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Milk trace elements in lactating cows environmentally exposed to higher level of lead and cadmium around different industrial units

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ABSTRACT

The present investigation was carried out to assess the trace mineral profile of milk from lactating cows reared around different industrial units and to examine the effect of blood and milk concentration of lead and cadmium on copper, cobalt, zinc and iron levels in milk. Respective blood and milk samples were collected from a total of 201 apparently healthy lactating cows above 3 years of age including 52 cows reared in areas supposed to be free from pollution. The highest milk lead (0.85±0.11 μg/ml) and cadmium (0.23±0.02 μg/ml) levels were recorded in lactating cows reared around lead–zinc smelter and steel manufacturing plant, respectively. Significantly ($P<0.05$) higher concentration of milk copper, cobalt, zinc and iron compared to control animals was recorded in cows around closed lead cum operational zinc smelter. Analysis of correlation between lead and other trace elements in milk from lactating cows with the blood lead level>0.20 μg/ml ($n=79$) revealed a significant negative correlations between milk iron and milk lead ($r=-0.273$, $P=0.015$). However, such trend was not recorded with blood lead level<0.20 μg/ml ($n=122$). The milk cobalt concentration was significantly correlated ($r=0.365$, $P<0.001$) with cadmium level in milk and the highest milk cadmium (>0.10 to 0.39 μg/ml) group had significantly ($P<0.05$) increased milk cobalt. It is concluded that increased blood and milk lead or cadmium level as a result of natural exposure of lactating cows to these environmental toxicants significantly influences trace minerals composition of milk and such alterations affect the milk quality and nutritional values.

1. Introduction

Contamination of environment with heavy metals and the insidious nature of their adverse ill health effects have become a matter of growing concern (Scheuhammer, 1987). Lead and cadmium are the two most abundant heavy metals in the environment, often coexist in a polluted environment (Phillips et al., 2003) and are mostly implicated in human and animal poisoning (Ozmen and Mor, 2004). Lead poisoning is one of the most frequently reported causes of poisoning in farm livestock; with cattle being most commonly affected (Blakley, 1984). A variety of exposure routes allow toxic heavy metals predominantly lead and cadmium to enter the food chain of farm animals, the commonest being the contaminated feed and water, lead paint, lead batteries, lead shot, automobile emissions, aluminum paints, textile, metallurgy and petrochemical based industries, combustion of coal and mineral oil, smelting, mining, alloy processing, paint industries,

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aluminum processing, phosphate fertilizer plant, lead–zinc smelter or coal mining areas (Sharma and Street, 1980; Dwivedi et al., 2001).

The chronic lead exposure in farm livestock and tissue lead concentration are receiving increasing attention, due to concern over the sub-clinical effects of elevated blood lead concentration in young children (Underwood and Suttle, 1999). Milk and milk products constitute an important component of diet in human beings especially growing children. Thus, contamination of milk by toxic metals can be a possible health risk to human population (Crout et al., 2004). These toxic chemicals may also influence the quality of milk with respect to its composition, particularly of trace elements essential for normal growth, production and reproduction (Doyle and Younger, 1984) and milk is an important dietary source of these minerals particularly for children. The mother's milk is the only source of nutrients available to neonatal offspring during their early life (Anderson, 1992).

Earlier from our laboratory, we reported higher blood and milk lead and cadmium levels in animals around different industrial areas and their higher levels were associated with higher concentrations of these toxic pollutants in forges and soil (Patra et al., 2005; Swarup et al., 2005). The lead concentration in fodder and soil samples collected from around the lead–zinc smelter was 29.1±11.3 (n=7) μg/g and 232.9±27.6 (n=2) μg/g as compared to 2.08±0.22 (n=8) and 28.66±2.53 (n=3) μg/g, respectively in non-industrialized area (Swarup et al., 2005). Similarly, cadmium concentrations in fodder and soil collected from steel manufacturing plant was 32.0±30.5 (n=3) and 168.9±0.0 (n=1) μg/g as compared to control level of 0.15±0.01 and 1.2±0.01 μg/g, respectably (Patra et al., 2005). Our pervious study also revealed a significant influence of blood lead level on milk lead concentration, and lactating cows with blood lead level>0.2 μg/ml (n=79) had significantly higher lead excretion in milk (Swarup et al., 2005). The cadmium excretion in milk remained relatively constant up to blood cadmium level of 0.02 μg/ml, showed an increasing trend from>0.02 to 0.05 μg/ml, and significantly higher cadmium excretion in milk as compared to that of control animals was recorded with blood cadmium level>0.05 μg/ml (Patra et al., 2005). We also observed that the blood lead (n=201) but not cadmium level had a significant negative correlation with blood copper (r=−0.339), cobalt (r=−0.224) and iron (r=−0.497) concentration (Patra et al., 2006). It was therefore hypothesized that increased blood lead and/or cadmium level in cows around industrial units, and the resultant changes in blood trace elements profile and milk lead and cadmium concentration may influence the concentration of trace elements in milk. Thus, the present work was undertaken to determine the toxic and trace mineral profile in raw milk from animals reared around different industrial units, and to examine the interaction between toxic heavy metals such as lead and cadmium, and trace elements such as copper, cobalt, zinc and iron in milk.

2. Material and methods

2.1. *Animals*

Respective milk and blood samples were collected from a total of 201 lactating cows (Non-descript/ Crossbred) of above 3 years of age reared either around different industrial units (n=149) or in non-polluted areas (n=52). These industrial units located at various parts of the India, were engaged in activities such as steel processing (n=22), aluminum processing (n=25), rock phosphate mining cum phosphate fertilizer production (n=21), lead–zinc smelting (n=21), coal mining (n=46), closed lead but operational zinc smelting (n=14). Cows in almost similar parity (1–3) and stages of lactation (2–3 months of lactation) were selected to rule out possibilities in variation due to stages of lactation and parity of cows. The animals reared since birth, used to graze on pasture within 2 km radial distance from industrial units or fed with the fodder/ grasses grown on those areas were selected for the present study. History regarding recent feeding practices and supplementation regimes (mineral mixture or drugs containing high amount of those mineral and metals under study) was also collected and cows receiving any extra feeding treatment were not included for the study to maintain uniformity in sampling to the maximum possible extent. Cows included in the present study typically had milk yield ranging from 3 to 10 L. Mostly the cows were pasture-dependent with once daily concentrate feeding.

2.2. *Sampling and processing*

Sample collection was executed by door-to-door visit preferably in the morning hours. Raw milk was collected in to clean vials directly from the udder or from milk bucket after morning milking. Milk samples (100 ml) were collected in nitric acid-washed glass vials and a drop of concentrated Hydrochloric acid was added to preserve its oxidation status. The samples were brought in ice packs for further processing in the laboratory, where it was kept in -20 °C till use.

Blood samples were also collected from respective cow by jugular venipuncture with heparin as anticoagulant. Approximately, 5 ml blood or milk sample was wet digested separately with nitric and perchloric acid mixture (HNO3: HCLO3=4:1 v/v) as per Kolmer et al. (1951). Two to three blank samples, where biosample was substituted by de-ionized triple distilled water, were run simultaneously with each batch of the digestion.

2.3. *Analysis of toxic and trace elements*

The toxic heavy metals such as lead and cadmium, and trace elements copper, cobalt, zinc and iron concentrations in the digested samples were estimated using atomic absorption spectrophotometer (Electronic Corporation of India Limited-4141, India) at the wave lengths of 217.0, 229.5, 324.7, 240.7, 213.9, 248.3 with 6, 6, 6, 7, 7, 5 mA current, respectively. The detection limits of lead and cadmium were 0.025 and 0.005 μg/ml respectively. The copper, cobalt, zinc and iron had the detection limits of 0.01, 0.02, 0.003 and 0.012 μg/ml, respectively. The standards procured (Sigma Aldrich Chemicals Corporation, New Delhi and Sisco Research Laboratory, Mumbai, India) for each element were used to calibrate the equipment and to check the analytical quality and accuracy with serial dilutions of test-specific standard solution, and to measure the absorbance of the test samples in reference to that of two fixed concentrations of the standard, and the values were expressed in μg/ml of blood or milk.

2.4. Analysis of data

The data were analyzed using one-way analysis of variance to find out the statistical difference among the mean values of a particular trace or toxic element. The correlations between toxic heavy metals and trace elements in blood and milk were analyzed using standard statistical methods. The blood and milk lead or cadmium levels (μg/ml) were sorted in to an increasing order irrespective of place of collection of samples, and grouped under four different increasing non-overlapping groups to examine the effect of different mean levels of these toxicants on the mean level of trace elements in milk. The mean values (±S.E.) of different trace elements within a particular range of blood and milk lead or cadmium and the statistical difference among these mean values were calculated using the standard statistical methods (Snedecor and Cochran, 1994).

3. Results

3.1. Milk level of toxic and trace elements

The highest mean milk lead (0.85±0.114 μg/ml) level was recorded in animals (n=21) reared around lead–zinc smelter followed by aluminum processing plant/ thermal power plant (n=25) and steel manufacturing plant (n=22) and these levels were significantly (P<0.05) higher than the mean milk lead level (0.25±0.03, n=52) recorded in cows reared in unpolluted areas (Table 1). However, lactating animals reared around coal mining areas (n=46), and phosphate fertilizer and mining areas (n=21) had milk lead level statistically comparable (P>0.05) to that of animals from un-polluted areas. The mean blood lead level in cows from either of these two polluted areas was also comparable to that of control area. Lactating cows around closed lead cum operational zinc smelter (n=14) with significantly (P<0.05) higher blood lead level as compared to that of controls (n=52) had milk lead level comparable (P>0.05) to that of animals from unpolluted area. The milk cadmium level was significantly (P<0.05) higher in lactating cows around steel manufacturing plant (n=22), aluminum processing plant (n=25) and lead zinc smelter (n=22) whereas, the blood cadmium level was significantly (P<0.05) higher than the control animals only in cows around steel manufacturing plant (Table 1).

No specific trend was observed in milk copper, cobalt, zinc or iron concentration with respect to increasing mean milk lead concentrations as per source (area-wise) of collection of samples (Table 1). Cows around closed lead cum operational zinc smelter had significantly (P<0.05) higher mean level of milk copper, cobalt, zinc and iron than respective value in control animals. The mean milk copper and cobalt level around aluminum processing plant was significantly lower as compared to respective value in control animals. Other than closed lead cum operational zinc smelter, the milk cobalt level was significantly (P<0.05) higher than control level in cows around phosphate fertilizer and mining areas and steel manufacturing plant, and milk zinc around phosphate fertilizer and mining areas and lead zinc smelter.

3.2. Correlation between trace mineral in milk and trace and toxic metal in blood

Analysis of data from all the 201 lactating animals irrespective of place of collection of samples and concentration of lead and cadmium in blood or milk, revealed a non-significant correlation of cobalt (r=0.130, P=0.067) and iron (r=0.062, P=0.380), a significant negative correlation of copper (r=−0.259, P<0.001) and positive correlation of zinc (r=0.293, P<0.001) between milk

Table 1 – Toxic heavy metals and trace elements in milk from lactating cows reared in different environments

	Toxic and trace elements in milk						Toxic metals in blood	
	Lead	Cadmium	Copper	Cobalt	Zinc	Iron	Lead	Cadmium
Unpolluted area (n=52)	0.25±0.03 [a] (.00–0.79)	0.033±.002 [a] (0.00–0.07)	0.101±0.006 [c] (0.02–0.29)	0.18±0.009 [b] (0.06–0.41)	3.95±0.40 [ab] (0.86–14.7)	5.10±1.06 [a] (0.00–35.4)	0.07±.009[a] (0.00 –0.25)	0.029±.002 [ab] (0.00–0.05)
Closed lead cum zinc smelter (n=14)	0.26±0.047 [a] (0.0–0.52)	0.052±0.005 [a] (0.03–0.09)	0.14±0.007 [d] (0.09–0.18)	0.23±0.037 [cd] (0.10–0.48)	12.50±0.73 [d] (7.96–15.95)	8.68±1.60 [b] (2.22–25.46)	0.59±0.078 [d] (0.13–0.96)	0.026±0.004 [a] (0.0–0.05)
Phosphate fertilizer and mining areas (n=21)	0.28±0.039 [a] (0.05–0.78)	0.037±0.005 [a] (0.0–0.10)	0.08±0.006 [b] (0.0–0.11)	0.25±0.010 [cd] (0.18–0.35)	6.34±0.63 [c] (0.86–13.25)	4.11±1.15 [a] (0.0–22.22)	0.14±0.018 [ab] (0.03–0.31)	0.045±0.003 [b] (0.02–0.07)
Coal mining areas (n=46)	0.35±0.024 [a] (0.07–0.79)	0.057±0.003[ab] (0.0–0.10)	0.08±0.004 [bc] (0.03–0.18)	0.21±0.008[bc] (0.03–0.34)	4.79±0.31 [b] (0.68–12.05)	2.19±0.33 [a] (0.12–12.25)	0.14±0.015 [ab] (0.0–0.60)	0.032±0.001 [ab] (0.01–0.07)
Steel manufacturing plant (n=22)	0.50±0.04 [b] (0.03–0.76)	0.265±0.02 [d] (0.11–0.39)	0.09±0.006 [bc] (0.05–0.15)	0.26±0.020 [d] (0.11–0.39)	3.68±0.25 [ab] (1.30–5.65)	2.78±0.42 [a] (1.28–10.59)	0.19±0.03 [b] (0.0–0.41)	0.232±0.02 [c] (0.09–0.41)
Aluminium processing plant/ Thermal power plant (n=25)	0.65±0.020 [c] (0.44–0.88)	.087±0.003 [c] (0.06–0.12)	0.05±0.006 [a] (0.0–0.13)	0.12±0.014 [a] (0.0–0.29)	3.04±0.25 [a] (1.37–6.66)	2.46±0.13 [a] (1.48–3.90)	0.33±0.015 [c] (0.22–0.48)	0.044±0.002 [b] (0.03–0.06)
Lead zinc smelter (n=21)	0.85±0.114 [d] (0.13–2.7)	0.078±0.014[bc] (0.02–0.27)	0.08±0.009 [bc] (0.03–0.20)	0.17±0.013[b] (0.07–0.32)	6.18±0.55 [c] (2.12–10.89)	3.62±0.95 [a] (0.25–17.36)	0.76±0.07 [e] (0.17–1.22)	0.034±0.002 [ab] (0.01–0.05)

Respective milk and blood samples were collected from 201 lactating cows reared and allowed to graze around different industrial units. The values were expressed in Mean (±SE) and values in parenthesis indicate minimum and maximum level recorded. The mean value with dissimilar superscripts vary significantly at P<0.05.

Table 2 – Correlation between milk and blood trace element

Trace elements	Lactating cows	Source and number	Number	Blood x milk r	Blood x milk P
Copper	Control animals	Unpolluted area	52	−0.349*	0.011
	Irrespective of place of collection	Industrial and unpolluted area	201	−0.259**	0.000
Cobalt	Control animals	Unpolluted area	52	0.103	0.467
	Irrespective of place of collection	Industrial and unpolluted area	201	0.130	0.067
Zinc	Control animals	Unpolluted area	52	−0.020	0.888
	Irrespective of place of collection	Industrial and unpolluted area	201	0.293**	0.000
Iron	Control animals	Unpolluted area	52	0.011	0.936
	Irrespective of place of collection	Industrial and unpolluted area	201	0.062	0.380

*P<0.05, **P<0.01.

and blood suggesting that the milk zinc level was influenced by place of collection or by the blood level of lead or cadmium (Table 2). A closer look to examine if significantly higher milk lead excretion as occur with blood lead level above 0.2 μg/ml in 79 lactating cows (Table 3) out of 201 animals in the present study, revealed a significant positive correlation between blood lead and milk zinc (r=0.476, P<0.001) and iron (r=0.298, P=0.008). However, blood lead level≤0.02 μg/ml (n=122) had non-significant correlation with milk copper and iron. Similarly, with blood cadmium level above 0.05 μg/ml (n=35), blood cadmium was significantly correlated (2-tailed) with milk cadmium (r=0.743, P<0.001) and cobalt (r=0.445, P=0.007) but not with milk copper (r=0.231, P=0.181), zinc (r=−0.143, P=0.413) or iron (r=0.072, P=0.680) (Table 3).

3.3. *Toxic and trace element correlation in milk*

Table 3 depicts the toxic and trace elements correlation in milk. The 2-tailed Pearson correlation was non-significant (P<0.05) between lead and trace elements levels in milk from all 201 cows. A non-significant correlation was also registered between milk cadmium with other trace elements except that cobalt concentration (r=0.365, P<0.001) was significantly correlated with cadmium level in milk.

Analysis of correlation between milk lead and other trace elements in lactating cows with significantly higher excretion of lead (n=79) irrespective of place of sampling revealed a significant negative correlation between milk iron with milk lead level (r=−0.273, P=0.015) unlike in animal population with blood lead<0.20 μg/ml where all the trace elements had a non-significant correlation with milk lead (Table 3).

The milk cadmium level in 35 lactating cows with blood cadmium level above 0.05 μg/ml documented a significant positive correlation with milk cobalt (r=0.726, P<0.001). However, other trace elements in milk such as copper, zinc and iron had a non-significant correlation with milk cadmium level in these animals. Animals with blood cadmium level≤0.05 μg/ml had a non-significant correlation with milk cobalt (r=0.002, P=0.980).

3.4. *Milk trace mineral in cows sorted in four groups*

Figs. 1–4 represent the effect of four different mean levels of blood and milk level of lead and cadmium on milk trace elements profile irrespective of environmental origin of the samples. Cows with blood lead level of >0.30 to 0.40 μg/ml (n=17) had significantly (P<0.05) lowered copper concentration as compared to other three groups and significantly higher milk zinc excretion (P<0.05) was associated with the highest

Table 3 – Correlation of trace element in milk with toxic element in blood or milk

Variable	Description of lactating cows	N	Milk Copper	Milk Cobalt	Milk Zinc	Milk Iron
Blood lead	Unpolluted area	52	0.167(0.236)	0.269(0.054)	0.135(0.339)	0.161(0.255)
	Cows with blood lead>0.20 μg/ml	79	0.212(0.061)	−0.024(0.834)	0.476**(0.000)	0.298**(0.008)
	Cows with blood lead≤0.20 μg/ml	122	0.033(0.720)	0.409**(0.000)	0.236**(0.009)	0.073(0.422)
	Cows irrespective of place of collection	201	0.049 (0.487)	0.026 (0.714)	0.384**(0.00)	0.113 (0.112)
Blood cadmium	Unpolluted area	52	0.094(0.505)	−0.246(0.079)	0.310*(0.025)	−0.047(0.741)
	Cows with blood cadmium>0.05 μg/ml	35	0.231(0.181)	0.445**(0.007)	−0.143(0.413)	0.072(0.680)
	Cows with blood cadmium≤0.05 μg/ml	166	−0.126(0.106)	−0.218**(0.005)	−0.038(0.625)	−0.132(0.089)
	Cows irrespective of place of collection	201	0.041 (0.561)	0.278**(0.000)	−0.140*(0.047)	−0.093 (0.191)
Milk lead	Unpolluted areas	52	0.096(0.498)	0.060(0.673)	0.042(0.768)	−0.080(0.572)
	Cows around industrial units	149	−0.100(0.224)	−0.192*(0.019)	−0.144(0.080)	−0.091(0.272)
	Cows with blood lead>0.20 μg/ml	79	−0.218(0.053)	−0.186(0.101)	−0.198(0.080)	−0.273*(0.015)
	Cows with blood lead≤0.20 μg/ml	122	0.067(0.465)	0.040(0.664)	−0.024(0.793)	−0.053(0.558)
	Cows irrespective of place of collection	201	−0.118(0.094)	−0.098 (0.165)	−0.040 (0.577)	−0.118 (0.094)
Milk cadmium	Unpolluted areas	52	0.254(0.069)	0.199(0.158)	0.158(0.263)	0.139(0.325)
	Cows with blood cadmium>0.05 μg/ml	35	0.260(0.132)	0.726**(0.000)	−0.114(0.514)	0.152(0.383)
	Cows with blood cadmium≤0.05 μg/ml	166	−0.213**(0.006)	0.002(0.980)	−0.005(0.948)	−0.052(0.508)
	Cows irrespective of place of collection	201	−0.016(0.819)	0.365**(0.000)	−0.121(0.088)	−0.078(0.270)

Figures in bracket indicate ‘P’ value, *P<0.05, **P<0.01.

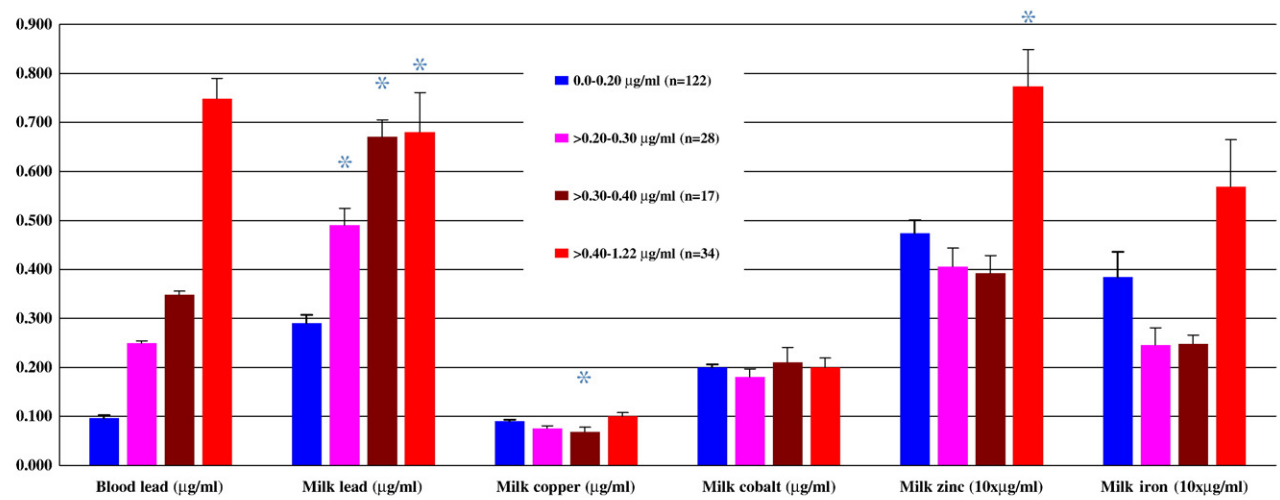

Fig. 1 – Toxic and trace elements in milk from lactating cows classified into different groups based on increasing blood lead level. Both blood and milk samples were collected from 201 lactating cows reared around different industrial units and in un-polluted areas. Animals were grouped into four non-overlapping groups based on blood lead level as per the range given in the legend. Data were analysed for toxic heavy metals in blood and milk and trace elements in milk. Values were expressed in Mean (±SE). 'n' in parenthesis of the legend represents number of animals in that range. Values for zinc and iron divided by 10 to get a uniform bar size. *Significantly different from the lowest blood lead group (0.0–0.20μg/ml).

blood lead concentration (Fig. 1). The mean trace elements level of copper, cobalt, zinc remained comparable ($P>0.05$) at different mean levels of milk lead. However, the milk iron level reduced significantly in all the milk lead groups with milk lead level above 0.20 μg/ml (Fig. 2).

The increasing mean cadmium level in blood (Fig. 3) or milk (Fig. 4) in four different groups was not associated with any significant ($P>0.05$) change in trace elements level except that the highest milk cadmium (>0.10 to 0.39 μg/ml) level (Fig. 4) was associated with significant increase in milk cobalt level.

4. Discussion

Lead and cadmium are considered as the commonest form of poisoning in farm animals because of natural curiosity, licking habits and lack of oral discrimination particularly in cattle (Radostitis et al., 2007). Chronic and in-apparent poisoning due to intake of smaller quantities leads to their higher accumulation in tissues, bones, hair and blood, and significantly enhanced excretion in milk, and their higher levels in

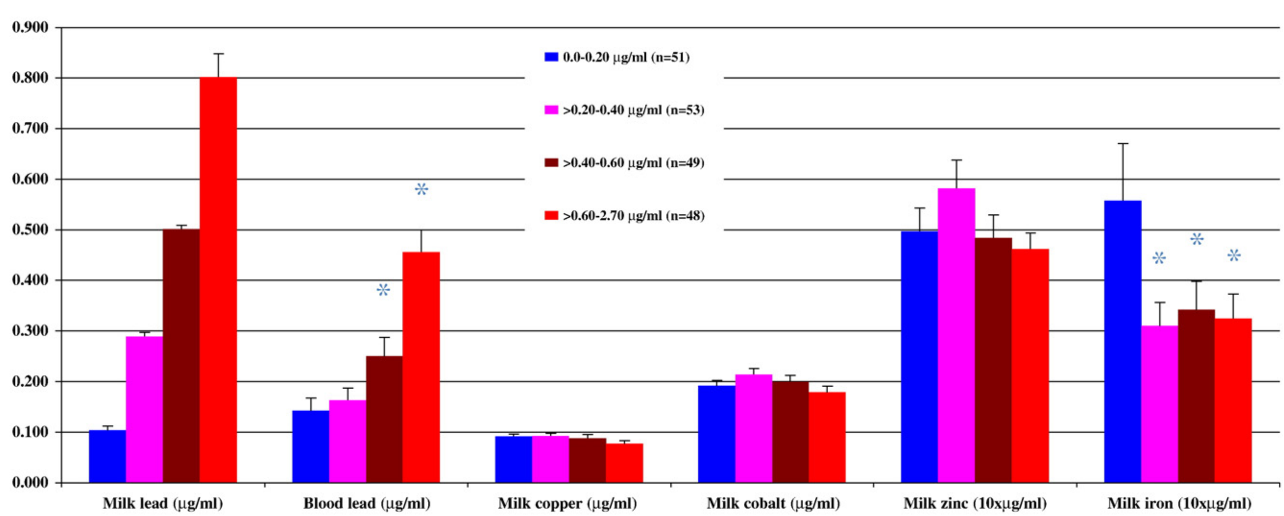

Fig. 2 – Toxic and trace elements in milk from lactating cows classified into different groups based on increasing milk lead level. Both blood and milk samples were collected from 201 lactating cows reared around different industrial units and in un-polluted areas. Animals were grouped into four non-overlapping groups based on blood lead levels as per the range given in the legend. Data were analysed for toxic heavy metals in blood and milk and trace elements in milk. Values were expressed in Mean (±SE). 'n' in parenthesis of the legend represents number of animals in that range. Values for zinc and iron divided by 10 to get a uniform bar size. *Significantly different from the lowest blood lead group (0.0–0.20μg/ml).

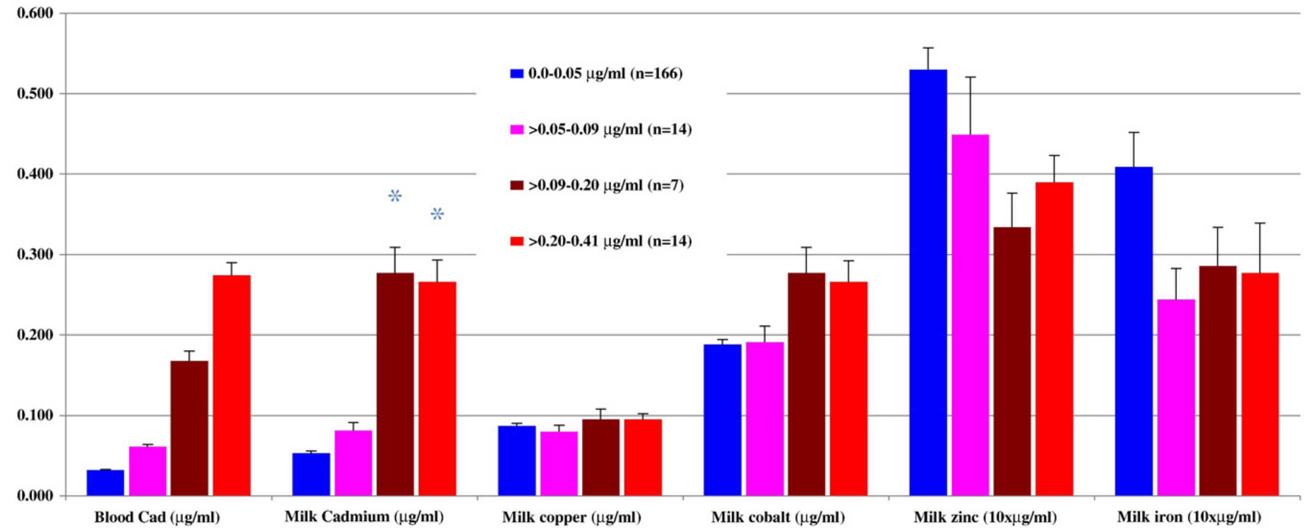

Fig. 3 – Toxic and trace elements in milk from lactating cows classified into different groups based on increasing blood cadmium level. Both blood and milk samples were collected from 201 lactating cows reared around different industrial units and in un-polluted areas. Animals were grouped into four non-overlapping groups based on blood lead levels as per the range given in the legend. Data were analysed for toxic heavy metals in blood and milk and trace elements in milk. Values were expressed in Mean (±SE). 'n' in parenthesis of the legend represents number of animals in that range. Values for zinc and iron were divided by 10 to get a uniform bar size.. *Significantly different from the lowest blood cadmium group (0.0–0.05µg/ml).

food and food products of animal origin (Dwivedi et al., 1995; Milhaud and Mehennaoui, 1988; Patra et al., 2005; Swarup et al., 2005).

Milk is produced by the epithelial cells of the mammary gland of a lactating animal. Some compounds of milk like fats, proteins, lactose are synthesized in the epithelial cells from blood precursors and then released into the lumen of the alveolus. The remaining constituents pass from the blood and released into milk ducts without any alterations by the cells. The rate of milk secretion in turn depends upon the rate of blood flow through the udder and the composition and uptake of blood constituents by the mammary gland. Trace minerals other than water and vitamins are transferred from blood plasma to milk without synthesis (Schmidt, 1973). But, there is

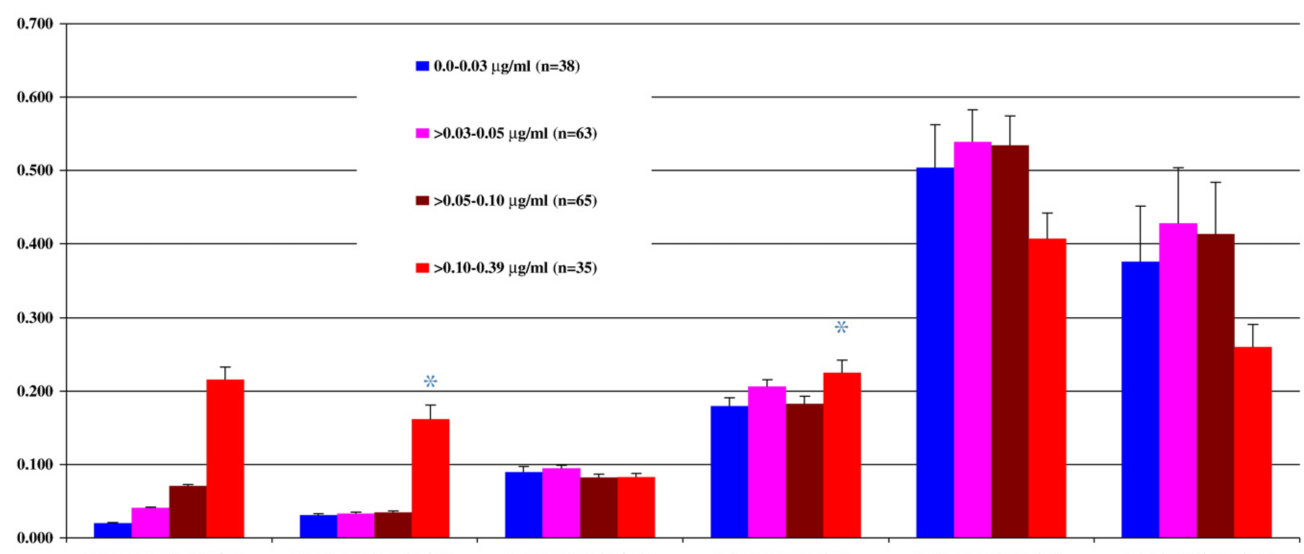

Fig. 4 – Toxic and trace elements in milk from lactating cows classified into different groups based on increasing milk cadmium level. Both blood and milk samples were collected from 201 lactating cows reared around different industrial units and in un-polluted areas. Animals were grouped into four non-overlapping groups based on blood lead levels as per the range given in the legend. Data were analysed for toxic heavy metals in blood and milk and trace elements in milk. Values were expressed in Mean (±SE). 'n' in parenthesis of the legend represents number of animals in that range. Values for zinc and iron divided by 10 to get a uniform bar size.. *Significantly different from the lowest blood cadmium group (0.0–0.03µg/ml).

a lack of data about the transport mechanism of these minerals across the mammary gland epithelium and about the regulation of zinc and copper. However, it has been observed that zinc concentration in breast milk varies among and within mothers (Stawarz et al., 2007). The importance of microelements in food including those occurring in ultra low concentrations is increasingly getting due importance from health point of view (Hermansen et al., 2005) and their presence in human diet especially, of infants is essential for growth and development (Tripathi et al., 1999; Flynn, 1992).

Trace elements including copper, cobalt, zinc, and iron are very much essential for normal growth, disease resistance, production and reproduction. Many of the essential trace elements have clinical properties in common and interactions among those and with other toxic elements influence the trace elements metabolism including their excretion from the animal body (Underwood, 1979). The management system and the environment have also been reported to influence the trace and toxic metals concentration as organically produced milk had a different composition as compared to conventionally produced one (Hermansen et al., 2005). Hejtmankova et al. (2002) recorded alterations in the concentration of selected macro and microminerals in milk from goat reared in farms around industrial sources of pollution. In the present investigation, milk from cows reared around closed lead cum operational zinc smelter with comparable milk lead and cadmium level with that of control animals had significantly ($P<0.05$) higher concentration of milk trace elements and such trend could be attributed to contamination of pasture with excess trace elements along with heavy metals emitted from the industrial unit.

Normal concentration of iron and copper in cow milk was reported to be 0.2 ppm and 0.05 ppm, respectively (Anderson, 1992). Milk from Chinese Peking black pied dairy cows has trace elements (ppm) as zinc (4.38 ± 0.86), iron (0.40 ± 0.15), copper (0.31 ± 0.009) and cobalt (0.0014 ± 0.0008) (Wun et al., 1981). Benemariya et al. (1993) reported normal average concentrations of Zn and Cu in cow's milk and colostrums from Africa as 4.40 and 0.10 ppm, and 12.40 and 0.24 ppm, respectively, these values fit well to the present observation. In a study on two groups of crossbred cows (Jersey x Assam local and Holstein x Assam local) reared in an organized farm in India, the mean iron, copper and zinc were recorded as 2.96 ± 0.23, 3.36 ± 0.21; 0.29 ± 0.04, 0.39 ± 0.05; and 4.11 ± 0.25, 4.72 ± 0.17 μg/ml, respectively and no significant difference was found in the levels of iron and zinc with respect to breed (Goswami et al., 2000). In the present investigation, levels of iron, lead and cadmium were comparatively high, and could be due to differing sources of collection of samples and diverse environmental conditions.

The milk level of cobalt, zinc and iron was not influenced by the blood trace minerals as there was no significant correlation between blood and milk level of either of these trace elements in cows ($n=52$) from un-polluted area. The findings substantiate the earlier report of Stawarz et al. (2007) who recorded zinc concentration in breast milk independent of maternal mineral status. However, the significantly negative correlation between blood and milk copper in control animals ($n=52$) or in all the animals ($n=201$) in the present study could not be explicitly explained. There are reports of diurnal and day to day variation of biogenic minerals in the breast milk of human being (Stawarz et al., 2007) and such variation might have been responsible for such a trend in copper. Irrespective of blood lead or cadmium level as a factor ($n=201$), there was a significant positive correlation between blood and milk zinc level suggesting that place of sampling or higher blood lead or cadmium might have influenced the zinc excretion. This was presumed as there was no significant correlation between blood and milk zinc level in control animals from unpolluted areas. Fig. 1 also shows significantly higher zinc level in milk in the group with the highest mean blood lead level compared to rest of the groups. This was also further substantiated by the findings of a significant positive correlation between blood lead and milk zinc in 79 lactating cows with blood lead level>0.2 μg/ml, the level where milk excretion of lead is significantly higher (Swarup et al., 2005). The analysis of data from these 79 cows also suggested a significant ($P=0.015$) negative influence of milk lead on milk iron level (Fig. 2). Similarly, cows with blood cadmium level>0.05 μg/ml, there was a significant positive correlation between blood cadmium and cobalt suggesting that higher blood cadmium level enhances cobalt excretion in milk. This was clearly evident from Fig. 4 that shows the highest milk cadmium level was associated with significantly higher milk cobalt excretion. There is paucity of earlier literature particularly in animals to compare the present finding. Experimental exposure of rats to either lead or cadmium or both concomitantly, has been demonstrated to influence the metabolism and tissue concentration of divalent cations like zinc, copper, iron etc (Doyle and Younger, 1984; Patra et al., 2001) and tissue specific changes in distribution of iron, zinc, copper, cobalt, and manganese have been documented after experimental administration of lead and cadmium in cattle and rats (Oishi et al., 2000; Patra and Swarup, 1998). However, Stawarz et al. (2007) did not find any correlation between zinc and lead but correlation between cadmium and zinc in the breast milk was significant ($r=0.279$) in their study involving a smaller human population. Strong positive correlations between Cd and Mg ($r=0.201$), Cd and Zn ($r=0.279$) have earlier been reported in breast milk (Stawarz et al., 2007). Lead, cadmium, zinc, and cobalt are divalent cations and secretion of more lead or cadmium with elevated blood concentrations might have a competition from trace elements for higher elimination. The alterations in trace elements in milk could be attributed to interactions among trace elements or with toxic minerals as absorption, utilization and excretion of trace elements in animal body are greatly influenced by interacting trace minerals or compounds (Underwood, 1979). Our results suggested that environmental heavy metals such as lead and cadmium are transported in to milk of lactating cows and their presence in milk was associated with changes in trace minerals profile and affects the nutritional quality including reduced iron content of milk with increased milk lead excretion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2008.06.010.

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