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Heavy metals analysis (Cd, Pb, Zn, Cu, Cr) and calcium in Padang and Padang Panjang fresh cow's milk

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Abstract. Cow's milk is important in a healthy food intake because of its high calcium content. However, the contamination in milk can be harmful to health. The acidity of cow's milk decreases with the increase of heavy metals concentration that is poisonous to the body. This research aims to investigate the content of heavy metals (Cd, Pb, Zn, Cu, Cr) and minerals Ca contained in fresh cow's milk samples from two different locations, which are Padang city and Padang Panjang city. The heavy metal content in fresh milk from these two places has never been tested. The quantitative method used in this research is Atomic Absorption Spectroscopy (SSA). The average heavy metal and Ca minerals contained in samples of fresh milk from the Lubuk Minturun area are: cadmium (Cd) not detected, lead (Pb) 13.58±1.01 ppm, zinc (Zn) 28.83±1.81 ppm, copper (Cu) 1.17±0.38 ppm, chromium (Cr) not detected, and calcium (Ca) 674.00±2.46 ppm. Meanwhile, fresh milk samples from Padang Panjang area: cadmium (Cd) not detected, Pb 20.58±2.02 ppm, Zn 53.08±2.40 ppm, Cu 2.17±0.38 ppm, chromium (Cr) not detected, and Ca 504.25±2.63 ppm. All samples from both regions showed heavy metal content of Pb, Zn, and Cu which exceeded the maximum limit set by the Environmental Protection Agency (EPA), consequently it could cause negative impacts on health when consumed. This is assumed to be caused by cattle food contamination by garbage and pesticides which requires further research.

1. Introduction

Citizen population growth and improvement in income that is followed by public awareness on the importance of a healthy lifestyle cause an increase in demand for fresh and processed cow's milk. Demand for milk is growing rapidly, this can be seen from Based on data from BPS (Statistics Central Bureau) data in the year 2021, the level of milk consumption per capita of the Indonesian people in 2020 is 16.27 kg/capita/year, it has increased by 0.25 percent from 2019. This makes milk to become an economic commodity that has strategic value.

Milk is considered a complete food because it contains essential nutrients including protein, essential fatty acids, lactose, vitamins, and minerals in balanced proportions [1]. However, milk can also contain chemical hazards and contaminants, which are technological risk factors for dairy products, for the associated commercial image, and most importantly, for consumer health [2]. One group of hazardous chemicals that can contaminate fresh milk are heavy metals.

In the periodic table, elements with a high atomic number and are metallic at room temperature are referred to as heavy metals. These metals have a gravitational force exceeding 5 g/cm3 [3]. Most of the heavy metals are toxic to living things if they accumulate in the body even at low concentrations [4] [5].

Generally, heavy metal contamination is infected from environmental sources such as soil and water or feed consumed by animals. In addition, metals in the composition of machinery and equipment used during milk storage and processing may leach into the product during milking [6].

When heavy metals enter the human body through different sources, it affects the cellular functions leading to metal poisoning. Some are excreted through the liver or kidneys or spleen, but some metals accumulate in some excretory organs and cause organ damage.

Heavy metals also cause food contamination which is one of the main reasons for maintaining food safety concerns. Major food contaminants include pesticides, toxins along heavy metal contamination [7]. Heavy metals can accumulate in appreciable amounts in crops such as rice, grasses, and some types of legumes for animal feed, including dairy cattle [8].

Lead and cadmium residues in milk are of particular concern because they are mostly consumed by infants and children. Food is the main route of lead and cadmium exposure in the general population (representing >90% of total Cd intake in non-smokers), although inhalation can be a major cause in highly contaminated areas [9]. Lead and cadmium are considered potential carcinogens and are etiologically associated with several diseases of the cardiovascular system, kidneys, nervous system, blood, and skeletal system. Heavy metals that enter the body through food, in addition to disrupting the nervous system, paralysis, and premature death, can also reduce children's intelligence levels [10].

Contamination of .copper metal in foods initially occurred due to excessive use of fertilizers and pesticides[8]. The maximum limit for the copper metal in drinking water set by the EPA is 1.3 ppm. However, copper is a constituent that must be present in the human diet and is needed by the body (Acceptance Daily Intake/ADI = 0.05 mg/kg body weight). At this level, there is no accumulation in the normal human body. However, the intake of large amounts in the human body can cause acute symptoms.

Sensitive organs that are the main targets of heavy metals are soft tissues, such as the kidneys, liver, and central nervous system. Accumulation of heavy metals in dairy animals harms health and processed production. Heavy metal contaminants enter animal systems due to pollution of air, water, soil, and consumption of contaminated feed; Improper manufacturing practices and use of contaminated equipment also contribute to milk contamination with heavy metals [4], [11], [12]. Heavy metals that can be transferred from livestock machinery and equipment are Cu, Zn, Cd, and Pb [13].

Because of the rapid developments in industry and agriculture, the assessment of heavy metal contamination in fresh milk and its derivatives has become very important [14]. This also applies in the city of Padang and Padang Panjang. The purpose of this study was to determine the metal content of Lead (Pb), Zinc (Zn), Copper (Cu), Cadmium (Cd), Chrom (Cr), and Calcium (Ca) in pure cow's milk from two different locations.

2. Methodology

2.1. Sample Collection

Samples of fresh cow's milk were obtained from dairy farms located in two different locations, which are: Lubuk Minturun in Padang City and Padang Panjang City to determine the levels of Lead (Pb), Zinc (Zn), Copper (Cu), Cadmium (Cd), Chrom (Cr) and Calcium (Ca) using the Atomic Absorption Spectrophotometry (SSA) method in the Chemistry laboratory of LL Dikti Region X, Padang, West Sumatra.

2.2. Sample Preparation

Fresh milk samples (5 mL or g) were destructed with a mixture of nitric acid and perchloric acid (HNO_3: $HClO_3$ = 4:1 v/v) until a transparent solution was obtained [15]. After digestion, the sample is filtered and diluted to a predetermined concentration. Standard solutions of Pb, Zn, Cu, Cd, Cr, and Ca were prepared by diluting certified standard solutions to the desired concentration. All reagents used are analytical reagent grade. Very high purity water is used for all dilutions. All glass and plastic items were washed and stored overnight in a 10% (v/v) nitric acid solution. After that, it is rinsed thoroughly with ultrapure water and then is dried.

2.3. Sample Analysis
Standard solutions with concentrations of 10 ppm, 20 ppm, 30 ppm, 40 ppm, and 50 ppm were measured using an Atomic Absorption Spectrophotometer at a wavelength and a cathode lamp according to the metal to be analyzed. The standard curve is made by plotting the absorbance value against the concentration of the solution (ppm). The same treatment was also used in the solution of fresh cow's milk samples.

2.4. Statistic analysis
Concentrations of all metals are reported as mean±SD. Each metal was analyzed at least three times for each sample.

3. Results and Discussion
The concentrations of heavy metals (Cd, Pb, Zn, Cu, Cr) and calcium contained in fresh milk samples from two different farm locations, namely: Lubuk Minturun Padang (LM) and Padang Panjang (PP) are shown in Table 1. Maximum metal limits The weight reference in this article is the Maximum Contaminant Level (MCL) set by the World Health Organization (WHO) in Geneva, Switzerland. The unit used is ppm which is equivalent to mg/Kg.

Table 1. Heavy metal and calcium concentrations of fresh milk samples from two different locations

Metal	LM (ppm)	PP (ppm)	MCL by WHO (ppm)
CD	ND	ND	0.005
Pb	13.58±1.01	20.58±2.02	0.02
Zn	28.83±1.81	53.08±2.40	5
Cu	1.17±0.38	2.17±0.38	1.3
Cr	ND	ND	0.1
Ca	674.00±2.46	504.25±2.63	-

*Mean±SD; *ND:Not Determined, ND means <LOD
*LM: Lubuk Minturun Area *PP: Padang Panjang Area
*MCL:Maximum Contaminant Level

Cadmium (Cd)
Cadmium contamination (ppm) of fresh milk samples from two different farm locations was not detected as can be observed in Table 1. This proves that the soil and water that are the source of dairy cattle feed are not contaminated by cadmium. In addition, the livestock equipment used also does not contain cadmium which can contaminate the fresh milk produced. The maximum limit for cadmium contamination in milk set by WHO is 0.005 ppm. From Figure 1, it can be concluded that fresh milk from Lubuk Minturun and Padang Panjang farms is free from cadmium contamination which can cause poisoning if consumed. Acute symptoms of cadmium poisoning are chest tightness, dry throat and chest tightness, shortness of breath, gasping for breath, distress, and can progress to pneumonia,[8]. Prolonged accumulation of cadmium in excretory organs can cause organ damage and also cause changes in cellular function. Continuous long-term exposure can even cause cancer [16].

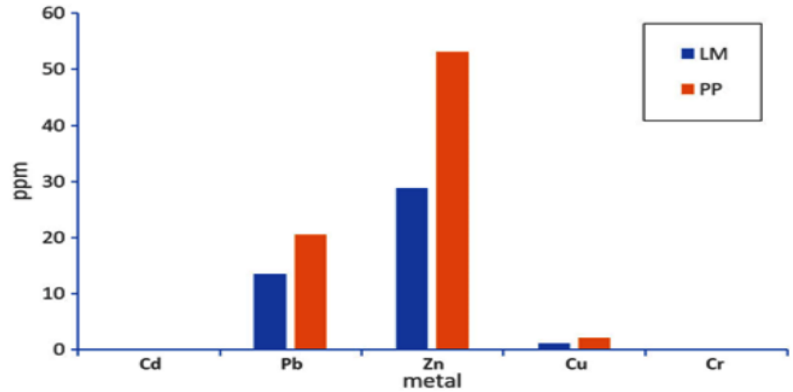

Figure 1. Heavy metal concentrations of fresh milk samples from two different locations (LM and PP).

Lead (Pb)

The lead content in fresh milk samples from Lubuk Minturun (LM) detected was 13.58±1.01 ppm, while the lead contained in the sample from Padang Panjang was 20.58±2.02 ppm as can be seen in Table 1. The maximum limit for lead contamination in fresh milk set by WHO is 0.02 ppm. From this data, it can be said that the fresh milk samples from the two places contain lead with concentrations far exceeding the maximum limit allowed by WHO, in other words, it is harmful to health if consumed both in the short and long term. The high lead content in fresh milk may be due to soil and water being exposed to high lead sources near polluted locations, such as landfills [17], [18].

The presence of high concentrations of lead in milk may also be due to the consumption of feed ingredients and water contaminated by industrial emissions and fertilizers (phosphate rock, which is the basis of commercial fertilizers and sludge), which can contaminate soil and crops that feed cattle. In addition, cows can inhale smoke and dust from industrial activities, and cadmium-coated metal utensils used in commercial food processing, kitchen utensils enamel, and incineration of cadmium-containing plastics [19]. The lead content in the samples from the Lubuk Minturun location is lower than the samples from the Padang Panjang location as shown in Figure 1. This indicates that lead contamination in the dairy farming environment at the Padang Panjang location is higher than in the Lubuk Minturun location.

Zinc (Zn)

Table 1 displays data on zinc content in fresh milk samples from two different locations, namely Lubuk Minturun (28.83±1.81 ppm) and Padang Panjang (53.08±2.40 ppm). The zinc content in samples from Padang Panjang was greater than those from Lubuk Minturun. Even so, both values far exceed the maximum zinc content in fresh milk that has been set by WHO, which is 5 ppm. The presence of zinc in high concentrations is thought to come from the use of livestock equipment used and feed contaminated with heavy metals. Within certain limits, zinc is needed by the body. Zinc is indispensable for the structure and activity of more than 300 enzymes responsible for nucleic acid and protein synthesis, cellular differentiation and replication, insulin secretion, sexual maturation and may also be involved in the functional performance of the immune system and other physiological processes [20]. However, zinc contamination in high concentrations can cause nausea and vomiting in children, anemia, and cholesterol problems in adults [21].

Copper (Cu)

Copper detected in fresh milk samples from the Lubuk Minturun location was 1.17±0.38 ppm. This value is lower than the maximum limit for copper content in fresh milk allowed by WHO, which is 1.3

ppm. Meanwhile, the copper content in the samples from Padang Panjang was 2.17±0.38 ppm exceeds the maximum allowable limit. This higher copper content could be due to contamination from the livestock equipment used. In addition, the feed and water used for dairy cows can also be contaminated with heavy metals from the surrounding environment.

Copper, as an essential trace element, is required for adequate growth, cardiovascular system integrity, lung elasticity, neuron-endocrine function, and iron metabolism [22]. Copper is also recognized as an important redox-active transition metal and an important micronutrient due to its multiple oxidation stages in vivo is involved in many structural and enzymatic activities as it is part of the structure in regulatory proteins and is involved in photosynthetic electron transport, mitochondrial respiration, oxidative stress response, metabolism. cell wall and hormone signaling for plant growth and development when present in optimal concentrations and environmental conditions [23]. The daily intake (mg/day) for copper in milk and dairy products ranged from 0.002 to 0.0191 mg/day. Nevertheless, copper harms the human body in high concentrations. Due to contamination, copper can reach high levels in milk and dairy products [21].

Chromium (Cr)

Chromium levels (ppm) in fresh milk samples from two different farm locations were not detected as shown in Table 1. Chromium contamination usually comes from the use of metal-based livestock equipment. In addition, chromium can also contaminate animal feed from soil and water near factory sites and landfills. From Figure 1, it can be concluded that fresh milk from Lubuk Minturun and Padang Panjang farms does not contain chromium with concentrations that can be harmful to health if consumed. WHO sets the maximum limit for chromium contamination in milk is 0.1 ppm. Chromium is known as an essential element for normal carbohydrate metabolism in animal and human nutrition [24]. However, in excess levels, chromium poisoning can cause skin irritation, accumulate in the liver, and systemic poisoning [25].

Calcium (Ca)

Calcium is responsible for many functions in the body such as heart rhythm, blood clotting, hormone secretion, muscle contraction, activation of enzymes in the body, and is also needed in bone structure. Calcium makes up 1.5-2% of the mass of an adult. Milk and its dairy products are foods rich in calcium, which is one of the most important minerals in fresh milk, and the amount varies according to the region and the breed of the dairy cow [26]. In this study, the average calcium content in the fresh milk from Lubuk Minturun was674.00±2.46 ppm. This value is higher when compared to the calcium content of the samples from Padang Panjang (504.25±2.63 ppm). These two data can be seen in Figure 2. The amount of calcium in the samples from these two different locations was higher than the average calcium content in fresh milk, which was 280 ppm [27]–[29]. Based on the results of this study, it appears that the calcium content in fresh milk samples from two locations (LM and PP) can be a good source of nutrition for humans regardless of heavy metal contamination due to contaminated equipment, feed, and water.

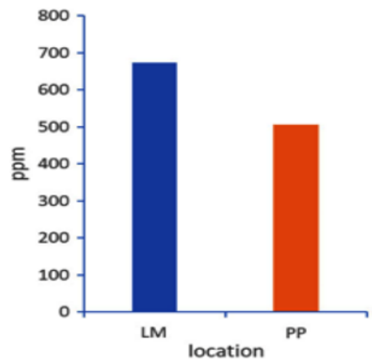

Figure 2. Calcium concentration of fresh milk samples from two different locations (LM and PP).

4. Conclusion

Information on the presence of heavy metals in dairy products from local farms is not available, which is necessary for policymaking, standard formation, and for taking corrective action, if available. This study is needed to evaluate the content of heavy metals and calcium in fresh milk samples from Lubuk Minturun Padang and Padang Panjang locations to confirm the health risks if the milk is consumed. Among all the heavy metals analyzed, cadmium, copper, and chromium contained in fresh milk samples from these two locations were below the maximum limit set by WHO. Meanwhile, the calcium content contained in the fresh milk samples from the two locations was quite high when compared to the average calcium content in fresh milk in general. However, for lead and zinc, the contamination is above the maximum contaminant level (MCL). The lead content in fresh milk samples were 13.58±1.01 ppm (Lubuk Minturun) and 20.58±2.02 ppm (Padang Panjang). And zinc content in fresh milk samples were 28.83±1.81 ppm (Lubuk Minturun) and 53.08±2.40 ppm (Padang Panjang). Therefore, fresh milk from these two locations is dangerous for human consumption. Further studies are needed to determine the exact cause of heavy metal contamination in fresh milk originating from the Lubuk Minturun and Padang Panjang locations so that a good solution can be found so that the fresh milk produced from these two locations is safe for consumption in the future.

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