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BIOACCUMULATION OF CADMIUM AND ZINC IN THE FRUITS OF SOME FORESTRY SPECIES OF SANOGENIC AND ECONOMICAL IMPORTANCE FROM THE AREA OF COPŞA MICĂ

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Abstract: *This paper presents the extent of heavy metal bioaccumulation in the fruits of some health promoting and economically important plant species grown around the area of Copşa Mică. Samples of fruits of hawthorn, blackberry, sea-buckthorn and desert false indigo were collected from the most polluted area around Copşa Mică city. To compare the results with "clean area'', one control plot was chosen at 26.40 km from the source of the main polluter, near the city of Blaj, Alba county. The study investigates the magnitude of the fruit's load with zinc and cadmium in the context of the major activity stop, from January-March 2009 main polluter, SOMETRA S.A. Copşa Mică.*

Key words: *cadmium, zinc, health promoting plants, bioaccumulation.*

1. Introduction

The adverse consequences of the pollution impact on terrestrial ecosystems have been under careful investigation since the beginning of the twentieth century.

Pollution represents the introduction of contaminants into an environment that causes instability, disorder, harm or discomfort to the physical systems or living organisms [9].

Heavy metals have been common pollutants since ancient times. The term of heavy metals refers to any metallic chemical element with a density exceeding a certain threshold value which varies in the literature between 3.5 and 6 g/cm^3.

Metals that are essential for plants, animals and humans include Fe, Zn, Mn, Cu and Co, whereas Pb, Cd and Hg have no known physiological function.

Essential metals may become toxic when exposures to biota become excessive. The implications associated with heavy metal contamination are of great concern, for human and animal organisms. These metals can pose a significant health risk to humans, particularly in elevated concentration above the very low body requirements. Dietary exposure to heavy metals Cd, Pb, Zn, and

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Cu has been identified as a risk to human health through the consumption of vegetable, crops and contaminated fruits. Excessive accumulation of dietary heavy metals in human body can develop systematic health problems. Harvesting areas near highways or in the areas around point polluters are heavily exposed to atmospheric pollution in the form of metal containing aerosols. These aerosols can be deposited on soil and are absorbed by plants or deposited on leaves and fruits and then absorbed [3].

The food chain is considered the main tract for transfer of trace elements to humans. There are several possible routes of transfer via food chain from soil to human: trace elements-soil-plant-animal, human; plant-human; animal-human; airborne dust-animal, human [8].

The oral intake of heavy metals has become the greatest concern and several official regulations have been established for their safety intake. Studies reported heavy metals as important contaminants of fruit and vegetables [2].

The use of medicinal plants in therapeutics or as dietary supplements has increased substantially in the last decades. Poisoning associated with the presence of toxic metals in medicinal plants is caused by bioaccumulation.

Plants can contain heavy metals from their presence in the soil, water or air. High levels of toxic metals can occur when the plants are grown in polluted areas such as near roadways or metal mining and smelting operations. Medicinal plants today are cultivated commercially in polluted environments, where soil and air [12] contain rather high levels of pollutants.

Toxic metals that can be accumulated in medicinal plants grown in polluted environments and translocated to humans and animals through the use of herbs grown in polluted zones, has concerned scientists who promote the use of herbal medicines.

1.1. Toxicology of Cd

Cd is a nonessential element for plants that negatively affects plant growth and development. The most evident symptoms of Cd toxicity in plants are chlorosis and stunting [8].

While chlorosis is the result of Cd toxicity on the uptake, transport and use of essential elements like Ca, Mg, Fe, Mn, Cu, Zn, P, K, lead to reduction of Mn and Fe absorption and changes in Fe: Zn ratios [4].

High concentrations of Cd in the air are associated with heavily industrialized cities, with refinery and smelting activities [7]. Cd emissions may be considered as arising from either point sources such as large manufacturing or production facilities or from diffuse sources such as those that may occur from the use and disposal of products by many consumers over large areas [10].

Extraction and manufacture of Zn, Pb, and Cu ores can result in pollution of the environment with Cd derivatives. Cd concentration in soil can reach high levels but the high acidity increases the release of Cd and its uptake by plants and bioaccumulation. Bioaccumulation in food and feed plants is of great concern [8].

In human and animal organisms Cd excess disturbs mineral metabolism and interferes with Zn and other enzymes. For common individuals Cd is slowly accumulated from foods. Ingestion of excess Cd from contaminated food gives, in time, several diseases like: renal damage, hypertension, emphysema, carcinogenic changes mainly of kidney and prostate, skeletal deformation, due to impaired Ca metabolism, low reproduction function. In acute poisoning, salivation, choking, nausea, vomiting, convulsion, collapse may occur [13].

1.2. The role of Zn in Plants

Zinc plays essential metabolic roles in plants, being an active component of a variety of enzymes. Thus the basic Zn functions are related to the metabolism of carbohydrates, proteins and phosphate and also to auxins, RNA, and ribosome formations. Zn stimulates the resistance of plants to dry and hot weather and also to bacterial and fungal diseases [8].

Zn is an essential nutrient present in all tissues of the human body; it is a structural component of over 300 enzymes, important for the metabolism of nucleic acids and all macromolecules. Zn acts as a nutrient but in higher concentrations it is toxic. Zn toxicity in plants is clearly visible with the inhibition of growth and decrease in biomass production. Excess Zn derives from pollution. Symptoms of acute poisoning are nausea, vomiting, diarrhea, lethargy, fever [13].

2. Objectives

The aim of this study is to determine the amounts of certain heavy metals Zn and Cd in of some species of fruits growing around the city of Copşa Mică in order to find out if they contain metals in amounts that could be toxic for human, animal consumption and for medical purposes, in the context of the main polluter's - SOMERTRA S.A. Copşa Mică major activity stops from January-March 2009.

3. Materials and Methods

3.1. Studied Plant characteristics

3.1.1. Common Hawthorn (Crataegus monogyna Jack)

Hawthorn is characterized by its phenolic constituents; in particular the flavonoid components to which many of the pharmacological properties associated with hawthorn have been attributed.

Hawthorn extract is sometimes used as aroma therapy and leaves, flowers and fruits are known for their benefits for the human organism. It is an adaptogen which is specific for the circulatory system and is used in numerous circulatory system problems [5].

3.1.2. The Common Sea-Buckthorn (*Hippophae rhamnoides*)

Sea Buckthorn has been used medicinally in China for at least 12 centuries and Sea Buckthorn oil (from the pulp and seeds) is currently used clinically in hospitals in Russia and China [11].

Bioactive oil is used for treating a wide variety of skin damage, including burns, bedsores, eczema, and radiation injury. The oil is also taken internally for diseases of the stomach and intestine [5]. The berries are high in essential fatty acids, which are important for the maintenance of a healthy skin.

3.1.3. Common Blackberry (*Rubus hirtus w.et K., sin. R. fruticosus*)

Common blackberry fruit are popular for use in desserts, jams, seedless jellies and sometimes wine. The astringent blackberry root and leaves are used in herbal medicine as treatment for diarrhea and dysentery [5].

They are a great source of vitamin C, E and K, folate, Mg and K as well as dietary fiber and Mn.

Blackberries have a high nutritional value. They are used in the preparation of juice, syrup, jam, jelly, liqueur, cider etc. [5].

Creeping blackberry fruits have laxative (on an empty stomach) and depurative properties, being indicated in diarrhea, meno-uterine, lung disease, and angina [5].

3.1.4. Desert False Indigo (*Amorpha fruticosa L.*)

Known by several common names, including desert false indigo and bastard indigo, this bush can be planted as a windbreak and also to prevent soil erosion. Amorpha seeds are consumed by pheasants (Phasianus colchicus) [5].

4. Study Site

The surrounding area, located in the vicinity of Copşa Mică industrial platform, consists of a mixture of forests and degraded land. The study site, the forest areas around the industrial platform of Copşa Mică, belongs to O.S. Medias, D.S. Sibiu.

The most affected forest ecosystems are located in UP II Micăsasa and UP III Târnava entirely belonging to the first area of pollution, a very strong one but also UP I Şeica Mică with 60% in the second area of pollution [1].

Fig. 1. *Localisation of sampling areas around Copşa Mică city*

4.1. Fruit sampling

Samples of fruits of the studied species in the forestry area surrounding the city of Copşa Mică (UP I Şeica Mică, UP III Târnava), were collected in September-October 2009. A total of 10 sampling sites, were selected at different distances from the main pollution source - S.C. Sometra S.A industrial platform.

4.2. Laboratory analysis methodology

In order to determine metals concentration the samples were washed with deionised water, dried at +60°C and homogenized. 0.3-0.5 grams of each dry sample were dry-ashed in concentrated HNO_3 Merck extra pure (65% concentration) $+H_2O_2$ (30% concentration) using the mineralization microwave, Berghof MWS-2. Zn and Cd concentration samples were estimated by an atomic absorption spectrometer ZEEnit 700, acetylene-air flame. The analysis was repeated two times. The absorbance was measured at a wavelength of 228.8 nm for Cd, and 213.9 nm for Zn atoms using background correction.

5. Results and Discussions

To evaluate the altitude's influence on the accumulation of Cd and Zn in the studied species' fruits, 5 altitude steps from 50 to 50 meters were established. The minimum altitude with the sample surface from which the sampling was made is of 285 m in sampling area 7, the maximum altitude being of 461 m in sampling area 5. The Shapiro-Wilk test was used for testing Cd and Zn distribution. The obtained results show that Zn and Cd present a normal distribution (Figures 2 and 3).

Using the *t*-test it was found that Cd and Zn don't differ significantly with altitude or with species. Also from the statistic data, it was observed that Zn differs significantly according to sample surface while the Cd does not differ depending on this variable. The distance measured from point "0" (considered the main exhaust flue from the industrial platform S.C. Sometra S.A.) to the 10 sampling areas was divided into 4 distance classes measured in km. The nearest sampling area is at 1.10 Km and the farthest is at 26.40 m near the city of Blaj where the control area is considered to be.

From the mean data, exceeding standard limits proposed by Herrick in 1990 [6], for vegetable and fruit that are observed for Cd, the only values below 0.5 $mg \cdot kg^{-1}$ Cd being with common blackberry in control plot S1 and amorpha in sampling plot S5. The maximum Cd concentration is found in the common blackberry in S9 of 2.69 $mg \cdot kg^{-1}$, 5.38 fold over standard limits.

Fig. 2. *Zn distribution in fruit samples*

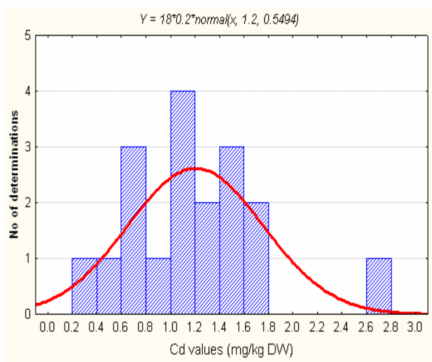

Fig. 3. *The adjustment after the normal distribution for Cd*

The lowest Cd quantity, of 0.38 $mg \cdot kg^{-1}$ DW, was determined in amorfa fruits from sampling area S5.

For Zn the values are distributed in standard limits of 5-10 $mg \cdot kg^{-1}$.

The highest Zn quantity, of 75.28 $mg \cdot kg^{-1}$ DW, was determined in amorfa fruits from sampling area S2 and the lowest Zn value, of 17.17 $mg \cdot kg^{-1}$, was found in control plot SP1 with hawthorn fruits. Data has been statistically analyzed using StatSoft 8 software.

6. Conclusions

By analyzing the fruit samples harvested in autumn 2009, it was observed that 88.8% of the samples have Cd content over toxicity threshold, being inedible by human beings. Also, by eating these fruits, Cd may bio-accumulate also in animal bodies belonging to the food chain of the forest ecosystems studied.

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