

1-1-2001

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ULVİ REHA FİDANCI

TEVHİDE SEL

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FİDANCI, ULVİ REHA and SEL, TEVHİDE (2001) "The Industrial Fluorosis Caused by a Coal-Burning Power Station and its Effects on Sheep," *Turkish Journal of Veterinary & Animal Sciences*: Vol. 25: No. 5, Article 16. Available at: <https://journals.tubitak.gov.tr/veterinary/vol25/iss5/16>

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The Industrial Fluorosis Caused by a Coal-Burning Power Station and its Effects on Sheep*

Ulvi Reha FİDANCI, Tevhide SEL

Ankara University, Faculty of Veterinary Medicine, Department of Biochemistry, 06110, Dışkapı, Ankara - TURKEY

Received: 21.07.2000

Abstract: The aim of this investigation was to examine the industrial fluorosis caused by the coal burning power station in Muğla-Yatağan. Blood and urine samples of sheep, and water, plant and soil samples from around the power station were collected four times throughout the year to cover all four seasons. Fluoride ion concentrations in the water, urine, plant and soil samples were detected potentiometrically using an ion selective electrode. Serum Alkaline phosphatase (ALP-EC 3.1.3.1), Alanine aminotransferase (ALT-EC 2.6.1.2), Aspartate aminotransferase (AST-EC 2.6.1.1) and Lactate dehydrogenase (LDH-EC 1.1.1.27) enzyme activities were analysed spectrophotometrically using Sigma commercial kits.

Significantly higher fluoride ion concentration levels ($p \leq 0.001$) were observed in the urine, water and plant samples from the surroundings of Yatağan power station with respect to the control areas. However, the fluoride ion concentrations of the water, plant and soil samples did not cause fluorosis. The fluoride ion concentrations of the urine samples (7.86 ± 0.77 ppm) indicated the presence of chronic industrial fluorosis in the sheep.

ALP, ALT and AST enzyme activities were found to be significantly higher ($p \leq 0.001$, $p \leq 0.05$ and $p \leq 0.001$ respectively) in sheep serum samples collected from the surroundings of Yatağan power station, but there was no significant change in LDH enzyme activities ($p \geq 0.05$). Positive correlations were found between the fluoride ion levels of urine and plants ($r = 0.48$, $p \leq 0.01$) and between the fluoride ion levels of urine and soil ($r = 0.28$, $p \leq 0.01$). Seasonal effects on the fluoride ion concentrations of urine, water and plant samples were found to be significant ($p \leq 0.01$). The same effects on the serum enzyme activities were also observed ($p \leq 0.01$).

Chronic fluorosis caused by industrial pollution from Yatağan power station was observed in the sheep. The release of the particulate and gaseous forms of F- into the air in Yatağan-Muğla is the cause of the chronic fluorosis.

Key Words: Industrial pollution, fluorosis, sheep, blood, urine, water, plant, soil

Muğla-Yatağan Termik Elektrik Santrali Çevresinde Endüstriyel Florozis ve Bunun Koyunlar Üzerine Etkisi

Özet: Muğla-Yatağan Termik Santrali çevresinde, yakılan linyite bağlı olarak endüstriyel florozis olgusunu araştırmak amacıyla kış, ilkbahar, yaz ve sonbahar mevsimlerinde olmak üzere bir yıl içerisinde 4 kez bölgeye gidilerek koyunlardan serum ve idrar örnekleri ile koyunların otlatıldığı bölgelerden su, toprak ve bitki numuneleri alınmıştır. İdrar, su, toprak ve bitki örneklerinde flor düzeyleri iyon selektif elektrot kullanılarak potansiyometrik olarak, serum örneklerinde ise flor zehirlenmesine bağlı olarak dokularda şekillenen hasarı göstermek için de Alkali fosfataz (ALP-EC 3.1.3.1), Alanin transaminaz (ALT-EC 2.6.1.2), Aspartat transaminaz (AST-EC 2.6.1.1) ve Laktat dehidrogenaz (LDH-EC 1.1.1.27) enzim aktiviteleri ise spektrofotometrik olarak ölçülmüştür.

Elde edilen sonuçlara göre Yatağan Termik Elektrik Santrali çevresinden sağlanan idrar, su, bitki örneklerinde flor düzeyleri kontrol bölgesine göre istatistiksel olarak $p \leq 0,001$ düzeyinde önemli olarak yüksek bulunmuştur. Ancak su, bitki ve toprak örnekleri flor düzeyleri florozis oluşturacak düzeyin altındadır. Buna karşın idrar örneklerinde saptanan $7,86 \pm 0,77$ ppm flor düzeyi koyunlarda endüstriyel kronik bir florozis olgusunu göstermektedir. Yatağan Termik Elektrik Santrali çevresindeki koyunlardan sağlanan serum örneklerinin ALP ve AST aktiviteleri $p \leq 0,001$ ve ALT aktivitesinde de $p \leq 0,05$ düzeyinde istatistiksel önemde artış saptanmıştır. LDH enzim aktiviteleri yönünden gruplar arasında anlamlı istatistik fark bulunamamıştır ($p \geq 0,05$).

İdrar flor düzeyi ile bitki ($r = 0,48$, $p \leq 0,01$) ve toprak ($r = 0,28$, $p \leq 0,01$) flor düzeyleri arasında pozitif bir korelasyon saptanmıştır. İdrar, su ve bitki örnekleri flor düzeyleri üzerinde mevsimlerin etkisi önemli bulunmuş ($p \leq 0,01$) olup mevsimin etkisi serum enzim aktiviteleri üzerinde de gözlenmiştir ($p \leq 0,01$).

Sonuç olarak Termik Elektrik Santrali çevresinde yakılan linyit kömürüne bağlı olarak koyunlarda kronik florozis olgusunun geliştiği ve bunun oluşumunda santralden çevreye yayılan, gaz ve partikül formundaki flor bileşiklerinin etkili olduğu kanısına varılmıştır.

Anahtar Sözcükler: Endüstriyel kirlilik, florozis, koyun, kan, idrar, su, bitki, toprak

* This project was supported by Ankara University Research Fund (Project No: 96-10-00-09).

Introduction

Water, soil and plants with natural high fluoride content are usually the main cause of fluorosis. The most important effects of fluoride are seen in the wild and in domestic animals that are exposed for long periods to excess fluoride due the industrial pollution (1-8).

Industrial activities may cause fluoride pollution of air. Steel production plants, superphosphate plants, ceramic factories, coal-burning power plants, brickworks and oil refineries are the main causes of industrial fluorosis (4, 9-14).

The coal-burning power station in Yatağan is known to cause air pollution and environmental damage because of the burning of low quality coals.

The aim of this research was to investigate the industrial fluorosis caused by the power station in Yatağan-Muğla burning fluoride-containing coal and the effects of fluorosis on animal health.

Materials and Methods

The research was carried out within the 5 km distance surrounding the coal-burning power station in Yatağan–Muğla. Ortaca-Muğla, where no evidence of industrial pollution has been seen, was chosen as the control area. Blood and urine samples of sheep, and water, plant and soil samples from the area surrounding the power station and the control area were collected four times periodically throughout the year to cover all four seasons.

Health checks were performed on the sheep routinely. Blood and urine samples were collected from two year-old sheep of the same breed. Blood samples were taken from the V. jugularis and put into evacuated collector tubes. Water and urine samples were collected in chemically clean polyethylene stoppered bottles. Soil and plant samples were collected in clean polyethylene bags.

Fluoride ion concentrations in the urine, water, plant and soil samples were analysed potentiometrically an using ion selective electrode (15-17). Serum Alkaline phosphatase (ALP–EC 3.1.3.1), Alanine aminotransferase (ALT–EC 2.6.1.2), Aspartate aminotransferase (AST – EC 2.6.1.1) and Lactate dehydrogenase (LDH-EC 1.1.1.27)

enzyme activities were analysed spectrophotometrically (18) using Sigma commercial kits.

Urine and water samples were instantly tested for fluoride. Soil and plant samples were dried and ashed before analysis.

Statistical evaluation: The significant differences between fluoride and enzyme values obtained from the different periods were determined using the T test. The relationship between seasonal periods and the areas was tested by General Linear Model variance analysis and Duncan test. Correlation tests were also performed (19).

Results

The concentrations of fluoride in urine, water, plant and soil samples collected from the control area (Ortaca) and from the surroundings of the power station in Yatağan are presented in Table 1. The enzyme activities of serum samples from the control area (Ortaca) and the study area (Yatağan) in sheep are presented in Table 2.

The urine, water and plant fluoride concentrations were higher in the study area than in the control area throughout the year ($p \leq 0.001$). There was a difference between the soil fluoride concentrations in Ortaca and Yatağan, but the difference was not significant ($p \geq 0.05$).

Serum ALP, ALT and AST enzyme activities were found to be significantly higher ($p \leq 0.001$, $p \leq 0.05$ and $p \leq 0.001$ respectively) in sheep serum samples collected from the study area than in those collected from Ortaca. There was no difference between the serum LDH activities in Ortaca or in Yatağan ($p \geq 0.05$).

In winter, the urine fluoride concentration and serum ALP activities were found to be significantly high ($p \leq 0.001$, Tables 1,2). In spring, serum ALT ($p \leq 0.001$) and AST ($p \leq 0.05$) activities were also found to be significantly high (Tables 1,2). In summer, there was a difference between Ortaca and Yatağan, but the difference was not significant ($p \geq 0.05$). In autumn, the urine, water and plant fluoride concentrations were found to be significantly high ($p \leq 0.05$) in Yatağan-Muğla, but the soil fluoride concentration was not found to be significant ($p \geq 0.05$). There was also no difference between the serum enzyme activities in autumn ($p \geq 0.05$).

Table 1. The fluoride concentrations of urine, water, plant and soil samples collected from Ortaca and Yatağan (ppm).

	Period	n	Urine	n	Water	n	Plant	n	Soil
Ortaca	I	22	0.71 ± 0.19	13	0.06 ± 0.01	10	0.28 ± 0.10	10	1.14 ± 0.16
	II	20	0.23 ± 0.05	21	0.13 ± 0.02	19	0.46 ± 0.07	19	1.18 ± 0.28
	III	15	0.53 ± 0.03	12	0.06 ± 0.03	14	1.05 ± 0.06	11	1.39 ± 0.22
	IV	16	1.38 ± 0.08	16	0.07 ± 0.01	13	1.18 ± 0.08	12	1.02 ± 0.10
	Total	73	0.69 ± 0.07	62	0.08 ± 0.01	56	0.74 ± 0.06	52	1.18 ± 0.11
Yatağan	I	14	7.54 ± 0.89	15	0.13 ± 0.01	13	0.63 ± 0.13	11	1.4 ± 0.11
	II	18	2.88 ± 0.45	20	0.55 ± 0.03	20	0.55 ± 0.09	19	2.12 ± 0.17
	III	15	13.67 ± 1.39	11	0.07 ± 0.02	15	1.96 ± 0.17	10	2.39 ± 0.40
	IV	15	8.32 ± 1.78	15	0.12 ± 0.02	13	2.23 ± 0.18	12	1.83 ± 0.11
	Total	62	7.86 ± 0.77	61	0.25 ± 0.02	61	1.27 ± 0.11	52	1.95 ± 0.11

I – Winter, II – Spring, III – Summer, IV – Autumn

Table 2. Serum ALP, ALT, AST and LDH enzyme activities in sheep samples collected from Ortaca and Yatağan (IU/L).

Period	n	ALP	n	ALT	n	AST	n	LDH	
Ortaca	I	20	57.25 ± 5.74	20	8.2 ± 0.29	20	44.75 ± 0.98	20	474.60 ± 12.86
	II	20	65.65 ± 6.11	20	8.20 ± 0.22	20	51.45 ± 1.17	20	600.75 ± 31.66
	III	15	40.33 ± 3.69	15	11.26 ± 0.34	15	50.40 ± 1.36	15	410.53 ± 31.89
	IV	16	50.81 ± 4.80	16	7.38 ± 0.81	16	38.18 ± 1.93	15	571.73 ± 23.15
	Total	71	54.59 ± 2.87	71	8.66 ± 0.27	71	46.35 ± 0.90	70	517.72 ± 15.50
Yatağan	I	20	77.10 ± 11.31	20	8.55 ± 0.35	20	42.75 ± 1.29	20	457.95 ± 23.84
	II	21	89.71 ± 9.97	21	11.28 ± 0.46	21	63.80 ± 2.60	21	573.71 ± 23.84
	III	15	56.20 ± 5.87	15	8.13 ± 0.44	15	39.13 ± 1.84	15	512.00 ± 19.29
	IV	15	75.53 ± 7.71	13	4.74 ± 0.37	15	38.20 ± 2.01	15	600.00 ± 27.02
	Total	71	76.08 ± 4.91	69	8.57 ± 0.34	71	47.25 ± 1.64	71	533.61 ± 13.51

I – Winter, II – Spring, III – Summer, IV – Autumn

Discussion

Natural drinking water with a high fluoride content, various plants growing in soil with fluoride and water and plant and food contaminated with fluoride consumed by humans and animals in industrial areas are the main cause of chronic fluoride toxicosis (1, 20-22).

Natural fluorosis seen endemically in Turkey and in other countries causes health problems and economic losses due to performance and product losses in animals (4,6,22,23).

There are many studies about the natural fluorosis in Turkey. However, there are insufficient studies about the industrial fluorosis in Turkey (14). Moreover, there are

no studies about industrial fluorosis caused by coal-burning power stations. In the present study, fluorosis due to pollution from coal-burning power stations was investigated in Turkey. The high fluoride content of the urine samples observed from the surroundings of Yatağan coal-burning power station indicated the presence of chronic industrial fluorosis in Turkey.

The water and food consumed by the animals are the main sources of fluoride. Eighty percent of fluoride intake by diet into the blood occurs via simple diffusion from gastrointestinal tract. Respiration is also another way of fluoride intake for the body. The majority of fluoride is stored as fluoroapatite in the calcify tissues and it is excreted via urine. Fluoride is present at low

concentrations in the body fluids and soft tissues. Fluoride concentration of urine is parallel to the fluoride concentration of the bones. Therefore, measurements of the fluoride concentrations of urine is an important practical criteria for the dental and skeletal fluorosis (6,22,24-28). Moreover, ruminants are more sensitive to the fluoride toxicosis than the other animals (2,27).

Excretion of fluoride via urine is normally less than 5 ppm (29). Ergun and colleagues (6) reported the fluoride content of urine in healthy sheep 1.49 ppm. Moreover, Fidancı and colleagues (14) found the fluoride content of urine in healthy sheep to be 1.00 ppm. The fluoride content of urine increases to 20-30 ppm in chronic fluorosis (14,30). The fluoride content of the urine in sheep was found to be 0.69 ppm in Ortaca. This is consistent with other reports. The fluoride content of the urine in sheep surrounding Yatağan power station was found to be 7.86 ppm, indicating chronic fluorosis (Table 1).

In addition to information on the fluoride levels in urine, fluoride levels in soil, food and water, and industrial contamination of the environment are also necessary to investigate the protection, diagnosis and treatment approaches (14,21,22,27,31).

Fluoride is present in various concentrations in water derived from the surface and under the soil. The content of fluoride of the drinking water is normally 0.01-0.3 ppm; however, it is present at around 1.3 ppm in sea water. WHO considers a maximum fluoride content of 1.5 ppm to be acceptable for normal health. Levels over 1.5 ppm may be the cause of fluoride toxicosis according to WHO (4,32).

Volcanic areas containing soil rich in fluoride possess water sources containing high levels of fluoride, and therefore, endemic fluorosis is frequently seen in these areas (6,7,30,33). Fluorosis may develop because of industrial water contamination (3,34). The fluoride content of the water from Yatağan was found to be statistically higher than that from the Ortaca area. However, the fluoride content of water in these areas is at normal levels according to WHO reports (Table 1). This shows that the water sources around Yatağan power station are not yet contaminated.

The fluoride concentration of the plants growing in the areas free from industrial contamination is 1–15 ppm (1,14). Robinson (35) reported that the fluoride content

of land plants except fluoride storing plants is 0.5–40.0 ppm. Fidancı et al. (14) reported that the natural fluoride content of plants is 13 ppm in the area of Anatolia. The stem and leaves of plants on soil may be contaminated via industrial sources (2,14,29,36-38). Fidancı et al. (14) detected the fluoride contents of plants to be 82.2 ppm and 41.4 ppm around plastic and aluminium factories respectively. However, the rate of the fluoride intake from the soil and its storage in the plants may be different from plant to plant according to the content of the soil (22). However, the fluoride content of the plants from Ortaca and Yatağan can be considered to be at normal levels (Table 1).

Fluorosis may occur due to the rich fluoride content of the soil. Soil in areas witnessing volcanic and seismic activity contains high levels of fluoride (6,7,30). Fluorosis is commonly seen in volcanic areas such as the small towns of the Van and Ağrı regions of eastern Anatolia (6,23,24,30). Potential fluoride reserves in the soil from the village of Kızılcaören in Eskişehir/Beylikova play an important role in the fluorosis cases in this area (8,14).

According to Robinson (35), a normal fluoride concentration in the soil should be 30-300 ppm. Fidancı et al. (14) measured the normal fluoride content of the soil to be 66.4 ppm in the Central Anatolia region. The fluoride contamination of the soil increases by industrial sources (14). The fluoride content of the soil from Ortaca and Yatağan was found to be at normal levels (Table 1).

In this study, we found a positive correlation between the fluoride content of urine and that plants ($r=0.48$; $p\leq 0.01$) and soil ($r=0.28$; $p\leq 0.01$). A negative correlation between water and soil ($r=-0.20$; $p\leq 0.05$) indicates seasonal changes in the fluoride content of the samples (14). Geography, seasons and geography-season interactions can affect the fluoride content of water, plants and urine at a $p\leq 0.01$ level. However, the fluoride content of the soil was only affected ($p\leq 0.01$) by the geographical distribution of the areas.

Although signs of chronic fluorosis were seen around Yatağan power station and the fluoride content in urine reached levels sufficient for the diagnosis of chronic fluorosis, the fluoride content was measured to be at normal levels in the samples of water, plants and soil. This may indicate fluoride contamination by air. The concentration of fluoride in the air is also an important factor in the formation of fluorosis. The usage of coal in

industry and for heating buildings contaminates the air by its dust, and thus, the increased amount of fluoride in the air contaminates the soil, plants and water and is taken up by living organisms (11,12,39).

Chen et al. (13) reported that the endemic fluorosis with high incidence seen in the area of Pingxiang in China was caused by the air pollution due to coal being burnt in homes. Cao (40) claimed that air pollution due to increased housing and industry in China is one of the major problems caused by the burning of coal. Fluoride and sulphur dioxide levels increase air pollution. This causes decreased levels of chlorophyll in the plants and inhibition of photosynthesis and increased fluoride levels.

Riet-Correa et al. (9) observed fluorosis in cows and sheep caused by the burning of coal at a distance of 1.2-9.6 km from a coal-burning power station in Brazil. They pointed out that the occurrence of fluorosis decreases with distance from the power station. This supports the idea that the chronic fluorosis seen around the Yatağan power station may be the result of the burning of coal in this area.

Riet-Correa et al. (9) also observed that cows at 6-7 years old and sheep at 3-4 years old lost their incisor teeth in fluorosis in a farm near a coal-burning power station.

Lesions of the bone and teeth develop in time in fluorosis. Therefore loss of appetite, nutritional disorders and insufficient energy production in fluorosis cause systemic changes in other tissues (3,20,22,25, 29,30,41).

The fluoride in vitro causes ALP to increase in the cells of bone and plasma (7,42,43). However, ALP activity does not change in in vivo studies (23,44-46). Moreover, Miller et al. (47) reported that increased ALP activity is directly proportional to the fluoride concentration of the bone. In our study, serum ALP activity of the sheep in Yatağan was found to be higher ($p \leq 0.001$) than that in the Ortaca area (Table 2).

Acute hepatitis and light degeneration in the liver develop following fluoride intake (48). As a result of this, serum transaminase activity increases (7,46). In the present study, there were no significant differences in the transaminase activity of the serum obtained from Ortaca and Yatağan. However, AST activity varied significantly ($p \leq 0.001$) between these two areas.

It is reported that LDH activity varies in fluorosis (46,49). However, serum LDH activity did not change significantly ($p \geq 0.05$) in our study.

The difference between the results of the serum enzyme activities of this study and other investigations may indicate the degree of chronic fluorosis.

In conclusion, chronic fluorosis caused by industrial pollution because of a coal-burning power station was observed in sheep. The release of the particulate and gaseous forms of fluoride into the air in Yatağan-Muğla is the cause of chronic fluorosis. Analysis of the serum enzymes suggested that chronic fluorosis has a negative effect on the bones and general metabolism in sheep. Hence, chronic fluorosis causes health problems in sheep that may lead to economic losses.

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