Review

Reduction of Heavy Metals Transfer into Food

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Abstract

Contamination of the natural environment by heavy metals is the main global ecological problem. Heavy metals present in the soil of agriculture areas could be transfered into crops and, subsequently, to the food chain.

Thus, methods for determination and speciation of heavy metals are still among the top interests of scientists working on treatment of waters, soils and sediments, transport of metals in the environment, and their influence on animals and plants.

Apart from methods destined for monitoring inorganic harmful substances in the environment, the methods for their elimination are even more desirable.

The screening of possibilities of elimination or at least reduction of transfer of heavy metals from the environment to food products is the main object of this review. Among them, the most promising are organic and inorganic amendments and special plants that remove heavy metals from soils.

Keywords: heavy metals, soils, phytoremediation, organic and inorganic amendments

Introduction

Large amount of heavy metals can be transfered to the environment as a result of human activity. Metal ore mining, fossil fuel combustion, and waste storage are a few examples of its antropogenic sources. On the other hand, natural geochemical processes, e.g. molten magma or erosion of rocks, can also increase environment contamination by metals [1-3].

During the last centuries, as a natural consequence of industrialization, heavy metal concentration in the evironment has been increasing all over the world [4-6].

Places that are particularly exposed to soil contamination are located in large industrial areas. Additional atmospheric deposition of heavy metals affect surrounding agricultural areas [7-9]. Moreover, agricultural practices such as the application of sewage sludge, phosphate fertilizers, and municipial solid waste composts, could cause increased metal concentrations in soils and plants [10-14].

The main places of pollution are located close to mining and smelting plants, or thermal power plants [15, 16].

In contrast to other organic pollutants, hazardous heavy metals are indestructible as they cannot be chemically or biologically degraded. What`s worse, some heavy metals can concentrate along the food chain and eventually accumulate in the human body, as we are at the top of the food chain.

The most important heavy metals with regard to potential hazards and occurrence in contaminated soils and water are: arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), and zinc (Zn).

Due to the heavy metal influence on human nutrition, there is a need to monitor their concentrations in the environment. The data collected should be a base for the creation of an agriculture environmental map indicating heavy metals contamination. In consequence, this could create the possibility for selection of the most suitable techniques for safe food production, particularly on farms.

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In order to realize this goal, it is necessary to develop:

1. Precise, easy-to-handle and relatively cheap analytical tools and procedures that allow for intensive monitoring of food production environments.
2. New food production technology that allows a decrease of heavy metals concentrations in food products as much as possible. Therefore, increasing attention has been paid in recent years to the remediation of polluted soils, among which the use of plants removing hazardous metal ions is particularly emphasized.

The purpose of this review is to highlight the need for heavy metals elimination from the environment by effective approaches using plants and organic and inorganic amendments in order to develop safe agriculture.

Methods of Heavy Metals Determination and Speciation

The most popular analytical methods for heavy metals determination in environmental samples are spectroscopic methods such as: flame atomic absorption spectrometry (FAAS) [17-19], graphite furnace atomic absorption spectrometry (GFAAS) [20, 21], atomic emission spectrometry (AES) [22], electrothermal atomic absorption spectrometry (ETAAS) [23], atomic fluorescence spectrometry (AFS) [24, 25], inductively coupled plasma mass spectrometry (ICP-MS) [26, 27], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [28, 29], inductively coupled plasma optical emission spectrometry (ICP-OES) [30-32], and cold vapor atomic absorption spectrometry (CVAAS) [33]. The popularity of these methods in quantitative analysis of heavy metals is not surprising, due to their high sensitivity and selectivity. Generally, the methods mentioned above are applied for determination of total concentrations of each metal.

To estimate the toxicity of heavy metals toward living organisms, information about total concentrations is not sufficient. The key is information about the chemical forms, valence state, and inorganic and covalent organometalic speciation. These parameters are of great importance and are decisive for metals mobility, bioavailability, bioaccumulation, and toxicity for living organisms.

According to IUPAC, speciation analysis [34-36] is defined as analytical activities of identifying and/or measuring the quantities of one or more individual chemical species in a sample. Simply put, it is identification and determination of individual physical-chemical forms present in the samples.

It is known that the interactions of metals with biota are highly dependent on their chemical forms, oxidation state, and/or organic or inorganic structure, rather than their total concentration [37-39].

The combination of separation techniques [40] coupled with a highly sensitive detector [41] are the most common tools for trace element speciation. In recent years the combination of chromatography, in its various modes, and sensitive spectroscopic detection methods such as atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS), atomic emission spectrometry (AES), and inductively coupled plasma mass spectrometry (ICP-MS) have joined into hyphenated techniques. These techniques are the most popular because of the following advantages: possibility of automatization, good reproducibility, and short analysis time.

The use of capillary electrophoresis [42] and multicapillary gas chromatography [43], which are specific separation techniques, could reduce analysis time. Moreover, the transformation of species during analysis is possible by using these techniques. Hyphenated techniques involving ICP-MS belong to the fastest growing research and application areas applied for speciation analysis [44-46].

Among the other non-chromatographic speciation techniques (e.g. solid-phase separation, complexation, distillation or vaporization), redox speciation can be applied. Redox speciation is defined as the capacity of discriminating between the common oxidation states of inorganic analyte species by an appropriate detector, without the need for previous separation. By using this approach, a wide range of element-species can be determined concerning such elements as As, Ge, Sb, Se, and Sn [47]. However, hydride generation cannot be applied to the determination of some organic compounds, unless the molecule is first destroyed by UV irradiation, and the reaction can be inhibited in the presence of high contents of organic compounds in the matrix.

Most of the above-described methods are precise and sensitive, but unfortunately the equipment used can be expensive. Additionally, staff with high qualification is required. This can be a big limitation for small local analytical laboratories that, in many cases exclude them from continuous environmental monitoring. In consequence, the data collection necessary for preparation of up-to-date maps of heavy metal pollution is not possible.

To solve these problems, electroanalytical methods could be applied for metal speciation. These methods are sensitive, selective, and relatively cheap due to the nature of the mechanisms involved in electrochemistry. Differential-pulse stripping voltammetry was applied to measure zinc, cadmium, lead, and copper by anodic stripping and selenium(IV) by cathodic stripping in rain water [48]. The anodic stripping voltammetry (ASV) methods using thin and gold electrodes were applied for speciation of heavy metals in wastewater or seawater [49] and in soil extracts [50]. The cathodic stripping voltammetry (CSV) methods using hanging mercury drop electrode have been employed for determination of lead in lake water [51]. Such methods facilitate the determination of the "labile" fraction in relation to total metal concentration levels, ligand concentration and related conditional stability constants [52]. One of the most popular applications of differential pulse anodic stripping voltammetry (DP-ASV) is lead speciation in seawater analysis [53]. Although rainy water, surface waters, estuarine waters, sediments, and marine organisms also have been investigated [54].

As has been seen, electrochemical methods could be a promising alternative to spectroscopic methods. They offer highly convinient tools to discriminate between toxic and non-toxic forms of many elements and, because of that, can be used as fast, cheap alternatives to the use of chromatographic-based speciation analysis. Ion selective electrodes [55-57], sensors and biosensors [58, 59] look especially interesting from this point of view. Popularization of electrochemical methods in consequence could allow us to collect data sufficient for preparation and/or updated heavy metal pollution maps.

Possibilites for Reduction of Heavy Metals Content in the Environment

As mentioned above, the second step of safe food production is the development and application of technologies leading to a decrease in concentrations of heavy metals in food.

The application of such technology should be relatively cheap and easy to introduce. The potential risk of metals introduction to the nutrition chain from soil depends entirely on their bioavailability. Bioavailability is defined as the fraction of metal that is available or can be made available for uptake and, as a consequence, could be accumulated in living organisms. Plants are important components of ecosystems, as they transfer elements from abiotic to biotic environments. So decreasing the bioavaibility of metals in soil for plants should be a main goal of developed technology. The bioavailability of elements to plants is controlled by many factors associated with soil and climatic conditions, plant genotype, and agronomic management. This means that the presence of the elements in soil does not imply that they are available in plants, particularly if they are insoluble in the soil solution [60, 61]. The concentration of metal in soil solution is key to their accessibility for plants. A low correlation between total contents of metals in soil and plants was detected [60]. Correlation coefficients significantly increased when the metal ion content in plants was related to the citrate-extracted fraction from soil. An assessment of the impact caused by a given contaminant involved the estimation of plant uptake from the soils with the use of the transfer factor (TF) model from the soil to the plant, if the dependence followed a linear pattern. Linearity dependence was found between citrate-soluble fractions (not between total soil concentration) and the plant for all the elements studied. This may suggest that plant absorption is controlled by the composition of the soil solution. The composition of which during the growing season could be related to the extraction method chosen [62, 63]. Determination of the composition of the citrate-soluble soil fraction and knowledge of transfer factors enables a prediction about whether plants cultivated on a given soil can be used as food or feed, on the basis of knowledge of soil extract composition.

Phytoremediation

One manner for reducing heavy metals concentrations in food products is decreasing their concentrations in soil, especially in soil solution.

Phytoremediation is the use of plants to remove pollutants from the environment. Usually, if a plant can accumulate more than 1,000 mg/kg of Cu, Co, Cr, Ni, or Pb, or more than 10,000 mg/kg of Mn or Zn, it is defined as a hyperaccumulator [64].

To date, more than 400 plant species have been identified as metal hyperaccumulators. The best hyperaccumulator varies according to regions with different climate and soil types.

Wild grown plants, tree species or herbs, are just a few examples of plants that could be applied for phytoremediation of soil [65, 66]. It was observed, that lavender could be successfully grown in highly heavy metal-polluted areas without any risk of essential oil contamination [67]. Similar results were obtained for peppermint and cornmint, in which no heavy metal contamination was found in the essential oils. Despite the yield reduction (up to 14%) caused by heavy metal contamination, mint remained a profitable crop and it could be used as substitute for other crops [68]. Other industrial crops suggested for cultivation on metal-contaminated soils were fibre plants like flax, cotton, and hemp [69, 70], and energy crops such as *Salix* trees and reed canary grass [71]. The presented results indicate that by choosing appropriate plants for phytoremediation of soil polluted with heavy metals could be done [72, 73].

Decreasing heavy metal concentrations in food products could be achieved by selecting crops with low heavy metal accumulation in edible parts.

Differences in plant uptake of mineral elements are well documented based on genotypic characteristics [74]. Cd and Pb are highly toxic and bioavailable. Therefore, these particular metals are subject to a number of studies focused on its accumulation. It was demonstrated that crop selection is effective for reducing their transfer to the human food chain [64, 75]. Cd and Pb accumulation by crop species decreased according the following order: leaf vegetables > root vegetables > grain crops [76, 77]. The large variation of Cd concentrations in the edible part of crops was found by performing an experiment [78] in which several plant species were grown in Cd-contaminated soil [79, 72, 80]. As another example, capeweed may be presented, which accumulate 10 to 40 times the Cd concentrations of subterranean clover and ryegrass, respectively [81]. This means that different plant species available for grazing animals via farm management had great impact on Cd transfer to the human food chain [82-84].

Large genotypic variations of Cd and Pb accumulation were found for maize shoots [85-88]. Among Austrian wheat cultivars, a 2.5-fold variation of Cd concentration in grain was observed [89]. Similarly, a 2.3-fold variation in seed Cd concentration was reported for 17 Australian lineseed lines [90]. These studies indicate that heavy metal transfer from soil into edible parts of crops may be highly influenced by the selection of low-uptake cultivars.

Soil Treatment Methods

Chemical or physical methods were early used and even endemically commercialized in the U.S. Physical methods (e.g. soil leaching and absorbent fixation) and chemical methods (e.g. bioreduction and chelate extraction) are still used in practice. In these methods, the use of chelators cannot be avoided. By adding synthetic chelators such as EDTA (ethylenediamine-tetracetic acid), both the solubility and bioavailability of heavy metals change. A chelating reagent's molecule can form several coordinative bonds to a certain metal atom. In consequence, increase of its concentration in soil aqueous phase and mobility is possible [91]. Considering that some metal ions strongly bond to the soil phase and are less bioavailable, powerful chelating reagents are employed such as Na salt of EDTA. However, such an approach requires not only expensive chemical reagent and machines, but also many technicians. Worse, excessive usage of chemical chelates has been proven to pollute ground water and negatively affect soil quality. Many ions are also chelated unselectively. Water supplying relates with transpiration, which plays a great role in the transportation of the heavy metals. Every plant and microbe has its optimum temperature, pH, water content, and nutrient supply for living, and satisfying these demands is important.

The Use of Organic Amendments

Effective reduction of bio-availability of heavy metals in soils could be achieved by using organic amendments such as compost, farmyard manure (FYM), bio-solids or bio-solid compost [92]. In the case where organic matter is introduced to the soil, such metals as Cd may remain in the soil, in spite of both leaching and crop uptake [93]. The various organic amendments were compared [94]. Based on the results obtained, it was concluded that quality of the organic matter is important for efficiency of metals reduction, especially on the acid soils with low cation exchange capacity used in this study. Gupta et al. [95] demonstrated the effectiveness of 2% farmyard manure application. They observed Ni concentration lowered by 39, 40, 45, and 35% in carrot, fenugreek, spinach, and wheat grain, respectively. The effectiveness of the incorporation of straw into contaminated soil has also been investigated [96] and decreases in the concentration of Cd and Zn in spinach by 40% and 25%, respectively, was observed. Similar results have been introduced by other scientists [97-100].

The Use of Inorganic Amendments

Inorganic, in contrast to organic, amendments are more effective in decreasing the metal bio-availability for the following reasons: the introduction of additional binding sites for heavy metals and pH effects [101]. Some examples of mineral amendments include: Al – montmorillonite, clinoptilolite, diammonium phosphate, ferrous sulphate, hydroxyapatite, lime, manganese oxide, red mud, and synthetic zeolites. Many of these amendments are inexpensive and available in large amounts becasue they are by-products of industrial activities [102]. One example is lime, which has been used for centuries to increase pH and thus decrease metal uptake by crops [103]. Successful reports on liming are available for pot and for field studies. In pot experiments [104, 105] a significant reduction of Cd and Zn concentrations was found. But Balik et al. [106] observed a decrease of Cd and Zn concentrations in spinach by 80% and 75%, respectively. Dongsen et al. [107] reported a field study about the effect of liming on the availability of heavy metals in a soil amended with sewage sludge 16 years previously. They adjusted pH of soil from 4.6 to 5.8, 6.5, and 6.9, and found the most consistent trends in plant concentrations for Cd, Ni, and Zn. The concentrations of these elements in cabbage and tomato fruit were significantly reduced at liming rates of 15 and 22 t/ha (pH 6.5 and 6.9, respectively). It should be noted that in some cases liming could not decrease the uptake of Cd due to the high buffer capacity of the soil [108]. Also, in saline soils, the effect of the limestone application may be negligible [109]. In conclusion, before lime application, it is important to estimate soil characteristics.

The other interesting mineral amendments are naturally occuring zeolites (clinoptilolitem philipsite) or synthetic zeolites. They belong to a family of hydrated aluminosilicates that have selective capacities for metals adsorption. That is why zeolites are considered to be the most effective mineral amendments for reducing heavy metal transfer to plants. Successful reports on zeolite application are summarized by Knox et al. [103].

In many studies phosphate compounds (apatite or hydroxyapatite) were used for the immobilization of metals. Knox et al. [103] found that hydroxyapatite from North Carolina (25 and 50 g P/kg) effectively bind Pb, Zn, and Cd.

The application of red mud to four different heavy metal-contaminated soils has shown a reduction in plant uptake of Cd, Pb, and Zn in *Festuca rubra* and *Amaranthus hybridus* by 38-87%, 50-81%, and 66-87% on certain soils [110]. Lombi et al. [105] found that the application of red mud, lime, and beringite was effective in reducing heavy metal uptake of rapeseed oil, pea, and wheat. However, in the case of red mud application, precaution is required due to possible content of Cr and As [110].

The main advantages of inorganic amendments applications are immediate effectiveness, long-term sustainability, reasonable costs, and availability. Nevertheless, the one physical limitation in their use is shallow contamination. Also, for continuation of its effectiveness, periodic application may be necessary [103].

Conclusions

The first step on the way to reduce the concentration of heavy metals in food products is the development of fast and cheap analytical methods for determining their total concentration, as well as concentrations of all their toxic forms in the environment. The electrochemical methods are promising from this point of view. Because of the relatively low price of equipment, they could be widely applied in small local laboratories. As a consequence, information coming from continuous monitoring of the environment could be a basis for making decisions connected with the production of safe food.

A second step is decreasing the concentration of heavy metals in soil by means of physical and chemical remediation and phytoremediation using crop rotation and cultivation of industrial or bio-energy crops.

The addition of various inorganic and organic amendments could be proposed as another effective approach for reducing bio-availability of heavy metals in soils. Organic amendments such as farmyard manure or inorganic additives such as lime, zeolites, and iron oxides where they arefound to reduce the transfer of metals into crops. The application of these materials into soil purification is relatively easy, because most of them are available in large amounts in nature. However, one cannot forget the necessity of repeated application and periodic soil condition monitoring, in order to obtain the most effective results.

In conclusion, most important is selecting the most effective methods and their combinations in relation to the specific site conditions, to keep heavy metal concentrations below guideline values. Therefore, the approach presented here may open possibilities for safe agriculture at simple and effective levels.

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