

## Cadmium and Lead Levels in Cow's Milk from a Milking Region in Santa Fe, Argentine

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Animals and man absorb cadmium and lead by the direct consumption of foods, from soil, atmosphere and water that are largely contaminated with risk elements (Fe, Al, Mg, Zn, As, Cd, Pb, Hg and Ni) arising from industrial environmental contamination. (Concon 1981, Robards and Worsfold 1991). In cattle, exposure to Cd may effect various clinical abnormalities such as loss of appetite, anemia, poor growth, abortions and teratogenic lesions or may pass without clinical signs (Webtubj et al. 1988, Kottferova and Korenekova 1995).

Milk and milk products are important components of human food. Cadmium and lead levels have been previously studied in ruminant species and their accumulation in some organs (kidney, muscle and liver, mainly) has been reported (Kuiters 1996, Khan 1995). Therefore, to ensure public health, the concentrations of Cd and Pb in milk need to be monitored (Jeng et al. 1994).

## MATERIALS AND METHODS

Cow's milk samples (n=52) were obtained from different farms located in the argentinean geographic area of Esperanza (Santa Fe). This is an important area including in the "Santafesina" milking region, one of the most important dairy region of South America.

Samples were taken and maintained at -5°C until analyzed. In each milk sample both cadmium and lead analyses were performed simultaneously. Analytical procedures are referenced in AOAC official methods (Cunniff 1996) and Jones et al. (1977). Homogenized sample (100 ml) were placed in a Pyrex 150 ml beaker and evaporated to dryness using a hot plate at low setting and a 120 °C oven overnight or until thoroughly dry. The vessel were placed in furnace, and heated in several steps to reach 500 °C, setting this temper&e for 24 h. It Should be necessary a concentrated nitric acid treatment, cooling the furnace and adding successive increments of 1 ml of  $\rm HNO_3(1:1)$  to the ashes and returned to heat at 500 °C until white, carbon free ash is obtained.

Ashes were completely dissolved in 10 ml HCl 1N and using aliquots of this solution, Cd and Pb were quantitatively analyzed by Differential Pulse Anodic Stripping Voltammetry (DPASV), in a EG&G Princeton Applied Research Corp. 264A, with Static Mercury Drop

Electrode (SMDE) 303 A model. The technique of standard additions were used, at hanging drop mercury electrode mode, stripping at a scan range of -0,80 V to -0,30 V vs Ag/AgCl. The detection limits were 0,5 ng Cd/ml and 1 ng Pb/ml. Procedure was validated and results were obtained under quality assurance principles.

Data are presented as means  $\pm$  SEM (SIGMA computer program). An ANOVA test was used to compare the difference of metal contents obtained from milk samples respective to different aging animals. Also, correlation analyses were performed to determine whether relationships exist between age and excretion of these metals in milk. Results were significant at p<0.05.

## RESULTS AND DISCUSSION

The cadmium and lead contents in the serum of raw milk samples in relation with age of animals, are listed in table 1. The mean content for cadmium was 1.47 ng/ml of milk with a range of 0.00 to 17.00 ng/ml (n=20) and for lead was 24.6 ng/ml with a range of 0.0 to 106.0 ng/ml (n=50). Some samples (63% for Cd and 6% for Pb) showed concentrations lower than the quantification limits calculated for the current analytical methods.

Concentrations were higher than the 0.44 ng of Cd/ml or 0.048 ng of Cd/ ml and 2.03 ng of Pb/ml or 1.76 ng of Pb/ml of milk reported by Jeng et al (1994) and by Narres et al. (1985), respectively. However, taking into consideration the maximum residue levels admitted for cadmium and lead in milk for the Argentinean Alimentary Codex (2 ppm for Pb in liquid and 20 ppm for Pb in solid foods; 50 ppm for Cd in milk) the concentrations found by us does not rise the safety limits in milk for these metals. It is necessary taking into account the maximum values accepted by International Organizations, as the International Atomic Energy Agency (1,7 ng of Cd/g and 54 ng of Pb/g in milk powder) (Table 2).

Previous studies have been shown that little cadmium is secreted into milk (0.00008% per day) due to the sequestration of cadmium by metallothionein-like proteins that have been isolated in mammary tissue and placenta (Miller et al. 1967, Neathery et al. 1974, Lucis et al. 1972). It has been reported that ingested lead transfer poorly to milk (0.0003%) although lead plasma or tissue levels were high and cows showed clinical signs of lead toxicity (Hammond and Aroson 1964, Antoniou et al. 1989).

Mean concentrations showed significative differences between young (< 5 years) and old (> 5 years) cows for both, cadmium (p<0.05) and lead (p<0.05) (Table 2), but the analyses of the variance due to age for lead levels showed a poor significance (0.10>p>0.05) and any significance was shown for cadmium levels. So, only for lead a poor correlation between age and metal milk concentration was found (r=0.038).

Table 1. Mean of Cd and Pb concentrations (ppb) in cow milk in relation with age of animals.

		AGE (years)								
		≤ 3	3-4	4-5	5-6	6-7				
	n	13	7	9	9	14				
Cd	mean ± SEM	$3.2 \pm 3.1$	$0.9 \pm 0.8$	$0.0 \pm 0.0$	2.4 ± 1.6	3.2 ± 1.4				
	range	0.0 - 4.0	0.0 - 6.0	0.0 - 0.0	0.0 - 13.0	0.0 - 17.0				
Pb	mean ± SEM	15 ± 5	$20 \pm 9$	18 ± 3	30 ± 8	37 ± 8				
_	range	0 - 60	0 - 70	10 - 40	0 - 70	10 - 106				

n= number of samples. SEM=standard error mean.

Table 2. Maximum residue limits of Cd and Pb in cow milk (ppb) compared with levels found in Esperanza region (Santa Fe, Argentine).

		Age (Years)	n		Mean Concentration		% Positive Samples		Maximum a b		% Samples upper maxim	
ſ	Cd	<b>&lt;</b> 5	29	52	1.47	0.37	24.1	37.0	1.7	2.0	0.0	0.0
١		≥5	23		ŀ	2.87	52.1					0.0
I	Pb	<b>&lt;</b> 5	29	52	25.0	17.0	89.6	93.0	54*	50	2.0	0.0
١		≥5	23	}		34.0	95.6					5.0

n= number of samples.

a= values from International Atomic Energy Agency.

b= values from Argentinean Alimentary Codex.

Generally, in ruminant species, cadmium accumulates in kidney and liver and lead accumulates in bone (Kuiters 1996, Fasset 1975) and, in these tissues, metal concentration increases with age. In the present study, cadmium and lead milk concentrations rend to increase with age although these enlargements are not significant. It could be due to no accumulation of cadmium and lead in mammary gland has been described.

The results of this survey confirm that it is possible to obtain residue levels of cadmium and lead in milk. Although, satisfactorily, the levels of these metals found in the Esperanza region of Argentine are slightly higher than those ones reported for other authors in other areas, they are well within the established tolerances by the different regulatory organizations. Neverless, the present work does not suggest the need to restrict the human consumption of milk but it shows the need to establish such monitoring program in order to improve the food safety.

<sup>\*=</sup> Values for milk powder.

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