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Heavy Metals Cd, Hg, and Pb in Fresh Milk from Dairy Farms in South Jakarta Analyzed by ICP-MS

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ABSTRACT

Determination of heavy metals cadmium (Cd), mercury (Hg), and lead (Pb) in fresh milk refers to the FDA 2020 method by inductively coupled plasma mass spectrometry (ICP-MS) was verified in this study. The objective of this study was to evaluate the heavy metal concentrations in fresh milk produced by traditional dairy farmers in Jakarta, a metropolitan city, analyzed by the verified method. Ninety-four milk samples were collected from 18 dairy farmers in southern Jakarta, which is the concentrated location of traditional dairy farms in Jakarta nowadays. Wet digestion was performed using microwave digestion with the reagents 65% HNO_3, 30% H_2O_2, and 30% HCl to extract these samples. The analytical performance of the method was as follows: linearity (R value ≥ 0.9975), precision (RSD range 7.66%–13.38%), recovery values (tested on 0.10 ng/g to 1.0 ng/g milk) at 88%-102%, limits of Cd, Hg, and Pb detections at 0.41 ng/g, 0.86 ng/g, and 1.20 ng/g respectively. The results showed that the heavy metals concentrations in fresh milk were obtained with a range of Cd from not detected (nd) to 1.92 ng/g, Hg from nd to 9.85 ng/g, and Pb from nd to 13.24 ng/g. The concentrations were below the national standards for Cd, Hg, and Pb in milk and milk products, and Pb was below the Codex standard for fresh milk. The results of rapid risk assessment on Cd and Hg in fresh milk are below the provisional tolerable monthly intake (PTMI) of Cd according to Joint FAO/WHO Expert Committee on Food Additives (JECFA 2023) and the provisional tolerable weekly intake (PTWI) of Hg according to JECFA 2011. Hence, the consumption of fresh milk in South Jakarta gave no health concern. Pb was not assessed due to no tolerable intake, according to JECFA.

Keywords: fresh milk; heavy metals; ICP-MS; method verification; metropolitan dairy farmer

INTRODUCTION

In a metropolitan city, Jakarta, there are traditional dairy farms which have been operated for ages since the colonial era. They are spread across four regions, namely South Jakarta, East Jakarta, Central Jakarta, and North Jakarta. This dairy farming business has its own challenges because, generally, dairy farming is carried out in rural areas and uses elephant grass as green fodder (Purbajanti *et al.*, 2023). The availability of green fodder in Jakarta is insufficient to meet the needs of the livestock due to the increasingly narrow grazing land. It is known that green fodder given to dairy cattle in Jakarta is generally fresh elephant grass. In overcoming the constraints on the availability of green fodder, farmers look for wild grass in nearby cities, Depok, Bogor, and Bekasi areas. With the increase in development and activities of the city of Jakarta and the increasing population, it directly or indirectly causes damage to the environment, such as air pollution and river pollution, which can come from domestic and non-domestic waste such as offices, factories, and industries. The need for clean water in the dairy farm cannot be ruled out for quality milk production. However, the use of well water for livestock is well-known for the dairy farm in Jakarta.

In recent years, there has been an increase in heavy metal concentrations in the environment due to their uses in several industrial, agricultural, domestic, and technological applications. Sources of heavy metal contamination reported from several studies are from industry, pharmaceuticals, household, waste, and air (Tchounwou *et al.*, 2012). Heavy metals Cd, Hg, and Pb are not essential elements and have no biological role, even at very low concentrations, they can have toxic effects (Varol & Sunbul, 2020). There are four heavy metals that can be found in food, namely As, Cd, Hg, and Pb. These metals can enter the human body in several ways, namely through the respiratory tract, by contact with skin, and by swallowing or drinking food or drinks contaminated with heavy metals. The concentrations of Cd and Pb in milk are reported to increase. Cd intake with low levels for a long period could cause the accumulation of Cd in the kidneys, which could damage the kidneys and cause brittle bones (ASTDR, 2012). The International Agency for Research on Cancer (IARC) 2023 determined that Cd is included in group 1 (carcinogenic to humans) with evidence of causing cancer in the lungs and kidneys, while Pb is in group 2A (probably carcinogenic to humans). Heavy metal toxicity becomes a threat to health if the heavy metal intake exceeds its maximum allowable limit. The limit is set according to a risk assessment by considering food intake or food consumption and the levels of heavy metals found in food. Currently, health-based guidance values for Pb have been withdrawn (evaluation in 2011) due to their toxic effects at the levels that have been proven. The value for Cd is 25 μg/kg BW/month according to the JECFA, whereas the value for Hg is 4 μg/kg BW/week. Heavy metal toxicity in milk is a serious problem because this product is consumed by the most vulnerable age groups, namely infants and the elderly. The toxicity of heavy metals to the human body depends on several factors, namely the route of entry into the body, the age, and sex of the exposed individual, as well as the levels of intake and absorption (Ismail *et al.*, 2019).

Heavy metal contaminants in green grass can come from air and water that contaminate the soil. It is known that all plants that grow on the ground will accumulate these metals in the plant roots, stems, leaves, and fruits. It can be said that green grass will harvest heavy metals and accumulate them in milk (Rohmawati & Wibowo, 2021) and other parts, namely the liver and kidneys (Hashemi, 2018). If milk containing heavy metals is consumed by humans, it can cause heavy metal accumulation in the human body. The introduction of high levels of heavy metals into milk can pose potential risks such as serious diseases and health problems. The determination of heavy metal content in milk is an important indicator of the hygiene conditions of the product and the level of pollution in the location where it was produced (Sobhanardakani, 2018).

Various heavy metal analysis methods are widely used to determine heavy metal levels in food, including atomic absorption spectrometry (AAS). This method has the disadvantage of low sensitivity for the determination of heavy metals in samples with very low concentrations and requires a relatively long time (Helaluddin *et al.*, 2016). Another instrument that is more sensitive and faster is inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS is a good analytical method for the simultaneous detection of heavy metals because it has high sensitivity, wide linear dynamic range, many elements coverage, multi-element analysis capability, accurate result output, and simple sample preparation. The liquid sample is pumped into the sample recognition system to form an aerosol (fine droplets) and then transferred to the argon gas plasma. The very high-temperature plasma atomizes and ionizes the aerosol-shaped sample and produces ions, which then the ions were directed into a quadrupole mass analyzer. The mass analyzer separates the ions according to their charge to mass ratio (m/z), and these ions are measured using a detector (Wilschefski & Baxter, 2019). Concentrations that can be measured by ICP-MS instruments up to parts per trillion (ppt or ng/kg or pg/g) (Khan *et al.*, 2014). Previous studies of heavy metal contents in fresh milk in Indonesia mostly used atomic absorption spectrometry (AAS) instruments that were limited to only two parameters, namely Cd and Pb, or Hg and Pb, and a small number of samples and concentrations that can be measured by AAS instruments up to parts per million (ppm or mg/kg). The use of this ICP-MS method for analysis of heavy metals Cd, Hg, and Pb in fresh milk samples refers to the FDA method, which was verified using milk as a sample matrix performed in this present study. The concentrations of heavy metals in fresh milk from Jakarta's dairy farms (concentrated in South Jakarta) were then evaluated for their levels according to some standards.

MATERIALS AND METHODS

Materials and Equipment

Standard solutions of Cd at a concentration of 1000 ± 2 mg/L, Hg at a concentration of 1000 ± 2 mg/L, Pb at a concentration of 1000 ± 2 mg/L, and Gold (Au) at a concentration of 999 ± 4 mg/L (Merck KGaA, Germany) were of ICP grade. Chemicals of supra purity grade for wet digestion were HNO_3 65%, H_2O_2 30%, and HCl 30% (Merck KGaA). Tuning Solution for ICP-MS at a concentration of 10 mg/L (Agilent) and ultrapure water from water purification system Direct Q3 (Merck-Millipore) were also used in this study.

According to the FDA 2020 method, all equipment used in the heavy metal analysis is free from heavy metal contamination, no glassware is used, equipment that can be used is made from fluorinated ethylene-propylene (FEP), perfluoro-alkoxy (PFA), and low-density polyethylene (LDPE). The equipment for the washing procedure was to use a detergent such as micro-90, then rinse using a cleaning reagent (a mixture of 65% suprapur HNO_3 and 30% suprapur HCl in a ratio of 10:1), and soaking in a 10% suprapur HNO_3 solution overnight after which to rinse with cleaning reagent and to dry in a rack in an inverted position.

Preparation and Homogenity Test of Sample

The materials used in this study were 94 fresh milk samples obtained from 18 dairy farmers in South Jakarta spread in 4 regions, namely Pancoran, Mampang, Pasar Minggu, and Jagakarsa. The mixed whole samples from the same farmers were then put into a plastic bag and sealed. The time required to bring milk samples from the farm to the laboratory is at most one hour by car. Milk samples were taken twice (morning and afternoon) and put into a cool box, and then the same samples were combined into composite samples. All samples were stored in a freezer at minus 20 °C prior to analysis. Frozen fresh milk samples were thawed within 2-3 hours and then homogenized before weighing for heavy metal analysis. Sample preparation for the verification method was carried out in the same way.

Instrumental Performance for Cd, Hg, and Pb Analysis by ICP-MS

Instrumental performance analysis using serial Cd, Hg, and Pb standard solutions was conducted. Linearity (R value ≥ 0.9975), precision (RSD ≤ 20%), and accuracy of 80%-120% (% recovery) based on the FDA (2020) method are used for the acceptability of the performance. Serial Cd standard solutions at concentrations of 1.0, 2.0, 3.0, 4.0, and 5.0 ng/mL, Hg solutions at concentrations of 0.5, 1.0, 1.5, 2.0, and 2.5, and Pb solutions at concentrations of 1.0, 2.0, 3.0, 4.0, and 5.0 ng/mL were used for the linearity test of the instrument.

Instrumentation and Condition of ICP-MS

The instrument used is ICP-MS type Aurora M90 (Bruker, USA) with recommended isotope analysis of Cd (m/z 111 and 114), Hg (m/z 201 and 202), and Pb (m/z 206, 207, and 208) refers to FDA method (Table 1). ICP-MS instrument setting was conducted as follows: plasma flow at 18 L/min (argon gas), auxiliary flow at 1.8 L/min, sheath gas at 0.17 L/min, nebulizer flow at 1.25 L/min, RF power at 1.5 KW, pump rate at 7 rpm, and CRI skimmer gas type hydrogen with flow at 80 mL/min (Table 2). Tuning solution at a concentration of 10 ng/mL for conditioning the plasma before sample analysis and Au solution at a concentration of 10 mg/L for washing after sample analysis were applied.

Sample Preparation

The initial stage is weighing the samples that have been homogenized, as much as 0.5 g. The sample was weighed in a vessel (110 mL capacity), then 8.0 mL of HNO_3 65% was added into the vessel and allowed to stand for 10 min. H_2O_2 30%, as much as 1.0 mL, was then added into the vessel and allowed to stand for 10 min, and finally, the vessel was closed tightly. All of the solution additions were done in a fume hood. The vessel was then put into a microwave for microwave digestion according to the microwave instruction (Table 4) as follows: maximum power 60% from 1600 watts with 3-stage processes, namely the first stage was to increase its temperature to 150 °C (for 15 min) and hold for 15 min at 150 °C, then continued to the second stage to increase its temperature from 150 °C to 180 °C (for 15 min) and hold for 15 min at 180 °C, and the final stage, to increase the temperature to 200 °C for 15 min and then hold for 15 min at 200 °C. The cooling process until the temperature reached 40 °C was then conducted. After this, the vessel is safe to be removed from the microwave digestion.

Method Verification

Verification of the analytical method using spiked samples (milk) at 3 spiking concentrations of Cd and Pb, i.e., 0.20 ng/g, 0.60 ng/g, and 1.00 ng/g samples (each with 5 repetitions) for low, medium, and high spiking concentrations was conducted by adding 100 µL, 300 µL, and 500 µL of each standard solution with a concentration of 1.0 mg/L to 0.5 g milk, respectively. For Hg analysis, verification of spiked samples was conducted by adding 50 µL (low), 150 µL (medium), and 250 µL

Table 1. Isotope recommendations for heavy metals analysis of Cd, Hg, and Pb by inductively coupled plasma-mass spectrometry (ICP-MS) (FDA, 2020)

m/z	Element	Elemental interferences	Polyatomic interferences
111	Cd	-	$^{95}Mo^{16}O$, $^{94}Zr^{16}OH$, $^{39}K_2{}^{16}O^2H$
114	Cd	^{114}Sn	$^{98}Mo^{16}O$, $^{98}Ru^{16}O$
201	Hg	-	-
202	Hg	-	$^{186}W^{16}O$
206	Pb	-	$^{190}Pt^{16}O$
207	Pb	-	$^{191}Ir^{16}O$
208	Pb	-	$^{192}Pt^{16}O$

Note: m/z= mass to charge ratio.

Table 2. Setting of inductively coupled plasma-mass spectrometry (ICP-MS) for Cd, Hg, and Pb analysis

Parameters	Value	Parameters	Value
Plasma flow	18 L/min	CRI skimmer gas type	Hydrogen (H_2)
Auxiliary flow	1.8 L/min	Skimmer flow	80 mL/min
Sheath gas	0.17 L/min	First extraction lens	-169
Nebulizer flow	1.25 L/min	Second extraction lens	-377
RF power	1.50 KW	Third extraction lens	-356
Sampling depth	6.5 mm	Corner lens	-366
Pump rate	7 rpm	Mirror lens left	50
Stabilization delay	30 s	Mirror lens right	9
Scan mode	peak hopping	Mirror lens bottom	56
Dwell time	30 s	Entrance lens	1
Points per peak	1	Fringe bias	-3.7
Scans/replicated	20	Entrance plate	-86
Replicate/sample	15	Pole bias	-2
Attenuation mode	None		

(high) of Hg standard solution with a concentration of 1.0 mg/L, to 0.5 g milk to obtain 0.10 ng/g, 0.30 ng/g, and 0.50 ng/g of spiked samples (each with 5 repetitions). After the standard addition, the vessels were allowed to stand for 30 min, and then the next process started from the stage of adding HNO_3 65% as in the sample preparation above.

After the destruction process was complete and the microwave digestion was cold, the vessel was removed, and the lid of the vessel was opened in a fume hood. After this step, 5 mL of 10% HCl was added and allowed to stand for 10 min. The solution in the vessel was then transferred into a 100.0 mL volumetric flask and adjusted to the volume of 100.0 mL with ultrapure water having a resistance of 18.2 MΩ and finally filtered using a syringe filter with a 0.2 μm PTFE filter disc.

The precision was calculated from the standard deviation of the 5 measurements of the spiked samples divided by the average value of the measurements, expressed in percent. There are 3 concentrations of spiked sample, namely Cd with concentrations of 0.20, 0.60, and 1.00 ng/g, Hg with concentrations of 0.1, 0.3, and 0.5 ng/g, and Pb with concentrations of 0.20, 0.60, and 1.00 ng/g milk. Instrument linearity was performed by measuring the count per second intensity of standard heavy metals solutions (Cd, Hg, and Pb) at various concentrations, with 3 repetitions. The acceptance criteria for verification of the analytical method according to FDA 2020 requirements consist of linearity value (R) ≥ 0.9975, precision by RSD value ≤ 20%, and accuracy by recovery value 80%–120%.

Statistical Analysis

Descriptive statistical analysis for the heavy metal concentrations was conducted using the Microsoft Excel 2019 program. Statistical analysis for significant differences was analyzed using IBM SPSS Statistics 29.0 (SPSS Inc, Chicago). Ninety-four fresh milk samples were tested for normality to determine whether the data came from a normally distributed population using the Kolmogorov-Smirnov method for a sample size of ≥ 50 (Mishra *et al.*, 2019). The normality test was carried out using IBM SPSS Statistics 29.0 (SPSS Inc, Chicago) and used alpha (α) = 0.05. After the normality test by Kolmogorov-Smirnov, the analysis of variance test using the Kruskal-Wallis test was applied if the non-normal distribution data were obtained. The Kruskal-Wallis test is a nonparametric test that aims to determine whether there is a statistically significant difference between two or more groups of independent variables on the dependent variable (Mishra *et al.*, 2019).

RESULTS

Instrumental Performance of ICP-MS for Heavy Metal Analysis

Serial Cd, Hg, and Pb standard solutions were used in instrumental performance analysis for the linearity test. The calibration curves determined (5 repetitions each) for Cd, Hg, and Pb analysis at 1.0–5.0, 0.5–2.5, and 1.0–5.0 ng/mL, respectively, had slope of linear regression at 1,810.64, 1.795.55, and 21,337.11, and intercept at 10.44, 74.76, and 4,247.17, respectively (Table 3). The results of linearity for Cd, Hg, and Pb showed R= 1.0000 (Table 3). Therefore, the relationship between standard concentrations and count per second (c/s) displays an accepted linearity, with R ≥ 0.9975 (FDA, 2020).

The results of the precision test obtained for Cd were 7.66%, 13.38%, and 11.84%; for Hg were 8.60%, 7.92%, and 5.03%; and for Pb were 9.48%, 8.67%, and 8.25% (Table 4). The precision values of all the measurements ranged from 5.03%-13.38%, meeting the requirements of the acceptance criteria of ≤ 20%.

Accuracy results showed the averaged recovery of Cd at 101.96%, 90.94%, and 98.12%, averaged recovery of Hg at 100.57%, 95.96%, and 88.27%, and averaged recovery of Pb at 95.25%, 96.70%, and 96.41% for respective low, medium, and high concentrations of spiking (Table 5). The results of the recovery values at 88.27%–101.96% are in the range of acceptability of 80% to 120%. Therefore, all verification results meet the FDA criteria

Table 3. Linearity result of heavy metal analysis by inductively coupled plasma-mass spectrometry (ICP-MS)

Standard	Concentration (ng/mL)	Average count/s	Slope	Intercept	R
Cd	1.0	1,825.13	1,810.64	10.44	1.0000
	2.0	3,628.67			
	3.0	5,440.87			
	4.0	7,255.20			
	5.0	9,063.20			
Hg	0.5	974.93	1,795.55	74.76	1.0000
	1.0	1,872.27			
	1.5	2,767.67			
	2.0	3,662.933			
	2.5	4,564.93			
Pb	1.0	25,951.00	21,337.11	4,247.17	1.0000
	2.0	46,918.60			
	3.0	68,278.20			
	4.0	89,531.47			
	5.0	110,899.93			

Note: R= correlation coefficient

Table 4. Precision result of heavy metal analysis by inductively coupled plasma-mass spectrometry (ICP-MS) in fresh milk

Variables	Cd			Hg			Pb		
	Low	Med	High	Low	Med	High	Low	Med	High
Sample (n)	5	5	5	5	5	5	5	5	5
Actual (ng/g)	0.20	0.60	1.00	0.10	0.30	0.50	0.20	0.60	1.00
Average (ng/g)	0.21	0.55	0.99	0.11	0.30	0.45	0.22	0.62	1.00
SD (ng/g)	0.02	0.07	0.12	0.01	0.02	0.02	0.02	0.05	0.08
RSD (%)	7.66	13.38	11.84	8.60	7.92	5.03	9.48	8.67	8.25

Note: SD= standard deviation; RSD= relative standard deviation.

Table 5. Recovery result of heavy metal analysis by inductively coupled plasma-mass spectrometry (ICP-MS) in fresh milk at low, Medium, and high spiking concentrations of Cd (0.20, 0.60, and 1.00 ng/g), Hg (0.10, 0.30, and 0.50 ng/g), and Pb (0.20, 0.60, and 1.00 ng/g)

Repeat samples	Recovery of Cd (%)			Recovery of Hg (%)			Recovery of Pb (%)		
	Low	Med	High	Low	Med	High	Low	Med	High
1	110.17	109.77	100.31	111.13	98.13	90.99	85.74	93.54	91.80
2	105.64	80.41	117.01	109.62	99.10	93.04	96.52	97.13	93.63
3	104.21	92.19	96.62	101.60	88.75	87.51	95.53	93.40	93.65
4	95.77	85.85	89.29	91.57	86.86	88.37	100.28	106.85	108.88
5	93.99	86.48	87.35	88.94	106.96	81.45	98.19	92.56	94.07
Average	101.96	90.94	98.12	100.57	95.96	88.27	95.25	96.70	96.41

for an analytical method. These methods have a limit of detection (LOD) for Cd at 0.41 ng/g, Hg at 0.86 ng/g, and Pb at 1.20 ng/g, which are relatively very low (sub ppb levels for Cd and Hg).

Heavy Metals of Cd, Hg, and Pb in Fresh Milk from Jakarta Dairy Farms Analyzed by ICP-MS

From the results of the normality test, the distribution of Cd, Hg, and Pb concentrations in fresh milk samples had an α value < 0.05, indicating that the data had a non-normal distribution. From these results, an analysis of the variance test was carried out using the Kruskal-Wallis non-parametric method for the non-normal distribution. Based on the test results, it is known that all data groups have a p value > 0.05, indicating that the test results of the data groups were statistically no significant.

The analytical results showed Cd, Hg, and Pb concentrations in 94 fresh milk samples from different regions in Jakarta (Tables 6, 7, and 8). Overall analytical results of 94 fresh milk samples showed the concentration ranges of Cd at not detected (nd) – 1.92 ng/g, Hg at nd – 9.85 ng/g, and Pb at nd – 13.34 ng/g. Samples from the Pancoran region consisted of 47 fresh milk samples had the ranges of Cd, Hg, and Pb at nd – 1.92 ng/g, nd – 9.85 ng/g, and nd – 13.34 ng/g, respectively. Samples from the Mampang region consisted of 43 samples had the ranges of Cd, Hg, and Pb at nd – 1.52 ng/g, nd – 8.27 ng/g, and nd – 10.37 ng/g, respectively. Samples from the Jagakarsa region consisted of 2 samples with the levels of Hg and Pb, both of which were not detected; meanwhile, Cd concentrations were at 0.54 and 0.61 ng/g. Samples from the Pasar Minggu region consisted of 2 samples with all levels of Cd, Hg, and Pb were not detected.

Most of the samples from the Pancoran and Mampang regions had not detected levels of Hg and Pb. Only 25.5% of the samples from the Pancoran region and 14.0% of the samples from the Mampang region were positively to contain Hg above its LOD. In contrast, only 4.3% of the samples from the Pancoran region and 11.6% of the samples from the Mampang region were to contain Pb above its LOD. In contrast to Cd results, 66.0% of samples from the Pancoran region and 60.5% of samples from the Mampang region were positively to contain Cd above its LOD.

Heavy metals in 10 water samples used for animal drinking (ground water) in 10 farmers have also been analyzed using the same method for milk samples. The results ranged from 0.34–1.17 ng/g Cd, 1.20–4.29 ng/g Hg, and 0.12–0.49 ng/g Pb.

DISCUSSION

The results of the verification test of Cd, Hg, and Pb analysis by ICP-MS using fresh milk as a sample matrix met the requirements of the acceptance criteria according to the FDA (2020). Therefore, the method was applied for the analysis of heavy metals in fresh milk samples collected from several regions in Jakarta, a metropolitan city. Heavy metals Cd, Hg, and Pb were found at relatively low concentrations compared to Indonesian national standards (Indonesian FDA Regulation No. 9 Year 2022) set for milk products: 0.05, 0.02, and 0.02 mg/kg or 50, 20, and 20 ng/g, respectively for Cd, Hg, and Pb. All of the fresh milk samples are below the standards. In the international situation, only the Pb standard has been set for fresh milk by the European Union (EC No. 1881/2006), 0.02 mg/kg or 20 ng/g, and this standard is the same as Codex standard for contaminants in food (Codex, 2019). Therefore, in the point of Pb concentrations, the levels of Pb found in fresh milk samples from 18 traditional dairy farms in the southern part of Jakarta city, the concentrated location of dairy farms in Jakarta, met the national and international standards.

Table 6. Distributions of Cd concentrations in fresh milk from Jakarta dairy farms (ng/g)

Region	Sample number	Mean*	SD	Min	Max	P50	P75
Pancoran	47	0.68	0.50	nd	1.92	0.54	0.97
Mampang	43	0.60	0.41	nd	1.52	0.52	0.92
Pasar minggu	2	nd		nd	nd		
Jagakarsa	2	0.57	0.05	nd	0.61		
Overall	94	0.63	0.45	nd	1.92	0.53	0.91

Note: *Mean was calculated by considering the not detected data as half of detection limit or ½ LOD (LOD of Cd analysis in milk was 0.41 ng/g). P50= 50% probability or median; P75= 75% probability.

Table 7. Distributions of Hg concentrations in fresh milk from Jakarta dairy farms (ng/g)

Region	Sample number	Mean*	SD	Min	Max	P50	P75
Pancoran	47	2.07	3.03	nd	9.85	nd	1.17
Mampang	43	0.91	1.13	nd	8.27	nd	nd
Pasar minggu	2	nd		nd	nd		
Jagakarsa	2	nd		nd	nd		
Overall	94	1.47	2.48	nd	9.85	nd	nd

Note: *Mean was calculated by considering the not detected data as half of detection limit or ½ LOD (LOD of Hg analysis in milk was 0.86 ng/g). P50= 50% probability or median; P75= 75% probability.

Table 8. Distributions of Pb concentrations in fresh milk from Jakarta dairy farms (ng/g)

Region	Sample number	Mean*	SD	Min	Max	P50	P75
Pancoran	47	0.94	1.91	nd	13.34	nd	nd
Mampang	43	1.29	2.22	nd	10.37	nd	nd
Pasar minggu	2	nd		nd	nd		
Jagakarsa	2	nd		nd	nd		
Overall	94	1.08	2.02	nd	13.34	nd	nd

Note: *Mean was calculated by considering the not detected data as half of detection limit or ½ LOD (LOD of Pb analysis in milk was 1.20 ng/g). P50= 50% probability or median; P75= 75% probability.

The results showed that the highest heavy metal concentrations in fresh milk were Pb 13.34, Hg 9.85, and Cd 1.92 ng/g following the order Pb > Hg > Cd, however, the prevalence of samples with heavy metal concentrations above LOD was present with the order from the highest prevalence Cd > Hg > Pb. Samples containing the highest contents of heavy metals Cd, Hg, and Pb all came from the Pancoran region. This region is the closest region to the center of Jakarta city. Perhaps the heavy metals from the environment affected the heavy metal concentrations in the fresh milk samples from the Pancoran region.

If the heavy metal concentrations found in this study are compared to those found in a previous study by Salundik *et al.* (2012), who reported Pb concentrations in 9 fresh milk samples from Bogor, West Java, at all in not detected (LOD was 400 ng/g), Harmini *et al.* (2020) reported Hg and Pb concentrations in the fresh milk from East Kalimantan ranged at 5–7 ng/g and 5–6 ng/g respectively, and Rohmawati & Wibowo (2021) reported Pb concentrations in the fresh milk from Boyolali, Central Java, ranged at 38–57 ng/g. It can be seen that the fresh milk samples from Jakarta were relatively of better quality than those from the other provinces in Java and comparable to those from a province in Kalimantan, a separate island from Java and has a much smaller population.

Heavy metals in water could contribute to their levels in milk. By considering roughly the volume of water intake (40 L) and the resulted milk (10 L) a day by an animal from an *in situ* interview with farmers in this study, the heavy metals in water contributed about 78% of Cd, 44% of Hg, and 4% of Pb found in milk.

Rapid risk assessment for heavy metals Cd, Pb, and Hg intake from milk consumption by considering the milk and dairy product consumption in South Jakarta (Andarwulan *et al.*, 2021) for adults (>19 years old) 19 g/capita/day, adolescents (13–18 years) 93 g/capita/day, and school-age group (6–12 years) 164 g/capita/day gave the mean intake of Cd at 11.97, 60.48, and 103.32 ng/capita/day for adults, adolescents, and school-age group, respectively. The mean intake was calculated by multiplying the consumption values with the overall mean concentration of Cd in 94 milk samples (Table 6). In the same way, the mean Hg intakes (considering the mean of overall samples in Table 7) for adults, adolescents, and school-age groups from milk consumption were at 27.93, 136.71, and 241.08 ng/capita/day, respectively. The mean Pb intakes by using the overall mean of Pb (Table 8) were at 20.52, 100.44, and 177.12 ng/capita/day for adults, adolescents, and school-age groups.

Health based guidance value (HBGV) for Cd intake according to JECFA is 25 μg/kg body weight (BW)/month or 833 ng/kg BW/day, whereas for Hg intake is 4 μg/kg BW/week or 571 ng/kg BW/day. There is no health base guidance value for Pb (JECFA evaluation in 2011). Given the lower values than HBGV of the Cd and Hg intakes from milk consumption, as discussed above, the intakes of Cd and Hg have no health concern for the South Jakarta population.

CONCLUSION

Verifications of Cd, Hg, and Pb analytical methods using ICP-MS have fulfilled the acceptance criteria based on FDA (2020) method requirements. The analysis method can be used for routine analysis of heavy metals Cd, Hg, and Pb in the laboratory. The maximum concentrations of heavy metals in fresh milk samples followed the order Pb > Hg > Cd, even though the average concentrations followed the order Hg > Pb > Cd, and most of the milk samples had not detected levels for Hg and Pb. More than 50% of fresh milk samples from South Jakarta contained Cd at the above detected level. Cd and Hg intake from fresh milk in South Jakarta gave no health concern.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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