THE ATMOSPHERIC CONTRIBUTION OF HEAVY METALS TO THE ARKANSAS RIVER

E-001

by

Marcia H. Bates, Ph.D.
Department of Civil Engineering

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INTRODUCTION

Heavy metal pollution of surface waters is resulting in serious water quality degradation and creating a problem of major concern. Metals contaminating aquatic systems are derived from many point and non-point sources, one of which is the atmosphere. The significance of this source will vary with geographical location and the proximity of the water body to urban and industrialized areas. Depending on particle size, aerosols containing heavy metals may be returned to earth close to the point of generation or may be carried into the upper reaches of the atmosphere where they pose a global problem. The two major mechanisms of deposition are wet deposition through precipitation and dry deposition either through sedimentation, diffusion, or impaction. Once in an aquatic system the metals may be metabolized, chemical precipitated, or absorbed onto sediments and algae, bacteria or other suspended matter. Changes in pH and oxidation-reduction potential may result in their resolubilization creating temporary increases in the aqueous heavy metal concentration.

The City of Tulsa, Oklahoma, in conjunction with the

Tulsa River Parks Authority is in the process of improving the east and west banks of the Arkansas River as it flows through an area adjacent to downtown Tulsa. Greenbelt areas, parks, and a proposed pool below a low-water dam are all being established to improve and enhance the aesthetic and recreational potential of the area and the Arkansas River. Water quality monitoring of the Arkansas River in the River Parks area as well as at other points indicates the existence of several important water quality problems that could limit the recreational potential of the river. One of the major problems is the presence of heavy metals. The effluents of two Tulsa urban storm drains, one at 23rd Street and one at 11th Street, are characterized by significant levels of lead, chromium, and cadmium. Zinc has also been found to be present. These two storm drains discharge into the proposed pool area below the River Parks low-water dam, and therefore the quality of their effluents is of particular importance. Probable sources of the metals in the storm water drainage include metal plating firms and many of the other industrial firms along the banks of the Arkansas River.

The atmosphere is also a potential source of metals for the Arkansas River. Metals generated and discharged in the Tulsa area can later be returned to the River in the form of bulk atmospheric fallout (dustfall, snow, rain, sleet, hail, and other types of precipitation). In addition, it is important to recognize that atmospheric sources could contribute metals other than those utilized in the Tulsa area to the

Arkansas River. Winds could carry pollutants from industries located many miles away from Tulsa to the River Parks area where the metals could be deposited.

The purpose of this study is to examine bulk atmospheric fallout to the Arkansas River for selected heavy metals and to determine the significance of the atmosphere as a non-point source of metal pollution to this aquatic system. The metals studied include cadmium, chromium, nickel, lead, and zinc.

EXPERIMENTAL METHODS

Six sampling sites were established along the Arkansas River both upstream and downstream from Tulsa, Oklahoma. The exact location of the sites are shown in Figure 1. Sites A and B were located in an industrialized area, and samplers were attached to poles at a height of 7-8 feet above ground level. Site C was located in a commercial-residential area on top of a five-story building. Site D, established in a residential area, was located on top of a two-story building. Samplers at sites E and F were attached to poles eight feet above ground level. Site E was in a residential district, and site F was in a largely residential area with a few small surrounding businesses. Sites A, B, D, and F were in heavily-traveled regions of the metropolitan area.

The samplers consisted of a polyethylene funnel inserted in a narrow-neck, one-liter polyethylene bottle. The funnel had a surface area of 176.7^{2}cm . All samplers were located in open areas away from trees and other vegetation. Samples

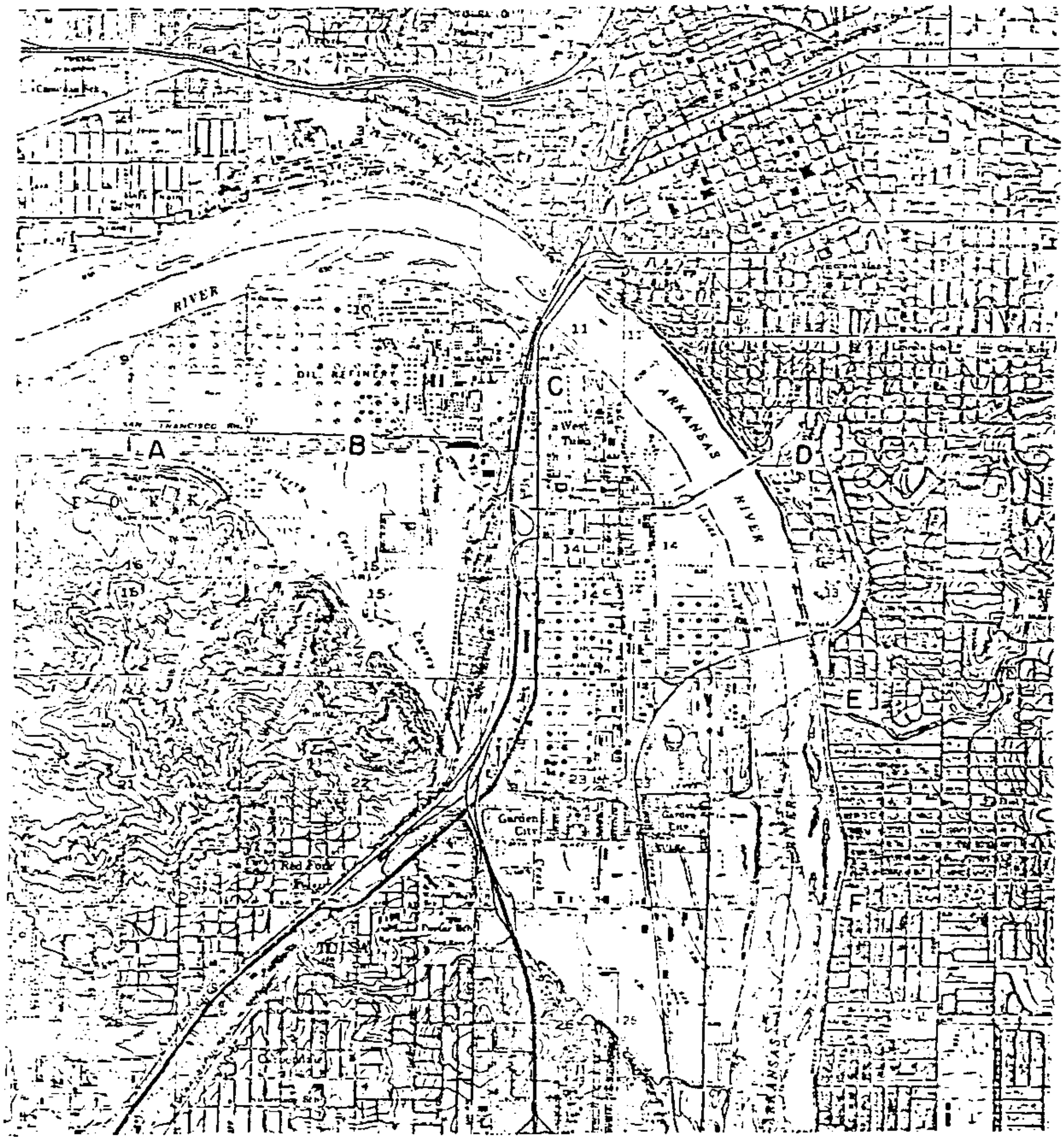

Figure 1. Location of six sampling sites along the Arkansas River.

were collected as soon as possible after each rainfall event to minimize evaporation. The sampling funnel and bottle at each site were replaced with clean acid-washed (HNO_3) funnels and bottles.

The collected samples were returned immediately to the labs where the amount of rainfall collected was determined. Fifty-milliliter aliquots were acid-digested using the digestion procedure of Perkin-Elmer Corporation. Metals were analyzed using a Perkin-Elmer HGA 400 Graphite Furnace coupled with a Perkin-Elmer 5000 Atomic Absorption.

RESULTS AND DISCUSSION

The data reported in this study was collected over a period extending from June 20, 1980 through the month of April 1981. Samples had been collected for approximately six months prior to June 20, 1980. However, problems with analyses, sensitivity, and contamination provided questionable results for some of the metals in these initial samples and the data was therefore not included.

During the period of June 20, 1980 through April 1981, there were twenty-three precipitation events. The only collectible snowfall occurred on February 5, 1981. Except for a few instances wet precipitation was collected from all sites for all 23 sampling events. On July 28, 1981, as a result of scattered rainfall, the samples at sites A, B, and F did not receive any precipitation. These funnels and bottles were washed down with 50 ml of distilled deionized water to suspend the dry deposition in an aqueous phase for digestion. At three other times either due to vandalism or broken sample bottles it was not possible to collect deposition at all six sites. On July 28, 1980, samples were not collected from site E and on November 22, 1980, and March 7, 1981, samples were not obtained from sites C and E respectively.

The data collected from the heavy metal analyses gave the concentration of the metals in the samples collected. Using the concentrations and the volume of rainfall collected the contribution of each metal in ug for each sampling period could be calculated. The metal found in the highest quantity was zinc followed by lead, chromium, nickel and cadmium in decreasing order. Figure 2 indicates the average micrograms of cadmium, chromium and nickel collected for all six sites for each sampling period. Figure 3 shows the average micrograms of lead and zinc collected for each sampling period. Figure 4 is a plot of the milliliters of rainfall collected versus the date of the corresponding precipitation event. Comparing Figures 2 and 3 to Figure 4, it can be generally said that as the amount of rainfall increased the loading of each metal increased. The highest average loading for zinc, lead, nickel, and chromium occurred on September 1, 1980 which also corresponded to the collection of the most rainfall. Other significant rainfall events that are associated with increases in the quantity of metals collected occurred on November 15, 1980, December 7, 1980, and April 18, 1981. The trend of increasing metal loadings with increasing rainfall is best illustrated by noting the similarities between the amount of zinc collected per sampling event (Figure 3) and the amount of rainfall collected (Figure 4).

A major exception to the trend occurred on June 20, 1980. Although this was a period of high rainfall (Figure 4) the loadings of none of the metals except possibly nickel are significant. A possible reason for the lack of metals in the precipitation is that June 20 was immediately preceded by several other days of heavy rainfall which probably served to cleanse the atmosphere of metals prior to the June 20, 1980 sampling date. Nickel (Figure 2), in addition to showing a peak amount on June 20, 1980 which did not correspond to peak rainfall also showed a peak on September 25, 1980, which could not be correlated with peak rainfall. Cadmium also had a peak loading which did not correspond to a significant rainfall event; this occurred on August 20, 1980. The reasons for this behavior of nickel and cadmium are unknown. However, it is possible that specific discharges of these two metals occurred at these times and resulted in elevated concentrations in the atmospheric fallout.

In order to ascertain if the quantity of metals collected was a function of site location, the total amount of each metal collected for all sampling events was plotted versus the site in Figure 5. The highest loading of lead, nickel, and cadium occurred at site E. The highest loading of chromium was found at site F and the highest loading of zinc at site B. The least variation in quantity collected with site was observed with zinc where the micrograms collected were very

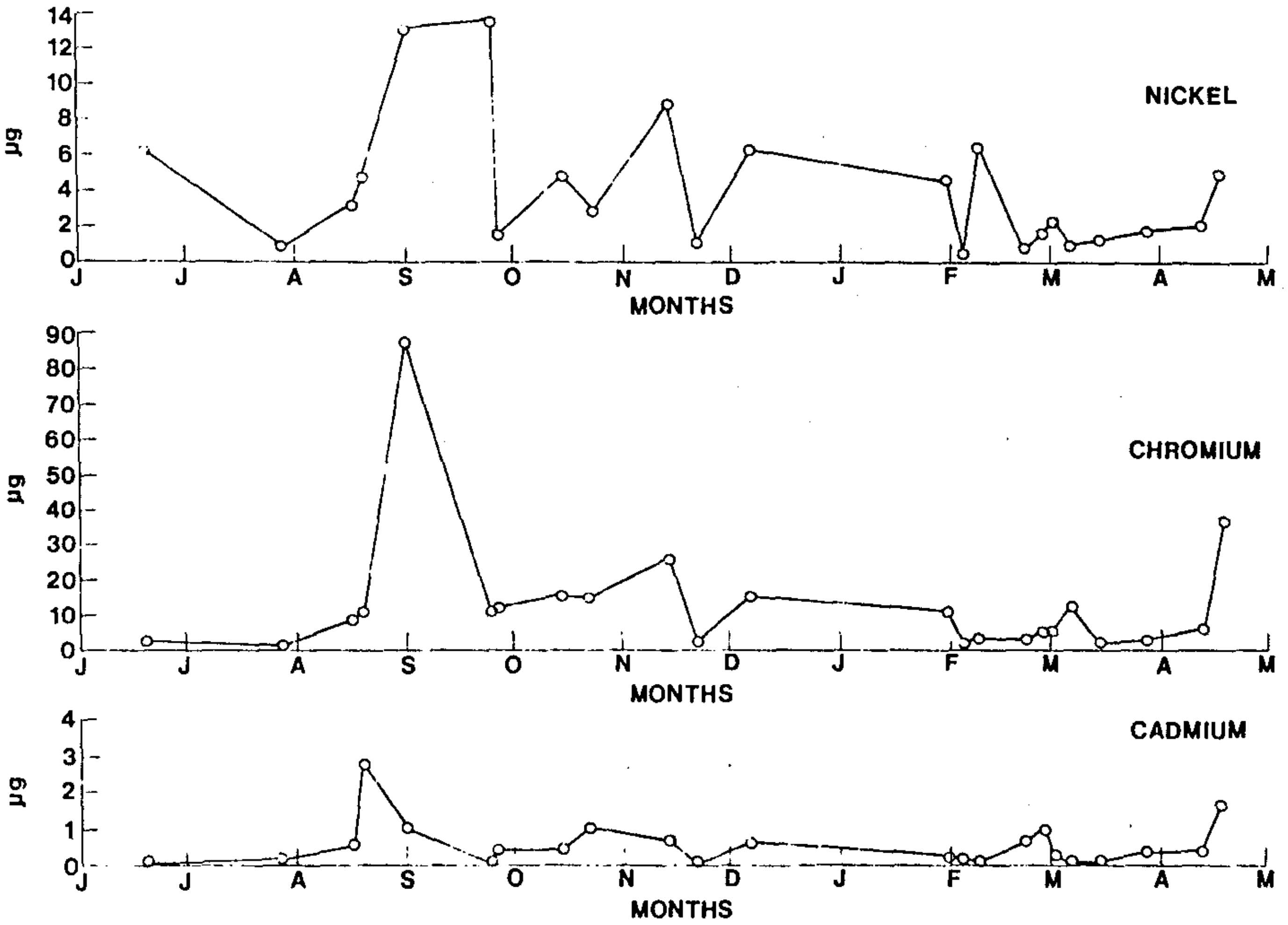

Figure 2. Average micrograms of cadmium, chromium, and nickel collected per sampling event.

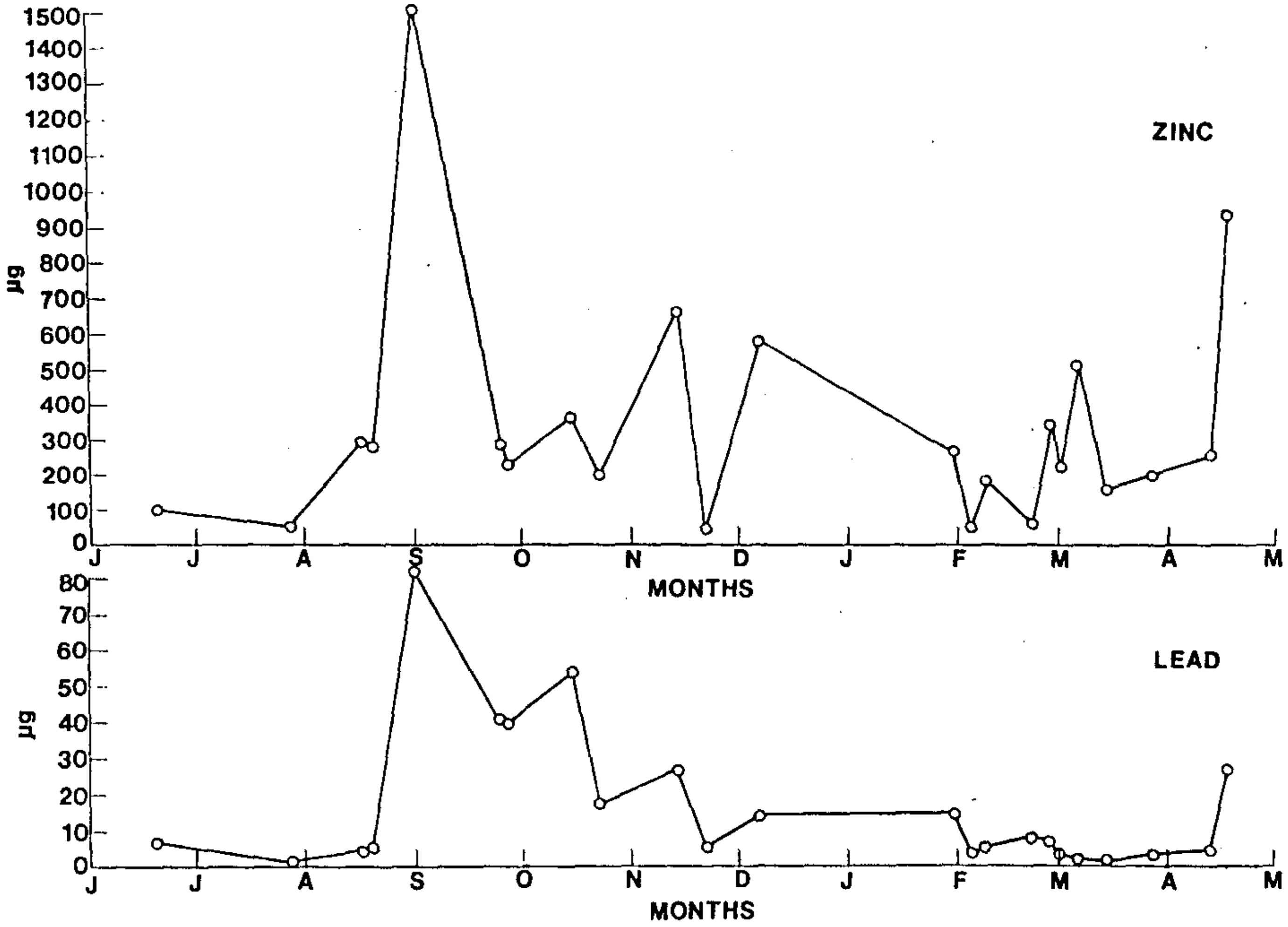

Figure 3. Average micrograms of lead and zinc collected per sampling event.

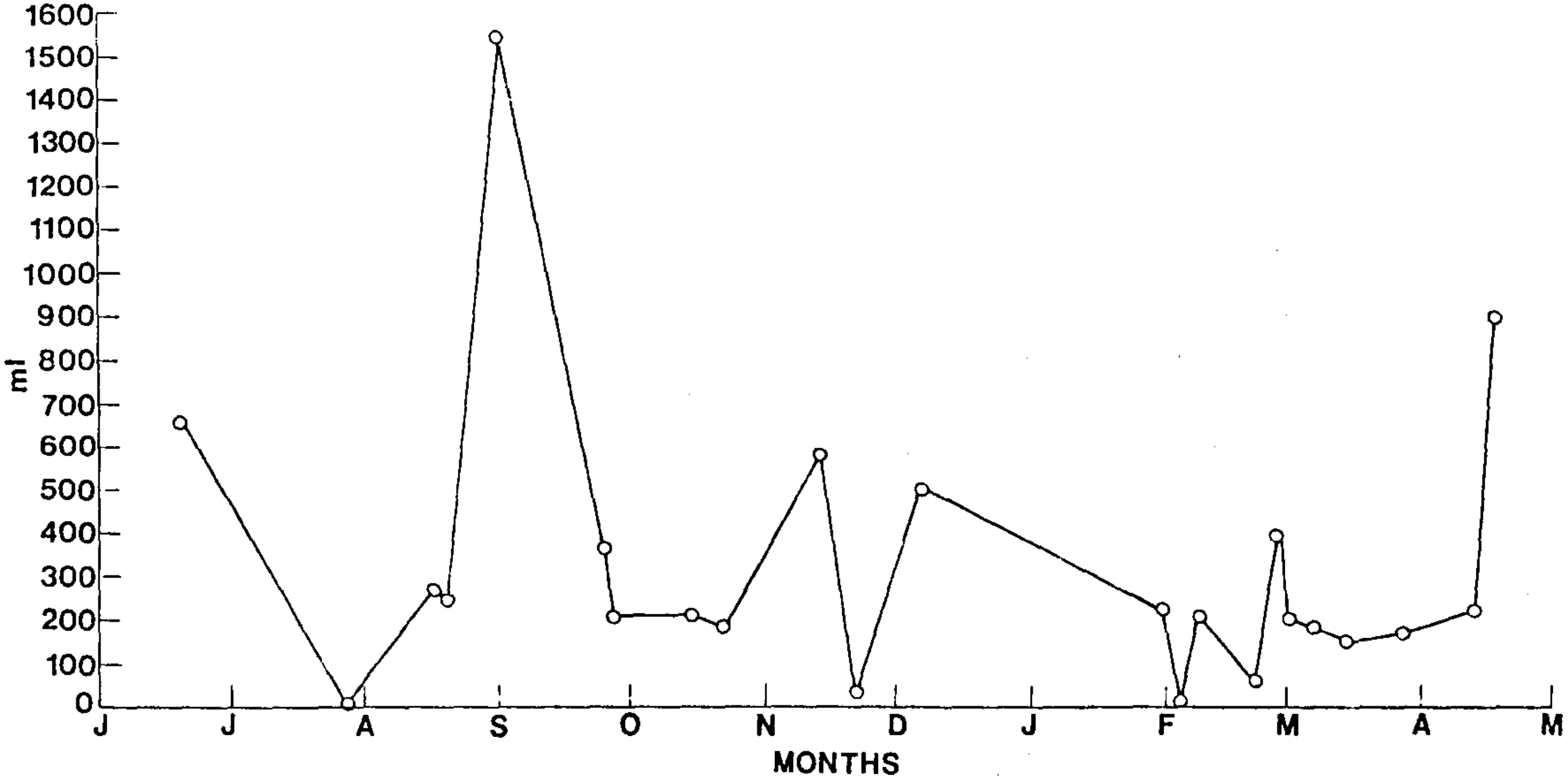

Figure 4. Average milliliters of rainfall collected per sampling event.

similar for all sites except for site C.

Figure 6 shows the total of all five metals collected at each site. From Figure 6 it can be seen that the highest total metal loading occurred at site F with a loading of 9119.07 ug. The loadings at the other sites in decreasing order are site B (9103.56 ug), site E (8861.11 ug), site A (8495.93 ug), site D (8123.72 ug), and site C (6159.35 ug). The total loadings, like those for zinc, did not vary much with the site except for site C. The lowest total loading (Figure 6) and the lowest loading for each metal (Figure 5) occurred at site C.

It is apparent that the quantities of individual metals collected are a function of sampler location. However, from the scope of this study, it would not be possible to establish any conclusions with respect to reasons for variations with site location. A complete inventory of all industries in Tulsa particularly along the Arkansas River and knowledge of their industrial processes and discharges would probably provide some insight into the variations observed.

SUMMARY

Loadings of cadmium, chromium, nickel, lead and zinc to the Arkansas River vary with sampler location and the amount of rainfall. During the 10 month period of 1980-1981 during which samples were collected, zinc was the metal in greatest abundance. Average loadings of zinc were approximately 10 times higher than the average loading of lead, 25 times higher than chromium, 80 times higher than nickel, and 582 times

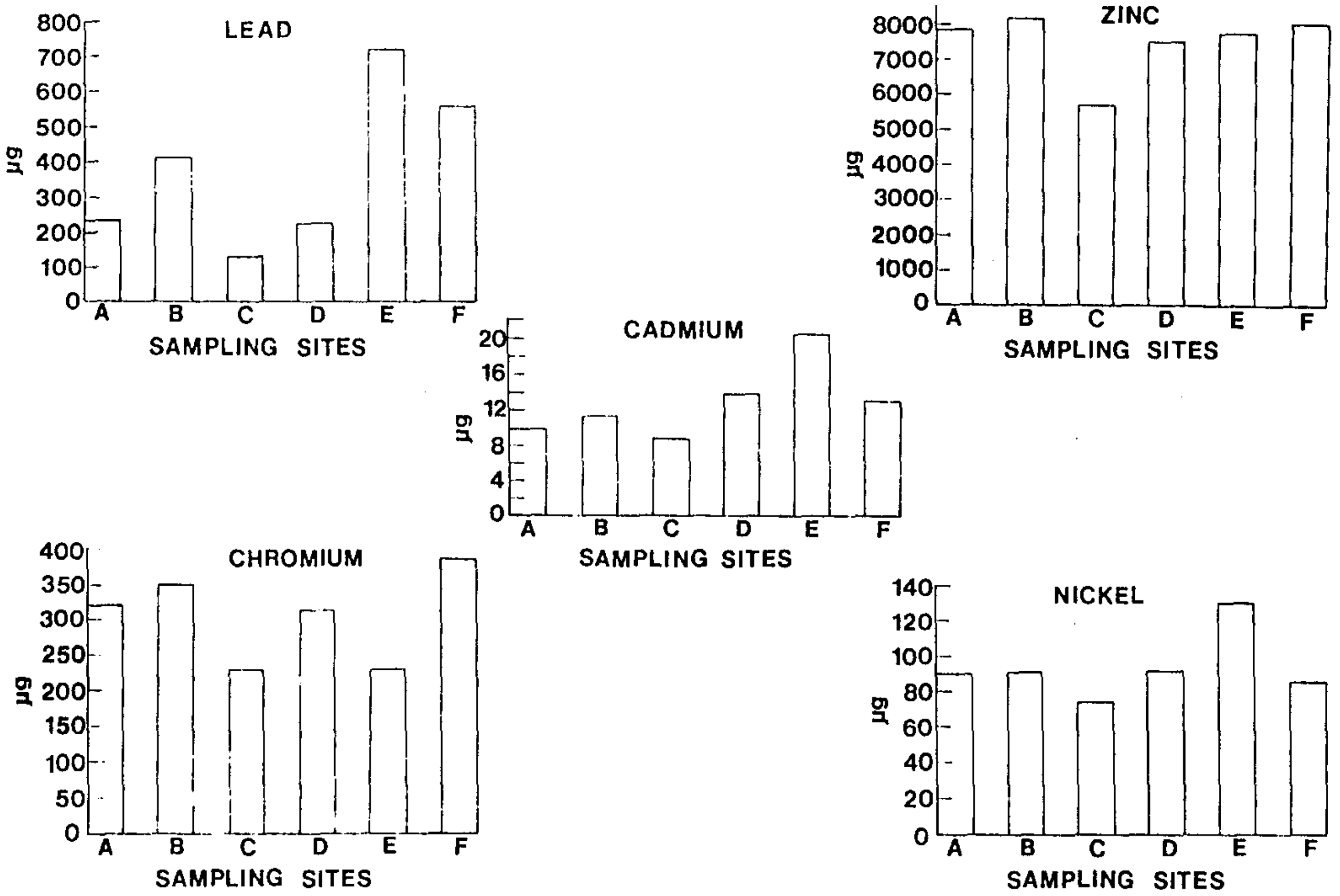

Figure 5. Total loadings of lead, zinc, cadmium, chromium and nickel collected versus site.

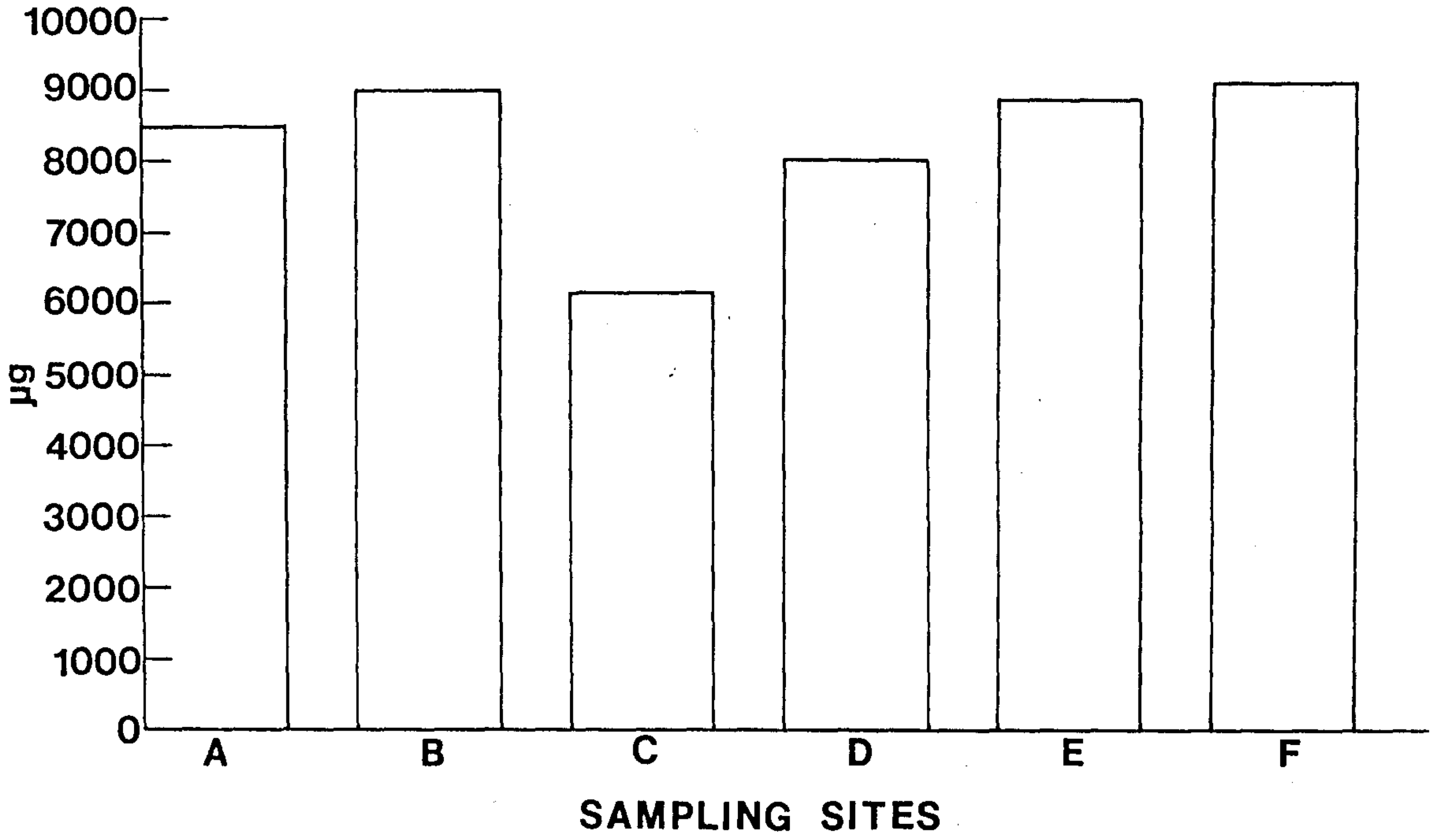

Figure 6. Total metal loading versus site.

higher than cadmium.

The total river area over which samples were collected was 766.7 acres and the total average loading for all six sites was 8295.47 ug. The equivalent loading per acre is 4.18 lbs/acre. Therefore the total loading over the entire area for the 10 month period was 3,207.45 lbs of 1.6 tons. It should be recognized that this figure just represents the contributions of five metals and that the total heavy metal loading to the river could be substantially higher. The atmosphere does appear to be a significant source of metals to the Arkansas River.

As long as conditions in the Arkansas River are aerobic these metals will ultimately become fixed in the sediments, and then during periods of high flow in the river, the bottom sediments containing the metals may be scoured and carried downstream. However, when the proposed River Parks low-water dam is constructed, a quiescent pool will be created and few sediments will be lost by scour. As a result, metals will accumulate in the pool bottom and the concentration will continually increase as the result of continual atmospheric inputs and potential discharges from other sources. Again, as long as the sediment-water interface is aerobic the majority of the metals should be bound to the sediments. However, if even temporary changes in pH or oxidation-reduction potential should occur, the metals could become resolubilized, which would result in serious water-quality degradation.