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October 13, 1970

Trace Elements - Hair 1509
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Lead file
NATIONAL AIR
POLLUTION CONTROL
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411 West Chapel Hill Street
Durham, North Carolina 27701

TO: Members, Lead Liaison Committee

1. As suggested by Dr. Douglas Hammer, the enclosed paper is being distributed to the members of the Lead Liaison Committee.
2. As indicated on the title page, it will be presented in Houston at the APHA meeting on October 26. It is to be published in the American Journal of Epidemiology in a few months.

Sincerely yours,

D. S. Barth
D. S. Barth, Ph.D.
Chairman
Lead Liaison Committee

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N36920

TITLE: HAIR TRACE METAL LEVELS AND ENVIRONMENTAL EXPOSURE

Running Head: AIR POLLUTION AND HAIR POLLUTION

Authors: D. I. Hammer,¹ J. F. Finklea,¹ R. H. Hendricks,²
C. M. Shy,¹ and R. J. M. Horton¹

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Houston, Texas

1. Division of Health Effects Research, Bureau of Criteria and Standards, National Air Pollution Control Administration, Environmental Health Service, Department of Health, Education and Welfare, Durham, North Carolina 27701.
2. Western Area Occupational Health Laboratory, Bureau of Occupational Safety and Health, Environmental Health Service, Department of Health, Education and Welfare, Salt Lake City, Utah 84108.

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Miniabstract

In fourth-grade boys, hair levels of As, Cd, and Pb accurately reflected community exposure while hair levels of Cu and Zn did not.

Key words: air pollution; environmental exposure; hair; arsenic; cadmium; copper; lead; zinc.

Abstract

Hair trace metal levels were related to environmental exposure in a study of fourth-grade boys in cities representing exposure dose gradients for arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn). Hair samples were carefully and stringently washed before analysis for As by spectrophotometry and for Cd, Cu, Pb, and Zn by atomic absorption spectroscopy.

Hair trace metal distributions for As, Cd, Cu, and Pb were positively skewed while those for Zn were symmetrical. Means were in accord with exposure rankings for As, Cd, and Pb but not for Cu and Zn. When grouped across a ranking gradient, differences among the means for As, Cd, and Pb were statistically significant while those of Cu and Zn were not.

The present study minimized possible effects of age, sex, hair color, varying hair length, and chemical treatments. Despite the problems of exogenous deposition, endogenous absorption routes, and relationships of hair metal to body burden, mean hair metals levels for As, Cd, and Pb accurately reflected community exposures.

HAIR TRACE METAL LEVELS AND ENVIRONMENTAL EXPOSURE

Introduction

Scalp hair has several of the characteristics of an ideal tissue for epidemiologic study in that it is painlessly removed, normally discarded, and easily collected. Since trace elements have been measured in hair, this tissue may prove a practical dosimeter for metallic environmental pollutants (1). Hair may also better reflect the total body pool of some elements than either blood or urine. Hair levels of two non-essential trace elements, arsenic and lead, have been useful in the diagnosis of clinical poisoning, while hair levels for cadmium, another non-essential metal, were recently reported (2,3,4).

The explicit hypothesis of this study was that mean hair levels of arsenic (As), cadmium (Cd), and lead (Pb) would differ among five cities in accord with the known environmental exposure gradients, while levels for two essential trace elements, copper (Cu) and zinc (Zn) would not (5).

Materials and Methods

An exposure ranking of four levels - low, intermediate, high, and highest - was constructed, with low approximating ordinary United States urban levels of each element (6). City exposure rankings were determined by combining aerometric, geologic, and industrial data (7, 8,9,10). The exposure ranking matrix for each metal and each city

studied is depicted in Table 1.

The study population consisted of fourth-grade school boys of similar socioeconomic status resident in a city for at least 3 years. With the cooperation of local school officials, explanatory letters and consent forms were sent to parents of eligible children. The overall volunteer response rate was 80 percent (168 of 211) with rates for the five cities ranging from 54 to 96 percent.³ Instruction sheets and plastic vials for hair collection were sent home with all volunteers. Virtually all of the samples were collected during the last two weeks of October 1969 when children underwent their regular haircuts at home or in the barber shop.

Hair samples were randomly numbered and brought to the laboratory² for analyses. Specimens were carefully cleaned by multiple washings with detergent, distilled water, alcohol, and EDTA (ethylene-diamine tetraacetic acid) heated to incipient boiling. They were then dried, weighed, and acid-digested for chemical analyses. Pb, Cd, Zn, and Cu were analyzed by atomic absorption spectroscopy and As by spectrophotometry (11,12). Control procedures included duplicate analyses of hair specimens and metal determinations on detergent, alcohol, and EDTA washings, as well as the original reagents.

Results

Trace metal analyses are summarized in Table 2. Geometric means and

³School principals thought that these response rates were similar to those observed for other activities in their schools.

medians were presented for each metal because all distributions except those of zinc were skewed, and the arithmetic means and standard deviations were tabulated for comparison with other published reports.⁴ Further discussion refers to geometric means unless otherwise stated.

Hair arsenic (As) distributions for each city were positively skewed (Figure 1). Fewer As determinations were made because this analysis required as much hair as analyses for the other four metals combined. City means were in accord with the known exposure gradient and ranged from 0.3 to 9.1 ppm. The mean of the highest city (III) was 3 times that of the high city (II) and 30 times that of the low city (V). Means for cities I, IV, and V (low and intermediate) were in agreement with other published values for hair As in unexposed populations, whereas means of cities II and III greatly exceeded them (13-17).

Hair cadmium (Cd) distributions for each city were also positively skewed (Figure 2). City means were again in accord with the exposure gradient and ranged from 0.7 to 2.1 ppm although the differences were not as striking as those of As. The mean of one high city (I) was 1.4 times that of the other high city (II) and 3 times that of the lowest low exposure city (V). Cadmium means from low exposure cities were lower than those previously reported (4).

⁴ Although comparisons to other published hair trace metal values will be made, differences in wash and analytic techniques as well as variation in sampling with respect to age and sex preclude exact inferences. Intercity comparisons for the data within this study are quite valid since these variables were carefully controlled.

Hair copper (Cu) distributions were positively skewed and the means did not follow the estimated exposure gradient (Figure 3). City means ranged from a low of 10.4 to a high of 17.1 ppm. The highest mean for an intermediate-exposure city (I) was 1.6 times the mean of the lowest low-exposure city (II). Since the Cu exposure gradient was only from low to intermediate, this relative homogeneity was not unexpected. Copper means were in the range of those reported by others (4,18).

As with the previous metals, hair lead (Pb) distributions were positively skewed (Figure 4). City means ranged from 6.1 to 57.7 ppm following the known exposure gradients. The mean for the highest exposure city (I) was 2.6 times that of the high city (II) and 9.5 times that for the lowest low-exposure city (V). The means of the three low cities were similar, ranging from 6.1 to 10.5 ppm. In addition, these means were lower than other reported "normals" (4,18,19).

Hair zinc (Zn) distributions, unlike those for As, Cd, Cu, and Pb were quite symmetrical. In addition, city means were quite similar, ranging from 141.9 to 154.3 ppm. Like those of copper, these means did not correlate with their exposure gradient. Zinc means were also lower than those previously reported (4,18).

Homogeneity of hair trace metal means over the exposure gradient was statistically tested by analysis of variance on log-transformed data

pooled for cities of equivalent exposure rank. As shown in Table 3, the exposure gradients for the three non-essential trace elements, As, Cd, and Pb, were confirmed by significant differences between means, $p < 0.0005$ in each case. On the other hand, means for the two essential trace elements, Cu and Zn, did not differ significantly. For each metal, additional contrasts were written to test homogeneity among city means within each exposure rank. No significant differences were found except for two cities (I, IV) with an intermediate exposure to As.

Analyses for Cd, Cu, Pb, and Zn were performed on washings from nine hair specimens and the arithmetic means shown in Table 4. Detergent and first EDTA washes contained substantial amounts of each metal and a second EDTA wash limited to these nine specimens lacked only Cd. Conversely, the routine post-detergent pre-EDTA ethanol rinse contained no detectable metals. No apparent relationships between hair and wash levels were noted for any metal except for a positive trend between hair and detergent Pb. The more rigorous washing technique used in this study probably accounted for the lower hair values found in low-exposure population segments.

Discussion

The amount of a trace metal in human hair is a function of many factors. The present study minimized any effects of age, sex, varying hair length, and personal chemical treatments. Ninety-two percent of the subjects had brown or blond hair and these hair colors, unlike red and black, have not been associated with alterations in metal levels (4,20). Further, hair trace metal determinations measure both endogenous and exogenous components. The former reflects metal from external deposition, e.g., hair preparations and dust, while the latter reflects internally deposited metal, i.e. by absorption through the skin, lungs, or gut. Moreover, hair treatments and wash techniques might add or remove hair trace metals (17). As our stringent pre-analysis wash included both detergent and hot EDTA, most or all of the superficially bonded trace metals were removed from the hair specimens before analysis. Chemical binding of exogenously and endogenously deposited hair trace metals is not fully understood although sulfhydryl and amino groups are involved. Likewise, the effect of competition for such binding sites is not known. Despite these problems, mean hair metal levels did reflect community exposures to As, Cd, and Pb.

If observed differences were not entirely due to external contamination, then a portion must have been caused by increased absorption of a given metal. Gastrointestinal and respiratory routes probably accounted for most absorption since both soil and air levels were increased in high-exposure cities. Further, differential absorption occurs. Only 5 to 10 percent of a gut Pb dose as opposed to up to 25 to 50 percent

of a respiratory dose is absorbed (21). Respiratory retention and absorption are primarily a function of particle size whereas gut absorption is more a function of diet, chemical form, and solubility.

How well hair reflects a body metal burden is not fully known since the hair metal pool represents only 0.5 to 1 percent of the total body pool and either pool might fluctuate independently of the other. Uptake of Pb in hair was greatly increased in anagen (growing) versus telogen (resting) hair and was affected by both total dose and dose fractionation (22). Hair Cd and Pb were shown to be log-dose related to dietary Cd and Pb (23). Schroeder suggested that hair Pb did not reflect the body burden because bone Pb increased with age while hair Pb did not (24). On the other hand, Jaworowski found that hair and bone lead correlated well in twenty autopsied females (25).

Increased hair metal levels, per se, do not indicate clinical illness (20,26). On the contrary, a metal may be accumulated in hair while other tissue levels are minimally or transiently elevated. Also, metals in hair may continue elevated for many months after exposure (27). Another consideration is that toxicity of these elements varies with chemical form as well as total dose. For example, trivalent but not pentavalent As is toxic (16,28). The present study was not designed to separate, analytically, the chemical forms of metals nor to detect clinical laboratory evidence of chronic poisoning. The questions of increased As and Pb burdens and subclinical biochemical abnormalities must be resolved by future investigation. Although Cd is known to be

highly toxic to humans, hair Cd levels have not been related to toxicity (29).

Mean hair levels of both Cu and Zn did not differ in accord with their postulated exposure gradients. The range of estimated environmental exposure for both elements was minimal, viz. intermediate versus low. In addition, Cu and Zn are considered to be essential trace elements whereas As, Cd, and Pb are considered to be non-essential; furthermore, the amount of Cu and Zn in the diet usually exceeds that in the environment (5,28,30-33). A full discussion of the possible variations of homeostatic mechanisms for essential versus non-essential trace elements is beyond the scope of this report.

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Table 1.

Exposure Rankings for Five Selected Metals
in Five Selected Cities*

CITY	MAJOR INDUSTRIES	METAL EXPOSURE RANKINGS				
		Arsenic	Cadmium	Copper	Lead	Zinc
I	Lead & zinc mining & smelting	Intermediate	High	Intermediate	Highest	Intermediate
II	Lead & zinc smelting	High	High	Low	High	Intermediate
III	Copper smelting	Highest	Low	Intermediate	Low	Low
IV	Government & commercial ⁺	Intermediate	Low	Low	Low	Low
V	Education & farm trading	Low	Low	Low	Low	Low

*Exposure ranking determined from aerometric, geologic, and industrial data with "low" $\leq$ ordinary United States urban exposures.

⁺Located near the lead and zinc smelting city.

Table 2.
Descriptive Summaries for Hair Trace Metal Levels;
Distribution by Metal and City

METAL	EXPOSURE RANKING (City)	DESCRIPTIVE SUMMARY				
		Geometric mean (ppm)	Median (ppm)	Arithmetic mean (ppm)	Standard deviation (ppm)	Sample size
Arsenic	Highest (III)	9.1	9.1	10.6	7.00	31
	High (II)	3.0	4.0	5.2	6.00	16
	Intermediate (I)	1.2	1.1	1.7	1.48	32
	Intermediate (IV)	0.7	0.7	0.8	0.33	13
	Low (V)	0.3	0.4	0.4	0.26	28
Cadmium	High (I)	2.1	2.1	3.5	4.94	45
	High (II)	1.5	1.6	2.0	1.54	25
	Low (III)	1.0	1.0	1.3	0.99	37
	Low (IV)	1.0	0.9	1.3	1.30	21
	Low (V)	0.7	0.8	0.9	0.58	37
Copper	Intermediate (I)	17.1	13.0	25.7	28.1	45
	Intermediate (III)	13.9	12.0	15.3	7.5	37
	Low (II)	10.4	11.0	11.8	3.0	25
	Low (IV)	11.5	11.0	12.6	6.0	21
	Low (V)	14.4	11.0	22.5	34.7	37
Lead	Highest (I)	57.7	52.0	107.1	131.8	45
	High (II)	22.3	20.0	44.3	49.3	25
	Low (III)	10.5	13.0	14.3	14.1	37
	Low (IV)	8.9	7.9	12.1	11.4	21
	Low (V)	6.1	6.5	7.6	5.0	38
Zinc	Intermediate (I)	149.6	160.0	154.0	33.7	45
	Intermediate (II)	141.9	145.0	145.2	30.8	25
	Low (III)	154.3	160.0	156.6	26.0	37
	Low (IV)	149.9	160.0	153.4	36.9	21
	Low (V)	149.9	155.0	154.2	32.5	38

Table 3.
One Way ANOVA* Tests of Equality of Geometric Hair Trace Metal Means
by Exposure Ranking Categories.

METAL	TEST OF EQUALITY	
	Contrast of Means	F Ratio
Arsenic	Highest($\bar{x}_{III}$) vs.High($\bar{x}_{II}$) vs.Intermediate($\bar{x}_{I+IV}$) vs.Low ($\bar{x}_V$)	66.60
Cadmium	High($\bar{x}_{I+II}$) vs.Low ($\bar{x}_{III+IV+V}$)	32.23
Copper	Intermediate($\bar{x}_{I+III}$) vs.Low ($\bar{x}_{II+IV+V}$)	3.90
Lead	Highest($\bar{x}_I$) vs.High($\bar{x}_{II}$) vs.Low ($\bar{x}_{III+IV+V}$)	64.37
Zinc	Intermediate($\bar{x}_{I+II}$) vs.Low($\bar{x}_{III+IV+V}$)	1.08

* ANOVA denotes analysis of variance.

Table 4
Trace Metal Means for Hair Washings*

TRACE METAL	ARITHMETIC MEAN (ppm)		
	Detergent	First EDTA	Second EDTA
Cadmium	0.2	0.6	0.0
Copper	2.9	4.8	7.6
Lead	10.8	5.0	0.9
Zinc	17.3	18.0	15.9

* Nine specimens

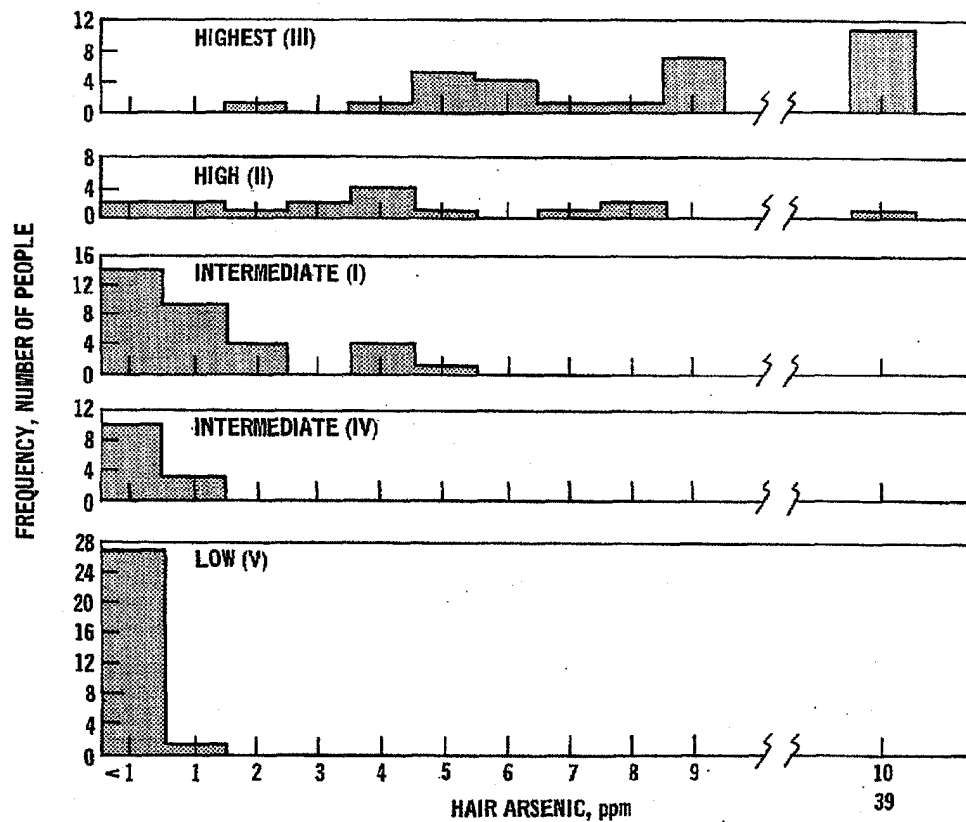


Figure 1. Distribution of hair arsenic levels, by city.

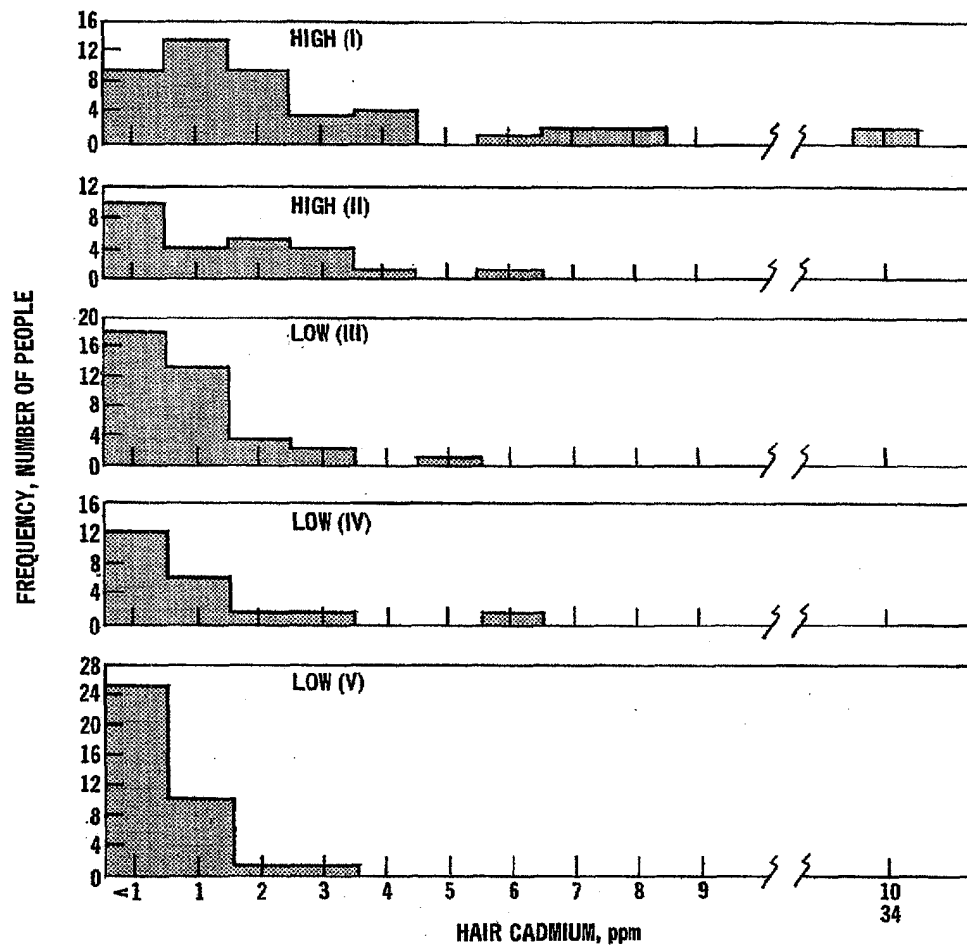


Figure 2. Distribution of hair cadmium levels, by city.

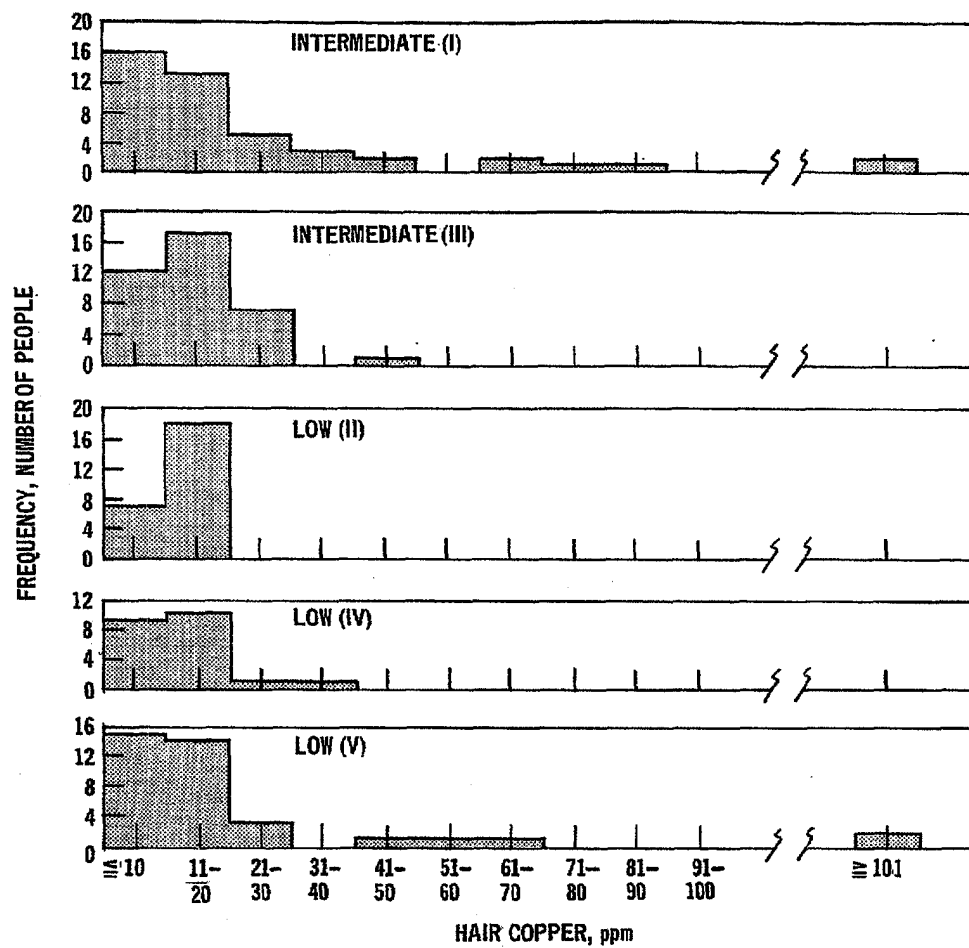


Figure 3. Distribution of hair copper levels, by city.

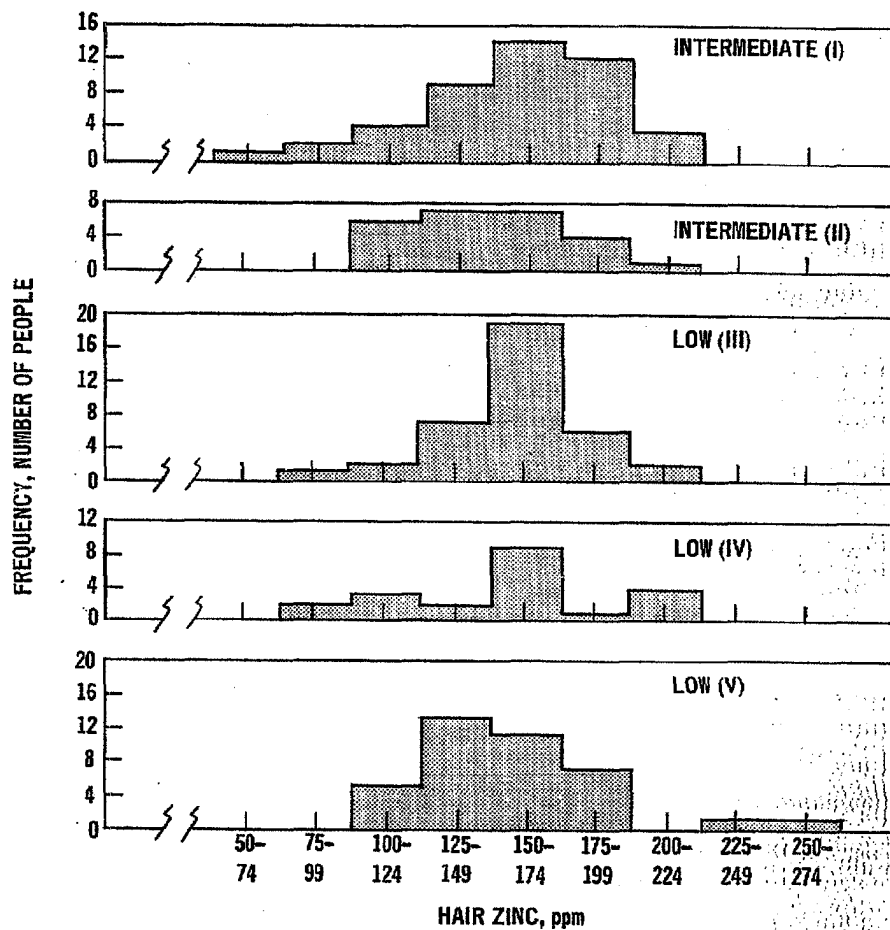


Figure 5. Distribution of hair zinc levels, by city.