Human health risk assessment of toxic metals

Ph.D. thesis

Emese Sipter, M.D., M.Sc.

Semmelweis University
Doctoral School of Pathological Sciences
Research in Public Health and Health Science

Study supervisors: Erzsébet Tátrai, M.D., Ph.D., D.Sc.
Katalin Gruiz, M.Sc., Ph.D.

Official reviewers: Tibor Kerényi, M.D., Ph.D., D.Sc.
Sándor Tömösközi, M.Sc., Ph.D.

Budapest
2008

INTRODUCTION

People are exposed to a variety of potentially harmful agents in the air they breathe, the liquids they drink, the food they eat, the surfaces they touch and the products they use. An important aspect of public health protection is the prevention or reduction of exposures to environmental agents that contribute, either directly or indirectly, to increased rates of premature death, disease, discomfort or disability.

Risk assessment is a conceptual framework that provides the mechanism for a structured review of information relevant to estimating health or environmental outcomes. The risk assessment paradigm divides the risk assessment process into four distinct steps: hazard identification, dose-response assessment, exposure assessment and risk characterization.

The "weakest link" in risk assessment processes is the exposure assessment. Exposure assessment requires the determination of the emissions, pathways and rates of movement of a substance and its transformation or degradation, in order to estimate the concentrations to which human populations or environmental spheres (water, soil and air) may be exposed. Three main exposure routes are determined in exposure assessment: dermal, oral and respiratory. The general equation of selected exposure route is the following:

$$\mathrm{ADD} = \frac{\mathrm{C} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}},$$

where C is concentration in environmental media (mg kg^{-1}), IR is ingestion rate (kg day^{-1}), EF is exposure frequency (days $year^{-1}$), ED is exposure duration (years), BW is body weight (kg), AT is average time (days).

By maintaining the spatial distribution of soil contaminant levels and receptors, it is possible, via the source-pathway-receptor paradigm to calculate more realistic contaminant intake and hence risks. Site-specific risk assessment is based on location specific exposure pathways and land-uses, hence get more realistic results, but often it is limited to high-profile studies and large projects.

The non-carcinogenic risk is characterized using a hazard quotient (HQ), which is the ratio of the average daily dose (ADD) to the reference dose (RfD). The aim of risk assessment is to determine, that the level of contamination is represent an acceptable risk or not for human being.

AIMS

The purpose of my study was to refine the human health risk assessment and exposure assessment of metal contaminated sites. We determined the differences in soil pollution and human health risk between the flooded and non-flooded vegetable gardens in the village of Gyöngyösoroszi. The arsenic, cadmium, lead and zinc content of soil and vegetables were analyzed in the area of an abandoned lead-zinc mine and geochemical maps were created from measured data.

We tried to model the plant uptake of metals with the most accumulating vegetable species in polluted and unpolluted soil in pot experiment. Site-specific exposure parameters were set by questionnaire derived data and more reasonable method for risk assessment was developed.

MATERIALS AND METHODS

Area description

The studied area is located in the South-Western part of Mátra Mountains, North-Eastern Hungary along the left side of the Toka creek. The creek flows from North to South through the village Gyöngyösoroszi (47.826°N, 19.894°E) and collects the runoff of the abandoned metal site. The mountain mostly consists of amphibole andesite, its pyroclastics and pyroxene andesite at the top together with 500-2000 m thickness. According to the postvolcanic hydrothermal activities chalcophile elements build up the mainly mesothermal ore minerals. In the Gyöngyösoroszi area the most frequent ore minerals are galenite (PbS), sphalerite (ZnS), pyrite (cubic FeS_2), marcasite (rhombic FeS_2) and chalcopyrite ($CuFeS_2$) (Vető, 1988). The mining activities were based on these minerals.

Mining began in the Middle Ages and was expanding rapidly throughout the 19th century until 1929. After two decades of interruption, mining continued more intensively and between 1954 and 1985 the total amount of 3920089 tons of ore were mined and transported to the flotation plant near Gyöngyösoroszi. To meet the water demand of the flotation technology an industrial water reservoir was constructed in the valley of the Toka creek.

The mining activity has ceased, but the final closing of the mine and remediation of the site has not been carried out yet. The sulphide minerals in the old drifts and headings have been oxidized and sulfurous acid is formed by infiltration. In 1996 a remarkable precipitation event (105 mm) occurred during one day, the water overflowed the dams and caused a huge flood in the village. The toxic sediment was spread over the surrounding vegetable gardens.

Field experiment

Sampling of soils and vegetables was carried out at 44 sampling sites from flooded and non-flooded vegetable gardens in the village Gyöngyösoroszi. Soil samples were collected also from the tailing dump at 13 sampling sites. At each sampling site duplicate samples were collected by random sampling method according to MSZ 21470-1. Six vegetable species were selected for this study; these were representative of species consumed in the studied area: tomato (*Lycopersicon lycopesicum*), squash (*Cucurbita pepo*), bean (*Phaseolus vulgaris*), onion (*Allium cepa*), carrot (*Daucus carota ssp. sativus*) and sorrel (*Rumex rugosus*).

Pot experiment

The pot experiment was planned on the basis of field experiment. Two soils were used: one was collected from non-flooded vegetable garden in the village (UP: unpolluted soil). The other soil sample (P: polluted soil) was a mixture of reference soil (80%) and tailing material (20%). This mixture modelled the flooding processes. 12 black plastic pots were filled with 1000 g air-dried soil. Vegetable seeds were sowed into the pots: sorrel (*Rumex acetosa*) (100 seeds) and carrot (*Daucus carota*) (100 seeds). The experiment was carried out in climate chamber for 106 days with 400 W m^{-2} light and 24°C for 16 hours and darkness and 16°C for 8 hours.

Laboratory analyses

Soil samples were dried at 30°C until constant weight and sieved through 2-mm nylon mesh according to MSZ 21470-2. The vegetable samples were washed with distilled water three times to eliminate the air-borne pollutants and soil particles and then blotted dry with tissue paper. Only the edible part of each vegetable was used for analytical purposes; the non-edible parts were removed using a plastic knife. The cook-ready vegetables were weighed, dried at 30°C until constant weight, weighed again to determine water content and then ground using a ceramic-coated grinder.

After digestion with *aqua regia* and microwave the arsenic, cadmium, mercury, lead and zinc contents were measured by inductively coupled-mass spectrometry according to US EPA 6020.

Questionnaire, statistical analyses and geochemical mapping

A standardized questionnaire was constructed to set the site-specific parameters for risk assessment. The survey included 67 vegetable gardens in the village and 90 participants (43 male and 47 female).

Median concentrations and median absolute deviation were calculated and compared to their Hungarian pollution limit value. In analyzing the differences among the two territory types the Mann-Whitney test was used for the statistical analysis taking $p<0.05$ as significant. The statistical parameters were prepared using Statistica 6.0 (StatSoft, Tulsa, OK 2001).

The sampling points were digitalized according to their GPS coordinates. Separated geochemical maps were created for arsenic, cadmium, lead and zinc concentrations using the grid based graphics program Surfer 8.0 (Golden Software, Golden, CO 2002).

Risk assessment

The average daily dose was calculated in the two selected exposure routes by default and site-specific equations. The site-specific equation of ingestion of vegetables was created from questionnaire derived data: $\mathrm{ADD} = \dfrac{\sum (C_{\mathrm{VEG}} \times \frac{Y_{\mathrm{VEG}}}{n}) \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}}$, where C_{VEG} is concentration in vegetable (mg kg^{-1} fresh weight), Y_{VEG} is the average yield of the selected vegetable in the garden (kg year^{-1}), n is the average family size (-), ED is exposure duration (years), BW is body weight (kg), AT is average time (days).

The average daily dose of soil ingestion was calculated separately for men, women and children, because of differences in bodyweight and ingestion rate soil. The non-carcinogenic risk was characterized using a hazard quotient (HQ), which is the ratio of the average daily dose (ADD) to the reference dose (RfD). If HQ is bigger than 1, then the ADD of particular metal exceeds the RfD, indicating that there is a potential risk associated with that metal.

RESULTS

Arsenic and heavy metal content of soils

The results obtained for the median concentrations are presented in Table 1. The arsenic and metal content of flooded vegetable gardens exceeded the pollution limit values, with the exception of lead, whereas the contents of non-flooded vegetable gardens were, bar arsenic, under these thresholds. The flooded and non-flooded vegetable gardens show highly significant differences, but the difference between the tailing dump and flooded vegetable gardens was non significant. The arsenic content of soils in the pot experiment also exceeded the Hungarian pollution limit value, but the zinc and cadmium content were under these thresholds. The mixing with tailing material increased the arsenic and lead content.

Table 1
Median concentrations of soil samples (mg kg^{-1})

	Soil sample	As	Cd	Pb	Zn
Field experiment	Tailing dump	55.7	1.46	125.5	436
	Flooded vegetable garden	46.6	1.31	85.2	366
	Non-flooded vegetable garden	31.4	0.43	27.8	142
Pot experiment	Polluted soil	202.5	0.49	391.5	159
	Unpolluted soil	34.5	0.27	30.8	124
Pollution limit value		15.0	1.00	100.0	200

Arsenic and heavy metal content of vegetables

The arsenic content of vegetables was under the limit of detection in every case in the field experiment. The measured heavy metal levels were higher in vegetables grown in flooded vegetable gardens in every case. The highest cadmium concentration was measured in carrot (0.130 mg kg^{-1}), lead in onion (1.060 mg kg^{-1}), and zinc in sorrel (60.50 mg kg^{-1}) in field experiment. In pot experiment the highest concentrations were measured in sorrel. (Cd: 1.273 mg kg^{-1}, Pb: 8.570 mg kg^{-1}, Zn: 139.57 mg kg^{-1}). In the case of pot experiment the arsenic content was measurable in the carrot grown in polluted soil.

Bioconcentration factors

The bioconcentration factor (BCF) was calculated from the ratio of the metal concentration of the vegetable (fresh weight) and the metal concentration of the soil. Figure 1 illustrates the bioconcentration factors of different species in flooded and non-flooded vegetable gardens.

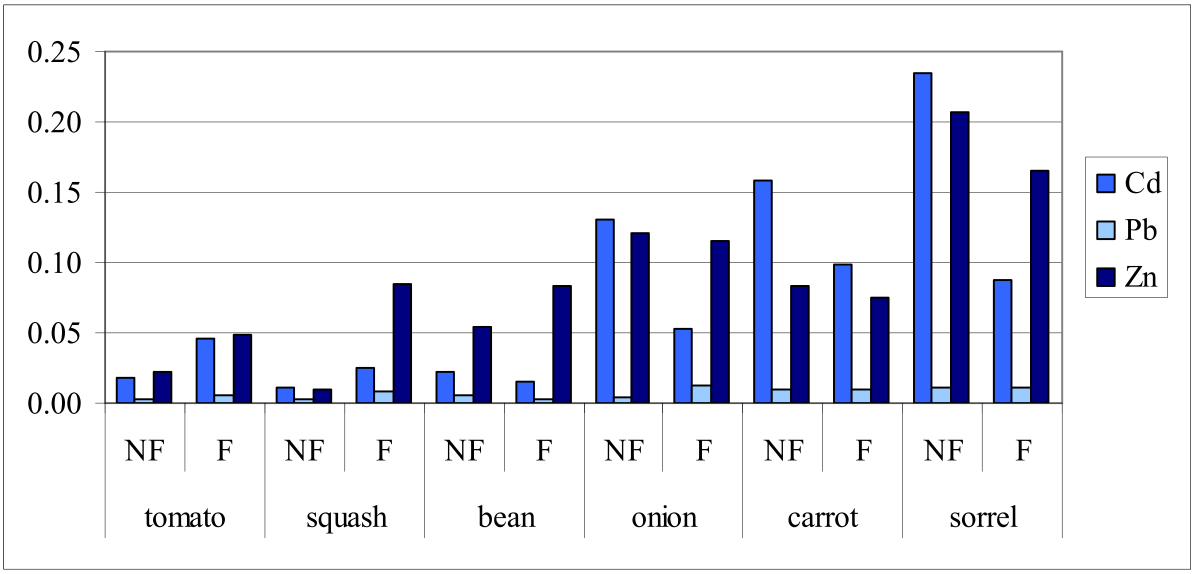

Figure 1.
Bioconcentration factors of vegetable gardens

NF: non-flooded vegetable gardens
F: flooded vegetable gardens

The highest bioaccumulation capacity has the sorrel in both experiments. In the field experiment higher BCFs were found in the non-flooded vegetable gardens, but in the pot experiment the BCFs of polluted soils were higher. (Sorrel: Cd: 0.606 in unpolluted and 2.59 in polluted soil, Zn: 0.348 in unpolluted and 0.882 in polluted soil.). In our experiments cadmium and zinc were the mobile elements, cadmium was more mobile than zinc in the pot experiment. In contrast with the field experiment, the bioconcentration values of polluted soil were higher, than the unpolluted soil. The high accumulating capacity in pot experiment can generate by the pH decreasing. The increased metal concentration in tailing material can decrease the pH of soil and hence stimulate the accumulating capacity

Risk assessment

The site-specific exposure parameters were the following: The average bodyweight was 80.07 kg for men and 73.66 kg for women. The average family size was 2.8. The yearly consumption of vegetables per capita was the following: 7.68 kg tomato, 6.21 kg squash, 2.74

kg bean, 2.44 kg onion, 2.15 kg carrot and 1.32 kg sorrel. The exposure frequency was 358 days.

The summarized hazard index of flooded vegetable gardens is 0.92835 and of non-flooded vegetable gardens is 0.55627 with default parameters. The largest contribution to hazard index was from As both in the flooded and non-flooded vegetable gardens. In all cases most hazard index was attributable to ingestion of home-produced vegetables. The summarized hazard index of flooded vegetable gardens is 0.3275 and of non-flooded vegetable gardens is 0.0922 with site-specific parameters, both of them are indicated acceptable risk. The largest contribution to hazard index was from Pb both in the flooded and non-flooded vegetable gardens. The contribution to the hazard index from soil ingestion was largest for children in flooded-vegetable gardens and 90% of the risk is derived from arsenic.

The risks were acceptable in every cases.

CONCLUSION

The toxic metal contents in the Gyöngyösoroszi area exceed the Hungarian limit value. The high arsenic content of the area is due to the natural background and is not available by vegetables. There are significant differences between the flooded and non-flooded vegetable gardens. Origin of the pollution is the tailing dump and the flotation plant.

The result of pot experiment suggests that mixing of unpolluted soil with tailing material does not model the flooding. The most mobile elements are cadmium and zinc and the most accumulating vegetable is sorrel.

The risk assessment was carried by default and site-specific exposure parameters. The results show that using the new equation $\mathrm{ADD} = \dfrac{\sum (C_{\mathrm{VEG}} \times \frac{Y_{\mathrm{VEG}}}{n}) \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}}$ can combine the amount of homegrown vegetables and the bioavailability of metals. Using site-specific parameters instead of default exposure parameters is more accurate in risk assessment process, because the default parameters overestimate the real hazard.

The consumption of homegrown vegetables does not pose unacceptable risk to the population although the main exposure route is consumption of vegetables.

PUBLICATIONS

Articles

1. **Sipter, E.**, Rózsa, E., Gruiz, K., Tátrai, E., Morvai, V., 2008. Site-specific risk asseessment in contaminated vegetable gardens. Chemosphere 71, 1301-1307.
   IF: 2.442
2. **Sipter, E.**, Auerbach, R., Gruiz, K., Máthé-Gáspár, G., 2008. Change of bioaccumulation of toxic metals in vegetable. Commun. Soil Sci. Plan. Accepted article.
   IF: 0.302
3. Máthé-Gáspár, G., **Sipter, E.**, Szili-Kovács, T., Takács, T., Máthé, P., Anton, A., 2008. Environmental impact of soil pollution with toxic element from the lead and zinc mine at Gyöngyösoroszi (Hungary).Commun. Soil Sci. Plan. Accepted article.
   IF: 0.302
4. Máthé, P., Máthé-Gáspár, G., Szili-Kovács, T., **Sipter, E.**, Anton, A., 2007. Changes in the parts of the rhizosphere phosphorus cycle influencing by heavy metal contamination. Cereal Res. Commun. 35, 761-764.
   IF: 1.037

Citable abstracts

1. **Sipter, E.**, Auerbach, R., Gruiz, K., 2005. Ecotoxicological testing and risk assessment of a heavy metal contaminated site, Toxicol. Lett. 158, S1:253–254.
   IF: 2.43
   42nd Congress of the European Societies of Toxicology, Cracow, Poland
2. **Sipter, E.**, Auerbach, R., Gruiz, K., Mathe-Gaspar, G., 2005. Bioaccumulation of toxic metals in vegetable species: A pot experiment
   ConSoil 2005, Bourdeux, France
3. **Sipter, E.**, Menczel, I., Gruiz, K., 2003. Methods for the site specific human health risk assessment of toxic metals containing cultivated plants
   ConSoil 2003, Gent, Belgium

4. **Sipter, E.**, Menczel, I., Gruiz, K., 2002. Human health risk assessment in a heavy metal polluted site
20th European Conference of the Society for Environmental Geochemistry and Health, Debrecen, Hungary
5. **Sipter, E.**, Menczel, I., Ferwagner, A., Gruiz, K., 2002. Natural processes in a toxic metal polluted site as potential risk source
European Conference on Natural Attenuation, Heidelberg, Germany
6. **Sipter, E**., Menczel, I., Gruiz, K., 2002. Egészségkockázat felmérésének lehetőségei toxikus fémekkel szennyezett területen
Országos Környezetvédelmi Konferencia és Szakkiállítás, Siófok, Hungary (in Hungarian)
7. Gruiz, K., Horváth, B., Molnár, M., **Sipter, E**., 2000. When the chemical time bomb explodes
ConSoil 2000, Leipzig, Germany
8. **Sipter, E**., 2000. Toxikus fémekkel szennyezett üledék környezeti kockázata
Magyar Kémikusok Egyesülete XXIII. Kémiai Előadói Napok, Szeged, Hungary (in Hungarian)