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ESTIMATION OF SOME INDUSTRIAL POLIUTANTS IN MILK AND MILK PRODUCTS
(With 7 Tables)

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قياس مستوى بعض الملوثات الصناعية في البان الجاموس الملوثة ومنتجاتها

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إرتبطت الألبان منذ قديم الزمان بحياة الإنسان والحيوان بما تتمتع به من قيمة غذائية عالية وهبها الله إياها ، بالإضافة إلى ذلك فإن لها العديد من المنتجات المرتبطة دوما بالإستهلاك اليومى ، ولما كانت منطقة منقباد والمناطق المحيطة بها تتعرض بصفة دائمة لأخطار التلوث بمخلفات مصانع السوبر فوسفات مما أدى إلى زيادة الملوثات الصناعية بالبان حيواناتها (الفلورين والكبريت) بالاضافة إلى إستخدام هذه الألبان في التصنيع لذا فقد هدفنا إلى دراسة هذه المنتجات المصنعة من الألبان الملوثة والمأخوذه من حيوانات ظهرت عليها الأعراض الإكلينيكية للتسمم وذلك لدراسة مدى تركيز هذه الملوثات الكيميائية في المنتجات المختلفة للألبان لتفادى الأخطار التى قد تنجم من إستعمالها على صحة المستهلك . لذلك فقد تم أخذ عينات من البان الجاموس المصرى المتواجد بمناطق منقباد والطوابية وجزيرة الاكراد بالإضافة إلى مدينة منفلوط كضابط للتجربة بواقع عشر عينات لكل منطقة . وقد تم إجراء الفحوص الطبيعية والكيميائية على العينات الممثلة للمناطق وتم تصنيعها إلى منتجات الزبادى والجبن والقشدة وتم قياس كل من عناصر الفلورين والكبريت والكالسيوم والفسفور والصوديوم والبوتاسيوم في جميع الالبان المفحوصة ومنتجاتها بالإضافة إلى شرش اللبن . وقد أوضحت النتائج أن كلا من الفلورين والكبريت قد إرتفعا إرتفاعاً معنوياً في الألبان المنتجة بالمناطق الثلاث المحيطة بمصانع السوبر فوسفات . كما أفادت النتائج أيضاً عن وجود إرتفاع بين معدلات الفلورين والكبريت في الجبن والقشدة بما يعادل ثلاثة إلى خمسة أمثال المتواجد في الالبان تقريباً على الترتيب . وقد إرتبط هذا الإرتفاع في عنصرى الفلورين والكبريت بنقص ملحوظ في معدلات الكالسيوم والفسفور في الالبان المفحوصة ومنتجاتها بالمقارنة بتلك التى أخذت من الضابط . أما عن نتائج تحليل عنصرى الصوديوم والبوتاسيوم فقد إختلف نسبتيهما في اللبن ومنتجاته . والخلاصة أنه بالرغم من إرتفاع معدلات الفلورين والكبريت في الالبان المفحوصة إلا أنها لاتمثل خطراً كالذى ينبغى أن نتنبه إليه من تصنيع هذه الألبان إلى منتجات الجبن والقشدة حيث تتركز فيه هذه العناصر (الفلورين والكبريت) كه أضعاف الموجود في اللبن تقريباً . كما أن الخطورة لاتتوقف عند هذا الحد بل تمتد الى النقص الواضح في عنصرى الكالسيوم والفسفور بالإضافة إلى خلل في الكتروذات الصوديوم والبوتاسيوم وجميعها من العناصر الهامة في الجسم ولكل الأعمار . ومن هنا ننصح بأنه إذا كان لزاماً إستخدام الألبان الملوثة فليكن بحذر شديد ، ناهيك عن تصنيعه إلى الجبن والقشدة لما بها من أخطار جسام على صحة المستهلك خاصة إذا أخذنا في الإعتبار الدور الهام والخطير الذى يلعبه الهواء والماء والغذاء في زيادة هذه الملوثات الكيميائية .

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SUMMARY

The present study estimate the levels of sulphur and fluorine in buffaloe's milk and their products in three localities (Manquabade, El-Tawabiya and El-Akrad) surrounding the superphosphate factory in Assiut governorate. Related elements as calcium phosphorus, sodium and potassium were also investigated.

The physical examination (colour and flavour) revealed that all examined milk samples were within normal limits. The chemical examination showed a significant decrease in chloride and fat perecentage. Statistical analytical results indicated a significant increase of sulphur (at 0.01 level) in milk, whey, cheese and yoghourt of the three examined areas. Moreover, a significant elevation of fluorine level was recorded in all milk samples and their products, accompanied with significant depletion in both calcium, phosphorus, and sodium, and increase in potassium level.

INTRODUCTION

Contamination of food supply by environmental pollutants is recieving an increasing attention. Attention has been focused on milk, particulary since it is nearly almost the perfect single food stuff as it contains high quality animal protein, butter fat and performed vitamins as well as its richness in minerals specially calcium and phosphorus. In addition to the elements that occur in milk in a relatively large proportions there are a large number of elements usually measured in ppm or ug per litre and reffered as trace elements e.g. copper, cobalt and fluorine. Fluorine is highly reactive element occures in soil, water and forage contaminated with fluorine as an air pollutant from various fluoride emitting industries. Fluorine has been widely reported as a prophylactic agent in the pervention of dental caries.

Interest in the biological significance of fluoride was at first confined to its toxic effects upon animals, following the discovery of chronic endemic fluorosis of man and farm stock in several countries in 1931. The most serious outbreaks of fluorosis are of industrial origin resulting from contamination of pastures by fluorine compounds emitted by industrial factories such as aluminum and superphosphate factories (TAWERS, 1954).

Transfer of fluorine across the mammary gland barrier appears to be small. In endemic fluorisis areas, or where the cows ration has been supplemented with fluorine to moderate levels, values within the normal range and appreciably higher have both been reported in milk (HARVEY, 1952). Evidence has also been produced that suckling rats and pupies subsisting on the milk of fluoride fed mothers accumulate more fluorine in their bodies than do similar animals consuming the milk of mothers on normal diets (MAPLESDEN, et al. 1960).

The total fluoride levels in milk from cows grazing in fluoride contaminated pastures are found to be about twice as high as those in milk from cows on a normal grass (GRREC and PLEBIN, 1986).

DUTOIT, et al. (1937) showed definite indications, that fluorine disturbs the normal metabolism of both calcium and phosphorus.

In subsequent study, IBRAHIM, et al. (1985) recorded the contamination of the environment at the areas surrounding the super-phosphate plant at Manquabade by both fluorine and sulphur. The high sulphur levels in animals feed affected the mucous membranes, gastro-intestinal tract,and central nervous system (WHITE, 1964).

As milk is life food for both newly born animals as well as for human consumption, therefore this study aimed to investigate, to what extent industrial pollution affects milk and milk products constituents (fluorine, sulphur, calcium, phosphorus, sodium and postassium) from buffaloes rearing in the areas surrounding the superphosphate plant Manquabade.

MATERIAL and METHODS

Three localities, (El-Akrad, El-Tawabiya and Manquabade) were studied and the fourth area (Manfaloute) was considered as control. Ten individual milk samples (2 litres each), representing 10 animals, from buffaloes were collected from every locality.

The samples were dispatched to the laboratory without delay and examined physically for colour and flavour (APHA, 1972), chemically for pH value using pH meter (Orion Model 701) equipped with standard electrode. Fat percentage was determined by the method of Gerber (A.P.H.A. 1972). Chloride percentage was done after LING (1963). Lactose percentage (Benedict method) was determined after HARVEY and HILL (1967). Then each milk sample was divided into equal 4 portions, the first three were manufactured according to the method of FAHMY and SHARARA (1950) to cheese and that of LAMPERT (1975) to cream and yoghourt. The fourth portion was used as original milk.

The original milk samples and milk products (cheese, cream and yoghourt) and milk by product (whey) were used for estimation of sulphur (STOCKHOLM and KOCH, 1923), calcium (BETT and FRASER, 1959), sodium and potassium (PEACH and TRACY, 1960), phosphorus (MORINL and PROX, 1973) and fluorine (KROOK and MAYLIN, 1979).

RESULTS

The physical examination (colour and flavour) of all milk samples were within normal limits.

The results of chemical examination, of milk for flourine, sulphur, phosphorus, calcium, potassium and sodium contents were recorded in tables 1, 2, 3, 4, 5, 6 and 7, respectively.

Table (1): Routine chemical examination of milk sample's collected from buffaloes at areas surrounding super-phosphate factory.

	AREAS			
	Control	Manquabade	El-Tawabiya	Ezbet El-Akrad
pH value	6.67 ±0.053	6.522 ±0.0604 *	6.53 ±0.0817 *	6.64±0.047
Lactose	4.25 ±0.098	4.226 ±0.0984	4.100±0.0954	4.13 ±0.0954
Chloride %	0.0767±0.00165	0.0657±0.003 **	0.059±0.0033 **	0.056±0.0047 **
Fat %	8.00 ±0.351	6.142 ±0.146 **	6.00 ±0.50 **	6.50 ±0.372 **

Table (2): Flourine content of investigated buffaloe's milk and its products.

AREA	(ppm)				
	Milk	Whey	Cheese	Yoghourt	Cream
El-Akrad	0.903±0.047 *+	0.573±0.015 **	3.00 ±0.535 **	0.896±0.028 **	2.462 ±0.156 **
El-Tawabiya	0.986±0.078 **	0.595±0.065 **	3.310±0.426 **	0.862±0.039 **	2.689±0.131 **
Manqubade	0.683±0.094 **	0.409±0.045 **	2.300±0.230 **	0.663±0.049 **	1.860±0.065 **
Control	0.233±0.047	0.139±0.009	0.700±0.021	0.197±0.040	0.650±0.015

** Significant at P ∠ 0.01 * Significant at P ∠ 0.05 S.E: Standard error.

Table (3): Sulpher level of investigated buffaloe's milk and its products.

AREA	(ppm)				
	Milk	Whey	Cheese	Yeghourt	Cream
El-Akrad	325.50±44.31 **	122.56±33.51 **	1719.62±19.2.15 **	330.76±32.65 **	76.62±25.00
El-Tawabiya	332.44±17.88 **	188.88±3.51 **	1756.28±211.70 **	342.52±12.30 **	77.55±30.10
Manquabade	226.04±9.42 **	78.28±11.54 **	1194.17±140.58 **	245.60±13.67 **	65.65±26.40
Control	120.00±22.75	45.55±3.76	633.96±100.19	122.25±25.79	35.55±18.63

** Significant at P ∠ 0.01   * Significant at P ∠ 0.05   S.E: Standard error.

Table (4): In-organic phosphorus level of investigated buffaloe's milk and its products.

AREA	(ppm)				
	Milk	Whey	Cheese	Yoghourt	Cream
El-Akrad	585.30±2.72 **	561.40±19.53 **	1351.60±42.88 **	1093.70±18.75 **	1093.80±13.27 **
El-Tawabiya	699.20±10.33 **	494.80±2.72 **	1382.80±32.80 **	1140.60±12.11 **	1135.40±21.67 **
Manqubade	765.6 ±19.90	677.00±14.32	1520.30±30.13 **	1312.50± 9.37	1114.60±46.24 **
Control	750.00± 7.65	703.20± 6.62	1710.90±28.00	1343.80±35.90	1307.80±17.68

** Significant at P ∠ 0.01   * Significant at P ∠ 0.05   S.E: Standard error.

Table (5): Calcium content of buffaloe's milk and its products.

AREA	(ppm)				
	Milk	Whey	Cheese	Yeghourt	Cream
El-Akrad	595.00±12.60 **	406.00±25.00 **	2916.60±161.30 **	600.00±56.00 **	202.30±13.20 **
El-Tawabiya	643.70±15.90 **	302.00±16.50 **	2918.60±110.20 **	659.70±10.90 **	222.50± 9.50 **
Manqubade	512.50± 4.40 **	325.00±27.60 **	2500.00±25.00 **	625.60±78.60 **	232.00± 8.90 **
Control	1366.00±13.08	1182.00±10.40	4027.70±113.60	1289.70±82.4	612.50±21.5

Table (6): Potassium level of buffaloe's milk and its products.

AREA	(ppm)				
	Milk	Whey	Cheese	Yeghourt	Cream
El-Akrad	1719.00± 49.10 **	1101.00±18.99 **	3537.00±171.49 **	2132.00±123.37 **	693.33± 46.31
El-Tawabiya	3316.00±310.33 **	1841.33±32.81 **	4390.00±80. 34 **	2007.00±161.93 **	1148.00±119.20 **
Manqubade	1778.00±123.15	1220.20± 5.00 **	3276.00± 53.04 **	1708.00± 50.96	669.33±15.38
Control	1510.00±21 .55	968.50±25.53	2285.33±50.64	1629.00±60 .59	632.50±25.21

Table (7): Sodium level of buffaloe's milk and its products.

AREA	(ppm)				
	Milk	Whey	Cheese	Yeghourt	Cream
El-Akrad	491.88±44.40 **	231.65±20.94 **	1380.00±47.05 **	436.75±25.60 **	258.0±12.32 **
El-Tawabiya	436.50±10.80 **	221.65±12.13 **	1380.00±79.87 **	393.25±28.20 **	291.00±12.58 **
Manqubade	425.80±24.50 **	310.00±29.40 **	1126.66±53.36 **	411.00± 8.03 **	445.70±46.90
Control	682.50±13.00	557.25±40.00	2047.50±18.18	571.50±19.15	427.70±22.50

* Significant at P $\angle$ 0.05 ** Significant at P $\angle$ 0.01 S.E: Standard error.

DISCUSSION

The measurments of environmental pollutants,in the first instance depends on the area considered control. Therefore, Manfaloute city was chosen for this purpose as it located 18 kilmeters north from the factory. The toxicological studies in this city revealed no clinical signs among animals pointing to exposure to any hazardous substance. The analytical finding of the elements in consideration were proved to be within the normal limits (IBRAHIM, 1983).

The chemical examination of milk samples obtained from the investigated areas (Table 1) revealed the same results of BEDDOWS and BLAKE (1982) that no change in the pH value. A significant decrease in both chloride and fat percentage in comparison with the control were recorded. A simillar decrease was recorded for sodium in examined samples of milk and milk products.

The analytical findings in the three studied localities, revealed a significant irregular elevation in sulphur (Table 3) of milk and its manufactured products (cheese, yoghourt) while cream showed non significant increase. The significant increase in milk sulphur was in agreement with the previous results recorded by IBRAHIM, et al. (1985) and correlated with the results of sulphur level in buffaloe's blood serum in the same area (IBRAHIM, 1983). The largest part of milk sulphur presented as a part of the amino acids methionine and cystine. BLOCK, et al. (1951) demonstrated the synthesis of cystine and methionine in milk protein and serum albumins of animals after feeding sulphate. The constant relation between sulphur and protein clarify the highly significant increase of both copper and molybdenum levels in milk was related to high sulphur content of milk (IBRAHIM, 1985). Rumen microflora reduce sulphur compound into sulphide, subsequent formation of insouble copper sulphide lower the avilability of dietary copper (DICK, 1954). Also sulphate decreases retention of molybdenum by decreasing its absorption by tubular epithelium and inhibits its absorption in the lower ilium (MASON and CARDIN, 1977).

The chemical analysis of milk, cheese, whey, yoghourt and cream, revealed a significant irregular elevation of fluoride in the three examined localities (Manquabade, El-Tawabiya and El-Akrad) in comparison with the control area (Manfloute). Inversely calcium and phosphorus showed a significant decrease. These results were in agreement with that recorded by SHEHATA, et al. (1984) in the area of Manquabade and SHLOSBERG, et al. (1980) in Israel, who recorded fluoride level in milk reach to 0.34 ppm.

Among products manufactured from contaminated milk, cheese and cream were highest. The same results were obtained by GRREC and PLEBIN (1986), who explained this phenomena due to the ability of fluorine to compined with lipid and protein to form a complexed compounds.

Inspite of the previously recorded by BEDDOWS and BLAKE (1982) that the addition of fluoride to milk not affect calcium and phosphorus levels, oppositely our results revealed a marked significant decrease in both elements (tables 4, 5). There is a corresponding decrease of calcium and phospharus in buffaloe's blood serum accompanied by significant intensive rates of excretion. Moreover, fluoride is able to withtrap calcium in urinary excretion even if it highly significant decreased in serum. Phosphates is seriously decreased in serum but not excreted in urine in excess. This could indicate the direct relationship of the three elements. The previous information explain the difference between addition of fluoride to milk in vitro and the metabalism of it inside the animal body in relation to calcium and phosphorus.

In conclusion, the investigation of milk and its products revealed a high concentration of the two pollutants (fluorine and sulphur) specially in cheese 3 to 5 folds of milk. Also, in cream fluoride level was 3 folds of milk. It is deemly necessary to warning about the hazardous effects of these pollutants on both newly born animals and human being in the studied areas. The consuming of such milk and their products considered as an additional source of exposure beside the direct sources of air and water. Moreover, the effect of infant requirements may contribute through distributing the levels of calcium, phosphorus, sodium and potassium in vital foods like milk and milk products.

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