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Trace Metals in Occupationally and Nonoccupationally Exposed Individuals

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An epidemiological survey was conducted in Houston, Texas on five trace metals in policemen, parking garage attendants, women living near freeways and three control groups of subjects. The controls were matched with the exposed groups for covariate information such as age, sex, smoking habits, ethnic background, socioeconomic status, hair color, and education. Each subject was sampled four times for blood, urine, hair, and feces, and these samples were analyzed for lead, cadmium, zinc, manganese, and copper. Lead and cadmium were correlated with airborne exposures but zinc, manganese and copper were not.

The second part of this paper deals with a market study of platinum and palladium markets and a design of an epidemiology survey of individuals occupationally and nonoccupationally exposed to these two metals. The market survey shows that although the catalytic muffler will have a major impact on the market, it is predicted that producers can meet these demands.

Measurement of Human Exposure to Fuel Additives

The most commonly used fuel additive in gasoline powered engines in the United States is tetraethyl lead. There are, however, a number of other fuel additives which may be used in greater quantities in the future that contain a variety of trace metals such as manganese, copper, and zinc. Other trace elements such as cadmium are present as impurities. It has been shown that trace metals such as these may accumulate in various tissuse and possibly contribute to the incidence of carcinogenic, mutagenic or teratogenic processes.

The objective of this investigation has been to develop methodologies for monitoring free-living populations for their exposure to trace elements that arise from automobile exhaust emissions. A large number of studies have been conducted similar to these for lead, but there have been relatively few involving the assay of other trace metals in free-living populations.

Methods

The monitoring program was conducted in the metropolitan area of Houston, Texas. Six groups of individuals were monitored: Group I, policemen on foot patrol; Group 1A, office workers in downtown Houston (controls for Group I); Group II, garage attendants; Group IIA, orderlies and custodians (controls for Group II); Group III, females living within two blocks of a freeway; Group IIIA, females living away from a freeway (controls for Group III).

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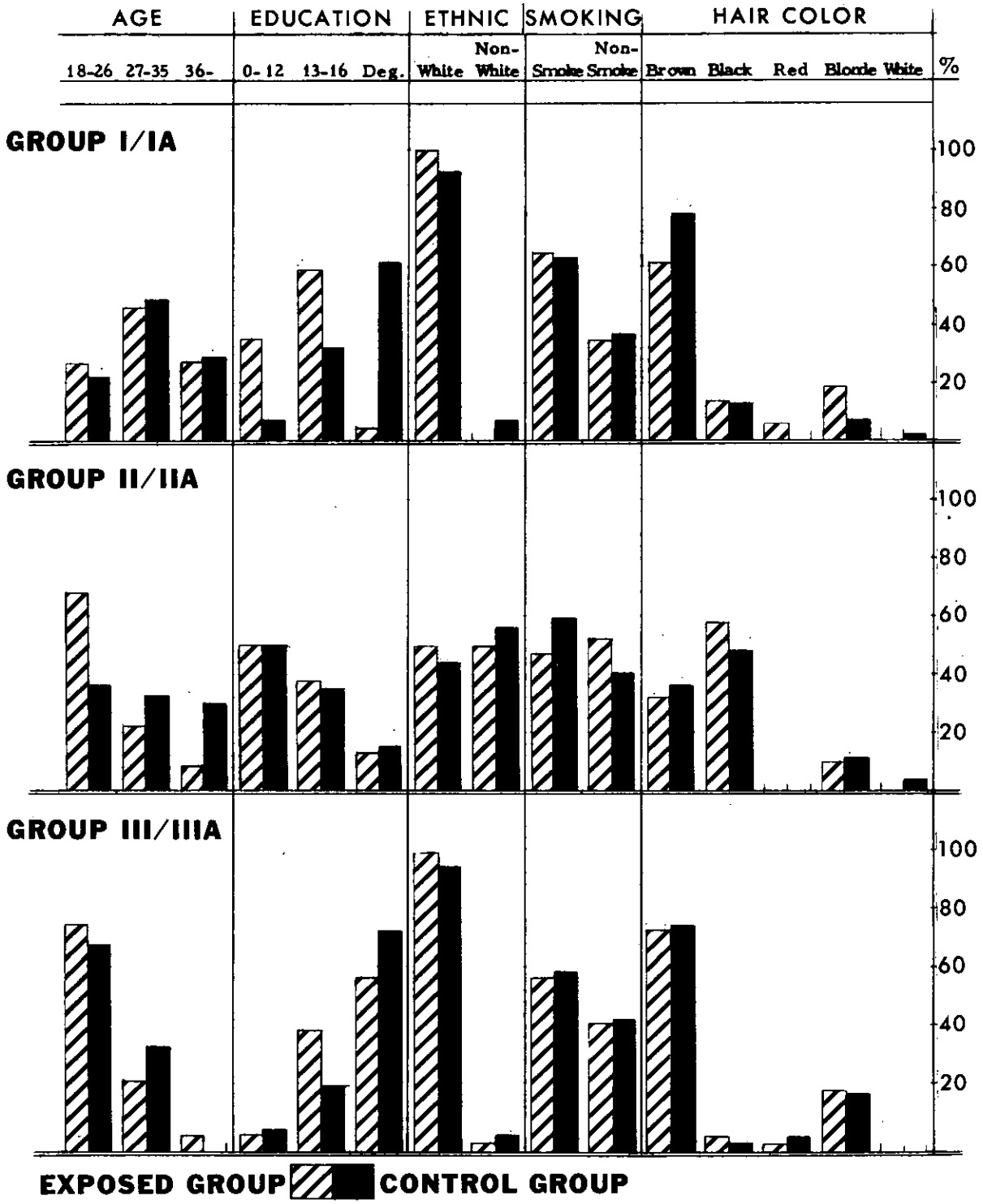

FIGURE 1. Schematic analysis of participants.

Thirty-six individuals were selected for study in each of these groups. Policemen, garage attendants, and females living near freeways were selected first, and then the control subjects were selected to match the appropriate group as closely as possible for covariate data such as age, sex, smoking habits, hair color, ethnic background, socioeconomic status, and education. Figure 1 shows the comparison of these groups for the variables mentioned. This type of matching is essential to make valid comparisons between groups of individuals for trace metals. The data illustrates that the groups were relatively well matched except for the education of the policemen versus their controls and a difference in age between the parking garage attendants and their controls.

Each subject was sampled four separate times for blood, urine, hair, and feces. Blood, urine, and hair were analyzed for all five metals, whereas feces was monitored for lead and cadmium only. Hematocrits and urinary coproporphyrin were monitored in each subject four times.

All samples were analyzed by atomic absorption spectrophotometry utilizing a deuterium arc background corrector. Each metal in each sample matrix (i.e., blood, hair, urine, feces) was analyzed by one of the following atomic absorption techniques: aspiration into an air–acetylene flame, micro sampling by using the Delves cup method, or graphite tube furnace.

Hair samples were washed and then digested with nitric–perchloric acid mixture (*1, 2*). The digest solution was then aspirated into an air–acetylene flame to analyze for each metal (*3*).

Blood samples were diluted with deionized water and allowed to hemolyze. Cadmium and lead were then determined by the micro sampling (Delves cup) technique (*4,5*). Copper and manganese were analyzed with the graphite furnace (*6,7*) and zinc by aspiration into an air–acetylene flame (*8,9*).

Urine was either analyzed without dilution or diluted with 0.1*N* HCl or deionized water. Cadmium was determined by the micro sampling technique (*10–12*). Lead, copper and manganese were determined by the graphite furnace (*7,12*), and zinc by aspirating into a flame (*8*).

Feces samples were digested with a nitric–perchloric acid mixture (*13*). The digest was analyzed for lead and cadmium with the graphite furnace.

Results

All of the data obtained were examined statistically by use of a *t*-test using paired comparisons. The data for copper, manganese, and zinc indicated that the values were not related to exposure to exhaust products. The median values were within normal for the groups of subjects. The results did indicate that there were larger quantities of copper in the blood, urine, and hair of females than male subjects. It has been reported previously that females have higher levels of copper than males. Also, there were lower levels of zinc in blood and urine for females, while higher levels were found in hair.

A summary of the data obtained for cadmium is shown in Table 1. Levels of cadmium are low in all specimens. These low levels pushed the analytical methods to the limit of effectiveness. In addition, there appear to be rather wide individual variations in cadmium content, particularly in hair samples. Statistical comparison of the data indicates that there are significant differences in cadmium levels in urine between Group I and IA and II and IIA at the 95% confidence limits. No differences were seen in the female subjects. The values reported here are consistent with data reported by others in nonoccupationally exposed individuals. It is possible that the levels of cadmium in urine are related to the exposure to air pollutants.

Table 2 presents the comparison between groups for lead values. There are significant differences (at the 95% confidence limit) for the male volunteers (policemen versus control and garage attendants versus control)

Table 1. Cadmium.

Group	Blood, μg/100 ml		Urine, μg/l.		Hair, μg/g		Feces, μg/g	
	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
I	0.5	0.67	1.4	1.05	1.1	2.09	0.19	0.07
IA	0.7	0.85	0.6	0.44	1.1	2.02	0.20	0.11
II	0.5	0.52	0.8	0.63	1.0	0.97	0.30	0.21
IIA	0.4	0.44	0.5	0.23	2.2	2.10	0.24	0.13
III	0.9	1.1	0.6	0.67	0.6	0.41	0.27	0.16
IIIA	0.8	1.7	0.6	0.40	0.7	0.55	0.23	0.13

Table 2. Lead.

Group	Blood, μg/100 ml		Urine, μg/liter		Hair, μg/g		Feces, μg/g	
	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
I	23.1	9.21	24.8	21.89	23.5	38.61	2.5	2.87
IA	18.4	7.38	19.0	19.64	13.1	15.92	2.3	2.72
II	28.3	10.33	26.5	25.38	47.6	46.42	2.4	1.68
IIA	21.3	9.70	27.8	19.80	29.7	29.62	2.2	2.44
III	12.9	4.47	32.0	25.47	7.4	10.61	2.9	2.18
IIIA	11.9	4.28	19.5	21.25	6.0	5.51	2.7	3.94

in blood and hair. There were slightly higher levels, although not significant, in females living near freeways versus their matched controls in blood. For urine, there were significant differences between the policemen and their controls and women living near freeways and their controls. Hematocrit data for the six groups of individuals were normal for their ages. There were no significant differences between the groups for the hematocrits. For the urinary coproporphyrins there were no statistical differences between policemen and their controls and garage attendants and their controls; however, there were significantly higher values for the females living near freeways versus thier controls.

Discussion

Comparison between the exposed groups and controls showed, as expected, that policemen and garage attendants had significantly higher blood and hair levels. Fecal lead measurements were included in this study to obtain data regarding the dietary consumption of lead. Fecal lead is a good indicator for dietary consumption, since 95% of orally ingested lead is not absorbed and is eliminated via feces. There were no statistically significant differences in fecal lead between any of the groups studied. From these results, it is concluded that the differences seen in body burdens of lead between the exposed and control groups are related to airborne exposures, probably from auto exhaust. For females living near freeways, there were higher levels than their control subjects for lead in blood, urine, and hair, although only urine was statistically significant at the 95% confidence limit.

In a recent position paper by the Environmental Protection Agency on health effects of lead from automobile emissions (*14*), results of several studies on exposed population were summarized. It was concluded that blood-levels of 40 μg/100 ml or above existed to a small but significant extent in the general adult population. The level of 40 μg/100 ml of lead in blood has been used by many agencies as the level in which some concern for health effects from lead is warranted. The results from this study show the following percentage of blood leads of 40 μg/100

ml or higher: policemen 6%, controls for policemen 2%, garage attendant 16%, controls for garage attendants 3%. The females, both exposed and control, had no blood lead values of 40 μg/100 ml.

The Seven City lead study included a study of females in Houston, Texas (*15*). Their blood lead values compared closely with values obtained in this study. Their data were 12.5 μg/100 ml of whole blood, whereas we obtained 12.9 and 11.9 μg/100 ml. The lead values found in this study indicate that females may metabolize lead differently than do males. Thus, males had blood-lead levels between 28.3 and 18.4 μg/100 ml, while females were 12.9 and 11.9 μg/100 ml for whole blood, and in hair, males' values ranged from 47.6 to 13.1 μg/100 ml, while female hair lead levels were 7.4 and 6.0 μg/100 ml. All of the females utilized in this study were employed in the metropolitan area of Houston. The control group of male subjects for the garage attendants worked in the same building as did the females utilized for this study. It is unlikely that exposure to different levels in the air or from dietary sources produced these significant differences in blood and hair lead levels. The values for fecal lead of females versus males are slightly higher for females. If the observations in this paper are correct, it could explain some of the lower lead values in blood of subjects examined in the Seven City study because their subjects were predominantly women.

Market Study of Platinum and Palladium and Design of Monitoring System

The catalytic muffler shows considerable promise for reduction of carbon monoxide, oxides of nitrogen, and hydrocarbons in the emission of automobiles. These muffler systems utilize platinum and palladium as the catalyst. Recent data indicate that these mufflers emit particles of platinum and palladium as well as sulfate. This project was designed to determine what effects the introduction of the catalytic muffler would have on the world market for platinum and palladium and to develop epidemiological procedures for use in monitoring body burdens of the general population for platinum and palladium.

Methods

A thorough review of the literature was made for identification of industrial uses of platinum and palladium to include production figures in the United States and foreign countries and the known reserves. The literature survey also included the documentation of human exposure cases and the toxicological information available for animals and man. The review covered the open literature through the end of 1973, and it also included contacts with various government and industrial concerns for additional information. Information obtained from the literature was used to assist in identifying industrial point sources of platinum and palladium and the design of analytical methods for assay of platinum and palladium in various media. An epidemiology survey was designed to determine the relationship between airborne concentrations of platinum and palladium and levels in various tissues of individuals occupationally exposed. The procedures developed will be used to monitor the general population for baseline levels prior to introduction of the catalytic muffler

Results

Table 3 shows the world population of platinum and palladium. The data (*16,17*) show that half of the world platinum and ⅙ of palladium production comes from the Union of South Africa, while ⅓ of platinum and ⅔ of palladium is from the U.S.S.R. Canada produces about 10% of both platinum and palladium, while the United States produces less than 1% of each.

Table 4 shows the world consumption of platinum and palladium as of 1971. The United States uses 37% of the total, while Japan uses 20%, Russia 16% and West Germany 12%. The data in these two tables point out clearly that the United States is

Table 3. World production of platinum and palladium. [a]

Source	1969–1972 annual average, troy oz×10⁻³		
	Platinum	Palladium	Total
Canada	188	187	375
Columbia	26	—	26
Ethiopia	0.3	—	0.3
Finland	0.2	0.3	0.5
Japan	3	5	8
Philippines	0.6	1	1.6
Republic of South Africa	909	321	1,230
U.S.S.R.	665	1,339	2,004
United States	9	13	22
Total	1,801	1,866	3,667

[a] Literature data (*16, 17*).

Table 4. World consumption of platinum and palladium. [a]

Nation	1971 consumption, troy oz×10⁻³
United States	1,376
Japan	758
U.S.S.R.	589
West Germany	451
France	313
Italy	74
Canada	68
United Kingdom	49
Netherlands	33
Sweden	17
Switzerland	12
Total	3,740

[a] Literature data (*16*).

heavily dependent on foreign sources of platinum and palladium.

Table 5 shows the future world demand for platinum and palladium. This table gives the median value of projected demands and reflects the impact of new demands for automotive exhaust emission control catalysts. Table 5 does not include a possible increase in consumption of platinum and palladium if countries other than the United States adopt the catalytic muffler for use in their countries. The data indicate that the use of the automotive catalyst will provide considerable increase in the consumption of platinum and palladium; however, a detailed analysis of the reserve situation and the potential of producers to meet these demands indicates that this production can be increased as the demand increases.

Table 5. Estimated future world demand for platinum and palladium. [a]

	Total annual demand, total oz×10⁻³		
	1971	1980	1990
United States			
Base platinum	541	734	1,044
Automotive catalysts	—	774	866
Total platinum	541	1,508	1,910
Base palladium	760	898	1,095
Automotive catayst	—	332	371
Total palladium	760	1,230	1,466
Total base	1,301	1,632	2,139
Total automotive	—	1.106	1,237
Total	1,301	2,738	3,376
Rest of World			
Platinum	1,283	1,826	2,703
Palladium	1,163	1,655	2,450
Total	2,446	3,481	5,153
Grand Total			
Platinum	1,824	3,334	4,613
Palladium	1,923	2,885	3,916
Total	3,747	6,219	8,529

[a] Literature data (*18*).

Platinum was considered harmless until the report published by Hunter, Hilton, and Perry in 1945 (*19*) which documented an investigation of exposure among workers in four refineries. It was found that the complex salts of platinum produced various symptoms such as asthma, eczemateous lesions and dermatitis in a high percentage of workers exposed. It was found that exposure to metallic platinum or palladium or the complex salts of palladium produced no apparent similar effects. Similar studies to those of Hunter et al. have confirmed that the soluble forms of platinum are toxic when the dosage is sufficiently high. Little information is available regarding assay of platinum levels in the work environment, although one report of Fothergill et al. (*20*) reported values of 5–70 μg of platinum/m^3 air. It is likely that refineries in plants of this type have significantly reduced these levels.

Very little information is in the literature

regarding toxicity studies in animals for palladium, although one report did indicate that palladium salts administered to animals showed damage to heart, kidneys, liver, and bone marrow. Studies are currently underway within the EPA in Cincinnati, Ohio to develop detailed toxicological data on platinum and palladium.

The review of the literature indicated that there are three primary categories of industrial point sources for possible exposure to platinum and palladium compounds: major categories are mining, refining and processing. The data indicate that the highest concentrations of exposure to significant number of individuals would occur in the refining and mining operations. The refining operation provides the possible exposure of predominantly the soluble forms of platinum and palladium following treatment with aqua regia, while in the mining operation the metals are found in the insoluble form as the free metal or other forms which are very insoluble. The data indicate that the insoluble form of platinum and palladium may be poorly absorbed. Thus, it has been demonstrated that the allergenic reactions are not produced by the insoluble forms in the human exposures.

There are two primary refineries located in the United States, with a number of much smaller operations. A follow-up study is planned to survey these refineries for platinum and palladium in air, soil and refinery workers. Blood, urine, hair, and feces samples will be collected from these individuals. Air samples will be taken in the plant environment, and correlations will be made between levels of platinum and palladium seen in the air versus levels produced in the tissues. A smaller study is planned for the mining operation to determine whether or not significant quantities of the insoluble form of platinum or palladium are absorbed into the miners. This is important because the catalytic muffler may under different circumstances produce soluble and/or insoluble forms of platinum and palladium.

A baseline survey is to be conducted in the Los Angeles basin prior to the introduction of the catalytic muffler and in a rural community relatively free of any source of air pollutants. The data from these surveys will provide a basis for comparison of future studies following the introduction of the catalytic muffler. Three age groups will be studied: young children, adults, and the aged. Both male and female subjects will be examined.

Very few methods are available for measuring platinum and palladium in biological tissues. This study has included the development of procedures for monitoring these two metals in urine, blood, hair, feces, and autopsy tissues. The procedures developed are based on atomic absorption spectrophotometry using an extraction procedure and the graphite furnace. It is likely that the quantities of these two metals in various tissues will be very low; thus, the assay methods must be extremely sensitive. The graphite furnace procedure offers an advance in sensitivity over the conventional flame techniques. The procedure developed thus far is able to detect 0.88 μg platinum/100 ml blood and 1.2 μg palladium/100 ml blood.

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