

ARSENIC and VANADIUM LEVELS in COW'S MILK in RELATION to POLLUTION*

Özden ANAL¹

Semra GEZER²

Cevval ULMAN²

İ. Ruhi TÖRE²

Ayşe YENİGÜN³

Nurten ÇELİKER⁴

N. Nevbahar TANELİ¹

Çevre kirliliği ile ilişkili olarak inek sütlerinde Arsenik ve Vanadyum düzeyleri.

ÖZET

Canlılar, birçok elementlerle hem organik, hemde inorganik biçimlere karşı karşıya gelirler. Bu çalışmada, termal aktivite alanlarında, örneğin sıcak su kaynaklarından zengin volkanik yörelerde ve trafiği yüklü karayolları çevresinde otlayan ineklerin sütlerinde, arsenik ve vanadyum düzeyleri araştırılmıştır. Çalışmaya alınan 36 Holstein inekten 30'u (Grup I, II ve III) ilkbahar başlangıcından yaz sonuna kadar, merada, doğal içme suları ve kirli hava koşullarında beslenirken; 6'sı (Grup IV) daha normal çevre koşullarında, kapalı barınaklarda ve sanayi yemleri ile beslenmiş ve şehir şebeke suyu ile sulanmışlardır. Yaz sonunda, iz elementlerden arındırılmış, teflon kapaklı tüplere alınan süt örneklerinde, usulüne göre küllleştirildikten sonra Atomik Absorbsiyon Spektrofotometresinde, arsenik ve vanadyum konsantrasyonları ölçülmüştür.

Kirli havada otlatılan ve yüzey suları verilen grupların birbiriyle ve kontrol grubu ile, sütteki arsenik ve vanadyum konsantrasyonları açısından anlamlı fark göstermemelerine ($P>0.05$) karşın, en büyük sayısal değerler (Ortalama± ortalamının standart hatası, sırasıyla, 4.245 ± 1.141 ng As/ml ve 0.0531 ± 0.0022 ng V/ml), beklendiği üzere, kontrol grubunda gözlenmiştir. En yüksek arsenik değere (4.932 ± 0.38 ng/ml) Grup III'de, en yüksek vanadyum değerine (0.629 ± 0.229 ng/ml) trafik yoğunluğu çok fazla olan bir anayola yakın otlatılan ineklerin (Grup I) sütlerinde rastlanmıştır.

Sonuçlar, lav yatakları ve termal kaynaklar açısından çok zengin olan yöremizde, bunlardan kaynaklanan bir arsenik kirlenmesi buldurmadığını düşündürmektedir. Buna karşın, motorlu araçların oluşturduğu hava kirliliğinin, sütte vanadyum konsantrasyonuna katkı yapabildiği gözlenmiştir.

ANAHTAR KELİMELER: Hava kirliliği, inek sütü, Arsenik, Vanadyum.

INTRODUCTION

Arsenic (As) was considered one of the inevitable contaminants for human beings and domestic animals and is well known as a potent toxin since ancient alchemists (15). It is present in minute amounts in foods, drinking waters and ambient air. Much effort has been devoted to ultra trace elements up to this time. Lately investigators even introduced As and Vanadium (V) as being new ultra trace elements essential for growth (9, 13).

During the last decade, it has been shown that free radicanls are the underlying culprit in many diseased states (7, 14). However, most studies are focused especially on in vivo release of iron (Fe) by a reductive mechanism (5, 10) triggered by several reducing agents, e.g. free radicals, xenobiotics and/or antioxidant, e.g. superoxide dismutase (SOD), glutathion

SUMMARY

Livestock are exposed to many chemical elements, both in organic and inorganic forms. In the present study, we aimed to investigate milk Arsenic and Vanadium levels of cows raised in areas of thermal activity (with extinct volcanoes, thermal baths, hot springs etc.) and at close vicinity to heavy traffic. A total of 36 Holstein cows were taken into study; 30 of them (Groups I, II and III) were let for grazing on pastures on lava ground and watered on natural sources under potential air-borne pollution conditions beginning from early May to the end of September, while 6 were kept in sanitary sheds within the city limits and fed on commercial pellet feeds and watered on city sources. Milk samples were collected into trace element-free teflon tubes with caps, at late summer, and, after wet digestion, they were analyzed by atomic absorption spectrofotometry.

Whilst the differences among the 'pollution groups' which were grazing in air polluted areas and watered with surface waters, and between the 'pollution groups' and the control group were not found significant ($P<0.05$). The lowest numeric Arsenic and Vanadium values (4.245 ± 1.141 ng As/ml and 0.0531 ± 0.0022 ng V/ml, respectively) were encountered in Group IV as expected. The highest Arsenic value was found in Group III being 4.932 ± 0.38 ng/ml, and the highest Vanadium value in Grup I being (0.629 ± 0.229 ng/ml) where the traffic is the heaviest.

Thus, these results show that although the area is on lava land and rich of thermal baths, Arsenic pollution was not important, however, air-borne pollution originated from heavy traffic could be complementary to Vanadium concentration in cows's milk.

KEY WORDS : Air pollution, cows's milk, Arsenic, Vanadium.

peroxidase (Gpx) and vitamins A, C and E, deficiencies (16). Tetravalent V, the vanadyl form, being another reducing agent, reacts with O_2 molecule to generate superoxide radicals (O_2^-).

In addition, vanadyl can induce NADH oxidation and promote biocellular lipid peroxidation; besides, it has the ability to release Fe from ferritin; however, a unique finding is tha while the universal antioxidant, SOD, is not effective in scavenging the vanadyl-released Fe from ferritin, Gpx is found effective (12). Livestock is exposed to many forms of ultra trace elements, in both organic and inorganic forms. Contamination of pastures where cattle graze, and of natural water sources many cause a wide variety of adverse effects on livestock and human beings, accordingly (3). In two recent studies (2, 18), we studied As and V in human milk, too.

In areas of thermal activity (volcanoes-even though extinct-, hot springs and thermal baths) and with smog-laden ambient air, a very high level of pollution could be encountered. Therefore, a study was planned to investigate As and V exposure of cows raising in localities at close vicinity to thermal baths and heavy traffic.

MATERIAL and METHOD

A total number of 36 Holstein cows were taken into study and 30 of them (Groups I, II and III) were let for grazing on pastures within hawthor enclosed hedges and watered by natural sources, under

* : This work was awarded by the 12th National Congress of Biochemistry, 13-16 April 1994, İstanbul, Turkey.

1: Dept. of Pediatrics, Dokuz Eylül Üniv. Fac. of Medicine, İnciraltı 35 340 , İzmir/ TURKEY.

2: Dept. of Biochemistry, Dokuz Eylül Üniv. Fac. of Medicine, İnciraltı-35 340 , İzmir/ TURKEY.

3: Dept. of Pediatrics, Aegean Üniv. Fac. of Medicine, Bornova-35 100, İzmir/ TURKEY.

4: Reserch Laboratory, Aegean Üniv. Fac. of Medicine, Bornova-35 100, İzmir/ TURKEY.

air-borne pollution conditions beginning from early May to the end of September, while a control group of 6 (Group IV) were kept in sanitary sheds within the city boundaries, were fed on commercial pellet feeds and given central city water. During the study period, the temperature was mild (no chimney smoke and soot) and the streets not as crowded as it naturally is in winter months.

Six cows (Group I) were let for grazing on lava ground pastures, at close vicinity to thermal activity, Agememnon thermal baths, Narlıbahçe, and heavy traffic where smog from motor-exhaust makes the area quite hazy at times. Fourteen cows (Group II) on ground pastures on the south-east shore of Gölcük, a crater lake, on the highest mountain, in the Aegean area, Bozdağ; and ten cows (Group III) on pastures at close vicinity to another thermal bath, Bayındır, alongside a highway with a traffic not so heavy as in Narlıbahçe. The heaviness of the traffic was calculated by the mean number of passing vehicles within a given time-morning, noon and evening on the every 15th days of May through September.

Milk samples were collected on the same day in late summer, by directly milking the cows, into trace element-free containers with teflon caps. After wet-ashing procedure, samples were kept at 70 degrees centigrade below zero till time for a batch assaying. Because of limitations related analyzes of biologic materials, only total values of As and V were assessed on a atomic absorption spectrophotometer (AA-680, Schimadzu).

Student's t-test was used for statistical analyzes.

RESULTS

The number of cows in each group, the mean (and standart error of mean, + SEM) total As and V concentrations in cow's milk are shown in Table 1.

Table 1. Arsenic (As) and Vanadium (V) Concentration in Cow's Milk (ng/ml).

| Groups | n | As | ±SEM | V | ±SEM |
|--------|----|-------|------|-------|-------|
| I | 6 | 4.710 | 0.46 | 0.629 | 0.229 |
| II | 14 | 4.457 | 0.49 | 0.627 | 0.114 |
| III | 10 | 4.932 | 0.38 | 0.459 | 0.024 |
| IV | 6 | 4.245 | 1.41 | 0.531 | 0.022 |

The differences between the pollution groups and the controls were found significant ($P < 0.05$) as well as among the pollution groups. However, while lowest values encountered in view of both As and V concentrations, were in the Control Group as expected; the highest values were found in Group IV where the livestock grazed in pastures alongside a highway with the heaviest traffic (Narlıbahçe). The As and V levels were the lowest in Group III- in the location of Gölcük lake being near the highest peak, in the Aegean region, Bozdağ, far away from ambient air.

DISCUSSION

The average amount of As in Earth's crust is known to be around 1.5-2.0 ppm and higher concentrations are particularly found in places of Sulfite and industrial waste deposits (8, 19). Although 97 per cent of ground water have been reported to contain 50 mg/L As in areas of high thermal activity, the hot springs in Searle, Ca. USA and ground waters in Chile, Argentine and Taiwan have been reported to contain much higher As, naturally (4).

With the exception of seafood, As content of foodstuff is found usually less than 1 mg/kg; marine fish could contain 1-10 mg/kg, some crustaceans and shellfish can even contain up to 100 mg/kg (4). In a future study, we are planning to assess As in seafood, e.g. fish, crayfish, mussels, sea urchin, caught in İzmir Bay. Although numerous thermal baths in

the vicinity drain into the Bay, we don't expect high As concentrations in contrast to methyl mercury concentrations found in Minemata Bay, Japan (4).

As in water from thermal baths or hot springs in the vicinity, in ground water in the surrounding meadows and in central city supplies has not been assessed in the present study. However, we do not expect any high concentrations either; since not even limited outbreaks of acute or chronic inorganic As poisoning have ever been reported from the region as reported from other regions of the world (4, 8, 19).

Our results show a gross median of 4.946 ng/ml of total As in cow's milk. When we compare it with the amount of daily dietary consumption in Canada, France and USA (0.5-4.2 mg/day) (11), the amount consumed through cow's milk in our vicinity could be considered trifle. There are no metal (copper) smelters in the vicinity, arsenical pesticides are prohibited and no sulfite and industrial waste burying grounds that contain As and V. Since the As concentration in milk of cows grazing in meadows with grass grown on lava ground and given ground water draining such meadows is not very high, then, we may consider that As concentration in the Aegean Region of Turkey, although a land of thermal activity, is not as high as it is in other countries, e.g. Argentina and Taiwan.

It is a known fact that V, for a long time, is considered a toxic element acquired through smog (ambient air, e.g. chimney soot, burned oil or motor-exhausted smoke). However tetra- and pentavalent V are known to be independent of the route of exposure whether air- or water-borne (6). Therefore, V was also assessed in cow's milk samples collected for As estimation. The only substantial difference between the groups was smog hanging over meadows alongside the highway with heavy traffic in Narlıbahçe (Group I).

At times, smog can be seen hanging heavil on the pastures where cattle graze. One could even come across cows grazing on the grass shoulder of the highway. A recent study (17) reports high lead and Cadmium in bush within 3 m to the same highway.

Substantial data are still lacking to relate the discussion of toxic or deficiency effects of As and V. However, these two elements have lately been considered as being essential for growth (13).

The pentavalent form of V, vanadate, has recently been shown to posses an insulinomimetic effect; since insulin is well known as a growth factor, vanadate is considered essential for growth (8). Nielsen (13) reports that As plays an important role in conversion is also a well known growth factor, As must be considered essential for growth, too.

In literature, we did not even come across any study relating to As and V concentrations in milk; however, our study group also investigated As (2) and V (18) concentrations in human milk and in cord blood of small for gestational age (SGA) babies of stunted mothers who were exposed to tobacco smoke during pregnancy (1).

In conclusion: lava ground-, water- and air-borne pollution of As and V contamination in cow's milk was studied in cows grazing on lava ground pastures even on the grass sholder of a highway with a heavy traffic at near vicinity to thermal baths and given ground water. Vigilant control of foodstuff and city water supplies must have been effective, since no serious outbreaks of As and V intoxication are reported from the region. However, smog from motor exhaust was seemingly found complementary to V concentrations.

REFERENCES

1. Anal Ö, Gezer S, Töre İR, Ulman C (1993) Importance of Vanadium in the Stunted Children, *J. Toxi. Occup. Environ. Health*, 2, 122.
2. Anal Ö, Ulman C, Gezer S, Töre İR, Yenigün A (1993) Arsenic in Breast Milk (Unpublished data).
3. Anon. (1973) Trace Elements in Human Nutrition: Report of WHO expert committee, WHO technical report series, Nr. 532, Geneva.

4. Chisholm JJ Jr (1984) Pediatric exposures to lead, Arsenic, Cadmium and Methyl Mercury. Presented at the 8th Nutrition Symposium, Munich.
5. Diplock AT (1985) Ultra trace elements and selenium, pp. 263-267 In: Trace elements in nutrition of children, ed. by RK Chandra, Vevey/Raven Press, New York. G. U.S.A.
6. Edel J, Sabioni E (1988) Retention of intratracheally installed and ingested tetravalent and pentavalent Vanadium in Rat, Trace elem. Electrolyte in Health. and Dis., 2, 23-30.
7. Feher J, Csomos G, Verecki A (1987) Free radical reactions in medicine. Springer-Verlag, Berlin.
8. Feinglass EJ (1973) Arsenic intoxication from well water in the United States, N. Engl. J. Med., 288, 828-830.
9. Hambidge KM (1985) Clinical deficiencies: When to suspect, there is a problem, pp. 1-11 In: Trace elements in nutrition of children, ed. by RK Chandra, Vevey/ Raven Press, New York, U.S.A.
10. Korkina LG, Cheremisina ZP, Abromova NE, Afanasev IB (1993) Influence of iron and cobalt ions on oxygen radical generation by human leucocytes, Turk. J. Med. Sci., 19 (Suppl.).
11. Magos L, Peristanis GC, Clarkson TW, Snowden RT (1980) The effect of lactation on Methyl Mercury intoxication, Arch. Toxicol., 45, 143-148.
12. Monteiro HP, Winterbourn CC, Stern A (1991) Tetravalent vanadium releases ferritin iron which stimulates vanadium-dependent lipid peroxidation, Free Rad. Res. Commun., 12/13, 125-129.
13. Nielsen FH (1991) Nutritional requirement for Boron, Silicon, Vanadium, Nickel and Arsenic: Current knowledge and speculation, Faseb J., 5, 2661-2667.
14. Sarkar B (1993) Free radical induced DNA damage by metals bound to DNA- binding proteins, Turk. J. Med. Sci., 19 (Suppl.).
15. Taiyab M (1987) Role of arsenic in health and disease, pp. 237-244 In: Elements in Health and Disease, ed. by M Said, MA Rahman, LA D'Silva, MAS Printers, Karachi, Pakistan.
16. Taneli NN, Anal Ö, Erdem N, Töre İR, Güner G (1993) Free Radica Scavenger Deficiency in Chronic, Presented at the 8th National Parasitology Congress, Trabzon, Turkey.
17. Turkan I (1986) İzmir İl merkezi ve çevre yol kenarında yetişen bitkilerde kurşun, çinko ve kadmiyum kirlenmesinin araştırılması, Doğa Tr. Biol. D., 10, 116-120.
18. Ulman C, Anal Ö, Gezer S, Töre İR, Yenigün A (1993) Vanadium in breast milk (Unpublished data).
19. Yamashita N, Doi M, Nishio M (1972) Current state of Toyoto children poisoned by arsenic tainted morinaga dry milk, Jpn. J. Hyg., 27, 364-399.