

A COMPARISON OF SELECTED
CHEMICAL CHARACTERISTICS IN RUNOFF
FROM DIFFERENT LAND TYPES,

by

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I. INTRODUCTION

Domestic and industrial waste discharges to streams have been recognized as a problem since about 1876 when the Royal Rivers Pollution Act was passed in England (1). Since then, efforts have been directed toward the development of methods to control water pollution from these sources. In recent years, however, land runoff also has been considered as a source of water pollution.

Land runoff is varied in both quality and quantity and is dependent upon meteorological, topographic, climatic, geologic, hydrologic, and land-use conditions (2). Thus, a determination of the effects of land runoff on water quality is a complex problem.

A method that is currently being used to describe the effects of pollutants on water quality is mathematical modeling. It is possible to predict the assimilative capacity of a stream by development of a mathematical model (3). The assimilative capacity is usually based on the amount of oxygen that is in the stream. If the oxygen level of a stream is low, then the stream will have a low assimilative capacity, and conversely, if the oxygen level is high the stream will have a high assimilative capacity. The amount of oxygen present in a stream is dependent upon many processes that take place in the stream. The processes are classified as either sources or sinks of oxygen (3).

One of the sinks of oxygen in a stream is the biochemical oxygen

demand (BOD) that is exerted by the addition of land runoff (4). It is usually estimated as 2.0 ppm or less (5), and, often, it is not considered at all. However, with the increasing attention that land runoff is receiving as a major source of pollution, it would be helpful to know how great an oxygen demand is exerted by runoff.

The general objective of this study was to investigate land runoff from several different drainage areas in and around the town of Blacksburg, Virginia. It was desired, in particular, to determine the amount of five-day biochemical oxygen demand (BOD₅) that was being exerted by each of the different types of runoff. It was also considered important to examine several additional parameters in order to determine other polluttional constituents that might be associated with land runoff. The other parameters examined were: chemical oxygen demand (COD), total phosphorous, orthophosphorous, nitrate, and total organic carbon (TOC).

II. LITERATURE REVIEW

Land Runoff - General Discussion

Historically, water pollution abatement policies have focused on the control of domestic and industrial discharges. Recently, interest in other potential pollution sources has increased as the nation has expanded its water pollution concerns. Certain potential pollution sources have always been considered as natural and generally uncontrollable. Sources of this type have included precipitation, drainage from urban areas, runoff from forested and rural lands, decaying vegetation and wastes from wild animals. They are generally called non-point sources, and have been assumed to be small in comparison to point sources such as municipal and industrial waste discharges. The validity of this assumption is being doubted, however, as more information is discovered about the characteristics and magnitude of non-point sources. The two non-point sources which have been studied perhaps more than any other are 1) drainage from urban areas and 2) runoff from rural lands.

Attention is being given urban runoff because of the problem of storm water. It is recognized now that, in many cases, storm water may require some type of treatment before it can be discharged to a receiving stream. Much research is being done to define the water pollution impact of urban storm water and to develop alternatives to reduce pollution from this source. Investigations of runoff from rural areas, or agricultural runoff, generally have been aimed at nutrient contributions, the reason

-being that nutrients, particularly nitrogen and phosphorous, greatly affect eutrophication, which is a major problem of many natural bodies of water today.

Precipitation

Precipitation is an efficient means in the earth's cleaning process by which gases and particulates in the atmosphere are brought to earth. As rainwater reaches surface waters directly, as on a lake, or indirectly, as runoff or seepage, its quality is a significant consideration in pollution control. Rainfall averages 30 inches annually over the United States, ranging from less than 2 inches in the Southwest, to some 150 inches in the Northwest (6). The sources of rainwater constituents are the earth's soil and the by-products of man's activities. These become atmospheric pollution and wash out with rainfall. Precipitation characteristics are influenced by man-made and natural events. Fuel burning, automobiles, manufacturing operations, forest and other fires, volcanic eruptions, and wind erosion are examples of activities that contribute to the constituents of precipitation.

Rainfall studies, or the analysis of precipitation, have been limited. Two studies were conducted in Ohio during the years 1963 and 1964 (7). One was at Cincinnati in an urban environment and the other in Coshocton in a rural environment. Results are shown in Table 1.

Concentrations of solids, chemical oxygen demand, and nutrients are low compared with those of storm water runoff, or combined-sewer

TABLE I
CONSTITUENTS IN RAINFALL, AVERAGES (mg/l)
(Reference 7)

Constituent	Cincinnati	Coshocton
SS	13	11.7
COD	16	9
Inorganic Nitrogen (N)	.69	.86
Total Nitrogen (N)	1.27	1.17
Total Hydrolyzable PO ₄ (P)	.08	.03

overflows, or sewage (6). For algal nuisances, however, the nitrogen and phosphorous levels are above the critical nutrient thresholds, found by Sawyer (8) to be about 0.3 mg/l, as N, for inorganic nitrogen, and 0.01 mg/l, as P, for inorganic phosphorous.

Urban Runoff

With the accomplishment of more complete control of sanitary and industrial wastewater discharges, urban stormwater runoff has taken on greater significance and is attracting more attention and concern. It has become increasingly obvious during the past few years that urban runoff is by no means "rainwater" in terms of quality. In many large urban areas, runoff is becoming a more serious source of pollutants than municipal sewage.

Conversion of once-vegetated land surfaces to roofs, streets, and parking lots, results in greater stormwater runoff. Although the runoff may be derived from both individual sources and varied sources, clean and unclean surfaces, the resulting mixture is polluted and cannot be ignored. The quantity and quality of stormwater runoff are highly variable and transient in nature. Runoff is dependent primarily on the land surface characteristics, such as environmental conditions, topography, and the degree of development of the area. Among the sources of pollution in urban runoff are debris and litter from streets, decayed vegetation, eroded soil, animal excreta, fertilizer, insecticides, air-deposited substances, ice-control chemicals, and dirt and contaminants washed from vehicles (9).

Urban runoff can contribute to a variety of problems. A portion of the runoff can drain to sewerage systems while the remainder may reach surface waters by natural drainage channels without receiving any treatment. The discharge to streams or sewage treatment plants results in an intermittent load that receptors may be unable to handle. Direct pollution of the receiving streams can result from the various pollutants contained within the runoff.

Numerous studies have been conducted to help define the problem of urban runoff, but only a few went further than presenting isolated, unrelated, pieces of data. Of the several, extensive studies of storm-water pollution, most failed to relate specific pollutants to conditions in the watershed such as land use, industry, and commercial activity. Current studies being conducted are aimed generally at determining the amounts of polluted substances involved, their sources, and possible means of control.

One of the earliest studies done on urban runoff in the United States was by Palmer (10) who, in 1949, sampled runoff from land surfaces at street catch basins in downtown Detroit. He found concentrations of BOD₅ ranging from 96 to 234 mg/l. He also reported similar samplings during a number of Detroit storms in 1960 (11). He stated that in some cases the quality of the runoff became worse as the storm progressed, in others it became better, and in still others, no pattern was apparent.

Results from some other early studies (12) indicated high values for BOD₅ in urban storm runoff. In Oxney, England, in 1954, BOD₅ con-

concentrations up to 100 mg/l were reported. Studies in Moscow, in 1936, reported a BOD₅ range of 186-285 mg/l. In Leningrad, in 1948-1950, a mean BOD₅ in storm runoff of 36 mg/l was noted. A study in Stockholm, Sweden, from 1945 to 1948, yielded BOD₅ values up to 80 mg/l with a mean reported at 17 mg/l. A mean COD value of 188 mg/l also was reported.

Stormwater samples from Seattle street gutters, reported in a study by Sylvester (13) in 1960, contained an average BOD₅ of 10 mg/l. Sylvester also found nutrient values of nitrate nitrogen, 0.53 mg/l, as N; soluble phosphorous, 0.08 mg/l, as P; and total phosphorous, 0.21 mg/l as P. The highest constituent concentrations usually were found when preceding rainfall had been low.

One of the more complete studies of stormwater pollution was performed in Cincinnati, Ohio, by Weibel et al. (14) during 1962. The study site was a 27-acre, residential and light commercial area. Values reported included BOD₅, 19 mg/l; COD, 99 mg/l; total nitrogen, 2.75 mg/l as N; and soluble phosphorous, 0.8 mg/l, as PO₄. The conclusion was that it was obvious from the information obtained that urban storm runoff could not be neglected considering waste loadings from urban sources.

Weibel et al. (7), in 1966 presented a study on pesticides in runoff. In this study, constituent yields during runoff events were compared with raw sanitary sewage yields during a similar length of time. Comparisons indicated that runoff yields varied from several to many times the yields from sanitary sewage for some constituents, including BOD₅.

An investigation of the pollution concentrations and loads from stormwater runoff was conducted in Tulsa, Oklahoma, during the period from October, 1968, to September, 1969 (12). Several parameters were measured on 15 urban watersheds. A BOD₅ range of 8.18 mg/l was reported with a mean of 11.8 mg/l; and a COD range of 42-138 mg/l, with a mean of 85.5 mg/l. It was observed that the largest portion of the pollutants resulted from washout of materials which were deposited on impervious areas.

DeFilippi and Shih (15), during a study in 1970 in Washington, D. C., were attempting to assess methods for control and/or treatment of combined sewer overflows. Sampling of separate storm flow revealed BOD₅'s in a range of 3-90 mg/l, with a mean of 19 mg/l; COD's from 29-1,514 mg/l, with a 335 mg/l mean; total phosphorous of 0.2-4.5 mg/l, as P, with a mean of 1.3 mg/l; and a total nitrogen range of 0.5-6.5 mg/l, with a mean of 2.1 mg/l. A conclusion derived from the study was that the approach of total separation of existing combined sewer systems should be reconsidered, because significant pollution loads were found in separated storm sewers.

A study on a 1,067-acre drainage basin in Durham, North Carolina (16), determined that the annual BOD₅ contribution attributable to storm runoff was approximately equal to the contribution of a secondary treated sanitary effluent, and the COD was estimated to exceed the amount in raw sanitary wastewater from a residential area of the same size.

In 1971, investigations were conducted in Sacramento, California (9), in order to assess the extent of water pollution resulting from stormwater runoff. A range of BOD₅ values from 24 to 283 mg/l was reported, along with a COD range of 21 to 176 mg/l. Samples of the separated stormwater runoff indicated certain trends. One was the pollutant concentration diminished as the wet season progressed and became of more equal value during the course of a single rainfall event.

A research study by Sartor and Boyd (17) was begun in 1972 to define the water pollution impact of urban stormwater discharge, and to develop approaches suitable for reducing pollution from urban runoff. The study pointed out that runoff from street surfaces generally is highly contaminated. Calculations based on a hypothetical, but typical, U.S. city indicated that the runoff from the first hour of a moderate-to-heavy storm (1/2 inch/hour), would contribute considerably more pollutorial load than would the same city's raw sanitary sewage during the same period of time.

The characteristics and control of urban runoff have been studied by many investigators. A summary of urban runoff characteristics, as recorded in a number of studies are presented, in Table II. It is evident that the pollutant concentrations in urban runoff are sizeable. Its true significance depends on water pollution control goals in the particular environment.

Rural Runoff

Almost 97% of the land area of the United States is rural in nature, and essentially all of the rural land is a source of nonpoint

TABLE II
CHARACTERISTICS OF URBAN STORMWATER RUNOFF

Location	Parameter (mg/l)										Refer- ence
	BOD ₅		COD		Nitrate-N		Soluble Phos-P ₀₄		Total Phos-P		
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	
Detroit	96-234										10
Oxney, Eng.	Max.100										12
Moscow	186-285										12
Leningrad		36									12
Stockholm	Max. 80	17	Max.3,100	188							12
Seattle		10				0.53		0.24		0.21	13
Cincinnati	2-84	19	20-610	99	0.1-1.5	0.4	0.07-4.3	0.8	0.02-7.3	1.1	14
Tulsa	8-18	12	42-138	86			0.54-3.49	1.15			12
Washington	3-90	19	29-1,514	335					0.2-4.5	1.3	15
Durham, N.C.	2-232	15	40-600	179					0.15-2.5	0.6	18
Sacramento	24-283		21-176								9

pollution (19). Nonpoint, rural sources are diffuse in nature, and discharge polluting substances to surface waters by widely dispersed pathways. Urban runoff, although considered a nonpoint source, is relatively localized in occurrence and lends itself more readily to some form of control. Rural runoff, however, is so diffuse in nature that control is difficult. The problem of rural runoff, like many other aspects of our total water resources, only recently has become of national interest and concern.

Rural runoff comes from a wide range of sources, the primary ones being areas of agricultural activity and forests. There also are different types of agriculture activity to be considered, such as cropland, pasture land, range land, and locations with high animal densities and each has its own potential pollution problems and solutions.

Rural runoff is varied in both quality and quantity. It consists of nonpoint discharges that can range from almost background or natural runoff from forests and unused fields, to that from confined animal feedlots and fertilized fields. In rural areas, a number of factors influence the amount of runoff from a given storm. They include storm characteristics, soil properties, topography, and plant cover. Constituents contained in rural runoff originate in rainfall, wastes from wildlife, leaf and plant residue decay, applied nutrients, pesticides, nutrient and organic matter initially in the soil, and wastes from pastured animals (19). Rural runoff constituents should not be considered together, because they originate from such diverse types of rural activity.

A review of the literature has revealed numerous studies aimed at specific problem areas such as erosion control, soil management, water management, and soil and water conservation. All of these problem areas have a relation to water pollution from rural areas. However, there was little information in the literature on the quality of rural runoff, particularly concerning organic waste loadings. The majority of investigators generally have limited their studies to determining nutrient contributions and sediment losses due to erosion. Aside from nutrients and sediment, little information is available on other constituents in rural runoff. Quantifying the pollutants in rural runoff, from data in the literature, also is difficult due to the different sources from which the runoff originates.

The major pollutants of rural runoff are nutrient elements, sediment, pesticides, organic wastes, and pathogens (19). The magnitudes of the impacts of these pollutants vary in direct proportion to the quality of the management of specific activities within agriculture and forestry.

The nutrients present in rural runoff have prompted many different studies, primarily because of the suspicion that they are important to eutrophication. Eutrophication is the overfertilization or accelerated aging of natural bodies of water. A complete review of the literature concerning eutrophication is not presented here. However, it is mentioned because runoff from rural land carries various nutrients which affect the rate of aging of surface waters.

Nutrient elements, chiefly nitrogen and phosphorous, are emitted from agricultural lands and any other rural land on which rainfall is sufficient to support plant and animal life. One of the best studies on nutrients in relation to wastes quality, was a task group report by the American Water Works Association (20). They reported that agricultural runoff is the greatest single contributor of nitrogen and phosphorous to surface waters. Their data also indicated that unit area contributions of nitrogen, especially nitrate, are much greater than those of phosphorous. It was noted that although improved land practices could substantially reduce the loss of fertilizer from cropland, the concentration of phosphorous and nitrogen in runoff remains high enough to significantly accelerate eutrophication in natural bodies of water. Therefore, they concluded that complete elimination of nitrogen and phosphorous from surface waters does not appear economically feasible. A bibliography of 63 references is included with the report.

Loehr (21) discussed the characteristics of agricultural and rural runoff, particularly nutrients, in a literature review. He reported that areas of fertile cropland could contribute greater amounts of nitrogen than any other rural area. He noted also that phosphorous contributions generally are at least an order of magnitude lower than nitrogen contributions. He concluded that although nutrient losses may be low from an agricultural stand point, they may be significant from an eutrophication and pollution standpoint.

Outside of nutrients, the greatest interest in rural runoff appears to be in the amount of sediment that is lost in runoff. It has

been one of the most studied phases of agriculture. Approximately 75% of the sediment load that reaches surface waters originates from rural runoff (21). Sediment consists of soil materials that erode from the surface of the land and are transported to streams by runoff water. In rural runoff, cropland is the chief source of sediment on a total mass basis (19). In the past, soil losses were viewed primarily from a crop production standpoint. Today, such losses must also be viewed from the environmental quality standpoint. Sediment is a carrier of plant nutrients, pesticide residues, plant and animal bacteria, and is considered a significant pollutant for this reason.

Soil losses are not the only consideration. Walker and Wadleigh, in a study of water pollution originating from land runoff (22), estimated that each ton of sediment carried about a pound of phosphorous attached to its surface. It also was found that eroded material may have from three to five times as much organic nitrogen content as the original soil.

Another major pollutant in rural runoff is organic waste. Rural land activities generate large quantities of natural organic waste materials that are potential nonpoint pollutants. These wastes have essentially the same adverse effects on streams and lakes as organic wastes of domestic and industrial origin. The major sources of organic wastes are livestock, crop debris, forest litter (including annual leaf fall), waste petroleum products, and numerous solid waste materials (19). On an overall basis, the organic waste load of rural runoff is degraded

fairly well as it flows overland, but a certain fraction, nevertheless, finds its way into surface streams.

The literature contains little information on organic loadings of rural runoff. Harms (23) in a study of pollutants in agricultural runoff in South Dakota, concluded that organic matter in surface runoff is low.

Weider et al. (24) reported on the quality of rural runoff from two, 1.5-acre watersheds near Coshocton, Ohio, and also from a 5-acre apple orchard at Ripley, Ohio. COD values ranged from 30 to 159 mg/l with a mean of 79 mg/l, and BOD₅ values ranged from 0.5 to 23 mg/l with a mean of 7 mg/l. From the study, it was concluded that rural runoff is a factor in stream pollution, and it must be considered when evaluating the quality of any stream or receiving body of water.

A study by Wallace and Dague (1), relating land runoff and dissolved oxygen, was conducted on the Iowa River Basin in 1972. The drainage basin consisted of 2953 square miles and 90% of the land area was used for agriculture. They found that agricultural land runoff caused low dissolved oxygen levels in the Iowa River at least once, and possibly several times, per summer. They also noted that the only cause of low dissolved oxygen levels in the Iowa River seemed to be land runoff, as wastewater discharges necessary to cause dissolved oxygen depressions equivalent to those caused by land runoff were many times the existing discharges.

Rural areas typically consist of a large percentage of forested land. As a result, forests are the source of much of the runoff that reaches streams and lakes. Forest drainage ordinarily carries only a minimal concentration of nutrient elements but may be sufficient to transport

quantities of erosion and sediment into surface waters. Forests are less influenced by the activities of man than are most other runoff sources. Forest runoff can therefore be one of the better indicators of pollutant constituents that result from natural conditions.

Established, well-managed forests are relatively free of pollution. Rainfall is deprived of most of its erosive force by tree cover, and rates of infiltration through ground cover are often high enough that rainfall will not produce any significant runoff.

Phosphorous and nitrogen levels are typically low in drainage from forest systems (6). Data obtained by Sylvester (13) for three forested areas in Washington State indicated an average soluble phosphorous concentration of 0.007 mg/l, as P, a total phosphorous concentration of 0.069 mg/l, as P, and a mean nitrate concentration of 0.13 mg/l, as N.

Perhaps the greatest pollutant found in forest runoff is sediment because it is estimated that much of the sediment which reaches streams and lakes originates from forested areas. The Environmental Protection Agency, however, in a study on nonpoint pollution (19), reports that well-managed forests are exceptionally free of erosion and sediment pollution.

III. MATERIALS AND METHODS

General

Because the main objective of this research was to determine the BOD₅ exerted by land runoff, it was considered essential to evaluate the runoff from several types of land. The general approach was to select a watershed with a single, predominant, land activity, with the following types of drainage areas chosen: urban land, agricultural land, construction site, and forested land.

Sampling site investigations and selections were made in the spring of 1973, and all sites were within 10 miles of Blacksburg, Virginia. Sampling and subsequent laboratory determinations were conducted on runoff samples collected during the summer of 1973. The samples were collected manually and were transported to the Sanitary Engineering Laboratory at Virginia Polytechnic Institute and State University where testing was begun immediately.

Sampling Sites

The selection of sampling sites was influenced by several factors. As previously mentioned, each drainage area was to have a single predominant land activity. In addition, the sampling sites were to be located near Blacksburg, so samples could be collected, transported, and analyzed with as little delay as possible. Other criteria were: the drainage areas were to drain to a single point and be large enough so that an adequate volume of sample could be collected, access to the sites

was to be on an all-weather road, and there were to be no known point sources of pollution in the drainage areas.

Five sampling sites were selected, each of which met the previously mentioned criteria and represented one of the different types of land uses in the area. Figure 1 shows the general location of the sampling sites. The area receives annually about 40 inches of precipitation, over 85% of which occurs as rainfall (26).

Site 1

Site number one was located at the construction site of the new high school building in Blacksburg. The drainage area was approximately 15 acres and the land had been cleared for construction. The school building was only partially completed at the time of the sampling. Runoff from the area drained to an open ditch where samples were collected.

Site 2

Site 2 was located in a residential area on Owens Street. The drainage area, approximately 45 acres, consisted of residential neighborhoods with most development five to ten years old. Good grass cover existed on the lawns, and a few shade trees were present. A few of the homes had backyard gardens. Runoff from the streets passed through inlet structures into storm sewers that subsequently emptied into an open channel where samples were taken. The area was well-kept, and there were no visible accumulations of rubbish that might contribute pollutants to the runoff.

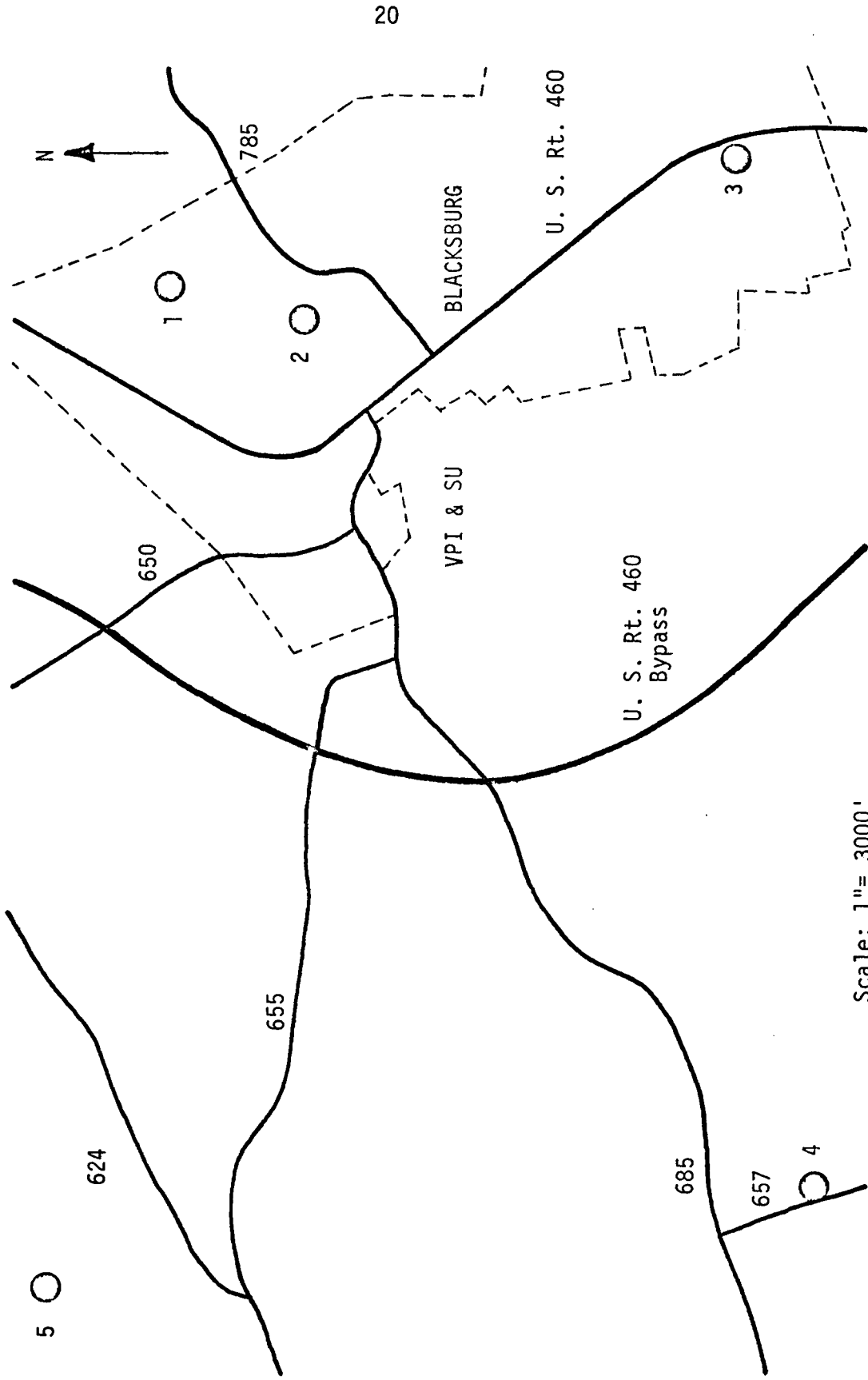


FIGURE 1: Map of Study Area Showing Location of Sampling Sites

Site 3

Site 3 was located at a shopping center in Blacksburg where runoff was from a commercial and business area. The shopping center was composed of retail shops and general merchandise stores, with an asphalt-paved parking area of approximately five acres. Streets adjacent to the shopping center were well-traveled. Runoff was by overland flow through the parking area to a point where it entered a drop inlet leading to a storm sewer. Samples were collected at that point. The only noticeable sources of pollution were oil, grease, and dirt from automobiles in the parking area, and some litter also in the parking area.

Site 4

Site 4 was located in a rural area outside of Blacksburg, and the runoff was from agricultural land. The drainage area was approximately 85 acres with a gently sloping terrain. Corn and grasslands were the primary crop covers. The soil texture was a silty loam. A small stream drained the area, and samples were collected from it at the lower end of the drainage area.

Site 5

Site 5 was in a forested area in the Jefferson National Forest near Blacksburg. The drainage area was approximately 160 acres, and the topography was steep and mountainous. There was no cleared land in the drainage area, and the wooded terrain consisted mainly of shrubs, saplings, and hardwood trees. Major species were oak, hickory, and maple. Samples

were collected from a small stream which drained the area.

Sampling Storm Runoff

Samples of storm runoff were collected manually from each site in clean glass containers of approximately two liters each. Because of the short duration and unpredictable occurrence of rainstorms, however, manual sampling was usually begun soon after the beginning of a rainstorm, but it took approximately one hour to travel to all the sampling sites. Sampling was not done uniformly, that is, the same order of visiting the sampling sites was not followed each time. If a sampling site was visited first for one runoff event, it would usually be visited last for the next runoff event. The samples were transported to the laboratory immediately after all samples were collected, and analyses begun.

Sampling Storage and Handling

Because BOD₅ determinations were of primary importance, the test for BOD₅ was set up immediately upon arrival at the laboratory. The tests for orthophosphorous and total phosphorous were subsequently performed without delay. The remaining three tests (COD, nitrate, and TOC) usually were completed within 48 hours. Samples then were stored until analyses for COD, TOC, and nitrate could be conducted. The preservation and storage procedures were as follows:

COD - samples were acidified using two drops of concentrated sulfuric acid (H₂SO₄) per 125 milliliter (ml).

TOC - samples were refrigerated inside a closed box, away from light.

Nitrate - samples were preserved by freezing.

Chemical Determinations

All chemical determinations were conducted in accordance with Standard Methods (25). Dissolved oxygen for five-day biochemical oxygen demand (BOD₅) was determined with a YSI Model 54 dissolved oxygen meter (Yellow Springs Instrument Company, Yellow Springs, Ohio). Chemical oxygen demand determinations were conducted using the standard dichromate reflux method with sample volumes of 20 ml. Orthophosphorous was determined colorimetrically using the stannous chloride method, as was total phosphorous following digestion in an autoclave. Nitrates were determined by the phenoldisulfonic acid method. Total organic carbon was determined on a carbon analyzer, after acidifying and purging samples with nitrogen gas to remove bicarbonate and carbonate carbon, as CO₂.

IV. RESULTS

Data for each of the five different types of runoff is summarized in Tables III through VII. The number of samples for each type of runoff differs in some cases. There were fewer samples collected of forest runoff because the site did not exhibit any runoff during some rainfall events. On one occasion, water was ponded at the sampling site for residential runoff, which prevented sampling.

The highest concentrations of BOD₅ and COD were in runoff from construction and commercial sites, as were the highest concentrations of total phosphorous and nitrate. Orthophosphorous concentrations generally were quite low, with the exception being in commercial runoff. Agricultural and residential runoff had the highest TOC concentrations.

Graphs comparing the chemical characteristics of low flow runoff with the characteristics of storm runoff are presented in Figures 2 through 7. Sampling to obtain the low flow characteristics was done during a period when there was no rainfall. This was necessary to establish a control or background level from which to make a comparison of characteristics exhibited during rainfall events. Sampling sites for construction and commercial runoff were dry during low flow periods; therefore, their background levels are zero. The other three sampling sites, however, did have flow during low flow periods. As shown by the graphs, the greatest variations in concentrations of most parameters was exhibited by runoff from construction and commercial sites.

TABLE III
CONCENTRATIONS OF CONSTRUCTION RUNOFF PARAMETERS

Parameter	Range (mg/l)	Mean (mg/l)	No. of Samples	Standard Deviation (mg/l)
BOD ₅	5-25	13	8	6.8
COD	35-174	83	8	
Orthophosphorous (P)	0.01-0.01	0.01	6	
Total Phosphorous (P)	0.11-1.25	0.47	6	
Nitrate (N)	0.11-0.84	0.37	6	
TOC	25-36	31	2	

TABLE IV
CONCENTRATIONS OF RESIDENTIAL RUNOFF PARAMETERS

Parameter	Range (mg/l)	Mean (mg/l)	No. of Samples	Standard Deviation (mg/l)
BOD ₅	1-7	6	7	2.2
COD	4-41	29	7	
Orthophosphorous (P)	0-0.03	0.01	5	
Total Phosphorous (P)	0.01-0.17	0.08	5	
Nitrate (N)	0.05-0.11	0.09	5	
TOC	50-63	57	4	

TABLE V
CONCENTRATIONS OF COMMERCIAL RUNOFF PARAMETERS

Parameter	Range (mg/l)	Mean (mg/l)	No. of Samples	Standard Deviation (mg/l)
BOD ₅	5-26	15	8	8.4
COD	27-141	71	8	
Orthophosphorous (P)	0.05-0.33	0.15	6	
Total Phosphorous (P)	0.06-0.50	0.20	6	
Nitrate (N)	0.07-0.93	0.36	6	
TOC	26-52	36	5	

TABLE VI
CONCENTRATIONS OF AGRICULTURAL RUNOFF PARAMETERS

Parameter	Range (mg/l)	Mean (mg/l)	No. of Samples	Standard Deviation (mg/l)
BOD ₅	3-11	7	8	3.2
COD	12-105	52	8	
Orthophosphorous (P)	0.01-0.05	0.02	6	
Total Phosphorous (P)	0-0.16	0.09	6	
Nitrate (N)	0.01-0.39	0.21	6	
TOC	50-57	54	5	

TABLE VII
CONCENTRATIONS OF FOREST RUNOFF PARAMETERS

Parameter	Range	Mean	No. of Samples	Standard Deviation (mg/l)
BOD ₅	3-5	4	5	0.5
COD	20-49	32	5	
Orthophosphorous (P)	0-0.01	0.01	4	
Total Phosphorous (P)	0.08-0.16	0.12	4	
Nitrate (N)	0.08-0.22	0.15	4	
TOC	25-29	27	3	

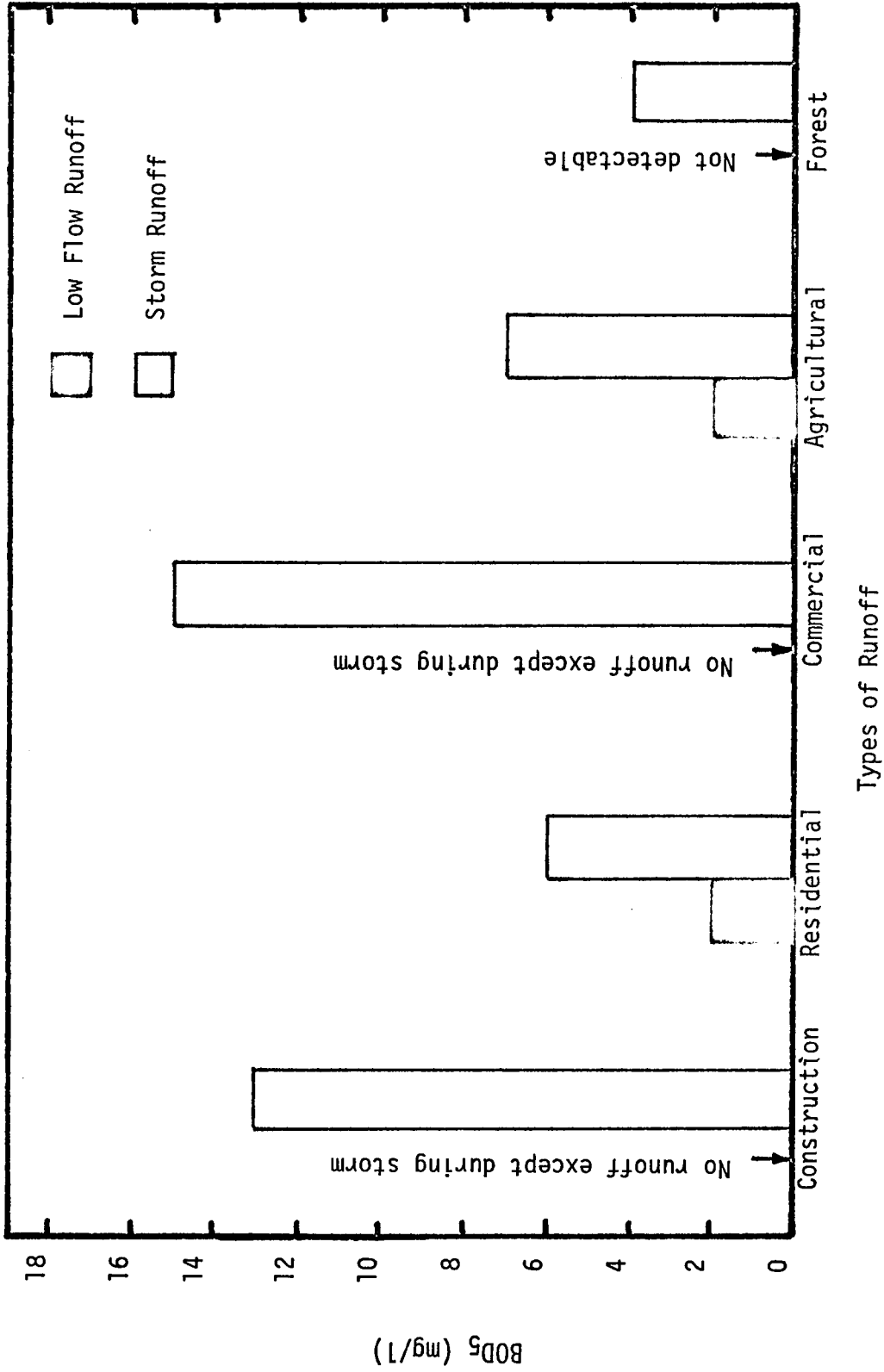


FIGURE 2. Comparison of BOD₅ Concentrations in Runoff During a Storm and During Low Flow for Different Land Types

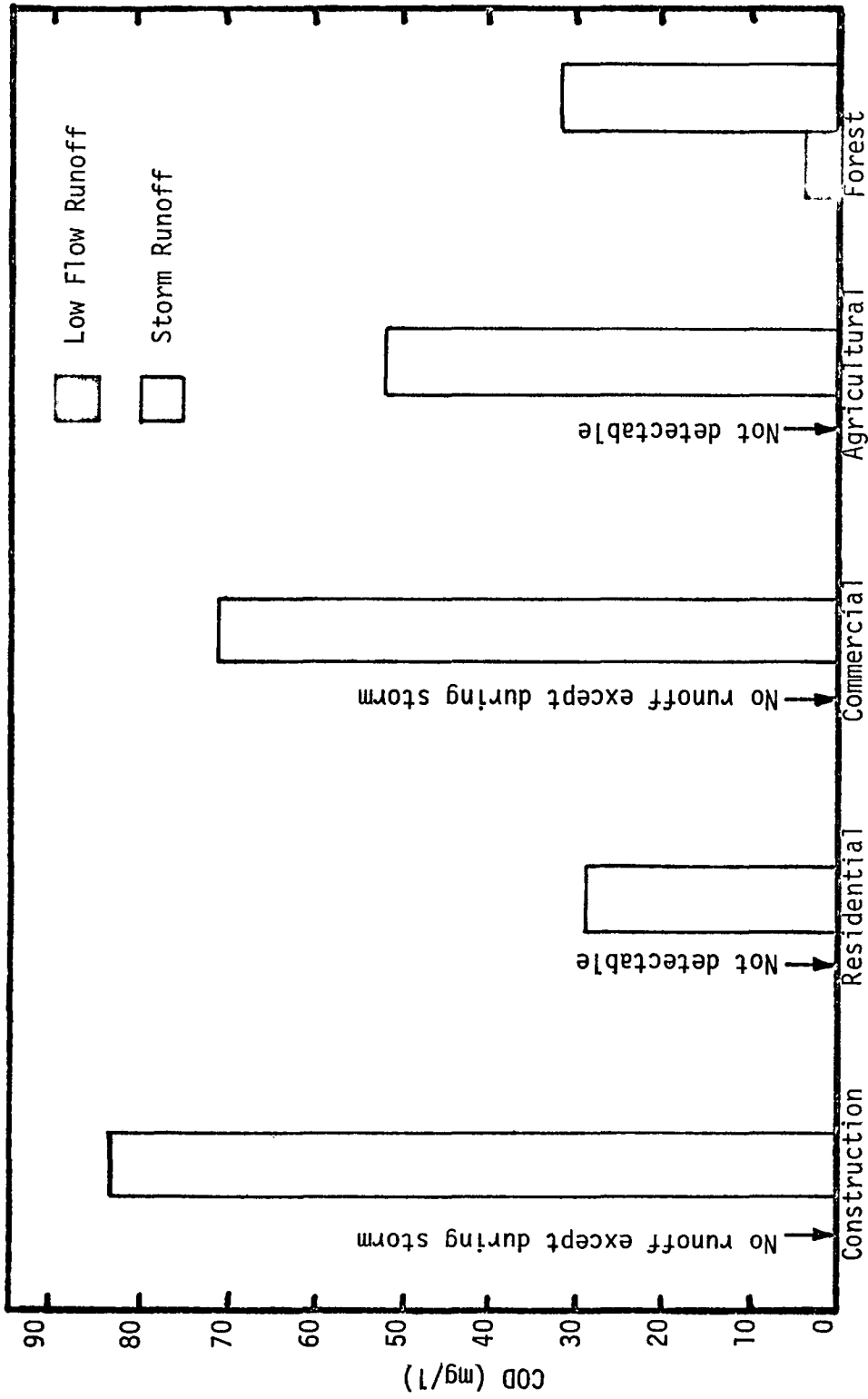


FIGURE 3. Comparison of COD Concentrations in Runoff During a Storm and During Low Flow for Different Land Types

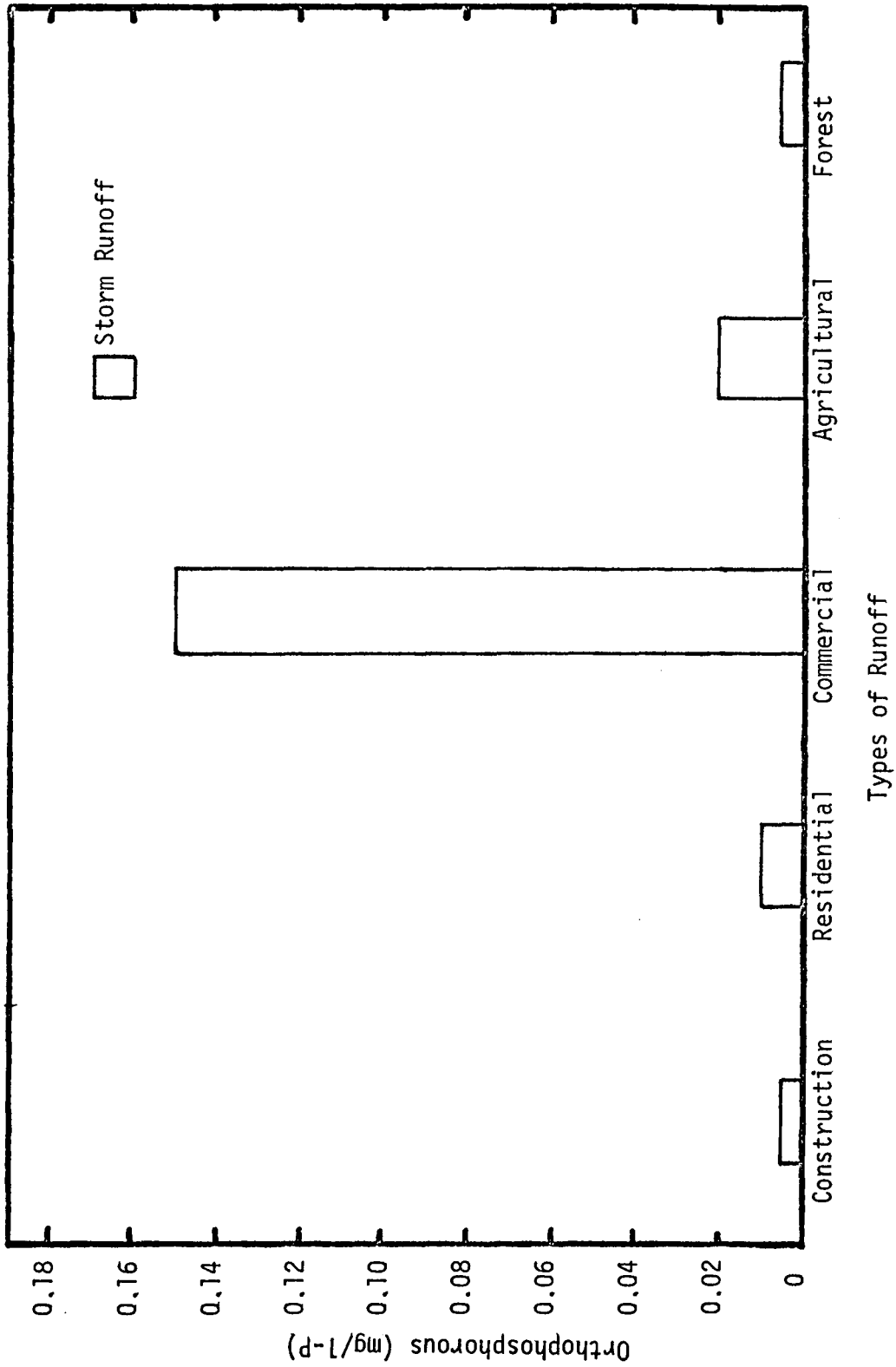


FIGURE 4. Comparison of Orthophosphorous Concentrations in Storm Runoff From Different Land Types

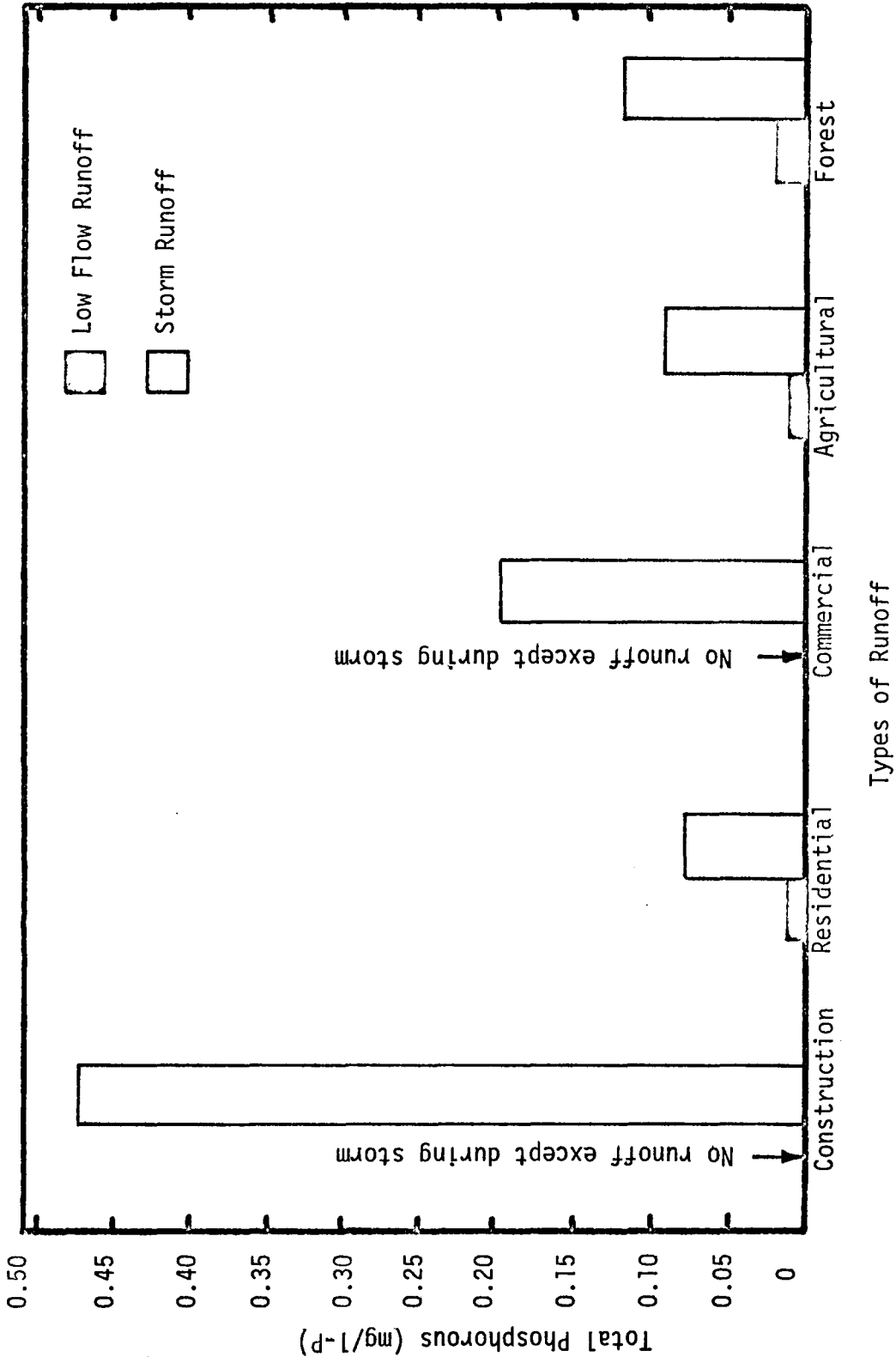
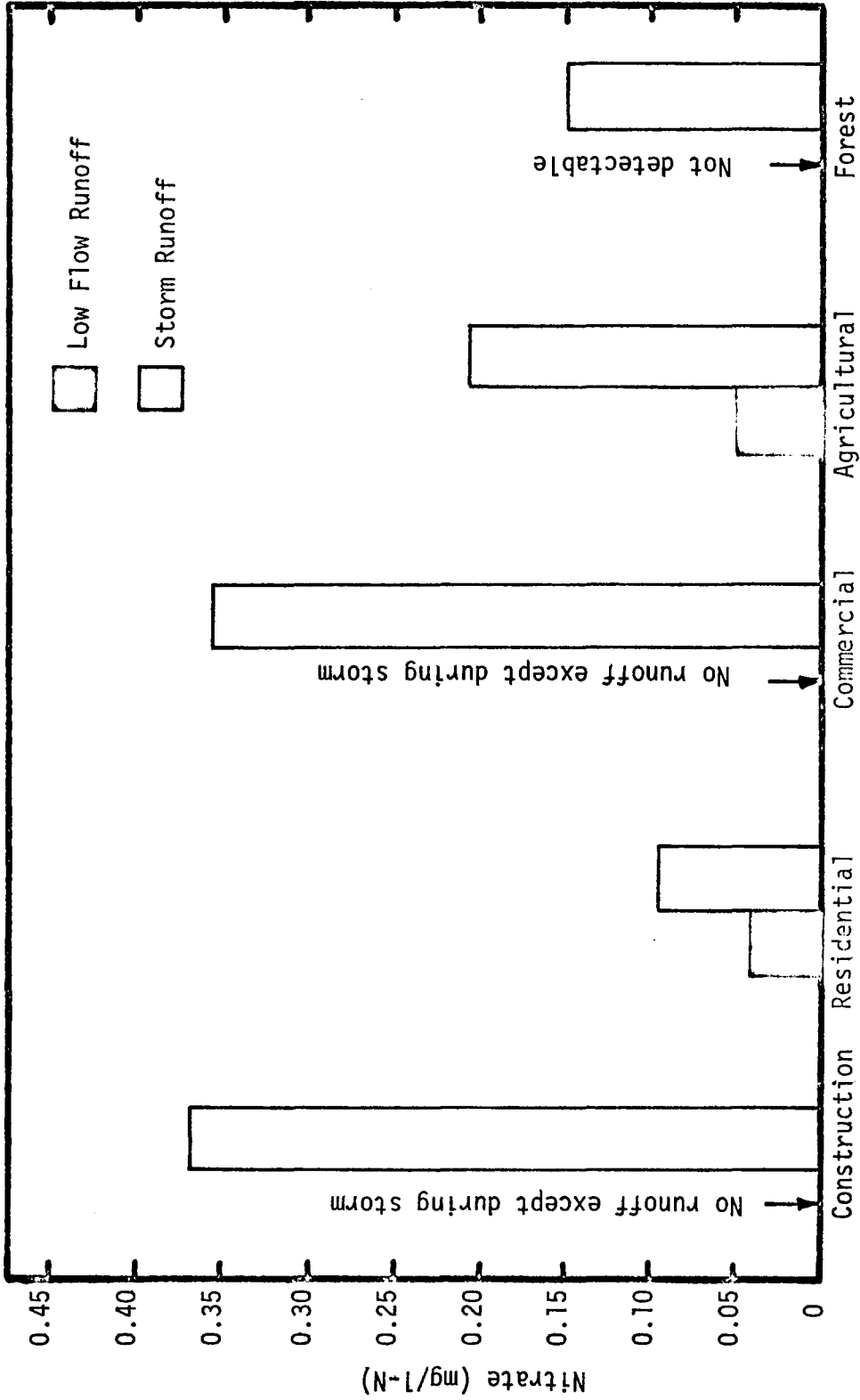


FIGURE 5. Comparison of Total Phosphorous Concentrations in Runoff During Storm and During Low Flow for Different Land Types



Types of Runoff

FIGURE 6. Comparison of Nitrate Concentrations in Runoff During a Storm and During Low Flow for Different Land Types

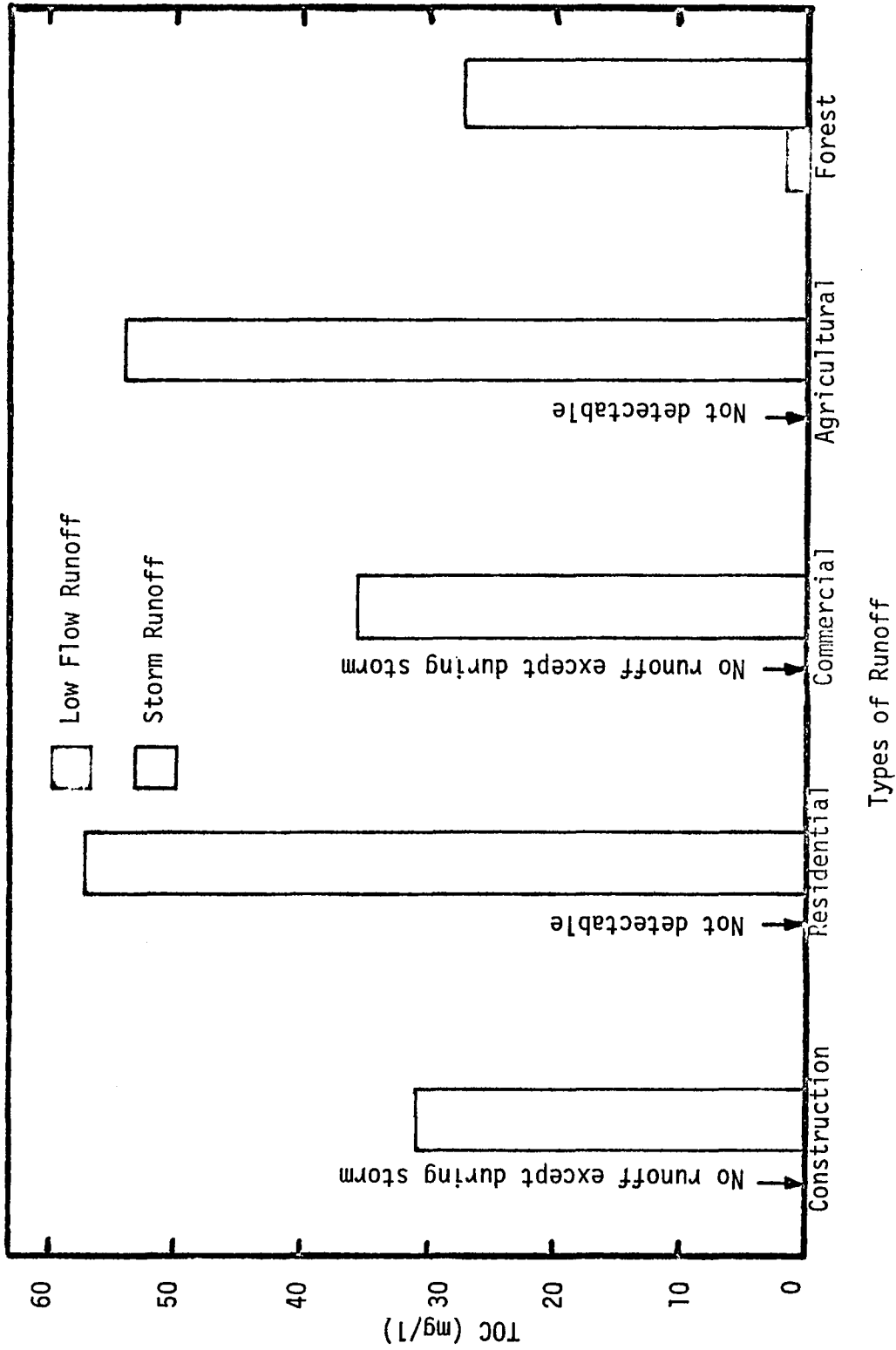


FIGURE 7. Comparison of TOC Concentrations in Runoff During a Storm and During Low Flow for Different Land Types

TABLE VIII
RELATIONSHIPS AMONG BOD₅, COD, AND TOC

Type of Runoff	Mean BOD ₅ (mg/l)	Mean COD (mg/l)	Mean TOC (mg/l)	$\frac{\text{BOD}_5}{\text{TOC}}$	$\frac{\text{BOD}_5}{\text{COD}}$	$\frac{\text{COD}}{\text{TOC}}$
Construction	13	83	31	0.42	0.16	2.68
Residential	6	29	57	0.11	0.21	0.51
Commercial	15	71	36	0.42	0.21	1.97
Agricultural	7	52	54	0.13	0.14	0.96
Forest	4	32	27	0.15	0.13	1.19

Table VIII shows the relationship among BOD₅, COD, and TOC, for each of the different types of runoff. The highest COD/TOC and BOD₅/TOC ratios are indicated for construction and commercial runoff, whereas the BOD₅/COD ratio is nearly the same for the different types of runoff.

V. DISCUSSION

The results of the chemical analyses during the study period indicate the polluttional aspects of land runoff. The parameter of primary importance in this study was BOD₅, and for each different type of runoff, concentration was found to exceed the values normally cited for land runoff.

There was little information in the literature concerning BOD₅ in runoff, with the exception of urban runoff. Mean BOD₅ concentrations of urban runoff studies were found to range from 10 mg/l (13) to 36 mg/l (12). The highest BOD₅ values measured during this study were in commercial runoff, which would be considered urban runoff. A mean BOD₅ concentration of 15 mg/l was obtained, with a standard deviation of 8.4 mg/l, and a range of 5 mg/l to 26 mg/l. A primary source of BOD₅ in the commercial runoff probably was debris and litter in the runoff area. The BOD₅ in construction runoff was probably mainly due to human and animal sources. The pollutants generated are often adsorbed or fixed to sediments and subsequently become a part of the runoff. Concentrations of BOD₅ from residential, agricultural, and forest runoff are lower than those in commercial and construction runoff and are caused primarily by the process of animal excreta and decayed vegetation.

The beneficial effects of land cover in holding nutrients is exemplified by the phosphorous data. The construction and commercial areas had no land cover, and the orthophosphorous and total phosphorous

levels were higher in runoff from these than from the other areas, primarily because particles of sediment bearing adsorbed phosphorous were trapped by vegetation on residential, agricultural, and forest drainage areas, but were eroded readily from commercial and construction sites.

Nutrient levels were of interest because of the emphasis placed on eutrophication. Concentrations of nitrogen and phosphorous that are considered to be the critical nutrient thresholds are 0.01 mg/l of inorganic phosphorous and 0.30 mg/l of inorganic nitrogen (8).

Mean concentrations of nitrate alone exceeded the 0.30 mg/l level in runoff from construction and commercial runoff. Nitrate concentrations in agricultural and forest runoff were 0.21 mg/l and 0.51 mg/l, respectively. If the other forms of inorganic nitrogen, particularly ammonia were added to these values, they too probably would exceed 0.30 mg/l. Phosphorous data showed concentrations in excess of 0.01 mg/l, indicating nitrogen and phosphorous in runoff may be important contributing factors to eutrophication in the area.

Mathematical modeling is currently becoming a useful and necessary tool in water quality engineering. With modeling, it is possible to predict the assimilative capacity of a stream, based on the amount of oxygen that is in the stream. When the oxygen level in a stream is low, the assimilative capacity of the stream is reduced. The amount of oxygen in a stream is dependent upon many processes, which are usually classified as either sources or sinks of oxygen.

One of the sinks of oxygen that is often ignored is the BOD that is exerted by land runoff.

The two models that are used primarily in Virginia are based on the Streeter-Phelps (27) equation, and TVA (28) equation. These models predict the amount of pollution, in terms of BOD, that can be discharged to a stream so that the dissolved oxygen (DO) in the stream will not be reduced below stream standards. The State Water Control Board of Virginia now requires that land runoff be considered in stream assimilation analysis. Land runoff is considered the background BOD in a stream, and 2 mg/l is commonly used for this parameter (5). Throughout this study, however, BOD₅ values were found to be consistently higher than 2 mg/l (Figure 2). The BOD₅ mean concentrations ranged from 4 mg/l for forest runoff to 15 mg/l for commercial runoff. Also, the BOD₅ concentrations in storm runoff were more than double those observed during low flow periods.

If a stream assimilation analysis is performed without considering the BOD exerted by land runoff, the results may be inaccurate and misleading. The assimilation capacity that is predicted without considering runoff will be higher than if the effect of runoff is considered. This could possibly lead to a oxygen deficit in the stream that would violate stream standards and be harmful to aquatic life.

The BOD₅ test is not always a useful test due to the long incubation time required to obtain a meaningful result. Therefore, it

is often necessary to develop correlations among BOD₅, COD and TOC, because the COD and TOC tests are more rapid. Of the three measures, however, the most difficult to correlate to the others is the BOD₅ test, because of the problems associated with it. The BOD₅ test is susceptible to variables that include seed acclimation, dilution, temperature, pH, and toxic substances. The COD and TOC tests are not as variable, so their ratio is a more useful parameter.

The BOD₅/COD ratios of the different runoff types are nearly the same, ranging from 0.13 to 0.21, a range similar to that reported for a clarified effluent from secondary sewage treatment plants (29). A BOD₅/COD relationship in this range indicates that a portion of the organics which were oxidized by dichromate in the COD test, were either nonbiodegradable or relatively resistant to biological degradation. Also, the COD may be due to the dichromate oxidation of ferrous iron, nitrogen, sulfites, sulfides, and other oxygen-consuming inorganics, which would not break down in the BOD₅ test.

The BOD₅/TOC ratios among the data ranged from 0.11 to 0.42, and COD/TOC ratios were in the range of 0.51 to 2.68. Although the BOD₅/COD ratio for each of the types of runoff closely parallels that of a secondary treated effluent, this was not true with the BOD₅/TOC and COD/TOC ratios. For a secondary treated effluent, the BOD₅/TOC and COD/TOC ratios vary from 0.30 to 0.60 and 2.00 to 2.70, respectively (29). Only the construction runoff and commercial runoff fall in these ranges.

When the COD/TOC ratio is less than 1.50, this indicates that there is some type of organic compound that is partially or totally resistant to dichromate oxidation, but is recovered in the TOC analysis. This may have been the case, but it does not seem reasonable that the COD/TOC ratio should have been as low as 0.51 in runoff, as was the case with residential runoff. Therefore, the TOC data is suspect, even though it was consistently high throughout the study. Good results were obtained with the construction runoff, COD/TOC ratio of 2.68, and commercial runoff, COD/TOC ratio of 1.97. If the TOC test results were correct, then there is no logical explanation for the low COD/TOC ratios that were obtained in this study. The COD/TOC ratio is normally in the range of 1.75 to 6.65 (29).

VI. SUMMARY AND CONCLUSIONS

This study was conducted in order to obtain information that would permit comparisons of nutrient concentrations, both organic and inorganic, in runoff from five different land types. The major interest was in BOD₅ concentrations because of the importance of runoff in modeling the assimilative capacity of streams. Analyses were performed for samples collected during low flow and during storm events.

The significant conclusions derived from this study were:

1. Concentrations of BOD₅ in runoff from all land types were higher than the 2 mg/l normally assumed as a value for runoff in stream assimilation models. The mass of oxygen-demanding material added to a stream by runoff may significantly affect the DO analysis and should be evaluated carefully.
2. Nitrogen and phosphorous concentrations in all runoff samples were high enough to constitute a significant contribution of fertilizer elements to streams.
3. Storm runoff from land types having a good vegetal land cover were shown to be of better quality than those having no cover.
4. Of the types of runoff tested, commercial and construction runoff were greater sources of pollution than residential, agricultural, or forest runoff.

VII. LITERATURE CITED

1. Wallace, D. A., and Dague, R. R., "Modeling of Land Runoff Effects on Dissolved Oxygen." Jour. Water Poll. Control Fed., 45, 1795-1809 (1973).
2. Clark, J. W., et al., Water Supply and Pollution Control, 2nd Ed., International Textbook Co., Scranton, Pa. (1971).
3. Eckenfelder, W. W., Jr., Water Quality Engineering For Practicing Engineers, Barnes and Noble, Inc., New York, N.Y. (1970).
4. Dobbins, W. E., "BOD and Oxygen Relationships in Streams." Jour. San. Eng. Div., Proc. Amer. Soc. Civil Engr., 90, 53-78 (1964).
5. Virginia State Water Control Board, Abingdon, Virginia, Personal Communication (November 2, 1973).
6. "Eutrophication: Causes, Consequences, Correctives." Proceedings of a Symposium, National Academy of Sciences, Washington, D.C. (1969).
7. Weibel, S. R., et al., "Pesticides and Other Contaminants in Rainfall and Runoff." Jour. Amer. Water Works Assn., 58 1075-1084 (1966).
8. Sawyer, C. N., "Fertilization of Lakes by Agricultural and Urban Drainage." Jour. New Eng. Water Works Assn., 61, 109 (1947).
9. "Urban Storm Runoff and Combined Sewer Overflow Pollution." 11024 FKM 12/71, Aerojet-General Corp., Rept. for EPA (December 1971).
10. Palmer, C. L., "The Pollutational Effects of Stormwater Overflows from Combined Sewers." Sewage and Industrial Wastes, 22, 154 (1950).
11. Palmer, C. L., "Feasibility of Combined Sewer Systems." Jour. Water Poll. Control Fed., 35, 162 (1963).
12. "Storm Water Pollution from Urban Land Activity." 11304 FKL 07/70, AVCO Economic Systems Corp., Rept. for EPA (July 1970).
13. Sylvester, R. O., "An Engineering and Ecological Study for the Rehabilitation of Green Lake." Univ. of Washington, Seattle, Wash. (1960).

14. Weibel, S. R., et al., "Urban Land Runoff as a Factor in Stream Pollution." Jour. Water Poll. Control Fed., 36, 914 (1964).
15. DeFilippi, J. A., and Shih, C. S., "Characteristics of Separated Storm and Combined Sewer Flows." Jour. Water Poll. Control Fed., 43, 2033 (1971).
16. Field, R., and Struzeski, E. J., Jr., "Management and Control of Combined Sewer Overflows." Jour. Water Poll. Control Fed., 44, 1393 (1972).
17. Sartor, J. D., and Boyd, G. B., "Water Pollution Aspects of Street Surface Contaminants." 11034 FUS 11/72, Rept for EPA (November 1972).
18. Bryan, E. H., "Quality of Stormwater Drainage from Urban Land Areas in North Carolina." Rept. 37, Water Resources Research Institute of North Carolina (1970).
19. Environmental Protection Agency, "Methods for Identifying and Evaluating the Nature and Extent of Non-Point Sources of Pollution." U.S. EPA-430/9-73-014, Office of Air and Water Programs (October 1973).
20. "Sources of Nitrogen and Phosphorous in Water Supplies." Task Group Report, Jour. Amer. Water Works Assn., 59, 344 (1967)
21. Loehr, R. C., "Agricultural Runoff-Characteristics and Control." Jour. San. Eng. Div., Proc. Amer. Soc. Civil Engr., 98, 909 (1972).
22. Walker, K. C., and Wadleigh, C. H., "Water Pollution from Land Runoff." Plant Food Rev., 14, 2 (1968).
23. Harms, L.L, "Quantification of Pollutants in Surface Runoff from Agricultural Lands in Brookings County, South Dakota." Ph. D. Thesis, S. D. State Univ., Brookings, S. D. (1973).
24. Weidner, R. B., et al., "Rural Runoff as a Factor in Stream Pollution." Jour. Water Poll. Control Fed., 41, 377 (1969)
25. "Standard Methods for the Examination of Water and Wastewater." 13th Ed., Amer. Pub. Health Assn., New York, N.Y. (1971).
26. Climatological Data for Virginia, Environmental Data Service, Asheville, North Carolina (1973).

27. Streeter, H. W., and Phelps, E. B., "A Study of the Pollution and Natural Purification of the Ohio River," Public Health Bulletin No. 146, Washington, D. C. (1925).
28. Comprehensive Water Resources Plan, Volume IV, Virginia Division of Water Resources, Richmond, Virginia (May 1972).
29. Eckenfelder, W. W., and Ford, D. L., Water Pollution Control, Jenkins Book Publishing Company, New York, N. Y. (1970).

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A COMPARISON OF SELECTED
CHEMICAL CHARACTERISTICS IN RUNOFF
FROM DIFFERENT LAND TYPES

by

William Morgan Skeen

(ABSTRACT)

This study was conducted in order to obtain information that would permit comparisons of six nutrient parameters, both organic and inorganic, in runoff from five different land types. Sampling and laboratory determinations were conducted on runoff samples collected during the summer of 1973, in and around the town of Blacksburg, Virginia.

The five different types of runoff that were studied were construction, residential, commercial, agricultural, and forest. The six parameters investigated during the study were five-day biochemical oxygen demand (BOD₅), chemical oxygen demand, orthophosphorous, total phosphorous, nitrate, and total organic carbon. The major interest was in BOD₅ concentrations because of the importance of land runoff in stream assimilation modeling. Analyses were also performed during low flow periods to permit a comparison with runoff collected during storm events.

Concentrations of BOD₅ in runoff from all six land types were higher than the 2 mg/l normally assumed as a value for runoff in

stream assimilation models. Also, nitrogen and phosphorous concentrations in all runoff samples were high enough to constitute a significant contribution of fertilizer elements to streams. Of the types of runoff tested, commercial and construction runoff were greater sources of pollution than residential, agricultural, or forest runoff.