ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 16, No. 3 2009

Magdalena BOROWIEC, Marta HUCULAK,
Krystyna HOFFMANN and Józef HOFFMANN[1]

ASSESSMENT OF LEAD AND CADMIUM CONTENT IN FOOD PRODUCTS IN ACCORDANCE WITH POLISH LAW IN FORCE

OCENA ZAWARTOŚCI OŁOWIU I KADMU W PRODUKTACH SPOŻYWCZYCH ZGODNIE Z OBOWIĄZUJĄCYM W POLSCE PRAWODAWSTWEM

Abstract: The research covered the determination of Pb and Cd content in selected fruits and vegetables from the Lower Silesian Province area. The samples contained very low amounts of the pollutants (Cd, Pb) according to the European Commission Regulation (EC) No. 466/2001 of 8 March 2001 setting the maximum allowable levels for some pollutants in foodstuffs. The amounts do not pose health hazard to the cultivated plants and so they do not pose such hazard to living organisms. The random taking of samples of plant products for monitoring purposes shows that plant products from the Lower Silesian Province area satisfy the requirements for foodstuffs. They contain amounts of the toxic metals close to their natural content in cultivated plants.

Keywords: Lead, cadmium, toxicity, maximum allowable levels

In recent years the protection of the natural environment has become an increasingly important social, economic and global issue. Global solutions based on the idea of *sustainable development* are aimed at eliminating or reducing the hazards to the environment, arising from any interference into natural ecosystems. Agenda 21, adopted at the Earth Summit in Rio de Janeiro in 1992 by the governments of most countries, obligates the signatories to action for the improvement of the environment in a systematic way making it possible to monitor and assess the environment using proper tools and indexes [1–3]. As a result of industrial, municipal and transport emissions, waste and sewage disposal, etc., increasing quantities of pollutants and dangerous substances are introduced into the environment. Among them heavy metals pose a very serious danger. As opposed to socially dangerous microbiological contaminations of

---

[1] Institute of Inorganic Technology and Mineral Fertilizers, Wroclaw University of Technology, ul. M. Smoluchowskiego 25, 50–372 Wrocław, tel. 071 320 30 39, email: jozef.hoffmann@pwr.wroc.pl

food, which immediately result in poisonings, chemical contaminations rarely cause acute poisonings. They may, however, cause diseases which manifest themselves much later. The largest amounts of metals (as much as 80 %) enter the body with food via the alimentary tract. Estimates of metal uptake in food rations show that over 30 % of the toxic compounds are supplied by vegetables [4, 5].

Besides microelements (highly valuable for human health), also elements having no nutritional value and posing a danger to health (because of their tendency to accumulate in the body) are ingested due to environmental contamination [6].

The consequence of the use of plant protectants and the accumulation of heavy metals products are deficient in natural nutrients, bioelements or vitamins and contain toxic elements (such as lead, arsenic, chromium, cadmium, mercury, nickel, tin, etc.) and other undesirable chemical compounds [6–8].

The main environment compartments from which trace elements pass to living matter are soil, water and air. Trace elements are particularly active and harmful because of their special role in biochemical processes and in the characteristic interactions of ions or chemical compounds as a result of which the biological effect of a given element depends on the occurrence and concentration of other ions or chemical substances. The interactions often disturb the chemical equilibrium in individual organisms or even in the ecosystem, which may lead to undesired biological consequences [4].

Heavy metals and their occurrence in soil

Soil is one of the vital links in the human food chain, which means that each change in its chemical composition brings about significant changes in the chemical composition of plants. Chemical soil pollutants are elements and chemical compounds which being not natural components of soil significantly affect its natural (formed long ago) properties. They may disturb the vegetation of plants and lower crops and the nutritional quality and technological usability of plant materials. Soil chemical contamination can be temporary, cyclic, long-lasting and practically irreversible. Particularly dangerous is soil contamination by such elements as: nickel, mercury, copper, cobalt, cadmium, beryllium and tin [9].

Soil is the main source of trace elements for plants. Trace elements are variously distributed among the particular components of soil, depending on: solubility, sorption, the formation of complex compounds, precipitation, occlusion, diffusion, oxidation, fixation by organic matter and uptake by microorganisms.

In the natural environment soil performs various functions, mainly filtration and buffering, which protect ecosystems against the excessive flow of trace elements into the other compartments of the biosphere [4].

The cycle of elements in soil and their transport to plant cells are highly complicated. They depend on, among other things, the soil pH, redox potential, mineral composition and moisture content, the kind of microorganisms and the abundance of organic compounds [8, 10].

Soil becomes contaminated with chemical compounds as a result of dust fall, sewage run-off and water migration of elements from solid waste heaps. Additional sources of heavy metal pollution are: the chemicalization of agriculture, some plant protectants and the transport and industrial wastes used for soil fertilization. The use of, for example, power plant ash as a mineral fertilizer brings about considerable chemical changes in soil – mainly the Mg and Ca content increases, which is beneficial for plants but at the same time a large load of heavy metals (particularly Pb, Zn and Cu) is introduced into the soil. Heavy metals easily migrate into the soil environment after its acidification [4, 11, 12].

A characteristic manifestation of soil contamination is the slow rate of change of the chemical compounds which do not naturally occur in it. This especially applies to heavy metals in cationic forms and to residues of some pesticides [9].

The soil reaction is one of the determinants of the agricultural usability of soils. In acid soils reduced plant growth, higher heavy metal concentrations and the loss of biological equilibrium are observed. The soil reaction regulates the uptake of nutrients and so it has a direct effect not only on the quality of the crops but also on their quantity. Increased soil acidity activates heavy metals in sparingly soluble compounds and blocks the uptake of beneficial forms assimilable by plants [13–15]. Soil liming is the most effective way of reducing the migration power of the existing and potential soil contaminations with heavy metals. Without improving the soil reaction it is impossible to achieve production objectives [16].

Heavy metals and their occurrence in plant products

Plants assimilate heavy metals occurring in the form of salts dissolved in soil solution or directly from atmospheric precipitation whereby there are differences in the heavy metal content between the aboveground and underground plant parts [17].

Heavy metals from dusts settle on plants, clogging their stomata and thereby reducing light absorption by plants and the rate of photosynthesis. Combined with water they form caustic compounds on the leaf's surface, damage the latter and after they get inside they change the structure of the cytoplasm and upset metabolism. Gaseous pollutants are even more harmful to plants than dusts. Dust pollutants on plants when ingested are harmful to consumers [8, 10].

The mechanism of trace elements uptake by the plant root system is complex, usually being the product of several processes such as cation exchange through the cell membrane, intracellular transport and rhizosphere processes. Ions (eg H^+, OH^-, HCO_3^-) and different substances released by the roots into the surrounding environment directly affect the mechanism of nutrient uptake. The oxidation or reduction of cations and the reaction of the solutions in the vicinity of roots are major factors in the assimilability of trace elements.

In natural conditions the trace element content considerably varies between species, and even between varieties of plants. The content also depends on the part of the plant and its developmental stage [4, 11].

A common feature of heavy metals, particularly lead and cadmium, is their capacity to accumulate in the body and their long biological half-life causes chronic toxicity whereby they pose extremely serious danger. Heavy metals are intensively taken up by plants growing on acid soils with $pH < 6.5$ [12].

Heavy metals penetrate into plants from both soil (via roots) and atmospheric dust. In the case of lead and cadmium, the hazard of their uptake from soil persists even after the pollution sources have been removed (the two elements are characterized by very high environmental persistence). Plants store the taken up metals mainly in their roots, but cadmium, being highly mobile, also passes to the aboveground plant parts. The uptake of metals from the substrate is a complex process which depends on many factors, such as the substrate's composition and reaction, the element's chemical form, the species of the plant (its accumulation capacity), the atmospheric conditions and so on. However, the highest toxic substance concentrations are found in sewage and industrial waste. Such substances can also penetrate into soils and ground and surface waters.

Vegetables quickly respond to an increase in the heavy metal content in the environment, increasing the amount of heavy metals in their tissues. Thus they reflect the state of the environment and the potential danger to humans [12, 18].

Cadmium

Cadmium significantly contributes to environmental contamination. Because of its toxicological properties and increasing abundance in the natural environment, it is included among food contaminations which deserve special attention.

The absorption of cadmium compounds by the human body depends on their solubility. Cadmium accumulates mainly in the kidneys and its half-life in the human body is as long as 10–35 years. The kidneys are the organs which are most exposed to the toxic action of cadmium. Cadmium absorbed through the airways has been proved to be carcinogenic [19–21].

For many years cadmium has been on the list of the main environmental contamination factors. In the environment, cadmium occurs in small amounts. It gets into air, soil and other compartments of environment as a result of human activities. Generally, there are two sources of environmental pollution: the production and use of cadmium and other nonferrous metals and the cadmium containing sewage of various origin. Small amounts of cadmium occur in phosphatic fertilizers [22].

Environmental pollution is the main source of cadmium in food. Soil cadmium pollution is dangerous since plants very readily take up cadmium and accumulate it in their roots. Plants can accumulate considerable quantities of cadmium which directly or indirectly (through interactions with other heavy metals) acts toxically on them. Cadmium can also migrate from everyday articles (eg kitchenware) into food [9].

Plants can accumulate cadmium from soil and the industry has considerably contaminated the environment with this element. Cadmium metabolism to a large extent depends on the uptake of zinc, copper and other metals [6].

Cadmium is taken up by plants exceptionally readily, both by the root system and leaves, generally proportionally to its concentration in the environment. The roots of plants readily take up cadmium in the form of cations Cd^{2+}, hydrated ions or chelates. Cadmium is assimilated by plants regardless of the properties of the soil. The transport of cadmium in plants is also easy but at its increased uptake it is accumulated mainly in roots, even when absorbed through leaf laminae. The exception are plants exposed to heavy atmospheric cadmium precipitation. Then cadmium accumulation in leaves is several times greater than in storage roots (eg carrot, beet). Plants resistant to high cadmium concentration form various protein compounds (phytochelatins) which by fixing this metal neutralize its phytotoxicity [4]. The ready assimilation of cadmium by plants entails a risk that excessive amounts of it will be incorporated into the human diet.

Lead

Lead is one of the dangerous heavy metals that have been more thoroughly researched. Liming and intensive phosphorous (with sulphur addition) fertilization can reduce lead uptake from soil by plants. Lead gets into the body through skin pores, the respiratory system and the alimentary canal and subsequently, into the blood, the bones and the body soft tissues, particularly the liver [6, 19, 21].

Lead is taken up by plants and accumulated mainly in their roots. But is also occurs in the aboveground parts of plants. Acid environment favours the migration of lead from technological containers and facilities into food. Lead acts on plants directly or through interaction with other components. It is highly toxic to animals [9, 15].

The harmful effect of lead on plants manifests itself mainly by photosynthesis, cell division and water balance disorders. The symptoms of toxicity include dark green colouring and withering of leaves and shortening of the roots.

The uptake of lead by roots is a passive process proportional to the occurrence of soluble forms in the substratum. As the lead concentration in the soil solution increases, so does its amount in plants, to a much higher degree in their roots than in their aboveground parts. The rate of lead uptake is determined by the properties of the plants and the soil conditions. The factors which markedly reduce lead uptake are: elevated soil reaction and lowered ambient temperature. Lead taken up by roots is stored in them and its transport to the green parts of the plant is very limited [19, 21].

Legal requirements

The maximum allowable levels (MAL) of heavy metals (Pb and Cd) are included in the Commission Regulation (EC) No. 466/2001 of 8th March 2001 setting the maximum allowable levels for lead (Pb) and cadmium (Cd) content in foodstuffs, section 3 [21]. The maximum allowable levels of lead (Pb) and cadmium (Cd) content in plant products are shown in Tables 1 and 2.

Table 1

MAL of lead (Pb) content in plant products [21]

Product	MAL of lead content [mg/kg of fresh product]
Vegetables, except for cabbage-like vegetables, leafed vegetables, fresh herbs and all mushrooms	0.1
Cabbage-like vegetables, leafed vegetables and all cultivated mushrooms	0.3
Fruits, except for berries and small fruits	0.1
Berries and small fruits	0.2

Table 2

MAL of cadmium (Cd) content in plant products [21]

Product	MAL of cadmium content [mg/kg fresh product]
Vegetables and fruits, except for leafed vegetables, fresh herbs, all mushrooms, stem vegetables, root crops and potatoes	0.05
Leafed vegetables, fresh herbs, root celery and all cultivated mushrooms	0.2
Stem vegetables, root crops and potatoes, except for root celery	0.1

Materials and methods

The aim of this research was to determine the heavy metal (Pb and Cd) content in plant products with regard to the current regulations. Commercial fruits and vegetables, coming from orchards and fields in Lower Silesia were tested for the content of the above contaminants.

The principles of taking up samples for the presence of Pb, Cd and Hg can be found in the Law Gazette No. 120 of 28th May 2004. This area is regulated by item 1257 of the Health Ministry Order of 30th April 2004 concerning the maximum allowable levels of chemical and biological pollutants, additives and processing aiding substances in food and food components or on the surface of food. The procedures and guidelines for taking and preparing samples are included in annex 1 to the Order [23].

Heavy metal content determination

Determination of lead and cadmium content in plant material

Samples for lead and cadmium content determination were mineralized in accordance with the ‘Determination of Lead, Cadmium, Copper and Zinc Content in Food Products by the Flame Atomic Absorption Spectrometry Technique’ [24].

The method consists in dry mineralizing samples and determining the metal content by the flame atomic absorption spectrometry (FAAS) technique after extracting Pb and Cd complexes from ammonium 1-pyrrolidinedithiocarbamate using methyl isobutyl ketone [24].

Prior to determining the Pb and Cd content the samples were subjected to dry mineralization. For this purpose, the product to be tested was homogenized and 10, 20, 50 g samples (depending on the plant material) were weighed out into quartz evaporating dishes. Since they contained much water (fruits, vegetables), the samples were dried and then carbonized. After incineration the samples were placed in a muffle furnace at a temperature of 250 ^{o}C. The temperature was gradually increased (at a step of 50 ^{o}C) up to about 400 ^{o}C (not exceeding 450 ^{o}C, which might result in losses of the elements to be determined). Incineration in the furnace was conducted until white ash was obtained. The residue was dissolved in 5 cm^3 of 1 M solution of HNO_3 and heated up on a water bath. Then it was filtered into a 50 cm^3 measuring flask and made up with 1 M solution of HNO_3.

30 cm^3 of the tested mineralizate, 20 cm^3 of deionized water, 100–200 mm^3 of bromocresol green were measured out into an extraction flask with a capacity of 100 cm^3. After mixing, 3 cm^3 of citrate buffer were added, the whole was mixed and titrated with an ammonia solution until the colour changed from yellow to blue. Then again 3 cm^3 of the buffer were added and the whole was mixed and heated up. 3 cm^3 of 2 % solution of 1-pyrolidinedithiocarbamate were added to the hot solution, the whole was mixed and cooled down to room temperature. Then 4 cm^3 of methyl isobutyl ketone were added and the whole was shaken for 0.05 h. Deionized water was added to the flask until the organic layer was in the upper part of the extraction flask neck. Then the organic layer was sucked in and the measurement was performed.

Results and discussion

The studies covered the determination of Pb and Cd content in selected vegetables and fruits coming from the Lower Silesian Province.

Pb and Cd in the product in [mg/kg] were calculated from this formula:

$$X_n = \frac{(C_n - C_{tr.}) \cdot V}{m}$$

where: C_n – the concentration of the element in the mineralizate;
$C_{tr.}$ – the concentration of the element in the reagent test, in μg/cm^3;
V – the total mineralizate volume in the tested sample, in cm^3;
m – the size of the analytical sample of the tested product, in g.

The arithmetic mean of the results from two simultaneously conducted determinations, differing from each other by no more than 15 % of the lower result, was adopted as the final result.

The results of the chemical analyses of the heavy metal content in the plant products are shown in the tables below.

The lead content in the selected fruit samples and vegetables is shown in Table 3 and Table 4, respectively.

Table 3

Lead content in fruits samples in mg/kg of fresh product

Fruits	Lead (Pb) [mg/kg of fresh product]
Apples	0.002
Peaches	0.000
Nectarines	0.000
Plums	0.000
Apricots	0.008

Table 4

Lead content in vegetables samples mg/kg of fresh product

Vegetables	Lead (Pb) [mg/kg of fresh product]
Soil-grown cucumbers	0.002
Mushrooms (*Agaricus*)	0.022
Carrots	0.008

No lead content was found in three of the eight tested samples. The other samples contain minimum amounts of the element with regard to the Commission Regulation (EC) No. 466/2001 of 8th March 2001 setting the maximum allowable levels for some pollutants in foodstuffs, section 3 [21].

The cadmium content in the fruit samples and in the vegetable samples is shown in Table 5 and Table 6, respectively.

Table 5

Cadmium content in fruits samples in mg/kg of fresh product

Fruits	Cadmium (Cd) [mg/kg of fresh product]
Apples	0.0000
Peaches	0.0004
Nectarines	0.0004
Plums	0.0024
Apricots	0.0010

Table 6

Cadmium content in vegetables samples in mg/kg of fresh product

Vegetables	Cadmium (Cd) [mg/kg of fresh product]
Soil-grown cucumbers	0.0030
Mushrooms (*Agaricus*)	0.0092
Carrots	0.0200

No cadmium was found in one of the eight tested samples while in the other samples cadmium content was minimal with regard to the Commission Regulation (EC) No. 466/2001 of 8 March 2001 setting the maximum allowable levels for some pollutants in foodstuffs, section 3.

Conclusions

The research covered the determination of Pb and Cd content in selected vegetables and fruits from the Lower Silesian Province area.

The elements were found to be absent in three of the eight plant material samples tested for Pb and Cd. The other samples contained minimum amounts of the pollutants with regard to the Commission Regulation (EC) No. 466/2001 of 8th March 2001 setting the maximum allowable levels for some pollutants in foodstuffs. The amounts do not pose health hazard to the cultivated plants and so they do not pose such hazard to living organisms.

The random taking of samples of plant products for monitoring purposes shows that plant products from the Lower Silesian Province area satisfy the requirements for foodstuffs. They contain minimum amounts of the toxic metals (close to their natural content in cultivated plants).

References

[1] Dokumenty końcowe Konferencji Narodów Zjednoczonych “Środowisko i Rozwój”, Rio de Janeiro 1992, Szczyt Ziemi, IOS, Warszawa 1998.

[2] Kowalski Z.: Czystsze produkcje jako strategia ochrony środowiska naturalnego, Mentor, Kraków 1998.

[3] Hoffmann J.N. and Radosiński E.: Polish J. Chem. Technol., 2007, **4**, 8–13.

[4] Kabata-Pendias A. and Pendias H.: Biogeochemia pierwiastków śladowych, PWN, Warszawa 1993.

[5] Lipińska J. and Oprządek K.: *Ocena zawartości metali w warzywach z Siedleckich ogrodów działkowych,* Rocz. Państw. Zakł. Hig., 1996, **2**(47), 211–216.

[6] Wiąckowski S.K.: Próba ekologicznej oceny żywienia, żywności i składników pokarmowych, PWN, Warszawa 1995.

[7] Kędzierska I. and Kędzierski W.: Ekologiczna profilaktyka chorób uwarunkowanych przez czynniki środowiskowe, Wyd. Med., Warszawa 1997.

[8] Meinhardt B.: Stan zanieczyszczenia roślin na terenie miasta Wrocławia i okolic, Bibl. Monit. Środow., Wrocław 1994.

[9] Smoczyński S. and Amarowicz R.: Chemiczne skażenia żywności, WNT, Warszawa 1988.

[10] Nabrzyski M. and Gajewska R.: *Zawartość rtęci, kadmu i ołowiu w owocach i warzywach oraz glebie,* Rocz. Państw. Zakł. Hig., 1982, **XXXIII**(3), 221.

[11] Nowak A.: Ecol. Chem. Eng., 1997, **6**(4), 869–893.

[12] Wacławek W., Kwak A., Koszałka-Niczypor A. and Sztamberek-Gola I.: Ecol. Chem. Eng., 1998, **12**(5), 1163–1178.

[13] Inspekcja ochrony środowiska, Wojewódzki Inspektorat Ochrony Środowiska we Wrocławiu, Raport o stanie Środowiska w województwie Dolnośląskim w 2001 roku, Bibl. Monit. Środow., Wrocław 2002.

[14] Lityński T. and Jurkowska H.: Żyzność gleby i odżywianie się roślin, PWN, Warszawa 1982.

[15] Ostrowska A., Gawliński S. and Szczubiałka Z.: Metody analizy i oceny właściwości gleb i roślin. Katalog Instytutu Ochrony Środowiska, Instytut Ochrony Środowiska, Warszawa 1991.

[16] Inspekcja ochrony środowiska, Wojewódzki Inspektorat Ochrony Środowiska we Wrocławiu, Raport o stanie Środowiska w województwie Dolnośląskim w 2002 roku, Bibl. Monit. Środow., Wrocław 2003.

[17] Popkow R. and Popokow H.: Przem. Ferment. Owoc.-Warzyw., 1995, **3**, 27–30.

[18] Godlewska-Żyłkiewicz B. and Dziwulska U.: Analityka: Nauka i Praktyka, 2003, (3), 47–49.

[19] Barałkiewicz D.: Analityka: Nauka i Praktyka, 2003, (2), 16–20.
[20] Wawrzyniak A. and Pawlicka J.: *Ocena pobrania kadmu z żywnością w gospodarstwach domowych w Polsce w latach 1993–1997*, Rocz. Państw. Zakł. Hig., 2000, **3**(51), 269–277.
[21] Rozporządzenie Komisji (WE) NR 466/2001 z dnia 8 marca 2001 r. ustalające najwyższe dopuszczalne poziomy dla niektórych zanieczyszczeń w środkach spożywczych.
[22] Kryteria zdrowotne środowiska, Kadm, Instytut Medycyny Pracy, t. 134, Łódź 1996.
[23] Rozporządzenia Ministra Zdrowia z dnia 30 kwietnia 2004 r. Dz.U. nr 120, poz. 1257.
[24] Metoda oznaczania ołowiu, kadmu, miedzi i cynku w produktach spożywczych techniką płomieniowej absorpcyjnej spektrometrii atomowej, Wyd. Metod. Państw. Zakł. Hig., 1996.

OCENA ZAWARTOŚCI OŁOWIU I KADMU W PRODUKTACH SPOŻYWCZYCH ZGODNIE Z OBOWIĄZUJĄCYM W POLSCE PRAWODAWSTWEM

Instytut Technologii Nieorganicznej i Nawozów Mineralnych, Politechnika Wrocławska

Abstrakt: Przeprowadzone badania obejmowały oznaczenia zawartości pierwiastków chemicznych Pb i Cd w wybranych owocach i warzywach. Badaniu zostały poddane owoce i warzywa pochodzenia krajowego z terenu województwa dolnośląskiego. W trzech z ośmiu zbadanych próbek materiału roślinnego nie stwierdzono zawartości Pb i Cd, pozostałe próbki zawierają niewielkie ilości badanych zanieczyszczeń w porównaniu z zaleceniami Rozporządzenia Komisji (WE) Nr 466/2002 z dnia 8 marca 2001 r. ustalającego najwyższe dopuszczalne poziomy dla niektórych zanieczyszczeń w środkach spożywczych. Nie stanowią więc zagrożenia dla uprawianych roślin, a tym samym dla organizmów żywych.

Słowa kluczowe: ołów, kadm, toksyczność, najwyższy dopuszczalny poziom