

ECOTOXICOLOGICAL STUDIES OF AKMOLA REGION LAKES

*Lyailya Akbayeva, Erdaulet Tulegenov, Ainur Omarbayeva, Nazira Kobetaeva,
Zina Nurgalieva, Yerlan Nurkeyev, Patricia Martišová, Vladimír Vietoris, Assylbek Zhanabayev*

ABSTRACT

The research object is water, bottom sediments in Akmola region lakes located in the intensive agriculture area. The territory of Akmola region is subjected to intensive human impacts, including the inevitable pollution with agricultural pesticides, which are ecotoxicants. The work has carried out hydrochemical studies in technogenic polluted lakes: general hydrochemical indicators, persistent organic pollutant content. The POPs in the samples were determined on the gas chromatograph Clarus 580 (PerkinElmer) with a mass spectrometer detector Clarus-SQ 8. According to the analysis results, the general hydrochemical pollution is classified as an average. The MPC excess indicators in the Akmola region lakes are observed for salt ammonium (up to 0.002 MPC), magnesium (up to 1.15 MPC), nitrites (up to 1.12 MPC), petroleum products (up to 1.98 MPC), iron (up to 2.0 MPC), SSAS (up to 3.8 MPC). High concentration indicators for the sulphate (3.5 MPC), copper (4.3 MPC), magnesium (1.125 MPC). Mainly the lakes are dominated by sulfates, ion chloride. But in general among 21 investigated POPs 8 substances are accumulated in bottom sediments of the investigated Zhalauly, Tastykol lakes, Unnamed Lake to the south of Akkol village, Itemgen lake, Zhalanash lake near Malinovka village (near Astana city), Kokay, Yesey, Bolshoe Chebachie.

Keywords: ecotoxicants; persistent organic pollutants; monitoring; accumulation; lake

INTRODUCTION

In Kazakhstan there is still no universal systematic monitoring of persistent organic pollutants (Kholubek et al., 2012). Upon that, a number of pilot projects of initial assistance to the Republic of Kazakhstan on obligations under the Stockholm Convention on Persistent Organic Pollutants has given reasoned conclusion that the problem is urgent in the republic (Kholubek et al., 2012; Zhanadilov et al., 2015.; Shabanova et al., 2010). This primarily relates to areas exposed to intense pollution by agricultural pesticides.

Ecological problems of Akmola region is largely determined by agro-industrial specialization of the region. The main branch of the region specialization is the production and processing of agricultural products (76%), including grain production – 56.8%. Akmola region has the highest percentage of rural population – 54.8% (Investment opportunities of the region, 2017; Sydykov et al., 2004; Seitkasymova, 2015).

The industry of this region is represented by the gold ore, uranium extraction, pharmaceutical and chemical industry, machine building and production of building materials (Sydykov et al., 2004; Press service of the Prime Minister of the Republic of Kazakhstan, 2018).

The area is rich in land resources. The total area of agricultural land is 13,791.7 thousand ha, areas of natural pastures are wide and occupy 6592.5 thousand hectares, the arable land is about 7,100 thousand ha. Almost all arable lands use some insecticides, fungicides - substances that are long-persistent in the environment, accumulated in the soil, in bottom sediments of stagnant water (Ljunggren et al., 2014; Jepson and Law, 2016).

In addition, the territory of the region under study still keep in some places some pesticides in abandoned warehouses without recycling, that were applied since the middle of last century. Names, respectively, contents of some pesticides are no longer possible to determine without analytical tests.

Thus, the territory of Akmola region is subjected to intensive human impacts, including the inevitable pollution with agricultural pesticides, which are ecotoxicants.

Detecting most POPs directly in water is not recommended (Kholubek et al., 2012; Ministry of Health of the USSR, 1987) because many of them are insoluble in water, and soluble POPs can be eliminated through bioaccumulation in living organism tissues. Thus, in our opinion, monitoring surface water for the POP content should begin with bottom sediments. In this case,

hydrochemical indicators should be analyzed as the accompanying background or synergistic factor increasing violations in biocenosis and pathomorphology of aquatic organisms (Yemlyanova and Lobchenko, 2002.; WHO, 2011; Kukeyeva et al., 2015; Grancová-Bielková and Sokol, 2010; Akbayeva et al., 2014).

The research aim: Study the content of ecotoxicants in the Akmola region lakes.

Scientific hypothesis

In Kazakhstan, by virtue of years of the uncontrolled POPs use and production of industrial toxins, violations of their operation and storage rules, a unique dangerous xenobiotic profile could emerge, which practically has not been studied (Akbayeva et al., 2016).

In the Republic of Kazakhstan, an average of up to 0.57 kg of pesticides was applied per 1 ha of arable land (Shabanova et al., 2010). Considering that pesticides were used from the 50s, about 475 tons of pesticides were used on the territory of the Akmola region with an area of 14,621.9 hectares until 2008, including POPs pesticides. In this regard, pesticides from contaminated soil should ultimately accumulate at the bottom of water bodies. Thus, lakes are the ultimate storage of POPs.

The research results should be informative and methodological rationale for more extensive researches in this area.

MATERIAL AND METHODOLOGY

In 2016 some of the chemical components was studied in the water and bottom sediments of the Akmola region lakes: Zhalauly and Tastykol lakes, the unnamed lake to the south of the district center of Akkol village and unnamed lake 40 km south from Astrakhanka village, Itemgen lake at Buland village, Zhalanash lake at Malinovka village (near Astana city). These lakes are located on the territory of the agricultural pesticides intensive use or places of POP substances storage. Lakes of the Korgalzhyn lake system: Kokay, Yesey, Sultankeldy are located in the south of the Akmola region territory in the lower part of the Nura River valley, which runs a large farmland. There have also been studied lakes of Shchuchinsk - Borov resort zone Borovoye and Bolshoe Chebachie that are under intensive anthropogenic impact.

In the lakes, hydrochemical samples of water and bottom sediment were selected in the summer months of July - August 2016.

These analyzes have determined the Hydrochemical water pollution index (WPI) (Sibagatullina and Mazurkin, 2009).

Determining POPs in bottom sediments

It has been carried out in accordance with the methodological guidelines for determining HCH and DDT in silt sulfide medical muds with gas-liquid chromatography (Ministry of Health of the USSR, 1987). The samples were selected with a bottom sampler from 10 – 70 cm depth from the surface. Samples were taken at five points by the "envelope" principle. Selected from all the mud was thoroughly mixed, and an average sample was selected in a glass jar of 500 mL. For further analysis, grounds were air dried.

The POPs in the samples were determined on the gas chromatograph Clarus 580 (PerkinElmer) with a mass spectrometer detector Clarus-SQ 8.

Chromatographic conditions: capillary column RestekRxi®-1 ms 0.25 mm x 30m x 0.25 mm, sample volume: 1.0 mL, the carrier gas, the carrier gas velocity: 1 mL.min⁻¹, flow division of 1:25, t columns: 40 °C, the rise of 2 °C.min⁻¹ to 280 °C, t evaporator – 280 °C, mass spectrometric detector: t – 240 °C, EI ±70 eV, the scanning time – 4 to 120 minutes, the ion scan mode – 39 – 500 m.z⁻¹.

Statistic analysis

All data were expressed as mean. The percentage components content was automatically calculated based on the peak areas of total ion chromatograms. The components were identified by mass spectra and retention times, using a NIST library.

RESULTS AND DISCUSSION

Indicators of the MPC excess in the Akmola region lakes for salt ammonium (up to 0.002 MPC), magnesium (up to 1.15 MPC), nitrites (up to 1.12 MPC), petroleum products (up to 1.98 MPC), iron (up to 2.0 MPC), SSAS (up to 3.8 MPC). High concentration indicators for the sulphate (3.5 MPC), copper (4.3 MPC), magnesium (1.125 MPC). Mainly the lakes are dominated by sulfates, ion chloride (Table 1).

Lakes the most salty and with a hard water are Zhalauly and Zhalanash lakes - the water hardness of 7.5 mg.dm⁻³ and 8.37 mg.dm⁻³, respectively.

According to the water pollution index (WPI) the first class (relatively clean) may only include Sultankeldy, Yesey, Kokay waters; the second class (slightly dirty) - Zhalauly, Itemgen, Unnamed Lake (Akkol village) Zhalanash, Borovoe, Bolshoe Chebachie; the third class (polluted) - Tastykol, Unnamed Lake (Astrakhanka village) (Sibagatullina and Mazurkin, 2009).

Water is not recommended as a key matrix for lipophilic and non-Arctic initial twelve POPs, so the analysis of surface water is not recommended: for aldrin, chlordane, DDT, dieldrin, endrin, HCB, heptachlor, mirex, PCB, PCDF/PCDF, toxaphene. Water-soluble POPs: chlordecone, α-HCH, β-HCH, γ-HCH, PFOS (perfluorooctanesulfonate). Besides, the POP concentration in water may vary seasonally due to the seasonal activity of phytoplankton and certain organic substances, and other impacting factors, such as rainfall, flow volume, etc. Based on this, we have not detected POPs in the lake waters, and immediately began to define in the bottom sediments, where they can sediment as lipophilic compounds on the adsorbent composed of dead biota, benthic microorganisms.

Almost in all the studied lakes (Table 2), certain POPs have been found, except for the Unnamed Lake (at Astrakhanka village), Borovoye and Sultankeldy. Among the pesticides investigated by us, no sample has such compounds detected as: alpha-hexachlorocyclohexane, beta-hexachlorocyclohexane, chlordecone, hexabromobiphenyl, hexabromodiphenyl ether, lindane, hexachloran, mirex, pentachlorobenzene (in quintozene), perfluorooctane sulfonate and its salts, endosulfan and

Table 1 Contents of the chemical components in the Akmola region lakes.

Component name	MPC	Akmola region lakes										
		Zhalauly Lake	Tastykol Lake	Itemgen Lake	Unnamed lake (Akkol village)	Unnamed lake (40 km south from Astrakhanka village)	Zhalanash Lake	Borovoe Lake	Bolshoe Chebachie Lake	Kokay Lake	Yesey Lake	Sultankeldy Lake
<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>	<i>10</i>	<i>11</i>	<i>12</i>	<i>13</i>
Temperature, °C		14	18	18.8	23	19	18.9	22	20	16	22	24
pH value		8.25	6.7	8.2	6.6	7.6	8.1	7.8	7.9	7.6	7.7	7.0
BOD 5 mg.dm ⁻³	3	1.28	3.15	1.48	2.2	3.5	1.89	1.63	2.15	2.35	1.78	2.6
Calcium, mg.dm ⁻³	180	76.6	10.23	84.2	21.63	63	90.8	68.5	78.3	65.3	55.2	45
Hardness, mEq.dm ⁻³	10.0	7.5	1.7	7.1	1.49	5.19	8.37	3.7	4.37	3.7	3.4	2.65
Nitrite nitrogen, mg.dm ⁻³	0.02	0.002	0.0012	0.009	0.001	0.002	0.001	0.002	0.013	0.004	0.003	0.001
Nitrite nitrogen, mg.dm ⁻³	9.1	4.47	8.3	0.67	4.36	9.06	0.54	2.4	3.8	4.31	8.0	3.16
Sulfate ions, mg.dm ⁻³	100	212	46.52	249	59.18	126.31	305	65.9	78.8	225	125	47.3
Chloride ions, mg.dm ⁻³	300	277	222	268	196	276	291	150	79	147	198	146
Salt ammonium, mg.dm ⁻³	0.5	0.98	0.42	0.02	0/07	0.61	0.06	0.33	0.47	0.014	0.24	0.003
Phosphates, mg.dm ⁻³	3.5	0.26	1.34	0.035	0.078	2.83	0.05	1.02	0.76	0.47	0.35	1.34
Total ferrum, mg.dm ⁻³	0.1	0.065	0.03	0.072	0.04	0.16	0.049	0.08	0.1	0.03	0.02	0.02
SSAS, mg.dm ⁻³	0.1	0.02	0.87	0.05	0.008	1.0	0.03	0.21	0.15	0	0	0.005
Magnesium, mg.dm ⁻³	40	45.5	14.63	35.3	5.07	25	48.6	3.92	5.77	5.41	8.12	5.47
Copper, mg.dm ⁻³	0.001	0.001	0.32	0.003	0.002	0.005	0.004	0.002	0.02	0	0.0002	0.0001
Petroleum products, mg.dm ⁻³	0.05	0.033	0.003	0.120	0.054	0.06	0.134	0.05	0.046	0.0007	0.0007	0.006
WPI	-	1.32	3.8	1.25	1.55	4.08	3.1	1.14	1.75	0.6	0.71	0.38

isomers, tiodan, paraquat. Thus, among 21 tested substances, 12 substances are not accumulated in the bottom sediments of lakes studied.

Lake, where studied chlorinated pesticides are found, are located in areas of the most intensive agriculture, in particular, Zhalauly lake – where 5 pesticides are found (endrin, heptachlor, hexachlorobenzene, DDT, polychlorinated biphenyl), in 3 lakes 3 pesticides are found: Tastykol (aldrin, hexachlorobenzene, DDT), Itemgen (heptachlor, DDT, polychlorinated biphenyl) and Zhalanash (dieldrin, hexachlorobenzene, DDT). One pesticide – (hexa hexachlorobenzene), Bolshoe Chebachie

(Aldrin) and Yesey (Aldrin). 2 pesticides were found in Kokay lake (chlordane, hexachlorobenzene).

The quantitative pesticides distribution in lakes is shown in Table 3: aldrin has been found in 3 samples of Tastykol lake (0.06×10^{-6} mg.kg⁻¹), Yesey (0.3×10^{-6} mg.kg⁻¹), Bolshoe Chebachie (1.8×10^{-6} mg.kg⁻¹), chlordane - in 1 Kokay lake (1.3×10^{-6} mg.kg⁻¹), dieldrin in 1 Zhalanash lake (0.04×10^{-6} mg.kg⁻¹), endrin - in 1 Zhalauly lake (0.6×10^{-6} mg.kg⁻¹), heptachlor - in 2 Zhalauly lakes (0.22×10^{-6} mg.kg⁻¹) and Itemgen (0.04×10^{-6} mg.kg⁻¹), hexachlorobenzene was found in 5 Zhalauly lakes (0.07×10^{-6} mg.kg⁻¹), Tastykol (0.47×10^{-6} mg.kg⁻¹),

Table 2a POPs content in the bottom sediments of the Akmla region lakes.

Lake name	Aldrin (mg.kg ⁻¹)	Alpha hexachlorocyclohexane (mg.kg ⁻¹)	Beta hexachlorocyclohexane (mg.kg ⁻¹)	Chlordane (mg.kg ⁻¹)	Chlordecone (mg.kg ⁻¹)	Dieldrin (mg.kg ⁻¹)	Endrin (mg.kg ⁻¹)	Heptachlor (mg.kg ⁻¹)	Hexabromobiphenyl (mg.kg ⁻¹)	Hexabromodiphenyl ether (mg.kg ⁻¹)
Zhalauly	-	-	-	-	-	-	0.6·10 ⁻⁶	0.22·10 ⁻⁶	-	-
Tastykol	0.06·10 ⁻⁶	-	-	-	-	-	-	-	-	-
Itemgen	-	-	-	-	-	-	-	0.04·10 ⁻⁶	-	-
Unnamed Lake in Akkol village	-	-	-	-	-	-	-	-	-	-
Unnamed Lake in Astrakhanka village	-	-	-	-	-	-	-	-	-	-
Zhalanash	-	-	-	-	-	0.04·10 ⁻⁶	-	-	-	-
Borovoe	-	-	-	-	-	-	-	-	-	-
Bolshoe Chebachie	1.8·10 ⁻⁶	-	-	-	-	-	-	-	-	-
Kokay	-	-	-	1.3·10 ⁻⁶	-	-	-	-	-	-
Yesey	0.3·10 ⁻⁶	-	-	-	-	-	-	-	-	-
Sultankeldy	-	-	-	-	-	-	-	-	-	-
Total amount of POPs accumulated in the bottom sediments of lakes	2.16·10 ⁻⁶			1.3·10 ⁻⁶		0.04·10 ⁻⁶	0.6·10 ⁻⁶	0.26·10 ⁻⁶		

unnamed lake in Akkol village (0.066 x 10⁻⁶ mg.kg⁻¹), Zhalanash (0.5 x 10⁻⁶ mg.kg⁻¹), Kokay (0.24 x 10⁻⁶ mg.kg⁻¹), DDT - in 4 Zhalauly lakes (2.3 x 10⁻⁶ mg.kg⁻¹), Tastykol (1.57 x 10⁻⁶ mg.kg⁻¹), Itemgen (3.05 x 10⁻⁶ mg.kg⁻¹), Zhalanash (2.34 x 10⁻⁶ mg.kg⁻¹), polychlorinated biphenyl - in 2 Zhalauly lakes (0.31 x 10⁻⁶ mg.kg⁻¹), Itemgen (1.87 x 10⁻⁶ mg.kg⁻¹).

For all studied Akmla region lakes, the POPs content was summed and their specific content identified in the bottom sediments in the region. It is possible to draw up the next POPs decreasing row: 54% (DDT) >12.71% (polychlorinated biphenyl) >12.59% (aldrin) >7.85% (hexachlorobenzene) >7.58% (chlordane) >3.49% (endrin) >1.51% (heptachlor) >0.23% (dieldrin).

The proposed POPs row in the Akmla region may be represented as a diagram (Fig.1).

Thus, the studied waters cannot be classified as toxic as the POPs content in the bottom sediments is of background character, even without exceeding the maximum allowable concentrations of these substances in the water. However, the presence of these substances in the water may indicate the threat growing as environmentally long persistent toxicants will continue to be accumulated by different migration routes, as they are in the water (Gopal et al., 2016). As a result, this can be a serious obstacle to the production of organic products (Kádeková et al., 2017).

Table 2b POPs content in the bottom sediments of the Akmola region lakes.

Lake name	Hexachlorobenzene (mg.kg ⁻¹)	Lindane, Hexachlorane (mg.kg ⁻¹)	Mirex (mg.kg ⁻¹)	Pentachlorobenzene (in quintozene) (mg.kg ⁻¹)	Toxaphene (mg.kg ⁻¹)	DDT (1,1,1-trichlor-2,2-di (p -chlorophenyl) ethane (mg.kg ⁻¹))	Perfluorooctane sulfonate and its salts (mg.kg ⁻¹)	Endosulfan and isomers, tiodan (mg/kg)	Paraquat (mg/kg)	Polychlorinated biphenyl (mg/kg)
Zhalauly	0.07·10 ⁻⁶	-	-	-	-	2.3·10 ⁻⁶	-	-	-	0.31·10 ⁻⁶
Tastykol	0.47·10 ⁻⁶	-	-	-	-	1.57·10 ⁻⁶	-	-	-	-
Itemgen	-	-	-	-	-	3.05·10 ⁻⁶	-	-	-	1.87·10 ⁻⁶
Unnamed Lake in Akkol village	0.066·10 ⁻⁶	-	-	-	-	-	-	-	-	-
Unnamed Lake in Astrakhanka village	-	-	-	-	-	-	-	-	-	-
Zhalanash	0.5·10 ⁻⁶	-	-	-	-	2.34·10 ⁻⁶	-	-	-	-
Borovoe	-	-	-	-	-	-	-	-	-	-
Bolshoe Chebachie	-	-	-	-	-	-	-	-	-	-
Kokay	0.24·10 ⁻⁶	-	-	-	-	-	-	-	-	-
Yesey	-	-	-	-	-	-	-	-	-	-
Sultankeldy	-	-	-	-	-	-	-	-	-	-
Total amount of POPs accumulated in the bottom sediments of lakes	1.346·10 ⁻⁶					9.26·10 ⁻⁶				2.18·10 ⁻⁶

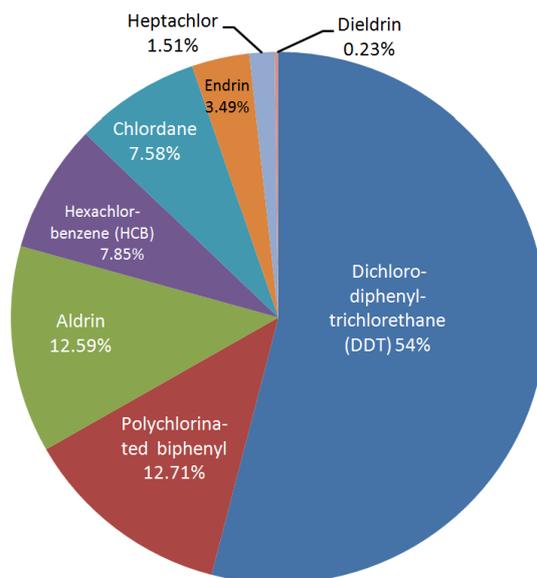


Figure 1 Generalized POPs share in bottom sediments of the Akmola region.

CONCLUSION

The obtained results of the work performed for 2016 allow for the following conclusions:

1. The MPC excess indicators in the Akmla region lakes are observed for salt ammonium (up to 0.002 MPC), magnesium (up to 1.15 MPC), nitrites (up to 1.12 MPC), petroleum products (up to 1.98 MPC), iron (up to 2.0 MPC), SSAS (up to 3.8 MPC). High concentration indicators for the sulphate (3.5 MPC), copper (4.3 MPC), magnesium (1.125 MPC). Mainly the lakes are dominated by sulfates, ion chloride. Lakes the most salty and with a hard water are Zhalauly and Zhalanash lakes - the water hardness of 7.5 mg.dm⁻³ and 8.37 mg.dm⁻³, respectively. For the studied water pollution index, the I class (relatively clean) can include Sultankeldy, Esey, Kokay waters; the II class (slightly dirty) - Zhalauly, Borovoye, Bolshoe Chebachie.

2. Thus, accordance with sanitary requirements, the studied waters cannot be classified as toxic as the POPs content in the bottom sediments is of background character, even without exceeding the maximum allowable concentrations of these substances in the water. However, the presence of these substances in the water may indicate the threat growing as environmentally long persistent toxicants will continue to be accumulated by different migration routes, as they are in the water.

3. But in general among 21 investigated POPs 8 substances are accumulated in bottom sediments of the investigated Zhalauly, Tastykol lakes, Unnamed Lake to the south of Akkol village, Itemgen lake, Zhalanash lake near Malinovka village (near Astana city), Kokay, Yesey, Bolshoe Chebachie.

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Contact address:

*Lyailya Akbayeva, Eurasian National University L. N. Gumilyov, Faculty of Natural Sciences, Department of Management and Engineering in the field of environmental protection, Satpayev Str., 2, 010008 Astana city, Kazakhstan, Tel.: +7(7172)709500(int33340), E-mail: akbaeva659@mail.ru

Erdaulet Tulegenov, Eurasian National University L. N. Gumilyov, Faculty of Natural Sciences, Department of Management and Engineering in the field of environmental protection, Satpayev Str., 2, 010008 Astana city, Kazakhstan, Tel.: +7(7172)709500(int33340), E-mail: er-daulet_kz@mail.ru

Ainur Omarbayeva, Eurasian National University L. N. Gumilyov, Faculty of Natural Sciences, Department of Management and Engineering in the field of environmental protection, Satpayev Str., 2, 010008 Astana city, Kazakhstan, Tel.: +7(7172)709500(int33114), E-mail: aynur.omarbaeva@mail.ru

Nazira Kobetaeva, Eurasian National University L. N. Gumilyov, Faculty of Natural Sciences, Department of Management and Engineering in the field of environmental protection, Satpayev Str., 2, 010008 Astana city, Kazakhstan, Tel.: +7(7172)709500(int33340), E-mail: kobetaeva.nazira@mail.ru

Zina Nurgalieva, Eurasian National L. N. Gumilyov, Faculty of Natural Sciences, Department of Management and Engineering in the field of environmental protection, Satpayev Str., 2, 010008 Astana city, Kazakhstan, Tel.: +7(7172)709500(int33340), E-mail: zina-nurgalieva@mail.ru

Yerlan Nurkeyev, Kazakh National Pedagogical University, Abai. Institute of Natural History and Geography, Department of Ecology and Tourism. Kazybek Bi St. 30, Almaty city, Kazakhstan, Tel.: +7(7272)914766, E-mail: nurkeev.e@mail.ru

Patricia Martišová, Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences, Department of Storing and Processing of Plant Products, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia, Tel.: +421376414608, E-mail: xmartisovap@uniag.sk

Vladimir Vietoris, Slovak University of Agriculture in Nitra, Faculty of Biotechnology and Food Sciences, Department of Storing and Processing of Plant Products, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia, Tel.: +421376414793, E-mail: vietoris@uniag.sk

Assylbek Zhanabayev, Saken Seifullin Kazakh Agro Technical University, Faculty of Veterinary and Livestock Technology, Department of Veterinary Medicine Zhenis avenue, 62, 10011 Astana city, Kazakhstan, Tel.: +7(7172)317547, E-mail: zhanabaev.asylbek@mail.ru

Corresponding author: *