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Introduction

Silver is a nonessential element of low toxicity. Its only well-established toxic effect results from the local corrosive or irritative action of large doses (1, 2). Prolonged exposure to high concentrations of silver produces argyria, which is characterized by a permanent bluish discoloration of the skin, the mucous membranes and the eyes, due to deposition of silver metal particles. A localized from is a result of the penetration of particles through the corneum, but generalized argyria is due to the absorption of silver compounds into the body. The signs of argyria occur especially as a result of occupational exposure (3-5). The medical use of silver than from occupational exposure, and occasionally, has led to toxic

Effects of Silver on Humans Living Near a Silver Mine

Abstract: The aim of this study was to determine the effects of silver mining on individuals living in Gümüş, a province of Kütahya in Turkey, which is located near a silver mine. For this purpose, two groups of subjects were chosen. The first group consisted of 59 people (n=59) above the age of 30 who had been potentially exposed to silver. The second group, which formed the control group of the study, were the same age as the first group (p>0.05) but had not been exposed to silver manufacturing, and lacked a history of silver medication. Blood, urine, hair, soil, rock, water, plant and cereal samples were collected and were analyzed for total silver content by Graphite Furnace Atomic Absorption Spectrometry, Statistical analyses were conducted using the "t test", "chi square test" or "pearson correlaction test". For the subjects, the mean concentration of silver in the blood was 11.356 μ g/L, in the urine it was 2.619 μ g/L, and in the hair it was 2.592 μ g/g. The same values for the control group were 6.059 µg/L, 1.700 µg/L, and 0.980 µg/g respectively. The values of the subjects were significantly higher than the ones in the control group (p<0.001, p<0.001, p<0.001 respectively). In addition to these findings, the mean concentrations of silver in the soil and rocks of the village were 3265.6 μ g/g, 7095.5 μ g/g respectively, which were significantly higher than the control group's means (p<0.001, p<0.001).

Both samples of water from the village and the control area had no silver content (0 μ g/L). The mean concentrations of silver in the cereals and plants from the village were 0.105 μ g/g and 3.589 μ g/g respectively, which were significantly higher than the control samples (p<0.001, p<0.001). None of the subjects had symptoms of argyria, but most of them had significantly higher systolic blood pressure than the control subjects (p<0.001). The results of our study indicate that generalized argyria is unlikely to occur in individuals who live near a silver mine, although they have high levels of silver in their blood, urine and hair.

Key Words: Silver, Argyria.

effects. The basic effect of silver is on the pulmonary and renal function, and on night vision (4). Normal concentrations of silver in human serum, urine and tissues are very low, less than 1 μ g/L.

In light of the literature, we decided to determine the effects of a silver mine on individuals living in Gümüş, which is located near a silver mine in the province of Kütahya, Turkey.

Material and Methods

The village: The silver mine is about 1 km from Gümüş. Between the village and the mine is arable land where cereal is grown and pasture areas where animals are grazed. 214 individuals were living in the village and

Age	Subject Group			Control Group			
	Male	Female	SUM	Male	Female	SUM	
30-39	1	2	3	1	2	3	
40-49	5	8	13	6	7	13	
50-59	6	5	11	6	5	11	
60-69	12	14	26	13	13	26	
70-79	2	2	4	1	3	4	
80-89	-	1	1	1	1	2	
90-99	-	1	1	-	-	-	
SUM	26	33	59	28	31	59	

Table 1. The distribution of the subjects in the subject group and the control group in terms of age and sex.

Study group		C	Concentration of silve	er
		Blood (µg/L)	Urine (µg/L)	Hair (µg/g)
Subjects	Mean	11.36	2.59	2.62
n=59	SD	4.25	1.64	1.09
	Range	6-20	0.8-9.5	1.2-4.5
Control Subjects	Mean	6.06	1.7	0.98
n=59	SD	2.56	0.66	0.37
	Range	3-12	0.9-3.6	0.1-2.1
		p<0.001	p<0.001	p<0.001

Table 2. Concentrations of silver in blood, urine and hair of the subjects and the control subjects.

68 of them were above the age of 30, and 63 of these 68 villagers had been living in the village more than 30 years.

Study group: In this study both the villagers and a control group were examined. Each study group consisted of 59 individuals. 59 of the villagers took part in the research, and all of them were over the age of 30 and been living in the village for 30 years or more (4 of the 63 villagers refused to give blood, urine or hair samples). An age limit of 30 was chosen because DiVincenzo et al. have reported that the time required for workers, potentially exposed to silver, to retain sufficient silver to develop signs of agryria is a minimum of 24 years of uninterrupted workplace exposure (4). The control group included 59 individuals who were not related to silver manufacturing and had no history of silver medication.

The villagers were between 31 and 90 years old with

a mean age of 56.9 ± 11.7 and the ages of the control group ranged from 31 to 89, with a mean of 57.8 ± 12.2 . The distribution of the subjects in the subject group and the control group in terms of age and sex are presented in Table 1.

The arterial tensions of both the subject and the control groups were measured by the same person, under similar conditions with the same equipment after a 20 minute rest.

Collection of biological samples: Blood, urine and hair samples were collected from both villagers and control subjects at the time of each persons' physical examination and were subsequently analyzed for total silver. About 5 ml of venous blood was collected in heparinized vacutainers and was refrigerated until analysis. Urine specimens were collected in plastic containers and were frozen. A minimum of 100 mg of

Study group		Concentration of silver			
		rock (µg/kg)	soil (µg/kg)		
Subject	Mean	7095.5	3265.6		
n=25	SD	3096	1136.1		
	Range	2706-11935	1551-6093		
Control Areas	Mean	3679	1725.6		
n=25	SD	1640.6	662.1		
	Range	1227-7689	1092-3963		
		p<0.001	p<0.001		

Table 3. Concentrations of silver in rock and soil specimens from the village and the control areas.

Parameter		Concentrat	Table 4.			
		plant (µg/kg)	cereal (µg/kg)			
	Mean	3589	105.2			
	SD	1167.9	35.3			
	Range	1858-6432	49-175			
5	Mean	1643	37			
	SD	581	20			

p<0.001

1017-3625

p<0.001

8-85

Concentrations of silver in plant and cereal specimens from the village and the control areas.

hair was removed from the suboccipital region of the head, placed in an acid-washed screw cap scintillation vial and stored at room temperature as described by DiVincenzo et al (4).

Range

Study group

Control Areas

Village n=25

n=25

Collection of environmental samples: The village water specimens were collected from tap water, fountains and from a stream flowing through the village, and the control specimens were from tap water, fountains in Eskişehir and from the Porsuk river flowing through the centre of Eskişehir, a city 127 km from the village. Soil, rock, plant and cereal specimens were collected from arable lands and pastures of the village and from control areas in Eskişehir.

Plant specimens consisted of different kinds of grass, flowers and leaves and cereal specimens included different kinds of grain such as beans wheat, barley, etc.

Sample preparation: Blood, urine and hair samples were prepared as described by DiVincenzo et al (4), rock, soil, plant and cereal samples were prepared as described by Que Hee SS et al (6, 7).

Analytical procedures: All of the samples were digested and analyzed for total silver using an Hitachi (180-70) Polarized Zeeman Atomic Absorption Spectrophotometer (Graphite Atomization Method) (4, 8-10).

Results

The mean silver concentrations of the blood, urine and hair of the subjects and the controls are presented in Table 2.

The mean silver concentrations of the rock and soil specimens from the village and the control areas are presented in Table 3.

The mean silver concentrations of the plant and dried cereal specimens from the village and the control areas are presented in Table 4.

		Systolic Arter	rial Tension			
	Lower than 159mmHg		Higher than 160mmHg		SUM	
Subject Group	30	%50.8	29	%49.2	59	%100
Control Group	42	%71.2	17	%28.8	59	%100
SUM	72	%61	46	%39	118	%100

Table 5. The system

The frequency distribution of systolic tensions of the subjects and the control subjects.

χ²=5.13 p<0.05

Both the samples of water from the village and the control areas had no silver content (0 μ g/L).

According to the physical examination of the subject and control groups, none had symptoms of argyria, but the subjects had high systolic arterial tension. The frequency distribution of the systolic tensions of the subjects and controls are given in Table 5.

With the recommendation of WHO, a systdic blood pressure of 160 mmHg was accepted as the hypertension limit (11).

Discussion

In this study, we established 6 μ g/L, 1.7 μ g/L respectively for blood and urine silver concentrations for control group, who were not related to silver manufacturing and had no history of silver medication. Wan TA. et al. established plasma silver concentrations in 26 individuals whose occupations were not related to silver manufactudring and had no history of silver medication as <1 μ g/L and for urine as <2 μ g/day (8). These findings are lower than those reported by DiVincenzo et al (4) who reported that normal human serum and urine contained silver concentrations less than 5 μ g/L.

In this study, the mean silver concentrations of the subjects' blood and urine were 11.36 ± 4.25 and 2.59 ± 1.64 , respectively. The mean silver concentration of the hair of the subjects was 2.62 ± 1.09 , and for control subjects it was 0.98 ± 0.37 . The values of the subjects were significantly higher than those of the control subjects p<0.001, p<0.001, p<0.001, respectively. DiVincenzo et al. have established silver concentrations in blood and urine of the photographic

industry workers exposed to silver to be 11 μ g/L and <0.005 μ g/g, respectively. The hair silver concentration of silver workers was significantly higher than that of the control subjects, 130±, 160 μ g/g and 0.57±0.56 μ g/g, respectively.

With age, or in other words, with exposure to time, no significant change was observed in the silver level in blood, hair or urine samples (r=0.1289, p>0.05; r=-0.0230, p>0.05; r=-0.1160 p>0.05; respectively).

Although most of the subjects were not workers in the mine, exposure can occur through the inhalation of silver particles and fumes, because the mine is so close to the village and it is an openpit rather than an underground mine. DiVincenzo et al. claim that occupational exposures can occur through the inhalation of silver particles and fumes also.

In our study the concentrations of silver in the hair were significantly higher than in the control subjects and the maximum concentration detected in control subjects was less than the mean concentraiton of the subjects. According to DiVincenzo et al., there is a potential for airborne silver particles to bind to hair and consequently, it may be difficult to discern between silver deposited during hair formation and silver bound from airborne contamination. But also they confirmed that no silver was detected in the inner portion of the hair by examining the hair by x-ray microanalysis. The importance of these later findings was questionable since airborne particles of silver can bind to hair and lead to apparent high values.

The mean concentrations of silver in the soil and rocks from the village were 3265.6 μ g/g, 7095.5 μ g/g, respectively. Silver concentrations of rocks ranged between 2706 μ g/g and 11935 μ g/g for the village and 1227-7689 μ g/g for the control areas, the values being

significantly higher for the subjects (p<0.001). The silver concentrations of soil ranged between 1551 and 6093 μ g/g for the village and 1092-3963 μ g/g for the control areas. Both the concentrations of rocks and soil from the village were significantly higher than the control areas (p<0.001, p<0.001).

The silver concentrations of fresh plants were significantly higher than the control samples (p<0.001) and also dried cereals from the village had higher values than the control samples (p<0.001).

We were not able to detect silver in any of the samples of water, either in the water from the village or in the water from the control areas.

In the physical examination of the subjects and controls, we recognized that systolic arterial tension values of the subjects were significantly higher than those

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of the control subjects (x^2 =5.13 p<0.05). There was no significant difference between the subjects and the control subjects in terms of diastolic tension. In the literature there was no evidence for the relationship between arterial tension and argyria. Because the control and the subject populations belonged to different social groups and their habits were very different from each other, no discussion was possible on this issue. None of the subjects or controls had any signs of argyria.

Conclusion

These findings clearly indicate that argyria is unlikely to occur in individuals who live near a silver mine, although they have high levels of silver in blood, urine and hair from exposure at the current levels.

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