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DISTRIBUTION OF SOME HEAVY METALS IN DIFFERENT HAWTHORN ORGANS

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Abstract: *This paper investigates the magnitude and distribution of Pb, Cd, Zn, Cu bioaccumulation in hawthorn flowers, leaves and fruits sampled from Copşa Mică surrounding areas affected by historical pollution. The accumulation and distribution of Cd and Zn is as it follows: flowers-leaves-fruits whereas for Cu the order is: flowers-fruits-leaves. According to the results, Pb accumulation isn't significantly influenced by the sampling organ. The Cd amounts in studied organs exceeded the proposed limit of 0.3 mg/kg by WHO for medicinal herbs and other herbal products and that is why their use as health promoting pharmaceuticals is not recommended due to their significant Cd contamination.*

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

1. Introduction

Most of the polluters which affect the environment have the propriety to bio-accumulate in different health promoting or economically important plants. Entering the food chain, they can bio-accumulate in different consumers manifesting toxic effects. The plants, which are essential elements in the ecosystem, represent the first link in the terrestrial food chain, being able to accumulate polluters both in soil and air. One of the main polluting sources is represented by the industrial pollution by point sources of polluting emissions.

Copşa Mică and its surroundings represent one of the most polluted areas of the country because of historical pollution due to the industrial platform S.C. Sometra S.A. Both forest and other forms of vegetation within the emissions' incidence suffer serious injury. The polluters' impact on plants leads to influencing and affecting biochemical processes, lowering body resistance to diseases, pests and other stressors [1].

2. Heavy Metals in Products of Health Promotion

Heavy metals like Cd, Pb, Cu, Cr and Hg are important polluters because of their toxicity at low concentrations in plant bodies.

Heavy metals enter into the composition of inorganic particles like dust and air suspension, Pb, Zn, Mn, Fe, Cu, As being found in particles in the form of oxides and other metal compounds. The atmospheric pollution with heavy metals presents

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consequences in time and space due to the high degree of spreading on long distances from the emission source (hundreds of kilometers) because of the depositing ability of plant organs or various degrees of bioavailability in soil [9].

The bioavailability of metals in soil depends on several factors of which the most important are: soil reaction, mineral colloids, soil humidity and organic matter content.

The metal content in plants is variable depending on the species, geographical area, drying and processing conditions [7].

The human consumption of contaminated plant organs for nutritional or medicinal purposes determines the insertion of heavy metals into the human body, thus leading to adverse health consequences.

Cadmium is one of the most toxic elements from the environment together with Hg, Pb and As, especially because of its ability to bind to the sulfhydryl groups of some proteins, especially enzymes, resulting in blocking their activity. Once absorbed by the intestinal lumen, Cd fixes itself into the liver and kidney.

The main toxic effects are: renal damage, hypertension, emphysema, carcinogenic changes, kidney, prostate skeletal deformation due to impaired Ca metabolism, low reproduction function [5].

The National accepted limit for Cu in tea is 0.5 $mg{\cdot}kg^{-1}$ product [10].

Lead is an important polluter in different diet food products. The Pb toxicity manifests itself by causing damage to the nervous system, inhibition of heme formation, kidney damage, anemia, impaired mental developments of young children, carcinogenicity and genotoxicity and impaired reproduction [5]. The National accepted limit for Pb in tea is 5 $mg{\cdot}kg^{-1}$ product [10].

Zinc plays an important role especially in protein, carbohydrate and DNA metabolism, entering also in the composition of several enzymes. It is less toxic than Cd and Cu. The ingestion of high quantities of Zn affects the gastrointestinal tract producing diarrhea and fever [5]. The National accepted limit for Zn in tea is 50 $mg{\cdot}kg^{-1}$ per product [10].

Copper is an essential metal component of several copper-enzymes acting as a cofactor and as an allosteric component. Dietary copper intake and total copper exposure, should take into account that copper is an essential nutrient with potential toxicity if the amount exceeds tolerance. A range of safe intakes should be defined to prevent deficiency and toxicity [8].

Cu deficiency in humans is a rare exception. The National accepted limit for Cu in tea is 50 $mg{\cdot}kg^{-1}$ product [10].

2.1. Quality of plant material and pharmaceutical products

The importance of medicinal plants in traditional medicine is well known. Medicinal plants and products are easily contaminated during growth and processing. In final dosage form the heavy metal enters the human body and may disturb the normal functions of the Central Nervous System, liver, lungs, heart, kidney and brain causing hypertension, abdominal pain, skin eruptions, intestinal ulcer and different types of cancer [6].

According to WHO and National Sanitation Foundation recommendations the maximum admitted limits for herbal medicines and other herbal products are of 10 mg/kg for Pb and 0.3 $mg{\cdot}kg^{-1}$ for Cd [12].

In 2002 the Medicines Safety Authority of the Ministry of Health of New Zealand withdrew from the market several traditional Chinese medicines because they had a considerable content of toxic substances in particular As. In testing of 251 samples of Asian medicine patents from California, 24% products contained at least 10 ppm Pb. In literature there are quoted cases of patients treated with Tibetan Herbal Vitamins, Ayurvedic products, Indian Herbal medicine and Chinese herbal medicine who suffered from Pb, Hg and As intoxications. A total of 54 samples of Asian remedies from Vietnam, Hong Kong, Florida and New Jersey were analyzed for heavy metal contamination and the conclusion was that 74% of samples exceeded published guidelines and 49% presented toxic concentrations [2].

2.2. Hawthorn's health promoting importance. Chemical composition and use of hawthorn pharmaceutical products

The hawthorn species studied in this paper is Crataegus monogyna Jack. It is a shrub with spreading throughout the country, growing especially at the forests' edge or isolated in area without forest vegetation. It is a species which is resistant to drought, heat, cold and little pretentious regarding the type of ground [4].

From the hawthorn, the flowers, fruits and leaves are used for medical purposes.

Major constituents are flavonoids (rutin, hyperosidae, vitexin, vitexin 2"rhamnosidae, acetylvitexyn -2"rhamnosidae) [3].

Hawthorn flowers and leaves contain pentacyclic triterpenes derivatives (oleanolic, ursolic, crategolic acids) essential oil (0.1-2%) catechin, epi-catechins, simple phenolic acids (chlorogenic acid 0.01%, caffeic acids).

Its fruits contain antociani, leucoantociani, catehine 1%, flavonoli 0.3%, beta-caroten 0.4 mg%, ascorbic acid 43.6 mg%, sterioli cumarine, pectins 2-6%, sorbita 20%, saponine, vitamin B, carbohydrates 4% and a fat oil [3], [4], [11]. Chemical formulas of the main constituents of hawthorn with pharmaceutical properties are shown in Figure 1.

Hawthorn flowers, leaves and fruits or extracts from these organs are used for the

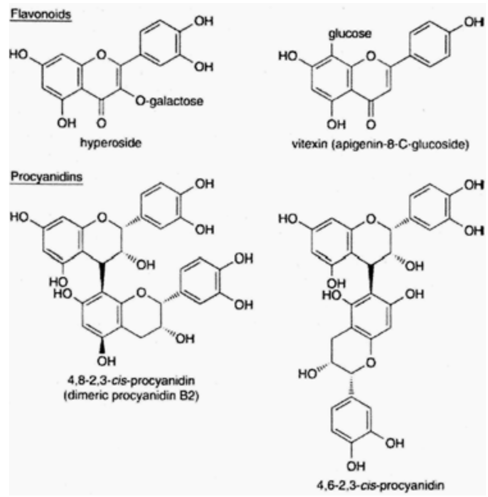

Fig. 1. *Major chemical constituents of hawthorn* [3]

treatment of chronic congestive heart failure stage II as defined by New York Heart Association. They are used also for anti-hypotensive, anti-inflammatory, sedative and diuretic effects. Cardiovascular activity has been documented for hawthorn and attributed to the flavonoid components [3]. Hawthorn based preparations decrease myocardial excitability and strengthen its activity; they improve irrigation and the supply of oxygen to the heart and brain thus showing hypotensive proprieties. Pharmaco-dynamic and therapeutic action of the hawthorn based preparations is given by all the active principles contained [4]. In traditional medicine these organs are dried and used as tea.

3. Objectives

The aim of this paper is to investigate the distribution of Pb, Cd, Zn, Cu in some hawthorn organs and compare the accumulated quantities with international safety levels for herbal medicines, in the context of the main polluter's major activity stop - SOMETRA S.A. Copşa Mică in January 2009.

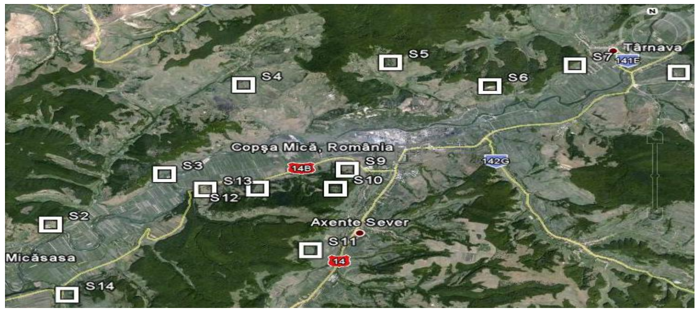

Fig. 2. *Localisation of sampling areas around Copşa Mică city*

4. Materials and Methods

Hawthorn flowers were sampled in May 2010, the leaves and fruits in September same year. The leaves and fruits were washed with distilled water in order to remove the eventual atmospheric depositions, dried at 60 °C and grinded. 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. Pb, Zn, Cd and Cu concentration samples were estimated by a Perkin Elmer AAnalyst 800 atomic absorption spectrometer, acetylene-air flame. The analysis was repeated two times. The absorbance was measured at a wavelength of 283.5 nm for Pb, 228.8 nm for Cd, 213.9 nm for Zn and 324.8 nm for Cu using background correction.

The data representing metal concentration in hawthorn organs from which the sample was taken were processed with the StatSoft 8 program. The statistic significance of the differences between the sampled organs regarding the size of some variables was examined with the nonparametric Kruskal-Wallis test. The data presented in Table 1 show no significant differences between the organs considering Pb accumulation ($p > 5\%$). Cd, Zn, and Cu are metals whose accumulation is influenced by the sampled hawthorn organ.

Table 1

The statistic significance of the differences between the sampled organs regarding the size of some variables

Variables	**Chi-Square**	***p* [%]**	**Significance level**
Pb	31.18	36.4	ns
Cd	8.61	3.48	*
Zn	9.56	2.27	*
Cu	10.9	1.18	*

For heavy metals which were significantly influenced by the accumulation organ, the distributions have been tested as shown in Figures 3-5.

From the heavy metal distribution graphic, the following accumulation tendency in the sampled organs for Cd and Zn can be observed: flowers > leaves > fruits and for Cu: flowers > fruits > leaves. Also from the Cd distribution graphic, the exceeding of the threshold of 0.3 $mg \cdot kg^{-1}$ proposed by WHO for herbal medicines and other medicinal product can be observed.

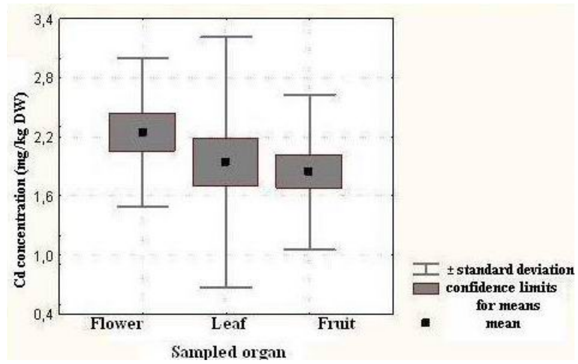

Fig. 3. *Cd distribution in hawthorn sampled organs*

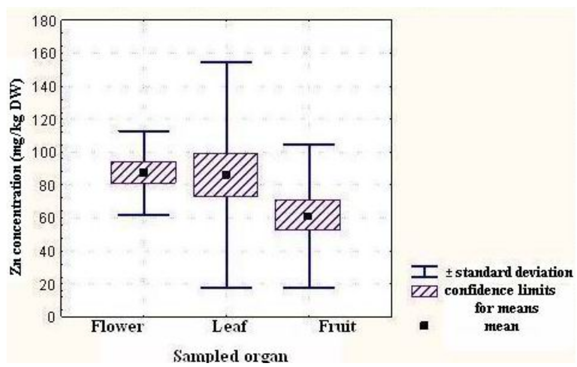

Fig. 4. *Zn distribution in hawthorn sampled organs*

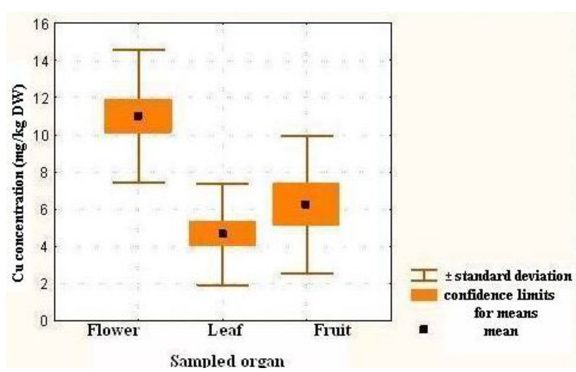

Fig. 5. *Cu distribution in hawthorn sampled organs*

5. Conclusions

From the analysis of hawthorn flowers, leaves and fruit samples harvested in 2010 from Copşa Mică surrounding areas, a high loading of Pb, Cu and Zn can be observed in studied organs manifested by overcoming the limits of toxicity of these metals in plants. The exceeding of the Cd limit proposed by WHO makes these products unsuitable for use within the eco-health promoting valences of herbal medicine.

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