

BULK ATMOSPHERIC METAL CONTRIBUTION TO A RIVER
IN AN INDUSTRIAL AREA

By

MICHAEL BOYD TATE

Bachelor of Science in Civil Engineering

Oklahoma State University

Stillwater, Oklahoma

1980

Submitted to the Faculty of the Graduate College
of the Oklahoma State University
In partial fulfillment of the requirements
for the Degree of
MASTER OF SCIENCE
December, 1981



BULK ATMOSPHERIC METAL CONTRIBUTION TO A RIVER
IN AN INDUSTRIAL AREA

Thesis Approved:

Marcia A. Bates

Thesis Adviser

John Vander

Don F. Keenan

Norman N. Durhan

Dean of the Graduate College

ACKNOWLEDGMENTS

I would like to use this space to recognize those persons who are primarily responsible for my being able to extend my education to this point. Firstly, my principal adviser, Dr. Marcia H. Bates, receives my utmost respect and appreciation for her exceptional guidance and instruction during my pursuit of this degree. Her patient and professional manner has made the time spent on this project both enjoyable and educational. I would also like to thank Dr. D. F. Kincannon and Dr. J. N. Veenstra for serving on my committee.

My fellow students in Bioenvironmental Engineering are to be thanked for their assistance and their friendship, along with friends outside of the department who have been most supportive.

Lisa Post deserves special recognition for her generosity in typing this paper, as well as Duane Phillips for his drafting.

My gratitude is also extended to my parents, Raymond and Mariana Tate. Their love, support, and moral upbringing has given me the ability to follow my academic desires where ever they may lead. My sisters, Paula and Julie, and their respective families have also provided me with an endless amount of emotional support throughout my schooling. I would also like to give my sincerest thanks to my grandmother, Bobbie Rosenberger. Her love and encouragement is deeply appreciated.

Lastly, I acknowledge my grandfather, the late Charles P. Rosenberger. His assistance and encouragement to grasp for academic excellence will always be remembered. To him I dedicate this work.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
II. LITERATURE REVIEW	4
Atmospheric Contribution of Metals	7
Factors Affecting Metal Concentrations and Contributions.	7
Trends Observed.	9
Methods of Sampling.	11
III. MATERIALS AND METHODS	14
Sample Collection.	17
Sample Digestion	17
Analysis	18
IV. RESULTS	19
V. DISCUSSION.	33
Seasonal Trends.	33
Precipitation Amount	34
Locational Trends.	36
VI. CONCLUSIONS	42
VII. RECOMMENDATIONS	44
BIBLIOGRAPHY	45

LIST OF TABLES

Table	Page
I. Metal Concentrations and Loadings	20
II. Comparison of Data to Previous Studies.	40

LIST OF FIGURES

Figure	Page
1. Locations of Sampling Sites.	15
2. Sample Collectors.	16
3. Average Precipitation Volume Versus Sampling Day	21
4. Average Concentration of Cadmium, Chromium, and Nickel Versus Precipitation Event	23
5. Average Concentration of Lead and Zinc Versus Precipitation Event.	24
6. Average Loading of Cadmium, Chromium, and Nickel Versus Precipitation Event.	25
7. Average Loading of Lead and Zinc Versus Precipitation Event.	26
8. Average Loading of Cadmium Versus Average Precipitation Volume	27
9. Average Loading of Chromium and Nickel Versus Average Precipitation Volume	28
10. Average Loading of Lead and Zinc Versus Average Precipitation Volume	29
11. Total Combined Metal Loading At Individual Sites	30
12. Total Loading of Cadmium, Chromium, Nickel, Lead, and Zinc at Individual Sites	32

CHAPTER I

INTRODUCTION

In recent years the detrimental effects of certain metals on human health as well as on other animals have been documented by medical professionals. Metals are an important pollution problem for several reasons; two of which are their tendency to bio-accumulate and their many avenues to the aquatic environment (i.e., direct discharge from industry- both air and water, natural contributions, and oil and coal burning). Evidence that metals are moving to the forefront of toxic pollutants can be witnessed by the fact that fifteen metals are included on the U.S. Environmental Protection Agency's (EPA) priority pollutant list which contains 129 toxic pollutants (21). The list of pollutants was originally ordered to be published by the Clean Water Act of 1977. The Act orders the EPA administrator to publish an up-to-date list of any pollutant or combination of pollutants which are toxic. Toxicity, as defined by the Act, is any disease-causing pollutant which, when assimilated into an organism can cause, among other things, death, disease, cancer, behavioral abnormalities, or deformation in off-spring (29).

All of the metals analyzed for in this project are toxic, but to varying degrees. The order of most toxic to least toxic is: cadmium, nickel, lead, chromium, and zinc. Cadmium is found naturally around coal and zinc mining areas, while atmospheric contributions result from the

smelting of metals, primarily zinc. The chief medical problems attributed to cadmium are cardiovascular disease and hypertension. Nickel pollution is associated with diesel oil combustion, coal burning, catalyst manufacturing, and steel alloying. Nickel is thought to be a health hazard only in its carbonyl form with strong evidence linking it to lung cancer. Lead is a major atmospheric pollutant because of its widespread use as a gasoline additive. Lead can cause brain damage, convulsions, and behavioral abnormalities (2). Chromium is released to the environment from metal plating, metal fabrication and, to some extent, from cooling towers where it is used as an anti-corrosive. Chromium is moderately toxic and will interfere with metabolic processes in both humans and animals. Zinc finds its way to the environment from plating operations, hot dip galvanizing, smelting of zinc ore and other metals. Zinc, also, is a moderately toxic pollutant which, when in excess, interferes with enzymatic reactions (16).

While all of the aforementioned metals are toxic at varying concentrations, two are essential for life. Chromium is necessary in insulin reactions. Zinc is of importance in enzymatic activity (16).

Natural scientists and medical doctors have detailed the gloomy results of organisms exposed to toxic amounts of metal pollutants generated mainly by industry. So-called "environmentalists" decry industry discharging pollutants to the environment and demand immediate action. It then becomes the responsibility of the engineering profession, particularly environmental engineers, to identify pollution sources and to devise means for reducing exposure to pollutants while helping industry to maximize production of beneficial goods.

The scope of this project was to identify and quantify five metals in bulk atmospheric precipitation collected from a highly industrialized area. An estimate was then made as to the amount of metal contributed by precipitation to a portion of an adjacent river basin.

One aim of this project is to identify any problems with respect to atmospheric metal pollution. Hopefully, this will provide an impetus for government and industry to further investigate the problem and to actively and wisely set a course of action to, if not solve, at least alleviate the problem.

CHAPTER II

LITERATURE REVIEW

Metal concentrations in the environment have increased considerably in the years since the industrial revolution. It is even feared that industrial activities, and the subsequent release of metals to the environment, could be altering natural geochemical cycles on earth (3). Murozumi et al. (15) analyzed annual snow layers from the North Pole and Greenland. The findings of this study indicated that concentrations of lead tripled from 1750 to 1950. Amounts of lead nearly tripled again from 1950 to 1970. The first jump was probably caused mainly by smelting lead, while the second increase was more than likely due to the use of lead in gasoline (16). Recent studies of lead-accumulating mosses in Sweden indicated a four-fold increase in lead content from the 1860's to the 1960's (24). Other investigations have also indicated a rise in the lead concentration of surface waters (12). Patterson (17) estimates that lead concentrations in surface waters have risen ten times since prehistoric eras.

The fact that Murozumi et al. (15) found detectable amounts of lead at the North Pole would lead to the conclusion that lead was transported there, most probably through the atmosphere. Several researchers have pointed out that both aquatic systems and land masses receive substantial amounts of many metal pollutants from dry and wet atmospheric deposition (8, 20, 31). Trace metals in the atmosphere have several natural sources

emanating from the surface of the earth: land masses, oceans, and volcanoes to name a few of the more important sources (20). Pierson et al. (20) state that large particulates, those greater than ten microns in diameter, will return to the earth's surface very rapidly by sedimentation, but that smaller particles may be carried worldwide.

Atmospheric deposition of metals is a major health problem to all forms of life. Hutchinson and Whitby (12) measured dry and wet deposition of several metals near a major nickel smelting region in Canada, the Sudbury Region. Results of the study showed that Ni and Zn appeared in above normal concentrations in plants and soil. Also mentioned in the report was that a major loss of vegetation, presumably because of acid rain and heavy metal deposition, resulted in only the hardiest of species remaining in the area analyzed. Another case study near a zinc smelter in Pennsylvania concluded that damage to vegetation around the smelter was due more to Cd and Zn than to acid rain (12).

A more profound problem of metal contamination is the pollution of aquatic environments. A large portion of the metals in plants and soils will eventually be cycled into groundwater, rivers, streams, lakes, and the oceans. Gatz (10) cites work done to determine the atmospheric contribution of metals to the Niagra River. Results show that metals from the atmosphere constitute 16-41% of the Pb in the river, 58-85% of the Zn and 12-15% of the Ni.

In lake studies, Hutchinson and Whitby (12) refer to work performed in 1973 and 1976 that showed toxic levels of Ni and Cu in lakes and algae which are in the Sudbury region of Canada. One study referenced by Gatz (10) estimated that the atmospheric contribution of Pb to Lake Michigan ranges from 20-33% of the total lead in the lake. Gatz concluded from

his own work that 3-15% (over 3 metric tons) of the metal emissions from the highly industrialized Chicago and northwest Indiana area were deposited in Lake Michigan. Ruppert (22) determined that a significant amount of numerous metals was contributed to German lakes and rivers encompassed by his study.

Contamination of surface waters is not limited exclusively to fresh water. Tsunogai and Nozaki (30) reported considerable amounts of Pb in water from the Pacific Ocean. The authors concluded that the Pb originated from atmospheric deposition. Fukuda and Tsunogai (9) also determined Pb pollution of the Sea of Japan and Pacific Ocean in their work and concluded that aerial deposition was the major source of the Pb.

Many researchers have reported the effects of atmospheric metal pollutants on vegetation and soil (2, 12, 25). The fact remains, however, that most metallic pollutants eventually find their way into water supplies, groundwater as well as surface water (16). Hutchinson and Whitby (12) determined that run-off and sheet erosion accounted for extremely high nickel concentrations in the Wanapitei River 48 miles from any major industry. The researchers also found large quantities of nickel in the Georgian Bay of Lake Huron. Major sources of the metal included erosion and leaching from soils.

Once in surface waters, metals are a health hazard because they are not biologically degraded; hence they persist in the environment. They are also toxic at low concentrations, and they biologically magnify, or accumulate, in aquatic life (16). Bio-accumulation, the concentration of pollutants by plants and animals, further increases the risk of poisoning or toxicity to humans. One study on the average amount of accumulation exhibited by 32 different fresh water plant species yielded the following

concentration factors for cadmium, chromium, and zinc: Cd--1620, Cr--695, and Zn--4600 (4).

Atmospheric Contribution of Metals

Atmospheric metal contributions to aquatic and terrestrial systems are broken into two groups, wet deposition and dry deposition. Wet deposition includes all forms of wet precipitation, rainfall, snow, ice, and sleet which entrap metal aerosols (20). Wet deposition contains metals in the soluble form and the insoluble form. Of greatest importance environmentally is the soluble form because it is more biologically active (10, 20). The term biologically active refers to the fact that the metals are mobile in soil and are actively taken up by vegetation (12). Insoluble or particulate metals tend to bind to the organic portion of a soil (18, 24).

Dry deposition of metals is dry fallout from the atmosphere through sedimentation, impaction and diffusion (5, 14). Dry deposition in conjunction with wet deposition is referred to as bulk, or total deposition (20).

Factors Affecting Metal Concentrations and Contributions

In any study area the surrounding industry will, to a great extent, affect the type and amount of metal in atmospheric deposition. Lazarus et al. (14) aptly pointed this out in their study across the entire U.S. A northeast to west downward gradient was found. This would implicate the more industrialized Northeast as a major contributor of metals. The major industries which contribute metals to the atmosphere are ore

smelting concerns and coal burning industries, most of which are utilized for energy generation (1, 11, 13, 14, 16, 24).

While anthropogenic sources are the greatest contributors of metals, natural sources also exist. As mentioned previously, blowing soils, oceans, volcanoes, forest fires, and ore deposits are the most common natural sources of metals (13, 20, 24).

Location of industry and natural sources are of utmost importance in determining the types and amounts of metals in the atmosphere, but meteorologic factors play the most important role in the distribution of metals. Andren and Lindberg (1) point out that the amount of precipitation, frequency of precipitation, wind direction, and wind speed are all important factors to be taken into account when analyzing rainfall data. Other considerations to be weighed are the geomorphological conditions in the sampling area (22). Andren and Lindberg (1), for instance, placed samplers in a valley behind a ridge to determine minimum atmospheric deposition. Ruppert (22) also reported that natural geographic barriers reduced atmospheric deposition to a minimum.

Man-made interferences must be reckoned with also. In populated areas, buildings may shield samplers from fallout; therefore, the sampler location is a significant factor in any study. In a populous industrial area, sampler height is of great importance. Janssens and Dams (13) noticed a marked difference in Pb concentrations along city streets in Antwerp, Belgium, due to sampler height. If samplers are too low, blowing soil might be picked up and this would not be truly indicative of atmospheric conditions (11, 20). If samplers are placed too high, localized, low-level pollution sources (i.e., automobiles) might not be

in evidence (13, 22). Schlesinger et al. (23), however, have shown sampler height to be relatively insignificant in unpolluted areas.

Trends Observed

Various natural and anthropogenic occurrences cause distinct trends in previous data which have been collected on metals in precipitation. The major trends observed in past studies include seasonal, rainfall amount, intensity, frequency, geographic location, and the relation of various metals to one another.

Seasonal trends are probably the most often observed in relatively unpolluted areas. Many researchers have noticed increased metal content in rainfall during the winter months (1, 9, 11, 14, 20). Pierson et al. (20) observed wintertime increases in Ni, Pb, Zn and other metals in a relatively unpolluted area in England. Lazarus et al. (14) found a general increase in atmospheric Pb during the winter months in the United States. Hallsworth and Adams (11) reported a generally higher metal content in precipitation in the winter than any other season. Again, their study was conducted in England. Andren and Lindberg (1) observed higher wintertime concentrations for Cr and Ni in northeastern Tennessee. Fukuda and Tsunogai (9), in a Japanese study, concluded that Pb deposition was higher during the winter months due to increased rainfall. Other authors concluded that in the winter, temperature inversions are more prevalent than in the summer and do not allow pollutants to disperse as well; thus, the higher concentrations (1, 14, 20). Hallsworth and Adams (12) attributed their increased winter concentrations to low level fog.

Janssens and Dams (13), in an investigation of Pb concentration in Swedish precipitation, found lower concentrations during the winter. Their explanation, however, had very little to do with meteorologic conditions. It was merely that more automobile traffic was present in the summer.

Some researchers are able to find correlations between the amount of precipitation collected and the amount of metals deposited. Dry and wet deposition are important factors to consider here. If the wet deposition is greater than the dry deposition, the indication is given that the chief mechanism for removal of atmospheric metals is rainout and not washout (9). That is to say, the process takes place in a cloud and not below a cloud by falling raindrops. Fukuda and Tsunogai (9) found a linear, increasing relationship in the deposition rate and amount of rainfall for Pb, thus indicating rainout instead of washout.

Several authors have found no significant relationship between amount of rainfall and metal concentration. Andren and Linberg (1) found this to be true for several metals including Cr, Ni, Pb, and Zn. Lazarus et al. (14) also could find no rainfall-concentration link for Ni, Pb, and Zn. Cadmium, Cr, Ni, Pb, and Zn showed little correlation between concentration and rainfall amount in work done by Ruppert (22).

Still other projects have shown an inverse relationship between rainfall amount and metal concentration. Hallsworth and Adams (11) found this definitive pattern in their work. Inverse relationships with Pb have also been observed by Chow and Earl (7) and Schlesinger et al. (23).

Rainfall frequency and intensity play a vital part in atmospheric metal analysis. Ter Harr et al. (28) pointed out that large

thunderstorms and rapid rainfall tended to lower metal concentrations, a slow, steady rain produced higher concentrations. Schlesinger et al. (23) and Lazarus et al. (14) found lower Pb concentrations in samples from heavy storms than from small storms. The reasoning to support this finding is that large storms quickly cleanse the atmosphere then serve only to dilute the samples. No significant correlation, however, could be drawn between either rainfall amount or frequency and metal concentration by Andren and Lindberg (1).

Often times trends can be observed in the correlation of one metal to another. If metals show a good correlation to one another, or to a non-metal, it can safely be assumed that the metals are being emitted from a common source (6). A common correlation between a metal and a non-metal is lead and bromine. Janssens and Dams (13) and Chan et al. (6) observed a Pb/Br relationship in their works. Both groups of investigators concluded that automobiles were the major source. The latter study also pin-pointed steel industries with iron-sulfur correlations. Hallsworth and Adams (11) observed a correlation between Cu and Cr near coal-fired power stations. Andren and Lindberg (1) attempted to find correlations between metals, but their results were inconclusive.

Methods of Sampling

Sampling for atmospheric metals involves various techniques. Some researchers wish to measure bulk precipitation only, while others separate the dry and wet components. Very few studies take bulk samples only (11, 22, 23). A more complex investigation involves taking bulk samples in conjunction with wet and/or dry precipitation. The usual bulk sampler involves a nitric acid-washed polyethylene or polypropylene funnel and

bottle arrangement supported in a holder several feet off of the ground (6, 11, 12, 20, 22, 23, 26). Those researchers attempting to capture only wet deposition used a sampler with a rain-sensing grid that activates the opening of doors sealing the sample bottle only during periods of wet precipitation, thus excluding dry fallout (1, 14).

Investigations attempting to ascertain only dry deposition basically involved two types of systems. One system drew air through filter paper by means of a suction device. Dry fallout trapped by the filter was then analyzed (1, 13). The other system suspended a piece of filter paper under a plastic cover to prevent rain from reaching it (20).

Once samples are collected, they must be stored. There is presently a great deal of concern as to what type of storage container is best. An in-depth study on this subject was performed by Struempfer (27) on borosilicate glass, polyethylene, and polypropylene containers. The author concluded that polypropylene was the least desirable container for storing trace metals because the metals adsorb to the container surface. Polyethylene was deemed the most appropriate for field work. To prevent any further adsorption to container surfaces and to prevent biological activity in the bottle, some authors recommended acidifying the sample upon collection (1, 12, 23, 26, 27). Freezing samples upon collection is another way to prevent biological activity or adsorption. This particular method was practiced by Chan et al. (6).

After retrieving rainwater samples, the analytical procedures utilized were varied. The most common method of analysis was by atomic absorption spectroscopy using either flame or graphite furnace analysis (1, 12, 14, 22, 23, 27). Some investigations utilized acid digestion procedures to solubilize any suspended metals (12, 26). Other authors

made no mention of any digestion procedure. Other methods used for metal determinations included charged particle induced X-ray emission (PIXE) (7), optical spectography with a quartz spectrograph (11), X-ray fluorescence (20), and a radiation counter to determine radioactive Pb-210 (9).

CHAPTER III

MATERIALS AND METHODS

The purpose of this research was to sample bulk precipitation in a moderately industrialized area (west Tulsa). Industries in the immediate area include 2 oil refineries, over 12 metal plating firms and 2 steel fabricating firms. Sampling points generally followed the shoreline of the Arkansas River, Figure 1, so that an estimate might be made as to the amount of metal entering that particular stretch of the river via precipitation.

Stations A and B were located approximately seven feet above the ground in a strictly industrial area. Stations C and D were located on top of buildings in the downtown area. Station C was located atop a five story building, while station D was located on top of a three-story structure. Stations E and F again were placed approximately seven feet above the ground, but situated in a residential area.

The collection devices were bulk samplers consisting of a polyethylene funnel and bottle combination with a total volume (bottle plus funnel) of 1550 ml, and a total surface area of 27.40 square inches. Samplers at stations A, B, E, and F were securely supported by a metal holder which was attached to a three-foot long two-by-four. The two-by-fours were attached to utility poles in right-of-way areas, Figure 2. Samplers at sites C and D were supported by a metal holder mounted to a five-foot high wooden stand which rested on the building roofs, Figure 2.

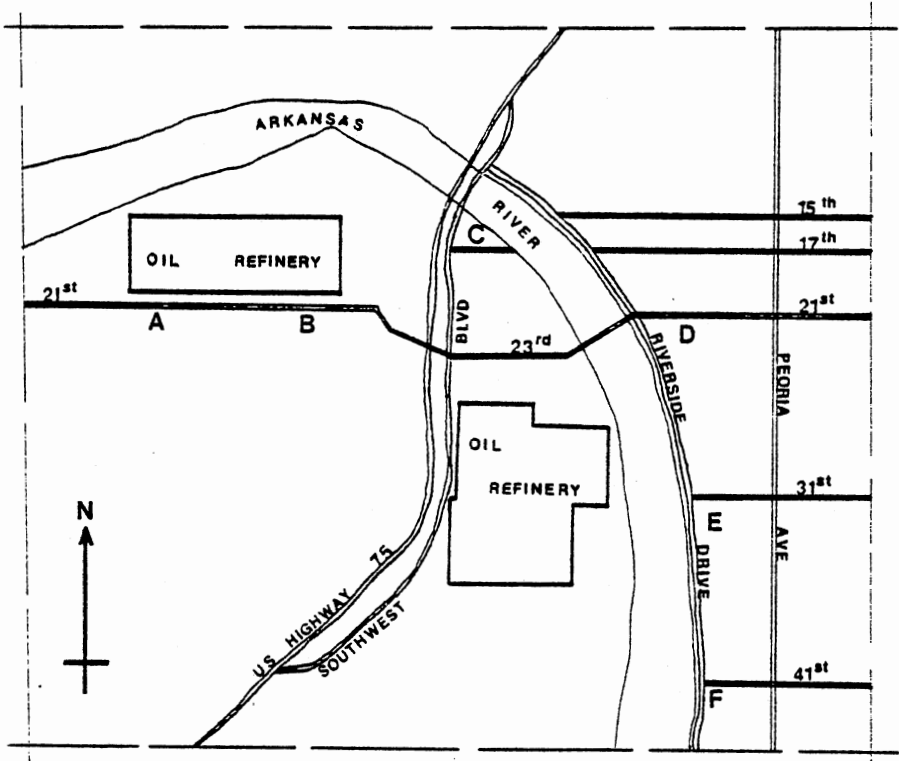


Figure 1. Location of Sampling Sites

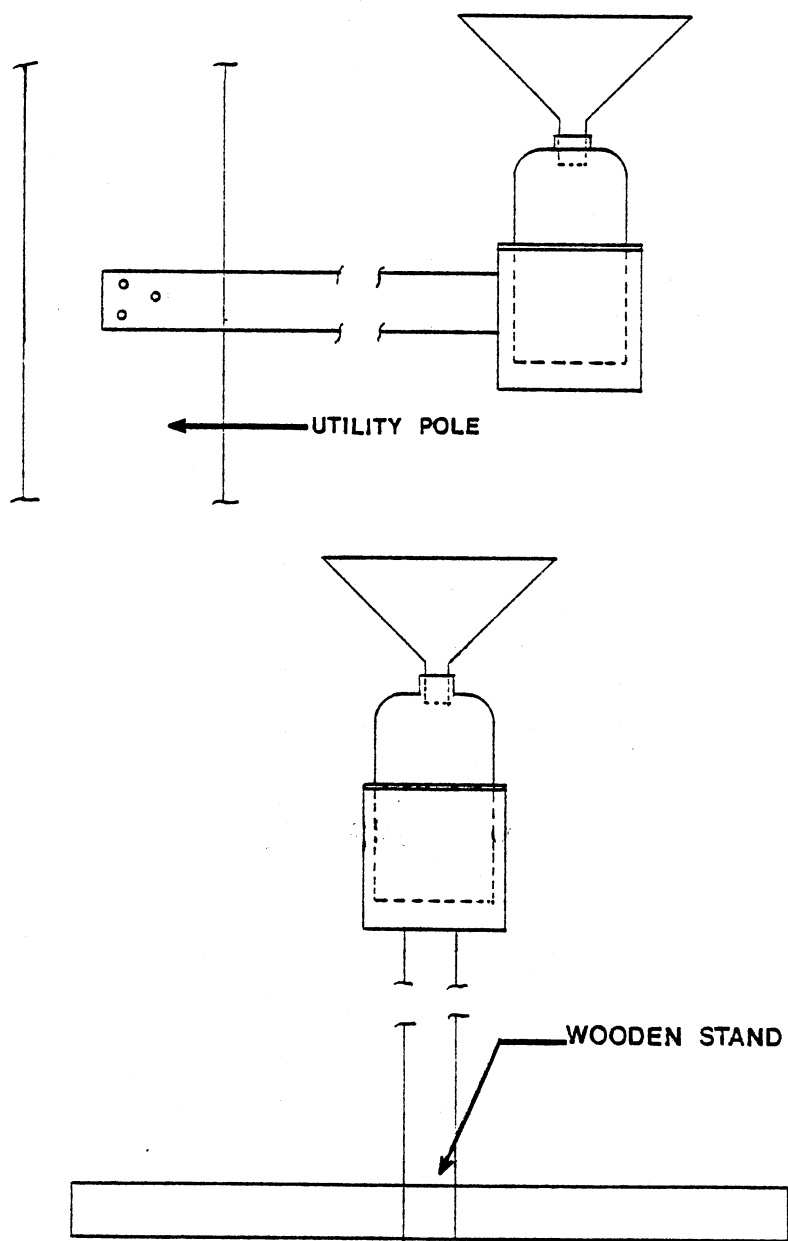


Figure 2. Sample Collectors

Sample Collection

Samples were collected the next working day following a precipitation event and new samplers were installed. If an entire month passed without rain, the sample bottles and funnels were collected and rinsed with deionized water. The collected samples were transported to Stillwater and the volume of each sample was measured and recorded. The samples were then transferred to polyethylene bottles with screw caps and placed in a freezer.

Following sample storage the sample bottles and funnels were nitric acid washed and placed in plastic bags until needed. It also became necessary to wash storage bottles with nitric acid and reuse them when needed.

Sample Digestion

Digestion was employed to ensure that all metals in the sample were soluble. Prior to digestion, the frozen samples were removed from the freezer and allowed to thaw at room temperature. As soon as possible after the samples had thawed, the digestion procedure was begun.

The samples were shaken to guarantee homogeneity. Fifty milliliters of each sample were measured in a volumetric flask. If the sample volume was less than 50 ml, deionized water was used to bring the sample to volume. The sample was then emptied into a 150 ml glass beaker. The heated nitric acid digestion process used was recommended by the Perkin-Elmer Corporation for use with their instruments (19). The procedure was followed in its entirety with two modifications; watch glasses covered the beakers at all times to prevent any organic contamination, and for the final step, any residue in the beaker was solubilized with nitric

acid instead of hydrochloric acid.

Following the digestion, the watch glasses and beaker walls were rinsed with deionized water into the beakers. The samples were poured back into 50 ml volumetric flasks and brought to volume with deionized water. The sample, then at approximately pH 1, was stored in a 60 ml polyethylene screw top bottle.

All glassware used in the digestion was used solely in the digestion of rainwater samples and was washed with dilute nitric acid and rinsed with deionized water just prior to its use.

Analysis

All analyses were performed using a Perkin-Elmer Model 5000 atomic absorption spectrophotometer equipped with a Perkin-Elmer HGA-400 graphite furnace. All blanks and standards were made with Fisher Scientific standard solutions.

Before any sample analysis was begun, a sensitivity check, a standard concentration which gives a known absorbance, was run to verify that the instrument was operating properly. Next an internal standard curve was set in the instrument. Previous work had determined the linear working range of the standard curve. Following standardization, two 20 ul sample injections were made per individual sample with Eppendorf automatic pipettes fitted with disposable plastic tips. The sample concentrations were read in mg/l and the two results were averaged and recorded. If the two injections yielded answers with more than 10-20% difference, two more injections were made.

All metals had minimum detection limits of 1 ug/l (ppb). Any sample below this limit was reported as zero.

CHAPTER IV

RESULTS

The results from the analyses are presented in three basic forms: precipitation data, concentration data, and loading data. Precipitation values are reported as the volume of the sample collected in ml, concentration is reported as mg/l, and loadings are given as ug of metal.

A portion of the loading and concentration data are given as averages. The term average concentration, as applied to each metal, refers to the mean of the concentrations taken over the six sites per sampling day. Finding a loading entails multiplying the concentration of a specific metal at a site by the corresponding precipitation volume. Average loading is merely the mean of the loadings at all six sites per sampling day.

Precipitation volume is also given as an average. Average precipitation volume is the mean of the volume of precipitation collected over all sites for each sampling day.

A summary of all data collected is presented in Table I. The ranges for each metal show a wide variation. For most metals the range is so wide that the data does not follow a normal distribution and standard deviation is of no significance.

Average volume of precipitation per sampling day is presented in Figure 3. The maximum volume, 1550 ml, was collected September 1, 1980. The minimum volume collected was 0 ml on July 27, 1980. This sample

TABLE I
METAL CONCENTRATIONS AND LOADINGS

Metal	Concentration (mg/l)		Loading (ug)		No. of Samples
	Range	Mean	Range	Mean	
Cd	0.000-0.017	0.003	0.000-4.640	0.569	135
Cr	0.009-0.158	0.028	0.765-187.550	13.544	135
Ni	0.000-0.091	0.016	0.000-18.600	4.171	135
Pb	0.000-0.990	0.116	0.000-213.900	16.860	135
Zn	0.392-1.292	1.061	46.200-1782.500	333.527	135

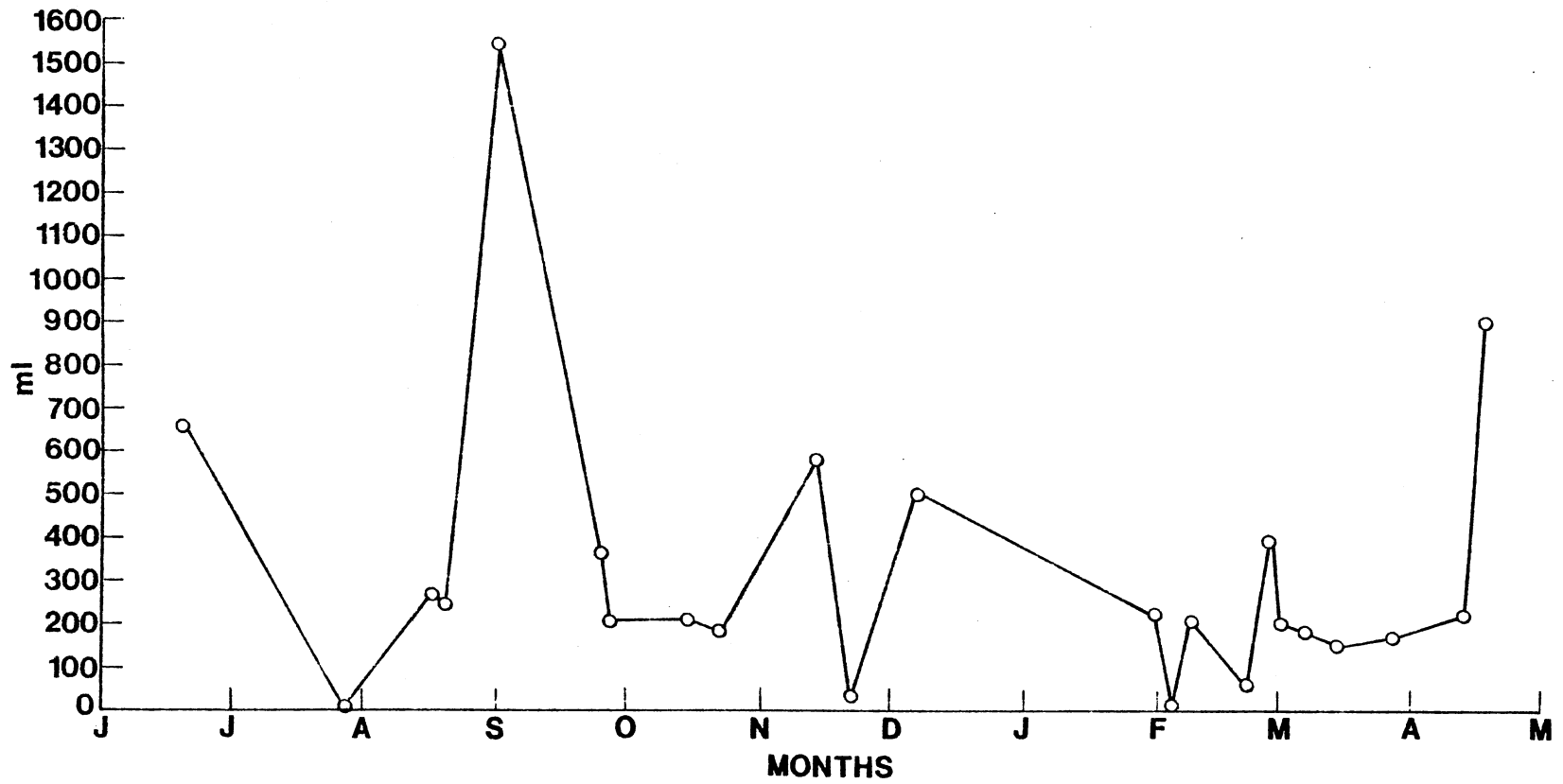


Figure 3. Average Precipitation Volume Versus Sampling Day

consisted of dry deposition on the collector washed down with deionized water.

The average concentrations per precipitation event for each metal are presented in Figures 4 and 5. Note that the maximum and minimum values, as well as the average concentrations vary somewhat from the values in Table I because these values are averages whereas Table I referenced the raw data. The minimum and maximum of the average values for each metal are: Cd, 0.000-0.012 mg/l; Cr, 0.014-0.084 mg/l; Ni, 0.004-0.051 mg/l; Pb, 0.015-0.205 mg/l; and Zn, 0.732-1.173 mg/l. The means of the average values determined from Figures 4 and 5 are: Cd, 0.003 mg/l; Cr, 0.042 mg/l; Ni, 0.017 mg/l; Pb, 0.064 mg/l; and Zn, 1.057 mg/l.

Average metal loadings per sampling day are given in Figures 6 and 7. Again, this data will differ somewhat from the raw data in Table I. The minimum and maximum of the average values for each metal are: Cd, 0.037-2.822 ug; Cr, 1.875-87.317 ug; Ni, 0.550-13.568 ug; Pb, 1.400-82.667 ug; Zn, 47.150-1522.88 ug. The means of the average values presented in Figures 6 and 7 are: Cd, .562 ug; Cr, 13.251 ug; Ni, 4.113 ug; Pb, 16.544 ug; and Zn, 342.293 ug.

In order to determine if any relationship existed between average loading and average precipitation, the two parameters were plotted. The resulting graphical analyses are presented in Figures 8, 9, and 10.

The last group of figures represents the total loading of metals at the individual sampling sites. Figure 11 shows the total loading of the combined metals at each site. The order of rank from highest loading to lowest loading is F (9119.07 ug), B (9013.56 ug), E (8861.16 ug), A (8495.93 ug), D (8123.72 ug), and C (6159.35 ug). The individual metal

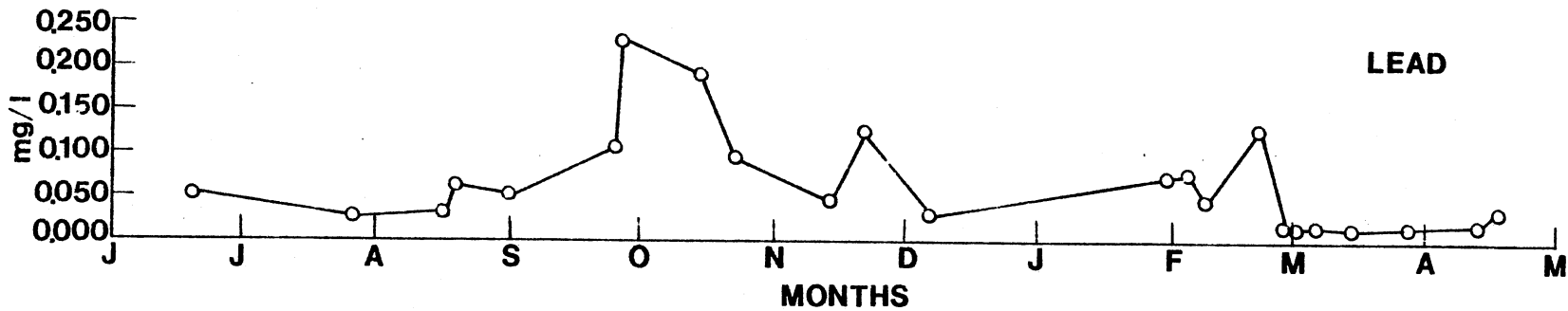
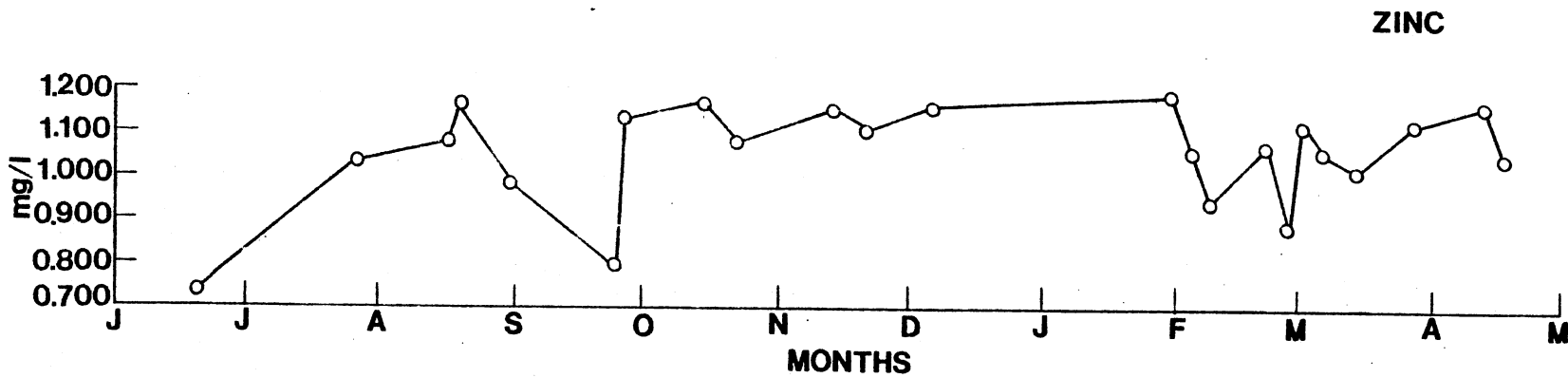


Figure 5. Average Concentration of Lead and Zinc Versus Precipitation Event

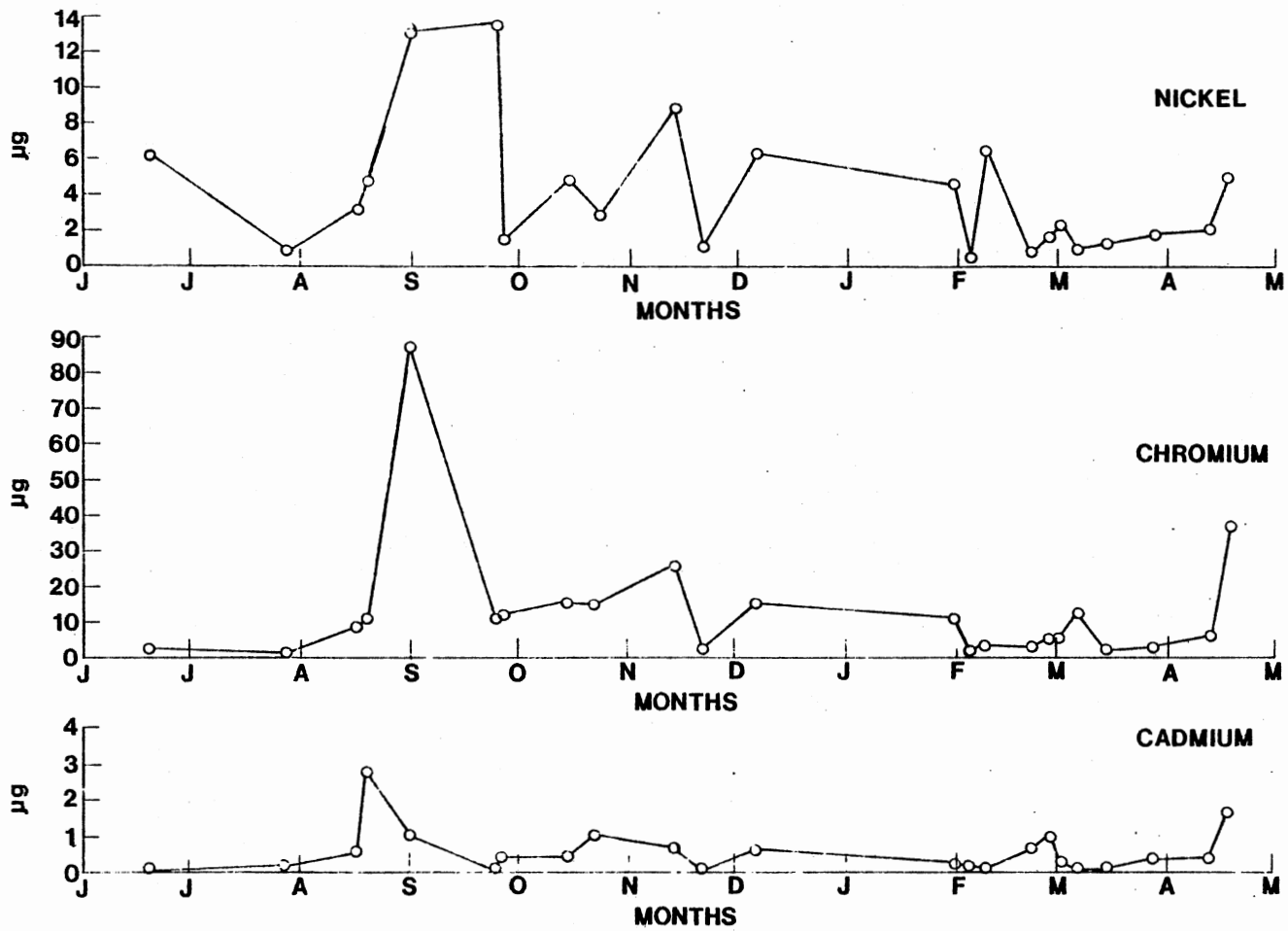


Figure 6. Average Loading of Cadmium, Chromium, and Nickel Versus Precipitation Event

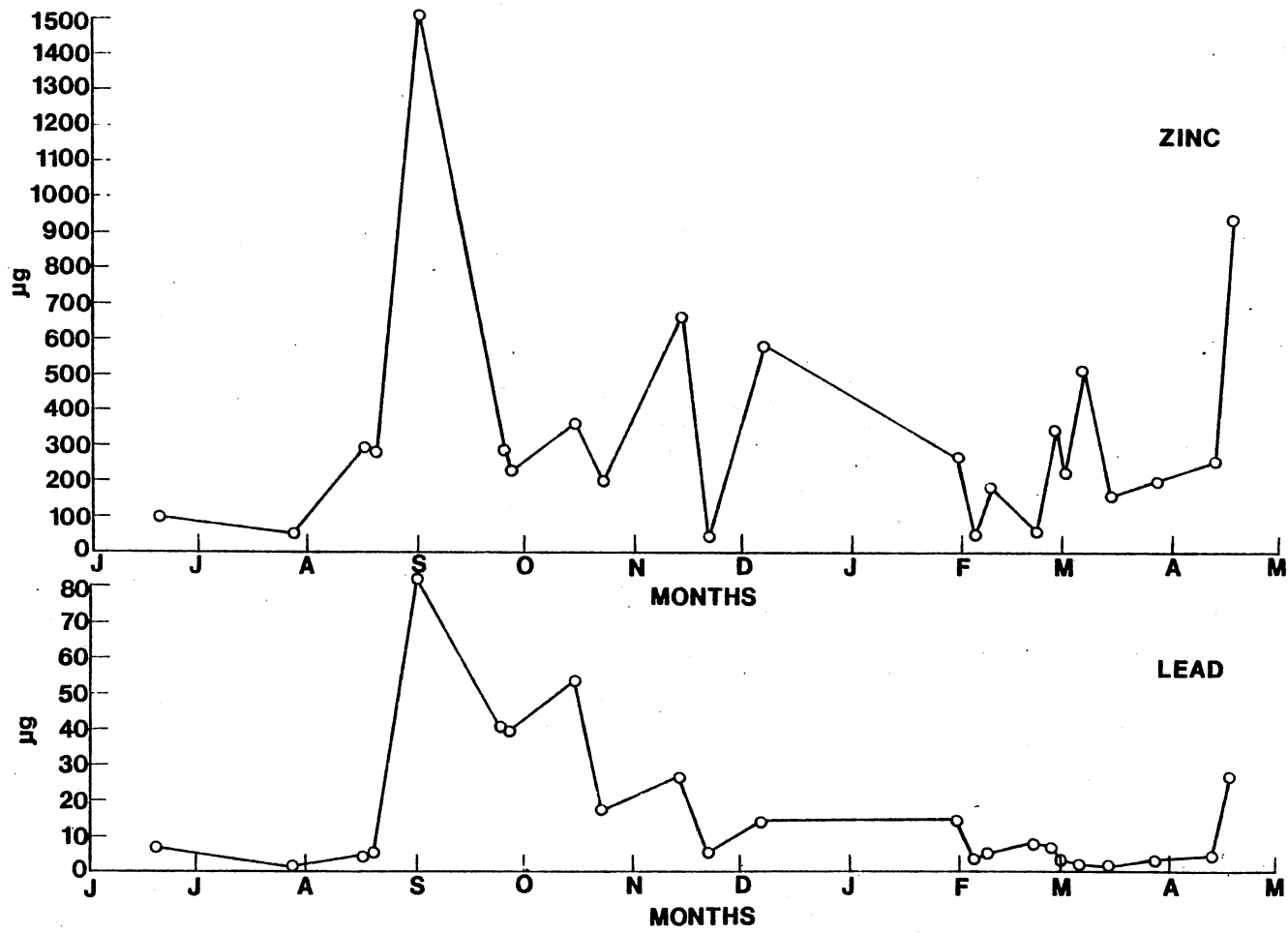


Figure 7. Average Loading of Lead and Zinc Versus Precipitation Event

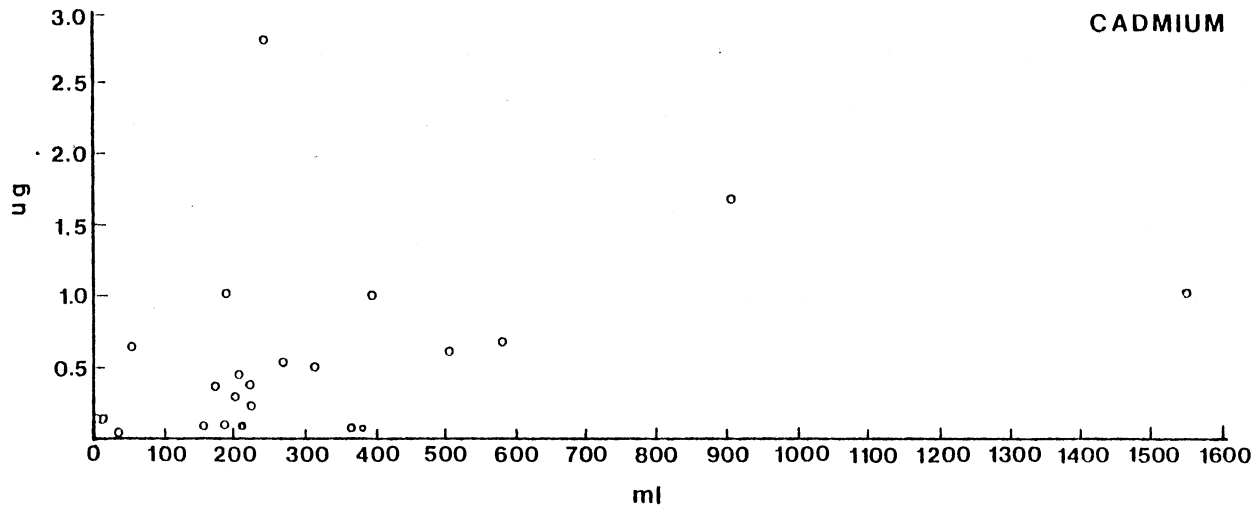


Figure 8. Average Loading of Cadmium Versus Average Precipitation Volume

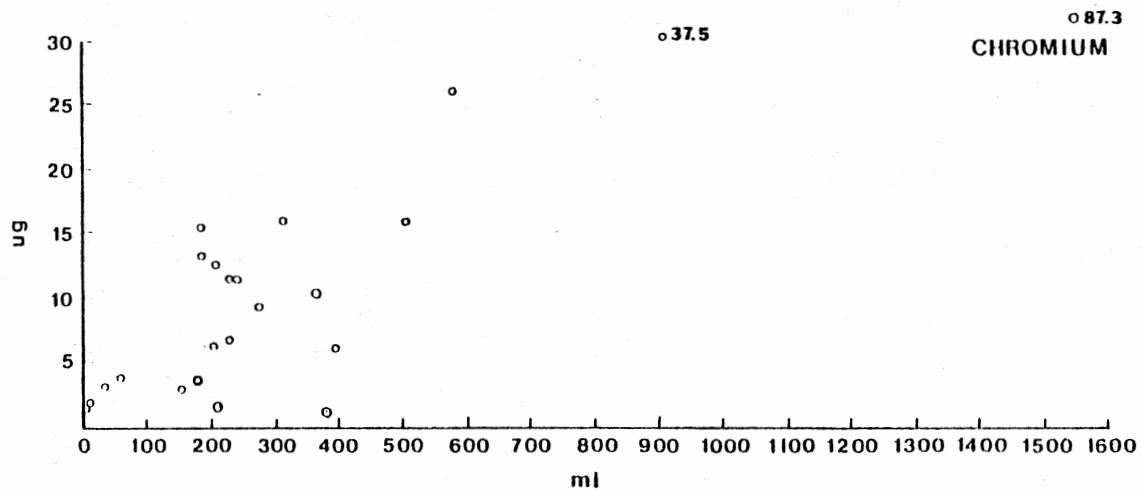
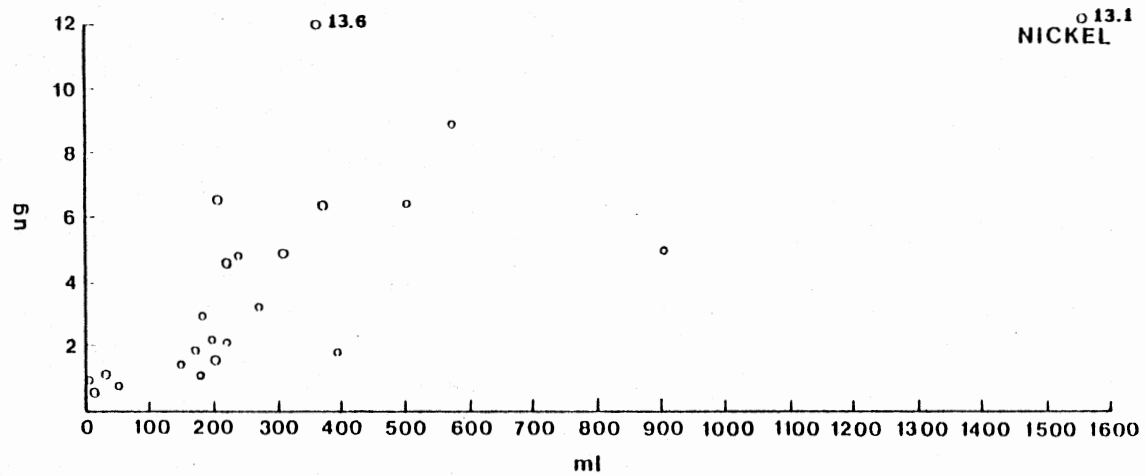


Figure 9. Average Loading of Chromium and Nickel
Versus Average Precipitation Volume

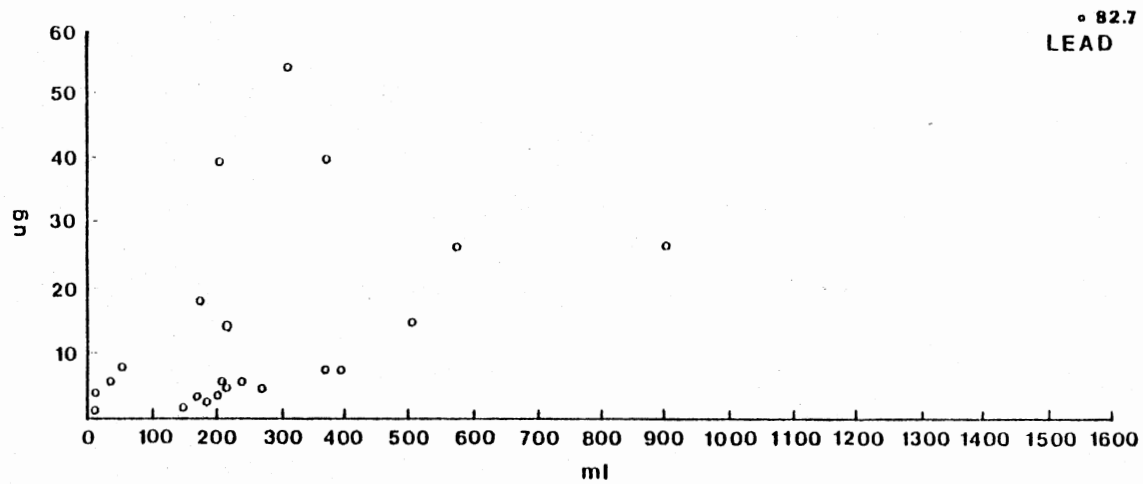
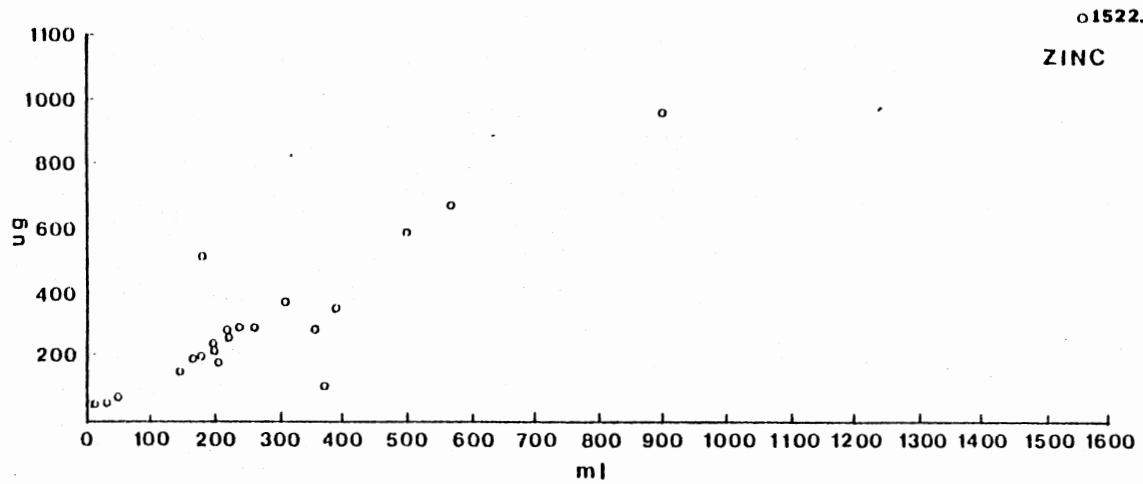


Figure 10. Average Loading of Lead and Zinc Versus Average Precipitation Volume

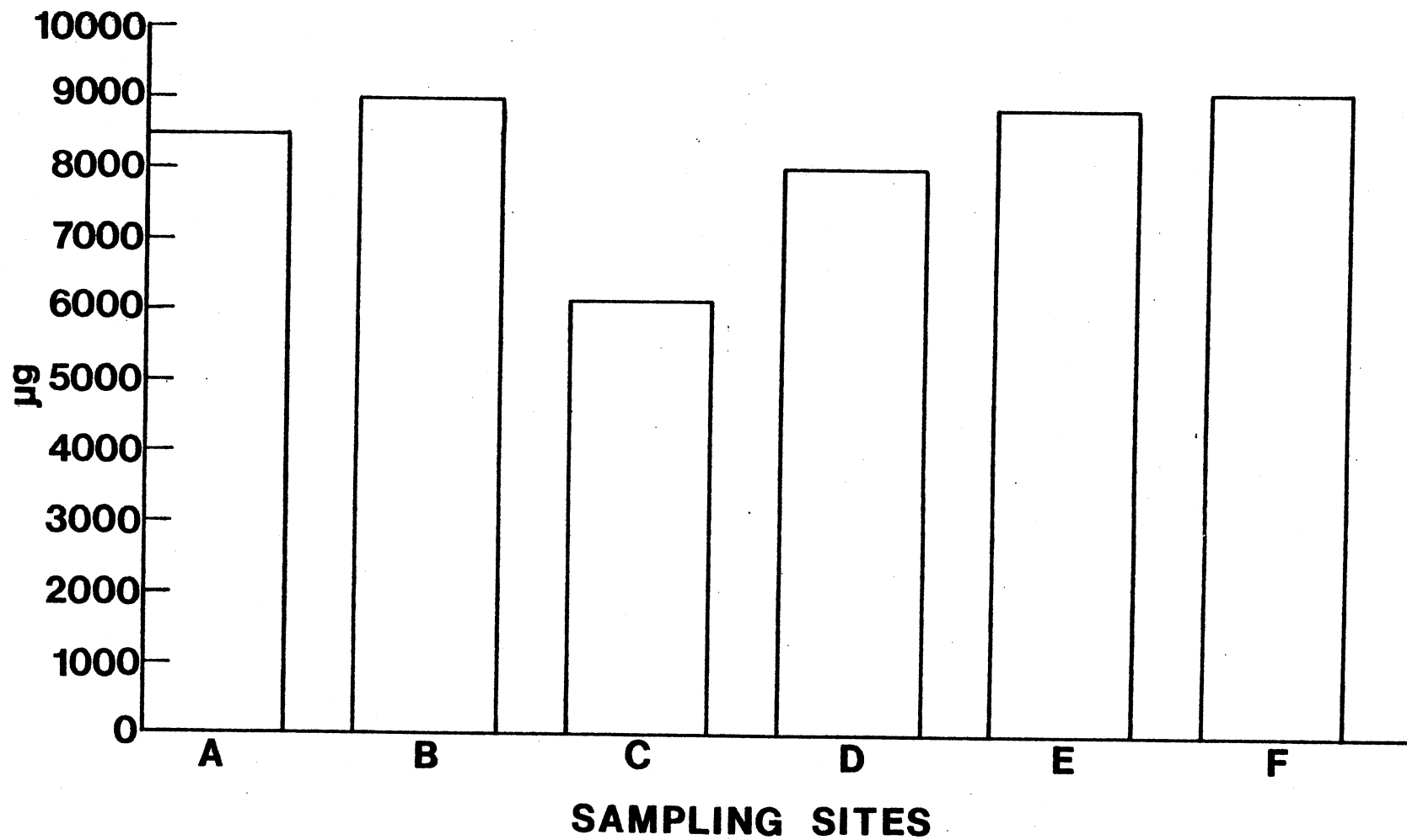


Figure 11. Total Combined Metal Loading at Individual Sites

loading components which comprise the combined loading are represented by Figure 12.

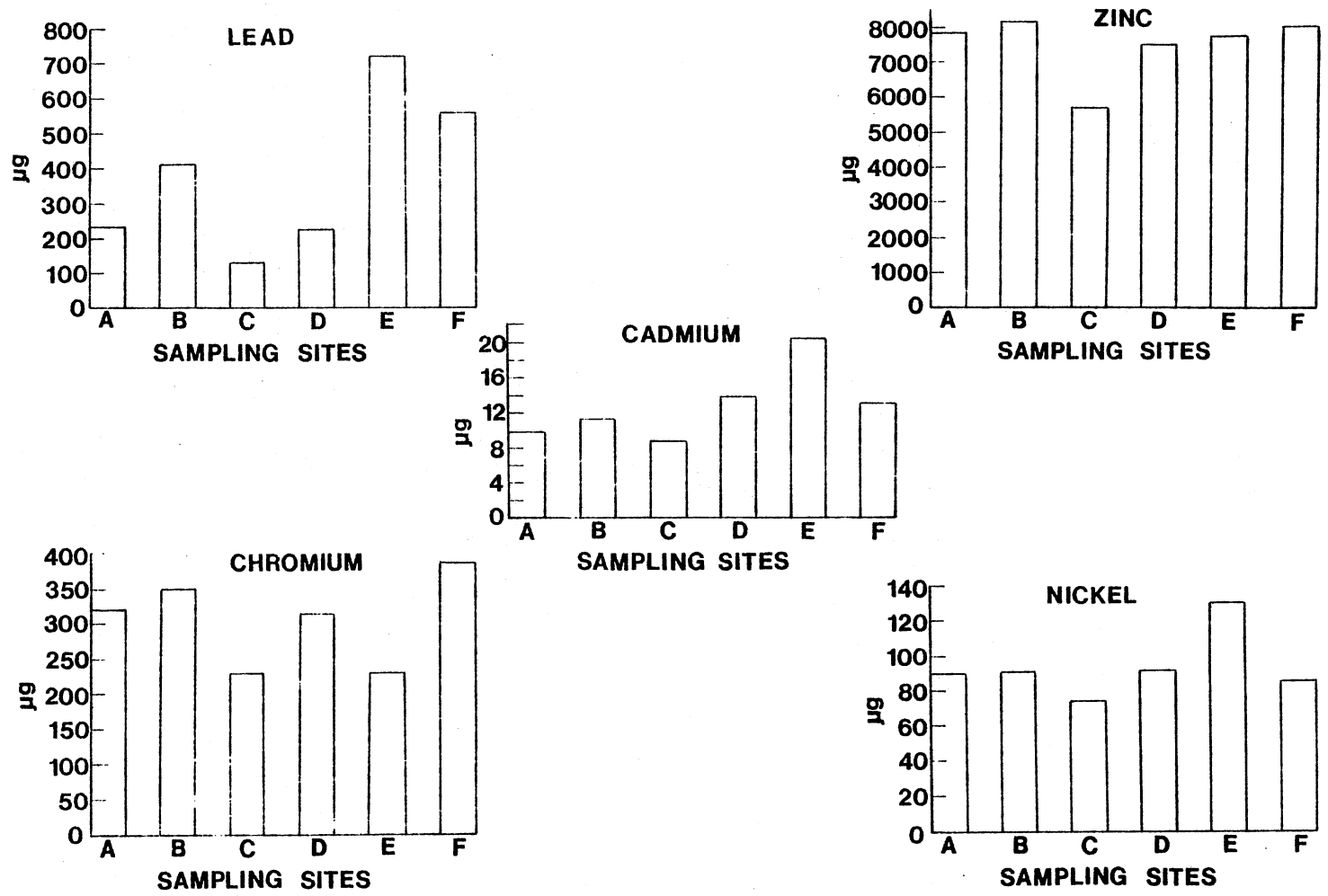


Figure 12. Total Loading of Cadmium, Chromium, Nickel, Lead, and Zinc at Individual Sites

CHAPTER V

DISCUSSION

The results were analyzed to determine if various trends in the precipitation data could be established. The possible trends for metal loading and concentration which were investigated were broken into three categories: seasonal, precipitation amount, and sampler location. Seasonal trends and those trends associated with precipitation amount take into account average metal loading as well as average concentration. Locational trends contrast site location with total metal loading for individual metals and combined metals.

Seasonal Trends

Seasonal trends are often reported to occur in studies conducted in relatively unpolluted areas (10, 21, 22). No conclusive seasonal trends, however, could be drawn from either concentration or loading data, Figures 4, 5, 6, and 7. This is not a very surprising revelation for this investigation because of the nature of the sampling area. The sampling sites are in a fairly industrialized portion of the city. Therefore, the major constraint on the amount of pollutant distributed in the atmosphere is industrial activity and not seasonal conditions. Janssens and Dams (13) reported the same basic conclusion in their work by linking Pb loading to industrial activity.

Precipitation Amount

The most obvious trends observed from data associated with precipitation amount can be drawn from precipitation amount in conjunction with either loading or concentration. If the graphical analyses of average loading per precipitation event, Figures 6 and 7, are compared to the amount of precipitation collected per event, Figure 3, a general observation can be made for all metals; loading is approximately proportional to the amount of precipitation. With the exception of a few data points, this is a definite trend for all metals but is most clearly evident for Pb and Zn.

The fact that loading increases as precipitation increases suggests that a mechanism of deposition involved in this study is rainout (8). In other words, the metals are combined with precipitation in the clouds and not washed out from below the clouds during a precipitation event. If rainout is occurring one can assume that the metals in question are generated from industrial processes and not natural sources (18). The rationale involved is that only industrial sources, as opposed to natural sources, will produce particulates small enough to reach cloud level.

Loading being proportional to precipitation volume is further illustrated in Figures 8, 9, and 10. The loading vs. precipitation plots yield a nearly linear relationship with a positive slope, thus indicating a direct proportion. Again, Zn is most representative of this trend.

The linear relationship occurs with Pb; however, two distinct lines are observed, Figure 10. The points which generate the upper line are composed of data from September 25, 1980 to February 22, 1981. The lower line is comprised of the remaining data. The upper line has the greater

positive slope which means that during the denoted time period the loading rate was greater than at other times.

The two line phenomenon for Pb was also observed by Fukuda and Tsunogai (8) in their work. The greater loading rate was observed during the winter months and was attributed to temperature inversions not allowing the Pb to disperse as readily. Temperature inversions may have been responsible for the results in Figure 10. However, because Pb is apparently the only metal affected, other unknown factors must be in effect.

Definitive patterns do not exist for all metals when concentration vs. precipitation event data, Figures 4 and 5, are compared to the precipitation-per-event data, Figure 3. The various metals analyzed for displayed individual traits. Lead showed an inverse relationship between amount of precipitation and Pb concentration over the entire sampling period, with only one or two data points out of line. Zinc, on the other hand, shows a "split" relationship. From June to November precipitation and concentration show an inverse relationship; while from November to May a proportional relationship between the two parameters is prevalent. Again it must be emphasized that some points do not follow this pattern, but the majority do.

Chromium and Cd data, while not providing as precise a pattern overall as Pb and Zn, do show an inverse relationship. Nickel had a very erratic concentration-precipitation plot. The only pattern present is an inverse relationship between concentration and precipitation amount for five of the six largest precipitation events.

The literature often cites cases where inverse proportionalities exist between concentration and precipitation data. Most authors

attribute the inversely related data to the idea that large amounts of precipitation tend to cleanse the atmosphere initially. The remainder of the precipitation serves only to dilute what has already been collected (6, 13, 22). Some researchers extend this theory of atmospheric cleansing to storm intensity, surmising that a very intense storm, which might produce only a moderate amount of precipitation, will quickly cleanse the atmosphere then serve only as a dilutant (13, 22, 27).

Locational Trends

Total metal loadings at the various sampling sites produced some interesting results. The loadings at most stations were close with respect to the amount of total combined metals deposited during the 10 month study period, Figure 11. The two building-top samplers (C and D), however, were markedly lower in loading than the remainder of the samplers. The same pattern was also observed by Janssens and Dams (13) in their studies on Pb. Assuming that the major contributor of Pb is automotive exhaust, the authors concluded that the bulk of the suspended Pb particulates was confined to fairly low levels.

Reduced loading at higher altitudes indicates that washout as well as rainout is a mechanism of deposition in this study. If only rainout was occurring the loadings should be consistent everywhere. The reduced loadings at the building top implies that some low-level particulate is washed out.

Not only did the height of sampler C play a role in its reduced loading characteristics, but its physical location on the building top was an additional factor. The sampler was somewhat shielded to the sides by the rooftop equipment, thus excluding some precipitation from the

sampler on windy days. As pointed out earlier, a proportional relationship exists between precipitation volume and loading. Therefore, low amounts of precipitation mean low metal loadings.

Improper interpretation of the total combined loading can produce some false impressions. In order to piece together the entire picture on metal loading, the individual components must be looked at, Figure 12. It can be seen that Zn is the major individual contributor to the total combined loading. Zinc loading is consistently high and fairly constant in amount from station to station. Because Zn appears in such inordinately large quantities, it tends to give a distorted picture as to which sites are receiving the greatest overall toxicity if only combined loading is considered. The fact that Zn tends to equalize the combined loading at all stations could overshadow the contribution of more toxic metals. The most obvious example of the combined loading not accurately reflecting the overall degree of toxicity at each site occurs at station E. This particular site has only the third highest combined loading primarily because the minimally toxic Zn loading at E ranks fourth among the Zn loadings at the six sites. However, the more toxic Cd, Ni, and Pb loadings at this site were the highest observed.

By further studying the individual metal loadings specific peculiarities are observed at various sampling sites. Cadmium and Ni, as did Zn, showed a fairly constant loading except at site E where both showed high loadings relative to the other sites.

The loading of Pb in the residential areas (sites E and F) is approximately twice as high as the average of the loadings from the other sites. Both sites are located near Riverside Drive, a heavily travelled and often congested city street. The great deal of traffic and

subsequent automobile exhaust is the probable cause of the high Pb loadings (11). Sites A and B border State Highway 51 (21st Street). This is also a fairly well-travelled road but the Pb loading at each site is much less than the loading recorded at either site E or F. A possible explanation might be that State Highway 51 is not as congested as Riverside Drive.

Stations C and D (located on building tops) have rather low Pb loadings compared to the other sites. That, coupled with the fact that Pb is the second largest contributing metal in this study (4.6% of the total), conceivably leads to the conclusion that Pb could make a difference in the overall ranking of the sites with respect to combined metal loading. It is unlikely that Pb loading alone is affected at high altitude. Any of the other metals used by plating firms in the area are also exhausted at low altitudes, and could make somewhat of a difference in the loading at sites C and D.

The residential sites also have relatively high loadings of other metals. The Cd and Ni loadings at site E are the highest for any of the stations. Chromium loading is greatest at site F. The probable reason for these high values is the proximity of these sites to metal emitters. Sites E and F are located approximately halfway between the two refineries mentioned earlier. The two sites are also situated across the river from a natural gas-fired electric generating station.

Sites A and B, which are located at the boundary of a refinery, show inordinately high concentrations for Cr only. Possible explanations for this are that chrome plating is taking place nearby or that some process at the refinery is releasing particulate Cr to the atmosphere. A potential source is cooling towers where Cr is used as an anti-scaling agent.

Chromium is also used as an anti-scalent in certain types of large industrial air conditioning units. This might explain the high Cr loading at site D because the sampler was located near an air conditioning unit.

The values for metal concentration presented in this study are for bulk precipitation in an industrialized area. In a review of the available literature, no comparable data was encountered. All of the data for bulk sampling was done primarily in rural, unpolluted areas. Pierson et al. (18) performed their sampling in a rural section of England, and Schlesinger et al. (22) sampled in White Mountain National Forest in New Hampshire. Only Ruppert (21) performed his investigations in an urban setting. The study was performed in Gottingen, West Germany. Gottingen was described as a "non-industrialized" town of 130,000 people, located in a rural area. Table II presents a summary of the data mentioned above, along with the data from this study. It can be seen from Table II that the concentrations of the metals in this study are considerably higher than those in the other studies. The concentration of zinc, for instance, is fifteen times higher than that observed by Ruppert (1972).

As stated in the scope of the project, an estimate would be made as to the total atmospheric metal loading to a portion of the Arkansas River. Planimetric analysis of a map of the river yielded an area of 766.7 acres which were encompassed by the sampling network. The total average loading was 4.18 lb/acre for the 10-month sampling period. The breakdown for the average loading of the individual metal in pounds per acre is: Cd, 0.007 lb/ac; Cr, 0.154 lb/ac; Ni, 0.047 lb/ac; Pb, 0.373 lb/ac; Zn, 3.781 lb/ac. The loading for the entire area is 3,207.45 lb.

TABLE II
COMPARISON OF DATA TO PREVIOUS STUDIES

	AVERAGE CONCENTRATION (mg/l)			
	Present Study	Pierson et al (1971)	Schlesinger et al (1971)	Ruppert (1972)
Cd	0.003	<0.018	0.0006	0.00058
Cr	0.028	0.003	--	--
Ni	0.016	<0.006	--	--
Pb	0.116	0.039	0.0134	0.035
Zn	1.061	0.085	--	0.071

for the 10-month period. Individual totals in pounds are: Cd, 5.37 lb.; Cr, 118.07 lb.; Ni, 36.03 lb.; Pb, 285.98 lb.; Zn, 2898.89 lb.

The loading values are unquestionably large. This is especially true when it is considered that atmospheric metals make up only a fraction of the metals entering the river. In a study on lakes, Gatz (9) estimated that 3-15% of the total input of the metals into Lake Michigan could be attributed to atmospheric desposition.

The unusually large deposition of metals to the river has a potential to adversely affect water quality and aquatic life. Metals entering an aquatic system may be taken up by fish or aquatic plants, chemically precipitated, or adsorbed onto sediments. That fraction which is precipitated or adsorbed may be resolubilized as the result of changes in pH and/or the oxidation-reduction potential. Presently, that portion of the metals which is not fixed will be carried down river and the concentration subsequently diluted. In addition, sediment scour may also provide for the transport of precipitated on adsorbed metals. However, when the proposed low-water dam is constructed on the river, quiescent flow conditions will prevail in the pool area allowing for the accumulation of metals in the aquatic system and resulting in further water quality degradation.

CHAPTER VI

CONCLUSIONS

The conclusions drawn from this work are:

1. No seasonal trends are apparent in the data.
2. Loading was approximately proportional to precipitation amount.
3. Lead, chromium, and cadmium concentrations were inversely proportional to precipitation amount.
4. Zinc concentrations were inversely proportional to precipitation amount during the first half of the study period, but the two parameters were proportional during the second half of the study.
5. Little difference existed between any of the sites with respect to combined metal loading.
6. Site elevation appeared to play a significant role in metal loading.
7. Zinc accounted for the majority of the combined metal loading.
8. The individual metal loadings, as opposed to the combined loading, provided a better idea as to which sites were receiving the greatest amounts of highly toxic metals.
9. High Pb loadings in the residential areas could probably be attributed to automobile exhaust.
10. The loading of atmospheric metals to the Arkansas River in the study area is high compared to background levels given in other studies.

11. Construction of a proposed low-water dam on the Arkansas River near 31st Street and Riverside Drive will lead to greater accumulation of metals than presently exists.

CHAPTER VII

RECOMMENDATIONS

Recommendations for future work are:

1. Determine the portions of the bulk atmospheric deposition that can be attributed to wet deposition and dry deposition. These two parameters will help to isolate the source of the pollution.
2. Determine the soluble and particulate fractions of the metals in precipitation in order to determine the relative mobility of the metals in soil and sediment.
3. Determine metal concentrations at various elevations at the same site to more precisely relate metal concentration and loading to elevational differences.
4. Collect a sample at a site isolated from industrial activity to determine a background level for metals in the general area being sampled.

BIBLIOGRAPHY

1. Andren, A. W. and Lindberg, S. E. "Atmospheric Input and Origin of Selected Elements in Walker Branch Watershed, Oak Ridge, Tennessee." Water, Air, and Soil Pollution, 8, 199 (1977).
2. Ault, W. U., Senechal, R. G., and Erlebach, W. E. "Isotopic Composition as a Natural Tracer of Lead in the Environment." Environmental Science and Technology, 4, 305 (1970).
3. Bertine, K. K. and Goldberg, E. D. "Fossil Fuel Combustion and the Major Sedimentary Cycle." Science, 173, 233 (1971).
4. Bowen, H. J. M. Trace Elements in Biochemistry. New York: Academic Press, 1966.
5. Chamberlain, A. C. and Harwell, A. E. R. E. "Aspects of the Deposition of Radioactive and Other Gasses and Particles." International Journal of Air Pollution, 3, 63 (1960).
6. Chan, K. C. Cohen, B. L., Frohlinger, J. O. and Shabason, L. "Pittsburg Rainwater Analysis By PIXE." Tellus, 28, 24 (1976).
7. Chow, T. J. and Earl, J. L. "Lead Aerosols in the Atmosphere: Increasing Concentrations." Science, 169, 577 (1970).
8. Duce, R. A., Quinn, J. G. Olney, C. E., Piotrowicz, S. R., Ray, B. J., and Wade, T. L. "Enrichment of Heavy Metals and Organic Compounds in the Surface Microlayer of Narragansett Bay, Rhode Island." Science, 176, 161 (1972).
9. Fukuda, K. and Tsunogai, S. "Pb-210 in Precipitation in Japan and Its Implication for the Transport of Continental Aerosols Across the Ocean." Tellus, 27, 514 (1975).
10. Gatz, D. F. "Pollutant Aerosol Deposition into Southern Lake Michigan." Water, Air, and Soil Pollution, 5, 239 (1975).
11. Hallsworth, E. G. and Adams, W. A. "The Heavy Metal Content of Rainfall in the East Midlands." Environmental Pollution, 4, 231 (1973).
12. Hutchinson, T. C. and Whitby L. M. "The Effects of Acid Rainfall and Heavy Metal Particulates on a Boreal Forest Ecosystem Near the Sudbury Smelting Region of Canada." Water, Air, and Soil Pollution, 7, 421 (1977).

13. Janssens, M. and Dams, R. "Man's Impact on Atmospheric Lead Concentrations--Pollution Sources and Baseline Levels in Western Europe." Water, Air, and Soil Pollution 5, 97 (1975).
14. Lazarus, A. L., Lorange, E., and Lodge, J. P., Jr. "Lead and Other Metal Ions in United States Precipitation." Environmental Science Technology 4, 55 (1970).
15. Murozumi, M., Chow, T. J., and Patterson, C. "Chemical Concentrations of Pollutant Lead Aerosols, Terrestrial Dusts and Sea Salts in Greenland and Antarctic Snow Strata." Geochemica Et Cosmochemica Acta, 33, 1247 (1969).
16. Oregon State University Water Resources Research Institute. Heavy Metals in the Environment. Corvallis: Oregon State University, 1973.
17. Patterson, C. C. "Contaminated and Natural Lead Environments of Man." Archives of Environmental Health, 11, 344 (1965).
18. Patterson, C. "Lead Pollution." Hygiene and Sanitation, 11, 89 (1971).
19. Perkin-Elmer Corporation. Analytical Methods for Atomic Absorption Spectrophotometry. Norwalk, Connecticut: Perkin-Elmer Corp., 1976.
20. Pierson, D. H., Cawse, P. A., Salmon, L., and Cambray, R. S. "Trace Elements in the Atmospheric Environment." Nature, 241, 252 (1973).
21. Proceedings of the Second Open Forum on Management of Petroleum Refinery Wastewater, Presented by the United States Environmental Protection Agency, American Petroleum Institute, and National Petroleum Refiners Association, and the University of Tulsa. EPA-600/2-78-058, March, 1978.
22. Ruppert, H. "Geochemical Investigations on Atmospheric Precipitation in a Medium-Sized City." Water, Air, and Soil Pollution, 4, 446 (1975).
23. Schlesinger, W. H., Reiners, W. A., and Knopman, D. S. "Heavy Metal Concentrations and Deposition in Bulk Precipitation in Montane Ecosystems of New Hampshire, USA." Environmental Pollution, 6, 39 (1974).
24. Shukla, S. S. and Leland, H. V. "Heavy Metals: A Review of Lead." Journal Water Pollution Control Federation, 45, 1319 (1973).
25. Siegel, S. M. and Siegel, B. Z. "Mercury Fallout in Hawaii." Water, Air, and Soil Pollution, 9, 113 (1978).

26. Slanina, J., Van Raaphorst, J. G., and Zijp, W. L. "An Evaluation of the Chemical Composition of Precipitation Sampled with 21 Identical Collectors on a Limited Area." International Journal of Environmental and Analytical Chemistry, 6, 67 (1979).
27. Struempfer, A. W. "Adsorption Characteristics of Silver, Lead, Cadmium, Zinc, and Nickel on Borosilicate Glass, Polyethylene, and Polypropylene Container Surfaces." Analytical Chemistry, 45, 2251 (1973).
28. Ter Harr, G. L., Holtzman, R. B., and Lucas, H. F. "Lead and Lead-210 in Rainwater." Nature, 216, 353 (1967).
29. The Clean Water Act Showing Changes Made By the 1977 Amendments. Serial No. 95-12. Washington: U. S. Government Printing Office, 1977.
30. Tsunogai, S. and Nozaki, Y. "Lead-210 and Polonium-210 in the Surface Water of the Pacific." Geochem Journal, 5, 165 (1971).
31. Zoller, W. H., Gladney, E., and Duce, R. "Atmospheric Concentrations and Sources of Trace Metals at the South Pole." Science, 183, 198 (1973).

VITA

Michael Boyd Tate

Candidate for the Degree of

Master of Science

Thesis: BULK ATMOSPHERIC METAL CONTRIBUTION TO A RIVER IN AN INDUSTRIAL AREA

Major Field: Bioenvironmental Engineering

Biographical:

Personal Data: Born in Tulsa, Oklahoma, January 19, 1957, the son of Mr. and Mrs. Raymond P. Tate of Bartlesville, Oklahoma.

Education: Graduated from College High School, Bartlesville, Oklahoma in June, 1975; Received Bachelor of Science in Civil Engineering from Oklahoma State University in May, 1980; completed requirements for Master of Science degree in Bioenvironmental Engineering at Oklahoma State University in December, 1981.

Professional Experience: Senior engineering student, May to August, 1979; Environment Control Group, Phillips Petroleum Company, Bartlesville, Oklahoma; graduate research assistant from June, 1980 to December, 1981, Oklahoma State University.