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Considerations regarding the presence of heavy metals in medicinal plants and their health risks

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Abstract. The presence of heavy metals in some species of medicinal plants is currently one of the important issues related to their use in various therapeutic purposes. Contamination with metal residues of the medicinal plants is mainly due to the phenomena of soil, water, air pollution and can be an environmental problem but also a health risk. Prolonged use of herbal supplements, teas, extracts or tinctures may be associated with the risk of accumulating large amounts of heavy metals in the body which can become toxic or dangerous.
Keywords: *heavy metals, medicinal plants, health risks*

1. Introduction

Medicinal plants are vegetal species, cultivated or spontaneous, which, by their chemical composition, have pharmaceutical properties and are used in therapeutics. The therapeutic value of medicinal plants is based on the relationship between the chemical structure of the active substances, also called active principles, and their pharmacodynamic action on the reactive elements of the body. Most medicinal plants have a complex chemical composition ranging from 2-3 compounds to 30-40 chemicals identified in some plants, such as species of the genera *Digitalis, Vinca, Claviceps, Papaver* etc., which explains the multiple pharmacodynamic properties of one and the same plants. [1]. In the pharmaceutical practice, plant mixtures known as "medicinal teas" or "medicinal species" or mixtures of tinctures, herbal powders, or other complex pharmaceutical forms are used as having a therapeutic action. Plants have the ability to absorb minerals from the soil through the roots, but also through the aerial organs, especially through their leaves. With the absorption of minerals from the soil, plants also accumulate heavy metals, so this property of the plant is not always beneficial. The use of medicinal plants, either for the preparation of teas, or by the use of parts of the plant (for the purpose of obtaining a medicinal product), or for the purpose of obtaining an extract or a tincture, causes heavy metals to enter the human body. In small amounts, they keep the body functioning, but in larger quantities heavy metals can become toxic or dangerous. [2]

It is well known that not all metals are harmful to the human body, some of them are essential in the development of the metabolic processes. Thus, metals such as Co, Cu, Fe, Mn, Mo, Ni, V and Zn are needed in small amounts for the body, but become toxic to it in large quantities.

Zinc is a metal of great biological importance, in the human body it acts as a true "circulating agent" because it controls and regulates a number of metabolic processes, influences the activity of enzymes and maintains the integrity of cells. Zinc is a vital enzyme complex that catalyzes many biochemical reactions, from those that contribute to cell development to those that participate in the synthesis of hormones (such as testosterone). In the human body, zinc has three major roles, namely: Lewis acid catalyst, control ion (regulation) and structural ion. Zinc can be said to be the most common metal

ion with catalytic function in the cytoplasm. Zinc enzymes are involved in a wide variety of cytoplasmic reactions. Zinc is involved in the proper functioning of the thyroid, immune system, reproductive system, etc. The daily intake required by an adult is 15 mg of zinc and, as only 8,6 mg reach the body through food, the deficiency should be supplemented by the administration of drugs containing sulfate, gluconate or other chelating complexes of zinc (ll). [3]
Another example of a transition metal with a very complex involvement in the biological processes in the body is the iron which participates in coordination reactions, redox reactions, some acid-base reactions and in many control systems. In the human body, iron is distributed in plasma in the form of hemoglobin, in tissues such as myoglobin and in cells in the bone marrow stored as ferritin. It also occurs in the form of complexes such as Fe^{2+} in enzymes and Fe^{3+} in transferrin, respectively. Lack of iron in the body causes iron anemia, called hyposideremia.
After iron, copper is the best known microelement, and its importance to the body has been reported since 1928 by Hart. In living systems (plants, animals and humans), copper participates in the performance of many biological functions such as transporting pigments (eg hemocyanin and cytochrome oxidase) or blue copper proteins, with the role of electron transfer. Cu^{2+} ions enter the structure of redox enzymes, participate in the synthesis of the hemoglobin and of adrenaline as well as in the activation of certain biological processes, such as glycolysis. In the physiology of animal organisms, copper is involved in major metabolic activities such as respiration, hematopoiesis, various connective tissue activities, pigmentation of skin and hair. [3,4]
On the other hand, the accumulation in the body of heavy metals from various sources such as contaminated food, herbal food supplements, herbal extracts with therapeutic action used in various long-term treatments, teas etc. can be very toxic. Side effects induced by some heavy metals that reach the body through various pathways, including the intake of herbal pharmaceuticals, can lead to metabolic disorders. For example, cadmium adversely affects the calcium metabolism, virtually replaces bone calcium, leading to various conditions (osteomalacia, osteoporosis, hypercalciuria, rheumatoid arthritis, etc.), replaces zinc in carboxypeptidase, the enzyme in the pancreas, and the intestine responsible for protein digestion. The excess of copper could cause anxiety or agitation, difficulty in concentrating, etc. In the case of lead accumulation, the acute symptoms are fatigue, loss of appetite, irritability, insomnia, digestive disorders. Mercury generates memory, respiratory, locomotor disorders etc. [5]

2. Potential sources of heavy metals in medicinal plants. Effects on the human body

The phenomena of soil pollution, more and more diverse and complex, determine the presence in the soil of some toxic heavy metals (arsenic, lead, cadmium) that can reach different species of medicinal plants. Sources of heavy metal pollution of the soil can be: excessive use of pesticides (fungicides containing mercury, copper, arsenic, zinc etc.), industrial activities generating sedimentary dusts containing heavy metals, emissions from road traffic, etc.

Depending on the type of soil and its geographical location, it may contain high amounts of heavy metals in areas with intense industrial or agricultural activity, the main source of contamination being anthropogenic activities or it may be deficient in them. High levels of metal concentrations in the soil can also result from geological processes, but for the most part result from agriculture and industrial activities.

Industrial pollution with heavy metal of the soils can lead to their passage in groundwater or surface water as well as in vegetable crops, with negative influences on the health of the population. Situations are known in which the loading of edible plants into chemical pollutants has increased greatly due to soil pollution. Industry in various fields can contribute to the chemical pollution of the soil by the deposition of pollutants spread in the atmosphere as in the case of lead or mercury. [6]

According to the World Health Organization, in the past, the nutrients used in agriculture were a clearly defined cycle, moving from soil to plants, from plants to animals and back into the soil. Lately, however, this cycle has been ”circulated” by the use of chemicals, mostly synthetic (fertilizers, biostimulators, pesticides etc.) to obtain higher amounts of agri-food products. Most of these substances, being of an organic nature, also undergo a process of decomposition or

biodegradation in the soil. They are metabolized by soil microorganisms that have a great ability to adapt, using them as nutrients. As a result, chemicals used in agriculture and penetrated into the soil disappear so that the soil can be re-treated.

However, this situation is not general for all chemicals, some being easier and others more difficult to biodegrade. Thus, lead or mercury compounds (organo-metals) as well as arsenic acid salts are difficult to decompose and tend to be persistently deposited in the soil. In the same sense, organochlorine products are difficult to decompose, which is why they remain degrading products in the soil for a long time, these substances having a long remanence in the soil.

Organochlorine pesticides, for example, persist in the soil after 5 years up to 5% of the amount initially used. For some of these substances it is not known whether the decomposition intermediates have a more toxic or less toxic action than the original. Under these conditions, the possibility of absorption in plants is possible not only at the time of treatment or immediately after it, but also after a very long time. [7]

Herbal food supplements obtained from contaminated raw materials (medicinal plants, plant products) due to the presence of heavy metal residues in their composition can be a health problem. The use of such products raises concerns regarding the safety of the combination in treatment, especially for long periods.

Air can be a source of contamination, a way of transporting heavy metals and depositing them on the ground and on plants (for example, the emission of lead from cars). Metal contaminants in the air come mainly from industrial processes but also from means of transportation. The most important of these are lead, mercury and cadmium, due to their increasing distribution in the environment as well as to the fact that they accumulate both in the environment and in the human body with the possibility of causing serious pathological alterations.

Numerous anthropogenic activities such as: combustion of coal, oil, production of non-ferrous metals, production of steel and iron, production of cement, installations for waste gas treatment, accumulation and incineration of waste, etc. lead to significant emissions into the air which may contain different concentrations of heavy metals. The lead is a widespread pollutant in the air from the industry for the extraction and processing of lead and its compounds, as well as from the exhaust gases of motor vehicles using petrol with the addition of tetraethyl or tetramethyl lead as an anti-knock agent. It is found in the atmosphere in the form of vapors and especially in the form of suspensions. [8]

Penetrating in circulation the lead is found in small amounts in plasma, most of which is fixed in red blood cells. Lead is mostly stored in the bones, especially in the long bones. About 50% of the lead in the human body is found in the bone system and about 90% of the stored one. It is also stored in hair, nails, etc. With age, some of the metabolized lead tends to accumulate in the soft tissues. However, the most important phenomenon is the increased risk of lead absorption. Since lead is a ubiquitous element, although it is not a bioelement, its absorption is inevitable. Up to certain load levels lead is perfectly tolerated by the body. Exceeding these levels, without causing signs of intoxication, lead, especially in children, can determine pathophysiological changes with repercussions on the state of health, characterized by nonspecific disorders.

Increased absorption of lead in the body can be manifested by nervous disorders such as irritability, insomnia, headache, digestive disorders such as loss of appetite, nausea, intestinal transit disorders, abdominal pain, joint and cardiovascular disorders. [9]

Water can also be a source of contamination with heavy metal on plants, with heavy metal salts (Mn, Co, Ni, Cr, As, Cd, Fe, Pb, Sn, Sb, Au, Ag, Cu, Hg) constituting a very serious form of pollution for surface waters due to their toxicity and stability, which can cause disturbances in the biological balance. Wastewaters used for soil irrigation is a source of contamination of edible plants that have the property of accumulating heavy metals from soil. Thus, for example, lead can pass into food chains and networks, being accumulated with varying intensities of different plant species depending on its concentration in the environment. [10]

For the detection of heavy metals in our body, the most relevant is the analysis of the hair (tissue mineral analysis). Blood or urine tests are inconclusive, as heavy metals build up in the fatty tissue, hair and nails. Heavy metal poisoning is usually severe, rapid, and may be associated with recent

exposure or ingestion of contaminated products. Symptoms of heavy metal poisoning include cramps, nausea and vomiting, headache, sweating, confusion, altered ability to think, speak, walk, convulsions, nervousness and emotional instability, insomnia, nausea, lethargy etc.

The effects of heavy metals on the body have consequences on important organs, they can damage the functioning of the brain, lungs, kidneys, liver, blood composition, etc. In the long run, exposure can lead to the gradual progression of physical, muscular and neurological degenerative processes. [11]

3. Absorption of heavy metals in plants. Dosing methods

The dosing of heavy metals in various medicinal plant species can be found out by known analytical methods, often by atomic absorption spectrometry (AAS). In principle, the method of atomic absorption spectrometry determines the concentration of an element in a sample, by measuring the absorption of electromagnetic radiation of a specific frequency and characteristic of the target element, when it passes through a medium containing uniform free atoms of the sample, uniformly distributed.

To carry out this analytical practice, several steps are taken. The analytical applications and the advantages of atomic absorption spectrometry in the determination of heavy metals are numerous. Atomic absorption spectrometry is a common method of analysis in general, and of trace analysis in particular. It is used both for routine analysis and in research. The sensitivity of the method varies from one element to another, usually remaining on the order of 1-100 $\mu g/cm^3$. In the analysis of heavy metals, the method has a higher sensitivity than other current methods and low detection limits for many of these elements, which is important in the analysis of traces and for the analysis of dilute solutions (in order to eliminate interference). The reproducibility is generally good and ensures adequate accuracy, the fields of use of the method are very varied and include a large part of the practiced dosages of heavy metals from different types of samples (soil, water, air, plant extracts). [12]

Heavy metals such as Cu, Ni, Zn, Mn, Cr, Cd, As etc. can be determined quantitatively from different parts of the plant (leaves, flowers, fruit). Samples can be taken from polluted areas so that they can be used as bioindicators if the soil is contaminated with traces of heavy metals.

Studies have shown that medicinal plants can absorb significant concentrations of heavy metals from soil and contaminated atmospheres, induced by car traffic, but also by emissions-producing industrial activities in the vicinity of land intended for their cultivation. Specially developed methods for determining the content of heavy metals have allowed the successful application to many matrices of plant products harvested from various medicinal species (rhubarb leaves, lavender flowers or cherry stalks), all having an important role in phytotherapy. Rhubarb leaves and lavender flowers are often associated in phytotherapy for their sedative and antispasmodic action and cherry stalks for their diuretic action. The existence of heavy metals in these plant sources, exceeded in doses compared to the maximum permitted limit, raises questions as to the safety in administration. [13]

Side effects in the body do not occur with occasional administration. Prolonged use of cherry stalk tea, for example, is recommended because it supports the normal functioning of the kidneys, urinary drainage, elimination of excess water accumulated in the body etc., can be a factor of insecurity in case of accumulation of excess heavy metals. Studies conducted by researchers in various countries have shown a bioaccumulation of heavy metals in plants that when used for medicinal or food purposes pose a health risk.

Pesticide residues and heavy metals have been detected through atomic absorption spectrometry in various medicinal plant species. Contamination of the soil with the excess of pesticides used is the main route of transmission to the plant of pesticide residues and heavy metals (Cd, As). The use in irrigation of agricultural lands of some wastewater with content of heavy metals (Co, Cu, Cd, Pb) insufficiently treated conduct to the accumulation of heavy metals in plants, and their content has been associated with the induced anatomical changes. [14]

Of interest in the conducted studies were a number of medicinal species sold frequently and used in the treatment of various diseases, especially those recommended for a long time, time being one of the factors that promote bioaccumulation.

Another aspect related to the capacity of plants to absorb heavy metals is that of their use in order to restore to the agricultural circuit the lands degraded by various anthropogenic activities generating emissions with high content in heavy metals. The importance of aromatic plant cultures has been demonstrated in order to remedy sites contaminated with heavy metals. The most promising results for phytoremediation of heavy metal contaminated sites have been identified in aromatic species of the *Poaceae, Lamiaceae, Asteraceae* and *Geraniaceae families*. The volatile oil obtained from aromatic crops used as phytostabilizers is not significantly contaminated with heavy metals, thus, herbs can be used successfully for phytoremediation. [15, 16]

4. Conclusions

The use of medicinal plants in order to obtain food supplements, teas, tinctures or medicinal preparations is based on the use of raw materials free of any type of contaminants. Due to the presence of heavy metal residues in the composition of medicinal plants, health problems may occur, the use of such products presents increased risks in terms of the safety of the combination in treatment, especially for long periods. The analysis of the chemical composition of medicinal plants and vegetal resources generally used as food or therapeutic raw materials is absolutely necessary for their safety in their recovery. Determining the content of heavy metals in medicinal plants is a priority especially for areas affected by industries generating heavy metal emissions, excessive use of pesticides, irrigation of land with wastewater containing varying concentrations of heavy metals, areas with heavy car traffic etc. , these being the main sources of contamination. The high absorption / bioaccumulation capacity of some aromatic plants is proved by the studies carried out, fact for which are mentioned possibilities of using certain species as bioindicators of heavy metal pollution.

The high content of heavy metals in the soil poses a direct risk of soil pollution, affects the plants that absorb them and implicitly have consequences for human health. If not properly recognized and treated, heavy metal toxicity can lead to morbidity and mortality. Heavy metals such as Pb, Cd and Hg have no beneficial effect on organisms and are therefore considered to be the main threats, as they are very harmful to both plants and animals and humans. Excess heavy metals even have mutagenic and carcinogenic properties, causing irreversible processes in the body.

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