

**CONTRIBUTIONS TO  
TRACE ELEMENT ANALYSIS OF  
HUMAN SCALP HAIR**

by

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## *ABSTRACT*

Levels of 19 elements in scalp hair samples taken from 122 children and 27 adults in three northern Alberta Indian villages were compared in an effort to trace contamination from the world's first tar sands oil extraction plants into the human population. One of the three communities (Fort McKay) is in close proximity to the plants; one is also in the tar sands ecosystem, but distant from the plants (Fort Chipewyan); the third is not in the tar sands ecosystem (Garden River). Children from Fort McKay (the exposed village) had highest average hair lead, cadmium and nickel levels. Unexpected results were found in the control village most distant from the tar sands plants (Garden River) where the children had significantly elevated levels of 8 metals. Water and air particulates were collected and analyzed for the 19 elements which were included in data analysis. Most of the results of the hair analysis can be explained by results from the environmental samples, but no immediate answer can be provided for large differences found between children and adults in Garden River. Detailed data analysis has revealed several sets of highly inter-correlated metals ('correlation clusters': Pb/Cd; Al/V/Fe; Ca/Mg/Sr/Ba), which may have important applications in metal toxicology and in assessing trace element status. Effects of age, sex, and sample washing procedure are discussed.

## *DEDICATION*

This thesis is dedicated to Professor Allan Davison who has been far more than a Senior Supervisor during the long course of development of this work. In addition to being the finest scientist I have had the opportunity to know, Allan is a friend and personal advisor to me and to all students who are fortunate enough to work in his laboratories.

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## *PREFERATORY COMMENTS*

This study was undertaken to address concerns expressed by the Fort McKay Indian Band, Fort McKay, Alberta, Canada, in regard to effluent discharges and stack emissions from the world's first oil sands extraction plants (Suncor and Syncrude). Both Fort McKay and the plants are situated on the banks of the Athabasca River, with the plants approximately 10 to 20 km upstream from Fort McKay, in the southern part of a large northern Alberta region referred to as the 'tar sands ecosystem'. Stack emissions from the two plants amount to around 1.5 metric tonnes per hour. Until recently, both plants have operated 24 hr per day. The particulates are composed of a number of metal contaminants, primarily Al, V, Ni, Mo, Sr, and Pb. In addition, contamination of the Athabasca River by organic pollutants has become so serious that people have been advised not to eat fish or drink water from the river.

In an effort to trace pollution from the plants into the human population, the study reported in this thesis was designed and conducted. Scalp hair samples were collected from children in each of three communities: Fort McKay, the exposed community, Garden River, a control community unexposed to any known source of industrial pollution, and Fort Chipewyan in the tar sands ecosystem, approximately 200 km north (downstream on the Athabasca River) from the plants. It was decided to attempt to trace pollution from the plants via inorganic (metal) contaminants. Human scalp hair has been used successfully to trace metal



contamination in many studies; we therefore used human scalp hair samples to investigate this problem.

The thesis is presented in three chapters. Chapter 1 presents the results of the hair analysis study, and has been published in *THE SCIENCE OF THE TOTAL ENVIRONMENT*, 1986, 54:107-125. Chapter 2 presents the results from water and air samples, and develops the concept of 'correlation clusters'. This chapter has been published in *THE SCIENCE OF THE TOTAL ENVIRONMENT*, 1988, 72:87-112. Chapter 3 deals with the effects sample washing on trace element content of hair. As well, the effects of age and sex -- the most important identified co-variables affecting trace element content of human scalp hair -- are presented and discussed with a review of the published literature. In addition to the three chapters that comprise the thesis, there are five appendices, containing the raw data, statistical treatment of the raw data and log-transformed data, and basic correlation analyses.

Great care was exercised in every aspect of the study, as may be appreciated from the following examples:

*STUDY DESIGN:*

1. An 'exposed' community and two 'control' communities (one in the same ecosystem; one far removed) were studied.
2. Children were chosen as the primary focus due to their continuous residence in each of the areas, and limited exposure to other

confounding factors such as smoking, hair dying, drugs, alcohol, and other exposures.

3. Participants were selected by random methods.
4. Samples were submitted and analyzed by investigators who did not know where any sample came from until after the analysis had been completed.

#### *SAMPLE COLLECTION:*

1. All samples were collected by a single individual (J.M.) and prepared in as uniform a fashion as possible.
2. Small scalp hair samples were gathered from 8 to 10 sites around each subjects head in order to insure that location on the scalp from which samples had been gathered would not influence results.
3. When samples were collected, the 8-10 small samples from each individual were placed with scalp ends aligned, tied with a nylon thread at the scalp end, folded into a weighing paper, and placed into a paper envelope for blinding. This envelope was then sealed into a zip-loc polyethylene bag until it was prepared for analysis.

#### *SAMPLE PREPARATION:*

1. Since samples were collected using metal scissors a glass blade was

used in the laboratory to shave several mm from the end of the hair that had come into contact with the scissors.

2. A separate glass blade was used for each sample.
3. Samples were cut to a uniform length to represent an approximately equivalent growth period.
4. For those samples that were separated for analysis both before and after washing, the sample was carefully separated a few hairs at a time to insure that the two samples were representative.

#### *SAMPLE ANALYSIS:*

1. All samples were washed and digested in exactly the same fashion.
2. Standards were checked against Environmental Protection Agency (EPA) water samples.
3. Accuracy of the instrument was checked by analyzing aliquots from 26 samples on a separate instrument in a separate laboratory.
4. A uniform hair sample was prepared by pooling the hair remaining after preparing the samples for analysis. The pooled sample was cut into extremely fine pieces, and mixed to uniformity. This uniform mixture was separated into 10 samples that were digested and analyzed along with the test samples.

5. In order to insure that any differences found were not due to surface contamination, all samples that were large enough to be separated into 2 samples (122 of the 149 samples) were analyzed both before and after washing.

#### *DATA ANALYSIS:*

1. Since the distributions of several elements were non-normal, data were log-transformed to make more normal distributions.
2. Although this study could be considered a repeated measures study, the available statistical analyses were unable to perform an appropriate repeated measures analysis. The BMDP repeated measures package excluded all samples that had not been analyzed twice, but the study design which was defined prior to data analysis, identified the washed samples to be of primary importance. Using the SPSSX MANOVA package, it was possible to write the program to perform the correct repeated measures analysis, but even expanded to its maximum, the package did not have the capacity to perform the analysis. Therefore data were analyzed using oneway analysis of variance, performed on log-transformed data.

#### *ENVIRONMENTAL SAMPLE COLLECTION:*

1. Water sample collection methods followed as closely as possible the methods recommended by the Energy Resources Conservation Board of Alberta (ERCB).

2. Containers for water sample collection were washed until pooled rinsings from 10 containers met the following standards: Pb 0.002 mg/l; Cd 0.001 mg/l; Ni 0.002 mg/l; Ca 1.0 mg/l; Na 0.5 mg/l; K 0.1 mg/l.
3. A separate Socorex pipette tip was used to collect each sample. Socorex pipette tips were soaked in 5% nitric acid for 15 hours, rinsed three times with deionised water, dried at 105°C, and stored in individual sealed polyethylene bags.
4. A field blank sealed in a polyethylene zip-loc bag accompanied each high-volume sampler. The field blank package was opened, and the field blank put into the sampler, then removed and placed back into its zip-loc by the individual responsible for looking after the sampler.

There are some minor points which can best be dealt with before coming to the main body of the thesis. These are as follows:

1. **CONTRIBUTIONS OF DIET TO DIFFERENCES AMONG THE COMMUNITIES:**  
We did not take specific information regarding dietary habits of the residents of the three communities. One of the primary problems that the residents of Fort McKay are facing is the forced change in eating habits that have come with the pollution of the Athabasca River. These changes have been discussed at length in a report issued by the Fort McKay Tribal Administration (*From Where We*

*Stand*, Fort McKay Tribal Administration, Box 5260, Fort McMurray, Alberta T9H 3G4). People have been advised not to eat fish from the river, or to drink water from the river, since contamination due to the oil by-products has made these unsuitable for human consumption. As well, the Fort McKay residents have claimed that there is a decrease in availability of berries and of all forms of wild life in the area, which has affected their diet. At the present time, most of the food consumed in Fort McKay is purchased in Fort McMurray, and probably differs little from the food consumed in Fort Chipewyan, where people also rely almost completely on food purchased in the local Hudson Bay store. In Garden River, the situation is different, since the village does not have a community store, and wild life such as water buffalo, deer, cariboo and fish are abundant. Thus there are distinct differences in dietary habits in the three communities, with two of the communities relying primarily on stores for food, and the third community relying most heavily on indigenous wild life. The question of the contribution of food to the differences observed remains an important question to be addressed in future research.

2. **SOURCES OF LEAD:** The elevated levels of lead in hair samples from Fort McKay children (and 2 adults) remains unexplained. What is even more striking is the fact that environmental lead levels are highest in Garden River.

We have suggested that the elevated lead levels in hair from Fort McKay residents may be due to the periodic seepage of lead and cadmium containing oil products from the holding tanks into the Athabasca River (see Chapters 1 and 2).

3. **POSSIBLE CONTRIBUTION OF GASOLINE SNIFFING TO LEAD IN HAIR:** A possible explanation for the elevated levels of lead in hair from Fort McKay residents which we will not consider further is the possibility of gasoline sniffing among the children. This, however, probably does not explain the high levels (>30 ppm) of lead in hair from 2 out of 8 adults from Fort McKay. Since these adults, along with the children had elevated levels of lead, it is doubtful that gasoline sniffing can explain the elevated lead levels among Fort McKay residents.
  
4. **FAILURE TO FIND ELEVATED VANADIUM LEVELS IN EXPOSED POPULATIONS:** The focus of the study was to attempt to document exposure of a human population to emissions from an industrial source. Since the oil sands plants constitute the greatest point sources of vanadium emissions in the world, we chose vanadium as a marker for exposure. It is remarkable, therefore, that these massive emissions are completely undetectable either in the environment or in the community. However, in retrospect, this can be understood. Vanadium is widely distributed in the earth's crust to an extent variously estimated to be between 0.01 and 0.05 per cent. For this reason, even emissions as high as those in the area of Fort McKay

contribute much less than amounts naturally present in the soil. Consequently, a minute amount of soil contamination of a hair sample can provide far more vanadium than the trace amounts that enter the hair through the human organism. Perhaps even the most careful washing will not remove all of the surface contamination (as discussed in Chapter 3), suggesting that hair analysis cannot be relied on for assessment of vanadium levels in people.

5. **THIS STUDY COULD NOT HAVE BEEN CONDUCTED WITHOUT THE COOPERATION OF THE INDIAN BANDS AND INDIVIDUAL SUBJECTS:**

Permission for collecting hair samples in each community was obtained from each of the participating Indian Bands. Consent forms were signed by parents of each participant, or by the participant in the case of adults. At the conclusion of the study, the Fort McKay Band was in the process of beginning to keep records of health and other aspects of life in the village, in order to document any further changes imposed on the community by the oil sands plants. As a result of this study, we have advised the band to set up a mechanism for continuing to monitor the population for lead and cadmium by way of collecting teeth from the children (as they are lost), to be analyzed at some future date.



**1. CHAPTER I: TRACE METALS IN SCALP HAIR OF CHILDREN AND ADULT  
OCCUPANTS OF THREE ALBERTA INDIAN VILLAGES**

**THE SCIENCE OF THE TOTAL ENVIRONMENT, 54 (1986):107-125**

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## 1.1 ABSTRACT

This study examined trace metal levels in scalp hair taken from 122 children and 27 adult residents of three small northern Alberta (Canada) Indian villages, one of which is situated close to the world's first tar sands oil extraction plants. The three communities studied were: Fort McKay (the exposed village), Fort Chipewyan (also in the tar sands ecosystem but distant from the plants), and Garden River (not in the tar sands ecosystem). Inductively coupled argon plasma emission spectroscopy was used to analyze hair sample metal content. Nineteen metals were included in data analysis. Children from Fort McKay had the highest average hair lead, cadmium, and nickel levels. Chromium levels were approximately equal in hair from Fort McKay and Garden River children, and significantly elevated above levels found in Fort Chipewyan children. Children from Garden River showed highest hair levels of eight metals: vanadium, aluminum, iron, manganese, barium, zinc, magnesium, and calcium. Fort Chipewyan children had the highest hair levels of copper, but the lowest levels of all other metals. Bioaccumulation of lead, cadmium, nickel, and chromium in hair from Fort McKay residents may be related to exposure to plant pollution. An increased number of significant metal-metal correlations in hair metal levels for Fort McKay children suggests a richer source of multiple metal exposure, relative to children in the other two communities.

## 1.2 INTRODUCTION

This study was undertaken to address concerns expressed by the Fort McKay Indian Band, Fort McKay, Alberta, Canada, in regard to effluent discharges and stack emissions from the world's first two oil sands extraction plants (Suncor and Syncrude). Both Fort McKay and the plants are situated on the banks of the Athabasca River, with the plants approximately 10 to 20 km upstream from Fort McKay, in the southern part of a large northern Alberta region referred to as the tar sands ecosystem.

The effluent discharge concerns are based upon Athabasca River pollution (Fort McKay Tribal Administration, 1983). Prior to 1975, the river was the major source of drinking water for Fort McKay. In 1975, two drinking water holding tanks for the community were constructed, with water delivered by truck first from the Syncrude water supply system (1975 to March, 1980), and subsequently from the Fort McMurray water treatment plant. The permitted effluent discharge of oil and grease from Suncor into the Athabasca River is 420 kg per day (Kostler, 1982). During the period December - February, 1982, one of the Fort McKay tanks burned and the second froze, forcing all community residents to rely upon river ice and snow for drinking water. During this same three-month period, operational problems at Suncor resulted in excessive effluent discharge into the river, which caused the fish to taste

of gasoline, and resulted in an order from Pollution Control Division of Alberta Environment requiring the plant to reduce its water-borne pollution and to inform the residents downstream of the operational problems responsible for the spillage (Kostler, 1982). Fort McKay residents were advised not to drink the river water or to eat fish from the river.

In March, 1982, each home in Fort McKay was provided with a 45-gallon water drum to store potable water, and water supplies have continued to be trucked in from Fort McMurray since that time. The only community running water system is in the school, which has its own reservoir. In addition to water-borne effluent, the plants emit massive amounts of particulates into the atmosphere. In June of 1983 the Air Quality Control Branch of Alberta Environment conducted the first surveys of stack emissions from the plants (Parsons, 1983A, 1983B). Particulates mass emissions from the Suncor powerhouse stack ranged from 547 to 780 kg/hr (Parsons, 1983A); the Syncrude Canada main stack mass emissions ranged from 713 to 1,067 kg/hr (Parsons, 1983B).

The fly-ash from Suncor stack emissions has been analyzed for its metals, and contains approximately 12% aluminum, 2.5% vanadium, 1% nickel, 0.2% molybdenum, 0.036% strontium, 0.026% lead, and 0.018% chromium, in addition to several other metals (Shelfentook, 1978). Table 1.1 presents

estimated average hourly emissions of these metals, computed from this information, and assuming that Syncrude stack emissions have a composition identical to that of Suncor emissions. The plants normally operate 24 hours per day.

Table 1.1. Estimated average emissions of particulates, Al, V, Ni, Mo, Sr, Pb, and Cr in Suncor and Syncrude fly ash (kg/hr)<sup>1</sup>

	<u>Suncor</u>	<u>Syncrude</u>
Total Particulates	664	890
Aluminum	77.0	103.2
Vanadium	30.5	40.9
Nickel	6.64	8.90
Molybdenum	1.53	2.05
Strontium	0.239	0.320
Lead	0.173	0.231
Chromium	0.120	0.160

<sup>1</sup>Calculated from particulates emission rates (Parsons, 1983A, 1983B), and metal analysis of Suncor fly ash (Shelfentook, 1978).

The overall question at issue in this matter is: What are the health effects of exposure of this community to the pollution from the oil sands plants? We concluded that before this question could be addressed, more definitive toxicologic evidence was needed regarding the degree of exposure by Fort McKay residents to stack emissions and plant effluent, relative to residents of villages not so directly exposed. Accumulation of metals in scalp hair was chosen as the measure of such exposure, based on the fact that metal levels in scalp hair are widely accepted as an index of exposure to metal contaminants in the environment (Underwood, 1971; Hemphill, 1972; Creason, *et al.*, 1975; Chattopadhyay, *et al.*, 1977; Ryabukhin, 1978). Moreover, oil sands plant stack emissions and liquid effluent contain substantial amounts of a number of metals which are known to bioaccumulate (Table 1.1; Shelfentook, 1978; Alberta Environment, 1976).

### 1.3 METHODS

#### 1.3.1 Study Design.

To test the hypothesis that hair metal bioaccumulation patterns are related to geographic proximity to the oil sands plants, we selected three Alberta native villages for study: Fort McKay (population approximately 300),

the exposed community in the immediate vicinity of the plants; Fort Chipewyan (population 2500 to 3000), in the oil sands ecosystem about 200 km downstream from the oil sands plants, on the major waterway (the Athabasca River), coming from the area; and Garden River (population approximately 250), a village of size, socioeconomic structure, and lifestyle tradition similar to Fort McKay, but in a different ecosystem away from the winds or waterways carrying plant pollutants. We decided to concentrate on children in each of the villages because of the likelihood that confounding effects of lifestyle, such as cigarette smoking and/or alcohol consumption, would be minimized, and because their residence within the various settlements was more stable. Many adults in each village travel extensively, and some work in the oil sands plants. However, a small, random sample of adults in each village also was studied.

Hair samples were chosen for metal analysis because they could be cut to a uniform length to represent a standardized time period and would therefore reflect exposure over a period of time rather than a single point in time. In addition, the hair sampling technique is minimally invasive and likely to be acceptable to the population. Samples were collected in November, 1983.

Samples were collected and analyzed in a double blind manner. They were submitted for analysis in a numbered fashion, and the coding key was not revealed until results were reported.

### 1.3.2 Subjects

An attempt was made to collect samples from all children from 5 to 18 years of age in Fort McKay and Garden River. From 53 children eligible in Fort McKay, 44 hair samples were gathered; from 59 children eligible in Garden River, 39 samples were gathered. In Fort Chipewyan, 48 children were selected by random methods and 39 samples were gathered. Adults were selected by random methods, but it was not possible to locate all of the selected adults, and some volunteers were accepted, to make a total of 8 adults from Fort McKay, 7 adults from Garden River, and 12 adults from Fort Chipewyan.

The age and sex distribution of children and adult subjects in each community from which hair samples were gathered were as follows: (1) Fort McKay: 22 girls, average age 9.0 years (range 5.3 to 14.8 years), and 22 boys, average age 9.6 years (range 5.8 to 15.1 years); 4 women and 4 men, average age 49.4 years (range 22.5 to 66.5 years). (2) Garden River: 22 girls, average age 10.7 years (range 5.1 to 18.4 years), and 17 boys,



average age 9.7 years (range 4.6 to 16.0 years); 5 women and 2 men, average age 40.7 years (range 22.5 to 62.8 years). (3) Fort Chipewyan: 16 girls, average age 10.4 years (range 5.2 to 18.4 years), and 23 boys, average age 10.6 years (range 5.6 to 16.1 years); 9 women and 3 men, average age 47.5 years (range 24.0 to 78.5 years).

#### **1.3.2.1 Hair Sample Collection**

Samples were collected using a pair of high-quality stainless steel barber scissors. A small amount of hair was cut from as close to the scalp as possible from each of 8 to 10 sites around the subject's head. These small samples were all placed together with the scalp ends aligned, tied with nylon thread at the scalp end, folded into a weighing paper and placed into a paper envelope which was labelled on a label that was taped to the envelope so that it could be removed for blinding. The paper envelope containing the sample was then placed in a zip-lock polyethylene bag, which was sealed until the sample was prepared for analysis.

#### **1.3.2.2 Sample Preparation**

Glass blades were used to shave the first one or two mm from the scalp end of the hair samples, and to cut the samples to a uniform length of 10 cm, measured from the scalp end. Since human scalp hair grows at a rate

of approximately 0.2 to 0.5 mm/day (Hopps, 1977), these 10 cm samples represent between 6.7 to 16.7 months of hair growth. The reason for using glass blades was to avoid any metal contamination that may have resulted from the use of metal scissors during sample collection. A separate glass blade was used for each sample. When there was sufficient hair (i.e., at least 0.4 gm, 10 cm long), samples were separated into two approximately equal samples; hair in one sample was washed according to the method recommended by the International Atomic Energy Association (Ryabukhin, 1978), and the hair in the other sample was analyzed without washing. Great care was taken in separating the sample, a few hairs at a time, in order to make the two samples as similar as possible. When there was insufficient sample for preparing two samples, the single sample was washed prior to analysis.

To minimize any sample contamination during sample preparation, cigarette smoking was not permitted in the laboratory.

*Reagents:* Metal standards were from SPEX Industries Inc., New Jersey; acetone, nitric acid and HCl were Baker Instra-Analyzed; perchloric acid was GFS Double Distilled; water with 18 meg-ohm resistance was obtained by passing distilled water through 2 mixed bed ion exchange resins and a 0.2 micron millipore filter.

*Washing Procedure:* Samples were placed on porous glass filters attached to a vacuum tube; twelve samples were washed at a time, first for ten minutes in acetone, followed by three ten minute water washings, and a final ten minute acetone wash. Samples were then dried with a drying lamp, transferred to digestion tubes, and weighed to four decimals.

*Digestion:* Three ml nitric acid were added, and the sample digested until the volume was reduced to about 1 ml. One-half ml perchloric acid was then added and taken to perchloric fumes. 0.1 ml HCl was added and the sample diluted to 4 ml with de-ionized water.

*Multiple Digests:* The preparation and certification of human hair powder reference material has recently been reported (Okamoto, *et al.*, 1985). However, there was no standard human hair sample available at the time these samples were analyzed, so it was necessary to prepare a uniform mixture of hair for checking the reproducibility of the over-all procedure. The hair remaining after the 10 cm samples were prepared was pooled, cut into very fine pieces, and carefully mixed to make as uniform a mixture as possible. This pooled sample was then separated into 10 samples, each of which was washed, digested and analyzed as described.

### 1.3.3 Sample Analysis

Samples were washed, digested, and analyzed at Quanta Trace Laboratories, Inc. (Burnaby, B.C., Canada), using inductively coupled argon plasma emission spectroscopy (ICAP) for the analysis (Fassel, 1978). Thirty-two metals were reported by Quanta Trace Laboratories. Thirteen of these metals were not included in data analysis for the following reasons: beryllium, uranium, thorium, arsenic, bismuth, cobalt, molybdenum, antimony, lithium, and mercury were generally below the detection limit of the instrument; selenium was excluded because results were highly variable and it was not believed to be of interest in this study; boron and silicon were excluded due to use of borosilicate blades to trim and cut samples.

Samples were analyzed in batches of approximately 20, and the instrument was standardized after each set of samples. The standard operating procedure involved running a standard followed by a blank, 11 samples, blank, 9-11 samples, and blank. As an external check, standards were checked against Environmental Protection Agency (EPA) water samples.

Accuracy of the instrument was checked by analyzing aliquots from 26 samples on a second instrument in a separate laboratory. This second analysis was carried out also using ICAP, except for nickel which was

analyzed by atomic absorption. These analyses were performed by CanTest Laboratories, Ltd. (Vancouver, B.C., Canada).

#### 1.3.4 Data Analysis

The purpose for analyzing unwashed samples was to establish whether or not differences among the three communities are due to metal that had been adsorbed onto the hair from external sources. Our primary interest is in the washed samples, since these are believed to provide a better indication of metals that have been absorbed by bioaccumulation (Ryabukhin, 1978). A comparison of the composition of the washed and unwashed samples is the topic of an article currently in preparation.

For values below the detection limit (b.d.l.) of the instrument, a value of one-half the detection limit was entered. The reasons for entering b.d.l. levels in this fashion are: 1) It is probable that each subject has a finite level of each metal in his or her hair; 2) It would be statistically inaccurate to enter b.d.l. values as 'missing values', since they have been measured, and are likely to be some low value which the instrument was incapable of measuring; 3) We assume that for b.d.l. values, the actual level is somewhere between 0 ppm and the detection limit of the instrument; and 4) Although the b.d.l. values for a given metal are probably

distributed in a fashion closer to the detection limit than to zero, we have no way of knowing the actual distribution, and therefore consider one-half the detection limit to be the best reasonable estimate. In this study, only vanadium was affected by b.d.l. values. For children, the significant differences found among the three communities for vanadium (Table 1.2) are confirmed using any other coding of b.d.l. values that are consistent with these data, i.e., the lowest possible value for the F statistic (36.6) is still highly significant. For adults, the significant differences reported for vanadium (Table 1.3) are found when b.d.l. values are coded either as one-half the detection limit, or as the detection limit; however, no significant differences are found among the three communities when b.d.l. values are coded as 0.

Analysis of the data obtained for washed samples showed the concentration distribution for most metals to be somewhat skewed right. The data were log-transformed resulting in more normal distributions. However, oneway analysis of variance of the log-transformed data gave exactly the same p-values as were obtained by oneway analysis of variance of the untransformed data. For simplicity, we have reported values from the untransformed data. The Duncan multiple range test was used for *post hoc* analysis.

## **1.4 RESULTS**

### **1.4.1 Quality Control Procedures.**

The following two subsections deal with results from the special quality control procedures adopted for this study. These quality control procedures are in addition to the standard operating procedures at Quanta Trace Laboratories, Inc. (Section 3.5).

#### **1.4.1.1 Results from Two Different Analytic Laboratories.**

For 26 hair samples, results of replicate analyses obtained from Quanta Trace Laboratories, Inc. and CanTest Laboratories, Ltd, for lead, aluminum, nickel, and strontium agreed within five percent. For vanadium, variability was within nine percent. Molybdenum was generally below detection limits in both analyses.

#### **1.4.1.2 Multiple Digests of a Uniform Hair Sample.**

For 18 of the 19 elements, ten separate digests gave results within  $\pm 7\%$ . Chromium was an exception with a variability of  $\pm 9\%$ , due largely to one analysis which gave a result more than twice as great as the other

nine samples.

#### 1.4.2 Metal Levels in Washed Hair Samples from the Entire Child Population.

Statistically significant differences in hair levels of twelve metals were observed among children from the three communities. These results are listed in Table 1.2, and are summarized below.

*Lead:* Fort McKay children had the highest ( $p < .05$ ) mean hair lead level ( $7.7 \pm 7.9$  ppm), compared to  $4.9 \pm 3.4$  ppm for Garden River children, and  $4.1 \pm 3.1$  ppm for Fort Chipewyan children.

*Cadmium:* Fort McKay children with  $0.454 \pm 0.297$  ppm, and Garden River children with  $0.415 \pm 0.264$  ppm, had significantly higher ( $p < .05$ ) hair cadmium levels than Fort Chipewyan children ( $0.243 \pm 0.187$  ppm). The difference between Fort McKay children and Garden River children were not significant ( $p < .05$ ).

*Chromium:* The level of hair chromium in Fort McKay children ( $0.499 \pm 0.410$  ppm) and Garden River children ( $0.523 \pm 0.291$  ppm) did not differ significantly, and both levels were higher ( $p < .05$ ) than that in Fort Chipewyan children ( $0.352 \pm 0.182$  ppm).



*Copper:* Fort Chipewyan children had significantly more ( $p < .05$ ) copper in their hair ( $13.6 \pm 9.7$  ppm) than Fort McKay children ( $10.5 \pm 3.7$  ppm) or Garden River children ( $9.8 \pm 1.7$  ppm).

*Vanadium:* The vanadium level in hair from children in Garden River ( $0.207 \pm 0.124$  ppm) was nearly two and one-half times as high ( $p < .05$ ) as that in Fort McKay children ( $0.086 \pm 0.071$  ppm), and Fort McKay children had about two times as much ( $p < .05$ ) hair vanadium as Fort Chipewyan children ( $0.039 \pm 0.026$  ppm).

*Aluminum, iron, manganese, barium, zinc, calcium, and magnesium:* The children of Garden River had highest hair levels of the rest of the metals for which levels differed significantly (aluminum, iron, manganese, barium, zinc, calcium, and magnesium). Aluminum, iron, manganese, and barium levels in hair from children from Garden River were about two times as great ( $p < .05$ ) as the highest levels found in children from either Fort McKay or Fort Chipewyan. The differences were not as great for zinc, calcium, and magnesium, but hair levels of these three metals again were significantly elevated ( $p < .05$ ) in Garden River children, compared to levels in children from either Fort McKay or Fort Chipewyan.

*Nickel, potassium, sodium, phosphorous, titanium, strontium, and zirconium:* When the entire child population was considered, there were no

significant ( $p < .05$ ) differences in hair levels among the three communities for the remaining metals: nickel, potassium, sodium, phosphorous, titanium, strontium, and zirconium.

#### 1.4.3 Metal Levels in Washed Hair Samples from Adults.

Among adult subjects from the three communities, as shown in Table 1.3, the only statistically significant (using  $p < .05$ ) differences observed were higher hair phosphorous and vanadium levels in Garden River adults. The hair phosphorous level was higher ( $p < .05$ ) in Garden River adults ( $142.4 \pm 17.9$  ppm) than in adult subjects from either of the other two communities ( $118.4 \pm 16.9$  ppm;  $116.7 \pm 16.3$  ppm). For vanadium, the level in hair from Garden River adults ( $.051 \pm .023$  ppm) was significantly elevated ( $p < .05$ ) above that for Fort Chipewyan adults ( $.020 \pm .011$  ppm), but did not differ significantly ( $p < .05$ ) from that for Fort McKay adults ( $.037 \pm .031$  ppm).

The mean hair lead level for Fort McKay adults ( $12.0 \pm 15.0$  ppm) was over three-fold higher than that for Garden River adults ( $3.4 \pm 2.2$  ppm) and over two times as high as that for Fort Chipewyan adults ( $5.3 \pm 7.1$  ppm). The mean hair cadmium level for Fort McKay adults ( $2.98 \pm 5.28$  ppm) was over thirteen-fold higher than that for Garden River adults ( $0.221 \pm 0.183$  ppm), and over eight-fold higher than that for Fort Chipewyan

adults ( $0.352 \pm 0.429$  ppm). The mean hair nickel level in Fort McKay adults ( $2.64 \pm 6.11$  ppm) was over nine times as high as that in Garden River adults ( $0.279 \pm 0.212$  ppm), and over eight times that in Fort Chipewyan adults ( $0.325 \pm 0.290$  ppm). However, because of variability in the data and the small sample number, these differences in hair lead, cadmium, and nickel levels from adults in the three communities are not statistically significant at the .05 level. However, the hair cadmium level for adults in Fort McKay was higher than that for either Garden River or Fort Chipewyan at  $p < .1$ .

#### **1.4.4 Sex-related Differences in Metal Levels in Washed Hair Samples.**

A number of studies have found significant differences in trace metals in the hair of males and females (Creason, *et al.*, 1975; Klevay, 1973; Petering, *et al.*, 1973; Petering, *et al.*, 1971). In these studies, females most often had higher hair metal levels than males. For instance, Creason and colleagues (1975) found that sex was the most important covariate influencing trace-element content of human scalp hair, being significantly associated with 12 of 16 trace elements examined in children. In all cases, females had higher values than males. In the case of adults, these workers reported that 9 of 16 trace elements showed differences between males

and females, with females having higher levels of all metals except cadmium and lead.

In the present study, several metals differed significantly ( $p < 0.05$ ) between boys and girls. These differences were as follows: For the total child population, girls had highest Ni, Ca, Mg, Ti, and Sr, while boys had highest Ba, K, Na, Mn, and P. In Fort McKay, girls had highest Cu, Ni, Ba, Ca, Mg, P, Ti, and Sr, while boys had highest Cr, Fe, K, and Na. In Garden River, girls had highest Cr, Ni, Ca, Mg, and Sr, while boys had highest K, and Na. In Fort Chipewyan, girls had highest Cr, while boys had highest Pb, K, Mn, Na, and Ti.

For the total adult population, women had highest levels of all eleven metals which were significantly ( $p < 0.05$ ) different: Cu, Ni, Zn, Ca, Fe, K, Mg, Mn, Na, Sr, and Ti. When each community was considered separately, differences were as follows: In Fort McKay, women had significantly ( $p < 0.05$ ) more Ni, Fe, K, Mg, Na, Sr, and Zr, while men had more Zn. In Garden River no significant ( $p < 0.05$ ) differences between males and females for any metal were observed, probably because of low sample sizes (5 females and 2 males). In Fort Chipewyan women had significantly ( $p < 0.05$ ) more Cu, Ni, Mg, and Zr, while men had significantly more Cd, Pb, and V.

The hair metal content data were analyzed to determine if there are any significant differences among the three communities for girls only, and for boys only. The adult population is too small for similar analysis.

Using oneway analysis of variance on either the original data or log-transformed data for differences among girls in the three communities, results are similar to those obtained when the entire child population is considered, except for hair nickel and strontium levels. Girls in Fort McKay had a significantly elevated ( $p < .1$ ) hair nickel ( $0.470 \pm 0.521$  ppm) level, relative to that for girls in Garden River ( $0.236 \pm 0.118$  ppm), and for girls in Fort Chipewyan ( $0.240 \pm 0.211$  ppm). Girls in Fort McKay had significantly more ( $p < .05$ ) hair strontium ( $3.62 \pm 2.70$  ppm) than did girls in Garden River ( $1.81 \pm 1.52$  ppm) and in Fort Chipewyan ( $1.62 \pm 1.17$  ppm).

Using oneway analysis of variance on either the original data or on log-transformed data for differences among boys in the three communities, results are similar to those obtained when the entire child population is considered as a whole. Strontium is an exception, with boys in Fort McKay having lower ( $p < .05$ ) hair levels ( $0.911 \pm 0.452$  ppm) than boys in Garden River ( $1.73 \pm 0.91$  ppm), and in Fort Chipewyan ( $1.42 \pm 1.06$ ).

#### 1.4.5 Comparison of Washed with Unwashed Hair Samples.

A detailed comparison of the 122 washed and unwashed hair samples analyzed in this study will be dealt with in a separate report. For most metals, some of the metal was generally removed by the washing procedure, whereas for lead, cadmium, copper, zinc, calcium, and strontium, very little metal was removed. We interpret these results to indicate that these latter metals appear in the hair primarily as a result of bioaccumulation, rather than via deposition onto the hair (Ryabukhin, 1978).

Table 1.2. Summary of results for washed hair samples from children (ppm  $\pm$  S.D.)<sup>1</sup>

	FORT MCKAY (N=44)	GARDEN RIVER (N=39)	FORT CHIPEWYAN (N=39)
Lead	7.7 $\pm$ 7.9 <sup>a</sup>	4.9 $\pm$ 3.4	4.1 $\pm$ 3.1
Cadmium	0.454 $\pm$ 0.297 <sup>a,b</sup>	0.415 $\pm$ 0.264 <sup>a</sup>	0.243 $\pm$ 0.187
Nickel	0.325 $\pm$ 0.401	0.226 $\pm$ 0.094	0.233 $\pm$ 0.192
Copper	10.5 $\pm$ 3.7	9.8 $\pm$ 1.7	13.6 $\pm$ 9.7 <sup>a</sup>
Vanadium	0.086 $\pm$ 0.071 <sup>a</sup>	0.207 $\pm$ 0.124 <sup>a</sup>	0.039 $\pm$ 0.026
Aluminum	28.9 $\pm$ 10.8	67.6 $\pm$ 30.8 <sup>a</sup>	22.6 $\pm$ 11.8
Iron	25.4 $\pm$ 14.6	55.2 $\pm$ 25.1 <sup>a</sup>	17.4 $\pm$ 6.8
Manganese	1.7 $\pm$ 0.83	3.6 $\pm$ 1.6 <sup>a</sup>	1.4 $\pm$ 1.4
Barium	1.4 $\pm$ 0.76	2.9 $\pm$ 1.1 <sup>a</sup>	1.5 $\pm$ 1.0
Zinc	109.3 $\pm$ 44.0	162.9 $\pm$ 39.3 <sup>a</sup>	124.7 $\pm$ 38.5
Magnesium	49.1 $\pm$ 52.2	71.3 $\pm$ 58.7 <sup>a</sup>	42.4 $\pm$ 27.9
Calcium	547.4 $\pm$ 514.2	696.0 $\pm$ 465.2 <sup>a</sup>	464.0 $\pm$ 274.0
Chromium	0.499 $\pm$ 0.410 <sup>a,b</sup>	0.523 $\pm$ 0.291 <sup>a</sup>	0.352 $\pm$ 0.182

<sup>a</sup>Significantly higher than the community (or communities) with lower averages ( $p < .05$ ).

<sup>b</sup>Does not differ significantly ( $p > .05$ ) from Garden River level.

<sup>1</sup> $p$ -Values computed by oneway analysis of variance. Duncan multiple range was used for *post hoc* analysis. The significant differences are confirmed using any other coding of values below detection limit that are consistent with these data, i.e., the lowest possible value for the F statistic (36.6) is still highly significant.

Table 1.3. Summary of results for washed hair samples from adults ppm  $\pm$  S.D.)<sup>1</sup>

	FORT MCKAY (N=8)	GARDEN RIVER (N=7)	FORT CHIPEWYAN (N=12)
Lead	12.0 $\pm$ 15.0	3.4 $\pm$ 2.2	5.3 $\pm$ 7.1
Cadmium	2.98 $\pm$ 5.28	0.221 $\pm$ 0.183	0.352 $\pm$ 0.429
Nickel	2.64 $\pm$ 6.11	0.279 $\pm$ 0.212	0.325 $\pm$ 0.290
Copper	10.6 $\pm$ 1.58	9.3 $\pm$ 1.3	16.9 $\pm$ 11.4
Vanadium	0.037 $\pm$ 0.031 <sup>b</sup>	0.051 $\pm$ 0.023 <sup>a</sup>	0.020 $\pm$ 0.011
Aluminum	20.7 $\pm$ 7.1	23.1 $\pm$ 8.4	15.6 $\pm$ 7.6
Iron	38.1 $\pm$ 63.3	20.7 $\pm$ 7.7	15.9 $\pm$ 12.8
Manganese	1.9 $\pm$ 2.1	2.7 $\pm$ 3.2	1.1 $\pm$ 0.84
Barium	1.3 $\pm$ 0.89	1.7 $\pm$ 1.3	1.4 $\pm$ 1.2
Zinc	116.2 $\pm$ 41.9	160.3 $\pm$ 19.0	145.7 $\pm$ 45.8
Magnesium	81.1 $\pm$ 107.2	89.8 $\pm$ 97.0	95.8 $\pm$ 85.5
Calcium	487.3 $\pm$ 335.2	812.8 $\pm$ 854.0	754.5 $\pm$ 607.4
Phosphorous	118.4 $\pm$ 16.9	142.4 $\pm$ 17.9 <sup>a</sup>	116.7 $\pm$ 16.3
Chromium	0.325 $\pm$ 0.185	0.444 $\pm$ 0.191	0.315 $\pm$ 0.166

<sup>a</sup>Higher than the remaining two communities ( $p < .05$ ).

<sup>b</sup>Higher than Fort Chipewyan ( $p < .05$ ).

<sup>1</sup> $p$ -Values computed by oneway analysis of variance. Duncan multiple range was used for *post hoc* analysis. The significant differences are found when b.d.l. values are coded as the detection limit, or as one-half the detection limit.



## 1.5 DISCUSSION.

The two crucial questions raised by the results described above deal with possible health implications of trace metal bioaccumulation indicated by the observed hair metal levels, and with possible sources of exposure (i.e., environmental, diet, etc.) to the observed metals. These questions are dealt with in the following two subsections.

### 1.5.1 Health Implications.

The choice of hair for assessing trace metal bioaccumulation complicates the question of inferring possible health implications from observed hair levels, because for many of the metals analyzed (Tables 1.2,1.3), little definitive information on the question exists (Underwood, 1971; Hemphill, 1972; Ryabukhin, 1978). For this reason, we focus in this section on five metals -- lead, cadmium, nickel, vanadium, and chromium -- with the greatest toxic potency, based on collective evidence from both human and animal studies (Casarett and Doull, 1975). Of these, lead and cadmium are of particular concern, in that subclinical effects have been documented for both metals (Pihl and Parkes, 1977; Thatcher, *et al.*, 1982), and hair levels of each have been shown to reflect environmental exposure (Chattopadhyay, *et al.*, 1977; Ryabukhin, 1978;

Hemphill, 1972).

*Lead.* Societal concern over human exposure to environmental lead has been dramatized with the 1984 announcement by the U.S. Environmental Protection Agency that the amount of lead in gasoline in the U.S. should be cut by 90% by 1986 (Keateny, 1984A, 1984B). Environment Canada had previously announced that Canadian gas lead levels would match the current U.S. standard by 1987 (Keateny, 1984A). Mr. William Ruckelshaus, administrator of the U.S. E.P.A. at the time, is quoted as saying, "The evidence is overwhelming that lead, from all sources, is a threat to human health" (Keateny, 1984A).

Environmental factors which have been shown to increase lead levels in human hair include urban living and cigarette smoking (Creason, *et al.*, 1975), residential proximity to industries with emissions containing lead (Chattopadhyay, *et al.*, 1977), and lead ingestion (Underwood, 1971; Hemphill, 1972). Creason and colleagues (1975) have shown that the relative amounts of trace metals, including lead, in hair from residents living in an urban area (New York) correlated with the relative amounts of the same metals in dustfall to which these residents are exposed. The two most important sources of body lead for most North Americans generally are accepted to be automobile exhaust emissions and ingested lead.

There is no standard for hair lead levels as there is for blood lead, for which both the U.S. E.P.A. and Canada Health and Welfare specify an acceptable limit of 30 micrograms ( $\mu\text{g}$ ) of lead per deciliter (dl) of blood (Ratcliffe, 1981). A comparison of human blood and hair lead levels suggests that a blood lead level of 30  $\mu\text{g}/\text{dl}$  would correspond (roughly) to a hair lead level of 24 ppm ( $\mu\text{g}/\text{g}$ ), assuming lead intake and excretion are in a steady state (Chattopadhyay, *et al.*, 1977).

Subclinical effects of lead on behavioral and cognitive function in children, at hair lead levels in the range 20 - 30 ppm, are suggested by at least two studies. Pihl and Parkes (1977) showed that a group of 31 learning disabled children had a mean hair lead level (23 ppm) over five-fold higher than the mean level (4 ppm) found in 22 normal children. These results anticipated those of Thatcher and colleagues (1982), who documented significant correlations of I.Q. and school performance in children with low levels of lead and cadmium in scalp hair samples.

Analysis of the results of the present study in light of findings from other studies suggest that the mean hair lead level in Fort McKay children of 7.7 ppm (Table 1.2), which is significantly higher than that found for children in the other two villages, is still typical of values of 9.1 ppm (Chattopadhyay, *et al.*, 1977) and 17.6 ppm (Weiss, *et al.*, 1972) found for rural North American

children in other studies. Individual data show that hair lead levels exceeding 20 ppm occurred in 4 children and 2 adults from Fort McKay. Results cited above (Pihl and Parkes, 1977; Thatcher, *et al.*, 1982) suggest that the children may display impaired cognitive and school achievement abilities, relative to their counterparts with lower hair lead levels.

*Cadmium.* This study, in agreement with other studies (Petering, *et al.*, 1973; Creason, *et al.*, 1975; Huel, *et al.*, 1981) found significant correlation between hair lead and hair cadmium levels (Tables 1.4,1.5,1.6). Important sources of environmental cadmium include industrial emissions, food, and smoking (Varma and Katz, 1978). Because blood cadmium levels do not correlate with either acute or chronic exposure, control levels for blood cadmium have not been specified (Lee and White, 1980). Hair cadmium levels correlate well with the degree of exposure, but no standards exist (Lee and White, 1980).

At least two studies (Pihl and Parkes, 1977; Thatcher, *et al.*, 1982) have shown that subclinical cognitive and performance impairment in children is correlated with hair cadmium levels. The study of Pihl and Parkes (1977) showed that learning disabled children had mean hair cadmium levels of 1.72 ppm, relative to a mean level of 1.08 ppm for their normal counterparts. Thatcher and colleagues (1982) found that I.Q. of Maryland school children was

negatively correlated with hair cadmium levels.

In the present study (Table 1.2), Fort McKay children had the highest mean hair cadmium level (0.454 ppm), which was significantly higher than that for Fort Chipewyan children (0.243 ppm). This value did not, however, differ significantly from that for Garden River children (0.415 ppm). Three children, two from Fort McKay and one from Garden River, had hair cadmium levels exceeding 1.0 ppm, with 1.4 ppm being the highest individual value found. Based on findings cited above (Pihl and Parkes, 1977; Thatcher, *et al.*, 1982), these results suggest that no subclinical effects due to cadmium exposure are likely to exist among children examined in this study.

Three adults from Fort McKay had hair cadmium levels exceeding 1.0 ppm. The two with highest hair cadmium levels (6.7 ppm and 14.8 ppm) also had the highest hair lead levels (33.5 ppm and 38.1 ppm). Two adults from Fort Chipewyan had hair cadmium levels exceeding 1.0 ppm (1.2 and 1.3 ppm).

*Nickel.* Nickel levels found in hair of children in this study (.325 ppm, .226 ppm, .233 ppm) are not much different from the 0.51 ppm reported by Creason, *et al.* (1975) for 265 children in New York. It is not likely that these nickel levels are associated with pathological effects.

One adult from Fort McKay had 17.7 ppm nickel in her hair, but this is still considerably below the 58 ppm reported for 7 Amazon Indian women (Perkons, *et al.*, 1977).

*Chromium.* Levels of hair chromium found in this study (for children: .499 ppm, .523 ppm, .352 ppm; for adults: .325 ppm, .444 ppm, .315 ppm) are very close to the levels reported by Creason, *et al.* (1975) for 265 children (.56 ppm) and 192 adults (.62 ppm) in New York. No pathology is likely to be associated with hair chromium levels found in this study.

*Vanadium.* Vanadium levels found in this study (for children: .086 ppm, .207 ppm, .039 ppm; for adults: .037 ppm, .051 ppm, .020 ppm) are not much different from the .25 ppm for 267 children and .18 ppm for 193 adults in New York reported by Creason, *et al.* (1975). Again, pathologic effects associated with these levels are unlikely.

#### 1.5.2 Possible Sources of Observed Hair Metal Levels.

This study was designed to obtain evidence for enhanced exposure to trace metals among Fort McKay residents, relative to exposure among residents in two other Indian communities further removed from an industrial source of such metals. The study was *not* designed to prove what the actual source of

metal exposure might be. Our results show that each village displays a distinctly different pattern of trace metal distribution in hair from both children and adults. The Fort McKay results are of concern, because the only metals which show the highest hair concentrations in both children and adults in this community, relative to levels found in residents of the other two communities, are lead, cadmium, and nickel (Tables 1.2 and 1.3). The first two of these metals have proven toxicity in humans, and both have documented subclinical effects on cognitive and behavioral functions in children. The only subjects found to have hair lead levels with possible subclinical implications (4 children and 2 adults) lived in Fort McKay. It is appropriate to speculate, therefore, on possible sources of exposure to lead and cadmium among residents of Fort McKay.

As noted above, ingestion, cigarette smoking and industrial pollution represent major sources of exposure to both lead and cadmium. Automobile exhaust emissions also represent a major source of exposure to lead. What differences among the three villages exist, in terms of these major sources?

*Ingestion.* The three villages studied are all native villages, with comparable socioeconomic status. Major differences in diet, and in pica (paint chip) ingestion among the three villages therefore are not likely. Differences in trace metal levels in the water supplies of the three villages may exist.

Therefore, differences in ingestion patterns cannot be ruled out as a possible source of the elevated hair Pb and Cd levels in Fort McKay residents. Further environmental studies to clarify this question are in progress.

*Cigarette Smoking.* When the samples were collected, we asked subjects about their cigarette smoking habits. Three children in Fort McKay, no children in Garden River, and 11 children in Fort Chipewyan admitted to smoking cigarettes. Since children from Fort Chipewyan had lowest levels of both lead and cadmium, and yet more children there admitted to smoking cigarettes than in the other two villages, it is not likely that cigarette smoking is involved in the elevated levels of lead and cadmium found among Fort McKay children. In addition, no correlation exists between cigarette smoking and hair lead or cadmium among adults in any of the communities. We conclude that cigarette smoking is not involved in the elevated levels of hair lead or cadmium found in Fort McKay residents.

*Automobile Exhaust Emissions.* Fort McKay is on a logging road with low vehicular traffic. Fort Chipewyan has no through roads leading to it. Garden River is isolated from any road. There probably is more vehicular traffic in Fort Chipewyan than in Fort McKay, because the former is a larger community with more vehicles using the community road system. All three communities display mean hair lead levels typical of those found by other studies of rural



residents. It does not seem likely that automobile exhaust emissions account for the elevated hair Pb and Cd levels among Fort McKay residents. Further studies are needed to clarify this question.

*Industrial Pollution.* The major difference among the three communities is that Fort McKay is in closer proximity to the two oil sands plants than the other villages. Recent source emissions surveys reported a mass atmospheric emission of 547 to 780 kg/hr for Suncor (Parsons, 1983A) and 713 to 1,067 kg/hr for Syncrude (Parsons, 1983B). This results in an average atmospheric emission of approximately .173 kg of lead per hour for Suncor, and .231 kg of lead per hour from Syncrude (Table 1.1). In addition, the two plants taken together, emit an estimated 15.5 kg of nickel per hour into the atmosphere (Table 1.1). Cadmium was not detected in the fly ash by Shelfentook (1978), using a method with a detection limit of 2ppm. Lead, cadmium, and nickel exist at elevated levels in the plants' holding tanks (Alberta Environment, 1976) which have been known to leak into the river (Kostler, 1982). Therefore, both air and water pollution by the oil sands plants represent possible sources of lead and nickel exposure. Water is also a possible source cadmium exposure.

Speculation about ingested water as a possible source of metal contamination in Fort McKay residents must be tempered by the observation that drinking water has been trucked into the community since March, 1982 for

storage in household tanks and the school reservoir. The 19-month interval from this date to the 11/83 hair sampling date exceeds the approximate 9-month growth period reflected in the 10 cm hair samples. Therefore, hair metal contamination from ingested water could arise from: 1) possible contamination of trucked water and/or storage tanks in Fort McKay; and 2) casual ingestion of snow and/or river water. We recently have completed a study to ascertain trace metal levels in drinking water supplies for each of the three communities.

There were no significant differences among the three villages in hair nickel levels, when the entire child population was considered. However, elevated nickel levels in Fort McKay girls, along with higher (though not statistically significant) levels of nickel in adults from Fort McKay, support the conclusion that there is an increased nickel burden in the Fort McKay environment.

Vanadium, aluminum, and molybdenum also represent likely markers of exposure to fly ash emissions by the plants, because of their appreciable occurrence in fly ash emissions. Hair levels of vanadium and aluminum are higher in Fort McKay than in Fort Chipewyan residents (Tables 1.2 and 1.3), but the levels for both of the villages are lower than Garden River levels. Hair molybdenum levels generally were below the detection limit, and are not

included in data analysis.

One way of possibly resolving the question of whether industrial pollution accounts for the pattern of trace metal distribution in the hair of Fort McKay residents is to examine the covariance pattern for the different hair metals measured for each village, by means of correlation matrices. The rationale for this approach is that if a group is exposed to a pollution source containing multiple trace metals, all known to bioaccumulate in hair, then hair levels of these metals should co-vary together and a correlation matrix may reveal such covariation. A group not so exposed will display a substantially different, and less extensive, pattern of hair metal covariation. This method of "fingerprinting" multiple contamination exposures by means of correlation patterns has been used successfully to pinpoint discrete pollution sources (Rahn and Lowenthal, 1984).

Our results (Tables 1.4, 1.5, 1.6) show that the number of pairs of hair trace metals which co-vary (either positively or negatively) in Fort McKay children (26 correlations) is substantially greater than the number for either Garden River children (10 correlations) or Fort Chipewyan children (14 correlations). These results suggest that Fort McKay children may be exposed to a richer source of multiple trace metal contamination than their counterparts in either of the other villages.

Table 1.4. Summary of Pearson product moment correlation analysis for metals in washed hair samples from Fort McKay children

---

	Pb	Cd	Cr	V	Al	Fe	Mn	Ba	Zn
Pb									
Cd	+								
Cr									
V	+	+	+						
Al		+	+	+					
Fe	+	+	+	+	+				
Mn	+	+		+	+	+			
Ba		+			+				
Zn	-	-	-	-		-	-	-	

---

+ Positive correlation ( $p < .01$ ).

- Negative correlation ( $p < .01$ ).

Table 1.5. Summary of Pearson product moment correlation analysis for metals in washed hair samples from Garden River children

---

	Pb	Cd	Cr	V	Al	Fe	Mn	Ba	Zn
Pb									
Cd	+								
Cr	+								
V			+						
Al				+					
Fe			+	+	+				
Mn									
Ba								+	
Zn	-	-							

---

+ Positive correlation ( $p < .01$ ).  
 - Negative correlation ( $p < .01$ ).

Table 1.6. Summary of Pearson product moment correlation analysis for metals in washed hair samples from Fort Chipewyan children

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	Pb	Cd	Cr	V	Al	Fe	Mn	Ba	Zn
Pb									
Cd	+								
Cr									
V									
Al	+			+					
Fe	+	+	+	+	+				
Mn	+	+					+		
Ba		+						+	
Zn	-								

---

+ Positive correlation ( $p < .01$ ).

- Negative correlation ( $p < .01$ ).

The present study provides grounds for concern over the substantial quantity of lead contained in the air emissions from these plants, in light of documented subclinical effects of lead on cognitive and behavioral function in children at relatively low levels, and in light of recent national initiatives in both Canada and the U.S. to attempt to substantially reduce existing atmospheric lead concentrations (Keateny, 1984A, 1984B). Further studies will be needed to document the extent to which air and/or water pollution by the tar sands plants contribute to the elevated levels of other trace metals, namely cadmium, nickel, chromium, and strontium, found in the hair of Fort McKay residents. To this end, we also have collected atmospheric particulates and water samples from the three villages, which will be subjected to trace metal analysis identical to that carried out for the hair samples. From these data, it will be possible to compare metal distribution patterns for environmental samples from the three villages with patterns for hair taken from residents of the villages.

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2. CHAPTER II. CORRELATION CLUSTERS IN THE ACCUMULATION OF METALS  
IN HUMAN SCALP HAIR: EFFECTS OF AGE, COMMUNITY OF RESIDENCE, AND  
ABUNDANCE OF METALS IN AIR AND WATER SUPPLIES.

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## 2.1 ABSTRACT

Scalp hair samples taken from 122 children and 27 adults from three native Indian villages in northern Alberta, Canada were analyzed for 32 metals, in an attempt to trace industrial pollution into the human population. One of the villages has been exposed since 1967 to increased levels of several metals due to its proximity to the world's first two oil sands petroleum extraction plants (Suncor and Syncrude), which release large amounts of metals into the environment. Metal-enriched particulates are emitted at a rate of 547 to 780 kg/hr for Suncor, and 713 to 1,067 kg/hr for Syncrude. To test the hypothesis that hair content reflected accumulation of environmental metals, water and aerometric samples were collected and analyzed for their metal content. These analyses demonstrated that elevated levels of 9 metals in hair from children in one of the control villages (Garden River) are (with the exception of Al) correlated with increased levels of metals in water and air. Moreover, increased levels of Cu, but lowest levels of all other metals were found in hair and environmental samples from one control village (Fort Chipewyan). Correlation matrices for metals in the hair samples revealed three sets of highly intercorrelated metals ('correlation clusters'): 1) Pb/Cd; 2) Al/V/Fe; 3)

Ca/Mg/Sr/Ba. These groups of metals were significantly intercorrelated ( $r > 0.6$ ,  $p < 0.001$ ) in the total population, and in both children and adults, or both males and females, as well as when the population was compared according to community of residence. The robustness of the clusters is particularly noteworthy in view of large differences in the proportions and absolute amounts of the various metals in hair from children in the three villages. Plots of metal levels in hair as a function of age of subject reveals a dramatic decrease in concentrations of Al, V, and Fe during the first years of life. The high levels of Al and V in hair from very young children may reveal a lower selectivity in metal absorption, and a higher risk of toxicity during a period of rapid growth when need for nutritionally essential metals is particularly high.

## 2.2 INTRODUCTION

A number of critical reviews of the use and misuse of hair analysis have appeared recently (Manson and Zlotkin, 1985; Rivlin, 1983; Fletcher, 1982; Hambidge, 1982), including a statement by the College of Physicians and Surgeons of Ontario (1982). These have been provoked by extensive

popularisation of hair analysis as a method of detecting nutritional deficiencies of various vitamins as well as minerals. As the College of Physicians and Surgeons of Ontario (1982) has pointed out, "present knowledge with respect to hair analysis does not justify its use in the detection of any nutritional deficiency or excess, with the possible exception of zinc deficiency." Nevertheless, the College (1982) also acknowledged that "On an experimental basis, the technique appears to hold the promise of providing insights into the longer term nutritional status of populations in the community, and the exposure of humans to environmental hazards."

There are many advantages in utilizing hair for assessment of toxic metal exposure and nutritional mineral status. These include the ease with which samples can be obtained, stored, shipped, and handled, as well as the fact that hair samples can indicate exposure or deficiencies over a period of time. The ability to analyze hair for several elements simultaneously is a definite advantage, especially in view of the growing knowledge of trace element interactions, and the inability to obtain similar information from blood or other body specimens. Also, a number of trace elements are considerably more concentrated in hair than in urine or blood.

At the same time, hair trace element analysis is not yet fully developed due to a lack of clear definition of normal ranges, and methods of analyzing data from multi-element analysis are not yet well-developed. Hopefully the present study will enhance the value of multi-element analysis of human scalp hair.

In the present study, scalp hair samples were taken from 122 native Indian children and 27 adults in 3 villages in northern Alberta, Canada, and were analyzed for 32 elements. Nineteen elements were selected for detailed analysis, 11 of which demonstrated distinctly different accumulation patterns in children but not in adults in each village. These results have been described by Moon and colleagues (1986). One of the villages (Fort McKay) is thought to be exposed to increased levels of a number of metals due to its proximity to two oil sands extraction plants, which emit large amounts of lead, cadmium, nickel, and other metals into the environment (Shelfentook, 1978; Parsons, 1983a,b). Levels of lead were highest in both children and adults in the exposed group, although the higher levels in adult hair were not significant at the .05 level. Surprisingly, in one of the control villages (Garden River) levels of 8 metals (V, Al, Fe, Mn, Ba, Zn, Mg, Ca) in hair from children but not adults were several

times higher than those found for either of the other two villages. These elevated levels were found in samples that were washed prior to analysis, making it unlikely that surface contamination was responsible for the differences. Children in the other control village (Fort Chipewyan) had highest levels of copper, and lowest levels of all other metals which were significantly different.

In an effort to explain these results, we obtained water and aerometric samples from each village. The time interval between hair sampling and environmental sampling was two years, but there is no reason to believe that substantial changes occurred during this time. The rest of this paper discusses the correlation of environmental parameters with hair trace element content, and inter-element correlations from hair trace element analysis.



## 2.3 METHODS.

### 2.3.1 Study Design

Three native Indian villages in Alberta, Canada, were selected for study: Fort McKay (population approximately 300), the exposed community in the immediate vicinity of the oil sands plants; Fort Chipewyan (population 2500 to 3000), in the oil sands ecosystem about 200 km downstream from the oil sands plants, on the major waterway (the Athabasca River) coming from the area; and Garden River (population approximately 250), a village of size, socioeconomic structure, and lifestyle tradition similar to Fort McKay, but in a different ecosystem away from the winds or waterways carrying plant pollutants. We decided to concentrate on children in each of the villages because of the likelihood that confounding effects of lifestyle, such as cigarette smoking and/or alcohol consumption, would be minimized, and because their residence within the various settlements was more stable. However, samples were also obtained from a few adults in each village.

Hair samples were chosen for metal analysis because they could be cut to a uniform length to represent a standardized time period and would

therefore reflect exposure over a period of time rather than a single point in time. In addition, the hair sampling technique is minimally invasive and likely to be acceptable to the population. Subjects were selected by random methods from children 5 to 18 years of age. Samples were collected in November, 1983, from 39 children in two of the villages (Garden River and Fort Chipewyan) and 44 children in Fort McKay. As well, 27 samples were collected from adult volunteers.

### **2.3.2 Environmental Samples**

In an attempt to investigate possible environmental sources for hair metal levels observed, water and aerometric samples were collected in September, 1985, and were analyzed for the 32 elements that were measured in the hair samples. Aerometric samples were obtained using a high volume sampling technique.

### **2.3.3 Hair Sample Collection**

Scalp hair samples were collected using a pair of high-quality stainless steel barber scissors. A small amount of hair was cut from as close to the scalp as possible from each of 8 to 10 sites around the

subject's head. These small samples were all placed together with the scalp ends aligned, tied with nylon thread at the scalp end, folded into a weighing paper, and placed into a paper envelope tagged with a label that could be removed for blinding. The paper envelope containing the sample was then placed in a zip-lock polyethylene bag, which was sealed until the sample was prepared for analysis. The procedure for hair sample preparation consisted of two steps: (1) using a glass blade the first one or two mm were shaved from the scalp end of the sample, to remove any metal that may have contaminated the sample by use of metal scissors to collect the samples; and (2) hairs were then cut to a uniform length (9 mm) to represent an approximate period of about 8 or 9 months of hair growth.

#### **2.3.4 Water Sample Collection**

Water samples were gathered from several sites in each of the three communities during September, 1985. A total of 19 samples were gathered from Fort McKay, 12 samples from Garden River, and 15 samples from Fort Chipewyan. Care was taken to obtain water from all of the community water supply sites in Fort McKay and Garden River. This was not possible

in Fort Chipewyan so water was drawn from the schools, nursing station, and several selected homes in the community. However, no water was taken directly from the Athabasca River, Lake Athabasca, or the Peace River.

Collection methods followed as closely as possible the methods described by the Energy Resources Conservation Board of Alberta (ERCB, 1984). Wide mouth polyethylene containers (500 ml), and their caps, were washed with non-ionic detergent, and rinsed three times with distilled and deionized water (18 meg-ohm resistance). They were then rinsed in 5 per cent nitric acid (Baker Instra-Analyzed for trace metal analysis), and again rinsed three times with deionized water. Analysis of washings from the final rinse water, pooled for each 10 containers, was required to meet the following standards: Pb 0.002 mg/l; Cd 0.001 mg/l; Ni 0.002 mg/l; Ca 1.0 mg/l; Na 0.5 mg/l; K 0.1 mg/l.

As a preservative, 1 ml concentrated nitric acid (J.T. Baker Instra-Analyzed for trace metal analysis) was added to each 500 ml sample immediately after sampling. Preservative was added using a Socorex pipette. Socorex pipette tips were soaked for 15 hours in 5 per cent nitric acid, rinsed three times with deionized water, dried at 105°C, and stored

individually in sealed plastic bags until use. Pipette tips were discarded after addition of preservative to each container.

### 2.3.5 Aerometric Sample Collection

General Metal Works high volume air sampling units (Model GMWL-2000 H) were set into place in each of the three communities during the water sampling trip in September, 1985. The units were run continuously for 48 hours per sampling period, and were calibrated to filter approximately 10,000 cu m air in the 48 hour period. The time period and the actual flow rate were continuously recorded on the disk recorders of the instruments. In each community, a member of the community was hired to change the filters and air volume recording disk. Filters were placed into pre-marked plastic bags, and sealed in a second zip-lock plastic bag, along with the air volume records. A 'field blank' which was sealed in a zip-lock bag accompanied each instrument. The field blank was put into place and removed without turning on the filter motor, then resealed in the zip-lock container by the same individual who was responsible for changing all filters. Six samples were successfully gathered at Fort McKay, eight from Garden River, and seven from Fort Chipewyan.

### 2.3.6 Sample Analysis

Hair samples were washed, digested, and analyzed by a commercial laboratory (Quanta Trace Labs., Inc., Burnaby, B.C.), using inductively coupled argon plasma emission spectroscopy. The preparation of hair samples for analysis, and analytic procedures have been described in detail (Moon, et.al., 1986). Hair samples were analyzed both before and after washing with a standard washing procedure (Ryabukhin, 1978). This paper deals only with results for washed samples; a detailed comparison of washed and unwashed hair samples will be published in a separate article. Samples were analyzed in a double blind manner. They were submitted for analysis in a numbered fashion, and the coding key was not revealed until after results were reported.

One hundred ml of each water sample was concentrated to 10 ml using a routine concentration procedure for inductively coupled plasma emission analysis (Thompson, et.al., 1982). This procedure allows for detection of lead and cadmium in the ppb range. Filters from high volume samplers were digested with perchloric acid (GFS Double Distilled) as previously described for hair sample digestion (Moon, et.al., 1986).

### 2.3.7 Data Analysis

Data were analyzed by oneway analysis of variance, using Duncan multiple range for *post hoc* analysis. The concentration distribution for most metals in the hair samples was somewhat skewed right. Therefore, the data were log-transformed, resulting in more normal distributions. Results for log-transformed data were identical with those obtained using the original data.

Pearson product moment correlation analysis was performed on results obtained for the concentration of 15 metals in the washed hair samples. The correlations were essentially the same for the original data and log-transformed data. The correlation matrices were analyzed using cluster analysis in order to determine if it is possible to identify members of the separate communities based on the results of the correlation analysis. For the cluster analysis we used squared Euclidean distances based on the average linkage between groups method (Norušis, 1985).

## 2.4 RESULTS

### 2.4.1 Correlation Analysis of Metals in Hair

Correlation matrices for metal levels for the 15 metals in hair from children from the three communities showed 38 significant ( $p < .001$ ) correlations for Fort McKay, 22 for Fort Chipewyan, and 23 for Garden River. Three sets of highly intercorrelated metals were identified: 1) Pb/Cd; 2) Al/V/Fe; 3) Ca/Mg/Sr/Ba. Table 2.1 lists the correlation coefficients for lead and cadmium in various subgroups of the population. Correlation coefficients for the Al/V/Fe cluster are given in Tables 2.2.1 - 2.2.4, and for the Ca/Mg/Sr/Ba cluster in Tables 2.3.1 - 2.3.4. For all elements in each cluster, the correlation coefficient is greater than 0.4900; all  $p$ -values are  $< 0.001$ . Several other metals, e.g., Zn, Ni, Cr, Cu, Ti, Zr, P, K, and Na, failed to form many significant correlations and did not fit into any of the identified clusters.



Table 2.1. Pearson product moment correlation coefficients for lead and cadmium in hair samples<sup>1</sup>

	Correlation Coefficient (r)	Number of Subjects (N)
Entire Population	0.6325	149
Adults	0.8684	27
Children	0.6675	122
Males	0.7382	71
Females	0.6498	78
Fort McKay	0.6376	52
Garden River	0.7713	46
Fort Chipewyan	0.8981	51

<sup>1</sup>High correlation coefficients were found between Pb and Cd for the entire population (122 children and 27 adults), and for each of the various subgroups of the population. All correlations are significant at  $p < .001$ .

Table 2.2. Pearson product moment correlation coefficients for the Al/V/Fe cluster in hair samples<sup>1</sup>

Table 2.2.1  
The entire child population (N=122)

	Al	V	Fe
Al	1.0000		
V	0.8331	1.0000	
Fe	0.8832	0.9161	1.0000

Table 2.2.2  
Girls (N=59)

	Al	V	Fe
Al	1.0000		
V	0.7849	1.0000	
Fe	0.8515	0.8750	1.0000

Table 2.2.3  
Boys (N=63)

	Al	V	Fe
Al	1.0000		
V	0.8841	1.0000	
Fe	0.9081	0.9637	1.0000

Table 2.2.4  
All children, separated by community of residence

Fort McKay (N=44)			
	Al	V	Fe
Al	1.0000		
V	0.6844	1.0000	
Fe	0.5775	0.6353	1.0000

Garden River (N=39)			
	Al	V	Fe
Al	1.0000		
V	0.7468	1.0000	
Fe	0.8536	0.9496	1.0000

Fort Chipewyan (N=39)			
	Al	V	Fe
Al	1.0000		
V	0.6474	1.0000	
Fe	0.7304	0.6678	1.0000

Tables 2.2 list the high correlation coefficients for the Al/V/Fe cluster for all children (Table 2.2.1), girls from the entire child population (Table 2.2.2), boys from the entire child population (Table 2.2.3), and for children in each community (Table 2.2.4). All correlations are significant at  $p < .001$ .

Table 2.3. Pearson product moment correlation coefficients for the Ca/Mg/Sr/Ba cluster for hair samples<sup>1</sup>

Table 2.3.1  
The entire child population (N=122)

	Ca	Mg	Sr	Ba
Ca	1.0000			
Mg	0.9460	1.0000		
Sr	0.9135	0.8832	1.0000	
Ba	0.6352	0.6313	0.5229	1.0000

Table 2.3.2  
Girls (N=59)

	Ca	Mg	Sr	Ba
Ca	1.0000			
Mg	0.9468	1.0000		
Sr	0.9020	0.8672	1.0000	
Ba	0.7218	0.7548	0.6164	1.0000

Table 2.3.3  
Boys (N=63)

	Ca	Mg	Sr	Ba
Ca	1.0000			
Mg	0.9219	1.0000		
Sr	0.9407	0.8920	1.0000	
Ba	0.7875	0.7785	0.7383	1.0000

Table 2.3.4  
All children, separated by community of residence

Fort McKay (N=44)

	Ca	Mg	Sr	Ba
Ca	1.0000			
Mg	0.9673	1.0000		
Sr	0.9644	0.9874	1.0000	
Ba	0.8842	0.8917	0.9054	1.0000

Garden River (N=39)

	Ca	Mg	Sr	Ba
Ca	1.0000			
Mg	0.9486	1.0000		
Sr	0.9690	0.9680	1.0000	
Ba	0.5047	0.4926	0.5787	1.0000

Fort Chipewyan (N=39)

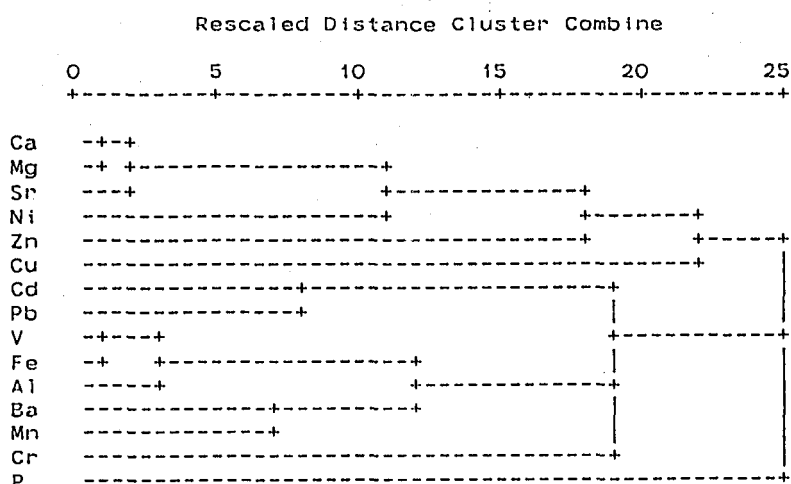
	Ca	Mg	Sr	Ba
Ca	1.0000			
Mg	0.8818	1.0000		
Sr	0.9333	0.8826	1.0000	
Ba	0.7571	0.6828	0.7538	1.0000

<sup>1</sup>Tables 2.3 list the high correlation coefficients for the Ca/Mg/Sr/Ba cluster for all children (Table 2.3.1), girls from the entire child population (Table 2.3.2), boys from the entire child population (Table 2.3.3), and for children in each community (Table 2.3.4). All correlations are significant at  $p < .001$ .

#### 2.4.2 Cluster Analysis of the Correlation Matrices for Metals in Hair

Cluster analysis of the correlation matrices for metals in hair for all children is given in the dendrogram in Figure 2.1. Figures 2.2.1–2.2.3 display dendrograms derived from cluster analysis of the correlation matrices for children in each community. The existence of the 'correlation clusters' is demonstrated by this analysis. One of the control communities (Garden River, Figure 2.2.2) is distinctive due to the occurrence of a Mn/Ba cluster combine at 6 on the combine scale. No clear distinction which can be related to environmental exposure in Fort McKay is apparent (Figures 2.2.1–2.2.3).

FIGURE 2.1  
 CLUSTER ANALYSIS OF THE CORRELATION MATRICES FOR 15 METALS  
 IN HAIR SAMPLES FROM ALL CHILDREN (N=122): DENDROGRAM USING  
 AVERAGE LINKAGE BETWEEN GROUPS FOR SQUARED EUCLIDEAN DISTANCES

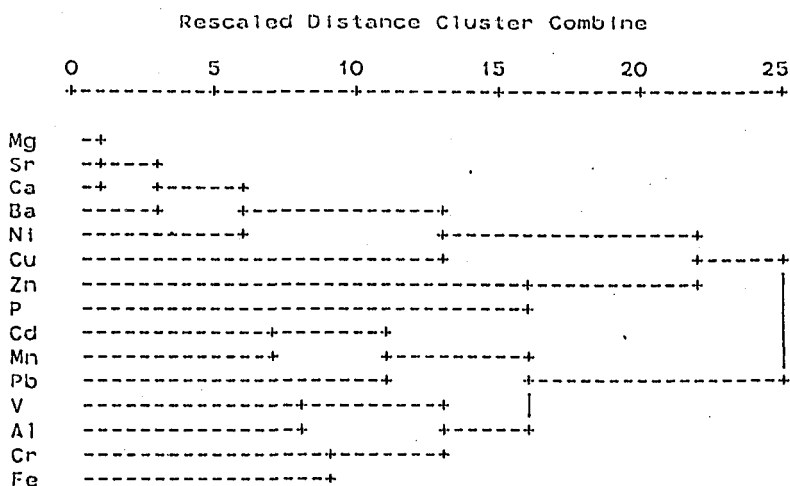


Dendrograms are read from left to right. "+" signs or vertical lines denote joined clusters. Distances are rescaled to fall in the range from 1 to 25. The closer to zero (the left margin) the "+" or connecting line falls, the more closely correlated are the joined metals.

In the above dendrogram, Ca is joined with Mg, and V is joined with Fe to make the first two (most closely correlated) sets of cluster pairs. Next, Sr is added to the Ca/Mg cluster, and Al is added to the V/Fe cluster, forming the Ca/Mg/Sr and Al/V/Fe clusters. Pb and Cd are combined at 8 on the scale. In this dendrogram, which represents all children in the study, Ba and Mn form a cluster that is more closely correlated than Pb and Cd. However, inspection of the dendrograms for the separate communities reveals that Ba and Mn are highly correlated only for children in Garden River; this correlation is so strong that it is seen in the dendrogram for all children.

CLUSTER ANALYSIS OF THE CORRELATION MATRICES FOR 15 METALS IN HAIR SAMPLES FROM CHILDREN: DENDROGRAM USING AVERAGE LINKAGE BETWEEN GROUPS FOR SQUARED EUCLIDEAN DISTANCES

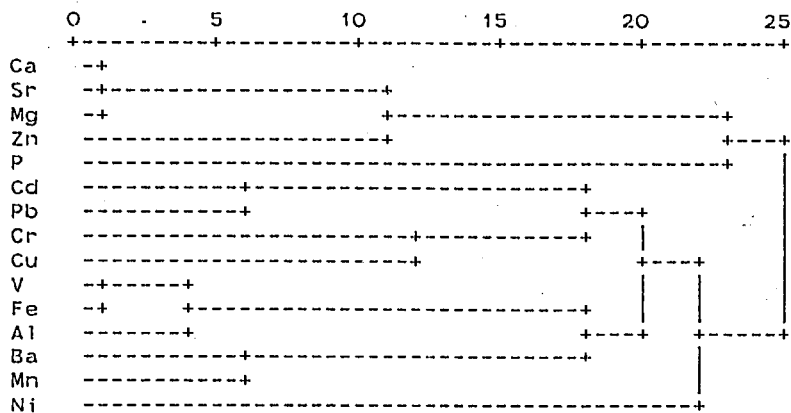
FIGURE 2.2.1  
CHILDREN FROM FORT MCKAY (N=44)



In the above dendrogram from cluster analysis of the correlation matrices for metals in hair from children in Fort McKay (the exposed village) Mg, Sr, and Ca form the most closely associated cluster. The Mg/Sr/Ca cluster is joined by Ba at 3 on the cluster combine scale. These four elements are joined by nickel at 6 on the scale. Cd and Mn are combined at 7, and are joined by Pb at 11 on the scale. V and Al combine at 6 while Cr and Fe combine at 9, and the 4 metals (V/Al/Fe/Cr) are combined at 13 on the scale. Although the dendrograms for children in Fort McKay (above) and Fort Chipewyan (Figure 2.2.3) are different, it would not be possible to distinguish children from these two communities based on cluster analysis of the correlation matrices of metals in hair samples.

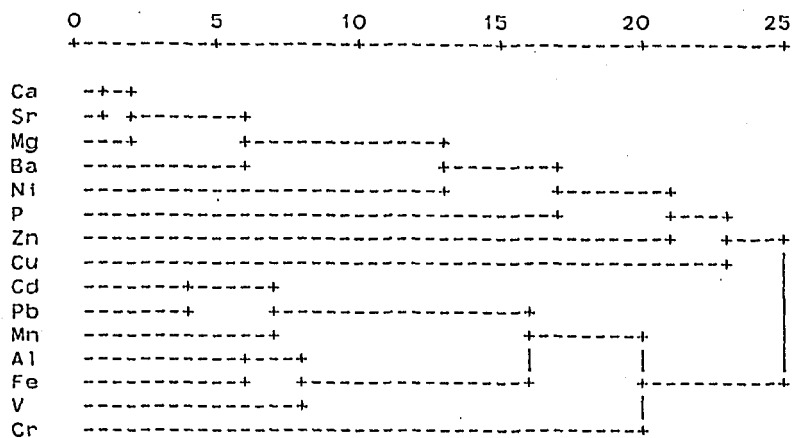


FIGURE 2.2.2  
CHILDREN FROM GARDEN RIVER (N=39)



In the above dendrogram from cluster analysis of the correlation matrices for metals in hair from children in Garden River, Ca/Mg/Sr, and V/Fe are combined at 1 on the scale. Al is added to the V/Fe cluster at 4. The Pb/Cd cluster is formed at 6. Ba is not added to the Ca/Mg/Sr cluster, but, instead, is combined with Mn at 6 on the scale. The strong association between Ba/Mn is distinctive for children from Garden River. The association is strong enough that it is seen in the dendrogram for all children (Figure 1). No comparable distinctive cluster was found for children from the other two villages (Figures 2.2.1 and 2.2.3).

FIGURE 2.2.3  
CHILDREN FROM FORT CHIPEWYAN



In the above dendrogram from cluster analysis of the correlation matrices for metals in hair from children in Fort Chipewyan, the Ca/Mg/Sr/Ba cluster is formed at 6 on the scale. The Pb/Cd cluster is formed at 4. Al/Fe join at 6, and the Al/Fe/V cluster is formed at 8. Although the dendrograms for children in Fort Chipewyan (above) and Fort McKay (Figure 2.2.1) are different, it is not possible to distinguish children from these two communities based on cluster analysis of the correlation matrices of metals in hair samples.

### 2.4.3 Water Samples

Water samples were analyzed: 1) by oneway analysis of variance to determine differences in water from the three villages; and 2) for metal-metal relationships using Pearson product moment correlation analysis. Results are discussed in the next two sections.

### 2.4.4 Metals in Water Samples

Table 2.4 lists levels of those metals for which significant differences were found in the water supplies of the three communities. Aluminum was from 4.5 to 5 times as high in Fort McKay water as in either of the other communities. Levels of cadmium, iron, manganese, and barium were highest in Garden River water. Magnesium and calcium were equivalent in Fort McKay and Garden River water, and higher in these communities than in Fort Chipewyan. Copper levels were far higher in Fort Chipewyan water than in water from either of the other communities - 145 times higher than in Garden River, and 16 times higher than in Fort McKay. Lead was found in five water samples, all from Fort Chipewyan, at low levels (approx. 0.007 mg/l).

Table 2.4. Metals present in water samples (mg/l)<sup>1,2</sup>

	Fort McKay N=19	Garden River N=12	Fort Chipewyan N=15
	<u>Mean</u> ± <u>S.D.</u>	<u>Mean</u> ± <u>S.D.</u>	<u>Mean</u> ± <u>S.D.</u>
Cadmium	.0005 ± .0001	.0021 ± .009*	.0009 ± .0001*
Copper	.018 ± .027	.002 ± .001	.292 ± .344*
Aluminum	.854 ± .254*	.183 ± .054	.172 ± .037
Iron	.034 ± .024	.612 ± .356*	.188 ± .086*
Manganese	.006 ± .003	.020 ± .007*	.004 ± .004
Barium	.050 ± .004*	.050 ± .015*	.023 ± .001
Magnesium	8.48 ± .370*	8.48 ± 3.1*	3.44 ± .142
Calcium	32.3 ± 2.1*	32.4 ± 6.7*	12.6 ± .560

\*Significantly higher than the community (ies) with lower value(s) at the 0.05 level.

<sup>1</sup>Only those metals that differ significantly in one or more community are given.

<sup>2</sup>Lead was below detection limit (0.005 mg/l) in all samples except five from Fort Chipewyan. Among these five samples were the only three that also contained detectable levels of Ni, and two containing Co.

#### 2.4.5 Correlation Analysis of Metals in Water

Results of correlation analysis for Ca, Mg, Sr and Ba in water samples from each community showed that Ca, Mg, and Sr form a correlation cluster for water samples as they did for the hair samples. However, Ba is an exception. Although Ba is highly correlated with Ca, Mg, and Sr in water samples from Fort McKay, it is not correlated with Mg in Garden River water, or with either Ca or Mg in Fort Chipewyan water. Lead was detected in only five water samples from Fort Chipewyan and undetectable in samples from the other communities. It therefore was not possible to obtain correlations for lead and cadmium in water samples. Moreover, aluminum and iron were not significantly correlated in water samples from any of the communities, so the Al/V/Fe cluster was not found in water samples.

#### 2.4.6 Aerometric Samples

Although results from this portion of the study may give insight into some of the hair findings, it is to be emphasized that there are complications associated with these samples. The samplers were placed at ground level; at least two samples from Garden River had a large amount

of visible sand. Since it was in a public place, it is possible that someone accidentally or maliciously contaminated the sampler. Moderate winds were reported for the area at the time, so it is also possible that these filters trapped airborne sand from the wind. Statistical results are essentially the same whether these samples are included or not. The only significant ( $p < .05$ ) differences are in lead, which was highest in samples from Garden River, and titanium which was highest in samples from Fort Chipewyan (Table 5). On a total weight basis, samples from Fort McKay were smallest ( $0.0816\text{g} \pm 0.068\text{g}$ ), Fort Chipewyan next ( $0.1974\text{g} \pm 0.0928\text{g}$ ), and Garden River highest ( $0.8192\text{g} \pm 1.21\text{g}$ ). However, these differences are not statistically significant ( $p > .05$ ). The small number of samples and large standard deviations are responsible for the lack of statistical significance.

Due to the problem of possible sample contamination, we performed correlation analysis on metal content of the sample, expressed in terms of  $\mu\text{g}$  per mg of deposited material. Ca and Sr were not included, since background levels on the filters were too high, i.e., greater on the blank than in the sample in many instances. Ba was reported as ">8000  $\mu\text{g}/\text{filter}$ " in all cases, and so is not included. Cd was not detected in the samples. Information is therefore available only for one cluster, the Al/V/Fe cluster.

All three elements were significantly correlated in samples from Garden River, while only Al and V were significantly correlated in aerometric samples from all three communities.

Table 2.5. Aerometric metal levels (ng/m<sup>3</sup>)

	Fort McKay	Garden River	Fort Chipewyan
	N=6	N=8	N=7
	<u>Mean</u> ± <u>S.D.</u>	<u>Mean</u> ± <u>S.D.</u>	<u>Mean</u> ± <u>S.D.</u>
Copper	296 ± 87	264 ± 194	314 ± 79
Nickel	.779 ± .774	4.97 ± 9.2	1.1 ± .57
Lead	6.2 ± 14.8	55.7 ± 53.1*	31.1 ± 15.7
Aluminum	405 ± 631	2838 ± 6942	317 ± 317
Vanadium	.767 ± .742	11.1 ± 18.2	1.35 ± .775
Iron	287.4 ± 313.5	6772 ± 14679	478.5 ± 226.2
Magnesium	136.3 ± 95.3	974.6 ± 1973	178.2 ± 82.4
Manganese	7.3 ± 8.1	151.4 ± 301.5	11.0 ± 7.5
Titanium	6.5 ± 5.4	21.0 ± 19.0	25.2 ± 11.3*
Chromium	.712 ± .310	5.7 ± 9.9	1.5 ± .71

\*Greater than the community with the lowest level (p<.05)

## 2.5 DISCUSSION.

### 2.5.1 Pearson Product Moment Correlation Analysis

Since our results (Moon, et.al., 1986), like those of others (for reviews see Hemphill, 1972; Ryabukhin, 1978; Brown, 1980), suggest that metal accumulations, or patterns of metal accumulation, in human scalp hair may have value in tracing environmental exposure from industrial sources, we examined metal correlation matrices in greater detail. Pearson product moment correlation analysis showed the villages with the highest and the lowest hair metal levels to be more similar than the other (exposed) village. Even though only lead was elevated in hair samples from children in the exposed village, there were nearly twice as many significant metal-metal correlations in that village as in either of the other two.

This analysis also revealed three sets of highly intercorrelated metals, which were significantly correlated in the total population as well as in each of the villages separately, and in various sub-groups of the populations studied. Previous reports of significant correlations between lead and cadmium (Petering, Yeager, and Witherup, 1973; Creason, et.al., 1975; Chittleborough and Steel, 1980; Huel, Boudene and Ibrahim, 1981), and



confirmed by our current data, convince us that the highly significant association between these two metals is a general phenomenon, and suggests that the other sets of intercorrelated metals may also be of more general interest.

Since synergistic effects of lead and cadmium have been reported (Ferm, 1969), and since concurrent exposure to the two metals is likely (Challop, 1971; Tsuchiya, 1976), it is important to assess both lead and cadmium levels at the same time. Hair is perhaps the best body tissue for concurrent assessment of lead and cadmium, since with teeth and nails it is one of the few tissues in which both metals can be measured, and for which there is evidence that levels may reflect exposure. Laker (1982) reviewed various specimens (blood, urine, hair, teeth, and nails) available for assessing trace element levels in humans, concluding that blood and hair are the most promising. Since blood cadmium levels may be maintained at a very low level even under conditions of relatively high exposure (Tsuchiya, 1976), hair is perhaps the only readily available specimen for concurrent assessment of lead and cadmium in the body. Multi-element analysis of human scalp hair samples may also provide interesting insights into relationships among elements other than lead and cadmium, as well as information relating environmental levels of minerals to scalp hair mineral

content, as indicated by the current study.

#### 2.5.1.1 The Lead/Cadmium Cluster

No matter how the population was separated, we found uniformly high Pearson product moment correlation coefficients for hair lead and cadmium in the entire population of 122 children and 27 adults, as well as in all sub-groups (Table 2.1). Others have also reported significant correlations between these two metals (Petering, et.al., 1973; Creason, et.al., 1975; Chittleborough and Steel, 1980; Huel, et.al., 1981), suggesting that the correlations found in this study are representative of a general phenomenon. The correlation coefficients found in this study are strikingly high when compared with previous studies.

Petering, Yeager, and Witherup (1973) reported a high degree of association of lead and cadmium in the hair of 95 males ( $r=0.4052$ ;  $p=.001$ ) and 83 females ( $r=0.2563$ ;  $p=.02$ ), in Cincinnati. Creason, et.al., (1975) reported inter-element correlations for 16 metals in 284 children and 207 adults in New York. Although values of correlation coefficients were not reported, Creason and coworkers (1975) stated that the elements that best intercorrelated in children and adults were cadmium, lead, and copper. Huel, Boudene, and Ibrahim (1981) reported a significant correlation between lead

and cadmium in hair from 110 newborn babies in Haguenu Maternity in eastern France (rank correlation coefficient,  $r=0.312$ ;  $p<.001$ ), but not in hair from the mothers. Chittleborough and Steel (1980) analyzed beard hair samples from a single individual (taken three times a week for a period of about 13 weeks), for lead, cadmium, copper and zinc. A correlation coefficient of 0.392 ( $p<.02$ ) for lead and cadmium was reported. Our results, when considered in view of these previous studies, indicates that correlation matrices may be of value in assessing simultaneous exposure to lead and cadmium. This similarly suggests that the other 'correlation clusters' may be of general interest as well.

We were not able to determine lead/cadmium relationships in environmental samples, since lead was not detected in water samples (except in five from Fort Chipewyan), and cadmium was not detected in aerometric samples.

#### 2.5.1.2 The Aluminum/Vanadium/Iron Cluster

In water samples, vanadium was detected in only a few samples at trace levels just over .0002 mg/l. Aluminum and iron were not significantly correlated in water from any community. For the aerometric samples, iron and vanadium were significantly correlated in all communities, but aluminum

and vanadium, and aluminum and iron were correlated only in Garden River. It is thus interesting that aluminum, vanadium, and iron levels in hair samples were highly inter-correlated in each of the communities, and in various groups within the communities. The hair samples were washed using a standard washing procedure to remove surface contamination (Ryabukhin, 1978), making it unlikely that these correlations are due to dust or soil contamination. In an effort to better understand this cluster of inter-correlated elements ('correlation cluster'), we have plotted levels of metals in hair as a function of subject age (Figures 2.3, 2.4, 2.5). The relationships between each of the metal pairs in the Al/V/Fe cluster are shown in Figures 2.6, 2.7, 2.8. These relationships which are represented by the high correlations among the three elements are strikingly illustrated by these plots. Since we did not record weight of subjects, it is not possible to determine if the elevated levels found in younger children are related more closely to age or to weight. Whether due to age or weight, the similarity of the curves and the relationships between metal pairs is striking. Similar curves are obtained for each separate community, or when data for girls or boys are plotted separately (not shown; a separate paper will deal with the effects of age, sex, and washing procedure on trace element content of human scalp hair).

FIGURE 2.3. ALUMINUM IN WASHED HAIR SAMPLES

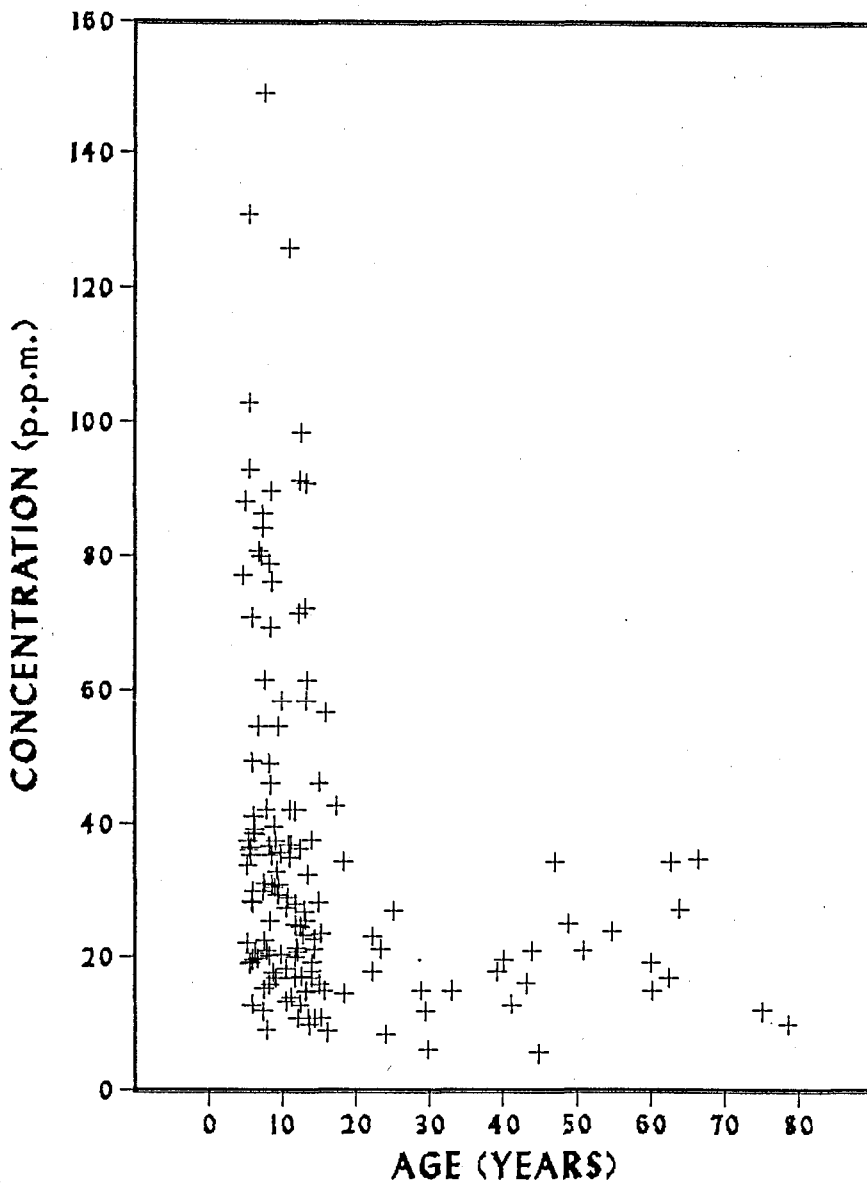


FIGURE 2.4. VANADIUM IN WASHED HAIR SAMPLES

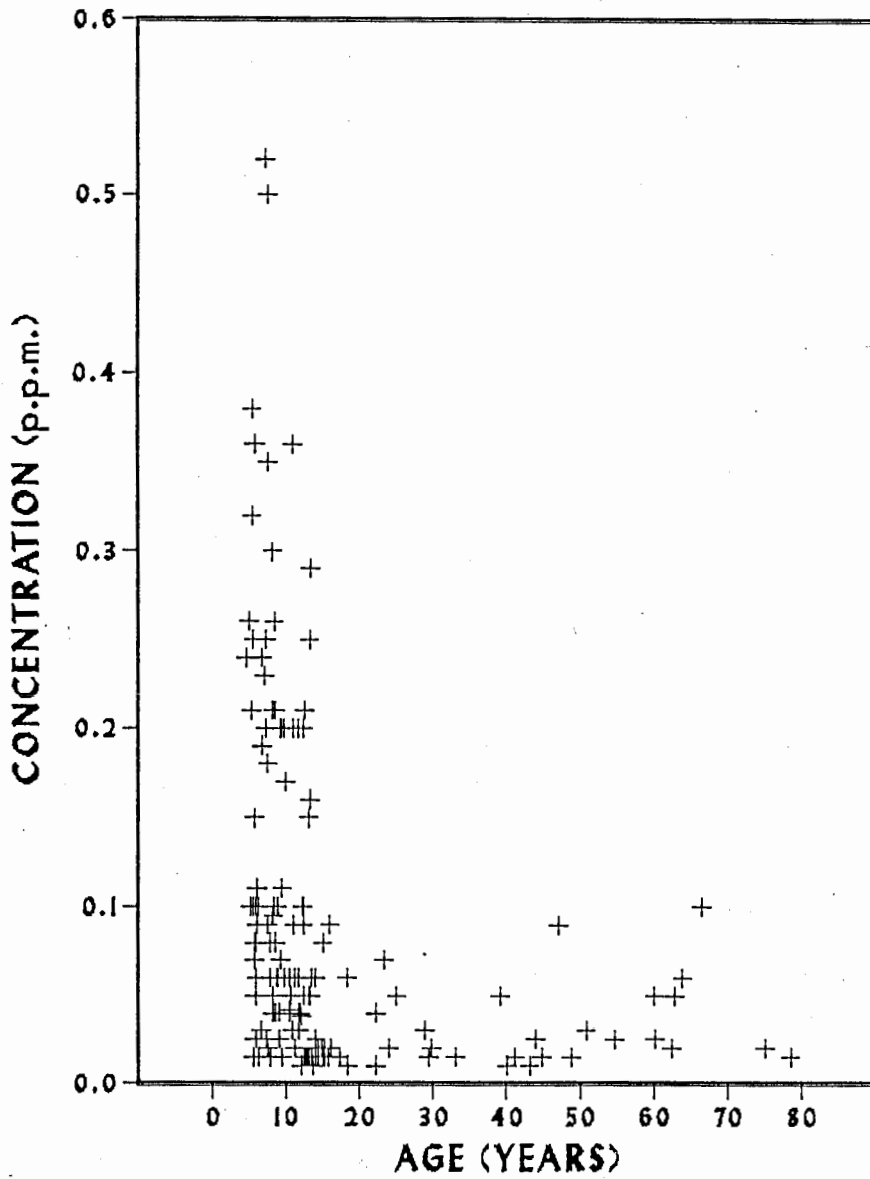


FIGURE 2.5. IRON IN WASHED HAIR SAMPLES

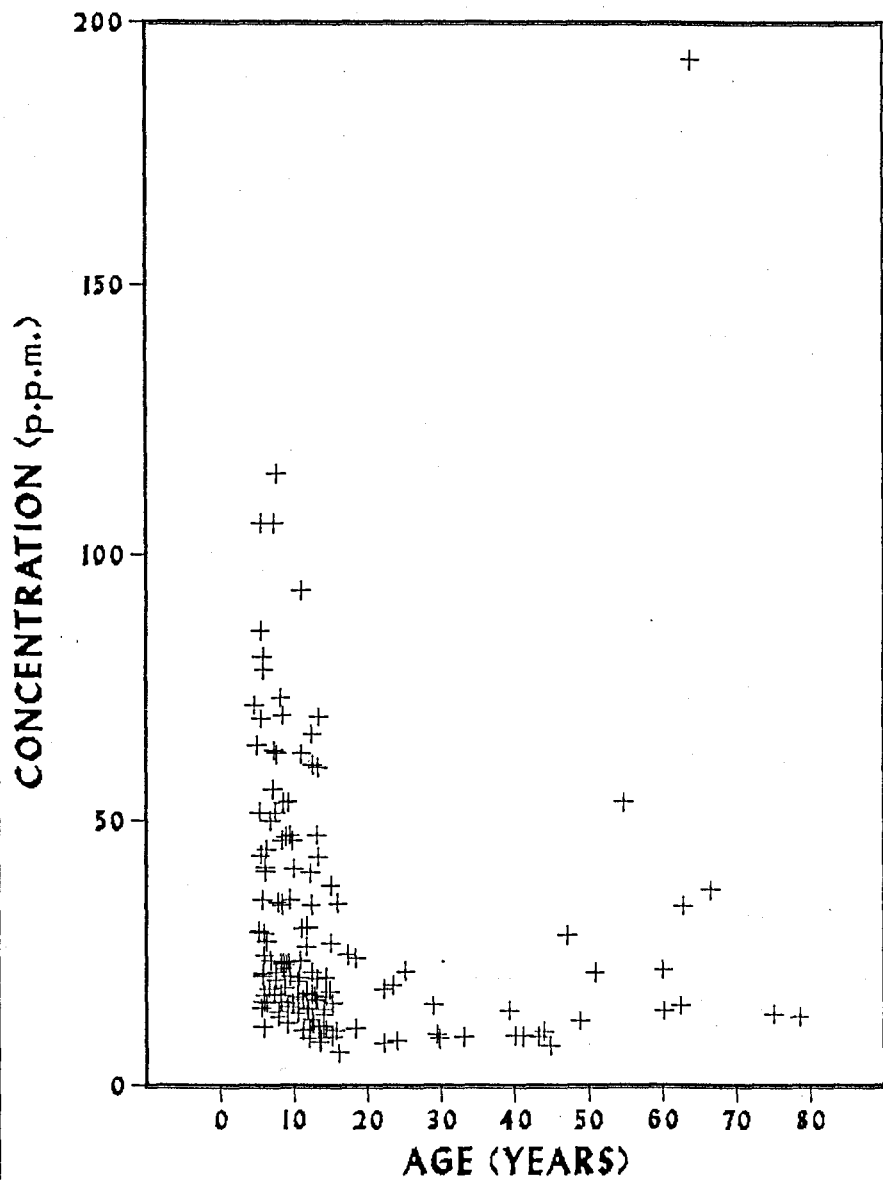


FIGURE 2.6. IRON VS ALUMINUM IN WASHED HAIR SAMPLES

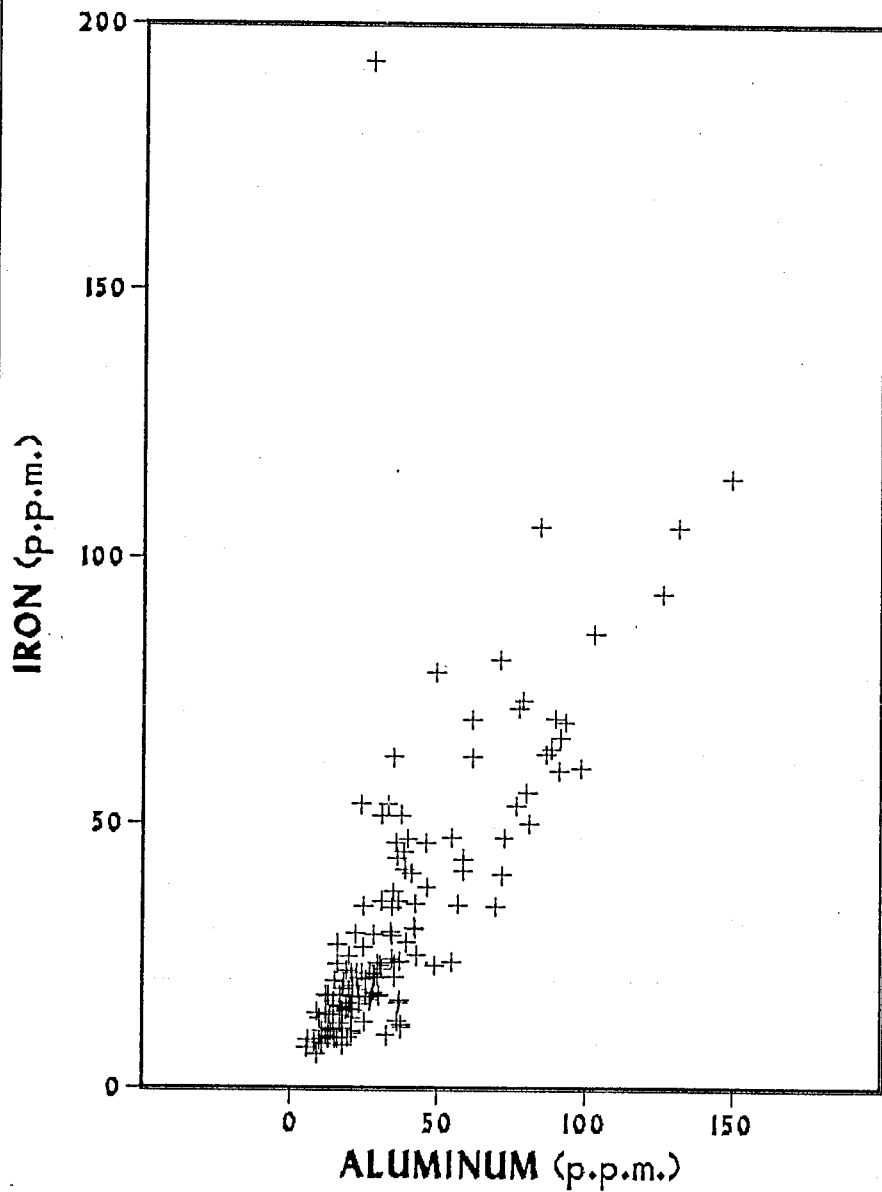




FIGURE 2.7. VANADIUM VS ALUMINUM IN WASHED HAIR SAMPLES

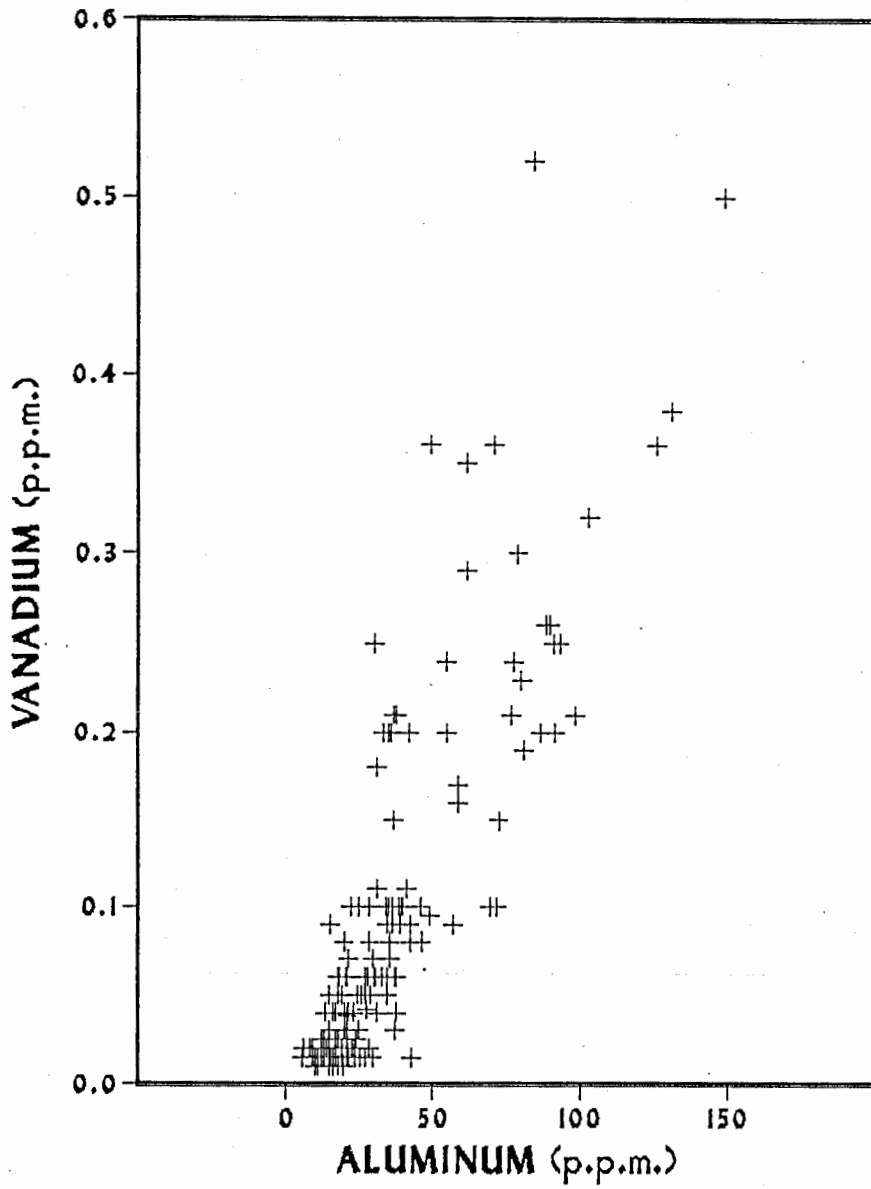
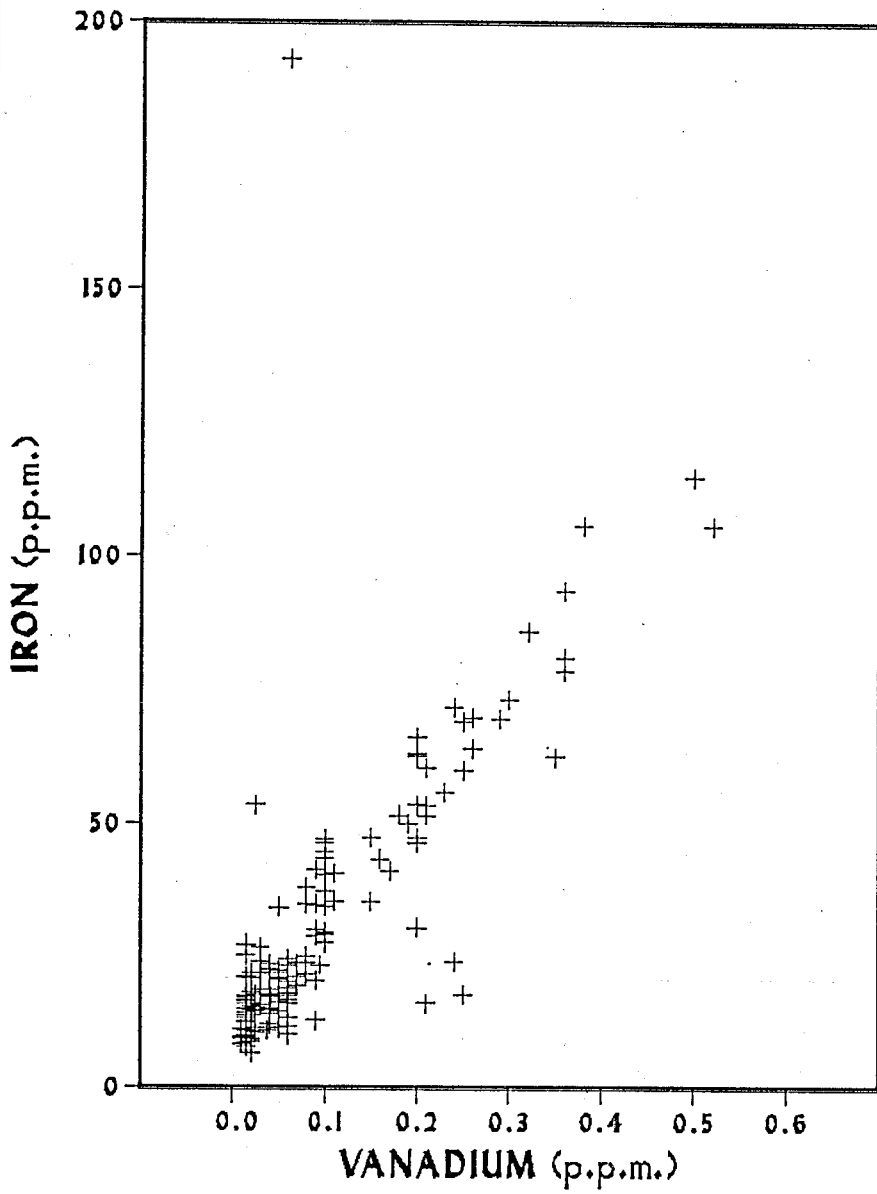


FIGURE 2.8. IRON VS VANADIUM IN WASHED HAIR SAMPLES



Growth promoting properties have been demonstrated for vanadium in chicks (Hopkins and Mohr, 1974) and rats (Schwarz and Milne, 1971). The current results provide evidence that vanadium levels in humans, are elevated during periods of growth. Aluminum is not considered to be an essential trace element (Sorenson, et.al., 1974; Frieden, 1984). On the contrary, aluminum accumulation may be associated with the neurological damage encountered in Alzheimer's disease (Bjorksten, 1982). Our results showing high levels of aluminum and vanadium in human scalp hair in young children awaits clarification. The high levels of Al and V in very young children may reveal a lower selectivity in metal absorption, and a higher risk of toxicity during a period of rapid growth when need for nutritionally essential metals is particularly high. Anthony and co-workers (1986) have shown that Al is more toxic in younger animals.

#### **2.5.1.3 The Calcium/Magnesium/Strontium/Barium Cluster**

Calcium, magnesium, strontium, and barium are all Group IIA elements. In the water samples, these metals correlated well with each other, with the exception of barium, which did not correlate with magnesium in Garden River or Fort Chipewyan, or with strontium in Fort Chipewyan. Levels of calcium, barium, and strontium are not available for aerometric samples, so

no comparisons can be made. Since these four elements are closely related chemically, always occurring in the divalent form in biological systems, and since they tend to be correlated in water samples (and possibly crustal deposits) their high degree of intercorrelation in hair samples is not surprising. However, the physiological significance (if any) of this relationship remains to be clarified. It has been demonstrated that vitamin D increases absorption and bone deposition of these four elements (Worker and Migicovsky, 1961). Thus either a common crustal distribution or common mechanisms in their absorption and disposition can account for their similar distribution in hair samples.

#### 2.5.1.4 Cluster Analysis of Correlation Matrices

The 'correlation clusters' were identified by examining the Pearson product moment correlation matrices. These clusterings demonstrate the similarities among the three communities. However, as we have reported (Moon, et.al., 1986), there were many more significant metal-metal correlations in the exposed community than in the other two communities. We, therefore, have attempted to determine if cluster analysis of the Pearson product moment correlation matrices will provide a method of distinguishing the exposed community from the other two communities. The dendrogram produced by

cluster analysis of the correlation matrix for 15 metals from all children in the study (Figure 2.1) clearly identifies the Pb/Cd, Al/V/Fe, and Ca/Mg/Sr clusters. However, in the entire child population Ba is not added to the cluster; instead, Ni is added at the tenth cluster combine. In each community, the metals are clustered somewhat differently. No relationships that would definitely identify the exposed community are apparent (Figures 2.2.1–2.2.3). However, a strong association between Ba and Mn found in children from Garden River (Figure 2.2.2) was not found in the other two communities (Figures 2.2.1, 2.2.3). This association is strong enough that it is reflected in the dendrogram for all children (Figure 2.1).

#### **2.5.2 Relationships between Metals in Hair Samples and Metals in Environmental Samples**

The following subsections will deal with various aspects of the association between air, water, and hair metal content, including an estimation of the amounts of metals that might be absorbed per day from air and water.

### 2.5.2.1 Time Lag between Hair Sample Collection and Environmental Sample Collection

Since hair samples were collected in November 1983, and environmental samples were collected nearly two years later, in September 1985, it must be asked if there were any major environmental changes during the intervening time that might affect the results. To the best of our ability to determine, there have been no major changes in water supply in the villages during this time interval. Fort McKay residents were supplied with 45 gallon drums for water storage in 1982, and these were still in use in 1985 when the water samples were collected. In Garden River, wells were sunk for water in 1981, and were still in use in 1985. The third village, Fort Chipewyan, has obtained its water supply from Lake Athabasca for many years. Thus, there appears to be no major change in water supply to any of the villages during the time interval in question.

Similarly, we have no reason to think that there have been any major changes in air-borne metals due to any new industry or due to any changes in atmospheric emissions from the oil sands plants during the time interval in question. However, it must be kept in mind that the air sampling period covered only 6 weeks, and therefore does not provide

information regarding long-term air levels of metals.

#### **2.5.2.2 General Comparison of Metals in Hair with Metals in Environmental Samples**

In the case of those metals for which we have measurable quantities of both water and hair, in 7 of 9 cases, the community with the highest level in the hair was also the one with the highest level (or joint highest level) in water. Where we have measurable quantities in both air and hair, in 5 out of 8 cases, the community with the highest level in hair was also the one with the highest level (or joint highest) in air. Finally, of elements where we have both air and water levels, the community with the highest level in the air was also the one with the highest level in water in 4 out of 5 cases. This latter observation makes it difficult to determine whether aerometric or water metal levels make the greatest contribution to levels of metals found in hair. Therefore in the following section we have attempted to estimate the amount of metal that might be absorbed from each source.

### 2.5.2.3 Estimation of Relative Contributions of Water and Air Metal Levels to Metal Levels in Hair

In an effort to help clarify the potential relative contributions of air metal levels and water metal levels to body stores of these metals, we have calculated approximate absorption levels. In order to arrive at values for absorption from water, we have used the model outlined by the Task Group on Metal Accumulation (1973). We assumed an approximate intake of 1 liter of water per day, with an average absorption of approximately 5% of the amount ingested. These values are given in Table 2.6, and plotted as  $\mu\text{g}$  absorbed per day in Figures 2.9 to 2.13.

For absorption from the respiratory tract we have used the model developed by the International Commission for Radiological Protection (ICRP, 1966). We have used the simplest ICRP model, realizing that, although the estimates are very approximate, we will still arrive at a better method of comparing air and water contributions to the body pool of elements than is provided by a simple comparison of air levels expressed as  $\text{ng m}^{-3}$ , and water levels expressed as  $\text{mg l}^{-1}$ , which are the common ways of expressing these values.



In arriving at an estimate of the contribution of air to body content of the metals, we have used the following methods (ICRP, 1966). The deposition of dust in the respiratory tract is calculated as 75% of the mass breathed. Of this 75%, two-thirds (50% of that inspired) is deposited in the upper respiratory passages and one-third (25% of that inspired) is classified as deposited in the lungs. Of this, approximately 50% is absorbed. To arrive at an approximation for the amount of metal inhaled, we have assumed a tidal volume of 750 cm<sup>3</sup> at a respiratory frequency of 15 cycles per minute (ICRP, 1966). The approximate levels of metals that might be absorbed ( $\mu\text{g}$  per day), using these approximations, are given in Table 2.7 and are plotted in Figures 2.9 to 2.13.

Table 2.6. Estimated amount of metal absorbed from water ( $\mu\text{g}/\text{d}$ )<sup>1</sup>

	<u>Fort McKay</u>	<u>Garden River</u>	<u>Fort Chip</u>
Copper	0.9	0.1	14.6
Aluminum	42.7	9.1	8.5
Iron	1.7	3.0	9.4
Manganese	0.3	1.0	0.2
Magnesium	425.0	425.0	172.0

<sup>1</sup>These estimations were calculated from levels of metals in water samples, assuming an approximate intake of 1 liter of water per person per day, with an average absorption of 5% of the amount ingested (Section 4.2.3).

Table 2.7. Estimated amount of metal absorbed from air ( $\mu\text{g}/\text{d}$ )

	<u>Fort McKay</u>	<u>Garden River</u>	<u>Fort Chip</u>
Copper	0.45	0.4	0.37
Aluminum	0.6	3.3	0.37
Iron	0.45	10.2	0.72
Manganese	0.01	0.2	0.02
Magnesium	0.2	1.5	0.27

#### 2.5.2.4 Comparison of Metals in Water with Metals in Hair

There was a definite relationship between several metals in water and hair samples. Of all the metals, only copper was elevated in hair from children from Fort Chipewyan. Copper was also highest in water samples from Fort Chipewyan, while the rest of the metals except cadmium, lead, and iron were lowest (Table 2.4). Levels of copper in water from Fort McKay were greater than those in water from Garden River, which corresponded with copper levels in hair from children in the two communities. The higher copper levels in water from Fort Chipewyan are probably due to the use of plumbing containing copper in that community, since Fort Chipewyan is

the only community with running water in homes. Fort McKay homes do not have piped in water, but the school does, and copper levels in water from the school were elevated, resulting in higher levels of copper there than in Garden River where everyone gathered water from community wells, using electric and hand pumps to pump water to the surface.

Garden River children had elevated levels of iron, manganese, barium, magnesium and calcium in their hair, and water levels of these metals (Table 2.4) were also elevated above those in Fort Chipewyan, where the lowest levels of these metals were found in children's hair samples. Iron, manganese, and barium in water samples from Garden River were also higher than those in Fort McKay (as were children's hair levels). However, magnesium and calcium were the same in water samples from Garden River and Fort McKay (Table 2.4), while magnesium and calcium were significantly higher in hair from Garden River children than from Fort McKay children.

Of the eight metals that were significantly different in water samples from the three communities, only aluminum and cadmium failed to display a direct relationship with results found for hair samples from children. As mentioned, adult hair samples did not display these relationships. Aluminum is striking in its failure to display a relationship between water and hair

sample levels. Fort McKay water contains many times more aluminum than water in either of the other communities (Table 2.4), whereas hair samples from Garden River children had at least twice as much aluminum as hair samples from children in the other communities. Elevated levels of aluminum in water samples from Fort McKay are probably related to the fact that Fort McKay water is trucked into the village, and stored in two large metal tanks, one at each end of town. In 1982, 45-gallon drums were provided for water storage for each home. It is possible that the elevated aluminum in water from Fort McKay come from these tanks. This might explain why hair aluminum levels do not reflect water aluminum levels in that community, since increased exposure would have occurred for only about 1 year before hair samples were collected, and it may take a longer time period to see a difference in hair aluminum levels.

Other failures to demonstrate a correlation between water metal levels and hair metal levels were as follows. Highest cadmium levels were found in hair from children from Fort McKay whereas highest water cadmium levels were in water from Garden River (Table 2.4). Lowest hair cadmium levels were found in children from Fort Chipewyan, but water from Fort Chipewyan had an intermediate level of cadmium.

#### **2.5.2.5 Comparison of Metals in Aerometric Samples with Metals in Hair**

Analysis of aerometric samples showed lead to be elevated in samples from Garden River, and titanium in samples from Fort Chipewyan (Table 2.5). These differences do not correlate with findings in hair samples, where highest levels of lead were found in Fort McKay children, and no differences were found for titanium. However, levels of vanadium, iron, manganese, magnesium, and chromium were highest in aerometric samples from Garden River (Table 2.5), which corresponds to the higher levels of these metals in hair from Garden River children.

Ely and co-workers (1981) studied the relationship between aerometric and hair levels of several metals (As, Cd, Hg, Pb, Se) in children in two schools in Akron, Ohio, and concluded that in their study, air was not a major source of hair trace metals, although it does add to the cumulative content of trace metals in hair. A similar conclusion seems to be indicated in this present study.

#### **2.5.2.6 Unexplained Results in Hair Samples from Fort McKay Residents**

It would appear that most of the results of the hair analysis in the two control villages can be explained by levels of metals contained in

FIGURE 2.9. LOG SCALE PLOT OF COPPER LEVELS IN ADULT HAIR (ppm), CHILD HAIR (ppm), WATER (ESTIMATED ABSORPTION IN  $\mu\text{g/d}$ ), AND AIR (ESTIMATED ABSORPTION IN  $\mu\text{g/d}$ )

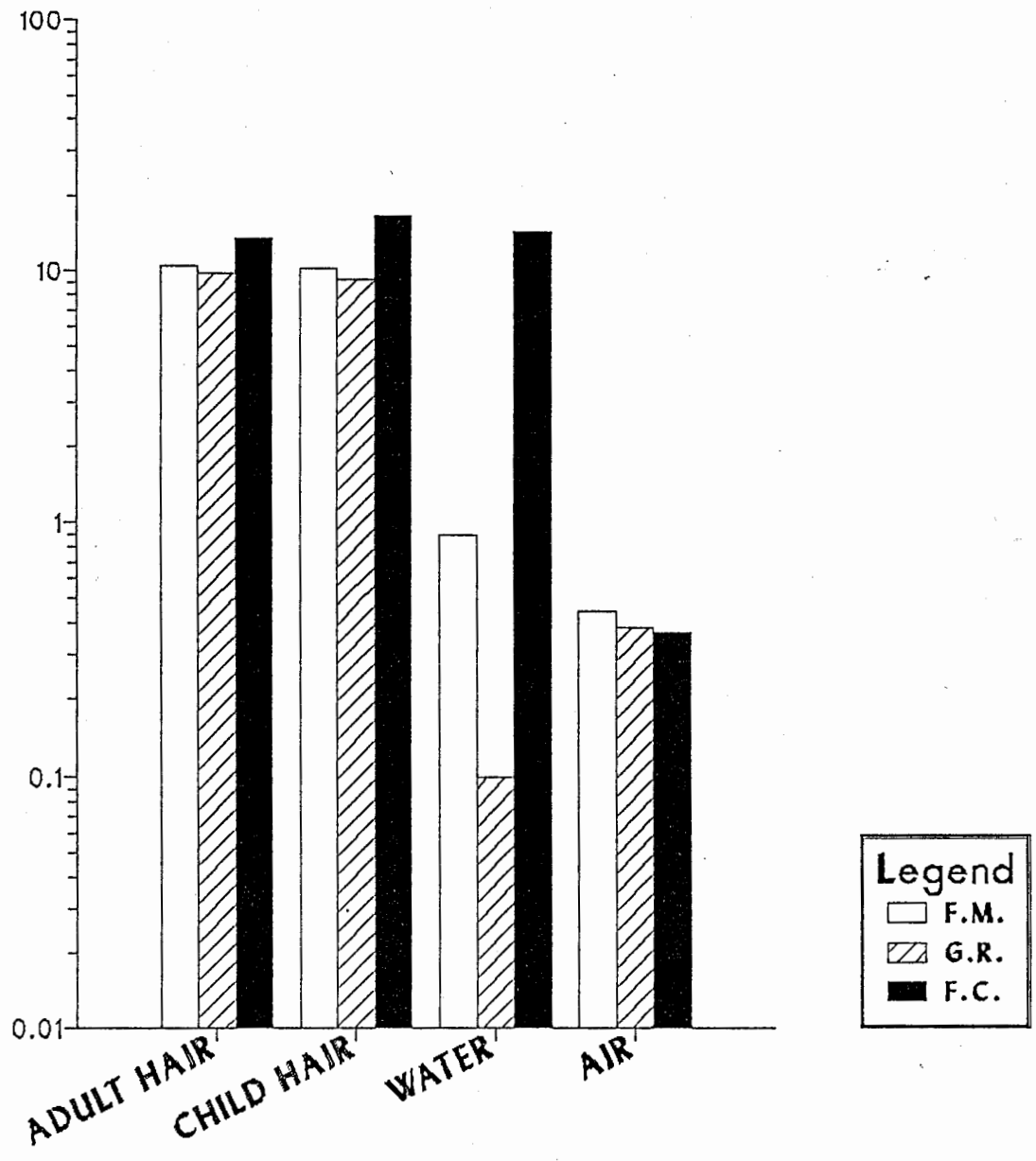


FIGURE 2.10. LOG SCALE PLOT OF MAGNESIUM LEVELS IN  
ADULT HAIR (ppm), CHILD HAIR (ppm),  
WATER (ESTIMATED ABSORPTION IN  $\mu\text{g}/\text{d}$ ),  
AND AIR (ESTIMATED ABSORPTION IN  $\mu\text{g}/\text{d}$ )

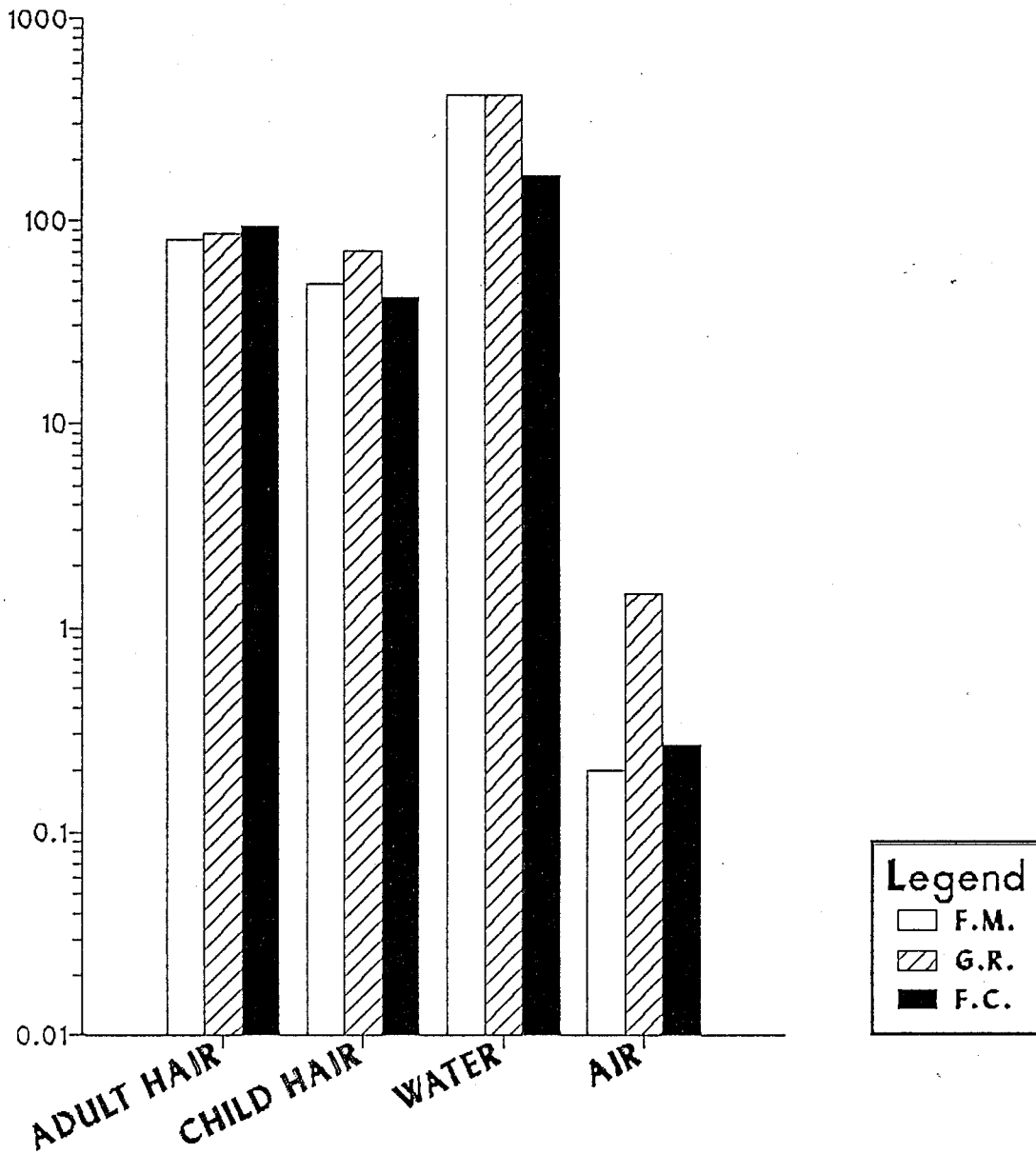




FIGURE 2.11. LOG SCALE PLOT OF ALUMINUM LEVELS IN  
ADULT HAIR (ppm), CHILD HAIR (ppm),  
WATER (ESTIMATED ABSORPTION IN  $\mu\text{g}/\text{d}$ ),  
AND AIR (ESTIMATED ABSORPTION IN  $\mu\text{g}/\text{d}$ )

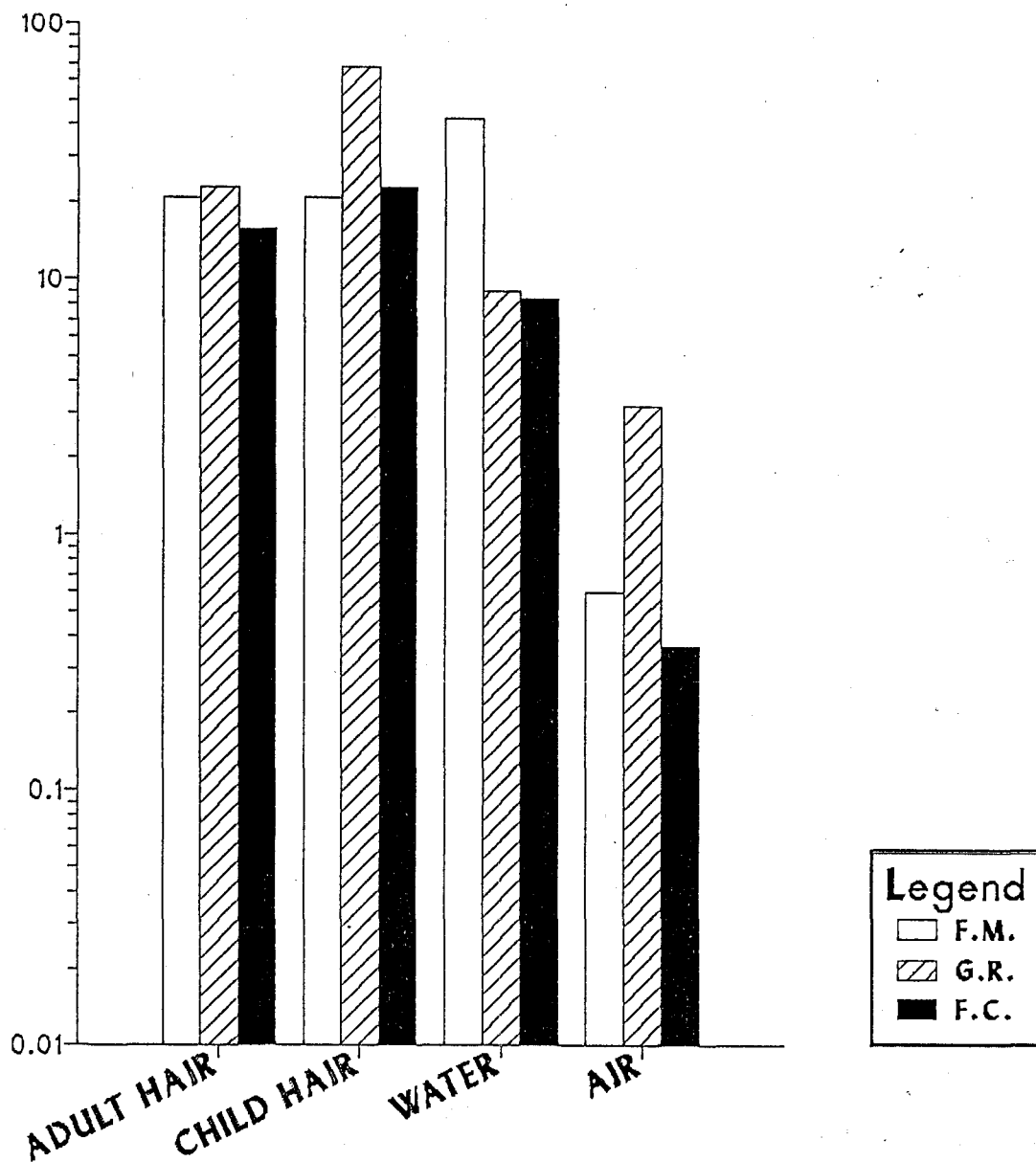


FIGURE 2.12. LOG SCALE PLOT OF IRON LEVELS IN  
ADULT HAIR (ppm), CHILD HAIR (ppm),  
WATER (ESTIMATED ABSORPTION IN  $\mu\text{g}/\text{d}$ ),  
AND AIR (ESTIMATED ABSORPTION IN  $\mu\text{g}/\text{d}$ )

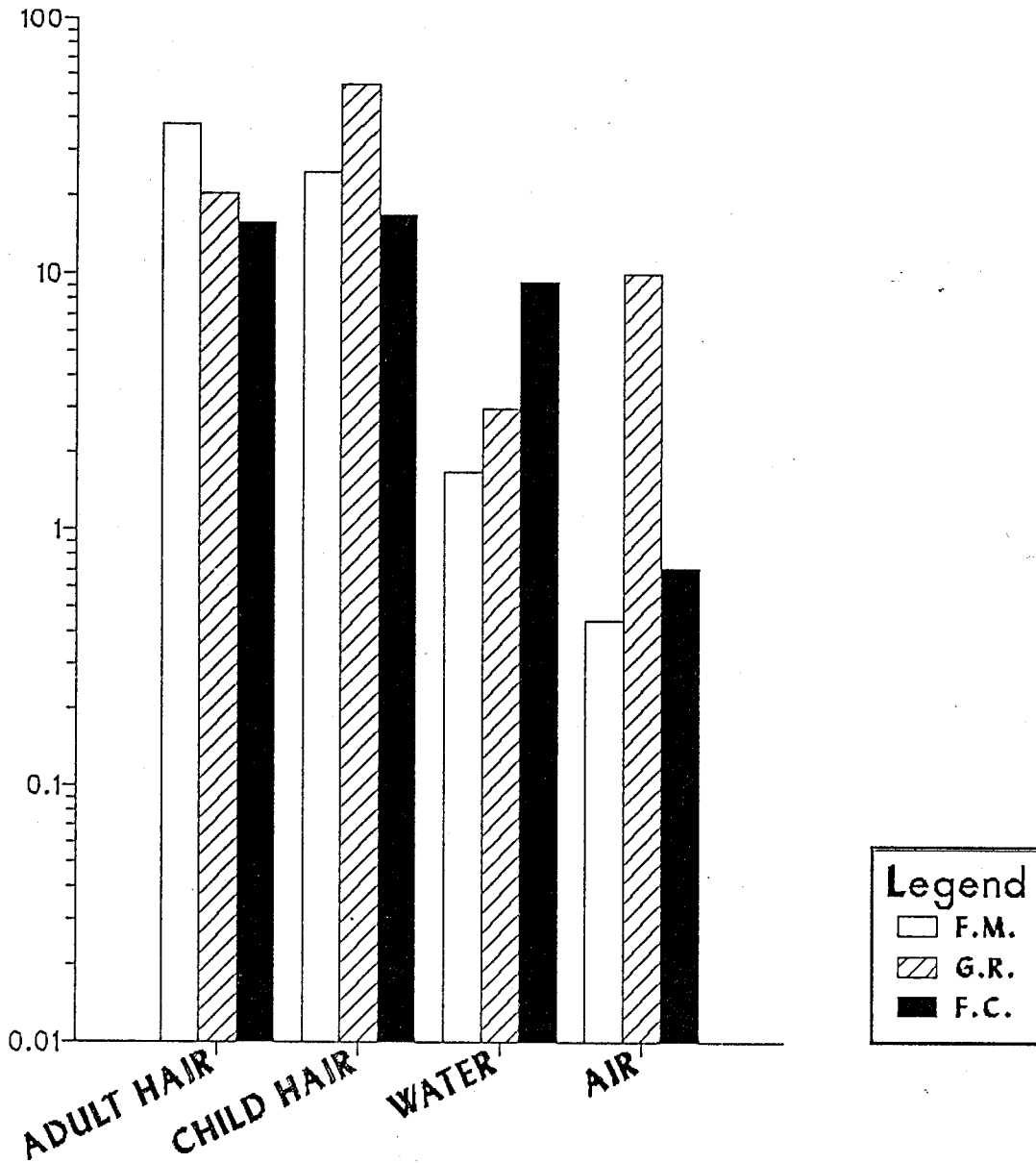
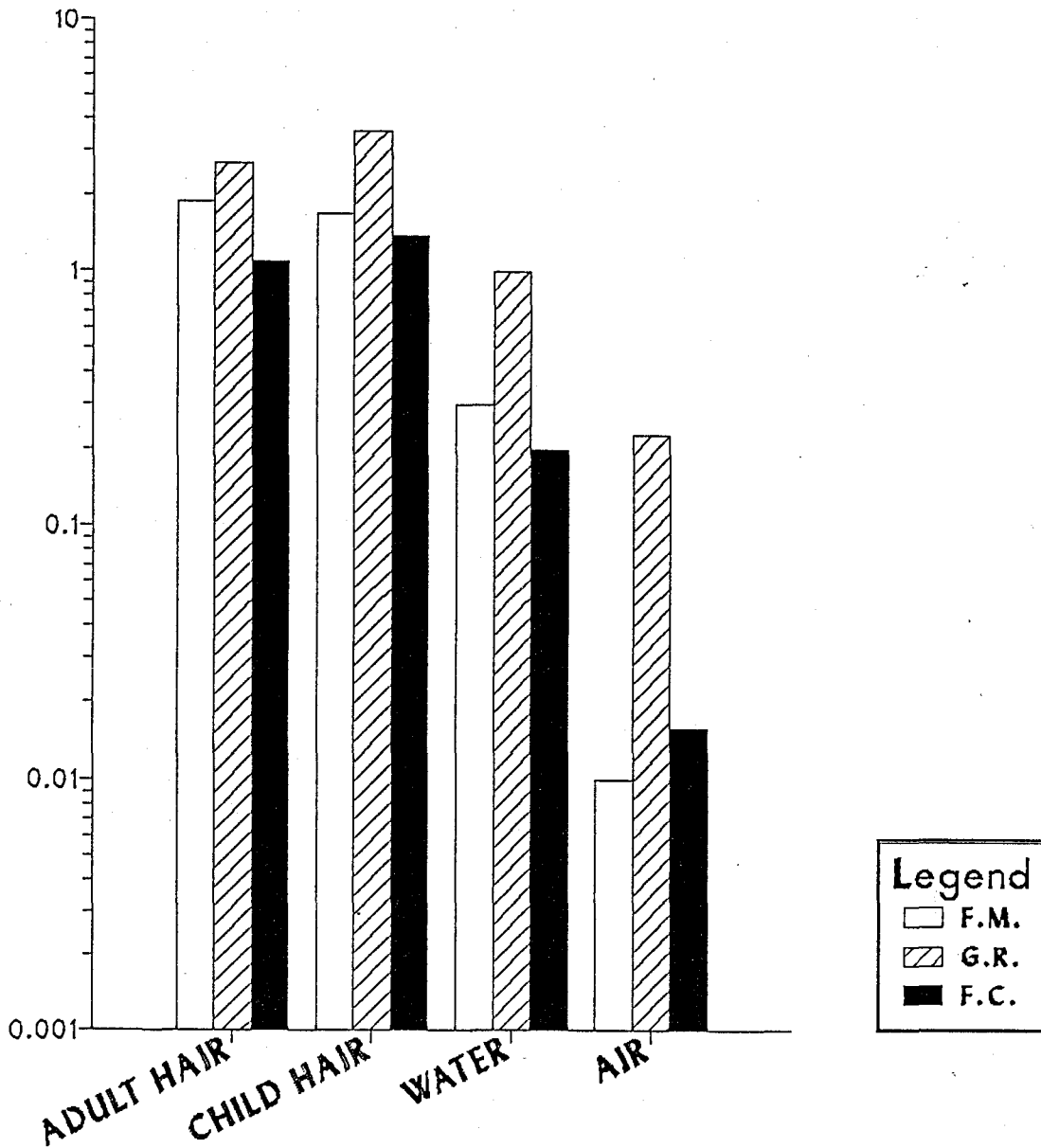


FIGURE 2.13. LOG SCALE PLOT OF MANGANESE LEVELS IN  
ADULT HAIR (ppm), CHILD HAIR (ppm),  
WATER (ESTIMATED ABSORPTION IN  $\mu\text{g}/\text{d}$ ),  
AND AIR (ESTIMATED ABSORPTION IN  $\mu\text{g}/\text{d}$ )



environmental samples. However, elevated levels of lead in hair samples from Fort McKay residents are not explained by the current studies. Since Pb, Cd, and Ni have been demonstrated in high levels in holding tanks from the oil sands plants (Alberta Environment, 1976), it is possible that the source of the increased levels of these metals in hair samples from Fort McKay residents is intermittent exposure to the contents of the holding tanks. These have been seen to leak periodically into the Athabasca River (Kostler, 1982). It is interesting that Fort Chipewyan water contained higher levels of cadmium, lead, and nickel - the three metals found to be highest in Fort McKay residents. This can be understood in retrospect, since Lake Athabasca, which is the water supply for Fort Chipewyan, is fed by the Athabasca River (as well as by other northern rivers). Increased levels in the lake result from elevated levels in the river. In the present study, we were unable to include river water samples, since this would have entailed sampling two rivers, (the Athabasca River and the Peace River), as well as Lake Athabasca. We recommend continuing, periodic analysis of the Athabasca River for Pb, Cd, and Ni.

## 2.6 CONCLUSIONS

Obviously the persistent correlations are due to similarities in the physico-chemical properties of the metals. These may be expressed through: (1) geochemical patterns of distribution in the materials comprising the earth's atmosphere, surface waters, or crust, (2) bioconcentration in the major food sources, and/or (3) common physiological mechanisms in metabolism, absorption, and disposition inside the human organism. Whichever of these is the cause, it is clear that the eventual result is expressed in the relative concentrations of these metals in human hair and individuals. It follows that the trace element composition of hair reproducibly reflects to some extent the environmental and/or metabolic history of the individual. The current data reinforce the need for additional studies to determine the relative contributions of the mechanisms. In practical terms, based on the results of the present study, we suggest that subject age is the most important covariate in hair analysis studies, and that younger children, approximately 5 to 12 years old, may represent the most sensitive populations for hair analysis studies of environmental contamination by several metals, including lead, cadmium, aluminum, and vanadium. Water metal levels are probably more effective than air levels in

affecting hair levels. This conclusion is based on the estimated amount absorbed by each route, and also on a closer correlation between amounts in water and associated patterns of accumulation in hair.

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### 3. CHAPTER III. SOURCES OF VARIABILITY IN TRACE ELEMENT CONTENT OF HUMAN SCALP HAIR: EFFECTS OF WASHING, AGE, AND SEX.

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#### 3.1 ABSTRACT

One hundred and twenty two scalp hair samples taken from native Indians in three northern Alberta villages were analyzed for 19 elements before and after washing using the washing procedure recommended by the International Atomic Energy Association. A significant ( $p < .05$ ) amount of each element was removed by the washing procedure, the amount removed varying from 4% for Zn to 92% for Na and K. Significant differences

( $p < .05$ ) between males and females were found for 5 elements, males having higher levels of Pb, and females having higher levels of the other 4 elements (Ca, Mg, Sr, Zn). Significant ( $p < .05$ ) age-related variations were found for 13 of the 19 metals, in washed hair samples. Pb and Cd were higher in 5 to 11 year olds than in 11.1 to 19 year olds, and also higher in the older age group ( $>19$ ) than in the 11.1 to 19 year olds. Al, Fe, V, and Cr decreased with increasing age of subjects, while Ca, Mg, Sr, Zn, Ni, Na, and K increased with increasing age.

### 3.2 INTRODUCTION

Human scalp hair has been used for many years to determine exposure to a number of metals (Kievay, 1973; Creason, *et al.*, 1975; Chattopadhyay, *et al.*, 1977; Brown, Ed., 1980; Wibowo, *et al.*, 1986; Moon, *et al.*, 1986), and has been used with limited success to assess mineral and trace element status (van Wouwe and van den Hamer, 1985). However, a number of factors such as variations in trace element content of human scalp hair due to age and sex of subjects (Petering, *et al.*, 1971, 1973; Briggs, *et al.*, 1972; Gordus, 1973; Gordon, 1985), location on the scalp from which samples are gathered (Alder, *et al.*, 1977; DeAntonio, *et al.*, 1983), length of hair samples (Hambidge, 1973; Obrusnik, *et al.*, 1973; Alder, *et al.*, 1976; Campbell, *et al.*, 1981), and methods used for preparing samples for analysis (Ryabukhin, 1978) are important co-variables that need to be taken

into account when designing studies involving trace element analysis of human scalp hair. As well, factors such as shampoos, frequency of hair washing, hair wave preparations, whether a subject smokes or not, and other personal factors may complicate hair analysis data (Creason, *et al.*, 1975; Taylor, 1986). Since these factors are not easy to control, and since there is widespread public interest in hair analysis which has resulted in frequent misuse of the procedure, numerous critiques have appeared in recent years (Errera, 1980; College of Physicians and Surgeons of Ontario, 1982; Fletcher, 1982; Hambidge, 1982; Laker, 1982; Holzbecher and Ryan, 1982; Gibson and Gibson, 1984; Manson and Zlotkin, 1985). The present paper addresses three of the most important factors that affect the trace element content of human scalp hair. These are washing of samples in preparation for analysis (Bate, 1966; Assarian and Oberleas, 1977; Ryabukhin, 1978; Scoble and Litman, 1978; Chittleborough, 1980; Fergusson, *et al.*, 1983; Buckley, *et al.*, 1984), and age and sex of subjects (Petering, *et al.*, 1971, 1973; Briggs, *et al.*, 1972; Gordus, 1973; Creason, *et al.*, 1975; Gordon, 1985; Moon, *et al.*, 1986). Although numerous washing procedures have been studied, there seem to be few (if any) studies in which a large number of samples have been analyzed both before and after washing. We therefore analyzed one hundred and twenty-two human scalp hair samples both before and after washing, using the standard washing procedure recommended by the International Atomic Energy Association (Ryabukhin, 1978).

### 3.3 METHODS

#### 3.3.1 Study design

This was a double blind study in that neither the person who submitted samples for analysis nor the analytic laboratory personnel knew where any sample came from until after all samples had been analyzed. Children were selected as the primary subjects for this study; defined as the child population in attendance at the local schools. These varied in age from 5.1 years to 19 years. Three communities were studied: a village in proximity to the oil sands extraction plants, and two control villages distant from the plants. An attempt was made to collect samples from all children in the two smaller communities, and a similar number of subjects selected by random methods from the larger community. A few adult volunteers who were not chosen by random methods were also included. Table 3.1 shows the age and sex distribution for the population. In order to evaluate age-related changes we have separated the child population into two groups, 5-11 and 11.1-19 years of age.

#### 3.3.2 Sample collection

Scalp hair samples were collected by a single individual from all subjects, using a pair of high-quality stainless steel barber scissors.

Approximately 150–200 strands of hair were cut from as close to the scalp as possible from each of 8 to 10 identified sites around the subject's head (Ryabukhin, 1978). These small samples were all placed together with the scalp ends aligned, tied with nylon thread at the scalp end, folded into a weighing paper and placed into a paper envelope which was labelled on a label that was taped to the envelope so that it could be removed for blinding. The paper envelope containing the sample was then placed in a zip-lock polyethylene bag, which was sealed until the sample was prepared for analysis. Using a glass blade, the first one or two mm were shaved from the scalp end to remove any metal that may have contaminated the sample by use of metal scissors to collect the samples, and were cut to a uniform length (7–9 cm) to represent an approximately uniform time period of about 7 to 11 months of hair growth. A total of 149 samples were collected from 78 females and 71 males whose ages were from 5.1 to 78.5 years; 122 of these samples were analyzed before and after washing as described below.

### 3.3.3 Sample washing procedure and analysis

When there was sufficient hair (at least 0.4 gm, 7–9 cm long), samples were separated into two approximately equal samples; hair in one sample was washed according to the method recommended by the International Atomic Energy Association (Ryabukhin, Ed., 1978); the other

sample was analyzed without washing. Great care was taken in separating the sample, a few hairs at a time, in order to make the two samples as similar as possible. When there was insufficient sample for preparing two samples, the single sample was washed prior to analysis. Samples were placed on porous glass filters attached to a vacuum tube; twelve samples were washed at a time, first for ten minutes in acetone (Baker Instra-Analyzed), followed by three ten minute distilled, de-ionized water (18 meg-ohm resistance) washings, and a final ten minute acetone wash. Samples were then dried with a drying lamp, transferred to digestion tubes, and weighed to four decimals. Three ml nitric acid (Baker Instra-Analyzed) were added, and the sample digested until the volume was reduced to about 1 ml. One-half ml perchloric acid (GFS Double Distilled) was then added and taken to perchloric fumes. 0.1 ml HCl (Baker Instra-Analyzed) was added and the sample diluted to 4 ml with distilled, de-ionized water (18 meg-ohm resistance).

Samples were washed, digested, and analyzed at Quanta Trace Laboratories, Inc. (Burnaby, B.C., Canada), using inductively coupled argon plasma emission spectroscopy (ICAP) for the analysis (Fassel, 1978). Samples were analyzed in batches of approximately 20, and the instrument was standardized after each set of samples. Three replicate determinations were made in each case and the analytic data represent means of these measurements.



At the time this study was conducted (1983-84) there was no reference hair sample, the first certified hair powder reference material being prepared by Okamoto *et al.* (1985). We therefore prepared a uniform hair sample from a finely chopped and mixed hair sample, which was analysed consecutively with each set of samples as a check on the entire procedure. Design of the study, subject selection, and sample collection, preparation, and analysis have been described in greater detail (Moon, *et al.*, 1986).

### 3.4 RESULTS

#### 3.4.1 Effects of sample washing.

As indicated in Table 3.1, a significant ( $p < .05$ ) amount of each of the 19 elements listed was removed by the washing procedure. The amount removed ranged from 4% for Zn to 92% for Na and K. Figures 3.1-3.4 show the effect of sample washing on the hair content of Pb, Al, V, and Fe in each of the communities. These elements were chosen to illustrate the different patterns of the effects of washing, and the close association found for Al, Fe, and V. The effect of washing on Pb content (Figure 3.1) is representative of several elements including also: Zn, Cu, P, and Cd. For these elements, a comparatively small amount was removed by the washing

procedure (4–13%), and the amount removed was similar in each of the three communities. Al, V, and Fe, on the other hand, are distinctive in that the amount of element washed off varies in the three communities, and a greater percentage (36–40%) of each metal was removed by the washing procedure. In spite of the relatively large amounts of Al, V, and Fe removed by the washing procedure, statistical analysis of the variations of these elements in the three communities were the same for washed and unwashed samples (Moon, *et al.*, 1986).

Table 3.1. Levels of 19 elements in 122 hair samples analyzed before and after washing (ppm)<sup>1</sup>

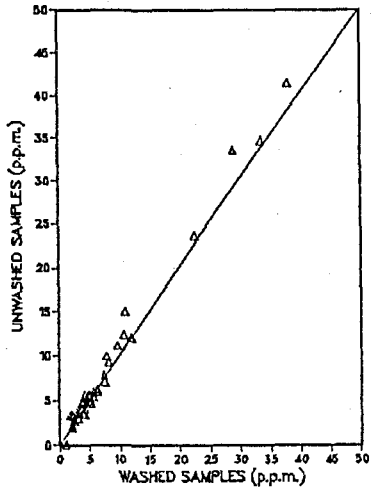
Element	Unwashed Mean±S.D.	Washed Mean±S.D.	Washed/Unwashed
Zn	138 ± 47	133 ± 46	0.96
Cu	12.5 ± 6.70	11.7 ± 6.6	0.94
Pb	6.38 ± 7.51	5.8 ± 6.8	0.91
P	139 ± 32.5	127 ± 27.2	0.91
Cd	.606 ± 1.36	.527 ± 1.45	0.87
Ca	719 ± 508	590 ± 491	0.82
Sr	2.33 ± 1.88	1.92 ± 1.80	0.82
Zr	.106 ± .072	.084 ± .063	0.79
Ti	9.31 ± 5.33	7.3 ± 3.9	0.78
Ni	.588 ± 1.24	.428 ± 1.61	0.73
Ba	2.42 ± 1.69	1.76 ± 1.15	0.73
Mg	81.5 ± 66.3	59.7 ± 60.5	0.73
Mn	2.99 ± 2.45	2.14 ± 1.80	0.72
Cr	.646 ± .544	.465 ± .320	0.72
V	.144 ± .165	.092 ± .102	0.64
Fe	49.4 ± 44.5	30.8 ± 26.5	0.62
Al	56.6 ± 53.8	34.2 ± 25.1	0.60
K	611 ± 767	51 ± 96	0.08
Na	928 ± 1148	80 ± 129	0.08

<sup>1</sup>All washed samples significantly less than unwashed samples ( $p < 0.05$ ).

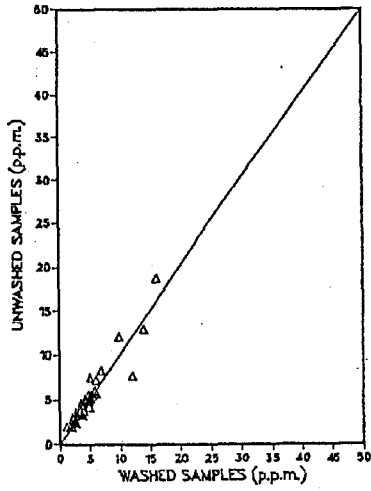
#### 3.4.2 Effects of age and sex.

Figures 3.6 and 3.7 show log/log plots of concentration vs age for Al, V, and Fe. We have plotted these in pairs to demonstrate the very

FORT MCKAY



GARDEN RIVER



FORT CHIPEWYAN

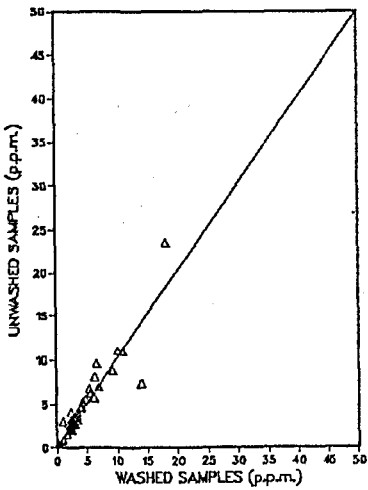
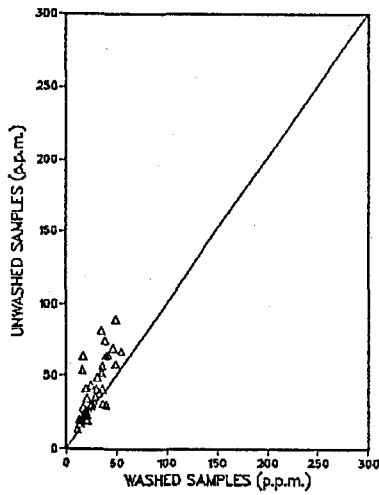
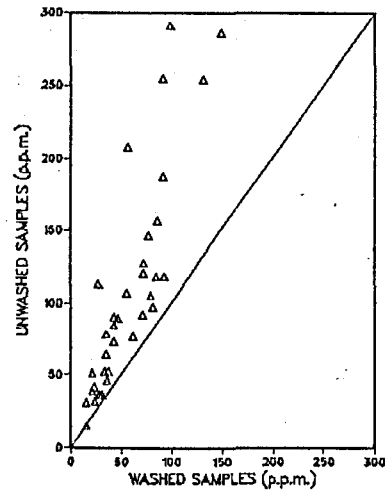


FIGURE 3.1. LEAD:  
Effect of washing on  
lead content of  
hair samples from  
three communities.

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GARDEN RIVER



FORT CHIPEWYAN

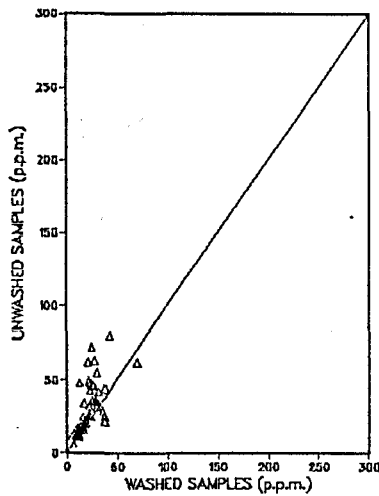
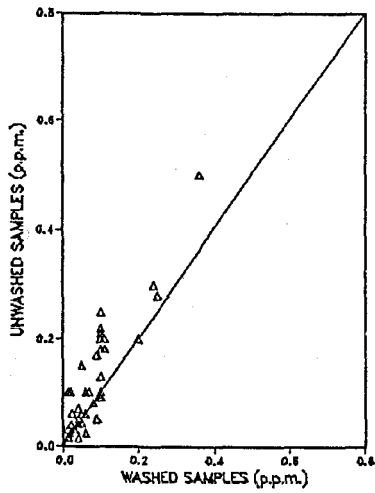
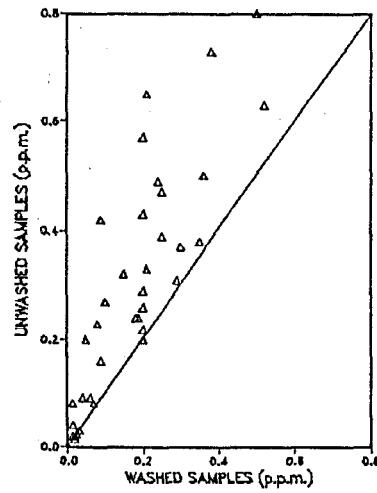


FIGURE 3.2. ALUMINUM:  
Effect of washing on  
aluminum content of  
hair samples from  
three communities.

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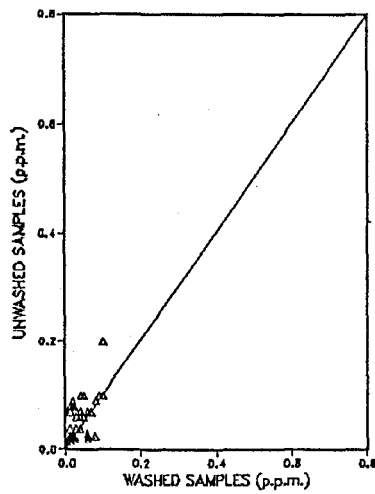
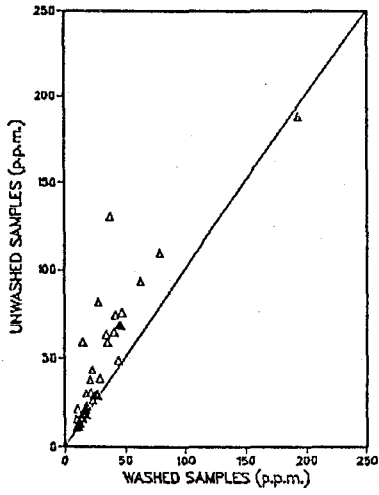
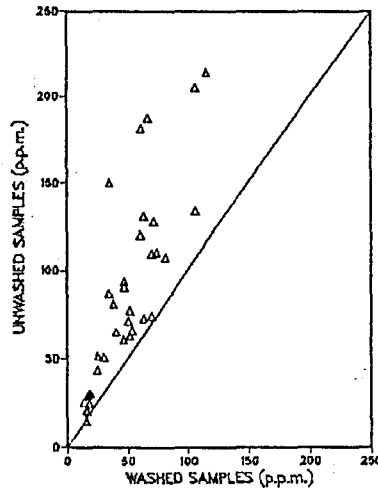


FIGURE 3.3. VANADIUM:  
Effect of washing on  
vanadium content of  
hair samples from  
three communities.

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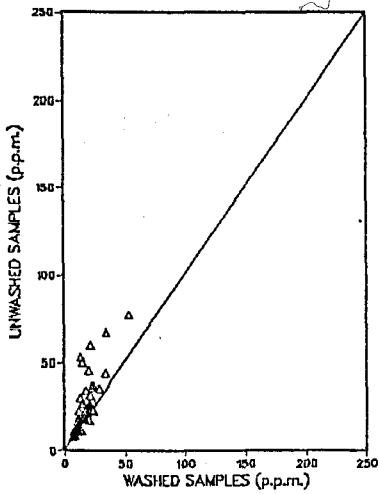
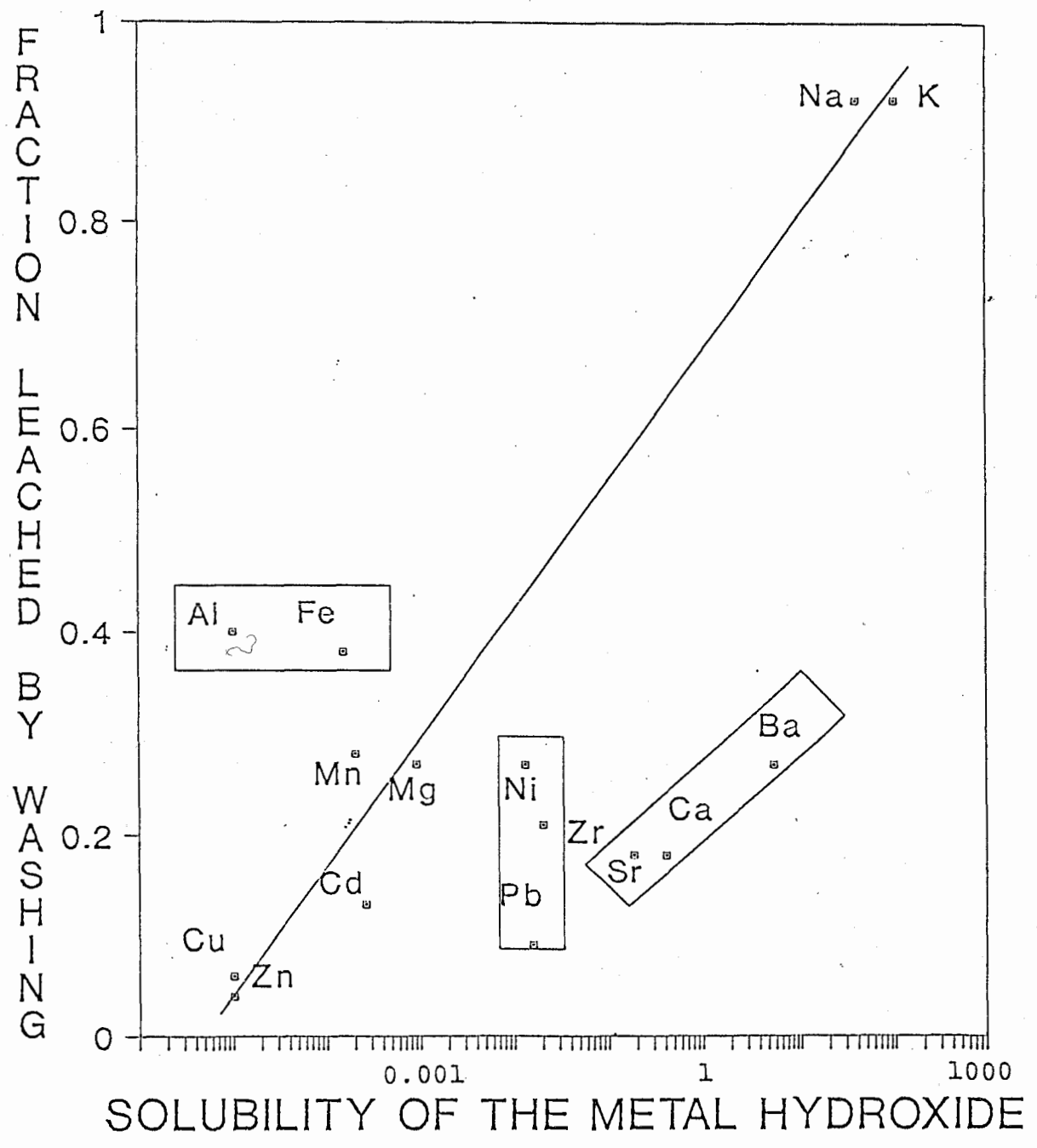


FIGURE 3.4. IRON:  
Effect of washing on  
iron content of  
hair samples from  
three communities.

Figure 3.5

# EXTENT OF LEACHING AS A FUNCTION OF SOLUBILITY





close age-related association among the three elements. Even though there is 1000 times as much Al and Fe in these samples as V, the three elements demonstrate very similar age-related concentration patterns, being highest among younger children, and decreasing during or around adolescence to the lower adult levels. Cr (Table 3.3; Figure 3.8) is very similar in its age-related concentration pattern to Al, V, and Fe. Pb (Table 3.3; Figure 3.9) and Cd (Table 3.3; not shown) are highly correlated with each other. These two elements tend to decrease from childhood levels to low levels during adolescence, followed by a gradual increase during adulthood.

Differences in scalp hair trace element content between males and females were found for 5 elements. Pb levels were higher in hair samples from males (Table 3.4; Figure 3.9), while Zn, Ca, Mg, and Sr were higher in hair samples from females (Table 3.4; Figures 3.10-3.13). Ni levels were elevated in hair from females (Table 3.4), but the difference was not significant ( $p > 0.1$ ). Zn displays interesting age- and sex-related changes in that males had lower concentrations of zinc in their hair during childhood, but no difference was found for adults between sexes (Tables 3.3 and 3.4; Figure 3.10). Ca, Mg, Sr, and Ba have been previously shown to form a highly intercorrelated cluster (Moon, *et al.*, 1988), which can be seen in Figures 3.11-3.13 (Ba is not shown since no significant difference between

sexes was found for Ba). It can be seen from the figures that an interaction between sex and age occurs for Ca, Mg, and Sr. Levels of these elements decrease with increasing age among males, but not among females. The age with sex interactions for Pb, Ca, Mg, Sr, and Zn are significant ( $p < .05$ ) when tested by multivariate analysis of variance.

Table 3.2. Age and sex distribution of the 149 individuals included in the study

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**AGE GROUPS**

<b><u>(YEARS)</u></b>	<b><u>FEMALES</u></b>	<b><u>MALES</u></b>
5 - 11	32	39
11.1-19	27	24
>19	18	9
<b>TOTAL</b>	<b>77</b>	<b>72</b>

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Table 3.3. Hair metal levels (ppm) in washed samples for the 13 metals that differed significantly ( $p < .05$ ) in three age groups

	Age Group 5-11 Years (N=71) <u>Mean±S.D.</u>	Age Group 11.1-19 years (N=51) <u>Mean±S.D.</u>	Age Group >19 years (N=27) <u>Mean±S.D.</u>
Cd	.4514±.2790	.2486±.1984	1.097±3.03**
Pb	7.10±6.60*	3.59±2.67	6.82±9.77*
Al	43.6±28.3**	33.1±26.0*	19.0±8.1
Fe	38.2±**24.6	23.9±18.6	23.7±35.5
V	.1390±.1158**	.0666±.0795	.0331±.0244
Cr	.5269±.3711**	.3632±.1918	.3515±.1800
Ca	435.8±309.3	759.0±527.9*	690.5±610.9*
Mg	40.8±35.0	73.1±60.3*	89.9±91.6*
Sr	1.48±1.48	2.45±1.92*	2.66±3.35*
Zn	117.0±47.7	152.0±35.8*	140.7±41.7*
Ni	.2514±.3088	.2816±.3088	.9981±3.35**
Na	54.4±42.7	75.2±61.2	168.7±271.8**
K	41.6±31.2	41.1±36.8	97.9±193.5**

\*\* Significantly higher than either of the other groups ( $p < .05$ ).

\* Significantly higher than the group with the lowest mean value ( $p < .05$ ).

Table 3.4. Hair metal levels (ppm) in washed samples for the 5 metals that differed significantly ( $p < .05$ ) between sexes

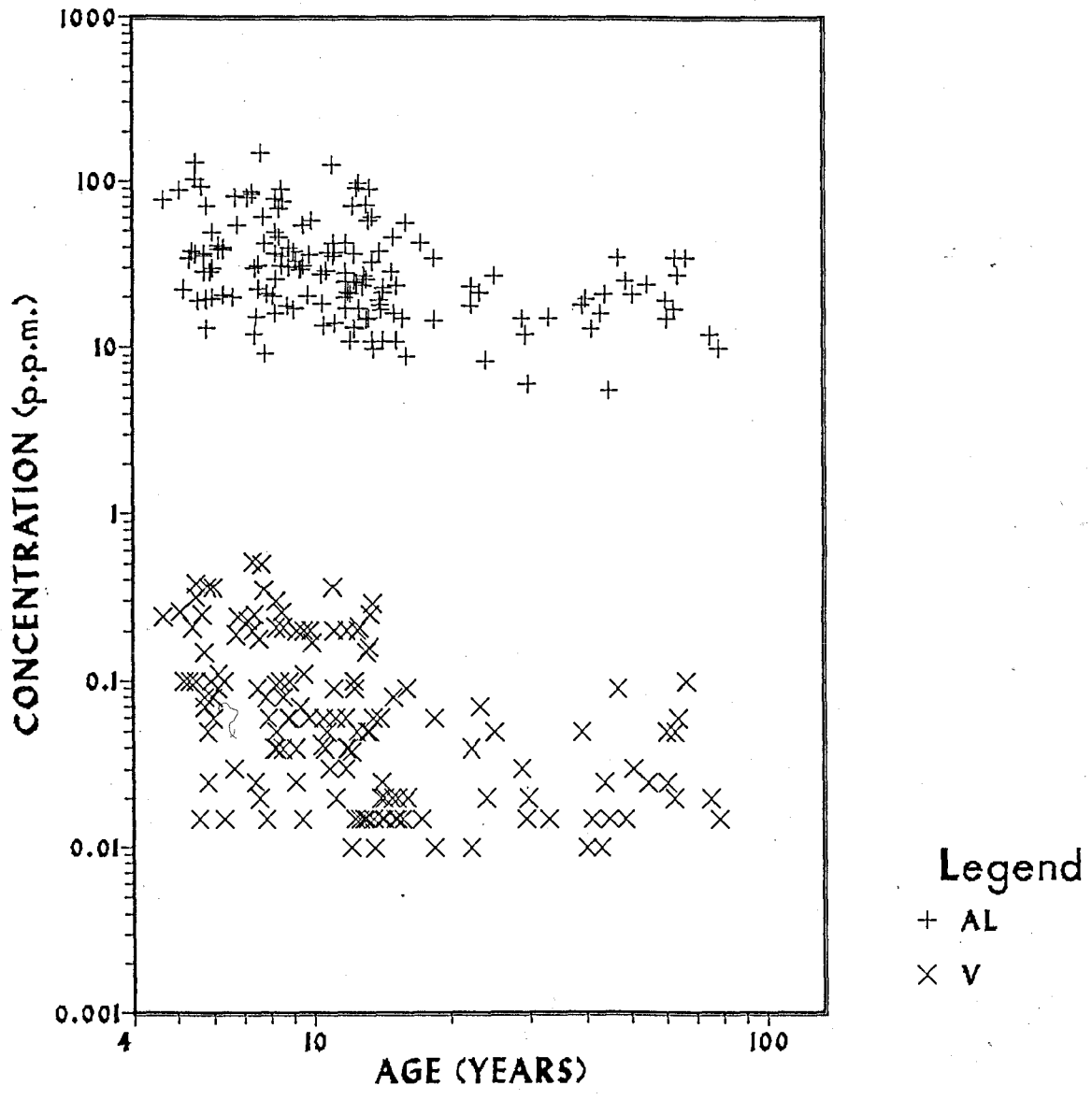
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	<u>FEMALES</u>	<u>MALES</u>
Pb	4.08 ± 6.56	7.01 ± 6.3
Ca	741 ± 571	429 ± 270
Mg	81.9 ± 73.8	37.7 ± 28.1
Sr	2.7 ± 2.7	1.3 ± 0.87
Zn	148.5 ± 45.9	116.6 ± 39.2
Ni <sup>1</sup>	0.56±2.0	0.22±0.22

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<sup>1</sup>This difference is not significant ( $p > 0.1$ ).

**FIGURE 3.6. AL AND V IN WASHED HAIR SAMPLES:  
LOG/LOG PLOT OF AGE-RELATED VARIATIONS.**



**FIGURE 3.7. FE AND V IN WASHED HAIR SAMPLES:  
LOG/LOG PLOT OF AGE-RELATED VARIATIONS.**

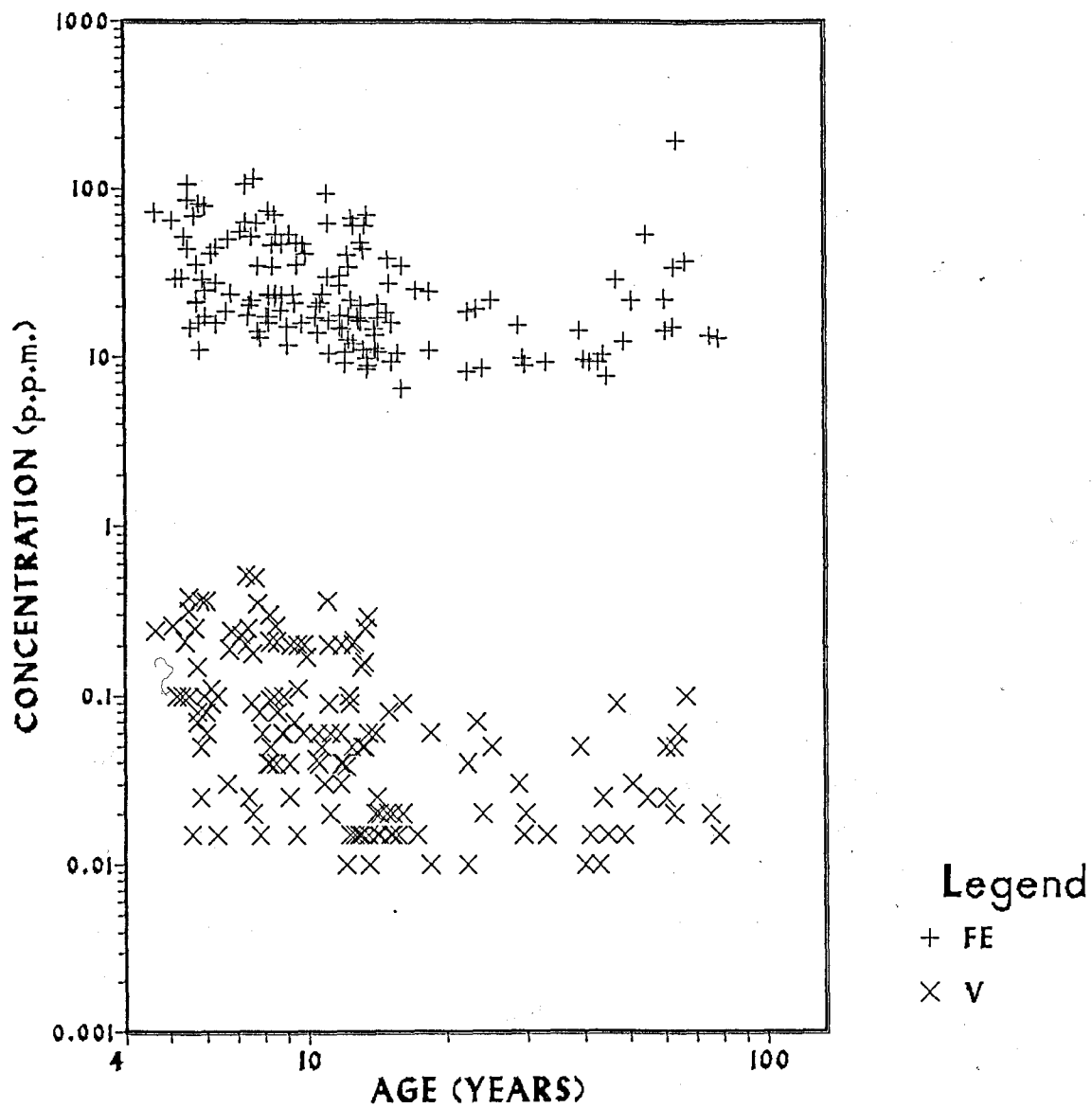


FIGURE 3.8. CHROMIUM LEVELS IN WASHED HAIR SAMPLES

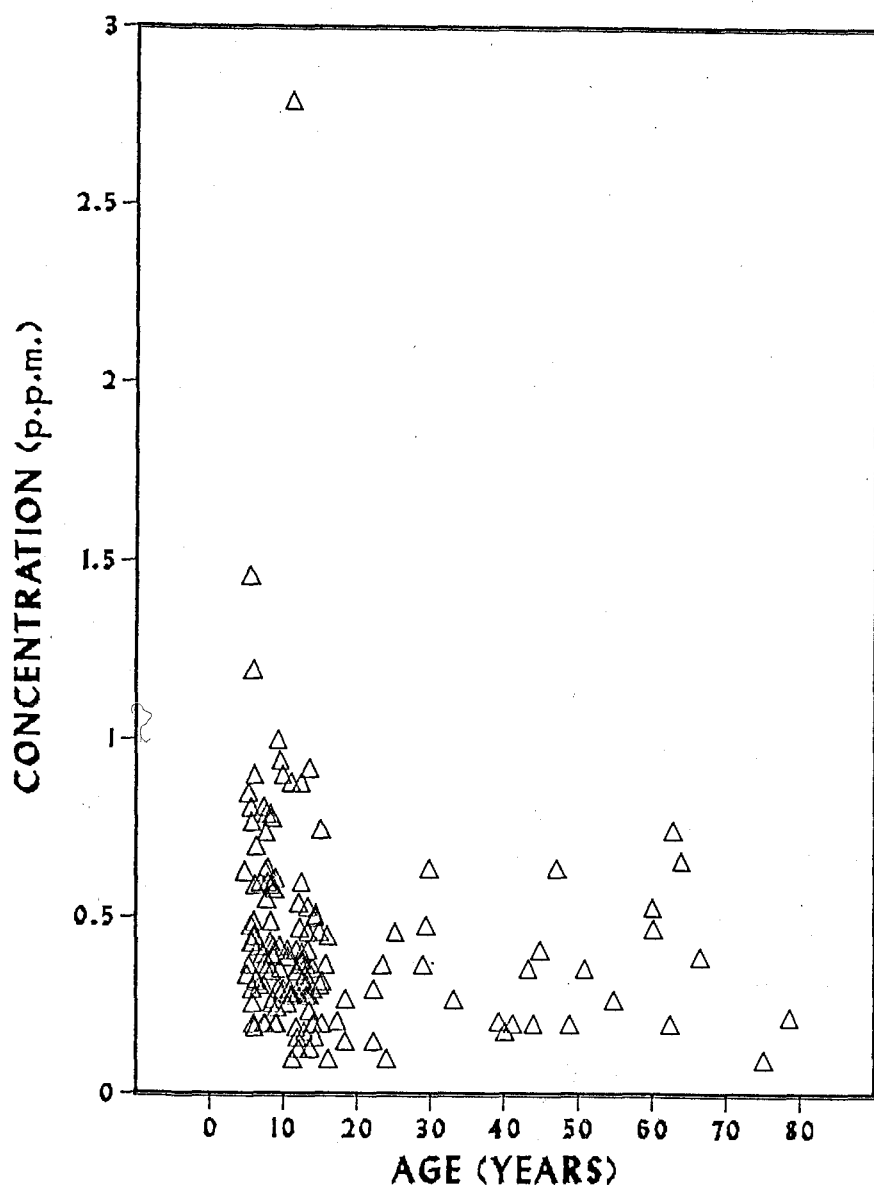


FIGURE 3.9. LEAD LEVELS IN WASHED HAIR SAMPLES

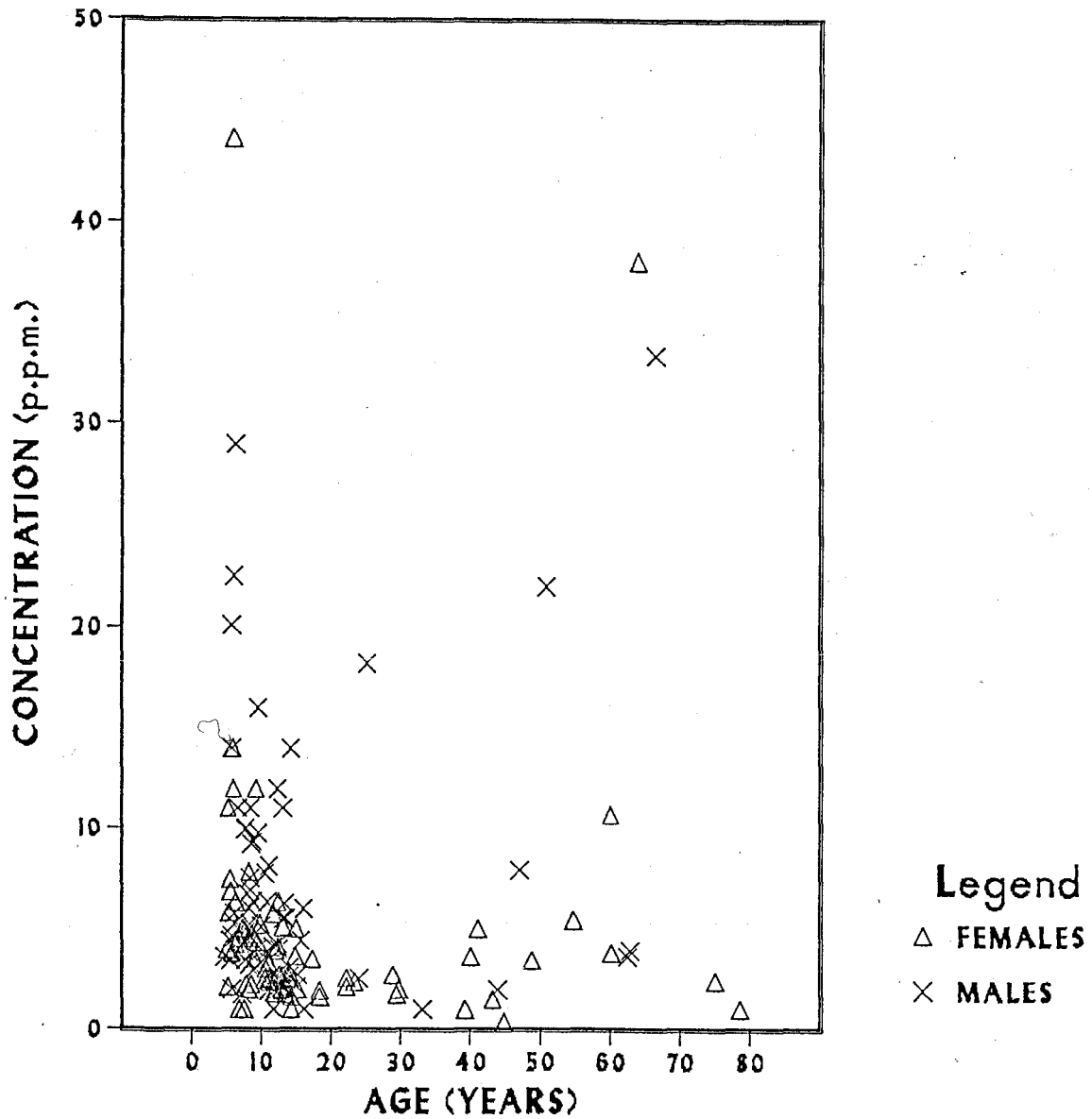




FIGURE 3.10. ZINC LEVELS IN WASHED HAIR SAMPLES

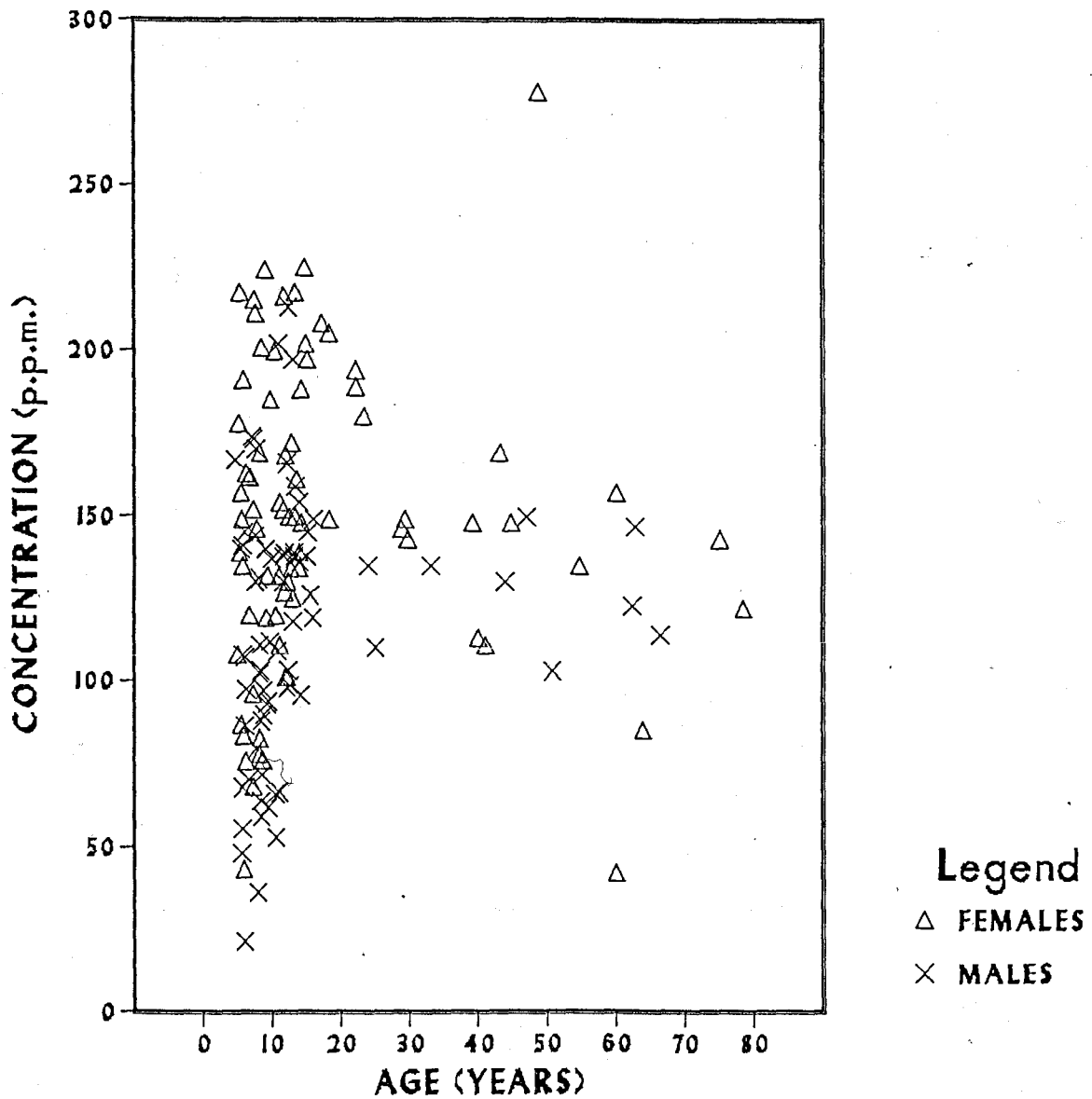


FIGURE 3.II. CALCIUM LEVELS IN WASHED HAIR SAMPLES

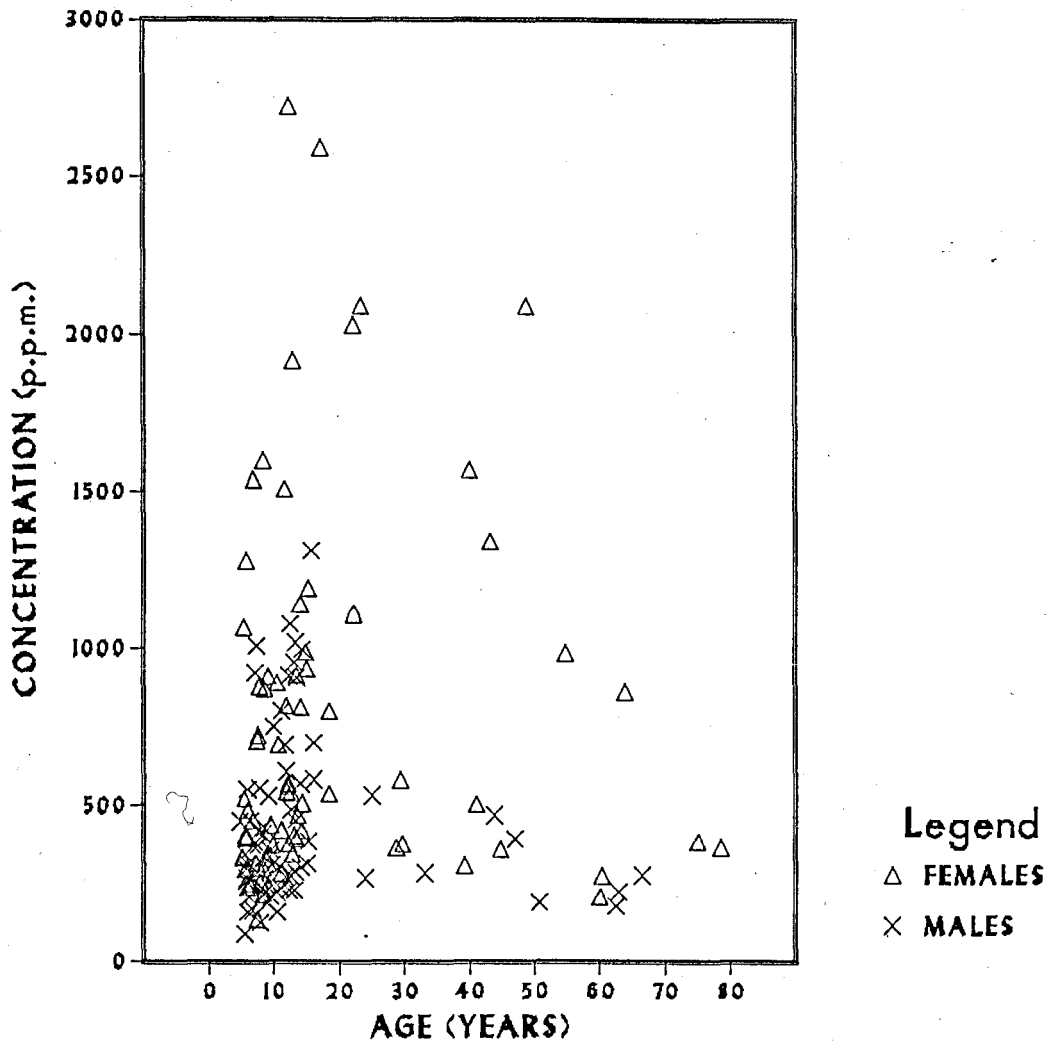


FIGURE 3.12. MAGNESIUM LEVELS IN WASHED HAIR SAMPLES

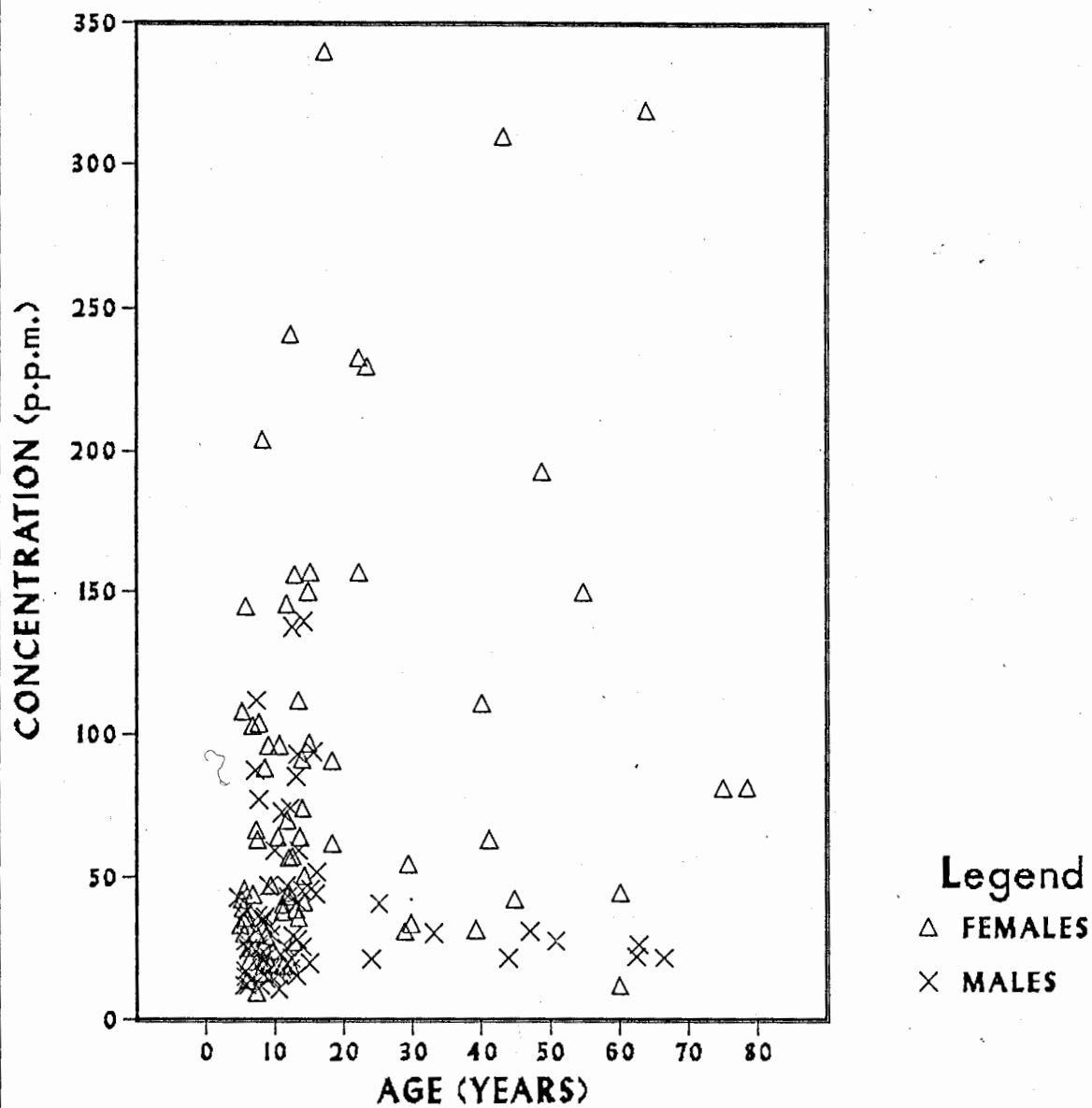
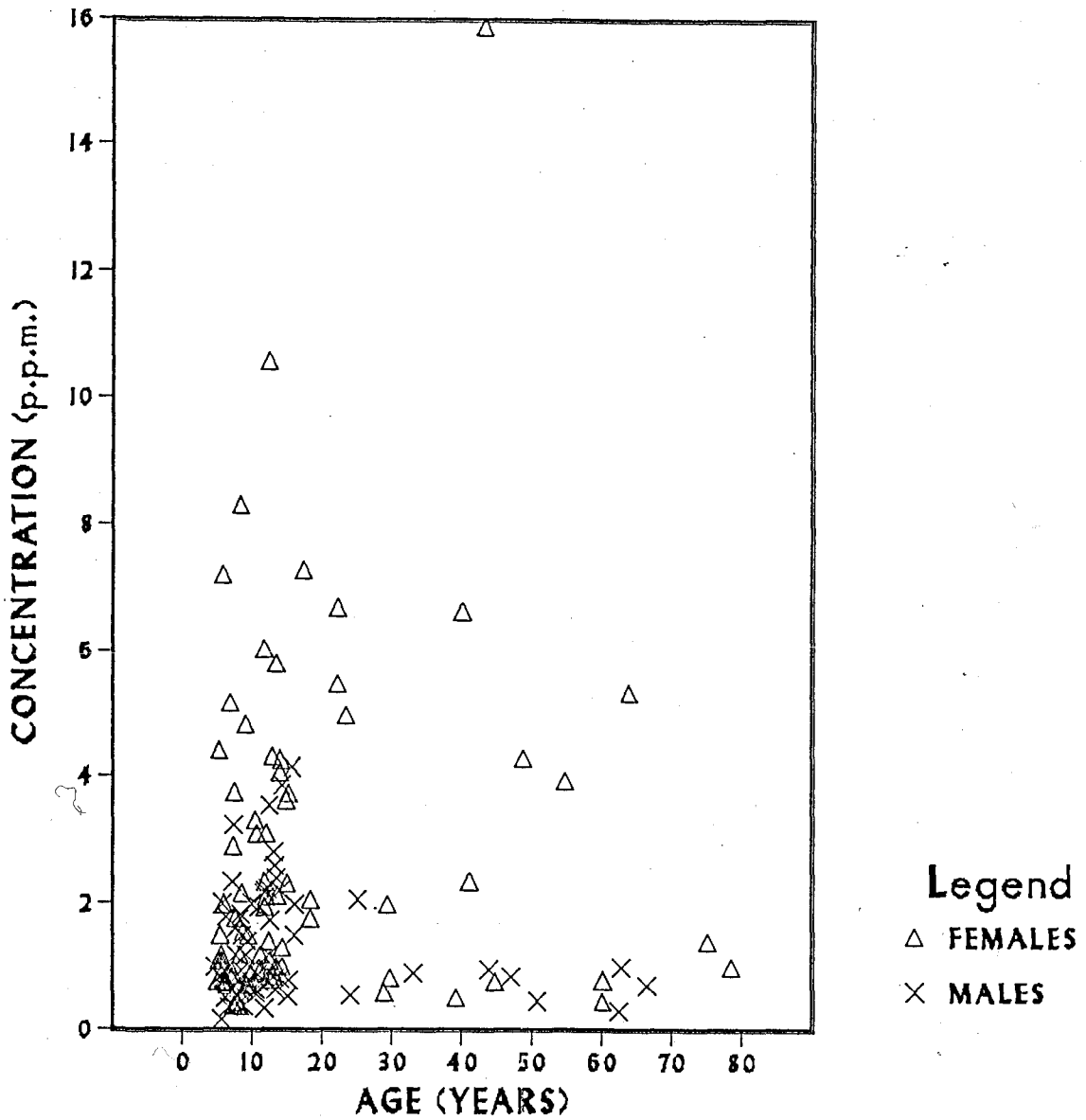


FIGURE 3.13 STRONTIUM LEVELS IN WASHED HAIR SAMPLES



### 3.5 DISCUSSION

#### 3.5.1 Effects of sample washing.

One of the primary problems encountered in interpreting results of trace element analysis of hair is that of separating exogenous from endogenous contributions. This is due to the fact that hair is hygroscopic and has ion-exchange capacity, thus enabling liquids and trace elements from external sources to enter the hair so that minerals adsorbed onto the hair from external sources become indistinguishable from minerals derived from endogenous sources (Bate, 1966; Nishiyama and Nordberg, 1972; Mossop, 1982; Fergusson, *et al.*, 1983; Buckley, *et al.*, 1984; Bos, *et al.*, 1985). A great deal of work has been done in an effort to solve this complicated problem, but no solution has yet been found. Chittleborough (1980) concluded that it is better not to wash hair samples prior to analysis; however, few have accepted the 'no-wash' procedure. Many workers have sought to overcome the question of external contamination by washing the hair in various ways (Assarian and Oberleas, 1977; McKenzie, 1978; Scoble and Litman, 1978; Ryabukhin, 1978; Salmela, *et al.*, 1981; Kollmer, 1983). This has led to a wide variety of washing procedures (see Pankhurst and Pate, 1979). An effort has been made to establish a standard

washing procedure (Ryabukhin, 1978), and it is this washing procedure that was used in the present study.

We have attempted to offer some explanation for the results obtained in the present study by plotting the extent of leaching of each element as a function of the solubility of the metal hydroxide (Figure 3.5). As can be seen, the elements with the most soluble hydroxides (Na and K) were almost entirely (92%) leached from the samples, whereas those with the least soluble hydroxides (Cu and Zn), very little metal was removed by the washing procedure. Although solubility effects may explain the extent of removal or lack of removal of some seven elements, the large amount of scatter in the plot demonstrates that leaching of some other elements is not well explained by their solubilities. In the cases of the metals which were removed relatively poorly in relation to their solubility we consider that more important factors are chelation of the metals in the hair by metal-binding ligands. Thus Pb and Ni which have highest affinities for sulphhydryl groups which are abundant in hair samples, were not readily removed by the washing procedure. Ca, Sr, and Ba have highest affinity for carboxylate groups, which are also abundant on hair, consistent with the observation that they are not readily washed from the samples. In contrast, some insoluble metals were rather readily removed and we explain this in terms of their occurrence as surface contamination. Thus, in the case of

Al and Fe, which were found in highest levels in air-borne particulates, it is likely that the large amounts removed by washing (approximately 40%) was due to the presence of these metals as dust or loosely adhering particles.

Hopps (1977) enumerated five sources of trace elements found in human scalp hair: 1) the matrix (the lower soft part of the hair root which encloses some blood vessels), 2) sebum, 3) sweat, 4) the epidermis and 5) exogenous sources. More recently, Bos and collaborators (1985), reported measurements on single hair strands at different positions in the root and outside the skin, as evidence that elements can enter the cortex via hair root sheaths, as well as via the matrix. Bos, *et al.* (1985) reported that Fe and Pb were found to be peaked on the periphery of the hair, while S, Zn, and Cu were distributed homogeneously across the hair diameter.

A number of interesting attempts to answer the question of the contribution of metals adsorbed from the environment to the total amount in hair samples have been made. In one of the earliest and most comprehensive studies, Bate (1966) placed a sample of hair in a solution with composition (NaCl, KNO<sub>3</sub>, lactic acid, urea) and pH (3.5-5.5) simulating that of perspiration, along with measured quantities of an element and a radiotracer. The sample was soaked for 16 hr in the solution, rinsed, and

washed using several washing procedures. The elements studied were Na, K, Cl, Br, Cu, Zn, Au, Se, Cr, I, As, Ag, Sb, Co, Fe, Mn, Ca, Ba, and Sr. All elements except Na and K were found to absorb, and the extent of absorption was pH dependent. Zn, Fe, Ba, Co, Mn, and Sb were removed by solutions containing EDTA, but no solvent was found that would remove Au, Ag, and Se.

Nishiyama and Nordberg (1972) studied adsorption and elution of cadmium on human and mouse hair, using a radioactive isotope technique. Hair with Cd accumulated solely from the hair follicle was obtained from mice injected with cadmium 109. Cd absorption onto human hair was found vary with individuals, from 0 to 100% of the Cd present in solution, possibly depending on hair acidity. Nearly complete removal of Cd from hair could be obtained using a sufficiently strong solution of an acid. Roberts and Green (1985) demonstrated that hair exposed to Cd containing cigarette smoke takes up cadmium in a form which can be removed by a washing procedure using a shampoo. Mossop (1982) performed an interesting study regarding arsenic adsorption onto hair. Hair from one individual was separated into several lots, one was maintained in an arsenic-free environment, and the others were exposed to an atmosphere polluted with arsenic trioxide resulting from roasting gold ore. Even after washing the samples left in the arsenic-polluted environment by a variety



of methods, all contained more than 30 ppm arsenic.

Buckley, *et al.* (1984) found that human hair adsorbs Zn and some other metals in a manner suggesting ion-exchange capacity for hair. Uptake of Zn was found to vary considerably between human hair samples, but usually accumulated to several times the levels found in control samples.

None of the washing procedures employed by Buckley *et al.* (1984) effectively removed all of the exogenous Zn, while all procedures extracted varying proportions of endogenous Zn.

In one of the most elegant studies conducted on the adsorption of metals onto human hair, Fergusson, *et al.* (1983), studied the sorption and desorption of  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{AsO}_3^{3-}$ . Fergusson, *et al.* (1983) observed that previous workers had employed very high aqueous concentrations of elements being sorbed and long soaking times, which are far from physiological. These workers attempted to overcome this problem by using lower levels and shorter soaking times. At an equilibrium concentration of  $0.3 \mu\text{g ml}^{-1}$  the sorptions were  $0.1 \mu\text{g g}^{-1}$  for As,  $1.1 \mu\text{g g}^{-1}$  for Mn,  $10 \mu\text{g g}^{-1}$  for Zn, and  $35 \mu\text{g g}^{-1}$  for Cu. Only in the case of Cu was the sorption significant relative to the indigenous levels of the elements in hair. According to Fergusson, *et al.* (1983), the greater sorption of  $\text{Cu}^{2+}$  may be correlated with better binding to hair fibre, probably both

electrostatically and to the sulphur in keratin. Inter-element binding effects were noted, where  $\text{Cu}^{2+}$  severely inhibits the sorption of  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ , and similarly the total sorption of  $\text{Cu}^{2+}$  is reduced on  $\text{Zn}^{2+}$  and  $\text{Mn}^{2+}$ -treated hair samples. Our data also support the concept that Cu and Zn are tightly bound to human hair, since very little Cu or Zn were removed by the washing procedure (Table 3.1; Figure 3.5). As well, the stability of Cu and Zn in hair samples after washing is reflected in the low solubility of the metal ions, indicating that both ligand binding and solubility are important factors.

Assarian and Oberleas (1977) studied the effect of several washing procedures on the Zn, Cu, and Mg content of a pooled hair sample. Using three washing procedures (detergent wash, hexane-ethanol wash, and acetone-ether-detergent wash), Assarian and Oberleas (1977) reported a significant difference for all three elements for the different washing procedures. Mg content of the hair was most affected by washing, containing less than half of the magnesium of the unwashed hair. The detergent wash removed the most Zn (9%) and Mg (60%); the acetone-ether-detergent wash removed the most copper (44%). In the present study, the washing procedure removed more Mg (28%) than Cu (6%) or Zn (4%), which is similar to the results of Assarian and Oberleas (1977). That we removed much less copper than Assarian and Oberleas (1977)

found using an acetone/ether/detergent wash is probably attributable to the absence of a detergent in the present study.

Salmela, *et al.* (1981) studied the effect of four washing procedures on concentrations of Mn, Fe, Cu, Zn and Cd for three pooled samples of human scalp hair. Washing agents included a non-ionic detergent, an ionic detergent, acetone, and a complexing agent (EDTA). For every element a level was found below which the concentration could not be further reduced. The number of washings required to reach this level varied considerably for each element and each washing procedure. Thus, the washing agent, the number of washings, and the length of time of each washing are important variables that must be taken into account in hair trace element studies. Salmela, *et al.* (1981) suggest that the duration and number of washes should be so long that further washes do not change the concentration of the element that is being studied. This, however becomes very difficult when doing multi-element analyses. Therefore, a standard washing procedure must be adopted for each study, according to the needs of the study. Values obtained by one washing procedure cannot generally be compared with results obtained using other washing procedures.

In a unique, but preliminary study, Scoble and Litman (1978) found that when hair samples were analyzed twice, one sample being stored for

one month prior to analysis, the amount of Na, K, Br, Au, and Zn removed by washing was much greater in the stored sample. Scoble and Litman (1978) also found that hair of older subjects loses a much larger portion of trace elements in the first wash than hair samples from younger subjects. In our study, hair from older subjects retained more Na and K than did hair from younger subjects (Table 3.3), although there was no age difference in the two elements prior to washing. Clearly, more work needs to be done to determine the effects of sample storage and age of subjects on the amount of element removed from hair samples during washing.

### 3.5.2 Effects of age and sex.

In the present study, age was a more important co-variate than sex, with 13 elements differing significantly ( $p < .05$ ) in one or more of three age groups (Table 3.3), while 5 only elements differed significantly between sexes (Table 3.4). In one of the previously most comprehensive reports regarding trace elements in hair, Creason *et al.* (1975) evaluated the importance of age, sex, hair color, cigarette smoking, and socio-economic status. In that study, the most important co-variate sex, with 12 of the 16 elements measured in children's hair, and 9 of the 16 elements in adult's hair differing between sexes. For all except Pb and Cd, female hair

contained more of the element than hair obtained from males. Although we found no significant difference in Cd content between males and females, we did find higher levels of lead in hair from males, with female hair containing more of the other four elements that differed significantly between sexes (Ca, Mg, Sr, Zn; Table 3.4).

In addition, nickel levels were found to be significantly ( $p < 0.05$ ) higher in female hair than in hair obtained from males when only the child population was considered (Moon, *et al.*, 1986). However, when the total population was considered, although females still had increased levels of Ni, the difference was not significant ( $p > 0.1$ ; Table 3.4). Our results are similar in sex-related differences to those reported for 17,380 hair mineral analyses by Gordon (1985), who found increased levels of Ca, Mg, Cu, Zn, and Ni in hair from females and increased Pb, Cd, and Cr in hair from males, although we did not find sex-related differences for Cu, Cd, or Cr (Table 3.4). The data reported by Gordon (1985), unfortunately, do not include children younger than 11 years of age. Since the greatest age-related changes in the present study occurred in the 5-11 year old age group, we cannot directly compare our results with those of Gordon (1985). Gordon (1985) reported a decrease in Zn levels with age after 30 in both sexes, and a dramatic and significant increase in hair nickel levels after age 40. Our results (Table 3.3) also indicate a significant increase in Ni levels with

increasing age after age 19, with a slight decrease in Zn after age 19, which is not significant ( $p > 0.05$ ). The lack of significance for decreased Zn levels among adults is possibly due to the small number of adult hair samples analyzed in the present study.

Erten, *et al.* (1978) reported Zn levels as a function of age, sex, and hair color for 115 children between the ages 0 to 15 years. Hair Zn levels increased as a function of age with no statistically significant difference with respect of sex or hair color. Petering, *et al.* (1971) reported that the concentrations of Zn and Cu in hair samples were directly related to the age of the individual, with an increase during childhood and a slow continuing decrease after maturity; a sex related difference was reported for Cu, but not for Zn. The results of Petering, *et al.* (1971) differ from those reported in the current study in that we found an increase (rather than a decrease) in hair Zn levels with age (Table 3.3), as well as a significant sex difference (Table 3.4). Deeming and Weber (1978) also found a sex-related difference in hair Zn levels among 11 male and 16 female adults in Tucson, Ariz., with females having higher levels, consistent with the present study, and with results reported by Gordon (1985). Hambidge, *et al.* (1972) reported a decrease in hair Zn levels shortly after birth, with a subsequent gradual increase from about 1 to 15 years of age.

### *CONCLUSIONS*

There are many important variables and co-variates that must be taken into account in designing studies involving the analysis of trace element content of human scalp hair. Among the most important are the methods used for preparing samples for analysis, and the age and sex of subjects. These factors place limitations on hair analysis data, restricting comparisons to individuals who are matched with respect to the latter two variables, and to samples that have been collected, washed, and otherwise treated as similarly as possible.

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*APPENDIX I. METAL LEVELS IN WASHED HAIR SAMPLES.*

21

FORT MCKAY CHILDREN

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
1	6.30	.3800	.10	7.96	.100	38.5	44.80	3.660	.78	75.9	25.2	239.0	.700
4	7.40	.6600	.10	7.67	.100	36.2	43.70	2.370	.97	86.7	30.4	297.0	.810
7	12.00	.6600	.40	9.34	.080	19.8	24.90	1.500	.87	43.5	14.0	237.0	.490
13	22.50	1.3700	.60	13.60	.360	49.3	78.70	2.940	1.16	21.6	12.0	159.0	.900
31	6.30	.5800	.10	8.16	.100	39.8	47.10	1.770	.86	97.1	21.8	244.0	.610
34	5.20	.3800	.20	7.93	.090	38.7	41.30	1.500	.67	86.5	15.8	210.0	.450
37	5.70	.5200	.20	7.80	.110	41.2	40.70	1.570	.94	107.0	25.1	286.0	.590
40	4.70	.4500	.20	7.05	.060	17.7	18.80	1.330	.96	76.1	29.4	334.0	.580
49	4.50	.4400	1.80	21.10	.240	54.7	23.80	1.100	2.59	120.0	103.0	1540.0	.600
58	7.50	.3100	.10	10.70	.100	46.0	46.40	1.860	1.10	63.8	16.0	217.0	.780
64	3.20	.1300	.10	8.63	.040	20.3	17.40	.770	.54	131.0	20.7	235.0	.430
76	9.70	.4200	.20	8.80	.110	30.9	35.40	1.710	1.00	62.0	15.2	210.0	.940
82	4.50	1.0800	1.00	20.80	.095	49.0	23.10	2.760	3.08	78.2	204.0	1600.0	.590
91	7.70	.2200	.10	6.79	.040	13.5	13.90	.880	.56	52.8	10.7	159.0	.390
103	1.80	.1000	.05	9.13	.040	17.0	17.60	.850	1.10	127.0	43.6	544.0	.350
109	2.10	.1000	.10	8.87	.015	16.0	27.20	.890	.52	138.0	19.9	316.0	.750
112	11.00	.2900	.05	10.30	.015	14.8	16.30	1.200	.79	118.0	15.5	229.0	.280
115	2.80	.2600	.20	10.40	.015	16.9	13.60	1.600	1.64	139.0	74.5	811.0	.300
122	4.20	.2000	.20	7.83	.050	24.5	21.70	.760	.80	103.0	21.7	277.0	.380
88	2.00	.1000	.05	9.46	.010	11.0	9.13	1.610	1.10	101.0	44.9	559.0	.130
10	3.80	.5300	.30	7.25	.070	35.4	20.90	1.710	2.98	135.0	145.0	1280.0	.260
43	29.00	.7800	.30	12.70	.100	39.4	27.40	3.170	2.10	97.5	28.4	452.0	.320
55	3.90	.5100	.70	12.30	.250	30.0	17.60	1.400	1.71	95.7	66.7	706.0	.370
70	3.30	.2000	.10	10.30	.060	20.5	15.90	1.600	1.10	112.0	19.0	309.0	.290
79	8.10	.5800	.20	8.96	.200	35.1	62.60	1.400	.93	66.6	17.6	232.0	2.790
106	12.00	.9100	.10	12.50	.100	24.7	34.40	2.140	1.20	97.6	18.0	229.0	.370
118	4.10	.3900	2.00	14.60	.090	36.3	12.60	1.300	3.45	130.0	241.0	2720.0	.880
119	2.00	.2200	.30	9.60	.060	32.5	9.93	.910	2.10	217.0	112.0	914.0	.280
46	4.20	.1000	.30	12.70	.015	20.7	15.90	.570	.93	163.0	20.8	250.0	.330
73	5.20	.2600	.20	8.18	.050	25.5	17.40	1.360	1.25	111.0	33.9	339.0	.490
85	5.70	.5600	.70	9.77	.030	24.9	26.50	2.100	2.87	152.0	146.0	1510.0	.410
94	2.47	.2700	.33	24.60	.042	27.5	17.10	.920	1.53	199.7	64.5	889.3	.410
100	3.90	.2900	.30	11.90	.038	20.9	10.70	1.100	1.54	168.3	57.0	569.0	.540
120	3.03	.1700	.20	11.10	.020	19.2	14.70	.653	1.00	154.0	45.3	570.0	.360
16	44.10	.9000	.30	10.60	.100	28.3	28.90	2.370	2.00	83.5	36.0	484.0	.450
97	2.30	.3300	.10	9.30	.020	14.0	10.60	.720	.77	111.0	19.0	284.0	.100
19	20.10	.9400	.60	9.48	.150	36.5	35.30	2.680	1.63	55.4	15.2	298.0	.300
22	11.00	.9800	.30	10.80	.100	33.9	29.50	3.160	2.54	139.0	108.0	1070.0	.370
25	4.50	.5400	.20	8.28	.060	30.0	17.40	3.050	1.42	145.0	24.3	315.0	.190
28	14.00	.7200	.10	8.61	.080	28.5	21.50	3.480	1.30	68.0	17.0	257.0	.430
52	3.80	.1400	.20	8.27	.060	18.3	19.90	1.460	.87	66.0	15.8	223.0	.260
121	4.60	.1700	.10	7.57	.050	19.4	16.00	1.000	.72	108.0	27.8	269.0	.200
61	3.50	.3700	.20	8.71	.040	37.6	11.90	.900	2.57	224.0	96.3	912.0	.250
67	7.80	.4500	.30	10.10	.210	36.7	16.00	1.100	1.30	82.8	20.7	301.0	.260

FORT MCKAY ADULTS

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
123	10.70	1.4300	.60	10.10	.050	19.3	22.20	1.500	1.25	42.4	12.1	208.0	.530
132	38.10	14.8000	17.70	12.80	.060	27.3	193.00	6.440	2.33	85.5	319.0	862.0	.660
126	33.50	6.7200	.40	13.10	.100	34.8	37.10	3.030	1.60	114.0	22.0	277.0	.390
135	3.60	.3400	.10	9.48	.020	17.0	15.30	.560	.32	123.0	22.3	180.0	.200
138	5.00	.2100	.20	9.12	.015	13.0	9.44	.630	1.20	111.0	63.6	506.0	.200
141	1.00	.0200	1.70	9.08	.015	15.1	9.38	.150	.38	135.0	30.6	285.0	.270
144	2.00	.1000	.10	10.10	.025	21.0	10.40	.320	.51	130.0	22.0	470.0	.200
129	2.10	.2400	.30	11.10	.010	17.9	8.18	2.300	2.68	189.0	157.0	1110.0	.150



GARDEN RIVER CHILDREN

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
8	3.70	.3100	.20	8.68	.250	93.0	69.20	1.830	2.16	149.0	34.9	395.0	.770
11	14.00	.9000	.40	10.80	.360	70.9	81.10	4.280	2.54	191.0	36.0	400.0	1.200
23	4.90	.4400	.20	10.60	.350	61.7	62.60	3.010	3.35	211.0	104.0	879.0	.790
26	5.80	.5800	.20	14.00	.210	37.5	51.70	3.440	3.04	217.0	39.1	523.0	1.460
32	12.00	.4800	.10	12.60	.200	33.0	53.60	2.490	1.70	119.0	20.0	246.0	1.000
38	5.00	.5100	.40	10.60	.520	84.4	106.00	2.550	1.99	152.0	30.2	315.0	.810
44	9.90	.7800	.20	12.50	.180	31.1	51.70	3.620	3.29	130.0	25.4	374.0	.740
59	5.20	.2700	.10	11.80	.200	35.7	46.50	1.600	1.70	185.0	24.6	374.0	.900
86	5.50	.3800	.20	11.20	.290	61.6	69.70	3.400	3.45	159.0	59.7	905.0	.920
14	6.80	.5600	.20	8.95	.380	131.0	106.00	4.860	3.11	157.0	45.8	402.2	.430
20	16.00	1.4000	.20	8.51	.200	47.50	106.00	6.510	3.11	93.8	29.9	357.0	.360
29	4.80	.4400	.20	10.80	.500	149.0	115.00	7.730	4.31	170.0	77.5	554.0	.550
41	4.20	.5800	.20	9.41	.200	86.4	63.20	5.400	6.10	173.0	112.0	1010.0	.310
65	5.10	.4200	.30	10.50	.150	72.3	47.50	4.210	2.78	125.0	38.9	405.0	.310
68	2.20	.2700	.20	7.56	.250	91.0	60.00	5.700	4.25	137.0	93.0	1020.0	.530
71	4.00	.4600	.30	12.80	.200	91.3	66.40	7.330	5.24	213.0	138.0	1080.0	.400
77	5.00	.4600	.20	12.50	.080	46.2	38.00	4.500	3.34	202.0	97.1	934.0	.310
92	3.30	.2800	.20	7.91	.090	42.2	30.00	3.420	2.08	132.0	40.5	422.0	.280
95	6.00	.3500	.20	9.11	.090	56.8	34.70	3.910	3.69	119.0	44.6	582.0	.450
98	2.00	1.000	.10	11.50	.020	23.5	15.90	3.580	2.39	197.0	157.0	1190.0	.200
104	1.60	.1500	.10	11.50	.015	21.3	17.10	1.400	.86	188.0	50.8	508.0	.160
107	1.90	.2400	.20	9.28	.060	34.4	24.40	2.270	1.40	205.0	91.0	798.0	.270
110	3.50	.2100	.20	8.52	.015	42.8	25.00	3.650	4.86	208.0	340.0	2590.0	.210
116	2.70	1.000	.50	10.10	.210	98.5	60.60	2.030	2.10	150.0	57.7	538.0	.380
80	2.40	.2700	.40	8.89	.200	42.1	30.30	2.300	1.80	216.0	70.3	815.0	.290
17	1.00	.9000	.10	8.32	.190	80.8	50.20	1.500	1.80	162.0	44.1	454.0	.310
35	6.00	.4300	.20	8.29	.300	78.9	73.50	3.600	2.49	102.0	28.1	283.0	.590
74	2.70	1.000	.20	7.59	.100	71.5	40.30	2.030	3.37	166.0	74.4	911.0	.470
89	2.00	1.000	.20	10.40	.015	27.0	16.50	5.920	3.11	172.0	156.0	1920.0	.340
101	3.60	.3400	.40	9.89	.020	28.3	18.20	3.840	2.76	225.0	150.0	988.0	.460
113	3.60	.4400	.10	8.88	.240	77.2	72.00	3.690	2.50	167.0	43.1	450.0	.630
2	4.00	.3500	.20	7.60	.260	88.3	64.20	2.010	2.27	108.0	33.3	334.0	.340
5	4.40	.6400	.20	8.28	.320	103.0	86.00	3.220	2.46	140.0	36.4	344.0	.430
47	1.70	1.000	.20	7.53	.230	80.1	56.00	3.960	3.86	174.0	87.7	921.0	.400
50	11.00	.6200	.20	8.45	.260	89.8	70.00	2.400	2.98	59.3	21.5	216.0	.390
53	1.90	1.000	.20	10.30	.360	126.0	93.60	3.750	3.35	202.0	73.0	799.0	.880
83	6.20	.4800	.30	9.05	.160	58.5	43.40	1.680	1.70	139.0	28.2	288.0	.410
56	2.20	.2200	.30	8.96	.210	76.3	53.50	2.630	2.85	201.0	88.5	872.0	.420
62	5.10	.4400	.30	8.19	.170	58.6	41.20	5.200	3.50	137.0	59.6	749.0	.300

GARDEN RIVER ADULTS

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
127	3.90	.2000	.05	9.70	.050	34.5	34.20	.840	.65	147.0	26.6	226.0	.750
142	2.70	.1000	.30	9.13	.030	15.0	15.50	.700	.53	146.0	31.2	365.0	.370
124	2.30	.2000	.30	8.07	.070	21.3	19.20	5.830	2.52	180.0	230.0	2090.0	.370
130	2.50	.2300	.20	10.50	.040	23.2	18.60	8.480	4.01	194.0	233.0	2030.0	.300
133	3.80	.2000	.70	9.22	.025	15.0	14.40	1.500	1.30	157.0	44.9	275.0	.470
136	7.90	.6000	.30	11.10	.090	34.5	28.80	1.400	2.17	150.0	31.2	395.0	.640
139	1.00	.0200	.10	7.15	.050	18.0	14.50	.210	.59	148.0	31.8	309.0	.210

FORT CHIPEWYAN CHILDREN

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
9	2.00	.1000	.10	13.90	.040	16.0	23.40	.330	.41	169.0	19.1	215.0	.790
42	2.10	.4600	.20	9.44	.100	22.2	29.10	1.600	1.20	178.0	42.1	336.0	.850
66	1.00	.2400	.10	13.40	.090	15.3	20.20	3.060	1.81	215.0	63.5	723.0	.630
69	2.20	.1000	.05	8.80	.015	9.2	14.30	.310	.34	146.0	16.4	255.0	.640
84	6.30	.3200	.80	56.30	.015	13.0	17.40	.350	.70	101.0	19.0	376.0	.600
117	1.00	.1000	.20	13.80	.015	11.0	10.70	.800	.93	148.0	41.5	419.0	.510
3	4.30	.3200	.10	9.67	.015	29.4	20.90	2.100	1.88	132.0	47.3	437.0	.420
48	10.00	.5200	.10	7.42	.080	42.3	34.80	3.100	1.73	79.7	22.7	238.0	.600
6	4.00	.3500	.30	29.80	.070	29.5	23.50	3.930	1.76	93.0	32.8	334.0	.300
12	3.00	.2100	.60	10.60	.050	29.0	20.80	1.200	3.19	120.0	96.4	690.0	.290
18	2.50	.1000	.20	11.40	.060	37.0	16.60	.980	.97	154.0	38.0	420.0	.280
21	1.90	.0900	.20	9.07	.015	23.4	17.30	.730	.99	134.0	27.5	344.0	.180
24	1.90	.1900	.30	30.80	.040	21.4	14.70	1.200	1.61	139.0	43.3	606.0	.160
45	3.40	.2600	.10	9.78	.020	22.5	21.70	1.600	1.10	144.0	36.4	416.0	.200
51	9.20	.3000	.30	7.87	.080	35.3	23.50	2.200	3.15	71.8	36.1	430.0	.270
60	6.90	.2700	.30	11.20	.100	69.5	34.40	1.400	1.85	103.0	35.4	409.0	.350
81	1.00	.0800	.20	8.29	.040	20.1	14.90	.280	.72	138.0	25.4	272.0	.190
87	1.70	.0400	.40	10.10	.015	11.0	8.42	.330	.39	150.0	35.8	394.0	.240
90	4.10	.2500	.30	10.10	.060	28.1	17.90	2.170	3.43	130.0	47.0	691.0	.350
108	2.50	.1000	.30	8.99	.060	37.7	11.40	.700	2.37	134.0	91.5	1140.0	.200
114	1.00	.0800	.10	27.90	.020	8.9	6.47	.310	.80	149.0	52.1	699.0	.100
15	6.30	.2000	.15	9.06	.030	37.0	23.80	1.300	1.60	109.0	23.0	306.0	.300
30	2.60	.1000	.10	9.00	.025	18.0	11.30	1.100	1.10	136.0	25.8	303.0	.200
33	5.50	.6600	.30	15.10	.050	25.5	20.40	2.940	2.75	197.0	85.4	957.0	.370
36	11.00	.3700	.20	7.39	.030	19.9	18.60	1.850	1.10	70.2	14.0	164.0	.420
39	3.40	.1700	.20	11.70	.015	19.1	14.90	.430	.29	48.1	12.0	88.4	.480
54	4.80	.2000	.10	7.51	.040	31.0	22.50	.770	1.40	87.8	23.6	265.0	.400
72	2.00	.0600	.10	8.05	.050	15.0	11.10	.460	.80	138.0	41.5	451.0	.460
78	6.70	.4000	.20	4.30	.060	21.0	13.10	.890	.72	36.5	12.0	126.0	.370
102	14.00	.9000	.30	12.00	.020	22.8	20.70	8.220	3.08	95.6	140.0	996.0	.500
105	2.80	.1000	.10	8.96	.015	17.2	12.10	.500	.93	98.5	29.7	487.0	.320
111	2.70	.1000	.10	9.66	.015	11.0	9.33	.780	.63	145.0	45.9	385.0	.320
27	2.00	.2000	.30	33.80	.025	13.0	11.10	.640	1.80	141.0	38.5	551.0	.200
57	3.00	.2000	.15	7.35	.025	17.0	15.20	1.100	1.40	140.0	47.1	530.0	.200
63	3.90	.3000	.15	9.05	.025	12.0	17.60	.680	.79	68.3	9.4	136.0	.200
93	4.40	.2900	1.00	14.80	.015	15.0	10.60	1.800	5.14	126.0	94.1	1310.0	.370
96	1.60	.0700	.10	15.50	.010	14.6	10.90	.740	1.11	149.0	62.2	540.0	.150
99	2.10	.0800	.10	14.20	.010	9.9	8.94	.800	1.33	161.0	64.6	469.0	.130
75	9.30	.6100	.20	14.40	.060	30.5	23.10	1.380	1.10	89.6	14.1	189.0	.200

FORT CHIPEWYAN ADULTS

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
125	.35	.0600	.05	8.93	.015	5.6	7.66	.330	.39	148.0	42.5	363.0	.410
128	1.70	.1000	.20	18.20	.015	12.0	9.83	1.100	1.20	149.0	55.0	582.0	.480
146	2.00	.1000	.10	38.30	.020	6.1	8.99	.440	.47	143.0	33.9	379.0	.640
140	2.40	.1000	1.00	16.40	.020	12.0	13.60	.810	.75	143.0	81.8	385.0	.100
131	3.40	.3000	.60	9.67	.015	25.1	12.50	2.550	1.61	278.0	193.0	2090.0	.200
134	5.40	.3000	.70	14.80	.025	24.0	53.60	2.750	2.10	135.0	150.0	986.0	.270
148	18.20	1.3000	.20	13.70	.050	27.1	21.80	.830	1.78	110.0	40.9	533.0	.460
143	2.50	.1000	.10	9.77	.020	8.4	8.59	.350	.45	135.0	21.3	268.0	.100
147	22.00	1.2000	.15	12.50	.030	21.0	21.70	.600	.79	103.0	28.0	192.0	.360
149	3.60	.1600	.30	42.40	.010	19.7	9.65	1.860	4.30	113.0	111.0	1570.0	.180
137	1.00	.3000	.20	8.26	.015	10.0	13.10	.530	.47	122.0	81.6	367.0	.220
145	1.50	.2000	.30	10.40	.010	16.1	9.42	1.000	2.80	169.0	310.0	1340.0	.360

*APPENDIX II. METAL LEVELS IN UNWASHED HAIR SAMPLES.*

FORT MCKAY CHILDREN

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
1	6.20	.4000	.30	8.86	.180	62.9	68.80	2.930	1.42	105.0	54.0	507.0	.950
4	7.80	.7400	.20	8.09	.130	40.5	48.30	2.660	1.09	90.8	36.0	333.0	.890
7	12.00	.6800	.50	9.71	.080	26.0	28.20	1.810	1.10	49.5	30.5	329.0	.470
13	23.70	1.6000	.90	14.30	.500	88.9	109.00	5.850	2.37	31.3	43.3	455.0	1.250
31	5.90	.6400	.30	8.98	.210	63.7	75.80	3.470	1.60	115.0	44.8	500.0	.860
34	4.60	.4800	.70	8.75	.170	74.1	74.10	3.210	1.40	112.0	36.9	448.0	.620
37	5.40	.6000	.40	8.37	.180	64.0	64.50	2.720	1.99	115.0	48.6	457.0	.720
40	5.60	.5600	.30	7.54	.060	21.9	22.20	1.730	1.23	83.9	45.4	435.0	.680
49	5.20	.4800	2.30	23.60	.300	66.5	27.90	1.100	2.65	109.0	119.0	1650.0	.650
58	7.00	.3200	.30	10.60	.220	69.2	68.60	3.520	1.78	84.5	37.0	455.0	.990
64	3.60	.1000	.05	9.51	.015	18.5	17.80	.900	.64	136.0	27.6	277.0	.350
76	11.10	.5100	.30	9.17	.200	48.2	59.10	2.840	1.51	65.5	35.1	372.0	1.220
82	4.60	1.0400	1.10	19.70	.094	57.6	26.80	2.980	2.64	65.2	222.0	1650.0	.680
91	9.90	.3000	.20	7.83	.040	18.8	16.30	1.310	.83	63.4	20.3	264.0	.430
103	3.30	.2400	.20	10.50	.070	27.8	29.40	1.200	1.30	136.0	82.1	595.0	.470
109	3.20	.1000	.30	9.80	.100	53.5	82.00	1.670	1.89	149.0	39.0	489.0	1.680
112	15.00	.4300	.05	11.80	.015	21.2	20.60	1.770	1.10	125.0	26.3	331.0	.320
115	3.50	.3400	.20	12.00	.015	21.3	15.90	2.140	2.14	156.0	108.0	1040.0	.360
122	5.50	.2600	.20	8.43	.060	29.6	29.90	1.490	1.10	102.0	35.5	389.0	.520
88	2.20	.1000	.10	10.20	.030	13.9	10.70	2.110	1.52	112.0	72.0	774.0	1.00
10	4.90	.8100	.50	9.11	.100	56.5	37.10	2.420	4.00	163.0	220.0	1690.0	.530
43	33.60	1.0000	.40	13.70	.100	29.4	28.70	3.020	2.00	78.4	26.2	398.0	.300
55	4.60	.7300	.90	13.00	.280	40.3	20.50	1.900	2.23	133.0	87.1	960.0	.350
70	4.10	.2400	.20	10.80	.060	20.0	18.10	1.700	1.30	119.0	26.9	375.0	.320
79	9.20	.7100	.30	9.73	.200	51.7	93.50	2.750	1.50	68.5	35.0	415.0	5.550
106	12.00	1.0000	.30	14.20	.200	43.4	63.50	3.870	1.80	110.0	37.9	383.0	.720
118	3.50	.3700	2.10	14.70	.050	30.0	12.40	1.600	3.22	122.0	219.0	2630.0	1.000
119	2.00	.3100	.40	9.56	.025	38.0	15.50	1.200	2.60	209.0	123.0	923.0	.300
46	4.10	.1000	.30	14.50	.017	34.4	18.40	1.870	1.50	195.7	38.8	350.7	.390
73	4.97	.2500	.27	8.14	.043	30.6	21.50	1.630	1.50	115.0	54.4	448.7	.630
85	5.83	.6300	.77	10.30	.030	28.8	29.10	2.300	3.08	157.0	182.0	1603.0	.420
94	2.70	.2600	.30	27.20	.050	31.9	20.80	1.100	1.62	213.0	81.1	1020.0	.400
100	3.50	.2600	.30	11.50	.040	23.1	11.60	1.100	1.50	164.0	66.8	610.0	.410
120	3.00	.1900	.30	11.20	.040	24.6	19.00	.880	1.30	154.0	75.2	740.0	.430
16	51.40	1.1000	.40	10.70	.090	34.6	38.00	3.540	2.83	94.1	59.7	699.0	.450
97	2.70	.4600	.15	10.10	.025	17.0	12.80	.980	1.10	122.0	40.7	458.0	.200

FORT MCKAY ADULTS

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
123	12.40	1.6400	.80	10.20	.150	40.8	42.80	2.900	1.94	48.0	37.5	442.0	.690
132	41.50	13.5000	13.00	13.30	.100	32.0	188.00	6.850	2.59	87.3	317.0	895.0	.770
126	34.70	7.0900	1.00	19.70	.250	81.1	130.00	5.910	2.76	126.0	64.6	573.0	.740
135	4.10	.5100	.80	11.60	.100	63.1	58.70	2.140	1.30	119.0	68.8	457.0	.660
138	5.60	.2500	.30	8.81	.015	19.8	11.80	.920	1.10	98.7	56.0	412.0	.270
141	.05	.0800	.90	9.36	.015	22.8	15.00	.430	.63	133.0	41.3	345.0	.590
144	3.40	.2000	.80	12.30	.060	22.0	21.30	.910	1.10	141.0	40.8	636.0	.440

GARDEN RIVER CHILDREN

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
8	3.30	.4200	.50	10.60	.390	118.0	109.00	2.910	2.69	185.0	68.9	645.0	1.100
11	13.00	1.0000	.70	12.10	.500	91.7	107.00	5.640	3.23	181.0	60.7	576.0	1.300
23	4.20	.6200	.20	10.10	.380	77.0	72.90	3.750	3.86	177.0	111.0	922.0	.753
26	6.00	.6800	.30	14.70	.390	51.8	77.50	3.500	3.40	234.0	52.6	588.0	1.300
32	7.60	.4800	.20	11.90	.260	51.6	66.50	3.640	2.44	160.0	46.5	509.0	.850
38	4.70	.5900	.50	10.40	.630	118.0	134.00	3.190	2.89	152.0	44.2	407.0	.980
44	12.00	.9000	.30	12.80	.240	36.1	62.80	3.650	3.19	120.0	30.7	399.0	1.200
59	5.10	.2900	.20	11.90	.220	45.6	61.00	1.750	1.97	189.0	32.7	404.0	.870
86	5.30	.4900	.30	10.90	.310	77.0	74.70	3.860	3.99	150.0	73.7	964.0	.950
14	8.20	.7300	.60	10.00	.730	254.0	205.00	7.810	6.62	178.0	98.8	692.0	.990
20	18.70	1.8000	.40	11.10	.290	107.0	93.50	9.000	5.60	101.0	51.9	520.0	.590
29	5.50	.5300	.50	11.00	.800	286.0	214.00	11.500	7.60	166.0	150.0	893.0	.890
41	5.10	.8300	.50	10.70	.430	156.0	131.00	7.250	8.34	179.0	167.0	1220.0	.650
65	5.60	.5300	.50	11.10	.320	127.0	90.60	5.660	4.73	125.0	60.9	546.0	.540
68	2.90	.3800	.40	8.58	.470	187.0	120.00	7.870	6.53	146.0	133.0	1210.0	1.130
71	4.70	.4900	.70	14.90	.570	255.0	187.00	8.970	7.58	183.0	198.0	1170.0	.920
77	7.50	.6200	.40	14.00	.230	89.6	80.90	6.150	4.59	167.0	142.0	1130.0	.590
92	3.60	.3500	.40	9.06	.160	73.4	50.60	4.100	3.39	143.0	61.3	534.0	.400
95	7.20	.6900	.50	12.50	.420	208.0	150.00	7.920	8.63	143.0	108.0	924.0	1.100
98	2.00	.2000	1.00	13.10	.020	31.3	19.90	4.100	2.76	221.0	195.0	1410.0	.230
104	2.00	.2300	.40	13.10	.080	51.0	29.30	2.200	1.40	204.0	78.9	658.0	.330
107	1.90	.2800	.30	11.70	.090	64.6	43.30	3.230	2.17	238.0	142.0	1060.0	.410
110	4.70	.3400	.50	11.30	.040	90.2	51.40	4.170	6.10	227.0	396.0	3090.0	.430
116	3.60	.3900	.90	11.60	.650	291.0	181.00	5.090	6.67	173.0	120.0	824.0	1.100
80	2.50	.3500	.60	9.57	.200	84.4	50.70	3.270	2.87	232.0	117.0	977.0	.370
17	2.00	.2000	.30	9.01	.240	97.3	71.30	2.200	2.67	167.0	73.2	573.0	.320
35	5.60	.6000	.30	9.58	.370	105.0	110.00	5.980	3.94	120.0	53.4	500.0	.730
74	3.20	.2900	.50	8.07	.270	120.0	65.20	3.150	4.57	165.0	112.0	1100.0	.770
89	3.10	.2000	.30	10.70	.020	113.0	21.20	13.700	4.34	177.0	214.0	2290.0	.540
101	3.40	.4100	.50	11.60	.015	35.8	24.30	4.510	3.05	256.0	178.0	1110.0	.480
113	4.50	.6800	.40	9.60	.490	146.0	128.00	6.010	4.59	175.0	77.3	647.0	.980



GARDEN RIVER ADULTS

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
127	4.40	.4500	.40	9.34	.200	78.3	87.00	2.360	1.85	137.0	59.8	392.0	1.400
142	2.40	.1300	.20	8.17	.030	14.9	15.30	.860	.68	130.0	41.2	425.0	.350
124	2.50	.2700	.60	8.93	.080	38.7	29.50	7.090	3.24	181.0	287.0	2440.0	.400
130	2.70	.2700	.40	10.40	.090	41.6	30.20	8.360	4.19	183.0	234.0	1890.0	.570
133	3.70	.2000	.90	10.40	.025	30.1	25.70	1.700	1.70	167.0	54.3	317.0	.570

FORT CHIPEWYAN CHILDREN

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
9	2.40	.2000	.40	13.50	.060	18.5	23.00	.460	.52	152.0	22.2	229.0	.860
42	2.00	.4800	.30	9.59	.200	26.2	35.40	2.050	1.60	182.0	57.9	392.0	.940
66	.90	.2500	.10	13.60	.100	16.7	21.80	2.430	1.63	222.0	69.3	755.0	.800
69	2.00	.1000	.15	8.58	.025	12.0	11.70	.500	.55	141.0	28.0	398.0	.830
84	5.70	.3700	1.00	55.30	.080	18.0	22.40	.480	.88	109.0	27.9	473.0	.610
117	1.00	.1000	.20	12.40	.015	12.0	10.90	.900	1.00	138.0	50.9	474.0	.520
3	5.30	.4000	.30	12.20	.015	34.8	26.00	2.630	2.31	132.0	66.4	565.0	.260
48	11.00	.6300	.40	8.26	.090	80.1	67.40	4.420	2.60	84.8	55.4	403.0	1.300
6	4.50	.4400	.40	35.60	.070	31.7	28.00	4.920	2.25	108.0	57.9	527.0	.280
12	3.50	.2500	.60	11.60	.100	54.8	27.20	1.200	3.36	110.0	94.2	690.0	.200
18	2.00	.2000	.30	12.00	.025	22.0	17.10	1.200	1.10	159.0	57.8	546.0	.350
21	2.80	.1800	.50	10.10	.070	47.2	34.10	1.400	1.89	141.0	47.1	466.0	.270
24	2.00	.2400	.40	33.60	.040	32.9	27.30	1.500	2.03	144.0	56.9	700.0	.350
45	4.10	.2700	.30	10.10	.080	43.0	31.70	1.950	1.40	152.0	50.7	497.0	.320
51	8.80	.2800	.30	7.73	.025	28.9	23.50	1.800	2.70	60.2	37.0	415.0	.270
60	7.00	.4800	.40	11.90	.100	61.9	44.10	2.060	2.14	98.5	50.5	517.0	.400
81	3.00	.2400	.70	10.50	.100	61.8	50.10	1.200	1.50	164.0	51.3	419.0	.540
87	1.60	.0500	.30	9.49	.015	14.0	9.79	.450	.87	142.0	51.0	451.0	.300
90	4.70	.3800	.50	10.90	.070	36.1	28.80	3.160	3.70	135.0	62.2	810.0	.580
108	3.00	.1500	.30	10.00	.030	25.2	13.90	1.000	2.60	146.0	119.0	1300.0	.280
114	1.00	.1000	.20	28.10	.025	17.0	7.66	.520	1.30	161.0	67.6	851.0	.260
15	8.10	.4200	.40	9.61	.060	44.3	37.20	2.000	2.20	112.0	32.9	356.0	.460
30	3.20	.2000	.30	9.04	.020	23.0	18.60	1.300	1.30	142.0	36.9	372.0	.340
33	6.30	.8500	.40	16.30	.100	46.0	45.50	3.610	3.27	202.0	92.1	945.0	.810
36	11.00	.4800	.10	8.28	.040	24.9	21.00	2.420	1.40	88.4	23.7	245.0	.590
39	3.20	.2000	.30	13.00	.020	21.3	17.40	.520	.38	49.6	19.9	154.0	.470
54	5.60	.3500	.50	7.89	.070	42.1	36.40	1.700	2.12	94.8	39.8	403.0	.550
72	2.10	.1000	.30	8.36	.060	24.9	16.70	.660	.76	138.0	50.1	495.0	.520
78	9.60	.6200	.20	7.79	.020	49.0	29.80	1.960	1.40	63.6	30.3	291.0	.530
102	7.40	.6100	.40	9.65	.025	25.6	17.30	9.260	3.24	105.0	183.0	1160.0	.570
105	2.90	.2000	.30	9.33	.020	34.0	22.50	1.200	1.30	91.2	40.4	543.0	.650
111	2.60	.1700	.20	8.82	.015	17.2	12.70	.870	.70	132.0	49.1	377.0	.350
27	2.00	.2000	.40	34.60	.025	16.0	12.50	.720	2.30	146.0	49.4	645.0	.260
57	2.80	.2600	.10	7.74	.020	20.0	18.20	1.500	1.50	141.0	52.8	587.0	.240
63	4.70	.3000	.10	8.95	.020	13.0	17.70	.750	.94	63.2	12.0	156.0	.250

FORT CHIPEWYAN ADULTS

SUBJECT	PB	CD	NI	CU	V	AL	FE	MN	BA	ZN	MG	CA	CR
125	.40	.0400	.10	10.70	.015	12.0	10.90	.460	.49	161.0	67.7	489.0	.550
128	1.60	.1600	.30	18.30	.040	11.0	13.10	1.100	1.10	147.0	60.5	547.0	.410
146	2.00	.1400	.05	36.40	.020	6.2	8.40	.440	.44	115.0	29.7	312.0	.470
140	4.10	.3700	4.60	18.50	.090	48.1	53.30	1.600	1.40	146.0	135.0	565.0	.570
131	3.70	.3500	.80	10.40	.015	36.4	17.20	3.600	1.85	290.0	217.0	2080.0	.250
134	6.80	.5000	1.00	16.90	.080	72.0	77.10	3.990	2.64	133.0	162.0	1010.0	.570
148	23.50	1.9400	.90	15.60	.100	62.7	59.70	2.520	2.50	113.0	60.9	593.0	.950
143	3.30	.2000	1.00	12.20	.025	12.0	11.90	.530	.72	170.0	33.7	383.0	.200

*APPENDIX III. DESCRIPTIVE STATISTICS AND ONEWAY ANALYSIS OF  
VARIANCE OF METALS IN WASHED HAIR SAMPLES FROM CHILDREN IN  
THE THREE VILLAGES.*

ANALYSIS OF VARIANCE: Variable LEAD by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.	95 PCT CONF INT FOR MEAN
BETWEEN GROUPS	2	292.0057	146.0029	4.9412	.0087	5.2545 TO 10.0865
WITHIN GROUPS	119	3516.1993	29.5479			3.8418 TO 6.0505
TOTAL	121	3808.2050				3.1077 TO 5.1026

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM
Grp 1	44	7.6705	7.9466	1.1980	1.8000	44.1000
Grp 2	39	4.9462	3.4067	.5455	1.0000	16.0000
Grp 3	39	4.1051	3.0770	.4927	1.0000	14.0000
TOTAL	122	5.6598	5.6101	.5079	1.0000	44.1000

MULTIPLE RANGE TEST

DUNCAN PROCEDURE RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
 THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $3.8437 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	
4.1051	Grp 3	G G G
4.9462	Grp 2	F F F
7.6705	Grp 1	P P P
		3 2 1
		* *

ANALYSIS OF VARIANCE: Variable CAOMIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	1.0117	.5059	7.7379	.0007
WITHIN GROUPS	119	7.7795	.0654		
TOTAL	121	8.7912			

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM	95 PCT CONF INT FOR MEAN
Grp 1	44	.4536	.2974	.0448	.1000	1.3700	.3632 TO .5441
Grp 2	39	.4154	.2641	.0423	.1000	1.4000	.3298 TO .5010
Grp 3	39	.2433	.1868	.0299	.0400	.9000	.1828 TO .3039
TOTAL	122	.3742	.2695	.0244	.0400	1.4000	.3259 TO .4225

MULTIPLE RANGE TEST

DUNCAN PROCEDURE RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
 THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.1808 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	G	G
.2433	Grp 3	r	r
.4154	Grp 2	p	p
.4536	Grp 1		
		3	2 1

ANALYSIS OF VARIANCE: Variable NICKEL by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	.2553	.1277	1.7579	.1769
WITHIN GROUPS	119	8.6429	.0726		
TOTAL	121	8.8983			

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM	95 PCT CONF INT FOR MEAN
Grp 1	44	.3245	.4006	.0604	.0500	2.0000	.2027 TO .4463
Grp 2	39	.2256	.0938	.0150	.1000	.5000	.1952 TO .2560
Grp 3	39	.2333	.1924	.0308	.0500	1.0000	.1710 TO .2957
TOTAL	122	.2638	.2712	.0246	.0500	2.0000	.2152 TO .3124

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.1906 * RANGE * DSQRT(1/N(I) + 1/N(J))$

NO TWO GROUPS ARE SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

ANALYSIS OF VARIANCE: Variable COPPER by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	324.2684	162.1342	4.4917	.0132
WITHIN GROUPS	119	4295.4475	36.0962		
TOTAL	121	4619.7159			

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM	95 PCT CONF INT FOR MEAN
Grp 1	44	10.4659	3.7062	.5587	6.7900	24.6000	9.3391 TO 11.5927
Grp 2	39	9.8038	1.6941	.2713	7.5300	14.0000	9.2547 TO 10.3530
Grp 3	39	13.6015	9.7275	1.5577	4.3000	56.3000	10.4482 TO 16.7548
TOTAL	122	11.2566	6.1790	.5594	4.3000	56.3000	10.1491 TO 12.3642

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $4.2483 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

G G G  
P P P  
P P P

Mean	Group	2	1	3
9.8038	Grp 2			
10.4659	Grp 1	*		
13.6015	Grp 3		*	*



ANALYSIS OF VARIANCE: Variable VANADIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	.5864	.2932	41.9887	.0000
WITHIN GROUPS	119	.8310	.0070		
TOTAL	121	1.4174			

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM	95 PCT CONF INT FOR MEAN
Grp 1	44	.0856	.0714	.0108	.0100	.3600	.0639 TO .1073
Grp 2	39	.2065	.1241	.0199	.0150	.5200	.1663 TO .2468
Grp 3	39	.0390	.0264	.0042	.0100	.1000	.0304 TO .0475
TOTAL	122	.1093	.1082	.0098	.0100	.5200	.0899 TO .1287

MULTIPLE RANGE TEST

DUNCAN PROCEDURE RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
 THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.0591 * RANGE * OSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	Group
.0390	Grp 3	G G G
.0856	Grp 1	r r r
.2065	Grp 2	p p p
	3 1 2	
	*	
	*	

ANALYSIS OF VARIANCE: Variable ALUMINUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	46884.9081	23442.4540	60.1957	.0000
WITHIN GROUPS	119	46343.0687	389.4376		
TOTAL	121	93227.9768			

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM	95 PCT CONF INT FOR MEAN
Grp 1	44	28.9000	10.8396	1.6341	11.0000	54.7000	25.6045 TO 32.1955
Grp 2	39	67.6051	30.7687	4.9269	21.3000	149.0000	57.6311 TO 77.5792
Grp 3	39	22.5974	11.8274	1.8939	8.9000	69.5000	18.7634 TO 26.4314
TOTAL	122	39.2582	27.7575	2.5130	8.9000	149.0000	34.2830 TO 44.2334

MULTIPLE RANGE TEST

DUNCAN PROCEDURE RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES. THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $13.9542 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	3	1	2
22.5974	Grp 3			
28.9000	Grp 1			
67.6051	Grp 2	*	*	*

ANALYSIS OF VARIANCE: Variable IRON by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	31230.0304	15615.0152	53.1769	.0000
WITHIN GROUPS	119	34943.5094	293.6429		
TOTAL	121	66173.5398			

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM	95 PCT CONF INT FOR MEAN
Grp 1	44	25.3673	14.6875	2.2142	9.1300	78.7000	20.9018 TO 29.8327
Grp 2	39	55.1872	25.1065	4.0203	15.9000	115.0000	47.0486 TO 63.3258
Grp 3	39	17.3759	6.7170	1.0756	6.4700	34.8000	15.1985 TO 19.5533
TOTAL	122	32.3452	23.3857	2.1172	6.4700	115.0000	28.1536 TO 36.5369

MULTIPLE RANGE TEST

DUNCAN PROCEDURE RANGES FOR THE 0.050 LEVEL

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
 THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $12.1170 * RANGE * DSORT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	G G G
17.3759	Grp 3	r r r
25.3673	Grp 1	p p p
55.1872	Grp 2	3 1 2

ANALYSIS OF VARIANCE: Variable MANGANESE by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	113.8100	56.9050	33.5492	.0000
WITHIN GROUPS	119	201.8440	1.6962		
TOTAL	121	315.6540			

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM	95 PCT CONF INT FOR MEAN
Grp 1	44	1.6564	.8289	.1250	.5700	3.6600	1.4044 TO 1.9084
Grp 2	39	3.6013	1.5801	.2530	1.4000	7.7300	3.0891 TO 4.1135
Grp 3	39	1.4118	1.4274	.2286	.2800	8.2200	.9491 TO 1.8745
TOTAL	122	2.1999	1.6152	.1462	.2800	8.2200	1.9104 TO 2.4894

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.9209 * RANGE * DSORT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	
1.4118	Grp 3	G G G
1.6564	Grp 1	F F F
3.6013	Grp 2	P P P
		3 1 2
		* *

ANALYSIS OF VARIANCE: Variable BARIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.	95 PCT CONF INT FOR MEAN
BETWEEN GROUPS	2	57.1336	28.5668	31.4533	.0000	1.1746 TO 3.4500
WITHIN GROUPS	119	108.0794	.9082			2.5655 TO 5.1400
TOTAL	121	165.2129				1.7076 TO 6.1000

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM
Grp 1	44	1.4055	.7592	.1144	.5200	3.4500
Grp 2	39	2.9138	1.0746	.1721	.8600	6.1000
Grp 3	39	1.4974	1.0184	.1631	.2900	5.1400
TOTAL	122	1.9170	1.1685	.1058	.2900	6.1000

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.6739 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group
1.4055	Grp 1
1.4974	Grp 3
2.9138	Grp 2

G G G  
 r r r  
 p p p  
 1 3 2  
 \* \*

ANALYSIS OF VARIANCE: Variable ZINC by Variable RESIDENCE

SOURCE	D. F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	61865.8272	30932.9136	18.5560	.0000
WITHIN GROUPS	119	198373.2994	1667.0025		
TOTAL	121	260239.1266			

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM	95 PCT CONF INT FOR MEAN
Grp 1	44	109.3250	43.9850	6.6310	21.6000	224.0000	95.9523 TO 122.6977
Grp 2	39	162.9000	39.3108	6.2948	59.3000	225.0000	150.1569 TO 175.6431
Grp 3	39	124.7462	38.5457	6.1722	36.5000	215.0000	112.2511 TO 137.2412
TOTAL	122	131.3811	46.3760	4.1987	21.6000	225.0000	123.0687 TO 139.6936

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $28.8704 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	
109.3250	Grp 1	G G G
124.7462	Grp 3	P P P
162.9000	Grp 2	P P P
		1 3 2
		* *

ANALYSIS OF VARIANCE: Variable MAGNESIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB	95 PCT CONF INT FOR MEAN
BETWEEN GROUPS	2	18067.2140	9033.6070	3.8696	.0235	33.1717 TO 64.9510
WITHIN GROUPS	119	277804.8171	2334.4943			52.3125 TO 90.3490
TOTAL	121	295872.0311				33.3241 TO 51.4041

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $34.1650 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	
42.3641	Grp 3	G G G
49.0614	Grp 1	r r r
71.3308	Grp 2	p p p
		3 1 2

ANALYSIS OF VARIANCE: Variable CALCIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	1079491.948	539745.9741	2.8614	.0611
WITHIN GROUPS	119	22447249.20	188632.3462		
TOTAL	121	23526741.15			

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM	95 PCT CONF INT FOR MEAN
Grp 1	44	547.3932	514.2197	77.5215	159.0000	2720.0000	391.0561 TO 703.7302
Grp 2	39	696.0308	465.2239	74.4954	216.0000	2590.0000	545.2227 TO 846.8389
Grp 3	39	464.0359	273.9883	43.8732	88.4000	1310.0000	375.2192 TO 552.8526
TOTAL	122	568.2615	440.9488	39.9216	88.4000	2720.0000	489.2261 TO 647.2969

MULTIPLE RANGE TEST

DUNCAN PROCEDURE RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
 THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 307.1094 \* RANGE \*  $DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	G G
464.0359	Grp 3	r r r
547.3932	Grp 1	p p p
696.0308	Grp 2	*



ANALYSIS OF VARIANCE: Variable CHROMIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	.6747	.3374	3.4320	.0356
WITHIN GROUPS	119	11.6975	.0983		
TOTAL	121	12.3722			

GROUP	COUNT	MEAN	STANDARD DEVIATION	STANDARD ERROR	MINIMUM	MAXIMUM	95 PCT CONF INT FOR MEAN
Grp 1	44	.4991	.4097	.0618	.1000	2.7900	.3745 TO .6236
Grp 2	39	.5231	.2914	.0467	.1600	1.4600	.4286 TO .6175
Grp 3	39	.3523	.1817	.0291	.1000	.8500	.2934 TO .4112
TOTAL	122	.4598	.3198	.0290	.1000	2.7900	.4025 TO .5172

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.2217 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	
.3523	Grp 3	
.4991	Grp 1	*
.5231	Grp 2	*

	Group	
	3	1 2
	G	G G
	F	F F F
	P	P P P

*APPENDIX IV. ONEWAY ANALYSIS OF VARIANCE OF THE LOGARITHM OF  
METAL LEVELS IN WASHED HAIR SAMPLES FROM CHILDREN IN THE  
THREE VILLAGES.*

ANALYSIS OF VARIANCE: Variable LN.LEAD by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	6.4819	3.2409	6.8830	.0015
WITHIN GROUPS	119	56.0328	.4709		
TOTAL	121	62.5147			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.4852 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	G G G
1.1735	Grp 3	r r r
1.4045	Grp 2	p p p
1.7288	Grp 1	* *

ANALYSIS OF VARIANCE: Variable LN.CADMIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	10.6864	5.3432	10.6977	.0001
WITHIN GROUPS	119	59.4371	.4995		
TOTAL	121	70.1235			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.4997 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	G G G
-1.6751	Grp 3	r r r
-1.0805	Grp 2	p p p
-1.0107	Grp 1	3 2 1

ANALYSIS OF VARIANCE: Variable LN.NICKEL by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	.4228	.2114	.4661	.6286
WITHIN GROUPS	119	53.9699	.4535		
TOTAL	121	54.3927			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $\text{MEAN}(J) - \text{MEAN}(I)$  IS...  
 $0.4762 * \text{RANGE} * \text{DSORT}(1/N(I) + 1/N(J))$

NO TWO GROUPS ARE SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL



ANALYSIS OF VARIANCE: Variable LN.VANADIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	49.3739	24.6869	35.2079	.0000
WITHIN GROUPS	119	83.4400	.7012		
TOTAL	121	132.8139			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.5921 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	G G G
-3.4709	Grp 3	r r r
-2.7664	Grp 1	p p p
-1.8833	Grp 2	3 1 2

ANALYSIS OF VARIANCE: Variable LN.ALUMINUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	25.4895	12.7448	61.7599	.0000
WITHIN GROUPS	119	24.5568	.2064		
TOTAL	121	50.0464			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.3212 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	G G
3.0045	Grp 3	r r
3.2908	Grp 1	p p
4.1033	Grp 2	3 1 2
		* *



ANALYSIS OF VARIANCE: Variable LN.IRON by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	25.7263	12.8632	56.1193	.0000
WITHIN GROUPS	119	27.2761	.2292		
TOTAL	121	53.0024			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.3385 * RANGE * DSORT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	G G G
2.7819	Grp 3	r r r
3.0985	Grp 1	p p p
3.8939	Grp 2	3 1 2
		* *
		* *

ANALYSIS OF VARIANCE: Variable LN.MANGANESE by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	28.0854	14.0427	40.1142	.0000
WITHIN GROUPS	119	41.6581	.3501		
TOTAL	121	69.7435			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
.0.4184 \* RANGE \*  $DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	G G G
.0163	Grp 3	r r r
.3874	Grp 1	p p p
1.1883	Grp 2	3 1 2
		* *
		* *

ANALYSIS OF VARIANCE: Variable LN.BARIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	16.7240	8.3620	30.5715	.0000
WITHIN GROUPS	119	32.5492	.2735		
TOTAL	121	49.2732			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $\text{MEAN}(J) - \text{MEAN}(I)$  IS...  
 $0.3698 * \text{RANGE} * \text{DSQRT}(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	G G
.1999	Grp 3	r r r
.2147	Grp 1	p p p
1.0016	Grp 2	3 1 2
		* *

ANALYSIS OF VARIANCE: Variable LN.ZINC by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	4.2902	2.1451	15.4065	.0000
WITHIN GROUPS	119	16.5687	.1392		
TOTAL	121	20.8588			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.2638 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	
4.6076	Grp 1	G G G
4.7688	Grp 3	r r r
5.0594	Grp 2	p p p
		1 3 2
		* *

ANALYSIS OF VARIANCE: Variable LN.MAGNESIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	6.9481	3.4740	6.8738	.0015
WITHIN GROUPS	119	60.1432	.5054		
TOTAL	121	67.0913			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.5027 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	
3.5088	Grp 1	G G G
3.5556	Grp 3	F F F
4.0409	Grp 2	P P P
		1 3 2
		* *

ANALYSIS OF VARIANCE: Variable LN.CALCIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	3.8738	1.9369	4.8991	.0090
WITHIN GROUPS	119	47.0471	.3954		
TOTAL	121	50.9209			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.4446 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	G G G
5.9769	Grp 3	r r r
6.0176	Grp 1	p p p
6.3789	Grp 2	* *

ANALYSIS OF VARIANCE: Variable LN.CHROMIUM by Variable RESIDENCE

SOURCE	D.F.	SUM OF SQUARES	MEAN SQUARES	F RATIO	F PROB.
BETWEEN GROUPS	2	3.2307	1.6154	5.6771	.0044
WITHIN GROUPS	119	33.8605	.2845		
TOTAL	121	37.0912			

MULTIPLE RANGE TEST

DUNCAN PROCEDURE  
RANGES FOR THE 0.050 LEVEL -

2.80 2.95

THE RANGES ABOVE ARE TABLE RANGES.  
THE VALUE ACTUALLY COMPARED WITH  $MEAN(J) - MEAN(I)$  IS...  
 $0.3772 * RANGE * DSQRT(1/N(I) + 1/N(J))$

(\*) DENOTES PAIRS OF GROUPS SIGNIFICANTLY DIFFERENT AT THE 0.050 LEVEL

Mean	Group	3	1	2
-1.1689	Grp 3			
-.8757	Grp 1	*		
-.7794	Grp 2		*	

*APPENDIX V. PEARSON CORRELATION COEFFICIENTS FOR THE 13 METALS  
OF INTEREST IN THE STUDY.*



METAL LEVELS IN WASHED HAIR SAMPLES FROM THE ENTIRE POPULATION

	PB1	CD1	NI1	CU1	V1	AL1	FE1	MN1	BA1	ZN1	MG1
PB1	1.0000	.6325**	.4041**	-.0253	.1451	.0458	.3576**	.2534**	.0407	-.4172**	-.0395
CD1	.6325**	1.0000	.8827**	.0117	.0548	.0286	.5346**	.2774**	.0695	-.1634	.2802**
NI1	.4041**	.8827**	1.0000	.0610	-.0164	-.0226	.4922**	.1986*	.0744	-.0872	.4061**
CU1	-.0253	.0117	.0610	1.0000	-.1389	-.1847	-.1393	-.1084	.0186	.0255	.0443
V1	.1451	.0548	-.0164	-.1389	1.0000	.8455**	.7665**	.4479**	.4146**	.0574	-.0915
AL1	.0458	.0286	-.0226	-.1847	.8455**	1.0000	.7454**	.5275**	.5706**	.1531	.0406
FE1	.3576**	.5346**	.4922**	-.1393	.7665**	.7454**	1.0000	.5548**	.3841**	-.0014	.1082
MN1	.2534**	.2774**	.1986*	-.1084	.4479**	.5275**	.5548**	1.0000	.7006**	.1840	.4205**
BA1	.0407	.0695	.0744	.0186	.4146**	.5706**	.3841**	.7006**	1.0000	.3398**	.5556**
ZN1	-.4172**	-.1634	-.0872	.0255	.0574	.1531	-.0014	.1840	.3398**	1.0000	.4281**
MG1	-.0395	.2802**	.4061**	.0443	-.0915	.0406	.1082	.4205**	.5556**	.4281**	1.0000
CA1	-.1617	.0049	.1283	.1290	-.0600	.0656	-.0647	.3781**	.6294**	.4807**	.8746**
CR1	.1699	.1058	.0677	-.0184	.4287**	.2187*	.4287**	.1297	.0426	-.0790	-.1019

	CA1	CR1
PB1	-.1617	.1699
CD1	.0049	.1058
NI1	.1283	.0677
CU1	.1290	-.0184
V1	-.0600	.4287**
AL1	.0656	.2187*
FE1	-.0647	.4287**
MN1	.3781**	.1297
BA1	.6294**	.0426
ZN1	.4807**	-.0790
MG1	.8746**	-.1019
CA1	1.0000	-.1004
CR1	-.1004	1.0000

\* - SIGNIF. LE .01      \*\* - SIGNIF. LE .001      (1-TAILED, " " PRINTED IF A COEFFICIENT CANNOT BE COMPUTED)

METAL LEVELS IN WASHED HAIR SAMPLES FROM RESIDENTS FROM FORT MCKAY

	PB1	CD1	NI1	CU1	V1	AL1	FE1	MN1	BA1	ZN1	MG1
PB1	1.0000	.6376**	.4406**	.1111	.3040	.2518	.5806**	.6690**	.1936	-.3822*	.1083
CD1	.6376**	1.0000	.8971**	.1585	.0646	.1064	.8401**	.7031**	.2210	-.1405	.5188**
NI1	.4406**	.8971**	1.0000	.1798	.0128	.0524	.8335**	.5996**	.2562	-.0704	.6626**
CU1	.1111	.1585	.1798	1.0000	.2567	.3638**	.0722	.1097	.4537**	.1889	.3889*
V1	.3040	.0646	.0128	.2567	1.0000	.7148**	.3164	.2693	.1534	-.4746**	-.0605
AL1	.2518	.1064	.0524	.3638*	.7148**	1.0000	.3206	.3883*	.4337**	-.1766	.1961
FE1	.5806**	.8401**	.8335**	.0722	.3164	.3206	1.0000	.7321**	.0858	-.3533*	.3876*
MN1	.6690**	.7031**	.5996**	.1097	.2693	.3883*	.7321**	1.0000	.3774*	-.3162	.4116*
BA1	.1936	.2210	.2562	.4537**	.1534	.4337**	.0858	.3774*	1.0000	.3129	.7950**
ZN1	-.3822*	-.1405	-.0704	.1889	-.4746**	-.1766	-.3533*	-.3162	.3129	1.0000	.3046
MG1	.1083	.5188**	.6626**	.3889*	-.0605	.1961	.3876*	.4116*	.7950**	.4006*	1.0000
CA1	-.1225	.0623	.2071	.4989**	.0108	.2759	-.0605	.0838	.8622**	.4006*	.8242**
CR1	.1062	.0834	.0841	.0385	.4347**	.3509*	.3925*	.1292	-.0306	-.3301*	.0039

CA1 CR1

PB1	-.1225	.1062
CD1	.0623	.0834
NI1	.2071	.0841
CU1	.4989**	.0385
V1	.0108	.4347**
AL1	.2759	.3509*
FE1	-.0605	.3925*
MN1	.0838	.1292
BA1	.8622**	-.0306
ZN1	.4006*	-.3301*
MG1	.8242**	.0039
CA1	1.0000	-.0100
CR1	-.0100	1.0000

\* - SIGNIF. LE .01 \*\* - SIGNIF. LE .001 (1-TAILED, " " PRINTED IF A COEFFICIENT CANNOT BE COMPUTED)

METAL LEVELS IN WASHED HAIR SAMPLES FROM RESIDENTS FROM GARDEN RIVER

	PB1	CD1	NI1	CU1	V1	AL1	FE1	MN1	BA1	ZN1	MG1
PB1	1.0000	.7713**	.0418	.2555	.2985	.0555	.2903	.1419	.0784	-.4570**	-.3559*
CD1	.7713**	1.0000	-.0276	.1423	.3821*	.2165	.3731*	.2364	.1822	-.3196	-.3161
NI1	.0418	-.0276	1.0000	-.0280	.0313	-.0199	-.0393	-.0094	-.0400	.0971	.0163
CU1	.2555	.1423	-.0280	1.0000	.0412	-.1818	.0577	.1446	.0874	.3711*	-.0177
V1	.2985	.3821*	.0313	.0412	1.0000	.8003**	.9559**	.1816	.2411	-.1504	-.3619*
AL1	.0555	.2165	-.0199	.1818	.8003**	1.0000	.8886**	.2695	.4278*	-.1669	-.1994
FE1	.2903	.3731*	-.0393	.0577	.9559**	.8886**	1.0000	.2222	.3212	-.1791	-.3349
MN1	.1419	.2364	-.0094	.1446	.1816	.2695	.2222	1.0000	.7534**	.1419	.4814**
BA1	.0784	.1822	-.0400	.0874	.2411	.4278*	.3212	.7534**	1.0000	.1680	.4868**
ZN1	-.4570**	-.3196	.0971	.3711*	-.1504	-.1669	-.1791	.1419	.1680	1.0000	.5363**
MG1	-.3559*	-.3161	.0163	.0177	-.3619*	-.1994	-.3349	.4814**	.4868**	.5363**	1.0000
CA1	-.3697*	-.3387	-.0237	-.0187	-.3594*	-.2161	-.3474*	.5106**	.5064**	.5102**	.9627**
CR1	.4183*	.2508	-.0154	.5017**	.4706**	.1074	.4297*	-.0897	-.0286	.0865	-.3447*

CA1	CR1
-.3697*	.4183*
-.3387	.2508
-.0237	-.0154
-.0187	.5017**
-.3594*	.4706**
-.2161	.1074
-.3474*	.4297*
.5106**	-.0897
.5064**	-.0286
.5102**	.0865
.9627**	-.3447*
1.0000	-.3008
-.3008	1.0000

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	PB1	CD1	NI1	CU1	V1	AL1	FE1	MN1	BA1	ZN1	MG1
PB1	1.0000	.8981**	.0299	-.0706	.2117	.3616*	.4059*	.3507*	.1749	-.4357**	-.0919
CD1	.8981**	1.0000	.0378	-.0425	.2584	.2652	.3939*	.4242**	.2067	-.2275	.0353
NI1	.0299	.0378	1.0000	.2911	-.0839	.0428	.1438	.1524	.4392**	.0774	.3843*
CU1	-.0706	-.0425	.2911	1.0000	-.1809	-.2161	-.1417	-.0299	.1006	.0193	-.0014
V1	.2117	.2584	-.0839	-.1809	1.0000	.6617**	.5170**	.2412	.1674	-.1096	-.2164
AL1	.3616*	.2652	.0428	-.2161	.6617**	1.0000	.6099**	.3048	.3375*	-.2377	-.0277
FE1	.4059*	.3939*	.1438	-.1417	.5170**	.6099**	1.0000	.3984*	.1604	-.1964	-.0201
MN1	.3507*	.4242**	.1524	-.0299	.2412	.3048	.3984*	1.0000	.5148**	-.0098	.3260*
BA1	.1749	.2067	.4392**	-.1417	.1674	.3375*	.1604	.5148**	1.0000	.0077	.4888**
ZN1	-.4357**	-.2275	.0774	.0193	-.1096	-.2377	-.1964	-.0098	.0077	1.0000	.4451**
MG1	-.0919	.0353	.3843*	-.0014	-.2164	-.0277	-.0201	.3260*	.4888**	.4451**	1.0000
CA1	-.0973	.0152	.4411**	.1703	-.1651	.0428	-.1042	.3534*	.6598**	.5292**	.8085**
CR1	.1379	.2097	-.1436	.0370	.3024	-.0076	.2584	.1445	-.0851	.0199	-.1333

	CA1	CR1
PB1	-.0973	.1379
CD1	.0152	.2097
NI1	.4411**	-.1436
CU1	.1703	.0370
V1	-.1651	.3024
AL1	.0428	-.0076
FE1	-.1042	.2584
MN1	.3534*	.1445
BA1	.6598**	-.0851
ZN1	.5292**	.0199
MG1	.8085**	-.1333
CA1	1.0000	-.1842
CR1	-.1842	1.0000

\* - SIGNIF. LE .01    \*\* - SIGNIF. LE .001    (1-TAILED, " " PRINTED IF A COEFFICIENT CANNOT BE COMPUTED)