утилизации и обезвреживание биоотходов, клиническое состояние животных, качество кормов, микроклимат помещений, система вентиляции и канализации, система профилактического карантирования. По результатам данного мониторинга выявлены нарушения ветеринарного-санитарного режима в молочно-товарных фермах, определен риск возникновения бруцеллеза, которая влияет на снижение продуктивности.

Ключевые слова: бруцеллез, мониторинг, контрольные точки, ветеринарно-санитарный режим, уровень риска, молочно-товарная ферма.

UDC 639.3.043.2:632.95.028

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PESTICIDE RESIDUES IN FISH FEED WHEN USING NON-TRADITIONAL FEED ADDITIVE TSEOFISH

Annotation

The article presents the results of the study of residual amounts (RA) of pesticides in fish using feed additives in their diet supplemented with 1%, 2%, 3% and 4%. It has been established that adding Tseofish to the feed, the level of RA of pesticides decreases. Without adding a feed additive, the presence of RA of pesticides is observed in 28.8% of feed samples; when the additive is added to the feed, 1% is 25%; when applying 2% of the additive - in 22%, with the addition of 3% - in 20%, when 4% - in 17% of the samples of feed. It was found that Tseofish based on zeolite due to sorption properties reduces the content of RA of pirimiphos methyl (PM) in meat of fish when using a pesticide in the composition of the feed. It has been shown experimentally that the content of RA of PM in fish meat with the addition of 4% of Tseofish in feed is reduced to 0.01 mg/kg in comparison with the control group (0.03 mg/kg).

Key words: Tseofish, pesticide, feed, feed additive, sample.

Introduction

Nowadays, more than 800 different kinds of pesticides are used for the control of insects, rodents, fungi and unwanted plants in the process of agricultural production. Although most of them leave the products or degrade in soil, water and atmosphere, some trace amounts of pesticide residues can be transferred to humans via the food chain, being potentially harmful to human health [1]. Pest control in intensive agriculture involves treatment of crops (fruits, vegetables, cereals, etc) pre and post harvest stages, rodenticides are employed in the post-harvest storage stage, and fungicides are applied at any stage of the process depending on the crop. These chemicals can be transferred from plant to animal via the food chain. Furthermore, breeding animals and their accommodation can themselves be sprayed with pesticide solution to prevent pest infestations. Consequently, both these contamination routes can lead to bioaccumulation of persistent pesticides in food products of animal origin such as meat, fat, fish, eggs and milk [2-4]. During the last decades much attention has been given to this group of substances and the international level after it became apparent that they are transported through the environment and critical concentrations have been reached in some areas even in places where they have never been produced or used.

Several countries banned the use of Organochlorine Pesticides (OCPs) during the 1970s and 1980s, although many of them continue to been used by other countries. OCPs have been identified as one of the major classes of environmental contaminants because of their persistence, long-range transport ability and human and animal toxic effects. OCPs are carcinogenic in animals as well as in human.

The immunotoxicity of selected OCPs has been also documented in vitro [5], in vivo [6], as well as in animals, in human fetal, neonatal and infant immune systems [4].

Materials and methods

This study involved the examination of 80 feed material samples in total, including 40 samples without addition to feed Tseofish feed additive (control), 10 samples with the addition to the feed Tseofish feed additive in an amount of 1% per 1 kg, 10 samples of feed with 2% Tseofish, 10 samples with the addition to the feed Tseofish feed additive in an amount of 3% per 1 kg, 10 samples with the addition to the feed Tseofish feed additive in an amount of 4% per 1 kg, from two provinces of Kazakhstan. All detected active substances were classified according to chemical classes as chloroorganic insecticides (IC), organophosphorus insecticides (IP), pyrethroid insecticides (IPYR) and fungicides (F). For feed, residues of chlorpyriphos methyl, diazinon, malathion, pirimiphos methyl (IP group), aldrine, DDTs (including metabolites), c-HCH (IC group), cypermethrin, deltamethrin (group IPYR) and tebuconazole (group F) were detected in the range of 0.02–0.88 mg* kg^{-1}.'

Results and discussion

Chlorpyriphos methyl was found in five samples at a concentration of 0.05–0.88 mg*kg^{-1}, pirimiphos methyl in three samples at concentrations ranging from 0.02 to 0.25 mg*kg^{-1} and malathion in one, at a concentration of 0.08 mg*kg^{-1}. No residues of plant protection products exceeded maximum residue levels (MRLs), which for chlorpyriphos is 3.0 mg*kg^{-1}, and for pirimiphos methyl and malathion: 5.0 and 8.0 mg*kg^{-1}, respectively [6].

Chlorpyriphos methyl, malathion and pirimiphos methyl, which are all insecticides, are active substances in such preparations as follow: Actellic 20 FU, Pro Store 157 UL, Pro Store 420 EC. Actellic 20 FU is used for disinfection of empty storehouses, grain and fodder silos, and the content of pirimiphos methyl in this preparation is 22.5%. Pro Store is used for disinfecting seed and consumption grain, and it contains 15–42% malathion. Plant protection products can be applied at the stage of primary production of plants, as well as during crop storage. Chlorpyriphos is a commonly applied insecticide, used for pest control in agriculture and industry all over the world [2]. Chlorpyriphos is efficient in controlling the population of many insects, and it is used as an insecticide in cereal, cotton, fruit, vegetables and nuts. Chlorpyriphos is moderately toxic for humans and can affect the central nervous system, cardiovascular system and respiratory system [3]. Bai et al. [6] have investigated organophosphorus pesticide residues in market food, including cereals in China, and they have found that organophosphorus residue levels were below MRLs in cereals. In our study, residues of chlorpyriphos methyl were detected below MRLs in 6.25% of samples.

Pirimiphos methyl was detected in 3.75% of samples in this study (the active substance of a preparation known under its commercial name of Actellic) and has been shown to inhibit acetyl cholinesterase. Literature data have established that, in research on mammals, the level which does not cause any harmful effects (determined as NOAEL) is 0.5 mg*kg^{-1} of body mass per day (mg* kg* $bw^{-1*}day^{-1}$). Pirimiphos methyl did not demonstrate carcinogenic effects in research that was carried out in doses up to 300 and 500 mg*kg^{-1} (the highest test dose) and does not demonstrate teratogenic effects in mice at levels of up to 16 mg*kg*bw^{-1}*day^{-1}. The research also indicates that this compound is rapidly expelled, and so far, no evidence has been found for its bioaccumulation in the organisms of the examined animals.

Malathion, detected in 1.2% of samples, is a commonly applied organophosphorus pesticide with a broad spectrum of insecticide effects. Malathion is used to control the populations of sucking and chewing insects, and is classified as slightly toxic. The most toxic of its metabolites is malaoxon – a product of oxidation, which is also responsible for the insecticidal activity of malathion. A strong relationship between malathion toxicity and the amount of protein in the diet of laboratory rats has also been found [4-7]. The largest share of samples with residues of plant protection chemicals was found for Kostanay (24.4%). Feed from the province of Almaty contained 20.5% of samples with residues.

Organochlorine pesticides were determined in five samples (6.25%): DDTs, aldrine and c-HCH. The presence of DDTs was found in two samples from Kostanay and one from Almaty. The metabolite p,p0-DDT was determined with the highest concentration (from 0.09 to 0.15 mg*kg^{-1}), the metabolite o,p0-DDT was detected to a lesser degree (from 0.05 to 0.13 mg*kg^{-1}), and o,p0-DDE had the lowest concentration (from 0.03 to 0.06 mg*kg^{-1}). The sum of isomers in samples amounted to 0.17, 0.2 and 0.34 mg*kg^{-1}, respectively, and exceeded the MRL in every case (0.01 mg*kg^{-1}). The accumulation of organochlorine compounds in foods is still a matter of major concern although the use of most organochlorine compounds (IC) has been banned or restricted in most countries, due to the uncertainty related to the adverse effects that their residues may have after a lengthy period of exposure at low doses. Organochlorine pesticides are not readily degradable in the environment and are lipophilic with a tendency to bioaccumulate, so they can be found at high concentrations in fatty foods, including cow milk. Distribution of organochlorine pesticides has been reported by authors in different types of samples [8]. This most probably reflects the usage pattern of these compounds, which are highly persistent, effective and cheap. Over 60% of total organochlorine contamination is due to DDTs components.

While the usage of DDTs in agriculture has been banned in Kazakhstan since 1983, nothing is known about its illegal use. Another explanation may be input from other countries around the Caspian Sea [9] assumption could be confirmed by measuring DDTs in local species at several points in Asia.

Lindane (c-HCH) was determined in 1 RGM-2M sample (Almaty) with a concentration of 0.12 mg*kg^{-1}. The World Health Organization (WHO) classifies lindane as moderately hazardous, and its international trade is restricted and regulated under the Rotterdam Convention on Prior Informed Consent. In 2009, the production and agricultural use of lindane was banned under the Stockholm Convention on persistent organic pollutants [10]. Lindane has been used to treat food crops and forestry products, as a treatment for seeds, soil, livestock, and pets. Lindane is a neurotoxin that interferes with GABA neurotransmitter function. Lindane is a persistent organic pollutant: it is relatively long-lived in the environment, is transported across long distances by natural processes like global distillation, and can bioaccumulate in food chains, though it is rapidly eliminated when exposure is discontinued.

Aldrine was determined in one feed sample without Tseofish (Almaty) with a concentration of 0.08 mg kg^{-1}. Aldrine was developed as a pesticide to control soil insects. Its use is now banned in the European Union (EU), but it is still used in developing countries. Although Aldrine is banned in the EU and Kazakhstan, its release into the environment can occur from products or materials which have been treated with it elsewhere. It directly contaminates soils in countries where it is still used as a pesticide. At an international level, Aldrine is the subject of two proposed UN treaties, is banned under the UNECE POPs protocol and proposed for elimination under the UNEP POPs Convention [11].

In recent decades, pyrethroids have increasingly replaced organochlorine pesticides due to their relatively lower mammalian toxicity, selective insecticidal activity, and lower environmental persistence than organochlorine pesticides. Although posing a minimal threat to mammals and avian species, pyrethroids are extremely toxic to bees [12] and aquatic organisms, including fish such as the bluegill and lake trout. Cypermethrin is a pyrethroid classified as a moderately toxic chemical [13]. In China, cypermethrin is one of the most potent insecticides, widely used in veterinary products to control lice, flies, and ticks on cattle and sheep, as well as in agricultural formulations to control numerous insect pests on fruits, vegetables, and field crops. It poses a great threat to fish and other aquatic organisms [14]. In one feed sample – with

ISSN 2304-334-02

1% feed additive Tseofish (Kostanay), pirimiphos methyl was detected with a concentration of 0.05 $mg*kg^{-1}$ and deltamethrin was detected in feed without adding the feed additive Tseofish (Almaty) with a concentration of 0.02 $mg*kg^{-1}$.

In our study, the percentage of samples containing pesticide residues varied between 28.8% in feed without adding the feed additive Tseofish (Figure 1), 20% in feed with 3% Tseofish (Figure 2) and 25 % in feed with 1% Tseofish (Figure 3) and 22% feed with 2% Tseofish (Figure 4), 17% feed with 4% Tseofish (Figure 5).

No multi-residue samples were found among the studied samples – The products that most frequently contained residues of the examined compounds included feed without feed additive Tseofish (28.8%), and residues were found the least frequently in feed with 3% Tseofish and feed with 4% Tseofish.

Levels, frequencies and ranges of concentrations of pesticide residues and maximum residue levels (MRL) found in the tested grain samples are shown in Table 1.

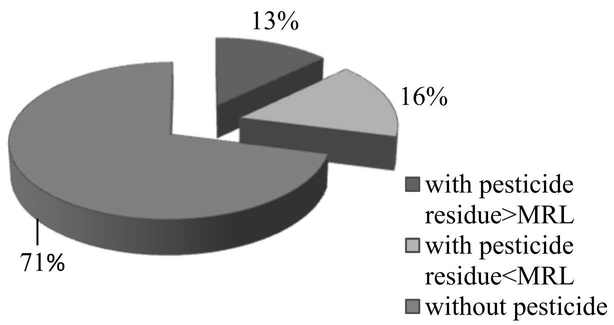

Figure 1 – Pesticide residues in feed samples without Tseofish feed additive

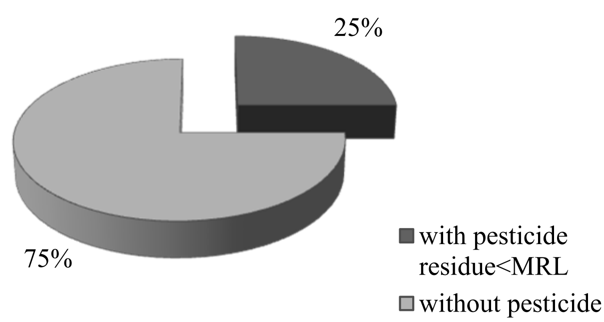

Figure 2 – Pesticide residues in feed samples with 1% Tseofish feed additive

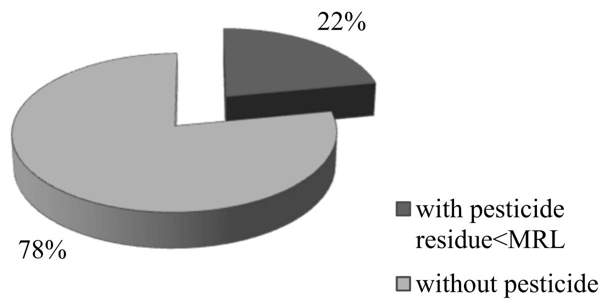

Figure 3 - Pesticide residues in tested feed samples with 2% Tseofish feed additive

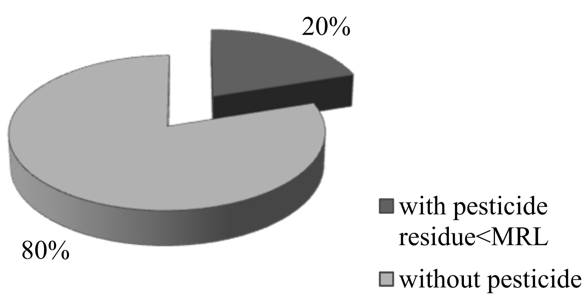

Figure 4 – Pesticide residues in feed samples while using 3% Tseofish feed additive

ISSN 2304-334-02

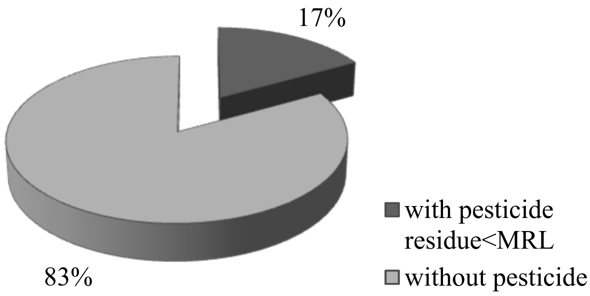

Figure 5 – Pesticide residues in feed samples while using 4% Tseofish feed additive

Table 1 – Levels, frequencies and concentration ranges of pesticide residues and maximum residue levels (MRL) found in tested grain samples

Active substance	Number of samples			MRL		Concentration range (mg kg^{-1})	LOD (mg kg^{-1})
	With residues	With residues >MRL EU	With residues <MRL EU	WHO	EU		
1	2	3	4	5	6	7	8
Feed without Tseofish feed additive (N=40)							
Aldrine (OC)	1	1	0	0,02	0,01	0,08	0,005
Chlorpyriphos methyl (OP)	3	0	3	10	3	0,05; 0,09; 0,16	0,005
Deltamethrin (IPYR)	1	0	1	5	2	0,02	0,01
p,p0-DDT (OC)				0,1	0,05	0,09; 0,10; 0,15	0,005
o,p0-DDT (OC)						0,05; 0,06; 0,13	0,005
o,p0-DDE (OC)	3	3	0			0,03; 0,04; 0,06	0,005
γ-HCH (OC)	1	1	0	0,01	0,01	0,12	0,005
Malathion (OP)	1	0	1	10	8	0,08	0,01
Pirimiphos methyl (OP)	2	0	2	7	5	0,05; 0,25	0,01
Tebuconazole (F)	1	1	0	0,15	0,2	0,25	0,01
Feed with 1% Tseofish (N=10)							
Chlorpyriphos methyl (OP)	1	0	1	10	3	0,05	0,005
Pirimiphos methyl (OP)	1	0	1	7	5	0,02	0,01
Feed with 2% Tseofish (N=10)							
Chlorpyriphos methyl (OP)	1	0	1	10	3	0,88	0,005
Pirimiphos methyl (OP)	1	0	1	7	5	0,02	0,01
Feed with 3% Tseofish (N=10)							
Pirimiphos methyl (OP)	1	0	1	7	5	0,02	0,01
Feed with 4% Tseofish (N=10)							

Pirimiphos methyl (OP)	1	0	1	7	5	0,02	0,01
Total	19	6	13	-	-	-	-

Conclusion

The results of the study of residual amounts of pesticides in fish using feed additives in their diet supplemented with 1%, 2%, 3% and 4%. In the course of the studies, it has been established that when the Zeofish feed is added to the feed, the level of residual amounts of pesticides decreases. Without adding a feed additive, the presence of residual amounts of pesticides is observed in 28.8% of feed samples; when you add 1% of additives to feed, 25%; when applying 2% of the additive - in 22%, with the addition of 3% of the additive - in 20%, when 4% - in 17% of the samples of feed. It was found that Zeofish feed supplement based on zeolite due to sorption properties reduces the content of residual quantities of pyrimiphos methyl in meat of fish when using a pesticide in the composition of the feed. It has been shown experimentally that the content of residual quantities of pyrimiphos methyl in fish meat with the addition of 4% of Zeofish fodder additive in feed is reduced to 0.01 mg/kg in comparison with the control group (0.03 mg/kg).

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ЦЕОФИШ АЗЫҚТЫҚ ҚОСПАСЫН ҚОЛДАНҒАН КЕЗДЕ БАЛЫҚ АЗЫҒЫНДАҒЫ ПЕСТИЦИДТЕРДІҢ ҚАЛДЫҚ МӨЛШЕРІ

Аңдатпа

Мақалада балықтардың рационына азықтық қоспаларды 1%, 2%, 3% және 4% қосқанда олардың құрамындағы пестицидтердің қалдық мөлшерін зерттеу нәтижелері көрсетілген. Зерттеу барысында цеолит негізіндегі 4% Цеофиш азықтық қоспасының сорбциялық қасиеті арқасында балық етінде пиримифос метилдің қалдық мөлшері төмендейтіні анықталды.

Кілт сөздер: Цеофиш, пестицид, азық, азықтық қоспа, үлгі.

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ОСТАТОЧНЫЕ КОЛИЧЕСТВА ПЕСТИЦИДОВ В КОРМАХ РЫБЫ ПРИ ИСПОЛЬЗОВАНИИ НЕТРАДИЦИОННОЙ КОРМОВОЙ ДОБАВКИ ЦЕОФИШ

Аннотация

В статье представлены результаты исследования остаточных количеств пестицидов в рыбах при использовании в их рационе кормовых добавок с добавлением 1%, 2%, 3% и 4%. В ходе исследований установлено, что 4% кормовая добавка Цеофиш на основе цеолита благодаря сорбционным свойствам снижает содержание остаточных количеств пиримифос метила в мясе рыбы при использовании пестицида в составе корма.

Ключевые слова: Цеофиш, пестицид, корм, кормовая добавка, образец.