Migration of heavy metals in the system "soil-plant-animal-livestock products"

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Abstract. Our article presents the study of the content of highly hazardous and moderately hazardous chemical elements in soils, plants, beef and cow milk. Their average amount is shown. A safe level of the concentration of these chemical elements in the links of the chain "soil - plant - animal – meat and dairy products" of the Republic of Tatarstan is revealed. The coefficients of biological absorption of chemical elements in the links of the system are calculated. An increase in the coefficient of accumulation of Zn in plants and As in milk and meat was found. Further research for ranking territories according to the actual content of chemical elements in environmental objects is required.

1 Introduction

Industry is the most important part of the national economy and it is very susceptible to technological innovation. Industry develops very fast and creates the basis for a better quality of life for people. At the same time, many problems come due the expansion and formation of new industries and they require different approaches and solutions. Environmental pollution by heavy metals is one of the challenges. For example, a number of toxic heavy metals enter the cow's food chain through the food and water and then accumulate in humans consuming milk and meat [1, 8].

There are two groups of metals found in nature depending on their density or specific atomic mass: heavy metals (HM) and light metals (LM). Heavy metals have specific gravity more than 5 g / cm^3 and include iron, lead, copper, zinc, mercury, cadmium. Well-known light metals include sodium, magnesium and potassium; their specific gravity is less 5 g / cm^3.

According to the level of involvement in biochemical processes of living organisms, metals are divided into three different groups. One group plays an important role in vitality, their removal from the body or their depletion can lead to unfavorable biological anomalies. This group includes sodium, potassium, magnesium, calcium, iron. Second group take part in growth, development, reproduction, but in a high amount, they become toxic. Molybdenum, bismuth, manganese, cobalt, copper and zinc are included in this group. Metals of the third group have no significant role in the vital process, but they are very toxic even in low amount, also they are able to accumulate in the body during prolonged exposure and do not play a significant role in the processes of life. Prominent representatives of such metals are cadmium, lead and mercury.

In recent years, environmental contamination by heavy metals is an object of increasing attention of ecological and global public. Among chemical pollutants, heavy metals are considered as one of the negative reasons that have serious environmental and biological consequences. Human consumption of products in excess of permissible concentrations of HM increases the risk of cancer [3].

The International Agency for Research on Cancer (IARC) classifies such chemical elements as lead and cadmium as probable carcinogens for humans [4].

Due to bioaccumulation, regular consumption of low concentrations of HM can lead to adverse effects on human health, including inhibition of renal function, mental disorders, changes in the chemical composition of blood and diseases of the cardiovascular system, etc. [6].

Once came in feed and food, heavy metals deteriorate their sanitary characteristic due to high migration ability, bioaccumulation tendency and specific toxic effects. When their content is above acceptable levels, they can be very dangerous for animal and human health [14]. The main source of soil contamination with metals are metallurgical enterprises, mines, thermal power plants and automobile transport. The contamination can cover areas of hundreds of square kilometers or more. Soils are most polluted within a radius of 2 km from mines and thermal power plants, in a strip of 0-50 (100) m from motorways.

A lot of Russian and foreign trials show that the content of heavy metals in the soils in most of industrial areas is approaching the ecologically acceptable maximal level and in the immediate vicinity of the polluter's enterprise even exceeds this limit.

Heavy metals can cause the local reaction or have the systemic toxic effect in animal. Their local action is

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mainly based on their ability to form albuminates when combined with proteins. Depending on the characteristics of the tissues with which the metal interacts, as well as on the concentration of the drug, the reaction may vary. In some cases, we can talk about incomplete coagulation of proteins and the reversibility of the process. In other cases, coagulation can be complete, and the process is irreversible. The local damage of most heavy metals is accompanied by cell dehydration and tissue fragility. The systemic effect of heavy metals on the body is not the same. Some of them affect the hematopoietic organs (iron, copper), others have antimicrobial and antispasmodics (silver, bismuth, mercury) effects, some do not have any noticeable effect (zinc, aluminum) or have only a toxic effect (lead, cadmium) [11].

Every chemical element has own effect on various systems of living organisms if it is taken in excess. Let see some of them.

Long-term exposure to cadmium (Cd) can lead to cancer and organ system toxicity in skeletal, urinary, reproductive, cardiovascular, central and peripheral nervous, and respiratory systems.

Lead toxicity is an important environmental disease. It is a serious and sometimes fatal condition. Lead poisoning usually occurs over a period of months or years and causes severe mental and physical impairment. Lead is more harmful to children because their brains and nervous systems are still developing. Lead poisoning can be treated, but any damage caused cannot be reversed.

Nickel (Ni) as a mineral has no any direct toxic effect. But when chemical compounds derived from Ni go through the respiratory system in high amount they can potentially cause lung cancer. Also, the chronic consumption of high quantities of Ni can lead to myocardial, brain, liver and kidney degeneration.

Arsenic (As) is considered as one of the inevitable contaminants for human beings. It has been well known as a toxic element since ancient times. Humans are exposed to many chemical forms of both inorganic and organic arsenic, but the highly stable organic forms are apparently nontoxic. Prolonged, chronic exposure to inorganic arsenic through breathing or drinking or ingestion has been linked to skin, lungs and urinary bladder cancer. In past decade, almost 13,000 Japanese infants have been afflicted with contaminated milk powder, majorly in the western part of the country where industrialization was considerable. Affected infants had diarrhea, fever, skin pigmentation, more than 100 died from acute poisoning [12].

Chronic copper (Cu) poisoning is associated with the slow accumulation in the liver of very small copper amounts ingested over a long period of time, but with no change in blood copper levels. Symptoms include profound depression, thirst, anorexia, pale or icteric mucous membranes and haemoglobinuria. When the liver's capacity to accumulate copper is overloaded, intravascular haemolysis occurs due to release of copper into the bloodstream. Also, there is a liver damage. All of this cause acute toxicosis and recumbency with affected animals often dying within 1-2 days.

Zinc (Zn) can suppress copper and iron absorption. The free zinc ion in the solution is highly toxic to bacteria, plants, invertebrates, and even vertebrate fish, but it is less toxic for humans [13].

It should be noticed that milk and dairy products, meat and meat containing products are one of the most widely consumed food by human and they make a significant contribution to the consumption of microelements. Therefore, strict control of the level of microelements in these products is recommended [5].

Therefore, it is very important to monitor the residual amount of toxic metals in milk and to make a risk assessment for consumers, especially for children. Due to the toxicity of heavy metals, many regulatory organizations have set acceptable limits for the content of heavy metals in raw milk to ensure its safety [10].

The aim of this study is to research the coefficient of the chemical elements transition in the parts of the chain «soil – plant – animal» to predict the quality and ecological safety of farm products. The following tasks were set:

1) measuring the content of chemical elements in soils, plants and cow milk and the largest pollutants determination;

2) calculating the coefficient of the transition of chemical elements in the links of the «soil-plant-animal» chain.

2 Materials and methods

The objects of the study were selected in the Republic of Tatarstan: gray forest soil (n = 107), plants (annual grasses) (n = 48), cow milk (n = 21), beef (n = 15).

The content of chemical elements in the objects was determined according to the State Standard (GOST 30538-97) using an atomic emission spectrometer with a microwave plasma Agilent 4210 (USA).

To predict the expected level of meat and dairy products contamination, we used the quantitative parameters of the transition (absorption) of chemical elements in the trophic chain of the system "soil - plant - animal – meat and dairy products". A quantitative characteristic of the ability to absorb and accumulate chemical elements is the dimensionless Biological Absorption Coefficient of the object (BAC) - the ratio of the content of the element in the aerial part to its gross content in the soil:

$$Ax = Ix / nx$$

where Ix - content of element x in the ash of plants; nx - content of element x in the rock or soil on which the plant grows.

Statistical processing of the obtained data was performed using the Microsoft Excel 2019 application package and the Jamovi statistical processing program.

3 Results

The presence and quantity of chemical elements in soils are determined by many factors, such as the parent rock composition, plant cover and the environment condition.

But the greatest influence is made by technogenic and anthropogenic factors.

Soil is a natural reservoir of toxic substances. For many years it can be a source of pollution of plant products used in animal feed and human food. There are three main groups of chemical elements in soils according to the degree of danger: class I - highly hazardous; class II - moderately hazardous; class III - slightly hazardous.

The gross content of chemical elements in grey soil occupying most of the Republic of Tatarstan forests was analyzed to evaluate the degree of soil contamination (Table 1).

Table 1. The content of chemical elements in soil and plants, mg /kg

Chemical element	Permissible concentration*	Actual content		
		Mean value	Minimum value	Maximum value
Soil (n=107)				
Cd	3.0	0.09±0.94	0.06	9.76
Pb	32.0	7.05±8.76	1.04	52.86
Ni	40.0	11.41±17.77	2.14	65.82
As	2.0	0.53±1.28	1.18	6.97
Hg	2.1	below the sensitivity threshold		
Cr	90.0	19.36±34.44	3.20	93.28
Co	100.0	4.21±3.28	1.12	7.48
Cu	66.0	11.58±10.73	1.09	46.29
Zn	110.0	19.79±31.86	1.37	173.02
plants (n=48)				
Cd	0.3	0.015±0.014	0.015	0.29
Pb	5.0	0.70±0.65	0.01	1.40
Ni	3.0	3.70±2.80	0.13	6.40
Cu	30.0	3.60±2.40	1.70	7.50
Zn	50.0	20.40±12.60	8.80	32.00

Note: * - GN 2.1.7.2041-06 Maximum permissible concentrations (MPC) of chemicals in soil; Temporary maximum permissible level (MDL) of certain chemical elements in feed for farm animals; Annex of October 31, 1996 to No. 46

It was established that the average quantity of chemical elements was significantly lower than MPC (maximum permissible concentrations). When analysing the variation of amounts of highly hazardous elements in soils - Cd, Pb, Zn, As, a number of samples exceeded their MPC 2-3 times. It indicates the local nature of contamination – it is spread around the industrial cities of the republic. The studies performed are comparable with the data of the authors, who also note a geochemical disadvantage around cities and towns of the Russian Federation with the developed metallurgical industry [2, 7].
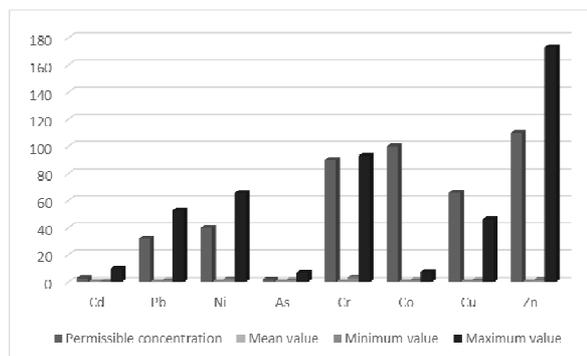

Fig 1. The content of chemical elements in soil
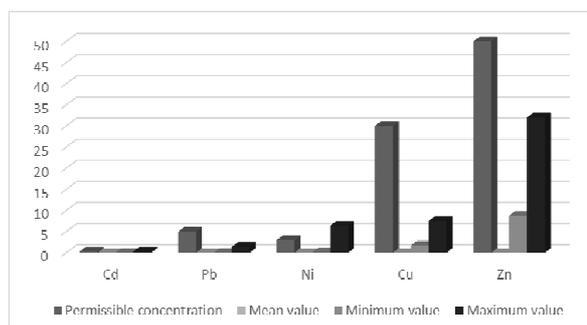

Fig 2. The content of chemical elements in plants

A number of moderately hazardous elements such as Ni, Co, chromium, and Cu in the soils of the Republic of Tatarstan were within acceptable concentrations or near the upper board of the normal rate with the exception of Ni. It should be noted the natural origin of Ni in the soils of the Republic of Tajikistan, since this element is part of the rocks of the mother plateau.

Soil is the main source of nutrition for plants. Plants have varying degrees of absorption and accumulation of chemical elements. There are a few groups of chemical elements according the degree of their ability to be accumulated in plants: group I – elements with a maximum degree of accumulation in plants (Cd and caesium), group II – elements with a moderate degree of accumulation in plants (Zn, Cu, Pb, Co), group III – elements with a low degree of accumulation in plants (Ni, chromium, manganese), group IV – elements with a minimal degree of accumulation in plants (iron, barium) [3].

The amount of Hg and As in plants was below the sensitivity limit of the device, and the content of other chemical elements did not exceed the values of the maximum permissible level (MRL). Data analysis in Table 1 showed that the average value of Ni in plants exceeded the MDL 1.2 times. The average values of Pb, Cu and Zn in plants did not exceed the permissible level. Single samples of plants had Cd in the amount near the upper border of the norm. These plant samples were localized in geochemical provinces contaminated with Cd.

Thus, such chemical elements as Cd, Pb, As, Ni, Zn were determined as major local soil pollutants and Ni and Cd as a major plant pollutant.

It was found that all indicators of average values of chemical elements in the cow milk were within the

borders of the "Hygienic requirements". At the same time, it was noted that the average values of Ni vary within the upper limits of the allowable value, and in some milk samples the amount of As is at the level of the extreme allowable limit (Table 2).

Table 2. The content of chemical elements in milk and meat, mg / kg

Chemical element	Permissible concentration*	Actual content		
		Mean value	Minimum value	Maximum value
Milk (n=21)				
Cd	0.03	0.006±0.058	0.006	0.065
Pb	0.1	0.01±0.01	0.004	0.13
Ni	0.3	0.30±0.28	0.02	0.56
As	0.05	0.02±0.02	0.001	0.05
Cu	1.0	0.023±0.018	0.020	0.036
Zn	5.0	0.35±0.09	0.34	0.37
Meat (n=15)				
Cd	0.05	0.003±0.005	0.002	0.025
Pb	0.5	0.053±0.070	0.032	0.170
Ni	0.5	0.50±0.13	0.10	0.72
As	0.1	0.04±0.08	0.01	0.10
Cu	5.0	0.95±0.62	0.02	2.40
Zn	70.0	4.41±2.35	1.20	10.40

Note: * - SanPiN 2.3.2.1078-01 Hygienic requirements for food safety and nutritional value
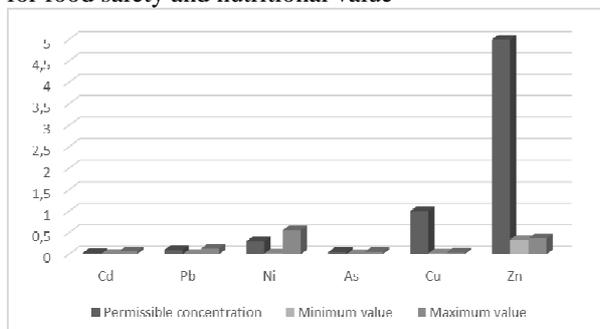

Fig 3. The content of chemical elements in milk

The average value of Ni in beef was at the upper border of acceptable values, but very few samples exceeded the standard 1.8 times. Similar results were found in the analysis content of As in beef.

The average values of As in the soil did not exceed permissible concentrations. Its content was below the sensitivity threshold of the device, less than 0.01 g / kg in plants. However, As traces were found in milk and beef indicating the potential for its accumulation in small amounts in animals.

Studies of the transition coefficients of major pollutants in the chains of the system "soil - plant - animal - livestock products" were made (Table 3).
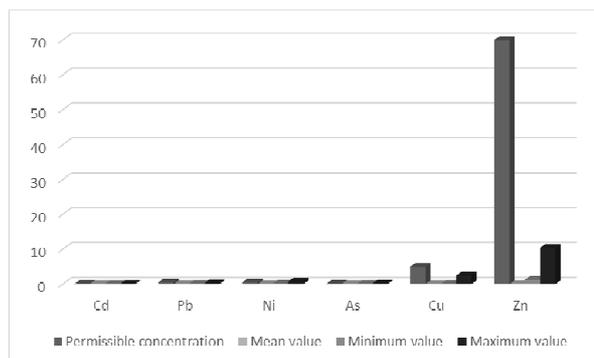

Fig 4. The content of chemical elements in meat

Table 3. Transition coefficients of chemical elements in the links of the system "soil - plant - animal - livestock products"

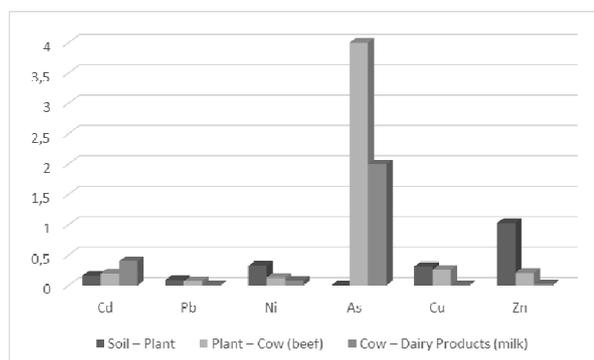| Systems chain	Chemical Elements					
	Cd	Pb	Ni	As	Cu	Zn
Soil – Plant	0.16	0.09	0.32	–	0.31	1.03
Plant – Cow (beef)	0.20	0.07	0.13	4.0	0.26	0.21
Cow – Dairy Products (milk)	0.40	0.01	0.08	2.0	0.01	0.02

Fig 5. Transition coefficients

When analysing the transition coefficient in the «Soil - Plant» chain, it was found that such chemical elements as Cd, Pb, Ni, Cu, As do not accumulate in plants, since all the coefficients are extremely low. Coefficients exceeding this value were found only in Zn, which indicated its accumulation by plants.

When analysing the «Plant to Milk» and «Plant to Meat» transition coefficient it was found that As accumulates with a sufficiently high degree. Its accumulation in the animal organism from the minimum incoming doses indicates necessity of the development of detoxification measures.

In calculating the transition coefficients, the average values for the elements from each link were used. At the same time, the concentration limits of some elements exceeded the permissible values. The content of the elements in different samples had a wide variety. So it is necessary to rank territories and zones according to the concentration of elements in environmental objects, which requires additional research.

4 Conclusion

In the study of the content of hazardous chemical elements in soils, plants, milk and beef in the Republic of Tatarstan, it was found that their average values do not exceed tolerable concentrations. A very few samples exceeding the normal level were obtained in the system facilities around industrial cities and settlements. The calculating the transition coefficients of elements in the links of the system as a whole throughout the Republic showed that Zn is accumulated in plants, and As is accumulated in milk and meat. The study has shown the importance of ranging the territory by the content of elements in environmental objects.

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