

CHARACTERIZATION OF POLYNUCLEAR  
AROMATIC HYDROCARBONS IN URBAN RUNOFF

by

PATRICIA FREEMAN BARRON

A THESIS

Submitted in partial fulfillment of the requirements for the  
degree of Master of Science in the Department of Civil  
Engineering in the Graduate School, The University of  
Alabama at Birmingham

BIRMINGHAM, ALABAMA

1990

## ACKNOWLEDGEMENTS

I would like to thank my major professor, Dr. Robert Pitt, whose counsel and encouragement were most instrumental in the completion of this effort. Thanks to the Environmental Protection Agency for the research grant that made this study feasible. Special thanks to the Water Works Board of the City of Birmingham for the use of their facilities. A debt of gratitude is owed to Patricia Hamaker for her assistance throughout the project. A very special thanks to my husband, Tim, for his support, patience, and understanding that made the project easier to complete.

## TABLE OF CONTENTS

	<u>Page</u>
ACKNOWLEDGMENTS . . . . .	ii
LIST OF TABLES . . . . .	v
LIST OF FIGURES . . . . .	vi
 <u>CHAPTER</u>	
1. INTRODUCTION . . . . .	1
2. LITERATURE REVIEW . . . . .	3
2.1 Problems Caused by Urban Runoff . . . . .	3
2.2 Pollutants in Urban Runoff . . . . .	4
2.3 Polynuclear Aromatic Hydrocarbons Detected During the NURP Project . . . . .	7
2.4 Sources of Polynuclear Aromatic Hydrocarbons . . . . .	7
2.4.1 Natural . . . . .	7
2.4.2 Anthropogenic . . . . .	7
2.5 Fates of Polynuclear Aromatic Hydrocarbons . . . . .	9
2.5.1 Adsorption . . . . .	9
2.5.2 Transport . . . . .	10
2.5.3 Volatility . . . . .	11
2.5.4 Photolysis and Oxidation . . . . .	12
2.5.5 Bioaccumulation . . . . .	13
2.5.6 Biotransformation . . . . .	14
2.6 Water Treatment . . . . .	15
3. METHOD OF ANALYSIS . . . . .	17
3.1 Sampling . . . . .	17
3.2 Sample Preparation and Analysis . . . . .	17
3.2.1 Liquid-Solid Extraction . . . . .	17
3.2.2 Liquid-Liquid Extraction . . . . .	18
3.2.3 Instrumentation . . . . .	19
3.2.4 Method Quality Assurance . . . . .	19
4. ANALYTICAL RESULTS . . . . .	21
4.1 Experimental Design . . . . .	21
4.2 Observed Concentrations . . . . .	23
4.3 Exploratory Data and Statistical Results . . . . .	29
4.3.1 Probability . . . . .	29
4.3.2 Box Plots . . . . .	32
4.3.3 Analysis of Variance . . . . .	34
4.4 Discussion . . . . .	39

TABLE OF CONTENTS (Continued)

	<u>Page</u>
5. SUMMARY AND CONCLUSIONS . . . . .	42
REFERENCES . . . . .	46
APPENDICES	
A LOG NORMAL PROBABILITY PLOTS FOR EACH COMPOUND DETECTED . . . . .	50
B BOX PLOTS FOR EACH COMPOUND DETECTED ACCORDING TO EACH LOCATION AND RAIN FACTOR . . . . .	64

## LIST OF TABLES

<u>Table</u>	<u>Page</u>
2.1	SUMMARY OF NURP PROJECT PAH OBSERVATIONS (EPA 1983) . . . . . 8
3.1	SPIKE RECOVERIES FOR 20 AND 25 PPB CONCENTRATIONS OF PAHs (PERCENT). . . . . 20
4.1	SAMPLES ACCORDING TO LAND USE . . . . . 22
4.2	SAMPLES ACCORDING TO SOURCE AREA . . . . . 22
4.3	RAIN VARIABLES FOR EACH SAMPLING PERIOD . . . . . 23
4.4	PAHs DETECTED IN EACH SAMPLE IN $\mu\text{g/L}$ . . . . . 24
4.5	COMPOUNDS AND THEIR DETECTION FREQUENCIES AND CONCENTRATION RANGES . . . . . 30
4.6	MEAN AND STANDARD DEVIATION OF THE COMPOUNDS DETECTED (REAL SPACE) . . . . . 31
4.7	LOG VALUE ONE-WAY ANOVA P RESULTS . . . . . 35
4.8	LOG VALUE TWO-WAY ANOVA P RESULTS . . . . . 37
4.9	LOG VALUE ONE-WAY ANOVA P RESULTS FOR PERVIOUS AREAS . . . . . 38
4.10	LOG VALUE TWO-WAY ANOVA P RESULTS USING PERVIOUS AREAS. . . . . 40
5.1	A COMPARISON OF THE STUDY RESULTS VERSUS EPA (1983) NURP RESULTS. . . . . 43

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
4.1	Description of a Box Plot . . . . .	33

## CHAPTER 1

### INTRODUCTION

Stormwater runoff has been identified as a major contributor to the degradation of streams and rivers. Point source pollution effects are much easier to identify due to their continuous discharges and specific location effects. However, with nonpoint source pollution (including stormwater) identifying runoff characteristics and pollutant sources are a critical first step when determining required levels of control.

This study is a preliminary investigation into the relationships between the rain characteristics, location characteristics, and the polynuclear aromatic hydrocarbons (PAH) characteristics in urban stormwater runoff. The experiment was designed to use rain events and sample locations to illustrate the variables associated with PAH concentrations in urban runoff. An attempt was made to specifically address the following questions.

1. What are the typical PAH contaminant levels in stormwater?
2. What are the origins of PAHs in stormwater?
3. What rain or land use factors affect PAH concentrations in stormwater?

Fifty-eight samples were collected under varying conditions during four rain events. Solid phase sep-pak extraction was tested using stormwater samples. Liquid-liquid was chosen as the final extract method. EPA Method 625 was used to analyze the samples; sample

extraction was altered to accommodate for small sample volumes and small solvent volumes.

Results were analyzed to determine typical detection frequencies and concentrations. Probability plots, box plots, and factorial analyses are used to determine the origins of PAHs in stormwater and to identify the rain or land use factors that have significant effects on PAH concentrations in stormwater.



CHAPTER 2  
LITERATURE REVIEW

2.1 Problems Caused by Urban Runoff

Government agencies have placed most of their concerns with water concentrations exceeding excepted standards (example: municipal and industrial discharges). Unfortunately, urban runoff behaves differently than point source discharges. The time period of an urban runoff event is relatively short. Bioassay tests indicate urban runoff has low short-term toxicity (Pitt 1979; Pitt and Barron, 1990). However, long term receiving water studies have indicated urban runoff causes habitat destruction, sediment loading, and chemical changes in the sediment materials. Pitt and Bozeman (1982) found that in-stream organisms were chronically stressed by the long-term toxicity of urban runoff.

Urban runoff is known for its high fecal coliform concentrations (EPA, 1983). Cities with urban watersheds for drinking water sources have high bacteria concentrations to treat. Drinking water treatment plants with urbanized watershed sources will have more difficulty meeting Drinking Water Regulations, which require monitoring for 68 constituents by 1991. In June, 1990, a proposal will be published in the Federal Register that will require the regulation of six PAHs in drinking water (EPA, 1990). These constituents will be regulated because they are considered carcinogens, or cancer causing agents.

Problems of urban runoff are linked more directly to long-term than to short-term effects. Mass loadings of the pollutants in urban runoff and receiving water effects indicate higher toxicities than shown during laboratory short-term bioassay tests.

## 2.2 Pollutants in Urban Runoff

Twenty four years ago, funds to study urban stormwater pollution management were made available by Congress under the Water Quality Act of 1965 (Field, 1988). Since then, much work has been done to characterize the quality of stormwater runoff.

In some of the earlier studies, total and fecal coliform were used to measure the quality of runoff. In two different studies, stormwater runoff from an Ann Arbor, Michigan watershed had high counts of total and fecal coliforms. Each study indicated maximum total and fecal coliform counts to be much greater during runoff events than during dry weather (EPA, 1982). Other tests also indicated higher nutrient concentrations during storm events.

Some of the main pollutants besides bacteria that occur in urban runoff are oxygen demanding organics, suspended solids, trace metals, and petroleum products (Field and Turkeltaub, 1981).

In the late 1970's, the Nationwide Urban Runoff Program (NURP) was initiated to address urban runoff issues. A major part of the NURP program was to assess the significance of priority pollutants found in urban stormwater runoff. Priority pollutants are toxic chemicals or classes of chemicals identified as potentially harmful substances of concern in the Clean Water Act of 1977. Organic priority pollutants were found less frequently and at lower concentrations than inorganic priority pollutants. Data was collected by 28 separate projects under NURP.

Pitt and Bissonette (1984) determined that urbanization causes degradation of stream habitat. Larger variations in flows and temperatures during dry and wet weather periods were also found during the study in Bellevue, Washington. Impervious areas were found to contribute more than half of the runoff flow from storms with rainfall exceeding one-tenth inch. However, much of the nutrient loadings were found to originate from precipitation washout.

Ellis and Mustard (1985) evaluated detention ponds and percolation pits as possible controls for urban runoff in Denver, Colorado. Urban runoff was declared a major source of suspended solids whether or not erodible land was present in the drainage area. Detention ponds and percolation pits were found to be effective in the control of the runoff pollutants, especially suspended solids.

In Winston-Salem, North Carolina, NURP project goals were to characterize urban runoff and to evaluate street sweeping as a pollution control device (North Carolina DNR, 1983). Street sweepers were found to be effective in the removal of the large particles, but not the fine particles. Sweeping frequently showed no noticeable improvement in stormwater quality. Much of the nutrient loadings were also attributed to rain washout.

Oakland (1983) evaluated grassed swales and vacuum-assisted street cleaning as runoff management practices in his Durham, New Hampshire NURP project. Grass swales were found to reduce particulate residue, bacteria, and phosphate content when used for runoff control. Grass swales were helpful in reducing suspended solids and some inorganic nutrients. The vacuum assisted street sweeping removed large materials very well, but not smaller particulate. Some degree of control has been noted by the capture of the large particulate. From the study's lake

sampling program, the freshwater impoundments were found to retain nutrients, causing abundant plant growth and low dissolved oxygen.

In Kansas City, Missouri, another NURP project sought to characterize urban runoff, to relate runoff loads to land use, and to determine the impacts of runoff (Mid-America Regional Council, et al., 1983). Land use was determined to have less of an effect on runoff loadings than slope and drainage patterns. Erosion and impervious areas were sources of runoff solids. Runoff volumes were found to have major influences on constituent loadings. Nutrients and metals in runoff were higher when land uses included heavy traffic or development.

Another NURP project in Austin, Texas characterized urban runoff from two residential land use locations, evaluated a detention basin and determined the effects of urban runoff on two urban lakes (City of Austin, et al., 1983). Increased nutrients in the lakes from urban runoff indicated short-term degradation. However, no long-term effects on the lakes were noted.

McGinn (1982) in Flint Pond, (Lake Quinsigamond) Massachusetts, studied the lake quality, the sources of pollutants, and how the urban runoff pollutants affected the lake quality. Urban runoff contributions to the lake raised nutrient levels and bacteria counts. It was estimated that the 1980 runoff added 96% of the suspended solids to the lake. The rest was attributed to tributaries and atmospheric fallout. The lake indicated it was capable of assimilating the loads, which disguised the potential problems.

Metroplan (1983) of Little Rock, Arkansas studied problems associated with Fourche Creek which drains approximately 90% of the Little Rock metropolitan area. The creek was noted for low dissolved oxygen and high concentrations of bacteria, nutrients, and suspended

solids. Sampling results indicated urban runoff was responsible for the high concentrations of bacteria, nutrients, and suspended solids. Concentrations of the constituents decreased as the stream passed through wetlands along the creek.

### 2.3 Polynuclear Aromatic Hydrocarbons Detected During the NURP Project

In an overview of the NURP study, ten of the sixteen PAHs studied were detected in more than 1% of the samples. These results were from storm drain outfall samples only. These data are shown in Table 2.1. Phenanthrene was found in 10% of the samples tested. Concentrations ranged from 0.3 to 21  $\mu\text{g/L}$  for each of the PAHs detected. When results were first determined in 1982, these organic priority pollutants were unlikely to exceed the Water Quality Criteria. However, in 1986, federal water quality criteria (EPA, 1986) was updated to decrease the PAH human consumption limit to 2.8 ng/L. This limit is the cancer risk associated with one additional cancer case per one million people. Therefore, a reevaluation of the 1982 results, indicates all PAH constituents detected were periodically above the updated limit.

### 2.4 Sources of Polynuclear Aromatic Hydrocarbons

Polynuclear aromatic hydrocarbons are generally derived from both natural and anthropogenic sources.

#### 2.4.1 Natural

Natural background levels of PAHs are detected in living organisms and the environment worldwide. PAHs have been found in borings as deep as 170 m that were nearly 100,000 years old. Benzo(a)pyrene is commonly found in all soils (Borneff, 1977).

#### 2.4.2 Anthropogenic

The main sources of PAHs in natural waters are soot particles from fossil fuel consumption (example: automobile use and coal burning power

TABLE 2.1 SUMMARY OF NURP PROJECT PAH OBSERVATIONS (EPA 1983)

Compound	Frequency of detection (%)	Range of detected concentrations ( $\mu\text{g/L}$ )
Acenaphthene	Not detected	
Acenaphthylene	Not detected	
Anthracene	7	1-10
Benzo(a)anthracene	4	1-10
Benzo(b)fluoranthene	5	1-5
Benzo(k)fluoranthene	3	4-14
Benzo(g,h,i)perylene	1	5
Benzo(a)pyrene	6	1-10
Chrysene	10	0.6-10
Dibenzo(a,h)anthracene	1	1
Fluoranthene	16	0.3-21
Fluorene	1	1
Indeno(1,2,3-c,d)pyrene	1	4
Naphthalene	9	0.8-2.3
Phenanthrene	12	0.3-10
Pyrene	15	0.3-16

plants) falling naturally or with rain, and petroleum spills.

Phenanthrene, one of the more often detected PAHs in the NURP program, is considered to be a product of wood and coal burning under incomplete combustion (EPA, 1982).

Fam, et al., (1987) noted that motor oil and diesel fuel were the major anthropogenic sources of hydrocarbons in urban runoff.

Hoffman, et al., (1984) has shown that industrial areas usually contribute more PAHs to urban runoff than residential areas. However, the PAHs detected during the NURP projects did not vary with the limited range of different land uses examined. However, Borneff (1977) noted that PAHs from natural sources and household sewage are as prominent a source of PAHs as industrial sites. He studied the Rhine River and found PAH concentrations to be associated with suspended particles and

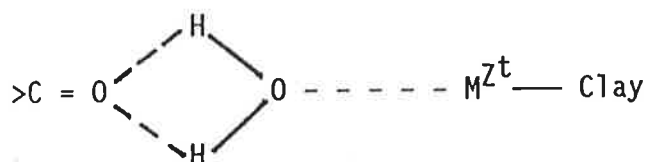
bottoms sediment. The concentrations were not only dependent on the particle volume, but also on the amount of sewage input. Also Borneff (1977) found PAHs in the river algae. However, the highest concentrations of the carcinogens were in the river bottom mud. City street surface runoff is considered one of the main sources of PAHs in receiving waters.

## 2.5 Fates of Polynuclear Aromatic Hydrocarbons

### 2.5.1 Adsorption

In surface waters, physical sedimentation is an important factor in reducing PAH concentrations in river and lake water. Algae adsorb PAHs and subsequently releases the compounds after algae die off.

Adsorption occurs in the sediment of receiving waters. This happens when the waters contain constituents that satisfy the sediment surface forces. Browman and Chester (1977) investigated pesticides and found that the major bonding reactions that occurred between soils and pesticides were Van der Waals forces, cation exchange, union exchange hydrophobic bonding, and coordination bonding. The H bond reported by Green (1974) associated with the "water bridge", is the union between the exchangeable cation and the polar organic molecules. According to Browman and Chester (1977) this bond has been illustrated:



The water bridge bonding is more favorable under moist soil conditions, or in river sediments. According to Browman and Chester (1977), Bailey and White (1970) found that absorption of organic constituents are dependent on several factors:

1. The characteristics of the functional groups such as alcohol (-OH), Ketone ( $=C=O$ ), carboxyl ( $-\overset{OH}{C}=O$ ) or amine ( $-NH_2$ );
2. The characteristics of substituted groups such as halogens that can change the shape of the molecule;
3. The possibility of the substituted group causing a hindrance for the functional group;
4. The possibility of the molecule being unsaturated, which affects hydrophilic-hydrophobic balance.

Browman and Chesters (1977) established that soil and sediment properties also contributed to their absorption properties. The important influencing properties include specific surface area, charge distribution, charge density, and functional group composition. The organic matter in sediment and soils is a mixture of humic and nonhumic materials. These materials interact with organic compounds in the water layer.

Pereira, et al., (1988) studying the Calcaseiu River in Louisiana found polycyclic aromatic hydrocarbons in water and bottom sediment samples analyzed by gas chromatography-mass spectrometry. Because they have a relatively high  $K_{ow}$  (octanol-water partition coefficient), polycyclic aromatic hydrocarbons absorb easily to the organic matter in sediment and tissue of the stream organisms. An equilibrium between bottom sediment and the water column contaminant concentrations was not found.

#### 2.5.2 Transport

Fine particles in water act to concentrate PAHs in water. In the water column, the highest concentrations of the PAHs are therefore found in association with the fine suspended particles. The transport and



dispersion of PAHs is highly dependent on the dispersal of fine particles in moving water.

To study the dispersal of pollutants in large bodies of water, such as lakes and oceans, knowledge from several disciplines must be intertwined. Wind drift currents, the altered velocity profiles of the current due to the earth's rotation, and density stratification must be considered. The mass of the pollutant material and the size of the turbulent eddies are critical factors in the mixing process. Therefore, knowledge of the behavior of a particular body of water, especially particulates transport, is necessary to predict the pollutant transport within it (Rumer, 1977).

### 2.5.3 Volatility

In bodies of water like the ocean, bubbles that break from the subsurface waters transport organic matter to the surface microlayer, according to Winchester and Duce (1977). As these bubbles cluster on the surface and burst, organic compounds are released to the atmosphere. Detailed composition of the organic matter is still incomplete. However, various types of fatty acids and hydrocarbons (including PAHs) have been identified.

Hoffman and Duce (1975) found that much of the organic matter that passes into the atmosphere was related to particles released when the bubbles burst.

The surface microlayer of the ocean has always been the boundary layer for atmospheric fallout. This surface microlayer is an important boundary between the atmosphere and the ocean that promotes the recycling of particles and substances (Winchester and Duce, 1977).

#### 2.5.4 Photolysis and Oxidation

Lane and Katz (1977) analyzed the photomodification of three PAHs under simulated atmospheric conditions. Concentrations of benzo(a)pyrene, benzo(b)fluoranthene, and benzo(k)fluoranthene were individually spread in thin layers in petri dishes. The petri dishes were covered tightly to produce an airtight seal. Each compound was exposed to three different conditions:

1. Lamp radiation without ozone present;
2. Several ozone concentrations in the dark; and
3. Several ozone concentrations with lamp radiation.

The most reactive PAH, benzo(a)pyrene, has the shortest half-life of only 0.2 hours when exposed to 0.70 ppm ozone and light radiation. Both benzo(b)fluoranthene and benzo(k)fluoranthene reacted similarly to each set of conditions. However, with increasing ozone concentrations, the oxidation of the two PAHs showed increasing differences. Under light illumination and without ozone exposure, the decomposition rates of the PAHs were found to be greater than under the conditions of ozone exposure in the dark. In all the ozone exposure cases, a rapid oxidation occurred initially followed by a much slower oxidation rate.

According to Lane and Katz (1977), degradation of these three PAHs is dependent on several things. First, the layering of PAHs on particle surfaces can affect the exposure to light or oxidants. This physical make-up can either increase or decrease the degradation of the compounds through synergistic effects of the constituents. Secondly, the length of time the compounds are exposed to light along with the concentrations of atmospheric oxidants will influence the decomposition of the PAHs.

When water and petroleum products come into contact, large quantities of organic compounds may dissolve in the aqueous solution.

Initially the transfer occurs naturally. Then, after two to seven days of contact, chemical and biological oxidation dissolution begins to occur (Lysyj and Russell, 1977).

#### 2.5.5 Bioaccumulation

The ultimate receptacles for trace amounts of organics in urban runoff are the rivers, lakes, estuaries and oceans. Perhaps the most serious problem caused from this polluted runoff is the concentration and accumulation of organics in the aquatic food web. This bio-concentration and bioaccumulation occurs either directly from the water, or through consumption of the contaminated food web. Concentrations of the benzo(a)pyrene increase in areas of human use and influence according to Borneff (1977). PAHs have been known to accumulate in food chains (Fam, et al., 1987).

According to Metcalf (1977), the rate of absorption from water can be explained by first order rate kinetics in a number of phases. In the form of Fick's law:

$$\frac{dS}{dt} = -DA \frac{dc}{dx}$$

D is the diffusion coefficient, A is the cross-sectional area of the exposed surface, x is the surface thickness, c is the diffusing substance concentration and S is the total amount of diffusing substances found on the surface. This relationship has been demonstrated to be true for DDT, 2,5,2'-trichlorobiphenyl, and di-2-ethylhexyl phthalate for different organisms, and is probably common for lipid soluble compounds.

The plateau principle implies that eventually the organism pollutant concentrations will increase until they reach equilibrium with

the surrounding water pollutant concentrations. However, the length of time required to reach equilibrium is usually longer than the life of the organism. The concentration in the organism,  $C_o$  can be determined by:

$$\frac{dC_o}{dt} = \frac{C_e K_a}{V} - K_c C_o$$

where  $V$  is the organism's mass or volume and  $K_c$  is the rate constant for clearance of the compound. This was originally used for the kinetics of drug absorption and metabolism by Kerr and Vass (1973). This equation may be over simplified, but it certainly makes it simpler to predict organism pollutant concentrations. When other environmental factors are included, the results become more complicated.

To measure the contaminant intake through food digestion, the equation above can be adjusted to account for the pollutant concentration in the edible substance, the weight of the substance and the concentration absorbed through digestion -  $C_p$ ,  $W_p$ , and  $c$ , respectively. Therefore,

$$\frac{dC_o}{dt} = \frac{c(C_p W_p)}{V} - K_c C_o$$

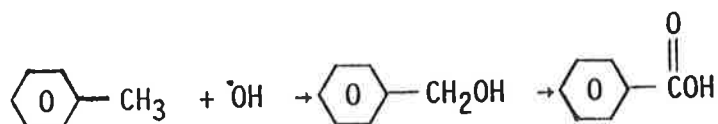
Metcalf (1977) showed that the percentage of certain pollutants being stored in body tissue decreased consistently with feeding.

#### 2.5.6 Biotransformation

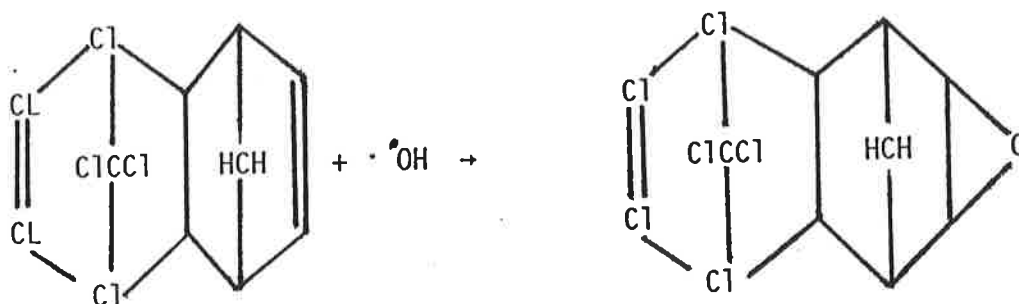
Many hydrocarbons are considered biodegradable, but are also toxic to marine life at high concentrations. Aquatic organisms have been known to metabolize and degrade contaminants using enzymes known as microsomal oxidases as noted by the National Academy of Sciences (1972). These enzymes use direct degradation. Metcalf (1966) pointed out some examples of the enzymes at work:



2. Side Chain Oxidation:



3. Epoxidation:



In most cases, the results are a less toxic substance. However, when epoxidation occurs to aldrin, dieldrin is formed.

Metcalf (1977) discussed the microsomal oxidases as being a genetic trait. Current data indicates that evolutionary changes seem to occur in organisms to help them cope with microcontaminants. However, this evolutionary process for organisms is very critical when the organism is exposed to multitudes of microcontaminants. The comparative biodegradability of individual compounds is related to the inherent polarity of the aromatic nucleus.

## 2.6 Water Treatment

Johnson and Gribberstab (1988) found that the presence of PAHs in drinking water sources will encourage formation of chlorinated PAHs when chlorine disinfection is used.

Kopfler, et al. (1977) reported the use of reverse osmosis as a treatment for cleansing drinking of organics. He found that the ability of the reverse osmosis treatment to work was dependent on the

distribution coefficient of a specific compound between the water and the membrane. This is further complicated with changing metal concentrations in the solution that will alter the efficiency of the membrane. In water treatment, it was found that by dosing the water with 1 mg/l chlorine, a 50 to 60% reduction of benzo(a)pyrene occurred. However, the chlorination of PAHs could produce carcinogenic by-products.

Borneff (1977) reported that chlorine dioxide could reduce benzo(a)pyrene by 90% in two to three hours. However, ozone was found to be a much faster oxidant than chlorine dioxide. With pre-purification, PAHs can be reduced to negligible concentrations when treated with ozone.

Borneff (1977) investigated activated carbon for treating drinking water contaminated with PAHs. Removal of 90 to 99% of the PAHs occurred when studied in the field and the laboratory.

By using sedimentation and sand filters in the treatment of drinking water, PAH concentrations were reduced 66%. Slow sand filtering was found to be more efficient in the removal of the PAHs than rapid sand filtration. Coagulation reduced PAHs by combining constituents with larger particles for settling. For groundwater, river bank filtration was effective for the removal of PAHs if the bank consist of fine sand particles, according to Borneff (1977). River bank filtration occurs when groundwater is recharged by the river through the bank of the stream.

CHAPTER 3  
METHOD OF ANALYSIS

3.1 Sampling

Sheetflow samples were collected in glass bottles with teflon lined caps. To simplify the sampling, a peristaltic hand pump was attached to the sample container using teflon tubing. The hand pump formed a vacuum and pulled a sample of the sheetflow through a teflon tube into the container. No headspace was allowed in the container. Special care was taken to prevent aeration of the sample. Samples were then stored at 4°C. No samples were held more than seven days prior to extraction.

3.2 Sample Preparation and Analysis

3.2.1 Liquid-Solid Extraction

Initially, the samples were to be extracted using solid phase extraction. Five filtered and nonfiltered samples were used to test the use of sep-pak solid phase extraction units with urban runoff samples. Residue analysis grade solvents used were dichloromethane, methanol and hexane. C18 silica bonded phase one milliliter (mL) sep-paks and filtration columns were purchased from Supelco, Inc. A Baker-21 SPE System was used for sample and solvent elation.

Six mL of hexane were slowly aspirated through the columns. Columns were then dried under a vacuum of 20-25 inches of Hg for two to three minutes. Next 12 mL of methanol were aspirated, followed immediately by six mL of organic-free water.

Seventy-five mL reservoirs were connected to the top of the columns for sample addition. For filtered samples, filters were added between the reservoir and the column. One hundred mL were then slowly aspirated through filtered and unfiltered apparatus for each sample. The columns were then washed with one mL of organic-free water and dried for ten minutes. Then, two mL of dichloromethane were allowed to drip through the columns and collected for analysis.

Results indicated problems with this extraction method. Filtered results were higher in concentration than for nonfiltered samples on some of the compounds that were analyzed. It was found that the solid particles in the unfiltered samples collected on the sorbent. This hindered the organic absorption of the bonded phase, therefore lowering the efficiency.

### 3.2.2 Liquid-Liquid Extraction

Because of the above stated problems with solid-phase extraction, liquid-liquid extraction methods were developed and used for the project. EPA (1982) Method 625 was used for sample analysis. However, the sample extraction was modified to allow for smaller sample and solvent volumes. Due to the method of sampling and the major objectives of the project, only a small volume of sample was available for extraction. One hundred mL were extracted with five mL of methylene chloride. The sample was measured and added to a 125 mL separation funnel. If necessary, the pH of the sample was adjusted for a neutral extraction. Then, five mL of solvent was added. The extraction shaking time was one minute. The mixture was then allowed to separate for ten minutes. The extract was drained through a disposable pipet packed with sodium sulfate and florisil into amber vials. Final volume of the extract was five mL. The vials were labeled and capped with teflon



lined tops and stored at  $-10^{\circ}\text{C}$  until analysis. Samples were analyzed within five days of the extraction.

### 3.2.3 Instrumentation

A Hewlett-Packard 5890 Gas Chromatograph, interfaced with a 5970 Mass Selective Detector, was used for the analysis. The instrument was equipped with a Supelco, Inc. DB-5 capillary column and a splitless injector. The helium flow rate through the column was one mL/min with 50 mL/min total flow. The temperature program included the following:

Temperature	Rate	Time
$45^{\circ}\text{C}$	$10^{\circ}\text{C}/\text{min}$	4.0
$300^{\circ}\text{C}$		10.0

The instrument was tuned prior to each run to meet the DFTPP tuning requirements in EPA Method 625. The data collection program was designed to use the single ion monitoring (SIM) mode - identifying the ion masses of the polynuclear aromatic hydrocarbon compounds. The electron voltage was increased 200 electron volts to improve sensitivity. The data was then analyzed using ion masses and retention times for compound identification. The concentrations of the identified compounds were determined using an external standard.

### 3.2.4 Method Quality Assurance

Sample blanks and spikes were used to verify the reliability of the method. Table 3.1 gives the excellent results for the spike recoveries of three different runs.

Parts per billion standards of 1, 5, 10, 20, and 30 were run on the instrument. The results began to degrade below ten ppb. Extract concentrations were 20 times that of the sample. Therefore, a detection limit of 0.5 ppb was determined.

TABLE 3.1. SPIKE RECOVERIES FOR 20 AND 25 PPB CONCENTRATIONS OF PAHs  
(PERCENT)

Concentrations	Samples				
	1 20 ppb	2 20 ppb	3 25 ppb	4 25 ppb	5 25 ppb
<u>Compounds</u>					
Naphthalene	94.4	105	93.3	87.8	106.5
Acenaphthylene	102.0	86.4	103.7	97.9	108.7
Acenaphthene	102.0	101	107.6	94.6	106.5
Fluorene	108.6	87.8	107.6	101.0	106.9
Phenanthrene	143.5	47.7	105.8	98.1	107.6
Anthracene	113.4	97.6	102.98	88.5	102.9
Fluoranthene	108.2	55.8	111.2	112.4	107.4
Pyrene	115.1	67.2	101.9	103.4	107.3
Benzo(a)anthracene	106.0	36.2	105.5	91.0	104.5
Chrysene	90.3	36.7	104.4	96.0	102.2
Benzo(b)fluoranthene	79.5	30.95	105.3	94.6	108.6
Benzo(k)fluoranthene	98.5	29.6	98.5	92.5	94.4
Benzo(a)pyrene	86.1	30.3	107.5	98.1	102.4
Indeno(123cd)pyrene	24.6	-	106.0	105.6	104.5
Dibenzo(ah)anthracene	76.3	-	103.0	111.7	124.0
Benzo(ghi)perylene	97.5	-	106.1	92.2	110.2

## CHAPTER 4

### ANALYTICAL RESULTS

#### 4.1 Experimental Design

Factorial analysis was used to design the project and to determine how much variation was explained by each experimental factor. Five different factors were initially considered: land use, source area, peak intensity, rain depth, and antecedent dry period. Source area sheetflow samples were obtained to represent these conditions, as described later. Individual effects were tested and combined effects were tested two at a time, using analysis of variance (ANOVA) procedures in the computer program Systat (Version 4.0, Evanston, IL, 1988).

Samples were collected from three different land uses: residential, commercial, and industrial. Table 4.1 indicates the samples collected according to land use. Area sources of the samples were roof runoff, parking areas, storage areas, streets, vehicle service areas, landscaped areas, urban creeks, and detention ponds. Table 4.2 indicates the source areas of the samples.

Information about each precipitation event monitored was secured from the National Weather Service (Oxmoor Road Station, 1989). Table 4.3 indicated the rain variables associated with each sampling period. For the ANOVA analysis, two categories for the rain depth were selected; a large rain was greater than one inch in depth, while a small rain was less than one inch in depth.

TABLE 4.1 SAMPLES ACCORDING TO LAND USE

Land Use	Samples
Residential	1, 6, 7, 11, 12, D, E, 23, 24, 25, 26, 32, 33, 41
Commercial	2, 3, 4, 5, 9, 10, 17, 27, 28, 29, 30, 31, 34, 35, 36, 37, 42, 43, 44, 45, 46
Industrial	8, 13, 14, 15, 16, A, B, C, 38, 39, 40, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58

TABLE 4.2 SAMPLES ACCORDING TO SOURCE AREA

Source area	Samples
Roof runoff	1, 7, 10, 14, 23, 24, 25, 31, 34, 49, 52, 58
Parking areas	2, 6, 9, 16, D, 27, 29, 30, 37, 39, 44, 48, 56
Storage areas	13, 43, 46, 51, 53, 54, 55
Streets	15, A, 26, 40, 42, 50
Vehicle service areas	5, 8, C, 38, 45, 47, 57
Landscaped areas	17, B, E, 28, 41
Urban creeks	4, 12, 33, 35
Detention ponds	3, 11, 32, 36

TABLE 4.3 RAIN VARIABLES FOR EACH SAMPLING PERIOD

Sampling period	Sampling date	Samples collected	Rain depth* (inches)	Antecedent dry period (days)	Peak intensity* (inches)
1	3/30/89	A-E	1.72	7	0.37
2	5/14/89	1-17	0.21	4	0.11
3	6/4/89	23-40	0.18	1	0.18
4	7/2/89	41-58	1.50	1	0.99

\* Prior to sampling.

Similarly, two categories were selected for the antecedent dry period. The antecedent dry period was selected to be "long", if greater than four days and "short", if less than four days. The peak intensity was rated as "high" if greater than 0.50 inches per hour and "low" if less than 0.50 inches per hour. This scheme allowed a complete factorial analysis to be attempted with the data.

#### 4.2 Observed Concentrations

The following information presents the results from the analysis of 58 samples. Samples were collected from the various locations under different conditions, as shown previously.

Thirteen of the sixteen polynuclear aromatic hydrocarbon compounds analyzed were detected. A complete listing of the samples and the concentrations detected are shown on Table 4.4. Twenty-two of the 58 samples analyzed contained some detectable PAH concentrations. Total PAH concentrations that were detected ranged from 0.74  $\mu\text{g/L}$  to 1200  $\mu\text{g/L}$ . Sixty-two percent of the samples had non-detectable PAH

TABLE 4.4 PAHS DETECTED IN EACH SAMPLE IN  $\mu\text{g/L}$ \*

	Samples											
	1	2	3	4	5	6	7	8	9	10	11	12
Acenaphthene												
Acenaphthylene												
Fluorene			18.4		36.7			104.0	71.8	187.1	67.7	296.2
Naphthalene								44.3		23.7	5.8	40.0
Anthracene			6.6		52.8	93.8		25.4	15.6	44.8	13.9	127.7
Fluoranthene						41.0		11.2	12.8	22.1	10.4	68.9
Phenanthrene						54.8		31.1	16.2	16.3		60.6
Benzo(a)anthracene					39.0			89.6	17.5	265.9		63.9
Benzo(b)fluoranthene	14.1	10.0		8.0	107.3	132.3	6.4					77.9
Benzo(k)fluoranthene	3.4	8.0		31.4	14.7	11.3	12.2	103.3	41.6	221.4		236.5
Chrysene					25.0	29.3				73.1		101.9
Pyrene			6.0		37.7	79.6		51.0	40.2	27.6	56.6	
Benzo(ghi)perylene						19.7						
Benzo(a)pyrene	10.9	21.4		19.1	59.7	78.3	34.0	119.7	19.5	300.2		126.4
Dibenzo(a,h)anthracene												
Indeno(1,2,3-cd)pyrene												
Total PAH	28.5	39.4	31.0	58.5	372.9	540.1	52.6	579.6	235.2	1182.2	154.4	1200.9

\* Results less than the detection limit (0.5  $\mu\text{g/L}$ ) are left blank.

TABLE 4.4 PAHS DETECTED IN EACH SAMPLE IN  $\mu\text{g/L}^*$  (CONTINUED)

	Samples												
	13	14	15	16	17	A	B	C	D	E	23	24	
Acenaphthene													
Acenaphthylene								1.9					
Fluorene		47.7			49.4			0.8					
Naphthalene					20.3								
Anthracene					38.1	0.6	1.3		1.0		0.7		
Fluoranthene	4.5	15.3			27.9								
Phenanthrene					54.1								
Benzo(a)anthracene		27.5	13.9		29.7								
Benzo(b)fluoranthene		11.5	15.4		61.4								
Benzo(k)fluoranthene													
Chrysene					8.2	1.0	2.3	0.7	1.0				
Pyrene	8.0												
Benzo(ghi)perylene													
Benzo(a)pyrene													
Dibenzo(a,h)anthracene													
Indeno(1,2,3-cd)pyrene													
Total PAH	12.5	153.5	48.1		343.1	1.6	3.6	3.4	2.0		0.7		

\* Results less than the detection limit (0.5  $\mu\text{g/L}$ ) are left blank.

TABLE 4.4 PAHS DETECTED IN EACH SAMPLE IN  $\mu\text{g/L}^*$  (CONTINUED)

	Samples											
	25	26	27	28	29	30	31	32	33	34	35	36
Acenaphthene												
Acenaphthylene												
Fluorene												
Naphthalene												
Anthracene												
Fluoranthene												
Phenanthrene												
Benzo(a)anthracene												
Benzo(b)fluoranthene												
Benzo(k)fluoranthene												
Chrysene												
Pyrene												
Benzo(ghi)perylene												
Benzo(a)pyrene												
Dibenzo(a,h)anthracene												
Indeno(1,2,3-cd)pyrene												

Total PAH

\* Results less than the detection limit ( $0.5 \mu\text{g/L}$ ) are left blank.



TABLE 4.4 PAHs DETECTED IN EACH SAMPLE IN  $\mu\text{g/L}^*$  (CONTINUED)

	Samples											
	37	38	39	40	41	42	43	44	45	46	47	48
Acenaphthene												
Acenaphthylene												
Fluorene												
Naphthalene												
Anthracene												
Fluoranthene												
Phenanthrene												
Benzo(a)anthracene												
Benzo(b)fluoranthene												
Benzo(k)fluoranthene												
Chrysene												
Pyrene												
Benzo(ghi)perylene												
Benzo(a)pyrene												
Dibenzo(a,h)anthracene												
Indeno(1,2,3-cd)pyrene												
Total PAH												

\* Results less than the detection limit ( $0.5 \mu\text{g/L}$ ) are left blank.

TABLE 4.4 PAHS DETECTED IN EACH SAMPLE IN  $\mu\text{g/L}^*$  (CONTINUED)

	Samples									
	49	50	51	52	53	54	55	56	57	58
Acenaphthene										
Acenaphthylene										
Fluorene										
Naphthalene										
Anthracene										
Fluoranthene				7.6						
Phenanthrene										
Benzo(a)anthracene										
Benzo(b)fluoranthene										
Benzo(k)fluoranthene										
Chrysene										
Pyrene										
Benzo(ghi)perylene										
Benzo(a)pyrene										
Dibenzo(a,h)anthracene										
Indeno(1,2,3-cd)pyrene										
Total PAH				7.6						

\* Results less than the detection limit ( $0.5 \mu\text{g/L}$ ) are left blank.

concentrations. Ten of the sixteen compounds were detected in samples with high total PAH concentrations. Ninety-five percent of the samples with PAH concentrations contained more than one PAH constituent.

Table 4.5 illustrates the compounds, the locations detected, the frequency of detection, and the range of detected concentrations. The most frequently detected PAH was fluoranthene (29%), followed by pyrene (26%). Similar results were found in the EPA (1983) NURP study.

### 4.3 Exploratory Data and Statistical Results

#### 4.3.1 Probability

Factorial analysis using the ANOVA procedure requires two sample conditions, according to Mason, et al., (1983).

1. The samples must be independent and random, and have the same standard deviation.
2. The sample groups being studied must have normal probability distributions.

The experimental design for location and water source were independent for each rain, though not independent of the rain. For example, unrelated parking lots and roof drains were sampled. No order was associated with the collection of the sample and care was taken to assure maximum representation for all experimental conditions. Log transformed data resulted in normal probability distributions and allowed the standard deviations to be compared, based on the slope of the probability plots.

Table 4.6 lists the mean and standard deviation for the PAH compounds detected, in real space. It is important to realize that the standard deviations listed are skewed by the number of none detected compounds.

TABLE 4.5 COMPOUNDS AND THEIR DETECTION FREQUENCIES AND CONCENTRATION RANGES

Compounds	Locations detected	Frequency of detection (%)	Range of detected concentrations ( $\mu\text{g/L}$ )
Acenaphthene	Not detected		
Acenaphthylene	C	2	1.9
Fluorene	C	2	0.75-9.3
Naphthalene	3, 4, 5, 8, 9, 10, 11, 12, 14, 17	17	7.7-300
Anthracene	8, 10, 11, 12, 17	9	5.8-44
Fluoranthene	3, 5, 6, 8, 9, 10, 11, 12, 13, 14, 17, A, B, C, D, E	29	0.62-130
Phenanthrene	6, 8, 9, 10, 11, 12, 17	12	10-69
Benzo(a)anthracene	5, 6, 8, 9, 10, 12, 17, D	14	1.8-61
Benzo(b)fluoranthene	1, 2, 4, 5, 6, 7, 8, 9, 10, 12, 14, 15, 17	22	6.4-270
Benzo(k)fluoranthene	1, 2, 4, 5, 6, 7, 8, 9, 10, 12, 14, 15, 17	22	3.4-220
Chrysene	5, 6, 10, 12	7	8.2-240
Pyrene	3, 5, 6, 8, 9, 10, 11, 12, 13, 17, A, B, C, D, E	26	0.96-102
Benzo(ghi)perylene	6	2	20
Benzo(a)pyrene	1, 2, 4, 5, 6, 7, 8, 9, 10, 12, 14, 15, 17	22	11-300
Dibenzo(a,h)anthracene	Not detected		
Indeno(1,2,3-c,d)pyrene	Not detected		

TABLE 4.6 MEAN AND STANDARD DEVIATION OF THE COMPOUNDS DETECTED (REAL SPACE)

Compound	Mean ( $\mu\text{g/L}$ )	Standard deviation
Naphthalene	15.6	48.8
Anthracene	2.8	8.5
Fluoranthene	8.1	22.6
Phenanthrene	3.8	11.3
Benzo(a)anthracene	5.2	14.0
Benzo(b)fluoranthene	13.9	42.5
Benzo(k)fluoranthene	11.0	34.1
Chrysene	6.7	32.5
Pyrene	7.7	20.1
Benzo(ghi)perylene	0.8	2.5
Benzo(a)pyrene	16.1	46.5
Acenaphthene	0.5	0.2
Fluorene	0.5	0.03

Log-normal distribution plots for individual PAHs are contained in Appendix A. The type of sample probability distributions can be estimated by plotting concentration versus probability on probability graph paper. If the plotted results are a straight line, then the samples represent normal distributions. These figures are on log-normal probability paper and the straight lines indicate that the sample values need log transformations before analyses that require normal probability distribution can be conducted. More scatter is apparent for anthracene, fluoranthene, benzo(a)anthracene, and pyrene plots than for the other PAHs.

Different symbols are used to represent PAH concentrations on the probability plots for different land uses. If PAH concentrations were greatly influenced by land use, similar symbols would be closely grouped. The results show that concentrations were not obviously influenced by land use.

The probability plots prove two factors: (1) Log transformation of the data was necessary to obtain normal distributions for factorial analysis, and (2) PAH concentrations during the study were not obviously influenced by land use.

#### 4.3.2 Box Plots

Box plots of the PAH concentrations, shown in Appendix B, are used to illustrate the basic distributions of the concentrations for the different experimental factors. Figure 4.1 shows how box plots are used. The hinge spread is located between the first and third quartile of the concentrations - between 25% and 75%. Whiskers are drawn adjacent to the outmost values. Values outside of the whiskers are 1-1/2 times the 25 to 50% spread. Far outside values are concentrations three times the spread. The median is the 50th percentile of the data. Notches are used to indicate the interquartile of the results (Systat, 1988). When box plot intervals noted by the notches do not overlap, the two populations are usually different at the 95 percent level.

Land use plots for each constituent in Appendix B show only far outside values, indicating that the hinged grouping is below the detection limit. Most of the PAH plots indicate groupings of concentrations where the median is located at the detection limit. This is because the majority of the constituents were not detected, as noted earlier.

Source area plots for benzo(k)fluoranthene and chrysene show only outside and far outside values for each category, except urban creeks. Only the urban creek category had enough detectable concentration observations (>25% detection) to result in relatively complete box plots. The box plots for almost all of the categories show significant overlapping of the box ranges. This indicates the population



concentrations are likely similar for each experimental category. This is a preliminary indicator that concentrations do not vary for most of the factors tested.

All of the rain variables are divided into two categories. For all of the PAH compounds, except fluoranthene, detectable concentrations were only found in one of the two rain categories. This is a preliminary indication that the rain factors may be significant. Except for one fluoranthene observation, all of the observed PAH values were associated with the following factor levels:

- long antecedent dry period
- low peak intensity
- small rain depth.

#### 4.3.3 Analysis of Variance

To further determine if any of the rain and location factors were significant, the PAH concentration results were analyzed using ANOVA. These tests were done using both zero and 0.5  $\mu\text{g/L}$  for the non-detectable observation values. No differences were noted in the ANOVA results.

The simplest form of ANOVA (one-way) occurs when one factor is tested alone for its produced responses on a concentration. Systat (1988) was used to conduct the ANOVA evaluations. One of the ANOVA results is the probability (P) that indicates at least one category of the factor being tested is different from the others. One-way ANOVA test results are shown in Table 4.7. Observed P values ranged from 0.000 to 0.861. The lower the P value, the more significant it is that at least one level of the factor being tested is different from the other factor levels. Commonly, a P value of 0.05, or less, is used to indicate significant differences.



TABLE 4.7 LOG VALUE ONE-WAY ANOVA P RESULTS

	Land use	Source area	Rain depth	Antecedent Dry Period	Peak Intensity
Naphthalene	0.474	0.477	0.009	0.000	0.031
Anthracene	0.725	0.572	0.065	0.003	0.128
Fluoranthene	0.625	0.808	0.018	0.000	0.031
Phenanthrene	0.211	0.792	0.024	0.000	0.065
Benzo(a)anthracene	0.304	0.558	0.035	0.000	0.052
Benzo(b)fluoranthene	0.437	0.610	0.001	0.000	0.008
Benzo(k)fluoranthene	0.405	0.503	0.001	0.000	0.009
Chrysene	0.206	0.606	0.102	0.009	0.178
Pyrene	0.406	0.634	0.016	0.000	0.014
Benzo(ghi)perylene	0.210	0.857	0.422	0.204	0.507
Benzo(a)pyrene	0.432	0.532	0.001	0.000	0.007
Acenaphthalene	0.475	0.411	0.220	0.204	0.507
Fluorene	0.475	0.411	0.220	0.204	0.507

Both the land use and source area categories have P values ranging from 0.206 to 0.857, therefore indicating insignificant effects on the constituents, indicated earlier by the probability and box plots. However, P values for rain depth, antecedent dry period, and peak intensity are below 0.05 for twenty-five of 39 tests. Eight of the thirteen tests for the rain depth variable had results between 0.001 and 0.035.

Antecedent dry period one-way ANOVA tests resulted in the lowest P values found. Ten of the PAHs tested had P values less than 0.01. The three compounds with P values greater than 0.05, were only detected once, in 58 analyses, as noted earlier. Peak intensity one-way ANOVA tests resulted in P values less than 0.05 for seven of the thirteen compounds.

Factorial tests for the combined effects of the variables on the constituent concentrations were tested two at a time using two-way ANOVA. Two-way ANOVA tests for three different combinations of effects - the concentration effect due to factor one, the concentration effect due to factor two, and the concentration effect due to both factors one and two combined. The one-way ANOVA provided the results for the individual factors. Table 4.8 shows the results for the two-way ANOVA analyses. Five combinations of the variables are indicated. Due to incomplete sampling conditions (for example, no storage areas or vehicle service areas were sampled in residential sections) the following combination effects could not be calculated:

- source area \* land use,
- source area \* rain depth,
- source area \* peak intensity,

TABLE 4.8 LOG VALUE TWO-WAY ANOVA P RESULTS

	Land use* rain depth	Land use* antecedent dry period	Land use* peak intensity	Source area* antecedent dry period	Rain depth *antecedent dry period
Naphthalene	0.957	0.082	0.890	0.258	0.004
Anthracene	0.986	0.713	0.993	0.548	0.071
Fluoranthene	0.959	0.145	0.900	0.766	0.004
Phenanthrene	0.752	0.127	0.830	0.820	0.020
Benzo(a)anthracene	0.843	0.073	0.791	0.365	0.046
Benzo(b)fluoranthene	0.998	0.069	0.937	0.064	0.000
Benzo(k)fluoranthene	0.958	0.021	0.887	0.067	0.000
Chrysene	0.601	0.116	0.734	0.533	0.118
Pyrene	0.925	0.229	0.968	0.399	0.021
Benzo(ghi)perylene	0.645	0.212	0.869	0.670	0.467
Benzo(a)pyrene	0.998	0.066	0.942	0.023	0.000
Acenaphthalene	0.706	0.237	0.545	0.199	0.009
Fluorene	0.706	0.238	0.545	0.199	0.009

peak intensity \* rain depth, and  
 peak intensity \* antecedent dry period.

The most significant two-way effect on PAH concentration shown in Table 4.8 is the combination of rain depth and antecedent dry period. Ten of the constituents tested had P values below 0.05 for the combined variables. The other variable combinations had much higher P values except for 0.021 and 0.023, for benzo(k)fluoranthene for the land use and antecedent dry period combination, and benzo(a)pyrene for the source area and antecedent dry period combination, respectively.

The most obvious incomplete sampling condition was source areas. To test source area effects in a complete experimental matrix, the source area samples were combined into only two groups: pervious and impervious source area categories. Table 4.9 gives the P values for one-way ANOVA using this sample description. None of the results have P values smaller than 0.2.

---

TABLE 4.9 LOG VALUE ONE-WAY ANOVA P RESULTS FOR PERVIOUS AREAS

Perviousness

---

Naphthalene	0.707
Anthracene	0.407
Fluoranthene	0.861
Phenanthrene	0.685
Benzo(a)anthracene	0.668
Benzo(b)fluoranthene	0.199
Benzo(k)fluoranthene	0.415
Chrysene	0.814
Pyrene	0.610
Benzo(ghi)perylene	0.439
Benzo(a)pyrene	0.249
Acenaphthalene	0.439
Fluorene	0.439

---

Table 4.10 shows the P values for two-way ANOVA for the different factors in combination with the perviousness factor. Of all the different combinations, only two compounds show perviousness conditions and the antecedent dry period to be a significant combination. Benzo-(b)fluoranthene and benzo(a)pyrene had P values of 0.008 and 0.015, respectively. However, this effect was not significant at the 0.05 level for any of the other PAHs.

#### 4.4 Discussion

The following major conclusions were found during these analyses:

- Probability plots indicated that log transformations were necessary to obtain normal distributions of the data. ANOVA calculations were then conducted using log transformed data.

- Because all source areas categories were not represented in all land uses, a complete two-way analysis for all land and rain factors was impossible. If lower detection limits had been available, more detectable PAH concentrations would have been found, and results for all analysis categories would have been more conclusive.

- Similar conclusions were obtained for the probability plots, box plots, and ANOVA calculations. All three analyses concluded that land use was not a significant factor. Source areas were shown to have overlapping concentration ranges in the box plots, illustrating little significance. Again, this was also shown by the ANOVA results.

- All three rain factors examined had significant effects on the PAH concentrations. The one-way ANOVA indicated that rain depth, antecedent dry period, and peak intensity were all significant factors. However, almost all of the detected PAH values were confined to only one level of each of these rain factors, as shown earlier. When the factorial analysis was performed on two factors at a time, the rain

TABLE 4.10 LOG VALUE TWO-WAY ANOVA P RESULTS USING PERVIOUS AREAS

	Perviousness* land use	Perviousness* rain depth	Perviousness* antecedent dry period	Pervious* peak intensity
Naphthalene	0.236	0.842	0.789	0.873
Anthracene	0.161	0.556	0.355	0.633
Fluoranthene	0.590	0.854	0.729	0.729
Phenanthrene	0.522	0.815	0.845	0.850
Benzo(a)anthracene	0.941	0.801	0.392	0.717
Benzo(b)fluoranthene	0.886	0.206	0.008	0.318
Benzo(k)fluoranthene	0.686	0.400	0.080	0.505
Chrysene	0.425	0.799	0.640	0.836
Pyrene	0.613	0.861	0.652	0.811
Benzo(ghi)perylene	0.312	0.523	0.294	0.601
Benzo(a)pyrene	0.795	0.249	0.015	0.363
Acenaphthalene	0.629	0.367	0.294	0.602
Fluorene	0.630	0.367	0.294	0.601

depth and antecedent dry period appeared to be the most significant two-way effect.

Independence problems may have occurred with the rain categories. Most all observed PAH values were associated with the following factor levels: long antecedent dry period, low peak intensity, and high rain depth. The three-way effect of peak intensity, antecedent dry period, and rain depth therefore could not be tested. The most significant one-way factor from all the analyses was antecedent dry period, but the two-way factor of antecedent dry period and rain depth must be used in preference to the one-way results (Box, et al. 1978).

This study also included filtered PAH observations for each of the 58 samples. Very few detectable filtered PAH values were found. The few data did not allow similar factorial analyses to be performed.

CHAPTER 5  
SUMMARY AND CONCLUSIONS

Twenty-two of the 58 samples analyzed contained some detectable PAH concentrations. Results are compared with NURP results in Table 5.1. Fluoranthene and pyrene had frequency of detections similar to the results found during the EPA (1983) NURP study. This study showed greater frequencies of detection for most compounds, compared to the NURP results. Only phenanthrene at 12% and benzo(ghi)perylene at 2% frequency of detection, were equal to or less than the frequencies of detection found during the NURP study. This study's samples were from source areas, where as NURP samples were from watershed outfall locations. Therefore, a high frequency of detection and higher concentrations can be expected in the undiluted source area samples obtained during this study. Results for all the compounds detected in this study showed higher concentrations than those detected by NURP.

Probability plots of each constituent showed that log transformations of the data were necessary to form a normal distribution that is required for many statistical analysis, including ANOVA. The probability plots did not indicate any influences by land use on PAH concentrations. Otherwise, grouping of similar symbols would have been noted on the plots. The majority of the PAH tests resulted in non-detected concentrations.



TABLE 5.1 A COMPARISON OF THE STUDY RESULTS VERSUS EPA (1983) NURP RESULTS

	Frequency of detection (%) Study	NURP	Range of concentrations ( $\mu\text{g/L}$ ) Study	NURP
Acenaphthylene	2	0	1.9	*ND
Fluorene	2	1	0.8	1
Naphthalene	17	9	7.70-300	0.8-2.3
Anthracene	9	7	5.8-44	1-10
Fluoranthene	29	16	0.6-130	0.3-21
Phenanthrene	12	12	10-69	0.3-10
Benzo(a)anthracene	14	4	1.8-61	1-10
Benzo(b)fluoranthene	22	5	6.4-270	1-5
Benzo(k)fluoranthene	22	3	3.4-220	4-14
Chrysene	7	10	8.2-240	0.6-10
Pyrene	26	15	1.0-100	0.3-16
Benzo(ghi)perylene	2	1	20	5
Benzo(a)pyrene	22	6	11-300	1-10
Dibenzo(a,h)anthracene	0	1	*ND	1
Indeno(1,2,3-cd)pyrene	0	1	*ND	4

\* ND - Not Detected

The overlapping box ranges on the box plots demonstrated that concentrations did not obviously vary for the factors tested. For all rain factors tested, almost all of the detectable PAHs were confined to one of the categories.

Most of the observed PAH concentrations were associated with long antecedent dry periods, low peak intensities, and small rain depths. More samples obtained under a greater variation of rain conditions would have lessened the potential independence problem.

This study also indicated the significance of location and rain factors on the concentrations of PAH compounds in urban stormwater runoff. The two-way factor of antecedent dry period in conjunction with rain depth was noted as the most significant factor affecting PAH concentrations. Another factor that indicated a significant effect on PAH concentrations was peak intensity. Two-way effects using rain intensity could not be calculated because the low peak intensity observations were only associated with the small rain depths.

Lower detection limits would have helped the analyses by increasing the number of valid observations available for the statistical tests. Detection limits were affected by the dirty water and the small volume of samples available. The use of liquid-liquid extraction gave better results than liquid-solid extraction for stormwater runoff samples. This was because the dirty samples interfered with the solid phase extraction. Particles collected on the solid phase decreasing the absorption efficiency and possibly absorbing PAH constituents. Analytical results could also have been improved by using larger sample volumes and larger solvent volumes. This would increase extraction time and the amount of solvent used, therefore, increasing the costs of the analysis. The biggest problem was the difficulty in collecting larger

volumes of sheetflow samples at many of the sampling locations. This would have greatly reduced the number of samples collected per rain.

Using hexane as the extraction solvent would have been beneficial. Better liquid-liquid separation occurs for small solvent quantity extractions with hexane. Further improvements in the verification of the results would have been observed with the use of surrogate and internal standards, along with the spike recovery adjustment method used, even though the methods used during this study were in compliance with the standard EPA methods.

Thirty-three percent of the PAH results were greater than the 1986 federal water quality criteria set for PAH human consumption (2.8 ng/L) (EPA, 1986). The short-term toxicity of urban runoff was measured to be low during the associated study (Pitt and Barron, 1990). However, long-term effects will be indicated by the carcinogenic effect due to human consumption, and probable contaminated sediment effects on receiving water organisms.

## REFERENCES

- Bailey, G. W., and J. L. White. Residue Review. 32:29, 1970.
- Borneff, J. Fate of Carcinogens in Aquatic Environments. In: Fate of Pollutants in the Air and Water Environments Part 2, I. H. Suffet, ed. John Wiley & Sons, Inc., 1977. pp. 393-408.
- Box, G. E. P., W. G. Hunter, and J. S. Hunter. Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building. John Wiley & Sons, Inc., 1978.
- Browman, M. G., and G. Chester. The Solid-Water Interface: Transfer of Organic Pollutants Across the Solid-Water Interface. In: Fate of Pollutants in the Air and Water Environments Part 1, I. H. Suffet, ed. John Wiley & Sons, Inc., 1977. pp. 49-106.
- City of Austin. Final Report of the Nationwide Urban Runoff Program in Austin, Texas. City of Austin and Engineering-Science, Inc., Austin, Texas, 1983.
- Ellis, S. R., and M. H. Mustard. A Summary of Urban Runoff Studies in the Denver Metropolitan Area, Colorado. Water Resources Investigations Report 84-4072, U.S. Geological Survey, Lakewood, Colorado, 1985.
- EPA. Base/Neutrals and Acids - Method 625. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 1982.
- EPA. Drinking Water Hotline. U.S. Environmental Protection Agency, Drinking Water Division, Washington, D.C., February 1990.
- EPA. Quality Criteria for Water. U.S. Environmental Protection Agency, Washington, D.C. PB87-226759, May, 1986.
- EPA. Results of the Nationwide Urban Runoff Program: Volume 1 - Final Report. U.S. Environmental Protection Agency, Water Planning Division, Washington, D.C., December 1983.
- EPA. Results of the Nationwide Urban Runoff Program: Volume 2 Appendices. U.S. Environmental Protection Agency, Water Planning Division, Washington, D.C., September 1982.
- Fam, S., M. K. Stenstrom, and G. Silverman. Hydrocarbons in Urban Runoff. Journal of Environmental Engineering, 113:1032-1046, 1987.

Field, R. Storm and Combined Sewer Overflow. An Overview of EPA's Disestablished Research Program. U.S. EPA, March 1988.

Field, R., and R. Turkeltaub. Urban Runoff Receiving Water Impacts: Program Overview. *Journal of Environmental Engineering*, 107:83-100, 1981.

Green, R. E. Pesticide - Clay - Water Interactions. *Pesticides in Soil and Water*. Soil Science Society of America Inc., Madison, Wisconsin, 1974.

Hoffman, E. J., and R. A. Duce. Factors Influencing the Organic Carbon Content of Atmospheric Sea Salt Particles: A Laboratory Study. Presented at the 55th Annual Meeting, Amer. Meteorol. Soc., Denver, Colorado, January 20-23, 1975.

Hoffman, E. J., G. L. Mills, J. S. Latimer, and J. G. Quinn. Urban Runoff as a Source of Polycyclic Aromatic Hydrocarbons to Coastal Waters. *Environmental Science and Technology*, 18:580-587, 1984.

Johnson, S., and I. S. Gribberstab. Influence of Human Substances on the Formation of Chlorinated Polycyclic Aromatic Hydrocarbons During Chlorination of Polycyclic Aromatic Hydrocarbon Polluted Water. *Environmental Science and Technology*, 22: 978-981, 1988.

Kerr, S. R.; and W. P. Vass. Pesticide Residues in Aquatic Invertebrates. In: *Environmental Pollution by Pesticides*, C. A. Edwards, ed. Plenum, London, 1973.

Kopfler, F. C., R. G. Melton, J. L. Mullaney, and R. G. Tardiff. Human Exposure to Water Pollutants. In: *Fate of Pollutants in the Air and Water Environments Part 2*, I. H. Suffet, ed. John Wiley & Sons, 1977. pp. 419-434.

Lane, D. A., and M. Katz. The Photomodification of Benzo(a)pyrene, Benzo(b)fluoranthene, and Benzo(k)fluoranthene Under Simulated Atmospheric Conditions. In: *Fate of Pollutants in the Air and Water Environments Part 2*, I. H. Suffet, ed. John Wiley & Sons, Inc., 1977. pp. 137-154.

Lysyj, I., and E. C. Russell. Transfer of Organics From an Oil Film into Water. In: *Fate of Pollutants in the Air and Water Environments Part 1*, I. H. Suffet, ed. John Wiley & Sons, 1977. pp. 135-144.

Mason, R. D., D. A. Lind, and W. G. Marchal. *Statistics: An Introduction*. Harcourt Brace Jovanovich, Inc., 1983. pp. 626.

McGinn, J. M. Watershed Management Plan for Lake Quinsigamond and Flint Pond. Office of Planning and Program Management, Massachusetts Department of Environmental Quality Engineering and Lakes Section, Technical Services Branch, Massachusetts Division of Water Pollution Control, 1982.

Metcalf, R. L. Biological Fate and Transformation of Pollutants in Water. In: Fate of Pollutants in the Air and Water Environments Part 2, I. H. Suffet, ed. John Wiley & Sons, Inc., 1977. pp. 195-221.

Metcalf, R. L. Metabolism and Fate of Pesticides in Plants and Animals. Scientific Aspects of Pest Control. National Academy of Sciences, Publication 1402, Washington, D.C., 1966.

Metroplan. Fourche Creek Urban Runoff Project. Metroplan, Little Rock, Arkansas, 1983.

Mid-American R.C. Nationwide Urban Runoff Program, Kansas City Area Project. Mid-American Regional Council and F. X. Browne Associates, Inc., Kansas City, Missouri, 1983.

National Academy of Sciences. Degradation of Synthetic Molecules in the Biosphere, Washington, D.C., 1972.

North Carolina DNR. Nationwide Urban Runoff Program, Winston-Salem, North Carolina. Division of Environmental Management, North Carolina Department of Natural Resources and Community Development, Raleigh, North Carolina, 1983.

Oakland, P. H. Summary Report, Durham Urban Runoff Program. New Hampshire Water Supply and Pollution Control Commission, Concord, New Hampshire, June 1983.

Oxmoor Road Station. Local Climological Data: Monthly Summary. National Weather Service, Oxmoor Road, Birmingham, Alabama, March, May, June, July 1989.

Pereira, W. E., D. K. Demcheck, C. E. Rostad, C. T. Chlou, T. I. Brinton, L. B. Barber, and C. R. Demas. Contamination of Estuarine Water, Biota, and Sediment by Halogenated Organic Compounds: A Field Study. Environmental Science and Technology, 22: 772-778, 1988.

Pitt, R. Demonstration of Nonpoint Pollution Abatement Through Improved Street Cleaning Practices. EPA 600/2-79-161, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1979.

Pitt, R., and P. Bissonette. Bellevue Urban Runoff Program, Summary Report. U.S. Environmental Protection Agency and the Storm and Surface Water Utility, Bellevue, Washington, 1984.

Pitt, R., and P. Barron. Assessment of Urban and Industrial Stormwater Runoff Toxicity and the Evaluation/Development of Treatment for Runoff Toxicity Abatement - Phase I. U.S. Environmental Protection Agency, Office of Research and Development, Edison, New Jersey, 1990.

Pitt, R., and M. Bozeman. Sources of Urban Runoff Pollution and Its Effects on an Urban Creek. EPA 600/52-82-090, NTIS PB 83-111021, U.S. Environmental Protection Agency, Cincinnati, Ohio, 1982.

Rumer, R. R. Physical Process for Pollutant Transport in the Water Environment. In: Fate of Pollutants in the Air and Water Environments Part 1, I. H. Suffet, ed. John Wiley & Sons, 1977. pp. 297-321.

Systat Version 4.0. Systat, Inc., Evanston, Illinois, 1988.

Winchester, J. W., and R. A. Duce. The Air-Water Interface: Particulate Matter Exchange Across the Air-Water Interface. In: Fate of Pollutants in the Air and Water Environments Part 1, I. H. Suffet, ed. John Wiley & Sons, Inc., 1977. pp. 27-48.

APPENDIX A  
LOG NORMAL PROBABILITY PLOTS FOR  
EACH COMPOUND DETECTED



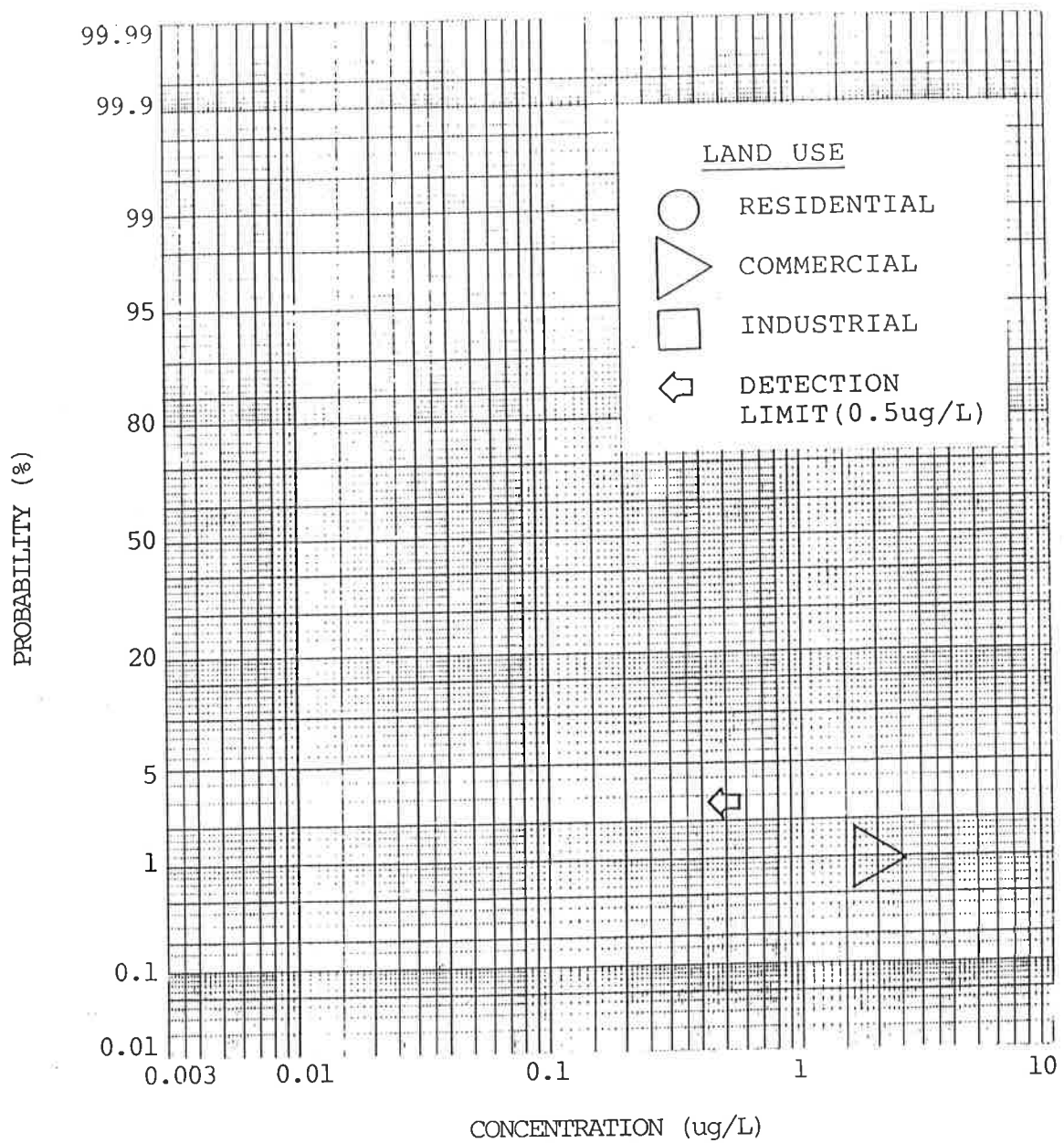


Figure A.1 Acenaphthene Log Normal Probability Plot Indicating Land Use for Each Sample Concentration Detected.

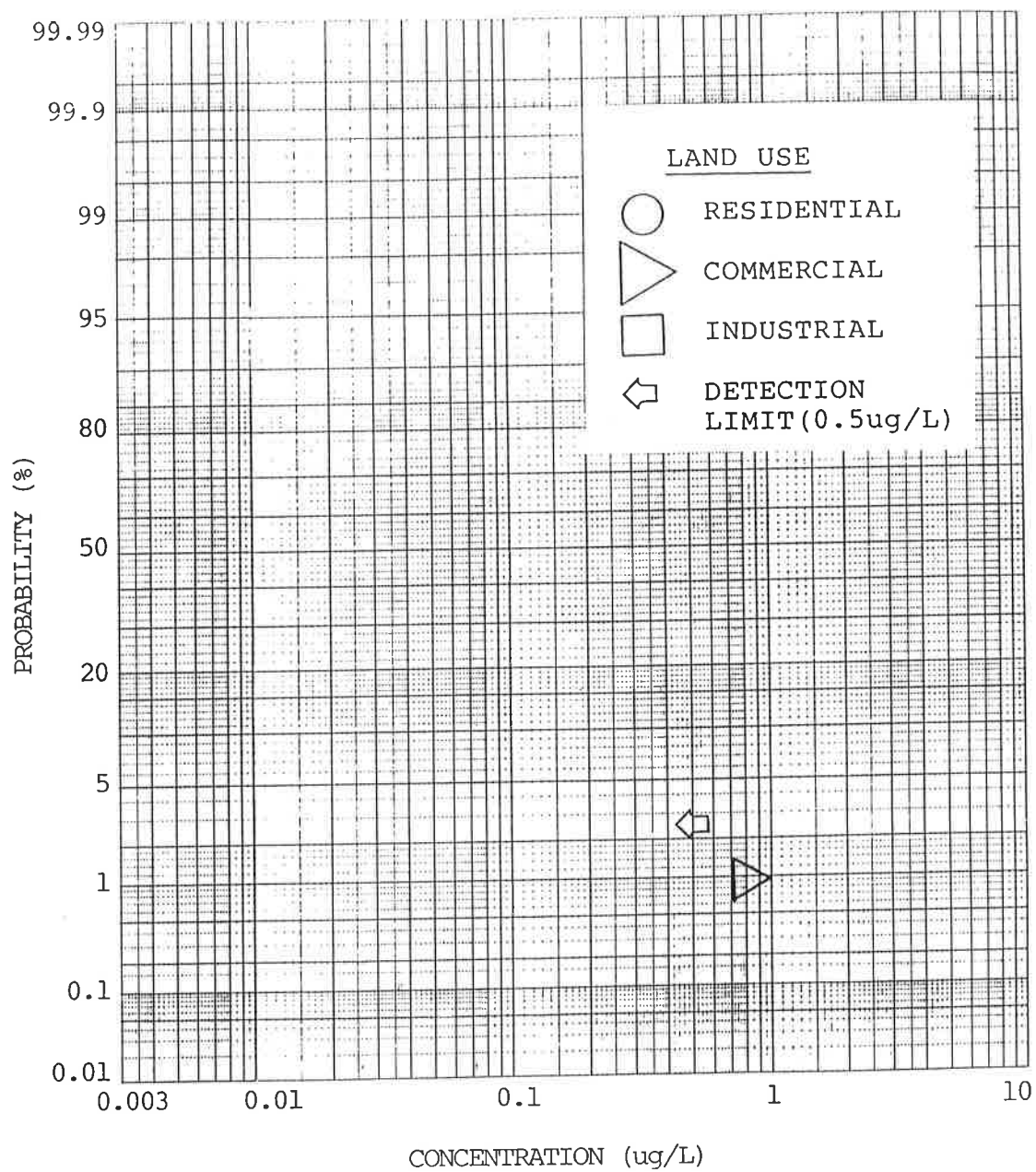


Figure A.2 Fluorene Log Normal Probability Plot Indicating Land Use for Each Sample Concentration Detected.

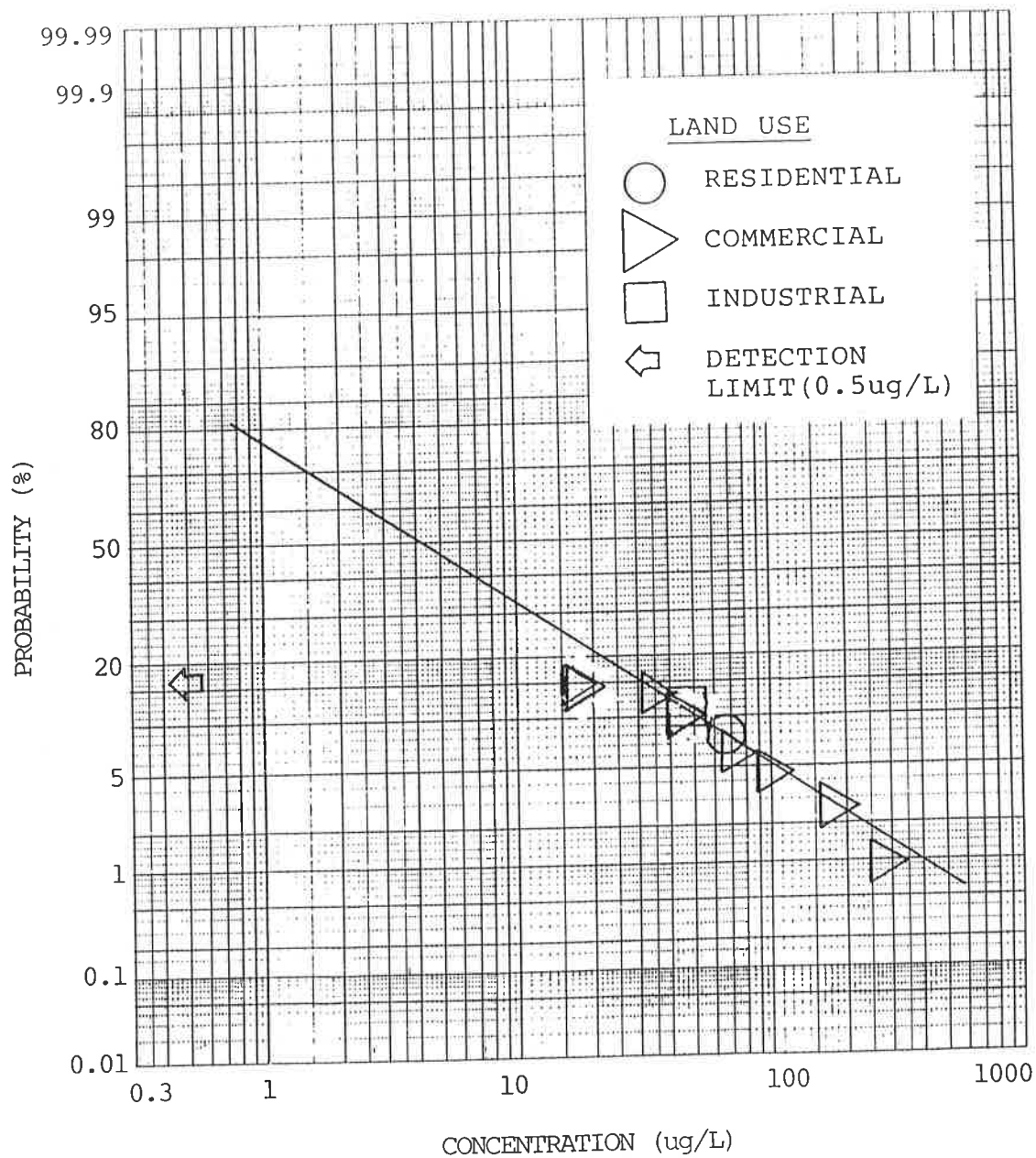


Figure A.3 Naphthalene Log Normal Probability Plot Indicating Land Use for Each Sample Concentration Detected.

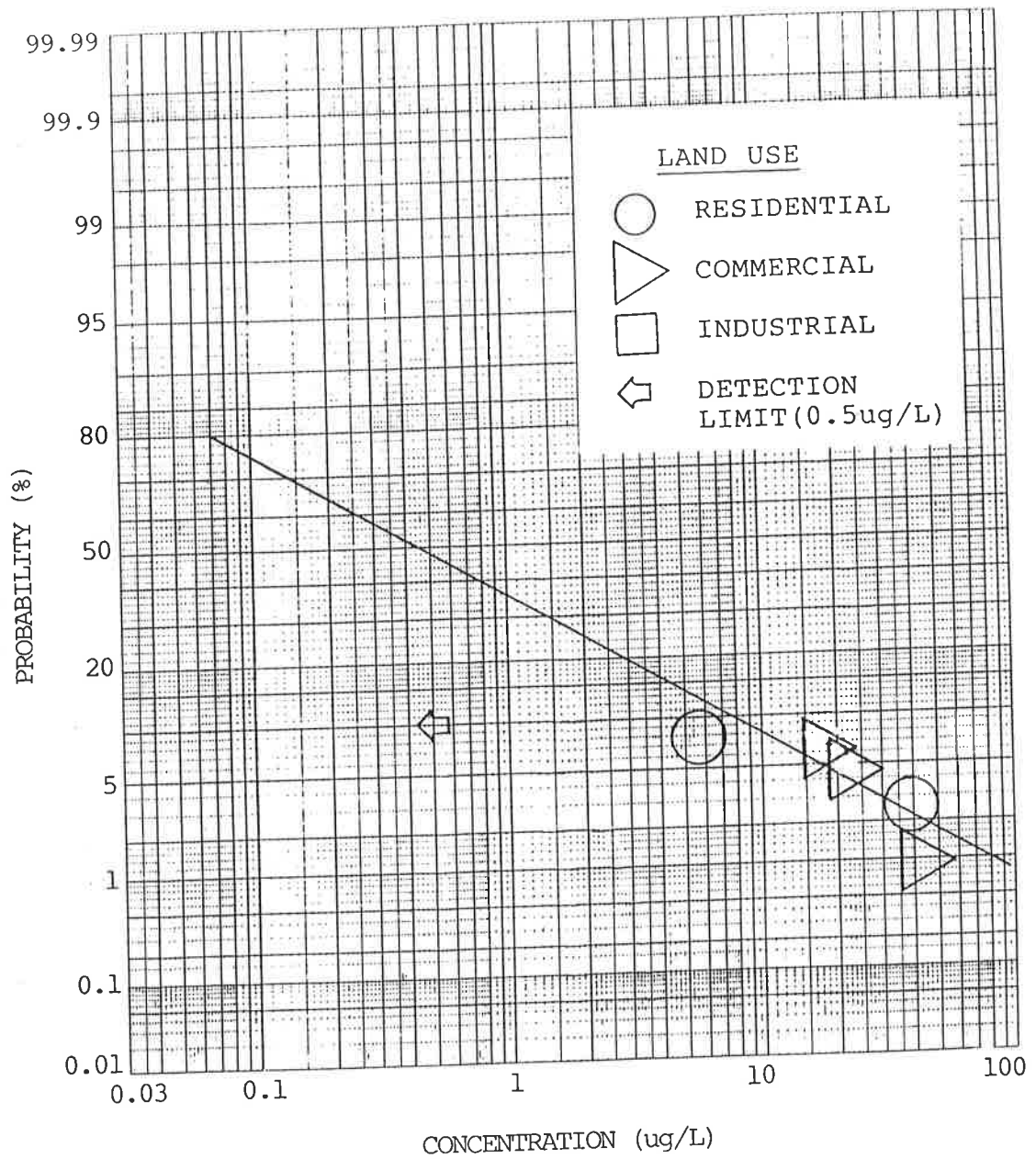


Figure A.4 Anthracene Log Normal Probability Plot Indicating Land Use for Each Sample Concentration Detected.

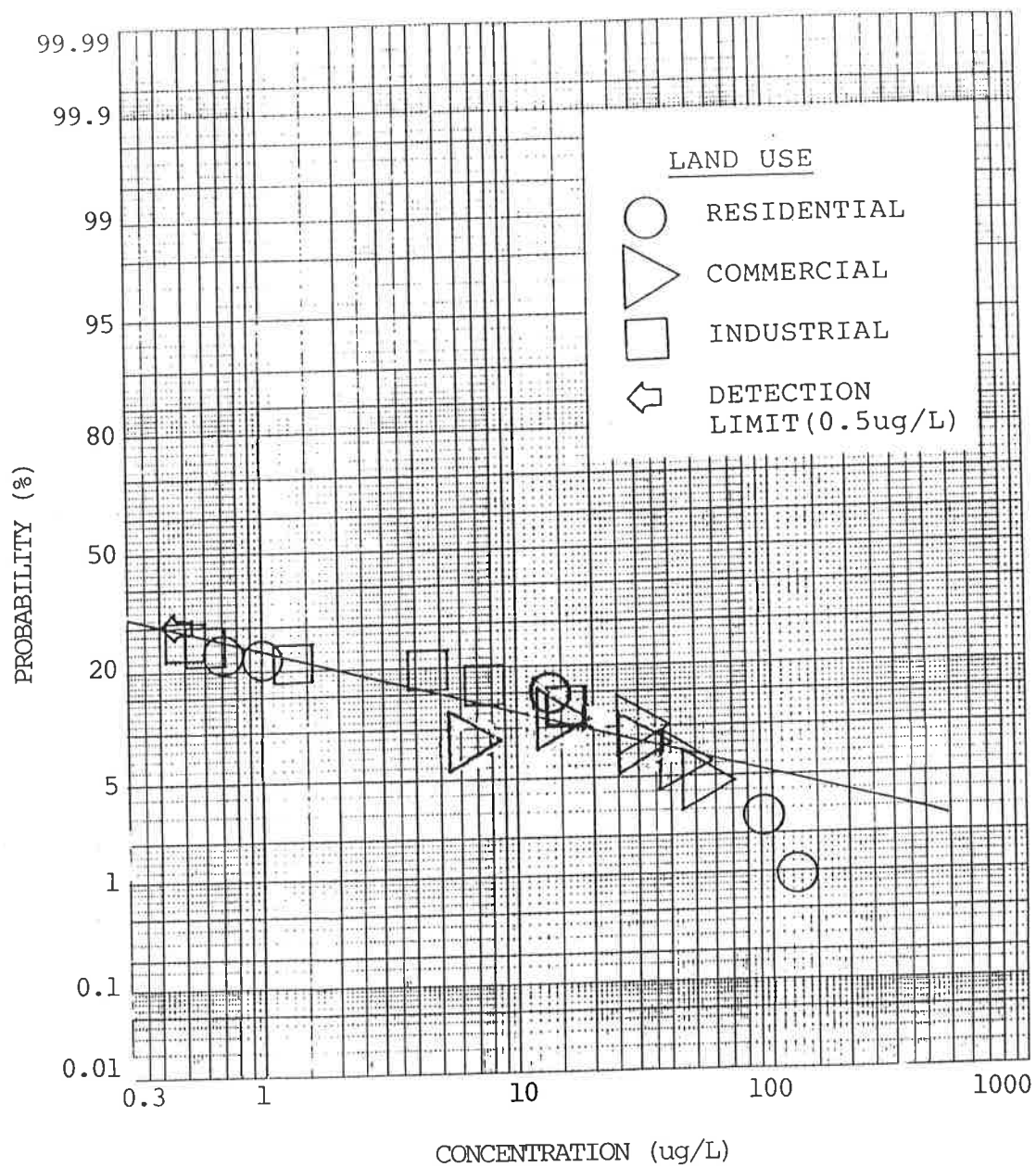


Figure A:5 Fluoranthene Log Normal Probability Plot Indicating Land Use for Each Sample Concentration Detected.

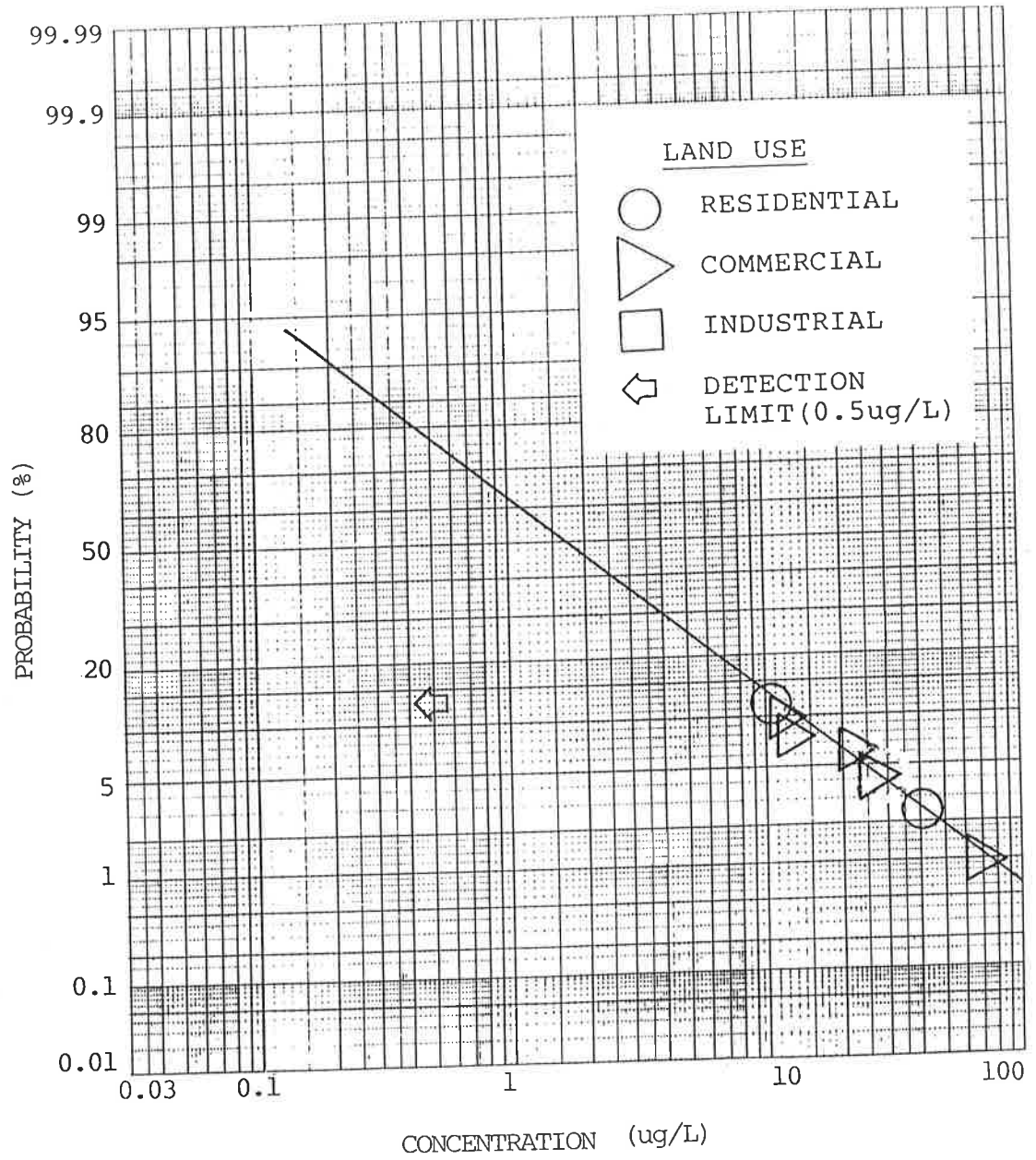


Figure A.6 Phenanthrene Log Normal Probability Plot Indicating Land Use for Each Sample Concentration Detected.



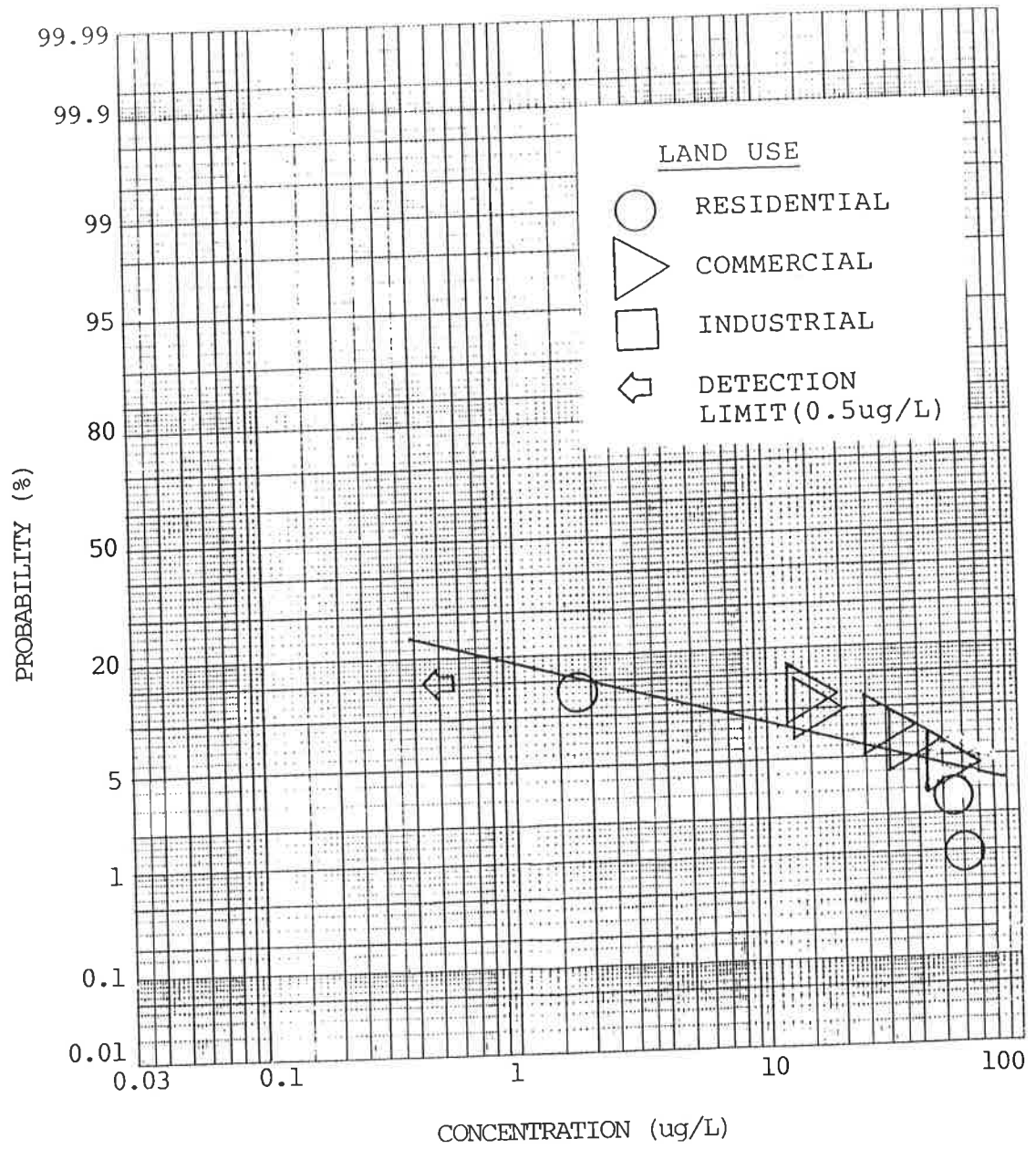


Figure A:7 Benzo(a)anthracene Log Normal Probability Plot Indicating Land Use for Each Sample Concentration Detected.

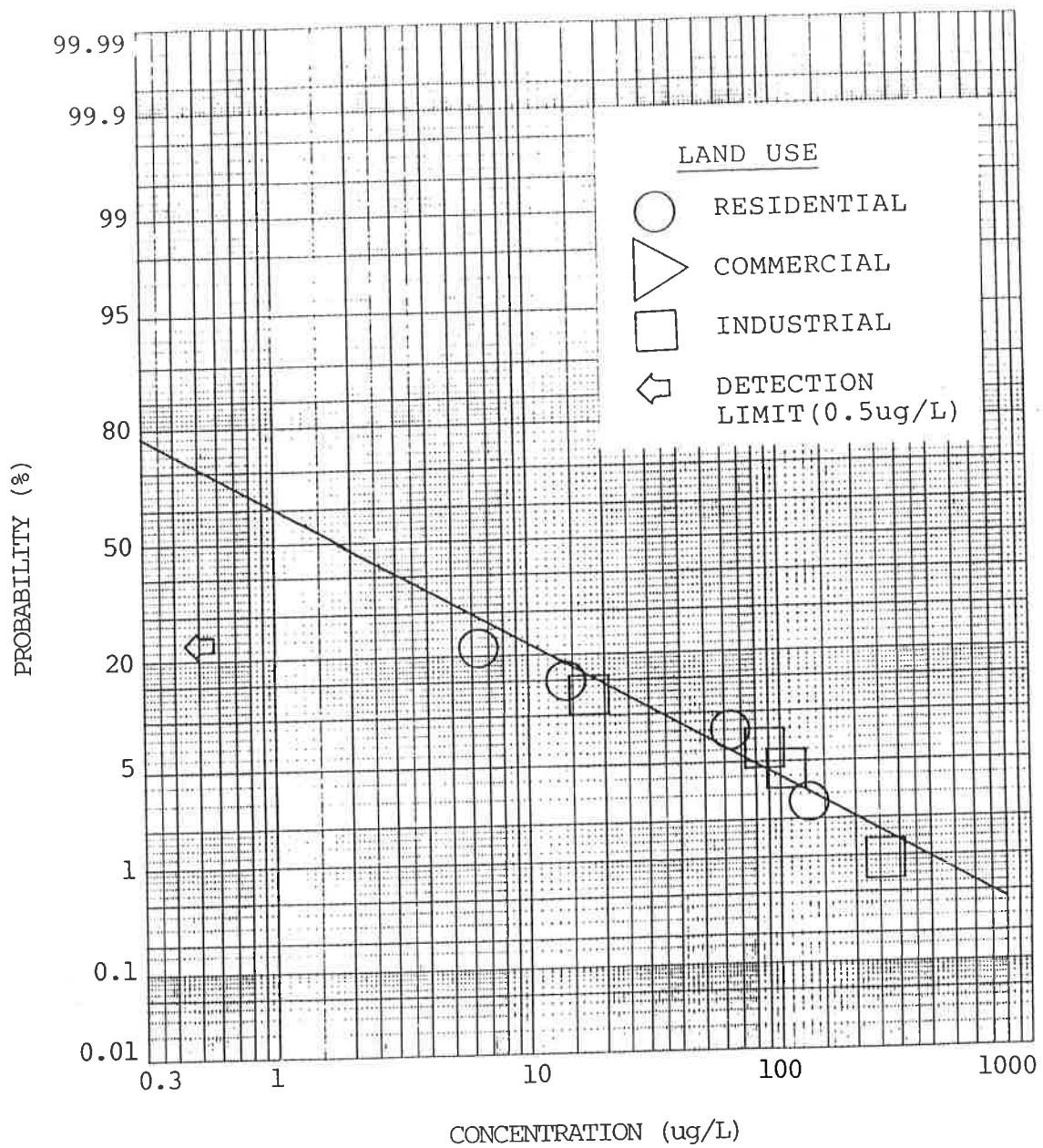


Figure A.8 Benzo(b)fluoranthene Log Normal Probability Plot Indicating Land Use for Each Sample Concentration Detected.



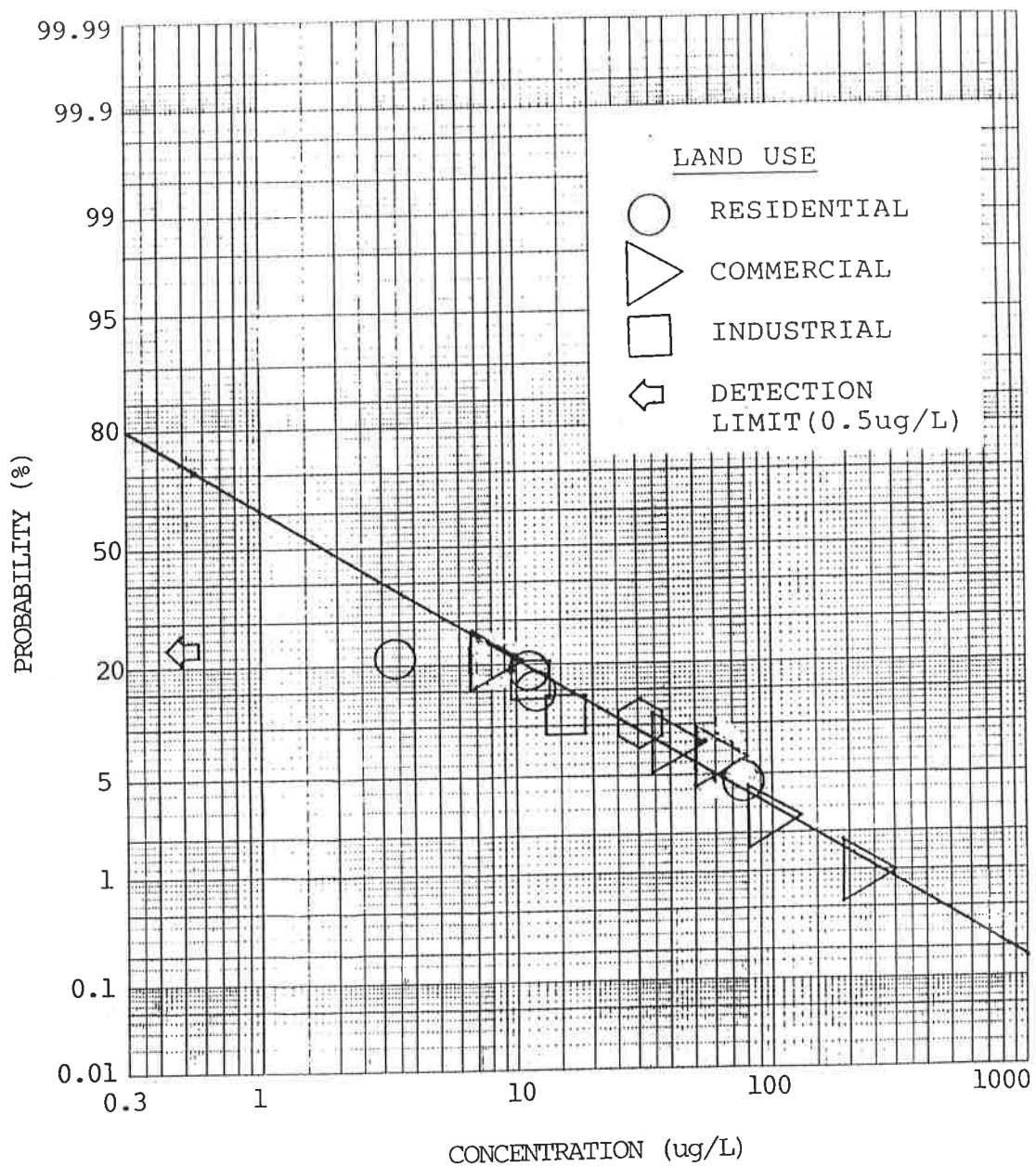


Figure A.9 Benzo(k)fluoranthene Log Normal Probability Plot  
 Indicating Land Use for Each Sample Concentration Detected.

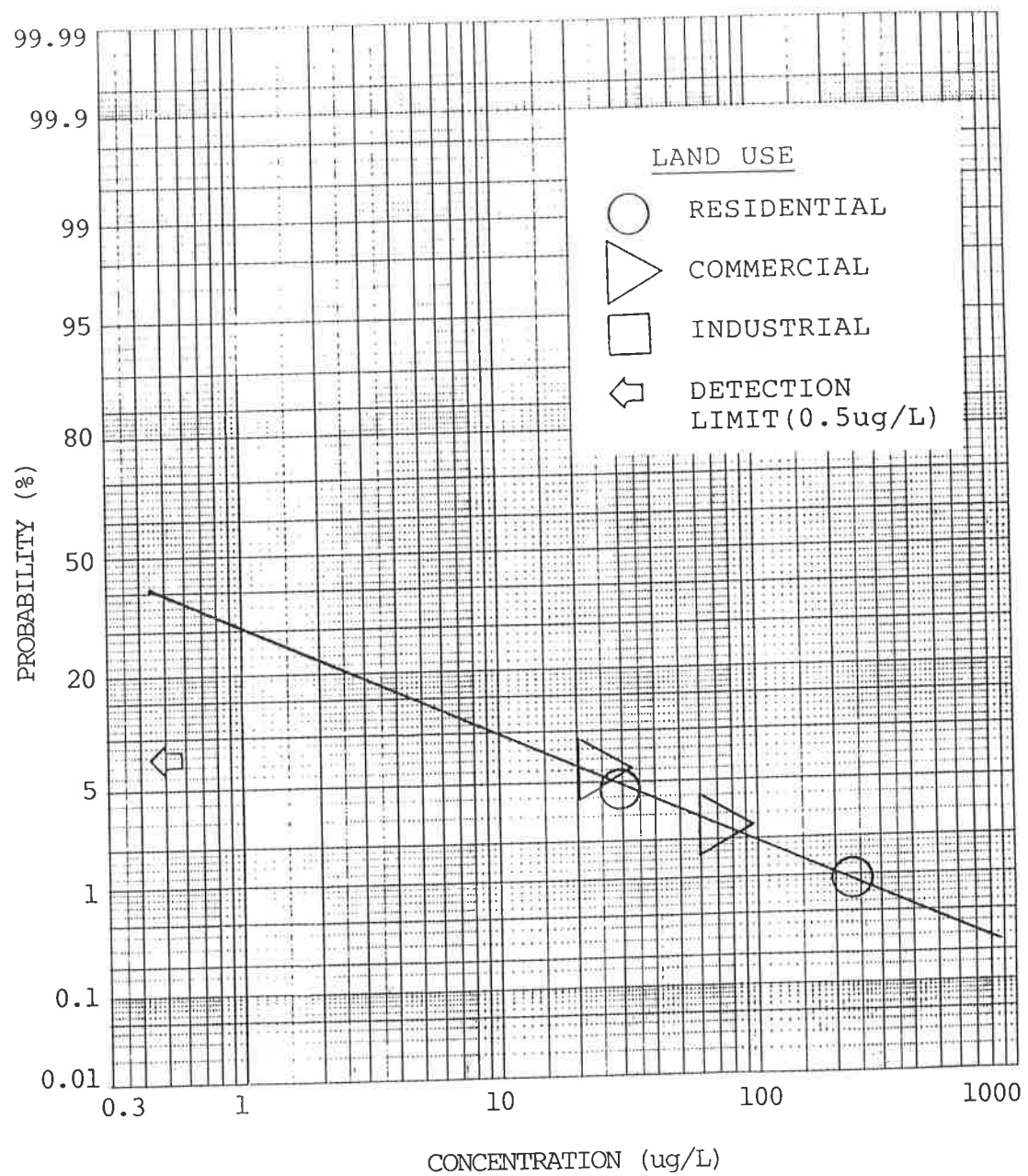


Figure A.10 Chrysene Log Normal Probability Plot Indicating Land Use for Each Sample Concentration Detected.

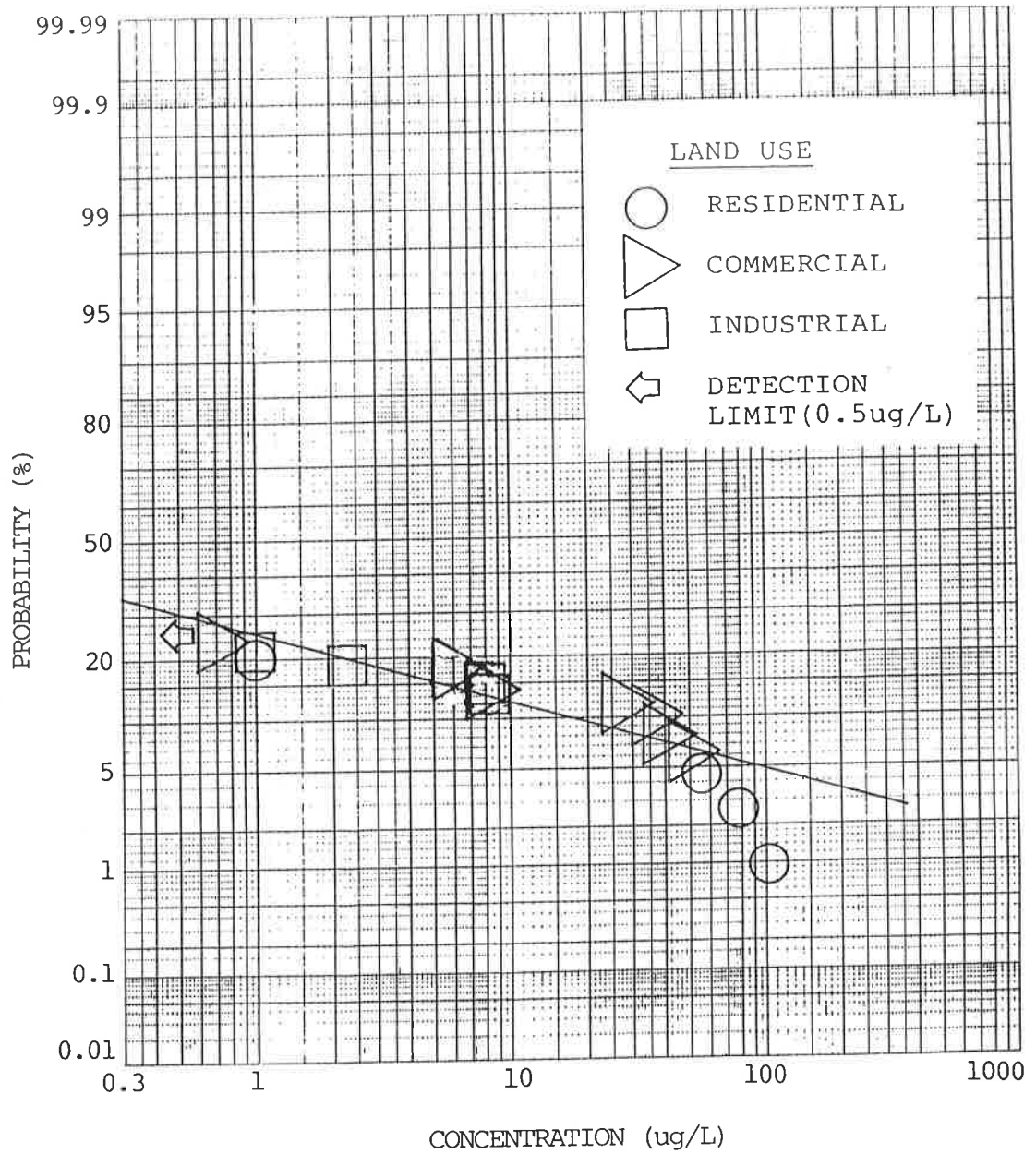


Figure A.11 Pyrene Log Normal Probability Plot Indicating Land Use for Each Sample Concentration Detected.

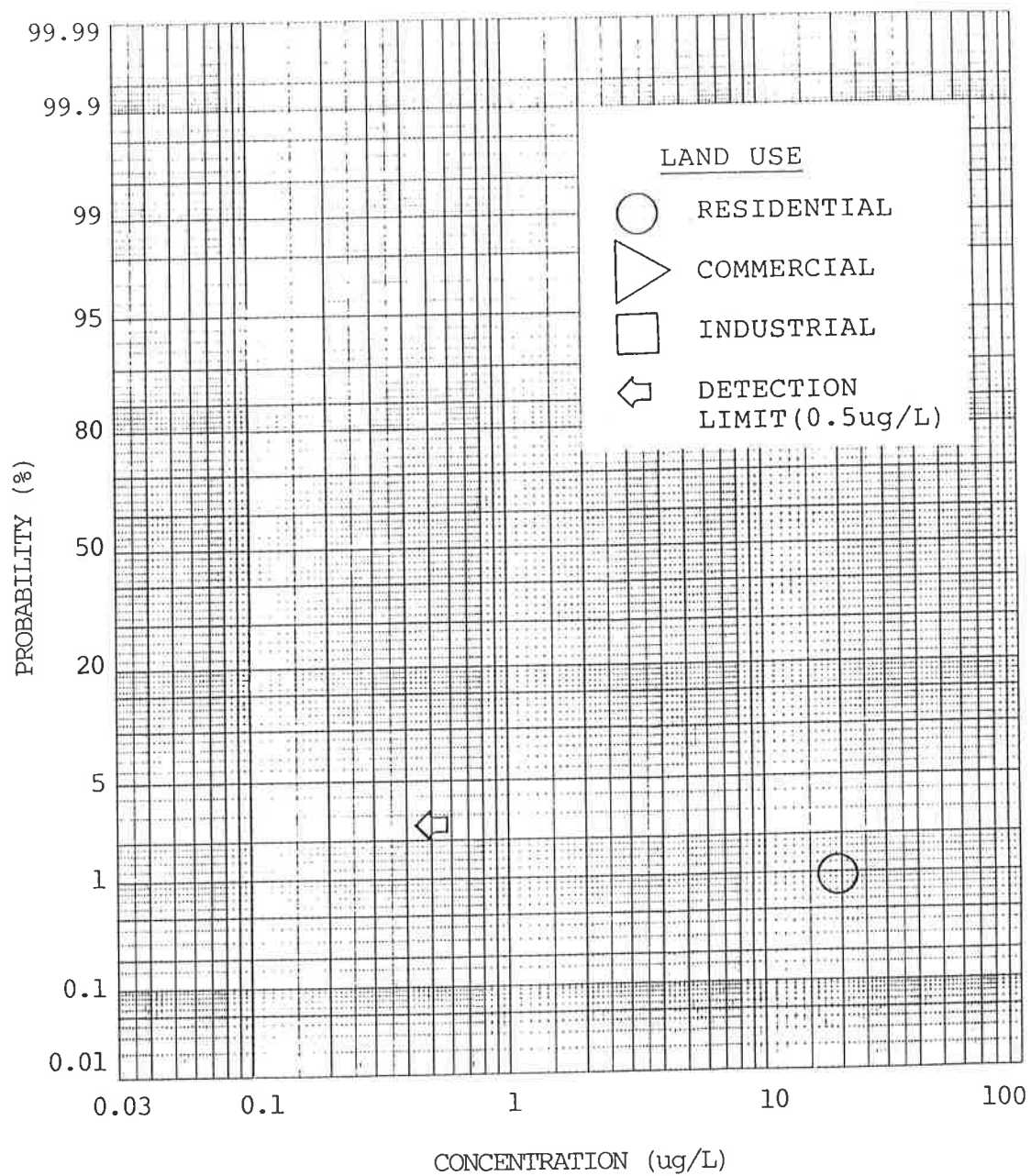


Figure A.12 Benzo(ghi)perylene Log Normal Probability Plot  
Indicating Land Use for Each Sample Concentration Detected.

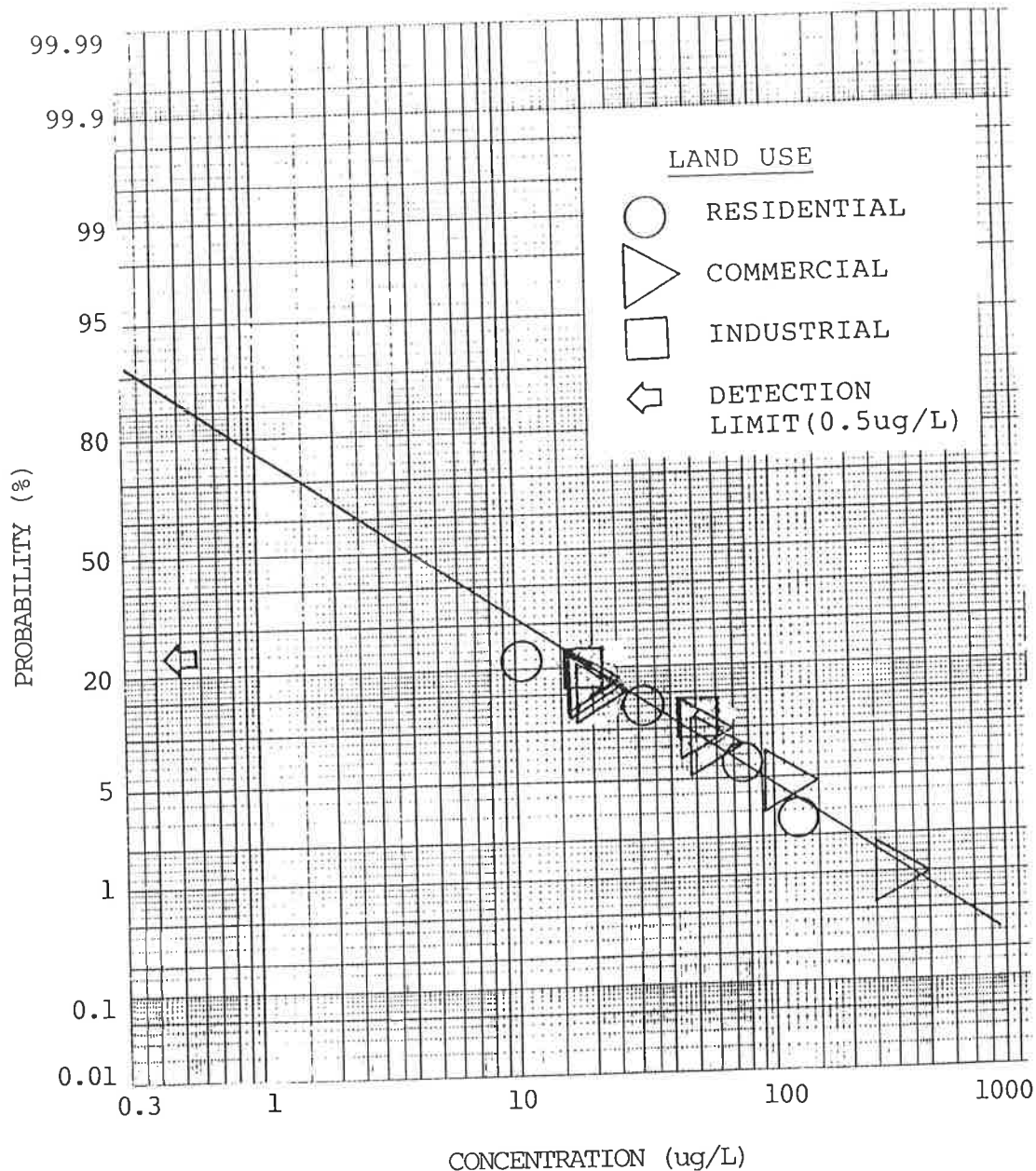


Figure A.13 Benzo(a)pyrene Log Normal Probability Plot Indicating Land Use for Each Sample Concentration Detected.

APPENDIX B  
BOX PLOTS FOR EACH COMPOUND DETECTED ACCORDING  
TO EACH LOCATION AND RAIN FACTOR

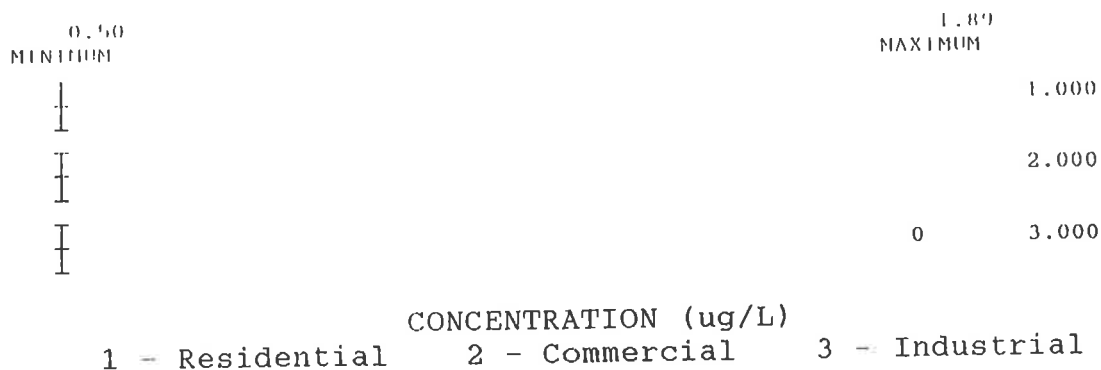


Figure B.1 Acenaphthene Box Plots of Land Use Categories.

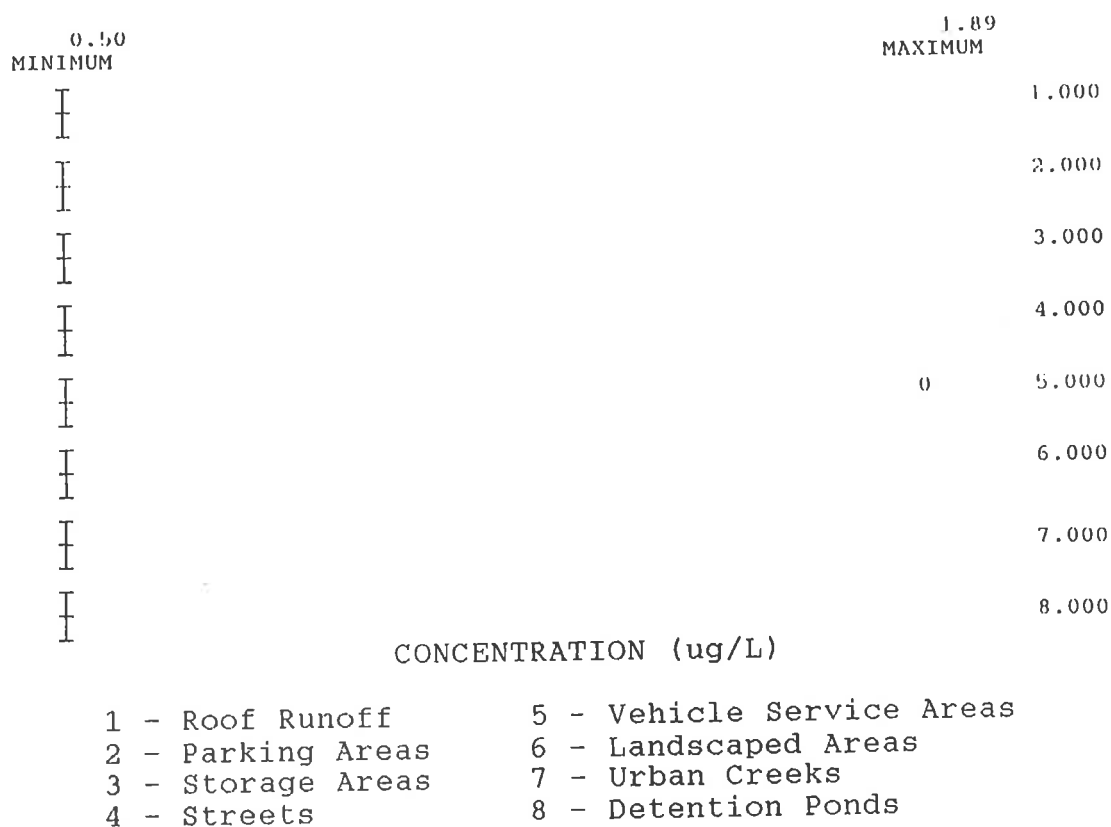


Figure B.2 Acenaphthene Box Plots of Source Area Categories.

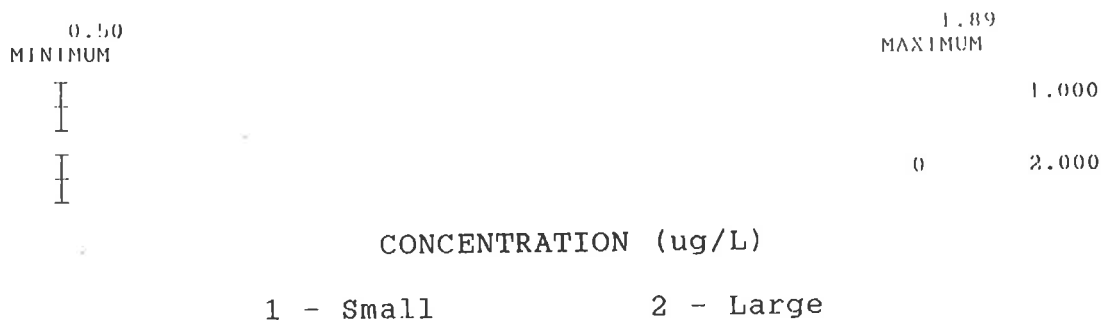


Figure B.3 Acenaphthene Box Plots of Rain Depth Categories.

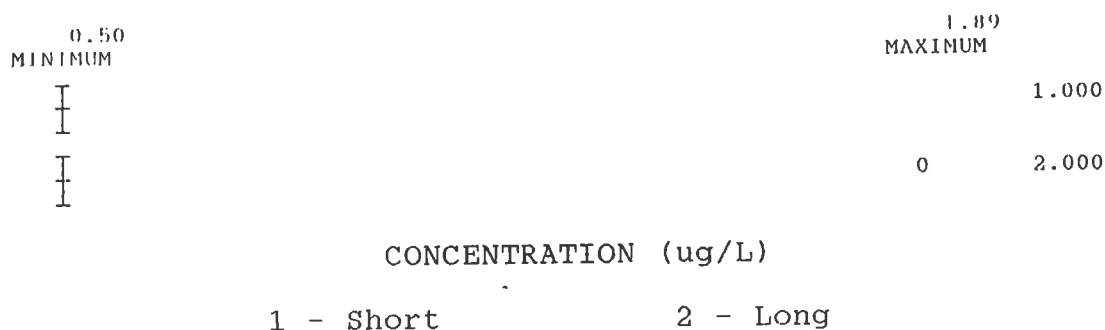


Figure B.4 Acenaphthene Box Plots of Antecedent Dry Period Categories.

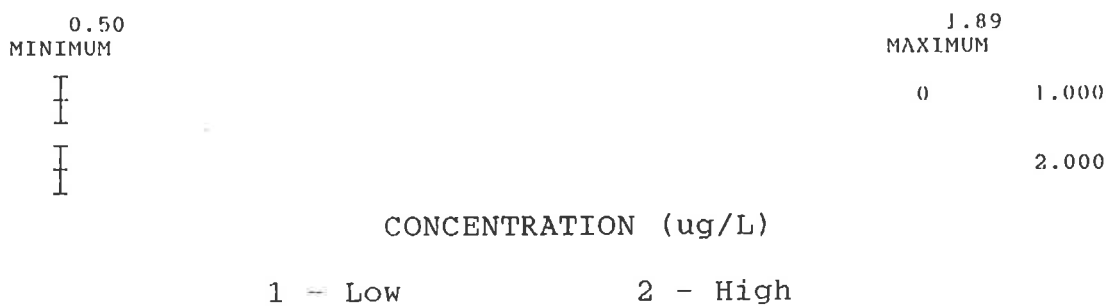


Figure B.5 Acenaphthene Box Plots of Peak Intensity Categories.



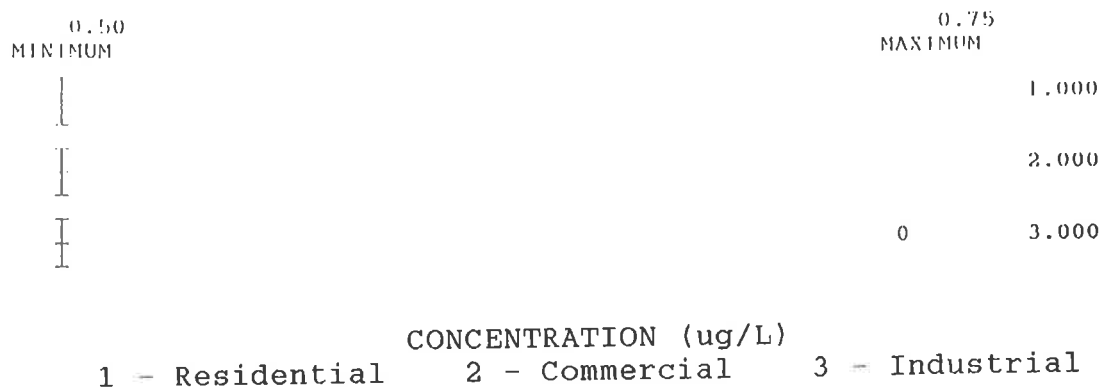


Figure B.6 Fluorene Box Plots of Land Use Categories.

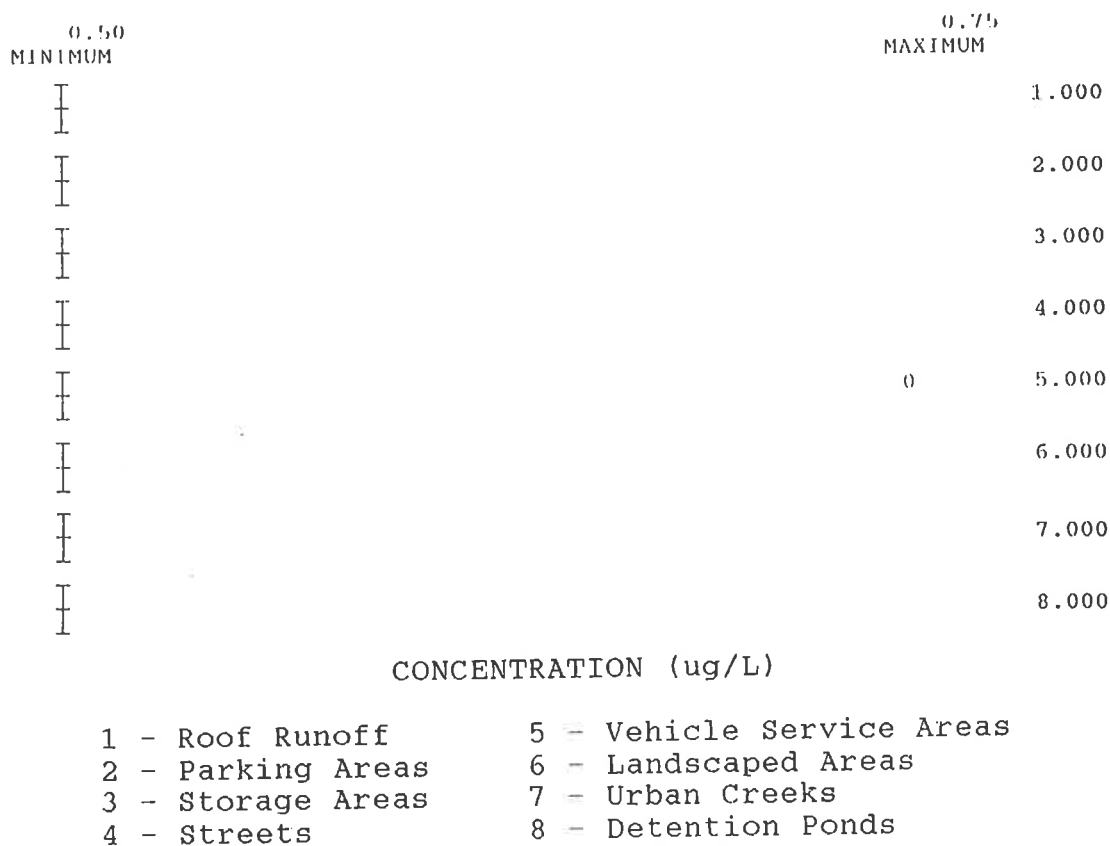


Figure B.7 Fluorene Box Plots of Source Area Categories.

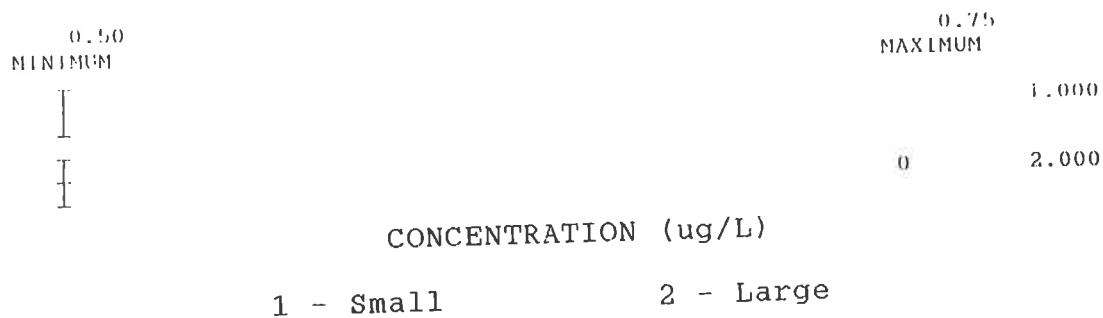


Figure B.8 Fluorene Box Plots of Rain Depth Categories.

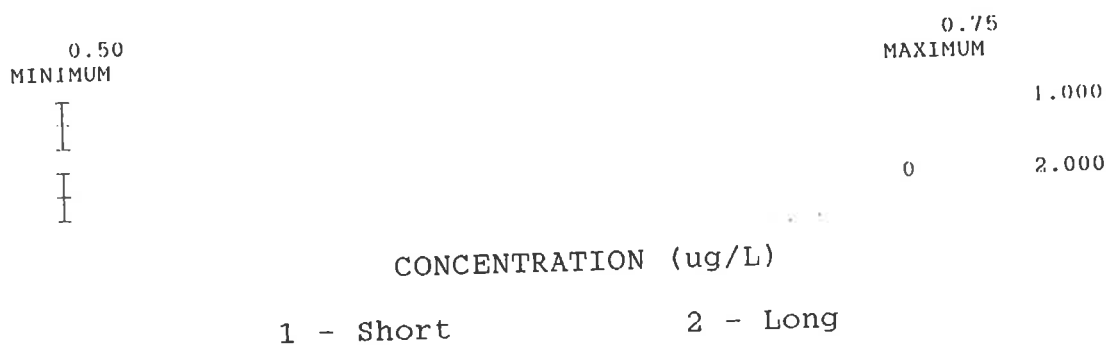


Figure B.9 Fluorene Box Plots of Antecedent Dry Period Categories.

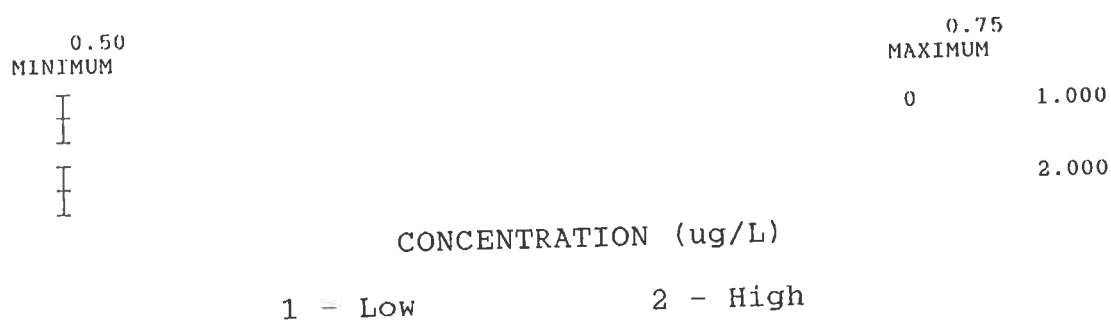


Figure B.10 Fluorene Box Plots of Peak Intensity Categories.

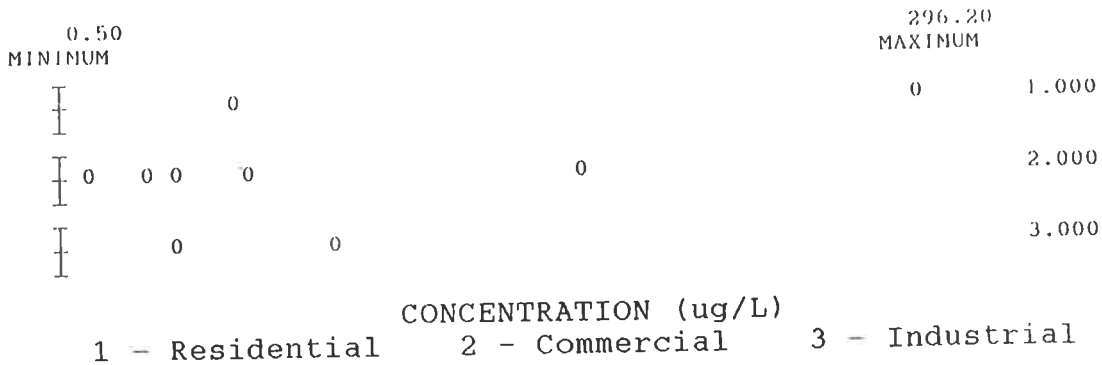


Figure B.11 Naphthalene Box Plots of Land Use Categories.



- 1 - Roof Runoff
- 2 - Parking Areas
- 3 - Storage Areas
- 4 - Streets
- 5 - Vehicle Service Areas
- 6 - Landscaped Areas
- 7 - Urban Creeks
- 8 - Detention Ponds

Figure B.12 Naphthalene Box Plots of Source Area Categories.

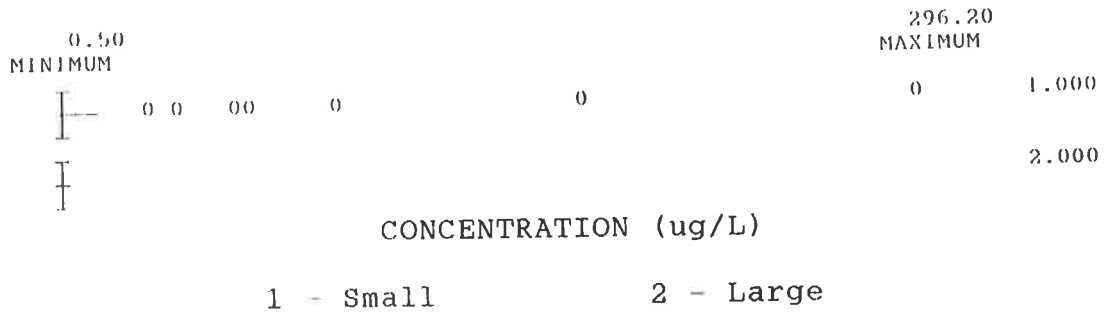


Figure B.13 Naphthalene Box Plots of Rain Depth Categories.

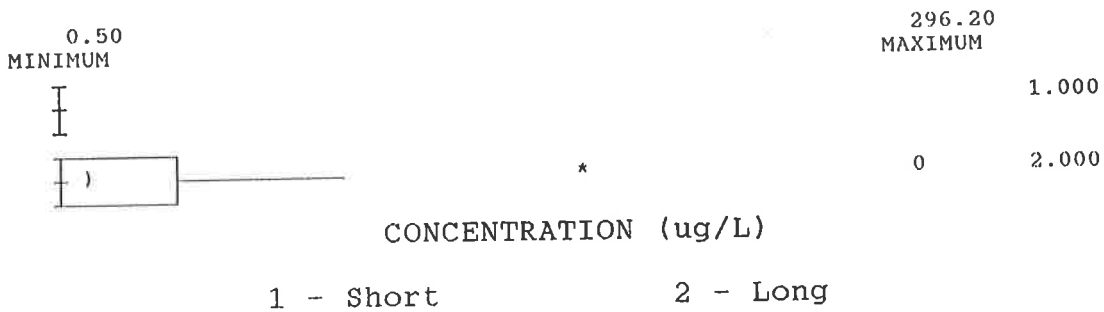


Figure B.14 Naphthalene Box Plots of Antecedent Dry Period Categories.

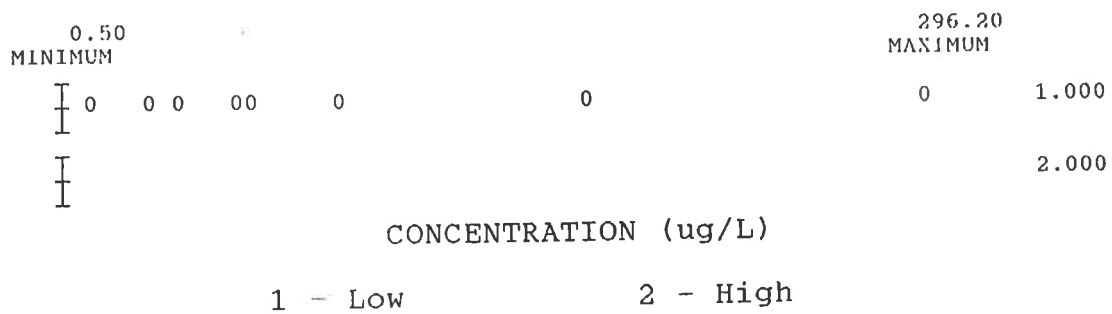


Figure B.15 Naphthalene Box Plots of Peak Intensity Categories.

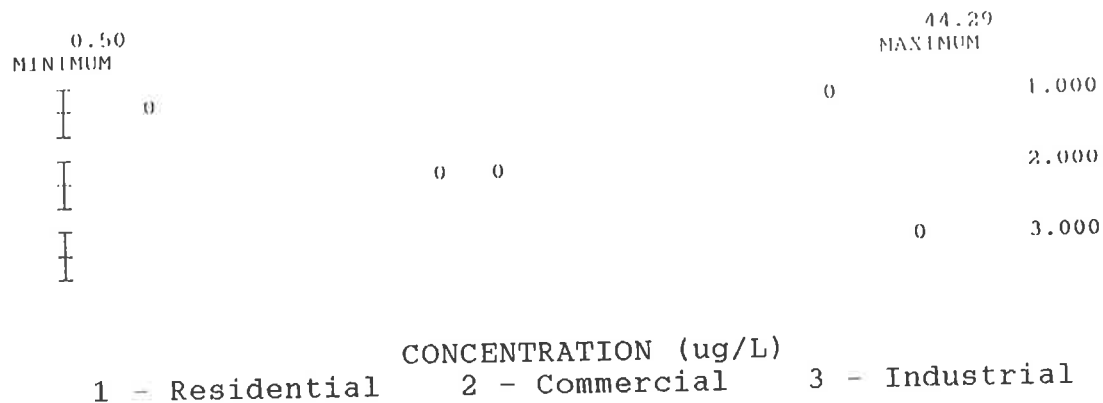


Figure B.16 Anthracene Box Plots of Land Use Categories.

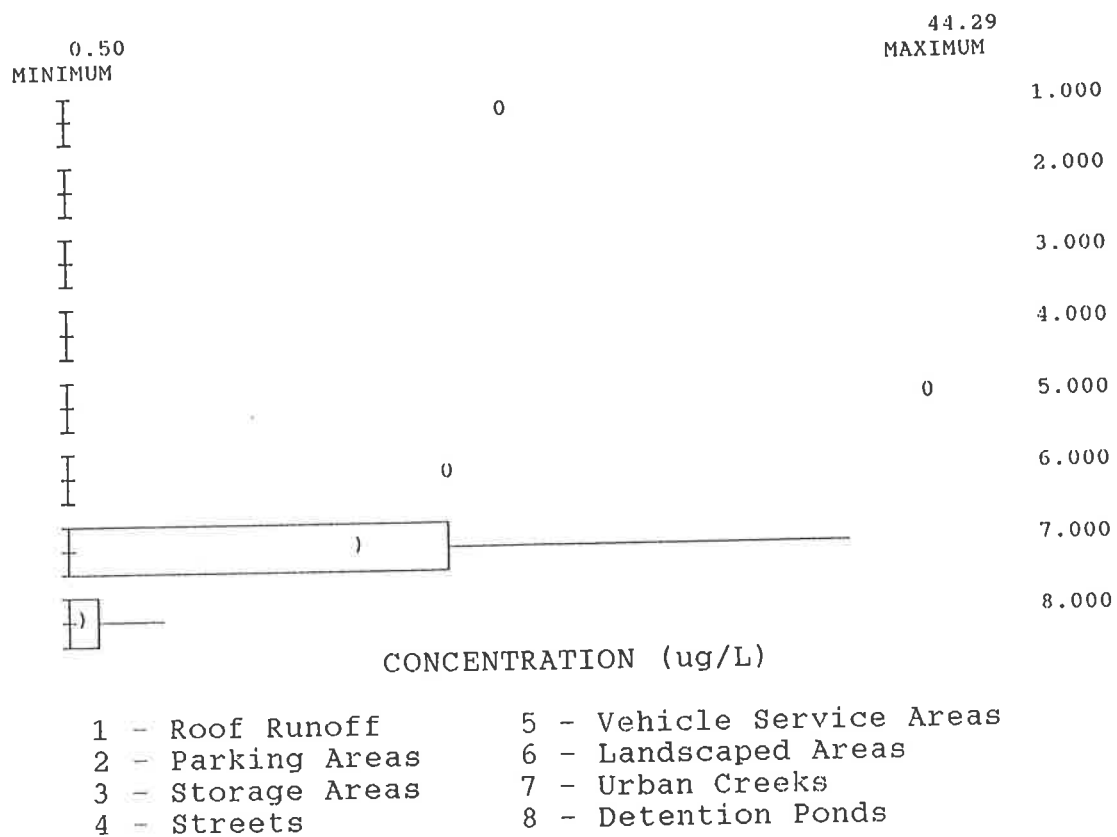


Figure B.17 Anthracene Box Plots of Source Area Categories.

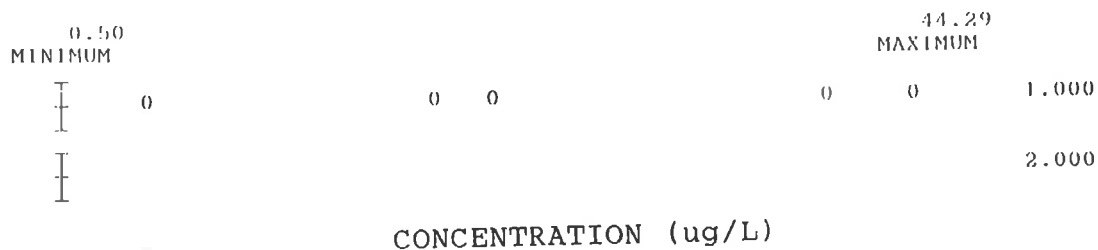


Figure B.18 Anthracene Box Plots of Rain Depth Categories.

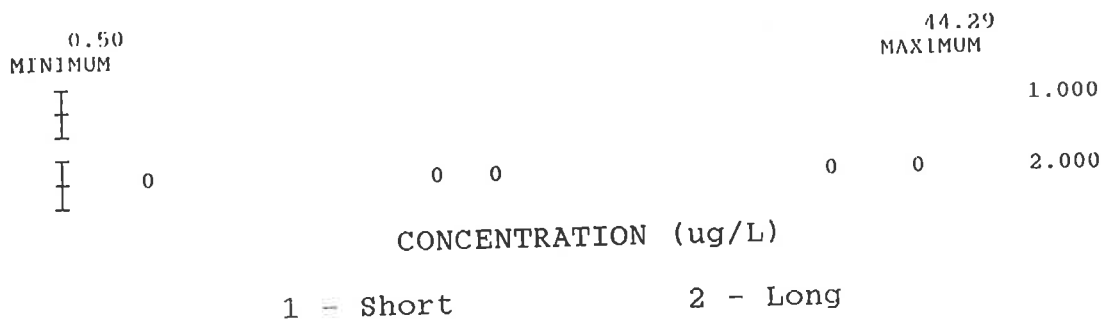


Figure B.19 Anthracene Box Plots of Antecedent Dry Period Categories.

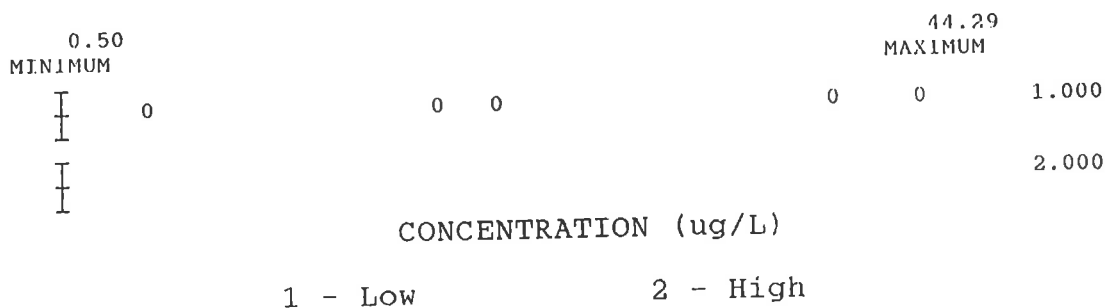


Figure B.20 Anthracene Box Plots of Peak Intensity Categories.

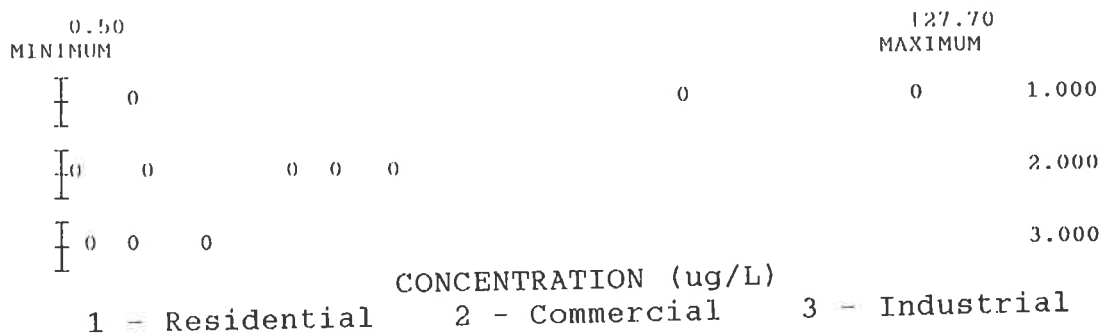
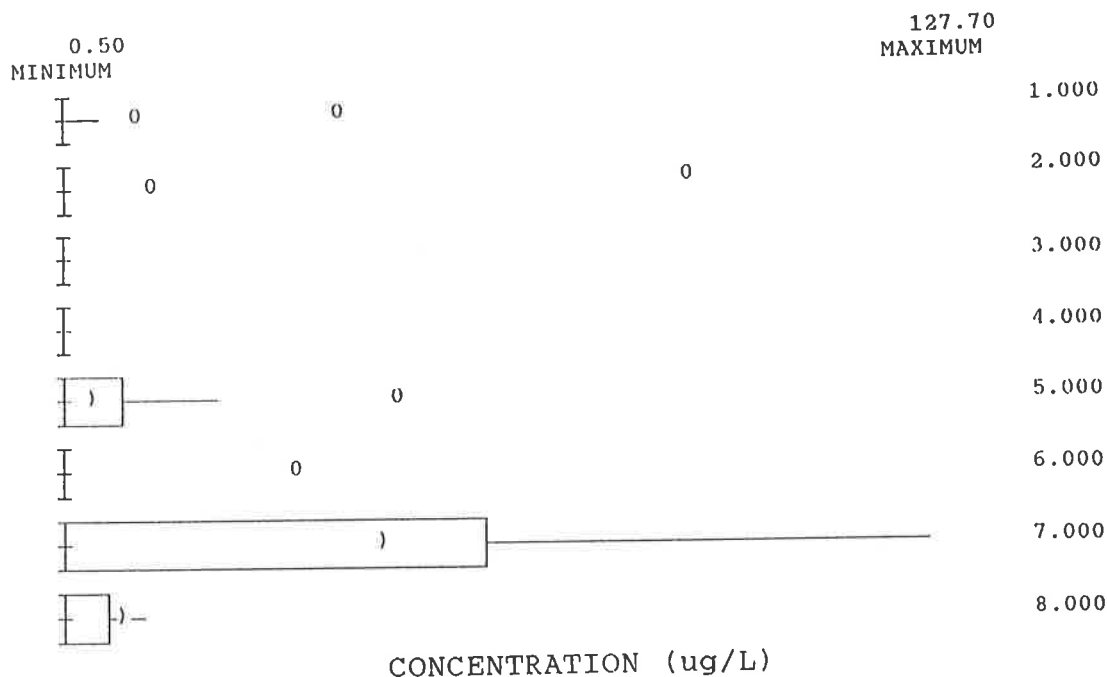


Figure B.21 Fluoranthene Box Plots of Land Use Categories.



- 1 - Roof Runoff
- 2 - Parking Areas
- 3 - Storage Areas
- 4 - Streets
- 5 - Vehicle Service Areas
- 6 - Landscaped Areas
- 7 - Urban Creeks
- 8 - Detention Ponds

Figure B.22 Fluoranthene Box Plots of Source Area Categories.

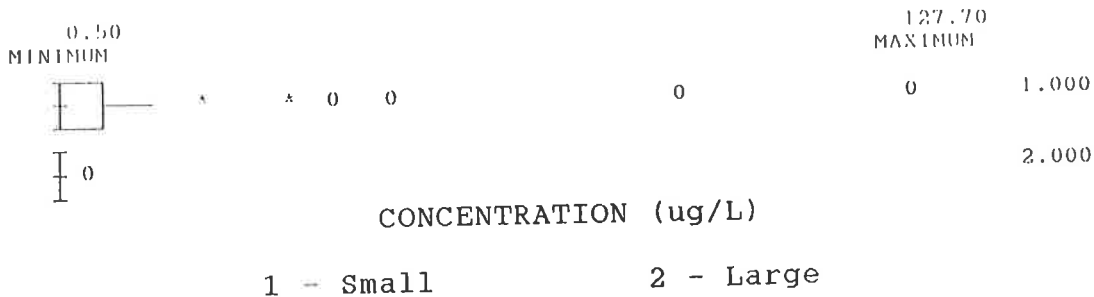


Figure B.23 Fluoranthene Box Plots of Rain Depth Categories.

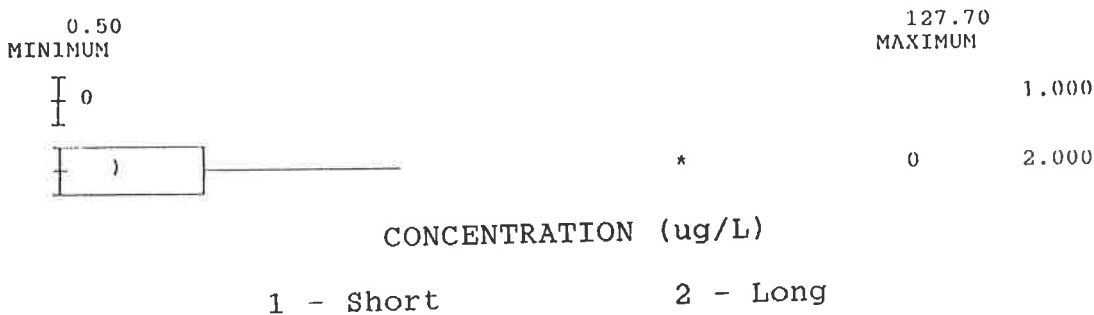


Figure B.24 Fluoranthene Box Plots of Antecedent Dry Period Categories.

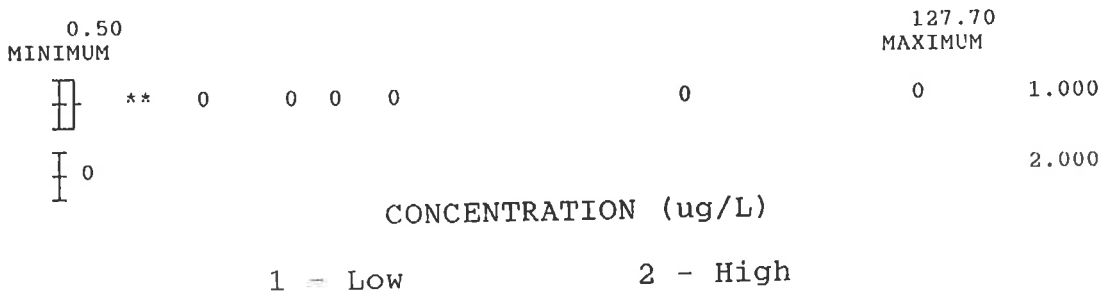


Figure B.25 Fluoranthene Box Plots of Peak Intensity Categories.



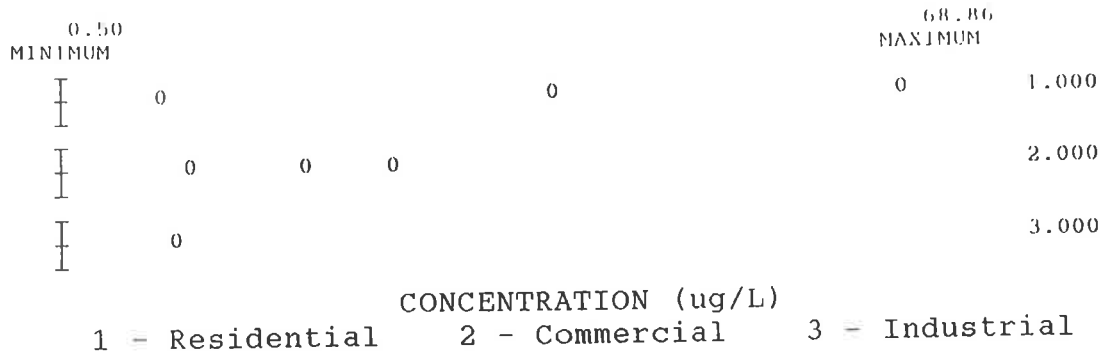
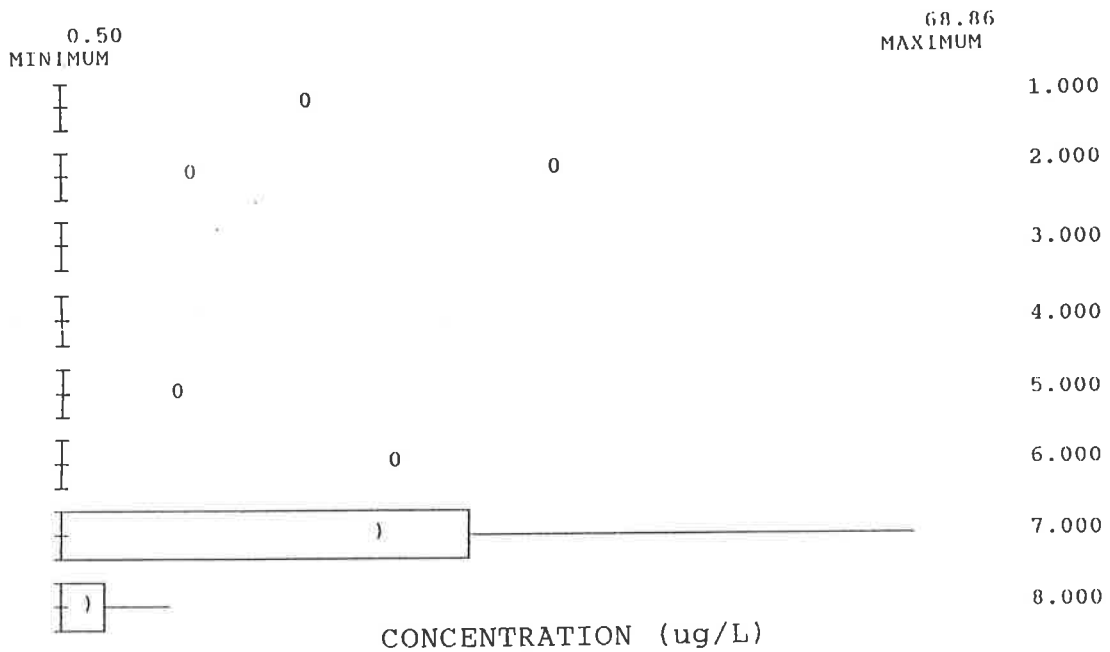


Figure B.26 Phenanthrene Box Plots of Land Use Categories.



- 1 - Roof Runoff
- 2 - Parking Areas
- 3 - Storage Areas
- 4 - Streets
- 5 - Vehicle Service Areas
- 6 - Landscaped Areas
- 7 - Urban Creeks
- 8 - Detention Ponds

Figure B.27 Phenanthrene Box Plots of Source Area Categories.

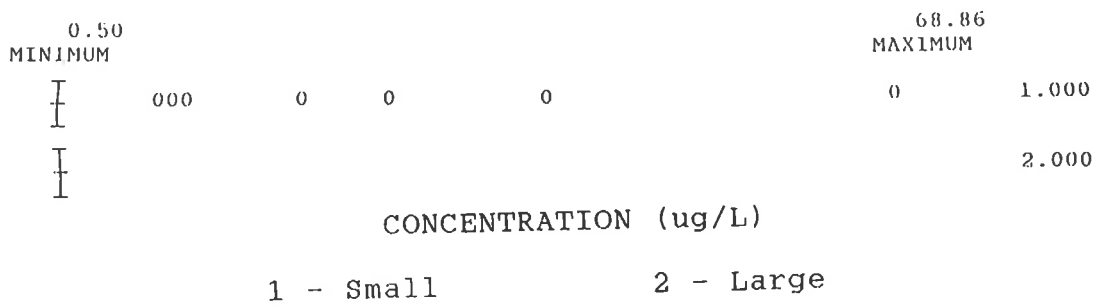


Figure B.28 Phenanthrene Box Plots of Rain Depth Categories.

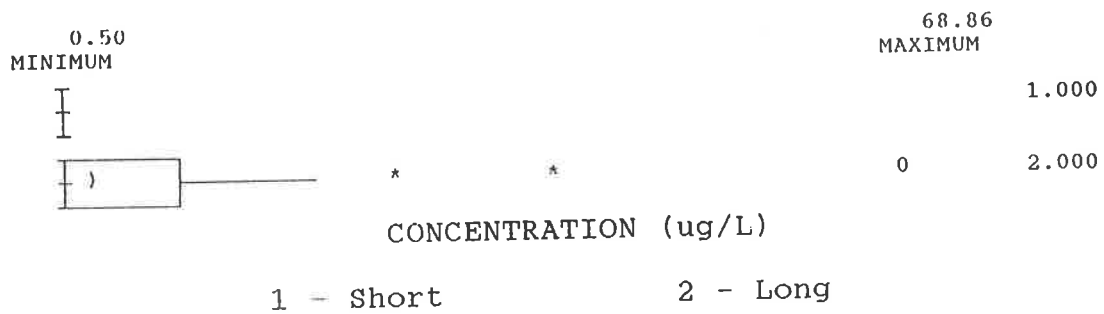


Figure B.29 Phenanthrene Box Plots of Antecedent Dry Period Categories.

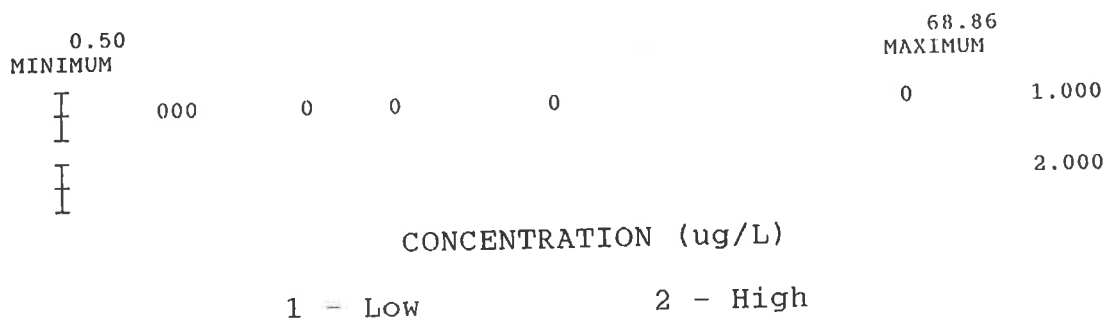


Figure B.30 Phenanthrene Box Plots of Peak Intensity Categories.

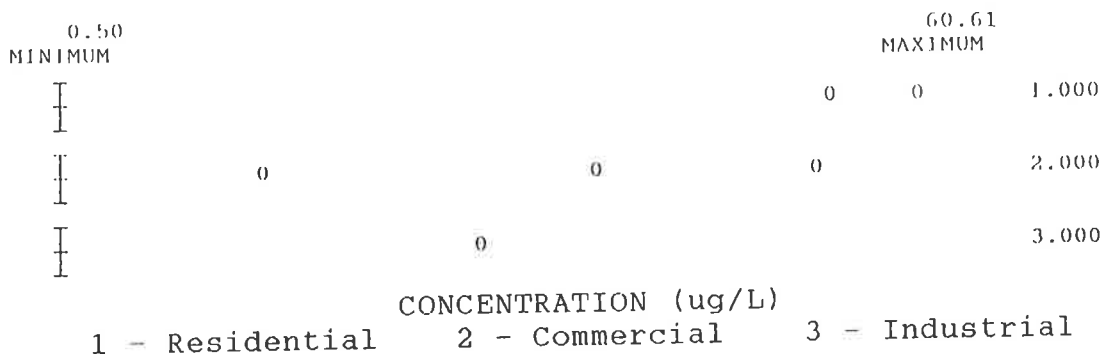
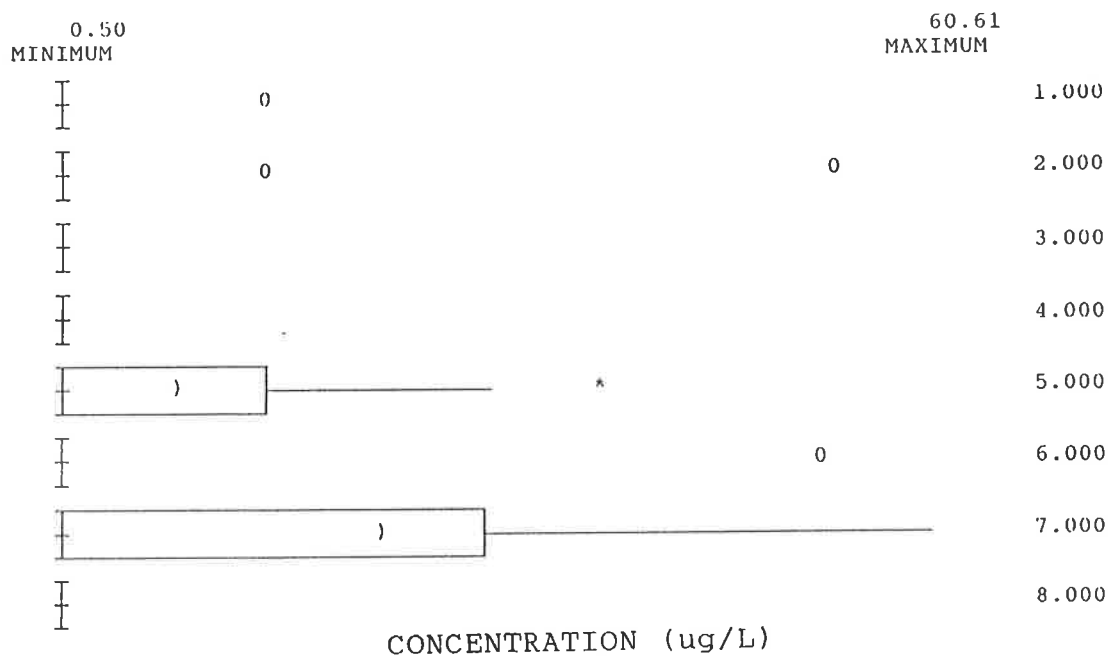


Figure B.31 Benzo(a)anthracene Box Plots of Land Use Categories.



- 1 - Roof Runoff
- 2 - Parking Areas
- 3 - Storage Areas
- 4 - Streets
- 5 - Vehicle Service Areas
- 6 - Landscaped Areas
- 7 - Urban Creeks
- 8 - Detention Ponds

Figure B.32 Benzo(a)anthracene Box Plots of Source Area Categories.

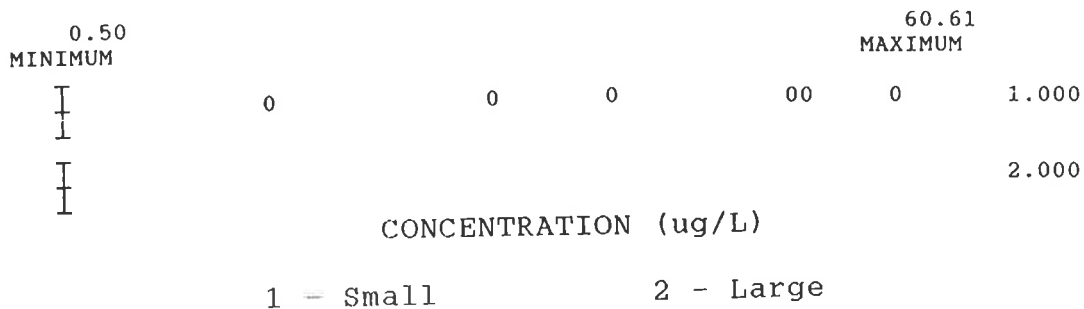


Figure B.33 Benzo(a)anthracene Box Plots of Rain Depth Categories.

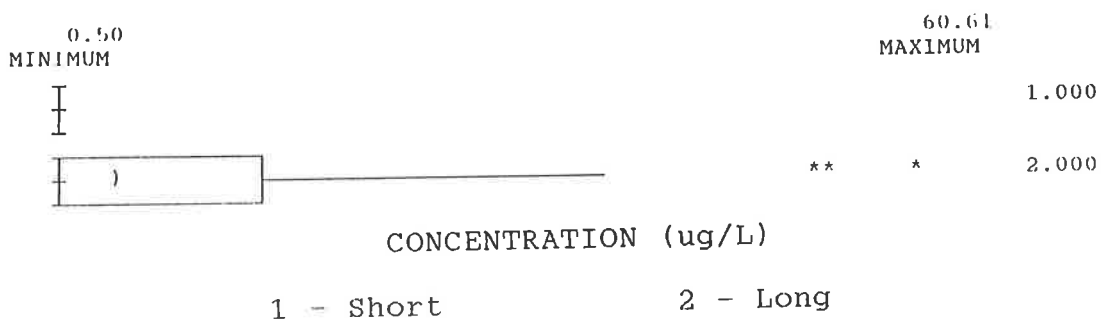


Figure B.34 Benzo(a)anthracene Box Plots of Antecedent Dry Period Categories.

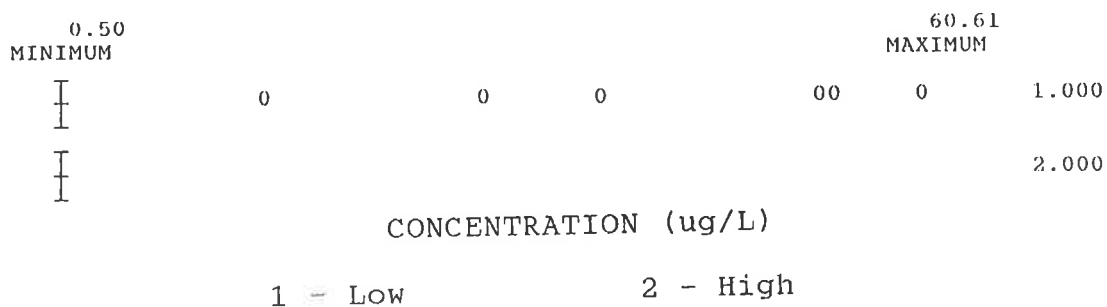


Figure B.35 Benzo(a)anthracene Box Plots of Peak Intensity Categories.

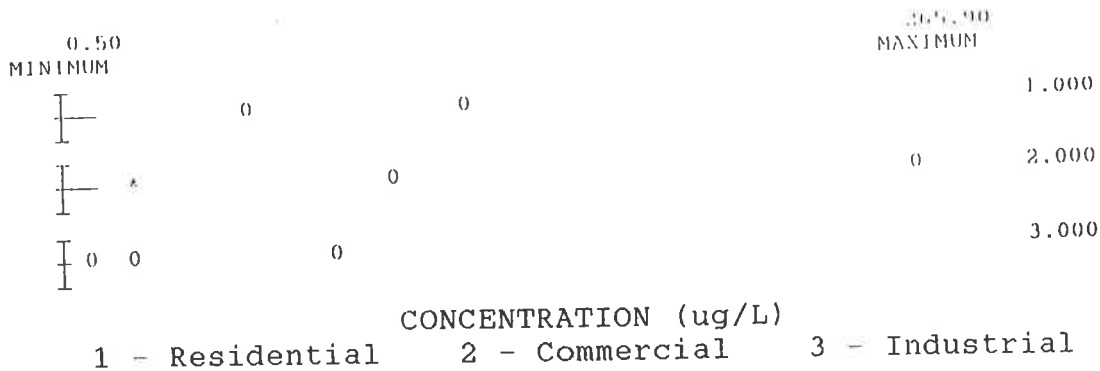


Figure B.36 Benzo(b)fluoranthene Box Plots of Land Use Categories.

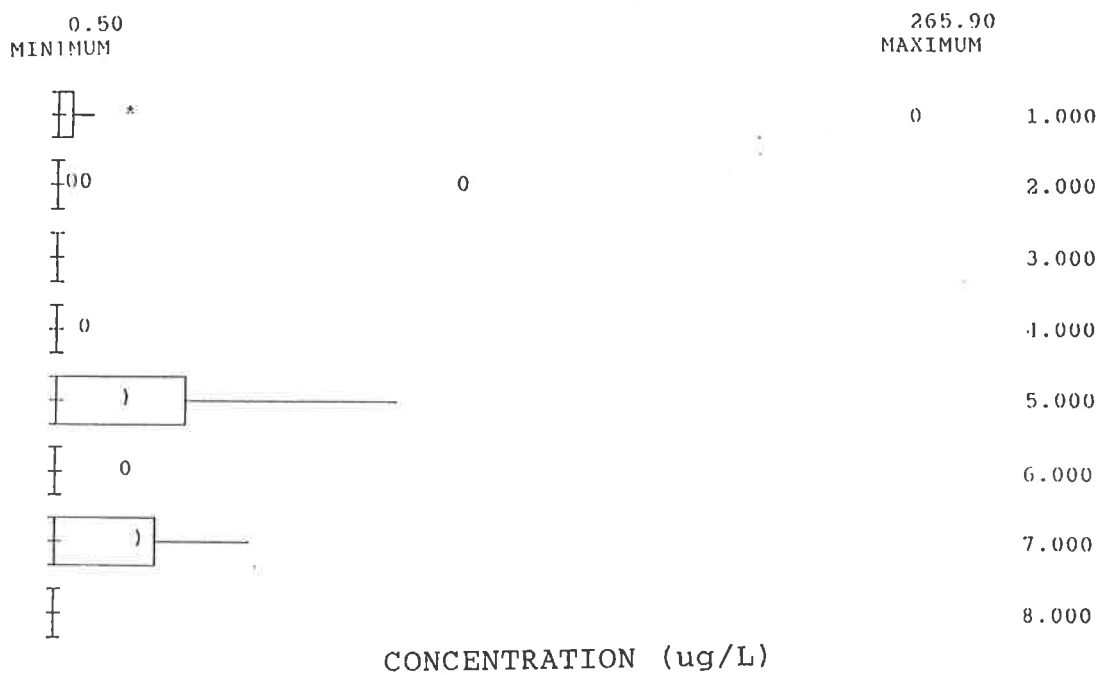
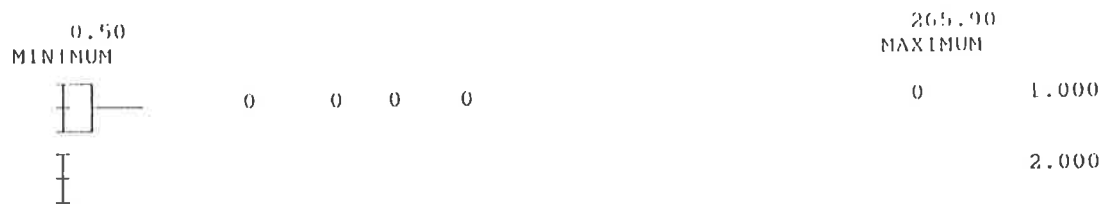


Figure B.37 Benzo(b)fluoranthene Box Plots of Source Area Categories.

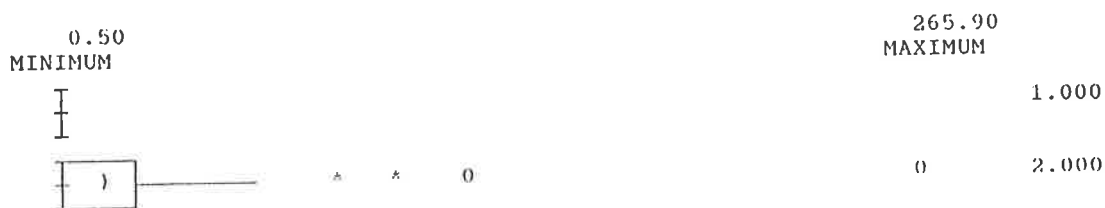


CONCENTRATION (ug/L)

1 - Small

2 - Large

Figure B.38 Benzo(b)fluoranthene Box Plots of Rain Depth Categories.

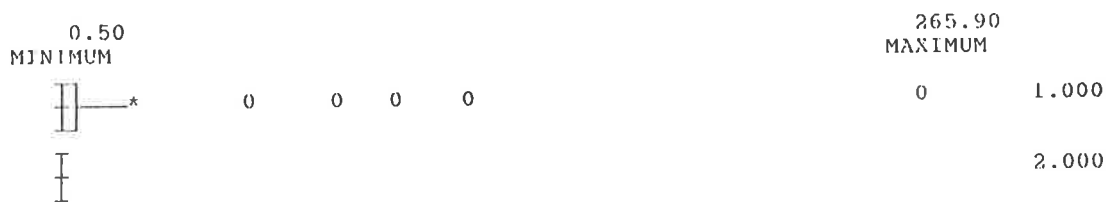


CONCENTRATION (ug/L)

1 - Short

2 - Long

Figure B.39 Benzo(b)fluoranthene Box Plots of Antecedent Dry Period Categories.



CONCENTRATION (ug/L)

1 - Low

2 - High

Figure B.40 Benzo(b)fluoranthene Box Plots of Peak Intensity Categories.

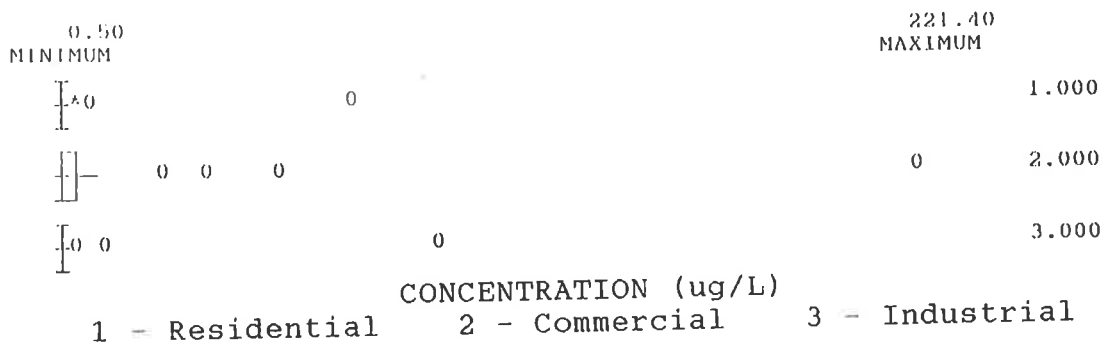


Figure B.41 Benzo(k)fluoranthene Box Plots of Land Use Categories.

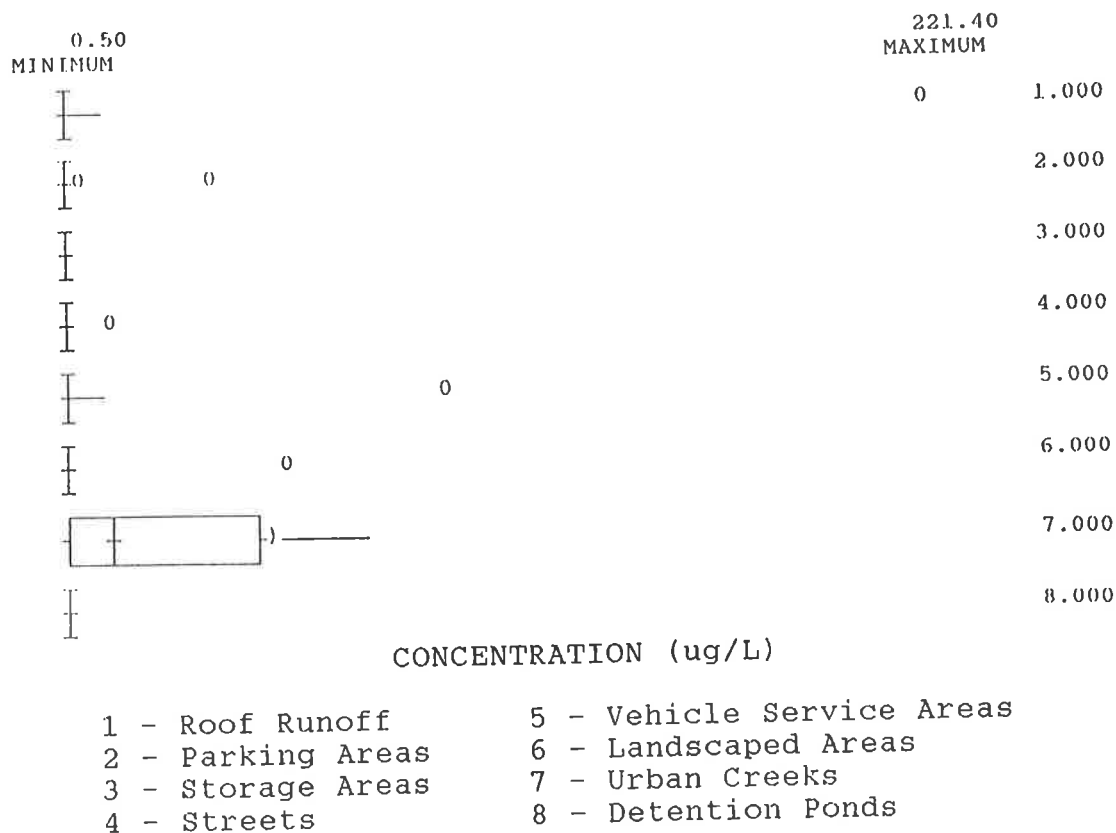


Figure B.42 Benzo(k)fluoranthene Box Plots of Source Area Categories.

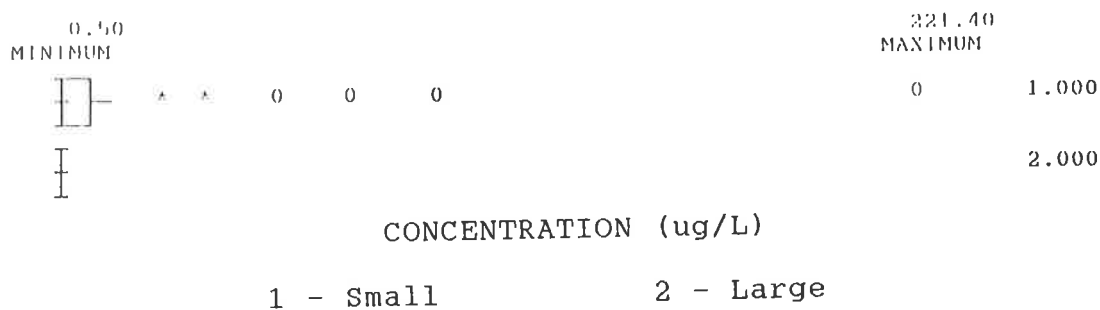


Figure B.43 Benzo(k)fluoranthene Box Plots of Rain Depth Categories.

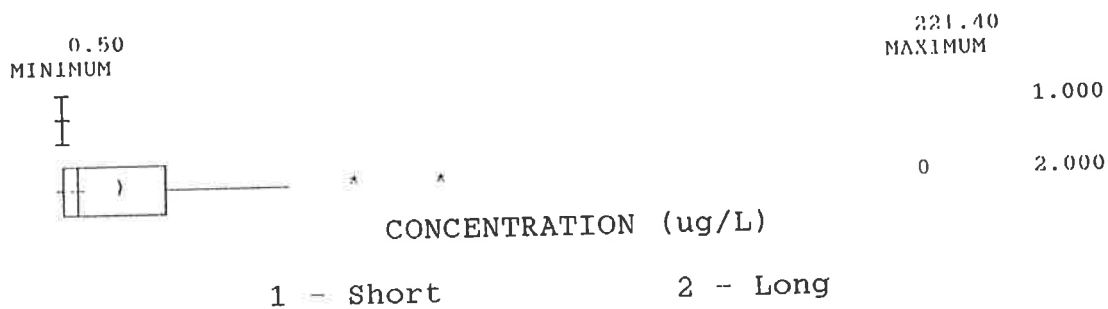


Figure B.44 Benzo(k)fluoranthene Box Plots of Antecedent Dry Period Categories.

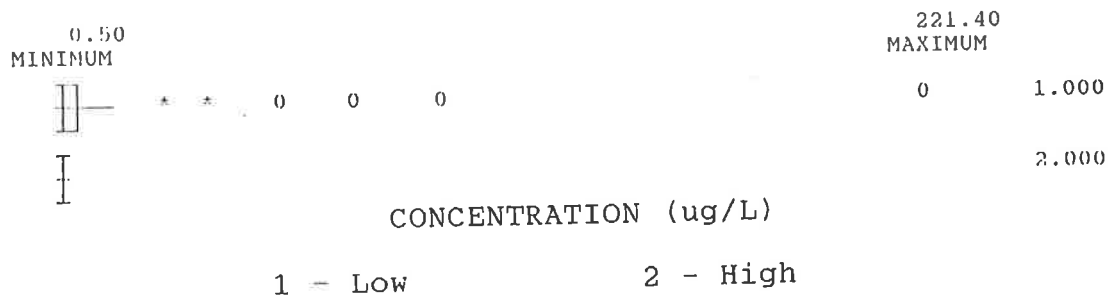


Figure B.45 Benzo(k)fluoranthene Box Plots of Peak Intensity Categories.



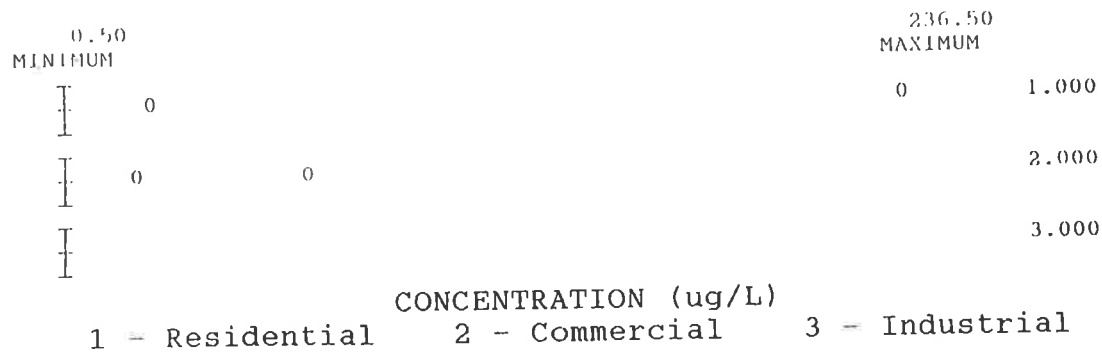
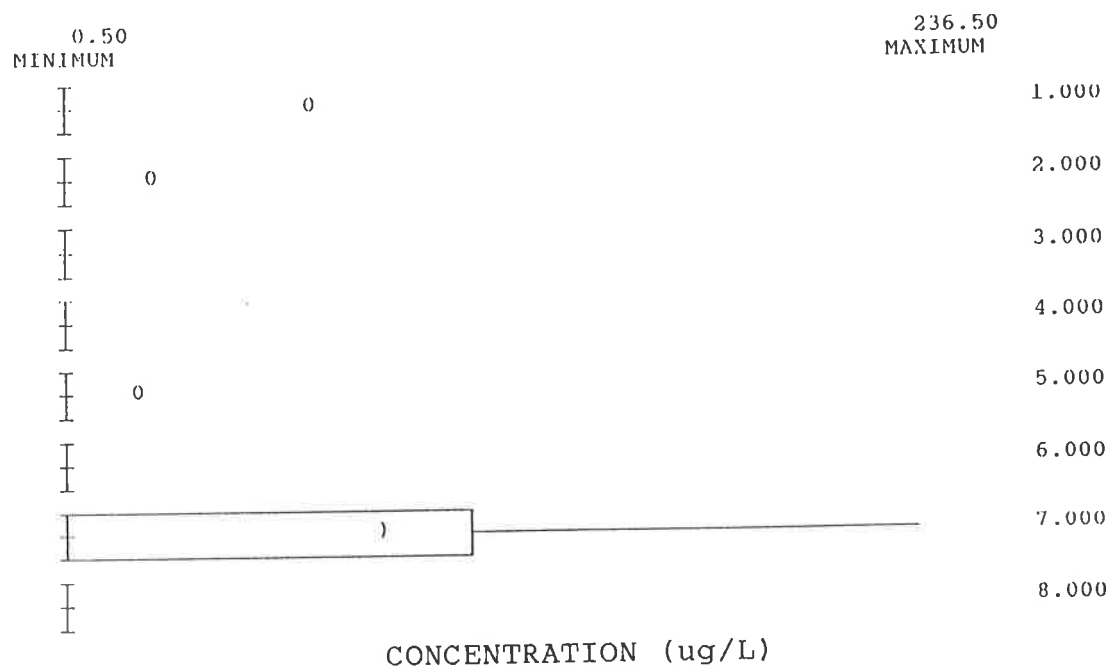


Figure B.46 Chrysene Box Plots of Land Use Categories.



- 1 - Roof Runoff
- 2 - Parking Areas
- 3 - Storage Areas
- 4 - Streets
- 5 - Vehicle Service Areas
- 6 - Landscaped Areas
- 7 - Urban Creeks
- 8 - Detention Ponds

Figure B.47 Chrysene Box Plots of Source Area Categories.

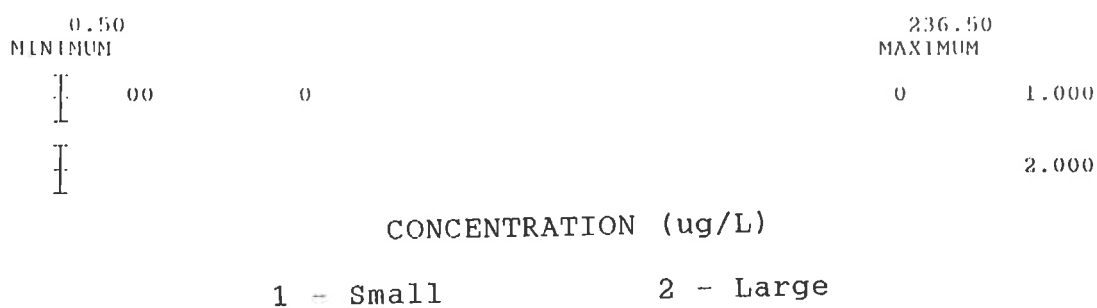


Figure B.48 Chrysene Box Plots of Rain Depth Categories.

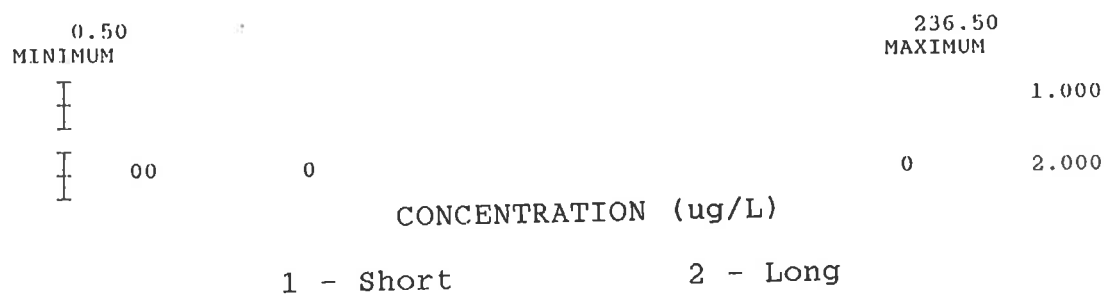


Figure B.49 Chrysene Box Plots of Antecedent Dry Period Categories.

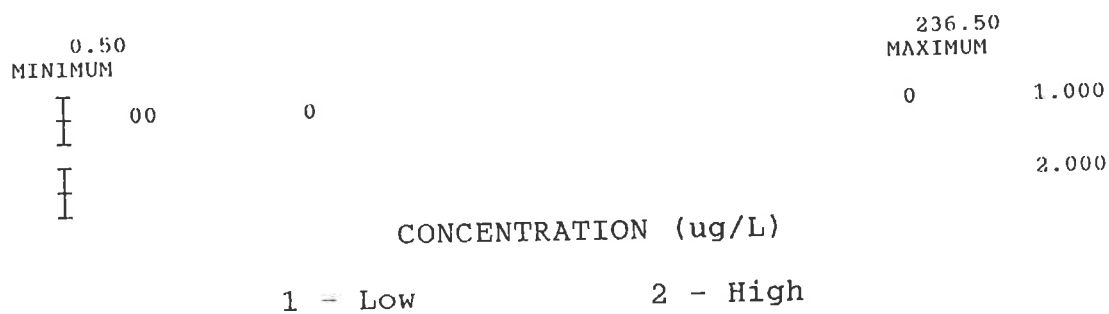


Figure B.50 Chrysene Box Plots of Peak Intensity Categories.

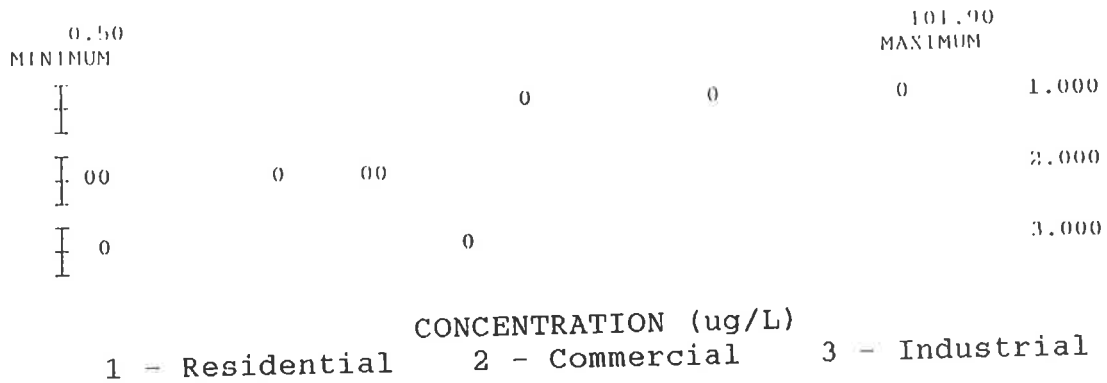


Figure B.51 Pyrene Box Plots of Land Use Categories.

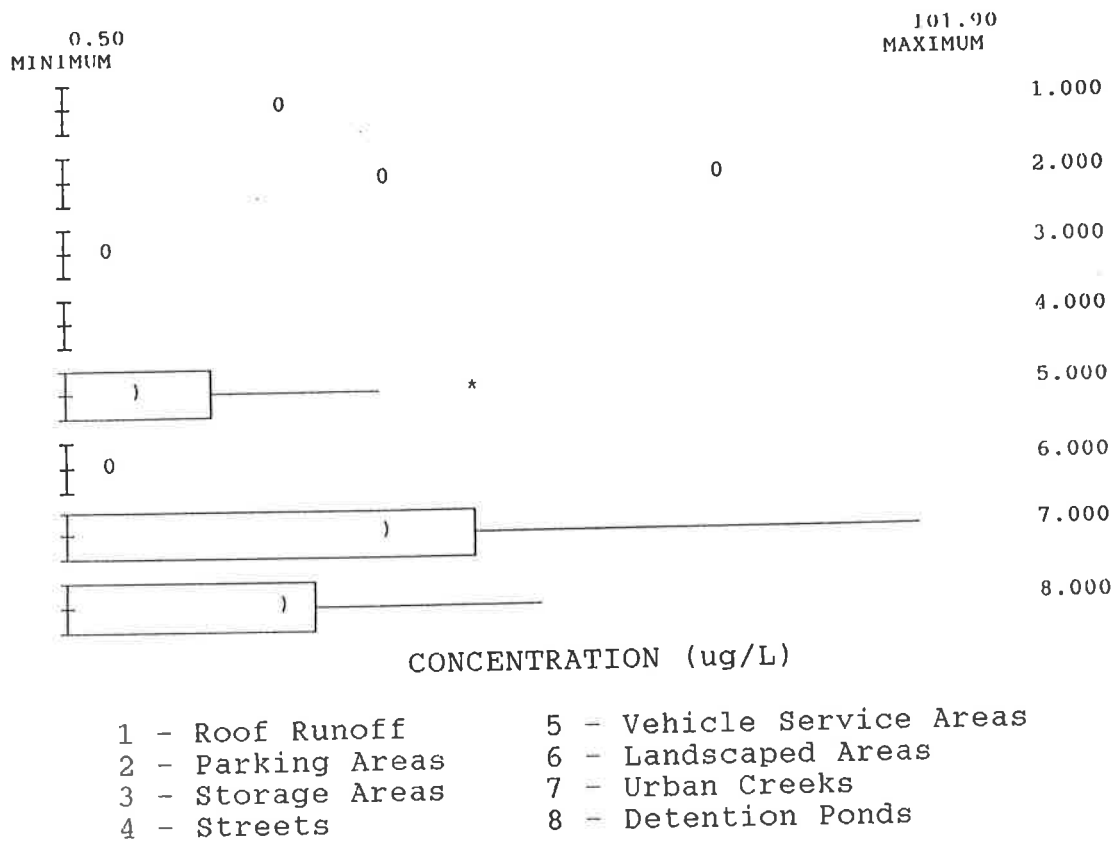


Figure B.52 Pyrene Box Plots of Source Area Categories.

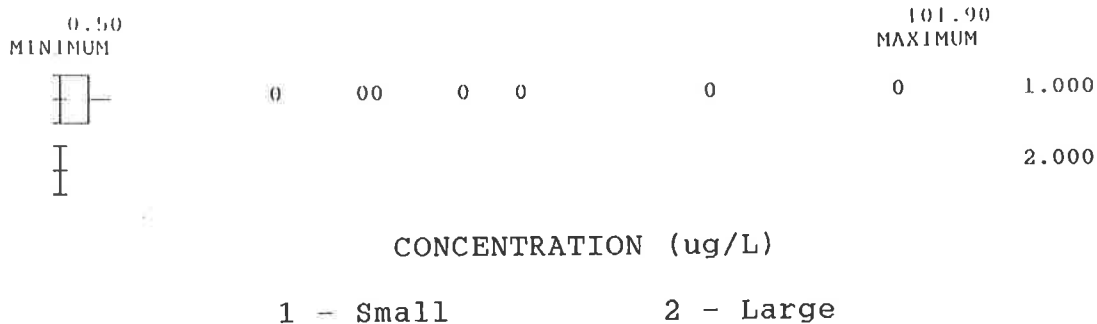


Figure B.53 Pyrene Box Plots of Rain Depth Categories.

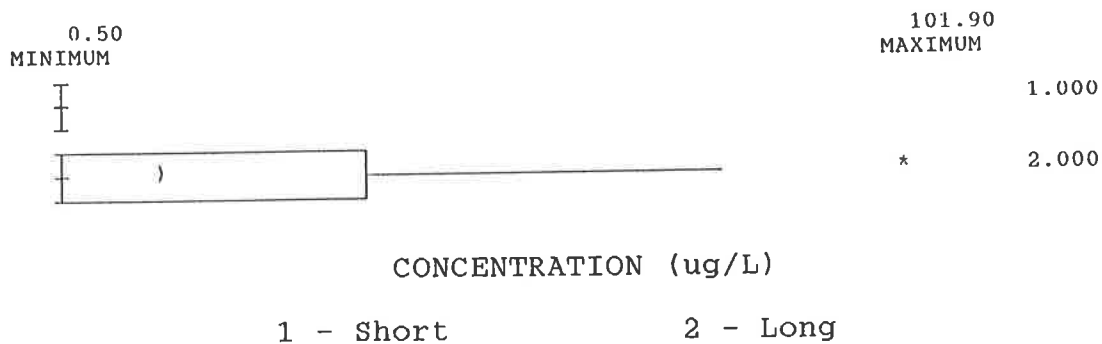


Figure B.54 Pyrene Box Plots of Antecedent Dry Period Categories.

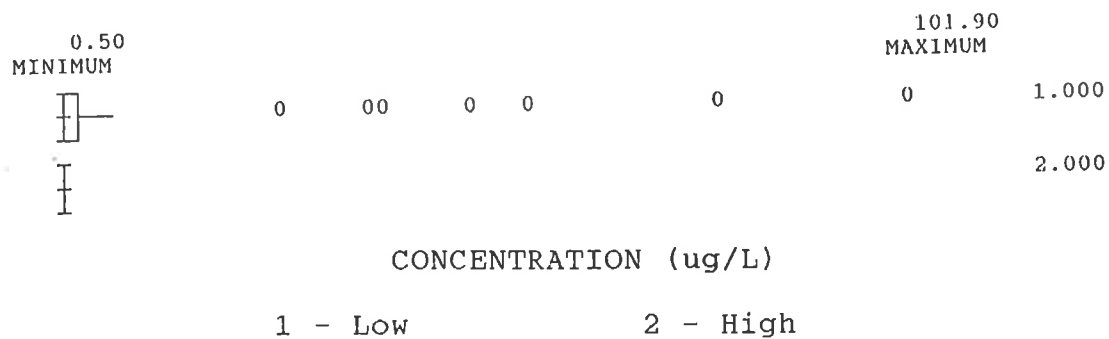


Figure B.55 Pyrene Box Plots of Peak Intensity Categories.

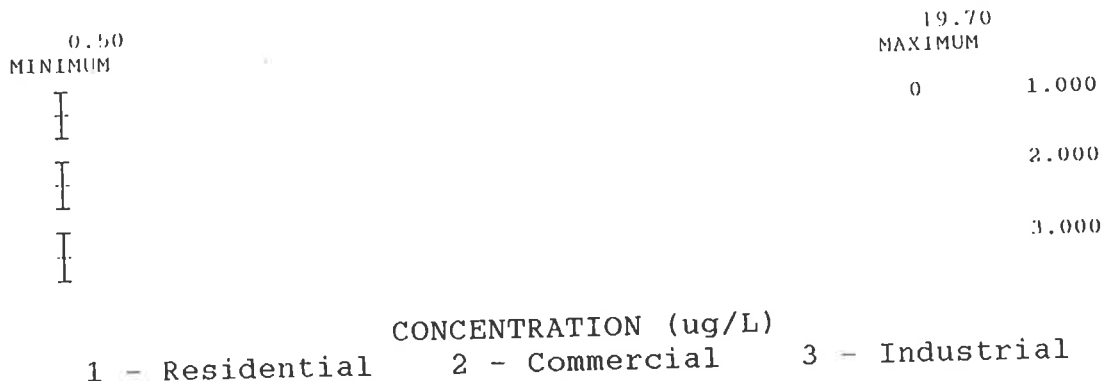


Figure B.56 Benzo(ghi)perylene Box Plots of Land Use Categories.

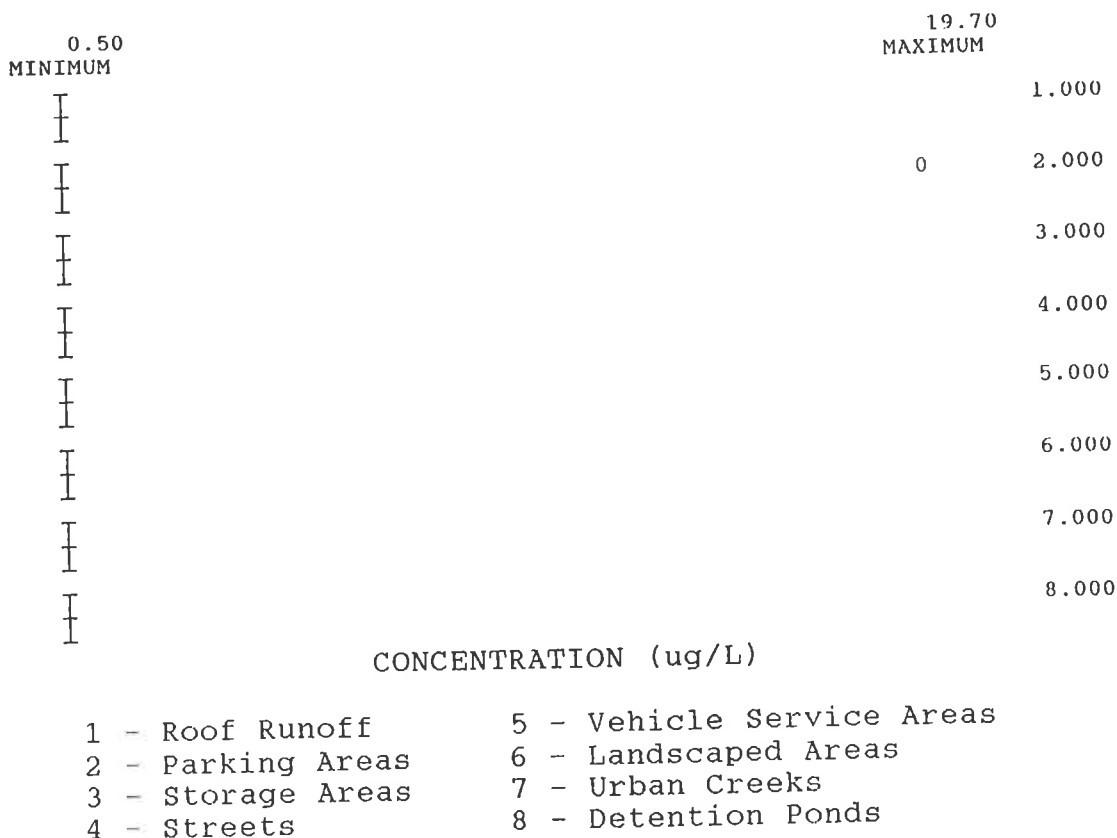


Figure B.57 Benzo(ghi)perylene Box Plots of Source Area Categories.

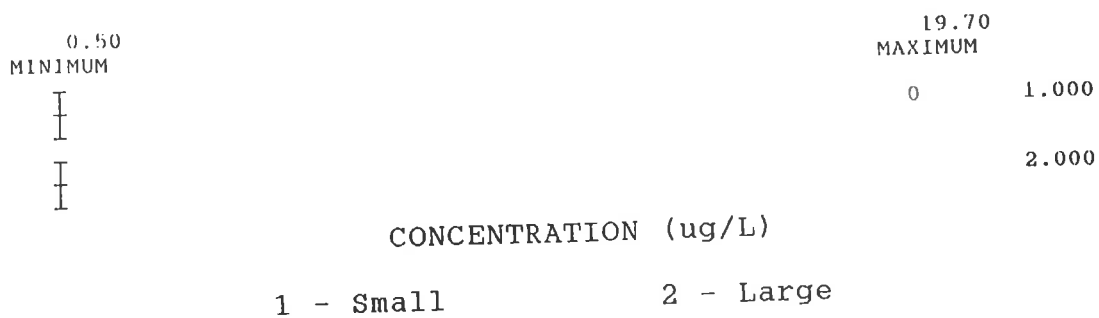


Figure B.58 Benzo(ghi)perylene Box Plots of Rain Depth Categories.

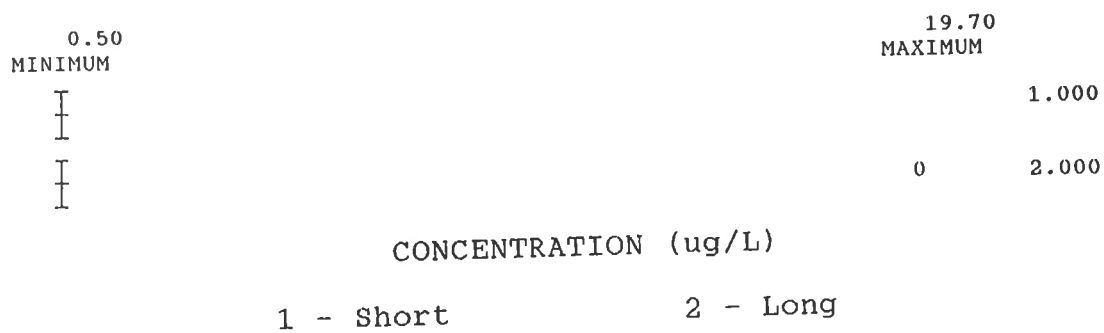


Figure B.59 Benzo(ghi)perylene Box Plots of Antecedent Dry Period Categories.

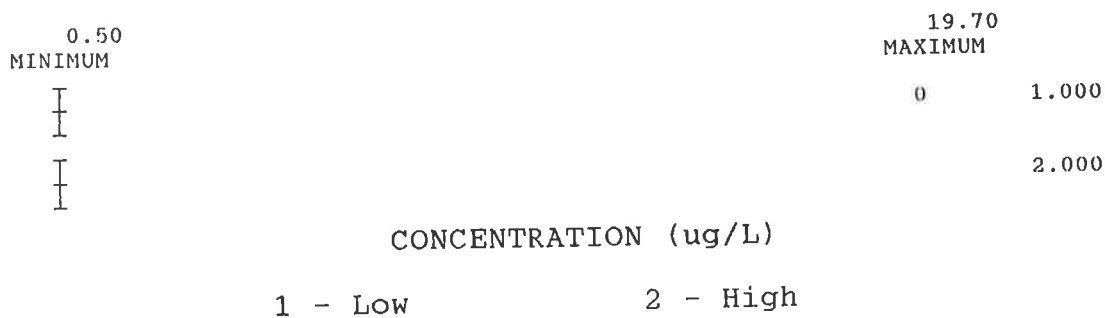


Figure B.60 Benzo(ghi)perylene Box Plots of Peak Intensity Categories.

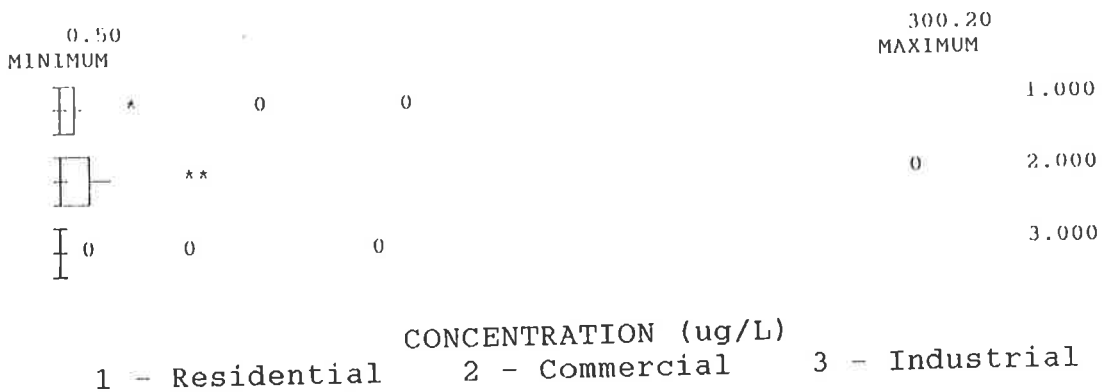
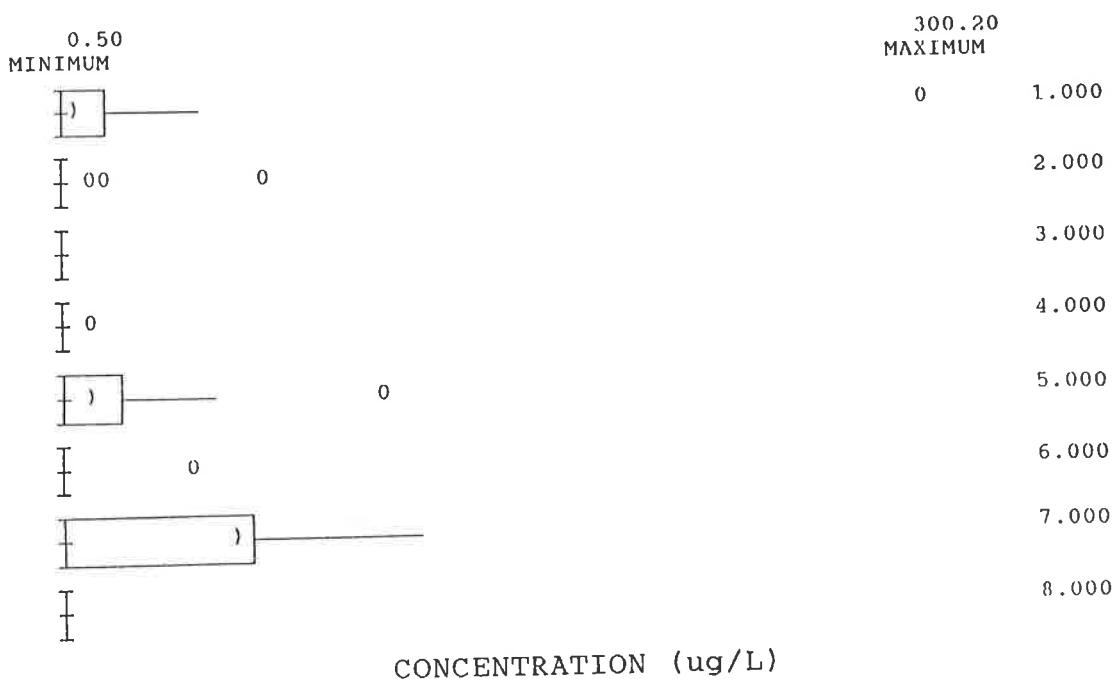


Figure B.61 Benzo(a)pyrene Box Plots of Land Use Categories.



- 1 - Roof Runoff
- 2 - Parking Areas
- 3 - Storage Areas
- 4 - Streets
- 5 - Vehicle Service Areas
- 6 - Landscaped Areas
- 7 - Urban Creeks
- 8 - Detention Ponds

Figure B.62 Benzo(a)pyrene Box Plots of Source Area Categories.



CONCENTRATION (ug/L)

1 - Small                      2 - Large

Figure B.63 Benzo(a)pyrene Box Plots of Rain Depth Categories.



CONCENTRATION (ug/L)

1 - Short                      2 - Long

Figure B.64 Benzo(a)pyrene Box Plots of Antecedent Dry Period Categories.



CONCENTRATION (ug/L)

1 - Low                      2 - High

Figure B.65 Benzo(a)pyrene Box Plots of Peak Intensity Categories.