RESIDUAL DISTRIBUTION OF LEAD, CHROMIUM AND COBALT IN DAIRY PRODUCTS AND THEIR BY-PRODUCTS MANUFACTURED FROM MILK SPIKED WITH THESE METALS

Hiba S. Al-Naemi
Department of Veterinary .Public Health, College of Veterinary Medicine, University of Mosul, Mosul ,Iraq

(Received 7 January 2018,Accepted 21 January 2018)

Keywords: Lead, Chromium, Cobalt, Dairy products.
Corresponding author E.mail: HSnaemi@yahoo.com

ABSTRACT

The research study the distribution patterns and residues behavior of Pb, Cr and Co between dairy products [yoghurt, cheese and fatty dairy products (kishfa, Gaymer and cream)] and their by-products (whey and skim milk) manufactured from experimentally polluted raw ewė s, buffalȯ s and coẇ s milk were investigated using Atomic Absorption Spectrophotometer (AAS). The studied metals (Pb, Cr and Co) were concentrated in both cheese and fatty dairy products (kishfa, gaymer and cream) as they recorded concentration factors in cheese produced from raw ewė s, buffalȯ s and coẇ s milk of 3.849, 3.466 and 2.452, 3.804, 2.938 and 2.342 and 2.995, 2.682 and 2.336 folds, respectively and 3.693, 3.164 and 2.339, 3.347, 2.773 and 2.242 and 2.601, 2.156 and 2.14 folds, respectively in kishfa, gaymer and cream produced from raw ewė s, buffalȯ s and coẇ s milk compared with metals concentrations reported in raw milk used for preparing these products, whereas the by-products of cheese and fatty dairy products processing (whey and skim milk, respectively) contained Pb, Cr and Co concentrations lower than these present in raw milk as they recorded reduction levels of 71.6, 58 and 31.7, 63.7, 39.5 and 27 and 31.4, 20 and 9.5%, respectively in whey and 37.3, 29.9 and 12.1, 41.7, 27 and 19.3 and 21.3, 7.8 and 5.2%, respectively in skim milk. Yoghurt processed from the raw ewė s, buffalȯ s and coẇ s milk contained Pb, Cr and Co metals at mean concentration levels similar to and slightly less than those found in raw milk as the reduction levels amounted 0, 0.6 and 1, 0.1, 0.7 and 1.4 and 0.6, 0.8 and 1.9%, respectively. Generally, metals exhibited significant differences ($p<0.05$) in their distribution and residues behavior in dairy products and their by-products and comparable to raw milk used in processing as they arranged as

follows: cheese> fatty dairy products (kishfa, Gaymer and cream)> raw milk> yoghurt> skim milk> whey, except yoghurt and raw milk which difference was not significant ($p<0.05$). Also, metals found in studying dairy products in the order of Pb > Cr > Co, in contrast to their by-products as they arranged reversibly. Finally, metals concentrated in cheese and kishfa produced from raw ewė s milk, in addition to cheese and gaymer produced from raw buffalȯ s milk at levels significantly higher ($p<0.05$) than those present in cheese and cream produced from raw coẇ s milk.

INTRODUCTION

Milk is a complete food that is widely consumed by children, adults and elderly people around the world, both in its original form and as various dairy products(1). Although milk is a good source of proteins, fats, sugar, vitamins, macro elements (Ca, K and P) and microelements (Cu, Fe, Zn and Se), it can carry numerous xenobiotic substances causing serious problems, both for the consumer health and for the related commercial image (2). Milk and dairy products can be a source of toxic metals due to environmental pollution with these metals, consumption of lactating animals to contaminated feed stuffs and water, in addition to the possibility of contamination through manufacturing and packaging processes (3). Metals are ubiquitous in the environment and human may be exposed to them via various pathways, especially food chain. Among them, Lead, chromium and cobalt may pollute dairy animals feeds, water and environment, the thereafter milk from these animals may constitute a threat to human health due to their toxic effects when exceeding the safe levels (4).

Lead is a major environmental pollutant (5) and has been mostly implicated in human and animal poisoning (6,7,8,9). In the dairy industry, One of the main sources of milk contamination with lead may be originated from metal vessels used for transporting milk to dairy factories (10). Furthermore, dairy product contamination with lead mostly arises from contamination of containers (11,12). Acute lead poisoning occurs by the ingestion of a large single dose of soluble lead salts (8). A cumulative poisoning can occur through regular ingestion of relatively small concentrations of lead for long periods and represent the greater problem of chronic poisoning (13). Lead is known to cause inhibition of the red blood cell synthesis. It is also affecting other organs, such as bone marrow, liver, nervous system, reproductive tissues, and kidney. Furthermore, lead cause injuries to mental development with reduction in intelligence, growth and cognitive function (9). In experimental animals, carcinogenic, mutagenic and teratogenic effects can be developed (14,15,16).

Chromium is ubiquitous in nature, occurring in air, water, soil and biological systems. It can be entered into the environment from industrial wastes and other sources as painting, plating, cooling tower waters and chromate production (17). Leather industry, inks and steel processing are also sources of contamination (18,19). Chromium is an essential metal for both humans and animals, but its excessive intake or intake exceeding the permissible limit may lead to poisoning in both of them. As other heavy metal toxicity, signs of chromium poisoning represented with depression, inappetance, diarrhea, dyspnoea, paralysis and death within few hours. Pathological changes in the lungs, kidneys and liver are found in cases of intoxication. Genotoxic and carcinogenic effects also has been reported with hexavalent chromium poisoning (20,21,22,23,24,25).

Cobalt may reach to our environment from both natural sources and human activities. Air, water, soil, rock, plants and animals naturally contain cobalt. High levels of cobalt may present in soils near ore deposits, phosphate rocks, or ore smelting facilities, (26,27). The main potential source for the general population to cobalt exposure is food which is most of them is inorganic. Children exposure may be happened by eating dirt. Cobalt absorption from foods and liquids in children may be more than adults (28). Cobalt exhibits both beneficial and harmful effects on human and animal health. It is an essential trace metal, as it is an integral part of vitamin B12, which is necessary for folate and fatty acid metabolism , (26,29,30,31,32,33,34). Also, cobalt is genotoxic and as determined by the IARC is possibly human carcinogenic (Group 2B) (28,35,36). In animals, Short-term exposure to high levels of cobalt in the food or drinking water has resulted in effects on the heart, liver, kidneys and blood, while long- term exposure to cobalt at low levels has resulted in effects on behavior and testes, in addition to effects on the tissues mentioned previously (28,37).

Due to the widely consumption of milk and dairy products all over the world and presence of metals in them exceeding the permissible limits represent potential hazards on the public health, so our research aimed to study the residual distribution of lead, chromium and cobalt in these products and their by-products which manufactured from milk experimentally spiked with them.

MATERIALS AND METHODS

Raw ewe̓ s and cow̓ s milk were purchased from the College of Agriculture and Forestry/ University of Mosul. Raw buffalo's milk was purchased from Al-Jazeera dairy factory in Mosul City. Each milk type was packaged in sterile plastic containers and immediately transferred to the laboratory for dairy products manufacturing. Before manufacturing processes, samples from each raw milk type were obtained in duplicate after thoroughly mixing for estimation levels of lead, chromium and cobalt.

Raw ewe̓ s, buffalo̓ s and cow̓ s milk (5 kg for each) were mixed well and 5 ml of standard solutions of lead, chromium and cobalt (1000 ppm) was added. After thoroughly mixing of each milk type with the standards, samples from each milk type were taken in duplicate for metals estimation and the remaining were exposed to manufacturing to some dairy products.

Yoghurt was prepared from raw milk of ewes, buffalos and cows. Milk was heated to 85°C for 30 min. and cooled to 45°C. The starter (1:1 mixture of *S. thermophilus and L. bulgaricus*) at a percentage of 2% was added to milk and incubated at 42°C for 3-4 hours (38).

Soft white cheese was made from raw ewe's, buffalo's and cow's milk after rennet addition, according to the procedure aforementioned by Fahmi and Sharara (39). Salt was not added to prevent the addition of any metals to cheese from it.

Fatty dairy products (cream, kishfa and gaymer) were prepared according to the methods clarified subsequently. Cream was produced from raw cow's milk after it was warmed to (32-38°C) and an electrical separator was used to obtain cream and skim milk. The obtained cream was pasteurized in a water bath at 80-82°C for 25 seconds, then cooled to 10°C or less (38). For kishfa preparation, the forming fat layer was scraped from raw milk of ewes after heating to approximately boiling point and cooling. This process was repeated several times in order to obtain kishfa (scraped fat layer) and skim milk (40). Gaymer which is also called plastic cream was manufactured by boiling of raw buffalo's milk for a minimum of 10 min. Boiled milk was poured into a flat container and cooled to temp. between 15-20°C. The upper fat layer (gaymer) was scrapped after cooling while skim milk remained beneath it (41).

Samples digestion was performed according to (42) with some modifications. Milk, dairy products and by-products samples were oven-dried at 70°C till constant dry weights were obtained. Afterwards, 0.3 g of each dried sample was weighed and digested on a hot plate by adding about 10 ml of 65% nitric acid, followed by the addition of 3 ml of 30% hydrogen peroxide. Samples are heating was persisting to near dryness, then samples dissolved in 30 ml of deionized water and filtered if necessary. The solution was completed to volume in a 100 ml flask and kept in a special container until analysis.

Determination of lead, chromium and cobalt carried out by using of Atomic Absorption Spectrophotometer (GBC SensAA). A specific hollow cathode lamp for each metal was used.

Before use, all laboratory glassware was washed with distilled water, soaked in 10% nitric acid solution for 48 h., then rinsed several times with deionized water and air dried.

The statistical analysis of data was done using Two Way Analysis of Variance procedure of Sigma Stat for windows Version 3.10 (2004) (43). Comparison of means was performed, depending on Duncan's Multiple Range Test at $p<0.05$ (44).

RESULTS

Results included distribution patterns of Pb, Cr and Co and their residues behavior between artificially polluted raw ewė s, buffalȯ s and coẇ s milk used for processing some dairy products, processed dairy products, in addition to their by-products presented significant differences ($p<0.05$) in their distribution and behavior between them with the exception distribution of Pb, Cr and Co between raw ewė s, buffalȯ s and coẇ s milk (0.988, 0.968 and 0.937; 1.006, 0.959 and 0.945 and 0.963, 0.925 and 0.902 mg/kg, respectively) and yoghurt (0.988, 0.962 and 0.928; 1.005, 0.952 and 0.932 and 0.957, 0.918 and 0.885 mg/kg, respectively), distribution of Cr between raw coẇ s milk (0.925 mg/kg), yoghurt (0.918 mg/kg) and skim milk (0.853 mg/kg), Co distribution between raw coẇ s milk (0.902 mg/kg), yoghurt (0.885 mg/kg), whey (0.816 mg/kg) and skim milk (0.855 mg/kg) and distribution of Co between cheese

(2.213 mg/kg) and gaymer (2.119 mg/kg) and between whey (0.690 mg/kg) and skim milk (0.763 mg/kg) produced from raw buffalȯ s milk as differences in metals mean values were not significantly different (p<0.05). Cheese and fatty dairy products (kishfa, gaymer and cream) manufactured from raw ewė s, buffalȯ s and coẇ s milk showed metals level significantly higher (p<0.05) than that recorded in raw milk. The concentration levels of metals (Pb, Cr and Co) in cheese were 3.849,3.466 and 2.452; 3.804, 2.938 and 2.342 and 2.995, 2.682 and 2.336 folds higher than those found in raw ewė s, buffalȯ s and coẇ s milk, respectively. Kishfa, gaymer and cream reported Pb, Cr and Co concentration levels of 3.693, 3.164 and 2.339; 3.347, 2.773 and 2.242 and 2.601, 2.156 and 2.14 folds more than levels recorded in raw ewė s, buffalȯ s and coẇ s milk, respectively. On the other hand, yoghurt and by-products of cheese and fatty dairy products (whey and skim milk, respectively) presented metals level lower than those found in raw milk, except Pb level in yoghurt prepared from raw ewė s milk showed mean concentration level resemble to that found in raw milk. The reduction levels for metals (Pb, Cr and Co) in yoghurt manufactured from raw ewė s, buffalȯ s and coẇ s milk were 0, 0.6 and 1; 0.1, 0.7 and 1.4 and 0.6, 0.8 and 1.9%, respectively, whey reported Pb, Cr and Co reduction levels of 71.6, 58 and 31.7; 63.7, 39.5 and 27 and 31.4, 20 and 9.5%, respectively, while skim milk recorded metals reduction levels of 37.3, 29.9 and 12.1; 41.7, 27 and 19.3 and 21.3, 7.8 and 5.2%, respectively. Regardless of animal species and type of studied metal, metals were significantly more concentrated (p<0.05) in cheese (2.865 mg/kg), then fatty dairy products (2.609 mg/kg), yoghurt contained metals at concentration (0.947 mg/kg) not significantly different (p<0.05) from that found in raw milk (0.955 mg/kg), where skim milk and whey contained the least metals content as mean concentrations (0.738 and 0.576 mg/kg, respectively) were significantly different (p<0.05) between them and from those present in raw milk and studied dairy products. So from the obtained results, metals presented significant differences (p<0.05) in their distribution patterns and residues behavior in dairy products and their by-products and comparable to raw milk used in their manufacturing as they found as follows: cheese> fatty dairy products (kishfa, gaymer and cream)> raw milk > yoghurt> skim milk> whey, with the exception of yoghurt and raw milk which was not significantly different (p<0.05).

Concerning metals levels in each dairy product and by-product, results displayed that Pb, Cr and Co in yoghurt showed no significant differences ($p<0.05$) in mean values between them in the product made from raw milk of the same and different animal species, except mean value of Pb in the product made from raw buffalȯ s milk (1.005 mg/kg) and Co in the same product made from raw coẇ s milk (0.885 mg/kg) which difference in values was significantly different ($p<0.05$). In cheese produced from raw ewė s, buffalȯ s and coẇ s milk, significant differences ($p<0.05$) in the mean values of the examined metals were reported, with the exception levels of Pb (3.803 and 3.827 mg/kg) and Co (2.298 and 2.213 mg/kg) in the product manufactured from raw ewė s and buffalȯ s milk, respectively and levels of Cr and Pb (2.818 and 2.884 mg/kg, respectively) in the product manufactured from raw buffalȯ s and coẇ s milk recorded no significant differences ($p<0.05$) between them. Levels of Pb and Cr in the by-product of cheese (whey) processed from raw ewė s milk revealed significant difference ($p<0.05$) in their mean concentrations (0.281 and 0.407 mg/kg, respectively) between them and others while no significant difference ($p<0.05$) was observed comparable with the mean concentration of Pb in the whey obtained from cheese processed from raw buffalȯ s milk (0.365 mg/kg). No significant differences ($p<0.05$) in the level of Co (0.640 mg/kg) in whey obtained from cheese processed from raw ewė s milk comparable to the levels of Cr and Co (0.580 and 0.690 mg/kg, respectively) in the same by-product obtained from cheese processed from raw buffalȯ s milk and with the levels of Pb and Cr (0.661 and 0.740 mg/kg, respectively) also in the same by-product obtained from cheese processed from raw coẇ s milk were reported. In addition, level of Cr (0.580 mg/kg) in the whey obtained from cheese, processed from raw buffalȯ s milk versus the level of Pb (0.661 mg/kg) in the whey obtained from cheese processed from raw coẇ s milk and level of Co (0.690 mg/kg) in the whey obtained from cheese processed from raw buffalȯ s milk versus the level of Pb (0.661 mg/kg) in the whey obtained from cheese processed from raw coẇ s milk showed no significant differences ($p<0.05$). Pb and Cr levels (0.661 and 0.740 mg/kg, respectively) in the whey obtained from cheese processed from raw coẇ s milk, also Cr and Co levels (0.740 and 0.816 mg/kg, respectively) in the same by-product, recorded no significant differences ($p<0.05$) between them. Fatty dairy products (kishfa, gaymer and cream) made from raw ewė s, buffalȯ s and coẇ s milk, respectively presented significant differences ($p<0.05$) in metals mean concentrations, except Co mean concentrations in kishfa and gaymer made from raw ewė s and buffalȯ s milk (2.192 and 2.119 mg/kg, respectively) and mean concentrations of Cr and Co (1.994 and 1.930 mg/kg, respectively) in cream made from raw coẇ s milk reported no significant differences ($p<0.05$) between them. Results of Pb in skim milk obtained from kishfa and gaymer produced from the raw ewė s and buffalȯ

produced from raw ewė s milk showed no significant differences ($p<0.05$). No significant differences ($p<0.05$) between Pb level (0.620 mg/kg) in skim milk obtained from kishfa produced from raw ewė s milk and Cr level (0.7 mg/kg) in skim milk obtained from gaymer produced from raw buffalȯ s milk, also between Cr level (0.679 mg/kg) in skim milk obtained from kishfa produced from raw ewė s milk, Cr and Co levels (0.7 and 0.763 mg/kg, respectively) in skim milk obtained from gaymer produced from raw buffalȯ s milk and Pb level (0.758 mg/kg) in skim milk obtained from cream produced from raw coẇ s milk. Co levels in skim milk obtained from kishfa and gaymer produced from raw ewė s and buffalȯ s milk (0.824 and 0.763 mg/kg, respectively) and Pb, Cr and Co levels (0.758, 0.853 and 0.855 mg/kg, respectively) in skim milk obtained from cream produced from raw coẇ s milk showed no significant differences ($p<0.05$) among them. As a result, metals found in the dairy products under study in the order of Pb > Cr > Co, comparable to their by-products where they arranged reversibly (Table 1).

Results reported in table (2) showed that studied metals (regardless of metal type) were significantly more concentrated ($p<0.05$) in cheese and kishfa processed from raw ewė s milk (3.152 and 2.968 mg/kg, respectively), yoghurt recorded metals mean concentration of 0.959 mg/kg which was not significantly different ($p<0.05$) from that reported in raw milk (0.964 mg/kg), whereas mean concentration of metals in skim milk decreased significantly ($p<0.05$) as it reached 0.708 mg/kg which was significantly different ($p<0.05$) from that found in whey (0.443 mg/kg) which reported the least concentration. Dairy products and by-products produced from raw buffalȯ s

Table 1:- The mean concentrations (mg/kg) of lead, chromium and cobalt in dairy products and their by-products manufactured from raw ewe's, buffalo's and cow's milk spiked with these metals*.

Raw milk type	Metal type	Raw milk	Yoghurt	Cheese	Whey	Fatty dairy products*	Skim milk
Ewe	Pb	0.988 a	0.988 ab	3.803 c	0.281 i	3.649 r	0.620 dy
	Cr	0.968 a	0.962 ab	3.355 d	0.407 j	3.063 s	0.679 yz
	Co	0.937 a	0.928 ab	2.298 e	0.640 koq	2.192 t	0.824 c
Buffalo	Pb	1.006 a	1.005 a	3.827 c	0.365 ij	3.367 u	0.587 y
	Cr	0.959 a	0.952 ab	2.818 f	0.580 kp	2.659 v	0.7 dz
	Co	0.945 a	0.932 ab	2.213 e	0.690 lo	2.119 et	0.763 clz
Cow	Pb	0.963 a	0.957 ab	2.884 f	0.661 lnpq	2.505 w	0.758 cz
	Cr	0.925 a	0.918 ab	2.481 g	0.740 mno	1.994 x	0.853 ac
	Co	0.902 ab	0.885 b	2.107 h	0.816 bm	1.930 x	0.855 bc
Dairy manufacturing effect		0.955 A	0.947 A	2.865 B	0.576 C	2.609 D	0.738 E

- Horizontally different small letters are significantly different ($p<0.05$).
- Vertically different small letters are significantly different ($p<0.05$).
- Different capital letters within last raw are significantly different ($p<0.05$).

* Metals were added to the milk used for preparation of dairy products at a conc. of 1 mg/kg.

* Kishfa, gaymer and cream processed from raw ewe's, buffalo's and cow's milk, respectively.

milk clarified that the mean value of metals in cheese (2.953 mg/kg) was significantly higher ($p<0.05$) than that found in gaymer (2.715 mg/kg) which was significantly higher ($p<0.05$) than others, yoghurt contained metals at level (0.963 mg/kg) not significantly different ($p<0.05$) from that reported in raw milk (0.970 mg/kg), the least significant metals levels??? ($p<0.05$) appeared in skim milk and whey where mean values (0.683 and 0.545 mg/kg, respectively) were not significantly different ($p<0.05$) among them. Raw cow̓ s milk used for preparation of dairy products and by-products under study revealed that cheese also recorded the highest metal level (2.491 mg/kg), then cream which contained metals at level (2.143 mg/kg) significantly ($p<0.05$) less than that found in cheese but higher than others, while yoghurt, skim milk and whey presented the lowest metals concentrations??? where mean values (0.920, 0.822 and 0.739 mg/kg, respectively) not significantly different ($p<0.05$) from that reported in raw milk (0.930 mg/kg). In cheese prepared from raw ewe̓ s and buffalo̓ s milk, metals were significantly more concentrated ($p<0.05$) (3.152 and 2.953 mg/kg, respectively) than that present in cheese prepared from raw cow̓ s milk which reported mean concentration level of 2.491 mg/kg, where metals concentration factors were 3.27, 3.044 and 2.678 folds, respectively more than those in raw milk. Kishfa prepared from raw ewe̓ s milk appeared metals concentration (2.968 mg/kg) significantly higher ($p<0.05$) than that found in gaymer and cream prepared from the raw buffalo̓ s and cow̓ s milk (2.715 and 2.143 mg/kg, respectively) where they also reported significant difference ($p<0.05$) between them and presented metals concentration factors of 3.079, 2.799 and 2.304 folds, respectively more than that in raw milk. Yoghurt processed from raw ewe̓ s, buffalo̓ s and cow̓ s milk presented metals mean concentrations (0.959, 0.963 and 0.920 mg/kg, respectively) not significantly different ($p<0.05$) among them and recorded metals reduction levels of 0.5, 0.7 and 1.1%, respectively than that found in raw milk. The by-product of cheese making (whey) produced from raw buffalo̓ s milk showed mean concentration of metals (0.545 mg/kg) significantly similar ($p<0.05$) to those found in whey obtained from cheese manufactured from raw ewe̓ s and cow̓ s milk (0.443 and 0.739 mg/kg, respectively) where they reported significant difference ($p<0.05$) between them and presented metals reduction levels of 54, 43.8 and 20.5% in this by-product obtained from cheese manufactured from raw ewe̓ s, buffalo̓ s and cow̓ s milk, respectively, whereas skim milk obtained from kishfa, gaymer and cream prepared from raw ewe̓ s, buffalo̓ s and cow̓ s milk showed no significant differences ($p<0.05$) in metals mean concentrations (0.708, 0.683 and 0.822 mg/kg, respectively) and reported metals reduction levels of 26.6, 29.6 and 11.6%, respectively than that reported in raw milk.

Table 2:- The mean concentrations (mg/kg) of metals in dairy products and their by-products processed from raw ewe's, buffalo's and cow's milk spiked with these metals.

Raw milk type	Raw milk	Yoghurt	Cheese	Whey	Fatty dairy products	Skim milk
Ewe	0.964 a	0.959 a	3.152 b	0.443 d	2.968 b	0.708 h
Buffalo	0.970 a	0.963 a	2.953 b	0.545 de	2.715 f	0.683 hd
Cow	0.930 a	0.920 a	2.491 c	0.739 ea	2.143 g	0.822 ha

- Horizontally different small letters are significantly different ($p<0.05$).
- Vertically different small letters are significantly different ($p<0.05$).

DISCUSSION

Metals residues have gained particular concern due to their ability to bio-accumulate (45). The Behavior of these residues in dairy products and by-products occupies special importance as these products are largely consumed by billions of people around the world every day and their by-products as whey entered in human food industry during the last decades due to nutritional value and the properties of its ingredients (46,47).

Patterns of metals distribution and their residues behavior in manufacturing dairy products and their by-products are changeable depending on the type of metal, milk origin, product and by-product type, in addition to environmental conditions at the processing sites.

Results showed that yoghurt presented metals level lower than that found in raw milk. (48) showed similar finding and reported Pb reduction level in yoghurt of 37% which was higher than Pb reduction levels presented in our research. Also (49) reported Pb, Cr and Co concentrations in cow's and buffalo's milk of 0.04, 0.026 and 0.002 and 0.062, 0.04 and 0.004 mg/kg, respectively higher than those recorded in yoghurt where they lowered to 0.039, 0.025 and 0.001 and 0.06, 0.038 and 0.003 mg/kg, respectively and recorded Pb, Cr and Co reduction levels in yoghurt produced from cow's and buffalo's milk (2, 3 and 50% and 3,5 and 25%, respectively) higher than those mentioned in our research (0.6, 0.8 and 1.9 and 0.1, 0.7 and 1.4%, respectively). Our results were also in acceptance to those displayed by (50) concerning Cr level in yoghurt which also showed a level lower than that present in raw milk and reported reduction level reached to 15.8% after 10 days of storage which was higher than Cr reduction levels reported in our research. This high percentage in metal reduction level perhaps belongs to yoghurt storage as it responsible for most reduction in metal level specially in the first 5 days of storage, in addition to the presence of metal at low level in milk and any small loss will lead to rise the percentage of reduction. In relation to Pb level in yoghurt, no reduction was reported comparable to that present in raw milk which was nearly similar to our results that recorded slight Pb reduction levels of 0, 0.1 and 0.6% in yoghurt produced from raw ewe̍ s, buffalo̍ s and cow̍ s milk, respectively. Generally, the reduction in metals concentration in yoghurt may belong to process of manufacturing and usage of starter for fermenting.

Concerning cheese, results revealed that metals were more concentrated in cheese than in milk used for manufacturing it and that whey contained metals at concentrations less than that present in milk. Many studies reflect these findings as (3) exerted Pb and Cr mean levels in ricotta (cheese produced from whey) of 0.391 and 0.32 µg/g, respectively and in fresh caciotta cheese (cheese made from raw ewe's milk) of 0.47 and 0.46 µg/g, respectively higher than those found in ewe's milk used for preparing of these cheese types which reported mean levels of 0.18 and 0.14 µg/g, respectively (as Pb concentration factors in ricotta and fresh caciotta cheese 2.17 and 2.61 folds, respectively and 2.3 and 3.3 folds, respectively for Cr than in ewe's milk). Another study presented from (51) also showed that kaşar cheese contained Pb level (1.1 mg/kg) higher than that found in milk powder (0.054 mg/kg), in addition to the study performed by (52) which recorded Pb average concentration of 2.73 mg/kg in pasteurized milk comparable to that present in hard cheese (4.05 mg/kg). Furthermore, (50) pointed that Pb and Cr were more concentrated in domiati cheese (0.112 and

0.305 mg/kg, respectively) than in raw milk used for producing it (0.099 and 0.205 mg/kg, respectively) and whey (0.096 and 0.179 mg/kg, respectively). Milk and manufacturing process used for preparing of each cheese type mainly influenced on the concentrations of certain metals in cheese. This remarkable increase in metals concentration in cheese may be primarily returns to that these metals are preferentially bound to milk proteins specially caseins so they will be transfer mainly to curd during cheese processing (3).

In fatty dairy products (kishfa, gaymer and cream), results referred that metals were detected in these products at concentrations higher than those present in milk used for preparing them and in skim milk which is the by-product of their processing. (53) presented similar results when found that skim milk contained trace levels of metals indicative that metals were concentrated in cream. (49) reported that Pb, Cr and Co concentration levels in cow's and buffalo's milk (0.04,0.026 and 0.002 and 0.062, 0.04 and 0.004 mg/kg, respectively) were lower than those present in cream (0.149, 0.117 and 0.01 and 0.230, 0.180 and 0.018 mg/kg, respectively) and found that Pb and Cr concentration factors in cow's and buffalo's cream were the same 3.7 and 4.5 folds, respectively, whereas Co concentrated in cow's and buffalo's cream 5 and 4.5 folds, respectively than in raw milk which was higher than our results that reported Pb, Cr and Co concentration factors in cream and gaymer processed from cow's and buffalo's milk of 2.601, 2.156 and 2.14 and 3.347, 2.773 and 2.242 folds, respectively. At last, displayed resemble findings when reported Pb and Cr mean values of 0.11 and 0.46 mg/kg, respectively in cram comparable to these reported in milk 0.07 and 0.44 mg/kg, respectively whereas recorded Pb and Cr concentration factors in cream lower than those reported in our research that amounted 1.58 and 1.05 folds, respectively than in initial raw milk. Metals were attached with the protein nitrogen, this complex proteinate will be adsorbed on the fat globule surface construing the reason for metals concentration in cream (54).

In our research, Pb presided metals in its residue concentration in the dairy products, then Cr whereas Co came at last, this perhaps ascribe to presence of variations among metals in their ability to bound to milk proteins and influence by manufacturing processes (50).

Eventually, results showed that metals were arranged in dairy products and their by-products and in comparable to raw milk used in processing in the order of cheese> fatty dairy products (kishfa, gaymer and cream)> raw milk> yoghurt> skim milk> whey and elucidated that metals were existed in cheese processed from raw ewė s and buffalỏ s milk at concentrations significantly higher ($p<0.05$) than those found in the same product processed from raw coẇ s milk, while they were significantly more concentrated ($p<0.05$) in kishfa processed from raw ewė s milk, then in gaymer processed from raw buffalỏ s milk, whereas cream processed from raw coẇ s milk contained the least concentration. (49) were in accordance to some degree to these results when reported that raw milk contained metals at levels higher than yoghurt but lower than cream and referred that metals were concentrated in dairy products processed from buffalo's milk at levels higher than these processed from cow's milk. The variations between ewė s, buffalỏ s and coẇ s milk, dairy products and their by-products in their chemical constituents percentages may explain these results precisely protein and fat percentages, in addition to the variations in the physical and chemical characters of the manufacturing processes of the dairy products .

ACKNOWLEDGMENTS

Author wish to thank the College of Veterinary Medicine, University of Mosul for support and providing facilities. Appreciation is also extended to the Department of General Science, College of Basic Education, University of Mosul for assistance in samples analysis with Atomic Absorption Spectrophotometer.

دراسة توزيع بقايا الرصاص، الكروم والكوبلت في منتجات الألبان ونواتجها العرضية المصنعة من حليب محقون بهذه المعادن

هبة صلاح الدين النعيمي

فرع الصحة العامة البيطرية, كلية الطب البيطري , جامعة الموصل, الموصل، العراق

الخلاصة

تناول البحث دراسة انماط توزيع وسلوك بقايا كل من عناصر الرصاص، الكروم والكوبلت في منتجات الالبان [اليوغرت، الجبن ومنتجات الالبان الدهنية (القشفة، القيمر والكريم)] ونواتجها العرضية (الشرش والحليب الفرز) المصنعة من حليب الأغنام، الجاموس والأبقار الخام والمحقون تجريبيا بهذه المعادن باستخدام جهاز قياس

طيف الامتصاص الذري. اظهرت النتائج تركز المعادن قيد الدراسة في كل من الجبن ومنتجات الالبان الدهنية (القشفة، القيمر والكريم) مقارنة بالتراكيز المسجلة في الحليب الخام لكل من الأغنام، الجاموس والأبقار المستخدم في تحضير هذه المنتجات حيث بلغ تركز المعادن (الرصاص، الكروم والكوبلت) في الجبن المحضر من الحليب الخام للأغنام، الجاموس والأبقار ٣,٨٤٩، ٣,٤٦٦ و ٢,٤٥٢، ٣,٨٠٤، ٢,٩٣٨ و ٢,٣٤٢ و ٢,٩٩٥، ٢,٦٨٢ و ٢,٣٦٦ مرة، على التوالي و ٣,٦٩٣، ٣,١٦٤ و ٢,٣٣٩، ٣,٣٤٧، ٢,٧٧٣ و ٢,٢٤٢ و ٢,٦٠١، ٢,١٥٦ و ٢,١٤ مرة، على التوالي في القشفة، القيمر والكريم المحضرين من الحليب الخام للأغنام، الجاموس والأبقار، في حين احتوت النواتج العرضية للجبن ومنتجات الالبان الدهنية (الشرش والحليب الفرز، على التوالي) على الرصاص، الكروم والكوبلت بتراكيز اقل من تلك المسجلة في الحليب الخام حيث وصلت نسبة الانخفاض الى ٧١,٦، ٥٨ و ٣١,٧، ٦٣,٧، ٣٩,٥ و ٢٧ و ٣١,٤، ٢٠ و ٩,٥%، على التوالي في الشرش و ٣٧,٣، ٢٩,٩ و١٢,١، ٤١,٧، ٢٧ و ١٩,٣ و ٢١,٣، ٧,٨ و ٥,٢%، على التوالي في الحليب الفرز. اليوغرت المصنع من حليب الأغنام ،الجاموس والأبقار الخام احتوى على المعادن (الرصاص، الكروم والكوبلت) بمستويات مشابهة واقل قليلا من تلك المتواجدة في الحليب الخام حيث بلغت نسبة الانخفاض ٠، ٠,٦ و ١، ٠,١، ٠,٧ و ١,٤ و ٠,٦، ٠,٨ و١,٩%، على التوالي. على العموم، فان المعادن اظهرت وجود فروقات معنوية ($p<0.05$) في توزيعها وسلوكها التراكمي في منتجات الالبان ونواتجها العرضية وبالمقارنة مع الحليب الخام المستخدم في تصنيعها متمركزة بالترتيب الاتي: الجبن> منتجات الالبان الدهنية (القشفة، القيمر والكريم)> الحليب الخام> اليوغرت> الحليب الفرز> الشرش، يستثنى من ذلك اليوغرت والحليب الخام اللذين لم يكن الفرق بينهما معنويا ($p<0.05$). تواجدت المعادن في منتجات الالبان بالترتيب الاتي: Pb> Cr> Co، في حين ترتيب عكسيا في نواتجها العرضية. وأخيرا، فان المعادن تركزت في كل من الجبن والقشفة المحضرين من الحليب الخام للأغنام، بالإضافة الى الجبن والقيمر المحضرين من الحليب الخام للجاموس بمستويات اعلى معنويا($p<0.05$) من تلك المتواجدة في الجبن والكريم المحضرين من الحليب الخام للأبقار.

REFERENCES-

1-**Licata, P., Trombbeetta, D., Cristani, M., Giofre, F., Martino, D., Calo, M. and Naccari, F**. (2004). Levels of toxic and essential metals in samples of bovine milk from various dairy farms in Calabria, Italy. Environ. Int. 30: 1-6.

2-**Drewnowski, A. and V. Fulgoni** (2008). Nutrient profiling of foods: creating a nutrient-rich food index. Nutr. Rev. 66: 23-39.

3-**Anastasio, A.; R. Caggiano.; M. Macchiato; C. Paolo; M. Ragosta; S. Paino and M.L. Cortesi** (2006**).** Heavy Metal Concentrations in Dairy Products from Sheep Milk Collected in Two Regions of Southern Italy. Acta. Vet. Scand. 47, 69-74.

4-**Montoro, R. and D. Velez** (2004). Detecting metal contamination. In: Watson, D.H. ed. Pesticide, veterinary and other residues in food. Woodhead Publishing Limited, Cambridge, England. pp: 610-640.

5-**Flora, S.J.S.; G.J.S. Flora and G. Saxena** (2006). Environmental occurrence, health effects and management of lead poisoning. In: Cascas, S.B. and J. Sordo, editors. Lead: Chemistry, Analytical Aspects, Environmental Impacts and Health Effects. Elsevier Publication, Netherlands. pp: 158–228.

6-**Liu, Z.P.** (2003). Lead poisoning combined with cadmium in sheep and horses in the vicinity of non-ferrous metal smelters. Scient. Total Environ. 309:117-126.

7-**Ozmen, O. and F. Mor** (2004). Acute lead intoxication in cattle housed in an old battery factory. Vet. Hum. Toxicol. 46: 255-256.

8-**Omaye, S.T.** (2004). Food and Nutritional Toxicology. CRC Press LLC, Boca Raton. pp: 163-173.

9-**Rubio, C.; I. Frias and A. Hardisson** (1999). Lead toxicology and its presence in food. Alimentaria. 305: 77-85.

10-**Azcue, J.P.M.; W.C. Pfeifer; C.M. Donangeio; M. Fiszman and O. Malm** (1988). Heavy metals in foods from the Paraiba do Sul Valley, Brazil. J. Food Comp. Anal. 1:250-258.

11-**Cabrera, C.; M.L. Lorenzo and M.C. Lopez** (1995). Lead and cadmium contamination in dairy products and its repercussion on total dietary intake. J. Agric. Food Chem. 43 (6): 1605-1609.

12-**Belgaied, J.E.** (2003). Release of heavy metals from Tunisian traditional earthenware. Food Chem. Toxicol. 41 (1): 95-98.

13-**Kosanovic, M.; M.Y. Hasan; D. Subramanian; A.F. Al-Ahbabi and A.O. Al-Kathiri** (2007). Influence of urbanization of the western coast of the United Arab Emirates on trace metal content in muscle and liver of wild red-spot emperor (*Lethrinus lentjan*). Food Chem. Toxicol. 45: 2261-2266.

14-**Bolger, M.; C. Carrington; J.C. Larsen and B. Petersen** (2000). Safety evaluation of certain food additives and contaminants: lead. WHO Food Addit. Series. 44: 273-312.

15-**Khaniki, Gh.R.J.** (2007). Chemical Contaminants in Milk and Public Health Concerns: A Review. Int. J. Dairy Sci. 2 (2): 104-115.

16-**Pitot, C.H. and P.Y. Dragan** (1996). Chemical carcinogenesis. In: Casarett and Doull's Toxicology. 5th ed. International Edition, Mc Graw Hill, New York. pp: 201-260.

17-**Paustenbach, D.J.; B.L. Finley; F.S. Mowat and B.D. Kerger** (2003). Human health risk and exposure assessment of chromium (VI) in tap water. J. Toxicol. Environ. Health Part A. 66 (14): 1295-1339.

18-**IULTCS (International Union of Leather Technologists and Cosmetics Societies)** (2004). IUE assessment for chromium containing waste from the leather industry published by IUE Commission.

19-**ATSDR (Agency for Toxic Substances and Disease Registry)** (2000). Toxicological profile for Chromium. U.S. Department of Health and Human Services, Public Health Service.

20-**Ellis, E.N.; B.H. Brouhard; R.E. Lynch; E.B. Dawson; R. Tisdell; M.M. Nichols and F. Ramirez** (1982). Effects of hemodialysis and dimercaprol in acute dichromate poisoning. J. Toxicol. – Clin. Toxicol. 19(3): 249-58.

21-**Saryan, L.A. and M. Reedy** (1988). Chromium determinations in a case of chromic acid ingestion. J. Anal. Toxicol.12 (3): 162-164.

22-**IARC (International Agency for Research on Cancer)** (1990). Monographs on the evaluation of carcinogenic risks to humans. Chromium, Nickel and Welding, International Agency for Research on Cancer, Lyon, France. 49.

23-**Cohen, M.D. and M. Costa** (2000). Chromium. In: Lippmann, M. ed. Environmental toxicants: human exposures and their health effects. Second edn, Wiley-Interscience, New York. pp: 173-191.

24-**Medeiros, M.G.; A.S. Rodrigues; M.C. Batoréu; A. Laires; J. Rueff and A. Zhitkovic** (2003). Elevated levels of DNA-protein crosslinks and micronuclei in peripheral lymphocytes of tannery workers exposed to trivalent chromium. Mutagenesis. 18 (1): 19-24.

25-**Pechova, A. and L. Pavlata** (2007). Chromium as an essential nutrient: a review. Vet. med. 52: 1-18.

26-**ATSDR (Agency for Toxic Substances and Disease Registry)** (2004). Toxicological profile for cobalt. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

27-**VKM (Vitenskapskomiteen for mattrygghet)** (2007). Risk assessment of health hazards from nickel, cobalt, zinc, iron, copper and manganese migrated from ceramic articles. Opinion of the Panel on Food Additives, Flavourings, Processing Aids, Materials in Contact with Food and Cosmetics of the Norwegian Scientific Committee for Food Safety adopted on 2 May 2007 (05/407-3 final). http://www.vkm.no/eway/default.aspx?pid=0&oid=-2&trg=__new&__new=-2:15799

28-**WHO (World Health Organization)** (2006). Cobalt and inorganic cobalt compounds. Concise International Chemical Assessment Document 69. World Health Organization, Geneva. http://www.who.int/ipcs/publications/cicad/cicad69%20.pdf

29-FSA (Food Standards Agency) (2003). Safe Upper Levels for Vitamins and Minerals, Expert Group on Vitamins and Minerals, Food Standards Agency, UK. http://www.food.gov.uk/multimedia/pdfs/vitmin2003.pdf

30-**Barceloux, D.G.** (1999). Cobalt. J. Toxicol. Clin. Toxicol. 37:201-6.

31-Elbirt, K.K. and H.L. Bonkovsky (1999). Heme oxygenase: recent advances in understanding its regulation and role. Proc. Assoc. Am. Phys. 111: 438-447.

32-**Maxwell, P. and K. Salnikow** (2004). HIF-1: an oxygen and metal responsive transcription factor. Cancer Biol. Ther. 3: 29-35.

33-**Thierse, H.J.; K. Gamerdinger; C. Junkes; N. Guerreiro and H.U. Weltzien** (2005). T cell receptor (TCR) interaction with haptens: metal ions as non-classical haptens. Toxicology. 209: 101-7.

34-**Lison, D.** (2007). Cobalt. In: Nordberg, G.F.; B.A. Fowler; M. Nordberg and L.T. Friberg. Handbook of the toxicology of metals. 3rd Ed. Elsevier-Academic Press, Amsterdam. pp:511-528.

35-**De Boeck, M.; M. Kirsch-Volders and D. Lison** (2003). Cobalt and antimony: genotoxicity and carcinogenicity. Mutat. Res. 533: 135-52.

36-IARC (International Agency for Research on Cancer) (2006). Monographs on the evaluation of carcinogenic risks to humans. Cobalt in hard metals and cobalt sulfate, gallium arsenide, indium phosphide and vanadium pentoxide. International Agency For Research On Cancer, Lyon, France. 86.

37-**Pedigo, N.G.; W.J. George and M.B. Anderson** (1988). Effects of acute and chronic exposure to cobalt on male reproduction in mice. Reproductive Toxicol. 2: 45-53.

38-**Alsafar, Th.A.; R.S. Alhamadani and M.E. Alomar** (1982). Liquid milk, 1st ed.

39-**Fahmi, A.H. and H.A. Sharara** (1950). Studies on Egyptian Domiati cheese. J Dairy Res. 17: 312-327.

40-**Aljawadi, I.M.S.** (1983). Kishfa and yoghurt properties processed from sheep milk. MSc thesis. College of Agriculture and Forestry, Mosul University, Mosul, Iraq.

41-**Baqir, A.W. and M.A. Munir** (1980). Microbiological study on local thick cream (gaymar) retailed in Basrah. The Arab gulf. 12 (12): 131

42-**AOAC (Association of Official Analytical Chemists)** (2000). Official Methods of Analysis International. 17th Ed. Washington D.C., USA.

43-**Steel, R.G. and J.H. Torrie** (1980). Principles and procedures of statistics: A biometrical approach. 2nd ed. Mc Graw-Hill, New York.

44-**Duncan, D.B.** (1955). Multiple range F-test. Biometrics. 11: 1-42.

45-**McCalley, M**. (2002). Life support: The environment and human health. MIT Press. pp: 65-83.

46-**Pearce, R.J.** (1992). Whey protein recovery and whey protein fractionation. In: Zadow, J.G. ed. Whey and lactose processing, Elsevier Science Publications, London.

47-**Huffman, L.M.** (1996). Processing whey protein for use as food ingredient. Food Technology 50.

48-**Bordajandi, L.R.; G. Gomez.; E. Abad.; J. Rivera.; M. del Mar Fernandez-Baston; J. Blasco and M.J. Gonzalez** (2004). Survey of persistent organochlorine contaminants (PCBs, PCDD/Fs and PAHs), heavy metals (Cu, Cd, Zn, Pb and Hg) and arsenic in food samples from Huelva Spain: Levels and health implications. J. Agric. Food Chem. 52: 992-1001.

49-**Enb, A.; M. A. Abou Donia; N. S. Abd-Rabou; A. A. K. Abou-Arab and M. H. El-Senaity** (2009). Chemical composition of raw milk and heavy metals behavior during processing of milk products. Global Veterinaria. 3 (3): 268-275..

50-**Elsayed Elham, M.; M. B. Sanaa; A. M. Amr and A. H. Ahmed** (2011). Evaluation of the factors influencing the content and retention of selected heavy metals in milks and some dairy products. Int. J. Dairy Sci. 6 (6): 305-313.

51-**Ayar, A.; D. Sert and N. Akin** (2009). The trace metal levels in milk and dairy products consumed in middle Anatolia—Turkey. Environmental Monitoring and Assessment. 152 (1-4): 1-12.

52-**Gradinaru, A.; O. Popescu and G. Solcan** (2011). Variation analysis of heavy metal residues in milk and their incidence in milk products from Moldavia, Romania. Environ. Engineering & Management J. (EEMJ). 10 (10): 1445.

53-**Abou-Arab, A.A.K.** (1991). Microbiological and compositional quality of dairy products in relation to some pollutants. Ph.D. Dissertation, Faculty of Agriculture, Ain-Shams University.

54-**Davies, W.L**. (1933). The mode of combination and distribution of trace of heavy metals in dairy products. J. Dairy Res. 4: 255-264.