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Heavy Metal Contents in Vegetable Oils of Kazakhstan Origin and Life Risk Assessment

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Abstract**—**The accumulation of heavy metals in food is a constant problem in many parts of the world. Vegetable oils are widely used, both for cooking and for processing in the food industry, meeting the main dietary requirements. One of the main chemical pollutants, heavy metals, is usually found in vegetable oils. These chemical pollutants are carcinogenic, teratogenic and immunotoxic, harmful to consumption and have a negative effect on human health even in trace amounts. Residues of these substances can easily accumulate in vegetable oil during cultivation, processing and storage. In this article, the content of the concentration of heavy metal ions in vegetable oils of Kazakhstan production is studied: sunflower, rapeseed, safflower and linseed oil. Heavy metals: arsenic, cadmium, lead and nickel, were determined in three repetitions by the method of flame atomic absorption. Analysis of vegetable oil samples revealed that the largest lead contamination (Pb) was determined to be 0.065 mg/kg in linseed oil. The content of cadmium (Cd) in the largest amount of 0.009 mg/kg was found in safflower oil. Arsenic (As) content was determined in rapeseed and safflower oils at 0.003 mg/kg, and arsenic (As) was not detected in linseed and sunflower oil. The nickel (Ni) content in the largest amount of 0.433 mg/kg was in linseed oil. The heavy metal contents in the test samples complied with the requirements of regulatory documents for vegetable oils. An assessment of the health risk of vegetable oils with a daily consumption of 36 g per day shows that all samples of vegetable oils produced in Kazakhstan are safe for consumption. But further monitoring is needed, since all these metals are toxic and their harmful effects become apparent only after several years of exposure.

Keywords**—**Kazakhstan, oil, safety, toxic metals.

I. INTRODUCTION

OVER the past three years, oil and fat production has been one of the most dynamically developing industries in the agro-industrial complex of Kazakhstan. Sown areas for oilseeds expanded thanks to the diversification of crop production, an increase in support within the framework of the state program for the development of the agro-industrial complex of the republic of Kazakhstan for 2017-2021 and favorable market conditions [1].

Currently, the oil and fat industry of Kazakhstan is in the development stage, demonstrating impressive results over the past decade.

Kazakhstan is the only country in the world which made so rapid breakthrough for short term: in 10 years the country from TOP-10 importers of sunflower oil surely entered in TOP-10 exporters of the sunflower oil [2].

In 2019, sunflower oil production amounted to 214,743 tons, which is 32% more than in 2017. Over 3 years, rapeseed oil production indicators increased significantly (Fig. 1) [1].

According to data in 2017, rapeseed oil production was at the level of 18,306 tons, then in 2019 it amounted to 66,124 tons, that is, it increased by 261.2% [1].

The increase in the level of heavy metals in the environment is a major concern worldwide because of their toxicity. Heavy metals such as As, Cd, and Pb are classified as toxic elements and according to confirmed data, Ni is a toxic and carcinogenic metal [3]. These toxic elements have been widely detected in the environment, including soil, water and air, as they are natural substances and pollutants from human activities [4]-[7]. Toxic elements cannot be decomposed, so they can accumulate in the food chain, causing serious problems for human health. Toxic elements in the environment can enter crops through root uptake or through air pollution. Consumption of crops or foodstuffs contaminated with toxic elements is the main route of human exposure.

The consumption of toxic elements can have adverse effects on human health [8]. Cd is a carcinogen and nephrotoxin causing damage to the renal tubules and skeleton [9]. Pb can damage the brain and nervous system, causing neurological disorders [10]. Therefore, it is important to monitor the levels of these toxic elements in crops or foods to protect human health [11].

The amount of vegetable oil in sunflower seeds reaches 60% or more. This oilseeds culture requires a warm and dry climate for good growth. Sunflower is sensitive to the presence of potassium and phosphorus in the soil.

In the Republic of Kazakhstan, sunflower is grown in the north east of the country. The main producer of sunflower seeds and the supplier of raw materials for vegetable oil production is East Kazakhstan region, where about 60% of the produced oil seeds is concentrated, as well as Pavlodar and Almaty regions [12].

Sunflower oil is recommended for patients with diabetes and cardiovascular disease [13], [14], as it contains more polyunsaturated fatty acids than lower low-density cholesterol and contains 66% linoleic acid, which washes cholesterol from the coronary artery.

Currently, rapeseed is beginning to take on great importance as an oilseeds, feed and sideral culture. In the EAEU states, two forms of rapeseed are cultivated: winter and

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spring (ring). Winter rapeseed seeds contain about 45-50% of vegetable oil, in spring seeds - 32-35%. They are rich in protein - 18-23%, which is well balanced in amino acid composition [12].

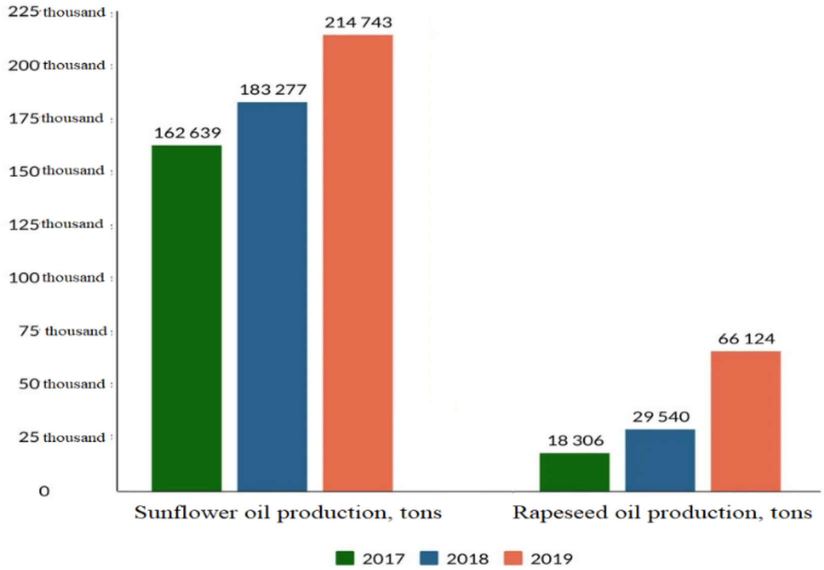

Fig. 1 Production of sunflower and rapeseed oil in Kazakhstan for 2017-2019 [1]

New varieties of rapeseed are characterized by a low amount of erucic acid and glycosinolates, which made it possible to widely use this culture as feed in animal husbandry. Rapeseed cakes and shrews are close in quality to soybean cakes and contain up to 40% protein. In addition, winter rape is also grown on a green mass to prepare silage, senage and herbal flour.

Rapeseed oil is no worse than sunflower oil. Antioxidants present in rapeseed and its products have attracted great attention due to their antioxidant properties and ability to purify free radicals, which can potentially have beneficial effects on human health [15]-[19]. It contains the useful acids Omega-3 and Omega-6. The balance between them is 1:2 and this, according to scientists, is almost an ideal ratio. In addition, the refined product includes a number of such vitamins: A, D, E. To provide the body with a daily dose of vitamin E, it is enough to consume 1 tbsp. l of rapeseed oil per day [20].

Safflower is one of the most drought-resistant oil plants. Seeds contain 25-32% of semi-drying oil, which is used for food and technical purposes. Safflower cake is used as a concentrated food with a large protein content - 15-40%. This crop is well adapted to a dry continental climate, to soil conditions is not required and can grow even on clogged soils [12].

Safflower oil also has a high content of polyunsaturated linoleic acid and tocopherol making it an excellent dietary product for people suffering from cardiovascular disease. High content of vitamin E converts it with a peculiar antioxidant and is produced for both food and medical purposes [21], [22].

Previously, saflor was grown in Kazakhstan mainly in the southern regions (South Kazakhstan, Zhambyl and Almaty regions), now there is a tendency to allocate an increasing number of areas in the northern and western regions of the country (Almaty, West Kazakhstan, Aktobe, Kostanay, Milyutinsky) due to the unpretentiousness and drought resistance of the culture [12].

In the EAEU states, two types of linseed seeds are cultivated: at first for the production of natural fiber, and second for the production of vegetable oil (linseed oil).

Olive flax is well adapted to the conditions of an arid and moderately arid steppe, is not very demanding for fertility, can be cultivated on almost any soil, with the exception of saline. Oil flax seeds contain up to 45-47% fat and 32-48% oil [12]. Linseed oil is used in the lacquer-paint industry and is widely used for food purposes. The remaining oil from the cake seeds is a valuable concentrated feed for livestock, especially for young cattle, since it contains up to 35% protein and about 32% nitrogen-free extractive substances.

In Kazakhstan, flax-curly for the production of vegetable oil is cultivated mainly in the northwestern part of the country - in the Akmola, Kostanay and North Kazakhstan [12]

Linseed oil is named as functional ingredient due to its being an excellent dietary source of the alpha-linolenic acid (ALA) (C18:3n-3). Linseed oil is highly unsaturated (90% of total fatty acids), and particularly rich in ALA (55.0%), oleic acid (21.2%), and linoleic acid (13.8%) [23].

The main purpose of this article is to determine the content of As, Pb, Cd and Ni in samples of vegetable oils available on the Kazakh market.

The content of toxic elements in vegetable oil samples is assessed in terms of their potential health risks to consumers. The concentrations of the installed elements were compared with the existing legal standards applicable in the European Union for heavy metals in food products. Potential health effects are estimated in light of weekly consumption limits for

Pb, As, Cd and Ni established by WHO and FAO [24].

II. Materials and Methods

The materials for the study were vegetable oils of Kazakhstan production: Sunflower oil (Eurasian Foods Corporation JSC), Rapeseed oil (Oil of Affairs LLP), Safflower oil (Kaz- Ir Agro LLP), Linseed oil (Dynasty Agro LLP).

Samples of vegetable oils for the study were purchased in areas of recognized markets in Kazakhstan. Samples were analyzed using standardized international protocols of methods.

The concentrations of Cd, Pb, As and Ni ions were determined in three repetitions. The accuracy of the method during the day (for samples taken on the same day and for samples taken on different days) were determined under optimal operating conditions by three-fold measurement of known Cd, Ni, As and Pb concentrations.

Determination of Cd, Pb by atomic absorption method was carried out in accordance with normative documents [32]. The method is based on the mineralization of the product by the dry or wet ozone method and determining the concentration of the element in the mineralizate solution (in 0.1 n nitric acid solution) by the flame atomic absorption method. Mineralization was carried out in accordance with normative documents [33]. The determination of As was carried out by the atomic absorption value at the resonance wavelength of 193.7 nm by the method of atomic absorption. All precautions were taken to prevent contamination of the sample [25], [26].

III. Results and Discussion

The use of nutrients is strictly important [27]. All products shall comply with the requirements for maximum pollution concentrations established by the Codex Alimentarius Commission. Currently, the following restrictions should be mandatory: the maximum concentration limit is 0.1 mg • kg^{-1} for lead (Pb); for arsenic - 0.1 mg • kg^{-1} (As). The US Department of Agriculture (USDA) has also established a maximum allowable level of simultaneous heavy metal content of 0.1 mg • kg^{-1} for Pb and As [26].

Concentrations of heavy metals in vegetable oils of Kazakhstan origin were analyzed in accordance with TR TS 021/2011 of the Technical Regulation of the Customs Union "On Food Safety." The established maximum permissible concentrations (MPC) of heavy metals are indicated and the results of comparison of the content of heavy metals in samples of vegetable oils of Kazakhstan origin are presented in Table I.

The results of the analysis of vegetable oil samples revealed that the largest lead (Pb) contamination was 0.065 mg/kg in linseed oil, which was 40% lower than the MPC. The content of cadmium (Cd) in the largest amount of 0.009 mg/kg was found in safflower oil, which is 80% lower than the maximum permissible norm. Arsenic content (As) was found in rapeseed and safflower oils at 0.003 mg/kg, then lower by 96% of the MPC, and not in linseed and sunflower oil. The nickel content (Ni) in the largest amount of 0.433 mg/kg was in linseed oil, 0.319 mg/kg in sunflower oil, 0.1541 mg/kg in rapeseed oil and the smallest amount in safflower oil - 0.0859 mg/kg.

TABLE I
CONTENT OF HEAVY METALS IN VEGETABLE OILS OF KAZAKHSTAN ORIGIN

Toxic elements, mg/kg	MAC	Sunflower oil	Rapeseed oil	Safflower oil	Linseed oil
Pb	0,1	0,0611	0,0207	0,0364	0,0654
Cd	0,05	0,0035	0,0016	0,009	0,0018
As	0,1	0	0,0037	0,0036	0
Ni	-	0,319	0,1541	0,0859	0,4334

In general, the content of heavy metals in the tested samples did not exceed the MPC for lead, cadmium and arsenic. For nickel, the MPC in vegetable oils is not normalized.

A. Modelling of Health Risk Assessment

The consumption of edible oil in Kazakhstan is about 36 g per day [28], while only 29 g per day is recommended. Sunflower oil consumed under this norm regularly consumes 1116 g per month. Predicted human consumption for the same is given in Table II. The health risk index [29]-[31] is calculated based on the consumption of edible oil for the average Kazakh adult (60 kg) using (1) and (2) as proposed by WHO are as follows:

$$\text{Health Risk Index} = \frac{\text{Daily assessment of vegetable oil consumption}}{\text{Permissible daily oil consumption}} \quad (1)$$

$$\text{Daily oil consumption estimate} = \frac{\text{Residual concentration} * \text{Oil consumption}\left(\frac{\text{gr}}{\text{day}}\right)}{\text{Average body weight (60 kg)}} \quad (2)$$

TABLE II
PREDICTED HEAVY METAL CONSUMPTION IN VEGETABLE OILS

Oil	Heavy metals	Presence mg/kg	36 gr of consumption per day			
			one month	four month	nine month	one year
sunflower oil	Pb	0,0611	0,0660	0,2640	0,5939	0,7919
	Cd	0,0035	0,0038	0,0151	0,0340	0,0454
	As	0	0	0	0	0
	Ni	0,319	0,3445	1,3781	3,1007	4,1342
rapeseed oil	Pb	0,0207	0,0224	0,0894	0,2012	0,2683
	Cd	0,0016	0,0017	0,0069	0,0156	0,0207
	As	0,0037	0,0040	0,0160	0,0360	0,0480
	Ni	0,1541	0,1664	0,6657	1,4979	1,9971
safflower oil	Pb	0,0364	0,0393	0,1572	0,3538	0,4717
	Cd	0,009	0,0097	0,0389	0,0875	0,1166
	As	0,0036	0,0039	0,0156	0,0350	0,0467
	Ni	0,0859	0,0928	0,3711	0,8349	1,1133
linseed oil	Pb	0,0654	0,0706	0,2825	0,6357	0,8476
	Cd	0,0018	0,0019	0,0078	0,0175	0,0233
	As	0	0	0	0	0
	Ni	0,4334	0,4681	1,8723	4,2126	5,6169

The contamination of vegetable oils with heavy metals in the compounds tested together with the predicted consumption (maximum number of residues) for 1 month (daily consumption for 30 days) is shown in Table III.

TABLE III
HEALTH RISK ASSESSMENT OF HEAVY METAL VEGETABLE OILS

Oil	Residues	Projected consumption for one month (36 g oil)	Risk index for one month	Health risk
sunflower oil	lead	0,0660	0,0410	no
	cadmium	0,0038	0,0023	no
	arsenic	0	0	no
	nickel	0,3445	0,2138	no
rapeseed oil	lead	0,0224	0,0139	no
	cadmium	0,0017	0,0011	no
	arsenic	0,0040	0,0025	no
	nickel	0,1664	0,1033	no
safflower oil	lead	0,0393	0,0244	no
	cadmium	0,0097	0,0060	no
	arsenic	0,0039	0,0024	no
	nickel	0,0928	0,0576	no
linseed oil	lead	0,0706	0,0438	no
	cadmium	0,0019	0,0012	no
	arsenic	0	0	no
	nickel	0,4681	0,2905	no

IV. CONCLUSION

The heavy metal content in the tested samples of vegetable oils does not exceed the permissible norms. The analyzed concentrations of arsenic (As), cadmium (Cd), lead (Pb) and nickel (Ni) in samples of vegetable oils of Kazakh origin showed that all tested samples of Kazakh vegetable oils are safe for consumption. Further monitoring is needed, as all these metals are toxic and their harmful effects become apparent only after a few years of exposure.

The findings of this study can be useful in reliably estimating the intake of toxic elements in the diet from plant oils of different species.

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Research interests: food safety and quality, technology of processing oilseeds and oil production, certification in the food industry.