STUDY ON THE DYNAMICS OF FOOD CONTAMINATION IN INDUSTRIALIZED AREA

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The paper approaches the food contaminations with chemical substances in industrialised area (in an area intensely polluted with heavy metals). We firstly studied accumulation in several types of vegetable matter and secondly, the evolution in time of cations mentioned in the paper. As a work method, we used flame and graphite furnace atomic absorption spectrophotometry as well as stripping methods.

Keywords: food contamination, food safety, polluted area,

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1. General aspects

Heavy metal pollution of the environment has lately been in the spotlight due to the extremely complex issues raised by this phenomenon, as most heavy metals are not soluble in water or if they are, the respective chemical species become compound with organic or inorganic binding agents, which radically influences their toxicity [1].

Inorganic noxious substances influence the growing and development of plants, the process of photosynthesis and the water absorption regime.

Physiological processes are ways of testing the interference pollution-normal development, preceding foliaceous symptomatology [2].

Soil charging with heavy metals led to their acidification and to the debasification of the absorbed complex. At the same time the degradation of organic matter quality occurs through an increase in the fulvic acid content (aggressive towards humic acids) and which, together with heavy metals, form compounds highly mobile and accessible to vegetation [3].

The global effect of the mentioned processes is the decrease of soil fertility and the worsening of nutrition conditions for plants. Consequently, mineral nutrition of plants becomes unbalanced. These nutrition unbalances are due to general unfavourable nutrition conditions (acid reaction, low content of phosphorous, calcium and magnesium) and to the passive absorption of polluting agents from air and soil, which are noxious to vegetal tissues. As a result, there is a slower growing process; vegetation withers sooner, fructification disappears thus leading to a production decrease [4].

The paper intends to approach this pollution aspect, respectively the contamination and dynamics of heavy metals in the vegetable matter from an industrial area. The research was conducted in the area of Zlatna, where heavy metals (Pb, Cd, Cu, Zn) are very active polluting agents, which in time have degraded agricultural and forest ecosystems, as a result of copper metallurgy from the ironworks of Ampelum Zlatna [5].

2. Experimental Part

Samples were gathered from four different areas and in several stages, taking into account the maturation degree of the studied plants, as follows:

Areas under study:

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

TA4 –Tudor Vladimirescu Street (the Morarus), 500 m away from the source, favouring currents S→E 2.1. Method and equipment

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 whole 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 [8].

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 HNO₃:HClO₄: H₂SO₄ 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: HNO₃:HClO₄:H₂SO₄ 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° C. 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].

Observation

As, for comparison, we also used the graphite furnace atomic absorption spectrophotometric method, (GFAAS) samples were subsequently solubilized with HNO_3 0,5 M in order to avoid heavy metal losses as metal chlorides in the graphite furnace [10], when HCl is used for solubilization.

The obtained extract is aspirated in AAS flame using a particular lamp for the dosed element. A blank sample (in order to verify the reagents' pureness) and a set of standards are prepared for each element under the same conditions.

3. Results and discussions

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 $\lambda = 324$, 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.

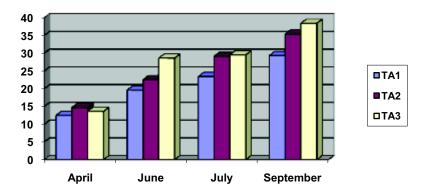


Fig.1. The dynamics of Cu²⁺ ion accumulation in spring onion (bulbs)

The evolution of cation content highlighted an increasing assimilation of the element studied, spaced out in different phases of vegetation, with extremely high values for the samples taken from the land TA2, 1,5 km from the source, under the influence of currents $S \rightarrow N$. High values can also be noted in the samples taken from land TA3, upstream towards West, air currents $E \rightarrow V$, 2 km away from the source of pollution,.

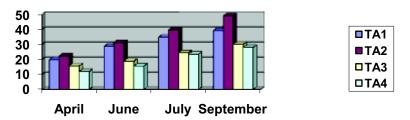


Fig. 2. The dynamics of Cu²⁺ accumulation in spring onion leaves

Green plants or their organs in photosynthetic activity accumulate larger quantities of heavy metals, which are better retained in leaves.

Besides the different accumulation in the plant's bulb or leaves, one can also notice an accumulation difference influenced b the soil of the agricultural land from where the samples were taken. The samples gathered from land TA2 registered the highest values.

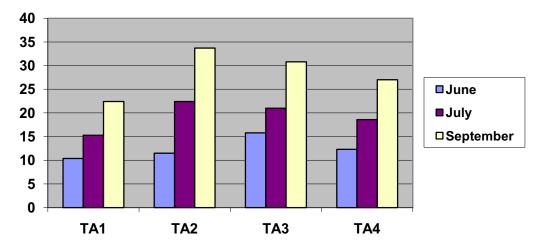


Fig. 3. The evolution of Cu ²⁺ accumulation in the potatoes gathered from the four studied agricultural lands.

With potatoes, the accumulation dynamics was studied during a period of three months (June, July and September); the highest accumulation was registered in the first period of vegetation. Comparing the four agricultural lands, one can notice that the samples taken from the agricultural land TA2 registered the highest values for the copper.

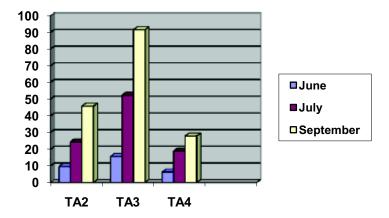


Fig. 4. The evolution of Cu²⁺ accumulation in the cabbage grown on three of the four agricultural lands studied

Of all studied vegetable matters, cabbage has the highest heavy metal accumulation potential. As it results from the presented diagrams, the most favourable area for copper accumulation is the agricultural land

TA3 located 2 km upstream from the source of pollution, favouring air currents $E \rightarrow V$.

Conclusions

Compared to the MAL (maximum allowed limit), which is of 10 ppm, one can notice exceeding values, much above this limit, 4 times higher in the case of onion (bulbs), 5 times for onion leaves, 3 times for the potato and 9 times for the cabbage. The process of heavy metal accumulation in plants differs after the soil contamination level, the element's nature and the analysed vegetable species or organ; this phenomenon is intensified by excessive acidity and mobile aluminium accumulations [11].

Natural acidity activated by the effect of polluting emissions becomes phytotoxic as a result of excessive mobile aluminium solubilization, a disturbing element for the vegetation growing on these soils. Mobile aluminium is a toxic element, which limits agricultural production in all acid soils or in soils that have become acid through pollution. When soils become acid at the level of an intense acid reaction, this toxic effect of mobile Al must be removed through agrochemical processes. The mobile aluminium content from the soils under research is differentiated and put in connection to the reaction status, and thus to that of the H⁺ion activity.

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