CONTAMINATIONS COEFFICIENTS OF HEAVY METALS IN AGRICULTURALLY FOOD

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ABSTRACT: *Food contamination represents the changes of the normal food composition due to the presence of foreign components, which by their action and concentration can affect public health. Contamination means the presence over the allowed limits of certain bacterial agents or their toxins, chemical agents etc. The contaminants adversely affect human health through various harmful effects they produce upon the human body. The paper is concerned with theoretical aspects of classification and effect of contaminants on consumers. In the second part, a case study on heavy metal contamination of food products from industrialized areas is presented. As a work method, we used flame and graphite furnace atomic absorption spectrophotometry as well as stripping methods. In finally we calculated the maximum allowed abundance index for the studied agricultural fields and heavy metal transfer coefficients in the studied vegetation.*

Key words*: heavy metals, coefficient transfer, agriculturally food*

1. Introduction

The supply of the population with quality food products is difficult to happen in when pollution is greatly present. The global development of food industry and service networks has caused some incidents with global characteristic focused on food safety. These problems implied withdrawing food products and important consequences on consumer health as well.

Romanian food product industry tends to align to the requirements of modern production necessary in the exploitation of methods and modern technologies in order to eliminate the risk of food contamination.

The policies of the European Union and of the World Health Organization are focused on food security as the responsibility of the food sector operator, ensured throughout the food chain beginning with the primary production "farm-to-fork".

Through a systemic approach of the food chain, it is possible to avoid product contamination. Therefore, it is essential that raw materials meet quality requirements, that the hygiene of staff, facilities, machines and equipments is appropriate. The result is reflected in the quality and the safety of the finished product.

From the food products perspective, three types of activities have appeared which contribute to the good organisation of the food processes:

1. agricultural production
2. food production
3. network of food services

The hygienic quality of foods is achieved by a series of rules [1]:

1. no physical, chemical, biochemical and microbiological deterioration
2. no micro-organisms, additives, foreign substances over the limits allowed by standards and laws.
3. no infestation with insects and parasites
4. no loss of the nutritional quality and psycho sensorial proprieties by mentioned degradation .

The knowledge of the food raw materials quality allows the obtaining of higher quality food products, applying an appropriate technology [2,3].

Despite having a system of quality monitoring and surveillance of food products, their contamination may occur by contaminants that are introduced naturally or accidentally or through the improper handling of food. Contamination of food products with microbiological agents, chemicals and physical or food allergens remains a key challenge for public health[2-4].

Contamination is the change in the normal composition of the food due to the presence of foreign components in action and their concentration can affect the health of consumers. The change of psycho, physical, chemical or biological properties of food products throughout the food chain can occur through contamination with various pollutants.

To ensure health security, food wholesomeness and maintaining control of the content of different contaminants, sanitation rules on consumer goods must be respected under specific legislation in all EU countries.

In the following, we present the results of our research on heavy metal contamination of food commodities in a highly polluted area, Zlatna.

2. Material and methods

In industrialized areas, there was the danger of food products being contaminated with various chemicals. Contamination can be made by foliar absorption of gas or dust (e.g. heavy metals) which exist in the atmosphere or transfer of such elements directly from the contaminated soil.

Metal translocation within the plant's roots and leaves is made with the vascular system, spreading throughout the plant. The proportion and amount absorbed depends on the concentration of metal inside the plant, plant organ and its age.

Samples from 4 points were taken respecting the sampling methodology and sample preparation according to the ICPA standards in force [7-10].

In order to obtain exact results, comparable to those of the specialty literature, in determining metal cations from soil, water and vegetable matter samples, we aimed at studying and applying modern methods of analysis [6]. We took comparative measurements through the three methods: flame atomic absorption spectrophotometry, graphite furnace atomic absorption spectrophotometry [7] and accumulation-dissolution methods [8].

Vegetable Matter Processing in View of Determining Heavy Metals

Vegetable Matter Preparation in view of Mineralization

Analysed plants were gathered during the entire vegetation period, at certain time spans (in relation to the growing periods). The sample size was of approximately 500 g fresh material.

The material was ground and dried at the room temperature in appropriate conditions so that it should not become contaminated with other substances.

The sample was subsequently ground and passed through a sieve with a 1 mm hole dimension and stored in sealed and labelled plastic boxes till the moment of analysis (the same as with the soil).

Vegetable Matter Mineralization

Through this method we determine the Pb, Cd, Zn or Cu content from leaves, fruits (grapes, apples, etc), cereals (corn beans, wheat beans) etc.

Method principle: in order to determine the Pb, Cd, Zn or Cu content, the biological material underwent wet mineralization or calcination. In the obtained solution, heavy metals were dosed through atomic absorption spectrophotometry or through other methods.

a) Wet mineralization was performed using a mixture of nitric acid, perchloric acid and sulphuric acid.

The organic substance from the vegetable matter was oxidised at high temperature using a mixture of HNO_3:$HClO_4$: H_2SO_4 in proportion of 2:1:0,2 (volume)

We weighed 1 g of fine vegetable material ground in a pestle mortar to which, in a Berzelius glass, we added 5 ml of oxidating mixture: HNO_3:$HClO_4$:H_2SO_4 of proportion 2:1:0,2.

The sample was left to rest for 24 hours after which it was evaporated dry, on a sand bath.

The samples were cooled and mixed with 5ml HCl conc., to a dry evaporation (yellowish). The samples were placed in a 50 ml rated balloon flask with a solution of HCl 0,5 N (or with distilled water where we added 2 ml HCl conc.)

The elements from the obtained extract were dosed using the atomic absorption spectrophotometer.

b) *Dry Mineralization* (through calcination)

The organic substance from the vegetable material is oxidised by the air oxygen in calcination in an electric furnace at a constant temperature of 450^0C.

The obtained residue formed of oxides and carbonates becomes soluble with 2 ml HCl 6,5 N, is passed to a 50 ml rated balloon flask, the blue stripe is filtered through filter paper and the balloon flask is brought to a sign with distilled water.

The elements from the obtained extract were dosed using atomic absorption spectrophotometry.

Mineralization through calcination has the advantage that it eliminates sample contamination by adding reagents. This method is recommended for the biological material that contains a high quantity of organic matter [9].

Location of the sampling points in Zlatna (the Studied Area)

1. TA1 – Pătrânjeni, to 1 Km away from the polluting source, South, downstream of Ampoi river, air currents V→E (Calea Motilor Street);
2. TA2 - Valea Morilor Street, 19, 1,5 Km away from the source, North, between two hills on the Valea Morilor river (affluent of Ampoi), favouring currents S "N;
3. TA3 – Stadionului Street (16), 2 km away from the source, upstream towards West, favouring iar currents E →V(obs. Samples were gathered from the confluence of rivers Valea Morilor and Ampoi);
4. TA4 –Tudor Vladimirescu Street, 500 m away from the source, favouring currents S→E

3. Results and discussion

The maximum allowed abundance index for the studied agricultural fields.

Results were registered on a period of 4 months encompassing all development phases of the studied plants. The analytical data on which we worked for Cu in vegetable matter are: spectral line λ = 324,7; Φ (slit) = 0,5; strength of current = 10mA; flame type air-acetylene; device sensitivity 0,07 ppm.

The obtained results were compared to the maximum allowed limits, which must not exceed 10 ppm for vegetation

- The maximum allowed abundance index was calculated – MAAI with:

$$MAAI_i = MAL_i / f_i \qquad (1)$$

where: $MAAI_i$ – the maximum allowed abundance index;
MAL – maximum allowed limit
f_i – the pedo-geochemical fund of the element

The abundance index of the element was calculated:

$$AI = D_i / f_i \qquad (2)$$

where: D_i – individual content, determined in soil, mg/kg

f_i - individual content of the pedo-geochemical fund;

The maximum allowed abundance index is shown in table 1.

Tab. 1 $MAAI_i$ in soils, for Cu^{2+}, Pb^{2+}, Cd^{2+}

The studied element	**f_i**	**MAL, mg/kg**	**$MAAI_i$**
Cu	14	100	714
Pb	31	100	322
Cd	1.20	3	25

The abundance index of polluting elements in the soil of researched fields is shown in tab. 2.

Tab. 2 The abundance index of Cu, Pb, Cd in the studied fields

Agricultural field	**AI_{Cu}**	**AI_{Pb}**	**AI_{Cd}**
TA1	77.1	22.9	5
TA2	45.6	18.5	275
TA3	55.5	24.4	941
TA4	36.4	14.2	33
$MAAI_i$	**7.14**	**3.22**	**25**

The area abundance degree for a chemical element (i) is considered to be **allowed** when:

$$AI_i \leq MAAI_i \qquad (3)$$

And to have an obvious polluting degree when:

$$AI_i > MAAI_i \qquad (4)$$

From the data presented in table 2, applying the relations (3, 4) it results that the polluting impact is obvious for copper and lead in all the land, and for cadmium, the impact is higher in agricultural land TA3.

Measuring the abundance of heavy metals in the soil allows more meaningful illustration of the phenomenon of pollution intensity, and a logical comparison of the values obtained for different zones or areas, these indices of abundance can be used to prepare distribution maps of soil heavy metals and to establish high risk areas for vegetation, animals and people[8].

Heavy metal transfer coefficients in the studied vegetation

In addition to knowledge of absolute and relative abundance of heavy metals in the studied soils, transfer coefficients of heavy metals in some plant species analyzed were determined, as described in the literature [20]

Although many factors related to soils and vegetation can affect the accumulation of heavy metals in plants, the amounts shown below are only important in magnitude of transfer coefficients.

Transfer coefficients calculation is based on the relation [3]:

$$Q_{tr} + C_p / C_s \qquad (5)$$

where:
Q_{tr} = the transfer coefficient of the metal to the plant;
C_p = metal concentration within the plant;
C_s = metal concentration into the soil.

Tab. 3 Transfer coefficient of the copper into the plant material
(mg/kg metal into the plant /mg/kg metal into the soil)

Land	**Plant material**	**Transfer coefficient Cu^{2+}**
TA1	cabbage	0.09
TA2		0.07
TA3		0.11
TA4		0.07
TA1	carrot	0.07
TA2		0.02
TA3		0.06
TA4		0.05
TA1	beet	0.08
TA2		0.05
TA3		0.10
TA4		0.06

Tab. 4 Transfer coefficient of the lead into the plant material (mg/kg metal into the plant /mg/kg metal into the soil)

Land	**Plant material**	**Transfer coefficient Pb^{2+}**
TA1	cabbage	1.08
TA2		0.74
TA3		1.4
TA4		2.06
TA1	carrot	0.12
TA2		0.03
TA3		0.10
TA4		0.09
TA1	beet	0.08
TA2		0.03
TA3		0.07
TA4		0.02

Tab. 5 Transfer coefficient of the cadmium into the plant material
(mg/kg metal into the plant /mg/kg metal into the soil)

Land	**Plant material**	**Transfer coefficient Cd^{2+}**
TA1	cabbage	3.1
TA2		2.5
TA3		2.9
TA4		2.8
TA1	carrot	0.3
TA2		0.2
TA3		0.3
TA4		0.1
TA1	beet	0.5
TA2		0.4
TA3		0.6
TA4		0.4

The highest transfer coefficients were calculated in the agricultural lands TA1 and TA3 for all the samples discussed (tab.5) High values were found in the cabbage sample but they are irrelevant because the plant contamination process also involved leaf absorption [8-9].

Conclusions

Based on a case study approach, we believe that a general methodology can be developed using predictive mathematical models.
It is important to take into account the factors favoring translocation from soil to plants such as soil acidity or the soil nutrient supply. With this, appropriate measures can be taken to reduce the effect of heavy metal contamination in food products grown and produced in industrial areas and not only.

References

1. Decun, M., Stoița, M., *Legislație pentru managementul calității produselor de origine animală,* Ed. Mirton Timişoara, 1999;
2. Diaconescu, I., Ardelean, D., Diaconescu , M., *Merceologie alimentară. Calitate şi siguranță,* Editura Universitară, Bucureşti, 2007
3. Jianu, I., *Concepte, sisteme şi tehnici de analiză şi control a produselor agroalimentare,* Editura Eurostampa, Timişoara, 2000
4. Popa, M., *Cercetari privind impactul poluarii mediului asupra calitatii produselor agroalimentare*, Marfa –Calitate-Globalizare- culegere de lucrari, Editura ASE, ISBN- 973-594-544-4, 2004;
5. Popa M., Glevitzky M., *Contaminarea marfurilor agroalimentare – Metode si tehnici experimentale de cercetare***,** Editura Casa Cartii de Stiinta, ISBN 978- 973-133-678-7, Cluj Napoca, 2009;
6. Popa M., *Calitate si siguranta alimentara*, ISBN 973-686-720-X, Editura Casa Cartii de Stiinta, Cluj Napoca, 2005;
7. Popa , M., Vica, M., Axinte, R., Glevitzky, M., Varvara**,** S., *Correlations on the microbiological and physical-chemical characteristics of different types of honey*, Journal of Environmental Protection and Ecology, (**2009**)1311-5065, p.234-236;
8. Popa M., Jitaru M., *Study On The Dynamics Of Cu^{2+} Cation Accumulation In The Polluted Vegetation* -Agriculture And Food Safety Within The Context Of European Union Directives, Journal Of Environmental Protection And Ecology, JEPE 904/02.09.05, 79(2) 2006, p.164-168,
9. Popa M., Jitaru, M., Achim I., *Recherches sur la presence des nitrites et des nitrates dans les marchandises alimentaire,* Sechage et Technologies post-recolte, ISSN-1728-9823, Camerun, 2004, p. 314-322
10.Popa, M., Achim, M., *Study on the impact of food additives on consumer's health***,** , Annales Universitatis Apulensis Series Oeconomica, 8(2006), vol 3, p.344-348;