To the Graduate Council:

I am submitting herewith a thesis written by Richard S. Brown entitled "Factors Affecting the Quality of Urban Runoff in Four Watersheds Within the City of Knoxville, Tennessee." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

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FACTORS AFFECTING THE QUALITY OF URBAN RUNOFF IN FOUR WATERSHEDS WITHIN THE CITY OF KNOXVILLE, TENNESSEE

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

Richard S. Brown

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ABSTRACT

This study is an extension of the model development done by Michael P. Barkdoll (1) to analyze the effects of various non-point sources, especially atmospheric fallout, on water quality in the Third Creek watershed of Knoxville, Tennessee; and of the study by Roger P. Betson (2) of non-point source contributions, surface water transport mechanisms, and land use effects in four watersheds within Knoxville, including Third Creek. In this study Barkdoll's models were applied to the other watersheds, and the results were examined relative to other published works in the field.

A complication was that in the Plantation Hills, First Creek, and Fourth Creek watersheds, which were the primary focus of this study, much of the potential runoff was lost into groundwater sinks and bypassed out of the watershed. This does not occur in the Third Creek watershed. In order to accurately represent the removal mechanisms in the three-study watersheds and to compare the results with those from Third Creek a simulation technique was developed for estimating the total stormwater volumes and the total pollutant loadings transported to groundwater as well as to stream channel sinks.

Results indicated slight differences in constituent concentrations and in factors involved in transport mechanisms

between watersheds of different land uses. In the watersheds characterized by karst terrain most of the contaminants reaching the stream channel seemed to be originating in the paved areas.

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CHAPTER I

INTRODUCTION

There is much evidence that the current strategy of trying to solve all of our water pollution problems by building treatment facilities will not prove to be adequate for achieving ecologically healthy rivers, streams, and lakes at a reasonable cost. A serious complication is that there is a factor in the water quality problem which we usually do not notice; stormwater scours all exposed land surfaces and transports pollutants associated with these surfaces to receiving waters. The magnitude of the pollution thus transported from many types of land use activities is comparable to that associated with sewage effluents (8). A point is often reached in waste treatment operations beyond which costs increase enormously for marginal increments in contaminant removal. Today we are usually constrained economically in our efforts to implement advanced waste treatment methods. If this relatively untouched aspect of the pollution problem were found to be a larger contributor than the as-yet uncontrolled or partially controlled segment of point sources, would not our money be better spent for stormwater quality management? Congress has addressed this question in Section 208 of the National Water Pollution Control Act of 1972, and some

municipalities are developing and submitting plans for the management of non-point sources of water pollution.

It must be realized that water pollution resulting from non-point sources cannot be understood unless one understands the mechanics of the transport mechanism--i.e. stormwater. A working knowledge of the rainfall runoff process is necessary for the development, understanding, and use of mathematical models for describing and predicting the behavior of various aspects of stormwater quality (8).

The urban sector is only one aspect of the stormwater pollution problem. Surface mines, construction projects, and agricultural activities also have a significant impact on water quality (8). Responsible water management objectives as well as our legal system of equal protection demand that control strategies must be based on a knowledge of the relative contributions of each sector.

This study is part of a project funded by the United States Air Force for the development of regionalized non-point source water quality models for Knoxville, Tennessee, and the surrounding region. The particular phase of this study which is presented here concentrates on the urban sector. It extends the previous work of Barkdoll (1) in one watershed within this city to three other urban watersheds of various land uses and geologic characteristics. Its objective is to explore comparisons between the

stormwater quality responses of these four watersheds and, if possible, to draw inferences which could affect water quality management schemes as well as future model development and refinement. The urban phase utilizes water quality and hydrologic data collected in these watersheds by the Tennessee Valley Authority for the purpose of furthering their own understanding of urban hydrology and water quality and for the refinement and regionalization of their own models (2).

CHAPTER II

LITERATURE REVIEW

The classic work dealing with the assessment and description of the water pollution aspects of urban stormwater discharges is that of Sartor and Boyd (3) of the URS Research Company of San Mateo, California who conducted research under the sponsorship of the U. S. Environmental Protection Agency. Their work included a comprehensive literature search to locate and evaluate all existing information concerning location, quantities, and environmental impact of street surface contaminants.

The review presented here is much more limited in scope, and the reader who desires a more comprehensive survey is referred to Sartor and Boyd's work (3). These researchers found little information regarding relationships between contaminants or runoff transport mechanisms; (3) therefore, they had to lay the groundwork in model development themselves. Their concepts have been expanded, refined, and applied by others (1, 4, 5).

Barkdoll (1) used models based on Sartor and Boyd's work as well as others of his own development to describe the impact of non-point sources and the transport mechanisms involved in one urban watershed of Knoxville, Tennessee. He surveyed existing literature in order to develop his

approach, and discussed the major influences on his work. The reader is referred to Barkdoll (1) for a more detailed account of the background of his model development.

The scope of this project was to apply Barkdoll's models (1) to three other urban watersheds in the city of Knoxville; therefore, this review concentrates on Barkdoll's results (1) and on the independent work of Betson (2), who used somewhat different approaches in studying hydrologic mechanisms and non-point source water quality impacts in the Knoxville area. Other modeling efforts which are considered to be relevant to the studies being done here are presented as examples and as sources of inspiration for further research of the types that we would like to see.

Although the topics of pollutant source identification, transport mechanisms, and stormwater quality are dealt with separately, it must be understood that these are highly interrelated aspects of the same problem. This approach has been adopted in order to provide a workable structure.

Some recent concepts concerning the statistical analysis of hydrologic and hydrology-related data are also discussed, together with the Wilcoxson significance tests which were used in this study.

Sources of Stormwater Pollution: Land Use Effects

Land use is described by Barkdoll (1) as a primary parameter governing variations in the water quality responses of watersheds within the same region to storm events. However, it would be a difficult parameter to quantify. An Environmental Protection Agency (EPA) study (4) approached this problem by suggesting an urbanization index, which would have the following components:

1. Population density.
2. Street types.
3. Street condition.
4. Fraction of the area as road surface.
5. Type of landscaping in the area beyond the sidewalk.
6. Average daily traffic.
7. Method of street cleaning.
8. Median income.
9. Age of homes.
10. Single or multiple housing units.
11. Percent commercial.
12. Percent industrial.
13. Type of industry.

The effect of land use on pollution loadings is better understood relative to the street surface sector of the urban environment than to the previous areas. The

reason for this is that the EPA has until now concentrated its studies on the street surfaces (1). Street surfaces contribute not only the expected pavement decomposition and automobile-associated by-products but also a variety of metals, pesticides, and nutrients (3), which are thought to be the result of atmospheric fallout (1). Studies conducted by the EPA have shown that the heaviest pollutant loadings are found on streets in industrial areas. Residential streets are less heavily loaded, and commercial streets have the lighest loadings. Total solids loading intensity as a function of land us is shown in Figure 1 (3).

Some knowledge of the potentially polluting aspects of construction activity is also available. Sediment resulting from soil disturbance and exposure is the chief pollutant associated with construction, but construction activities can also release a host of wasted or spilled chemicals and building materials into the environment (6). Sediment production from construction activities can be reduced by site planning for the control of runoff volume and velocity, and by various strategies for entrapping the sediment itself (6).

A high percentage of impervious, paved areas is usually associated with an urban environment. Paved areas and other impervious surfaces, such as buildings prevent the infiltration of stormwater into the soil. Moreover,

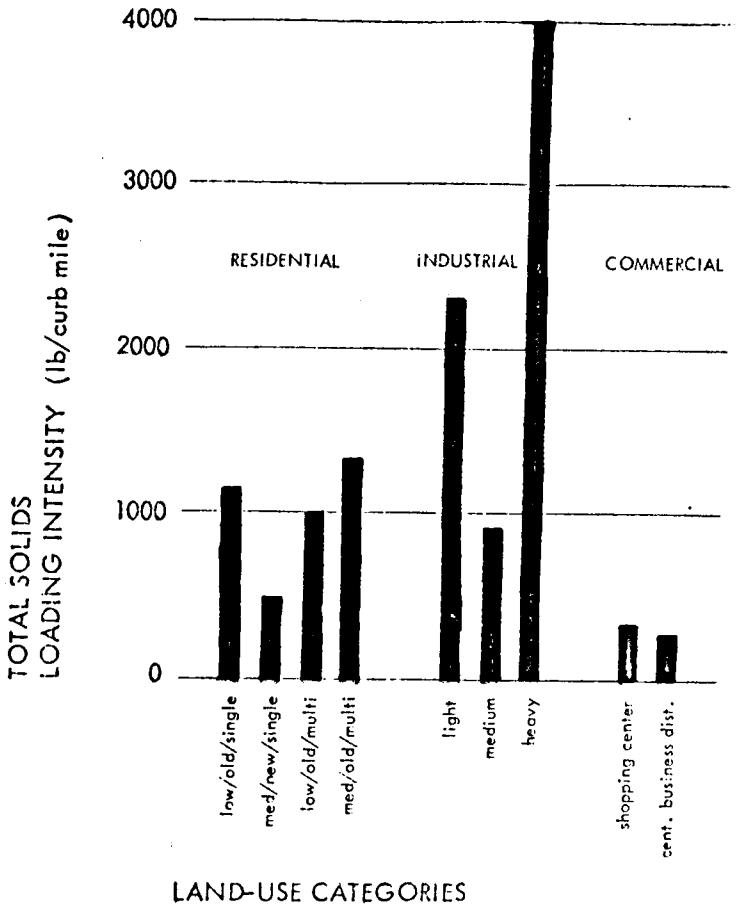

Figure 1

Total Solids Loading on Street Surfaces:
Variation with Land Use

paved areas are usually smooth and offer less resistance to flow than do vegetated areas. The combination of these two effects increases both the volume and the velocity of the stormwater runoff. The result is the "flashy" hydrograph usually associated with urban watersheds, characterized by a short time to peak and a high peak flow relative to base flow. This type of watershed response can result in erosion of the stream banks and flooding and sediment deposition downstream (6).

Barkdoll (1) and Betson (2) have theorized that a weather modification effect may be occurring in the Knoxville area. Betson (2) pointed to the fact that a number of improbable floods occurred during the three-year study period. He attributed this effect to the production of aerosols at two large coal-burning power plants, one located 35 miles and the other 14 miles west of Knoxville. Surface heating in the city could produce convection currents which could transport these aerosols into the upper layers of clouds, from which they would fall as precipitation. The total effect would result in a larger amount of rainfall near the city than would otherwise occur.

Contaminant Accumulation and Removal Mechanism

According to Barkdoll (1), transportation of pollutants into an area results from man's activities, wind, and rain. Wind transportation, commonly called

dustfall, involves sedimentation, coagulation, and impaction mechanisms. If dustfall per se were to be studied it should be separated from rainfall and snowfall. However, dustfall, rainout, and washout taken together provide a measure of total atmospheric fallout. Barkdoll used Rasool's definition of rainout as particles removed by condensation processes within clouds, and of washout as particles captured and removed by falling hydrometers (1).

Barkdoll reported an estimate by Heaney and Sullivan that 70 percent of the material found on street surfaces in Chicago could be attributed to dustfall (1). He described a study conducted by Rassano and Johnson in Seattle to determine the impact of direct atmospheric fallout into water supply reservoirs on the quality of the reservoir water. They concluded that no constituents could affect the water quality, except for lead at certain times of the year. Their sampling network included stations in several different land use districts. Phosphates were found to be most abundant in urban areas. Lead correlated well with traffic flow. Dustfall rates were rather constant throughout the year except for a pronounced peak during the spring months (1).

Total atmospheric fallout was collected at one station in each of four watersheds in the Knoxville, Tennessee area between 1972 and 1975 by the Tennessee Valley Authority

(TVA). Betson (2) compared the results obtained through this sampling program with the results of other studies. For many constituents the Knoxville data was comparable to that collected elsewhere in both rural and urban watersheds, but the quantities of potassium, manganese and lead were somewhat higher than at most other locations. A problem with comparing atmospheric fallout data was that some investigators sampled total fallout while others sampled only rainfall. The results of this study are shown in Table 1.

Transportation of contaminants from a land surface area results from resuspension by wind, sanitary practices such as street cleaning, and urban runoff (1). Contaminants may be absorbed onto soil particles; these may remain in the area or they may be removed by one of the vectors mentioned above. Barkdoll (1) reports the work of Andren, Lindberg, and Bate, who sampled wet deposition (rainout and washout) and dry decomposition (impaction) in a rural watershed near Oak Ridge, Tennessee, for which they performed a mass balance. The ratio of dry deposition to total deposition was found to be .045, .206, .032, .200, .165, .331, and .092, respectively for Cd, Cr, Cu, Hg, Mn, Pb, and Zn. They calculated that the watershed retained 98-99 percent of Pb; 94-95 percent of Cd; 82-84 percent of Cu; 59 percent of Cr; 57 percent of Mn; 73-75 percent of Zn; and 69-75 percent of the Hg which was transported into the study area (1).

TABLE 1

AVERAGE CONSTITUENT CONCENTRATIONS IN BULK PRECIPITATION

Location	Fe	Ca	Mg	Na	K	SO_4	Cl	Org N	NH_3 N	Total PO_4	pH	Mn	Pb	Hg	$NO_{2,3}$ N	SS	COD	Comment	Reference
Urban Areas																			
Knoxville, TN	.18	3.8	.74	1.5	2.6	7.1	4.0	2.5	.41	1.1	5.1	.05	.05	.0009	.47	16	65	Bulk Precip - Four watershed average	
Menlo Park, CA		6.7	3.0	3.9	0.7	12.2	7.3				6.4				.58			Bulk Precip.	(Whitehead & Feth, 1964)
St. Louis, MO	.67		.24								4.9	.01	.034					Downwind from St. Louis	(Huff, 1973)
Cincinnati, OH										.24						13	16	Rainfall	(Weibel, et al., 1966)
Heidleburgh, Germ.	1.8			.8	.8		1.5					.03		.0013				Rainwater	(Bogen, 1974)
Gottingen, Germ.	1.4	3.0	0.7	.8	1.0	8.8	.9			1.1		.04	.04	.0015				Bulk Precip	(Ruppert, 1975)
Rural Areas																			
Oak Ridge, TN		1.0	.19	.25	.2				.13	.12					.25			Bulk Precip. - Forest Area	(Swank & Henderson, 1974)
Oak Ridge, TN												.01	.02	.0002				Rainfall - Forest Area	(Andren, et al., 1975)
Clyde, NC					1.2	19		1.2	.8	1.5					.62			Rainfall - Pasture	(TVA, 1974)
Coshocton, OH										.1						12	9	Rainfall	(Weibel, et al., 1966)
Inland Stations USA		1.4		.42		2.1	.2											Mid-1950's	(Whitehead & Feth, 1964)
Inland Sta. - N. Europe		1.5		1.22		5.4	2.6											do	do
St. Louis, MO	.15		.11								4.9	.006	.007					Upwind from St. Louis	(Huff, 1973)
Blairsville, GA	.70	.1	.00	.70	.8	2.9			.3		5.5	.09	.01		.10			Bulk Precip	(Giddens, 1975)
Gatlinburg, TN		0.2	.03	.05	.1	3.2	.15		.18		4.2				.28			Exp. Station Rainfall Resort Area	(Cogbill & Likens, 1974)

All values are mg/1 (except pH)

(Betson, 2)

Betson (2) performed a mass balance on the Knoxville watersheds, calculating input from the atmospheric fallout samples and output from the stormwater quality samples and streamflow measurements. His results are shown in Table 1. He urges that the fact that measured atmospheric fallout values are highly dependent on the location of the sampler be kept in mind, and suggests that average values of atmospheric input across the four watersheds should be examined (2). Atmospheric sources were found to approximately account for loadings of silica, flouride, lead, mercury, arsenic, and COD. However, they could not account for all of the iron, calcium, magnesium, potassium, total dissolved solids, hardness, manganese, alkalinity, or suspended solids in any of the watersheds (2).

Sartor and Boyd (3) found that the pollutant accumulation rate on street surfaces was constant for one to two days after a street cleaning or storm event; then it decreased asymptotically. Amy and Pitt (4) reported a study of street debris samples from Chicago; it was determined that the very fine, silt-like portion of the debris (less than 43 u) which was less than 5.9 percent of the total weight of the debris, contained approximately one-fourth of the total oxygen demand, more than half of the heavy metals, and nearly three-fourths of the total pesticides. This is an important discovery

because particle size affects the design of street sweeping equipment (3, 4) and stormwater treatment facilities (4, 5), and can also affect transportation and accumulation of pollutants in receiving waters (1).

The EPA studied removal rates of contaminants from paved surfaces by artifically produced runoff (4). Runoff rates were varied from .1 to 1.0 times per hour, and runoff durations were varied from .25 to 6.0 hours. It was found that removal percentage was a function of total runoff volume, but that it could not be precisely related to runoff intensity. Ninety percent removal resulted from .5 inches of total runoff. They developed the equation,

$$\text{Percent removal} = (1 - e^{-P/.217}) * 100 \qquad (1)$$

Where

P = total runoff in inches

The coefficient .217 represents the easiest removal case; that is, for impervious surfaces. This coefficient would be expected to be larger for semi-pervious and pervious areas.

Using streamflow and water quality measurements from actual storm events, Barkdoll (1) determined generally larger runoff coefficients for Knoxville's Third Creek watershed. His runoff coefficients varied from contaminant to contaminant, whereas the EPA street surface coefficient was essentially constant for all contaminants.

Hey and Waggy (9) are developing an overall probabilistic watershed model which would consider stormwater contributions together with point source discharges, and chemical and biological interactions in receiving waters, as components of a total system. They propose contaminant accumulation and removal functions for inclusion in the stormwater segment of the model. Accumulation between storms would be represented by the equation,

$$P(T) = P(T-1) * (1-r) + Y \qquad (2)$$

Where

P(T) = surface removal at time (T)
r = in-situ removal rate
Y = in-situ accumulation rate

Computations would be carried out in a stepwise manner from the end of one storm event to the beginning of the next one. The removal factor includes all removal mechanisms. The equation assumes that a maximum contaminant load, Y/r, exists for a given watershed, and that this value is approached asymptotically as a function of time.

They describe the removal of pollutants during a storm event by the equation,

$$Pw = Po* (-e^{-brt}) \qquad (3)$$

Where

Po = surface pollutants at beginning of time step
pw = surface pollutants washed off during time step
b = runoff coefficient
r = rate of runoff per unit Time
t = duration of time step

This is obviously a modification of the EPA street surface removal equation but it is more flexible in that it allows for variable runoff rates during a storm event.

The researchers suggest that a better approach might be to relate pollutant washoff to sediment movement. Considering the proportion of contaminants bound to small particles, this argument appears to have merit. Their proposed equation is,

$$SER(t) = KSER * OVQ(t)^{JSER} \qquad (4)$$

Where

SER(t) < SRER(t), and
SER(t) = sediment fines in transport during step t
KSER = washoff coefficient
OVQ(t) = overland flow during time step t
JSER = washoff exponent, and
SRER(t)= reservoir of soil fines at beginning of step t

In Bakersfield, California, EPA researchers artificially flushed streets and tested the quality of the runoff. They found that initially the runoff was quite dirty, but that the water quality improved as flushing continued (3). Barkdoll (1) reported results from the work of Wilbur in New Jersey which show the same effect; also, Colston (5) in North Carolina described similar results for a variety of contaminants in urban watersheds. The graphical representation of pollutant concentration versus time during a storm event became known as a

"pollutograph." Most pollutographs exhibit what is referred to as the "first-flush effect"; that is, concentrations decrease as the storm progresses. Stormwater quality responses may also be described by a "loadograph," which is a plot of cumulative stream load versus time during a storm event. Colston, Wilbur, and others (4) have shown that loading usually increases rather linearly with time at first, and asymptotically approaches a limiting value.

Barkdoll (1) reported a discovery by Wilbur that high settleable solids concentrations are associated with the rising limb of the hydrograph, and high non-settleable solids concentrations are associated with the falling limb. He postulated that this effect is due to the scouring action of high-kinetic energy, high volume flows which occur early in the storm, and which can remove the larger particles. Since kinetic energy is velocity-related this hypothesis challenges the conclusion of other researchers (4) that contaminant removal is not a function of velocity. Betson (2) believed that the large sediment loadings observed in Knoxville's Fourth Creek are caused at least in part by the high-velocity runoff from paved areas, which erodes the stream channel.

Barkdoll (1) ranked antecedent dry period along with intensity and duration of runoff, contaminant removal mechanisms, and land use as primary factors governing between-storm variations in surface water quality. The antecedent dry period not only is a limiting factor for

contaminant accumulation in the watershed, but in pervious areas it also affects infiltration rates.

Barkdoll (1) developed a deterministic model for use in analyzing the relationship between dustfall, stormwater runoff, and water quality. His equation is,

$$C = \frac{D * N}{Vol} \qquad (5)$$

Where

C = average constituent concentration during a storm event
D = dustfall rate (weight/unit time)
N = antecedent dry period, and
VOL = runoff volume

The model is based on the following assumptions:

1. Removal of contaminants by runoff is 100 percent efficient.

2. There is no carry-over from storm to storm; i.e. each storm is an isolated event.

3. All dustfall becomes a water contaminant.

4. Dustfall is the only source of water quality impairment.

5. Dustfall jar measurements are true values for dustfall.

Admittedly the model is ". . . very simplistic and has severe limitations" (1). Barkdoll thought that it would be helpful in assessing the magnitude of the effects of

dustfall on water quality. Predicted versus measured stream concentrations were compared, and "K" values (predicted divided by observed concentration) and coefficients of determination were reported for various constituents in the Third Creek watershed.

For most contaminants the model indicated that dustfall contributions were more than adequate to account for stream concentrations. Barkdoll suggests that these findings should be used with caution, chiefly because they are based upon a single dustfall jar (1).

Barkdoll also used a parametric model similar to the EPA equation for contaminant removal from street surfaces. His equation (modified for use in a computer program) is,

$$C*RO = M_T(1-e^{-RO/RO_C}) \qquad (6)$$

Where

C = average concentration during a storm event

M_T = the total mass of contaminant material within a watershed which could be removed by runoff

RO = runoff volume, and

RO_C = that amount of runoff which removes 63.2 percent of accumulated contaminants

The variate C*RO is obviously an estimate of the total cumulative stream loading during the storm event. A

nonlinear least squares program was used to evaluate streamflow and water quality data in order to develop optimized values of the parameters M_T and RO_C. RO_C is, of course, the runoff coefficient. The average coefficient of determination for Third Creek was .72.

The RO_C values were found to be higher than the street surface coefficient for all contaminants. This is an indication that pervious areas contributed significantly to stream loadings. Total mass M_T was divided by the dustfall rate in order to determine the time period necessary for the accumulation of this mass. In nearly all cases M_T/D was longer than the average antecedent dry period for Third Creek (4.4 days), indicating that there were contributing sources other than dustfall.

Stormwater Quality

Stormwater discharges from urban areas can produce a broad spectrum of water pollution problems. The magnitude of this problem varies. During the wet periods of the year of 1972 (about 20 percent of the time) in Durham, North Carolina, the COD of urban runoff was approximately 4.5 times that of the raw municipal sewage while the suspended solids yield was approximately 100 times that of the raw sewage. It was inferred that if the sewage treatment plant were to achieve zero discharge that the net annual reduction

in stream loadings would be only 52 percent of the COD, 59 percent of the ultimate BOD, and only 5 percent of the suspended solids (5). At Lodi, New Jersey, higher heavy metals concentrations were found in stormwater than in secondary sewage effluent (7). Betson (2) compared water quality data collected in the four Knoxville watersheds during storm events with data from Durham, North Carolina, and other cities, as well as with data from rural watersheds. He found that while the quality of stormwater in Knoxville was generally similar to that in other cities it was little, if any, more polluted than runoff from rural areas. It should be noted, however, that yields of suspended solids and lead from Third and Fourth Creeks were higher than yields which would have resulted from raw sewage discharges, and loadings of COD were higher than those from secondary sewage effluent (2). Betson's work is presented in Table 2 (2).

Barkdoll (1) used principle components analysis to screen the matrix of 20 water quality constituents which resulted from the water quality sampling program for Third Creek. Principle components analysis is a statistical technique which mathematically transforms a matrix of interdependent variates into a new set of mutually independent components, which are linear combinations of the old variates,

TABLE 2

AVERAGE ANNUAL WATERSHED LOADINGS: BULK PRECIPITATION AND STREAMFLOW FOR COMPARABLE PERIODS[a]

	SiO_2	Tot. Fe	Ca	Mg	Na	K	SO_4	Cl	Org.* N	NH_3 N	Tot. PO_4	TDS	Hardness$_3$	Mn	F	Pb	Hg*	As*	Alk	$NO_{2,3}$ N	SS	Sol PO_4	5-day BOD	COD*
Fourth Creek																								
Average Input	14	2.1	24	11	16	18	93	44	23	3.4	14	270	180	.75	2.1	1.8	.008	.08	180	4.4	180	6.5	-	450
Average Output	16	130	110	25	17	56	94	38	9	.44	15	590	340	3.1	.58	.86	.011	.22	240	3.1	8200	2.7	55	450
Third Creek																								
Average Input	18	2.1	49	8.6	14	27	95	58	17	4.3	11	510	230	.48	1.8	.59	.008	.06	170	9.0	230	7.4	-	750
Average Output	57	27	370	74	80	65	170	89	8.4	.82	13	2050	1200	3.1	1.5	1.1	.003	.07	1000	5.6	1100	7.3	95	570
First Creek																								
Average Input	6.7	1.2	23	5.7	20	11	65	41	18	2.3	4.4	260	180	.22	1.4	.55	.007	.04	62	3.9	140	2.6	-	480
Average Output	13	2.1	43	9.5	14	9.4	28	21	.63	.23	3.7	390	190	.37	.55	.23	.001	.01	150	1.3	95	2.9	14	37
Plantation Hills																								
Average Input	14	1.6	41	7.4	14	18	100	38	10	2.1	2.9	150	210	.38	1.5	.85	.008	.082	110	3.6	63	1.9	-	380
Average Output	5.2	1.2	8.9	1.5	2	2.1	8	4.3	.98	.11	1.3	140	51	.05	.35	.05	.002	.004	42	.47	20	1.1	2.2	31

All values are kg/ha

[a]Based upon data collected through May 1973.

also eliminating scale effects in the process. Each component explains a certain portion of the total variance of the original variates. Hopefully a small number of components will explain a large proportion of the original variance and these components will be heavily weighted by a small number of the original variates. If this is the case, these variates may be selected for study purposes, and the rest may be discarded. Although he reported that Mahlock, using principle components analysis to screen water quality data from the Pascagoula River in Mississippi had reduced the number of variates from 17 to 6 while retaining 76 percent of the original variance of the data, Barkdoll (1) was unable to reduce the number of variates in the Third Creek data matrix. He attributed his difficulty to the fact that his water quality data were analyzed by two different laboratories, which reported inconsistent results. An attempt to reduce the dimensionality of a matrix of nine of the variates for which problems with the data were less severe was also successful.

Barkdoll (1) utilized nonlinear least squares combined with components analysis to develop a linear regression model for streamflow as a function of these nine variates. His model was of the form,

$$\text{Discharge} = 105.1 * Mg - 56.4 * Na - 10.6 * SO_4 - 46.7 * Cl - 469.4 * PO_4 - 396.8\ Mn + 83382.2\ NO_2NO_3 + .955.*SS \qquad (7)$$

The coefficient of determination was .25, which in his opinion was not high enough to justify using the model with any confidence.

Betson (2) used a rating curve between constituent concentration and streamflow to predict the concentrations of various pollutants which would have occurred if these watersheds had been rural. His model was of the form,

$$Conc = a \left(\frac{Q}{DA}\right)^b \qquad (8)$$

Where

Conc = Constituent concentration
Q = streamflow discharge
DA = drainage area
a,b = coefficients

A linear regression model was used to determine regionalized values for a and b as functions of forested percentage and geologic features of the watershed. Data from 66 rural watersheds which were free from significant point sources of pollution was used to regionalize the model. In tests for watersheds not included in the calibration procedure, average prediction errors were on the order of ±50 percent for all constituents except for pH (±10 percent) and for iron, nitrate, and color (±100 percent).

Using this model, Betson (2) concluded that average concentrations of silica, magnesium, ammonia, TDS, hardness, conductance, pH, flouride, mercury, and nitrate-nitrogen were largely unaffected by urbanization. However, average

concentrations of sodium, potassium, sulfate, chloride, organic nitrogen, phosphate, color, iron, manganese, lead, suspended solids, BOD, COD, and possible alkalinity and arsenic, were somewhat elevated over expected rural values, even more so in the industrial and commercial Third Creek and Fourth Creek watersheds. In no case were average concentrations above any existing water quality criteria. Betson (1) suggested that his computations could have been biased due to the fact that his model was calibrated using "fair weather" rural watershed water quality samples. If the model had been developed from rural stormwater samples the simulated rural values could have been closer to the measured urban concentrations.

Statistical Analysis of Hydrologic Processes

Fiering (14) reported an analysis by Hurst of extensive records of natural phenomena, including rainfall, river statistics, tree rings, and mud varves, pertaining to the Nile River. Hurst found that long-term shifts in the moments of records and other non-random effects existed which could not be encompassed by simple correlation structures.

In a study of the records from 227 streamflow stations within the United States for which flow had been essentially unregulated and records had been kept continuously for at least 30 years, Beard (15) admitted that the true form of the population distribution for the data was not known, and

that it was quite possibly non-normal.

In this study the Wilcoxson two-sample test was used. This is a non-parametric or distribution-free test; that is, it assumes no knowledge about the distribution and parameters of the population. It is therefore suitable for use with hydrologic and hydrologic-related data populations which may not be normally distributed.

The null hypothesis Ho is that $\mu_1 = \mu_2$ for two populations represented by the two samples (the alternate hypothesis is that $\mu_1 \neq \mu_2$). (μ = the mean of the population represented by the sample.) The smaller sample is called sample (1) and the larger sample is called sample (2). The samples are ranked together in ascending order if $x_1 < x_2$ and in descending order if $x_2 < x_1$. ($\bar{x}$ = the median of the sample.) The sum of the ranks of the n_1 observations of the smaller sample is called w; w_2 is the sum of the ranks of the larger sample. Then,

$$u = w_1 - (\text{minimum value of } w_1)$$

Or

$$u = w_1 - n_1 * \frac{(n_1 + 1)}{2} \qquad (9)$$

U is a statistic of which u is a particular value. The significance test is as follows:

(1) Choose a level of significance α.

(2) Compute w, and u, from the data.

(3) Critical region:

(a) All values for which Pr (U<u/Ho is true) $< \alpha$, for one-tailed test.

(b) All values for which $2Pr(U < \mu / Ho$ is true$) < \alpha$, for two-tailed test.

Critical probability values and values for various sample sizes are given by Walpole and Myers (13).

(4) Conclusion: Reject Ho if u falls in the critical region; otherwise accept Ho.

Wilcoxson also developed a test for paired observations (13). In this test the null hypothesis is that or the mean of the differences between paired observations of the two samples is equal to zero or to some other stated value. The positive differences and the negative differences are ranked and added separately. The smaller sum of the rankings is called w. W is a statistic of which w is a particular value. The significance test is as follows:

(1) Choose a level of significance a.

(2) Critical region:

(a) All w values for which $Pr(W < w$ / Ho is true$) < \alpha$, for one-tailed test.

(b) All w values for which $2Pr(W < w$ / Ho is true$) < \alpha$, for two-tailed test.

Critical w values for a range of sample sizes are given by Walpole and Myers (13).

(3) Conclusion: Reject Ho if w falls in the critical region; otherwise accept Ho.

CHAPTER III

METHODS AND PROCEDURES

Study Area Description

Four watersheds within the city of Knoxville, Tennessee, having different land use and geologic characteristics, but possessing relative stability of land use patterns and lack of major point sources of pollution, were chosen for study by the Tennessee Valley Authority. Rainfall, stormwater quantity and quality, and atmospheric fallout data were collected in these watersheds from 1972 to 1975. The purposes of the study were to expand our understanding of urban watershed hydrology and to regionalize some first-generation models (2).

The watersheds are characterized by carbonate rock formations overlain by permeable soils of varying depth. A few older homes in the First Creek watershed have septic tanks, but all other residences and establishments in the study area are served by sanitary sewers. Streets are cleaned in each of the watershed areas at least once per month by flushing followed by manual sweeping into a "vac-all" unit. Some important characteristics of the watersheds are summarized in Table 3 (2).

The Plantation Hills watershed, shown in Figure 2, is located in a subdivision of the same name in

TABLE 3

KNOXVILLE STUDY WATERSHEDS

Watershed	Drainage Area km^2	Drainage Area (mi^2)	Impervious Percent	Primary Land Use
Fourth Creek	2.12	(0.82)	45	Commercial
Third Creek	4.14	(1.60)	28	Industrial-Residential
First Creek	1.3	(0.50)	16	Residential
Plantation Hills	0.62	(0.24)	23	Suburban

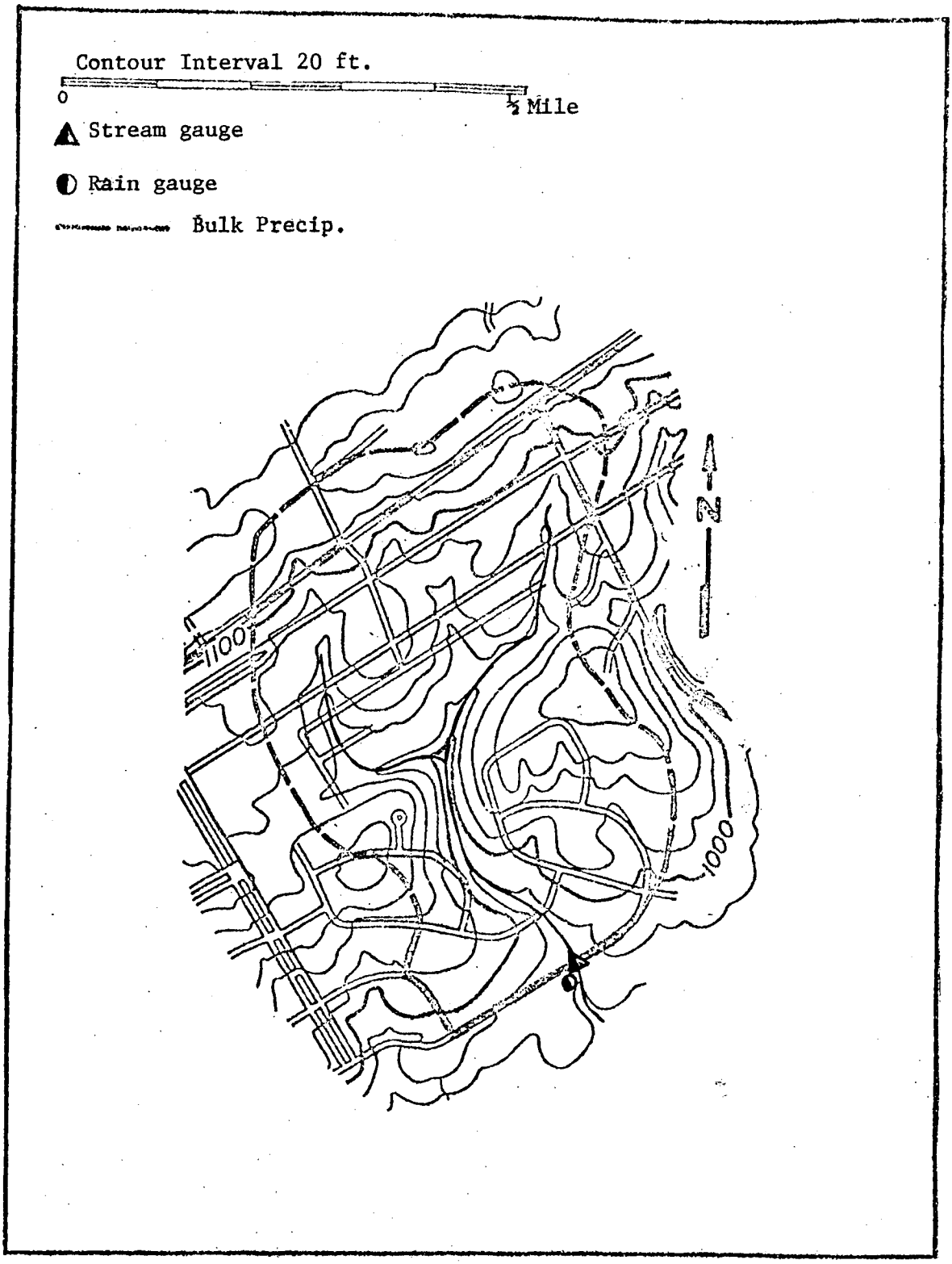

Figure 2

Map of Plantation Hills Watershed

East Knoxville, which was developed between 1950 and 1965. It is located near an interstate highway, I-75. Lot sizes are one-half to three-fourths acre, and the population density (1970) was 3.5 per acre. The entire watershed is underlain by dolomite limestone, which is quite soluble and is associated with a karst terrain characterized by sinkholes, blind drainage, caves, and springs. Much of the runoff generated in this watershed disappears into a very permeable section of the stream channel upstream from the stormwater runoff gauge. Often the only source of stormwater runoff is the street is located immediately above the stream gauge. Stormwater runoff usually lasts only a short time in this watershed (2).

The First Creek watershed, shown in Figure 3, is in a primarily residential neighborhood of North Knoxville. Most of the homes are about 50 years old and are located on one-fourth to one-half acre lots, but along the ridge which forms the northern boundary of the watershed there are some newer homes built between 1950 to 1965 on one-half to three-fourth acre lots. A major urban artery, Highway 441, traverses the watershed. There are a number of commercial establishments along this highway, including several gas stations and a garage. The elevation drop between the crest of the ridge and the stream gauge is more than 300 feet. Nearly all of the watershed except for the upper portion of the ridge is underlain by soluble dolomite rock (2).

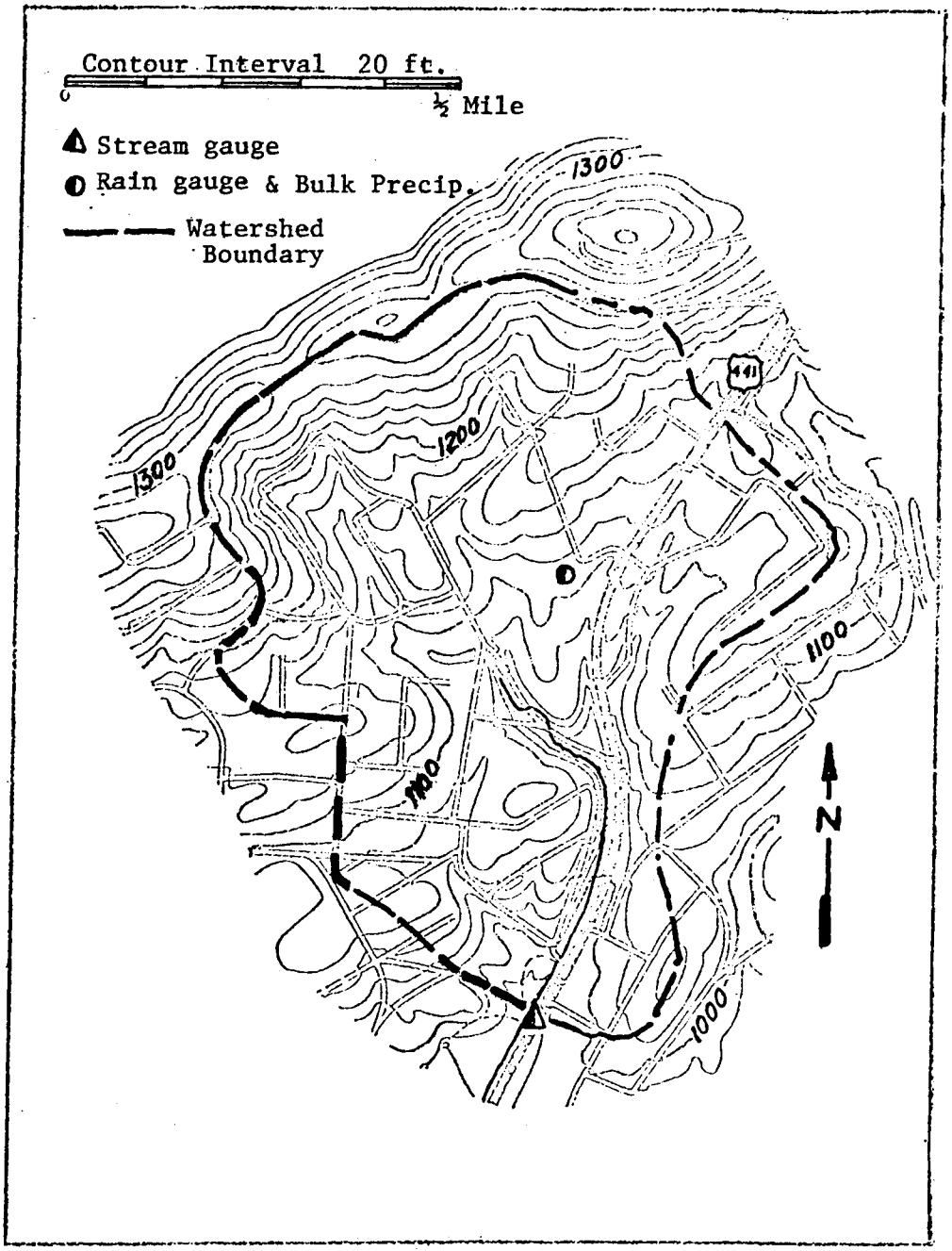

Figure 3

Map of First Creek Watershed

The Third Creek watershed, shown in Figure 4, is atypical among Knoxville watersheds for several reasons. The land use is a combination of commercial and industrial patterns. The residential sector includes older single-family homes, some of them blighted, located on one-fourth acre lots, and three high-density low-income housing developments. The industrial sector includes some trucking companies, a plastics molding plant, a veneer mill, a marble company, and an iron foundry. An automobile recycling operation near the headwaters of the creek has large exposed, easily erodable soil surfaces. A settling pond for the foundry overflows during large storms. These sites resemble point sources for sediment and other pollutants during storm events. The geology of this watershed is also different from that characteristic of the others. A ridge composed of Copper Ridge dolomite forms a seal across the southern boundary of the watershed. Also, the underlying strata of most of the watershed is a mixture of Rutledge and Maryville limestone and Rogersville shale; this combination is much less soluble than the types of dolomite found in the other watersheds. Because of these two factors very little water is lost from this watershed except via the stream channel. Third Creek maintains a year-round flow, with a significant groundwater contribution (2). The elevation drop is more than 300 feet from Sharp's Ridge at the northern boundary to the valley along

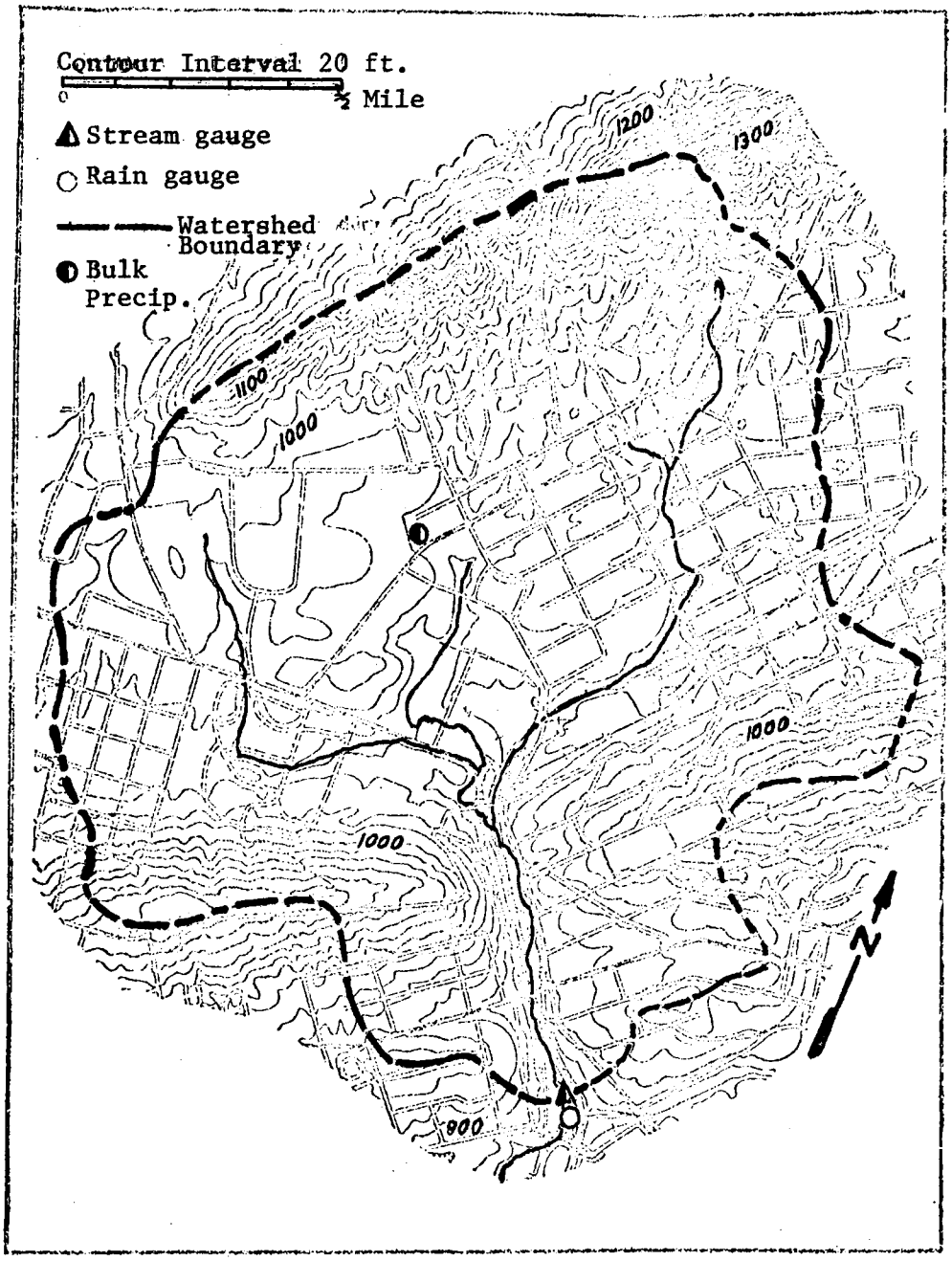

Figure 4

Map of Third Creek Watershed

Third Creek.

The Fourth Creek watershed, shown in Figure 5, is located in a largely commercial area of West Knoxville. United States Highway 11-70 and Interstate 40-75 run parallel to one another through the watershed in an East-West direction. United States Highway 11-70 is lined with commercial establishments. The stream itself rises in a large shopping center, in which it is enclosed under the parking lot as a storm sewer. There are some rather new homes along the fringes of the watershed--mostly on one-acre lots. The entire watershed overlays soluble dolomite, but the presence of pavement prevents surface water from reaching these strata in much of the watershed (2).

Betson (2) used the TVA Continuous Daily Streamflow Model as an analytical tool to quantify changes in the water yield from the four watersheds during the study period. The results indicated that watershed losses by-passed through subsurface channels decreased considerably in the Fourth Creek watershed during a period when urbanization was increasing. Slight decreases in losses were also calculated for the Plantation Hills and First Creek watersheds. Average losses during the study period were 50, 81, and 89 percent of the expected runoff for Fourth Creek, First Creek, and Plantation Hills, respectively. Losses were negligible in the Third Creek watershed (2).

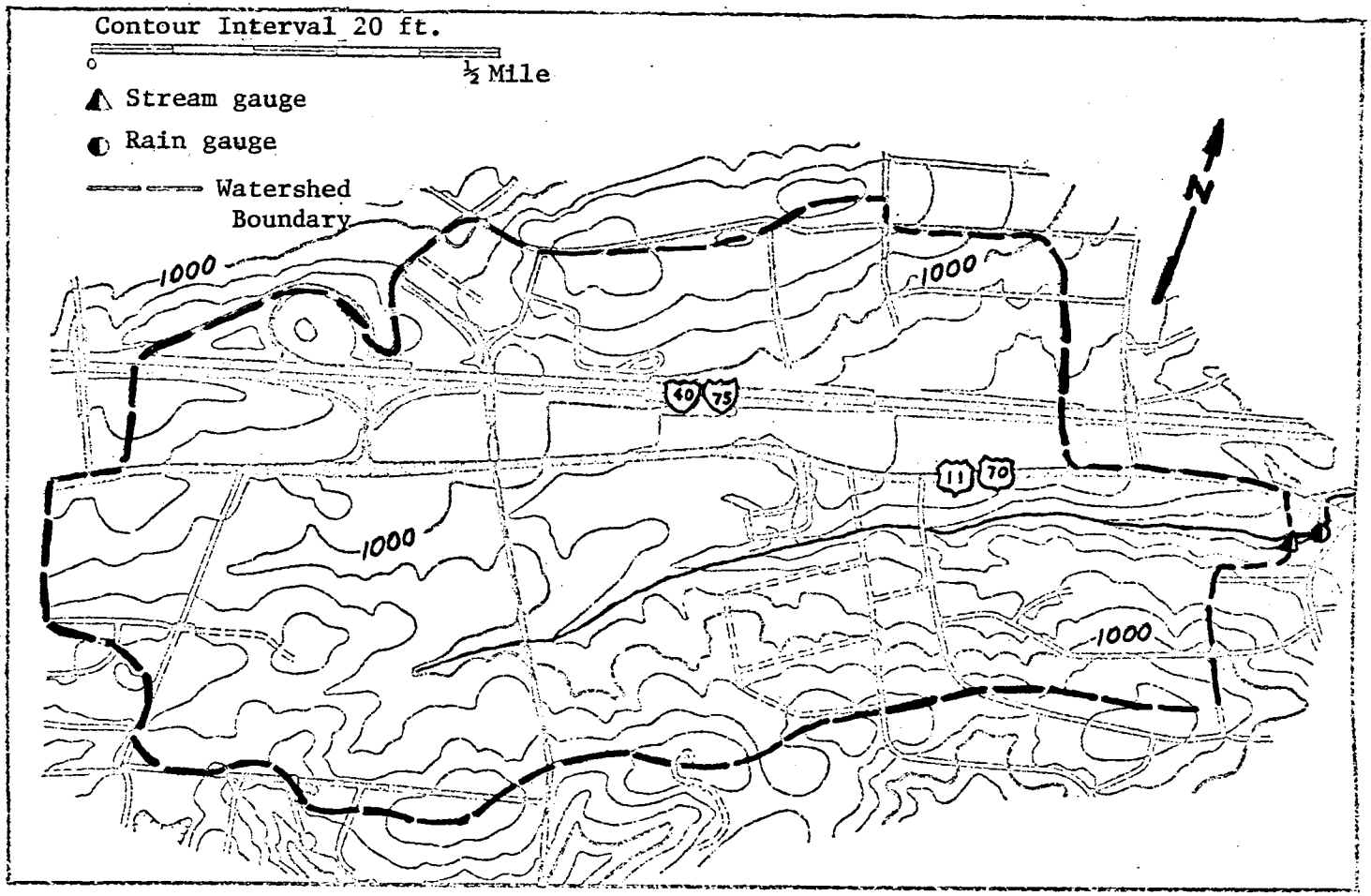

Figure 5

Map of Fourth Creek Watershed

Data Acquisition

Recording streamflow gauges were installed at the lower boundary of each watershed during 1971. In the First Creek watershed a rain gauge and an atmospheric fallout sampler was placed more than one-half mile from the stream gauge, but in the other watersheds these instruments were located near the stream gauge.

The atmospheric fallout samplers have a height of 8.1 inches and an effective top diameter of 7.7 inches. They are equipped with a bird ring. The sampling period for atmospheric fallout was generally about one month.

Two water quality sampling devices were used. One was the ISCO automatic water sample collector, model 780, manufactured by the Instrument Specialties Company, Lincoln, Nebraska. The sampler was modified so that it would be activated whenever the stage of flow reached a certain height. The sampler was mounted in a trailer and was moved from First Creek to Fourth Creek. Sampling was done from May 1972 to October 1973 on Fourth Creek, and from November 1973 to February 1975 on First Creek (2).

The other sampler was a PS69 water sampler designed at the Federal Inter-Agency Sedimentation Project, St. Anthony Falls Hydraulic Laboratory, Minneapolis, Minnesota. It was planned that this unit would be moved from Third Creek to Plantation Hills, but the unit was so

large that there was no room for it at the Plantation Hills site. Therefore, it remained at Third Creek; it was used from May 1972 to December 1974. The sampler utilizes a variable sampling interval adjusted to the stream gauge rating curve, so that the sampling interval is proportional to the discharge (2).

Sampling at Plantation Hills took place between August 1974 and March 1975. All sampling was done by hand (2).

At First, Third, and Fourth Creeks the stream gauge charts were usually marked at the times when sampling was done. At Plantation Hills this was not done. This was a serious problem; the only knowledge available concerning time of sampling was the date, which was indicated in the water quality data. It was necessary to assume that the sampling for the date indicated took place during hydrograph peaks. There is no assurance that this assumption is valid, because in some of the other watersheds, samples were taken when there was no storm event. (These samples were discarded for our study purposes.) As much as possible, events were limited to single storms during one day, but this guideline could not be entirely followed because there was not enough useable data. No reliability can be claimed for the results from Plantation Hills. The study of this watershed was useful for developing and refining computational procedures and the results are useful

for comparison with those from the other watersheds.

This study utilized data from Plantation Hills, First Creek, and Fourth Creek. The study of Third Creek by Barkdoll (1) was considered to be complete and the results are reported for purposes of comparison. The collection of dustfall and water quality data in the study watersheds often was not synchronized. In addition, some of the sampling units malfunctioned at times, and some data is lost that is not accounted for. A larger data base would have been very beneficial, because it would have allowed more screening of events according to guidelines reported by Barkdoll (1). In each watershed, only eight or nine storm events were found to have all of the necessary data available. It must be mentioned, however, that the requirements for this study were not foreseen by the researchers who organized the data collection project.

From the beginning of the project in 1972 until May 1973, all water quality samples were shipped by bus to the TVA Water Quality Laboratory in Chattanooga, Tennessee, shortly after they were taken. The analytical procedures used conformed to either the Environmental Protection Agency Methods (EPA, 1971) or to Standard Methods (APHA, 1971) (2).

Due to manpower limitations the TVA laboratory was unable to analyze the samples after mid-1973. For the remainder of the project the samples were analyzed at the Mark C. Whitaker Water Treatment Plant operated by the

Knoxville Utilities Board (KUB). Sample analysis conformed to Standard Methods (APHA, 1971) except for pH (Potentiometric method); ammonia (specific ion); and silica and calcium (atomic absorption method). Four constituents (organic-N, Hg, As, and COD) were not analyzed during this latter phase of the project (2).

Barkdoll (1) noticed that for many constituents the reported concentration values for Third Creek did not appear to be consistent between the two phases of analysis. He performed a split-data test on those constituents which were analyzed by both laboratories; he found that the data from the two phases represented statistically different populations at a significance level of at least .05 for the constituents Fe, K, NH_3, TDS, pH, color, and SS. For this reason he dropped these constituents from his matrix for principle components analysis screening (1). In this study, the only significant overlap between the two laboratories' work occurred in the Fourth Creek data. This data did not present any unusual difficulties in our experience. Time and manpower limitations precluded the type statistical analysis of this data which was done by Barkdoll for Third Creek.

Data Analysis

The streamflow gauges record depth or stage of flow. The TVA has developed rating curves for discharge as a

function of depth for Plantation Hills, Third Creek, and Fourth Creek. There is no verified rating curve for First Creek because a small dam has been placed across the channel just below the stream gauge, changing the flow characteristics, since TVA last rated the stream. A theoretical rating curve was developed for this stream using Bresse's function and empirical weir equations given by Streeter (12). This rating curve is shown in Figure 6.

In this study principle components analysis was performed and linear regression water quality models were developed using the TVA's water quality and average discharge data. The BMDOIM Principle Components Analysis program (16) and Betson and Green's DIFCOR program (17) were used in this phase of the analysis. Since there was no need to synchronize the water quality data with actual hydrographs nearly all of the water quality data from each watershed could be used; therefore, the data base was large.

Barkdoll's parametric and deterministic models were used to provide insight into the sources of stream degradation as well as into pollutant transport mechanisms for these watersheds. It was also hoped that this work would provide an opportunity for evaluating Barkdoll's results relative to those obtained from other area watersheds having different characteristics. Requirements for the deterministic model are dustfall rate, antecedent dry period, total runoff volume, and average constituent

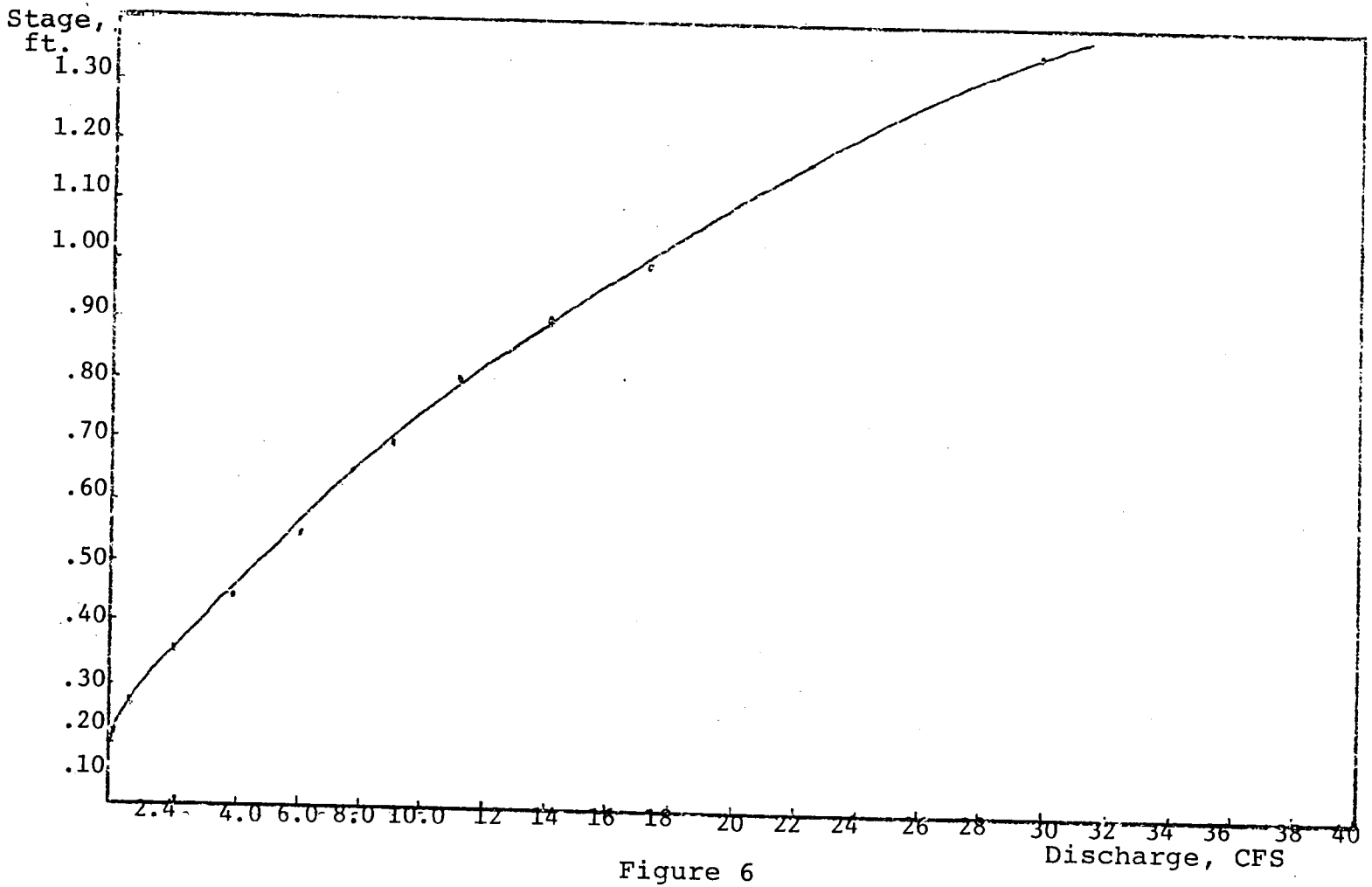

Figure 6

Theoretical Rating Curve for First Creek at Gresham Road, Fountain City

concentration during each storm event. Requirements for the parametric model are total loadings for each constituent and total runoff volume for each storm event.

Runoff volumes were developed from the stream hydrographs, using the rating curves. Base flow, where it existed, was subtracted from the total volume. Total loadings were calculated by multiplying the total runoff volume during a storm event times the average measured constituent concentration during the event as determined from the water quality samples. Dustfall rates were determined from the atmospheric fallout samples. Antecedent dry periods were taken from the rainfall charts.

The parametric model was evaluated using the BMD07R nonlinear least squares computer program (16). Correlation coefficients for both models were evaluated using a program developed by David Jessup, a graduate research assistant at the University of Tennessee.

Principle components analysis and regression modeling were used to describe relationships between a manageable number of water quality variates. The deterministic model was used to describe water quality as a function of dustfall and storm frequency and magnitude, and to assess the predictive utility of this model. The parametric model was used to assess the source of pollutants and the magnitude of loadings in various land-use areas. Each of the models is an independent approach to the stormwater impact problem.

CHAPTER IV

PRESENTATION OF RESULTS

Principle Components Analysis and Water Quality Model Development

For Plantation Hills watershed, 25 water quality variates were reduced to 7; 7 components represented by these 7 variates explained 81.9 percent of the total variance of the original matrix. These variates were SiO_2, PO_{40RG}, CA, NH_3-N, Pb, Color, and K.

For First Creek, 25 original variates were reduced to 8. These were Fe, Ca, Mg, TDS, Ca CO_3, Mn, F, and Pb. Eight components explained 81 percent of the original variance.

For Fourth Creek, 20 original variates were reduced to 8; these were pH, $PO_{4\ ORG}$, NH_3-N, ORG-N, NO_2-NO_3, TDS, Hg, and As. Eight components explained 94.6 percent of the variance.

An admitted weakness in this screening effort is that several variates were almost equally weighted across the first component for each watershed. This was also Barkdoll's experience in attempting to screen the Third Creek Data (1). In this study that constituent having a large data base, a relatively large weighting, and a relatively high correlation with average discharge was chosen to represent

the first component. The choice was usually obvious in components of lower rank.

Parametric linear regression models were developed for discharge as a function of the screened water quality variates from each watershed. The model for Plantation Hills is,

$$\text{DISCHARGE} = .1253 * SiO_2 + .2591 * PO_{4\ ORG} + 2.147 * NH_3\text{-}N + 1.733 * Pb + .0037 * COLOR + .0754 * K.$$

The coefficient of determination is .3798.

For First Creek the model is,

$$\text{DISCHARGE} = .0060 * Fe + 2.798 * Ca + 4.296 * Mg + .9377 * TDS + .0068 * CaCO_3 - .0297 * Mn + 8.591 * F + .1024 * Pb.$$

The coefficient of determination is .2086.

The model developed for Fourth Creek is,

$$\text{DISCHARGE} = -.4384 * pH + 12.24 * PO_4\text{-SOL} - 11.37 * NH_3\text{-}N - 237.2 * ORG\text{-}N + 6.2.6 * NO_2\text{-}NO_3 + .3683 * TDS - .0447 * Hg + 5.638 * As.$$

The coefficient of determination is .5343.

Deterministic Model

Barkdoll's model (1), $C = \frac{D*N}{Vol}$, was used to analyze data from Plantation Hills, First Creek, and Fourth Creek watersheds. The results are shown in Table 4, together

TABLE 4

RESULTS OF DETERMINISTIC MODEL

Group	Constituent	Watershed							
		Plantation Hills		First Creek		Third Creek		Fourth Creek	
		K	Coeff. of Det.	K	Coeff. of Det.	K	Coeff. of Det.	K	Coeff. of Det.
Limestone Associated Minerals	Ca	10.33	.0016	1.644	.0560	-	-	1.437	.0145
	Mg	5.90	.1305	2.839	.0034	.39	.0729	1.979	.0002
	$CaCO_3$	6.43	.2401	6.362	.1439	.75	.0961	2.154	.4627
	ALK	9.18	.0262	1.045	.0296	-	-	-	-
Other Minerals	SiO_2	3.18	.0089	1.532	.0249	1.73	.0100	1.039	.0874
	Na	15.00	.0418	12.40	.0128	.52	.0256	2.267	.2842
	K	14.4	.1104	10.67	.0802	1.52	.2601	5.535	.1604
	SO_4	40.1	.0020	1.902	.4661	2.23	.0016	3.558	.0008
	Cl	20.88	.0097	21.91	.0383	4.63	.1024	7.254	.1525
	F	290.4	.0250	14.43	.0529	4.01	.0196	5.230	.7149
Solids	SS	-	-	2.356	.0358	.27	.5776	.5291	.0885
	TDS	1.375	.4173	2.243	.1373	2.19	.3721	6.050	.0102

TABLE 4 (Continued)

Group	Constituent	Watershed							
		Plantation Hills		First Creek		Third Creek		Fourth Creek	
		K	Coeff. of Det.	K	Coeff. of Det.	K	Coeff. of Det.	K	Coeff. of Det.
Metals	Fe	9.20	.1671	2.106	.0282	.12	.3249	.1870	.2495
	Mn	3.48	.1310	9.521	.0218	.27	.0729	.4506	.2028
	Pb	-	-	-	-	.83	.2809	7.844	.3173
	Hg	-	-	-	-	5.84	.0169	6.119	.2638
	As	-	-	-	-	1.14	.2304	1.144	.0141
Nutrients	ORGN	-	-	-	-	-	-	1.154	.0620
	NH_3N	42.0	.0192	24.49	.0709	152.11	.2304	243.3	.0274
	NO_2-NO_3	9.52	.9968	8.528	.2944	18.21	.0001	30.80	.1028
	PO_4-T	2.10	.0074	1.898	.0008	-	-	.6951	.0025
	PO_4-SOL	1.13	.0813	1.616	.3058	-	-	5.990	.7932
	COD	-	-	-	-	2.88	.1521	1.659	.0038

with Barkdoll's results from Third Creek (1). The "K" values are mean values (C predicted/C observed) for the events analyzed. The coefficients of determination were calculated from predicted and observed concentrations also. Barkdoll (1) divides the "K" values into three classes. Case I ($K < 0.8$) represents underprediction by the model. In this case there may be pollutant sources within the watershed other than dustfall, or dustfall is not the only mode of contaminant transport into the watershed. Case II ($0.8 < K < 1.2$) indicates approximate prediction of observed concentrations by the model. Case III ($1.2 < K$) represents overprediction by the model. There may be environmental sinks for dustfall contaminants, or removal by runoff may be less than 100 percent efficient (1).

The constituents have been divided into groups so that behavioral trends for various classes of pollutants might be identified, if they exist.

A large proportion of the potential runoff generated in the Plantation Hills, First Creek, and Fourth Creek watersheds is lost into groundwater channels; therefore, it was realized that the model does not represent the system if only that fraction of the runoff which reaches the stream is considered to be a dilution factor for the accumulated dustfall. In the First Creek watershed Betson (1) calculated that 81 percent of the potential runoff is bypassed; therefore, the runoff measured at the

stream gauge is only 19 percent of the potential runoff volume. This total volume of dilution water was calculated and average concentrations were recalculated for certain constituents (see Table 5). First Creek was used for this purpose because this watershed has a high percentage of losses and the data are reasonably reliable. One constituent from each group which had a relatively large number of measurements and a relatively good coefficient of determination in the previous trial was used. The model assumes that the quality of the water transported from the watershed by whatever mechanism, whether by runoff into the stream or by infiltration into the ground, is uniform over the entire watershed. This is admittedly a simplistic assumption; however, it was hoped that this approach could shed light on the problem of whether the large overpredictions resulting from this model are due to the dustfall rates or to a lack of accounting for all of the dilution water.

Parametric Model

The results of Barkdoll's parametric model (1), $C^*RO = M_T\ (1-e^{-RO/ROC})$, for the study watersheds, are shown in Tables 6 and 7. Barkdoll's results from Third Creek are also presented.

It was realized that this model, also, cannot represent the system unless the watershed losses are considered. The loadings removed by a small portion of the

TABLE 5

ADJUSTED RESULTS FOR SELECTED CONSTITUENTS: FIRST CREEK

Constituent	K Value
$CaCO_3$	1.20
K	2.07
TDS	.418
Fe	.400
PO_4-T	.307

TABLE 6

VARIATION OF M_T AMONG WATERSHEDS

Group	Constituent	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		M_T, lb.			
Limestone Associated Minerals	Ca	3.607	200.2	143695	646.8
	Mg	.6045	22.10	1808	187.6
	$CaCO_3$	.1492	656.6	44084	2807
	ALK	17.50	501.7	-	1480
Other Minerals	SiO_2	1.368	43.73	2336	131.1
	Na	.5238	33.86	2761	90.00
	K	.6288	16.00	-	759.7
	SO_4	7.100	141.2	22299	697.9
	Cl	1.505	39.11	2347	199.2
	F	.1013	2.306	76.34	2.004
Solids	SS	-	343.3	1145804	85271
	TDS	100.0	1354	-	3403

TABLE 6 (Continued)

Group	Constituent	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		M_T, lb.			
Metals	Fe	.3009	13.11	402.6	1505
	Mn	.0125	.4503	95.04	49.12
	Pb	.0050	1.046	.1100	8.022
	Hg	-	-	2.816	.0515
	As	-	-	-	3.412
Nutrients	ORGN	-	-	-	56.22
	NH_3N	.0545	.7169	-	6.019
	NO_2.3-N	.2746	3.993	1074	13.22
	PO_4-T	.7101	11.00	-	120.0
	PO_4-SOL	.6575	8.812	-	3.592
	COD	-	-	25689	3749

TABLE 7

VARIATION OF RO_c VALUES AMONG WATERSHEDS

Group	Constituent	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		RO_c, in.			
Limestone Associated Minerals	Ca	.0103	.0700	21.0	.1533
	Mg	.0104	.0665	1.41	.1794
	$CaCO_3$	.0042	.0904	1.50	.2111
	ALK	.0102	.0947	-	.1670
Other Minerals	SiO_2	.0105	.0820	1.64	.2378
	Na	.0086	.0923	1.92	.2120
	K	.0108	.0578	-	.2091
	SO_4	.0113	.1001	5.71	.1857
	Cl	.0110	.0957	.99	.1422
	F	.0130	.0853	2.16	.0816
Solids	SS	-	.0959	15.0	.3178
	TDS	.0367	.0875	-	.1897

TABLE 7 (Continued)

Group	Constituent	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		RO_c, in.			
Metals	Fe	.0099	.0801	-	.1521
	Mn	.0088	.0897	2.78	.2808
	Pb	.0129	.0980	1.30	.2040
	Hg	-	-	0.50	.1712
	As	-	-	1.46	.3744
Nutrients	ORG-N	-	-	-	.2256
	NH_3-N	.0043	.0753	-	.2886
	HO_2-NO_3	.0109	.0893	10.0	.2777
	PO_4-T	.0117	.0897	-	.2074
	PO_4-SOL	.0106	.0490	-	.1086
	COD	-	-	0.74	.2590

potential runoff in the study watersheds cannot be expected to compare with those removed by the total potential runoff in the Third Creek watershed. Therefore, the parameters were recalculated, based on estimated total loads removed by estimated total runoff, in an approach similar to that used with the deterministic model. In order to do this it was necessary to assume that the removal of contaminants into groundwater sinks follows a mechanism approximately the same as that by which surface runoff conveys contaminants into the stream. This would usually be a weak assumption, because the laws of groundwater hydrology are somewhat different from those for surface water hydrology. However, in this case the assumption may have some validity, because a large portion of the losses are thought to occur through discreet sinks or rapid infiltration areas rather than through pervious soil surfaces in a uniform manner (2). Surface water and its associated loadings is conveyed to these sinks, of course, by the runoff process.

To allow comparison of the results between watersheds the M_T values were also normalized to a per-acre basis so that the effect of the varying sizes of the watersheds would be eliminated.

Table 8 gives normalized M_T values based on runoff volumes measured at the stream gauge. Tables 9 and 10 show normalized M_T values and RO_C values based on the total

TABLE 8

NORMALIZED M_T VALUES FOR STUDY WATERSHEDS

Group	Constituent	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		M_r, lb./acre			
Limestone Associated Minerals	Ca	.0234	.6256	140.3	1.232
	Mg	.0039	.0690	1.766	.3575
	$CaCO_3$	.0010	2.052	43.05	5.349
	ALK	.1139	1.568	-	2.820
Other Minerals	SiO_2	.0087	.1366	2.281	.2498
	Na	.0034	.1058	2.696	.1715
	K	.0041	.0500	-	1.448
	SO_4	.0462	.4412	21.78	1.158
	Cl	.0098	.1222	2.292	.3796
	F	.0006	.0072	.0746	.0038
Solids	SS	-	1.073	1119	162.5
	TDS	.6510	4.231	-	6.484

TABLE 8 (Continued)

Group	Constituent	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		M_r, lb./acre			
Metals	Fe	.0020	.0410	-	2.867
	Mn	.0001	.0014	.3932	.0094
	Pb	.00003	.0033	.0928	.0153
	Hg	-	-	.0001	.0001
	As	-	-	.0028	.0065
Nutrients	ORG-N	-	-	-	.1071
	NH_3-N	.0004	.0022	-	.0115
	NO_2-NO_3	.0018	.0125	1.049	.0252
	PO_4-T	.0046	.0344	-	.2286
	PO_4-SOL	.0043	.0275	-	.0068
	COD	-	-	25.09	7.144

TABLE 9

NORMALIZED M_T VALUES BASED ON PROJECTED RUNOFF VOLUMES

Group	Constituent	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		M_T, lb./acre			
Limestone Associated Minerals	Ca	.2127	3.293	140.3	2.464
	Mg	.0354	.3632	1.766	.7150
	$CaCO_3$	.0091	10.80	43.05	10.70
	ALK	1.035	8.252	-	5.640
Other Minerals	SiO_2	.0791	.7189	2.281	.4996
	Na	.0309	.5568	2.696	.3430
	K	.0372	.2632	-	2.898
	SO_4	.4200	2.322	21.78	2.316
	Cl	.0891	.6432	2.292	.7472
	F	.0054	.0379	.0746	.0076
Solids	SS	-	5.647	1119	325.0
	TDS	5.918	22.26	-	12.97

TABLE 9 (Continued)

Group	Constituents	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		M_T, lb./acre			
Metals	Fe	.0182	.2157	-	5.734
	Mn	.0009	.0073	.3932	.0188
	Pb	.0003	.0174	.0928	.0306
	Hg	-	-	.0001	.0002
	As	-	-	.0028	.0130
Nutrients	ORG-N	-	-	-	.2142
	NH_3-N	.0036	.0116	-	.0230
	NO_2-NO_3	.0164	.0658	1.049	.0504
	PO_4-T	.0418	.1810	-	.4572
	PO_4-SOL	.0391	.1447	-	.0136
	COD	-	-	25.09	14.29

TABLE 10

RO_c VALUES BASED ON PROJECTED RUNOFF VOLUMES

Group	Constituent	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		RO_c, in.			
Limestone Associated Minerals	Ca	.0936	.3684	21.0	.3066
	Mg	.0945	.3500	1.41	.3588
	$CaCO_3$	.0382	.4758	1.50	.4222
	ALK	.0927	.4984	-	.3340
Other Minerals	SiO_2	.0954	.4316	1.64	.4756
	Na	.0782	.4858	1.92	.4240
	K	.0982	.3042	-	.4182
	SO_4	.1027	.5268	5.71	.3714
	Cl	.1000	.5037	.99	.2844
	F	.1182	.4489	2.16	.1632
Solids	SS	-	.5047	15.0	.6356
	TDS	.3336	.4605	-	.3794

TABLE 10 (Continued)

Group	Constituent	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		RO_c, in.			
Metals	Fe	.0900	.4216	-	.3042
	Mn	.0800	.4721	2.78	.5616
	Pb	.1173	.5158	1.30	.4080
	Hg	-	-	0.50	.3424
	As	-	-	1.46	.7488
Nutrients	ORG-N	-	-	-	.4512
	NH_3-N	.0391	.3963	-	.5772
	NO_2-NO_3	.0991	.4700	10.0	.5554
	PO_4-T	.1064	.4721	-	.4148
	PO_4-SOL	.0964	.2579	-	.2172
	COD	-	-	0.74	.5180

volume of water available for runoff. Table 11 presents coefficients of determination calculated from observed and predicted loadings for the study watersheds. Coefficients of determination for Barkdoll's work (1) are also shown.

The M_T values were divided by dustfall rates so that accumulation times for the various constituents in the study watersheds could be compared with those computed by Barkdoll (1) for Third Creek. These ratios expressed in days, are shown in Table 12. The average antecedent dry period for the watersheds is about four days.

One constituent having a relatively complete representation across the study watersheds and a relatively high coefficient of determination was chosen from each group. For the constituents the M_T/D ratios were recalculated from the adjusted M_T values given in Table 9. It was hoped that this approach would provide a clearer understanding of the actual contribution of dustfall to pollutant loading in these watersheds. Adjusted M_T/D ratios are given in Table 13.

Statistical Analysis

Overton and Meadows (8) asserted that if a model produces different predictions or simulations given different scenarios for a particular problem, these variations need to be placed relative to the errors associated in fitting the model to the data. In order to gain understanding of

TABLE 11

AVERAGE COEFFICIENT OF DETERMINATION FOR VARIOUS WATER QUALITY CONSTITUENTS: PARAMETRIC MODEL

Group	Constituent	Average Coefficient of Determination	Number of Cases (Watersheds)
Limestone Associated Minerals	$CaCO_3$	.86	4
	ALK	.81	3
	Ca	.81	4
	Mg	.78	4
Other Minerals	Na	.74	4
	K	.72	3
	Cl	.67	4
	F	.60	4
	SO_4	.59	4
	SiO_2	.55	4
Solids	TDS	.67	3
	SS	.35	2

TABLE 11 (Continued)

Group	Constituent	Average Coefficient of Determination	Number of Cases (Watersheds)
Metals	As	.81	2
	Fe	.73	3
	Hg	.71	2
	Pb	.50	4
	Mn	.47	4
Nutrients	ORG-N	.92	1
	PO_4-T	.88	3
	COD	.80	2
	NO_2-NO_3	.77	4
	PO_4-SOL	.76	3
	NH_3-N	.50	3

TABLE 12

COMPARISON OF M_T/D RATIOS AMONG WATERSHEDS

Group	Constituent	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		M_T/D, days			
Limestone Associated Minerals	Ca	.315	27.38	1070	11.85
	Mg	.305	4.28	118	12.29
	CaCO	.0020	4.07	80	9.66
	ALK	.398	8.88	-	11.16
Other Minerals	SiO_2	.702	4.66	41	21.20
	Na	.113	2.76	90	7.63
	K	.215	3.74	-	22.07
	SO_4	.214	3.20	-	4.18
	Cl	.179	1.37	14	1.90
	F	.106	1.51	25	1.43
Solids	SS	-	16.68	320	289.8
	TDS	2.57	14.48	-	3.30

TABLE 12 (Continued)

Group	Constituent	Watershed			
		Plantation Hills	First Creek	Third Creek	Fourth Creek
		M_T/D, days			
Metals	Fe	1.82	.713	-	348.6
	Mn	.326	1.67	366	39.36
	Pb	-	3.61	61	2.74
	Hg	-	4.49	6	4.29
	As	-	-	20	27.34
Nutrients	ORG-N	-	-	-	1.38
	NH_3-N	.099	.713	-	.44
	NO_2-NO_3	.421	1.67	40	1.26
	PO_4-T	2.21	3.61	-	3.00
	PO_4-SOL	4.49	4.41	-	-
	COD	-	-	14	-

TABLE 13

SELECTED M_T/D RATIOS ADJUSTED FOR PROJECTED RUNOFF VOLUMES

Constituent	Watershed			
	Plantation Hills	First Creek	Third Creek	Fourth Creek
	M_T/D, days			
$CaCO_3$	.018	21.4	80	19.3
K	1.95	19.7	-	44.1
Fe	16.5	107.7	-	697.2
TDS	23.4	76.2	-	6.6
PO_4	40.8	23.2	-	-

the significance of the variations in the data for this study, the Wilcoxson test was used to determine the significance of between-watershed variations in normalized measured loadings. It was hoped that a context would be provided for assessing the significance of predicted M_T and RO_c values.

It was hoped that one constituent for which analysis was complete in all watersheds and which produced a high coefficient of determination could be chosen to represent each group. However, no constituent of the non-limestone associated metals met these criteria. Lead was the only constituent meeting the needs of this test for which data from Third Creek was readily available. The Plantation Hills watershed was not included in this analysis because of the uncertainties concerning the data which were previously mentioned. It was felt that First Creek could be considered representative of a residential watershed, and Third Creek and Fourth Creek could be considered to be representative of industrial and commercial watersheds, respectively. Results obtained through the Wilcoxson two-sample test are shown in Table 14.

Note that the null hypothesis that the population means for normalized stormwater loadings in two different watersheds are equal is accepted at the .05 level of significance in every case except for the comparison of lead between First Creek and Third Creek.

TABLE 14

WILCOXSON TWO-SAMPLE TEST

Watersheds Compared	Constituent	Critical Region	(Probability)
First Creek	$CaCO_3$	12	26
versus	TDS	17	34
Fourth Creek	Pb	Pr(u < 22.51/Ho True)=.05	Pr(u <22.5/Ho True)=.178
	NO_2-NO_3	12	26
First Creek	Pb	29	25
versus			
Third Creek			
Third Creek	Pb	29	33
versus			
Fourth Creek			

Ho: $\mu_1 = \mu_2$, $\alpha = .05$ significance level.

The Wilcoxson test for paired observations was used to determine whether there were significant differences between RO_c values for different pollutant groups. The calculated RO_c values given in Table 10, page 60, representing two constituents for a given watershed were considered to be a pair. $CaCO_3$, Pb, and NO_2-NO_3 represented the limestone associated minerals, heavy metals, and nutrients, respectively. In no case were the differences statistically significant at the $\alpha = .05$ significance level.

CHAPTER V

DISCUSSION OF RESULTS

The fact that some of the same constituents are retained after screening in more than one watershed indicates that principle components analysis is a promising tool for reducing the complexisty of the problem of storm-water quality analysis. Some of the difficulties encountered in screening the data by principle components analysis could have been caused by discrepancies and gaps in the data itself.

The coefficients of determination suggest that the regression model for Fourth Creek and possibly the Plantation Hills model as well could be used for some purposes with a limited degree of confidence.

The deterministic model generally produced low coefficients of determination for predicting constituent concentrations. This could be due to the fact that the model structure does not reflect the nonlinear nature of surface water transport mechanisms or the first-flush effect in contaminant removal. Results for some constituents are sufficiently impressive, however, to indicate that this model could be used in some cases in which rough estimates are needed.

It is instructive to compare prediction patterns produced by the deterministic model with the results reported by Betson (2) for the mass balance on these same watersheds (see Table 1, page 10). Both approaches revealed that atmospheric sources were more than sufficient to account for all water quality constituent measurements in Plantation Hills. In the First and Fourth Creek watersheds results of the two approaches were similar for all non-limestone associated minerals except for SiO_2, Na, and K in Fourth Creek watershed; both approaches indicated that atmospheric sources could not account for all of the limestone-associated minerals found in the stream. Both approaches indicated that atmospheric sources were more than sufficient to account for the metals (Hg and As) and nutrients (NH_3, NO_2-NO_3, and COD) studied in this watershed.

Of course the deterministic model predicts constituent concentrations during storm events and the mass balance compares annual input (dustfall) and output (streamflow) loadings. Actually, the model structures are similar, and since both approaches address the question of the degree to which dustfall is responsible for stormwater pollution, it was hoped that the results could be compared in order that our understanding of the magnitude of the dustfall contribution for various constituents could be better understood. In all cases where there were discrepancies between the two approaches the deterministic model overpredicted while the

mass balance showed that inputs were actually smaller than outputs. It has previously suggested that concentrations predicted by the deterministic model may have been too high because not all of the dilution water was taken into account. Betson's input loadings could also have been too small. They were based on precipitation volumes taken from the atmospheric samplers; since these samplers were only serviced at approximately monthly intervals, the evaporation losses could have been considerable (2).

The parametric model predicted large differences in ultimate pollutant loading M_T between watersheds if runoff volumes measured at the stream gauge were used. The prediction that the loadings are heaviest in the industrial Third Creek watershed is consistent with Sartor and Boyd's work (3); the prediction that loadings in the commercial Fourth Creek watershed are generally about double those of residential First Creek is not. This could be a real occurrence, but this effect could also be due to the difference between bypassed losses for the two watersheds. Table 8, page 56, shows that if projected available runoff volumes were used to determine the parameters the differences in M_T values between the two watersheds became slight. This response is more consistent with the results of other work in the field (3). Notice that lead and suspended solids were still relatively high for Fourth Creek.

The lead loadings could be caused by heavy traffic around the shopping centers and on the highways in this watershed. The suspended solids loadings could be elevated because of the erosion of the streambed by high-volume high-velocity stormwater runoff (2).

RO_C values computed using measured runoff volumes were less than the EPA street surface runoff coefficient in all of the watersheds except for Third Creek. This indicates that most contaminants which are actually washed into the streams originate from impervious surfaces. If the projected total available runoff volumes were used the RO_C values became larger than the street surface coefficient for most constituents in the First and Fourth Creek watersheds, indicating that pervious surfaces may also be involved in the total contaminant removal process. It appears that contaminants which find their way into First and Fourth Creeks are mostly originating in the paved areas of these watersheds, and that most contaminants associated with the pervious areas are lost into the groundwater channels. If this conclusion is valid, it would certainly have implications for stormwater management strategies in these watersheds.

There does not appear to be a pervious area contribution to even the total pollutant removal process in the Plantation Hills watershed, as the revised RO_C values are smaller than the street surface coefficient for all

constituents except for TDS.

The large RO_C values for Third Creek indicate contaminant removal from pervious areas. Removal only by direct runoff mechanisms is not necessarily implied. A portion of the contaminant loadings could come from the foundry's settling pond, which only overflows into the creek when surface runoff feeding the pond reaches a certain magnitude (11). In addition, it should be remembered that subsurface leaching could be a source of pollution, since groundwater flows feed the stream channel in this watershed. Groundwater flow is indirectly linked with surface runoff, since runoff volume affects infiltration rates (8). Therefore, the large RO_C values could be reflecting this process as well as surface runoff per se.

If M_T/D ratios are determined from measured runoff volumes the conclusion would be that dustfall could account for all contaminant accumulations in Plantation Hills; for all minerals except for Ca; for all metals except for Fe; and for all nutrients in First Creek; and for the minerals SO_4, Cl, and F; dissolved solids; the metals Pb and As; and all nutrients in the Fourth Creek watershed. Only in the case of Hg does the M_T/D ratio approach the typical antecedent dry period for Third Creek.

It should be realized that the M_T values used in this determination for the Plantation Hills, First Creek, and Fourth Creek watersheds represent only the fraction of the

total mass which contributes to stream loadings, while D represents the atmospheric input to the entire watershed. Therefore, these figures could be misleading. If M_T values representing the total mass contributing to all vectors of contaminant removal from these watersheds is used the M_T/D ratios are more similar to those developed by Barkdoll (1) for Third Creek, indicating that dustfall should not be considered to be the only contributor to pollutant loading in the study watersheds (see Table 12, page 63).

The Wilcoxson test does not indicate statistically significant differences between loadings during storm events for any constituents in any two watersheds except in the case of lead, between First Creek and Third Creek. Differences between the results in the study watersheds for the various constituents should be interpreted relative to this fact as well as to the size and quality of the data base.

No inference could be drawn concerning the behavior of the various pollutant groups for different land uses from this study. Land use appeared to have an effect, but this effect was different for each pollutant.

The results of this study should not be considered to be conclusive; however, some general trends in the

stormwater quality responses of various types of land-use areas are indicated. Since pollution problems associated with stormwater do exist at times in these watersheds (2), and since there is some impetus for developing stormwater management plans, a continuation of this study seems justifiable.

A larger data base is needed so that a greater degree of preliminary screening and of significance testing could be done. It might not be necessary to collect additional data for all of the constituents investigated in this study; one possibility would be to sample those constituents which were retained by the principle components analysis screening reported in this study, together with certain others which could pose serious environmental or public health problems. There should be a greater effort in the future to insure that collection of hydrologic, water quality, and dustfall data is synchronized and that all equipment is functioning properly. We agree with R. Gregory Bourne (11) that "(infrequent) sampling, use of time-composited samples, missing data, and quality data without accompanying flow data are factors limiting the utility of available information."

Both Barkdoll (1) and Betson (2) have expressed the opinion that a more extensive dustfall sampling network would have produced more reliable results. Barkdoll (1) also recommended a shorter sampling period for the dustfall jars.

In this study only average constituent concentrations during a storm event were available. Better results could be obtained if concentrations were available for five-minute or ten-minute time intervals for the duration of the storm event. If this type of data were available, loadings could be calculated by a time-variant scheme which would be more reflective of the removal process. Perhaps a more refined deterministic model could be developed which would reflect the unsteady nature of surface runoff. An overall pollutant transport model linking infiltration and groundwater transport vectors with surface water transport effects would be very useful for expanding our understanding of systems which affect urban stormwater quality. Perhaps the TVA Continuous Daily Flow Model (2) and the work of the Hydrocomp Corporation (9) could supply ideas for the development of such a model. This type of model would necessitate a program of groundwater sampling in conjunction with streamflow and water quality data collection.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

1. Principle components analysis was somewhat successful in pointing out some of the water quality constituents which would probably be most profitable for future measurement.

2. The deterministic model is too simplistic to adequately represent the process. It would only be useful to acquire rough approximations of stream concentrations for a few constituents.

3. The parametric model is a useful tool for assessing the sources of water quality impairment, the magnitude of such sources, as well as the variations in loading magnitude and removal mechanisms with land-use and geologic factors.

4. A larger and more accurate data base is necessary in order to acquire statistical confidence in this type of work.

Recommendations

1. Use results from principle components analysis to decide which constituents to include in further sampling efforts. Collect water quality and flow data on short sampling intervals in as many of these watersheds as

monetary and manpower resources permit. Develop pollutographs and loadographs from the data.

2. Set up a groundwater sampling network synchronized with the streamflow network.

3. Sample dustfall in the study watersheds using a larger number of collection devices and a shorter sampling interval.

4. Use the expanded and improved data base to verify the results obtained with the parametric model and to develop a more refined deterministic model.

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VITA

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