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Heavy Metals in Common Foodstuff: Quantitative Analysis

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The presence of heavy metals in human body always draws scientific concern as these are considered responsible for affecting health, especially in these days where the release of toxic wastes in the environment has been increased.

Some metals are essential for life, others have unknown biologic function, either favourable or toxic and some others have the potential to produce disease. Those causing toxicity are the ones which accumulate in the body through food chain, water and air (Lucas 1975, Tsoukali et al 1989, Morris 1970).

The purpose of this study is the determination of Pb, Cd, Ni, Mn, Zn in different foodstuff consumed by inhabitants of the city of Thessaloniki, northern Greece, according to their dietary habbits.

MATERIAL AND METHOD

Sampling was performed from the market of the city of Thessaloniki during three years period. For each type of foodstuff, 30 specimens were analyzed. All samples were kept at -4^0 C, while meat and fish at -15^0 C.The groups of foodstuff studied were:

- -Meat (bovine,chicken)
- -Liver (bovine,lamb)
- -Pastes
- -Bread (white, brown)
- -Fish
- -Vegetables (leafy,tomatoes,etc.)
- -Diary (milk,feta cheese,cheese)
- -Fruits (apples, pears)
- -Fruit juices

Before chemical analysis, samples were subjected to pretreatment (Tsalev 1983, Giron 1973, EEC method 1982):

- Twenty grams of each specimen was rinsed with tab water and separated in two. In one of them, Pb and Cd

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Table 1. Mean (n=30) Pb, Cd and Ni concentrations in ppb (± SD) for common foodstuff

No	Foodstuff	Pb	Cd	Ni
1.	Bread (white)	64.6±18.8	49.4±14.1	40.9±10,2
2.	Bread (brown)	63.1±13.6	33.0± 8.9	46.1± 8.7
3.	Pastes	156.3±15,0	62.9±14.0	40.0± 5.7
4.	Beef meat	160.0±56.7	52.5±18.9	75.2±20.1
5.	Beef liver	477.2±35.0	113.2±15.4	87.9± 7.9
6.	Lamb liver	473.9±89.2	178.3±15.3	91.1± 9.3
7.	Chicken	173.4±13.2	25.4± 4.0	81.0± 5.1
8.	Fish	194.1±65.0	47.8±12.4	80.9±20.1
9.	Milk (paster.)	13.6± 2.5	0.9± 0.1	23.0± 5.3
10.	Milk (concen.)	24.5± 2.7	1.5± 0.2	41.6± 4.8
11.	Cheese (feta)	48.1± 5.7	5.0± 1.1	116.3±14.3
12.	Vegetables	146.0±34.7	74.3±17.5	110.3±11.3
13.	Bulbs	174.2±34.5	49.5±22.4	86.9± 8.9
14.	Tomatoes	209.7±33.8	26.3± 3.8	79.6±21.7
15.	Apples	171.2±25.2	22.5± 7.3	61.2± 8.6
16.	Fruit juice	49.8±13.9	10.0± 1.2	23.9± 4.7
17.	Wine dark	210.3±24.4	15.1± 3.0	43.6± 8.2
18.	Wine white	180.6±19.6	15.2± 1.6	39.7± 4.8
19.	Retsina wine	185.2±14.3	13.3± 1.9	27.0± 3.9

Table 2. Mean (n=30) Mn and Zn concentrations in ppm (± SD) for common foodstuff

No	Foodstuff	Mn	Zn
1.	Bread (white)	1.44±0.26	6.89± 1.25
2.	Bread (brown)	2.11±0.33	12.36± 1.31
3.	Pastes	1.48±0.15	9.88± 1.11
4.	Beef meat	0.26±0.07	26.24± 4.19
5.	Liver beef	0.51±0.05	28.31± 3.90
6.	Liver lamb	2.09±0.37	31.86± 2.58
7.	Chicken	0.21±0.02	17.55± 0.63
8.	Fish	0.44±0.12	20.90±14.75
9.	Milk (paster.)	0.07±0,01	4.44± 0.62
10.	Milk (concen.)	0.11±0.01	7.93± 0.58
11.	Cheese feta	0.17±0.02	32.45± 2.11
12.	Vegetables	2.72±0.85	8.41± 1.42
13.	Bulbs	1.77±0.35	3.56± 0.38
14.	Tomatoes	0.50±0.06	3.44± 0.86
15.	Apples	0.22±0.08	0.62± 0.20
16.	Fruit juice	0.12±0.05	0.94± 0.22
17.	Wine dark	0.72±0.15	0.96± 0.37
18.	Wine white	0.27±0.04	0.49± 0.11
19.	Retsina	0.39±0.14	0.60± 0.20

were to be measured and in the other Mn, Zn and Ni.

- Sixty to eighty milliliters of HNO_3 and $HClO_4$ were added with mild increase of temperature till boiling. This wet digestion lasted about 3-4 hours. At the end, 5ml of 30% H_2O_2 were added and heating continued till specimens became clear, Finally, 5ml of ammonium acetate 10% was added and heating at 80^0 C followed.

- Specimens were filtered and diluted with distilled water. Those for Pb and Cd determination, were adjusted to pH 3 with ammonium hydroxide.Four ml of APDC 1% was added with vigorous shaking for 2 min to allow complex formation and with 5ml of MIBK, the complex was removed to the organic layer. Aspiration of the organic layer to Atomic Absorption Spectrometer equiped by graphite furnace (HGA-400) was the next step of procedure. Those for Mn, Zn and Ni were properly diluted and directly aspirated.

Metal measurement was performed with a Perkin-Elmer model 2380 Atomic Absorption Spectrometer, double beam and deuterium background correction. Hollow cathode lamps of Pb, Cd, Mn, Zn and Ni were used at 283.3, 228.8, 279.5, 213.9 and 232.0 nm respectively (Tsoumbaris 1990, Roschnic 1973, Evans 1978). Measurements were done against metal standard solutions.

RESULTS AND DISCUSSION

On tables 1 and 2, mean metal concentrations are presented. For each kind of foodstuff, 30 samples were treated and mean concentration (± SD) is presented. Concentrations are expressed in ppb for Pb, Cd and Ni, while in ppm for Mn and Zn.

Mean concentration (± standard deviation) of 30 specimens per kind of foodstuff and per metal in ppb for Pb, Cd, Ni and in ppm for Mn, Zn are given. Statistic analysis "z test" of data followed (Armitage 1987, Katsougiannopoulos 1990).

The significant deviation from mean value of Zn in fish is mainly attributed to conserved tuna fish in relation to other kinds of fish.

The difference of Pb mean values in brown bread to white one is not statistically significant ($z=0.35$, $0.5<P$). For Cd though, the difference is significant ($z=5.29$, $P<0.001$) being lower in brown bread. For the essential elements Zn and Mn, there are differences ($z=8.51$ and $z=16.23$ respectively, $P<0.001$), higher in brown bread. For Ni there is also, significant difference ($z=2.09$, $0.02<P<0.05$). All these differences in concentrations of toxic and essential metals show that brown bread is healthier than the white one.

Between beef meat and chicken, the difference in Pb mean values is not statistically significant ($z=1.43$, $0.1<P<0.5$). For Cd the difference is significant ($z=8.84$, $P<0.001$) with lower in chicken. For Zn and Mn the differences are significant ($z=12.93$ and $z=3.83$ respectively, $P<0.001$) with lower in beef meat. For Ni the difference is not significant ($z=1.757$, $0.05<P<0.1$).

Between beef meat and fish, Pb mean concentration is significant ($z=2.86$, $0.001<P<0.01$). For Cd the difference is not significant ($z=1.27$, $0.1<P<0.5$). For Mn and Zn the differences are significant ($z=7.46$ $P<0.001$ and $z=1.99$ $P<0.05$ respectively). For Ni the difference is not significant ($z=1.20$, $0.1<P<0.5$).

Between beef meat and liver, all mean values for Pb, Cd, Mn, Zn, Ni are significant ($z=28.48$, $z=10.44$, $z=15.36$, $z=2.09$, $z=3.63$ respectively) being higher in liver.

Between beef and lamb liver, for Pb and Ni the differences are not significant ($z=0.11$, $0.5<P$ and $z=0.94$, $0.1<P<0.5$ respectively). For Cd, Mn and Ni they are significant ($z=11.16$, $z=12.63$, $z=3.13$ respectively $P<0.001$) with higher values in lamb liver. This fact may be attributed to the area of sampling which is located near Mn factories.

Between pasteurized and concentrated milk, the differences of all mean values for Pb, Cd, Mn. Zn and Ni are significant ($z=17.30$, $z=14.47$, $z=13.66$, $z=21.85$ and $z=14.31$ respectively, $P<0.001$) with higher in concentrated milk.

Between pasteurized milk and feta cheese, the differences of all mean values for Pb, Cd, Mn, Zn and Ni are significant ($z=31.50$, $z=20.50$, $z=24.89$, $z=69.33$ and $z=33.42$ respectively, $P<0.001$) with higher concentrations in cheese. Also, Ni and Zn in cheese are in much higher levels than in milk probably due to packing.

Between green vegetables and bulves, the differences of all mean values for Pb, Cd, Mn, Zn and Ni are significant ($z=3.13$, $z=4.73$, $z=3.66$, $z=17.85$ and $z=8.91$ respectively, $P<0.001$) with higher in greev vegetable besides Pb.

Similar results appear between green vegetables and tomatoes ($z=6.88$, $z=14.67$, $z=14.23$, $z=15.89$ and $z=6.53$ respectively for Pb, Cd, Mn, Zn, Ni $P<0.001$) with higher in green vegetables, besides Pb.

Between fruit and juices, the differences are significant ($z=21.71$, $z=8.63$, $z=4.98$, $z=5.35$, $z=19.63$ respectively for Pb, Cd, Mn, Zn, Ni $P<0.001$) with higher in fruits besides Zn.

Between dark and white wine, the differences for Pb, Mn, Zn, Ni, are significant ($z=4.79$, $z=14.24$, $z=6.04$, $z=2.06$ respectively, $P<0.001$, $0.02<P<0.05$), with higher in dark wine. For Cd the difference is not significant ($z=0.15$, $0.5<P$).All differences between dark wine and retsina are significant ($z=4.46$, $z=2.57$, $z=8.00$, $z=4.71$, $z=9.22$ respectively, $P<0.001$, $0.01<P<0.02$) being higher in dark wine.These differences are attributed to the way of preparation.

It can be generally said that for Pb and Cd the highest concentrations appeared in liver and the lowest in pasteurized milk. For Mn, the highest concentration appeared in salads and brown bread, while the lowest in milk and fruit juices. For Zn, the highest concentrations appeared in cheese, meat, liver and fish, while the lowest in fruit, fruit juices and wines. Finally, for Ni, the highest concentrations appeared in cheese and salads, while the lowest in pasteurized milk and fruit juices.

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