

LEAD AND CADMIUM LEVELS IN RAW COW'S MILK IN LITHUANIA DETERMINED BY INDUCTIVELY COUPLED PLASMA SECTOR FIELD MASS SPECTROMETRY

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Raw milk from 15 districts in Lithuania was analysed in winter and grazing seasons in 2005. Lead and cadmium were determined by inductively coupled plasma sector field mass spectrometry. Mean cadmium concentrations in winter milk samples amounted to 0.37 $\mu\text{g}/\text{kg}$ (0.25–0.49 $\mu\text{g}/\text{kg}$) and in summer ones 0.18 $\mu\text{g}/\text{kg}$ (0.11–0.23 $\mu\text{g}/\text{kg}$). The mean concentrations of lead in samples collected in winter and in summer were 0.47 $\mu\text{g}/\text{kg}$ (0.17–1.0 $\mu\text{g}/\text{kg}$) and 0.54 $\mu\text{g}/\text{kg}$ (0.06–1.76 $\mu\text{g}/\text{kg}$), respectively. No individual sample exceeded the Lithuanian norm value for lead (20 $\mu\text{g}/\text{kg}$). The health quality of Lithuanian milk can be considered as very high in the aspect of cadmium and lead contamination.

INTRODUCTION

Milk is a primary source of nutrients in diets all around the world [Buldini *et al.*, 2002]. Technical progress, various industrial activities and increased roadway traffic resulted in significant increase of environmental contamination [Licata *et al.*, 2004]. By their spread speed in biosphere and increasing concentrations heavy metals are considered to be among the most hazardous pollutants [Staniškienė & Garalevičienė, 2004]. The almost ubiquitous presence of some metal pollutants, especially cadmium and lead, in the environment facilitates their entry into the food chain, thus increasing the hazard of human and animal health [Licata *et al.*, 2004].

There were several studies of heavy metals contamination in milk some years ago in Lithuania [Urbienė & Čiučkinas & 1993; Čiučkinas & Urbienė, 1994; Paškauskienė *et al.*, 1995; Ramonaitytė, 1996]. However, the results differed according to the various sampling areas and the analytical methods employed.

The aim of the study was to determine lead and cadmium concentrations in cow's milk collected during indoor feeding and pasture season

MATERIALS AND METHODS

Sampling. Raw milk was collected in winter (March and April) and grazing (June and July) seasons of 2005 at two milk factories in Lithuania (Figure 1). Samples of collecting milk originated from five industrialised districts (fuel factory in Mazeikiai district, cement works – in Akmene district and



FIGURE 1. Map of milk samples collection.

main highways: Vilnius – Kaunas in Kaunas and Kaišiadoriai districts and Siauliai – Klaipėda in Siauliai district), five areas near industrialised districts (Marijampolė, Prienai, Sakiai, Skuodas, Telsiai districts) and five unpolluted districts (Alytus, Salcininkai, Silalė, Ukmergė and Vilkaviskis districts).

Milk was sampled two times from every district every season in milk factories from milk truck into 12-mL plastic containers and stored at a temperature of $0\pm 6^{\circ}\text{C}$ during delivery and until analysis.

Precautions against contamination. Plastic containers and all other laboratory ware used were new and were

cleaned by soaking them for 24 h in the bath containing 10% HNO₃ solution and for 24 h in ultra pure water. After rinsing with ultra pure water they were dried in a class 10 clean bench.

Reagents and sample preparation. Closed, pressurised, high-performance microwave digestion unit (Anton Paar, Austria) was used for mineralisation. Device is equipped with a rotor for six quartz vessels designed for pressures up to 75 bar. Weighed 5 g milk samples were placed into the digestion vessels and mixed with 2.5 mL of concentrated HNO₃ (Suprapur®, 65.3%, Merck). Mineralisation was made by the optimised procedure. The samples were diluted to 50 g with purified water before ICP-SFMS analysis.

Apparatus. Measurements were carried out by means of high resolution ICP-SFMS ELEMENT2 (Thermo Finnigan MAT, Bremen, Germany) with a double focusing mass separator. Instrumental operating conditions are outlined in Table 1.

TABLE 1. Operating conditions for the instrument.

Parameter	Value
Resolution	Low (R=300): ²⁰⁶ Pb, ²⁰⁷ Pb, ²⁰⁸ Pb High (R=10000): ¹¹⁰ Cd, ¹¹¹ Cd, ¹¹² Cd, ¹¹³ Cd, ¹¹⁴ Cd
Cooling gas	14.00 L/min
Auxiliary gas	0.75 L/min
Sample gas	1.25 L/min
Plasma power	1073 W
Sample time	0.01 s
Nebulizer	MCN600
Spray chamber	Scott double pass
Sample and skimmer cones	Ni

The certified reference material BCR-063R (skim milk powder) was used for validation purposes. Detection limits were defined as 3 times the standard deviation of an average of procedural blanks. The corresponding values for lead and cadmium were obtained equal to 0.04 ng/g and 0.01 ng/g. The repeatability of the measurement of the analytical signals usually was not worse than 2–3%. To control the stability of the analytical signals the measurements for the standard solutions were repeated before and after the measurements of the samples.

Statistical analysis. The results were evaluated by a single-factor variance analysis. The significance of differences was checked with the Student's t-test at a significance level of $p=0.05$ with the use of Statistica 6.0 software.

RESULTS AND DISCUSSION

Mean concentrations of cadmium and lead in cow's milk samples from Lithuania are presented in Figure 2. The levels of cadmium in milk did not differ significantly ($p=0.05$) between winter (0.37 $\mu\text{g}/\text{kg}$) and summer (0.18 $\mu\text{g}/\text{kg}$) seasons. The highest concentration of cadmium was found in winter in the Kaunas district (0.49 $\mu\text{g}/\text{kg}$) and in summer in

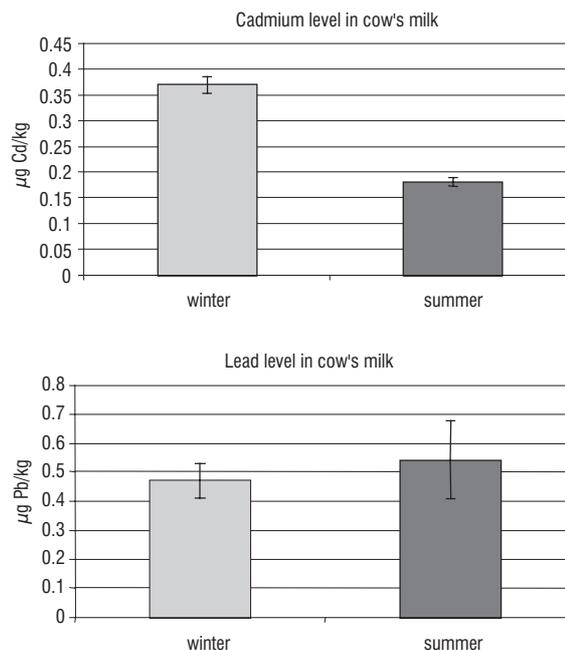


FIGURE 2. Cadmium and lead concentrations in cow's milk.

the Salcininkai district (0.23 $\mu\text{g}/\text{kg}$) and the lowest ones in winter and summer in the Siauliai district (0.25 $\mu\text{g}/\text{kg}$) and in the Telsiai district (0.11 $\mu\text{g}/\text{kg}$), respectively. Cadmium levels did not differ significantly ($p=0.05$) in milk samples compared to the industrialised and other districts in both winter and grazing seasons.

The mean concentration of lead in winter milk samples was 0.47 $\mu\text{g}/\text{kg}$ and 0.54 $\mu\text{g}/\text{kg}$ summer. The highest level of lead was in winter in the Kasiadoriai district (1.00 $\mu\text{g}/\text{kg}$) and in summer in the Salcininkai district (1.76 $\mu\text{g}/\text{kg}$). The lowest level of lead was detected in the Marijampole district (0.17 $\mu\text{g}/\text{kg}$) and in the Skuodas district (0.06 $\mu\text{g}/\text{kg}$), respectively.

The highest concentrations of lead in winter milk samples were determined in two industrialised districts (Kaunas and Kasiadorys) but in the others they were less than average. Lead levels in other districts were similar and did not differ significantly from the average.

The mean concentration of lead in summer milk samples from the industrialised districts was 0.4 $\mu\text{g}/\text{kg}$ and varied from 0.11 $\mu\text{g}/\text{kg}$ to 0.75 $\mu\text{g}/\text{kg}$. The highest level of lead (1.76 $\mu\text{g}/\text{kg}$) was in grazing season milk sample from the district grouped as not polluted. Significantly ($p=0.05$) higher concentration of lead was found in summer than in winter and this suggests that there is no lead contamination during milk collection and transport.

Lead levels in all examined milk samples were lower than the maximum allowed levels (MAL) of Lithuanian Hygiene Norm [Hygiene Norm, 2001] which allows concentrations up to 20 $\mu\text{g}/\text{kg}$. There are no specific MAL for other heavy metals in milk both in Lithuanian Hygiene Norm and Commission Regulation (EC) No 466/2001.

Higher lead and cadmium levels were detected in milk in Lithuania 10 years ago. In 1991 lead concentrations of 60–80 $\mu\text{g}/\text{kg}$ were determined in some samples though concentrations <10 $\mu\text{g}/\text{kg}$ were found as well [Urbienė &

Čiučkinas, 1993]. Cadmium concentrations amounted to $<10 \mu\text{g}/\text{kg}$. Lead levels of $20\text{--}30 \mu\text{g}/\text{kg}$ were detected in 1990–1993 [Čiučkinas & Urbienė, 1994].

Our results are similar or lower than those reported from other countries currently. Licata *et al.* [2004] analysed milk samples of 40 cows in Calabria, Italy. The highest lead concentrations amounted to $9.92 \mu\text{g}/\text{kg}$. The cadmium levels were below the detection limit of $0.01 \mu\text{g}/\text{kg}$ in almost all the samples. Only in three milk samples were the cadmium concentrations higher: 1.14, 3.42 and $22.8 \mu\text{g}/\text{kg}$. Rodriguez *et al.* [1999] determined the heavy metals in samples of raw cow's milk in Spain. The concentration of cadmium accounted for $4.88 \mu\text{g}/\text{L}$ ($0.7\text{--}23.1 \mu\text{g}/\text{L}$), whereas that of lead – for $14.82 \mu\text{g}/\text{L}$ ($1.3\text{--}39.1 \mu\text{g}/\text{L}$). National monitoring studies in Poland reported mean concentration of lead at 3 and that of cadmium at $<1 \text{mg}/\text{kg}$ in 2000 [Report..., 2001] and similar levels in 2001 [Report..., 2002].

CONCLUSIONS

Lead and cadmium concentrations in raw cow's milk in Lithuania were very low, irrespective of the place of sample origin. The only significant ($p=0.05$) differences were found in lead concentration (higher in summer than in winter). We can conclude that the health quality of Lithuanian milk is very high in the aspect of cadmium and lead contamination.

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REFERENCES

1. Buldini P.L., Cavalli S., Sharma J.L., Matrix removal for the ion chromatographic determination of some trace elements in milk. *Microchem. J.*, 2002, 72, 277–284.
2. Čiučkinas A., Urbienė S., Kai kurių Lietuvos rajonų pieno užterštumo toksinė mis medžiagomis tyrimai (Investigation of contamination levels of milk delivered from some areas of Lithuania.). *Food Chem. Technol.*, Vilnius, 1994, 28, 10–15.
3. Higienos norma 54:2001 Maisto produktai. Didžiausios leidžiamos teršalų ir pesticidų likučių koncentracijos (Hygiene Norm 54: 2001 Foodstuffs. Maximum allowed levels of pollutants and pesticides residues).
4. Licata P., Trombetta D., Cristani M., Giofre F., Martino D., Calo M., Naccari F., Levels of “toxic” and “essential” metals in samples of bovine milk from various dairy farms in Calabria, Italy. *Environ. Res.*, 2004, 30, 1–6.
5. Paškauskienė V., Ramonaitytė D., Bernatoniš J., Sunkieji metalai pieno produktuose (Heavy metals in milk products). 1995, Scientific publication, LMAI, KTU, Kaunas, pp. 1–25.
6. Ramonaitytė D.T., Sunkieji metalai pieno produktuose ir jų biocheminis aktyvumas. (Heavy metals in milk products and biochemical activity). 1996, Monograph, Kaunas, pp. 16–43.
7. Report on monitoring of soils, plants and food quality in 2000. 2001. Ministry of Agriculture & Land Development, Warsaw, pp. 134–126.
8. Report on monitoring studies of soils, plants and food quality in 2001. 2002. Ministry of Agriculture & Land Development, Warsaw, pp. 42–44.
9. Rodriguez E.M., Uretra E.D., Romero C.D., Concentrations of cadmium and lead in different types of milk. *Z. Lebensm Uters Forsch. A.*, 1999, 208, 162–168.
10. Staniškienė B., Garalevičienė D., Sunkieji metalai žuvų mėsoje ir kauluose (The amount of heavy metals in fish bones and meat). *Vet. Zootech.*, Kaunas, 2004, 26, 46–52.
11. Urbienė S., Čiučkinas A., Sunkiųjų metalų ir toksinių elementų kiekis kai kurių Lietuvos rajonų piene (The amount of heavy metals and toxic elements in milk delivered from some areas of Lithuania). *Food Chem. Technol.*, Vilnius, 1993, 27, 54–55.

ZAWARTOŚĆ KADMU I OŁOWIU W MLEKU SUROWYM NA LITWIE OZNACZONA METODĄ SPEKTROMETRII MASOWEJ Z PLAZMĄ SPRĘŻONĄ INDUKCYJNIE

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Analizie poddano mleko surowe pobrane w 2005 roku w okresie żywienia oborowego i pastwiskowego na terenie piętnastu powiatów Litwy. Zawartość ołowiu i kadmu oznaczono metodą spektrometrii masowej z plazmą sprężoną indukcyjnie. Średnie stężenie kadmu w mleku pobranym zimą wynosiło 0.37 µg/kg (0.25–0.49 µg/kg), zaś latem – 0.18 µg/kg (0.11–0.23 µg/kg). Średnie stężenie ołowiu w próbkach mleka z okresu żywienia oborowego i pastwiskowego wynosiło odpowiednio 0.47 µg/kg (0.17–1.0 µg/kg) i 0.54 µg/kg (0.06–1.76 µg/kg). W żadnej z próbek zawartość ołowiu nie przekraczała wartości dopuszczalnej na terenie Litwy. Jakość zdrowotną w aspekcie zanieczyszczenia ołowiem i kadmem mleka na Litwie można uznać za bardzo wysoką.