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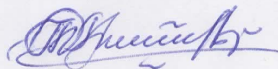
BIOTECNOLOGIA DEGLI ALIMENTI - XXVIII Ciclo.

HEALTH RISK ASSESSMENT OF ENVIRONMENTAL CONTAMINANTS FOR POPULATION VIA
CONSUMPTION OF VEGETABLES AND FRUITS GROWN IN MINING AREAS. A CASE STUDY:
ARMENIA

AGR/15 SCIENZE E TECNOLOGIE ALIMENTARI

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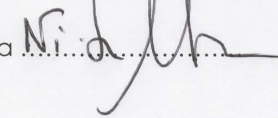
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ABSTRACT

This PhD thesis is aimed to carry out risk assessment of trace elements, especially of first-class toxic elements, in some mining regions of Armenia, where production of plant origin food is developed and produced fruits and vegetables are the major source of food for local population.

Exposure of pollutants is one of major environmental and public health concerns.

Taking into consideration the fact that in the study region consumption of plant origin food in overall diet is significantly higher, so the estimation of dietary intakes of potentially toxic elements via consumption of selected vegetables and fruits can be considered as an efficient tool for health risk assessment, simultaneously for providing appropriate information about any threat and risk regarding exposure of environmental contaminants.

To conduct dietary exposure assessment of toxic elements it is necessary to combine data of concentration of contaminants in selected food commodities and the consumption data of those selected food items.

The present study was conducted to assess the human health risk posed by environmental contaminants through the intake of vegetables and fruits grown in some of Armenia's mining regions.

The main activities included.

1. *Elaboration of sampling plan, monitoring, analyses and compilation of a database of environmental contaminants in selected vegetables and fruits.*
2. *Dietary study and creation of food consumption survey.*

To achieve the goal the following tasks were set and executed:

- *Estimation of chemical concentrations by up-to-date methods in compliance with international requirements*
- *Assessment of dietary exposure*
- *Investigation of daily intake of metals (DIM)*
- *Estimation of dietary toxicity through calculation of Health Risk Index (HRI) and Target Hazard Quotient (THQ).*

Concentrations of Cu, Mo, Ni, Cr, Pb, Zn, Hg, As and Cd in different vegetables were detected and the consumption data calculated. Moreover, combining concentration data with consumption data DIM and HRI were calculated.

The results obtained showed that the mean concentrations of Cu, Cr, Pb and Hg in some

vegetables and fruits exceeded maximum acceptable levels, moreover $HRI > 1$ for Cu, Mo, Cr, Hg and Pb were detected.

In conclusion the results of combined HRI suggest that except cucumber and onion bulb consumption of other studied vegetables and fruits (maize, bean, potato, pepper sweet, eggplant, tomato, beet, onion leaves, carrot, fennel, basil, cabbage, plum and grape) have a high potential to pose health risk to both male and female population.

1. INTRODUCTION

Food safety is a major public health concern worldwide [29]. Presently, Armenia is developing a food safety system within the framework of European Neighbourhood Policy. Since 2009, Armenia's Government has been involved in Harmonization of Food Safety Structural and Functional Capacities. In 2010 by President Decree State Service for Food Safety was established designated for implementation of a risk-based food safety inspection system.

The main steps include implementation of food safety requirements in compliance with Regulation 178/2002 laying down the general principles and requirements of food law, establishing the European Food Safety Authority and laying down procedures in matter of food safety [51]. The state control must be based on risk analyses [52]. Article 3 of Regulation 178/2002 gives a definition of risk analyses as a process consisting of three interconnected components: risk assessment, risk management and risk communication.

To implement scientifically risk based food safety system by Prime Ministers's decree (N835-N from Oct. 21, 2010) was created the Center for Risk Assessment (after Center) at the Center for Ecological Noosphere Studies (after Ecocenter).

The Ecocenter possesses a large database related to soil, irrigation water and contamination of some food commodities, but lack of dietary exposure prevents from getting a completed risk assessment. The main obstacles are absence of harmonized methods for food consumption data collection, dietary intakes of different contaminants and particularly toxic elements which level exceeding in soils and irrigation water, and there exists is a high probability of food contamination, too.

Appropriate knowledge of risk assessment components emphasizing exposure assessment is not sufficient yet. So far, the country has had no officially approved TDS program and methodology.

Mining industry is one of priority sectors of Armenia's economy. Along with the solution of some socio-economic development, it brings about numerous environmental problems, which largely influence safety of agroproduction. Lack of treatment facilities in the mining plants, immediate discharge of untreated mine waters into surface waters and irrigation system, presence of idle tailing repositories in the study region and lots of other violations have a grave environmental impact [102].

Pollution of components of agrobiocoenosis brings to migration and accumulation of heavy metals in agricultural produce and food chain [101].

Apart mining industry, sustainable rural development and development of agrarian sector is strategically important to the Republic of Armenia in general. The investigated area also historically was famous both for mining and agrarian sector development.

Armenian government has elaborated and set a food safety and export oriented food production development strategy, where plant origin food is one of the priority branches.

As there is high risk of contamination of plant origin products the aim of study is to measure the levels of toxic elements (Hg, As, Cd, Pb, Cu, Mo, Zn, Ni, Cr) found in common vegetables grown in contaminated mining areas to determine their potential detrimental effects via calculation of the daily metal intake (DIM) and Target Hazard Quotients (THQ) for normal daily consumption of these vegetables, for males and females.

Heavy metal contamination of food items is one of the most important aspects of food quality assurance [85]. It is public concerns are fruits and vegetables cultivated in polluted soils safe for human consumption [19].

There are reports indicating that some plant species may accumulate specific heavy metals [84], particularly crop species grown in contaminated medium can pose serious health risk to human health when consumed [81].

Fruits and vegetables accumulate heavy metals both in edible and non-edible parts and accumulation of heavy metals in edible parts is a direct pathway for their penetration into a human food chain [131, 53]. Vegetables, particularly leafy ones, accumulate higher amounts of heavy metals [113]. It has been stated that roots and leaves of the plants accumulate higher concentration of heavy metal than stems and fruits [153].

Heavy metal contamination of vegetables cannot be under estimated as these foodstuffs are important components of human diet [76]. Some elements, such as lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), chromium (Cr), copper (Cu) and selenium (Se) (IV) can be harmful for plants and humans even at very low concentrations [14]. The adverse health effects of several chemical elements are famous throughout history, currently the development of toxicology has improved knowledge about human exposure and recent investigations related intake of heavy metals through the food chain by human populations are available [88, 89]. Different natures of effects are reported, such as toxic (acute, chronic or sub-chronic), neurotoxic, carcinogenic, mutagenic or teratogenic [49].

Having non-biodegradable and persistent nature, heavy metals are able to be accumulated in important vital organs such as the kidneys, bones and liver and cause serious adverse effects and health disorders [33]. McCluggage reported harmful biotoxic effects when consumed above the bio-recommended limits. Although individual metals exhibit specific signs of their toxicity, general signs for lead, arsenic, mercury, zinc, copper and aluminium

poisoning have been implicated with gastrointestinal disorders, diarrhea, stomatitis, tremor, hemoglobinuria causing a rust-red color to stool, ataxia, paralysis, vomiting and convulsion, depression and pneumonia [87]. Lead and cadmium are the most toxic elements. The excessive content of these metals in food can cause a number of diseases, especially cardiovascular, renal, and nervous as well as bone diseases [141, 142].

It is also known, that permanent consumption of fruits and vegetables rich in heavy metals such as Cd, Pb sometimes Cu and Zn can cause carcinogenic effects. Particularly there are evidences of gastrointestinal cancer [118].

During the recent years by the Ecocenter [101, 102] were largely investigated the contamination of the mining areas, peculiarities of migration of elements, and was declared that several toxic elements enter to the food chain, which can have both short- and long- term health impact.

The previous investigations were directed to understand the characteristics of contamination, but not the exposure assessment of environmental contaminations via consumption of those products, as there are no data about consumption levels of the vegetables.

1.1. CHEMICAL AND TOXICOLOGICAL PROFILE OF ENVIRONMENTAL CONTAMINANTS IN FOOD

CADMIUM

Cadmium (Cd) naturally occurs in the environment in its inorganic form with zinc and lead in sulfide ores [34, 90]. Cadmium is not degradable in nature [91]. Cadmium in ambient air is transferred to soil by wet or dry deposition and can enter the food chain [146].

The main contribution of dietary cadmium is provided by agricultural products [65, 91]. Certain crops contain naturally elevated amounts of cadmium, so individuals' consuming these materials might be at increased risk [96, 144]. Iron deficiency is more important determinant of cadmium uptake than is the actual amount of cadmium ingested [65, 130].

In 2004 the European Commission carried out investigation and updated exposure assessment data served for setting the maximum levels for cadmium in foodstuffs [103,110]. Food is the main source of cadmium exposure [148]. Cadmium is absorbed via the lungs, gastrointestinal tract, and skin in both humans and experimental animals [16]. Cadmium bioavailability varies according to content, the nutritional status, gender, the smoking status, age and the presence of divalent or trivalent cations [10]. Zn and calcium deficiencies may

result in increased accumulation of cadmium in the intestinal wall, liver and kidney [95]. Studies have shown increasing blood cadmium with decreasing serum ferritin in women at fertile age and during pregnancy [3]. Low iron stores were associated with increased Cd accumulation, but only at adequate zinc status [13, 77]. Cd may bind SH-rich low-molecular weight peptides or amino acids such as glutathione and cysteine respectively [34, 154].

Degree of uptake is largely dependent on several factors: age, pH, type of a diet and production of metallothionein [5]. The distribution of Cd to the kidneys is of particular importance because the kidney is the critical organ after long-term exposure [90, 92]. The distribution rates to the liver increased dose-dependently, whereas those to the kidney decreased when dose increased [34, 80]. Approximately 50% of the total cadmium body burden at autopsy is found in the kidney and 15 % in the liver, and only a relatively small part is stored in bone [90].

Cadmium can be detected in virtually all tissues in adults from industrialised countries, with the greatest concentrations in the liver and kidney [20]. Cadmium exposures are associated with kidney and bone damage [148]. Kidney is a the target organ of toxicity during chronic Cd exposure [39, 111]. In addition, long-term exposure to higher doses of cadmium has been associated with teratogenicity, mutagenicity, and carcinogenicity. However, there is no evidence of carcinogenicity by the oral route and no clear evidence that cadmium is genotoxic [150], but the IARC [61] classified cadmium and cadmium compounds as carcinogenic to humans (Group 1). EC has classified some cadmium compounds as possibly carcinogenic (Carcinogen Category 2) [97]. US EPA declares the three aspects of the carcinogenic assessment [119, 120]. No reliable unit risk can be derived to estimate the excess lifetime risk for lung cancer [146].

ARSENIC

Arsenic (**As**) is a metalloid that occurs in different inorganic and organic forms [42]. Arsenic is present in more than 200 mineral species. Terrestrial abundance of arsenic is approximately 5 mg/kg [147]. In the agricultural industry, arsenic has historically been used in a range of applications (pesticides, herbicides, insecticides etc.) [63]. The actual total arsenic concentrations in foodstuffs from various countries vary widely depending on the food type, growing conditions (type of soil, water, geochemical activity, use of arsenical pesticides) and processing techniques [147]. Public health actions are needed to reduce human exposure to arsenic, particularly in areas with naturally high levels in groundwater [149].

The primary route of arsenic exposure for the general population is via the ingestion of contaminated food or water [63]. The highest concentration of arsenic has been found in

seafood followed by meats, cereals, vegetables, fruit, and dairy products [63]. After absorption arsenic is transported by the blood to other parts of the body [90].

Total tissue arsenic accumulation (measured as the sum of inorganic arsenic, methylarsonate and dimethylarsinate) was greatest in kidney > lung > urinary bladder > skin > blood > liver [42, 63]. Arsenic and metabolites are readily excreted in urine and bile [42]. Inorganic arsenic is eliminated primarily via the kidney in humans as well as laboratory animals [90, 147]. Arsenic is excreted by routes other than just urine and faeces, but in general these routes of excretion are quantitatively minor. The inorganic forms of arsenic are more toxic as compared to the organic arsenic [42]. Inorganic arsenic can have acute, subacute and chronic effects, which may be either local or systemic [146]. Symptoms of chronic arsenic poisoning include weakness, debility, and lassitude, loss of hair, hoarseness and loss of weight [110].

Conclusions on the causality of the relationship between arsenic exposure and other health effects are less clear-cut. The evidence is strongest for hypertension and cardiovascular disease, suggestive for diabetes and reproductive effects and weak for cerebrovascular disease, long-term neurological effects, and cancer at sites other than lung, bladder, kidney and skin [8, 90, 149].

MERCURY

Mercury (Hg) is a metal that is released into the environment from both natural and anthropogenic sources [44]. On a global scale, the estimated natural emission of mercury represents about one-third of the total, and anthropogenic emissions represent about two-thirds [148]. Methylmercury compounds are formed in aquatic and terrestrial [61]. Humans, plants, and animals are exposed to mercury, potentially resulting variety of health impacts [44].

The major proportion of the mercury in fish is methylmercury [90]. The gastrointestinal absorption rate varies substantially depending on the chemical compound in question. Smaller amounts of inorganic mercury can be absorbed through the skin, but ingestion is the main pathway into the body [148].

Absorbed inorganic mercury accumulates in the kidneys but does not cross placental or blood - brain barriers as easily as Hg^0 or methylmercury. However, inorganic mercury does accumulate in placental tissues [148].

The highest proportion of the body burden is located in the kidney. The other largest deposition is a liver [44]. In contrast to mercuric mercury, in human blood methylmercury is accumulated to a large extent (>90 %) in the erythrocytes, where it is bound to the cysteinyl

residues of hemoglobin [69]. Mercuric mercury in the brain is generally the result of either in situ dealkylation of organic mercury species, including methylmercury and thiomersal, or oxidation of elemental mercury [100].

The main pathway of excretion of absorbed mercuric mercury is via the urine and, to a lesser extent, via faeces [86].

LEAD

Lead (Pb) is an environmental contaminant that occurs naturally and, to a greater extent, from anthropogenic activities such as mining and smelting and battery manufacturing [74]. Lead is a metal that occurs in organic and inorganic forms; the latter predominates in the environment [9, 43, 64]. Control measures have been taken to regulate lead in paint, petrol, food cans and pipes in Europe since the 1970s [43].

Lead is incorporated into several crops through absorption, by the roots, from soil and through direct deposition on plant surfaces. In leafy vegetables, the accumulation of airborne lead largely exceeds the soil-borne part taken up via the roots [64, 148].

The main exposure of the general non-smoking adult population is from food and water [74]. Food is the predominant source of lead uptake in the general population [43, 148].

The rate of absorption of lead after ingestion can range from 3% to 80% [74].

Gastrointestinal absorption of ingested lead is influenced by physiological factors (e.g., age, fasting, nutritional calcium and iron status, and pregnancy), physicochemical characteristics of particles (size, solubility and lead species) and the amount of food intake [9, 64]. In human adults, approximately 90% of the total body burden of lead is found in the bones [43]. Body does not change lead into any other form. Once it is taken in and distributed to organs, the lead that is not stored in bones leaves body via urine or feces [9].

Lead has been described as a classic chronic or cumulative chronic poison. Health effects are generally not observed after a single exposure [72, 74]. Toxic effects may occur in the central and peripheral nervous systems, blood (including inhibition of heme synthesis, which also affects other cells), kidney, and cardiovascular, endocrine and immune systems, gastrointestinal tract, and male reproduction [90]. Lead causes increase of blood pressure [9, 90]. The US EPA has determined that lead is a probable human carcinogen. The IARC has determined that inorganic lead is probably carcinogenic to humans [64]. Substantial increases in lead uptake are said to have occurred when dietary iron and iron status were low [145].

ZINC

Fiftyfive zinc (Zn)-containing minerals are known [90]. Zinc is an essential nutrient, present in all tissues of the human body [32, 92]. Zinc has an ability for fast exchange coupled with strong binding to organic molecules [47]. Zinc is necessary for growth [56]. It also has an important role for gene expression. In the human genome, about 10% of proteins have the potential for binding zinc [90, 92]. The main dietary sources are meat, fish and poultry, with cereals and dairy products also making a significant contribution [56]. Meat, legumes, eggs, fish, and grains and grain-based products are rich dietary zinc sources [47]. Milk, fruit and vegetables are low in zinc [105].

In EU average zinc intake ranged from 4.6 to 6.2 mg/day in children aged one to less than three years, from 5.5 to 9.3 mg/day in children aged 3 to < 10 years, from 6.8 to 14.5 mg/day in adolescents (10 to < 18 years) and from 8.0 and 14.0 mg/day in adults [47]. Zinc is present in food as a complex. The majority (>85%) of total body zinc is stored in skeletal muscle and bone [56]. Zinc and copper are mutual antagonists, interfering for absorption in the intestine [92]. Sensitivity to phytate as antagonist of zinc is likely to be significant only when diets are based on unrefined and when calcium intake is also high [145].

The relationship between the quantity of zinc absorbed and that ingested is best fit with saturation response modeling [152]. The zinc pool was found to be correlated to endogenous intestinal excretion of zinc and to total daily absorption of zinc [105].

The quantity of zinc secreted into and excreted from the gastrointestinal tract depends on zinc intake and status [47].

Zn seems to support normal growth and development in pregnancy, childhood, and adolescence [55]. Zinc deficiency is more likely to develop during childhood, when the daily requirement of zinc is higher [32]. Nutritional correction of zinc deficiency may have a significant impact on different aspects of human health [32, 145]. Excess zinc derives from pollution [92]. Zinc is not stored in the body and excess intakes result in reduced absorption and increased excretion [105].

Chronic zinc toxicity, undoubtedly, is associated with symptoms of copper deficiency [105]. Chronic high zinc intake can result in severe neurological diseases attributable to copper deficiency [47]. Very high intakes of zinc over long periods have resulted in anaemia and changes in red and white blood cells indicative of copper deficiency [105].

CHROMIUM

Chromium (Cr) is a metal widely distributed in the environment and can exist in a variety of oxidation states, with the trivalent (Cr (III)) and hexavalent (Cr (VI)) states [45]. Chromium is an essential element involved in the action of insulin [56]. The Cr concentrations are generally highest in lung tissue [90]. There is little information available on chromium (VI) in food [63]. The EFSA CONTAM Panel noted that if even a small proportion of total chromium in food was in the form of Cr (VI), it could contribute substantially to Cr (VI) exposure. Processing and geochemical factors can greatly affect the chromium content of foods [56].

Since chromium is a required nutrient in the body and is normally present in food, chromium is normally present in blood, urine, and body tissues [11]. Chromium has been viewed as an essential element with a role in the maintenance of carbohydrate, fat, and protein metabolism [78].

In 1989, the US National Research Council established the daily dietary intake range 50 to 200 g per day [54]. The UK Committee on Medical Aspects of Food Policy (COMA) suggested 25 g/day chromium for adults [45]. The suggested intakes were 29-30 µg/day during pregnancy and 44-45 µg/day during lactation [68]. Only a small amount (0.4-2.5%) of ingested chromium is absorbed [56]. In humans, the site of absorption also includes the jejunum [78].

Cr is excreted through the urine and feces, predominantly through the urine. Besides, absorbed Cr can be excreted in small quantities in the hair and sweat [11, 78]. In humans, chromium is stored in bone, soft tissue, and organs such as the liver, kidneys and spleen [56]. Cr (VI) is more toxic than Cr (III) [11, 92]. Cr (VI) was classified as carcinogens by IARC [62]. It is also has genotoxic effects [92].

COPPER

Copper (Cu) is present naturally in the environment in the elemental form. Copper in soils may come from a variety of anthropogenic sources: mining and smelting activities [6, 92].

Copper is essential for the normal growth [92], is a component of some enzymes and proteins in the body [46]. Act as oxidases in a variety of biological reactions [56]. Ruminant liver and kidney can be high in copper [145]. Copper is found in a wide range of foods, with major dietary sources being offal, seafood, legumes, nuts and seeds, and to a lesser extent, wheat bran cereals and wholegrain products [56].

Copper absorption is strongly influenced by the amount of dietary copper [92, 106]. Copper is absorbed primarily in the small intestine [56]. Copper is widely distributed in biological tissues [145]. Cu uptake and excretion are efficiently regulated in humans, but when it occurs, it is found more often in children than in adults [55, 92]. Excessive dietary Zn can cause Cu deficiency [55]. Cu deficiency is accompanied by a hypochromic microcytic anaemia similar to that produced by iron deficiency [46]. Excess dietary intakes can in some circumstances be toxic. Similarly to copper deficiency, many of the pathologic effects of copper overload are consistent with oxidative damage to the membrane or to macromolecules [92]. Copper accumulation in the liver and brain results in hepatitis, haemolytic crisis and hepatic failure may ensue [106]. Although, chronic dietary copper toxicity is not generally considered as a significant human health concern [92]. US EPA does not classify copper as a human carcinogen because there are no adequate human or animal cancer studies [6, 121].

NICKEL

Nickel (Ni) is one of many trace metals widely distributed in the environment, being released from both natural sources and anthropogenic activity [18]. Terrestrial plants take up nickel from soil primarily via the roots [143]. Natural nickel is a mixture of five stable isotopes; nineteen other unstable isotopes are known. Although it can exist in several different oxidation states [18, 41]. Some of the metals that nickel can be alloyed with are iron, copper, chromium, and zinc [7]. Nickel may serve as a cofactor of specific metalloenzymes of various functions [68].

Ingestion of nickel in food is the primary route of exposure [7, 63]. Vegetables such as legumes, spinach and lettuce contain more nickel than other food items [82].

Nickel has been measured in a variety of foodstuffs as “total nickel”. Average concentrations are in the range of 0.01-0.1 mg/kg, but can be as high as 8-12 mg/kg in certain foods [63]. The average contribution of this source to the oral intake of nickel is unknown, but could augment dietary exposure by as much as 1 mg/day [62]. The absorption of nickel is dependent on its physicochemical form, with water-soluble forms being more readily absorbed [143]. The rate of absorption of nickel salts can be reduced in the presence of food, such as milk, coffee, tea and orange juice [41]. In the plasma, nickel is transported by binding to albumin [68, 114].

Because of the poor absorption of Ni, the majority of ingested Ni is excreted in the feces. Ni that is absorbed is excreted primarily in the urine [68, 90, 143]. Ni has not been demonstrated to be essential for humans [7, 41, 90]. Some studies have shown that Ni compounds induce oxidative stress, genomic instability, and chromosome damage [82, 114].

The IARC classified nickel compounds as group 1 carcinogen (confirmed carcinogen) to humans [62].

MOLYBDENUM

Molybdenum (Mo) is a transition metal. It exists in several oxidation states, the most stable being +4 and +6. Mo is widely distributed in nature [151]. Mo is ubiquitous in food and water as soluble molybdates [107]. Plants grown on neutral or alkaline soil are rich in molybdenum, those grown on leached acid soil are molybdenum deficient [54, 68, 145].

Molybdenum is an essential trace element [92, 114]. It is required as a component of enzymes involved in the catabolism of sulphur amino acids and heterocyclic compounds, as well as in the metabolism of aromatic aldehydes [40, 107]. Good food sources of Mo are sorghum, pulses, nuts, leafy vegetables, legumes (beans), grains (cereals, wheat germ), organ meats (liver, kidney), milk and eggs. Fruits, root vegetables, and muscle meat are poor sources [40, 92, 107, 151].

There are no reliable estimates of human requirements for Mo and no recommended intake has been established by the EC. Intakes for Mo of 75-250 µg for adults and older children, based on average reported intakes. Mo could be approximately 25 µg/day, corresponding to approximately 0.4 µg/kg bw [54, 107, 145]. Mo in herbage and green vegetables are absorbed by man from 40-50% [145]. Molybdenum absorption is affected by the presence of copper and sulfates [92]. Mo was rapidly cleared from the blood within 24 hours [107].

Absorbed molybdenum is rapidly excreted via the kidney [54, 68, 90]. An important excretion route related to the gastrointestinal excretion is the bile [40].

Mo compounds appear to have low toxicity in humans [68]. Severe Mo toxicity has only been reported in ruminants [114]. Clinical signs of dietary Mo have not been described [40, 68, 92]. There are no relevant studies about carcinogenicity in animals or man [107].

In an area in Armenia, where the population is exposed to a high dietary intake of Mo for geophysical reasons from soil levels of 77 mg Mo/kg and 39 mg Cu/kg, aching joints and goutlike symptoms have been reported. The daily intakes of Mo and Cu, calculated from analysis of levels in different foods, were 10-15 mg Mo/day (equivalent to 0.14-0.21 mg Mo/kg bw/day for a 70 kg adult) and 5-10 mg Cu/day, compared to intakes of 1-2 mg Mo and 10-15 mg Cu in a control area. Biochemical investigations showed abnormally high serum uric acid levels in humans and livestock (81 mg/L in humans with symptoms). Tissue XO activity was also high. Individuals with symptoms had hyperuricosuria and a raised Mo blood level (310 µg/L). Serum molybdate and XO levels were positively correlated with serum uric

acid levels. Serum uric acid levels increased with residence time from 37.5 mg/L after 1 year to 68 mg/L after 5 years. Weaknesses of this study were the low blood Cu level of 1130 µg/L in affected persons vs. 1830 µg Cu/L in controls (possibly contaminated samples) and the ratio of 5 controls to 52 exposed cases. The US NRC concluded that the involvement of Mo was speculative [107].

Because of the deficiencies in the study conducted in Armenia, inadequate data exist to identify a causal association between excess molybdenum intake in normal, apparently healthy individuals and any adverse health outcomes [68].

HEALTH-BASED GUIDANCE VALUES OF METALS

The EFSA Panel on Contaminants in the Food Chain noted that average dietary exposure of **Cd** in European countries is close to or slightly exceeding the TWI of 2.5 µg/kg body weight [34].

Regulation (EC) No 1881/2006 of 19 December 2006 set MRLs for Cd in foodstuffs [28] (See APPENDIX, Table 36). According to USDA GAIN Report [129] ML for Cd is shown in APPENDIX,

Table 37.

The UL for Cd is 0.064 mg/day [59]. The TDI for oral exposure is 0.5 µg/kg bw/day [12, 30]. A health based guidance value for Cd of 7 µg/kg body weight (b.w.) per week (PTWI) was established previously by the JECFA [73] and endorsed by the SCF [34]. US-EPA established an oral RfD (reference dose) of 1 µg/kg bw/day in food [12, 120].

There is no evidence available to define the mechanisms of **As** carcinogenesis and no data to support a threshold, it is not possible to establish health-based level of inorganic arsenic in food and drinking water [68]. Currently, there are no MLs established for arsenic in food at EU level, although MLs are laid down in national legislation in some Member States (MSs) [35, 42, 110]. According to USDA GAIN Report [129] ML for As (inorganic) is shown in APPENDIX,

Table 37. No UL was set for arsenic [68]. Inorganic arsenic was evaluated within the scope of RIVM project. They derived a TDI of 2.1 µg arsenic per kg body weight (bw) per day. The value was based on a PTWI of inorganic arsenic by JECFA in 1989 [12]. The CONTAM Panel concluded that the PTWI of 15 µg/kg b.w. The JECFA's data had shown that inorganic arsenic causes cancer of the lung and urinary bladder in addition to skin, and that a range of adverse effects had been reported at exposures lower than those reviewed by the JECFA [35, 42]. The US-EPA lists an oral RfD for arsenic of 0.3 µg/kg bw/day [12, 123]. Data on European sub-groups with high dietary inorganic arsenic exposure were not available [42].

MLs are established for **Hg** in fishery products and muscle meat of fish and in food supplements. An ML of 0.5 mg/kg wet weight (w.w.) applies to fishery products and muscle meat of fish (including crustaceans, excluding the brown meat of crab and excluding head and thorax meat of lobster and similar large crustaceans [28, 44].

According to USDA GAIN Report [129] ML for **Hg** (total) is shown in APPENDIX,

Table 37. The TDI of organic mercury for oral exposure is 0.1 µg/kg bw/day and TDI of inorganic mercury for oral exposure is 2 µg/kg bw/day [12, 30]. The JECFA set PTWI for methylmercury of 1.6 µg/kg body weight (b.w.) and of 4 µg/kg b.w. for inorganic mercury

[44]. The Panel has therefore proposed a TWI for methylmercury of 1.3 µg/kg bw, which is lower than JECFA's 1.6 µg/kg bw [36, 44]. EPA did not propose a RfD for inorganic mercury [12]. The dietary exposure assessment was based on occurrence of total mercury. The estimated dietary exposure to inorganic mercury in Europe does not indicate a concern [44].

Regulation (EC) No 1831/2003 of 22 September 2003 set MRLs for Pb in foodstuffs [28] (See APPENDIX, Table 1). According to USDA GAIN Report [129] ML for Pb is shown in APPENDIX,

Table 37. The UL for Pb is 0.240 mg/day [59]. The TDI of lead for oral exposure is 3.6 µg/kg bw/day. At this intake level a net accumulation of lead in human organisms is considered highly unlikely [30]. At the JECFA meeting in 1978, the PTWI of 50 µg/kg b.w. for adults was maintained. In 1986, the JECFA addressed the evaluation of the risks associated with the exposure to lead from all sources, specifically as it impacts on infants and children. For this sensitive group the PTWI was set to 25 µg/kg b.w [43].

In 1985, the U.S. EPA considered deriving an RfD for **Pb**, but judged it inappropriate, given the evidence that some adverse health effects (e.g. alterations of some blood enzyme levels and of children's neurobehavioural development) occurred at blood lead levels so low as to be essentially without a threshold [43, 122]. The RDI for Pb is 0 mg/day/person [59]. The EFSA CONTAM Panel evaluated the risk to human health related to the presence of lead in foodstuffs by applying the Margin of Exposure (MOE) 26 approach as there was no evidence for a threshold for the critical endpoints, systolic blood pressure, chronic kidney disease and IQ scores [43]. After due consideration to both limitations of epidemiological data and health significance of observed changes associated with blood lead levels, the CONTAM Panel concluded that the risk of clinically important effects on either the cardiovascular system or kidneys of adult consumers, at current levels of lead exposure is low to negligible. In infants, children and pregnant women, there is potential concern at current levels of exposure to lead for effects on neurodevelopment. Protection of children and women of child-bearing age against the potential risk of neurodevelopmental effects would be protective for all other adverse effects of lead, in all populations [43].

Recommendations on limits for the tolerable intake of **Zn** can be confusing, sometimes conflicting to some extent with recommended nutrient intakes [50]. No available MRL for Zn.

According to Harmanescu M. et al. [59] MAL for Zn is 15 mg/kg (See APPENDIX,

Table 37). An UL of 25 mg/day is recommended (applies also to pregnant and lactating women) [47, 105, 104]. In the opinion of EGVM the Safe Upper Level for daily consumption (UL) over a lifetime is also 25 mg zinc/day for supplemental zinc [48].

According to IOM the UL for adults is 40 mg/day, a value based on reduction in erythrocyte copper-zinc superoxide dismutase activity [68]. A report by the Dutch RIVM in 2001 determined a TDI of 1 mg/kg bw/day for oral intake [12].

WHO proposed a PMTDI of 0.3-1.0 mg/kg, corresponding to 18-60 mg/day for a 60 kg adult [50]. The US-EPA proposed a RfD of 0.3 mg/kg bw/day for zinc and zinc compounds [12, 50, 124]. According to FDA a RDI for Zn is 15 mg/day [128].

According to USDA GAIN Report [129] ML for **Cr** is shown in APPENDIX, Table 37.

The limited data from studies on subchronic, chronic, and reproductive toxicity on soluble trivalent **Cr** salts and the available human data do not give clear information on the dose response relationship. Therefore, a UL can't be derived [68, 104]. WHO considered that supplementation of Cr should not exceed 250 µg/day [104, 145].

A report by the Dutch RIVM in 2001 determined a TDI of 5 µg/kg/day for oral exposure to chromium [12, 50]. The EFSA CONTAM Panel derived a TDI of 0.3 mg/kg b.w. per day for Cr(III) [45]. In the UK it has been recommended that dietary intakes should exceed 0.025 mg/day for adults. In the opinion of the EGVM a total daily intake of about 0.15 mg trivalent chromium per kg body weight and day (or 10 mg/person) would be expected to be without adverse health effects. It was also noted that no adverse effects were observed at intakes of 1000-2000 mg/day Cr III [48, 50].

US EPA oral RfDs for Cr III and Cr VI are 1.5 mg Cr/kg/day and 0.003 mg Cr/kg/day respectively (corresponding to 105 and 0.21mg/day based on EPA assumed 70 kg body weight) [45, 50, 126].

The US FDA has selected a RDI for chromium of 120 µg/day [50, 128].

It should be noted that on the basis of the currently available data it is questionable whether Cr is an essential element. In its opinion on nutrient and energy intakes, the SCF was unable to define a specific physiological requirement for Cr (III) [108]. The mechanism of action of Cr (III) as an essential element has not been identified yet and the reports of clinically relevant chromium deficiency in humans are rare and controversial. The role of Cr (III) as an essential element is currently under evaluation by the EFSA NDA Panel [45].

Mean dietary **Cu** intakes from food of adults in different European countries have been estimated with a range of 1.0-2.3 mg/day for males and 0.9-1.8 mg/day for females [106].

No available MRL for Cu, meanwhile according to Harmanescu M. et al. [59] MAL for Cu is 5 mg/kg (See APPENDIX,

Table 37). According to SCF UL has been established for Cu as 5 mg/day in adults [106]. The upper level of 5 mg/day is not applicable during pregnancy or lactation because of

inadequate data relating to this critical life stage [104]. For children and adolescents UL was established as 1 mg/day for 1-3 years, 2 mg/day for 4-6 years, 3 mg/day for 7-10 years, 4 mg/day for 11-17 years [46]. Besides, according to IOM the UL for adults is 10 mg/day, a value based on protection from liver damage as the critical adverse effect [68].

In the opinion of the EGVM the Safe Upper Level for total daily consumption over a lifetime is 0.16 mg/kg bw/day (equivalent to 10 mg/day in a 60 kg adult) [48].

A report by the Dutch RIVM in 2001 determined a TDI of 140 µg/kg bw/day [12, 50].

The US-EPA proposed RfD for subchronic and chronic toxicity respectively 0.05 mg Cu/kg/day and 0.005 mg Cu/kg/day [50]. According to FDA a RDI for Cu is 2 mg/day [128].

The EFSA CONTAM Panel considers that cause and effect relationship has been established between the dietary intake of copper and the protection of DNA, proteins and lipids from oxidative damage. However, the evidence provided does not establish that inadequate intake of copper leading to impaired protection of DNA, proteins and lipids from oxidative damage occurs in the general EU population [46].

The available studies show that the mean copper intakes of adults and children in EU countries are below the UL. The 97.5 percentile of total copper intakes for all age groups are close to the ULs, which, in the view of the Committee, are not a matter of concern. The Committee notes that the additional copper intakes from drinking water may be appreciable and may need to be taken into account [104].

In the EU, there are currently no maximum levels for Ni in food. Nickel in drinking water intended for human consumption and in natural mineral waters, should not exceed 20 micrograms per litre [36, 37].

According to SCF in the absence of adequate dose-response data for adverse health effects, it is not possible to establish a tolerable upper intake level [104].

The EFSA is asked to derive an upper level for the intake of nickel from food that is unlikely to pose a risk of adverse health effects [41]. The EFSA Scientific Panel on Dietetic Products, Nutrition and Allergies concluded that it was not possible to establish a tolerable upper intake level for intake of nickel from food [37].

According to US IOM the UL for nickel is 1 mg/day [68].

WHO derived a TDI of 5 µg/kg/day through use of an uncertainty factor of 1000 (to compensate for the absence of reliable chronic toxicity / carcinogenicity / reproductive toxicity data) [50].

A report by the Dutch RIVM in 2001 determined a TDI of 50 µg/kg bw/day for oral intake [12].

In February 2015, EFSA published a scientific opinion on the risks to human health from nickel in food, particularly in vegetables, and also in drinking water. EFSA set a safe level, known as the TDI, of 2.8 µg/kg/day. Although, the TDI of 2.8 µg Ni/kg b.w. per day may not be sufficiently protective of individuals sensitized to nickel [36, 37].

US EPA set an RfD of 20 µg Ni/kg/day after employing an uncertainty factor of 300 [12, 37, 50, 125].

The RDI for Ni is 0.5 mg/day/person [59].

Consumption of food with high nickel content and additional exposure from first-run drinking water and kitchen utensils could result in an intake higher than the critical dose. Any additional nickel intake from supplements would further increase the risk. In this context, the EFSA CONTAM Panel draws attention to the high prevalence of nickel sensitisation in the population and to the fact, that many individuals may not be aware that they are sensitized [41, 104]. However, everybody should keep in mind that, at present, nickel, although not released extensively into the environment, may represent a hazard to human health [18].

There are no available data concerning maximum levels for nickel. The UL of approximately 0.01 mg/kg bw/day, equivalent to 0.6 mg/person/day for adults, which also covers pregnant and lactating women [40, 107, 104]. According to US IOM the UL is 2 mg/day [68]. In the opinion of the EGVM there are insufficient data from human or animal studies to establish a Safe Upper Level for molybdenum [48].

A report by the Dutch RIVM in 2001 determined a TDI of 10 µg/kg bw/day for oral intake of Mo [12, 50]. The US EPA proposed a RfD of 5 µg/kg bw/day [12, 50]. According to FDA a RDI for Mo is 75 µg/day [128]. There are no well-designed chronic studies in man which can be used for risk assessment [107]. Because there is no information from national surveys on percentile distribution of Mo intakes, the risk of adverse effects cannot be characterized [68].

1.2. RISK ASSESSMENT AND DIETARY EXPOSURE OF ENVIRONMENTAL CONTAMINANTS

LEGAL AND NORMATIVE FRAME

The food regulation aims at the establishment of a balance between risks and benefits of substances, the European Union (EU) legislation must meet high levels of consumer protection as requested by the Treaty on the Functioning of the European Union (TFUE), Article 169 (Sect.1.2) [26].

Food regulatory system must be based on so called "Risk analysis" approach as ruled by the framework Regulation (EC) No 178/2002 [51] (hereinafter, General Food Law, or GFL) Article 6.

The definition of risk analysis, established by Article 3 of GFL - means a process consisting of three-interconnected components: risk assessment, risk management and risk communication.

"Risk assessment" means a scientifically based process consisting of four steps:

1. Hazard identification
2. Hazard characterization
3. Exposure assessment
4. Risk characterization.

By article 62 of GFL was established that maximum residue levels shall be replaced by the reference to the Standing Committee on the Food Chain and Animal Health.

The regulation No 1881/2006 [28] setting maximum levels for certain contaminants in foodstuffs regulates also the maximum residue limit (MRL) of metals; the section 3 of the annex is related to metal maximum levels in foodstuff. The Regulation (EC) No 629/2008 [24] and Regulation (EU) No 420/2011 [25] amended the previous regulation.

The regulation (EC) No 333/2007 [23] laying down the methods of sampling and analysis for the official control of the levels of lead, cadmium, mercury, inorganic tin, 3-MCPD and benzo(a)pyrene in foodstuffs. Another requirement for analysis is the accreditation of laboratory in compliance with ISO/IEC 17025 standard [66].

APPROACHES OF RISK AND EXPOSURE ASSESSMENT

Principles

The presence of chemical contaminants or other undesirable substances in food and feed is often unavoidable as these substances may occur ubiquitously or are of natural origin [39]. Therefore, human exposure to such substances is also unavoidable. The risk assessment of chemical contaminants in food relies on the integration of two components: knowledge about the human exposure to these substances via food and other routes, and their potential to cause adverse health effects.

Risk assessment at international level provides the scientific bases for the establishment of Codex standards. The Codex Alimentarius Commission Procedural Manual [22] defines the exposure assessment as "the qualitative and/or quantitative evaluation of the intake of biological, chemical and physical agents via food as well as exposures from other sources".

Dietary exposure assessment combines food consumption within the data on concentration of chemicals in food. The resulting dietary exposure estimate is then compared with the relevant toxicological or nutritional reference value for the food chemical. Long-term exposure covers average daily exposure over the entire lifetime.

The general equation for both acute and chronic dietary exposure would be expressed as follows:

$$\text{Dietary exposure} = \frac{\sum(\text{Food chemical concentration} \times \text{Food consumption})}{\text{Body weight}}$$

Total Diet Studies

A Total Diet Study (TDS) can be a complementary approach to traditional monitoring and surveillance programs, which instead of focusing on compliance is designed to provide a solid basis for calculating population dietary exposure and assessing potential impact on public health [38]. The advantages of the TDS approach are as follows:

- They focus on chemicals in the diet rather than individual foods.
- They provide more accurate estimates of human exposure, as the levels are measured in foods as consumed (e.g. peeled or cooked).
- They provide an assessment of background exposures not obtainable from regulatory.

TDS approach offers one of the best means for setting priorities to enable risk managers. The EFSA defines [38] essential principles of a TDS:

1. Representative of the whole diet

2. Pooling of foods
3. Food analysed as consumed.

The TDS can be used as a screening tool and for a refined dietary exposure assessment [139, 140].

Concentration data in a TDS are not based on historical composition data, because estimated dietary exposures are based on the edible portions of the food [134]. Analytical methods should be capable of measuring concentrations of chemicals in foods at appropriate levels. Typically, methods with LODs/LOQs 10-1000 times lower than those needed for enforcement purposes are used for TDSs [38, 137].

Selective studies of individual foods

In some cases, surveys such as a TDS that encompass the whole diet may not be necessary. It is sufficient for a dietary exposure when one, two, or a limited range of foods predominantly influences chemical. This approach involves the measurement of contaminants in representative samples of staple food, either unprocessed or processed with or without cooking. The purpose of such studies is to obtain data about average dietary exposure to a contaminant in order to estimate average population risk [132].

Sampling

The sampling procedure selected and how it is carried out are critical to the validity of the results obtained. Different sampling plans and methods are required, depending on the objectives of the studies.

For a chronic dietary exposure assessment, data based on random composite samples for selected food items may be used. Food items may be taken from different regions, locations, and seasons from different brands, varieties, and even food types in order to be nationally representative [132].

Sample preparation and processing

Sample preparation includes actions taken to prepare the analytical sample from the laboratory (bulk) sample. The chemical concentrations in the edible portion of the commodities are the main interest of the investigation. Sample processing includes physical operations performed to prepare homogeneous matrix to form the analytical sample, from which the test portions for the analysis are taken. In some cases, cooking of food needs to be based on one or more recipes or methods for each food item, in order to account food habits [1]. Special care should also be taken to ensure that the size of the test portion is representative and sufficient for the accurate and reproducible determination of the average chemical/residue content of the analytical sample [21].

Specific design approaches for generating concentration data

A good study design is the most important element of any exposure study [135]. There are two main approaches to analysing foods when generating analytical data from surveys.

Approaches for food consumption data collection

1. Population-based methods

Food supply data at the national level, such as food balance sheets or food disappearance data provide gross annual estimates of the national availability of food commodities. These data may also be used to calculate the average per capita availability of energy and macronutrients and exposure to chemicals. These data do not include water consumption [136].

2. Household-based methods

These methods include data on foodstuffs purchased by a household, follow-up of consumed foods, or changes in food stocks. However, these data do not provide information on the distribution of food consumption among individual members of the household. Household Budget Surveys (HBS) are national surveys mainly focusing on consumption expenditure [38]. They are conducted in all EU Member States and their primary aim (especially at national level) is to calculate weights for the Consumer Price Index. In contrast to food balance sheets, household surveys can supply information on the distribution of food consumption at household level but not for the individuals belonging to the household.

3. Individual-based methods

Data from individual dietary surveys are also understood to more closely reflect actual consumption [79]. Data collected by individual-based methods provide detailed information on food consumption patterns. For instance, several studies [83, 17, 75] have found that nutrient intakes derived from 24-h recalls tend to underestimate true intakes of some macronutrients for some subjects.

a) Food record survey

The food record requires that the subject report all foods consumed during a specified period (usually seven days or less). These surveys generally collect information not only about the types of food consumed but also about the source of the foods. Amounts of each food item consumed may or may not be recorded.

b) Twenty-four-hour recall survey

The 24-h dietary recall consists of a listing of foods and beverages (including drinking-water and sometimes dietary supplements) consumed the previous day or during the 24 h

prior to the recall interview. These surveys collect information not only about the types and amounts of food consumed, but also about the source of the foods and the time of day at which and place where the foods are consumed [117, 94].

c) Food frequency questionnaire

The FFQ, sometimes referred to as a “list-based diet history”, consists of a structured listing of individual foods or food groups. For each item on the food list, the respondent is asked to estimate the number of times the food is usually consumed per day, week, month, or year.

The validity of dietary patterns assessed with FFQs depends on the representativeness of the foods listed in the questionnaire. While some [15, 99] have concluded that FFQs produce valid data for dietary exposure assessments. Schaefer et al. [109] have found that FFQs do not produce reliable estimates of intake of some macronutrients.

d) Diet history survey

The dietary history assesses the daily food of individual and usual meal pattern over varied periods of time [38]. The meal-based diet history is designed to assess usual individual food consumption. It consists of a detailed listing of the types of foods and beverages commonly consumed at each eating occasion over a defined time period, which is often a “typical week”. A trained interviewer probes for the respondent’s customary pattern of food consumption on each day of the typical week [137].

4. Combined methods

Methods for the collection of food consumption data may be combined to improve accuracy and facilitate the validation of the dietary data. They may also be combined for practical reasons. For example, the food record has been combined with the 24-h recall. The FFQ that focused on selected nutrients has been used in addition to the 24-h recall. The 24-h recall is frequently used to help establish the typical meal plan. This information can be used for getting better information from the diet history method. The FFQ may also be used as a cross-check for the other three types of methods [137].

2. MATERIAL AND METHOD

2.1. STUDY SITE

This study covered cities of Kapan (N 39°12'15.60", E 46°27'59.75") and Kajaran (N 39° 9'4.52", E 46° 9'35.71") located in the Republic of Armenia (Picture 1) and recognized as large mining centers with own mining bases. The cities home huge active processing enterprises. Another source of contamination are active and abandoned tailing repositories and untreated industrial wastewater used in watering either directly or when mixed with irrigation waters [101]. These facts largely predetermine specificities of native agro-ecosystems located within natural biogeochemical provinces in mountain river Voghchi valley.

The main minerals of the minefield are molybdenite and chalcopyrite with associated pyrites, magnetite, hematite, sphalerite as well as native tellurium (Te) and gold (Au). Concentrates contain significant amounts of rhenium (Re), selenium (Se) and silver (Ag).

The main food source to local communities includes different fruits and vegetables. The basic source of food staples for local urban population are minimarkets and supermarkets controlled by national authorities, and open markets which sell products both local and brought mostly from other urban settlements of the study region. Another food source for local citizens has been urban agriculture. Highly probable risks of contamination are common to rural communities where the key food source is homegrown produce and barter with neighbors and where no food safety control is exercised by national authorities. So during research the study region was divided based on population groups (urban and rural) and different approaches were employed to conduct risk assessment.

2.2. PLANT SAMPLING

Rural area

With an intention to conduct a chronic risk assessment, this research included random sampling of fruits and vegetables which was done in compliance with WHO and FAO requirements [132]. This was the first ever attempt to analyze dietary exposure in one of Armenia's mining regions; therefore the individual food approach was selected. The approach allows estimating contribution of individual foods to exposures as well as assures the greater flexibility in calculating dietary exposures for various segments of the population, provided appropriate food consumption information is available. In order to get the best representative sample across the diet, multiple samples of the same food were gathered from rural sites throughout the mining region.

All major fruits and vegetables growing in home gardens and intended for home consumption were collected between July and September 2013. Additional details on the sampled plants are given in Table 1.

Agricultural lands selected for this research lie close to mining areas of Kajaran and Kapan and rural communities. From each sampling site seven (7) subsamples were collected and then mixed to obtain a composite sample to ensure its representativeness. Due to availability of fruits and vegetables during a period of sampling at least 3 samples of each fruit and vegetables were collected, the number of samples of a few food items (widely spread and widely consumed throughout the region and largely contributing to the diet) reaching 10.

Totally 84 samples from rural communities were collected and then placed in special clean polyethylene bags intended for plant-origin samples.

Urban area

The farmer markets of Kapan and Kajaran cities were selected for sampling as they are main source for urban population. In each market 2 or 3 vendors were identified and samples were obtained twice from each at different times. About 7-10 fruits/or vegetables of each type were randomly procured from each vendor making in total of 45 samples.

After transportation to the lab the samples were washed with distilled water to remove surface dust and soil particles, then dried and ground until 1mm size particle was reached, and kept at a room temperature for subsequent analyses.

Data of rural and urban communities were separated and analyzed saperately.

In some cases the zone was divided in two areas to avoid from very high standard deviation and to make appropriate assessment of dietary toxicity. Tales located near to Kapan city and Syunik village community were grouped as a 1st zone and tales located near to Kadjaran city grouped in 2nd zone.

2.3. DIGESTION OF SAMPLES

Plant samples were digested by destruction of organic matter through the use of both heat and acids. Acids that have been used in these procedures include sulfuric (H_2SO_4), nitric acid (HNO_3), and perchloric (HClO_4) acids in combination. Hydrogen peroxide (H_2O_2) also was used to enhance reaction speed and to complete the digestion [71]. 1.0 g of dried (80°C) plant material (which has been ground 1.0 mm and homogenized) was placed in a tall-form beaker. After 5.0 mL concentrated HNO_3 with watch glass was added in the mouth of digestion tube and allowed to stand overnight. Covered beaker was placed on a hot plate and heated at 125°C for 1 hour (except As and Hg samples). 2 mL 30% H_2O_2 were added and digested at the same temperature. Heating was continued by 30% H_2O_2 additions until

receiving clear digest. Then a watch glass was removed and temperature lowered to 80°C. Heating was continued until near dryness.

An advantage of wet digestion method is the sampling preparation eliminates elemental loss by volatilization.

2.4. ANALYZES OF HEAVY METALS

Concentrations of Cu, Mo, Ni, Cr, Pb, Zn, Hg, As and Cd in the filtrate of digested plant samples were estimated by using an atomic absorption spectrophotometer (AAS). A Perkin Elmer AAnalyst 800 AAS was used to quantify the total metal concentrations. The instrument was fitted with specific lamp for chemical elements and was calibrated using manually prepared standard solution of respective heavy metals as well as drift blanks. Standard stock solution of 1000 ppm for all the metals was obtained from SchelTec Authorized Distributor of Perkin Elmer. These solutions were diluted for different concentrations to calibrate the instrument. As a fuel was used acetylene gas. Support was provided through distribution of air.

Quality assurance and quality control

To ensure the appropriate quality of data, standard operational procedure was established and several procedures were implemented in order to verify reliability of the results. Water was purified by bio-distillation. Double distilled deionized water was used for solution preparation. Appropriate cleaning of glassware was provided by washing with 10% HNO₃.

Blanc and drift standards obtained from authorized distributor of Perkin Elmer were run after five determinations to calibrate the instrument. The coefficients of variation of replicate analyses were determined and variation less than 10% were considered correct.

Precision and accuracy of analyses was guaranteed by repeated analyses of samples against Standard Reference Material (SRM 1570a) for all heavy metals. The replicate analyses of samples were carried out. The results were found to be within $\pm 2\%$ of the certified values, which declare the accuracy of the purchased results.

2.5. DIET ASSESSMENT METHODS

For a diet study individual based approach was selected; a 24 - hour recall method was combined with a food frequency questionnaire (FFQ) to improve accuracy and facilitate the validation of the dietary data. The 24-h recall was used for establishing typical meal plan. Disadvantage of the method is a seasonal change of diet, for this reason FFQ was used as a “list-based diet history” consisted of a structured listing of individual foods [137].

The 24-hour recall

The survey aims at revealing the degree of contaminant exposure through food consumption. Its findings are expected to contribute to the risk assessment study. 116 males and 129 females at the age 25 to 65 residing close to mining sites, both in urban and rural areas were asked about their food consumption behavior through a 24-hour diet questionnaire. The recall data were collected in-person using a paper-and-pencil approach. The data-collection phase of the research was carried out in August-September, 2013.

Food frequency questionnaire

This study included development of a food frequency questionnaire (FFQ).

The whole set of examined food commodities was included to understand not only portion size, but also frequency of consumption. 97 males and 103 females at age 25 to 65 residing in mining areas were asked for filling out the FFQ. The data-collection phase of the research was carried out in August-September, 2014. All the collected data coded, inputted into a relevantly developed data entry field, processed and analyzed with the help of SPSS software. The food consumption survey involved both male and female respondents in order to implement exposure assessment by gender.

2.6. DATA ANALYSES

Statistical analysis

The significance of difference between food consumption of male and female and also the difference of THQ values between rural and urban areas were analyzed by using Student's t-test. The data of heavy metal concentrations in vegetables and fruits were subjected to analyses of variance (ANOVA) test to assess heavy metal content between different food groups. All the statistical tests were performed using Excel and SPSS software (SPSS Ins., version 11).

Daily intake of metal (DIM)

$$\text{Daily intake of metal (DIM)} = C_{\text{metal}} \times D_{\text{food intake}} / B_{\text{average weight}},$$

where, C_{metal} - heavy metal concentrations in vegetables

$D_{\text{food intake}}$ - daily intake of vegetables

$B_{\text{average weight}}$ - average body weight [115].

Health risk index (HRI)

By using Daily Intake of Metals (DIM) and reference oral dose (RfD) we obtain the health risk index. The following formula is used for the calculation of HRI.

$$HRI = DIM / RfD,$$

where, R_fD - food reference dose for the metal (mg/ kg of body weight per day).

If the value of HRI is less than 1 then the exposed population is said to be safe [58].

Target hazard quotient (THQ)

$$THQ = E_F \times F_D \times DIM / RfD \times W \times T [59].$$

where, E_F - exposure frequency,

F_D - exposure duration,

DIM - daily metal ingestion (mg/person/day),

RfD - oral reference dose (mg/kg/day),

W - average body weight (kg),

T- average exposure time for noncarcinogens (365 days/year × number of exposure years).

For this project E_F was set up at 182.5 days/year, in this area from Armenia (mining areas of Kapan and Kajaran) peoples eat vegetables and fruits from own garden only 6 months a year. Length of exposure (F_D) was set to 59.20 for males and 67.10 for females based on the average life expectancy, starting from 8 years of age [155].

Table 1. Plant samples collected from the experimental sites		
Edible part of sample	Common name	Botanical name
Leaf	Beet	<i>Beta vulgaris</i>
Leaf	Cabbage	<i>Brassica oleracea</i>
Leaf	Potato	<i>Solanum tuberosum</i>
Leaf	Basil	<i>Ocimum basilicum</i>
Leaf	Fennel	<i>Foeniculum vulgare</i>
Root	Carrot	<i>Daucus carota</i>
Root	Onion	<i>Alium cepa</i>
Grain	Maize	<i>Zea mays</i>
Grain	Bean	<i>Phaseolus vulgaris</i>
Friut	Peper sweet	<i>Capsicum annum</i>
Friut	Zucchini	<i>Curcubita pepo</i>
Friut	Tomato	<i>Solanum melongena</i>
Fruit	Cucumber	<i>Cucumis sativus</i>
Fruit	Plum	<i>Prúnus</i>
Friut	Grape	<i>Vitis vinifera</i>
Friut	Eggplant	<i>Solanum melongena</i>
Friut	Cornel	<i>Cornus mas</i>
Friut	Dewberry	<i>Rubus flagellaris</i>

3. RESULTS AND DISCUSSION

3.1. DATA ON VEGETABLES AND FRUITS OBTAINED FROM RURAL COMMUNITIES

3.1.1. The contents and distribution of contaminants in fruit vegetables and grains

The results of investigation (Table 2,

Figure 1) declare that the content of environmental contaminants in fruit vegetables and grains is varying in a wide range. The high content of **Cu** was identified in the samples of *bean* (2nd zone), *maize* and *pepper sweet*. The lowest concentration was recorded in *cucumber* samples.

The highest content of **Mo** was also detected in *bean* samples. The concentration is more than 100 times higher, than the content of the element in *cucumber*, *plum* and *tomatoes*. The high content of **Mo** was detected in *maize* samples.

Maize and *bean* contain relatively high content of **Ni**, while the lowest content was detected in *cucumber* samples.

The highest content of **Cr** also was detected in *maize* samples. Relatively high contents were detected in *bean*, *grape*, *eggplant* and *pepper sweet*. The lowest content of **Cr** was detected in *cucumber*.

Bean, *pepper sweet*, *eggplant* and *grape* contain high concentrations of **Pb**, while the lowest content was detected in *cucumber* samples.

The highest content of **Zn** was detected in *maize* (below the safety limit). Relatively high contents were identified in *bean*, *pepper sweet*, *grape* and *eggplant* samples. The lowest content of **Zn** was detected in *cucumber* samples.

In respect to **Hg**, **As** and **Cd** content in investigated vegetables and fruits, there are not significant concentrations in majority of species. *Bean* (2nd zone) and *grape* contain high content of **Hg**, while *bean* (2nd zone) samples show content of **As** as well.

Table 2. The content of contaminants in fruit vegetables and grains from investigated areas										
Species	Mean/ SD	Content (mg/kg fresh matter)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Safety levels (mg/kg)								
		5	-	-	0,5	0,1	15	0,01	0,05	0,05
Bean (1st zone)*	M	8,78	0,56	2,67	1,85	1,88	8,50	0,002	0,002	0,001
	SD	4,16	0,17	1,18	0,66	0,80	3,27	0,001	0,001	0
Bean (2nd zone)**	M	15,55	58,06	2,70	1,28	1,05	6,80	0,019	0,047	0,012
	SD	3,92	8,46	1,33	0,80	0,20	1,13	0,002	0,001	0,001
Pepper sweet	M	9,53	1,13	1,80	1,30	1,80	8,68	0,004	0,004	0,002
	SD	3,57	0,36	0,54	0,29	0,43	2,25	0,003	0,003	0,001
Maize	M	15,73	6,00	3,87	3,10	2,33	11,77	0,001	0,003	0,001
	SD	0,87	2,78	0,81	0,46	0,25	3,36	0	0,001	0
Plum	M	2,07	0,23	0,63	0,43	0,53	2,80	0,001	0,001	0,001
	SD	0,90	0,06	0,15	0,15	0,12	0,35	0,001	0	0
Grape	M	7,40	1,13	1,60	1,35	1,25	5,68	0,058	0,012	0,003
	SD	1,10	0,51	0,80	0,65	0,45	2,59	0,002	0,008	0,002
Eggplant	M	4,68	0,73	1,18	1,05	1,03	6,32	0,002	0,003	n/d
	SD	1,71	0,33	0,28	0,41	0,40	1,71	0,001	0,003	-
Tomato	M	3,46	0,44	0,88	0,78	0,64	3,22	0,002	0,001	0,002
	SD	1,73	0,25	0,41	0,33	0,19	0,89	0,001	0,001	0,001
Cucumber	M	0,63	0,05	0,14	0,10	0,09	0,49	0,001	0,001	n/d
	SD	0,17	0,01	0,05	0,04	0,02	0,05	0	0,001	-

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to Kadjaran city

With red colour are illustrated the data exceeding safety levels

With blue colour are illustrated the data closed to safety level

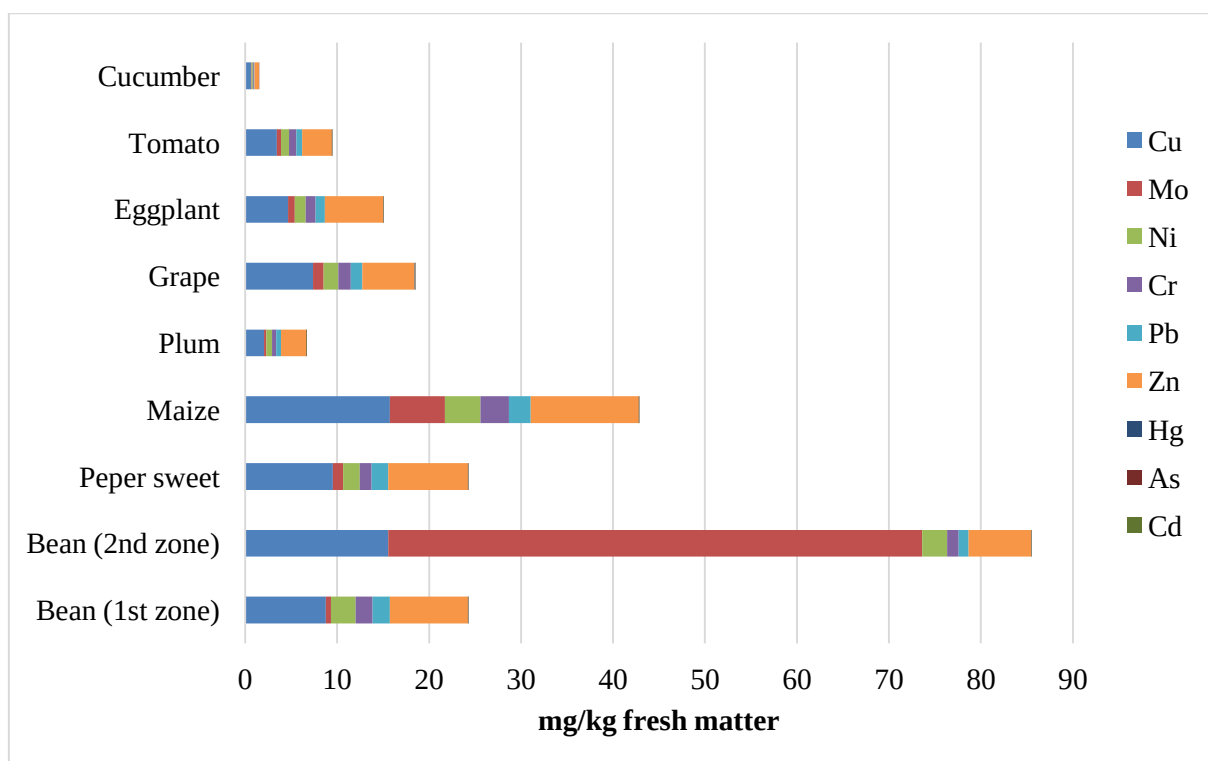


Figure 1. The content of contaminants in fruit vegetables and grains from investigated areas

3.1.2. The content and distribution of contaminants in root vegetables

The Table 3 declares that highest content of **Cu** was detected in *beet* (2nd zone). The relatively high contents were detected in *potato* and *carrot*. The lowest content was identified in *onion bulb*.

The highest content of **Mo** was detected in *potato* (2nd zone). High concentrations of **Mo** were detected in *beet* (2nd zone) and *carrot*. Relatively low content was detected in *onion bulb* samples.

Potato and *beet* contain relatively high content of **Ni**. The lowest concentration was identified in *onion bulb*.

The high content of **Cr** was detected in *beet* (1st zone). The high content was detected in *potato* samples, while the low concentrations were detected in samples of *onion bulb* and *carrot*.

The content of **Pb** in beet and cucumber is exceeding the safety level. Onion bulb contains the lowest quantity of lead.

The highest content of **Zn** was detected in carrot, while the lowest concentration was detected in *onion bulb*.

The significant concentrations of **Hg** were detected in samples of *bean* (1st zone) and *potato* (2nd zone).

Regarding the concentrations of **As** and **Cd**, it was not detected any significant content of mentioned elements.

To conclude, it is possible to declare, that relatively high content of environmental contaminants was detected in *beet* (2nd zone), while *onion bulb* is containing lower concentrations of the same elements (Figure 2).

Table 3. The content of contaminants in root vegetables from investigated areas										
Species	Mean/ SD	Content (mg/kg fresh matter)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Safety levels (mg/kg)								
		5	-	-	0,5	0,1	15	0,01	0,05	0,1
Beet (1st zone)*	M	3,20	0,50	1,40	1,10	0,77	4,00	0,44	0	0,002
	SD	1,71	0,20	0,72	0,50	0,38	2,00	0,17	-	0,001
Beet (2nd zone)**	M	20,43	10,90	1,60	0,83	0,97	5,00	0	0,003	0,008
	SD	6,65	2,69	0,40	0,40	0,40	1,10	n/d	n/d	n/d
Potato (1st zone)	M	9,30	4,67	1,61	0,73	0,73	4,53	0,004	0,003	0,002
	SD	2,33	1,61	0,50	0,06	0,06	0,31	0,001	0,001	0,001
Potato (2nd zone)	M	17,41	12,58	1,55	0,83	0,69	4,24	0,45	0,004	0,014
	SD	4,13	4,50	0,68	0,37	0,19	0,44	0,16	0,001	0,002
Onion bulb	M	0,45	0,43	0,08	0,22	0,01	2,84	0,003	0,002	0,001
	SD	0,04	0,23	0,03	0,16	0,00	1,35	0,00	0,00	0,00
Carrot	M	10,33	11,25	1,49	0,68	0,79	5,38	0,00	0,00	0,01
	SD	1,67	4,75	0,62	0,03	0,09	0,68	0,00	0,00	0,00

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to Kadjaran city

With red colour are illustrated the data exceeding safety levels

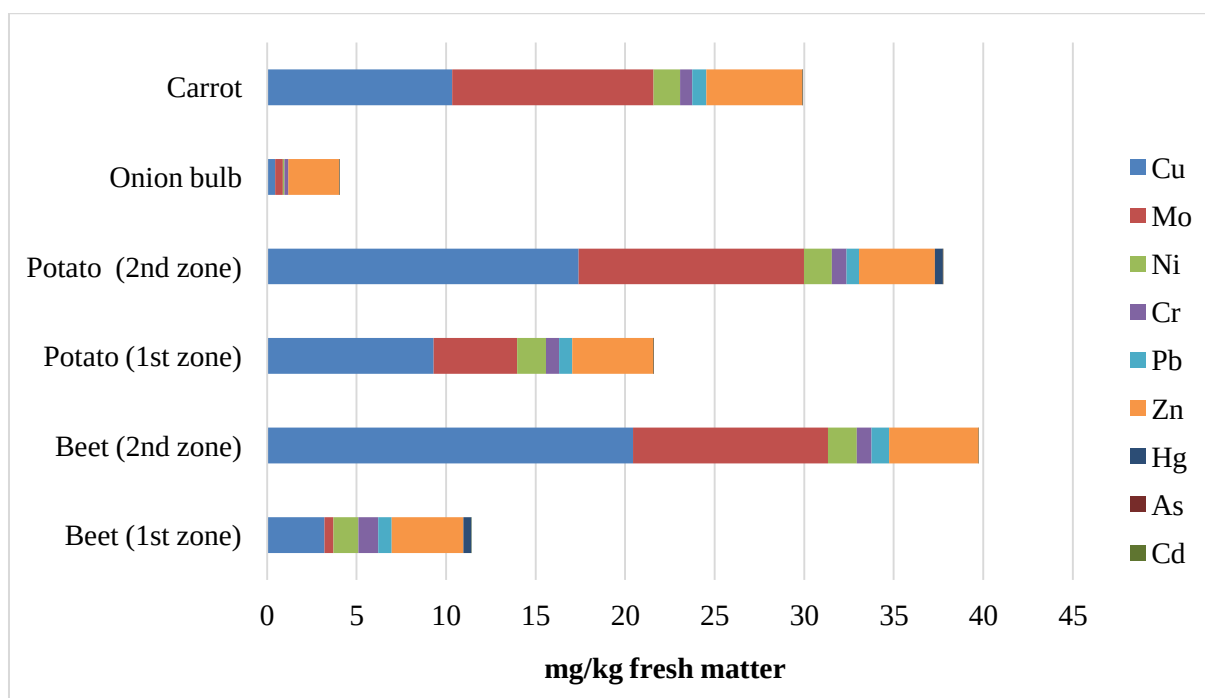


Figure 2. The content of contaminants in root vegetables from investigated areas

3.1.3. The content of contaminants in leafy vegetables

The high concentrations of **Cu**, **Mo**, **Ni** and **Cr** chrome were detected in *fennel* (2nd zone), while the lowest content was in samples of *cabbage* (Table 4).

The samples of *fennel*, *basil* and *onion leaves* showed high content of Pb. Relatively low concentration was detected in *cabbage*.

The highest content of **Zn** was detected in *onion leaves*; meanwhile the lowest concentration was in *cabbage*.

Significant concentration of **Hg** was detected in samples of *fennel* (2nd zone). Regarding to **Cd** there is no any significant content.

Generalizing the obtained data, one may conclude that the samples of *fennel* from 2nd zone have a high level of contamination with environmental contaminants (Figure 3).

Table 4. The content of contaminants in leafy vegetables from investigated areas										
Species	Mean / SD	Content (mg/kg fresh matter)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Safety levels (mg/kg)								
		5	-	-	0,5	0,3	15	0,01	0,05	0,05
Fennel (1st zone)*	M	6,20	0,77	2,57	3,00	1,33	5,63	0,002	0,006	0,001
	SD	0,40	0,21	0,70	1,51	0,06	2,84	0	0,001	0
Fennel (2nd zone)**	M	32,48	80,88	5,53	5,81	1,57	8,57	0,94	0,1	0,024
	SD	6,42	20,22	2,39	1,92	0,46	0,94	0,12	0,011	0,008
Basil	M	6,30	0,62	1,58	1,28	1,66	6,54	0,002	0,001	0,002
	SD	3,11	0,28	0,83	0,66	0,63	3,17	0,001	0	0,001
Cabbage	M	0,99	0,38	0,33	0,63	0,53	3,03	0,001	0,003	n/d
	SD	0,28	0,13	0,06	0,15	0,06	0,15	0,001	0,001	-
Onion leaves	M	24,03	44,10	3,73	3,77	1,13	9,17	n/d	n/d	n/d
	SD	2,24	16,60	0,15	2,68	0,40	1,25	-	-	-

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to Kadjaran city

With red colour are illustrated the data exceeding safety levels

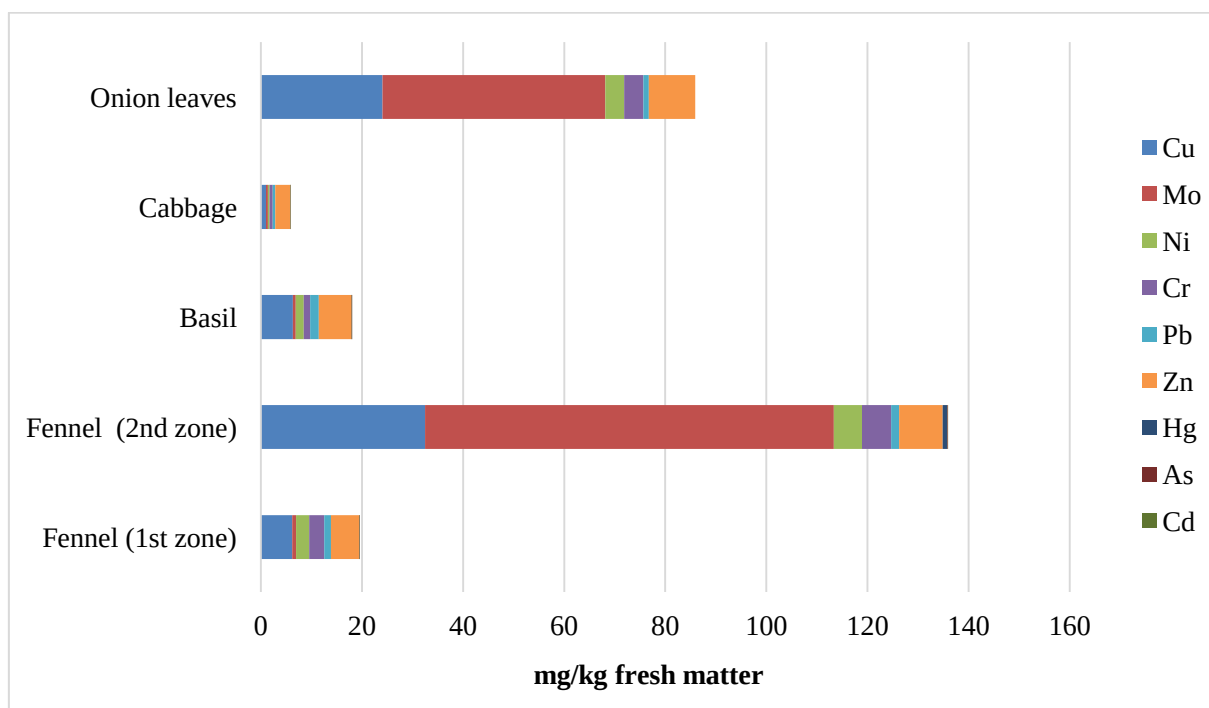


Figure 3. The content of contaminants in leafy vegetables from investigated areas

3.1.4. Comparing characteristics of the investigated elements in different food groups

As it was already mentioned, the food samples were divided in 3 groups based on edible part of food commodity: fruit and grains, root and leafy vegetables. So, the comparing of distribution of the element in different vegetables and fruits is giving an opportunity to understand which vegetables and fruits are accumulating more effective to take into consideration for cultivation. The content of the element was compared for different groups. So, it worth mentioning that the comparing was realized with mean values of concentrations as there is high variation and consequently high standard deviation. The naturally rich soil environment from one site and the pollution from the mining industry from another site are creating not homogenous contamination in different sites of tailing repositories. Therefore, in consequence the high standard deviation of contamination is inevitable.

The distributions of investigated elements are concluded in Figure 4-12.

Table 5. Cu contents in vegetables and fruits from investigated areas (mg/kg fresh matter)										
Species	M	SD		Species	M	SD		Species	M	SD
Bean (1st zone)	8,78	4,16		Beat (1st zone)	3,20	1,71		Fennel (1st zone)	6,20	0,40
Bean (2nd zone)	15,55	3,92		Beat (2nd zone)	20,43	6,65		Fennel (2nd zone)	32,48	6,42
Pepper sweet	9,53	3,57		Potato (1st zone)	9,30	2,33		Basil	6,30	3,11
Maize	15,73	0,87		Potato (2nd zone)	17,41	4,13		Cabbage	0,99	0,28
Plum	2,07	0,90		Onion bulb	0,45	0,04		Onion leaves	24,03	2,24
Grape	7,40	1,10		Carrot	10,33	1,67				
Eggplant	4,68	1,71								
Tomato	3,46	1,73								
Cucumber	0,63	0,17								



- Fruit vegetables and grains



- Root vegetables



- Leafy vegetables

Table 6. Mo content in vegetables and fruits from investigated areas (mg/kg fresh matter)														
Species			M	SD	Species			M	SD	Species			M	SD
Bean (1st zone)			0,56	0,17	Beat (1st zone)			0,50	0,20	Fennel (1st zone)			0,77	0,21
Bean (2nd zone)			58,06	8,46	Beat (2nd zone)			10,90	2,69	Fennel (2nd zone)			80,88	20,22
Pepper sweet			1,13	0,36	Potato (1st zone)			4,67	1,61	Basil			0,62	0,28
Maize			6,00	2,78	Potato (2nd zone)			12,58	4,50	Cabbage			0,38	0,13
Plum			0,23	0,06	Onion bulb			0,43	0,23	Onion leaves			44,10	16,60
Grape			1,13	0,51	Carrot			11,25	4,75					
Eggplant			0,73	0,33										
Tomato			0,44	0,25										
Cucumber			0,05	0,01										

Table 7. Ni contents in vegetables and fruits from investigated areas (mg/kg fresh matter)										
Species	M	SD		Species	M	SD		Species	M	SD
Bean (1st zone)	2,67	1,18		Beat (1st zone)	1,40	0,72		Fennel (1st zone)	2,57	0,70
Bean (2nd zone)	2,70	1,33		Beat (2nd zone)	1,60	0,40		Fennel (2nd zone)	5,53	2,39
Pepper sweet	1,80	0,54		Potato (1st zone)	1,61	0,50		Basil	1,58	0,83
Maize	3,87	0,81		Potato (2nd zone)	1,55	0,68		Cabbage	0,33	0,06
Plum	0,63	0,15		Onion bulb	0,08	0,03		Onion leaves	3,73	0,15
Grape	1,60	0,80		Carrot	1,49	0,62				
Eggplant	1,18	0,28								
Tomato	0,88	0,41								
Cucumber	0,14	0,05								

Table 8. Cr content in vegetables and fruits from investigated areas (mg/kg fresh matter)										
Species	M	SD		Species	M	SD		Species	M	SD
Bean (1st zone)	1,85	0,66		Beat (1st zone)	1,10	0,50		Fennel (1st zone)	3,00	1,51
Bean (2nd zone)	1,28	0,80		Beat (2nd zone)	0,83	0,40		Fennel (2nd zone)	5,81	1,92
Pepper sweet	1,30	0,29		Potato (1st zone)	0,73	0,06		Basil	1,28	0,66
Maize	3,10	0,46		Potato (2nd zone)	0,83	0,37		Cabbage	0,63	0,15
Plum	0,43	0,15		Onion bulb	0,22	0,16		Onion leaves	3,77	2,68
Grape	1,35	0,65		Carrot	0,68	0,03				
Eggplant	1,05	0,41								
Tomato	0,78	0,33								
Cucumber	0,010	0,04								

Table 9. Pb content in vegetables and fruits from investigated areas (mg/kg fresh matter)										
Species	M	SD		Species	M	SD		Species	M	SD
Bean (1st zone)	1,88	0,80		Beta (1st zone)	0,77	0,38		Fennel (1st zone)	1,33	0,06
Bean (2nd zone)	1,05	0,20		Beta (2nd zone)	0,97	0,40		Fennel (2nd zone)	1,57	0,46
Peper sweet	1,80	0,43		Potato (1st zone)	0,73	0,06		Basil	1,66	0,63
Maize	2,33	0,25		Potato (2nd zone)	0,69	0,19		Cabbage	0,53	0,06
Plum	0,53	0,12		Onion bulb	0,01	0,00		Onion leaves	1,13	0,40
Grape	1,25	0,45		Carrot	0,79	0,09				
Eggplant	1,03	0,40								
Tomato	0,64	0,19								
Cucumber	0,09	0,02								

Table 10. Zn content in vegetables and fruits from investigated areas (mg/kg fresh matter)										
Species	M	SD		Species	M	SD		Species	M	SD
Bean (1st zone)	8,50	3,27		Beta (1st zone)	4,00	2,00		Fennel (1st zone)	5,63	2,84
Bean (2nd zone)	6,80	1,13		Beta (2nd zone)	5,00	1,10		Fennel (2nd zone)	8,57	0,94
Peper sweet	8,68	2,25		Potato (1st zone)	4,53	0,31		Basil	6,54	3,17
Maize	11,77	3,36		Potato (2nd zone)	4,24	0,44		Cabbage	3,03	0,15
Plum	2,80	0,35		Onion bulb	2,84	1,35		Onion leaves	9,17	1,25
Grape	5,68	2,59		Carrot	5,38	0,68				
Eggplant	6,32	1,71								
Tomato	3,22	0,89								
Cucumber	0,49	0,05								

Table 11. Hg content in vegetables and fruits from investigated areas (mg/kg fresh matter)										
Species	M	SD		Species	M	SD		Species	M	SD
Bean (1st zone)	0,002	0,001		Beta (1st zone)	0,44	0,16		Fennel (1st zone)	0,002	0
Bean (2nd zone)	0,019	0,002		Beta (2nd zone)	n/d	-		Fennel (2nd zone)	0,94	0,12
Peper sweet	0,004	0,003		Potato (1st zone)	0,004	0,001		Basil	0,002	0,001
Maize	0,001	0		Potato (2nd zone)	0,45	0,15		Cabbage	0,001	0,001
Plum	0,001	0,001		Onion bulb	0,003	0,002		Onion leaves	n/d	-
Grape	0,058	0,002		Carrot	0,002	0,001				
Eggplant	0,002	0,001								
Tomato	0,002	0,001								
Cucumber	0,001	0								

Table 12. As content in vegetables and fruits from investigated areas (mg/kg fresh matter)										
Species	M	SD		Species	M	SD		Species	M	SD
Bean (1st zone)	0,002	0,001		Beta (1st zone)	n/d	-		Fennel (1st zone)	0,006	0,001
Bean (2nd zone)	0,047	0,001		Beta (2nd zone)	0,003	0		Fennel (2nd zone)	0,1	0,011
Peper sweet	0,004	0,003		Potato (1st zone)	0,003	0,001		Basil	0,001	0
Maize	0,001	0		Potato (2nd zone)	0,004	0,001		Cabbage	0,003	0,001
Plum	0,001	0,001		Onion bulb	0,002	0,001		Onion leaves	n/d	-
Grape	0,058	0,002		Carrot	0,002	0,001				
Eggplant	0,002	0,001								
Tomato	0,002	0,001								
Cucumber	0,001	0								

Table 13. Cd content in vegetables and fruits from investigated areas (mg/kg fresh matter)										
Species	M	SD		Species	M	SD		Species	M	SD
Bean (1st zone)	0,001	0		Beta (1st zone)	0,002	0,001		Fennel (1st zone)	0,001	0
Bean (2nd zone)	0,012	0,001		Beta (2nd zone)	0,008	0		Fennel (2nd zone)	0,024	0,008
Peper sweet	0,002	0,001		Potato (1st zone)	0,002	0,001		Basil	0,002	0,001
Maize	0,001	0		Potato (2nd zone)	0,014	0,002		Cabbage	n/d	-
Plum	0,001	0		Onion bulb	0,001	0		Onion leaves	n/d	-
Grape	0,003	0,002		Carrot	0,01	0,005				
Eggplant	n/d	-								
Tomato	0,002	0,001								
Cucumber	n/d	-								

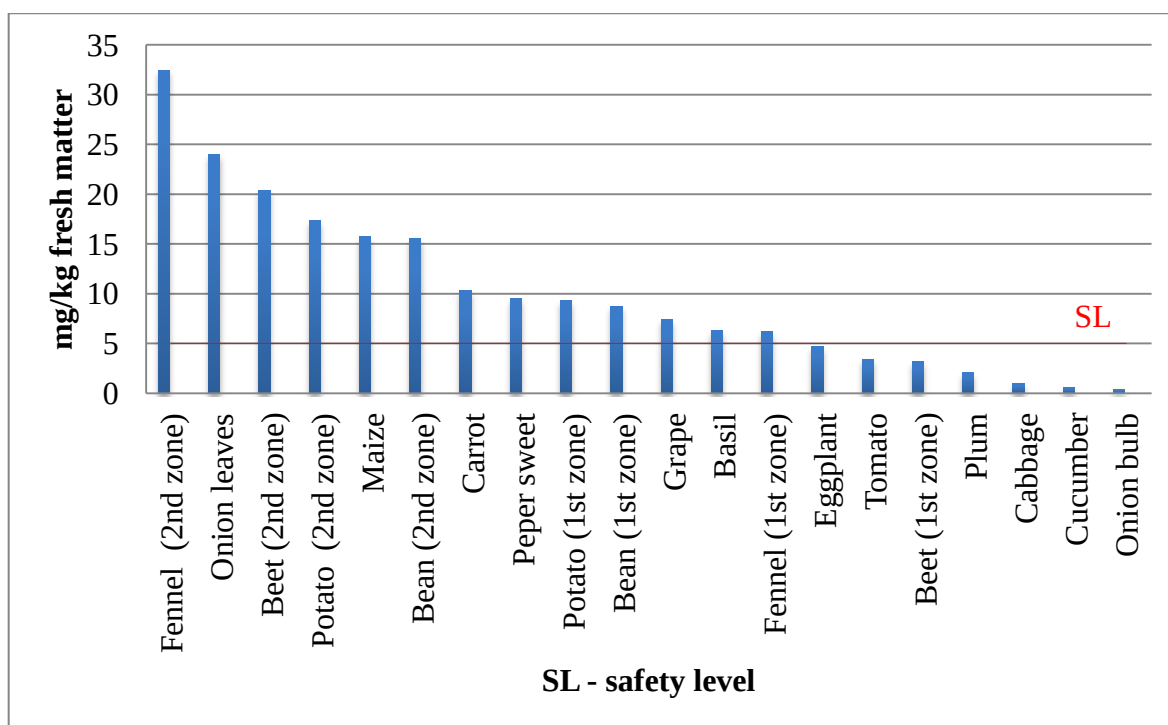


Figure 4. Cu distribution in vegetables and fruits

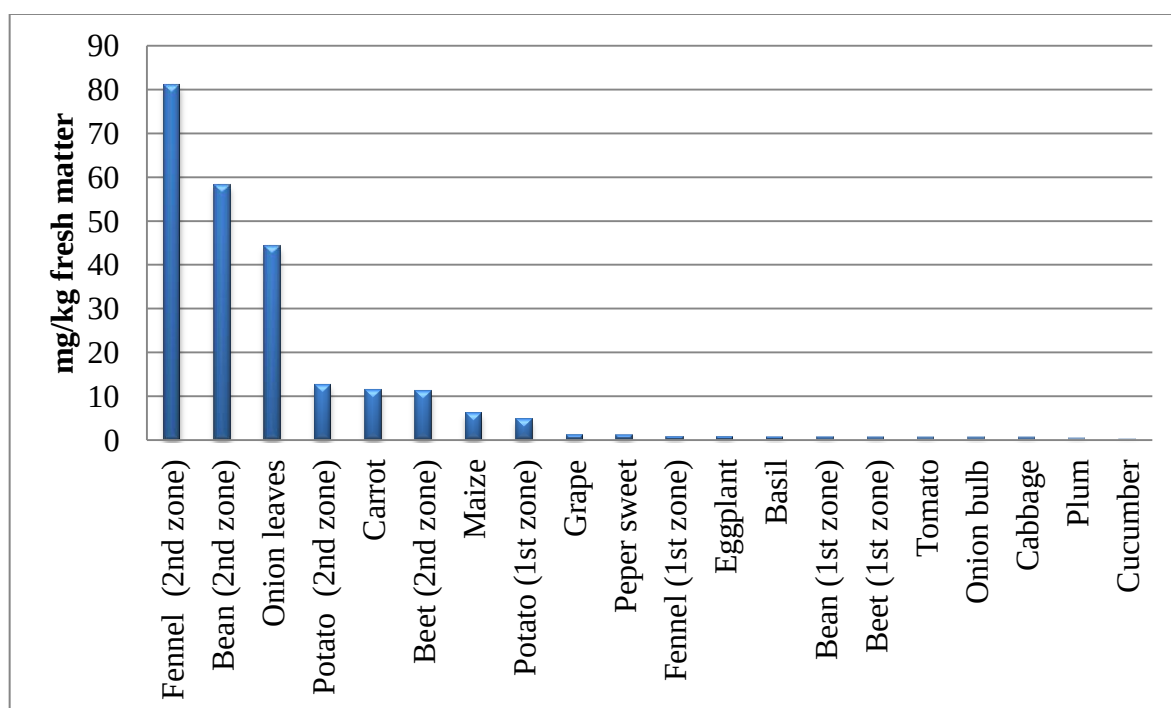


Figure 5. Mo distribution in vegetables and fruits

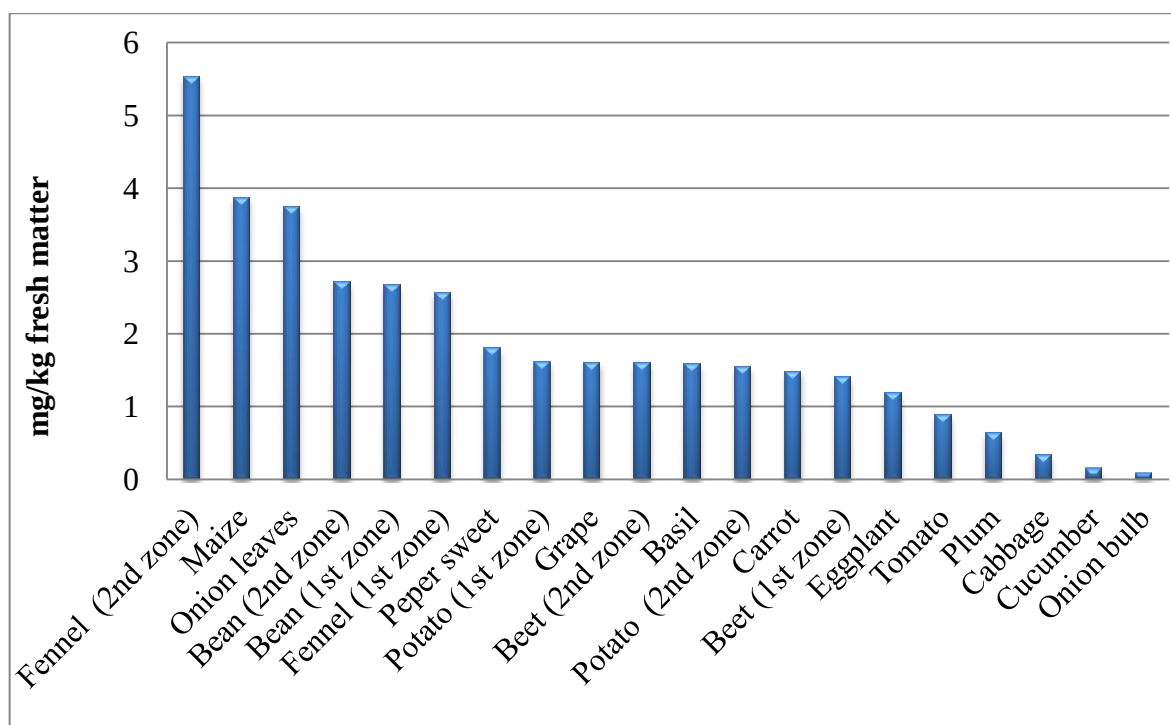


Figure 6. Ni distribution in vegetables and fruits

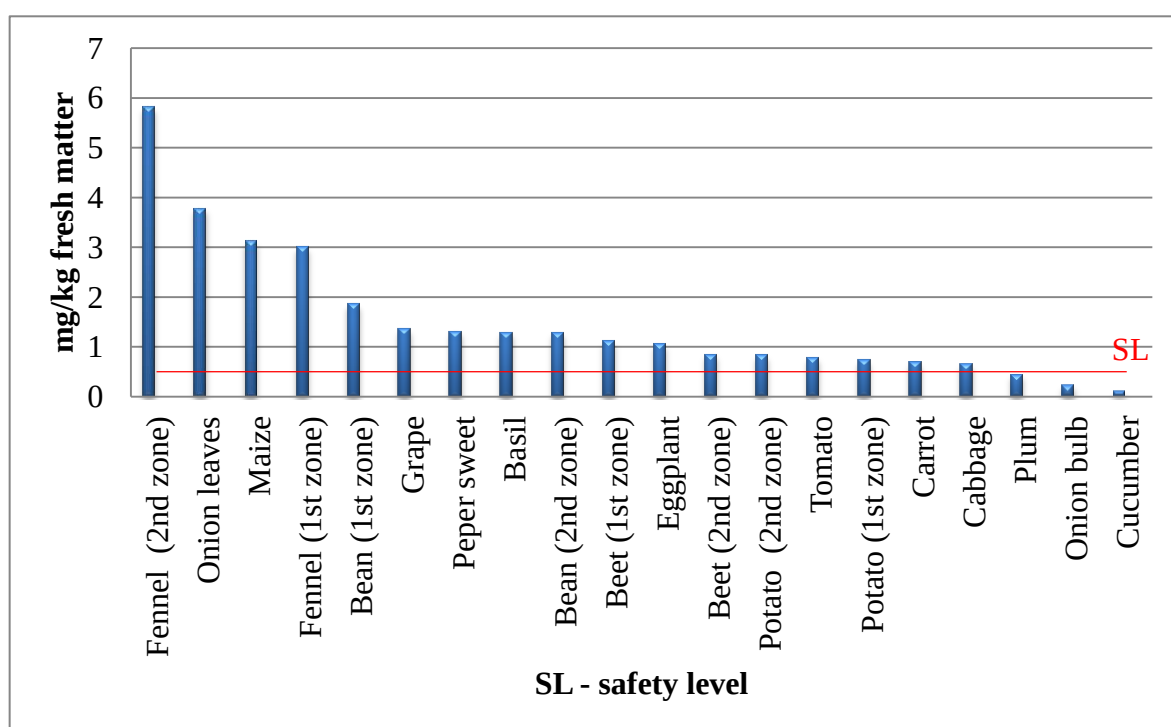


Figure 7. Cr distribution in vegetables and fruits

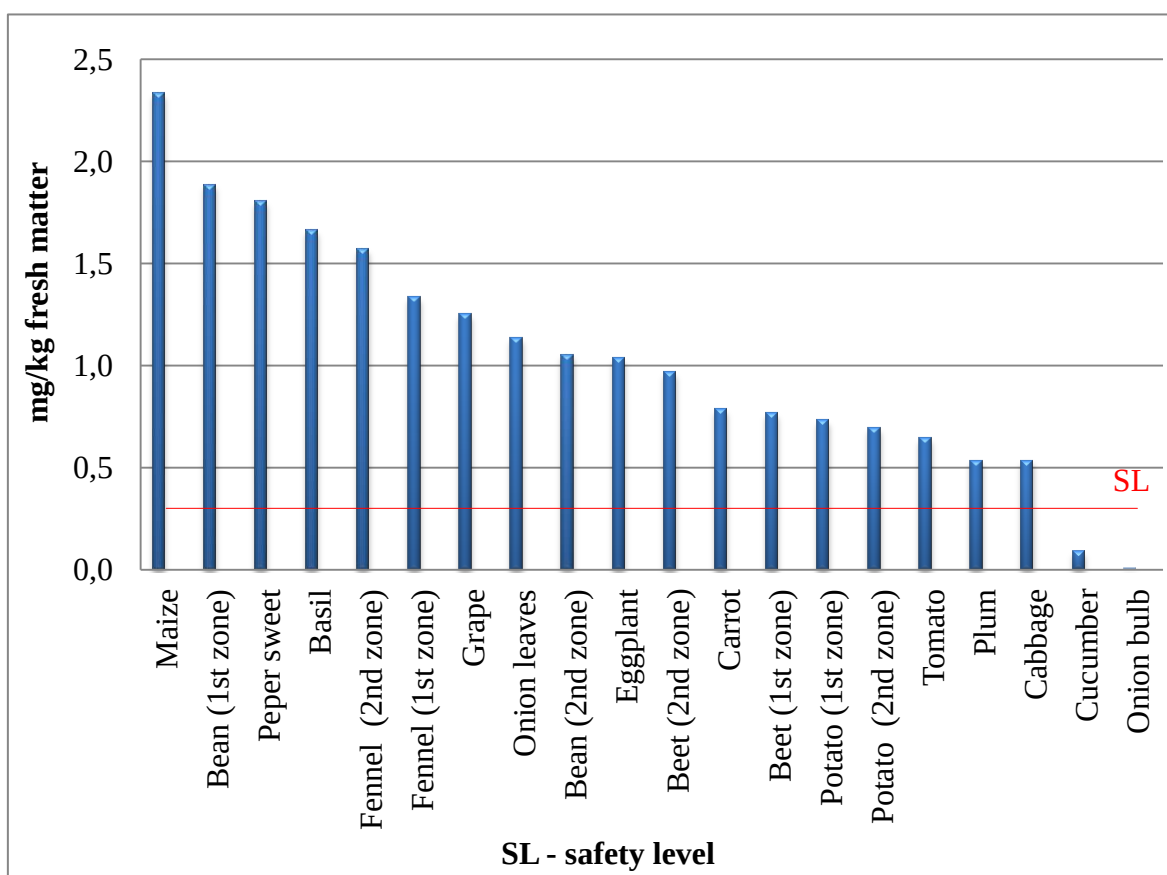


Figure 8. Pb distribution in vegetables and fruits

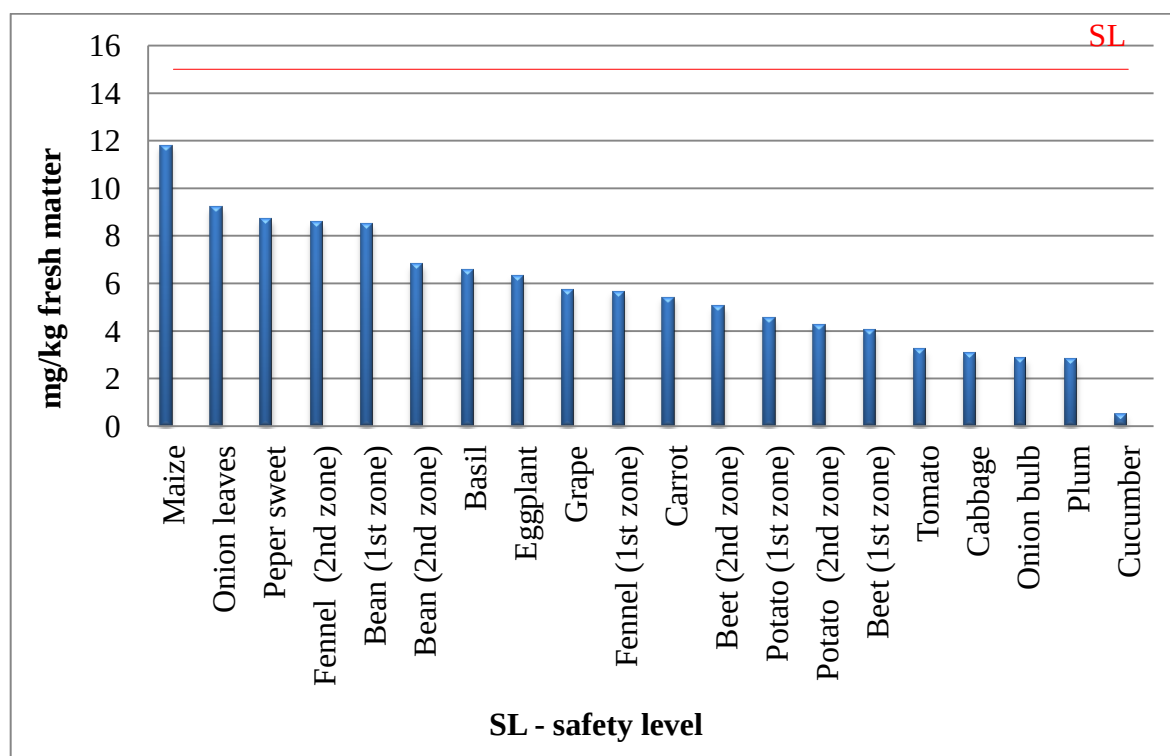


Figure 9. Zn distribution in vegetables and fruits

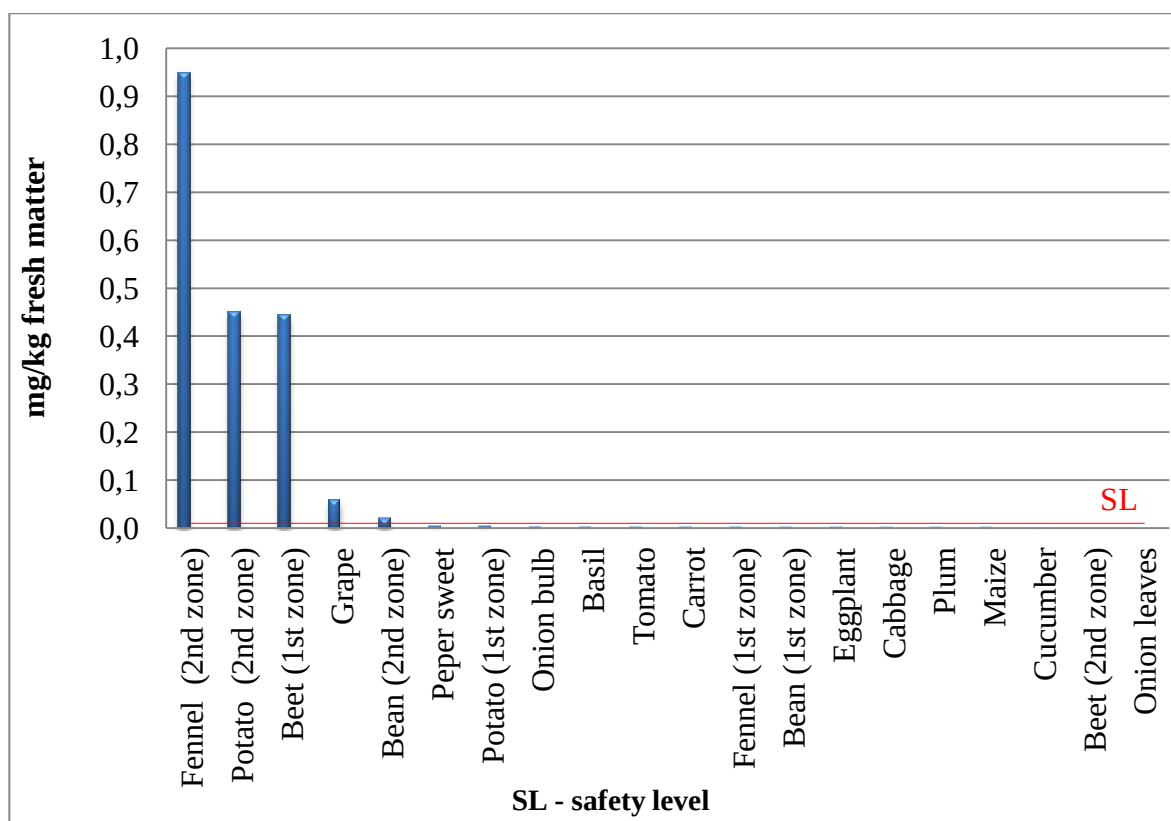


Figure 10. Hg distribution in vegetables and fruits

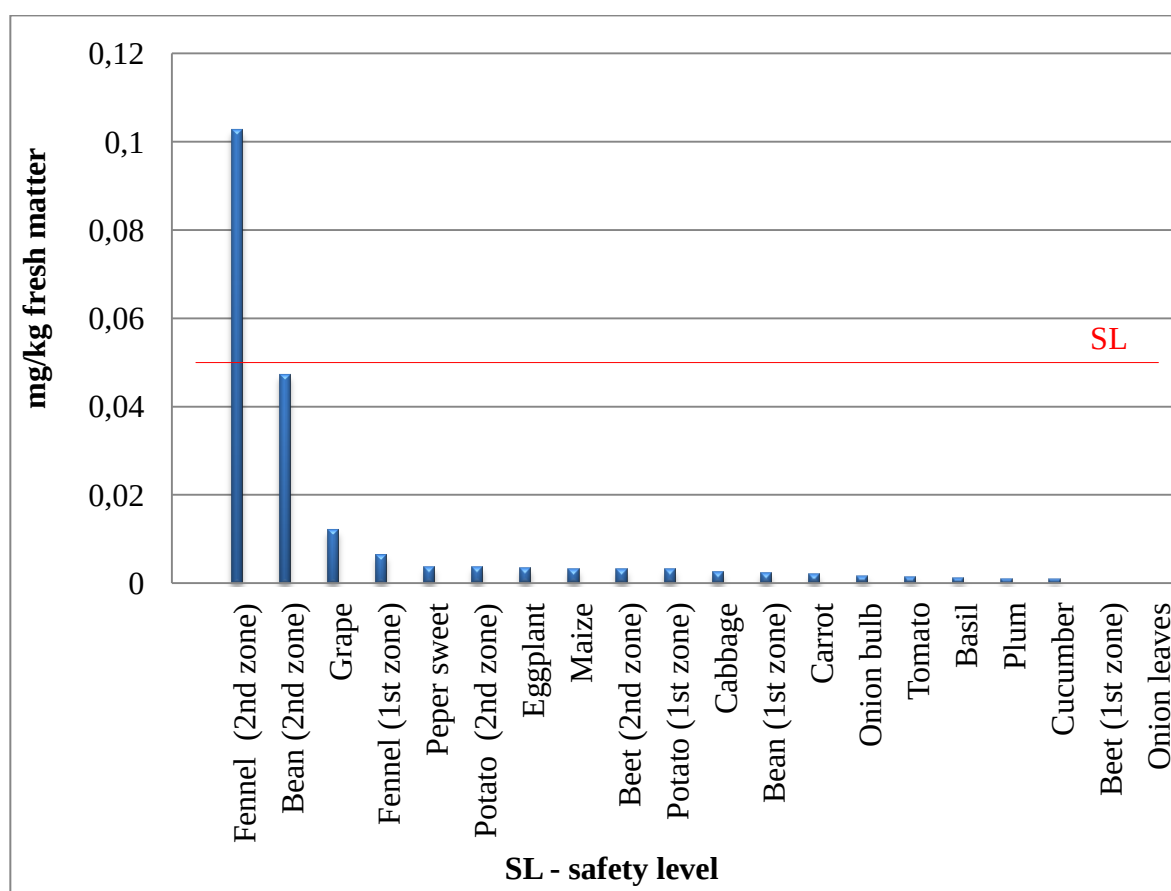


Figure 11. As distribution in vegetables and fruits

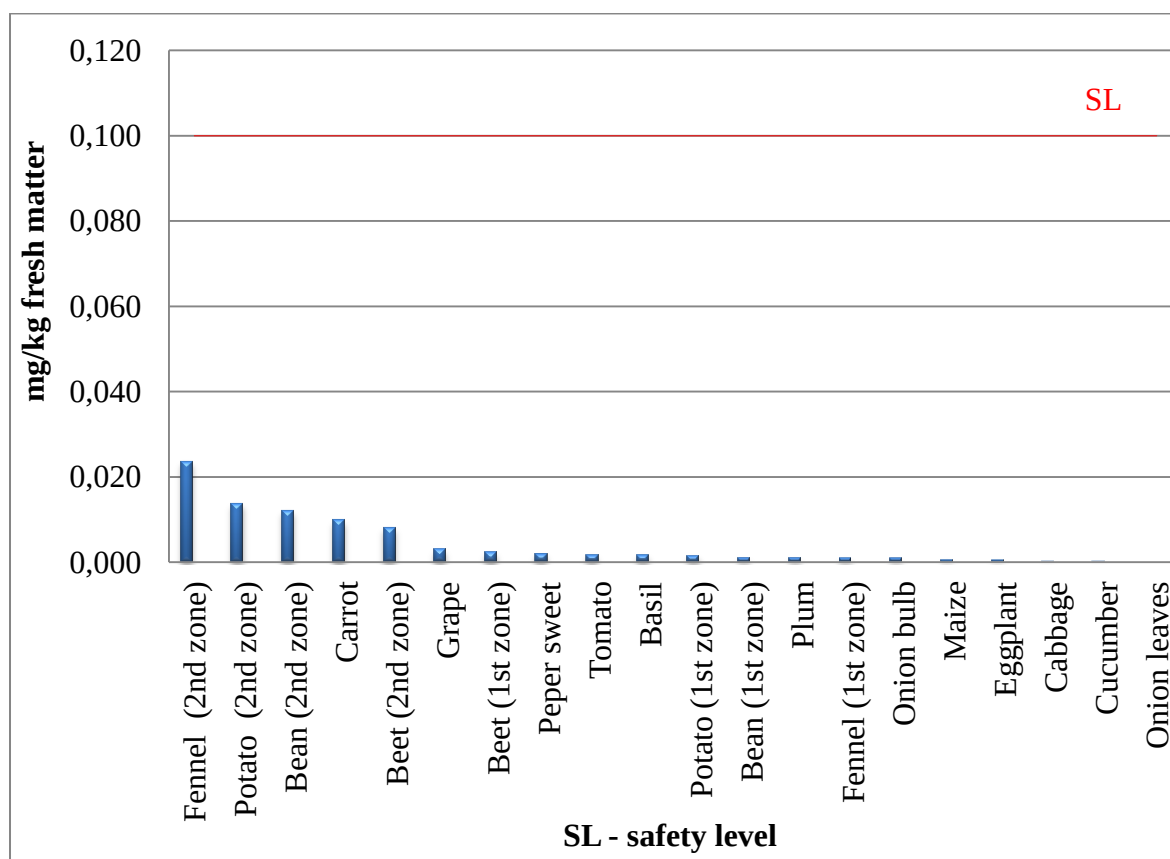


Figure 12. Cd distribution in vegetables and fruits

Concluding the obtained data it is possible to declare that data about concentrations of Cu, Mo, Ni, Cr, Pb, Zn, Hg, As and Cd in different vegetables grown in mining areas of Armenia (rural community) show that there is a significant contamination and the risk assessment is necessary to understand the level of threat and prepare measures of prevention.

The result shows that for Cu (Table 5), Mo (Table 6) and Hg (Table 11) high concentrations were discovered for leafy vegetables and the lowest concentration in fruits. The highest content of Ni (Table 7), Cr (Table 8), Zn (Table 10) and As (Table 12) were detected in samples of leafy vegetables, while the lowest concentrations were discovered in onion bulb and root vegetables.

The mean contents of **Cu** in investigated plants ranged from 0,45-32,48 mg/kg. The obtained results (Table 5, Figure 4) showed that the high content of **Cu** was observed in various vegetables. The highest concentration was detected in *fennel of 2nd zone* (32,48 mg/kg), meanwhile the lowest content was detected in onion bulb.

In *onion leaves*, *beet* (2nd zone), *potato* (2nd zone), *maize*, *carrot*, *pepper sweet*, *potato* (1st zone), *bean* (1st zone) and *grape* were detected high concentrations (respectively 24,03; 20,43; 17,41; 15,73; 10,33; 9,53; 9,30; 8,78 and 7,40 mg/kg) which exceed permissible level (5 mg/kg) [59].

High concentrations can be explained by two important factors: 1) this area is one of Armenia's natural biogeochemical province to which copper-molybdenum mining area belongs 2) presence of 3 tailing repositories (Darazami, Voghchi, Pkhrut) in the surroundings of the Zangezur copper-molybdenum enterprise, where some farmlands are located.

It was found that the peculiarity of accumulation in fruit vegetables is related to the leaves contact with air [4]. Demirezen and Ahmet [31] also declared that Cu (22,19-76,50 mg/kg) content was higher in leafy vegetables in Turkey. Singh et al., [116] reported higher copper contents in spinach in India.

Mean contents of **Mo** contents (Table 6) is highly varying (0,05 - 80,88 mg/kg) depending also on the geochemical peculiarities of the farmlands. Although the highest content was detected in fennel of 2nd zone (80,88 mg/kg), high contents were detected also in vegetables such as bean (2nd zone), onion leaves, potato (2nd zone), carrot and beet (2nd zone) (respectively 58,06; 44,10; 12,58; 11,25 and 10,90 mg/kg) (Figure 5). Such kind of difference is related with the location of farmlands. As described earlier, Kajaran is located in biogeochemical province naturally high in Mo and in this area actively exploits local mine, so vegetables growing in the vicinity of the city show noticeable difference of uptake.

Our study revealed that **Ni** (Table 7) and **Cr** (Table 8) were accumulated more in *leafy vegetables* (except cabbage samples), than in *root vegetables*. The highest contents of **Cr** (Figure 7) and **Ni** (Figure 6) were detected in *fennel*, *maize* and *onion leaves*.

Sharma et al. [112] declare that **Cr** concentration in different vegetables grown in the lands irrigated by wastewater is within the safe limits. Our results are compatible with those of Itanna [67], who noted that *cabbage* was the least accumulator of **Cr**.

Zn contents were similar in all groups of vegetables and there is no significant difference between groups (Table 10, Figure 9).

Fytianos et al. [57] reported that in industrial areas of Greece there is a significant accumulation of Zn in spinach. Radwan and Salama [93] declared that in Egypt the highest levels of Pb, Cd, Cu and Zn were present respectively in strawberries, cucumber, dates and spinach.

The detected concentrations of **Pb** were higher compared with safe limits set by EU commission regulation [28]. Average concentration in fruit vegetables and grains was 1,18

mg/kg (*Table 9*), meanwhile safe limit is 0,4 mg/kg. Only in cucumber samples the concentration is within the safety limit. In root and leafy vegetables the mean concentration is respectively 0,68 mg/kg and 1,1 mg/kg, while the safe limit is 0,5 mg/kg.

Muchuweti et al. [89] reported that concentration of **Pb** (6,77 mg/kg) in vegetables irrigated with mixtures of wastewater and sewage from Zimbabwe were over 22 times the permissible levels allowed by both EU standards and UK guidelines. Sharma et al. [112] declared that Pb concentration (17,54 – 25,00 mg/kg) in vegetables grown in wastewater industrial areas also were exceeding safe limit.

As and **Cd** contents (respectively shown in *Table 12* and *Table 13*) were below safety limit [28]. Mercury concentration over safety level was detected in beet (0,44 mg/kg). Abbas et. al [2] declared that in Pakistan the range of concentration of mercury (0,003 and 0,01 µg/g) in food and feed was over the safety levels (0,03 µg/g) established by the WHO.

3.1.5. Daily Intake of Metals (DIM) for rural population

Dietary exposure of environmental contaminants to humans depends on daily intake. The standard of FAO/WHO [70] has adopted a reference value for tolerable daily intake (TDI). The DIM values for heavy metals are firmly based not only on contamination level, but also on consumption of vegetables grown in contaminated areas.

DIM values both for males and females are generalized in *Table 14-16*.

The DIM value of **Cu** ranged from 0,0003 to 0,094 mg/day. From *Table 15* it is obvious, that except *onion bulb*, the group of root vegetables have higher DIM values, than leafy vegetables (*Table 16*).

The highest DIM of Cu both for males and females was detected in potato of 2nd zone (respectively 0,0945 and 0,0746 mg/kg bw/day), which is higher than RfD of the metal (0,04 mg/kg bw/day). The smallest contribution of DIM of Cu has the samples of cabbage, cucumber and onion bulb.

Established TDI of copper is equal to 0,14 mg/kg bw/day. From obtained data it is obvious, that mixed vegetables exceed the tolerable level also.

DIM values of **Mo** (*Table 14-Table 16*) ranged from 0,0002 to 0,2654 mg/kg bw/day, while the tolerable daily intake established by FAO [70] is 0,01 mg/kg bw/day. The highest DIM values of Mo was detected for *bean* (2nd zone), while the lowest contribution was detected for *cucumber* and *onion bulb* both for males and females.

In some cases individual contribution of selected vegetables exceeded the **TDI** of **Mo**. Both for male and female DIM_{Mo} of beat (2^{nd} zone), potato, carrot, fennel (2^{nd} zone), onion leaves, bean (2^{nd} zone) and maize exceeded tolerable intake (0,01mg/kg bw/day).

Estimated DIM values of Ni (Table 14-Table 16) ranged from 0 to 0,0137 mg/kg bw/day.

The highest DIM values for **Ni** were noticed for *bean*, while *onion bulb* did not contribute detectable DIM values. EFSA established TDI for Ni 2.8 $\mu\text{g/kg/day}$ [36].

Except cucumber, plum and onion bulb DIM values for investigated fruit and root vegetables exceeded tolerable daily intake both for male and female. Except the samples of fennel (2^{nd} zone) the DIM values of Ni for leafy vegetables were below TDI.

DIM values of **Cr** ranged from 0,0001 to 0,0102 mg/kg. The highest values were detected in maize samples, while onion bulb didn't have any significant contribution. Estimated DIM values of Cr were over the TDI for majority of investigated fruit vegetables. DIM values of Cr were below TDI for root and leafy vegetables.

The results shown in Table 14 declare that fruit vegetables and grains have higher DIM value of **Pb** than root and leafy vegetables (Table 15 and Table 16). The highest DIM values of **Pb** were detected in *bean* (1^{st} zone) both for male and female. Onion bulb didn't showed any contribution of DIM values of Pb.

The FAO/WHO adopted a provisional tolerable weekly intake (PTWI) of 25 $\mu\text{g Pb/kg}$ body weight for humans [70]. In Canada the dietary intake of lead is 168 $\mu\text{g/week}$ for a 60 kg person [60].

Only weekly consumption of beans during summer (almost 1 kg per week) provide higher intake, than the FAO/ WHO PTWI.

DIM values of Zn ranged from 0,0016 to 0,0437 mg/kg. The view is another in the case of Zn as in all investigated vegetables and fruits DIM values were below TDI (1 mg/kg bw/day).

Significant DIM values of Hg were detected in samples of potato (2^{nd} zone). For As and Cd significant DIM values were not detected.

Cui et al. [27] reported high exposure of Cd and Pb for local residents in Nanning, China, but for Cu and Zn there was no risk.

Concluding the obtained results of DIM values it is possible to declare, that in several cases even single consumption of selected vegetable contributes higher level of intake, than the reference dose or even TDI. For bean and maize even single consumption provides high values of intake of Mo, Ni, Cr and Pb. So, this fact must be taken in consideration and the

population must be aware about risks of cultivation of mentioned vegetables. Cucumber, onion bulb, cabbage and plum have small contribution of DIM of copper.

Table 14. Daily intake of metals estimate for fruit vegetables and grains from rural areas										
Species	Gender	Daily intake of metals (mg/kg/day)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Tolerable daily intak of metals (mg/ kg/day)								
		0,14	0,01	0,0028	0,005	0,0036	1	0,002	0,0021	0,0005
Bean (1st zone)*	male	0,0452	0,0029	0,0137	0,0095	0,0097	0,0437	0,0000	0,0000	0,0000
	female	0,0402	0,0026	0,0122	0,0085	0,0086	0,0389	0,0000	0,0000	0,0000
Bean (2nd zone)**	male	0,0578	0,2157	0,0100	0,0047	0,0039	0,0253	0,0001	0,0002	0,0000
	female	0,0711	0,2654	0,0124	0,0058	0,0048	0,0311	0,0001	0,0002	0,0001
Pepper sweet	male	0,0340	0,0040	0,0064	0,0046	0,0064	0,0310	0,0000	0,0000	0,0000
	female	0,0299	0,0035	0,0057	0,0041	0,0057	0,0273	0,0000	0,0000	0,0000
Maize	male	0,0517	0,0197	0,0127	0,0102	0,0077	0,0387	0,0000	0,0000	0,0000
	female	0,0494	0,0189	0,0122	0,0097	0,0073	0,0370	0,0000	0,0000	0,0000
Plum	male	0,0077	0,0009	0,0024	0,0016	0,0020	0,0104	0,0000	0,0000	0,0000
	female	0,0056	0,0006	0,0017	0,0012	0,0014	0,0076	0,0000	0,0000	0,0000
Grape	male	0,0317	0,0049	0,0069	0,0058	0,0054	0,0244	0,0002	0,0001	0,0000
	female	0,0264	0,0040	0,0057	0,0048	0,0045	0,0203	0,0002	0,0000	0,0000
Eggplant	male	0,0238	0,0037	0,0060	0,0053	0,0053	0,0321	0,0000	0,0000	0,0000
	female	0,0221	0,0035	0,0056	0,0050	0,0049	0,0298	0,0000	0,0000	0,0000
Tomato	male	0,0188	0,0024	0,0048	0,0042	0,0035	0,0175	0,0000	0,0000	0,0000
	female	0,0173	0,0022	0,0044	0,0039	0,0032	0,0161	0,0000	0,0000	0,0000
Cucumber	male	0,0029	0,0002	0,0007	0,0005	0,0004	0,0022	0,0000	0,0000	0,0000
	female	0,0025	0,0002	0,0006	0,0004	0,0004	0,0019	0,0000	0,0000	0,0000

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to KaKajaranjan city

With red colour are illustrated the data exceeding TDI

With blue colour are illustrated the data closed to TDI

Table 15. Daily intake of metals estimate for root vegetables from rural areas										
Species	Gender	Daily intake of metals (mg/kg/day)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Tolerable daily intake of metals (mg/ kg/day)								
		0,14	0,01	0,0028	0,005	0,0036	1	0,002	0,0021	0,0005
Beet (1st zone)*	male	0,0082	0,0013	0,0036	0,0028	0,0020	0,0103	0,0011	0,0000	0,0000
	female	0,0091	0,0014	0,0040	0,0031	0,0022	0,0114	0,0013	0,0000	0,0000
Beet (2nd zone)**	male	0,0525	0,0280	0,0041	0,0021	0,0025	0,0129	0,0000	0,0000	0,0000
	female	0,0584	0,0311	0,0046	0,0024	0,0028	0,0143	0,0000	0,0000	0,0000
Potato (1st zone)*	male	0,0505	0,0253	0,0088	0,0040	0,0040	0,0246	0,0000	0,0000	0,0000
	female	0,0399	0,0200	0,0069	0,0031	0,0031	0,0194	0,0000	0,0000	0,0000
Potato (2nd zone)**	male	0,0945	0,0683	0,0084	0,0045	0,0038	0,0230	0,0024	0,0000	0,0001
	female	0,0746	0,0539	0,0066	0,0036	0,0030	0,0182	0,0019	0,0000	0,0001
Onion bulb	male	0,0003	0,0002	0,0000	0,0001	0,0000	0,0016	0,0000	0,0000	0,0000
	female	0,0003	0,0002	0,0000	0,0001	0,0000	0,0016	0,0000	0,0000	0,0000
Carrot	male	0,0266	0,0289	0,0038	0,0017	0,0020	0,0138	0,0000	0,0000	0,0000
	female	0,0339	0,0370	0,0049	0,0022	0,0026	0,0177	0,0000	0,0000	0,0000

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to Kajaran city

With red colour are illustrated the data exceeding TDI

With blue colour are illustrated the data closed to TDI

Table 16. Daily intake of metals estimate for leafy vegetables from rural areas										
Species	Gender	Daily intake of metals (mg/kg/day)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Tolerable daily intake of metals (mg/ kg/day)								
		0,14	0,01	0,0028	0,005	0,0036	1	0,002	0,0021	0,0005
Fennel (1st zone)*	male	0,0044	0,0005	0,0018	0,0021	0,0010	0,0040	0,0000	0,0000	0,0000
	female	0,0044	0,0005	0,0018	0,0021	0,0010	0,0040	0,0000	0,0000	0,0000
Fennel (2nd zone)**	male	0,0232	0,0578	0,0039	0,0042	0,0011	0,0061	0,0007	0,0001	0,0000
	female	0,0232	0,0578	0,0039	0,0042	0,0011	0,0061	0,0007	0,0001	0,0000
Basil	male	0,0045	0,0004	0,0011	0,0009	0,0012	0,0047	0,0000	0,0000	0,0000
	female	0,0045	0,0004	0,0011	0,0009	0,0012	0,0047	0,0000	0,0000	0,0000
Cabbage	male	0,0034	0,0013	0,0011	0,0022	0,0018	0,0104	0,0000	0,0000	0,0000
	female	0,0028	0,0011	0,0010	0,0018	0,0015	0,0087	0,0000	0,0000	0,0000
Onion leaves	male	0,0137	0,0252	0,0021	0,0022	0,0006	0,0052	0,0000	0,0000	0,0000
	female	0,0137	0,0252	0,0021	0,0022	0,0006	0,0052	0,0000	0,0000	0,0000

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to Kajaran city

With red colour are illustrated the data exceeding TDI

3.1.6. Health Risk Index (HRI) for rural population

Health risk index was calculated to assess the potential of investigated vegetables and fruits to cause adverse health effects. The results of investigation are generalized in Tables 17-19 and in Figures 13-15.

From indicated tables it is obvious, that Cu, Mo, Ni and Cr have high health risk indexes. In several cases, the health risk index is high even for single vegetable consumption.

The HRI for Cu was more than 1 for beet (2nd zone) potato, bean and maize both for males and females. It means that even single consumption of those vegetables can have negative health impact. For several vegetables it was closed to safety limit, such as pepper sweet (0,85 for males and 0,75 for females) and grape (0,79 for males and 0,66 for females). Only cucumber and onion bulb have low HRI.

Mo HRI ranged from 0,04 to 53,08. This means, that several vegetables do not have significant health risk, while selected vegetables from 2nd zone such as bean, potato and fennel have a value more than 10, which declares that risks are obvious and precautions must be undertaken. The results of investigation show, that cucumber and onion bulb don't have any significant contribution for Mo exposure, while some vegetables such as maize, beet (2nd zone), potato (1st zone), carrot and onion leaves can have a probability to cause negative health impact.

It should be stressed that the significant difference (almost 100 times) was established between DIM values for bean from 1st and 2nd zones.

For Ni the high HRI were detected for bean, maize and pepper sweet. The lowest index for Ni was detected in cucumber, while onion bulb didn't have detectable value. None of vegetables and fruits has a HRI of Ni, which exceeds the safety level, but combined HRI data is more than 3 for 1st zone and more than 1 for 2nd zone. HRI_{Ni} of bean and maize for female is equal to 0,61, while for males it is respectively 0,69 and 0,64 which declares that mixing of this vegetables in a diet will contribute the HRI more than 1. Generalizing obtained data it is possible to argue that risks exist for Ni also.

The HRI data for Cr show potential to cause health risks, as for several vegetables such as bean, pepper sweet, maize, grape, eggplant, tomato, beet (1st zone for female), potato and fennel (2nd zone) the HRI is more than 1, which is a fact that consumer health protection is not guaranteed.

The view of Pb in the sense of HRI is quite diverse. In some cases, particularly for vegetables such as bean, maize, grape, eggplant, the values exceed the safety limit till 2 times even for single consumption, while for cucumber it is equal to 0,1. Obtained data of HRI for Pb declare that there is a potential to cause health problems.

In the present study Zn, Hg, As and Cd were not found to cause any risk to the local population for majority of analyzed vegetables. For Hg only beet (1st zone) and potato (2nd zone) indicated HRI more than 1.

Concluding the results it is possible to declare that health risk index bases on high proportion of vegetables in diet. Observed contamination in plants have greatest potential to pose health risk to the consumers.

Table 17. Health risk index for rural population for fruit vegetables and grains										
Species	Gender	HRI of metals								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
Bean (1st zone)*	male	1,13	0,57	0,69	3,17	2,77	0,15	0,01	0,04	0,01
	female	1,00	0,51	0,61	2,82	2,46	0,13	0,01	0,04	0,00
Bean (2nd zone)**	male	1,44	43,13	0,50	1,58	1,12	0,08	0,07	0,58	0,04
	female	1,78	53,08	0,62	1,95	1,37	0,10	0,09	0,72	0,05
Pepper sweet	male	0,85	0,80	0,32	1,55	1,84	0,10	0,01	0,04	0,01
	female	0,75	0,71	0,28	1,36	1,62	0,09	0,01	0,04	0,01
Maize	male	1,29	3,94	0,64	3,4	2,19	0,13	0,00	0,03	0,00
	female	1,24	3,77	0,61	3,25	2,10	0,12	0,00	0,03	0,00
Plum	male	0,19	0,17	0,12	0,54	0,57	0,03	0,00	0,01	0,00
	female	0,14	0,13	0,09	0,39	0,41	0,03	0,00	0,01	0,00
Grape	male	0,79	0,97	0,34	1,93	1,53	0,08	0,25	0,17	0,01
	female	0,66	0,81	0,29	1,61	1,28	0,07	0,21	0,14	0,01
Eggplant	male	0,60	0,75	0,30	1,78	1,50	0,11	0,01	0,06	0,00
	female	0,55	0,69	0,28	1,65	1,39	0,10	0,01	0,05	0,00
Tomato	male	0,47	0,48	0,24	1,41	0,99	0,06	0,01	0,03	0,01
	female	0,43	0,44	0,22	1,3	0,91	0,05	0,01	0,02	0,01
Cucumber	male	0,07	0,05	0,03	0,15	0,12	0,01	0,00	0,01	0,00
	female	0,06	0,04	0,03	0,13	0,10	0,01	0,00	0,01	0,00

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to Kajaran city

With red colour are illustrated the data exceeding 1

Table 18. Health risk index for rural population for root vegetables										
Species	Gender	HRI of metals								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
Beet (1st zone)*	male	0,21	0,26	0,18	0,94	0,56	0,03	1,14	0,00	0,01
	female	0,23	0,29	0,20	1,05	0,63	0,04	1,27	0,00	0,01
Beet (2nd zone)**	male	1,31	5,61	0,21	0,73	0,71	0,04	0,00	0,03	0,02
	female	1,46	6,23	0,23	0,79	0,79	0,05	0,00	0,03	0,02
Potato (1st zone)	male	1,26	5,07	0,44	1,32	1,13	0,08	0,02	0,05	0,01
	female	1,00	4,00	0,35	1,04	0,89	0,06	0,02	0,04	0,01
Potato (2nd zone)	male	2,36	13,66	0,42	1,5	1,07	0,08	2,44	0,06	0,07
	female	1,87	10,78	0,33	1,18	0,85	0,06	1,93	0,05	0,06
Onion bulb	male	0,01	0,05	0,00	0,04	0,00	0,01	0,00	0,00	0,00
	female	0,01	0,05	0,00	0,04	0,00	0,01	0,00	0,00	0,00
Carrot	male	0,66	5,79	0,19	0,58	0,58	0,05	0,01	0,02	0,03
	female	0,85	7,39	0,24	0,74	0,74	0,06	0,01	0,02	0,03

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to Kajaran city

With red colour are illustrated the data exceeding 1

Table 19. Health risk index for rural population for leafy vegetables										
Species	Gender	HRI of metals								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
Fennel (1st zone)*	male	0,11	0,11	0,09	0,71	0,27	0,01	0,00	0,02	0,00
	female	0,11	0,11	0,09	0,71	0,27	0,01	0,00	0,02	0,00
Fennel (2nd zone)**	male	0,58	11,55	0,20	1,38	0,32	0,02	0,68	0,24	0,02
	female	0,58	11,55	0,20	1,38	0,32	0,02	0,68	0,24	0,02
Basil	male	0,11	0,09	0,06	0,31	0,34	0,02	0,00	0,00	0,00
	female	0,11	0,09	0,06	0,31	0,34	0,02	0,00	0,00	0,00
Cabbage	male	0,08	0,26	0,06	0,72	0,52	0,03	0,00	0,03	0,00
	female	0,07	0,22	0,05	0,60	0,44	0,03	0,00	0,02	0,00
Onion leaves	male	0,34	5,04	0,11	0,72	0,19	0,02	0,00	0,00	0,00
	female	0,34	5,04	0,11	0,72	0,19	0,02	0,00	0,00	0,00

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to Kajaran city

With red colour are illustrated the data exceeding 1

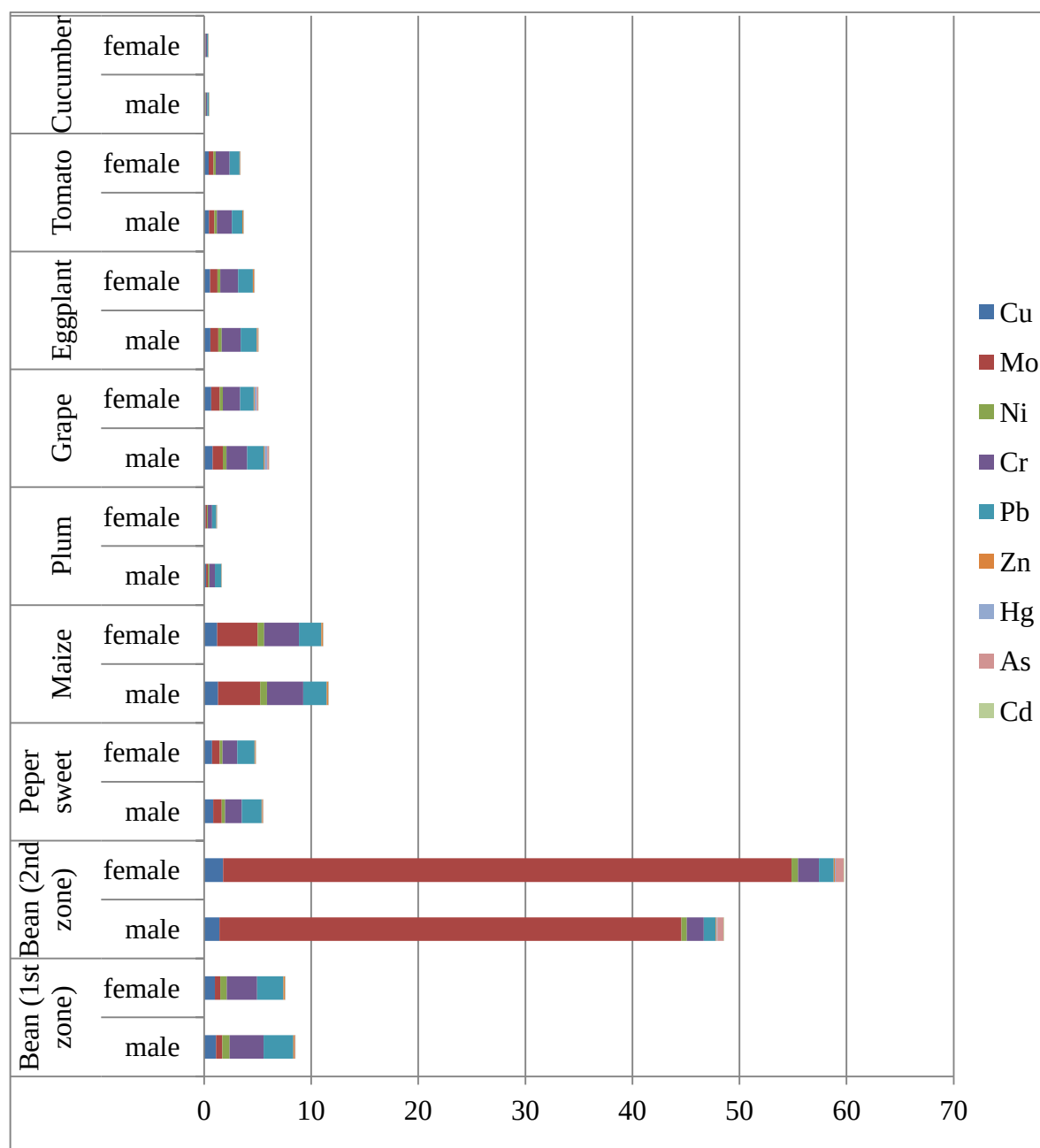


Figure 13. HRI for rural population for fruit vegetables and grains

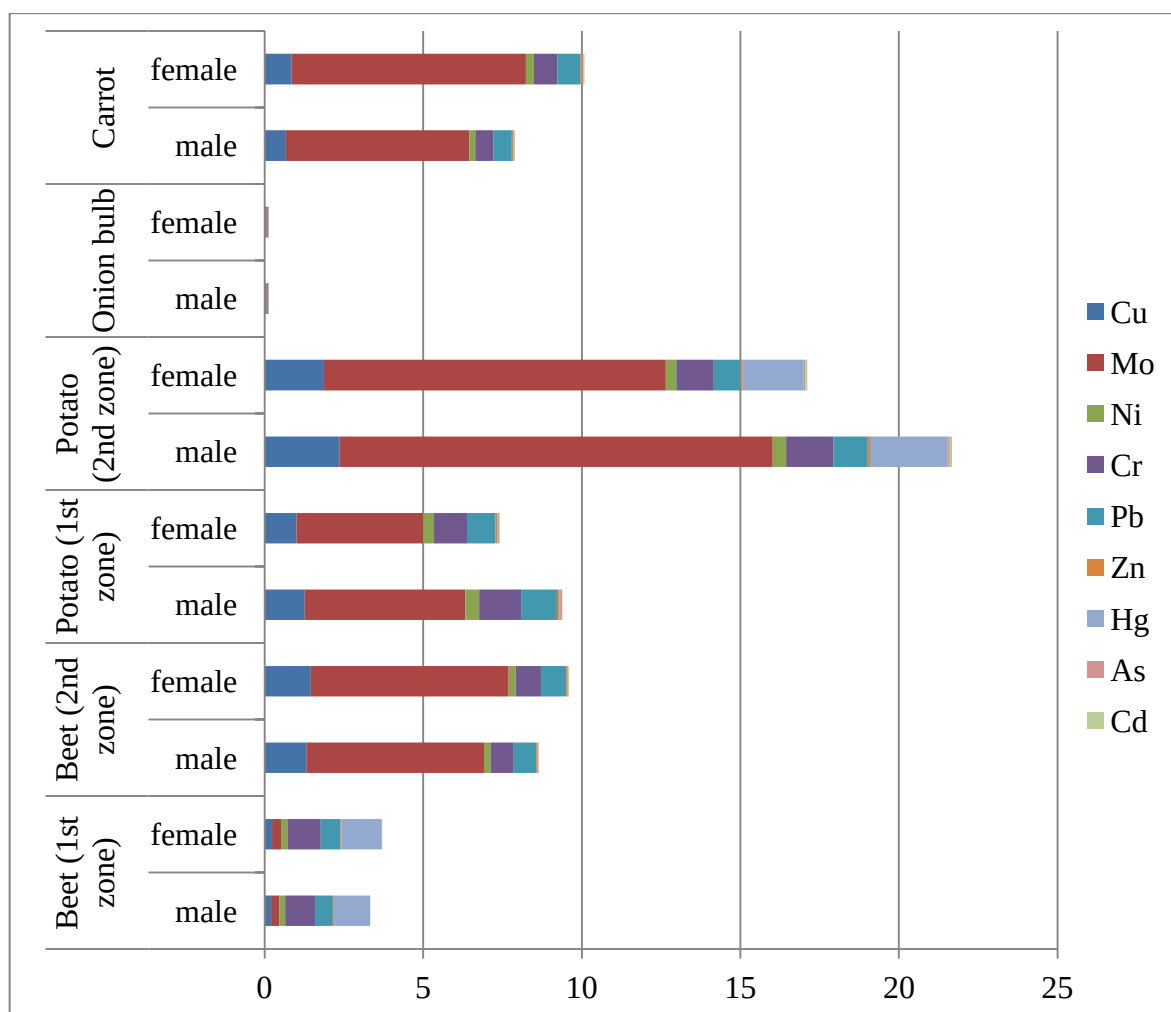


Figure 14. HRI for rural population for root vegetables

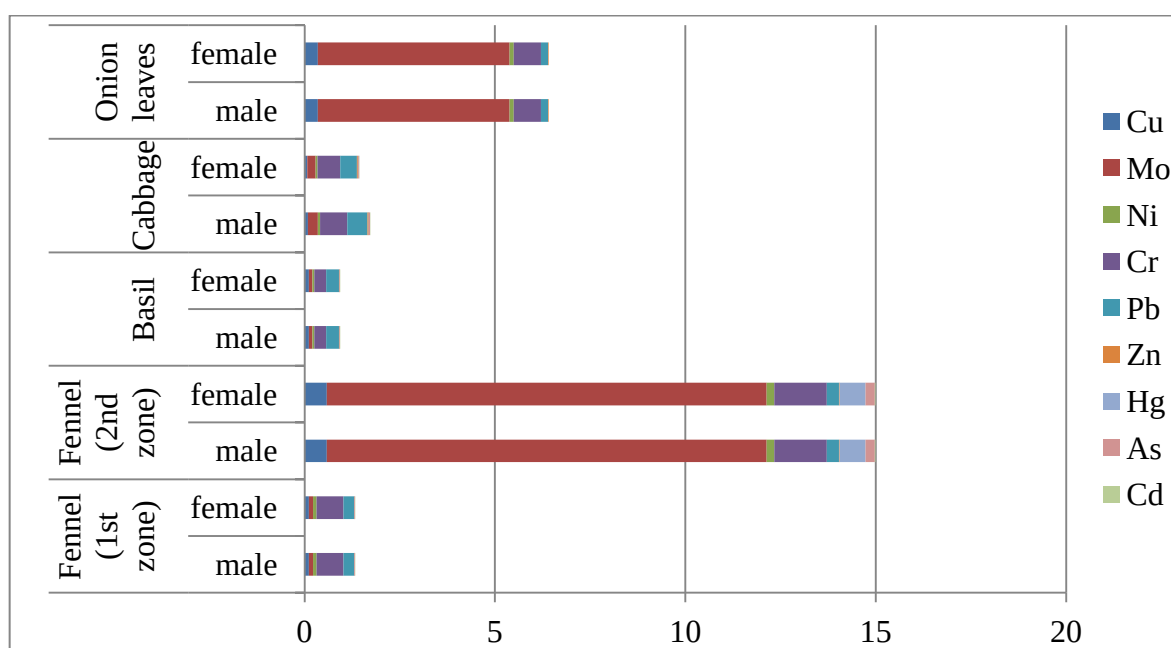


Figure 15. HRI for rural population for leafy vegetables

3.1.7. THQ for rural population

The results of Table 20 declare that for Mo, Cr and Pb THQ values for both males and females are more than 1, which means that the exposed population is in a level of concern interval [59]. The THQ_{Mo} of bean (2nd zone) for male is higher than 10, which means that the precautions are needed immediately. The THQ values of Cr and Pb in bean (1st zone) and maize are exceeding the safety level.

Table 20. THQ for fruit vegetables and grains for rural population									
Species/metals	Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
For males									
Bean (1st zone)*	0,56	0,29	0,34	1,59	1,38	0,07	0,00	0,02	0,00
Bean (2nd zone)**	0,72	21,57	0,25	0,79	0,56	0,04	0,04	0,29	0,02
Pepper sweet	0,43	0,40	0,16	0,77	0,92	0,05	0,01	0,02	0,00
Maize	0,65	1,97	0,32	1,70	1,10	0,06	0,00	0,02	0,00
Plum	0,10	0,09	0,06	0,27	0,28	0,02	0,00	0,01	0,00
Grape	0,40	0,49	0,17	0,96	0,77	0,04	0,12	0,09	0,01
Eggplant	0,30	0,37	0,15	0,89	0,75	0,05	0,00	0,03	0,00
Tomato	0,23	0,24	0,12	0,71	0,50	0,03	0,01	0,01	0,00
Cucumber	0,04	0,02	0,02	0,08	0,06	0,00	0,00	0,01	0,00
For females									
Bean (1st zone)*	0,50	0,26	0,30	1,41	1,23	0,06	0,00	0,02	0,00
Bean (2nd zone)**	0,89	26,54	0,31	0,97	0,69	0,05	0,04	0,36	0,03
Pepper sweet	0,37	0,35	0,14	0,68	0,81	0,05	0,01	0,02	0,00
Maize	0,62	1,89	0,30	1,62	1,05	0,06	0,00	0,02	0,00
Plum	0,07	0,06	0,04	0,20	0,21	0,01	0,00	0,00	0,00
Grape	0,33	0,40	0,14	0,80	0,64	0,03	0,10	0,07	0,01
Eggplant	0,28	0,35	0,14	0,83	0,70	0,05	0,00	0,03	0,00
Tomato	0,22	0,22	0,11	0,65	0,46	0,03	0,01	0,01	0,00
Cucumber	0,03	0,02	0,01	0,07	0,05	0,00	0,00	0,01	0,00

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to Kajaran city

With red colour are illustrated the data exceeding 1

The results shown in Table 21 declare that Cu and Hg THQ values of potato (2nd zone) for male are in the interval 1-5, as well as for Mo in beet (2nd zone), potato (1st zone) and carrot for male.

Table 21. THQ for root vegetables for rural population									
Species/metals	Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
For males									
Beet (1st zone)*	0,10	0,13	0,09	0,47	0,28	0,02	0,57	0,00	0,00
Beet (2nd zone)**	0,66	2,80	0,10	0,36	0,36	0,02	0,00	0,01	0,01
Potato (1st zone)	0,63	2,53	0,22	0,66	0,57	0,04	0,01	0,03	0,00
Potato (2nd zone)	1,18	6,83	0,21	0,75	0,54	0,04	1,22	0,03	0,04
Onion bulb	0,00	0,02	0,00	0,02	0,00	0,00	0,00	0,00	0,00
Carrot	0,33	2,89	0,10	0,29	0,29	0,02	0,00	0,01	0,01
For females									
Beet (1st zone)*	0,10	0,13	0,09	0,46	0,28	0,02	0,56	0,00	0,00
Beet (2nd zone)**	0,64	2,75	0,10	0,35	0,35	0,02	0,00	0,01	0,01
Potato (1st zone)	0,44	1,76	0,15	0,46	0,39	0,03	0,01	0,02	0,00
Potato (2nd zone)	0,82	4,76	0,15	0,52	0,37	0,03	0,85	0,02	0,03
Onion bulb	0,00	0,02	0,00	0,02	0,00	0,00	0,00	0,00	0,00
Carrot	0,37	3,26	0,11	0,33	0,33	0,03	0,00	0,01	0,01

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to Kajaran city

With red colour are illustrated the data exceeding 1

The results generalized in Table 22 show that THQ values for leafy vegetables are less, than those of fruit and root vegetables. Anyway the obtained results show that THQ values for Mo and Cr are in a level of concern interval ($1 < \text{THQ} < 5$).

Table 22. THQ for leafy vegetables for rural population									
Species/metals	Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
For males									
Fennel (1st zone)*	0,06	0,05	0,05	1,07	0,14	0,01	0,00	0,01	0,00
Fennel (2nd zone)**	0,29	5,78	0,10	2,08	0,16	0,01	0,34	0,12	0,01
Basil	0,06	0,04	0,03	0,46	0,17	0,01	0,00	0,00	0,00
Cabbage	0,04	0,13	0,03	1,09	0,26	0,02	0,00	0,01	0,00
Onion leaves	0,17	2,52	0,05	1,08	0,09	0,01	0,00	0,00	0,00
For females									
Fennel (1st zone)*	0,05	0,05	0,04	0,36	0,12	0,01	0,00	0,01	0,00
Fennel (2nd zone)**	0,26	5,10	0,09	0,69	0,14	0,01	0,30	0,11	0,01
Basil	0,05	0,04	0,02	0,15	0,15	0,01	0,00	0,00	0,00
Cabbage	0,03	0,10	0,02	0,36	0,19	0,01	0,00	0,01	0,00
Onion leaves	0,15	2,22	0,05	0,36	0,08	0,01	0,00	0,00	0,00

Note * - tales located near to Kapan city and Syunik village community

** - tales located near to Kajaran city

With red colour are illustrated the data exceeding 1

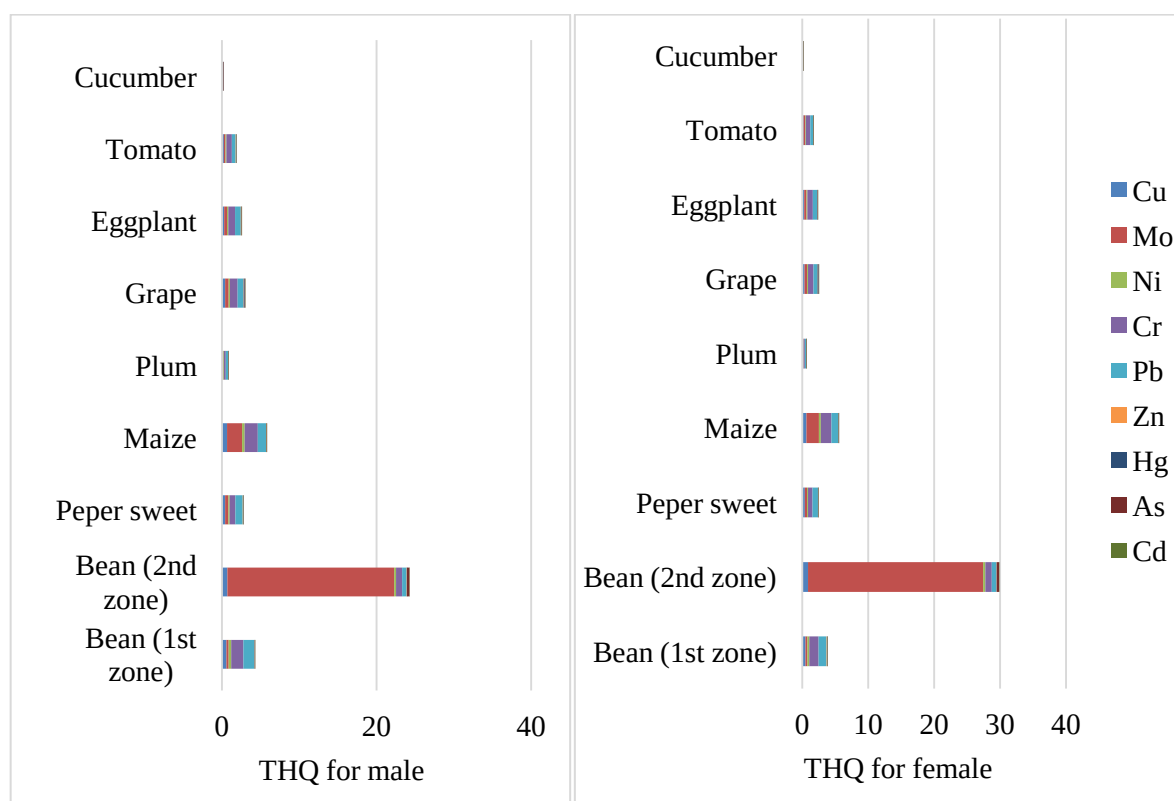


Figure 16. Combined THQ for fruit vegetables and grains for rural population

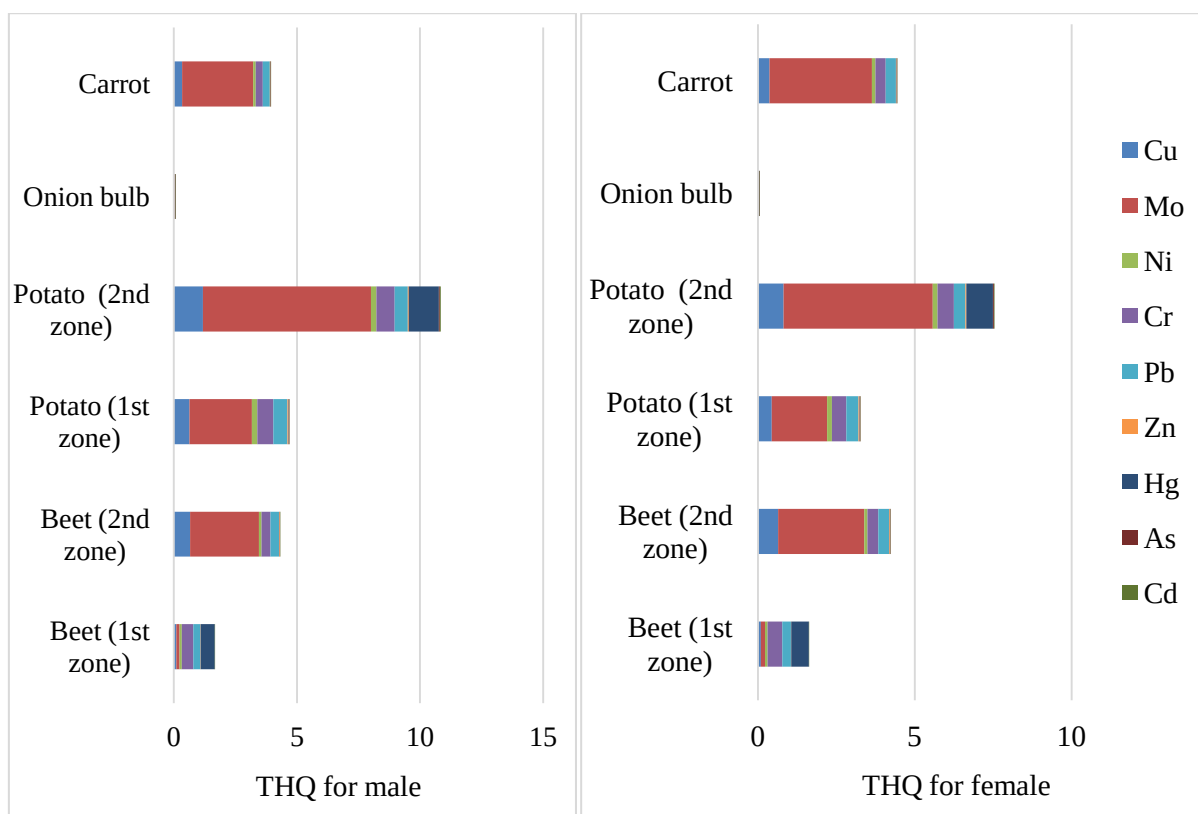


Figure 17. THQ for root vegetables for rural population

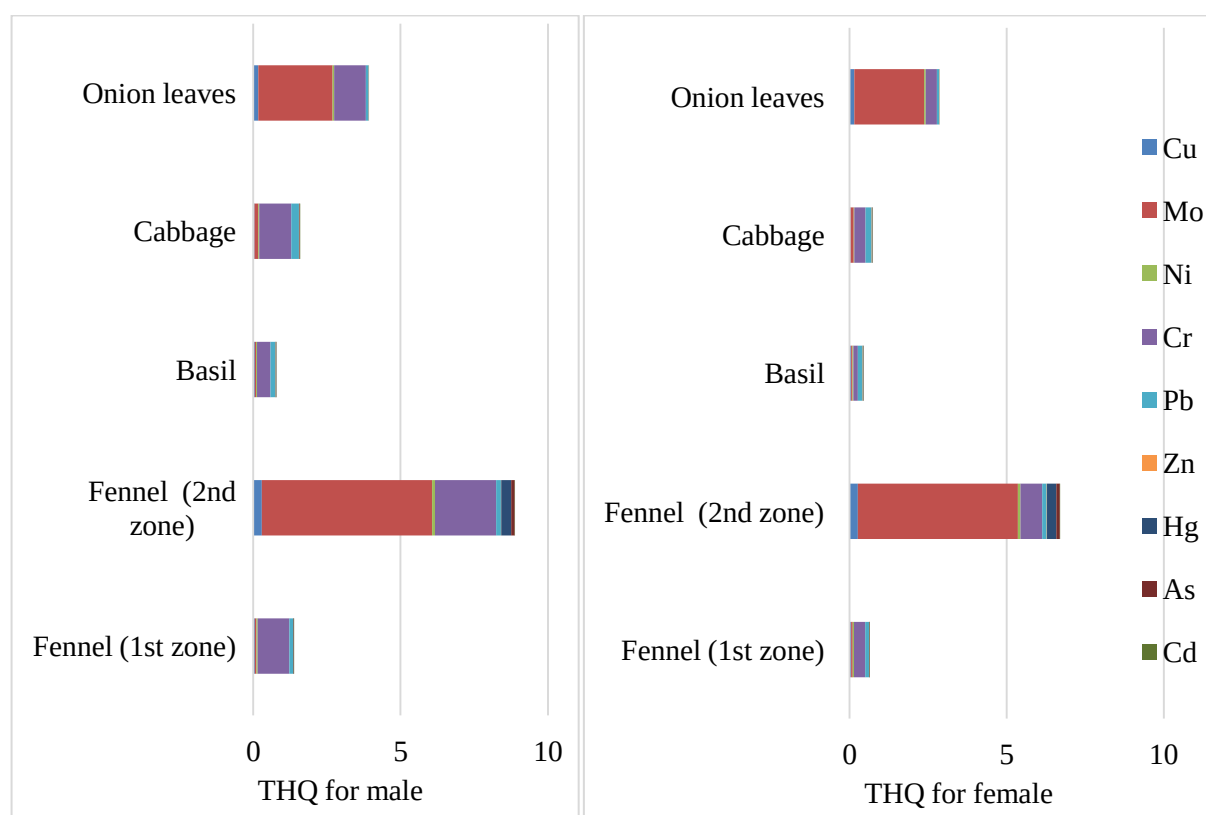


Figure 18. THQ for leafy vegetables for males (rural population)

3.2. DATA ON VEGETABLES AND FRUITS OBTAINED FROM FOOD MARKETS OF TOWN OF KAPAN

3.2.1. The content of contaminants in fruit vegetables and grains

The highest contents of Cu were detected in samples of dewberry and bean. In other vegetables the content was relatively high; the lowest contents were detected in cornel and tomato samples.

The highest content of Mo also was detected in bean samples. Relatively high contents were detected in samples of pepper sweet and cornel. Small contents were found in samples of dewberry, eggplant, cucumber and zucchini.

High Ni concentration also was detected in bean samples. Except pepper sweet, other vegetables contain 30 times less Ni, than bean samples.

Regarding to Cr concentration the highest value was detected in beans, although the relatively high contents were detected in dewberry and in other vegetables also. The lowest content of mentioned metal was detected in zucchini samples.

The Zn content was detected in all investigated vegetables, and highest content was in bean samples.

The contents of Pb, Hg, Cd and As were not significant.

Table 23. Heavy metal contents in fruit vegetables and grains from urban markets										
Species	M/ SD	Content (mg/kg fresh matter)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Safety levels (mg/kg)								
		5	-	-	0,5	0,1	15	0,01	0,05	0,05
Dewberry	M	0,76	0,057	0,052	0,208	0,00038	1,99	0,00150	<LOD	0,00142
	SD	0,32	0,006	0,027	0,023	0	0,593	0	0	0,0001
Cornel	M	0,36	0,602	0,084	0,145	0,00038	1,790	0,00150	<LOD	0,00064
	SD	0,18	0,049	0,036	0,024	0	0,141	0	0	0,00007
Eggplant	M	0,53	0,097	0,094	0,190	0,00038	2,273	0,00150	<LOD	0,00355
	SD	0,10	0,040	0,004	0,034	0	0,285	0	0	0,000568
Pepper sweet	M	0,62	0,705	0,113	0,150	0,00038	1,803	0,00150	<LOD	0,00241
	SD	0,19	1,15	0,063	0,070	0	0,166	0	0	0,002
Bean	M	0,937	0,895	0,309	0,211	0,00100	3,29	0,00150	<LOD	0,00131
	SD	0,403	1,082	0,040	0,029	0,001	1,160	0	0	0,00074
Tomato	M	0,397	0,212	0,033	0,114	0,00038	1,665	0,00150	<LOD	0,00762
	SD	0,127	0,26	0	0,020	0	0,44	0	0	0,00303
Zucchini	M	0,415	0,069	0,098	0,095	0,00068	1,967	0,00438	<LOD	0,00038
	SD	0,021	0,04	0,022	0,1117	0,00042	0,456	0,00407	0	0,000007
Cucumber	M	0,45	0,018	0,076	0,107	0,00038	1,966	0,00150	<LOD	0,00077
	SD	0,036	0,016	0,027	0,023	0	0,37	0	0	0

3.2.2. The content of contaminants in root vegetables

The highest contents of Cu, Mo, Ni and Cr were detected in potato samples, while the lowest content of Cu was detected in carrot and for Mo, Ni and Cr in beet.

Pb contents were equal for all investigated root vegetables.

The contents of Hg and Cd were not significant.

In beet and carrot samples the content of Zn was quite similar; the exception was the potato, for which the concentration is higher, than in other vegetables.

Table 24. Heavy metal contents in root vegetables from urban markets										
Species	M/ SD	Heavy metal contents (mg/kg fresh matter)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Safety levels (mg/kg)								
		5	-	-	0,5	0,1	15	0,01	0,05	0,05
Beet	M	0,467	0,030	0,048	0,169	0,00038	1,99	0,0015	<LOD	0,003
	SD	0,14	0,005	0,001	0,006	0	0,834	0	0	0,001
Potatoes	M	0,785	0,191	0,084	0,193	0,00038	3,73	0,0015	<LOD	0,006
	SD	0,516	0,038	0,035	0,055	0	0,69	0	0	0,0002
Carrot	M	0,313	0,103	0,072	0,179	0,00038	2,1	0,0015	<LOD	0,004
	SD	0,02	0,05	0,03	0,073	0	0,509	0	0	0,002

3.2.3. The content of contaminants in leafy vegetables

The highest content of Cu, Cr and Ni were detected in greens. The lowest content was detected in lettuce samples.

The highest content of Mo was detected in cabbage, while the lowest was in greens.

The contents of Pb, Cd and Hg were not significant.

Table 25. Heavy metal contents in leafy vegetables from urban markets										
Species	M/ SD	Heavy metal contents (mg/kg fresh matter)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Safety level (mg/kg)								
		-	-	5	0,5	0,3	15	0,01	0,05	0,05
Greens	M	0,95	0,11	0,13	0,25	0,0002	1,99	0,0015	<LOD	0,028
	SD	0,47	0,04	0,03	0,01	0,0001	0,55	0	0	0,02
Cabbage	M	0,40	2,4	0,08	0,14	0,0002	2,01	0,0027	<LOD	0,001
	SD	0,04	0,2	0,01	0,07	0,0002	0,53	0,003	0	0,001
Lettuce	M	0,32	0,22	0,01	0,13	0,0003	0,8	0,0001	<LOD	0,002
	SD	0,18	0,288	0,01	0,01	0	0,023	0	0	0,0005
Onion leaves	M	0,43	0,18	0,1	0,13	0,0003	2,06	0,0009	<LOD	0,003
	SD	0,028	0,187	0,069	0,039	0	0,14	0,0007	0	0,001

3.2.4. Comparing characteristics of the investigated elements in different food groups

For urban market also were compared the mean values as there is high standard deviation (Table 26). Cu content didn't show any significant difference between fruit, root and leafy vegetables.

Regarding to Mo content it is possible to declare, that the content is higher in leafy vegetables, which is a result of effective accumulation. The metal content was 3-8 times higher, than in other vegetables.

Ni, Cr and Hg didn't show any significant difference.

Pb detected with higher contents in fruits, and the lowest content was detected in leafy vegetables.

The highest content of Zn was detected in root vegetables, while the lowest in leafy vegetables.

Table 26. The content of contaminants in different food groups (mg/kg)								
Mean / SD	Cu	Mo	Ni	Cr	Pb	Zn	Hg	Cd
Fruit vegetables and grains								
Mean	0,559	0,332	0,107	0,153	0,00056	2,094	0,002	0,002
SD	0,201	0,347	0,086	0,046	0,00027	0,517	0,001	0,002
Root vegetables								
Mean	0,499	0,127	0,077	0,168	0,00038	2,47	0,00136	0,00443
SD	0,202	0,077	0,024	0,027	0,00001	0,841	0,00028	0,00118
Leafy vegetables								
Mean	0,561	0,913	0,099	0,177	0,00026	1,603	0,00145	0,01099
SD	0,345	1,290	0,028	0,068	0,0001	0,691	0,00128	0,01529

3.2.5. Daily intake of metals (DIM) for urban population

The results shown in Table 27-29 indicate, that DIM values didn't exceed the tolerable daily intake for single consumptions.

Following to the Table 27-29 the DIM_{metal} of Pb and Hg for fruits and vegetables is equal to 0 mg/kg/day both for males and females. The same view is for Cd, but the DIM of green leaf both for males and females is 0,0001 mg/kg/day. For these 3 elements there is no accession of TDI values.

The DIM of **Cu** for investigated metals has the following series: Bean_(0.0043) - potato_(0.0039) - greens_(0.0029) - eggplant_(0.0026) - dewberry_(0.0022) - pepper sweet_(0.0021) - zucchini,

cucumber_(0.0020) – tomato, beet_(0.0018) - cabbage_(0.0014) - carrot, lettuce, dewberry_(0.0010) – onion_(0.0008) (for males).

Bean_(0.0035) - potato_(0.0034) - green leaf_(0.0030) – eggplant, dewberry_(0.0022) - pepper sweet = cucumber_(0.0020) - zucchini_(0.0017) - tomato_(0.0016) - beet_(0.0015) - cabbage_(0.0012) – lettuce, dewberry_(0.0010) - carrot_(0.0008) - onion_(0.0007) (for females). The DIM values of Cu do not exceed the TDI (0,14mg/kg/day).

The DIM of **Mo** has a following series: Cabbage_(0.0082) - bean_(0.0041) - pepper sweet_(0.0024) - dewberry_(0.0017) - potato, tomato_(0.0010) - lettuce_(0.0007) - eggplant_(0.0005) - zucchini, onion, carrot, greens_(0.0003) - dewberry_(0.0002) - cucumber, beet_(0.0001) (for males).

Cabbage _(0.0069) - bean _(0.0033) – pepper sweet _(0.0023) - dewberry _(0.0017) - potato, tomato _(0.0008) - lettuce _(0.0007) - eggplant, greens _(0.0004) - zucchini, onion _(0.0003) - carrot, dewberry _(0.0002) - cucumber, beet _(0.0001) (for females). The DIM values of Mo do not exceed the TDI (0,01mg/kg/day).

The DIM of **Ni** in investigated vegetables has a following series: Bean _(0.0014) - eggplant, zucchini_(0.0005) - pepper sweet, potato, greens_(0.0004) - cucumber, cabbage _(0.0003) - tomato, beet, onion, carrot, lettuce, cornel_(0.0002) - dewberry_(0.0001) (for males).

Bean _(0.0011) - eggplant, zucchini _(0.0004) - pepper sweet, potato, greens _(0.0004) - cucumber_(0.0003) - cabbage, beet, onion, carrot, lettuce, cornel _(0.0002) – tomato, dewberry _(0.0001) (for females). The DIM of Ni don't exceed the permitted level (0,0028mg/kg/day).

DIM of **Cr** has a following series: Bean, potato _(0.0010) - eggplant _(0.0009) - greens _(0.0008) - beet _(0.0007) - carrot, dewberry_(0.0006) - pepper sweet, tomato, cucumber, cabbage_(0.0005) - zucchini, lettuce, cornel_(0.0004) - onion_(0.0002) (for male).

Potato, eggplant, greens, bean _(0.0008) - dewberry _(0.0006) - pepper sweet, tomato, cucumber, beet _(0.0005) - carrot, zucchini, lettuce, cabbage, cornel _(0.0004) - onion_(0.0002) (for female). The DIM values are exceeding the safety limit both for males and females as TDI is 0,0003 mg/kg/day.

Zn DIM series is following: Potato _(0.0187) - bean _(0.0151) - eggplant _(0.0110) - zucchini_(0.0093) - cucumber _(0.0087) - beet _(0.0077) -tomato _(0.0076) - cabbage, carrot_(0.0069) - pepper sweet_(0.0062) - greens _(0.0060) - dewberry_(0.0057) - cornel_(0.0051) - onion_(0.0038) - lettuce_(0.0024) (for males).

Potato_(0.0160) - bean_(0.0122) - eggplant_(0.0094) -cucumber_(0.0087) -zucchini _(0.0079) -tomato_(0.0069) – beet, greens _(0.0063) -pepper sweet_(0.0059) - cabbage, dewberry_(0.0057) - carrot, cornel_(0.0051) - onion_(0.0035) - lettuce_(0.0025) (for females). DIM of Zn doesn't exceed the TDI values (1mg/kg/day).

Table 27. Daily intake of metals estimate for fruit vegetables and grains from urban areas										
Species	Gender	Daily intake of metals (mg/kg/day)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Tolerable daily intake of metals (mg/ kg/day)								
		0,14	0,01	0,0028	0,005	0,0036	1	0,002	0,0021	0,0005
Dewberry	male	0,0022	0,0002	0,0001	0,0006	0,0000	0,0057	0,0000	0,0000	0,0000
	female	0,0022	0,0002	0,0001	0,0006	0,0000	0,0057	0,0000	0,0000	0,0000
Cornel	male	0,0010	0,0017	0,0002	0,0004	0,0000	0,0051	0,0000	0,0000	0,0000
	female	0,0010	0,0017	0,0002	0,0004	0,0000	0,0051	0,0000	0,0000	0,0000
Eggplant	male	0,0026	0,0005	0,0005	0,0009	0,0000	0,0110	0,0000	0,0000	0,0000
	female	0,0022	0,0004	0,0004	0,0008	0,0000	0,0094	0,0000	0,0000	0,0000
Pepper	male	0,0021	0,0024	0,0004	0,0005	0,0000	0,0062	0,0000	0,0000	0,0000
	female	0,0020	0,0023	0,0004	0,0005	0,0000	0,0059	0,0000	0,0000	0,0000
Bean	male	0,0043	0,0041	0,0014	0,0010	0,0000	0,0151	0,0000	0,0000	0,0000
	female	0,0035	0,0033	0,0011	0,0008	0,0000	0,0122	0,0000	0,0000	0,0000
Tomato	male	0,0018	0,0010	0,0002	0,0005	0,0000	0,0076	0,0000	0,0000	0,0000
	female	0,0016	0,0009	0,0001	0,0005	0,0000	0,0069	0,0000	0,0000	0,0000
Zucchini	male	0,0020	0,0003	0,0005	0,0004	0,0000	0,0093	0,0000	0,0000	0,0000
	female	0,0017	0,0003	0,0004	0,0004	0,0000	0,0079	0,0000	0,0000	0,0000
Cucumber	male	0,0020	0,0001	0,0003	0,0005	0,0000	0,0087	0,0000	0,0000	0,0000
	female	0,0020	0,0001	0,0003	0,0005	0,0000	0,0087	0,0000	0,0000	0,0000

Table 28. Daily intake of metals estimate for root vegetables from urban areas										
Species	Gender	Daily intake of metals (mg/kg/day)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Tolerable daily intake of metals (mg/ kg/day)								
		0,14	0,01	0,0028	0,005	0,0036	1	0,002	0,0021	0,0005
Beet	male	0,0018	0,0001	0,0002	0,0007	0,0000	0,0077	0,0000	0,0000	0,0000
	female	0,0015	0,0001	0,0002	0,0005	0,0000	0,0063	0,0000	0,0000	0,0000
Potatoes	male	0,0039	0,0010	0,0004	0,0010	0,0000	0,0187	0,0000	0,0000	0,0000
	female	0,0034	0,0008	0,0004	0,0008	0,0000	0,0160	0,0000	0,0000	0,0000
Carrot	male	0,0010	0,0003	0,0002	0,0006	0,0000	0,0069	0,0000	0,0000	0,0000
	female	0,0008	0,0002	0,0002	0,0004	0,0000	0,0051	0,0000	0,0000	0,0000

Table 29. Daily intake of metals estimate for leafy vegetables from urban areas										
Species	Gender	Daily intake of metals (mg/kg/day)								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
		Tolerable daily intak of metals (mg/ kg/day)								
		0,14	0,01	0,0028	0,005	0,0036	1	0,002	0,0021	0,0005
Greens	male	0,0029	0,0003	0,0004	0,0008	0,0000	0,0060	0,0000	0,0000	0,0001
	female	0,0030	0,0004	0,0004	0,0008	0,0000	0,0063	0,0000	0,0000	0,0001
Cabbage	male	0,0014	0,0082	0,0003	0,0005	0,0000	0,0069	0,0000	0,0000	0,0000
	female	0,0012	0,0069	0,0002	0,0004	0,0000	0,0057	0,0000	0,0000	0,0000
Lettuce	male	0,0010	0,0007	0,0002	0,0004	0,0000	0,0024	0,0000	0,0000	0,0000
	female	0,0010	0,0007	0,0002	0,0004	0,0000	0,0025	0,0000	0,0000	0,0000
Onion leaves	male	0,0008	0,0003	0,0002	0,0002	0,0000	0,0038	0,0000	0,0000	0,0000
	female	0,0007	0,0003	0,0002	0,0002	0,0000	0,0035	0,0000	0,0000	0,0000

3.2.6. Health risk index (HRI) for urban population

The results of investigation are concluded in Tables 30-32 and in Figure 19.

Table 30. Health risk index of metals for fruit vegetables and grains from urban areas										
Species	Gender	HRI of metals								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
Dewberry	male	0,1	0,0	0,0	0,20	0,0	0,0	0,0	0,0	0,0
	female	0,1	0,0	0,0	0,20	0,0	0,0	0,0	0,0	0,0
Cornel	male	0,0	0,3	0,0	0,13	0,0	0,0	0,0	0,0	0,0
	female	0,0	0,3	0,0	0,13	0,0	0,0	0,0	0,0	0,0
Eggplant	male	0,1	0,1	0,0	0,30	0,0	0,0	0,0	0,0	0,0
	female	0,1	0,1	0,0	0,27	0,0	0,0	0,0	0,0	0,0
Pepper	male	0,1	0,5	0,0	0,17	0,0	0,0	0,0	0,0	0,0
	female	0,1	0,5	0,0	0,17	0,0	0,0	0,0	0,0	0,0
Bean	male	0,1	0,8	0,1	0,33	0,0	0,1	0,0	0,0	0,0
	female	0,1	0,7	0,1	0,27	0,0	0,0	0,0	0,0	0,0
Tomato	male	0,0	0,2	0,0	0,17	0,0	0,0	0,0	0,0	0,0
	female	0,0	0,2	0,0	0,17	0,0	0,0	0,0	0,0	0,0
Zucchini	male	0,0	0,1	0,0	0,13	0,0	0,0	0,0	0,0	0,0
	female	0,0	0,1	0,0	0,13	0,0	0,0	0,0	0,0	0,0
Cucumber	male	0,0	0,0	0,0	0,17	0,0	0,0	0,0	0,0	0,0
	female	0,0	0,0	0,0	0,17	0,0	0,0	0,0	0,0	0,0

Table 31. Health risk index of metals for root vegetables from urban areas										
Species	Gender	HRI of metals								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
Beet	male	0,0	0,0	0,0	0,23	0,0	0,0	0,0	0,0	0,0
	female	0,0	0,0	0,0	0,17	0,0	0,0	0,0	0,0	0,0
Potatoes	male	0,1	0,2	0,0	0,33	0,0	0,1	0,0	0,0	0,0
	female	0,1	0,2	0,0	0,27	0,0	0,1	0,0	0,0	0,0
Carrot	male	0,0	0,1	0,0	0,20	0,0	0,0	0,0	0,0	0,0
	female	0,0	0,0	0,0	0,13	0,0	0,0	0,0	0,0	0,0

Table 32. Health risk index of metals for leafy vegetables from urban areas										
Species	Gender	HRI of metals								
		Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
Greens	male	0,1	0,1	0,0	0,27	0,0	0,0	0,0	0,0	0,1
	female	0,1	0,1	0,0	0,27	0,0	0,0	0,0	0,0	0,1
Cabbage	male	0,0	1,6	0,0	0,17	0,0	0,0	0,0	0,0	0,0
	female	0,0	1,4	0,0	0,13	0,0	0,0	0,0	0,0	0,0
Lettuce	male	0,0	0,1	0,0	0,13	0,0	0,0	0,0	0,0	0,0
	female	0,0	0,1	0,0	0,13	0,0	0,0	0,0	0,0	0,0
Onion leaves	male	0,0	0,1	0,0	0,07	0,0	0,0	0,0	0,0	0,0
	female	0,0	0,1	0,0	0,07	0,0	0,0	0,0	0,0	0,0

Note. With red colour are illustrated the data exceeding 1

From indicated tables it is obvious, that for fruit and root vegetables Cr had high health risk indexes for wide range of vegetables, such as dewberry, eggplant, bean, beet, potato and carrot.

The HRI for Mo was high in cabbage (Table 32).

For other metals, the HRI values were not significant.

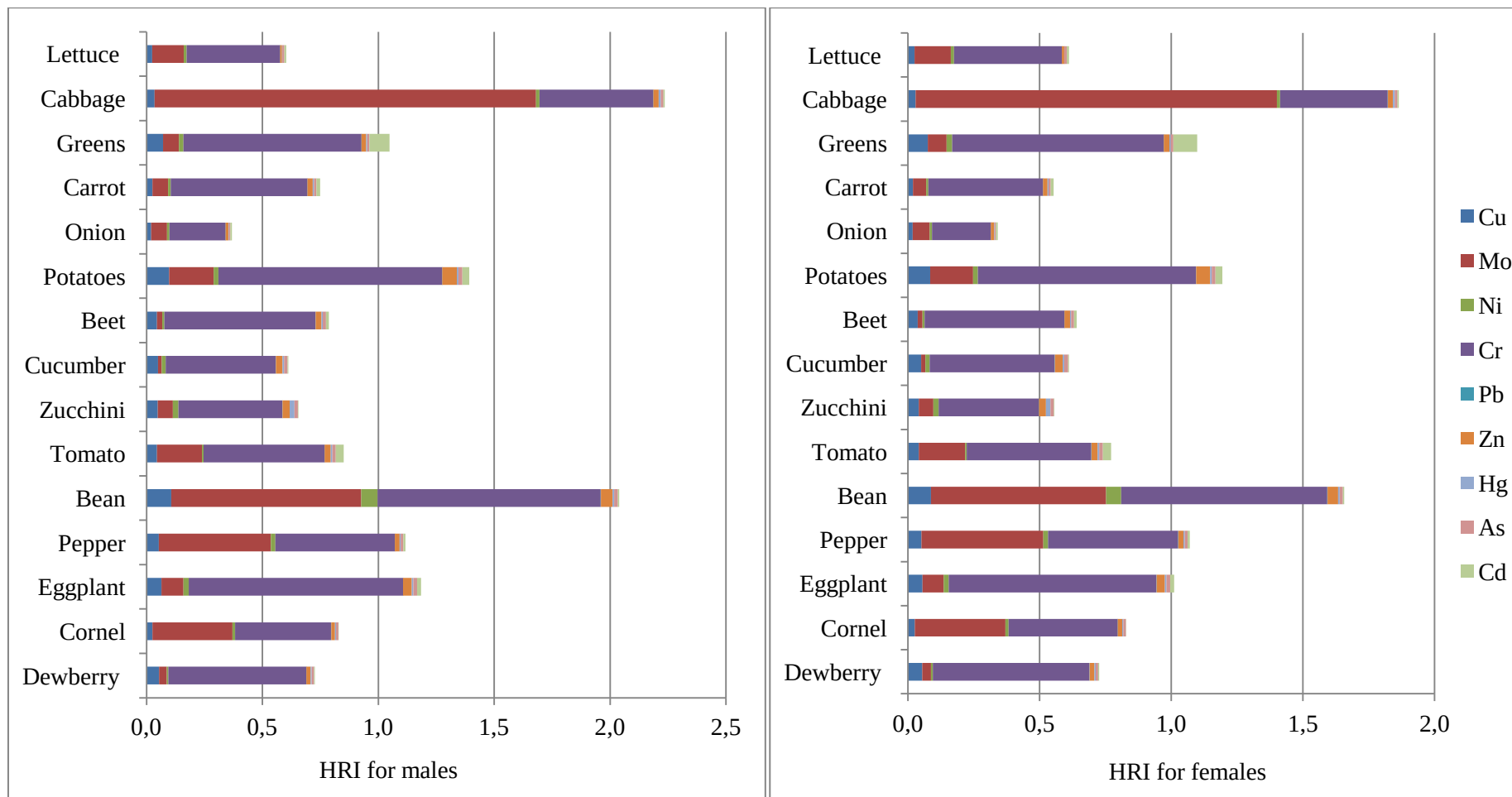


Figure 19. Combined HRI for vegetables and fruits for urban population

3.2.7. THQ for urban population

The THQ values for urban population are concluded in Tables 33-35 and in Figure 20-24. From the tables it is obvious, that there is no any vegetable, for which THQ value exceeds safety level.

Table 33. THQ for fruit vegetables and grains for urban population									
Species/metals	Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
For Males									
Dewberry	0,0271	0,0163	0,0037	0,0991	0,0002	0,0095	0,0021	0,0048	0,0020
Cornel	0,0130	0,1721	0,0060	0,0690	0,0002	0,0085	0,0021	0,0048	0,0009
Eggplant	0,0322	0,0472	0,0114	0,1542	0,0003	0,0184	0,0036	0,0081	0,0086
Pepper	0,0264	0,2416	0,0097	0,0859	0,0002	0,0103	0,0026	0,0057	0,0041
Bean	0,0535	0,4094	0,0354	0,1605	0,0007	0,0251	0,0034	0,0076	0,0030
Tomato	0,0227	0,0969	0,0038	0,0869	0,0002	0,0127	0,0034	0,0076	0,0174
Zucchini	0,0245	0,0326	0,0116	0,0747	0,0005	0,0155	0,0103	0,0079	0,0009
Cucumber	0,0249	0,0081	0,0084	0,0791	0,0002	0,0145	0,0033	0,0074	0,0017
For females									
Dewberry	0,0271	0,0163	0,0037	0,0991	0,0002	0,0095	0,0021	0,0048	0,0020
Cornel	0,0130	0,1721	0,0060	0,0690	0,0002	0,0085	0,0021	0,0048	0,0009
Eggplant	0,0274	0,0403	0,0097	0,1315	0,0002	0,0157	0,0031	0,0069	0,0074
Pepper	0,0253	0,2316	0,0093	0,0823	0,0002	0,0099	0,0025	0,0055	0,0040
Bean	0,0435	0,3326	0,0287	0,1304	0,0005	0,0204	0,0028	0,0062	0,0024
Tomato	0,0205	0,0879	0,0034	0,0788	0,0002	0,0115	0,0031	0,0069	0,0158
Zucchini	0,0208	0,0277	0,0098	0,0634	0,0004	0,0131	0,0088	0,0067	0,0008
Cucumber	0,0249	0,0081	0,0084	0,0791	0,0002	0,0145	0,0033	0,0074	0,0017

Table 34. THQ for root vegetables for urban population									
Species/metals	Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
For Males									
Beet	0,0225	0,0114	0,0046	0,1087	0,0002	0,0128	0,0029	0,0064	0,0066
Potatoes	0,0491	0,0955	0,0105	0,1609	0,0003	0,0311	0,0038	0,0083	0,0150
Carrot	0,0129	0,0337	0,0059	0,0982	0,0002	0,0115	0,0025	0,0055	0,0076
For females									
Beet	0,0183	0,0093	0,0038	0,0885	0,0002	0,0104	0,0024	0,0052	0,0053
Potatoes	0,0421	0,0818	0,0090	0,1380	0,0002	0,0266	0,0032	0,0071	0,0129
Carrot	0,0095	0,0249	0,0044	0,0726	0,0001	0,0085	0,0018	0,0040	0,0056

Table 35. THQ for leafy vegetables for urban population									
Species/metals	Cu	Mo	Ni	Cr	Pb	Zn	Hg	As	Cd
For Males									
Greens	0,0359	0,0342	0,0099	0,1279	0,0001	0,0100	0,0023	0,0050	0,0430
Cabbage	0,0174	0,8230	0,0073	0,0818	0,0001	0,0115	0,0046	0,0057	0,0030
Lettuce	0,0122	0,0680	0,0061	0,0673	0,0002	0,0041	0,0002	0,0051	0,0040
Onion leaves	0,0100	0,0345	0,0049	0,0404	0,0001	0,0064	0,0009	0,0031	0,0034
For females									
Greens	0,0376	0,0358	0,0103	0,1340	0,0001	0,0105	0,0024	0,0052	0,0450
Cabbage	0,0145	0,6858	0,0060	0,0682	0,0001	0,0096	0,0039	0,0048	0,0025
Lettuce	0,0123	0,0689	0,0062	0,0682	0,0002	0,0041	0,0002	0,0051	0,0040
Onion leaves	0,0092	0,0319	0,0045	0,0373	0,0001	0,0059	0,0008	0,0029	0,0032

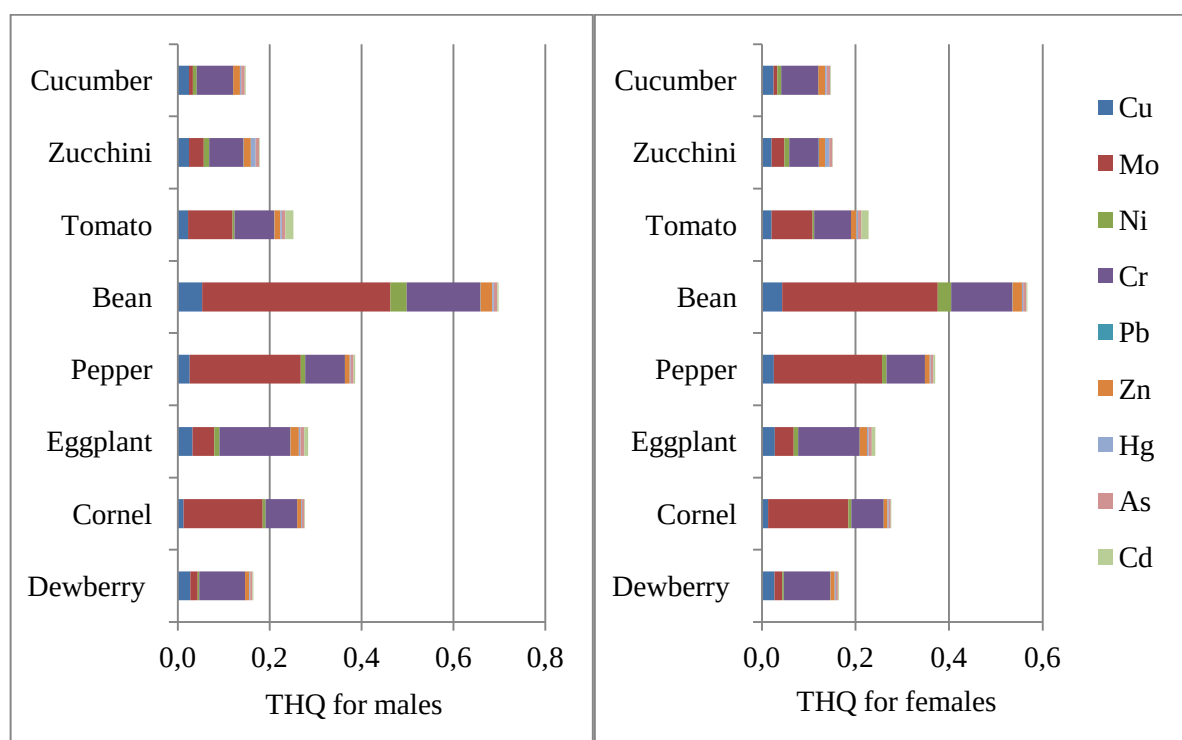


Figure 20. Combined THQ for fruit vegetables and grains for urban population

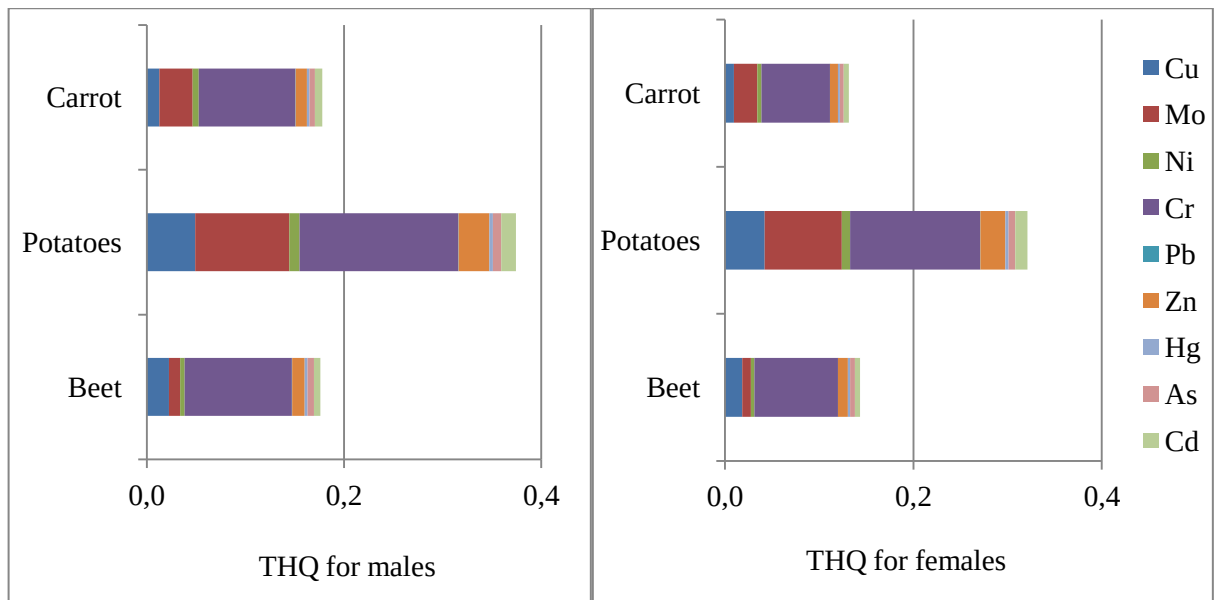


Figure 21. Combined THQ for root vegetables for urban population

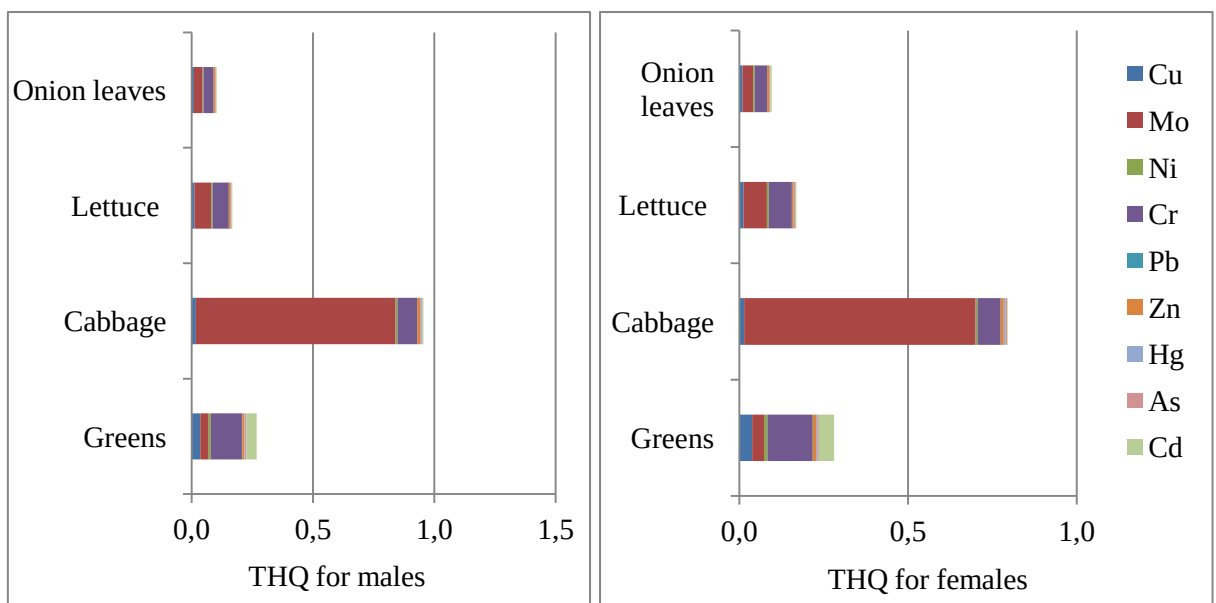


Figure 22. Combined THQ for leafy vegetables for urban population

3.3. COMPARING CHARACTERISTICS OF THQ FOR RURAL AND URBAN COMMUNITIES

THQ (Cu)

The results of investigation declare, there is significant difference between THQ values of rural (*Figure 16-18*) and urban (*Figure 20-22*) communities. The THQ of Cu of rural community is several times higher, than in samples of urban community. For several vegetables the difference is more than 10 times both for males and females. The highest difference is detected for samples of carrot: in rural community the THQ value is exceeding those of urban community 39 times for males and 25 times for females. Significant difference is existing also for pepper sweet (14-16 times), bean and tomato (10 times). The small difference of THQ values is for cucumber and zucchini (almost 1,5-2,5 times), but anyway, THQ values for all vegetables and fruits were higher in a samples from rural community.

THQ (Mo)

For Mo also the samples from rural community have higher values than those of urban community. The unique exception is a bean, where the picture is another. The most significant difference is for carrot, where the THQ values are higher both for males and females, consequently 85 and 130 times higher, than those of rural community. The smallest difference is for pepper sweet and bean.

THQ (Ni)

The THQ values of Ni also were higher in samples of rural community. The smallest THQ values were identified in samples of urban market. The highest difference is detected for tomato (31 times). A significant difference is available also for potato, bean and carrot (approximately 17-25 times).

THQ (Cr)

The THQ values of Cr in samples of rural community are exceeding the safety limit (more than 1) except cucumber and carrot. The THQ values of rural community are exceeding those values of urban community several times, except the cucumber. The difference between THQ of cucumber between rural and urban communities is very small. The highest difference of THQ values were detected in samples of bean (4 times). The smallest values of THQ were detected in samples of urban market.

THQ (Pb)

In case of Pb also the values of THQ are higher for samples of rural community. The highest THQ was detected in bean 1,4 (males) and 1,2 (female). In other vegetables the values were below 1. The lowest THQ values were detected for cucumber 0,05-0,06, but anyway the values are higher than in urban market. In samples of urban market THQ values are varying between the ranges 0,0001-0,0006. So, except cucumber samples the THQ values of Pb from rural community are exceeding significantly from those of urban market.

THQ (Zn)

The same picture is in case of Zn: THQ values are exceeding those of samples from urban market. The unique exception is cucumber. In urban market the highest THQ values were detected in following vegetables: potato > bean > eggplant. In samples from rural community the THQ series were following: bean > eggplant > pepper sweet > potato.

THQ (Hg)

The THQ values for samples of urban market were less than those of rural community. The difference is significant only for bean (almost 100 times), for other vegetables it was 2-3 times. In rural areas THQ values are varying within a range 0.001 to 0.009. The THQ of Hg didn't exceed the safety limit.

THQ (Cd)

The picture of difference of Cd THQ is different. In case of Cd the samples from urban market have higher values than those of rural community. But there is no accession of safety limit as none of samples has a value more than 1.

4. CONCLUSION

Concluding the obtained results of the investigation it is possible declare.

1. The data of concentrations of Cu, Mo, Ni, Cr, Pb, Zn, Hg, As and Cd in different vegetables grown in mining areas of Armenia (rural community) showed significant contamination, so the risk assessment is essential to understand the level of threat and prepare measures of prevention.
2. The high concentrations of Cu, Mo and Hg were detected in leafy vegetables and the lowest concentrations in fruits grown in mining areas. The highest content of Ni, Cr, Zn and As were detected in sample of greens, while the lowest concentrations were discovered in onion bulb and root vegetables. So, it is possible to declare that greens are accumulating effectively the heavy metals and there is higher contamination with environmental contaminants. This fact must be taken in consideration during the planning of Species for cultivation.
3. The obtained results of investigation declared that concentrations of some elements, particularly Cu, Cr, Pb and Hg were exceeding recommended maximum acceptable levels proposed by the Joint FAO/WHO Expert Committee on Food Additives and other international organizations.
4. The obtained results of DIM values declare that in rural communities for some vegetables even single consumption contributes higher level of intake, than the reference dose or even safety value. For bean and maize even single consumption provides high values of intake of Mo, Ni, Cr and Pb. So, this fact must be taken in consideration and the public awareness is necessary in the area for consumer protection.
5. Cu, Mo, Ni and Cr have high health risk indexes. In several cases the health risk index is high even for single vegetable consumption. Concluding the results it is possible to declare that health risk index bases on high proportion of vegetables in diet.
6. Observed contamination in plants have greatest potential to pose health risk to the consumers, which was proved by the data of health risk indexes.
7. The THQ values for Mo, Cr and Pb for both males and females are more than 1, which means that the exposed population is in a level of concern interval. The THQ of bean (2nd zone) and maize for male is higher than 5, which means that the exposure of population can cause adverse health effects. This fact is very important

for risk management, as long-term health effect must be taken into consideration to guarantee the high level of consumer protection.

8. The investigation declares that in samples from urban market the concentrations of contaminants are less than in rural areas. High concentrations can be explained with two important factors: this area is one of Armenia's natural biogeochemical province to which copper-molybdenum mining area belongs and the presence of 3 tailing repositories (Darazami, Voghchi, Pkhrut) in the surroundings of the Zangezur copper-molybdenum enterprise, where some farmlands are located. In markets not only locally grown fruits and vegetables are available, but also from other regions and areas, which is decreasing the overall level of contamination and consequently the level of risk.
9. The DIM values of contaminants for urban population are less compared with those of rural community. Cr has high DIM values both for male and for female. Other contaminants have a small contribution of DIM, which is not exceeding the safety limit.
10. High HRI for urban population was detected for Mo and Cr.
11. Comparing the THQ values of rural and urban communities it is obvious that there is significant difference. Except Cd for all other elements the THQ values of rural community were higher from those of urban community.

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APPENDIX

Table 36. MRLs for metals in fruits and vegetables

Metal	Product	MRLs for metals (mg/kg) (EC) No 1881/2006 [28]
Cd	Vegetables and fruit, excluding leaf vegetables, stem vegetables, root vegetables and potatoes	0,05
	Leaf vegetables	0,2
	Stem vegetables, root vegetables and potatoes (peeled potatoes)	0,1
As	Fruit and vegetables	-
Hg	Fruit and vegetables	-
Pb	Vegetables, excluding brassica vegetables, leaf vegetables, potatoes (peeled potatoes)	0,1
	Brassica vegetables, leaf vegetables	0,3
	Fruit, excluding berries and small fruit	0,1
	Berries and small fruit	0,2
Zn	Fruit and vegetables	-
Cr	Fruit and vegetables	-
Cu	Fruit and vegetables	-
Ni	Fruit and vegetables	-
Mo	Fruit and vegetables	-

Note: «-» - No available date.

Table 37. MAL/ML for metals in fruits and vegetables

Metals	MALs and MLs (mg/kg)					
	CAC (FAO/WHO) [74]		USDA GAIN report [129]		Harmanescu M. et al. [59]	
	Product name	MLs	Product name	MLs	Product name	MALs
Cd	Brassica, bulb, fruiting vegetables	0,05	Fruit	0,05	Fruiting and leafy vegetables	0,2
	Leafy vegetables	0,2	Stem vegetables (exclud. celery)	0,1		
	Legume Root, tuber, stalk, stem vegetables, Potato, Pulses	0,1	Leaf vegetables, celery, edible mushrooms	0,2		
			Other vegetables	0,05	Root vegetables and onion	0,1
As	Fruit and vegetables	-	Fruit and vegetables	0,05	Fruit, Leafy, Root vegetables and onion	-
Hg	Fruit and vegetables	-	Fruit and vegetables	0,01	Fruit, Leafy, Root vegetables and onion	-
Pb	Citrus, Pome, Stone fruits, Bulb, Fruiting, Root, Tuber vegetables	0,1	Fruits, Vegetables (excluding stem, leaves and edible mushrooms)	0,1	Fruit, Leafy, Root vegetables and onion	0,5
	Berries and other small fruits, Legume vegetables, Pulses	0,2	Fruitlet, Berries, Grapes, Potato products	0,2		
	Brassica, leafy vegetables	0,3	Leafy and stem vegetables	0,3		
Zn	Fruit and vegetables	-	Fruit and vegetables	-	Fruit, Leafy, Root vegetables and onion	15
Cr	Fruit and vegetables	-	Fruit and vegetables	0,5	Fruit, Leafy, Root vegetables and onion	-
Cu	Fruit and vegetables	-	Fruit and vegetables	-	Fruit, Leafy, Root vegetables and onion	5
Ni	Fruit and vegetables	-	Fruit and vegetables	-	Fruit, Leafy, Root vegetables and onion	-
Mo	Fruit and vegetables	-	Fruit and vegetables	-	Fruit, Leafy, Root vegetables and onion	-

Note: «-» - No available date.

Table 38. UL for metals

Metals	UL (mg/day)	
Cd	0,064 [59]	
As	No UL was set [68]	
Hg	-	
Pb	0,240 [59]	
Zn	25 [47, 48, 105, 104]	40 [68]
Cr	No UL was set [68, 104]	
Cu	5 [106]	
Ni	1 [68]	
Mo	0,6 [40, 107, 104]	2 [68]

Note: «-» - No available data.

Table 39. TDI/ PTWI/ TWI for metals

Metals	TDI	PTWI	TWI
Cd	0,5 µg/kg bw/day [12, 30]	7 µg/kg bw/week [34]	3,5 µg/kg bw/week [12]
As (inorganic)	2,1 µg/kgbw/day [12]	15 µg/kg bw/week [42,35]	-
Hg	0,1 µg/kg bw/day* [12, 30]	1,6 µg/kg bw/week* [44]	1,3 µg/kg bw/week* [36]
	2 µg/kg bw/day** [12, 30]	4 µg/kg bw/week** [44]	4 µg/kg bw/week** [44]
Pb	3,6 µg/kg bw/day [30]	50 µg/kg bw/week [43]	-
Zn	1 mg/kg bw/day [12]	-	-
Cr	5 µg/kgbw/day [12, 50]	-	-
	0,3 mg/kgbw/day*** [45]		
Cu	140 µg/kg bw/day [12, 50]	-	-
Ni	2,8 µg/kg/day [36]	-	-
Mo	10 µg/kg bw/day [12, 50]	-	-

*Note: «-» - No available data, * - organic (methylmercury), ** - inorganic, *** - for Cr (III).*

Table 40. RfD for metals

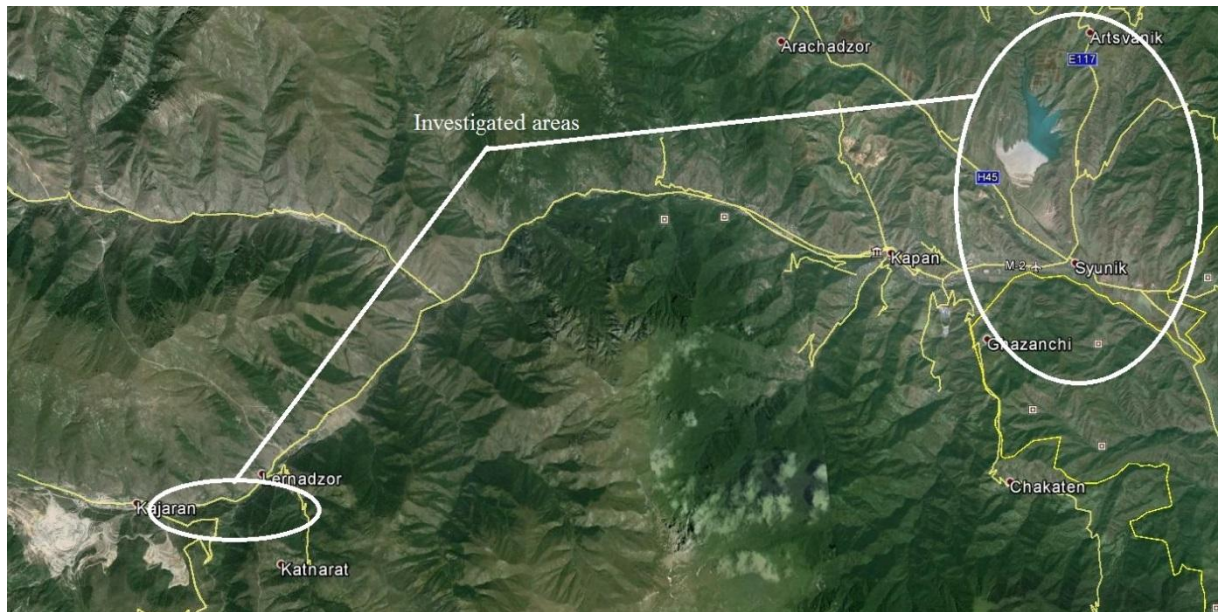
Metals	RfD
Cd	1 µg/kg bw/day [12]
As	0,3 µg/kg bw/day [12, 123]
Hg (organic)	0,1 µg/kg bw/day [12]
Hg (inorganic)	No RfD was set [12]
Pb	0,0035 mg/kg/day[43, 122]
Zn	0,3 mg/kg bw/day [12, 50, 124]
Cr (III)	1,5 mg/kg/day [45, 50, 126]
Cr (VI)	0,003 mg/kg/day [45, 50, 127]
Cu	0,04 mg/kg/day [59]
Ni	20 µg/kg/day [12, 37, 50, 125]
Mo	5 µg/kg bw/day [12, 50]

*Note: * - for subchronic RfD, ** - for chronic RfD.*

Table 41. RDI for metals

Metals	RDI
Cd	0 mg/day/person [59]
As	-
Hg	-
Pb	0 mg/day/person [59]
Zn	15 mg/day [128]
Cr	120 µg/day [50, 128]
Cu	2 mg/day [128]
Ni	0,5 mg/day/person [59]
Mo	75 µg/day [128]

Note: «-» - No available data.



Picture 1. The map of investigated area



Picture 2. Mining wastes



Picture 3. Mining repository of Artsvanik



Picture 4. Cultivation of beans near to Mo miner



Picture 5. Wild collection of dewberry



Picture 6. Collection of samples from rural farmlands



Picture 7. Sampling from farmer market



Picture 8. Sampled fruits and vegetables



Picture 9. Sample preparation

ABBREVIATIONS

AI	Adequate intake
ATSDR	Agency for Toxic Substances and Disease Registry
CONTAM Panel	The Panel on Contaminants in the Food Chain
DNA	Deoxyribonucleic acid
EC JRC	European Commission Joint Research Centre
EFSA	European Food Safety Authority
EGVM	Expert Group on Vitamins and Minerals
FAO	Food and Agricultural Organization
FNB	Food and Nutrition Board
IARC	The International Agency for Research on Cancer
JECFA	Joint FAO/WHO Expert Committee on Food Additives
LOD	Limit of Detection
LOQ	Limit of Quantification
MAL	Maximum Allowable Limits
ML	Maximum Level
MRL	Maximum Residue Limit
NDA Panel	The Panel on Dietetic Products, Nutrition and Allergies
PMTDI	Provisional Maximum Tolerable Daily Intake
PTWI	Provisional tolerable weekly intake
RDI	Recommended Daily Intake
RfD	Oral Reference Dose
RIVM	National Institute of Public Health and The Environment (Rijksinstituut voor Volksgezondheid en Milieu)
SCF	Scientific Committee on Food
SCOOP	Scientific Co-Operation on Questions Relating to Food
TDI	Tolerable Daily Intake
TWI	Tolerable Weekly Intake
UL	Tolerable Upper Intake Levels
US EPA	United States Environmental Protection Agency
FDA	Food and Drug Administration
IOM	Institute of Medicine
NRC	National Research Council
USDA GAIN	United States Department of Agriculture, Global Agricultural Information Network
WHO	World Health Organization

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