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ASSESSING HUMAN RISKS THROUGH *CSOIL* EXPOSURE MODEL FOR A SOIL CONTAMINATION ASSOCIATED TO HEAVY METALS

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Obiectivul acestui studiu a fost evaluarea riscurilor la expunere asociate poluării solului cu metale grele. Probele studiate au fost soluri poluate cu metale grele (Pb, Cd, Cu, Zn) peste limitele de intervenţie, datorate industriei metalelor neferoase. În scopul evaluării riscului uman, a fost utilizat modelul CSOIL pentru calcularea unor parametii ca: expunere medie zilnică, expunere de-a lungul vieţii şi cale principală prin care poluanţii ajung la receptor. Rezultatele obţinute prin modelare au demonstrat că expunerea zilnică la cadmiu depăşeşte cu mult riscul maxim permis, deci, reprezintă o ameninţare serioasă pentru sănătatea umană.

The goal of this study was to assess the human exposure risk associated to heavy metal soil pollution. The studied samples were heavy metals polluted soils (Pb, Cd, Cu, Zn) with concentrations above the intervention limits, because of smelting activities. In order to assess human risk, CSOIL exposure model was used for calculating parameters like: average daily exposure, lifelong exposure, main pathway through which the pollutants reach the receptor. The results obtained through modeling showed that cadmium daily exposure is well above the maximum permissible risk, so it represent a threat to human health.

Keywords: heavy metals, contamination, soil, exposure, risk assessment, CSOIL, Zlatna

1. Introduction

Human impacts on the environment have risen steadily. Previously, our impacts were primary felt locally. However, in the last few decades we have seen impacts spread across regions [1].

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One of the challenges we have to face is particulate matter deposition on soil which represents an important source of soil pollution with heavy metals. Soil, as being a dynamic system which has many important functions and it is vital to ecosystems and humans survival, should receive a higher attention when speaking about heavy metals because of their high persistence and toxicity [2]. Heavy metals can be removed from soil just when occurring following processes: phytoextraction and leaching through soil to groundwater or to deeper horizons.. Therefore, as the pollution sources are multiples: metalliferous mining and smelting, industry, fossil fuel combustion, agriculture, waste disposal on land and not only, heavy metal concentrations in soil increased gradually becoming an urgent issue to solve.

Metalliferous mining and smelting processes gained attention because of the high mobility of heavy metals caused by soil acidification through high concentration of sulfur oxides eliminated from these processes into atmosphere [3].

The present study was performed on soil from the small town of Zlatna, Alba County, Romania. The town is located in a depression being surrounded by Metaliferi (Ore) Mountains and Trascau Mountains, stretches along the main road and follow the Ampoi River. The local extraction of sulphide ores, which are mainly contained in alpine magnetite associated with sedimentary cretaceous rocks [4], conducted in the 1990s to declare Zlatna "one of the most polluted areas in Europe". SC. Ampelum S.A. worked until 2004 and used to process 80 000 t of ore concentrate per annum by a two-stage method of production. The two main types of Cu produced were black copper (Cu concentrate), and blister copper containing 98.8–99.5% pure Cu [4].

The slag is disposed of in a landfill that was closed in 2010 and is placed inside the town. Before this action, no measures were taken to prevent wind-borne transportation of the slag dust, which accumulates on exposed surfaces of nearby houses and gardens.As a result of intensive pollution, the herbal and wooden vegetation suffered greatly or disappeared completely leading to erosion and landslides [5].

2. Human health in the studied area

Human health in the Zlatna area has been considerably affected. A study carried out by U.S. Agency for International Development concluded that in 2009, while the smelter was operating, young children had lead levels in blood in the range of 20 to 65 µg/dL, while lower concentrations as low as 10 or 15 µg/dL are significantly associated with learning disabilities and low IQ scores. More than that, the effects seem to be irreversible. In addition, it has been shown that, due to their natural behavior, young children are usually more exposed to lead in their environment and absorb more lead through their gut than older children or adults. In addition, there is evidence that risk of fetal exposure is significant for pregnant women who are occupationally exposed to lead, such as smelter workers [6].

REACH regulation (19907/2006) [7] has reported that lead may be "probable human carcinogen". The human studies investigated occupational settings to which workers primarily were exposed by inhalation. It is unknown whether exposure by ingestion has a cancer risk as high as the exposure by inhalation. Also, cadmium was classified as a probable human carcinogen by inhalation based on limited evidence of an increase in lung cancer in humans [7], [8].

Even though we can consider that after 8 years from smelter closure the total concentration of heavy metals in soil decreased, a recent study [9] shows that the values are still higher than the intervention limits [10]. Furthermore, in the muscles of 7 out of 8 tested animals the lead concentration exceeded maximum threshold up to 4 times [11].

So, it is essential to evaluate which is the present human risk generated by the exposure to soil contaminated with heavy metals, in order to know if there is an imminent need for intervention.

3. Materials and methods

3.1. Soil characterization

The soil was sampled from gardens (used for grown of vegetables and potatoes) located in the impacted area on a distance of 500 m from the smelter stack. The samples were collected from the depth of 20 cm because usually, the roots does not reach depths higher than this value. In this respect we assume that that heavy metals having a low mobility are not reach under this level.

There were carried out determination of soil texture through Bouyoucos hydrometer method after dispersion of the sample with Na-hexametaphosphate, organic carbon by using an NA 2100 Protein CE Instruments equipment (ISO 10694, 1995), and pH (ISO 10390, 1994).

The pseudo – total concentration of heavy metals in soil was determined by microwave digestion of soil with Aqua Regia (0.5 g of dry soil in 10 mL of extractant, at a ratio $HCl:HNO_3$ of 3:1 (ISO Standard 11466).

The concentration of heavy metals in soil pore water was sampled by Rhizon Moisture Samplers - porous plastic samplers which have no cation exchange capacity, which avoids sorption, and the pore size of 0.2/µm ensures the solution collected is free from microbial and colloidal contamination [12], [13].

The Pb amount available for plant was evaluated through EDTA Extraction (5 g of soil extracted with 50 mL of ethylenediaminetetraacetic acid, pH = 4.65 with CH_3COOH for 2 h at room temperature with continuous shaking at 50 rpm). EDTA has been used to increase the availability of metals for phytoextraction by accumulating plants [14].

3.2. Exposure model

In order to evaluate the exposure and to assess the risk for humans, CSOIL Model was used. The model calculates the risk humans are exposed to if they come into contact with contaminated soil and determines the value of exposure. Humans can be exposed to contaminated soil *via* different exposure routes (inhalation of soil, ingestion of soil, water, plants and dermal contact). The soil use, such as a vegetable garden, determines the measure of exposure. Physico-chemical properties of the contaminant in soil air, soil particles and soil solution also have an influence on the exposure. The model calculates the maximum concentration of a contaminant in the soil at which it is still safe for humans, a reason for which this model is used by UK and Dutch Environmental National Agencies. This maximum concentration is useful in determination of the intervention value. In soil contamination the intervention value differentiates between lightly and seriously contaminated soils. The urgency of remediation is, therefore, determined by the level at which soil contamination exceeds the intervention value.

The CSOIL model was developed with the help of previous models like HESP, SOILRISK, RIVM model and extensive studies of the literature behind these models. One of the advantages of this model is that calculates risk for humans taking into account all the possible pathways for pollutants to reach the receptor. Another advantage is that if there is a missing secondary parameter, the model can still be applied considering that the general influence of the different parameters decrease in the following order: density of the solid phase > organic matter content > depth of contamination > depth of groundwater table > contribution of crop consumption from own vegetable garden to total vegetable consumption > pore air fraction [15].

The behavior and characteristics of humans, the scenario used and the contaminants are described with a set of parameters. The most relevant parameters for the calculation of human exposure to contaminated soil and groundwater are identified on the basis of model analysis. For metals, the soil-to-plant bioconcentration factor (BCF) and the partition coefficients, soil/sediment-water (Kp) are critical. The relationship with standard soil characteristics (pH, clay content and organic carbon) is considered for both BCF and Kp metals.

When a contaminant enters the soil, it can be partitioned over different soil phases. From these phases the contaminant can enter different transfer routes, from which it can expose humans. In CSOIL the pollutant concentration in water phase, air phase and soil phase is calculated. The partition amounts in the different phases can be calculated if assumed that there is equilibrium in the three soil phases. The software calculate contaminant concentration in all phases with knowledge about soil-water partition coefficient, air-water Henry coefficient and soil parameters [16].

3.2.1. Soil ingestion

Soil ingestion is a major contribution to the total exposure of humans to contaminants. Either soil is ingested by accident from unwashed hands or vegetables (adults case), or if is ingested on purpose (children case), it enters in digestive tract where is released and adsorbed into the body. The ingestion of heavy metals can seriously cause depletion of some essential nutrients in the body, which in turn causes a decrease in immunological defenses, intrauterine growth retardation, psychosocial dysfunctions, disabilities associated with malnutrition and a high prevalence of upper gastrointestinal cancer [17], [18].

The main equation used by CSOIL for calculating the exposure *via* ingestion of soil is:

$$DI = AID*Cs*Fa/BW \qquad (1)$$

DI = exposure *via* ingestion of soil [mg/kg of BW/d]
AID = daily intake soil [ADULT $5.0/10^5$ kg dw/d, CHILD $1.0/10^4$ kg dw/d]
Cs = initial soil concentration (total concentration in gas-, water- and solid phase) [mg/kg]
Fa = relative absorption factor (general) [-]
Fag = relative absorption factor soil [-]
BW = bodyweight [ADULT 70 kg, CHILD 15 kg]

3.2.2. Soil inhalation

Soil inhalation has a high contribution to the total exposure of humans to pollutants either from indoor, but especially from outdoor. Soil inhalation depends on wind velocity, soil texture, soil humidity and not only.

$$IP = Cs*ITSPc*Fr*Fa/BW \qquad (2)$$

IP = exposure *via* inhalation of soil particles [mg/kg of BW/d]
Cs = initial soil concentration (total concentration in gas-, water- and solid phase)[mg/kg]
ITSP = inhaled amount of soil particles [ADULT $8.33/10^7$ kg/d, CHILD $3.13/10^7$ kg/d]
Fr = retention factor soil particles in lungs [0.75 -]

Fa = relative absorption factor [-]
BW = bodyweight [ADULT 70 kg, CHILD 15 kg]

$$ITSP = TSP * frs * AVc * t * tf \quad (3)$$

TSP = amount of suspended particles in air [mg/m^3]
Indoors 0.75 * 70 = 52.5 g/m^3
Outdoors 70 g/m^3
Frs = fraction soil particles in air [-]
Indoors 0.8
Outdoors 0.5
AV = air volume [CHILD 0.317m^3/h, ADULT 0.833 m^3/h]
T = length of time of exposure [h]
Indoors 16 h
Outdoors 8 h
Tf = correction factor exposure daily _ yearly [-]
Indoors 1.322
Outdoors 0.357

3.2.3. Dermal uptake

Dermal uptake of pollutants in contact with the contaminated soil is an exposure pathway with a small amount form the total exposure. The skin has an outer layer that protects humans against different external metals and other pollutants having a low probability to pass through. CSOIL software take into consideration that the dermal uptake for metals is 0.

3.2.4. Exposure *via* permeation in drinking water

Pollutants from pore water can be transported to the groundwater. If the contaminated groundwater is used for drinking, the compound is automatically harmful to humans.

$$DIW= QDW*Cdw*Fa/BW \quad (4)$$

DIW = exposure *via* permeation of drinking water [mg/kg of BW/d]
QDW = consumption of drinking water [CHILD 1 dm^3/d, ADULT 2 dm^3/d]
Cdw = concentration in drinking water [mg/dm^3]
Fa = relative sorption factor [-]
BW = bodyweight [CHILD 15 kg, ADULT 70 kg]

3.2.5. Exposure *via* crop consumption

There are two main exposure pathways for vegetation described in CSOIL 2000. These are *via* the air (deposition of soil dust/ soil re-suspension) and *via* uptake by plant roots. CSOIL 2000, also, calculates the transport of the compound from the roots to the leaves of the plant.

The exposure to humans depends on the concentration in the crops, the amount of consumption and the fraction of the total vegetation that comes from a contaminated soil.[19] Rather than total metal concentration the potential risk associated with soil contamination depends on heavy metals speciation in soil.[20], [21].

For metals, an empirical approach is used in which the uptake by the plant is within the use of a BioConcentration Factor (BCF). This is due to the poor understanding of the mechanisms of accumulation for metals. In order to get the BCF, experimental data are used. If these data are not present, the BCF can be calculated with the following equation:

$$VIcmet = (B146*Cpr1)*Fa/BW \quad (5)$$

VIcmet = exposure *via* ingestion of crops [mg/kg of BW/d]
DCC = crops daily consumption [kg dw/d]
Cpr1 = consumption average amount in crop [mg/kg ds]
Fa = relative sorption factor [-]
BW = bodyweight child [CHILD 15 kg, ADULT 70 kg]

$$DCC = (QK\_c*Fdwr*fvk)+(QB\_c*Fdws*fvb) \quad (6)$$

QK = root crop consumption [CHILD 0.0595 kg fw/d, ADULT 0.122 kg fw/d]
Fdwr = dry matter content root crops [0.167 kg dw/kg fw]
fvk = fraction contaminated root crop [0.1 -]
QB = leafy crop consumption [CHILD 0.0583 kg fw/d, ADULT 139 kg fw/d]
Fdws = dry matter content of leafy crop [0.098 kg dw/kg fw]
fvb = contaminated leafy crop fraction [0.1 -]

3.2.6. Total exposure inhalation, oral and dermal and the derivation of human risk

The maximal permissible risk (MPR) is defined as the concentration at which there is annually 1 death per million. For substances with a threshold level, the MPR for humans is set to the exposure level without effect (NOAEL = no observed averse effect level). The MPR can be expressed as tolerable daily intake

(TDI) or an excess carcinogenic risk *via* intake (CRoral, mg/kg bw/d). The MPR can, also, be expressed as a tolerable concentration in air or an excess carcinogenic risk *via* air (CRinhal, μg/m3). The total exposure is calculated using the following equation:

$$Risk - child/adult = SUMO/MPR + SUMA/MPR\_A \qquad (7)$$

SUMO = total exposure oral and dermal child/adult [mg/kg bw/d]
MPR = maximum permissible risk [mg/kg bw/d]
SUMA = total exposure *via* inhalation child/adult [mg/kg bw/d]
MPR_A = TDI inhalation child/adult [mg/kg bw/d] (Brand et. al, 2007)

4. Results and discussion

CSOIL software was used taking into account the following simplifying hypothesis: (i) the land was residential with vegetable garden (Fig. 1);

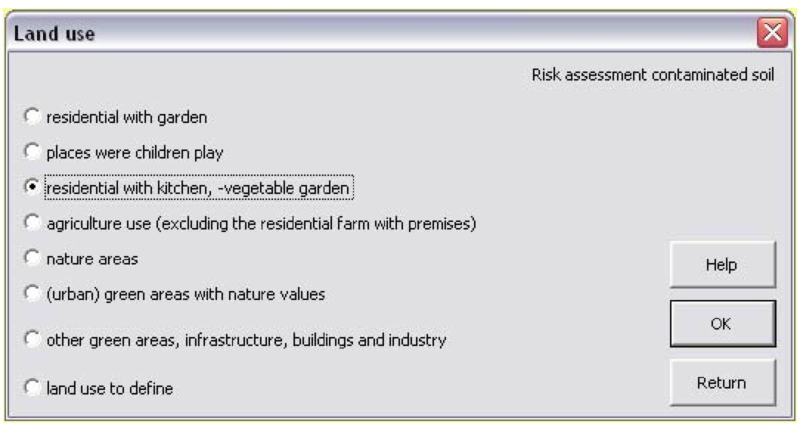


Fig. 1. Soil use

(ii) the exposure pathways taken into account were: soil ingestion, soil inhalation, dermal contact, inhalation of outdoor air, consumption of drinking water and consumption of crops from kitchen garden; (iii) the receptors were both children and adults (Fig. 2); (iv) the contamination depth was 0.5 m; (v) crawl space contributed with 0% to indoor air pollution.

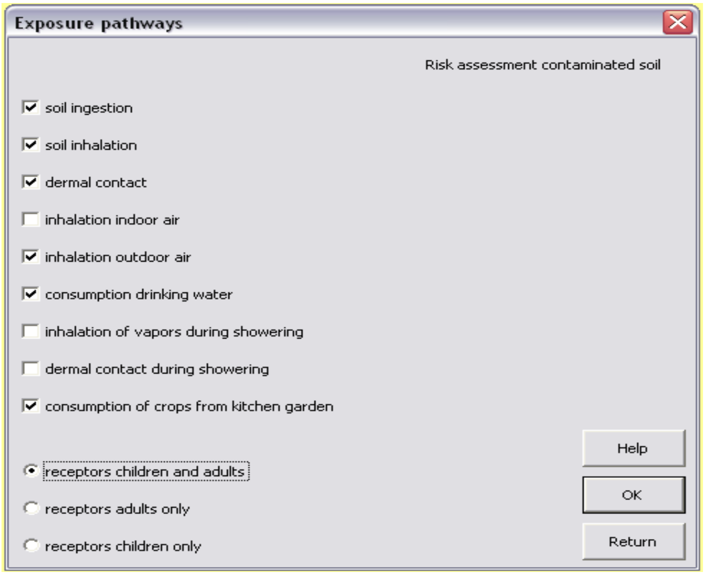


Fig. 2. Exposure pathways and receptors

In Table 1 is presented soil characterization for 5 garden samples. In order to apply CSOIL software for human risk assessment, the average values of clay, silt, sand, organic matter content and the average pH were calculated.

Table 1

Garden soils characterization

Sample	**Clay %**	**Silt %**	**Sand %**	**Organic Carbon %**	**pH (H_2O)**
g1	6	18	76	1.56	7.3
g2	12	26	62	2.23	7.3
g3	7	32	61	1.75	7.3
g4	8	26	66	1.63	7.5
g5	6	27	67	2.13	7.2
AVERAGE	7.8	25.8	66.4	1.86	7.32

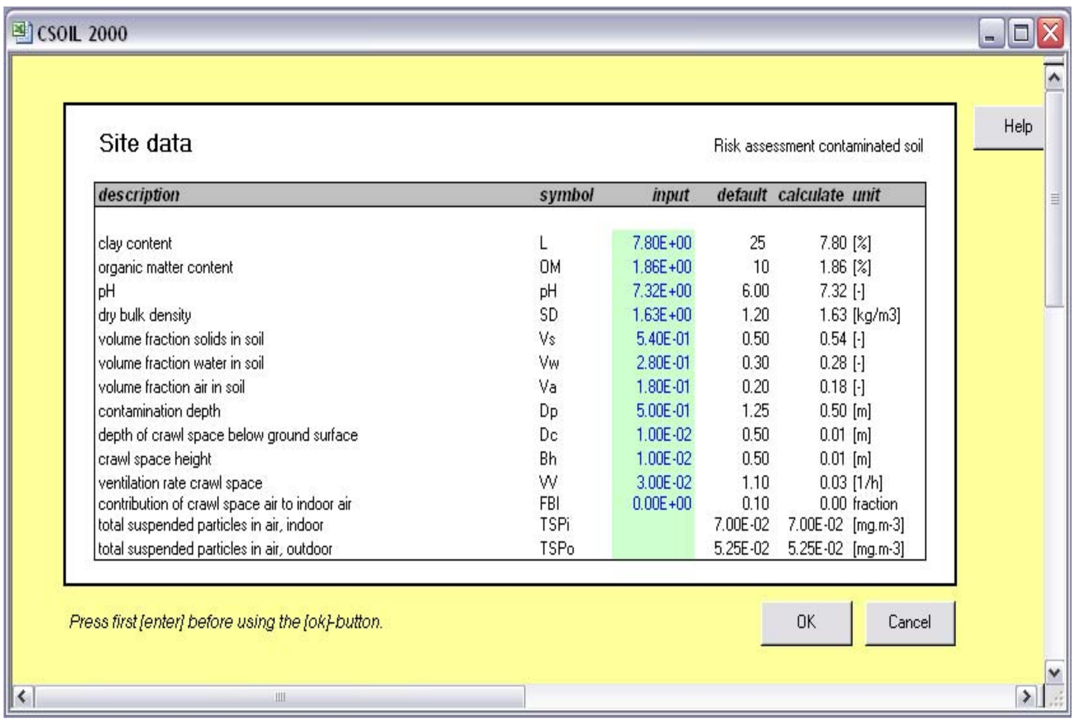
The first input parameters include: clay content, organic matter, pH, dry bulk density, volume fraction of solids, water and air in soil, contamination depth, and even it was not required to take into consideration indoor air inhalation pathway the software need depth of crawl space below ground surface, crawl space height, ventilation rate of crawl space and contribution of crawl space air to indoor air.

Clay content was determined through wet sedimentation (7.8 %), organic matter content was determined with solid elemental analyzer (1.86 %) and pH was determined with a pH-meter (7.32). For calculating dry bulk density the equation (8) was used, and for calculating the proportionality between volume fraction of solids, of water and of air, the values for clay, silt and sand presented on [22] were used.

*RHO_soil = Vs*RHOsolid+Vw*RHOwater+Va*RHOair* (8)

where:

RHO_soil = calculated dry bulk density (default 1550) [kg/m3]
Vs = volume fraction of soil [-]
RHOsolid = solid soil density [2500 kg/m3]
Vw = volume fraction of water [-]
RHOwater = water density [1000 kg/m3]
Va = volume fraction of air [-]
RHOair = air density [1.3 kg/m3]



description	symbol	input	default	calculate	unit
clay content	L	7.80E+00	25	7.80	[%]
organic matter content	OM	1.86E+00	10	1.86	[%]
pH	pH	7.32E+00	6.00	7.32	[-]
dry bulk density	SD	1.63E+00	1.20	1.63	[kg/m3]
volume fraction solids in soil	Vs	5.40E-01	0.50	0.54	[-]
volume fraction water in soil	Vw	2.80E-01	0.30	0.28	[-]
volume fraction air in soil	Va	1.80E-01	0.20	0.18	[-]
contamination depth	Dp	5.00E-01	1.25	0.50	[m]
depth of crawl space below ground surface	Dc	1.00E-02	0.50	0.01	[m]
crawl space height	Bh	1.00E-02	0.50	0.01	[m]
ventilation rate crawl space	Vv	3.00E-02	1.10	0.03	[1/h]
contribution of crawl space air to indoor air	FBI	0.00E+00	0.10	0.00	fraction
total suspended particles in air, indoor	TSPi		7.00E-02	7.00E-02	[mg.m-3]
total suspended particles in air, outdoor	TSPo		5.25E-02	5.25E-02	[mg.m-3]

Fig. 3. First set of parameters required by CSOIL

In this scenario, indoor air pollution is not relevant to gardening exposure, therefore the values for depth of crawl space below ground surface, crawl space height and ventilation rate of crawl space were the minimum ones accepted by the software and the contribution of crawl space air to indoor air it was considered 0 (Fig. 3).

After performing the first step, the software requires selection of pollutants, type of compounds and selection of compounds of interest. After this step, it is necessary to introduce the second set of parameters: contaminant concentrations for each compound of interest (in this case, lead, cadmium, copper and zinc).

Table 2

Heavy metal concentration in soil, in leafy crops and in potatoes

Heavy metal	**Conc. in soil** mg/kg soil	**Conc. in leafy crops – lettuce [23]** mg/kg soil	**Conc. in potatoes [23]** mg/kg soil
Pb	1290.0	40	1.50
Cd	3.8	5	0.12
Cu	335.0	15	1.75
Zn	800.0	110	9.00

The requested values are total contaminant concentration in soil, contaminant concentration in pore water, contaminant metal concentration in leafy crops and in potato or root crops

After all the required parameters were introduced, the software calculates risk index, exposure concentrations (Table 3), average daily exposure and lifelong both for adults and children (Table 4), and contribution of the pathways taken into account at total exposure (Table 5).

Table 3

Risk index and exposure concentrations

Contaminant	**Soil content** mg/kg ds	**Risk index** exp/mpr	**MPR** mg/kg bw.day	**TCA** mg/m3	**Metals conc. Potato** mg/ kg fw	**Metals conc. Vegetables** mg/kg fw
Lead	1.29E-01	0	3.60E-03	0.00E+00	7.00E-04	4.00E-03
Cadmium	3.80E+00	20.29	5.00E-04	0.00E+00	1.25E-01	2.73E+00
Copper	3.35E-02	0	1.40E-01	1.00E-03	1.74E-02	1.50E-03
Zinc	8.00E-02	0	5.00E-01	0.00E+00	8.00E-03	5.00E-02

Table 4

Average daily exposure and lifelong for children and adults

Contaminant	**Soil content mg/kg ds**	**Children (0-6 years) mg/kg l.g.*d**	**Adults (6-70 years) mg/kg l.g.*d**	**Lifelong (0-70 years) mg/kg l.g.*d**
Lead	1.29E-01	2.08E-05	1.50E-05	1.55E-05
Cadmium	3.80E+00	1.30E-02	9.87E-03	1.01E-02
Copper	3.35E-02	4.49E-05	2.20E-05	2.40E-05
Zinc	8.00E-02	2.51E-04	1.86E-04	1.92E-05

Maximum permissible risk for humans (MPR) is defined by WHO [24] as the amount of substance that any human individual can be exposed to daily, during a full lifetime without significant health risk. In order to assess the risk posed by lead, cadmium, copper and zinc to humans, daily exposure concentrations were calculated assuming that average bodyweight for child is 15 kg and for adult is 70 kg.

Table 5

Contribution of different exposure pathways to the total exposure

Contaminant	**Soil intake** %	**Consumption from own garden** %
Lead	0.8	99.2
Cadmium	0.0	100.0
Copper	0.2	99.8
Zinc	0.1	99.9

According to values for MPR introduced in CSOIL, cadmium exceeds daily exposure concentration, both for children and adults, and because the only important pathway for cadmium is consumption from own garden, there is an increased risk for humans. Lead, copper and zinc daily exposure concentrations were below MPR values, so, risk is estimated to be low.

5. Conclusion

Using CSOIL software, the main pathway through which pollutants reach human receptors in Zlatna was estimated to be the consumption from private gardens. Also, the calculated daily exposure concentration of cadmium was found to be above the maximum permissible risk value. It is necessary to raise public awareness about the identified risks, because cadmium has an increased probability to be phytoextracted by vegetables. Additional investigation should be performed, but the first measures to be adopted should avoid the consumption of vegetables with increased affinity for Cd, and the removal of animal liver and kidney from food chain [25], in order to substantially reduce the dietary Cd intake. The solution which can decrease the risk of exposure is to plough and consume just vegetables with a low probability of Cd phytoextraction, and/or to improve agricultural practices, like ploughing deeper, for the decrease of metal concentration in the rhizosphere.

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