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DETERMINATION OF THE RISKS OF ADVERSE IMPACT ON THE POPULATION OF NITRATES IN PLANT PRODUCTS GROWN IN THE TERRITORY OF THE NORTHERN INGULETSK MINING AND PROCESSING COMPLEX

An important task in the field of food safety expertise is to ensure the quality of plant materials and the production of safe food products. Conducting research on the content of nitrates in plant products of local production is especially relevant in industrial regions. Many studies by scientists on the effects of nitrates and nitrites on humans prove that they are one of the sources of threat to human health. Comparative characteristics of the nitrate content in plant products sold on the market and in stores are given. The nitrate content exceeds the MAC in early potatoes, which were bought at the market, and early tomatoes. Long-term nitrate load, even in small doses, is one of the important toxic risk factors for public health, reduces the body's resistance. The research involved samples of locally produced agricultural crops grown in the area near the enterprises of the Northern and Ingulets Mining and Processing Plants. The levels of nitrate content in the main types of plant-based food products were determined, the risks of adverse effects of controlled nitrates supplied by plant products were calculated, which confirmed the need for continuous monitoring of food raw material safety. Food products were ranked by their contribution to the overall exposure value. Cabbage and potatoes have the highest nitrate load on the region's residents, mg per day. The HQ values were less than one. The paper presents the main ways to reduce nitrate content in plant products.

Key words. Food safety, nitrates, risk assessment, safety of plant raw materials, food expertise, methods for determining nitrates.

INTRODUCTION

The intensive development of agriculture, the use of nitrogen-containing fertilizers, and the irrigation of crops with water polluted by industrial effluents have led to the accumulation of nitrates in plant material and have had a negative impact on human health. The Kryvyi Rih iron ore basin is one of the main mining centers of Ukraine, located within the Dnipropetrovsk region. The development of enterprises in the mining and metallurgical complex has caused a significant man-made load on the basins of the Ingulets and Saksagan rivers, which have become receivers of wastewater discharges.

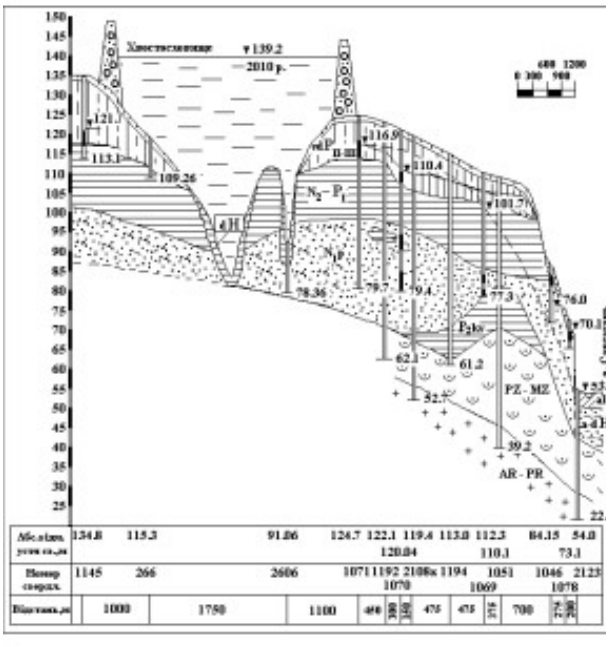

Fig. 1 – Geological and hydrogeological section on the territory of the Northern GZK

The waters of these rivers are used for irrigating agricultural land (Fig. 1).

The main mass of nitrates (70-80% of the daily intake) enters the human body through plant products (vegetables and leafy greens). Small amounts of nitrates are ingested with fruits, berries, dairy and meat products, and drinking water. Therefore, it is currently relevant to conduct research on the nitrate content in locally produced vegetables (potatoes, carrots, cucumbers, cabbage, tomatoes, onions). This is due to the irrational use of fertilizers, which increases the level of nitrates in the soil and plants [1–5].

Nitrates are a necessary component of nitrogenous plant nutrition. Nitrogen, entering the plant in the form of nitrate ions, undergoes complex transformations, reducing nitrogen from an oxidation state of +5 to -3 [6–8]. Features of nitrogen metabolism in plants:

$NO_3^- \rightarrow NO_2^- \rightarrow (HNO)_2 \rightarrow NH_2OH \rightarrow NH_3 \rightarrow$
$\rightarrow$ Imino acid $\rightarrow$ Amino acid

The first stage:

$$NO_3^- + НАДФ(H) + 2e \xrightarrow{Nitrate\ reductases} NO_2^- + НАДФ^+ + H_2O$$

The second stage:

$$NO_2^- + 6FD(restored) + 8H^+ + 6e \xrightarrow{Nitrite\ reductases} \xrightarrow{Nitrite\ reductases} NH_4^+ + 6FD(oxidized) + 2H_2O$$

The third stage:

$$KGA + NH_4^+ + NADH + H^+ \xrightarrow{Glutamate\ dehudrogenas} Glutamic\ asid + H_2O + NAD^+$$

$$SHUK + NH_4^+ + NADH + H^+ \xrightarrow{Glutamate\ dehudrogenase} Aspartic\ asid + H_2O + NAD^+$$

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In order to control the chemical composition of water in rivers

Saksagan and Ingulets researchers proposed a permanent hydrochemical model of Kryvbas water bodies:

1) organization of the hydrochemical monitoring system;

2) analysis of the main trends of changes in the content of the main ions in the water of water bodies;

3) assessment of the development of the main hydrochemical processes;

4) forecast of stabilization of the chemical composition of water and

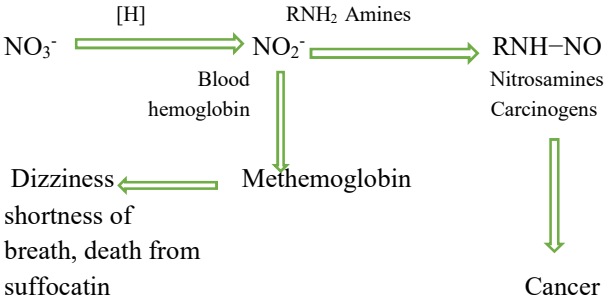
analysis of the obtained results;

5) development and implementation of environmental protection measures.

The absorption of nitrates by plants occurs through a number of stages. First stage Nitrates are reduced to nitrites through the enzymatic action of nitratereductase. Nitrite is then reduced to ammonia by nitrite reductase. Third stage The resulting ammonia is quickly incorporated into glutamic acid under the action of glutamine synthetase, into aspartic acid, alanine. Therefore, plants urgently need the addition of nitrate fertilizers to the soil. However, excess nitrates accumulate in plants and have a negative effect on humans.

The toxic effect of nitrates on the human body is associated with the formation of nitrite, ammonia, and hydroxylamine reduction products that occur under the action of enzymes. The nitrites formed react with secondary amines to form carcinogenic nitrosamines.

Nitrates also oxidize the divalent iron of hemoglobin into trivalent iron with the formation of methemoglobin, which is unable to transport oxygen to the tissues.



Large doses of nitrates cause shortness of breath, diarrhea, nausea, and palpitations. Long-term exposure to nitrates leads to allergies, metabolic and nervous system disorders [9-11].

Objet, subject and methods of research

The objects of the study were vegetables taken in the spring and autumn periods, purchased in a store and on the market from a private owner, which were grown with the use of irrigation with water from the reservoirs of the adjacent territories of the Northern and Ingulets GZK.

Nitrates were determined by methods by the ionometric method according to DSTU 4948:2008. The essence of the quantitative ionometric method consists in the determination of nitrates from the analyzed material with a solution of alumakalium alums and the subsequent measurement of the concentration of nitrates in the hood with an ion-selective electrode.

The exposure was calculated according to the formula:

$$\text{Exp} = \frac{\sum_{i=1}^{N}(C_i \times M_i)}{BW},$$

where Exp is the contaminant exposure value, mg/kg of body weight/day;

Ci – the content of the contaminant in the ith product, mg/kg;

Mi – consumption of the ith product, kg/day;

BW – human body weight, kg; N is the total number of products included in the study.

The contribution of each group of food products to the total value of exposure to the contaminant was calculated:

$$\text{Contr } i = \frac{(C_i \times M_i)}{\sum_{i=1}^{N}(C_i \times M_i\}},$$

where Contr i is the contribution of the i-product to the total exposure value; Ci – the content of the contaminant in the ith product, mg/kg; Mi – consumption of the ith product, kg/day.

The risk of developing non-carcinogenic effects was assessed through the calculation of hazard ratios (HQ). The calculation of HQ was carried out taking into account the average dose according to the formula:

$$\text{HQ} = \frac{Exp}{PDD},$$

Exp – value of contaminant exposure by average content, mg/kg of body weight/day; PDD – permissible daily dose of contaminant intake with food products, mg/kg;

Values of non-carcinogenic risk were estimated as a negligible risk of developing toxic effects – at HQ ≤1.0, high – at HQ >1.0 [12].

A social survey (interview) of the population of Shevchenkivske, Andriivaka and Zavyalivka villages was conducted regarding the use of agricultural products. The age of citizens who participated in the survey was from 18 to 50 years.

Results

Sampling of vegetables was carried out in the period from May to October, and seasonal dynamics of nitrate content and comparison of their analysis methods were studied.

The results of the analysis were listed in Table 1.

Research results have shown that not all plants accumulate nitrates equally. A large amount was found in potatoes, cabbage, tomatoes.

Nitrates are mainly accumulated in the head of cabbage, in the core of carrots, in the skin of cucumbers, and potatoes. However, the detected residual content of nitrates did not exceed the MPC in all products of vegetable origin, except

The seasonal dynamics of plant production showed that the largest number of vegetables with a high nitrate content is in the spring period. The largest amount of nitrates accumulates in cabbage in the autumn period, cabbage, cucumbers, potatoes and tomatoes in the spring period. Until the autumn period, the amount of nitrates in products decreased.

Table 1 – Concentration of nitrate ions in mg/kg spring/autumn period

The name of the vegetable	Ionometric method	MPC, mg/kg
Store products		
Potato	210/135	250
Cucumbers	294/134	300/150
Tomatoes	156/96	150
Cabbage	770/360	900/500
Carrot	-/230	400/250
Onion	-/70	80
Market products		
Potato	270/175	250
Cucumbers	238/134	300/150
Tomatoes	147/88	150
Cabbage	644/426	900/500
Carrot	-/156	400/250
Onion	-/46	80

Analyzing the research data shown in Table 2, it has been established that the maximum limit is exceeded for early market potatoes by 8 − 12%, and in early store tomatoes by 4%.

Vegetables, such as cucumbers, tomatoes, and cabbage, purchased in the spring contain much more nitrates than those purchased in the fall. The maximum nitrate content during the research period is 770 mg/kg in store-bought early cabbage.

Table 2 – Results of the ionometric method for determining nitrate ions in the spring period in different parts of vegetables

The name of the vegetable	Concentration of nitrate ions in mg/kg		% Nitrate Reduction
	With skin	Without skin	
Potato	320	289	9,7
Cucumbers	450	250	44,4
Carrot	300	178	40,7

Another reason for the increased content of nitrates in early vegetables is the fact that plants grown indoors have a lack of ultraviolet light, which leads to the accumulation of nitrates due to a violation of their metabolism in plants. In addition, the high price of early vegetables during this period forces the use of nitrogen fertilizers in order to obtain a higher yield and a higher profit.

In the autumn period, almost all vegetable products met hygienic standards Nitrogen in plants is mainly accumulated in the stems, roots, roots, petioles and veins of the leaves and less in the fruits.

In the fruits of cucumbers, potatoes, and carrots, the nitrate content is approximately three times higher in the peel than in the pulp (table 3).

It was established that removing the skin from carrots, potatoes and cucumbers is an effective measure for reducing nitrates in experimental samples (by 9 − 45%).

Speaking about the examination of the safety of food products when determining nitrate ions, it is necessary to first of all ask questions about the accuracy of express methods for determining vegetable raw materials, regulating the content of nitrates in the water used for growth and the use of nitrate fertilizers.

Table 3 – Results of the actual human burden of nitrates obtained with vegetables

The name of the vegetable crop	The level of total nitrate loading when consuming 1 kg of product, mg/kg	Actual annual consumption of products per capita, kg/year.	Actual daily food consumption per capita, kg/day.	Real nappy per person with nitrates mg per day
Potato	197,5	94	0,257	50,8
Tomatoes	122	51	0,140	17,1
Onion	48	66	0,181	8,6
Cabbage	550	67	0,184	100,9
Carrot	193	68	0,186	35,9
Cucumbers	200	62	0,170	33,9

The obtained results of the actual content of nitrates in vegetable products were used later in the calculation of the intake of these compounds into the body from food products. Data on the actual consumption of food products (averaged taking into account the season of the year) by the population of Shevchenkivske, Andriyivaka and Zavyalivka villages are presented in the table. 4.

Table 4 – Consumption of nitrates with vegetables

Product	Nitrates, mg/ per kg of body weight		
	year	sunday	day
Vegetables	1288	24,72	3,53

To evaluate the level of nitrate intake with vegetables per kilogram of human body weight, the average value of body weight was calculated: 70.0 ± 1.2.

Data on the actual consumption of vegetables, the average body weight of an adult and the results of studying the content of nitrates in vegetables made it possible to calculate the nitrate exposure of vegetables for the population living in the villages of Shevchenkivske, Andriyivaka and Zavyalivka.

The calculation of the daily load of food contaminants per population was carried out on the basis of data from a social survey on the volume of food consumption with rations.

Based on the data of the social survey of the population of Shevchenkivske, Andriyivaka and Zavyalivka villages (564 people), the variable intake of nitrates with food products was determined and the contribution of plant products to the total value of exposure of the city population was determined.

The ranking of food products by contribution to the total value of exposure was (%): potatoes − 20.6; cabbage − 40.8; cucumbers − 13.7; tomatoes – 6.9; carrots − 14.5; onion − 3.5. Thus, the products with the greatest contribution to the exposition are potatoes and cabbage.

The dietary burden of nitrates for the population did not exceed the recommended PDD and amounted to 3.53 mg/kg of body weight per day (70.6% of PDD).

Calculation of the hazard coefficients of only the content of nitrates in plant products:

$$HQ = 3,53 / 5 = 0.706$$

The HQ values were less than one, so an in-depth exposure assessment is not required, the non-carcinogenic risk is at an acceptable level.

Non-carcinogenic risks are related to the fact that nitrates, entering the human body daily with food and accumulating inside, can affect the circulatory and cardiovascular systems.

Summarizing, it should be noted that the issue of security is certainly relevant in the field of health care. Plant raw materials, the level of contamination with contaminants does not exceed permissible values, can be sold to the population without restrictions. But we must not forget that contaminants in raw materials and products put a strain on the human body. Long-term exposure to nitrates, even in small doses, is one of the important chemical risk factors for public health.

Application of thermal and mechanical plant processing processes products, such as cleaning, cooking, blanching, canning, salting and fermentation, leads to a decrease in the level of nitrates, but at the same time the content of minerals and vitamins also decreases.

It is recommended to use fresh salted cabbage, cucumbers and other fermented vegetables after 10 − 15 days. With long-term soaking of parsley and dill leaves in water, 10 − 15% of nitrates are washed out of them [13].

So,

• established levels of nitrate content in the main types of food products of plant origin;

• a calculation of the risks of the adverse effects of controlled nitrates coming from plant products grown on the territory near such enterprises as Severnyi and Inguletsky GZK was carried out;

• The need for constant monitoring of the safety of food raw materials has been confirmed.

In order to prevent the accumulation of nitrates in crops, it is necessary to revise agricultural techniques and reduce the use of mineral fertilizers.

Recommendations for reducing the content of nitrates in vegetables:

– washing and cleaning (for example, potatoes, carrots, etc.);

- when grinding or rubbing is required, it should be done shortly before cooking;

– blanch vegetables with a high content of nitrates in boiling water for 1 − 3 minutes and leave them in water until consumption (soaking);

- store vegetables until the next meal in a refrigerator (below 4°C) or a freezer (at a temperature below -18°C);

- it is necessary to store fresh leafy vegetables in the refrigerator, if they are not prepared immediately;

- cooked food taken out of the refrigerator or freezer must be reheated immediately, boiled thoroughly for 1 minute and consumed immediately [12–13].

Conclusions

To summarize, it should be noted that the issue of safety is certainly relevant in the field of preventive health care. Technological solutions and organizational principles of achieving a satisfactory state of the environment are outlined.

A qualitative analysis of nitrate ions in vegetable raw materials: cucumbers, cabbage, potatoes, tomatoes, carrots and onions was carried out by the ionometric method. It was established that the most nitrate ions are contained in products from closed soil, compared to products collected from open soil.

Quantitative determination of the content of nitrate ions in food products was carried out and it was investigated that nitrates are contained in all products.

The content of nitrates exceeds the MPC in early potatoes bought on the market and early tomatoes.

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О. О. ЧЕРНУШЕНКО, І. Р. КОЛЄСНІКОВ

ВИЗНАЧЕННЯ РИЗИКІВ НЕГАТИВНОГО ВПЛИВУ НА НАСЕЛЕННЯ НІТРАТІВ У РОСЛИННІЙ ПРОДУКЦІЇ ВИРОЩЕНОЇ НА ТЕРИТОРІЇ ПІВНІЧНОГО І ІНГУЛЕЦЬКОГО ГЗК

Важливим завданням у галузі експертизи харчової безпеки є забезпечення якості рослинної сировини та виробництво безпечної харчової продукції. Проведення досліджень на вміст нітратів у рослинницькій продукції місцевого виробництва є актуальним особливо у промислових регіонах. Багато досліджень вчених щодо впливу нітратів і нітритів на людину доводять, що вони є одним із джерел загрози здоров'ю людей. Наведено порівняльні характеристики на вміст нітратів у рослинній продукції, що реалізується на ринку та в магазинах. Вміст нітратів перевищує ГДК у ранній картоплі, що була куплена на ринку, та ранніх помідорах. Тривале навантаження нітратами навіть у малих дозах є одним із важливих токсичних факторів ризику для здоров'я населення, що знижує стійкість організму. Для досліджень було взято зразки рослинницької сільгосппродукції місцевого виробництва вирощеної на території поблизу підприємств Північного та Інгулецького ГЗК. Встановлено рівні вмісту нітратів в основних видах харчових продуктів рослинного походження, проведено розрахунок ризиків несприятливого впливу контрольованих нітратів, що надходять рослинною продукцією, що підтвердило необхідність проведення постійного моніторингу безпеки харчової сировини. Проведено ранжування харчової продукції за вкладом у загальне значення експозиції. Найбільше навантаження на жителів регіону нітратами мг на добу надає капуста та картопля. Значення HQ склали менше одиниці. У роботі викладено основні способи зменшення вмісту нітратів у рослинницькій продукції.

Ключові слова. Безпека харчових продуктів, нітрати, оцінка ризику, безпека рослинної сировини, експертиза харчових продуктів, методи визначення нітратів..