MINERAL BALANCE IN FOOD - A FOOD QUALITY, ANIMAL WELFARE AND ENVIRONMENTAL ISSUE

Liliana TUDOREANU, Mario D. CODREANU, Elena ROTARU, Victor CRIVINEANU, Gheorghe V. GORAN, Laura POP

Interdisciplinary Laboratory for Heavy Metals Accumulation in the Food Chain and Modeling (HEVMETFOOD), University of Agronomic Sciences and Veterinary Medicine of Bucharest, Romania

Corresponding author email: liliana tudoreanu223@hotmail.co.uk

Abstract

Data over 20 to 40 years showed historical decline in the mineral content of food and feed plant from USA and UK rising questions on the evolution of the environment quality and its implication on human and animal wellbeing. Although the "intensive varietal improvements of vegetable crops for high yield and improved nutritional quality are primary breeding objectives of various national and international programs little attention have been paid to below threshold concentrations of pollutants in soils, such as Cd, which may significantly influence the mineral concentrations in vegetable crops and pasture plants. Over the years the mineral status of pasture and feed crops were found to be insufficient for a balanced nutrition of farm animals and to support high yields of produces of animal origin. Therefore feed supplements are provided to farm animals,, however it is unclear how these practices support animal welfare and are generating a healthier food.

A survey of the mineral status of foods of animal and plant origin marketed in the Bucharest areas, mineral status of milk produced in farms near Bucharest and pot experiments for lettuce plants (2001-2003) were conducted between 2008 and 2012. The aim of the survey and experiments were to bring into light information on the mineral status of food for the population leaving in the Bucharest area and to better understand how the environment quality is influencing the mineral balance in food and the wellbeing of humans and animals.

Keywords: food, minerals, survey.

INTRODUCTION

Devare et all (2011) mentioned that —minerals are the basic spark-plugs in the chemistry of life, on which the exchange of energy in the combustion of foods and building of living tissues depend". Metals present in the body in trace concentrations carry out a large number of enzymatic reactions. Thus their deficiency or overdose can cause severe disorders in different metabolic pathways. The minerals are interrelated with each other, as well as being linked with the metabolism of proteins, carbohydrates, fats, and vitamins.

Cunningham et al, 2005 and Mayer, 1997 observed historical declines (for data over 20 to 40 years) in the mineral content of food from USA and UK (i.e. K in potatoes from 650mg/100g in 1948 to 450mg/100g in 1991 and to 380mg/100 in 2000).

Much effort have been put into the identification of the pathways of potentially

toxic metals such as Cd and Pb in the food chain and for the characterization of their influence on plants development and toxicity too. Moreover a large number of studies were developed to quantify the effects of the accumulation of potentially toxic metals in humans and animals. In 2010 the JECFA (Joint FAO/WHO Expert Committee on Food Additives) reviewed its previous evaluation of cadmium accumulation in humans. As a result, the JECFA withdrew its previous PTWI (provisional tolerable weekly intake of 7 μg/kg b.w. and established a provisional tolerable monthly intake (PTMI) of 25 µg/kg body weight (b.w). The JECFA concluded that the tolerable dietary intake should be expressed as a monthly value because of the long half-life of cadmium. This PTMI corresponds to a weekly intake of 5.8 µg/kg b.w. The dietary cadmium exposure (µg/kg b.w. per day) that equates to a concentration of 5.24 µg cadmium/creatinine in urine (break

point) was estimated to be 1.2 µg/kg b.w. per day at the 5th population percentile, 0.8 and 1.8 µg/kg b.w. per day, corresponding to the break point CI 4.94-5.57 µg cadmium/g creatinine in urine, respectively. The JECFA used the lower bound of 0.8 µg/kg b.w. per day as critical dietary intake to account for particularly susceptible individuals to ensure that 95 % of the population will maintain urinary cadmium levels with 95 % probability below 5.24 µg cadmium/g creatinine, i.e. -below the point at which renal pathology is increased B2M levels" indicated by (FAO/WHO, 2011).

Although the effect of minerals on cadmium accumulation in organisms is well documented the balance of minerals in the human diet was not taken into account for the previous calculations.

.Worldwide -intensive varietal improvements of vegetable crops for high yield and improved nutritional quality are primary breeding objectives of various national and international programs" little attention have been paid to below threshold concentrations of pollutants in soils, such as Cd, which may significantly influence the mineral concentrations in crops and thus the total mineral intake for humans. Several food nutritional value databases are available worldwide among which the USDA Nutrient Data Laboratory, Health Canada and the Danish Food Composition Databank (Department of Nutrition, National Food Institute, Technical University of Denmark). The Canadian Nutrient File database published by Health Canada is a database that reports up to 150 nutrients in over 5807 foods. This database provides entries on values for nutrients such as vitamins, minerals, protein, energy, fat etc, which are updated periodically The usefulness of such databases stems from several issues such as the need for considering the risks of excessive nutrient intakes and establishing upper levels of intake where data exist regarding risk of adverse health effects. The activity for reviewing components and measuring concentrations of food components that may not meet the traditional concept of a nutrient but are of possible benefit to health, or an indicator of animal welfare (Tudoreanu et.al 2011) and environmental quality status is

another important aspect in food mineral concentrations monitoring.

Usually database refers to food produced in a specific country (USA, Canada, Denmark, etc). The main entries to these databases are generally grouped in proximate such as water, energy, protein, total lipid (fat), ash, carbohydrate, sugars (total), fiber; minerals such as Ca, Fe, Mg, P, K, Na, Zn, Cu, Mn, Se, Cr, Ni, I. Other components which are represented in the databases are vitamins, lipids and other components such as alpha and beta carotene, lycopene, Caffeine, theobromine etc. However the databases are very different due to difference in food groups' information and data offered by food group.

Moreover the presence of information on micronutrients total concentrations will provide valuable data for studies population's heath consuming traditional foods. For some population categories the consumption of high quantities of traditional foods such as common beans (Phaseolus vulgaris L.) is very common. It has been reported that Phaseolus vulgaris L. may also produce negative dietary effects such as interference with micronutrient absorption, protein digestibility or glucose metabolism (Doria et al., 2012). Therefore information on micronutrients concentrations in food may be valuable to scientist studying the link between clinical pathology and mineral nutrition as well, and might generate the reconsideration of the provisional tolerable monthly intake for toxic metals such as Cd and Pb.

MATERIALS AND METHODS

Between 2008 and 2012 were analyzed over 800 samples of food commodities which were considered having the highest acceptability and to be most frequently bought such as: bread, meat, meat products, eggs, milk and milk products, legumes vegetables, fruits and drinks (wines, beer and soft drinks) including water, were All the samples were bought from the Bucharest local markets and supermarkets. In all sample the total concentration of 24 minerals was measured. The total mineral concentrations were analyzed by ICP OES and ICP-MS.

For the dairy products 1ml of milk or yogurt was digested in a microwave oven as described by (Gerber et al, 2008). A Thermo XS series2 ICP-MS spectrometer was used for the total minerals concentration analyses in meat, fish and beverage samples. The operating conditions for Thermo XS series 2 ICP-MS were: Sample uptake 40s; Washout Sample uptake;: 0.7 l/min; 60s; Runs 3; Sampling depth 15mm; Sampler 1.0mm, Ni Skimmer 0.4, Ni; Internal standard 103Rh; Neb. 1,9 bar; Spike recoveries from 80% to All operating conditions optimized to yield the highest signal/ background ratio for ⁹Be, ¹¹⁵In, ²³⁰U, ⁵⁵⁶Fe, ²⁰⁹Bi, ¹⁴⁰Ce, ¹⁵⁶CeO, ⁷⁵As, ²⁷Al. Prior to analysis each sample was spiked with the internal standard (Rh). The dilution factor for each sample is 10. All elements were determined against external calibration using synthetic standard acid multielemental standard (24 elements MS standard MERCK). Four standards were prepared by dilution containing 1ppb, 10ppb, 100ppb and 1000ppb of the 24 elements. The accuracy of the calibration was assessed by using reference materials such as NIST SRM 1546 and SRM1577b.

Milk, yogurt, eggs and bread were analysed by ICP-OES spectrometry (Thermo series). The operating conditions were 27.12 MHz, Rf=1.5 Kw, Ar flow 14 l/min, integration time 5-3 sec, Spectral range 200-800 nm. Theree standars were used 0.001ppm, 0.1ppm şi 50ppm from The standars were obained from a merck standard of 1000mg/l containing: Al, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, Li, Mg, Mn, Ni, Pb, Se, Sr, Te, Tl and Zn.

A pot experiment to test the mineral status of letuce plants cultivated on subtrates containing Cd was conducted. The experiment and sample analyses were describe in details elsewere (Tudoreanu, 2004).

RESULTS AND DISCUSSIONS

The international food nutritional value database do not always include the concentrations of potentially harmful elements such as Cd, Pb, however some databases (the Danish database) included the concentrations of Cr and Ni and other elements

concentrations such as Pb, Cd and Al (The British diary database). The three international databases mentioned in this paper (table 1) do not contain information on Sr concentrations in foods. The analyses conducted include and macronutrients micro as well potentially harmful minerals such as Cd and Pb as well as Sr and Co. We believe that a clear picture of the influence of the mineral content of foods on human health may be found only if data on major nutrients (micro and macro nutrients) are known in relation to the potential harmful elements concentrations. (Tudoreanu et al. 2011). The impact on human health of these foods will also be influenced by overall quantity of each food groups in the daily diet.

Cobalt is an essential trace mineral that is a constituent of vitamin B12 and which plays a cofactor role for making the thyroxine hormone. Another mineral which is less studied as possible micronutrient is Ni. Nickel is associated lately with vitamin C. and also been linked to skin allergies or dermatitis. Iit is also thought to be a factor in lipid and hormone, cel1 membrane metabolism. Insulin response is increased after ingesting nickel, which may be related to its activation of enzymes associated with the breakdown or utilization of glucose.

However a very few international database gives information on the total concentration of Ni and no database gives information on Co in food and feed

Table 1. Comparison between the available data on minerals concentrations in foods which are available from international food databases and from the Romanian survey data.

National abase for eference,	Food	survay
USDA Nutrient Data Standard R. Release 24 [.	Danish Composition Databan [].	2008-2012 (Bucharest markets)
Ca Fe Mg P	Ca Fe Mg	Ca
Fe	Fe	Fe
Mg	Mg	Mg
P	P	P
K	P K	K
Na	Na	Na
Na Zn	Na Zn	Fe Mg P K Na Zn Cu
Cu	Cu	Cu
Mn	Mn	Mn

USDA National Nutrient Database for Standard Reference, Release 24 []	Danish Food Composition Databan [].	2008-2012 survay (Bucharest markets)
Se	Se	Se
-	Se I	Cr
-	Cr Ni	Ni
-	Ni	Co
-	-	Sr
-	-	Al
-	-	Se Cr Ni Co Sr Al Cd Pb
-	-	Pb

Data obtained on milk and yogurt during the survey (mean values) are presented in table 2. Although many food nutritional value databases are available none of them is offering information on microelements such as Co and B.

Table 2. Mean value of survey data for the period 2009-2012 for yogurt, milk, fish (carp trout and pike), pork meat and white bread samples.

Ele- me nt	Yogurt (ppm) wet weight	Milk (ppm) wet weight	Fish (ppb) wet weight	Pork (ppm) wet weigh basis	Whitebr ead (ppm) dry weight
Li	0.00546	<0.001-	527.03	<0.001	<0.001-
Be	0.00004	<0.001-	-<0.001	< 0.001	<0.001-
В	0.33367	0.278	348.74	< 0.001	<0.001-
Mg	6.122	3.695	< 0.001	25.782	0.711
Al	0.40988	0.0862	660.377	<0.001-	0.572
Cr	0.01325	0.0186	35.547	-<0.001	<0.001-
Mn	0.02385	0.01385	136.767	0.0278	0.0134
Fe	503.0244	0.0634	611.450	0.795	0.0705
Со	0.00221	0.00072	4.644	<0.001-	<0.001-
Ni	0.01596	0.0218	21.224	<0.001-	<0.001-
Cu	246.92406	0.0631	654.727	0.178	0.0061
Zn	900.80057	0.2711	470.173	1.376	0.045
Se	0.02727	0.0058	2.254	0.086.	< 0.001
Sr	0.04879	0.0256	69.519	1	0.05
Cd	0.00584	0.0136	277.82	0.063	< 0.001
Pb	0.0489628 57	0.0507-	58.063	0.02	< 0.001
Ba	0.07434	<0.001-	<0.001-	< 0.001	< 0.001
Tl	0.00002	-<0.001	<0.001-	< 0.001	< 0.001
Bi	0.0019275 71	-<0.001	-<0.001	<0.001	<0.001

Strontium was present in brine cheese, eggs from local traditional private farms, and in root vegetables but not in honey (Tudoreanu et.al., 2012), however further investigations are needed to elucidate the source of its presence and the level; that were detected.

Milk from cows farmed near Bucharest showed a large variability in minerals among individuals and the mineral decline in Ca or other elements were related to the individual pathology (table 3).

Usually mastitis is associated with reduced intake or quality of grass or silage; unpalatable herbage (reduced intake on certain paddocks, sometimes associated with high quality but low fiber). An adequate diet containing sufficient Vitamin E and Se and Zn reduce the incidence of subclinical mastitis in some deficient herds For dairy cows apart from hypomagnesaemia, mineral deficiency may cause poor milk yield, and occasionally deficiency of P, Na, Cu, Se, I or Co may be involved too. If the levels of Cu, Se, I, Zn, Co or P are low in blood samples there are risks of developing mastitis.

Letuce (Brasiliana cv) plants cultivated on substrates containing below threshold total cadmium concentration (1ppm dry weight) had a significant decrease of total mineral content after 45 days from planting although they had the total Cd concentration in leaves largely below the maximum admissible limit (table 4). These results are supporting the ideas developed by the open letter of Cheryl Long (1999), the Senior Editor of Organic Gardening (Rodale Press), addressed to USDA Secretary Dan Glickman who raised the question: -Is Chemical Farming Making Our Food less Nutritious? —(James and Phillip, 2000). The letter mentioned two studies which show that the vitamin and mineral content of American and British food appear to be declining. One of these studies (Mayer 1997) -eompared British data over a fifty year period -significant reductions" in the levels of minerals in fruit and vegetables and questioned if modern agriculture could be responsible for the reduction" (James and Phillip, 2000).

The Diminishing Nutritional Values of Australian Grown Fruit and Mineral nutritional value of vegetables comparison between 1948 and 1991 by the C.S.I.R.O.

showed a clear decline in mineral concentrations too. A survey of minerals in Australian food have been conducted for the period 1990-2000. In 2001 Australian media reports (Patty 2001, Moynihan 2001) raised questions about whether or not nutrient levels in Australian horticultural produce are

declining due to changing soil conditions and horticultural practices.

Up to date no attempt was made to generate complex data on the total diet mineral nutritional value and on the implication of minerals and potentially toxic metals on health

Table 3. Mineral content of milk from dairy cows farmed near Bucharest

Element	Mean concentration (mg/l)	Median concentration (mg/l)	Std Err Mean (mg/l)	Upper 95% Mean (mg/l)	Lower 95% Mean (mg/l)	Min (mg/l)	Max (mg/l)	FAO/ OMS (mg/l)
Ca	1058.00	1074.83	47.61	1157.02	959.01	601.571	1487.582	1250
K	1449.96	1563.89	55.48	1565.25	1334.88	673.554	1711.532	1300-1500
Fe	2.89	1.62	0.75	4.46	1.33	0.31	14.90	0,5
Cu	0.77	0.23	0.34	1.48	0.06	0.11	6.60	600
Li	0.24	0.12	0.09	0.43	0.05	0.06	1.80	
Mg	139.27	133.30	6.47	152.75	125.80	70.00	227.70	90-240
Mn	0.05	0.03	0.01	0.07	0.03	0.00	0.16	10-40
Na	541.49	438.40	72.54	692.34	390.63	269.60	1759.50	350-500
Pb	0.33	0.31	0.03	0.40	0.26	0.05	0.69	20-80
Cd	0.06	0.04	0.017	0.10	0.02	0.01	0.40	1-20
Co	0.15	0.14	0.01	0.18	0.11	0.00	0.33	0,4-1,1
Se	0.43	0.44	0.04	0.52	0.34	0.00	0.81	
Sr	0.41	0.37	0.03	0.47	0.34	0.24	1.00	
Zn	3.847	3.84	0.16	4.19	3.50	2.35	5.35	3-5

Table 4. Minerals and cadmium concentration in leaves of Brasiliana lettuce plants, after 45 from planting. Daily mean temperature: 22C to 39C. In brackets the standard error. Values from each row followed by the same letter are not significantly different for α =0.05 (all pairs Tukey –Kramer and Each pair Student's tests). No comparison between values from different rows can be made. T1, T3. T10 are treatments of the substrate.

Treatment	Control	T1	T3	T10	ANOVA
		(1ppm added Cd	(3ppm added Cd in	(10ppm added Cd	p value
Element		in the substrate)	the substrate)	in the substrate)	_
Cd (ppm DW)	0.4800 b	0.5775 b	2.4025 b	7.3400 a	0.0001
	(0.0500)	(0.0594)	(0.2050)	(1.1766)	
Ca (% DW)	1.3150 a	1.2000 a	0.9425 b	1.1525 a	0.006
	(0.0050)	(0.0385)	(0.0201)	(0.0815)	
K(% DW)	8.4500 a	6.1250 b	7.4750 b	5.1750 a	0.002
	(0.4500)	(0.5297)	(0.3816)	(0.2393)	
P (% DW)	0.6100 a	0.4000 b	0.3325 с	0.4825 d	0.009
	(0.0700)	(0.0244)	(0.0246)	(0.0540)	
Cu (ppm DW)	6.3000 a	4.9500 a	3.9500 с	5.0750 b	0.003
	(0.5106)	(0.0500)	(0.0500)	(0.4714)	
Mg (% DW)	0.4000 a	0.3300 a	0.2670 с	0.3600 ab	0.0003
	(0.0011)	(0.0070)	(0.0110)	(0.0160)	
Mn (ppm DW)	42.5000	39.2500	34.5000	41.2500	0.18
	(2.5000)	(2.5290)	(0.9574)	(5.4371)	
Fe (% DW)	631.500	917.250	661.500	937.500	0.69
	(106.50)	(281.54)	(34.71)	(257.69)	

CONCLUSIONS

The survey conducted between 2008 - 2012 on food commodities from local Bucharest markets revealed that Sr, Co and Ni concentration in foods as well as Cd, Pb,

concentrations should be taken into consideration for food surveys and food nutritional value databases as they may influence the metabolism of other minerals. Data from the xperiments conducted on lettuce plants in 2001-2003 showed that there

is a clear decline of minerals concentration in plants gorn on substrates containing less than 1ppm of total cadmium concentration in soil (1ppm wet weight). Unfortunately historical databases on minerals concentrations and potentially toxic metals in food of animal and vegetal origin are not available in Romania. However many valuable data exists from Romanian published research before 1990 but their collection and organization in historical food database is a costly and time consuming activity. However during the last decade many Romanian publications reported mineral content of locally produced food all over Romanian. Comparison of food mineral nutritional value data from the Bucharest region with data from other Romanian areas will be a valuable tool in evaluating the trends in the evolution of the environment quality and to identify the influence of food and feed quality on human and animal welfare.

REFERENCES

Cunningham JH, Milligan G., Trevisan L. 2004. Minerals in Australian fruits and vegetables – a comparaison of levels between the 1980's and 2000. Food Standards Australia, New Zealand

Doria E., Campion B., Sparvoli F., Tava A., and Nielsen E. (2012). Anti-nutrient components and metabolites with health implications in seeds of 10 common bean (*Phaseolus vulgaris* L. and *Phaseolus lunatus* L.) landraces cultivated in southern Italy. Journal of Food Composition and Analysis Volume 26, Issues 1–2, May–June 2012, Pages 72–80

Duizer L.M, James B., Corrigan V.K., Feng J, Hedderley D.I. and Haker F.R.(2011). Use of a panel knowledgeable in material science to study sensory perception of texture. Journal of texture Studies nr. 42 p 3009- 3011

Gerber N, Brogioli R, Hattendorf, B., Scheeder M.R.L., Wenk C., and Gunther D. (2009) Valability of selected trace elements of different meat cuts

determined by ICP-MS and DRC-ICPS . Animal. 3:1, pp166-172 Print ISSN 1843-5246; Electronic ISSN 1843-5386

Hartkopp, H.B., Hess Ygil, K., Hels, O.H.:Danish (2008). Food Composition Databank, revision7. Department of Nutrition, National Food Institute, Technical University of Denmark

James W. L. and Phillip B. 2000 . Are Depleted Soils Causing a Reduction in the Mineral Content Of Food Crops?. Annual Meetings of the ASA/CSSA/SSSA, Nov 5-9, 2000, Minneapolis MN.

Mayer, A-M. (1997). Historical changes in the mineral content of fruits and vegetables: a cause for concern?. p. 69-77 In W. Lockeretz, (ed). Agriculture Production and Nutrition: Proc. Sept 1997. Tufts University.

1. Moynihan, R. (2001). The value of the vegetable – the debate over the declining nutrients in fruits and vegetables. Australian Financial Review, 21 July 2001, p 25

Patty, A. (2001). Test for goodness. Fruits and vegetables in the spotlight. Daily Telegraph, 13 October, p 12

Saxholt, E., Christensen, A.T., Møller, A. Hartkopp, H.B., Hess Ygil, K., Hels, O.H.: (2009).The official Danish Food Composition Database

Tudoreanu L.(2004). Cercetari cu privire la acumularea cadmiului si influenta acestuia asupra plantelor de salata. Teza doctorat.(USAMVB).

Tudoreanu L., Codreanu M, Crivineanu V, Goran Gh. (2012). The Quality of Romanian Honey Varieties - mineral content and textural properties. Bulletin UASVM Agriculture, 69(2)/

Tudoreanu L., Codreanu M, Goran Gh, Crivineanu V. (2011). Plant-animal models for heavy metals accumulation in agricultural systems. Simpozionul FMVB Iasi. Lucrarii stiintifice Medicina Veterinara .vol 53(12), ISSN 1454-7406

Tudoreanu L., Codreanu MD, Crivineanu V, Goran GV, (2011), Modeling heavy metals transport and accumulation in plat-animal systems, Ed. Printech.

***Danish Food Composition Databank,(2008) revision Department of Nutrition, National Food Institute, Technical University of Denmark. 2008.

***International Food Composition Tables Directory. United Nations University. International Network of Food Data Systems (INFOODS).