

SHALLOW-WATER ROADSIDE DITCHES  
FOR STORMWATER PURIFICATION

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## ABSTRACT

The potential of shallow-water ditches adjacent to impervious roadways for hydrocarbon-degradation and deposition of heavy metals was assessed. Bacteria present in soils at the edge of pavement and in aerobic ditches produced significantly greater degradation of petroleum products relative to anaerobic ditches and dry areas 20 feet from the pavement. The metals examined in the field were those from automobile emissions and wear of automotive parts. These are: lead, zinc, copper, chromium, and nickel. Cadmium content was also measured. The highest concentrations of metals were found in the plant and animal populations. However, these contained the least mass. Soils adjacent to the edge of pavement contain the greatest mass of metals. In general, the top soil contained higher concentrations of metals relative to subsurface soils. Lead was shown to be relatively immobilized by the soil. Other metals were more mobile. Soils in areas where rainfall excess appears as overland flow most likely can retain more than 10 times their existing lead content.

## PREFACE

This research was made possible by the State Related Research Program (STAR) of the State University System, the State Department of Transportation, and Florida Technological University. The research was conducted by an interdisciplinary team of Environmental Engineers and Biologists at Florida Technological University. The initial objectives were to document the levels of heavy metals and petroleum degradation in the environments adjacent to highways. These objectives were accomplished. The metal content in soils was so significant that design and maintenance suggestions for metal removal by soils were developed. This work is arranged with an introduction followed by summary, results, and recommendations in Chapter II. Details of the work follow in the remaining chapters. The research team at Florida Technological University is grateful for the assistance provided by personnel from the State Department of Transportation and the State Board of Regents.

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## CHAPTER I. INTRODUCTION

Stormwater runoff in the United States is receiving considerable technical and social attention primarily as a result of the water pollution control act and amendments<sup>36</sup>. Other countries also have recognized the problems of documentation and management of stormwater. A first international conference on stormwater management was held in Southampton, United Kingdom with 28 countries participating<sup>15</sup>. Runoff pollutants from highway surfaces had been documented as early as 1957<sup>26</sup>, when high concentrations of lead in soils adjacent to highways were reported. More recent studies by Shaheen<sup>29</sup> in 1975 and Sartor and Boyd<sup>28</sup> in 1972 identified zinc, copper, chromium, cadmium, nickel, and others as present in highway runoff waters. On a mass basis, Shaheen compared highway runoff to sanitary sewage for comparable land uses and populations. He determined that the mass of lead, zinc, and chromium were respectively 1000, 20, and 300 times greater than that encountered in sanitary sewage. Hydrocarbons also were identified as organic constituents of highway runoff. Residential and industrial roadway runoff was analyzed and it was concluded that grease, oils, and unburned exhaust hydrocarbons are the major organic constituents of highway runoff waters<sup>25</sup>. The ultimate fate of metals and hydrocarbons depends to a great degree on the areas immediately adjacent to the paved surfaces and the methods of disposal of the runoff waters.

Environments adjacent to paved roadways are not similar. The shoulder and ditch areas may be impervious or pervious to various degrees. In addition, overland flow of water or channelization to a discharge point are options in design. Ditches parallel to the edge of pavement can be designed to store or remove water. A cross-section of a typical roadway shoulder and ditch are shown in Figure 1. If the ground water table is usually lower than the ditch, water will percolate. Water retained on the ground surface due to a high water table also can be purified by assimilation and biological degradation. Standing water can promote mosquito breeding, thus removal of the water after purification or within 5 days may be required. In this work, shallow-water ditches are defined as those aerobic waters holding natural vegetation and receiving highway runoff. Retention areas are natural or man-made storage ponds providing storage of surface runoff water resulting in evapotranspiration and percolation.

### OBJECTIVES

The major objective of this research was the management of stormwater runoff to reduce metal and hydrocarbon concentrations. It was postulated that the shallow-water (aerobic) roadside ditch with overland flow of stormwaters from the impervious surfaces to a ditch would be more effective for stormwater management before discharge to lands or surface water bodies adjacent to highway right-of-ways. Field sampling and statistical analyses were conducted to determine for the shoulder and ditch areas adjacent to paved roadway surfaces the

following:

1. Metal concentrations in soils, plants, animals, surface water, and ground water.
2. The relative mobility of metals resulting from overland flow with distance from the edge of pavement and with depth into the soil.
3. The total metal carrying capacity of soils.
4. Hydrocarbon concentrations and degradation in soils, aerobic water, and anaerobic water.
5. The relative degradation of hydrocarbons resulting from overland flow with distance from the edge of pavement.
6. The volume of shallow-water retention areas required to remove impurities if channelized flow (not overland flow) is the stormwater conduit design.

The last activity was done to recognize the fact that some bridge and roadway drainage must be done without overland flow.

## CHAPTER II. SUMMARY, RESULTS, AND RECOMMENDATIONS

Soil, plant, animal, groundwater, and surface water samples were obtained from the shoulder and ditch areas adjacent to highway right-of-ways. These samples were analyzed for metal content and hydrocarbon degradation. Two thousand two hundred twenty-one (2221) metal determinations, two hundred fourteen (214) gas chromatograph traces for hydrocarbons and over twenty four hundred twenty (2420) selective media plate counts for hydrocarbon utilizing bacteria were done during the research which extended over an 18-month period. Eleven field sites were used to represent aerobic water environments, partly anaerobic water (1-3 meters deep) environments, and different soil conditions.

Research completed prior to this work provided valuable guidance and is important for the summary, conclusions, and recommendations of this research.

1. Deposition rates of hydrocarbons and metals from automobiles have been well-documented<sup>29</sup>. The quantities of these pollutants in the runoff waters have been documented.
2. Hydrocarbons from the automobile are transmission fluid, crankcase oil, non-volatilized diesel and gasoline, hydraulic fluid, and gear lubricants.
3. Aerobic microorganisms capable of degrading hydrocarbons are frequently isolated from petroleum polluted environments.
4. In treated sewage disposal by land spreading, metals are found primarily in the soil.
5. Soil properties generally considered important for retention of heavy metals are pH, cation exchange capacity, clay mineral content, and organic matter content.
6. Lead is particularly significant as a public health problem.
7. In laboratory studies, the retention of lead can be reasonably predicted by pH and cation exchange capacity.

### RESULTS

The results will be presented in summary format with hydrocarbon findings followed by the results of the metal studies. Relative to hydrocarbons, the results are:

1. Hydrocarbon utilizing bacteria populations are at most 90 percent higher during rainy months than during dryer months of the year. Thus, runoff waters have a significant effect on bacterial growth.

2. Concentrations of hydrocarbon utilizing bacteria are greatest at the edge of pavement and decrease with distance from the edge of pavement until a ditch is encountered.
3. Total nitrogen and phosphorus concentrations decrease with distance from the edge of pavement. Forty feet from the edge of pavement with no surface water (ditches) present, phosphorus and nitrogen concentrations are 70 and 94 percent less respectively than edge of pavement concentrations.
4. Shoulder areas with no surface waters in the ditches were capable of degrading at most 48 percent of hydrocarbon substrates in sixty days. The hydrocarbon substrates were those found in kerosene. The degradative potential decreases with distance from the pavement. Degradative potential is related to species diversity, bacterial concentration, and total nutrients. All decrease with distance from the pavement.
5. The degradative potential of shoulders with ditches (aerobic) exceeds the potential of shoulders alone. Under optimum temperature and nutrient conditions, ninety-nine percent of the hydrocarbon substrates are degraded within 60 days by bacteria present within the aerobic ditches. Degradation was measured by chromatographic tracings.
6. Weathered kerosene chromatograph tracings served as controls. The weathered tracings were approximately 400 times greater than the aerobic bacterial degradation tracings measured in total mass of hydrocarbons.
7. Hydrocarbon utilizing bacteria were present in higher concentrations in the surface waters ( $5 \times 10^5$  organisms/ml) than in the anaerobic ditch sediments ( $2 \times 10^5$  organisms/ml). However, under optimum aerobic conditions, the degradative potential of anaerobic sediment is approximately equal to that of aerobic water.
8. The shoulder soils and water from the aerobic and anaerobic ditches were examined for the suspect carcinogenic compounds: Benzidine, Alpha-naphthylamine, and Benzo(a)-pyrene. None of these compounds were found in the roadside environments.

Results relative to metal depositions in shoulders and ditches are:

1. Highest concentrations of metals are found in animal life. However, animal life resident in these areas is difficult to detect. Over 100 square feet of top-soil had to be "turned over" to collect a sufficient quantity of soil insects (grubs) to allow one metal detection analysis.
2. The greatest mass of metals is found in the soil of the shoulder areas. For example, the mass of lead found in the soil is approximately 5000 times greater than that found in animals.
3. With one exception, ditch water, surface and ground water concentrations of metals were not greater than the Florida State drinking water standards. The one exception was one chromium sample of sixteen.



4. Lead concentrations were considerably higher in the surface soils (top 2-3 cm) than in subsurface soils (15-20 cm) at the same location. This was not consistently found for the other metals. Therefore, lead is generally immobilized in roadside soils.
5. Metal concentration in the soil decreased with distance from the edge of pavement.
6. Based on a regression equation developed by Zimdahl and Skigerboe<sup>41</sup> which relates pH and cation exchange capacity to lead retention of a soil, the soils tested have over 10 times their existing lead content remaining for additional lead retention.
7. Organic matter is important and correlates well with the ability of soil to retain metals. However, in general, other factors are important, such as clay minerals, pH, and chemical reactions. No one removal mechanism or soil characteristic was determined as being most important.

## RECOMMENDATIONS

In areas where surface water discharges from highway right-of-ways to adjacent lands are limited, the following recommendations for design and maintenance of the land and water are advanced. The underlying concepts for these recommendations are based on land percolation rates, water aerobic conditions, and metal interactions with soil. In the design of highways,

1. Rainfall excess (runoff) should be directed as overland flow as much as possible to promote water percolation and metal removal.
2. Shallow-water ponding of runoff in aerobic maintained ditches should be encouraged to increase petroleum (hydrocarbon) degradation.
3. Diversion of runoff from open or closed conduits into shallow holding areas can be used to remove specified quantities of pollutants.
4. A "muck" blanket should be spread on the soil before vegetation is planted to promote metal removals.
5. Subsurface soil should be alkaline to promote metal removals. Also, organic matter and clay minerals aid in removal of metals.

When overland flow of surface runoff waters is not possible, the first flush of runoff water can be diverted for treatment. The volume of water diverted depends on the discharge limitation. Treatment may be accomplished by storage and percolation in medium or shoulder areas. Formulas for diversion volume and percent efficiency are given in the text.

In the maintenance of highways,

1. Soils adjacent to pavements need to be replaced on a periodic basis because of metal saturation. Care should be exercised in disposal of these soils.

2. Roadside vegetation should remain on the ground after cutting to allow nutrients to recycle.
3. Planting of leguminous plants, such as clover, will provide nitrogen which is a limiting factor in petroleum degradation and therefore necessary.

#### LIMITATIONS

The field work was done in the East Central Florida highway environment. A previous study<sup>17</sup> was completed for the South Florida Environment. Efforts were made to obtain soil samples that would represent clay, sand, organic, and limestone soils commonly found in Florida. However, at the present time, the results are limited to the East Central Florida highway environments. National studies now underway by the Transportation Research Board may be beneficial in expanding the results of this work. Metal concentrations in minnows were determined, but larger fish were not measured for metal concentrations. Larger fish living exclusively in roadside ditches could not be found in the study area. Along the Florida Turnpike, catfish were found but these were able to travel to water bodies adjacent to highway right-of-ways.

#### FUTURE RESEARCH

There exist many different field conditions of soil, percent impervious area, water table depth, conduct configurations, and others which effect the application of the design recommendations of this report. The results can be used directly, but a manual of design related to design storms and local conditions would be of benefit to the designers. Therefore, it is suggested that a design manual should be developed for use by drainage engineers. This may also require a short course that would provide design reasons and example problems. The short course also would be attended by State and Federal regulatory people.

With the many aquatic areas adjacent to roadways within the State of Florida, it appears reasonable that some may be useful as aquaculture areas. In addition, hay or clover may be planted in the dry areas. Shoulder areas within right-of-ways can be productive. The type of crops that can yield a revenue and not concentrate metals or other toxics needs to be examined.

Retention of stormwater without subsequent release to surface waters was a suggested solution for stormwater management. If hydrocarbon degradation was the limiting parameter, rate degradation studies at field sites could provide data on the holding time of runoff waters before surface water discharge. Determination of in situ rates using  $C^{14}$  radiolabeled hydrocarbons are currently being performed at Florida Technological University. The results should be available in September 1978.

Finally, methodologies to predict soil saturation by metals is needed. Soils will need replacement, however, no field or laboratory column (breakthrough) studies were done in this research. This is feasible and needed in the near future.

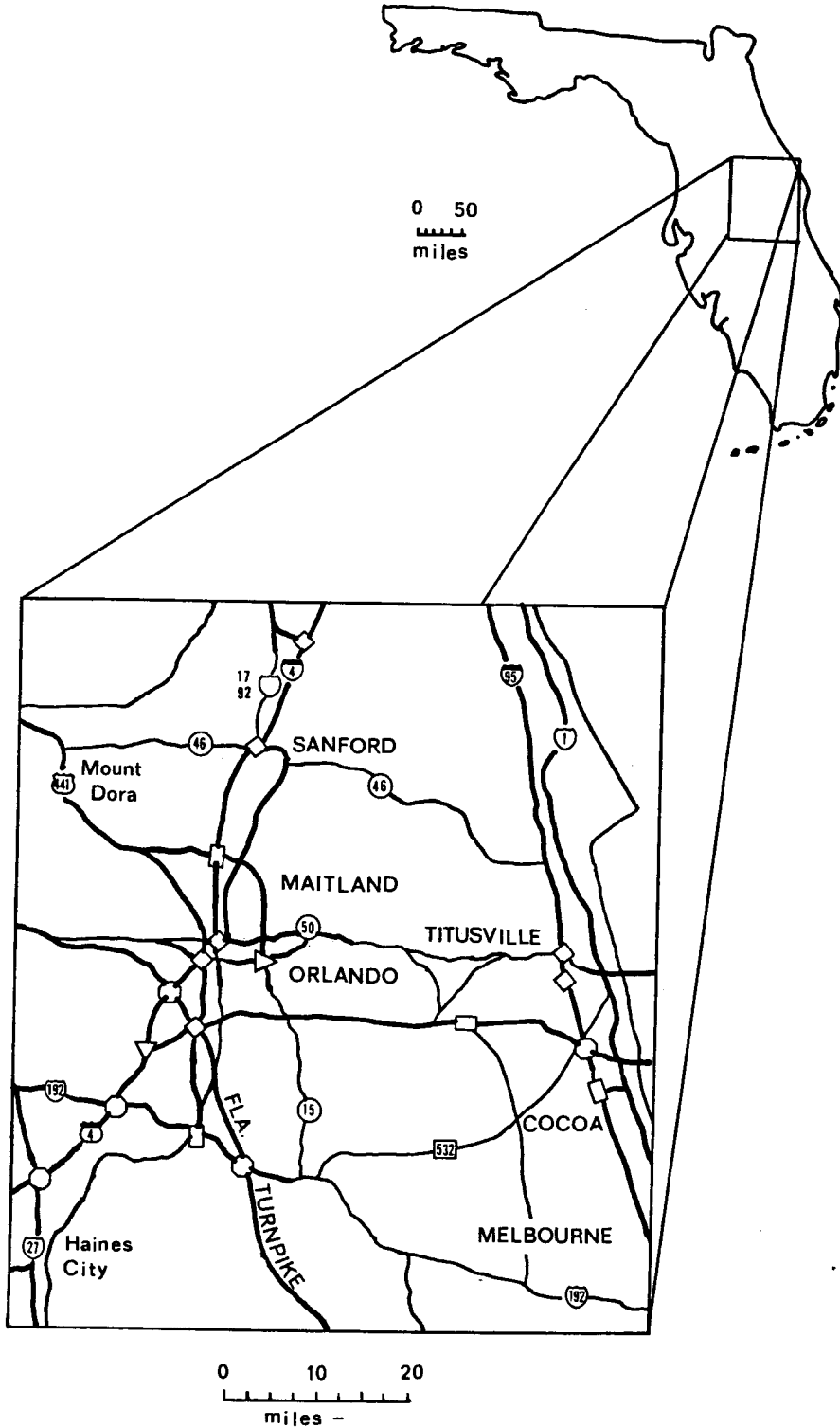


FIGURE 2. STUDY AREA

## CHAPTER III. SOURCES, LOADINGS, AND MAJOR SINKS OF METALS AND HYDROCARBONS

Before evaluating the effectiveness of shoulders and ditches as sinks for highway related metals and hydrocarbons, a discussion of the sources and loadings (deposition rates) near highways is appropriate. This discussion, with evidence showing the importance of the soil in retaining highway related heavy metals and aerobic ditches for degrading hydrocarbons will be presented in this chapter.

### LEAD, ZINC, CHROMIUM, COPPER, NICKEL, AND CADMIUM

There are essentially three sources of metals near highways. These include: 1) natural sources, 2) "background" sources due to ambient levels of metals in the atmosphere, and 3) highway related sources including automotiles, paints, preservatives, and to some extent, herbicide spraying.

Most soils contain heavy metals in trace amounts as a result of natural processes. Naturally occurring levels of metals in soils are a function of the parent materials from which the soil was derived and the processes of weathering to which these materials have been subjected. The background and natural concentrations of metals can be expected to vary widely with geographic location. Most highway related metals are not distinguishable from background and natural at distances greater than 30 meters (Motto et. al. 1970). Thus background and natural conditions in Florida adjacent to highways were assumed to be determined by measurements greater than 30 meters from the edge of pavement. However, this distance will have to be determined by statistical analysis of concentrations as a function of distance from the edge of pavement.

The atmosphere is known to contain certain amounts of lead, zinc, and chromium because of industrial activity and oil or coal combustion. These amounts of metals are "background" to levels existing near highways. Lead concentrations in urban atmospheres are on the order of  $1 \mu\text{g}/\text{M}^3$  while chromium concentrations are on the order of  $.01 \mu\text{g}/\text{M}^3$  in urban atmospheres<sup>12</sup>. These values will likely be lower in rural areas. Some "background" metals from the atmosphere can contaminate the soil.

The predominant source of lead, zinc, chromium, copper and nickel near highways is the automobile. Cadmium is generally not believed to be from the automobile. The combustion of leaded gasoline is generally acknowledged to be the major source of lead, but some lead also results from the wear of tires in which lead oxide is used as a filler material<sup>29</sup>. Zinc also results from tire wear and from the leakage of crankcase oil in which high concentrations of zinc is used as a stabilizer<sup>18</sup>. Chromium, copper and nickel are from the wear of metal plating, bearings, bushings and other moving parts within the engine<sup>29</sup>.

Lead is added to gasoline in the form of tetra-alkyl lead compounds at a concentration of about 150 ppm<sup>20</sup>. Much of this added lead is not exhausted,

but is retained in the engine. Exhausted lead is probably in the range of 50-80 percent of lead added<sup>27</sup>, depending on driving conditions. The most common compounds of lead found in the exhaust are lead bromochloride ( $\text{Pb}\cdot\text{Cl}\cdot\text{Br}$ ), mixed oxide and halide ( $\text{PbO}\cdot\text{PbCl}\cdot\text{Br}\cdot\text{H}_2\text{O}$ ), and ammonium chloride and lead halide ( $\text{NH}_4\text{Cl}\cdot 2\text{PbCl}\cdot\text{Br}$  or  $\text{ZNH}_4\text{Cl}\cdot\text{PbCl}\cdot\text{Br}$ ). These compounds are very unstable; 75 percent of the bromides and 30-40 percent of the chlorides break down into lead oxides and carbonates within 18 hours<sup>10</sup>. The effect of aging on exhausted lead compounds has been shown by Terhaar<sup>33</sup>, who determined that the lead compounds in aged exhaust particles are carbonates (30%), oxides (20%), oxycarbonates (27%), oxysulfates (5%), and sulfates (3%). Olson and Skogerboe<sup>22</sup> have suggested that atmospheric or soil reactions may convert most of the exhausted forms into lead sulfate.

From an environmental health viewpoint, lead is not required by any form of life and is known to be toxic to plants, animals and humans at elevated levels<sup>2,35</sup>. While zinc, copper, and chromium are essential to most life forms in trace amounts, elevated levels of either have been shown to be toxic<sup>2</sup>.

#### SOURCES OF HYDROCARBONS

Highway related hydrocarbons are primarily waste lubricants derived from vehicular transportation. These oil pollutants enter the roadside environment as a constituent of highway runoff. Analysis of roadside runoff of both residential and industrial areas indicate that grease and waste oil are the major organic constituents<sup>25</sup>. According to EPA estimates of the 616 million gallons of waste oil produced by automobiles in 1974, 148 million gallons or 24 percent entered the environment<sup>40</sup>.

Hydrocarbons deposited on the surface of highways is primarily crankcase oil and the non-volatile portion of diesel and gasoline. Other petroleum pollutants include transmission fluid, hydraulic fluid, and gear lubricants<sup>40</sup>. These waste oils originate from hot engines, machine joints, grease fitting, brakelines, and from exhaust as burnt motor oil. Vehicular fuels, i.e., gasolines and diesels, contain volatile hydrocarbons which rapidly evaporate from the road surface. The less volatile compounds remain on the pavement. Hydrocarbons deposited on the road surface combine with sand and organic matter. These deposits remain on the surface until a rain of sufficient intensity removes them into the roadside environment. The hydrocarbon pollution then enters the roadside environment where it may undergo chemical changes, i.e., photooxidation, bioconversion, and biodegradation.

The classes of hydrocarbons associated with waste oils and the non-volatile portion of fuels entering the roadside environment represent some of the more resistant hydrocarbons. Aromatic and cycloalkanes occur in waste petroleum in percentages ranging from 35-70%. The average percentage of hydrocarbon classes in petroleum and fuels, i.e., gasolines, are given in Table 1. It should be noted that no two lubricants or fuels are identical in concentrations and these represent only average percentages.

Factors which influence microbial growth also influence petroleum degradation. Biodegradation and bioconversion of hydrocarbons is an extremely complex process involving intercellular enzymes and metabolic pathways. Several reviews on hydrocarbon oxidation by bacteria at the molecular level have been

published in recent years<sup>7,8,23,36</sup>.

TABLE 1. AVERAGE AMOUNTS OF MAJOR CLASSES OF HYDROCARBONS AND RELATED COMPOUNDS PRESENT IN DIFFERENT PETROLEUMS AND GASOLINES

Component	Percentages in	
	Petroleums	Gasolines
Aliphatic or paraffinic (alkanes)	15-35	25-68
Cycloparaffinic (cycloalkanes;naphthenes)	30-50	5-24
Aromatic (benzene and polynuclear series)	5-20	7-55
Asphaltic (asphaltenes; heterocyclic compounds with oxygen, sulfur, or nitrogen)	2-15	0.1-0.5
Olefinic (alkenes or ethylene series)	nil	0-41

From Zobeil<sup>42</sup>

#### LOADING RATES

Traffic dependent rates of deposition of roadway surface contaminants were determined by Shaheen<sup>29</sup> based on a study of urban roadways in the Washington, D. C. area, and others<sup>25,30</sup>. These rates are shown in Table 2 and are expressed in Kg/axle-Km. They represent the dry weather accumulation of pollutants on the roadway surface and do not include pollution from other non-traffic related sources such as atmospheric fallout, litter, and runoff from adjacent areas.

The data in Table 2 can be used to estimate the traffic related pollutant loading for a specific section of roadway by applying the following formula:

$$Y_i = y_i \sum_j TD_j AX_j$$

where

$Y_i$  = loading of pollutant  $i$ , Kg/day

$y_i$  = deposition rate of pollutant  $i$ , kg/axle-km

LH - length of roadway section, km

TD<sub>j</sub> = traffic density of vehicle with "j" axles, vehicles/day

AX<sub>j</sub> = number of axles per "j" vehicle

The approximate rate of emission of air pollutants by motor vehicles is shown in Table 3.

To determine the loading rates of atmospheric pollutants from motor vehicles for a specific section of roadway, the following formula is used:

$$Y_{i(\text{atm})} = \frac{Y_{i(\text{atm})} \text{ TD LH}}{1000 \text{ M}}$$

where

Y<sub>i(atm)</sub> = loading of atmospheric pollutant i, lb/day

y<sub>i(atm)</sub> = emission rate of atmospheric pollutant i, lb/1000 gal fuel

LH = length of roadway section, miles

TD = traffic density, vehicles/day

M = average vehicle fuel consumption, miles/gal

#### OTHER SOURCE CONSIDERATIONS

The types of contaminants which originate from non-traffic related sources will vary according to land use. Studies by Pitt and Amy showed widely varying pollutant loads between city streets, rural roads and highways. In addition to the automobile related pollutants listed above, roadways are contaminated by loadings of BOD, PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>, N, Cd, Fe, Mn, and Sr which usually arise from land use related sources.

Other sources of pollutants in the highway right-of-way are herbicides, preservatives, and paints. Herbicides are used to control weeds in ditches and around guardrails. They contain toxic, but readily degradable hydrocarbons. A preservative is used on wooded fence posts. It is a chemical containing hexavalent chromium (33-50%), Copper (as CuO, 17-22%), and AsS<sub>2</sub>O<sub>5</sub> (30-48%). Zinc is also present in paints used for guardrails and chain link fences. Silica lead chromate is used in yellow paint. Paints are used for pavement marking and their weathering results in various compounds of lead.

#### THE SOIL AS A SINK FOR METALS

The transport of metals from the impervious highway surfaces ultimately results in large amounts of these metals being deposited in adjacent soils. This is evident from the high concentrations observed in roadside soils. Studies by Motto et. al.<sup>21</sup>, Lagerwerff and Specht<sup>18</sup>, Singer and Hanson<sup>30</sup>, and Olson and Skogerboe<sup>22</sup>, to name but a few, have shown elevated levels of lead and zinc in roadside soils. Concentrations of lead as high as 7000 ppm have been reported<sup>22</sup>.

TABLE 2. DEPOSITION RATES OF TRAFFIC-RELATED MATERIALS  
(Shaheen, 1975)<sup>29</sup>

	DEPOSITION RATE (kg/axle-km unless otherwise stated)
Dry Weight	$6.67 \times 10^{-4}$
Volume	$1.77 \times 10^{-4}$
	(quarts/axle-km)
Volatile solids	$3.39 \times 10^{-5}$
BOD	$1.52 \times 10^{-6}$
COD	$3.58 \times 10^{-5}$
Grease	$4.26 \times 10^{-6}$
Total Phosphate - P	$4.03 \times 10^{-7}$
Nitrate - N	$5.29 \times 10^{-8}$
Nitrite - N	$6.33 \times 10^{-9}$
Kjeldahl - N	$1.04 \times 10^{-7}$
Chloride	$6.16 \times 10^{-7}$
Petroleum	$2.39 \times 10^{-6}$
n-Paraffins	$1.68 \times 10^{-6}$
Asbestos	$1.08 \times 10^5$
	(fibers/axle-km)
Rubber	$3.47 \times 10^{-6}$
Lead	$7.81 \times 10^{-6}$
Chromium	$5.18 \times 10^{-8}$
Copper	$7.95 \times 10^{-8}$
Nickel	$1.23 \times 10^{-7}$
Zinc	$9.8 \times 10^{-7}$
Magnetic Fraction	$3.53 \times 10^{-5}$

Some of the atmospheric pollutants are deposited on the roadway surface and are accounted for by the deposition rates Table 2.

TABLE 3. EXHAUST EMISSIONS  
USPHS, 1968<sup>34</sup>

Pollutant	(lb/1000 gal fuel)	
	Autos	Diesel
Aldehydes (as formaldehyde)	4	10
Carbon Monoxide	2300	60
Hydrocarbons (as Carbon)	200	136
Nitrogen Oxides (as NO <sub>2</sub> )	113	222
Particulates	12	110
Organic Acids (as acetic acid)	4	31
Sulfur Oxides (as SO <sub>2</sub> )	9	40



The physical factors related to these metal concentrations are generally found to be traffic volume, distance from the highway and depth into the soil.

A study of the mass inputs and outputs of highway related lead in urban and rural basins was performed by Rolfe and Jennett<sup>27</sup>. They calculated that 75 percent of the total lead input by automobiles in the urban basin was leaving the basin via streamflow while only 2 percent of the total lead input to the rural basin was output as streamflow. They concluded that the soil was responsible for accumulating a large portion of the lead input to the rural basin and estimated, based on soil lead measurements, that an equivalent to 30 years of auto lead emissions were contained in the soil. The quantity of metals retained in the soil is dependent upon many physicochemical reactions, such as absorption, coordinated chemical complexing, oxidation-reduction, and filtration<sup>16,32</sup>. The tendency of a metal to be removed by one of these reactions depends on its chemical form and contact with the soil. John H. Bell<sup>3</sup> has completed an extensive examination of soils in the Central Florida area. His work forms the basis for part of this report.

#### AEROBIC DITCHES FOR HYDROCARBON DEGRADATION

The natural process of hydrocarbon degradation involves microbial utilization of hydrocarbons as substrates. Microorganisms capable of degrading hydrocarbons oxidize these highly reduced compounds and derive energy for metabolism. This degradation is most common in aerobic environments. Aerobic microorganisms capable of oxidizing various hydrocarbon substrates are widely distributed in soil and water. The greatest varieties and numbers of bacteria occur in environments contaminated with petroleum.

Walker and Collwell<sup>38</sup> demonstrated the number of bacteria capable of utilizing petroleum in estuaries to be on the order of  $10^3$  to  $10^4$  organisms per ml of water.

Aerobic microorganisms most frequently isolated from petroleum polluted environments are:

1. Pseudomonas species are the most versatile of all known hydrocarbon utilizing bacteria. These strict aerobes possess the ability to oxidize paraffins, cycloparaffins, naphthenes, phenols, m-creosols and asphalt<sup>4</sup>.
2. Achromobacterium species can oxidize polysulfide polymers and many classes of hydrocarbons occurring in highway related waste oils.
3. Micrococcus species can utilize paraffins and oxidize phenols.
4. Nocardia species are highly effective in oxidizing paraffins to cellular components, some species can also co-oxidize aromatic compounds.
5. Flavobacterium species are capable of oxidizing benzene ring compounds. Other less predominate aerobic microorganisms capable of hydrocarbon oxidation include members of the genus Corynebacteria, Arthrobacteria, Bacillus, Acinetobacter and Vibrio<sup>8,38</sup>.

## CHAPTER IV. RESULTS OF METAL STUDIES

Metal concentrations and mass with estimates of retention capacity in the "sinks" adjacent to the paved highways were determined. The eleven sampling sites are listed in Table 4. The sites were chosen to provide a range of geographic locations, age of highway, number of traffic lanes, drainage conditions, soil conditions, and traffic volume.

TABLE 4

### SITE LOCATIONS AND DESCRIPTIONS

I-95	Northbound lane, near Titusville, overland flow area characterized as a low water table area
I-95	Same area as above but at a discharge closed conduit
I-95	Northbound lane, near Titusville, overland flow area with a ditch in a high water table area
I-75	Florida Turnpike, Southbound lane near Canoe Creek Plaza, overland flow with a ditch in a high water table area
I-75	Florida Turnpike, Canoe Creek pond with overland flow
I-75	Florida Turnpike, Southbound lane near Canoe Creek Plaza, overland flow in a low water table area
I-4	Maitland interchange, Northeast pond of the interchange with closed conduit discharges
I-4	Same area as above but at the discharge pipe
SR-50	Eastbound lane, near St. Johns River, with a high water table area
US-1	Northbound lane, near Titusville, very sandy with no vegetation and a low water table
SR-405	Eastbound lane, near Titusville, very sandy with no vegetation and a low water table

### SUMMARY STATISTICS

Much variability exists in the measurement of the metal concentrations.

Summary statistics aid in an understanding of the average concentration and measures of variability. Lead summary statistics are shown in Table 5. For lead, the highest concentration was found in animals. The least concentration was in surface and ground water. Comparative data also are shown in Table 5. The drinking water standards or the maximum contaminant levels (MCL) show that surface and ground water samples are below the standards, in all but one sample for chromium out of sixteen chromium samples. The dissolved fraction of lead in surface waters was about 10 percent. The greatest mass of lead is found in the soils subjected to overland flow. However, plant life has greater concentrations relative to soil concentrations. The coefficient of variation illustrated that more consistent estimates of the average were possible for animal and plant samples. The greatest mass of lead is found in the soils subjected to overland flow. However, plant life has greater concentrations relative to soil concentrations. The coefficient of variation illustrated that more consistent estimates of the average were possible for animal and plant samples. The greatest variability generally was found among the soil samples. However, soil at various depths and distance from the edge of pavement were included in the average statistics. Variability should be expected.

Relative concentrations from Table 5 for lead are shown in Figure 3. Lead, zinc, copper, chromium, cadmium and nickel comparative concentration charts all illustrate that the highest concentrations are found in animal life. However, very little animal life is resident in the roadside environments. Thus, if the concentrations are converted to mass loading of metals per meter of highway, the greatest quantity of metals are found in the soils. For lead, a comparative loading chart is shown in Figure 4. Similar figures for the other metals are found in Appendix A.

Sampling procedures and methods conformed to the latest editions of Standards Methods<sup>1</sup> and Bergey's Manual<sup>4</sup>. The methods and procedures are discussed in greater detail in Appendix B.

The assumptions used to convert concentration averages to mass per meter of roadway were average conditions at the sampling sites along I-75, I-95, SR-50, SR-405, and US-1. The shoulder width not including the ditch area was calculated at approximately 12.25 meters. The weight of soil in a 12x1 meter area, 15 centimeters deep is approximately 2200 Kg. Samples of grass were weighed and for twelve square meter area the weight was estimated at 5.91 Kg. Grubs or resident animals were difficult to find. A total of 12 one square meter areas, 15 cm deep were examined. Approximately 4 grubs/m<sup>2</sup> were found. The average weight is equal to 0.35 g/animal. The volume of water per meter of highway was estimated at 560 liters which assumes a 1 foot average depth, 2 meters wide. Thus, by knowing concentration and mass of media, the mass of metals can be calculated. Example calculations for copper are:

	<u>Calculations/Meter of Roadway</u>	<u>Mass (mg)</u>	<u>Ratio</u>
Water:	0.033 mg/l x 560 liters	= 18.48	23
Soil:	0.688 mg/kg x 2200 kg	= 1514.00	1892
Plants:	36.3 mg/kg x 5.91 kg	= 214.00	268
*Animals:	43.4 mg/kg x 0.018 kg	= 0.80	1

\*Average weight of grubs and minnows/meter.

TABLE 5  
LEAD SUMMARY STATISTICS  
CONCENTRATION

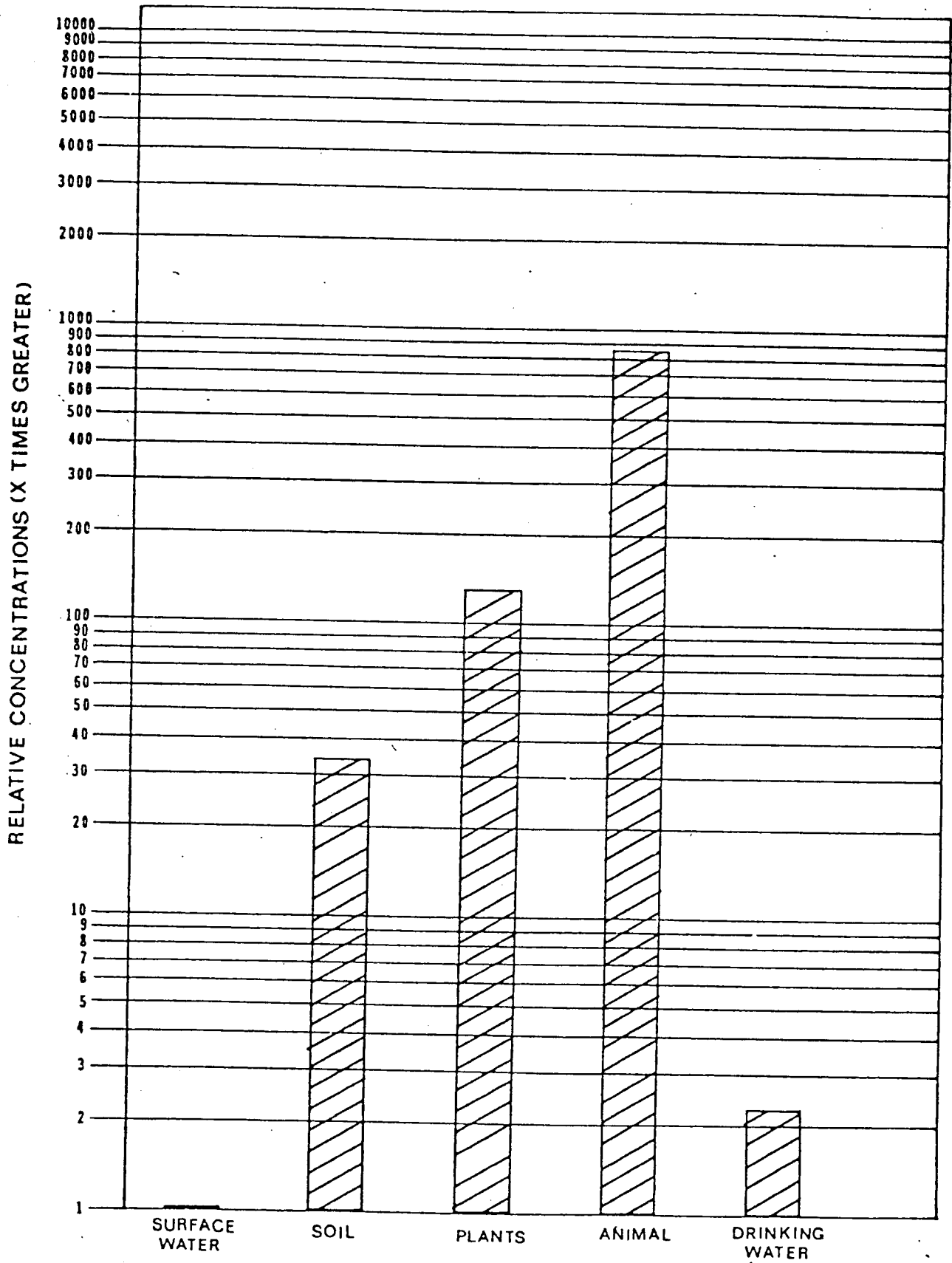
DESCRIPTION	SAMPLE SIZE	AVERAGE (ppm)	STANDARD DEVIATION	COEFFICIENT OF VARIATION	RANGE (ppm)	
					From	To
<u>Study Data</u>						
Surface water, Total	28	0.218	0.265	122	0.0012	0.27
Surface water, Dissolved	27	0.026	0.041	158	0.0009	0.04
Surface water, Sediment	3	1.949	3.335	171	0.001	5.8
<hr/>						
Soils, All Samples	85	7.787	10.600	136	0.16	53.0
Top Soil	47	10.591	11.823	112	0.25	53.0
5 inches deep	38	4.320	9.600	222	0.16	25.0
<hr/>						
Plants, All Samples	17	29.57	17.38	59	3.15	65.0
Dry sites	11	27.34	15.46	57	26.4	65.0
Wet Sites	6	33.65	16.03	48	3.15	53.4
<hr/>						
Animals, All Samples	4	191.1	176.5	92	27.6	429.0
Dry sites - Grubs	2	324.8	147.4	45	220.5	429.0
Wet sites - Minnows	2	28.4	1.1	4	27.6	29.2

Comparison Data

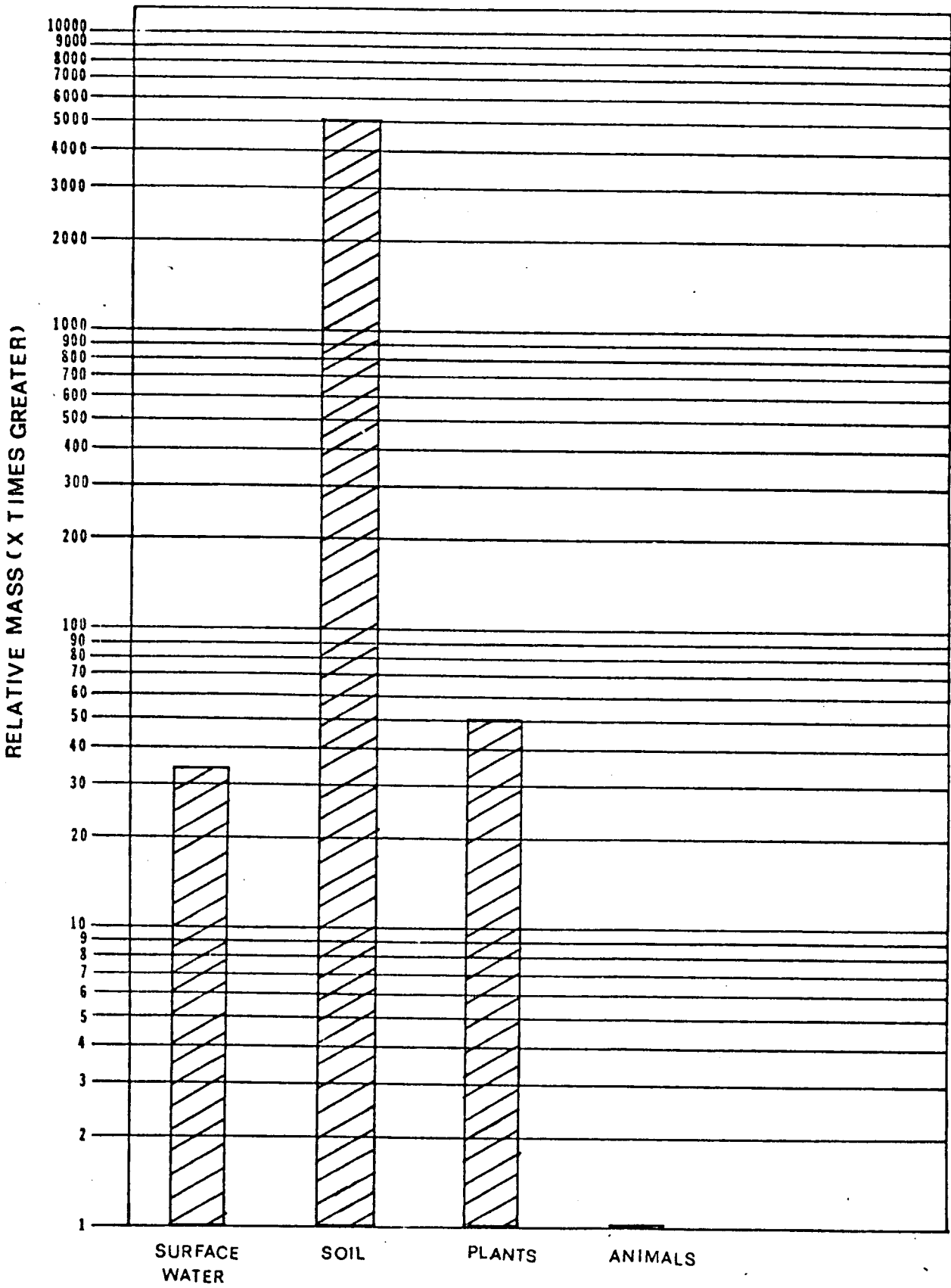
Maximum Contaminant Level (MCL) - Florida Safe Drinking Water Act	-	-	-	-	-	-
Primary - Health	-	0.5	-	-	-	-
Groundwater from Dry Sampling Site I-95	-	-	-	-	-	-
Titusville, FL	-	0.01	-	-	-	-
Upper Floridan Aquifer, Orlando, FL	-	<0.5	-	-	-	-
Lower Floridan Aquifer Orlando, FL	-	<0.005	-	-	-	-
Apalachicola River	-	-	-	-	0.0021	0.0062
<u>Toxicity</u>						
Human	-	2.0 to 4.0 ppm of Lead	-	-	-	-
Guinea Pig	-	1000 ppm of Lead Carbonate	-	-	-	-
Dog	-	300 ppm of Lead Acetate	-	-	-	-

FIGURE 3

RELATIVE LEAD CONCENTRATIONS



RELATIVE LEAD MASS - METER OF HIGHWAY



## DEPTH AND DISTANCE

At every sampling site, metal concentrations decreased with both depth into the soil and distance from the edge of roadway. Using dilute acid extractions, comparison of edge of road surface samples is made with background samples taken 30-40 meters from the edge of pavement. This comparison is shown in Table 6. The concentrations of nickel were below the detection levels in most samples and thus too low for valid comparison purposes. From Table 6 and the summary statistics, it was apparent that lead, zinc, cadmium, and chromium were most likely being retained by the soil and/or roadway concentrations were significant enough to produce differences from background and sub-surface concentrations. Since cadmium was not directly related to automotive wear or use, it was decided to do additional retention studies using total and dilute extraction procedures for lead, zinc, and chromium.

The average lead concentrations with respect to depth and distance from this research are compared with that of 4 other study locations. This study appears to be consistent with other areas as shown in Table 7. The weight of lead is the total extractable lead by concentrated acid solution. In areas where a ditch contained sediment, high metal concentrations were found in the sediment. To determine the mobility or retention of metals, it was necessary to measure additional soil parameters and the most probable physicochemical forms of lead in the soil.

## SOIL CHARACTERISTICS

Fourteen soil samples at seven sites were further analyzed for metal retention capacity. Three metals were examined, namely, lead, zinc and chromium. Bell<sup>3</sup> has a more extensive discussion of these results.

Soil characteristic, including organic matter content, grain size, cation exchange capacity and pH are related to the ability of soil to retain metals. In addition, they give an indication of the classification of soils being analyzed (i.e., sandy, muck, alkaline, etc.), the nature of soils found adjacent to paved areas, and the differences which exist between soils in the shoulder areas relative to those found in ditch areas. The characteristics are summarized in Tables 8 and 9 for each soil sample.

The organic matter content of the soils tested ranged from approximately 0.6 percent to 20 percent by weight. Most samples were between one and six percent organic matter which is typical of mineral soils. Sample S106 taken from a ditch area contained over 20 percent organic matter. Surface samples at three of the edge of pavement sampling sites had higher organic matter contents than subsurface samples reflecting the presence of an organic "muck" layer for plant growth. The samples taken from the ditch areas generally had higher organic matter contents than edge of pavement samples which is likely due to the more well developed vegetation existing in these areas.

Most samples contain small amounts of fine (<0.074 mm) material, generally less than 5 percent. The amount given represents the sum of both silt and clay size particles and additional fine material larger than silt size (>0.020 mm). The USDA textural classification of all samples is "sand".

The soil samples tested had cation exchange capacities ranging from less

TABLE 8  
SOIL CHARACTERISTICS:  
EDGE OF PAVEMENT SAMPLES (2 Depths)

Depth (cm)	Sample	Location <sup>a</sup>	Grain Size <sup>b</sup> (Percent Finer Than 0.074 mm)	Cation Exc. Capacity <sup>c</sup> (meq Ba <sup>++</sup> /100g)	pH <sup>d</sup> (Units)	Percent Organic Matter <sup>e</sup>
2-3	S100	S. R. 50	3.8	3.4	8.2	1.37
2-3	S102	I-95	3.0	5.31	7.7	--
2-3	S108	U. S. 1	4.0	4.35	7.6	2.69
2-3	S110	S. R. 405	1.1	0.82	8.1	1.26
2-3	S112	Turnpike	4.4	--	8.0	1.62
15-20	S101	S. R. 50	3.2	1.91	7.9	0.96
15-20	S103	I-95	11.4	2.40	8.2	3.78
15-20	S109	U. S. 1	1.8	1.49	8.1	0.58
15-20	S111	S. R. 405	1.2	--	8.4	0.87

<sup>a</sup>For a detailed description, see Table IV-1

<sup>b</sup>Percent Passing No. 200 seive

<sup>c</sup>By barium chloride - triethanolamine method of Chapman and Pratt<sup>5</sup>

<sup>d</sup>By 1:1 dilution

<sup>e</sup>By peroxide digestion



TABLE 9  
SOIL CHARACTERISTICS:  
IN DITCH SAMPLES (2 Depths)

Depth (cm)	Location <sup>a</sup>	Percent Filter <sup>b</sup> Than 0.74 mm	Capacity <sup>c</sup> (meq Ba <sup>++</sup> /100 g)	pH <sup>d</sup> Units	Percent Organic Matter <sup>e</sup>
2-3	I-95 (near outfall)	1.8	6.45	7.8	3.01
2-3	I-95	3.3	26.8	4.8	20.5
2-3	Turnpike	1.2	--	5.7	6.37
15-20	I-95 (near outfall)	1.3	6.12	8.0	6.04
15-20	I-95	1.4	5.12	7.3	1.01

<sup>a</sup>For a detailed description, see Table IV-1

<sup>b</sup>Percent Passing No. 200 sieve

<sup>c</sup>By barium chloride - triethanolamine method of Chapman and Pratt<sup>5</sup>

<sup>d</sup>By 1:1 dilution

<sup>e</sup>By peroxide digestion

than one milliequivalent per 100 grams to approximately 27 milliequivalents per 100 grams. Surface edge of pavement soils had higher exchange capacities than subsurface soils at the same locations and surface soils from ditch sites had higher exchange capacities than edge of pavement soils. These cation exchange capacities are representative of sand or sandy loam soils.

A majority of the soil samples are in the moderately alkaline pH range. The highest pH values occur in those samples adjacent to the pavement while two of the ditch samples had the lowest pH values. Low pH values in the ditch samples (S106 and S113) may be the result of organic and inorganic acids from organic matter decay. The ditch samples from near the outfall did not have similar low pH values.

The concentrations of lead, zinc, and chromium as determined for each sample are listed in Tables 10 and 11. The extractable metals are those dissolved in dilute acid solution as described in Appendix B. Total metals are those extracted by a concentrated acid solution. The total metal concentration for each sample was determined by adding the weight of metal extracted from each soil density fraction and dividing by the total weight of the soil sample. In general, the total metal concentrations were approximately an order of magnitude higher than extractable metal concentrations.

A comparison between surface and subsurface samples at the edge of pavement sites shows that large differences in both extractable and total lead concentrations, the subsurface concentration being lowest. It suggests a relative immobility of lead with respect to downward movement into the soil. Two of the three edge of pavement locations at which both surface and subsurface samples were analyzed had higher concentrations of zinc in surface layers. However, the difference in zinc concentration between layers was large only for one location (US-1). The sample from SR-50 (S100) had a higher zinc concentration in the subsurface layer. Thus it is possible, based on limited data that zinc is relatively more mobile than lead with respect to downward movement into the soil. Concentrations of chromium differed little between surface and subsurface layers at edge of pavement sites, suggesting that this metal also may be a relatively mobile metal.

The regression equation developed by Zimdahl and Skogerboe<sup>41</sup> allows a comparison between the capacity for lead fixation and the total lead content of a given soil. The equation, as presented, is:

$$N = 2.81 \times 10^{-6} \text{CEC (meg/100g)} + 1.07 \times 10^{-5} \text{pH} - 4.93 \times 10^{-5}$$

where N is the moles of lead per gram of soil at saturation (maximum capacity). Entering the values for CEC and pH for each sample from Tables 7 and 8, N was calculated to range from  $3.97 \times 10^{-5}$  to  $7.74 \times 10^{-5}$  moles Pb per gram for the soils analyzed in this study. The corresponding concentrations (mg/Kg) range from 8,220 Mg/Kg to 16,030 Mg/Kg. This means that if the soils analyzed in this work behaved similarly to those tested by Zimdahl and Skogerboe,<sup>41</sup> they would have additional capacity to fix lead ranging from 10 to 500 times their existing lead content.

#### ORGANIC MATTER CONTENT

Bell<sup>3</sup> separated the soils of the study area into different density fractions

TABLE 10  
METAL CONCENTRATIONS:  
EDGE OF PAVEMENT SAMPLES (2 Depths)

Depth (cm)	Sample	Location	Extractable Metals <sup>a</sup> (mg/kg)			Total Metals <sup>b</sup> (mg/kg)		
			Lead	Zinc	Chromium	Lead	Zinc	Chromium
2-3	S100	S. R. 50	46.8	7.70	0.105	370	20.6	9.54
2-3	S102	I-95	43.2	14.7	0.101	822	70.1	16.1
2-3	S108	U. S. 1	75.0	7.70	0.263	1320	146	13.8
2-3	S110	S. R. 405	11.4	11.0	0.141	778	58.2	8.89
2-3	S112	Turnpike	--	--	--	51.3	43.9	6.69
15-20	S101	S. R. 50	3.14	1.40	0.137	36.9	35.3	8.60
15-20	S103	I-95	0.20	13.70	0.050	124	68.4	25.2
15-20	S109	U. S. 1	5.12	2.00	0.330	26.6	4.71	9.84
15-20	S111	S. R. 405	1.56	10.0	0.263	--	--	--

<sup>a</sup>Extractable by 0.075 N Acid Solution

<sup>b</sup>By summation of metal extracted from density separations

TABLE 11  
 METAL CONCENTRATIONS:  
 IN DITCH SAMPLES (2 Depths)

Depth (cm)	Sample	Location	Extractable Metals <sup>a</sup> (mg/kg)			Total Metals <sup>b</sup> (mg/kg)		
			Lead	Zinc	Chromium	Lead	Zinc	Chromium
2-3	S104	I-95 (near outfall)	52.0	10.7	0.284	699	93.3	22.2
2-3	S106	I-95	9.40	7.30	0.468	31.8	78.8	8.89
15-20	S105	I-95 (near outfall)	44.8	12.3	0.294	360	62.2	16.4
15-20	S107	I-95	0.99	1.30	0.410	4.88	50.5	6.28

<sup>a</sup>Extractable by 0.075 N Acid Solution

<sup>b</sup>By summation of metal extracted from density separation

to determine the most probable physicochemical form of metal in the soil. A strong correlation (0.95) existed between organic matter and metal content indicating the organic fraction of the soil is of considerable importance for the retention of metals. The percentage of metals contained in the density range less than  $2.0 \text{ g/cm}^3$  is significant. This density fraction is most likely all organic material. Table 12 illustrates the organic matter content of each sample as determined by peroxide digestion and the weight percent of soil in the less than  $2.0 \text{ g/cm}^3$  density range. These percentages are similar. Since the weight percent is less than the percent organic matter, some organic matter must be included in the higher density ranges.

Examination of other soil component density fractions indicated that no single soil characteristic or physicochemical form exists for total metal retention. Illustrated in Table 13 are the average results of density gradient and metal analysis<sup>3</sup>. The averages in general illustrate that the greatest percentages of metals are in the density range between  $2.5$  and  $2.9 \text{ g/cm}^3$  which contains the bulk of the soil (approximately 84 percent). The metals in this density range are most likely absorbed by minerals or in the case of zinc and chromium, they are present as discrete compounds or precipitates. Tables B-2 and B-3 present data for most probable soil components within a density range.

The fraction of soil in the density range less than  $2.0 \text{ g/cm}^3$  contains an average of 30 percent of the lead, 29 percent of the zinc and 32 percent of the chromium, while the bulk of the soil is only 1.1 percent of the total.

The fraction of soil in the density range greater than  $3.3 \text{ g/cm}^3$  contains 28 percent of the lead but a less significant portion of zinc and chromium. These metals are likely in the form of discrete compounds or are associated with dense minerals.

By density separation, it is evident that no single soil characteristic or physicochemical form exist for metal retention. The site specific nature of the soil characteristics and physicochemical reactions are all most likely important.

TABLE 12  
 COMPARISON BETWEEN ORGANIC MATTER CONTENT\*  
 AND WEIGHT PERCENT OF SOIL LESS DENSE THAN 2.0 g/cm<sup>3</sup>

---

<u>Sample</u>	<u>Percent Organic Matter</u>	<u>Weight Percent of Soil 2.0g/cm<sup>3</sup></u>
S100	1.37	1.4
S101	0.96	0.6
S103	3.78	1.8
S104	3.01	2.1
S105	6.04	2.5
S106	20.48	14.0
S107	1.01	0.7
S108	2.69	3.4
S109	0.58	1.2
S110	1.26	3.3
S112	1.62	3.4
S113	<u>6.37</u>	<u>3.6</u>
AVERAGE	4.10	3.2

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From Reference 3

\*Organic Matter Content Determined by Peroxide Digestion

TABLE 13

RESULTS OF DENSITY GRADIENT ANALYSIS:  
AVERAGE FOR ALL SAMPLES<sup>3</sup>

Density Range (g/cm <sup>3</sup> )	Average Weight Fraction of Soil (%)	Lead % of Total <sup>*</sup>	Zinc % of Total <sup>*</sup>	Chromium % of Total <sup>*</sup>
< 1.5	1.1	18.4	16.2	15.1
1.5 - 2.0	2.3	11.8	13.4	17.0
2.0 - 2.5	11.7	10.7	12.7	16.3
2.5 - 2.9	83.8	27.1	36.2	37.6
2.9 - 3.3	0.5	4.2	7.2	5.9
> 3.3	0.6	27.8	14.3	8.1

<sup>\*</sup> Average percent of bulk total metal in all samples.

## CHAPTER V. RESULTS OF HYDROCARBON STUDIES

The sampling locations for the hydrocarbon degradation studies were the same as those used for the metal analyses along I-95 and I-75. Hydrocarbon retention within the shoulder and ditch areas is a function of the quantity of volatile compounds, weathering (no biological) processes, and biological degradation. Highly volatile compounds will be dispersed within a short period of time (minutes) and the more weather resident hydrocarbons will be subject to biological degradation.

The diversity of hydrocarbon utilizing bacteria were documented for 3 roadside environments. The different kinds of bacteria present in the three environments are shown in Table 14.

TABLE 14

### HYDROCARBON BACTERIA ISOLATED FROM SHOULDER AND DITCH ENVIRONMENTS

Shoulders - Minimum Overland Flow (0, 1, 1.8, 2.5, 3 and 6 meters from edge of pavement)	<u>P. aeruginosa</u>
Shoulders - Overland Flow - High water table area (6 meters from edge of pavement)	<u>P. testosteroni</u> <u>P. alcaligenes</u> <u>Z Pseudomonas</u> like organisms
Ditches, 15 cm of water (8 meters from edge of pavement)	<u>P. pseudomallei</u> <u>P. fluorescens</u> <u>P. fluorescens</u> like <u>Flavobacterium</u> sp. <u>Pseudomonas</u> sp.

Diversity is more evident in the aerobic ditch and overland flow shoulder areas. Substrate is more available in these areas and should have an effect on diversity and total number of bacterial populations. Total counts of heterotrophic and petroleum degrading bacteria were determined at various distances from the edge of pavement and average values are presented in Table 15. With distance from the edge of pavement, the percentage of hydrocarbon degrading bacteria decrease until the ditch area is encountered. The ditch area populations of hydrocarbon degrading bacteria are similar to the edge of pavement populations.



TABLE 15  
Average Bacterial Populations Along I-95 Near Titusville

Distance from Edge of Road (Feet)	Total Count of Heterotrophic Population (#/g soil)	Hydrocarbon Degrading Bacteria (#/g soil)	Percent of Total Population Capable of Hydrocarbon Degradation (%)
0.0	$3.7 \times 10^6$	$3.2 \times 10^6$	86.5
2.5	$2.5 \times 10^6$	$1.5 \times 10^6$	60.0
5.0	$2.0 \times 10^6$	$4.7 \times 10^5$	23.5
10.0*	$3.1 \times 10^6$	$2.3 \times 10^6$	74.0
20.0	$2.3 \times 10^6$	$4.2 \times 10^5$	18.0

\* Area of Ditch at the dry site

NOTE: 4 sampling events, one each in January, February, March and April of 1977.

In this area the soils had high percolation rates. Thus, substrate for the hydrocarbon utilizing bacteria were more available in the edge of pavement and ditch areas. Overland flow in shoulder areas of good percolation can promote hydrocarbon degradation before discharges to adjacent highway environments.

Substrate is not the only limiting factor for hydrocarbon degradation. Nutrient availability, predation, temperature, and toxic metal effects are limiting factors. A typical plot of hydrocarbon utilizing bacteria, substrate and nutrients with distance from edge of pavement is shown in Figure 5.

Total nutrients in the form of total trivalent nitrogen and total phosphates decrease with distance from the pavement. The concentration of nitrogen in roadside soils are 94 percent less at 40.0 feet distance from the highway than at 0.0 feet. Nitrogen compounds are present as a constituent of highway runoff. The concentration of phosphate is 70 percent greater at 0.0 feet than at 40.0 feet distance from the highway. Areas of the roadside environment not exposed to surface runoff (40.0 feet) have decreased nutrient concentration, hydrocarbon utilizing bacteria, and little substrate.

Hydrocarbon utilizing bacteria in the shoulder areas increase with increasing rainfall and thus rainfall excess (runoff). Bacteria concentrations at the edge of pavement are 90 percent higher during the rainy season (June-September) than during the dry months of May and June. Hydrocarbon utilizing bacterial populations at other distances from the edge of pavement also increase during wet weather relative to dry weather conditions. These positive correlations are shown in Figure 6.

Biological hydrocarbon degradative potentials were measured by inoculating known concentrations of mixed hydrocarbon substrates (kerosene) with the hydrocarbon utilizing bacteria from the I-75 and I-95 roadside environments. After 60 days degradation, the remaining hydrocarbons were estimated by integration under the chromatograph curve. A typical chromatograph is illustrated in Figure 7. Generally, the gasoline and part of the kerosene will weather. Under optimum conditions, the bacteria associated with the edge of pavement are capable of degrading at most 48 percent of the mixed hydrocarbon substrates. Biological degradation potential is related to species diversity, bacterial concentration, and total nutrients. All these factors decrease with distance from the pavement.

The biological degradative potential of various wet roadside environments (overland flow, aerobic ditch, wet ditch) exceeds the potential of the dry shoulder environments. Figure 8 illustrates the comparison of three wet roadside environments. The environments degraded all the substrate. Ninety-nine percent of the mixed hydrocarbon substrates were degraded within 60 days by bacteria present within wet roadside environments. Figure 9 is the chromatographic tracing of kerosene remaining after 60 day degradation by bacteria found in the water from wet roadside environments. The area under these tracings correspond to the degradative potential of the wet roadside environments given in Figure 8. The hydrocarbon degradation potential was measured in micrograms kerosene degraded after 60 days incubation at optimum conditions.

The weathered kerosene tracing represents the sterile control which takes into account the volatilization effects and chemical weathering. It should be

FIGURE 5  
OVERLAND FLOW WITH NUTRIENT AND SUBSTRATE AVAILABILITY

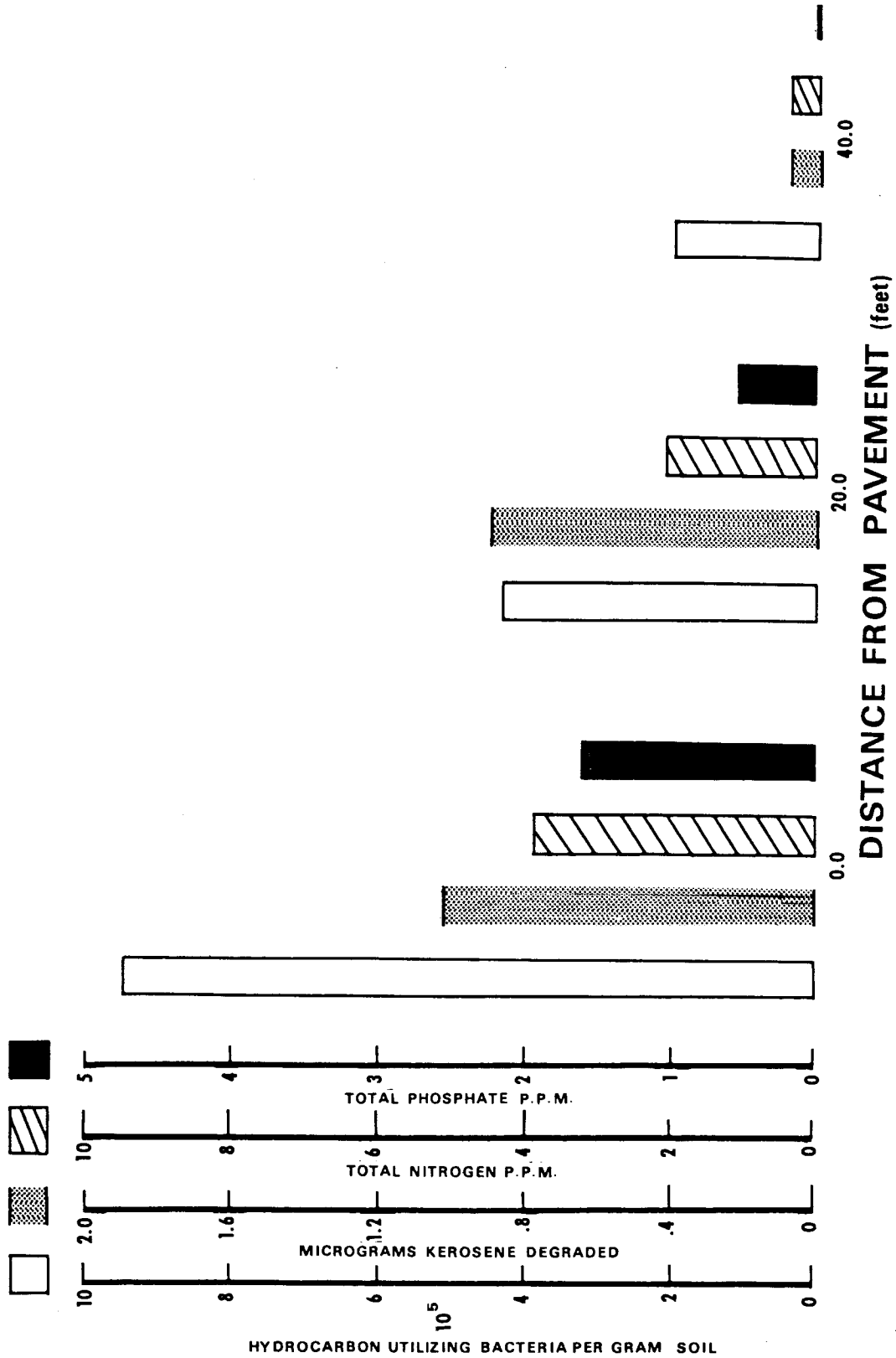


FIGURE 6  
RAINFALL - HYDROCARBON UTILIZING BACTERIAL POPULATIONS

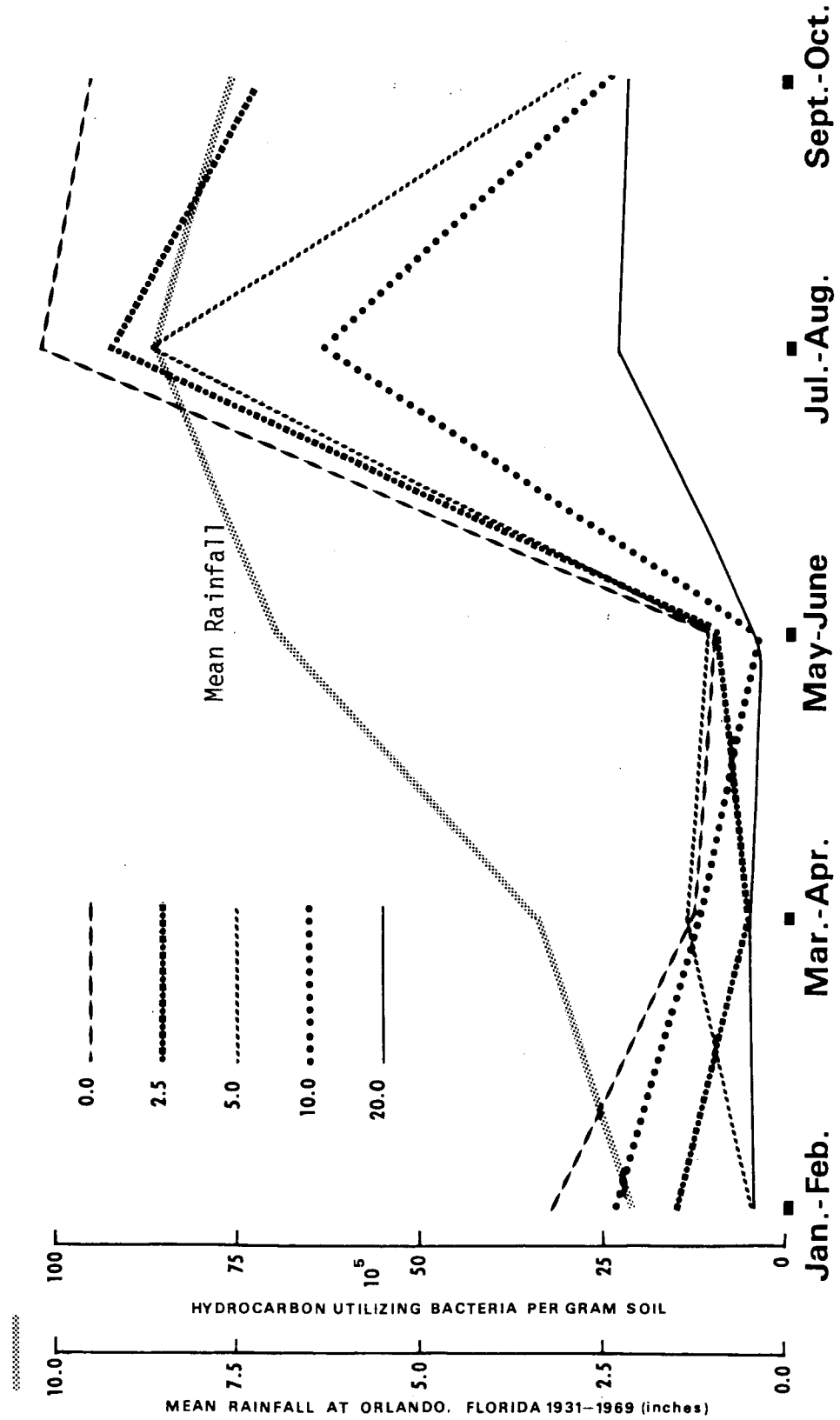


FIGURE 7

**IDEALIZED CHROMATOGRAPH**  
**3% DEXSIL 300, 100/120 CHROMO WHP**  
**1/8" x 6 FT. COLUMN, FLAME IONIZATION DETECTOR**  
**HEWLETT PACKARD MODEL 5750**

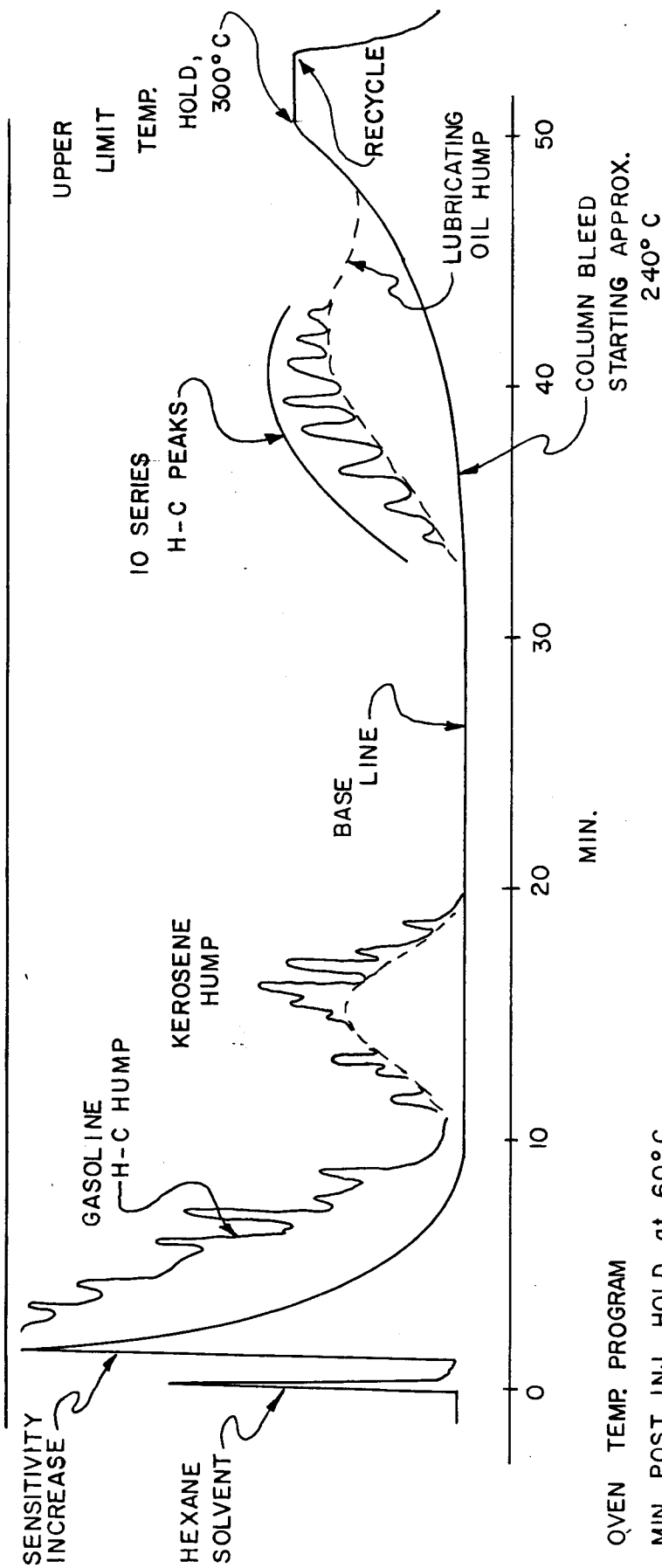


FIGURE 8  
WET ROADSIDE ENVIRONMENTS AND HYDROCARBON DEGRADATION

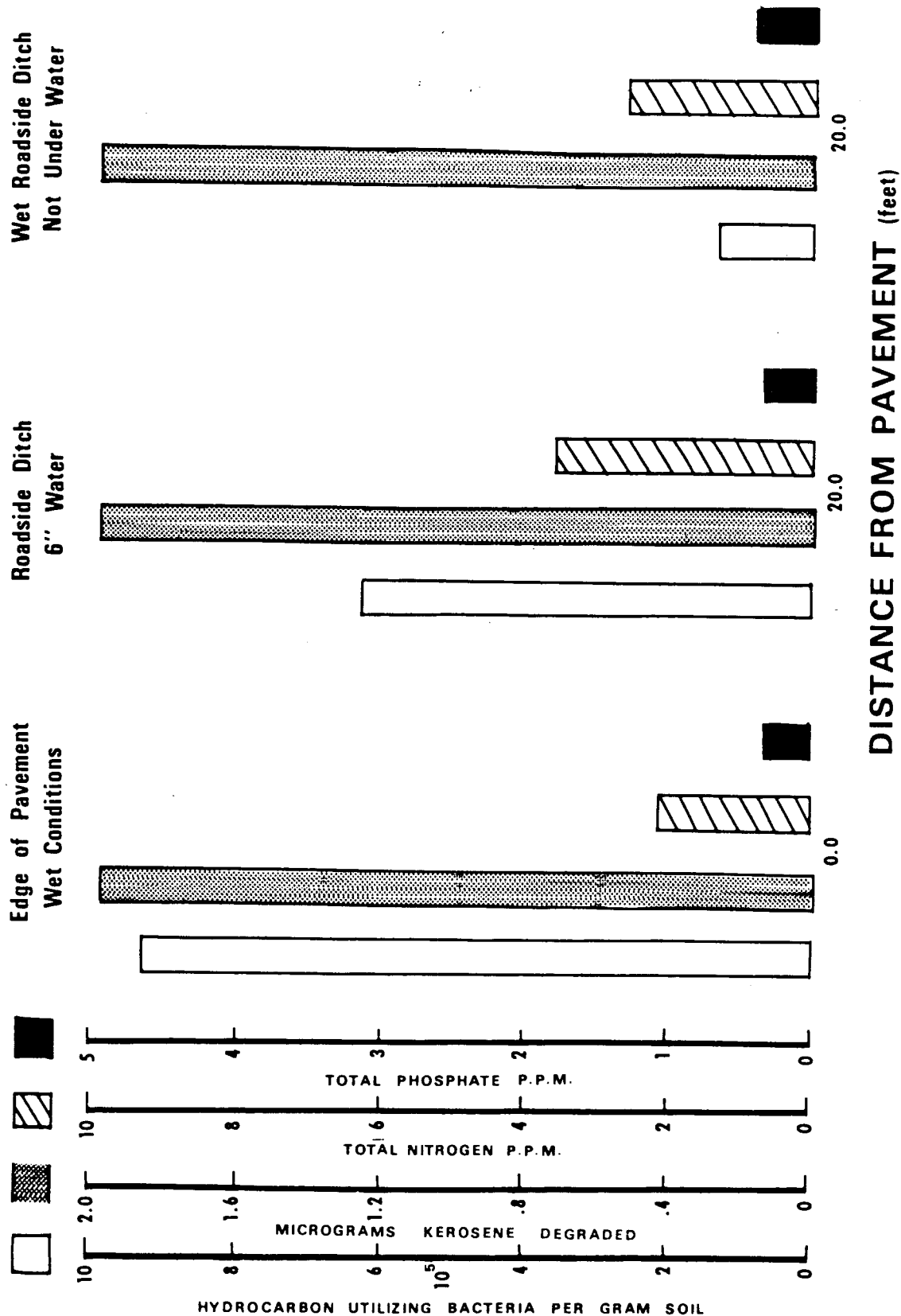
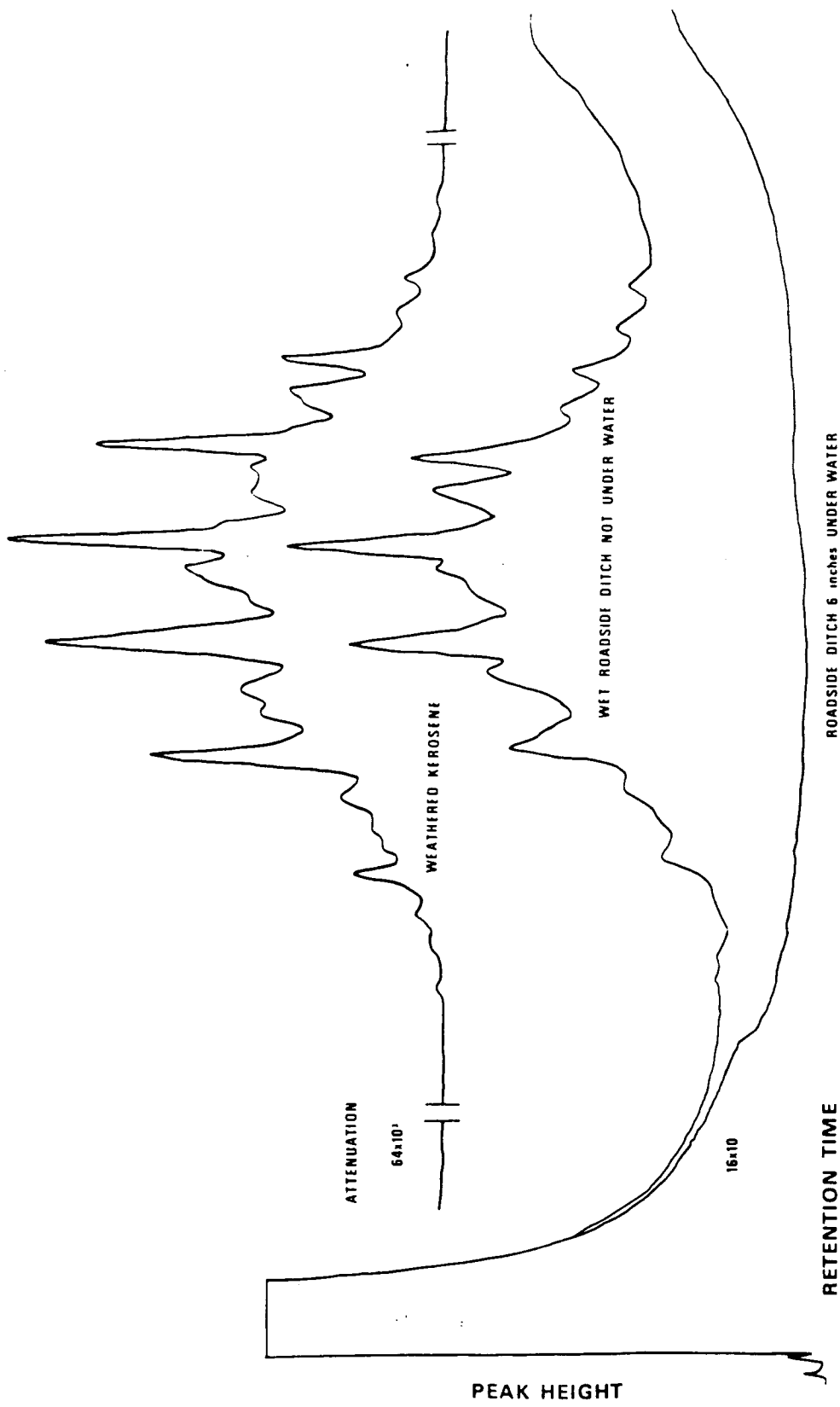


FIGURE 9  
COMPARATIVE CHROMATOGRAPHS



noted that control has a concentration 400 times greater than the degraded samples.

The chromatographic tracings of kerosene degraded by bacteria associated with roadside ditches with 15 centimeters depth of water indicate that degradation was extremely efficient. These water environments were aerobic. Virtually, all hydrocarbon substrates were degraded at the end of 60 days. Wet shoulders at the edge of pavements (not under water) were also 99 percent effective in degrading the hydrocarbons. However, various classes of hydrocarbons usually the 10 series persist in small concentrations.

Aerobic microorganisms using oxidative pathways are the principal hydrocarbon decomposers found in nature. Free or dissolved oxygen is essential for optimum degradation. The surfaces of soils and shallow wet ditches have an oxygen tension sufficiently high to support aerobic bacterial growth and hydrocarbon decomposition. When anaerobic conditions are present in the roadside environment, oxidative degradation is reduced significantly and probably ceases.

Anaerobic bacteria are not as efficient in oxidizing hydrocarbons as their aerobic counterparts. A few highly specialized sulfur reducing bacteria utilize hydrocarbons under anaerobic conditions. These specialized anaerobes require sulfur for metabolism and can only utilize a limited class of sulfur containing hydrocarbons.



## CHAPTER VI. HYDROLOGIC CONSIDERATIONS

To limit the quantity of pollutants discharged from a highway right-of-way, the infiltration characteristics of the shoulders can be used to retain some metals and promote hydrocarbon degradation by weathering and biological activity. The more mobile metals and other potential pollutants can be retained in shallow water ditches where most metals will deposit in the sediment and the hydrocarbons will undergo biological degradation. When shoulders or earthen areas are not available for overland flow, such as rainfall excess (runoff) from bridge or limited right-of-way areas, then retention ponds with underdrains or natural percolation would be valuable for treating the first flush of stormwater. The major question is what size (Acre-Feet) and area (Acre) should be allocated for retention of stormwaters? Other stormwater treatment methods are available and should be examined before the use of shallow-water ditches or retention ponds are constructed.

A general equation to express the allocation of waters within a highway right-of-way would be:

$$R_T = R_{RW} + R_0$$

where:

$R_T$  = total runoff needing treatment, volume measure

$R_{RW}$  = runoff from right-of-way, volume measure

$R_0$  = runoff from outside of the right-of-way, volume measure

At the beginning of a storm event, the precipitation infiltrates into the ground, is stored in surface depressions or is otherwise abstracted. Rainfall intensity and distribution is variable during a storm producing variable runoff quantities. Eventually, a saturation level is reached and runoff water is equivalent to precipitation. Thus, the highway shoulders and ditches receive runoff at a variable rate but the volume of runoff for a storm can be predicted. Depending on the water table and soil water conditions, the runoff waters will percolate or remain on the surface as rainfall excess (runoff).

The factors which affect the amount of runoff from a given area are intensity and duration of rainfall, soil drainage characteristics, amount of vegetative cover, amount of impervious surfaces (i.e. pavement), and topographic characteristics (i.e. slopes, depressions, etc.). There are numerous mathematical formulas which have been developed to model rainfall-runoff relationships. One such formula has been developed by the Soil Conservation Service (SCS) for use on urban watersheds. It is also useful for predicting roadway runoff and will be applied here as an illustrative example.

### EXAMPLE: PART 1

Consider a section of roadway 94 feet wide with 34 feet of paved or otherwise impervious area. The length of roadway drainage is 2424 feet (similar to

the I-95 area). The entire area drains by overland flow into an outfall at the lowest elevation.

The runoff from this highway section during a storm event is calculated as follows using the SCS procedure<sup>31</sup>.

1. From an evaluation of soil type, soil moisture, ground cover, and percent impervious area, a weighted curve number is established. The curve number is used to estimate the potential for infiltration and the total infiltration or saturation capacity of a soil. For the roadway under consideration it is assumed the soil is type B (moderately well drained) under average moisture conditions (condition 2). The ground cover is assumed to be fair grass over 50-75% of the pervious area. The percent of impervious area is 36. The weighted curve number is determined as follows:

<u>Land Type</u>	<u>Percent of Total Area</u>	<u>Curve Number (CN)*</u>	<u>Weighted Curve Number</u>
Pavement . . . . .	36	90	32
Pervious (grassed slope and ditch) . . .	64	69	<u>44</u>

\*From reference 31 or 11

Total CN = 76

2. The total storage,  $S'$ , (initial abstraction, infiltration and evapotranspiration) is then estimated using the formula

$$S' = \frac{1000}{CN} - 10 = \frac{1000}{76} - 10$$

$$S' = 3.16 \text{ inches}$$

3. Using this storage term, the runoff,  $Q$ , is calculated as follows:

$$Q = \frac{(P - 0.2S')^2}{P + 0.8S'}$$

where  $P$  is the amount of precipitation in inches. Substituting the value obtained for  $S'$ :

$$Q = \frac{(P - 0.63)^2}{P + 2.53}$$

and for a 3-inch rainfall (1 in 10 year storm)

$$Q = \frac{(3 - 0.63)^2}{3 + 2.53} = 1.01 \text{ inches}$$

4. If it were decided to store the 1.01 inch of runoff, the volume of storage required is traditionally calculated using:

$$\text{Volume} = \text{Area} \times \text{Runoff (in)} / 12(\text{in/ft})$$

$$\text{FT}^3 = (2424 \times 94) \times 1.01/12 = 19178$$

or Volume = 0.44 AC-FT

#### VOLUME CALCULATIONS CONSIDERING ANTECEDENT CONDITIONS

The problem with the above calculation is the fact that the volume is considered sufficient to store all the runoff water for each storm event. During the rainy season, a storm of different quantities may occur each day for a long period of time (weeks). Water in the storage area will be displaced into adjacent lands or surface water bodies. This displaced water will carry pollutants. If the water stored could be treated before the next storm event producing runoff, then the storage capacity of the holding area is available.

Work completed by Wanielista<sup>11,39</sup> for the East Central Florida Regional Planning Council indicated that diversion of first flush stormwaters into percolation ponds, underdrained storage areas, and overland flow with percolation are cost-effective. In roadway right-of-ways, these land areas are already available in most cases, thus additional land purchases may not be necessary making diversion for percolation, underdraining, or overland flow much more cost effective. Coaxial graphs to aid in computing the volume of treatment (storage) as a function of watershed area, soil percolation, curve number, and depth of pond were developed. These equations considered the antecedent conditions of rainfall using data for the Florida Environment. The coaxial graphs were difficult to use and not available for watershed areas greater than 150 acres. Therefore, the coaxial graphs were extrapolated for larger watersheds and series of equations were developed using bi-variate regression analysis. The correlation coefficients for the bi-variate equations were never less than 0.97. For two types of soil drainage conditions in the ditch or pond areas, the equations for estimating "pond" volume are shown in Tables 16 and 17.

It has been suggested in previous chapters to maintain shallow aerobic water conditions. Thus, a one foot deep ditch adjacent to a roadway would most likely be aerobic and percolate fast during and after runoff conditions. Other depths are also possible up to 5 feet for type A soils and 3 feet for type D soils. These maximum depths were established to drain the areas by percolation to prevent mosquito breeding problems.

If overland flow into ditches parallel to the roadway surface is the design, and the first inch of every stormwater runoff can be stored and treated, then the quantity of pollutants removed from direct surface discharge to adjacent lands and water bodies is about 99 percent of yearly runoff mass<sup>11</sup>. This level of treatment is more efficient than most advanced wastewater treatment processes for industrial and sewage wastes. However, the shoulders and ditches must be designed to always retain the first runoff volume.

When conduits are used to transport a number of first flushes entering the conduit at various areas (and times) the concept of first flush is no longer valid because the pollution concentrations are random. In this case, the efficiencies calculated from cumulative runoff distributions for associated rational runoff coefficients are shown in Table 18. These efficiencies would be

TABLE 16

POND VOLUME FOR TYPE "A" SOILS

For "A" Soils in Percolation Pond Area (Minimum Percolation Rate = 1.0"/hr)

Diversion Volume (Inches)	P O N D V O L U M E (AC-FT)				Pond Depth = 1 Foot
	5 Feet Deep Pond Impervious Watershed	5 Feet Deep Pond Composite Land Use	1 Ft < Pond Depth < 5 Ft Composite Land Use		
0.25	$V_I = 0.016(A)^{1.28}$	$V_5 = V_I (0.59 + 0.37 \frac{CN}{100})$	$V_D^A = V_m + \frac{(V_5 - V_m)(D-1)}{4}$	$V_m = \frac{A \times DI}{12}$	
0.50	$V_I = 0.046(A)^{1.18}$				
0.75	$V_I = 0.09(A)^{1.11}$				
1.00	$V_I = 0.14(A)^{1.07}$				
1.25	$V_I = 0.20(A)^{1.04}$				

where:  $V_m$  = minimum basin volume (AC-FT)

A = contributing watershed area (AC)

DI = diversion volume (IN)

12 = conversion factor (IN/FT)

$V_D^A$  = volume of basin at depth "D" in Type "A" soil (AC-FT)

D = depth of basin (FT)

CN = composite curve number

$V_5$  = basin volume at 5" Depth (AC-FT)

$V_I$  = basin volume for impervious area, 5' Depth, (AC-FT)

TABLE 17

Pond Volume For Type "D" Soils

For "D" Soils in Percolation Pond Area (Minimum Percolation Rate = 0.25"/hr)

Diversion Volume (Inches)	P O N D V O L U M E (AC-FT)			Pond Depth =0.5 Feet
	3 Feet Deep Pond Impervious Watershed	3 Feet Deep Pond Composite Land Use	0.5 Ft<Pond Depth<3 Ft Composite Land Use	
0.25	$V_I = 0.02(A)^{1.31}$	$V_3 = V_I (0.07 + 0.92 \frac{CN}{100})$	$V_D = V_m + \frac{(V_3 - V_m)}{2.5} (D - 0.5)$	$V_m = \frac{AxDI}{12}$
0.50	$V_I = 0.05(A)^{1.24}$			
0.75	$V_I = 0.13(A)^{1.11}$			
1.00	$V_I = 0.20(A)^{1.07}$			
1.25	$V_I = 0.29(A)^{1.04}$			

where:  $V_m$  = minimum basin volume (AC-FT)  
 $A$  = contributing watershed area (AC)  
 $DI$  = diversion volume (IN)  
 $12$  = conversion factor (IN/FT)  
 $V_D^D$  = volume of basin at depth "D" in Type "D" soil (AC-FT)  
 $D$  = depth of basin (FT)  
 $CN$  = composite curve number  
 $V_3$  = basin volume at 3' Depth (AC-FT)  
 $V_I$  = basin volume for impervious area, 3' Depth, (AC-FT)

applicable to large sewerred areas.

TABLE 18

YEARLY MASS REMOVAL EFFICIENCIES

Conduit System (no first flush)	% Efficiency			Diversion Volume (inches)
	*c=0.8	c=0.4	c=0.2	
	96	95	90	1.25
	95	93	82	1.00
	93	90	72	0.75
	90	82	60	0.50
	82	60	40	0.25

\*c is the rational coefficient in  $Q = c i A$

Table 18 was developed using rainfall data at the Tallahassee Airport. This was the rainfall data producing the least efficiency between Orlando Jetport and Tallahassee Airport data. Orlando has fewer storms or less intensity duration and quantity. The Orlando area efficiencies are estimated to be at least 2-4 percent higher than Table 18.

EXAMPLE: PART 2

For the previous example, calculate the required ditch volume if the ditch on the average is one foot deep and the percolation rate is estimated at a minimum of 1/4 inch per hour. It is desired to store and treat at least one inch of runoff. Using Table 17, one calculates the needed volume as:

$$V_1 = 0.20 (5.23)^{1.07} = 1.17 \text{ AC-FT}$$

$$V_3 = 1.17 (0.07 + 0.92 \frac{76}{100}) = 0.90 \text{ AC-FT}$$

$$V_1 = \frac{5.23(1)}{12} + \frac{(0.90 - 0.44)}{2.5} (0.5) = 0.54 \text{ AC-FT}$$

Therefore, at a one foot depth, the area of ditch is 0.54 Acres. For a 2424 feet long area, the width of the ditch is 9.7 feet, or rounded to 10 feet.

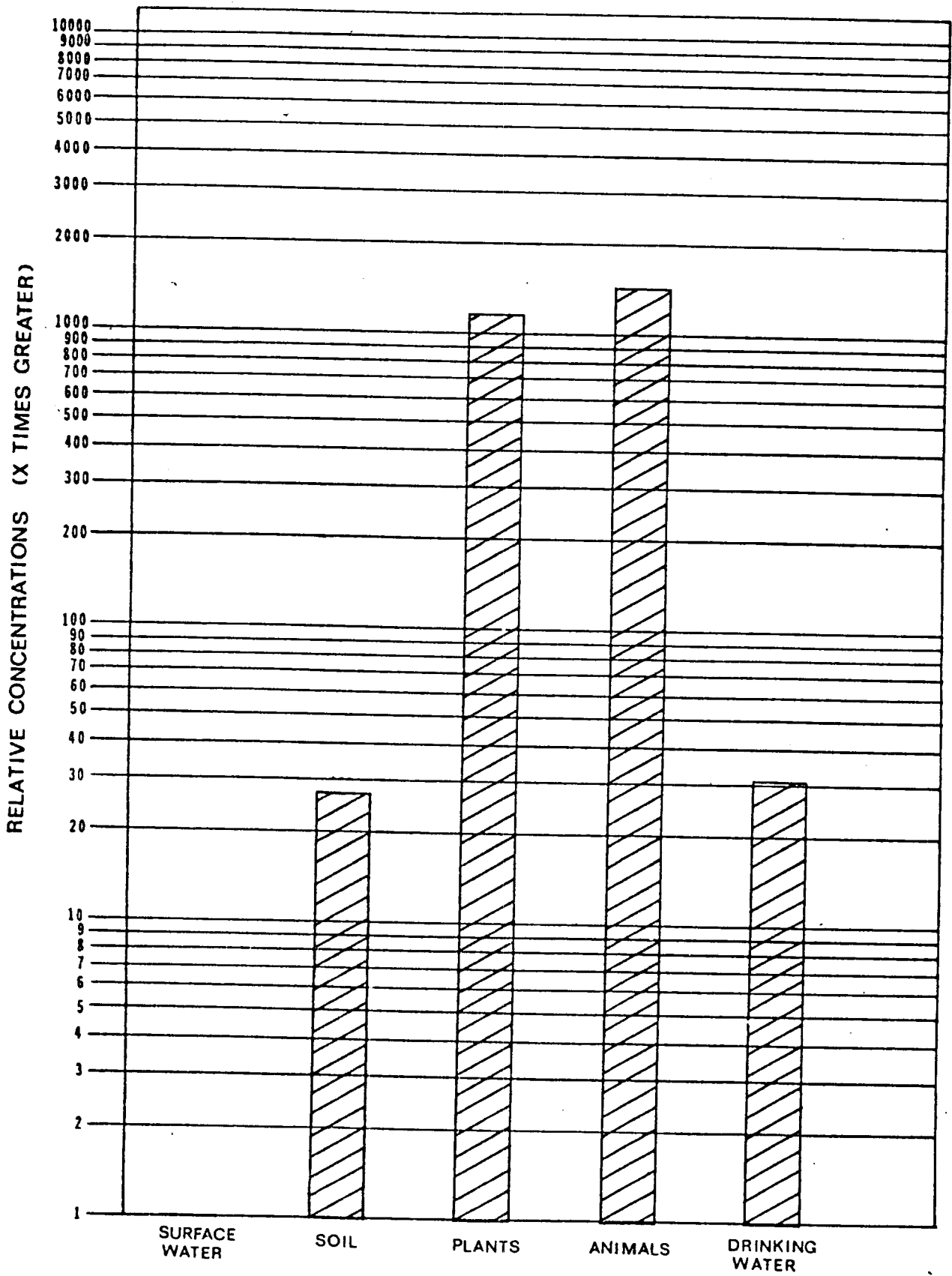
Overland flow of highway runoff into a ditch parallel to a roadway can be designed using the equations of this chapter. If no percolation is available in the ditch area, then consideration should still be given to overland flow with possibly a 1-2 deep ditch occupying a larger area. It is believed that the metals and hydrocarbons from highway runoff can be retained for the most part in the right-of-way areas.

## APPENDIX A. METAL CONCENTRATIONS AND MASS

TABLE A-1  
COPPER SUMMARY STATISTICS  
CONCENTRATIONS

DESCRIPTION	SAMPLE SIZE	AVERAGE (ppm)	STANDARD DEVIATION	COEFFICIENT OF VARIATION	RANGE (ppm)	
					From	To
<u>Study Data</u>						
Surface water, Total	16	0.033	0.069	209	0.0124	0.228
Surface water, Dissolved	15	0.023	0.010	43	0.0076	0.034
Soils, All Samples	24	0.688	0.310	45	0.10	1.38
Top soil	11	0.700	0.290	41	0.40	1.28
5 inches deep	8	0.510	0.220	43	0.10	0.87
2 inches deep	5	0.950	0.320	34	0.65	1.38
Plants, All Samples	18	36.3	18.6	51	15.0	84.0
Dry sites	7	48.3	26.6	55	15.0	84.0
Wet sites	11	28.7	8.2	29	23.5	46.0
Animals, All Samples	4	43.4	28.8	66	3.7	72.7
Dry sites - Grubs	2	61.5	15.8	26	50.4	72.7
Wet sites - Minnows	2	25.2	30.4	121	3.7	46.7
<u>Comparison Data</u>						
Maximum Contaminant Level (MCL) - Florida Safe Drinking Water Act	-	-	-	-	-	-
Secondary - Esthetic	-	1.0	-	-	-	-
Groundwater Under Stormwater Percolation Pond	3	0.069	-	-	-	0.120
Winter Park	-	-	-	-	-	-
Upper Floridan Aquifer, Orlando, FL	1	0.0025	-	-	-	-
Apalachicola River	-	0.0018	-	-	0.0021	0.0051
<u>Toxicity</u>						
Human - 10,000 ppm of Copper	-	-	-	-	-	-
Dog - 400 mg/day of Cupric Sulfate	-	-	-	-	-	-
Rat - 140 ppm of Cuprous Nitrate	-	-	-	-	-	-

RELATIVE COPPER CONCENTRATIONS





RELATIVE COPPER MASS - METERS OF HIGHWAY

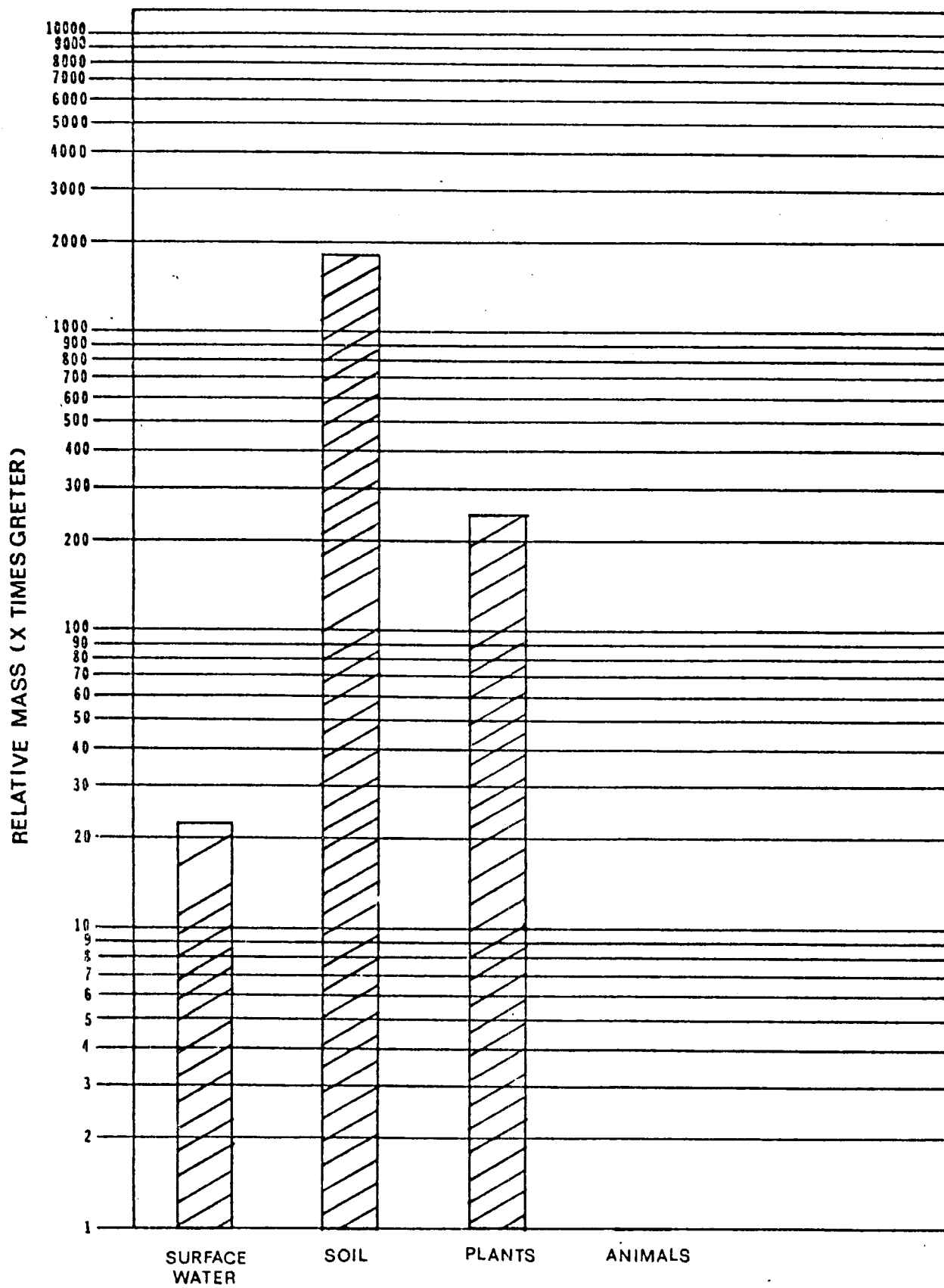


TABLE A-2  
ZINC SUMMARY STATISTICS  
CONCENTRATIONS

DESCRIPTION	SAMPLE SIZE	AVERAGE (ppm)	STANDARD DEVIATION	COEFFICIENT OF VARIATION	RANGE (ppm)	
					From	To
<u>Study Data</u>						
Surface water, Total	28	0.056	0.099	177	0.012	0.165
Surface water, Dissolved	25	0.053	0.093	175	0.012	0.135
Surface water, Sediment	3	0.381	0.614	161	0.019	1.09
Soils, All Samples						
	87	7.765	7.940	102	0.45	49.0
Top soil	47	10.327	10.823	105	1.90	49.0
5 inches deep	40	4.755	4.548	96	0.45	19.5
Plants, All Samples						
	18	51.24	25.71	50	5.6	130.1
Dry sites	11	46.54	29.09	63	5.6	90
Wet Sites	7	58.63	23.78	41	30.1	130.1
Animals, All Samples						
	4	490.3	217.2	44	197.2	664.3
Dry sites - Grubs	2	549.8	135.3	25	454.1	645.5
Wet sites - Minnows	2	430.8	330.3	77	197.2	664.3

Comparison Data

Maximum Contaminant Level (MCL) - Florida Safe Drinking Water Act	-	-	-	-	-	-
Secondary - Esthetic	-	5.0	-	-	-	-
Groundwater 1½-3 feet under a Stormwater Percolation pond, Winter Park	3	0.21	-	-	-	0.33
Upper Floridan Aquifer, Orlando, FL	-	<0.20	-	-	-	-
Lower Floridan Aquifer, Orlando, FL	-	0.02	-	-	-	-
Southeast Water Basin, (USA)	-	0.052	-	-	-	-
<u>Toxicity</u>						
Human - 45,000 mg of Zinc Sulfate and 6,000 mg of Zinc Chloride						
Dog - 8-16 mg of Zinc Sulfate						
Rat - 350 ppm of Zinc Chloride						
Fish - 45 ppm of Zinc Sulfate (except minnows)						

TABLE A-3  
CHROMIUM SUMMARY STATISTICS

DESCRIPTION	SAMPLE SIZE	AVERAGE (ppm)	STANDARD DEVIATION	COEFFICIENT OF VARIATION	RANGE (ppm)	
					From	To
<u>Study Data</u>						
Surface water, Total	16	0.009	0.017	189	<0.003	0.07
Surface water, Dissolved	15	0.007	0.009	129	<0.003	0.03
Soils, All Samples	83	0.204	0.185	91	0.004	1.0
Top soil	45	0.175	0.161	92	0.037	1.0
5 inches deep	38	0.239	0.195	82	0.004	0.32
Plants, All Samples	19	2.49	1.51	61	0.473	8.70
Dry sites	12	2.76	3.83	139	1.64	8.70
Wet sites	7	2.03	1.22	61	0.473	4.60
Animals, All Samples	4	15.28	17.86	117	2.23	40.99
Dry sites - Grubs	2	22.59	26.03	115	4.18	40.99
Wet sites - Minnows	2	7.97	8.12	102	2.23	13.71
<u>Comparison Data</u>						
Maximum Contaminant Level (MCL) - Florida Safe Drinking Water Act						
Primary - Health		0.05				
Groundwater 1½-3 feet under a Stormwater Percolation Pond, Winter Park	3	0.005				0.006
Upper Floridan Aquifer, Orlando, FL		<0.2				
Lower Floridan Aquifer, Orlando, FL		<0.005				
Apalachicola River					0.002	0.0078
Toxicity						
Rat - 500 ppm Cr <sup>6+</sup>						
Fish - 5-200 ppm Cr						

FIGURE A-3

RELATIVE ZINC CONCENTRATIONS

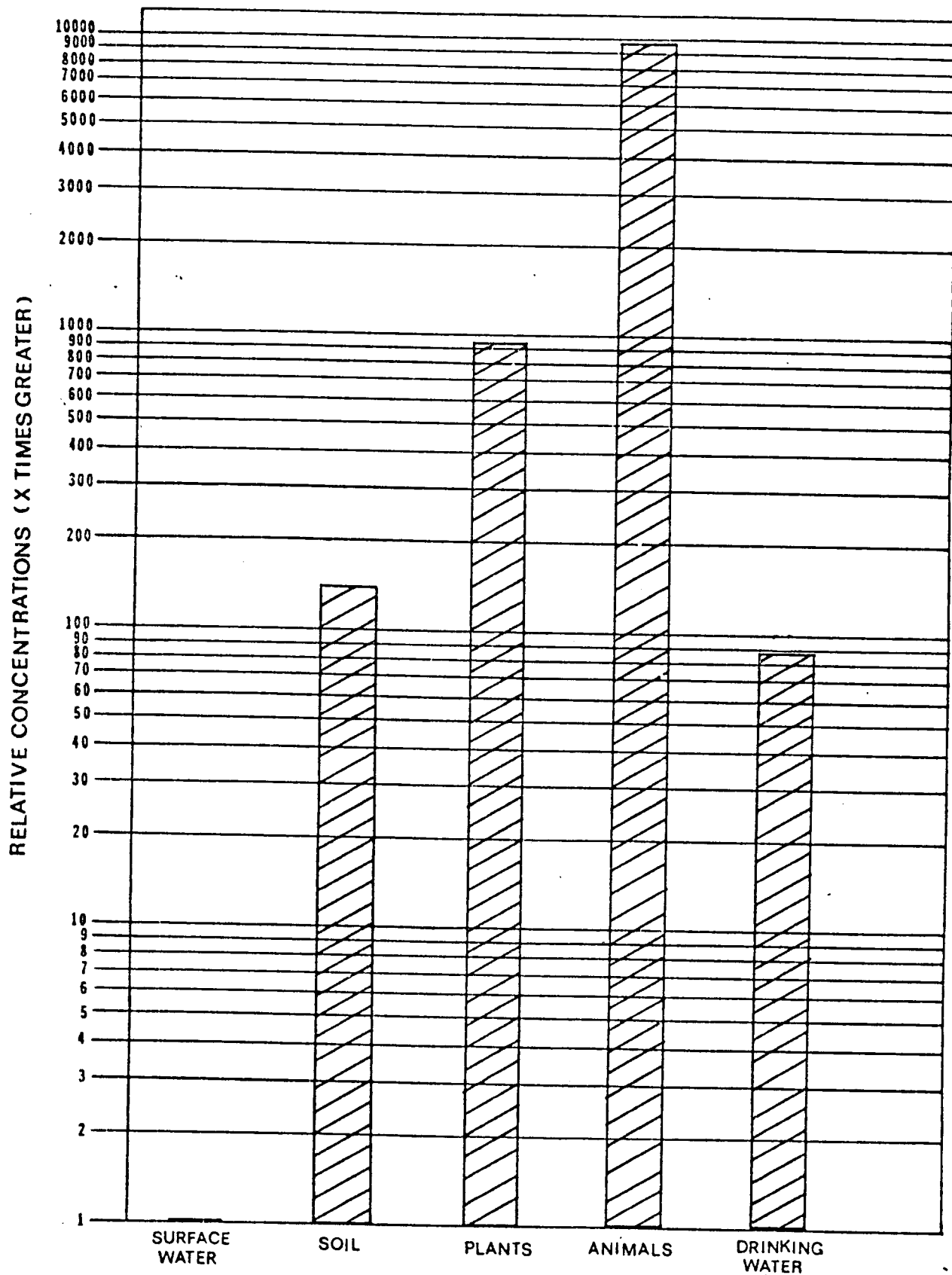
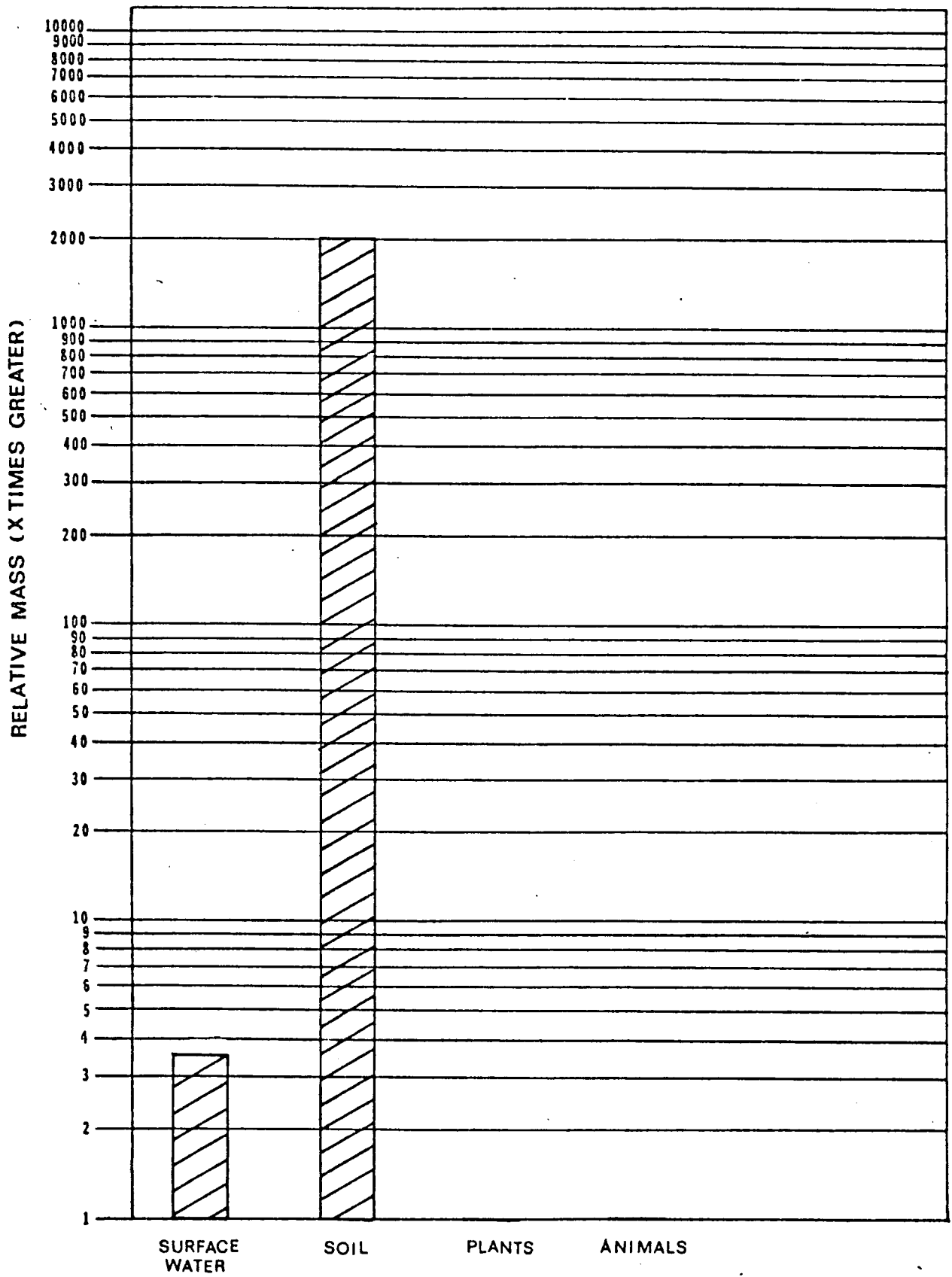
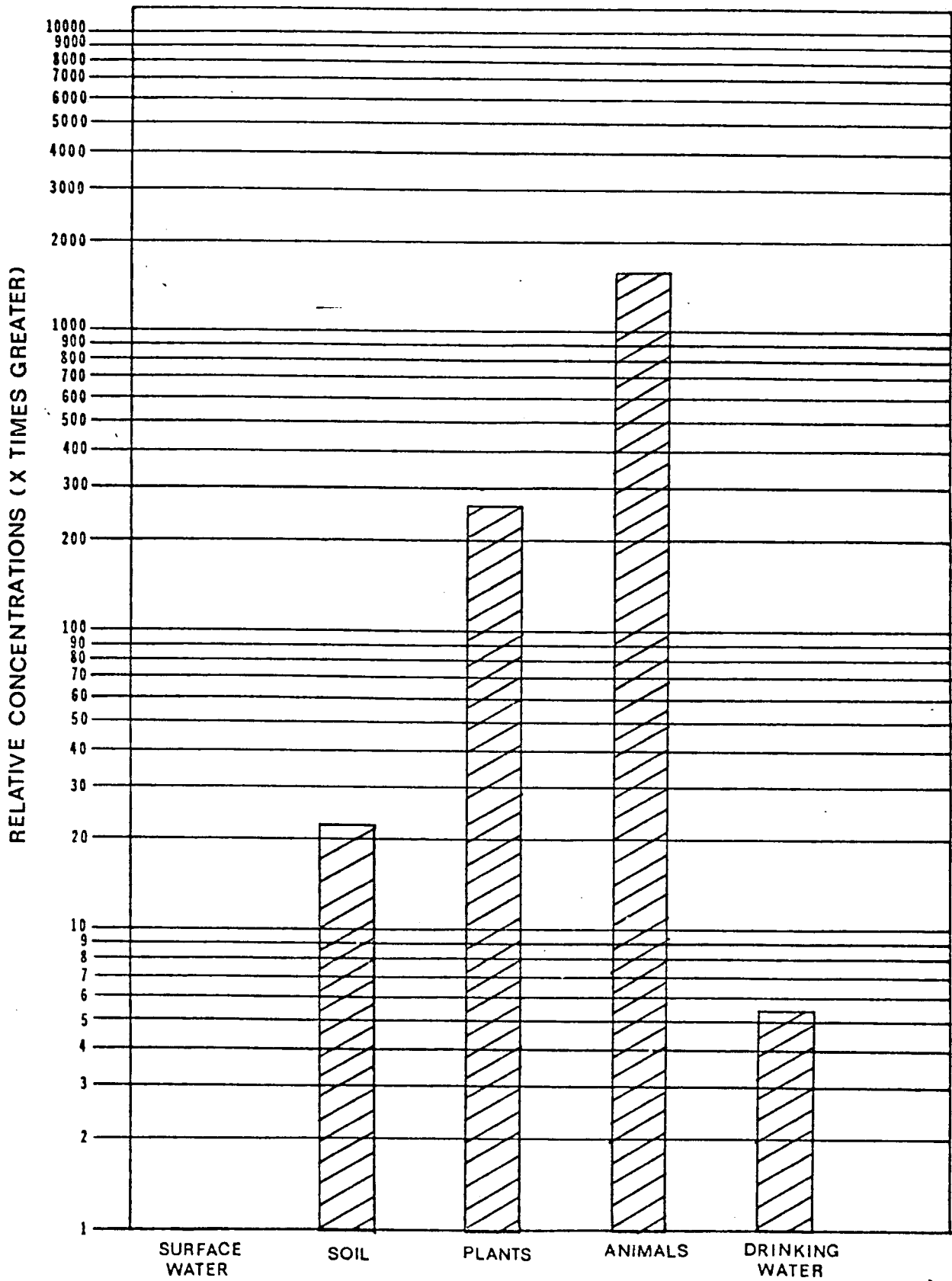


FIGURE A-4  
RELATIVE ZINC MASS - METER OF HIGHWAY



RELATIVE CHROMIUM CONCENTRATIONS



RELATIVE CHROMIUM MASS - METER OF HIGHWAY

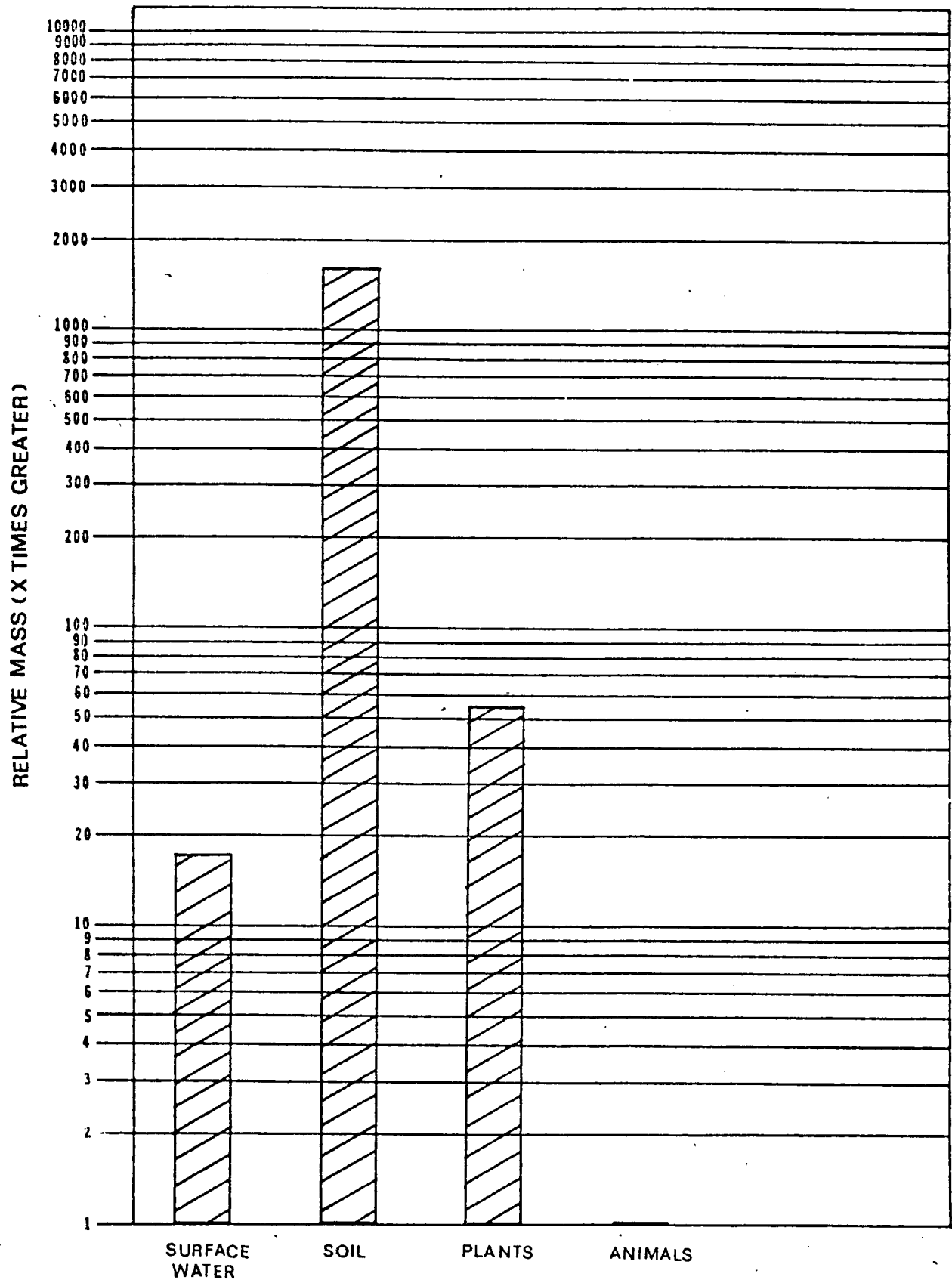


TABLE A-4  
CADMIUM SUMMARY STATISTICS

DESCRIPTION	SAMPLE SIZE	AVERAGE (ppm)	STANDARD DEVIATION	COEFFICIENT OF VARIATION	RANGE (ppm)	
					From	To
<u>Study Data</u>						
Surface water, Total	13	<0.002	-	-	<0.002	-
Surface water, Dissolved	11	<0.002	-	-	<0.002	-
Soils, All Samples	14	0.187	0.190	102	0.08	0.60
Top soil	6	0.217	0.205	95	0.12	0.60
5 inches deep	8	0.165	0.177	107	0.08	0.60
<u>Comparison Data</u>						
Maximum Contaminant Level (MCL) - Florida Safe Drinking Water Act	-	0.01	-	-	-	-
Primary - Health	-	0.01	-	-	-	-
Groundwater 1½-3 feet under a Stormwater Percolation Pond	-	-	-	-	-	0.004
Winter Park	3	<0.003	-	-	-	-
Upper Floridan Aquifer, Orlando, FL	-	<0.2	-	-	-	-
Lower Floridan Aquifer, Orlando, FL	-	<0.0005	-	-	-	-
Southeast Water Basin, (USA)	-	0.005	-	-	-	-
<u>Toxicity</u>						
Human	-	14.5 mg of Cadmium	-	-	-	-
Minnows	-	1000 ppm of Cadmium	-	-	-	-
Rabbit	-	300-500 ppm of Cadmium	-	-	-	-
Rat	-	88 ppm of Cadmium Chloride	-	-	-	-



RELATIVE CADMIUM CONCENTRATION

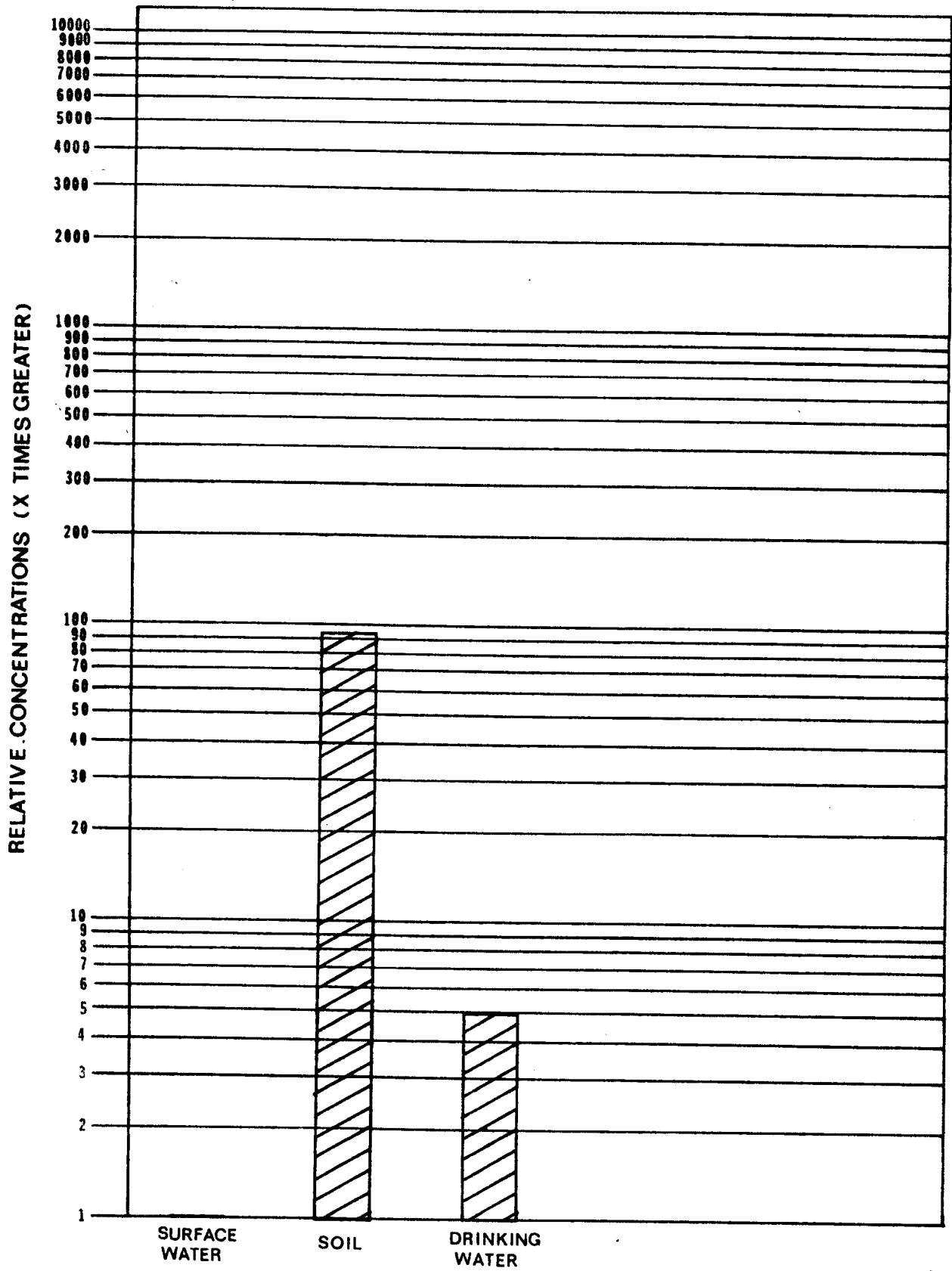


FIGURE A-8

RELATIVE CADMIUM MASS - METER OF HIGHWAY

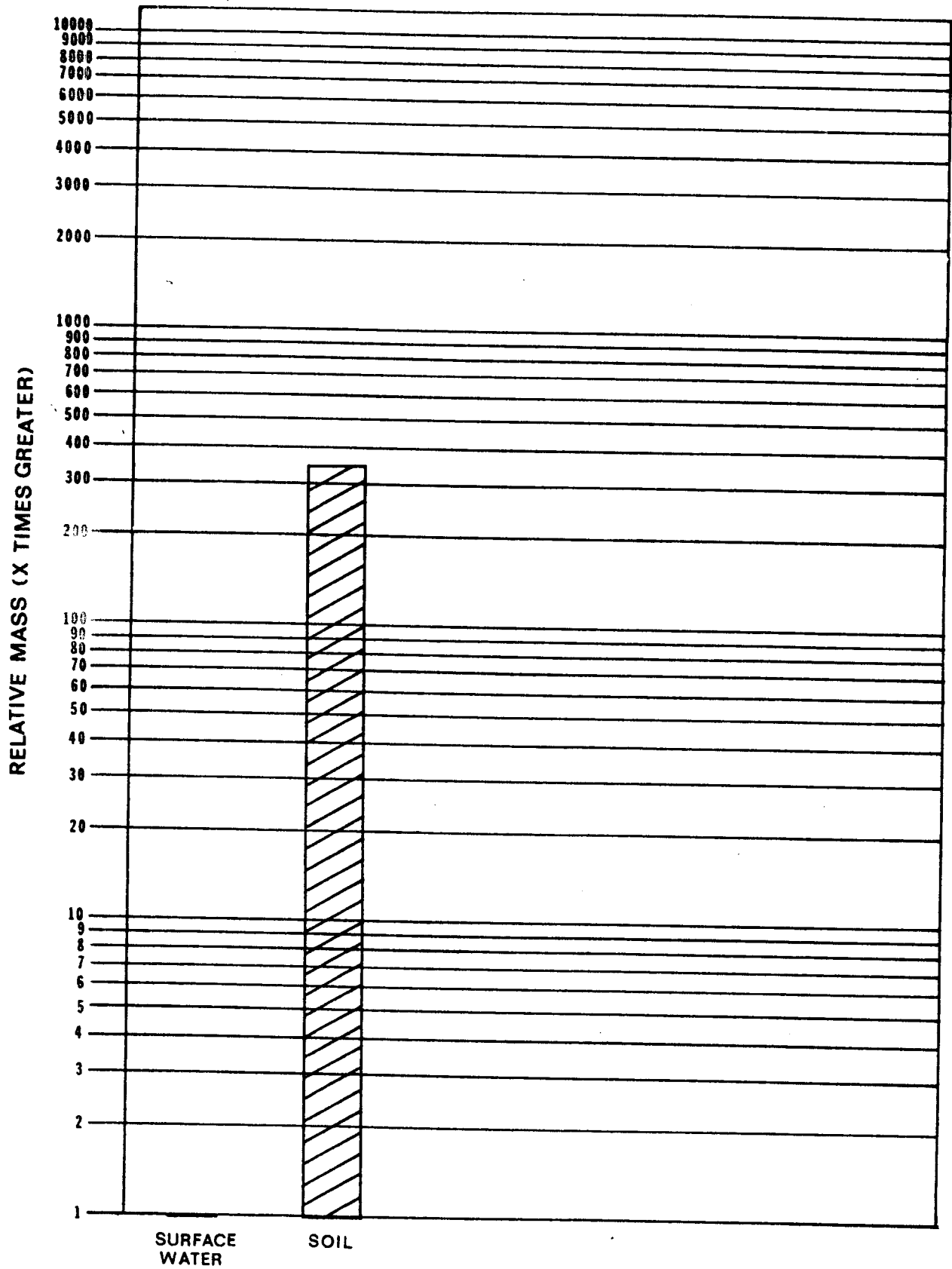


TABLE A-5

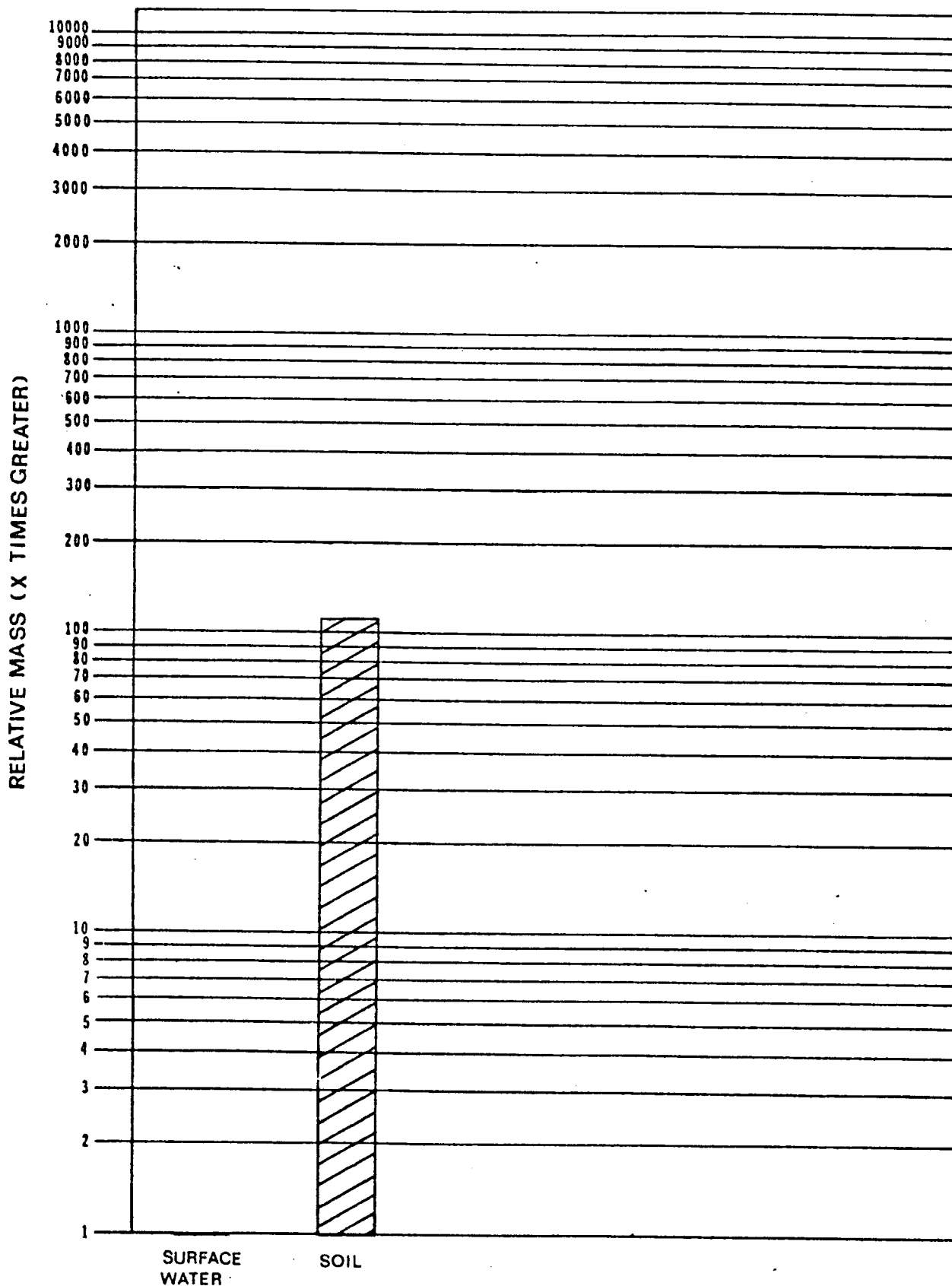
## NICKEL SUMMARY STATISTICS

## CONCENTRATION

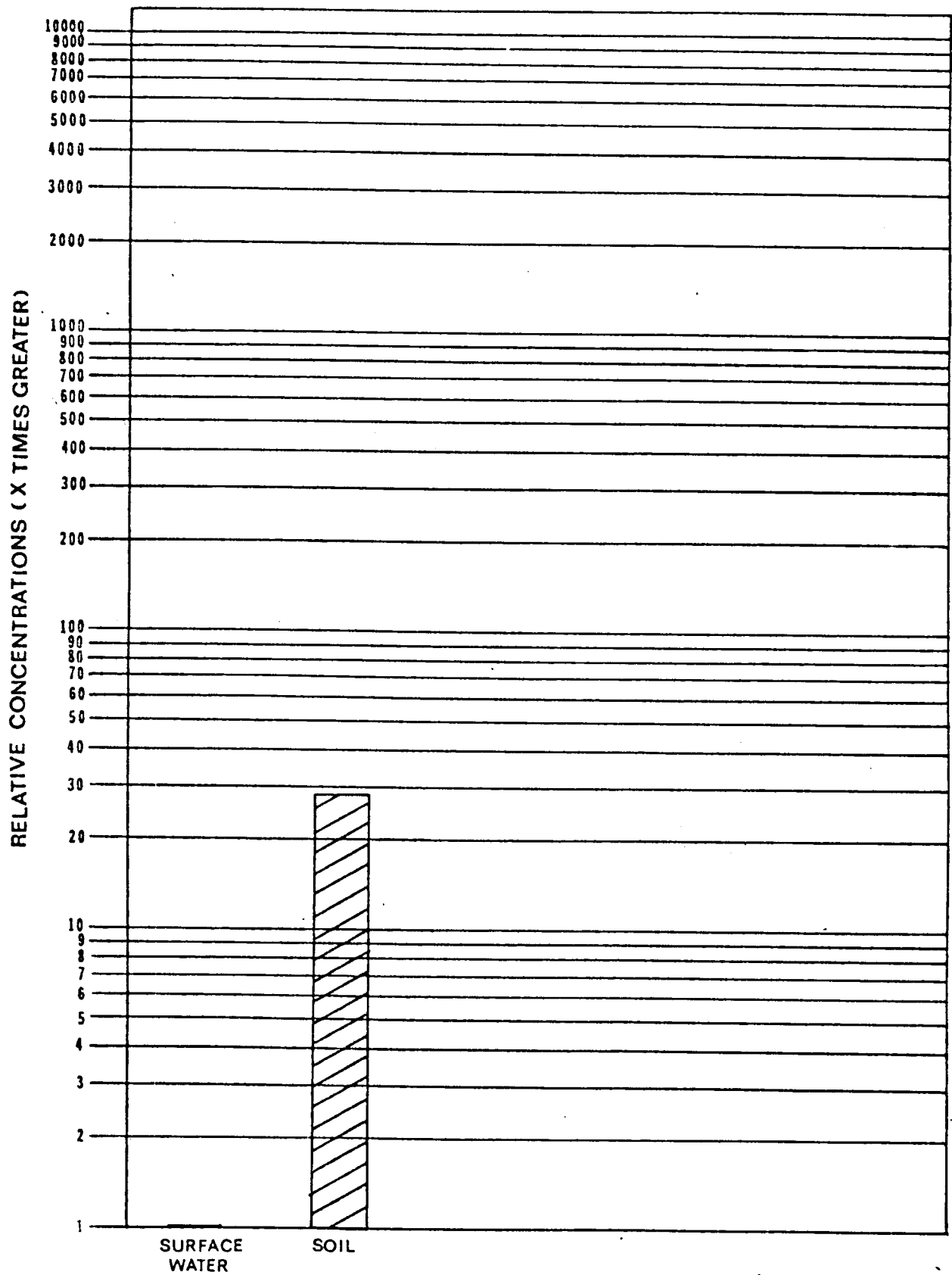
DESCRIPTION	SAMPLE SIZE	AVERAGE (ppm)	STANDARD DEVIATION	COEFFICIENT OF VARIATION	RANGE (ppm)	
					From	To
<u>Study Data</u>						
Surface water, Total	4	0.020	0.010	50	0.014	0.028
Surface water, Dissolved	4	<0.014	-	-	<0.014	-
<u>Soils, All Samples</u>						
Top soil	2	0.720	0.030	4	0.014	0.74
5 inches deep	3	0.472	0.396	84	0.0148	0.70
<u>Comparison Data</u>						
No Drinking Water Standard	-	-	-	-	-	-
Apalachicola River	-	-	-	-	0.0026	0.034
Southeast Water Basin, USA	-	0.004	-	-	-	-
<u>Toxicity</u>						
Rat - 250-1000 ppm of Nickel Carbonate	-	-	-	-	-	-
Dog - 1.5-30 ppm of Nickel Chloride	-	-	-	-	-	-

FIGURE A-9

RELATIVE NICKEL MASS - METER OF HIGHWAY



RELATIVE NICKEL CONCENTRATION



## APPENDIX B. MATERIALS AND METHODS

Surface and subsurface soil samples from various locations within the right-of-way of several Central Florida highways were obtained. These samples were analyzed for pH, cation exchange capacity (CEC), organic matter content, and grain size. Plant, soil, animal and water samples were analyzed. The content of metals in the samples was found by both dilute and concentrated acid extractions.

The second step in the analysis of soils was designed to enable a quantitative determination of the relative importance of soil components (i.e. organic matter, clay minerals, etc.) for heavy metal retention and to enable a quantitative determination of the relative importance of soil components (i.e. organic matter, clay minerals, etc.) for heavy metal retention and to enable a speculative determination of the probable forms (i.e. absorbed, precipitated, etc.) taken by the heavy metals following reaction with the soil. The procedure used in this step involved a separation of each soil sample into fractions according to density and analyzing the fractions for metal content. In this manner, some of the soil components, in particular organic matter of low density and some heavy metal precipitates of high density, could be isolated to a certain extent from the bulk inorganic soil components including sand, silt, and clay. Analysis of the isolated components for metals would indicate their importance to heavy metal immobilization by the soil.

A more detailed description of the methodology is presented in the following sections.

### SAMPLES FOR METAL ANALYSES

Field soil samples were obtained from eleven locations near major Central Florida highways. Seven sites were used for metal retention studies. These are described in Table B-1. Different geographical areas and different locations within the highway right-of-way were chosen as sampling sites to insure that soils of varying characteristics would be obtained and to enable a comparison between edge of road and ditch environments and among soil, plant, animal, surface water, and ground water. All sites were in rural areas with no apparent sources of metals other than the highway, natural and "background" sources. The ditch sites are covered by 5 or more centimeters of water during the wet seasons.

At each sampling location, both a surface soil sample (Top 2-3 cm) and a subsurface soil sample (15-20 cm) were taken. These depths were chosen because of the existence of an organic layer which was 2-3 cm thick at most locations. Beneath this layer was usually a thick layer of sandy soil with apparently limited organic matter content. Surface samples were taken by cutting a 30 cm by 75 cm rectangle of soil with a shovel to a depth of 3 cm and retaining all material including grass. For subsurface samples, the soil beneath the top cut was excavated to a depth of 15 cm. Then a 3 cm thick layer was removed with either a shovel or a post hole digger and retained. The samples were allowed to air

TABLE B-1  
DESCRIPTION OF SAMPLES

SAMPLE IDENTIFICATION	LOCATION	DEPTH	DESCRIPTION
S100	SR 50 near St. Johns River East bound lane, 35 cm from edge of pavement	Surface 2-3 cm	Contains grass, organics, cohesive
S101	Same as above	Surface 15-20 cm	Mosit, cohesive
S102	I-95, Titusville, Northbound lane, 35 cm from edge of pavement	Surface 2-3 cm	Fairly dry, contains grass
S103	Same as above	Surface 15-20 cm	Contains lime-rock, moist, clayey
S104	I-95, Titusville, Northbound lane in ditch adjacent to outfall. Receives direct runoff from roadway.	Surface 2-3 cm	Sandy with organics and some asphalt, moist
S105	Same as above	Surface 15-20 cm	Same as above
S106	I-95, Titusville, Northbound land in drainage ditch, 6 cm from edge of pavement	Surface 2-3 cm	Peak-like; decayed plant material with some sand. Loos and moist.
S107	Same as above	Surface 15-20 cm	Moist, sandy, not as much organic material.
S108	U.S. 1, Titusville, Northbound land, 35 cm from edge of pavement	Surface 2-3 cm	Dry, sandy
S109	Same as above	Surface 15-20 cm	Moist, sandy
S110	SR 405, Titusville, near U.S. 1 Eastbound lane, 35 cm from edge of pavement	Surface 2-3 cm	Very sandy, no vegetation
S111	Same as above	Surface 15-20 cm	Sandy, dry
S112	Fla. Turnpike, Southbound land near Canoe Creek Service Plaza, 35 cm from edge of pavement	Surface 2-3 cm	Moist, loose
S113	Fla. Turnpike, Southbound land near Canoe Creek Plaza, in ditch, 18 M from edge of pavement. Under 7 cm of water.	Surface 2-3 cm	Sample saturated

dry for approximately one week and then were sieved to No. 20 mesh size to remove any large debris. Grass and other undecayed plant material were removed for plant metal determination.

Animal samples were the most difficult to obtain because of the scarcity of animals. In addition only resident populations were considered.

#### pH MEASUREMENT

The pH of each sample was measured according to a procedure used by Hanna<sup>14</sup>. Fifty grams of sample were placed in a 100 ml beaker and 50 ml of distilled water were added. After stirring occasionally for 1 hour, the pH of the solution was measured using a Corning Model 10 pH meter.

#### EXTRACTABLE LEAD, ZINC, AND CHROMIUM

Each sample was analyzed for "extractable" (easily removable) lead, zinc, and chromium using the procedure suggested by Perkin-Elmer. The extraction solution was a 0.075N acid mixture (0.05N HCl + 0.025N H<sub>2</sub>SO<sub>4</sub>), 20 ml of which was added to 5 g of sample and shaken for 15 minutes. The solution was then filtered through a Whatman No. 44 filter paper into a 50 ml volumetric flask, diluted to volume with extraction solution, and analyzed by atomic absorption spectrophotometry.

#### CATION EXCHANGE CAPACITY

The cation exchange capacity of each sample was determined by the modified barium chloride-triethanolamine method of Chapman and Pratt<sup>5</sup>. In accordance with this method, 2.5 g of sample were sequentially saturated with 25 ml of 0.1N HCl (twice), distilled water, a buffer solution of barium chloride (0.5N) and triethanolamine (0.2N), a 0.5N barium chloride replacement solution (three times), distilled water, (twice), methanol (twice), and neutral normal ammonium acetate (four times). Each saturation involved shaking the soil and solution for 10 minutes on a mechanical shaker and then centrifuging for 5 minutes. The liquid was discarded following centrifugation in each step except following the saturation with NH<sub>4</sub>OAC. The four NH<sub>4</sub>OAC solutions (containing replaced barium) were combined in a 100 ml volumetric flask following centrifugation and diluted to volume with distilled water. Barium was then determined using a Beckman DU flame photometer and the results were determined in ppm barium in the soil. The CEC of each sample was calculated as follows:

$$\text{CEC (meq/100g)} = \frac{\text{ppm Ba}^{++} \text{ in soil}}{686.8}$$

#### GRAIN SIZE ANALYSIS

The grain size distribution of each sample was determined according to the combined analysis procedure of Lambel<sup>19</sup>. The samples were washed through a No. 200 sieve with distilled water and both fractions (larger and finer than No. 200) were dried at 105°C. Following dessication, the fraction larger than No. 200 was analyzed for grain size by standard sieve analysis procedures. Since none of the samples contained sufficient fine material (finer than No. 200) for hydrometer analysis, the portion washed through the No. 200 sieve was simply dried



and weighed. This weight was added to the weight of the coarse fraction passing the No. 200 sieve.

#### ORGANIC MATTER DETERMINATION

The organic matter content of each sample was determined by a peroxide digestion. The samples were oven dried (103°C) for one hour and approximately two grams of each were weighed to  $10^{-3}$  g (after dessication) into a tare weighed crucible. Approximately ten milliliters of 30% peroxide solution were added and the mixture was heated at 90°C, to dryness. The samples were reweighed and the net weight of soil was obtained. Then, another ten milliliters of the peroxide solution were added and heated to dryness as above. The samples were again weighed and the net weight of soil obtained was compared with that of the previous digestion. If the weights did not differ by more than 0.1 percent, digestion was taken as complete and the weight of organic matter was obtained by subtraction from the initial oven dry weight. If a significant difference in weight was obtained between the two digestions, the procedure was repeated until a stable weight was obtained.

#### DENSITY GRADIENT ANALYSIS

As stated earlier, the purpose of this portion of the analysis is to determine, on a quantitative basis, the relative importance of the soil components for the soil's capacity to retain lead, zinc, and chromium, and to enable a speculative determination of the probable metal forms which result from soil-heavy metal interactions in road-side areas. The density gradient analysis method was selected for this purpose following a review of studies with similar objectives. Several different techniques were illustrated in these studies and used with varying degrees of success. In general, these techniques fall into three categories:

- a) Interelement Correlations
- b) Chemical Extractions
- c) Physical Separation

The first two categories were outlined by DeWalle<sup>9</sup> in a review of the literature. He found numerous examples of techniques employing correlations between heavy metal concentrations and the concentrations of other elements or components such as organic carbon, clay minerals, iron and manganese in sediments and soils. These correlations were used to assess the physicochemical form taken by the heavy metals. He also documented the use of different chemical extractants to characterize the form of heavy metals in soils and sediments. Examples of extractants used are EDTA or hydrogen peroxide to estimate the quantities of metals associated with organic material, and acetic acid or ammonium acetate to determine the quantities of metals retained by exchange processes ("exchangeable" phase). However, some of the studies reviewed found that chemical extractants may remove some metals from all forms with little absolute selectivity.

The use of physical separation by density gradient to assess the forms of heavy metals in soils and sediments has been illustrated in two recent studies. Pita and Hyne<sup>24</sup> used this technique in an analysis of lead and zinc in

reservoir sediments. They found most of the lead and zinc in the density range between 2.0 and 2.9 g/cm<sup>3</sup> and generalized that the metals were probably in the form of organo-metallic complexes adhering to clay minerals or adsorbed directly into clay minerals in ionic form. This generalization was based on the fact that clay minerals would likely have densities in the range between 2.0 and 2.9 g/cm<sup>3</sup>. Olson and Skogerboe<sup>22</sup> used a density gradient separation technique as a means of preconcentration of lead compounds from automotive sources in soils adjacent to highways prior to analysis by x-ray diffraction. This analysis was aimed mainly at the identification of lead compounds in the most dense fractions of the soil (>3.3 g/cm<sup>3</sup>) which were found to contain the majority of the lead. Lead sulfate was determined to be the principal constituent in the soils analyzed. However, it was also found that significant quantities of the lead was in density ranges less than 3.3 g/cm<sup>3</sup>. This lead could not be identified by x-ray diffraction, inferring that it may exist in ionic form, absorbed or held at exchange sites.

Following a detailed consideration of the advantages and disadvantages of the three approaches outlined above, the density separation technique was chosen for use. While sophisticated analytical methodologies such as x-ray diffraction were not available for compound identification it was felt that separation of the soil into various density fractions and subsequently analyzing each fraction for lead, zinc and chromium by acid extraction and atomic adsorption spectrophotometry would isolate, to a reasonable extent, some of the soil components taking part in heavy metal interactions. This is based on the assumption that each soil component (i.e., sand, silt, clay, organic material, metal oxides, or discrete heavy metal precipitates) will have a unique density. In most cases the differences between the component densities is too small to enable complete isolation with available methods, but by separating the soil into density ranges, a certain degree of isolation is obtained which allows qualitative generalizations about the soil component or components present in a given range.

Six density ranges were selected to be analyzed and are shown in Table B-2. Also shown in the table are the probable soil components and metal forms present in each range. The most dense soil fraction (>3.3 g/cm<sup>3</sup>) is likely composed of dense minerals and other dense compounds including some heavy metal precipitates. Table B-3 lists the densities of some common compounds of lead, zinc, and chromium. All of the lead compounds shown have densities greater than 3.3 g/cm<sup>3</sup> as do all of the zinc compounds except the hydroxide (OH<sup>-</sup>) and chloride (Cl<sup>-</sup>) forms. Only three of the listed chromium compounds have densities greater than 3.3 g/cm<sup>3</sup>. Possible heavy metal forms in the density range greater than 3.3 g/cm<sup>3</sup>, other than discrete precipitates, are ionic forms adsorbed either by metal oxides or possibly clay minerals (since adsorbed heavy metals would increase the density of clay minerals).

The previously mentioned study by Olson and Skogerboe<sup>22</sup> provides evidence that the lead in the soil fraction greater than 3.3 g/cm<sup>3</sup> may be in the form of a discrete compound or precipitate. They separated edge of pavement (within 2 m) surface soil samples into density ranges by a procedure similar to that used in this study. Using x-ray diffraction techniques, they found that the bulk of the lead was in the most dense soil fraction and that lead sulfate (PbSO<sub>4</sub>) was the predominant form present. If analysis of the samples used in this study indicate a similar tendency of lead to be found in the most dense soil fraction, it can be taken as circumstantial evidence that this lead is in

TABLE B-2  
 DENSITY RANGES ANALYZED AND PROBABLE SOIL  
 COMPONENTS OR METAL FORMS IN EACH RANGE

Density Range (g/cm <sup>3</sup> )	Probable Soil Components and Metal Forms
< 1.5	Organic matter and organically bound metals
1.5 - 2.0	Organic matter and possibly clay with adsorbed organic matter. Metals organically bound or adsorbed on clay minerals directly. Cr may be present as a precipitate (See Table B-3)
2.0 - 2.5	Some organic matter, light minerals and light clays. Metals organically bound or adsorbed on clay minerals. Cr may be present as a precipitate.
2.5 - 2.9	Will comprise the bulk of the inorganic soil components including sand, clay, silt and other minerals. Very few organics are likely present. Metals will likely be adsorbed by clay minerals or in precipitated form (Cr and Zn).
2.9 - 3.3	Dense minerals and possibly clays with adsorbed heavy metals. Probably no organics. Metals in adsorbed or precipitated form (Cr and Zn, precipitates have densities in this range, but not Pb. See Table B-3.)
> 3.3	Dense minerals, possibly some clay with adsorbed heavy metals. Metals probably in precipitated form (Pb, Zn, Cr)

TABLE B-3  
 DENSITIES OF SELECTED FORMS OF LEAD,  
 ZINC, AND CHROMIUM (g/cm<sup>3</sup>)

Anion	Pb	Zn	Cr
Hydroxide	-	3.05	-
Carbonate	6.6	4.40	1.77
Sulfate	6.2	3.54	1.8 - 3.01
Orthophosphate	6.9 - 7.3	4.00	2.42 - 2.12
Chloride	5.85	2.91	2.76
Oxide	9.53	5.61	5.21
Sulphide	7.5	3.98 4.10	4.85
Flouride	8.4	4.95	3.8

SOURCE: CRC Press, Inc.<sup>6</sup>

the form of a discrete compound, possibly lead sulfate.

The less dense soil fractions ( $<2.0 \text{ g/cm}^3$ ) are probably composed predominantly of organic material. A linear correlation between the weight percent organic matter in each sample as determined by the peroxide digestion and the weight percent of soil in the density range less than  $2.0 \text{ g/cm}^3$  should result in a correlation coefficient of near unity if this were true. Metals in the density range less than  $2.0 \text{ g/cm}^3$  are probably adsorbed or complexed by organic material.

The bulk portion of soils such as those analyzed will have a density in the range between  $2.5$  and  $2.9 \text{ g/cm}^3$ . This is the range in which most mineral components including sand and clay will be found; the density of quartz sand being approximately  $2.65 \text{ g/cm}^3$ . Other mineral components, for example clay with adsorbed organic material, may have densities as low as  $1.9$  to  $1.8 \text{ g/cm}^3$ . Some minerals may have densities greater than  $3.3 \text{ g/cm}^3$ , however these would not likely be active in heavy metal interactions. Metals in the density range between  $2.5$  and  $2.9 \text{ g/cm}^3$  would likely be adsorbed by clay minerals or, in the case of zinc and chromium, be present as a precipitate (no common compounds of lead have densities in this range).

While the density gradient analysis does not allow absolutely certain identification of the soil components responsible for retention of heavy metals by the soil, it will yield results that are probably more quantitative than any other technique available. The procedure used for this analysis follows.

A  $10 \text{ g}$  portion of each sample was separated into six fractions according to density. The density range of each fraction is as shown in Table B-3. The separation was accomplished by sequentially suspending the soil in five solutions having densities equal to the extremes of each range. These solutions were either bromoform (density =  $2.88 \text{ g/cm}^3$ ), diiodomethane (density =  $3.3 \text{ g/cm}^3$ ), or bromoform diluted with acetone (density =  $0.79 \text{ g/cm}^3$ ) to a given density.

TABLE B-4  
DENSITY CALCULATIONS FOR SEPARATION SOLUTIONS

Solution	Bromoform (ml)	Acetone (ml)	Density (Calculated)	Density (Weight)
1	35	65	1.52	1.51
2	60	40	2.04	2.04
3	80	20	2.46	2.54
4	100	0	2.88	2.88

The bromoform dilutions were prepared by pipetteing the amounts of bromoform shown in Table B-4 into tare weighed volumetric flasks and diluted to volume with acetone. The density of the solutions were calculated as follows:

$$\text{Solution Density} = \frac{\text{mlBrCH}_3(2.88) + (\text{mlAcetone}) (0.79)}{100}$$

for 100 ml of total mixture, where:

$$\text{mlBrCH}_3 = \text{volume of Bromoform (ml)}$$

$$\text{mlAcetone} = \text{volume of Acetone (ml)}$$

The density of each solution was checked after mixing by reweighing the flasks and calculating the density based on weight.

The 10 grams of soil were placed in a 250 ml separatory funnel and approximately 50 ml of solution (1) (Density = 1.5 g/cm<sup>3</sup>) were added. The funnel was stoppered and the mixture was shaken for one minute. The sides of the funnel were then washed down with the remainder of the solution (1) and the suspension was allowed to separate for 5 minutes. The floating soil and the liquid were decanted and filtered through a tare weighed Whatman number 44 filter paper. The filtrate was recovered in a tare weighed graduated cylinder so that its density could be readily checked before reuse and adjusted if necessary. The filter paper and the soil it contained were placed aside for air-drying. This soil is the fraction of the sample having a density of less than or equal to 1.5 g/cm<sup>3</sup>.

Approximately 50 ml of solution (2) (Density = 2.0 g/cm<sup>3</sup>) were then added to the soil which had settled to the bottom of the funnel and the mixture was again shaken for one minute. The suspension was allowed to separate and was decanted and filtered as above. The soil thus obtained is the fraction having a density greater than 1.5 g/cm<sup>3</sup> and less than or equal to 2.0 g/cm<sup>3</sup>. The entire process was repeated for solution (3) (Density - 2.5 g/cm<sup>3</sup>).

The soil remaining in the funnel after mixing with solution (3) was mixed with approximately 50 ml of solution (4) (Density - 2.9 g/cm<sup>3</sup>). The resulting separation results in almost all of the soil floating. The small portion of soil settling to the bottom of the funnel was drained off through the stopcock into an evaporating dish and allowed to dry. The floating soil and the liquid were filtered as above.

Once the soil in the evaporating dish had dried at approximately 23°C (usually overnight) it was scraped with a metal spatula into the separatory funnel, approximately 5 ml of diiodomethane (Density - 3.39 g/cm<sup>3</sup>) was added and the mixture was agitated for one minute. Following a 5 minute separation period, the settled portion of the soil was drained through the stopcock into a tare weighed filter paper. The floating portion was then drained through a separate filter paper.

The six filters and the soil they contained were reweighed after drying overnight at approximately 23°C and the net weight of soil in each density

fraction was obtained to the nearest  $10^{-3}$  gram. The soil was subsequently removed from each filter, weighed to  $10^{-3}$  gram and placed in a 20 ml test tube for metal analysis. The portion of soil in the density range between 2.5 and 2.9 g/cm<sup>3</sup> was too large to be extracted in total. Therefore, only 1.000 g of this portion was retained for metal analysis.

Each solution used in the separation process was analyzed for lead, zinc, and chromium to ensure that they were not dissolving these metals from the soil.

#### EXTRACTION OF METALS

A modification of the Standard Methods<sup>1</sup> procedure for total metals extraction of suspended metal was used. The samples were digested in 5 ml of concentrated HNO<sub>3</sub> at 90°C for 3 to 4 hours, depending on the amount of organic material present. Digestion was taken as complete when all soil at the bottom of the tube appeared light gray in color. A thermoline "dri-bath" aluminum block assembly was used for heating.

After cooling for 20 minutes, the nitric acid solutions were filtered through acid-washed Whatman 44 filter papers into 50 ml volumetric flasks. The filters were rinsed with 10 ml of 1N HCL and the mixture in the flasks was diluted to volume with distilled water. The extractions were analyzed for lead, zinc, and chromium by atomic absorption spectrophotometry.

#### HYDROCARBONS

Water and sediment samples were collected in sterile one liter glass jars, placed on ice and processed on the day of collection. The sampling sites were not connected to surface waterways and were free from agricultural, residential and industrial influences.

The media used in this study for isolation and enumeration of petroleum-utilizing aerobic microorganisms consisted of 10.0 ml kerosene, 1.0 g. NH<sub>4</sub>Cl, 0.05 KH<sub>2</sub>PO<sub>4</sub>, 0.05 NaH<sub>2</sub>PO<sub>4</sub>, 0.6 g. NaCl, 0.05 g. FeCl<sub>3</sub>, 15.0 g. Agar, in 1000 ml distilled water. Bacterial identification was accomplished using Bergey's Manual of Determinative Bacteriology<sup>4</sup>. Enumeration of bacteria were determined using a standard plate count procedure.

One hundred milliliter salts solution as previously described were buffered with 0.5 m NaHPO<sub>4</sub> and the pH adjusted to 7.2 with 1.0 m NaOH solution. The sterile solutions were overlaid with 2.5 ml sterile kerosene in 250 ml Erlinmeyer flasks. The flasks were inoculated with 1 ml of a  $10^{-2}$  dilution of soil or 1 ml of a surface water sample. Flasks were incubated at room temperature for 60 days on a rotary shaker at 100 rpm with a 2-inch throw. The cultures were extracted for gas chromatographic determination of degraded kerosene at the end of the 60-day incubation.

#### EXTRACTION PROCEDURE

1. After incubation, the flasks were emptied into separate 250 ml separatory funnels and extracted with 20 ml chloroform.
2. The chloroform layer containing the residual kerosene was filtered

through a 10 cm 0.45 micron fluoropore filter to remove the cell mass (Millipore Co.). An additional 20 ml of chloroform was utilized to dissolve any kerosene bound to the surface of glass during the filtration procedure.

3. The extracted contents were placed in a 500 ml round bottom flask and flash evaporated at 55°C to a volume of 5 ml.
4. 1 Microliter samples of the extract were injected into a gas-liquid chromatograph and quantitatively determined by measuring the area under the chromatogram excluding the chloroform solvent peak.

#### GAS-LIQUID CHROMATOGRAPHY

The chromatograms were obtained on a Hewlett Packard 5750 Gas-Liquid Chromatograph equipped with a dual flame ionization detector. Stainless steel columns 10 feet in length packed with 10 percent SP-2100 on 80/100 supelcoport (Supelco, Inc.) were used to resolve the various hydrocarbon components of kerosene. The details of the gas-liquid chromatography procedure in this study are given in Table B-5.

#### STANDARDS

Initial calibrations were performed with n-alkanes, isomers of branched alkanes, and decane; the branched hydrocarbons from 2- and 3-methylpentane, C<sub>6</sub>, to 2, 2, 5-trimethylhexane, C<sub>9</sub>, and methylcyclohexane, C<sub>7</sub>; the aromatic hydrocarbons ranged from benzene, C<sub>6</sub>, to n-decylbenzene, C<sub>16</sub>.

As a result of field sample tests indicating that the lighter hydrocarbons decayed rapidly under atmospheric conditions in exposed environments and that a residual of high carbon alkanes remained, a set of normal-alkanes containing eicosane, C<sub>20</sub>; docosane, C<sub>22</sub>; tetracosane, C<sub>24</sub>; octacosane, C<sub>28</sub>; dotriacontane, C<sub>32</sub>; tetratriacontane, C<sub>34</sub>; and hexatriacontane, C<sub>36</sub> standards were used. This range of standards appeared to cover those hydrocarbons being found in the field samples.

Also, three chemical carcinogen standards; benzidine, alpha-naphthylamine, and benzo(a)pyrene were obtained along with the polycyclic aromatic hydrocarbon (non-carcinogenic)pyrene; to determine their peaking characteristics on the columns and the feasibility/possibility of finding these carcinogens in the field samples. Based on literature warnings of potential risks, toluene was used as the solvent to dilute these compounds. Benzidine, a biphenyl diamine, C<sub>12</sub>H<sub>12</sub>N<sub>2</sub> appeared to elute during the solvent tailoff and could not be identified as a peak. Alpha-naphthylamine, 1-amino-naphthalene, C<sub>10</sub>H<sub>9</sub>N, eluted at approximately 19 minutes on the OV-101 column and 22 minutes on the Dexsil column, it had a low sensitivity and was characterized as a peak having a sharp rise with considerable tailoff.



TABLE B-5  
GAS-LIQUID CHROMATOGRAPHY PROCEDURE

PARAMETER	HEWLETT PACKARD 5750
Column Length	10 Ft.
Column Inside Diameter	1/8 inc.
Liquid Phase	10% SP 2100
Support Material	Supelcoport
Support Mesh Size	80/100
Initial Column Temperature °C	50
Final Column Temperature °C	270
Programming Rate	10°C per min hold at 270 for 10 min.
Carrier Gas	N <sub>2</sub>
Carrier Gas Flow ml/min	30
Hydrogen Flow ml/min	40
Air Flow ml/min	425
Detector	FID
Detector Temp °C	310
Injection Temp °C	300
Sample Size Microliter	1
Recorder	Hewlett Packard IMV
Chart Speed	1/2 in/min.

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