grant financing of the Committee of Science, Ministry of Education and Science of the Republic of Kazakhstan on the topic:"Improving environmental criteria evaluation of soil contaminated with chemicals to regulate grain food security agroecological monitoring», № state registration 0112RK02635

References

[1] M.Suleimenov, J.R. Thomas,“Ecosystems and carbon sequestration challenges, «Climate change and TerretrialCarbon Sequestration in Central Asia”. Taylor and Francis Group London, 2007, pp. 165 – 174.

[2] D.K.Gupta, S.Chatterjee, S.Datta, V.Veer, C.Walther,“Role of phosphate fertilizers in heavy metal uptake and detoxification of toxic metals”. Chemosphere, 108, 2014, pp. 134-144.

[3] M.Cupit, O.Larsson, C.De Meeuˆs, G.H.Eduljee, M.Hutton, “Assessment and management of risks arising from exposure to cadmium in fertilizers – II. Science of the total environment”, 291, 2002 pp. 189–206.

[4] M.Molina, F.Aburto, R.Calderóón, M.Cazanga, M. Escudey, “Trace element composition of selected fertilizers used in Chile: phosphorus fertilizers as a source of long-term soil contamination. Soil Sediment Contamination International Journal, 18”2009, pp. 497–511.

[5] R.E.Franklin, L.Duis, R.Brown, T.Kemp, “Heavy metal content of selected fertilizers and micronutrient source materials.Community soil science and plant analysis, 36”2005pp. 1591–1609.

[6] M.I.Sheppard, S.C.Sheppard, C.Grant, “Solid/liquid partition coefficients to model trace element critical loads for agricultural soils in Canada”.Canadian Journal of Soil Science, 87: 2007 pp,189–201.

[7] G.Brümmer, K.G.Tiller, U.Herms, P.M.Clayton, “Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils”. Geoderma, 31, 1983 pp. 337-354.

[8] R.Lambert, C.Grant, S.Sauve, “Cadmium and zinc in soil solution extracts following the application of phosphate fertilizers”. Science of the Total Environment, 378: 2007 pp. 293–305.

[9] H.F.Li, C.Gray, C.Mico, F.J.Zhao, S.P. McGrath,“Phytotoxicity and bioavailability of cobalt to plants in a range of soils”. Chemosphere, 75,2009, pp. 979-986.

[10] D.Luo, H.Zheng, Y.Chen, G.Wang, D. Fenghua, “Transfer characteristics of cobalt from soil to crops in the suburban areas of Fujian Province, southeast China”. Journal of Environmental Management, 91, 2010 pp. 2248-2253.

[11] D.McGrath, H.Tunney“Accumulation of cadmium, fluorine, magnesium, and zinc in soil after application of phosphate fertilizer for 31 years in a grazing trial”. Journal of Plant Nutrition and Soil Science, 173, 2010 pp. 548–553.

[12] D.Cakmak, M.Saljnikov, V.Mrvic, M.Jakovljevic, Z.Marjanovic, B.Sikiricn, S.Maksimovic, “Soil properties and trace elements contents following 40 years of phosphate fertilization”. Journal of Environmental quality, 39: 2010 pp. 541–547.

[13] R.Carrillo-Gonzalez, J.Simunek, S.Sauve, “Mechanisms and pathways of trace element mobility in soils”.Advances in Agronomy, 91, 2006, pp.111–178.

[14] C.A. Grant, S.C. Sheppard, “Fertilizer impacts on cadmium availability in agricultural soils and crops”. Human and Ecological Risk Assessment, 14, 2008, pp. 210–228.

[15] W.P.Chen, A.C.Chang, L.C. Wu, “Assessing long-term environmental risks of heavy metals in phosphate fertilizers”. Ecotoxicological Environmental Safety Journal, 67, 2007, pp. 48–58.

[16] P.Takáč, T.Szabová, L.Kozáková, M.Benková, “Heavy metals and their bioavailability from soils in the long-term polluted Central Spiš region of SR”. Plant, Soil Environment, 55, 2009, pp, 167–172.

[17] M.D.Taylor,“Accumulation of cadmium derived from fertilizers in New Zealand soils”.Science of the Total Environment, 208, 1997, pp. 123–126.

[18] J.J. Mortvedt, “Cadmium levels in soils and plants from some long-term soil fertility experiments in the United States of America”. Journal of Environmental Quality, 16, 1987, pp.137–142.