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RESEARCH PAPER

The Occurrence of Arsenic, Cadmium, and Lead Residues in Cattle Feed Collected in Kırıkkale, Türkiye: A Preliminary Study

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Abstract

The aim of this study is to investigate the occurrence of arsenic (As), cadmium (Cd), and lead (Pb) residues in 15 cattle feed collected from dairy and beef cattle breeding farms located in 6 different districts (Kırıkkale Province, Yahşihan, Karakeçili, Balışeyh, Delice and Keskin) of Kırıkkale. The quantitative analysis of the As, Cd and Pb levels of the samples was analyzed by ICP-MS. Arsenic and Pb residues were found in all of the collected samples, while Cd residues were found in 13 (86. 67%) of the collected samples. In the samples with heavy metal residues; the mean value ± standard deviation for As, Cd, and Pb were found as 0.1475±0.1060 mg/kg, 0.0382±0.0079 mg/kg and 0.1944±0.1074 mg/kg respectively. The maximum tolerable limit in cattle feed is 2 mg/kg for As, 5 mg/kg for Pb, and for Cd in cattle feed is 1 mg/kg for Cd according to an official announcement (2014/11) of the Ministry of Agriculture and Forestry Turkey. The results of this study showed that detected As, Cd and Pb levels in cattle feeds were below the tolerable limit. Therefore, it is suggested that the heavy metal pollution in terms of As, Cd, and Pb in feed does not pose a risk for cattle farming in Kırıkkale province.

Introduction

The term heavy metal can be used for elements having an atomic mass of 200 or more like mercury, thallium, lead and bismuth. In practice, heavy metals include metals that is clinically cause undesirable effects and potentially dangerous for health (Baldwin and Marshall, 1999). Some metals such as cobalt, copper, chromium, and iron are necessary to maintain many biochemical and physiological processes in living organisms including animals and plants. On the other hand, metals such as As, Cd, Pb, and mercury (Hg) do not play a role in biological functions, and these undesirable substances in animal feeds are called contaminants. These metals threaten public health at high doses, and may even cause organ damage at low doses (Hejna *et al*., 2018). It is known that especially Cd, Pb and less commonly Hg cause kidney damage (Garcia *et al*., 2018). There are also findings reporting that these heavy metals cause cardiovascular diseases and chronic heart diseases (Chowdhury *et al,*. 2018).

The source of heavy metal accumulation in the environment is through natural and anthropogenic sources. Anthropogenic activities such as rapid industrialization, overgrowing urbanization and environmental manipulation lead to environmental pollution with heavy metals. Emissions from rapidly expanding industrial areas, mine residues and the accumulation of heavy metals through the disposal of high metal waste pollute the soil and water (Verma *et al*., 2018).

Arsenic is ubiquitous element, and has many forms on earth. Arsenite and arsenate forms of As are highly toxic to human and animals health. Exposure to As

occurs in many ways. Industrial activities are one of the most important reason of As exposure. Also drinking water and feed may contaminated with As that found in wood preservatives, herbicides, pesticides, fungicides and dyes (Engwa *et al*., 2019; İriş and Çınar, 2019). Cadmium is another highly toxic metals both for humans and animals. It accumulates in the soil and contaminates pastures (Reis *et al*., 2010). Cadmium is released into the environment through coal and waste incineration, disposal of metal-containing products, and the use of phosphate fertilizers (İriş and Çınar, 2019). Some plants can accumulate Cd. Therefore, they can be toxic to animals that consume these plants. While the performance of cattle decreases when consuming 5-10 mg/kg of Cd, it affects the health of animals above 30 mg/kg (Reis *et al*., 2010). Lead is one of the most important contaminants because of its largely use in industrial products. Exposure to lead can occur in many ways such as drinking water, food, cigarettes, industrial processes and domestic sources (Engwa *et al*., 2019). Because of eating habbits cattle reported widely in terms of Pb toxication. Lead toxication mostly affect gastrointestinal, central nervous and hematological systems in living organisms (Thompson, 2007).

Heavy metals can be found as residues in soil, ingestion of plants, sewage wastes, fertilizers and feeds. Apart from these, mine wastes, gasoline with Pb, paints and pesticides are among the causes of metal pollution (Kanbur and Tekeli, 2017). Considering all these reasons, it is important to investigate the level of undesirable substances especially in terms of heavy metals. The aim of this study is to investigate the presence of As, Cd, and Pb metal residues in cattle feed collected from some ruminant farms in Kırıkkale province.

Materials and Methods

Sample Collection

The feeds were collected from local enterprises of dairy and beef cattle breeding farms in Kırıkkale Province. A total of 15 total mixed rations samples were collected from the Districts of Kırıkkale Province (4 samples), Yahşihan (3 samples), Karakeçili (1 samples), Balıseyh (1 samples), Delice (2 samples), and Keskin (4 samples). The feed samples were total mixed rations that were prepared by the farm owners. Environmental differences such as the distance of the enterprises from each other were taken into account in the selection of the enterprises. Feed samples were collected in May, 2021. Containers and bags conforming to standards were used for sampling. The samples were stored at +4^{o}C and analyzed in the Nanolab Special Food Control Laboratory for the necessary analysis as soon as possible.

Sample analysis

The As, Cd, and Pb levels in feed samples were analyzed according to the procedures ISO27085-2009 E modified by Nanolab Special Food Control Laboratory In-house Method- "K.SOP.148"using, inductively coupled plasma mass spectrometry (ICP-MS, AGILENT/7700e, Japan). All chemicals were of analytical reagent quality. Arsenic, Cd, Pb standard stock solutions (1000 mg/L) (Merck) were used (0.05, 0.1, 0.5, 1, 5, 10, 20, 50 µg/L). For calibrations 50, 20, 10, 5, 1, 0.5, 0.1, 0.05 µg/L (ppb), appropriate solutions were made using stock standard solutions.

Table 1. Arsenic, cadmium and lead levels in cattle feed samples (mg/kg).

		Contamination (mg/kg)			
Metal	**Sample number**	**Positive**	**min-max**	**Mean ±SD**	**Samples exceeding legal level**
	n	***n (%)***			***n* (%)**
Arsenic	15	15 (100%)	0.027-0.385	0.1475±0.1060	-
Cadmium	15	13 (86.67%)	0.023-0.053	0.0382±0.0079	-
Lead	15	15 (100%)	0.050-0.403	0.1944±0.1074	-

n: sample number, min: minimum level, max: maximum level

Data were given as mean ± SD. The maximum tolerable value is 2 mg/kg for arsenic, 5 mg/kg for lead, 1 mg/kg for cadmium in catle feed (Republic of Turkey Ministry of Agriculture and Forestry No: 2014/11 Undesirable substances in animal feed)

Approximately 0.5 g of the prepared test sample was weighed into a vessel. Then, 8 ml HNO_3 (%65, Merck) and 2ml H_2O_2 (%30, Merck) were added, mixed, and burnt at microwave oven for 45 minutes. Samples were cooled and diluted to 50 ml using de-ionized water and shaken several times. It was filtered with cellulose asetate filtrate into a 15 ml falcon tube. After filtrated samples were applied to the ICP-MS device. A blank test tube was also prepared with the same procedure as for feed samples. Arsenic, Cd, and Pb heavy metals in test samples were measured at 75, 111, and 208 mass, respectively. The results were calculated according to the calibration.

The data of the study are given as mean ± standard deviation (SD). The evaluation of the data is based on the Republic of Turkey Ministry of Agriculture and Forestry No: 2014/11 Notification of undesirable substances in animal feed.

Results

Arsenic and Pb residues were found in all of the collected samples, while Cd residues were found in 13 (86.67%) of the collected samples. In the samples with heavy metal residues; the mean value±standart deviation for As was found as 0.1475 ± 0.1060 mg/kg ranging from 0.027-0.385 mg/kg. The mean value±standart deviation for Cd was found as 0.0382 ± 0.0079 mg/kg ranging from 0.023-0.053 mg/kg. The mean value±standart deviation for Pb was found as 0.1944 ± 0.1074 mg/kg ranged from 0.050-0.403 mg/kg. The maximum tolerable limit for As in feed is 2 mg/kg, for Pb in feed stuff is 5 mg/kg, for cadmium in cattle feed is 1 mg/kg (The Republic of Turkey's Ministry of Agriculture and Forestry Announcement No: 2014/11). The results of this study showed that the detected values were below the tolerable limit (Table 1).

Discussion

Heavy metals are extensively dispersed into the environment along with industrial wastes, as a result, they bio accumulate in the environment. These metals are known as environmental pollutants that pollute natural environments such as water, air and soil, and have toxic effects on humans through animals, plants and the food chain. Arsenic, Cd and Pb are known as the most exposed heavy metals (Yiğit ve Kabakçi, 2018). The main source of As accumulation in agricultural soil is the use of pesticides containing As (Adriano, 2001). Pesticides are commonly used in orchards. High levels of As have been found in pastures that were previously used as orchards (Willett *et al*., 1993).

Arsenic levels in grain and protein feed mix were reported 10 times higher than those in homegrown feed, probably due to the addition of other ingredients to the feed mix by the feed mill (for example, mineral mixtures containing P) (Li *et al*. 2005). The highest As concentration was reported in mineral mixtures by Li *et al*. (2005). However, acute poisonings with As in cattle are rare (Yiğit and Kabakçi, 2018). In a study conducted in China, the average As content in cattle feed samples was found to be between 0.80-1.38 mg/kg (Zhang *et al*., 2012). Cang *et al*. (2004) reported 0.13 mg/kg average As content in cattle feed in Jiangsu province. Wang *et al.* (2013) determined an average value of 0.3 mg/kg As in 35 dairy cow feeds in Jiangsu province of China. Nicholson *et al.* (1999) reported an average of 0.37 mg/kg in pelleted dairy cattle feed, 0.49 mg/kg in pelleted beef cattle feed, <0.10 mg/kg As in oat-barley mixture collected from the Wales province of England. Li *et al*. (2005) determined As values of 433 µg/kg in dairy feed, 490 µg/kg in dairy feed (substitute) and 450 µg/kg in heifer feed. In the presented study, it was revealed that As levels (0.1475 ± 0.1060 mg/kg) were higher than cattle feeds in the Izmir region declared an average value of 0.046 ± 0.127 mg/kg (Güvercin, 2010), and lower than dairy feeds in Jiangsu city of China with an average value of 0.3 mg/kg As (Wang *et al*., 2013). Arsenic levels of this study did not exceed the legal level recorded as 2 mg/kg.

High concentrations of Cd (up to 10 mg/kg) have been found in forages grown in fields near industrial zinc coating areas where urban sludge is used as fertilizer (Smith, 1986). Cadmium is a human carcinogen associated with lung and prostate cancer therefore it should not be found in feed and feedstuff (Hadjey and Trombetta, 2004). According to the legal restrictions in Turkey Cd in cattle feed should not be more than 1 mg/kg. Nicholson *et al.* (1999) found an average of 0.37 mg/kg Cd in dairy cattle feed, 0.49 mg /kg in pelleted cattle feed, and <0.10 mg/kg in oat barley mixture. Li *et.al*. (2005) determined an average of 51 µg/kg in dairy feed, 159 µg/kg in dairy feed (substitude), and 63 µg/kg Cd in heifer feed. Li *et al*. (2010) totally collected 210 feed samples from poultry, cattle, pig, and sheep feed and declared that over % 88.6 of the samples contain Cd residue. The authors reported that the average value of Cd residue in 71 cattle feed collected from Bejing and Fuxin cities in China was 2.79 mg/kg. Güvercin (2010) collected 216 cattle feed from 3 different areas (Kemalpaşa, Torbalı and Kiraz) in Izmir province and detected an average of 0.07 ± 0.06 mg/kg Cd. Cerit *et al.* (2007) stated that the mean Cd value was 2.016 ± 1.46 mg/kg in 4 cattle feed samples collected from 4 different regions (Bursa-İstanbul Highway, Bursa-İzmir Highway, Uludag University Faculty of Veterinary Medicine, Demirtaş) in Bursa. Wang *et al.* (2013) determined that there is 0.42 mg/kg Cd in 35 dairy cow feeds in Jiangsu province of China. The occurance of Cd in feed may be due to the addition of Zn sulfate, phosphates and Zn oxide supplements to the feed as Cd generally found in these mineral supplements (Li *et al.,* 2010). Thus some resaerchers demonstrated 1–3.6% of Cd in the Zn sulfate additive which shows that phosphate and zinc sulfate were the main sources of Cd in the animal compound feeds (Nong, 2002; Zhong and Jiang, 2005). In the presented study, it was revealed that Cd levels (0.0382

± 0.0079) were lower than cattle feeds in Izmir region that declared an average value of 0.07 ± 0.06 mg/kg (Güvercin, 2010) and in Beijing and Fuxin city of China with an average value of 2.79 mg/kg Cd (Li *et al.,* 2010).

Animal species have different susceptibility to Pb poisoning. Cattle and sheep are considered to be more susceptible to Pb poisoning (Şanlı, 2002). Wang *et al*. (2013) determined an average value of 5.2 mg/kg Pb in 35 dairy cow feeds in Jiangsu province of China. Nicholson *et al.* (1999) found an average value of 2.00 mg/kg Pb in pelleted dairy feed, <1.00 mg/kg Pb in pelleted cattle feed, 1.16 mg/kg Pb in the oat-barley mixture, Cerit *et al.* (2007) detected an average value of 0.902 ± 0.517mg/kg Pb residue in cattle feed. Güvercin (2010) detected an average value of 0.28 ± 0.52 mg/kg Pb, which was higher than the average Pb value of 0.1944 ± 0.1074 mg/kg that was found in this study.

Conclusion

The results of this study showed that the detected values of As, Cd and Pb were below the tolerable limit for cattle feed. For this reason, it has been revealed that heavy metal pollution in terms of As, Cd and Pb do not pose a risk to use cattle feed. Apart from this, it should be taken into account that metal pollution can be encountered in many situations. A more comprehensive analysis should be made not only of feed but also of other nutrients such as water consumed by the animal. When heavy metals are collectible materials, analyzes in terms of metal pollution in the animal's hair, milk, as well as in blood will contribute to the protection of human and animal health.

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