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# 3<sup>rd</sup> INTERNATIONAL CONFERENCE

on

## Agriculture and Life Sciences (ICOALS III)

Campobasso - Tirana 2021

# PROCEEDINGS

**PROCEEDINGS OF  
INTERNATIONAL CONFERENCE ON AGRICULTURE AND LIFE SCIENCES  
(ICOALS III)**

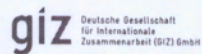
Due to Covid-19 restrictions, this conference is partly organised online /Universita di Molise

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## Determination of heavy metals and radionuclides in animal feeds of plant origin

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**Abstract.** This study was carried out to determine the presence of heavy metals and radionuclides in animal feeds of plant origin used in the territory of North Macedonia. Obtained results covered the levels of lead, arsenic, and mercury, as well as the levels of <sup>40</sup>K, <sup>226</sup>Ra and <sup>137</sup>Cs in a variety of plant-based pig and poultry feeds. A total number of 121 samples were collected from local representatives and feed industry, and the content of contaminants of concern was analyzed. Analyses were performed using electrothermal atomic absorption spectroscopy (ETAAS) for detection of lead (Pb) and arsenic (As), and cold vapor atomic absorption spectrometry (CVAAS) for mercury (Hg) concentrations in the collected samples. The radionuclide analysis was performed by means of HPGe gamma spectrometry. The highest detected average concentrations of the selected toxic metals were 0.277±0.376 mg/kg for Pb, and 0.105±0.201 mg/kg for As in pig feeds, as well as 0.030±0.028 mg/kg for Hg in poultry feeds. All tested samples contained toxic metal concentrations much below the MLs. The mean values from the measured activities in pig feeds were in the range 3.20 - 3.65 Bq kg<sup>-1</sup> for <sup>226</sup>Ra, 184.54 - 201.11 Bq kg<sup>-1</sup> for <sup>40</sup>K, and <1 Bq kg<sup>-1</sup> for <sup>137</sup>Cs. The activity levels for poultry feeds were from 0.23 to 2.11 Bq kg<sup>-1</sup> for <sup>226</sup>Ra, from 40.7 to 43.2 Bq kg<sup>-1</sup> for <sup>40</sup>K, and <1 Bq kg<sup>-1</sup> for <sup>137</sup>Cs. The food of plant origin used in North Macedonia has generally shown safe levels for all three heavy metals analyzed. Additionally the activity level in the analyzed radionuclides was within sufficient limits to conclude that there are no hazards to animal and human health. The preventive measures for feed safety would be continuous monitoring of radioactivity and heavy metals in animal feeds.

**Keywords:** poultry feeds, pig feeds, radionuclides, heavy metals

### Introduction

The presence of radionuclides and heavy metals is an integral unavoidable part of the environment. Their concentrations depend on the geological and geographical conditions (1). The large number of activities in everyday life such as application of soil fertilizers, processing of phosphate ore, and deposition of particles, increase the concentration of radionuclides and heavy metals in the environment, feed and food products (2, 3). Due to the toxic effects and present levels, they are considered as the major environmental pollutants (4). Lead, As and especially Hg, rank among the priority elements that are important for animal and human health. There has been a significant need for radiological analysis of the presence of heavy metals in the environment, especially analysis of animal feed, considering that it reaches humans through the food chain. In order to enrich the nutritional value, elements that may increase the amount of radionuclide activity in animal feed are increasingly being added, which was an issue of discussion (5).

This study was conducted in order to determine the content of heavy metals and radionuclides in animal feed of plant origin marketed on the territory of North Macedonia. The obtained results included levels of Pb, As and Hg, as well as levels of <sup>40</sup>K, <sup>226</sup>Ra and <sup>137</sup>C in different types of plant-based animal feed for pigs and poultry.

### Material and Methods

#### Sampling and sample preparation

In total 121 samples were collected from local wholesale and feed producers. For radiological analysis, after the homogenization, the samples were placed in 0.5 L Marinelli beakers which were fully filled, sealed and stored for some time before the measurements was performed, in order to establish a balance between <sup>226</sup>Ra and <sup>222</sup>Rn (6). For heavy metals testing, the homogenized samples were mineralized in PTFE lined vessels with a mixture of concentrated nitric acid (65%) and hydrogen peroxide (30%), through a wet digestion process in a microwave oven (Ethos up, Milestone Corporation, Italy) (7, 8). The digests were diluted with high-purity water and directly analyzed for heavy metals contents applying ETAAS for Pb and As and CVAAS for Hg analysis (7, 8).

#### Instrument

For radiological assessment the samples were measured on gamma spectrometer instrument (Canberra Packard) with a high purity germanium detector. GENIE 2000 software was used for data acquisition and analysis. The specific activity of <sup>226</sup>Ra was calculated from the energy line of 186.1 (keV), <sup>40</sup>K was determined from its  $\gamma$ -line at 1460 keV, while the activities of <sup>137</sup>Cs were determined by means of an estimation of the  $\gamma$ -line at 661.66 (keV). The time interval for calculation (counting) was 65000 seconds.

Lead and arsenic analysis was performed using ETAAS (Perkin Elmer AAnalyst 600), and CVAAS by means of flow injection mercury system (Perkin Elmer, FIMS 100) was used for determining mercury in the selected samples. The

measured absorption lines were: 283.3 nm for Pb, 193.7 nm for As, and 253.7 nm for Hg. Palladium was added as chemical modifier to standards and samples for stabilization of Pb and As at charring temperatures of 1850 °C, while alkaline sodium borohydride was used as the reducing agent for mercury determination in animal feeds (7, 8).

The internal quality control of the gamma-spectrometry procedure was performed by means of periodical energy and efficiency calibration with standard source MBSS2 (Czech Metrology Institute, Brno, Czech Republic), and weekly control of the background spectrum of the acquisition system. For heavy metals, the quality control check was performed using proficiency test material IMEP 38 (EURL for heavy metals, Geel, Belgium). The obtained measurement data were subjected to analysis of arithmetic means and standard deviations using MS Excel (MS Office 2013, Redmond, USA).

## Results and Discussion

The obtained results showed that highest level of natural  $^{40}\text{K}$  was present in both types of examined samples. The mean values for the measured activities in the pig feed were 3.20 to 3.65 Bq kg<sup>-1</sup> for  $^{226}\text{Ra}$ , from 184.54 to 201.11 Bq kg<sup>-1</sup> for  $^{40}\text{K}$  and <1 Bq kg<sup>-1</sup> for  $^{137}\text{Cs}$ . In addition, for poultry feed the measured values were from 0.23 to 2.11 Bq kg<sup>-1</sup> for  $^{226}\text{Ra}$ , from 40.7 to 43.2 Bq kg<sup>-1</sup> for  $^{40}\text{K}$  and <1 Bq kg<sup>-1</sup> for  $^{137}\text{Cs}$ . Anthropogenic radionuclide  $^{137}\text{Cs}$  was not detected in none of the tested samples.

The determined trend for toxic element levels, according to the average concentrations found in the studied feed samples (pig feeds and poultry feeds), was as follows: Pb>As>Hg. The mean values of Pb and As were detected to be higher in pig feeds (0.277±0.376 mg/kg for Pb, and 0.105±0.201 mg/kg for As) corresponded to ones in poultry feeds which were 0.103±0.092 mg/kg for Pb and 0.036±0.021 mg/kg for As. On the other hand, mercury mean levels have been shown to be higher in poultry feed.

Table 1. Mean values of specific activities (A) of  $^{226}\text{Ra}$ ,  $^{137}\text{Cs}$  and  $^{40}\text{K}$  in pig and poultry feeds

Sample type	N*	A $^{40}\text{K}$ ±SD (Bq kg <sup>-1</sup> )	A $^{226}\text{Ra}$ ±SD (Bq kg <sup>-1</sup> )	A $^{137}\text{Cs}$ ±SD (Bq kg <sup>-1</sup> )
Pig feeds		192.85±8.50	3.42±1.22	<1
Poultry feeds		41.95±3.00	1.17±0.23	<1

\*N – number of tested samples

Table 2. Mean concentrations and standard deviations (mg/kg) of Lead (Pb), Arsenic (As) and Mercury (Hg) in pig and poultry feeds

Matrix	N*	Pb (mg/kg)	As (mg/kg)	Hg (mg/kg)
Pig feeds	72	0.277±0.376	0.105±0.201	0.020±0.024
Poultry feeds	49	0.103±0.092	0.036±0.021	0.030±0.028

\*N – number of tested samples

Our research and the obtained results show that the samples do not pose a risk to animal and human health. However, as preventive measure continuous monitoring of radioactivity and heavy metals in animal feed should be conducted. Strict safety control will also need to be performed when importing different types of animal feed. Furthermore, a monitoring plan to monitor radiation and heavy metals can prevent the entry of high levels of radionuclides and heavy metals in the food chain. If there are high levels in the analyzed samples, above the permissible limits, they should be diluted with appropriate nutrients, or should be removed from the market and safely destroyed.

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