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Heavy metals concentration in milk from the Baia Mare depression

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Abstract

The presence of lead in animal products is a consequence of the environmental pollution in all its segments, accidental introduction of this element in animal products, the addition of spices and adjuvants contaminated with lead or lead concentration due to storage in various containers containing lead and under the influence of certain factors,as a result being transferred to the food product.

Keywords: milk, heavy metals, lead, cadmium, manganese, iron, zinc, cooper

1. Introduction

A number of 25 samples of cow's milk from the area of industrial pollution in Baia Mare have been analysed and distributed as follows: Baia Sprie – Satu Nou de Sus – 7 samples; Groşi – 6 samples; Baia Mare – Ferneziu – 8 samples; Tăuții Măgherăuş - 2 samples; Tăuții Măgherăuş - Bozânta Mare – 2 samples. As an sample area, we have chosen Sighetu Marmatiei, an area located 60 km from major pollution sources and which is divided by the same mountain chain Gutai. From this area there have been taken a number of 25 samples of milk. These samples of milk were mineralized. The mineralization was achieved through wet cleaning.

2. Materials and method

The results which have been obtained are presented in the following tables:

The concentration of heavy metals in cow's milk raw material in the area polluted

Table no 1

Sample no	The concentration of heavy metals in polluted area (mg/kg)					
	Pb	*Cd*	*Mn*	*Fe*	*Zn*	Cu
1	0,157	0,031	0,216	1,358	1,941	0,243
2	0,206	0,019	0,206	1,254	1,847	0,211
3	0,149	0,017	0,183	1,247	1,347	0,197
4	0,274	0,022	0,201	1,357	1,975	0,214
5	0,159	0,017	0,148	1,651	1,875	0,235
6	0,147	0,021	0,194	1,541	1,752	0,197
7	0,241	0,019	0,171	1,314	1,687	0,168
8	0,114	0,034	0,182	1,112	1,287	0,215

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9	0,167	0,034	0,172	1,487	1,978	0,247
10	0,104	0,042	0,189	1,297	1,642	0,214
11	0,135	0,036	0,211	1,262	1,952	0,211
12	0,417	0,032	0,167	1,249	2,358	0,211
13	0,216	0,031	0,187	1,357	2,674	0,192
14	0,147	0,015	0,177	1,364	2,981	0,159
15	0,157	0,014	0,184	1,249	2,198	0,148
16	0,354	0,017	0,198	1,547	2,458	0,257
17	0,145	0,021	0,208	1,213	2,354	0,149
18	0,487	0,014	0,178	1,351	2,221	0,247
19	0,617	0,021	0,184	1,162	2,354	0,157
20	0,248	0,019	0,168	1,647	2,354	0,168
21	0,543	0,016	0,197	1,246	2,101	0,157
22	0,152	0,012	0,183	1,254	1,952	0,157
23	0,392	0,018	0,162	1,206	1,387	0,179
24	0,246	0,022	0,192	1,119	1,297	0,141
25	0,097	0,019	0,183	1,182	1,287	0,177
$\overline{X}$	0,24284	0,02252	0,18564	1,32104	1,97024	0,19404
ds	0,144197	0,00812	0,016238	0,149645	0,449699	0,035324

The concentration of heavy metals in cow's milk raw material in the unpolluted area

Table no 2

Sample no.	**The concentration of heavy metals in the unpolluted area (mg/kg)**					
	Pb	Cd	Mn	Fe	Zn	Cu
1	0,081	0,0081	0,055	0,652	1,250	0,243
2	0,078	0,0033	0,0458	0,918	0,894	0,211
3	0,067	0,0041	0,0587	0,875	1,035	0,197
4	0,058	0*	0,0257	0,478	1,614	0,214
5	0,068	0*	0,0354	0,592	0,957	0,235
6	0,051	0*	0,0478	0,749	0,875	0,197
7	0,068	0,0048	0,0579	0,687	0,689	0,168
8	0,054	0,0052	0,0457	0,955	0,759	0,215
9	0,047	0*	0,0547	0,825	1,358	0,247
10	0,035	0*	0,0748	0,694	1,241	0,214
11	0,049	0*	0,0498	0,487	0,971	0,211
12	0,061	0,0035	0,0428	0,679	0,873	0,211
13	0,031	0,0031	0,0415	0,681	1,498	0,192
14	0,024	0,0036	0,0294	0,543	1,574	0,159
15	0,061	0*	0,0485	0,679	1,035	0,148
16	0,064	0*	0,0628	0,971	1,211	0,257
17	0,035	0*	0,0483	0,612	0,976	0,149
18	0,042	0*	0,0241	0,654	0,958	0,247
19	0,043	0,0069	0,0151	0,687	0,962	0,157
20	0,051	0,0046	0,0254	0,729	0,753	0,168
21	0,061	0,0037	0,0347	0,519	1,113	0,157
22	0,051	0,0045	0,0134	0,549	1,628	0,117
23	0,033	0*	0,0112	0,556	1,121	0,125
24	0,052	0*	0,0214	0,671	1,427	0,124
25	0,037	0*	0,0579	0,922	0,921	0,268
$\overline{X}$	0,05208	0,002216	0,0585	0,69456	1,10772	0,1442
ds	0,014843	0,002567	0,090022	0,145188	0,276567	0,031894

* = below the limit of detection

The average concentration (mg / kg) of heavy metals in the cow milk collected from cattle in the polluted and unpolluted areas compared with the maximum limit allowed (MLA):

Table no 3

No	Harvest Area	No of samples taken	ELEMENTS (mg/kg)					
			Pb	Cd	Mn	Fe	Zn	Cu
			x±s	x±s	x±s	x±s	x±s	x±s
1	Polutted area	25	0,242 ±0,144	0,022 ±0,008	0,185 ±0,016	1,321 ±0,149	1,970 ±0,449	0,194 ±0,035
2	Unpolutted area	25	0,052 ±0.014	0,002 ±0,002	0,058 ±0,090	0,694 ±0,145	1,107 ±0,276	0,144 ±0,031
3	The significance of the difference		***	***	***	***	***	***
4	M.L.A		0.1	0.01	-	-	5	0.5

The lead's concentration (mg / kg)in the milk samples from the polluted area was on average of 0242 ± 0144 mg / kg (between 0097 - 0617 mg / kg of MLA exceeding 0.97 times respectively 6.17 times) compared to milk samples from the unpolluted area which was 0052 ± 0014 mg / kg.

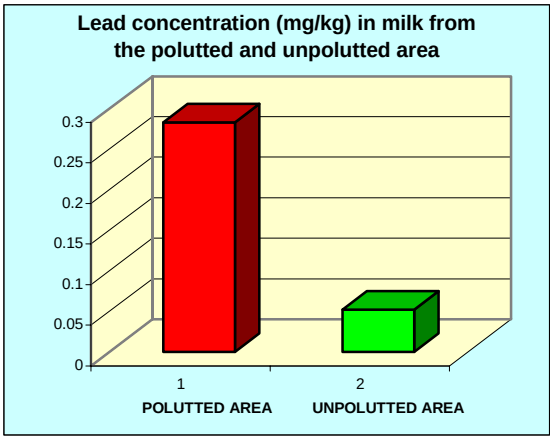
The average of the milk samples from the cows in the polluted area exceeded the maximum limit allowed by 2.42 times, the statistic difference between those two lots of milk samples being very significant.

In milk samples collected from the polluted area the results obtained exceeded the maximum limit allowed by 0.1 mg / kg as established by the Order of the Ministry of Health 975/1998 for 24 samples.

The lead's elimination through milk is made, especialy, by a protein fraction in the proportion of 90 - 96%. The cows' grazing in the polluted areas near the industrial pollutants units can cause the contamination of milk with lead and cadmium The lead transfer in milk is not made immediately, it is realised in time [5].

The obtained results are represented in chart number one, as follows:

Chart No 1

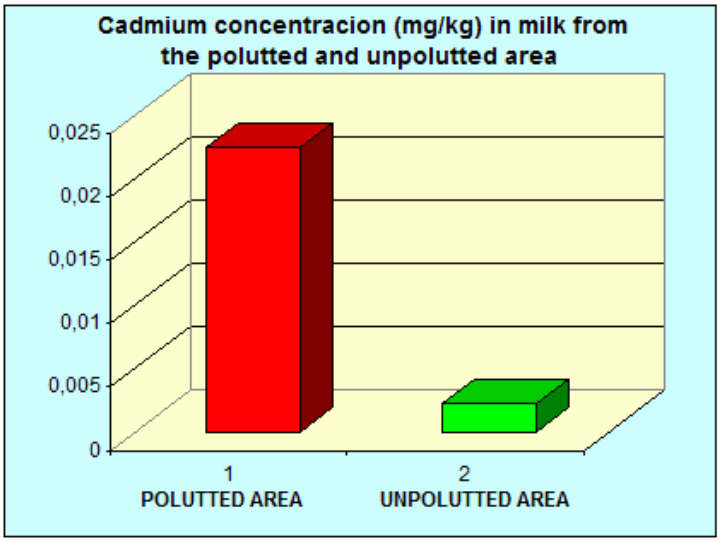


The cadmium concentration in the milk sample from the polluted area was never situated under the MLA of 0.01 mg / kg, set by the Order of the Ministry of Health 975 / 1998[3], all samples exceeding this worth, the average being of 0022 ± 0008 mg / kg (between 0012 - 0042 mg / kg exceeding the MLA 1.2 times or 4.2 times respectively), compared to a witness sample who was 0002 ± 0002 mg / kg (between 0 - 0.0069), the statistic difference between those two lots of milk samples being very significant.

Cadmium is present in milk in particular related to the protein fraction of the proportion of 72%. Distribution of cadmium in the milk remains at a very low value in blood 5-10% which does not meet the high values even in case of a high intake [2]

The obtained results are represented in the chart number 4 as follows:

Chart No 2

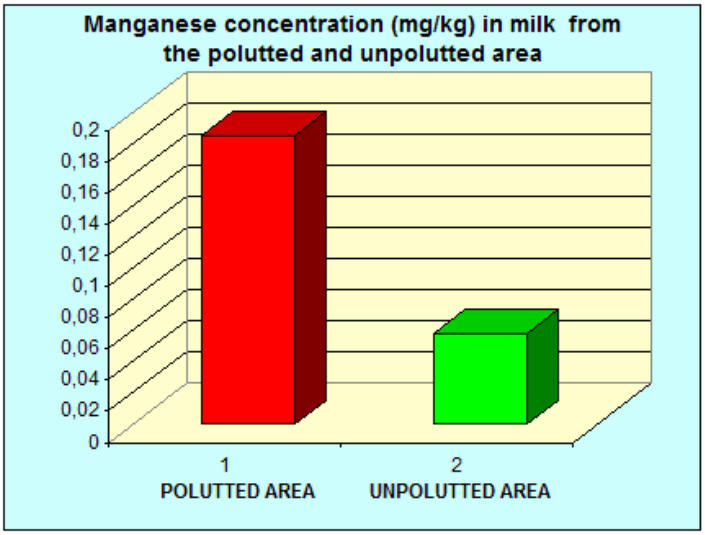


Manganese concentration in the samples of milk collected from the polluted area was 0185 ± 0016 mg / kg (between 0148 - 0216 mg / kg) compared to samples of milk collected from the witness area in the area that was 0058 ± 0090 mg / kg (with values in the 0011 - 0048 mg / kg).

Although for manganese, The Ministry of Health [3] does not stipulate MLA compared to the values considered normal 0.02 mg / kg [1] average level of the evidence that the milk in the unpolutted area is exceeded on average by 2.9 times the milk samples from the polluted area the environment of the normal concentration exceeds by 9.25 times the statistical difference between the two lots of samples of milk, thus being highly significant[3]

The obtained results are represented in chart number three as follows:

Chart No 3

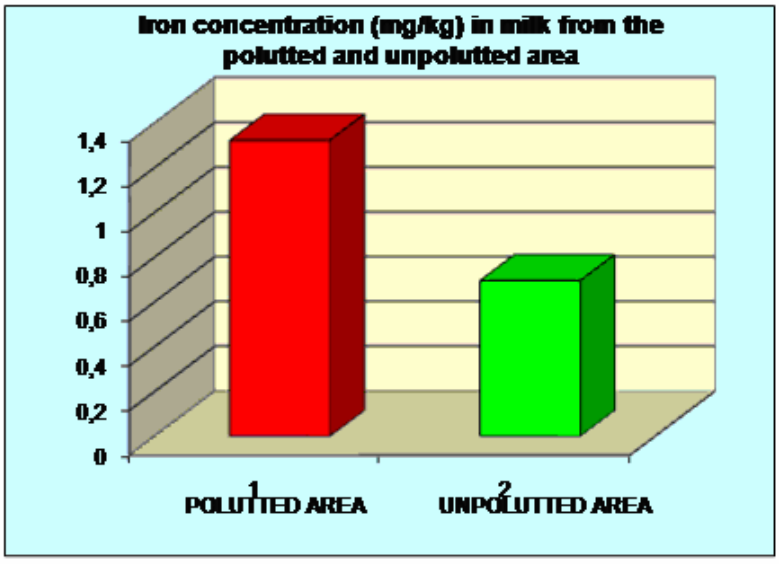


Concentration of iron in the lot of samples taken from the polluted area was 1321 ± 0149 mg / kg (between 1112 - 1651 mg / kg) versus a lot of samples taken from the witnesses who were 0694 ± 0145 mg / kg (worth between 0478 - 0971). The Ministry of Health Order[3] does not provide AML for this item.

Cow's milk is a food poor in iron, he found the regular cow's milk in quantities of 0450 - 0650 mg / kg[8]. Compared with these,the values considered as a normal amount of iron in cow's milk collected from the polluted area was higher by 1.71 - 2.54 times in the unpolutted area and this was exceeded by 1.49 times, the statistical difference between the two groups was very significant .

The obtained results are represented in the chart number four, as follows:

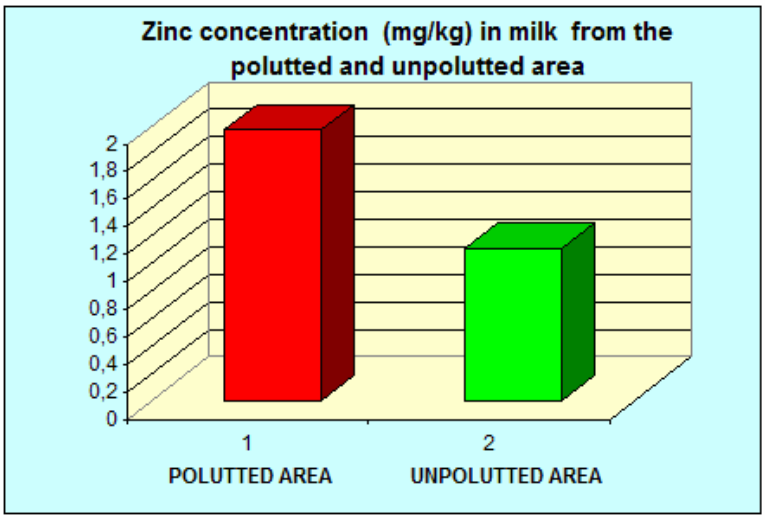
Chart No 4



Zinc concentration has not presented any evidence from the milk lot of samples collected from the area regarded as polluted and the unpolutted values over MLA provided by the The Ministry of Health Order [4]. Non-milk samples from polluted area was 1970 ± 0449 mg / kg (between 1287 - 2981 mg / kg) versus batch of samples of milk collected from the clean area which was 1107 ± 0276 mg / kg (between 0689 - 1628 mg / kg), the statistical difference between the two lots of samples is very significant (***).

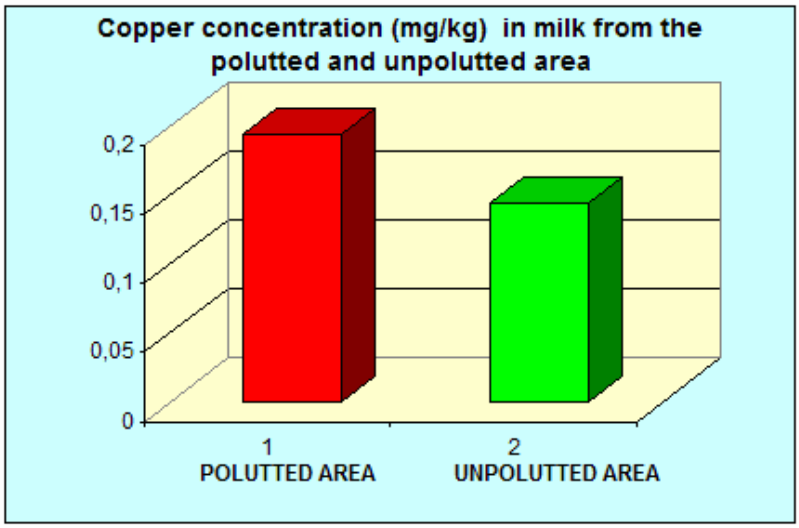
Zinc concentration in the cow milk reflects the amount of zinc in serum and daily intake. The maximum quantity of zinc in milk is the protein fraction of milk [2] and it differs depending on the stage of lactation and breed of cows being higher in the first days postpartum [2].

Chart No 5



Copper concentration in the lot of samples from polluted area was 0194 ± 0035 mg / kg (between 0141 - 0257 mg / kg) versus lot of samples of milk collected from the unpolluted area which was 0144 ± 0031 mg / kg (the limit values was between 0111 - 0268 mg / kg). Neither in this case the copper, was not value over the maximum allowed limit (MLA) provided by the Ministry of Health Order [3]of 0.5 mg / kg, both samples taken from the area and considered polluted area between the statistical unpolluted. Statistical difference between two groups is very significant.

Chart No 6



4. Conclusions

From the analysis of data submitted the following conclusions can be made:

1. Feeding cows with excessive vegetation polluted with heavy metals cause the pollution of the milk with these metals

2. Major pollutants milk in the area of industrial pollution in Baia Mare are represented by lead, cadmium and manganese

3. The average lead concentration in the milk reaches values of 0.242 mg / kg exceeding MLA of 2.42 times

4. The average concentration of cadmium in the milk reaches values of 0022 mg / kg exceeding MLA by 2.2 times

5. The average concentration of manganese reaches values of 0185 mg / kg, exceeding the amounts allowed by technical literature by 9.25 times.

6. Although the concentration of lead and cadmium far exceeds the maximum allowes limits set by the Ministry of Health Order 975/1998, the toxic deficiencies events are not of clear clinical reason because of the many interrealations which can be established with other metals.

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