# TREND ANALYSIS OF CADMIUM IN FEEDSTUFF

# ANALIZA TRENDA KADMIJUMA U HRANI ZA ŽIVOTINJE

**Boris Pisinov**, research associate[1]*
**Sanja Đurović**, research associate[2]
**Zoran Sekulić**, PhD - environmental protection engineer[3]
**Tijana Dudić**, BSc - biochemistry[4]
**Tanja Keškić**, research associate[5]
**Maja Petričević**, research associate[6]
**Tamara Stamenić**, research assistant[7]

**Abstract:** *Heavy metals are potent metabolic inhibitors. Cadmium is considered a non-essential element and has high emissions in the biosphere due to anthropogenic activities. The aim is to indicate the importance of cadmium in feedstuff as a potential contamination source. Microwave digestion and graphite furnace atomic absorption spectrometry were used to examine 298 feedstuff samples. A high amount of cadmium above permitted is present in 0.67% of samples. Continuous cadmium monitoring is necessary to prevent its uncontrolled entry into the food chain.*

**Key words**: *cadmium, pollution, feed, GFAAS, regulations*

**Apstrakt:** *Teški metali su snažni metabolički inhibitori. Kadmijum se smatra neesencijalnim elementom i ima visoke emisije u biosferi usled antropogenih aktivnosti. Cilj je da se ukaže na važnost kadmijuma u hrani za životinje kao potencijalnom izvoru zagađenja. Mikrotalasna digestija i grafitna peć atomska apsorpciona spektrometrija su korišćeni za ispitivanje 298 uzoraka hrane za životinje. Visoka količina kadmijuma iznad dozvoljene je prisutna u 0.67% uzoraka. Neophodan je stalan nadzor kadmijuma da bi se sprečio njegov nekontrolisani ulaz u lanac ishrane.*

**Ključne reči:** *kadmijum, zagađenje, štočna hrana, GFAAS, propisi*

## 1. INTRODUCTION

Under intensive urbanization and industrialization conditions, there are also negative consequences, primarily to large-scale pollution and environmental destruction. Pollutants of anthropogenic origin,

[1] Institute for Plant Protection and Environment, Teodora Drajzera 9, 11040 Belgrade, Serbia, e-mail: boriss752002@yahoo.com (*Corresponding author)
[2] Institute for Plant Protection and Environment, Teodora Drajzera 9, 11040 Belgrade, Serbia, e-mail: stojakovicsm@yahoo.com
[3] Institute of Public Health of Belgrade, Bulevar Despota Stefana 54a, 11108 Belgrade, Serbia, e-mail: zoran.sekulic@zdravlje.org.rs
[4] Institute for Plant Protection and Environment, Teodora Drajzera 9, 11040 Belgrade, Serbia, e-mail: tijanadudic44@gmail.com
[5] Institute for Animal Husbandry, Autoput Belgrade-Zagreb 16, 11080 Belgrade-Zemun, Serbia, e-mail: tanjakeskic@gmail.com
[6] Institute for Animal Husbandry, Autoput Belgrade-Zagreb 16, 11080 Belgrade-Zemun, Serbia, e-mail: majanovakovic@live.com
[7] Institute for Animal Husbandry, Autoput Belgrade-Zagreb 16, 11080 Belgrade-Zemun, Serbia, e-mail: tstamenic169@gmail.com

including heavy metals and their compounds and alloys, in the chemical, automotive, textile, and electronics industries, agriculture, metallurgy and mining, and wastewater from heavy industry lead water, land, and air pollution. Heavy metals and their salts represent a very important group of environmental pollutants since they are potent metabolic inhibitors. The inherent toxicity of a metal depends upon its capacity to disturb the dynamic life processes in biological systems by combining with cell organelles, macromolecules, and metabolites.

Cadmium (Cd), as a heavy metal, can damage the structure of the natural ecosystem, so it is built into the food chain, creating the need to establish criteria of health safety food not only of plant and animal origin but also the various nutrients used in animal feed. In the 1950s and 1960s, industrial pollution with cadmium was high. Still, when the toxic effects of cadmium became apparent, the boundaries of the industrial release were reduced in most industrialized countries, with the approval of further reduction. Considering that there is a possibility of accumulation of heavy metals, therefore also cadmium, from the environment in the food and living organisms, as well as the fact that the least amount of heavy metals can affect the metabolism of plants, animals, and people, there is a need for determining the content of cadmium in various materials (water, soil, etc.). The buildup of cadmium levels in the water, air, and soil has been occurring, particularly in industrial areas.

Food is another source of cadmium. Plants may only contain small or moderate amounts in non-industrial areas, but high levels may be found in the liver and kidneys of adult animals [1]. Environmental exposure to cadmium has been particularly problematic in Japan, where rice consumed was grown in irrigation water contaminated with cadmium, causing Itai-Itai disease in humans, which was recognized in 1968th as the first illness caused by pollution of the environment [2]. Cadmium from various sources (water, air, food, dust) slowly accumulates in the body during the 50-60 years, and the biological half-life is 10-30 years [3].

Some phosphate sources in fertilizer contain cadmium in amounts of up to 100 mg $kg^{-1}$, which can lead to an increase in cadmium concentration in soil [4-5]. Cadmium is found in low concentrations in rocks, coal, and oil and is often naturally found in groundwater rather than surface water. Soft water of low pH value can contain multiple values of the concentrations of cadmium. In surface waters, cadmium can run in discharging unrefined wastewater, released from the soil where sewage sludge is added or applying pharmaceutical products for stock breeding, with the waste from farms uncontrolled distributed on agricultural land [6].

Cadmium is a serious, lethal occupational and environmental toxin known for its high toxicity, which may affect living systems in various ways. Therefore, it has been ranked seventh among the top 20 hazardous substances [7]. The International Agency for Research on Cancer (IARC) has classified cadmium as a group 1 human carcinogen of the prostate and lung [8].

The maximum permitted concentrations (MPC) in water, soil, food, and animal feed define the cadmium content. It occurs naturally in almost all agricultural soils, and the average concentration in Earth’s crust is 0.1-0.5 mg $kg^{-1}$; therefore, the European Union (EU) sets a limit on the concentration of sewage sludge used on agricultural land as 20-40 mg $kg^{-1}$ dry matter, and 1-3 mg $kg^{-1}$ Cd when sewage sludge is used on agricultural soil [9-10]. In Serbia, MPC for cadmium in soil is 0.8 mg $kg^{-1}$ dry matter, for sediment is 6.4 mg $kg^{-1}$, while for tap and bottled water are 0.003 mg $l^{-1}$ and 0.005 mg $l^{-1}$, respectively [11,12,13]. Depending on the type of food, national and EU legislation prescribe cadmium MPC values from 0.020 to 1.20 mg $kg^{-1}$ [14]. According to the national Regulation on the quality of animal feed, MPCs for cadmium, depending on the categorized group, are in the intervals 1 to 10 mg $kg^{-1}$ for feed and 0.5 to 7.5 mg $kg^{-1}$ for mixtures, while 15 mg $kg^{-1}$ is for premixes [15].

In order to determine the potential risk of contamination with cadmium and its entering into the food chain system as a bioaccumulation toxin, in terms of the tendency of getting safe food, tests were carried out on samples of animal feed (feedstuffs, premixtures, and mixtures).

## 2. MATERIAL AND METHODS

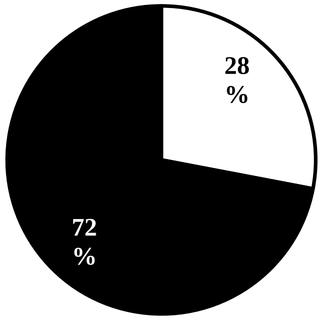
The tests were performed on 298 samples received to the laboratory over two years period, of which 130 feed samples (75 samples of mineral feed, 55 samples of animal origin feed), 112 samples of premixes (97 samples of vitamin-mineral premix, 15 samples of mineral premixes), 56 samples of the mixture.

Sample preparation and cadmium analyses were performed according to EN 15550 [16] using an advanced MARS 6 iWave microwave digestion system (CEM Corporation, Charlotte, NC, USA) and PinAAcle 900T graphite furnace atomic absorption spectrometer (GFAAS) equipped with furnace autosampler AS 900, electrodeless discharge lamps (EDL) and hydride generation FIAS 100 System (Perkin-Elmer Inc., Shelton, CT, USA). Ground test samples up to 0.5 g were digested in 9 ml of concentrated nitric acid (≥ 65%) and 2 ml of hydrogen peroxide (≥ 30%) by microwave heating in the microwave system. The temperature profile was specified to start at 16 ± 4 °C, reach 165–170 °C within 10 min, and hold for 10 min to complete reactions. After cooling for at least 30 min, the samples were filtered and analyzed. The operating conditions of GFAAS for cadmium determination were set as follows: power supply 10.1 kW, element-specific analytical wavelength of 228.8 nm, slit width 0.7 nm, pyrolysis and atomization temperature of 900 °C and 1600 °C, output pressure of argon (purity ≥ 99.996%) gas stream at 350-400 kPa with maximum flow rate of 0.7 l $min^{-1}$, autosampler injection volume of 10 µl. A temperature program for the graphite furnace consists of four steps: drying, pyrolysis, atomization, and cleaning. Palladium nitrate/magnesium nitrate matrix modifier (Perkin-Elmer Inc., Shelton, CT, USA), Zeeman's effect background correction, and blank solution were used to eliminate interferences and obtain reliable results. Cadmium was quantified in the samples by subtracting the analyte concentration of the blank solution and using an external calibration curve. Individual commercial standard (AccuStandard Inc., New Haven, CT, USA) was used to prepare standard calibration solutions. Working (calibration) standard solutions were prepared at the concentration range of 0.0, 0.1, 0.2, 1.0, and 2.0 mg $l^{-1}$.

## 3. RESULTS AND DISCUSSION

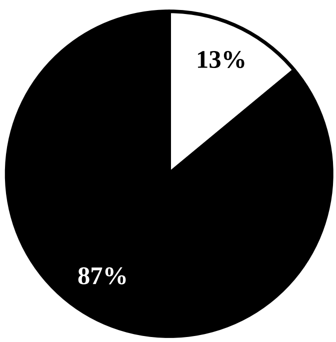
In the period of two years, were obtained in the feed samples (mineral feed, animal origin feed), premix (vitamin-mineral premixtures, mineral premixtures) mixture following results we have shown in Graphs 1, 2, 3, 4.

In mineral feeds, cadmium was detected in 54 samples (72% of the total surveyed samples of mineral feed) (Graph 1). Of these, in 52 samples (69%), its concentration was below 10 mg $kg^{-1}$, the maximum permitted concentration specified in the Regulation on the quality of animal feed [15]. In only two samples (3%), cadmium was proven to be above MPC (10 mg $kg^{-1}$). Similar to our research, Sigarini et al. [17] investigated eleven mineral feeds with Cd concentrations ranging from lower than the limit of quantification to 6.1 mg $kg^{-1}$. It was found that 60% of samples showed values above the recommended by the EU (1.0 mg $kg^{-1}$), but regarding Brazilian national legislation, all values were below the maximum recommended (10 mg $kg^{-1}$). The wide result variations can be attributed to inhomogeneous impurity levels of used batches of phosphate rocks.



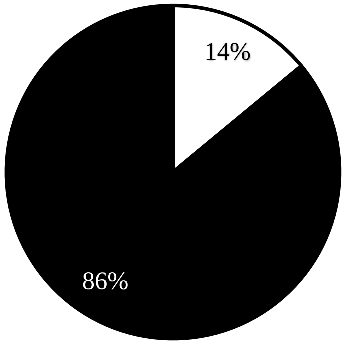

Graph 1. Total percentage of samples where cadmium was measured (dark field).

In the animal-origin feed, cadmium was determined in 48 samples (87% of the total surveyed samples of animal-origin feed) (Graph 2). In samples containing cadmium, its concentration was below 2 mg $kg^{-1}$, the maximum permitted concentration defined in the Regulation on the quality of animal feed [15]. All 48 samples where cadmium was quantified were fish meal, in other animal-origin feed samples its amount was below the limit of quantification. The findings of Adamse et al. [18] were partly in agreement with ours, where was stated in the period 2000-2013, of the 401 analyzed animal origin feed samples, 249 (62%) had values above the limit of quantification (> 0.02 mg $kg^{-1}$) but four samples (1%) exceeded recommended MPC (2 mg $kg^{-1}$) of EU Regulation [19].



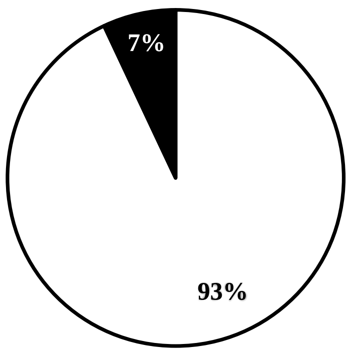

Graph 2. Total percentage of samples where cadmium was measured (dark field).

In premixtures, 96 samples contained cadmium (86% of the total number of tested premixes samples) (Graph 3). However, for premixes, 15 mg $kg^{-1}$ is the maximum permitted concentration of cadmium according to the Regulation on the quality of animal feed [15]. Further, obtained results for cadmium content in premix samples indicate that neither of them had concentrations greater than prescribed for premixes. The findings of Adamse et al. [18] were in agreement with ours, who stated in the period between 2000 and 2013, of the 734 analyzed premixture samples, 577 (79%) had values above the limit of quantification (> 0.02 mg kg-1), but neither exceeded recommended MPC (15 mg $kg^{-1}$) of EU Regulation [19].




Graph 3. Total percentage of samples where cadmium was measured (dark field).

In the mixtures, cadmium was determined in four samples (7% of the total number of samples in the tested mixture) (Graph 4). The cadmium content did not exceed the maximum permitted concentration of 1 mg $kg^{-1}$, prescribed in the Regulation on the quality of animal feed [15].




Graph 4. Total percentage of samples where cadmium was measured (dark field).

Our findings contradicted the findings of Marçal et al. [20], who examined 37 mixture samples and in 33 samples (89%) found cadmium concentrations greater than 0.5 mg $kg^{-1}$ (ranged < 0.5 to 11.2 mg $kg^{-1}$), which is the maximum concentration recommended by the Brazilian national legislation. The sufficient content of cadmium may cause toxicity in animals.

## 4. CONCLUSION

Based on the obtained results, it can be concluded that the content of cadmium was mainly below the maximum permitted concentration in animal feedstuff and that it complies with the legislation's requirements on the quality of animal feed in part related to the harmful substance.

However, according to the presented information on the toxicity of cadmium and all possibilities for it to enter the food chain, in order to obtain safe food, it is necessary to continue monitoring toxic elements for preventive reasons and also for locating possible contamination at any part of the system water-soil-plant-animal-human.

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