Investigation Of Heavy Metals Content in Raw Milk Samples from Dairy Cows – A Systematic Review

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Abstract
Heavy metals toxicity, as well as the cumulative effects on the human body, require regular monitoring of their concentration in cow's milk. In dairy cows, heavy metals can cause loss of appetite, reproductive imbalances, and long-term consequences on milk production, among other concerns. Cow feed quality is directly related to environmental quality and agricultural aspects such as plant type, soil quality, fertilization processes, harvesting, processing, and storage. This literature review highlights various sources of heavy metals in raw milk, methods of decontamination and prevention, as well as classical and innovative techniques for determining the presence of heavy metals in milk. Due to the high concentrations of heavy metals in milk samples, particularly lead and cadmium, health and environmental protection organizations should conduct rigorous assessment. The relevant regulatory agencies should establish and implement more precisely the permitted levels of cadmium, nickel, cobalt, and copper in milk, and each unit that processes milk should be required to adhere to practices and a food safety management program.

Keywords: decontamination, heavy metals, milk, prevention, rapid methods.

Introduction

The presence of heavy metals into milk and other dairy products, food, water, as well as processes of manufacturing and packaging, is a serious concern because they can cause adverse health effects for humans [1].
Soil – forage – milk – consumer is a short food chain through which metals can pass to humans, causing problems in health. In this particular case, soils are the primary source of metals that can be passed to plants that become animal fodder, and then move through the animal's digestive system and are deposited in lipid-rich tissues and partially excreted through milk [2].
Heavy metals are among the world's most harmful pollutants, despite the fact that many of them, such as zinc, iron, copper, and selenium, are bio-elements required for the proper functioning of the human body under the right conditions [3].
Long-term exposure of the human body to even small concentrations of heavy metals, resulting from persistent involvement in a polluted area, may be the trigger of subclinical changes, sometimes permanent [4]. Some of the most important and daunting contaminations is due to heavy metals like mercury, cadmium, cobalt, nickel, arsenic and tin [5-7]. The density of heavy metals relative to other metal elements is greater than 5 gr / cm^3 on average [8].
Today, heavy metals contaminating milk and dairy products, in particular lead and cadmium, play a significant role in public health because of the prevalence of various diseases. [5,7]. After reaching the body, Lead starts to accumulate in various tissues, including liver and kidneys and disrupts its physiological efficiency.
Lead is also regarded as a factor in respiratory inflammation, insufficiency and tumour [6,9,10].

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Heavy metals are not metabolized in the host's body and are vulnerable to numerous bacterial, viral, and fungal diseases [5,8].

It was also reported that the influence of high concentrations of heavy metals has similar effects in a short time as low concentrations in a long-term environmental organization introduced lead and cadmium as the most dangerous heavy metals [11, 12]. Sewage, waste from factories, garbage, dust and so on are common ways for heavy metals to get into the food. The cow's body acts like a heavy metal biological filter, particularly cadmium and the absorbed lead and cadmium transfer to its bones and begin to accumulate. For this reason, water and feed must be regulated and inspected before use, for both animals and plants [13].

Lead (Pb) and cadmium (Cd) are the essential trace elements that may come, in particular, from manufacturing processes, livestock diets, polluted water and industrial activities in the vicinity of milk production sites. As a result, they may be easily transferred through food chains. The Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) has set the approved threshold for lead and cadmium in raw cow milk for this purpose. The urge to assess heavy metals and nutrients in milk and its by-products has been recorded in many studies. In addition, the consistency and concentration of raw milk in terms of protein, fat, and heavy metal content are of vital importance to the dairy industry [14].

This study covers the possible sources of metals that reach the milk, the methods and rapid techniques for determining the heavy metals in milk as well as possible methods of decontamination.

Sources possible of heavy metals in milk

Heavy metals are commonly found in nature and their concentrations in food items are increasing day by day as a result of utilization of untreated sewage water and industrial effluents for irrigation of crops. Animals are reported as efficient filter of metals and as a result minute quantities are naturally added to milk through animal bodies [15].

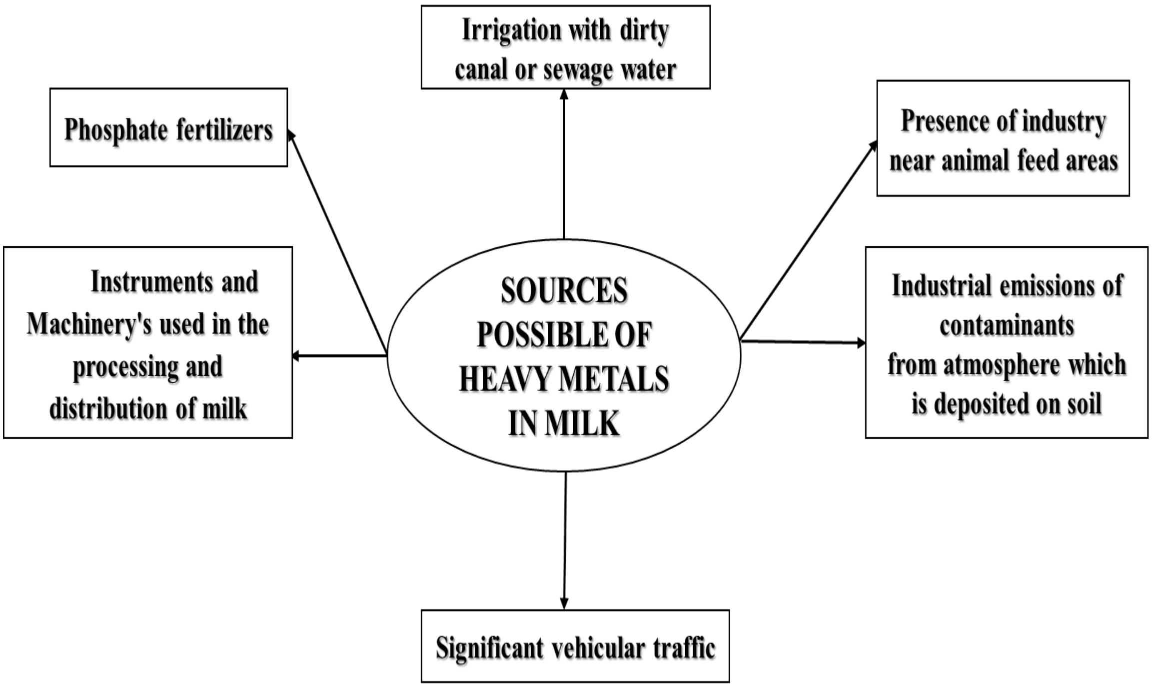

Figure 1. Sources possible of heavy metals in milk

Metals may contaminate cow milk through instruments and machinery used in the processing and distribution of milk. For this reason, processed milk is reported to have higher concentrations of heavy metals as compared to raw milk [16]. Heavy metals may also enter milk from contaminated animal feed, which may be caused by irrigation with dirty or sewage water, pesticide and fungicide, or due to the presence of industry near animal feed areas [17,18].

Heavy metal contamination of water, soil, and crops has been reported by a number of researchers [19-22]. A common farming practice of driving milk-producing animals to water canals in developing countries may also be one of the causes of heavy metals contamination in milk.

Heavy metals may be transferred from industrial sites to canals and rivers through direct discharges and runoff of contaminated sites. Water storm runoff from city roads may also contain significant amounts of heavy metals.

These heavy metals reach the agricultural land used for growing animal feed. Ultimately, the feed or water contaminated with metals is consumed by dairy animals. Infants may also be exposed to heavy metals through dirty water such as canal water or contaminated food [23].

Phosphate fertilizers, which are produced using heavy metals like cadmium and nickel, are another source of contamination. In addition to building up in the soil, excessive fertilizer use also reduces soil microbial activity, which is then absorbed by plants and passes through the animal and human food chain. Cadmium is easily distributed in the environment, and is primarily found in industrial compounds and phosphate fertilizers.

Due to continuous industrialization and urbanization activities, heavy metal pollution becomes a major cause of environmental degradation. Heavy metals are commonly found in nature and their concentrations in food items are increasing day by day as a result of utilization of untreated sewage water and industrial effluents for irrigation of crops. Among different metals, it was suggested that Cd would be the most mobile element in the soil and more available to crop.

Industrial emissions of contaminant to the atmosphere which is finally deposited on soil or dumping of industrial wastes on disposal land may cause problem in the environment beyond limit. In India, many urban and dense cities with significant industrial waste generation have been found to have contaminated soil. Metals may contaminate animal milk through instruments and machinery used in processing and distribution of milk. For this reason, processed milk is reported to have higher concentrations of heavy metals as compared to raw milk [16].

Decontaminating Methods

Heavy metals can be distributed in the atmosphere by direct drainage and runoff of polluted areas, from industrial points into canals and rivers. Storm water runoff from urban roads can also contain large amounts of heavy metals.

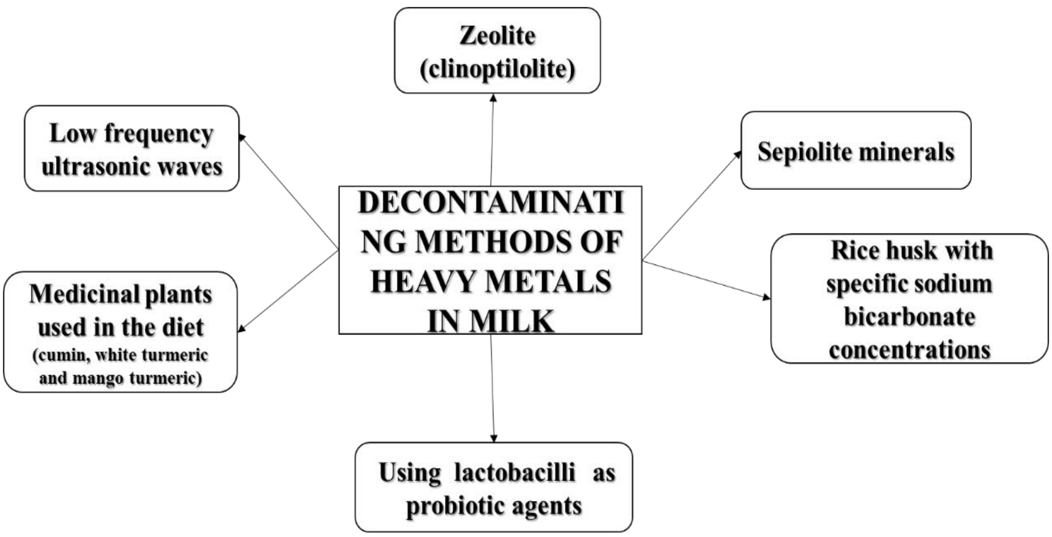

Figure 2. Decontaminating methods of heavy metals in milk

Metals may enter milk by ingestion of metal-contaminated feed or water from dairy animals, or by utensils used in the transportation and processing of milk, and milkmen may be involved in the adulteration of milk with polluted water such as canal water, which may be a major source of heavy metals. There are few options for extracting heavy metals from milk. Porova and collaborators in 2014 [24], successfully used low frequency ultrasonic waves to decontaminate heavy metals Pb, Hg, and As in milk without adversely affecting their chemical and physical properties [25].

Nurdin and collaborators in 2013 studied the impact of some medicinal plants used in the diet that may minimize the amount of lead excreted in the milk. Their findings showed that cumin, white turmeric and mango turmeric can reduce lead content in milk [26]. The studies proved that some lactobacillus species use heavy metals in their metabolism. The use of these lactobacilli as probiotic agents may reduce the contamination, heavy metals being absorbed from fermented dairy products such as yogurt [27]. Heavy metals bond with some lactobacilli specific proteins, afterwards they are absorbed and eliminated biologically [28].

Another research introduced Sepiolite minerals and zeolites as adsorbents and heavy metal correctives [29].

Thanks to its filtering properties zeolite has been using for centuries as a natural remedy for heavy metal reducing. Few experiments have targeted the use of zeolite, in particular clinoptilolite, to demonstrate its ability to reduce the heavy metal content in milk from dairy cows that have consumed zeolite.

By linking and converting heavy metals into insoluble compounds, which are then expelled from the body together with the remaining undigested material, zeolites increase the adsorption of heavy metals in the digestive system. In a different investigation, modified rice husk with particular proportions of sodium bicarbonate was utilized to absorb trace amounts of cadmium in aqueous environments [13].

Further efforts should be made to find a process for decontaminating heavy metals in milk which is economically viable and easily implementable [25].

Methods and techniques for the analysis metals heavy

Due to the high concentration of organic matter in the sample matrix, analysing heavy metals in milk involves a predigesting stage. Acid digestion, or also known as wet digestion, is the preferred form of pre-digestion, though less commonly dry digestion or ashing is also practiced [30, 31].

A variety of techniques may be used to measure heavy metals in milk, including particle-induced X-ray emission [32] mid-infrared spectrometry [33], potentiometric stripping complexometric titration [34] and capillary zone electrophoresis [35.]

Flame atomic absorption spectrophotometer is the most widely used tool by developing countries for quantifying heavy metals in milk [16,31]. The advantages of flame spectrophotometer atomic absorption over other methods are low cost, relatively fast detection, and simple operating system [36].

The inductively coupled plasma mass spectrophotometer (*ICPMS*) has been used for for more sensitive detection of mineral elements, but is more widely used by developing countries due to its higher costs [25]. The determination of heavy metals may be performed by several instrumental techniques [37] (Figure 3).

Innovative and rapid methods

A biosensing *tool* was recently developed for the detection of Cd using B. Badius phenol-red whole cells as biosensing agent. The biosensing agent was immobilized on circular plastic disks with a sol-gel method, and a fibre optic transducer device was used to detect urease enzyme cadmium inhibition in milk. The detection limit of 0.1μg / L was achieved with a sample volume of 10μL [40].

Nanohorns modified screen-printed electrochemical sensor - The developed sensor was applied to quantitatively determine Cd (II) and Pb (II) ions levels for honey and milk sample extracts with satisfactory results [39].

Another method for rapid determination of metals in milk (Pb and Cd) is the ***graphene based disposable bismuth film electrode,*** which is a sensitive, stable, and reliable sensing platform with sensibility by up to 0.5 μg L^{-1} for cadmium ion and 0.8 μg L^{-1} lead ion. Milk sample analysis demonstrates that the developed electrode could be effectively used to detect low levels of cadmium ion and lead ion [40].

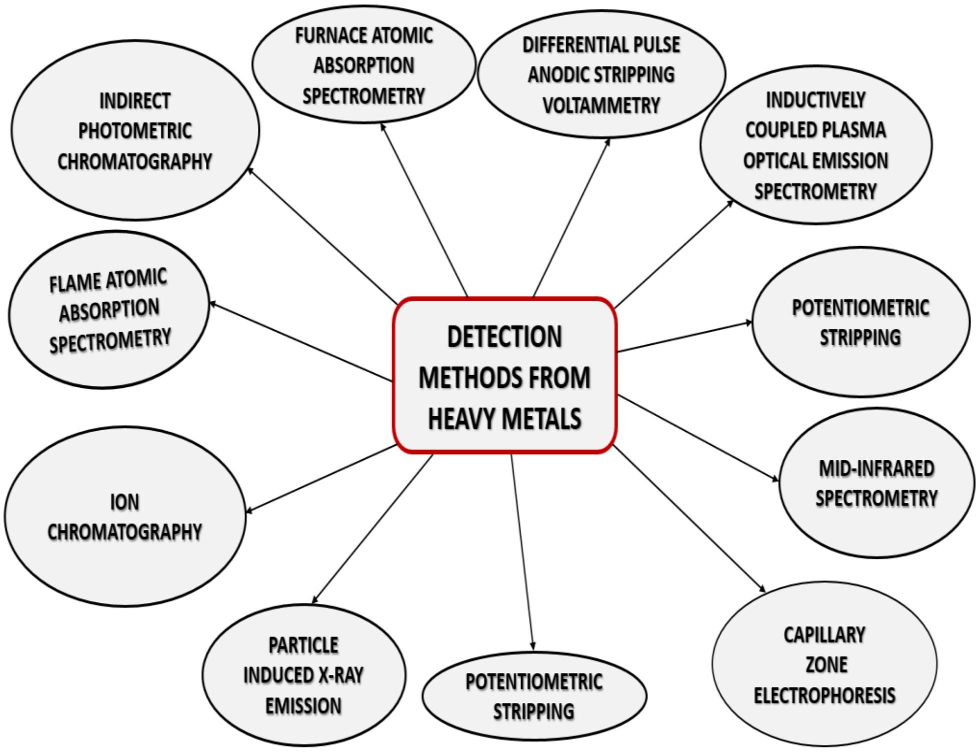

Figure 3. Instrumental techniques for the analysis of heavy metals in milk

Conclusions

Heavy metals may have a variety of health implications for humans. Rapid urbanization and industrialization in developing countries, less rigorous controls, and inadequate implementation due to the inefficiency of law enforcement agencies have resulted in high rates of heavy metals in milk.

The high levels of heavy metals in milk samples, especially lead and cadmium, demand

strict monitoring from health and environmental protection agencies. The relevant regulatory agencies should more specifically define and implement the allowable limits for cadmium, nickel, cobalt, and copper in milk.

Practices and Food Safety Management Program should be made compulsory for each unit that processes milk. Further work is required to identify commercially implementable and effective methods for heavy metal decontamination in milk and milk products.

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