

PRELIMINARY ASSESSMENT OF HEAVY METALS CONTENT OF VEGETABLES GROWN IN INDUSTRIAL AREAS IN ROMANIA

MIRELA NEDELESCU¹, DAN BĂLĂLĂU², DANIELA BACONI^{2*}, MIHAI JULA³, DALIA MORAR³, ALINA GLIGOR³, CRISTIAN BĂLĂLĂU⁴

¹Hygiene and Environmental Health Department, University of Medicine and Pharmacy "Carol Davila", Bucharest

²Toxicology Department, Faculty of Pharmacy, University of Medicine and Pharmacy "Carol Davila", Bucharest

³Hunedoara Sanitary Veterinary and Food Safety Directorate, Deva, Hunedoara County

⁴Department of General Surgery, University of Medicine and Pharmacy "Carol Davila", Emergency University Hospital "St. Pantelimon", Bucharest

*corresponding author: daniela_baconi@yahoo.com

Manuscript received: May 2014

Abstract

Heavy metals represent an important health risk to people living in historically contaminated areas with these substances, especially due to their bioaccumulation in soils, through the transfer to vegetables affecting the health of consumers. The aim of this study was to determine the concentrations of heavy metals (Pb, Cd, Cu and Zn) in vegetables grown in two non-ferrous metallurgical industrial areas in Romania: Copșa Mică and Zlatna. Samples of potato, carrot and yellow onion harvested in these regions were analysed through atomic absorption spectrophotometric techniques and the results revealed elevated Pb and Cd concentrations in carrots and yellow onion grown in Copșa Mică area, while the concentrations of Pb and Cd in vegetables harvested in Zlatna area exceed the maximum limits only in carrots. Concentrations of Cu and Zn in vegetables analysed were below the maximum permissible limits, both in Zlatna and Copșa Mică area.

Rezumat

Metalele grele reprezintă un risc pentru sănătatea populației care locuiește în zone poluate istoric cu aceste substanțe, mai ales datorită bioacumulării în sol, de unde prin intermediul legumelor ajung să afecteze sănătatea consumatorilor. Scopul studiului a fost să determine conținutul în metale (Pb, Cd, Cu și Zn) al unor legume cultivate în două zone cu industrie metalurgică neferoasă din România – Copșa Mică și Zlatna. Au fost analizate prin tehnici de spectrofotometrie de absorbție atomică probe de cartof, morcov și ceapă galbenă recoltate din aceste zone. Rezultatele relevă valori crescute de Pb și Cd în zona Copșa Mică la morcovi și ceapă galbenă, pe când concentrațiile de Pb și Cd în legumele recoltate în zona Zlatna depășesc limitele maxime admise doar în morcovi. Concentrațiile de Cu și Zn în legumele analizate s-au situat sub concentrația maxim admisă, atât în zona Zlatna, cât și în zona Copșa Mică.

Keywords: heavy metals, industrial pollution, GF-AAS, F-AAS, vegetables

Introduction

Manufacturing and processing of non-ferrous ore mining was the main source of heavy metal pollution in the second half of the last century in Romania. Pollution problem still persists, in historically contaminated areas heavy metals were deposited in large quantities in the environment, especially in soils, exposing continuously the resident population. Such areas are Copșa Mică and Zlatna cities which are strongly marked by the heavy metal pollution phenomenon due to emissions from non-ferrous metallurgy plants, Sometra SA Copșa Mică and Ampelum SA Zlatna. The industrial platform of Ampelum SA has an area of about 5 hectares and is located in the south of the Zlatna city. Zlatna metallurgical plant worked continuously from 1747 until 2004 when it was closed due to unprofitable activity and debts accumulated. With industrial activities stopped in

2004, there remained the 3 tailings dams near Zlatna where there are deposited about 3.5 million tons of tailings resulting from the manufacturing processes. In 2009, these tailings ponds have entered into a process of closing, the first two located in the Podu lui Paul village (1.73 ha) and Valea Mică village (tailing dam II, 5.6 ha) were closed in 2010 and the closing of the third tailing dam (10.2 ha) situated in Galați village is almost completed [19].

Established as an economic unit in the years 1939-1940, the non-ferrous metallurgical enterprise from Copșa Mică [3], the current Sometra SA, has the obligation to reduce pollution levels of sulphur dioxide and dust containing heavy metals by the end of 2014, through modernization and monitoring measures.

Lead contamination of the main pollutants emitted by the non-ferrous metallurgical plants occurs in

particular in the form of steams that are rapidly converted into fine aerosols which condense and are oxidized by air. Due to their size, lead aerosols remain suspended in the atmosphere for a long time so that they can be transported to 5-10 km from the release site. Air contamination occurs also in the process of production and processing of other nonferrous metals such as zinc, cadmium, manganese and copper.

In contrast to other impurities, which are neutralized in contact with air or soil, lead maintains its characteristics even if it is absorbed by plants, with a continuous increasing of its concentration in the environment [7]. The mobility of heavy metals from soils and bioavailability to plants depends on the pH of soil, presence and concentration of organic and inorganic ligands and redox reactions which are controlling the oxidation state of heavy metals and metalloids and thus, the mobility and the toxicity of these compounds [10, 13].

Metals in particulate form, having the origin in contaminated soils and waste dumps in industrial areas circulate by air and hydrological system at considerable distances from sources of pollution [1], which is why a large population is exposed to the toxic effects of heavy metals.

Heavy metals are pollutants with toxic systemic effects in the body, where they have actions on various organs and systems such as: blood, nervous system, cardiovascular system, gastrointestinal tract, kidneys etc. Chronic exposure to lead is responsible for different organ-specific syndromes: haematological (anaemia), neurological (brain dysfunction, psychological changes, disturbance of attention, hyperactivity, saturnine encephalopathy), cardiovascular (atherosclerosis, hypertension, heart disease), renal disease (chronic renal failure), gastrointestinal (saturnine colic). Cadmium affects the pulmonary apparatus with the appearance of emphysema and increase the risk of lung cancer, and kidney (glomerular and tubular destructions), its increased concentration in the body interfering with zinc and calcium levels [8, 9].

Materials and Methods

This study assessed the concentrations of lead, cadmium, copper and zinc in vegetables grown in soils historically contaminated with heavy metals in two areas of non-ferrous industry: Copșa Mică and Zlatna, Romania. Measurements were made by a spectrophotometer ZEE nit 650 using atomic absorption spectrometry with graphite furnace technique (GFAAS) for the determination of Pb and Cd and by a spectrophotometer with continuous source Analytik Jena contraAA 300 in order to

determine concentrations of Cu and Zn through flame atomic absorption spectrometry (FAAS).

Sampling. Three sampling surfaces in Copșa Mică area (SS1, SS2 and SS3) and two sampling surfaces in Zlatna (SS1 and SS2), located at different distances from the source of pollution, were chosen in order to collect the vegetables samples. Samples of potatoes, carrots and yellow onions were collected randomly during the month of August 2014 from established areas.

Sample preparation. Collected vegetables samples were processed in order to determine the above mentioned trace elements according to SR EN 13804:2003 [16]. After washing and peeling, the vegetables were chopped and homogenized using a mincer. From each sample there were weighed 10 g of sample in a crucible, followed by the drying in a programmed oven at the initial temperature of 105°C, increasing gradually to 450°C. To the resulting ash there were added 5 mL of perchloric acid, which was then evaporated putting the crucible on the stove. The residue was dissolved in 10 mL of nitric acid, after which the solution was transferred to a 50 mL volumetric flask and the volume was made up using *aqua regia* [2, 6]. All the chemical reagents used were of analytical grade.

For the choice of the determination technique of trace elements we took into account the instrumental methods developed for food analysis [6, 13, 17, 18], the expected concentrations of these elements in vegetables samples grown in studied areas [3, 4, 5] and the maximum permissible concentrations for these elements [11, 14, 15]. The results were expressed as mg/kg dry matter and represent the average of the determinations from a sampling surface.

Verification of performance parameters in order to determine lead and cadmium by GFAAS and copper and zinc by FAAS. Linearity, concentration range and sensitivity of the determination method were evaluated by drawing the 5-point calibration curve using standard solutions with concentrations between 10 and 30 ppb for Pb, 0.8 and 2.4 ppb for Cd, 0.1 and 1.6 ppm Cu and 0.06 to 0.6 ppm for zinc. The calibration curves for Pb by graphite furnace atomic absorption spectrometry method and for Zn by flame atomic absorption spectrometry can be found in Figure 1, respectively in Figure 2.

In order to determine the limit of detection (LOD) and limit of quantification (LOQ), a series of five solutions of the same concentration were prepared: lead standard solution having the lower concentration used to draw the calibration curve (10 ppb) was diluted 50 times (LOD = 0.002 ppm and LOQ = 0.24 ppm); Cd standard solution with a concentration of 0.8 ppb was diluted 40 times (LOD = 0.014 ppm and LOQ = 0.06 ppm); the

copper standard solution with a concentration of 0.1 ppm was diluted 20 times (LOD = 0.02 ppm and LOQ = 0.18 ppm) and the standard zinc solution with a concentration of 0.06 ppm was diluted 10 times (LOD = 0.04 ppm and LOQ = 0.32 ppm).

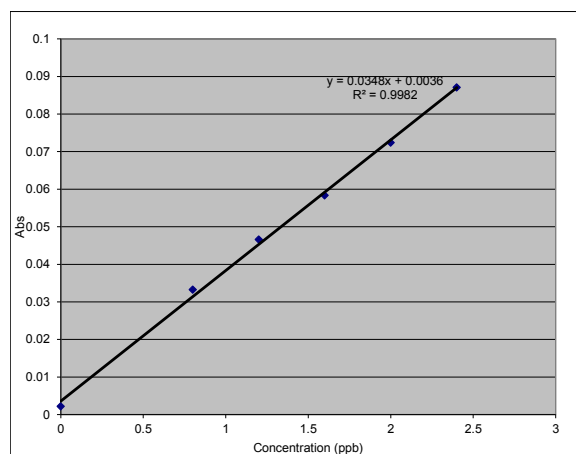


Figure 1.

Calibration curve for lead through GFAAS

Statistical analysis. Analysis and interpretation of data was made using SPSS program version 21. The statistical analyses used were as follows: ANOVA was used to test the effect of the sampling locations, the t test pairs for comparisons between species of vegetables and regions.

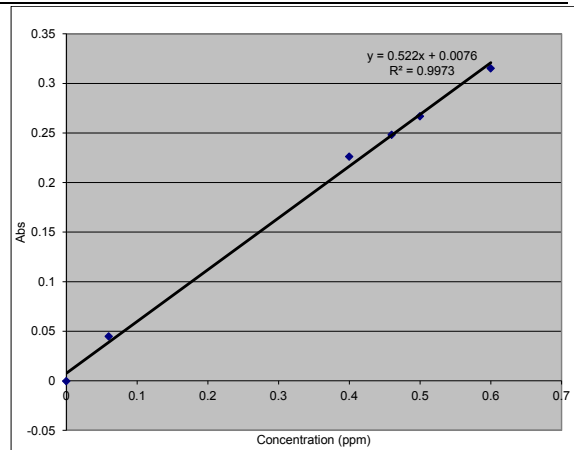


Figure 2.

Calibration curve for zinc through FAAS

Results and Discussion

For the determination of heavy metals in vegetables grown in the study areas, harvesting was made in three sampling areas in Copșa Mică area numbered SS1, SS2 and SS3 and the two sampling surfaces in Zlatna - SS1 and SS2. The identification of sampling areas and harvested samples is shown in Table I and Figures 3 and 4 locate the sampling surfaces of vegetables in relation to sources of heavy metal pollution in the two areas.

Table I

Identification of sampling surfaces and no. of samples

Study area	Sampling surface	Location	No. of samples		
			Potato	Carrot	Yellow onion
Copșa Mică	SS1	Copșa Mică	7	5	6
	SS2	Târnavioara	-	5	5
	SS3	Axente Sever	8	-	7
Zlatna	SS1	Valea Morilor	7	8	7
	SS2	Pătrângenii	8	5	6
Total samples (84)			30	23	31

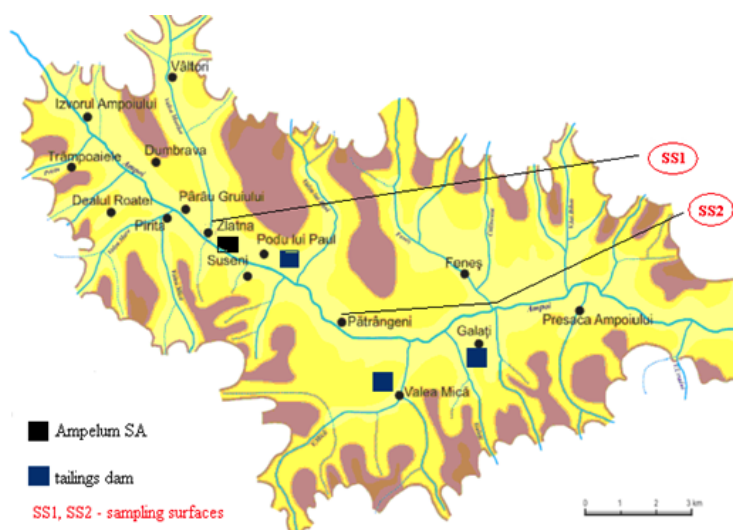


Figure 3.

Zlatna area and correspondence with sampling surfaces of assessed vegetables

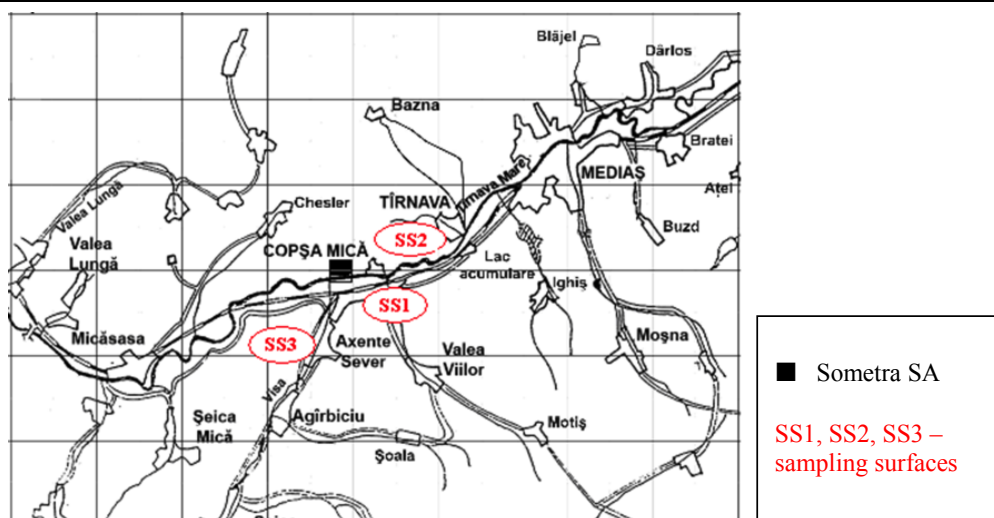


Figure 4.

Copșa Mică area and correspondence with sampling surfaces of tested vegetables

The average concentrations of heavy metals found in vegetable samples is shown in Table II. Values

were compared with the maximum levels for heavy metals admitted in vegetables (Table III).

Table II

The average concentrations of heavy metals found in edible parts of vegetables in the studied areas (mg/kg)

Sample surfaces	Sample	Pb		Cd		Cu		Zn	
		Average	SD	Average	SD	Average	SD	Average	SD
Copșa Mică SS1	potato	0.04	0.02	0.10	0.04	2.39	0.76	3.9	0.89
	carrot	0.22*	0.06	0.27*	0.14	0.80	0.23	3.3	0.82
	yellow onion	0.02	0.007	0.30	0.17	0.51	0.20	2.1	0.78
Copșa Mică SS2	carrot	0.54*	0.06	0.37*	0.18	1.01	0.30	5.7	0.93
	yellow onion	0.03	0.005	0.27*	0.13	0.55	0.20	4.6	0.09
Copșa Mică SS3	potato	0.11	0.04	0.05	0.02	2.05	0.25	9.3	0.07
	yellow onion	0.01	0.002	0.1	0.06	0.55	0.20	10.6	0.08
Zlatna SS1	potato	0.05	0.03	0.01	0.003	3.17	0.56	7.4	0.08
	carrot	0.11*	0.03	0.05	0.02	0.65	0.10	2.9	0.04
	yellow onion	0.01	0.0065	0.01	0.0016	0.51	0.15	2.1	0.03
Zlatna SS2	potato	0.06	0.01	0.01	0.0010	1.37	0.27	6.9	0.03
	carrot	0.14*	0.05	0.03	0.01	0.90	0.28	3.3	0.01
	yellow onion	0.02	0.01	0.01	0.0009	0.54	0.19	4.6	0.03

*p value < 0.05

Table III

Maximum limits for heavy metals admitted in vegetables

Element	Maximum permissible limits (mg/kg)*	
	Fresh or frozen vegetables except leafy vegetables	Leafy vegetables
Pb	0.1	0.3
Cd	0.1	0.2
Cu	5	-
Zn	15	-

*EU Regulation no. 1881/2006 setting maximum levels for certain contaminants in foodstuffs and European Food Safety Authority

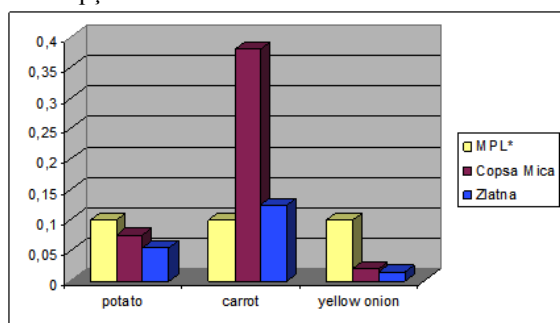
Following the spectrometric determinations, the concentrations of lead and cadmium found in vegetables harvested in Copșa Mică area exceeded the maximum limits in carrots and yellow onions, the concentration decreasing with the increase of the distance from the source of pollution.

Lead and cadmium content in vegetables collected from the two study areas is shown in Figure 5 and Figure 6. In vegetables grown in Copșa Mică area

lead was found in quantities exceeding 2-5 times the maximum permissible level in carrots, for other analysed vegetables the average concentration was below the maximum permissible limit. It was noted that in Zlatna area the average concentrations of cadmium were in the order: yellow onion < potato < carrot, these values being below the maximum allowed concentrations, while in Copșa Mică area, the average Cd concentrations

exceed 2 or 3 times the maximum permissible limit in yellow onion and carrot samples.

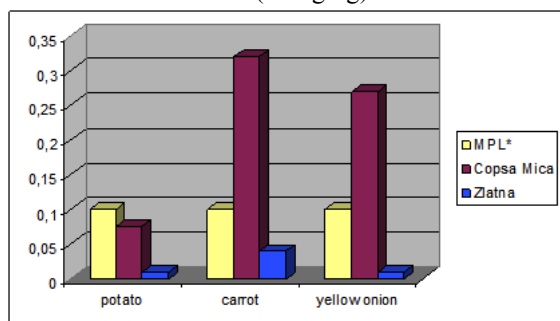
Concentrations of Cu and Zn in the vegetables analysed were within normal limits in both Zlatna and Copșa Mică area.



*MPL (maximum permissible limit) = 0.1 mg/kg

Figure 5.

Lead content of vegetables grown in the studied areas (in mg/kg)



*MPL (maximum permissible limit) = 0.1 mg/kg

Figure 6.

Cadmium content of vegetables grown in the studied areas (in mg/kg)

Conclusions

Measurements of the content of heavy metals in vegetables grown in two areas with non-ferrous metallurgical industry in Romania were revealed quantities exceeding the maximum limits for lead and cadmium, the concentration decreasing with the increase of the distance from the source of pollution. Copper and zinc content was found within permitted limits.

In order to have a complete assessment of environmental contamination and a better correlation with environmental factors in the two considered areas, research for assessing the concentration of heavy metals in other environmental factors (soil, surface water and groundwater) are ongoing.

References

1. Agarwal S.K., Heavy metal pollution. APH Publishing Corporation, 2009: 3-7.
2. Aldjain I.M., Al-Whabi M.H., Al-Showiman S.S., Siddiqui M.H., Determination of heavy metals in the

fruit of date palm growing at different locations of Riyadh. *Saudi Journal of Biological Science*, 2011; 18: 175-180.

3. Bardac D., Brezai C., Florescu E., Copșa Mică – elemente de monografie socială și medicală. Sibiu, Casa de Presă și Editură „Tribuna” Sibiu, 1999.
4. Beccanoli E., Vanni F., Beccaloni M., Carere M., Concentrations of arsenic, cadmium, lead and zinc in homegrown vegetables and fruits: Estimated intake by population in an industrialized area of Sardinia, Italy. *Microchemical Journal*, 2013; 107: 190-195.
5. Gergen I., Harmanescu M., Application of principal component analysis in the pollution assessment with heavy metals of vegetable food chain in the old mining areas. *Chemistry Central Journal*, 2012; 6: 156-169.
6. Ionita, C., Mititelu M., Morosanu E., Analysis of heavy metals and organic pollutants from some Danube River fishes. *Farmacia*, 2014; 62(2): 299-305.
7. Kabata-Pendias A., Pendias H., Trace Elements in Soils and Plants – Third Edition. CRC Press, Boca Raton, London, New York, Washington, D.C., 2001: 158-170.
8. IPCS – International Program on Chemical Safety, Environmental Health Criteria 3: Lead (www.inchem.org).
9. IPCS – International Program on Chemical Safety, Environmental Health Criteria 134: Cadmium, 1992 (www.inchem.org).
10. Jolly Y.N., Islam A., Akbar S., Transfer of metals from soil to vegetables and possible health risk assessment. *SpringerPlus*, 2013; 2: 385-393.
11. Magnuson B., Munro I., Abbot P., Review of the regulation and safety assessment of food substances in various countries and jurisdictions. *Food Additives & Contaminants: Part A*, 2013; 30(7): 1147-1220.
12. Vartolomei A., Vlase L., Cuciureanu M., Cuciureanu R., Saveta Popa D., Determination of ochratoxin in food by LC-MS/MS. *Farmacia*, 2014; 62(2): 287-298.
13. Violante A., Cozzolino V., Perelomov L., Caporale A.G., Pigna M., Mobility and bioavailability of heavy metals and metalloids in soil environments. *J. Soil Sci. Plant Nutr.*, 2010; 10(3): 268-292.
14. *** - European Food Safety Authority. Scientific Opinion of EFSA Panel on Contaminants in the Food Chain (CONTAM) (www.efsa.europa.eu).
15. *** - Regulation CE no. 1881/2006 setting maximum levels for certain contaminants in foodstuffs (<http://eur-lex.europa.eu>).
16. *** - SR EN 13804: 2003; Produse alimentare. Determinarea microelementelor. Criterii de performanță, considerații generale și pregătirea probei.
17. *** - SR EN 14083:2003 Produse alimentare. Determinarea microelementelor. Determinare plumb, cadmiu, crom și molibden prin spectrofotometrie de absorbție atomică cu cuptor de grafit (GFAAS) după digestie sub presiune.
18. *** - SR EN 14084:2003 Produse alimentare. Determinarea microelementelor. Determinare plumb, cadmiu, zinc, cupru și fier prin spectrofotometrie de absorbție atomică (SAA) după digestie cu microunde.
19. *** - http://www.geo.edu.ro/Catmin/Rom/cncsis/halde/index.php/lazuri_de_decantare.