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SADRŽAJ:

Human health risk assessment of intake Cd and Cu from agricultural soils in Mostar and Tomislavgrad

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Abstract

The aim of the research was to determine the total content of cadmium (Cd) and copper (Cu) in agricultural soils and to determine the potential toxicity of different intake routes for children and adults. Two locations were selected (Tomislavgrad and Mostar) where field crops were grown. Taking soil samples and determining the content of Cd and Cu was carried out according to the Instructions on determining the permitted amounts of harmful and dangerous substances in the soil and their testing methods (Official Gazette of FBiH, no. 96/22). A health risk assessment model based on the guidelines of the US Environmental Protection Agency (USEPA, 1996; USEPA, 2002; USEPA, 2011) was used to calculate the human health risk assessment. The measured values of the total content of copper and cadmium at the Tomislavgrad location are in accordance with the prescribed limit values. The copper content at the Mostar location was 205.90 mg/kg, which is above the limit value, and the cadmium content is in accordance with the prescribed limit values. When the HI value is less than 1, then there is no risk to human health, but if the values are greater than 1, then there is concern about non-carcinogenic risks (USEPA, 2004). The USEPA considers a carcinogenic risk in the range of 1×10^{-6} to 1×10^{-4} to be acceptable to human health. Calculations for non-carcinogenic and cancerous health risks were following the limit values.

Key words: copper, cadmium, risk assessment, Tomislavgrad, Mostar.

Introduction

Agriculture is primarily classified as a diffuse source of soil and water pollution. According to the data of the United Nations, i.e. the Economic Commission for Europe (UN/ECE, 1996), the most common

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water pollution in agricultural production occurs due to excessive and unprofessional use of nitrogen and phosphorus fertilizers, then pesticides and heavy metals (Petošić et al., 2011). The use of mineral and organic fertilizers (Cu, As) and the use of processed sewage sludge (Cu, Cd, Fe, Pb) contribute to the pollution of agricultural soil with heavy metals (Gimeno – Garcia et al., 1996).

A large part of pesticides, fungicides, and herbicides also contain Cu, Zn, Fe, Mn, and As, and some heavy metals such as Cd and Pb are introduced into the soil as impurities present in fertilizers. Phosphate fertilizers have the greatest importance among mineral fertilizers in terms of heavy metals as impurities, i.e. raw phosphates as individual fertilizers or as raw material for the production of individual and complex fertilizers. The main source of phosphorus to produce mineral fertilizers is phosphate ore. As much as 80 % of phosphorus from the phosphate rocks that are exploited is used precisely to produce fertilizers. In addition to phosphorus, phosphate ore contains a larger amount of cadmium and radioactive uranium (Contract, 2004).

In doing so, we pay the greatest attention to the concentration of Cd in phosphate minerals, although the share of other heavy metals is also very significant.

As a worldwide environmental problem, Cd was listed in seventh place as a toxic substance of concern by the American Agency for Toxic Substances and Disease Registry (ATSDR). Moreover, it was listed as a highly toxic, hazardous, and carcinogenic substance by the European Union (Zenith, H.A et al., 2020). Research shows that long-term exposure to soil environments with high Cd content leads to skeletal damage, renal failure, reproductive effects, and cancers (Syfullah, S.et al., 2020).

Metals are natural components of soil. Contamination is the result of industrial activity, such as mining and smelting of ores and metals, electrolysis, exhaust gases, fuels and energy sources for production, fertilizers and pesticide application, as well as the generation of municipal waste (Wuana and Okieimen, 2011).

Cu is not a potentially toxic element, yet its elevated level can cause respiratory problems, dizziness, nausea, and diarrhea in human beings (Nihal G. et al., 2021).

Due to their ability to accumulate in the human body, heavy metals can cause poisoning, which affect the central nervous system and cause a number of other serious disorders, which can lead to death.

Cadmium poisoning can be acute or chronic. Acute poisoning occurs by inhalation of vapor or particles of cadmium salts (oxide, chloride, sulfide, sulfate, carbonate, and acetate) (Wentz, 2000). Chronic poisoning can occur due to long-term exposure to cadmium by inhalation or by oral route, and systemic exposure to cadmium leads to increased calcium excretion (Godt et al., 2006).
In 1987, cadmium and its components were classified by the International Organization for Research on Cancer (IARC) as probable carcinogens (Group 2A) based on occupational exposure.

Recent data indicate that human exposure in the general population is statistically associated with an increased risk of endometrial, bladder and breast cancer. In 1993, IARC classified cadmium and its components in Group 1 as human carcinogens based on evidence of lung cancer in humans due to occupational inhalation exposure, and based on animal studies (IARC, 1997, 2008).

Almost the entire amount of copper in the body is bound to proteins, so the concentration of free copper ions is very low, unless there are other disorders in the body. It is believed that even 35 % of the population does not consume sufficient amounts of copper with food. The recommended daily intake of copper is about 2 mg (Tasić et al., 2004). Excessive accumulation of copper in the body leads to Wilson's disease, the basis of which is a defect in the process of incorporation of Cu^{2+} ions into ceruloplasmin (Fuentealba et al., 2000). Chronic exposure to high concentrations of copper has been shown to damage the liver, kidneys, and brain (Scheinberg et al., 1996). Increased copper content in the body has a harmful effect on the cardiovascular system, leading to coronary heart disease, atherosclerosis, and hypertension.

A number of studies have been published whose role was to examine the content of heavy metals in fruit samples and assess the risk of dietary exposure to metals in fruit. Toxic metals, especially arsenic, mercury, cadmium and lead, represent a major problem in the field of food safety. It is estimated that their intake in most European countries is 30-40 % compared to the recommended tolerant weekly intake and is sometimes significantly higher. European Food Safety Agency (EFSA) for the period from 2003-2007. found that in 5 % of food samples the concentrations of heavy metals were above the permitted values.

Health risk assessment

Risk to human health is defined as a probability that describes the degree of threat to the health of an individual exposed to the action of a certain pollutant or group of pollutants.

The risk depends on several factors:

• contaminants present in food,

• contact sizes (exposure levels),

• and toxicity of contaminants.

Combining the knowledge described in these three factors is fundamental to most risk assessments. Assessing the human health risks of chemicals can help answer questions about the potential hazards of exposure to chemicals. Professionals in the field of risk assessment must understand the concept of risk, must predict, recognize, and analyze it, and make decisions related to all the above. Risk assessment for human health provides an overview of the evaluation of past, present, and future cases of exposure to food hazards and can be qualitative and/or quantitative. It is based on a scientific understanding of pollutant properties, exposure, doses, and toxicity. Two dimensions of risk, which are a combination of the probability or frequency of a bad event and the magnitude of the consequences of that event, must be considered.

Risk assessment is a scientifically based process of assessing a possible harmful impact, which consists of:

• hazard identification,

• hazard characterization,

• exposure assessments

• risk characterization (Knežević and Serdar, 2011).

Material and methods

Two localities in Tomsilavgrad and Mostar were selected for the research. Field crops corn and wheat are grown in the researched localities. The locations were chosen due to the intensive use of pesticides and mineral fertilizers. Taking soil samples and determining the content of Cd and Cu was done according to the *Instructions on determining the permitted amounts of harmful and dangerous substances in the soil and their testing methods (Official Gazette of FBiH, no. 96/22)* Chemical and physical analyzes of the soil, analyzes of the content of organic matter and nutrient elements in the soil were performed in the laboratory of the Federal Institute for Agropedology in Sarajevo.

FIELD RESEARCH included:

a) Selection of locality,

b) Soil sampling,

c) Monitoring of the fertilization and protection plan.

LABORATORY RESEARCH included:

a) physical and chemical analyzes of the soil:

b) physical and chemical characteristics,

c) organic matter and nutrients,

d) content of heavy metals: cadmium (Cd), copper (Cu).

RISK ASSESSMENT

Hazard Identification basically aims to investigate chemicals that are present at any given location, their concentrations, and spatial distribution. In the study area, Cd, and Cu were identified as possible hazards for the community.

The purpose of exposure assessment is to measure or estimate the intensity, frequency, and duration of human exposures to an environmental contaminant. In the study, exposure assessment was carried out by measuring the average daily intake (ADI) of heavy metals earlier identified through ingestion, inhalation and dermal contact by adults and children from the study area. Adults and children are separated because of their behavioural and physiological differences.

The dose-response assessment estimates the toxicity due to exposure levels of chemicals. The cancer slope factor (CSF, a carcinogen potency factor) and the reference dose (RfD, a non-carcinogenic threshold) are two important toxicity indices used. RfD values are derived from animal studies using the "No observable effect level" principle. For humans, RfD values are multiplied 10-fold to account for uncertainties.

Risk characterization predicts the potential cancerous and non-cancerous health risk of children and adults in the study area by integrating all the information gathered to arrive at quantitative estimates of cancer risk and hazard indices.

The potential exposure pathways for heavy metals in contaminated soils are calculated based on recommendations by several American publications. ADI (mg/kg-day) for the different pathways were calculated using the following exposure Equations, prescribed by US Environmental Protection Agency (USEPA, 1996; USEPA, 2002; USEPA, 2011).

$ADI_{oral} = (C \times IR \times EF \times ED \times CF) / (BW \times AT)$

$ADI_{dermal} = (C \times SA \times FE \times AB \times EF \times ED \times CF) / (BW \times AT)$

$ADI_{inhal} = (C \times IRair \times EF \times ED) / (PEF \times BW \times AT)$

ADI_{oral}, ADI_{dermal} and ADI_{inhal} are daily amounts of corresponding exposure to soil elements (mg/kg day).

The assessment of non-cancer risk was calculated according to the calculation model for non-cancer hazards:

$$\boldsymbol{HI = \sum_{k=1}^{n} HQ_k = \sum_{k=1}^{n} \frac{DI_k}{RfD_k}}$$

The assessment of carcinogenic risk was calculated according to the calculation model for carcinogenic hazards:

$$Risk_{input\ method} = \sum_{k=1}^{n} DI_k\, CSF_k$$

Table 1. *Exposure parameters used for the health risk assessment through different exposure pathways for soil. (Kamunda C., 2016.)*

Parameters	Unit	Definition	Value	
			Children	**Adult**
ABS	--	Dermal absorption factor	0.1	0.1
AF	mg/cm^2	Soil adhesion factor for skin	0.2	0.07
BW	kg	Average weight	15	70
ED	godina	Exposure time	6	30
EF	d/godina	Exposure frequency	350	350
FE	--	Dermal exposure ratio	0.61	0.61
IngR	mg/d	Soil ingested factor	200	100
Irair	m^3/d	Inhalation factor	10	20
SA	cm^2/event	Exposed skin surface	2.8	5.7
Atnc	D	Averaging time for noncarcinogens	ED x 365	
Atca	D	Averaging time for Carcinogens	70 × 365	
CF	kg/mg	Calculation factor	10^{-6}	
PEF	kg/mg	Soil particulate emission factor – air	1.36×10^9	

Sampling was carried out before sowing the crops by taking five individual samples along the diagonal of the plot, which were collected into one average sample, weighing about 1 kg. The obtained average samples were prepared by being crushed, packed in plastic bags and marked, after which they were delivered to the Federal Institute for Agropedology in Sarajevo for the analysis of the total content of heavy metals, and the analysis of the physico-chemical properties of the soil.

The samples taken are labeled as follows:

- Uz.1 Mostar (0-30 cm)

- Uz.2 Tomislavgrad (0-30 cm)

Determination of the content of Cd and Cu in the soil by AAS method

The preparation of samples for the instrumental analysis of the content of heavy metals in the soil is carried out using aqua regia, and then their content in the extract is determined by the method of atomic absorption spectrometry (AAS). The extraction of heavy metals in aqua regia was carried out according to the international standard ISO11464. This standard specifies a method for the extraction of trace elements with a gold nugget using an adequate atomic spectrometric technique. According to the principle of this standard, the soil sample is ground into particles smaller than 2 mm before digestion with aqua regia. Such grinding achieves a more homogeneous sample from which a sub-sample is taken and an increase in the efficiency of the action of the acid by increasing the surface area of the particles. The dried sample is then extracted with a mixture of hydrochloric/nitric acid by leaving it for 16 hours at room temperature, followed by boiling under reflux for two hours. The extract is clarified - purified (filtered) and the volume is made up with nitric acid. The international standard ISO11047 specifies the method of atomic absorption spectrometry for the determination of one or more elements in extracts from soil, extracted with aqua regia, obtained in accordance with ISO11466.

The delegated legislation that is currently in force in the territory of the Federation of Bosnia and Herzegovina, and is directly related to the research topic, is the Instruction on determining the permitted amounts of harmful and dangerous substances in the soil and their testing methods (*Official Gazette FBiH*, number 96/22) (Table 2.) in which the limit values of pollutants in the soil in their total form are defined, which apply only to agricultural soils, while the limit values for other soils have not yet been legally defined.

Table 2. *Limit values of heavy metals in soil in total form*

Element	**Limit value (mg/kg)**		
	Sandy soil	**Powdery clay soil**	**Heavy soil**
Cadmium (Cd)	0.5	1	1.5
Copper (Cu)	50	65	80

Source: Instructions on determining the permitted amounts of harmful and dangerous substances in the soil and their testing methods (Official Gazette FBiH, No. 96/22)

Table 3. *Copper content in soil*

Location	**Texture tag**	**Cu mg/kg**
Mostar	Loamy clay	205.90
Tomislavgrad	Loamy clay	25.47

The measured value of copper content above MDK was measured at the location of Mostar. According to the Instructions on determining the permitted amounts of harmful and dangerous substances in the soil and their testing methods *(Official Gazette of FBiH, no. 96/22),* the copper content in this type of soil is up to 65 mg/kg, and in our research, it is 205.90 mg/kg. Also, according to Soriano et al. 2012, such soils are classified as moderately polluted.

The measured value of the copper content at the Tomislavgrad location was in accordance with the Instructions on determining the permitted amounts of harmful and dangerous substances in the soil and their testing methods *(Official Gazette of FBiH, no. 96/22).* Also, according to Soriano et al. 2012, such soils are classified as uncontaminated.

More copper is usually found in heavy clay soils than in light sandy ones (Kastori, 1983). According to Kabata-Pendias (2011), copper concentrations in soils around the world range from 14-109 mg/kg. According to research by Šukalić, A. 2017, the copper content in the locations of Mostar, Čapljina and Stolac in 2015 and 2016 ranged from 19 mg/kg to 57.7 mg/kg. In our research, the total content of copper in all localities did not exceed the maximum allowed concentration, which is in accordance with the research of Ramović et al. (2012) where at one location in Zenica (Pehare) the measured value of copper was 51.3 mg/kg. According to research by Bukalo et al. (2013) an increased content of total copper was determined in the location of the city of Mostar, more precisely Mostar/Kokorina, where the content of total copper was 165.58 mg/kg.

In this research, it was determined that the copper content is much higher in the Mostar location and is 205.90 mg/kg.

A possible reason for the excessive amount of copper in this location is that earlier there were potatoes in that place that were treated with preparations based on copper, and it is possible that the excessive accumulation of copper in the soil occurred precisely because of this.

Table 4. *Cadmium content in soil*

Location	Texture tag	Cd mg/kg
Mostar	Loamy clay	0.79
Tomislavgrad	Loamy clay	0.33

At both investigated locations, the measured cadmium content was within the limit values (Table 3).

According to the Instructions on determination of permitted quantities of harmful and dangerous substances in the soil and their testing methods *(Official Gazette of FBiH, no. 96/22)*, the cadmium content in the powdery loam type of soil is 1 mg/kg.

In nature, cadmium rarely occurs in pure form and is a constant companion of zinc, copper and lead, with which it is similar in geochemical characteristics. In uncontaminated soils, its content depends on the texture of the soil: in sandy soils, it is 0.01-0.3 mg/kg, and in clayey soils, it is 0.2-0.8 mg/kg**.** (Šukalić, A. 2017.)

In soils around the world, the cadmium content is estimated to be around 0.41 mg/kg, and Kabata-Pendias (2011) and Branković et al. (2016) state that a cadmium content of 2.5 mg/kg was determined at the investigated locations. The content of cadmium in the soils of Serbia varied in the range of 0.01-2.0 mg/kg (Kastori, 1993).

According to research by Bukalo et al. (2013) an increased content of total cadmium was determined in three locations of Mostar: Mostar/Bogodol with a measured value of 4.17 mg/kg, Mostar/Goranci 4.13 mg/kg and Mostar/Kokorina where the content of total cadmium was 2.73 mg / kg. According to the research of Šukalić, A. 2017, the content of cadmium in the localities of Mostar in 2015 and 2016 were above the permitted limit values.

In our research, the measured value of the cadmium content in the Mostar location was 0.79 mg/kg, while in the Tomislavgrad location this content was 0.33 mg/kg. In both localities, the values were in accordance with the Instruction (*Official Gazette of FBiH, no. 96/22)*, although in the Mostar locality, this value is close to the limit value.

Risk assessment calculation

Table 5. *Average daily intake values (ADI) in mg/kg/d from soil for adults at locations*

Average daily intake value for heavy metals in mg/kg/day for adults by location			
Location	**Routes of exposure**	**Cd**	**Cu**
Mostar	Ingestion	1.08E-05	2.82E-03
	Inhalation	1.59E-10	4.15E-08
	Dermal	3.76E-08	9.81E-06
	Total	1.09E-05	2.83E-03
Tomislavgrad	Ingestion	4.52E-06	3.49E-04
	Inhalation	6.65E-11	5.13E-09
	Dermal	1.57E-08	1.21E-06
	Total	4.54E-06	3.50E-04

Table 6. *Average daily intake values (ADI) in mg/kg/d from soil for children at locations*

Average value of daily intake for heavy metals in mg/kg/day for children by location			
Location	**Routes of exposure**	**Cd**	**Cu**
Mostar	ingestion	1.01E-04	2.63E-02
	inhalation	3.71E-10	9.68E-08
	dermal	8.63E-08	2.25E-05
	total	1.01E-04	2.63E-02
Tomislavgrad	ingestion	4.22E-05	3.26E-03
	inhalation	1.55E-10	1.20E-08
	dermal	3.60E-08	2.78E-06
	total	4.22E-05	3.26E-03

Table 7. *Non-carcinogenic hazard index (NHI) in mg/kg/d from soil for adults at locations*

NHI for heavy metals in mg/kg/day for adults by location			
Location	Routes of exposure	Cd	Cu
Mostar	ingestion	2.16E-02	7.62E-02
	inhalation	2.79E-06	
	dermal	7.53E-05	4.09E-04
	NHI	2.17E-02	7.66E-02

NHI for heavy metals in mg/kg/day for adults by location			
Location	Routes of exposure	Cd	Cu
Tomislavgrad	ingestion	9.04E-03	9.43E-03
	inhalation	1.17E-06	
	dermal	3.14E-05	5.05E-05
	NHI	9.07E-03	9.48E-03

Table 8. *Non-carcinogenic hazard index (NHI) in mg/kg/d from soil for children at locations*

NHI for heavy metals in mg/kg/day for children by location			
Location	**Routes of exposure**	**Cd**	**Cu**
Mostar	ingestion	2.02E-01	7.11E-01
	inhalation	6.51E-06	
	dermal	1.73E-04	9.37E-04
	NHI	2.02E-01	7.12E-01
Tomislavgrad	ingestion	8.44E-02	8.80E-02
	inhalation	2.72E-06	
	dermal	7.21E-05	1.16E-04
	NHI	8.45E-02	8.81E-02

When the HI value is less than 1, then there is no risk to human health, but if these values are greater than 1, then there is concern about non-carcinogenic risks (USEPA, 2004).

The average values of daily intake (inhalation, oral and dermal) of Cd and Cu from soil for adults and children at the locations of Mostar and Tomislavgrad were calculated based on a health risk assessment model based on the guidelines of the US Environmental Protection Agency (USEPA, 1996; USEPA, 2002; USEPA, 2011), parameters for risk assessment and concentration of heavy metals at sites and RfD and CSF reference doses for Cd and Cu.

Based on the ADI, the values of the non-carcinogenic hazard index (NHI) were calculated, and for adults, the total value of the NHI by different routes of Cd intake at the Mostar location is 2.17E-02, and at the Tomislavgrad location 9.07E-03.

The total value of NHI by different intake routes for Cu at the Mostar location is 7.66E-02, while at the Tomislavgrad location, this value is 9.48E-03.

For children, the total value of NHI through different routes of Cd intake at the Mostar location is 2.02E-01, and at the Tomislavgrad location 7.12E-01. The total value of NHI by different intake routes for Cu at the Mostar location is 8.45E-02, while at the Tomislavgrad location, this value is 8.81E-02.

Mičijević et al. (2019) investigated the content of Cu, Pb, and Zn at three locations in Herzegovina, and the values of the hazard index (HI) for all examined heavy metals were lower than 1 (1.62E-1 for adults, 2.44E-1 for children), and have no non-carcinogenic health risks due to ingestion, dermal contact and inhalation.

Šukalić et al. (2018) in their research on 7 heavy metals and assessment of non-carcinogenic risks, report HI values for adults Cd 5.3E-4 and for Cu 3.6E-2, and for children Cd 5.34E-4 and Cu 3.08E- 2.

Kamunda C. et al. (2016) report a hazard index value of 2.13 for all routes of intake, which makes non-carcinogenic effects significant for the adult population. For children, the value of the hazard index was 43.80, which represents a serious non-cancerous risk for children living in the researched area. In a study by Luo et al. (2012), concern about the non-carcinogenic risk of oral lead intake for children was expressed, although the HI value is lower than 1.

In our research, the HI values for adults through the oral, dermal, and inhalation routes of entry of heavy metals into the body were lower than 1 in all locations, which means that there is no risk to the health of adults and children.

Calculation of carcinogenic risk assessment of heavy metals for adults and children

***Table 9**. Average daily intake (CDI) values in mg/kg/d from soil for adults at the sites*

Average daily intake value for heavy metals in mg/kg/day for adults by location			
Location	**Routes of exposure**	**Cd**	**Cu**
Mostar	Ingestion	4.64E-06	1.21E-03
	Inhalation	6.82E-11	1.80E-08
	Dermal	1.61E-08	4.20E-06
	Total	4.65E-06	1.21E-03
Tomislavgrad	Ingestion	1.94E-06	1.50E-04
	Inhalation	6.65E-11	5.13E-09
	Dermal	6.74E-09	5.20E-07
	Total	1.94E-06	1.50E-04

***Table 10**. Average chronic daily intake (CDI) values in mg/kg/d from soil for children at the locations*

Average value of daily intake for heavy metals in mg/kg/day for children by location			
Location	**Routes of exposure**	**Cd**	**Cu**
Mostar	Ingestion	8.66E-06	2.26E-03
	Inhalation	3.18E-11	8.30E-09
	Dermal	7.39E-09	1.93E-06
	Total	8.66E-06	2.26E-03
Tomislavgrad	Ingestion	3.62E-06	2.79E-04
	Inhalation	1.33E-11	1.03E-09
	Dermal	3.09E-09	2.38E-07
	Total	3.62E-06	2.79E-04

***Table 11.** Carcinogenic hazard index (CHI) in mg/kg/d from soil for adults at locations*

CHI for heavy metals in mg/kg/day for adults by location			
Location	**Routes of exposure**	**Cd**	**Cu**
Mostar	Ingestion	1.76E-06	/
	Inhalation	4.30E-10	/
	Dermal		/
	CHI	1.76E-06	/
Tomislavgrad	Ingestion	7.36E-07	/
	Inhalation	4.19E-10	/
	Dermal		/
	CHI	7.37E-07	/

Table 12. *Carcinogenic hazard index (CHI) in mg/kg/d from soil for children at the locations*

CHI for heavy metals in mg/kg/day for children by location			
Location	**Routes of exposure**	**Cd**	**Cu**
Mostar	Ingestion	3.29E-06	/
	Inhalation	2.01E-10	/
	Dermal		/
	CHI	3.29E-06	/
Tomislavgrad	Ingestion	1.37E-06	/
	Inhalation	8.38E-11	/
	Dermal		/
	CHI	1.37E-06	/

In our research, the carcinogenic hazard index (CHI) was calculated only for Cd, because it is a proven carcinogen, both through oral and inhalation intake. CHI for adults at the location of Mostar is 1.76E-6 and at the location of Tomislavgrad 7.37E-07. CHI for children at the location of Mostar is 3.29E-06, and at the location of Tomislagrad 1.37E-06.

The USEPA considers a carcinogenic risk in the range of 1×10^{-6} to 1×10^{-4} to be acceptable to human health. If the carcinogenic risk is < 10^{-6}, the carcinogenic risk to health can be considered negligible, and if it is je > 10^{-4}, it is considered that there is a significant risk for the development of cancer in humans.

In the research Šukalić et al. (2020) report values of carcinogenic hazard calculations for oral intake of Cd, and oral intake and dermal contact of Pb via soil for adults and children. The values were close to the limits recommended by the USEPA at the three investigated sites (2E-6 for Cd and 1.99E-6 for Pb).

In the research of Kamunda C. et al (2016), the carcinogenic risk is 1.7 E-4, which indicates that one person may be affected in 5882 adults. In addition, 1 child per 2725 children may be affected (3.67 E-4). Those carcinogenic risk values were more than acceptable.

Huabin H. et al (2019) in a study of uncultivated soils report the total carcinogenic index for Cr, Cu, Zn, As, Cd, Pb and Hg for adults (2.80±0.79)E-5 and children (1.36±0.39)E-5.

In our research, the calculated values for the assessment of carcinogenic risks are < 10^{-6}, so there is no risk to human health.

Conclusion

The measured value of the copper content above the MDK was measured at the Mostar location and is 205.90 mg/kg.

The value of NHI by different routes of Cd intake for children at the Mostar location is 2.02E-01, and at the Tomislavgrad location 7.12E-01. The total value of NHI by different intake routes for Cu at the location of Mostar is 8.45E-02, while at the location of Tomislavgrad this value is 8.81E-02. The values of HI for adults oral, dermal and inhalation routes of entry of heavy metals into the body were lower than 1, which means that there is no risk to the health of adults and children.

The carcinogenic hazard index (CHI) in our research was calculated only for Cd, because it is a proven carcinogen and that is through oral and inhalation intake into the body. CHI for adults at the Mostar location is 1.76E-6, and at the Tomislavgrad location 7.37E-07. CHI for children in Mostar is 3.29E-06, and in Tomislagrad 1.37E-06. USEPA considers that a carcinogenic risk in the range of 1×10^{-6} to 1×10^{-4} is acceptable for human health, which was also the case in this study.

Based on the research conducted on the content of cadmium (Cd) and copper (Cu) in agricultural soils in Tomislavgrad and Mostar with an assessment of the risk to human health, it can be concluded that the importance of permanent monitoring of agricultural soil should be given, and that would enable the identification of risk areas depending on the type and the severity of threats to the soil as a resource necessary for food production.

It is also necessary to include in the monitoring the implementation of the methodology for assessing the risk to human health from contaminants both from agricultural soil and from food in order to reduce potential risks to a minimum.

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