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Assessment of Dairy Feeds for Heavy Metals

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Abstract

Heavy metals are by definition metals having densities higher than 5 g mL−1, for example, Fe, Cu, Pb, Cd, Hg, Ni, Zn, and Mn. Heavy metals can be classified into four major groups on their health importance: essential, non-essential, less toxic and highly toxic heavy metals. Approximately fifty three of the ninety naturally occurring elements are called heavy metals and many of these, such as Cu, Mn, Fe, and Zn, are essential micronutrients, but can become toxic at concentrations higher than the amount required for normal growth. Other heavy metals, such as Cd, Hg, and Pb, have so far unknown roles in living organisms, and are toxic even at very low concentrations. Zinc and Cu are essential trace minerals required for many biological processes, particularly enzyme functions, and they have a positive influence on livestock growth and reproduction. Due to the low Zn and Cu content in some homegrown feeds compared with recommendations and varying bioavailability, supplementation of these metals is necessary for most livestock species, and they are commonly added to dairy rations as mineral supplements. When these nutrients are added above requirements, however, the dairy cow may restrict undesired accumulation of Zn and Cu in tissues by adaptation of absorption and excretion leading to an increase in the Zn and Cu content of manure. In addition to Zn and Cu, heavy metals such as Cr, As, Cd, and Pb are generally considered contaminants of dairy feed that are imported into the ration involuntarily, generally via phosphate-containing concentrates and supplements. Most work concerning heavy metals in animal feed has focused on pig and poultry production where it is common practice to add Cu and Zn at rates much higher than animal requirements. Very little is known about the heavy metal concentration of dairy feeds and feed components. Typical concentrations of Cu and Zn have been published in the United States and Europe, but only a few studies have reported concentrations of contaminant heavy metals (e.g., Pb and Cd), which are of more concern for animal and human health

Keywords: Heavy metals; dairy feed; concentrations; contaminants.

1. Introduction

Heavy metals are by definition metals having densities higher than 5 g mL−1 [47], for example, Fe, Cu, Pb, Cd, Hg, Ni, Zn, and Mn. Approximately fifty three of the ninety naturally occurring elements are called heavy metals [49], and many of these, such as Cu, Mn, Fe, and Zn, are essential micronutrients, but can become toxic at concentrations higher than the amount required for normal growth [36]. Other heavy metals, such as Cd, Hg, and Pb, have so far unknown roles in living organisms, and are toxic even at very low concentrations [53,36]. Heavy metals such as zinc (Zn), copper (Cu), chromium (Cr), arsenic (As), cadmium (Cd), and lead (Pb) are potential bioaccumulative toxins of the dairy production system as soils tend to act as long term sinks or these metals [4] via sorption onto metal oxides, particularly iron and manganese oxides [12], clay minerals, soil organic material, and other forms of humified natural organic material.

Although different heavy metals display a range of different properties and mobilities in the soil, losses are generally low and may occur through crop removal, leaching, and soil erosion [3]. The long-term accumulation of heavy metals in agricultural soils has the potential to reduce soil productivity by inhibiting soil microbial [10] and fauna [20] populations, and may pose a risk to animal, human, and ecosystem health [4]. Since many heavy metals can be very toxic and thus may threaten the health of organisms, studies have been conducted to investigate heavy metal levels in environmental samples, as well as heavy metal accumulation in and effects on organisms, and factors affecting heavy metal accumulation by various organisms. However, studies conducted in tropical environments are rare [28].

The results of the researches undertook until now, are showing that a lot of the vegetable or animals products are chemically contaminated, having harmful agents of great risk like heavy metals (Pb, Cd) and other chemical substances. The danger that fodders or animal products become potential harmful for the animal or for the human body, results from their contamination degree with different chemical pollutions. The animals could be contaminated with heavy metals through ingesting polluted feeds. Heavy metals with a potential toxicity arrived in feeds on multiples ways [33,2]. The pollutants toxicity depends on animal species, chemical dose and lasting of their action upon the organism [33]. Lead and cadmium have a toxic effect and oncological action, leading to hepatic, cutaneous and pulmonary cancer and changed haematological parameters [2]. Thus, the objectives of this review were: to define heavy metals, to classify them, to look for their amount on dairy feed and dairy products, and their toxicity to animals.

2. Classification of heavy metal

Heavy metals can be classified into four major groups on their health importance.

- Essential: Cu, Zn, CO, Cr, Mn and Fe. These metals also called micronutrients and are toxic when taken in excess of requirements [41].
- Non-essential: Ba, Al, Li and Zr
- Less toxic : Sn and Al

- Highly toxic : Hg, Cd and Cd. Heavy metals are also called trace element due to their presence in trace (10mg Kg-1) or in ultratrace (1µg kg-1) quantities in the environmental matrices.

Cadmium (Cd): Pure cadmium is a soft, silver-white metal. The physical property of cadmium is atomic number 48, atomic weight 112.411, electro-negativity 1.5, crystal ionic radius (Principal valence state) 0.97, ionisation potential 8.993, oxidation state +2, Electron configuration Kr 4d1 5S2, Density 8.64 g/cm3, Melting point 320.9°C and Boiling point 765°C at 100 kPa. It is usually found as a mineral combined with other elements such as oxygen (cadmium oxide), chlorine (cadmium chloride), or sulphur (cadmium sulphate, cadmium sulphide). Cadmium is a toxic to virtually every system in the animal body. It is almost absent in the human body at birth, however accumulates with age. An average man accumulates as about 30 mg cadmium in his body by the age of 50 years. Refined foods, water foods, water pipes, coffee, tea, coal burning and cigrates are all the most important source of Cd. Daily dietary intake of Cd ranges from 40-50 µg/ day [51]. Cadmium accumulated with in the kidney and liver over long time [32]. It is interact with numbers of minerals mainly Zn, Fe, Cu and Se due to chemical similarities and competition for binding stage. It is also reported that Cd can affected Ca, P and bone metabolism in both industrial and people exposed to Cd in general environment [23].

Lead (Pb): Lead is a bluish or silvery grey soft metal with atomic number 82; atomic weight 207.19; specific gravity 11.34, melting point 327.5 ^{o}C and boiling point 1740 ^{0}C. It is the most common industrial metal that has become widespread in air, water, soil and food. Lead is slightly soluble in water and is transported mainly through the atmosphere. It behaves like calcium in body and accumulates in bone, liver, kidney and other tissues. The problem of lead poisoning in animals has widely been recognized which needs a special attention for the environmentalist and health personnel. It is a cumulative tissue poison and gets stored in different parts of the body especially in bones, liver, kidney and brain. Besides, direct ingestion of lead leading to increased blood lead levels, accumulated lead in the body also acts as a significant source of blood lead burden [48]. Accumulated lead is mobilized from the storage sites with decreasing blood lead level or following treatment with chelator, thus enhancing the chelator blood lead level without the animal being exposed to lead in the immediate past. Chelation treatment sometimes leads to fatal outcome due toimmediate surge of lead from the deposited site to blood causing severe damages to kidney and brain. Lead produces mainly acute or chronic poisoning. In acute lead poisoning case fatality in lead poisoning may go up to as high as 100%. In acute lead toxicity in cattle, there is sudden onset of signs and the animal at pasture may succumb within 24 hours.

Arsenic (As): The organoarsenicals in food are one of the most poisoning in livestock now a day because of the displacement of arsenic form almost all phases of farming activities. The common of source of arsenic is in fluid used for dipping and spraying of animal to control ecto-parasites. Clinical signs of arsenic toxicity in cattle vary from gastrointestinal to nervous signs. Arsenic were killer including sodium or sodium arsenate, Arsenic pentaoxide and monosodium or disodium acid. It toxicity produces goiter in rats, thyroid antagonism in man and inhibited the growth of rumen bacteria in pure culture as well as reduces the fermentative activity. Chronic arsenic toxicity is mostly manifested in weight loss, capricious appetite, conjunctively and mucosal erythematic lesion including mouth ulceration and reduce milk yield. Acute toxic effects include abdominal cramping, hyperesthesia in extremities, abdominal patellar reflexes and abdominal electrocardiogram (Franzblau and Lilis, 1989). Such effects generally occur at the levels of exposure equal to 50µg/kg weight/day. However, chronic poisoning of As includes anemia, liver and kidney damage, hyper pigmentation and keratosis i.e. skin damage [55,7]. It is reported that As toxicity produced goiter in rats, thyroid in man. Arsenic inhibited the growth of rumen bacteria in pure culture as well reduced the fermentative activity.

Mercury (Hg): Mercury is considered a highly toxic contaminant. The toxicity of mercury depends on its chemical form methyl mercury being the most hazardous metal and stable form of mercury that has been attributed to the suffering of most avian and mammalian predators at the top of contaminated tropics. Industrial wastes and sewage water from the chloroalkali industry are a major source of mercury pollution. The symptoms of toxicosis in most species of animals include in coordination of movement, visual aberration and decline in awareness. Fishes containing more than 0.4 ppm Hg are unfit human consumption, the critical urinary concentration of Hg has been suggested as 1 to 2 µg/ml. Minimata disease is characterized bysymptoms of fatigue, loss of memory and concentration, tremors' constriction of visual field, cortical blindness etc. [22]. The intake of mercury as suggested by WHO is 43 µg [25]. The animal consumed high mercury containing vegetation will be affected and will suffer from alopecia, neuropathy, and visual and gastrointestinal tract disorder.

3. Heavy metals in dairy feed

Heavy metals such as zinc (Zn), copper (Cu), chromium (Cr), arsenic (As), cadmium (Cd), and lead (Pb) are potential bioaccumulative toxins of the dairy production system as soils tend to act as long term sinks or these metals [4] via sorption onto metal oxides, particularly iron and manganese oxides [12], clay minerals, soil organic material, andother forms of humified natural organic material. Although different heavy metals display a range of different properties and mobilities in the soil, losses are generally low and may occur through crop removal, leaching, and soil erosion [3]. The long-term accumulation of heavy metals in agricultural soils has the potential to reduce soil productivity by inhibiting soil microbial [10] and fauna [20] populations, and may pose a risk to animal, human, and ecosystem health [4].

In a closed system, the cycling ofmany heavymetals through the dairy food chain is likely to be limited by the soil-plant barrier [14]. The soil barrier limits transmission of metals through the food chain by chemical processes that limit bioavailability. Principally this is the soil cation exchange capacity, but it is affected, in turn, by other soil chemical properties such as pH, salinity, micro- and macronutrients, and metal concentration [4].Where soils receive amendments, such as biosolids or manures, bioavailability will be affected by these respective properties in the amendment [14]. The plant barrier limits transmission of certain heavy metals through the food chain where metals are phytotoxic, and substantial yield reduction occurs before the crop would comprise risk during lifetime ingestion by livestock. The exception to this rule is Cd. Cadmium has the greatest potential for transmission through the food chain at levels that present risk to consumers. In the 1980s, the adult population in the United States was reported to receive about 20% of theWorld Health Organization's allowable daily intake of Cd from the consumption of grain and cereal products [54].

Zinc and Cu are essential trace minerals required for many biological processes, particularly enzyme functions, and they have a positive influence on livestock growth and reproduction. Due to the low Zn and Cu content in some homegrown feeds compared with recommendations and varying bioavailability, supplementation of these metals is necessary for most livestock species, and they are commonly added to dairy rations asmineral supplements [37,17,18]. When these nutrients are added above requirements, however, the dairy cow may restrict undesired accumulation of Zn and Cu in tissues by adaptation of absorption and excretion leading to an increase in the Zn and Cu content of manure [34,31].

In addition to Zn and Cu, heavy metals such as Cr, As, Cd, and Pb are generally considered contaminants of dairy feed that are imported into the ration involuntarily, generally via phosphate-containing concentrates and supplements [31]. Ingestion of these contaminant heavy metals is likely to increase their concentration in manure. Heavy metal application to soils in the form of manure can be taken up by feed crops, perhaps exacerbating heavy metal exposure to dairy cows over the long-term. The trivalent form of Cr is considered essential for normal carbohydrate and lipid metabolism [37]. However, Cr (III) is ubiquitous in nature, occurring in air, water, soil, and biologicalmaterials, and supplementation is generally not considered essential. Favorable responses to Cr supplementation have been reported in swine production but not in dairy cattle, although studies are limited [19]. Although Cr (III) is relatively harmless tomost animal species, ingestion of a high dose (30 to 40 mg/kg of BW/d) of Cr (VI) has induced toxicosis in dairy calves [19].

Arsenic has been shown to be an essential trace element in rodents, and some organic arsenic compounds (e.g., arsanilic acid, 4-nitrophenylarsonic acid, 3 nitro-4-hydroxyphenylarsonic acid, and their salts) have been used as feed additives for disease control and improvement of weight gain in swine and poultry in high concentrations for some time.However, no evidence exists that arsenic is an essential nutrient for dairy cattle. The toxicity of arsenic is dependent on chemical form and valency. Inorganic forms of arsenic are generally much more toxic than organic forms. Ruminants are less susceptible to As toxicosis and do not show any sign of toxicity unless the feed offered contains more than 200 to 300 mg/kg of inorganic As [37].

Cadmium and Pb are nonessential nutrients that are of direct concern to human and livestock health and may accumulate in the body, particularly in the kidney, liver, and to a lesser extent in the muscle. Only a limited number of instances have been reported where levels in cattle tissue exceeded maximum acceptable limits for human consumption [42,24], but recent work has suggested that dairy cattle may be more susceptible to the accumulation of Cd and Pb than beef cattle [5]. Although it is unlikely that Cd would accumulate in products intended for human consumption, accumulation has been observed in the ovaries and uteri of dairy cows [44] that may have an impact on reproduction.

Most work concerning heavy metals in animal feed has focused on pig and poultry production where it is common practice to add Cu and Zn at rates much higher than animal requirements. Very little is known about the heavymetal concentration of dairy feeds and feed components. Typical concentrations of Cu and Zn have been published in the United States [37, 38] and Europe [19], but only a few studies have reported concentrations of contaminant heavy metals (e.g., Pb and Cd), which are of more concern for animal and human health [34,39].

4. Source of heavy metal contamination

Naturally, all soils contain varying concentrations of heavy metals depending on the type of parent material from which the soil was formed. Heavy metals may be added to pasture soils through the application of mineral and organic fertilizers, direct defecation and urination by animals, pesticides, soil amendment practices (e.g. liming and gypsum applying) [1,57], and atmospheric deposition (e.g.radionuclides, vehicle and industrial emissions) [33,3,4]. The heavy metal content of cattle faeces and urine vary by animal diet. Dairy and beef cattle waste contain greater heavy metal concentrations when they are fed with concentrated feed rather than forage or silage [33]. Also, the heavy metal content of cattle manure depends primarily on the concentration in the animal feed. In consideration of the potential impact of heavy metals on the pollution of pasture soils in the long-term, it is important to quantify metal concentrations in pasture soils to detect the possible long-term buildup of heavy metals, especially in tropical regions with acidic soils. The availability of metals to plants is high in acidic soils [28].

It is reported that the application of dairy sludge to grassland soils does not lead to the accumulation of heavy metals to a harmful level in the short or medium-term (1 and 4 years) [27]. The impact of heavy metals entering pasture soils is affected by the characteristics of the soil [16]. The concentration of metals in the soil varies with the type of source, presence of metals in the environment [47] and soil chemical characteristics. The distribution and localization of heavy metals within the soil profile are governed by the type of clay minerals and organic matter percent [11] leaching, erosion, and biological and microbial processes. The distribution of heavy metals is not identical throughout the soil profile [29]; however, heavy metals are normally located within the top 25 cm of the soil in cultivated soils [52].

Heavy metals pollution can also originate from natural and anthropogenic sources. Activities such as mining & smelting operation and agriculture, have contaminated extensive area of world such as Japan, Indonesia, and China mostly such as Cd, Cu and Zn [21] Cu and Pb in north Greece [56], Cu, Pb, Cu, Ni, Zn, and Cd in Austrilia [44].

5. Route of entry to the animal body

Heavy metals may enter the dairy production system in a variety of ways. These include atmospheric deposition, land application of inorganic fertilizers, biosolids, agrochemicals, and animal manures [35]. However, the magnitude of these direct inputs will be determined by many indirect factors, such as farm location, and the use of imported feed and fertilizer. In animal body, metals are entering through animal feeds, green fodder, drinking water and pharmaceutical medicines etc. Other sources are accidental access to limed field, mineral supplements with high content of trace metal and licking of painted surfaced containing metallic pigments.

6. Heavy metal concentration in dairy products

Milk is a complex, bioactive substance that promotes growth and development of mammalian infants. It is considered as a nearly complete food since it is a good source of proteins, fats, sugars vitamins and minerals. Therefore, milk and dairy products are important components of human diets that are widely consumed by human children and adults especially elderly people around the World [13,40]. Although, milk is an ideal source of macroelement (Ca, K and P) and microelemts (Cu, Fe, Zn, Se), addition amounts of contaminant metals might enter milk and dairy products reaching levels that are harmful to humans [40]. Milk and dairy products become contaminated with heavy metals either through food stuff and water or through manufacturing and packaging processes [6,8].

The authors in [9] investigated the concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb, Se and Zn in cheese samples packaged in plastic and tin containers. They found that there were considerable differences among of the studied element contents of cheese samples packaged in tin and plastic containers. They concluded that, cheese types and packaging materials play a key role in the content of trace metal. Altogether, milk, dairy products and chicken eggs constitute a major food source around the World. Therefore, monitoring heavy metal levels in milk, dairy products and chicken eggs is of great importance for nutritional, toxicological and environmental purposes. In the West Bank, studies concerning heavy metal levels in milk, dairy products and chicken eggs are completely lacking, although these products are typical food stuff that is largely consumed [9].

7. Toxic effect of heavy metals in livestock health

Heavy metals are persistent contaminants in the environment that can cause serious environmental and health hazards. They are released into the environment from natural as well as man-made activities. Some heavy metals (like Cu and Fe) are essential to maintain proper metabolic activity in living organisms; others (like Pb and Cd) are non-essential and have no biological role [8,40]. However, at high concentrations, they can cause toxicity to living organisms [26].

Heavy metals constitute a very heterogeneous group of elements widely varied in their chemical properties and biological functions. Heavy metals are kept under environmental pollutant category due to their toxic effects in plants, human animals and food. Some of the heavy metals i.e. arsenic (As), Cadmium (Cd), Lead (Pb), Mercury (Hg) are cumulative poison. These heavy metals are persistence, accumulate and not metabolized in other intermediate compounds and do not easily breakdown in environment. These metals are accumulating in food chain through uptake at primary producer level and than through consumption at consumer level.

Heavy metals disrupt metabolic functions in two ways:

1. They accumulate and thereby disrupt function in vital organs and glands such as the heart, brain, kidneys, bone, liver, etc.
2. They displace the vital nutritional minerals from their original place, thereby, hindering their biological function. It is, however, impossible to live in an environment free of heavy metals. There are many ways by which these toxins can be introduced into the body such as consumption of foods, beverages, skin exposure, and the inhaled air [43].

Several metals and their compounds have been stated to be toxic to animals. The As, Cu, Pb, Hg and Cd have been reported to be the most toxic heavy metals. It is believed that many toxic metals exert their bad effects by distressing the enzyme systems of animals. Many of them bind to specific enzymes and proteins necessary for cellular function and thus compete with other substances essential for maintenance and the continued function of cells. Thus, the poisons can also have the effect of inducing mineral deficiencies. Additionally, many toxic appear to assist in the formation of the paramagnetic anion, superoxide (O_2^-), which itself is toxic and seems widely responsible for the spontaneous cell death [15].

Table 1: Heavy metal toxicity, source and description [50].

Metal	Sources	Description
Arsenic (As)	Chemical processing plants, cigarette smoke, drinking water, fungicides, meats and seafood, metal foundries, ore smelting plants, pesticides, polluted air, specialty glass products, weed killers, wood preservatives, etc.	Extremely poisonous as well as colorless and odorless, arsenic can enter the body through the mouth, lungs and skin. Arsenic toxicity seems to predominantly affect the skin, lungs and gastrointestinal system, and may cause nervous disorders, deteriorated motor coordination, respiratory diseases, and kidney damage as well as cancers of the skin, liver, bladder and lungs.
Cadmium (Cd)	Air pollution, batteries, ceramic glazes/enamels, cigarette smoke (both first and second hand), tap and well water, food (if grown in cadmium-contaminated soil), fungicides, mines, paints, power and smelting plants, seafood, etc	Exposure to cadmium can occur through inhalation or ingestion in places or situations where cadmium products are used, manufactured, or ingested. Cigarette smoke is the biggest source of cadmium toxicity, which seems to primarily affect the lungs, kidneys, bones, and immune system. It may lead to lung cancer, prostate cancer and heart disease, and also causes yellow teeth and anemia. Cadmium also seems to contribute to autoimmune thyroid disease.
Chromium (Cr)	Stainless steel welding, chromate or chrome pigment production, chrome plating, leather tanning, handing or breathing sawdust from chromium treated wood	Exposure to high level chromium can damage and irritate your nose, lungs, stomach, and intestines. Ingesting very large amounts of chromium can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death.
Lead (Pb)	Air pollution, ammunition, auto exhaust, batteries, containers for corrosives, contaminated soil, cosmetics, fertilizers, foods (if grown in lead-contaminated soil), hair dyes, insecticides, lead-based paints, lead-glazed pottery, pesticides, solder, tobacco smoke, water (if transported via lead pipes), etc.	Lead is a naturally-occurring neurotoxin. Although many lead-containing products (such as gasoline and house paints) were banned in the 1970s, contamination still occurs today mostly by drinking lead-contaminated water, breathing lead-polluted air, and living in or near older painted buildings and certain toxic industrial areas. Lead toxicity primarily targets the nervous system, kidneys, bones, heart and blood, and poses greatest risk to infants, young children and pregnant women. It can affect fetal development, delay growth, and may also cause attention deficit disorder, learning disabilities, behavioral defects, and other developmental problems.

Mercury (Hg)	Air pollution, barometers, batteries, cosmetics, dental amalgam fillings, freshwater fish (such as bass and trout), fungicides, insecticides, laxatives, paints, pesticides, saltwater fish (such as tuna and swordfish), shellfish, tap and well water, thermometers, thermostats, vaccines, etc.	Both poisonous and dangerous, mercury is found throughout our environments in many forms and also in many household items. Mercury as used in dental fillings is the primary source of toxic exposure, and in vapor form accounts for the majority of all exposures (via inhalation). Mercury toxicity can affect the central nervous system, kidneys and liver. Research suggests that this heavy metal may also contribute to autism and multiple sclerosis.
Thallium (Tl)	Infrared and electric eye optical devices, foods (if grown in thallium-contaminated soil), light-sensitive crystals, photocells, rodent and ant poisons (now discontinued), contaminated cocaine (or what is thought to be cocaine), semiconductors, etc.	Thallium is a toxic heavy metal with no known biological function. Human contamination can occur from oral ingestion as well as through the skins and lungs, especially if exposed to thallium-contaminated dust from lead and zinc smelting plants, pyrite burners, and similar processing sites. Thallium toxicity mainly affects the nervous system, and can lead to maladies such as hair loss, nerve degeneration, extremity numbness, and cataracts.

8. Conclusions

The heavy metals, viz., As, Cd, Pb and Hg are most toxic to all human beings, animals, fishes and environment. The excess levels of heavy metals cause severe toxicity. Though some heavy metals are essential for animals, plants and several other organisms, all heavy metals exhibit their toxic effects via metabolic interference and mutagenesis. The Pb and Hg cause severe toxicity in all. Zinc (Zn), copper (Cu), chromium (Cr), arsenic (As), cadmium (Cd), and lead (Pb) are potential bioaccumulative toxins of the dairy production system as soils tend to act as long term sinks or these metals via sorption onto metal oxides, particularly iron and manganese oxides, clay minerals, soil organic material, and other forms of humified natural organic material. Although different heavy metals display a range of different properties and mobilities in the soil, losses are generally low and may occur through crop removal, leaching, and soil erosion. The long-term accumulation of heavy metals in agricultural soils has the potential to reduce soil productivity by inhibiting soil microbial and fauna populations, and may pose a risk to animal, human, and ecosystem health.

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