

State of Delaware Delaware Geological Survey Robert R. Jordan, Director



Open-File Report No. 44

Storm-Water and Base-Flow Sampling and Analysis
In the Delaware Inland Bays
Preliminary Report of Findings
1998-2000

William J. Ullman University of Delaware College of Marine Studies

and

A. Scott Andres University of Delaware Delaware Geological Survey

Joseph R. Scudlark, Karen B. Savidge University of Delaware College of Marine Studies

University of Delaware Newark, Delaware

2002

Table of Contents

		page
Overview		1
Introduction		1
Watershed Characteristics		2
Sampling and Analytical Methods		5
Hydrographic Methods		9
Results		11
Base-Flow Discharge		11
Stormwater Discharge		22
Discussion		24
Base-Flow Loadings		24
Storm-Flow Loadings		30
Conclusions		33
References Cited		40
Eigen	Illustrations	
Figure	et stations in the Inland Dave systemshed	page
	et stations in the Inland Bays watershed.	4 5
	C and CISNet watersheds	_
<u> </u>	e Cape Henlopen rain site	12
4. Concentrations and loadings of N	· · · · · · · · · · · · · · · · · · ·	1.4
1	w discharge at Munchy Branch	14
5. Concentrations and loadings of N		1.5
•	w discharge at Bundicks Branch	15
6. Concentrations and loadings of 1	· · · · · · · · · · · · · · · · · · ·	17
•	w discharge at Swan Creek	17
7. Concentrations and loadings of 1		10
<u>*</u>	w discharge at Millsboro Pond	19
8. Concentrations and loadings of 1	· · · · · · · · · · · · · · · · · · ·	20
<u>-</u>	w discharge at Blackwater Creek	20
9. Concentrations and loadings of N		
	w discharge at Beaverdam Ditch	21
10. Concentrations and loadings of N		
<u> </u>	ro Pond for a summer storm	23
11. Concentrations and loadings of N	· · ·	
•	reek for a storm in October 1999	25
12. Concentrations and loadings of N		
	as Branch for a summer storm	26
13. Concentrations and loadings of N	N, P, and organic C species	
and suspended solids in Munchy	Branch for a storm in January 2000	27
14. Concentrations and loadings of I	N, P, and organic C species	
and suspended solids in Blackwa	ater Creek for a storm in January 2000	28
15. Concentrations and loadings of N	N, P, and organic C species	

16	and suspended solids in Beaverdam Ditch for a storm in January 2000 Comparison of quarterly areal base-flow loading rates of	2
10.	N, P, C, and suspended solids	3
17.	Comparison of areal loadings of N, P, C, and suspended	
	solids and unit discharge for two storms.	3
Ta	ble	
1.	DNREC sampling sites.	
2.		
3.	Land use/land cover characteristics of Inland Bays watersheds	
4.	Dates of base-flow sample collection at DNREC and CISNet sites	
5.	Dates and success of storm-water sampling at DNREC sites	
6.	Water quality measurements at DNREC and CISNet sites	
7.	Typical precision achieved for each analytical procedure used	
	in this report	
8.	Total base-flow loads and discharge per time period specified	
	for DNREC watersheds	3
9.	Areal base-flow loads and discharge per time period specified	
	for DNREC watersheds	3
10.	Provisional cumulative mass loads for storms	3
11	Provisional areal storm loadings and discharges	2

STORM-WATER AND BASE-FLOW SAMPLING AND ANALYSIS IN THE INLAND BAYS: PRELIMINARY REPORT OF FINDINGS

1998-2000

OVERVIEW

This report provides initial research results of a storm-water and base-flow sampling and analysis project conducted by the University of Delaware College of Marine Studies (CMS) and the Delaware Geological Survey (DGS). Base-flow samples were collected from six tributary watersheds of Delaware's Inland Bays on 29 occasions from October 1998 to May 2000. Water samples were filtered in the field to separate dissolved nutrients for subsequent analysis, and a separate sample was collected and returned to the laboratory for particulate nutrient determinations. On each sampling date, temperature, conductivity, pH, and dissolved oxygen concentrations were determined at each sampling station. Stream discharge measurements at each of these sites were made by the U.S. Geological Survey (USGS) under a joint-funded agreement with the Delaware Department of Natural Resources and Environmental Control (DNREC) and the DGS. Together, the nutrient and discharge data were used to determine the total and unit (normalized to watershed area) nutrient loading from base flow to the Inland Bays from each of these watersheds on a quarterly and annual basis. At the same six stations, storm water was collected during eight storms from May 1999 to April 2000. Storm-water loadings of nutrients from each watershed were calculated from the concentrations of nutrients in water samples collected at fixed time intervals from the beginning of the storm-water discharge period until recession to base flow. These data provide DNREC with a more complete picture of the seasonal dependence of nutrient loading to the Bays from which to establish goals for total maximum daily loads in the Inland Bays watershed.

INTRODUCTION

The impact of agricultural, domestic, municipal, and industrial practices on the environmental status of Delaware's Inland Bays and their tributaries (Sussex County, Delaware) has been well documented over the last ten years by the U.S. Environmental Protection Agency's National Estuary Program, DNREC, the Center for the Inland Bays, the DGS, the University of Delaware, and other agencies. The documentation of the effects of these practices and the impact of regulation on the ecological status of the Inland Bays is an important consideration for the management of this environmentally, recreationally, and economically important resource. Until now, however, there has not been a sufficient database to determine the impact of particular land uses and land use practices on nutrient and carbon fluxes, the seasonal variations of these fluxes, and the impact of storm events on the Inland Bays. Determining the magnitudes and mechanisms of transport of the nutrient elements, nitrogen and phosphorus, and organic carbon (a contribution to estuarine oxygen demand) through the watershed to the Inland Bays has become a priority for federal, state, and local government agencies with management responsibilities in this watershed.

In 1998, DNREC proposed a cooperative program between the CMS and the DGS to collect and analyze waters from selected discharge points in the Inland Bays watershed under

base-flow and storm conditions. The discharges of water, nutrients, and organic carbon were to be determined from several contrasting watersheds within the Inland Bays watershed during the 1999 water year. This contract was subsequently extended to cover the period until March 2000. The proposed work was designed to supplement and augment the routine water sampling and analysis performed by DNREC and the monitoring and research effort funded under the U.S. Environmental Protection Agency Coastal Intensive Site Network (CISNet) Program. Coinvestigators of the Delaware CISNet program, "Nutrient Inputs as a Stressor and Net Nutrient Flux as an Indicator of Stress Response in Delaware's Inland Bays Ecosystem," are William J. Ullman, Kuo-Chuin Wong, Joseph R. Scudlark, John A. Madsen, David E. Krantz, A. Scott Andres and Thomas E. McKenna. The collaborative program included four tasks:

- 1. Acquisition of water-quality samples for a total of at least six rainfall events from each of six gaging stations selected by DNREC.
- 2. The acquisition of base-flow discharge samples a minimum of four times during the 1999 water year from each of the sampling sites.
- 3. The preparation and analysis of the collected water samples using documented methods of analysis.
- 4. Quality control, quality assurance, and reporting of the analytical results obtained under (1), (2), and (3), above.

This document describes the preliminary results of the DNREC collaborative program. Further analysis of these results will be undertaken in the context of the CISNet project and the auxiliary data collected by this and other ongoing research and monitoring projects. The data on which this document is based are separately reported in a Microsoft Access database (Andres et al., 2002). This database is equipped with queries that permit easy uploading of analytical data, quality control of these data, and display of the data in various formats. The database includes results of water sampling from both the DNREC (Table 1) and CISNet (Table 2) sampling sites and will continue to be updated until the completion of the CISNet project. Future updates will be available on the Delaware Geological Survey WWW site:

http://www.udel.edu/dgs/ftp/cisnet/CHEMDATA/.

This report focuses on the results of sampling at the DNREC (Table 1) sites. The present discussion of the CISNet sites is limited to land use and land cover. Copies of reports related to the CISNet sites will be forwarded to DNREC as they become available.

WATERSHED CHARACTERISTICS

Thirteen streams and their respective watersheds were sampled as part of the joint DNREC/CISNet efforts (Figure 1). These watersheds vary in size from 1.3 to 157.2 km² and have a wide range of differing land uses. The total area of land drained by these streams that were sampled (348.1 km² for both the DNREC and CISNet sites) represents 48% of the total area of the Inland Bays watershed (Rehoboth, Indian River, and Little Assawoman bays). Based on the analysis of digital orthophotographs taken in 1997 (Delaware Office of State Planning Coordination, 1999), the watersheds have a range of distributions of land uses (LU) and land

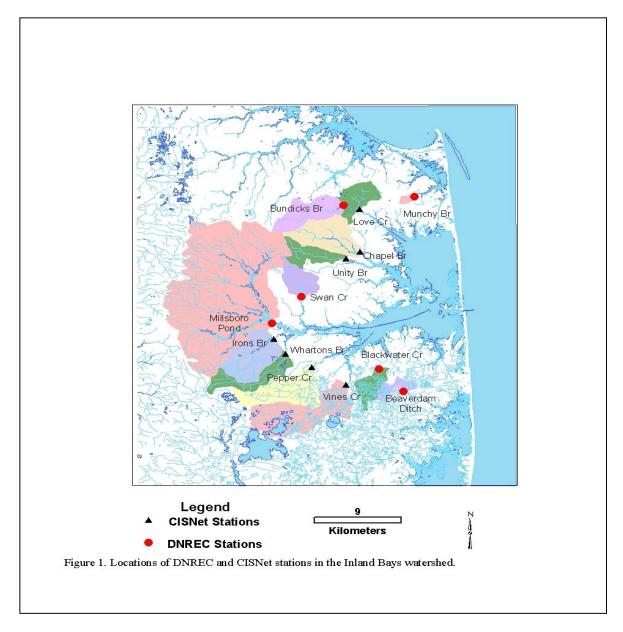
covers (LC) from built-up (LU/LC classes 100-199), agricultural (LU/LC classes 200-299), forest (not including forested wetland; LU/LC classes 400-499), and wetland (including forested

Table 1. DNREC sampling sites. The results of sampling at these stations are discussed in this report.

	Site Description (Reason for Selection)	USGS Identifier
1.	Munchy Branch near Rehoboth Beach (at Rd. 270A, commercial, residential, trailer park, partial canopy)	01484668
2.	Bundicks Branch at Robinsonville (at Rt. 23, mixed forest, unditched cropland with wetland/woodland stream corridor)	01484654
3.	Swan Creek near Millsboro (at Rd. 297, mixed forest, partially ditched cropland)	01484534
4.	Millsboro Pond Outlet at Millsboro (at Rt. 24, mixed land use, main flow into Indian River Bay)	01484525
5.	Blackwater Creek near Clarksville (at Rd. 54, heavily ditched cropland, poultry production, partial canopy over stream)	01484600
6.	Beaverdam Ditch near Millville (at Rd. 368, heavily ditched cropland, poultry production, partial canopy over stream)	01484695

Table 2. Additional CISNet sampling sites. The results of sampling at these stations are not discussed in this report. See Figure 1 for locations.

	Site Description (Reason for Selection)	USGS Identifier
7.	Love Creek at Robinsonville (at Rd 277, Goslee Millpond, mixed built- up, agricultural, and forest. increasing development, impoundment upstream)	01484655
8.	Chapel Branch at Angola (at Rt. 24, Burton Pond, mixed agriculture and forest, impoundment upstream)	01484677
9.	Unity Branch at Angola (at Rd 302, mixed agriculture and forest)	01484678
10.	Iron Branch near Millsboro (at Rt. 113, high iron content waters)	01484530
11.	Whartons Branch near Millsboro (at Rt. 113, mixed agricultural and wetlands)	01484531
12.	Pepper Creek at Dagsboro DE (at Rt 20, mixed agricultural and wetlands; high iron content waters)	01484550
13.	Vines Creek at Omar (at Rt 20, mixed agricultural and wetlands; high organic content waters)	01484548



wetland; LU/LC classes 600-699) that are representative of the range of land uses found elsewhere in the Inland Bays watershed (Table 3; Delaware Office of State Planning Coordination, 1999; Mackenzie and McCullough, 1999). Brushland/rangeland, barren, and water, not including the open waters of the Bays, are minor components of land use in the Inland Bays watershed and are summed together in "other" in Table 3). The range of land use and the relative sizes of the watersheds sampled are shown in Figure 2.

The evaluation of land use characteristics as a predictor of base-flow and storm-water loadings of nutrients and organic carbon are the subject of a separately funded investigation currently underway (Delaware Water Resources Graduate Fellowship, "Base-flow and Storm Discharges of Nutrients to Delaware's Inland Bays," William J. Ullman and Joseph R. Scudlark, co-investigators). Results of this study will be reported to DNREC as they become available.

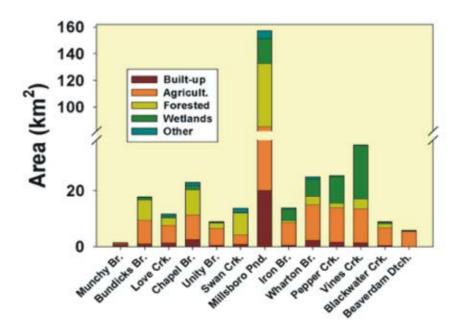


Figure 2. Land use/land cover in DNREC and CISNet watersheds.

Table 3. Land Use/Land Cover (LU/LC) characteristics of Inland Bays watersheds. LU/LC of individual watersheds determined by analysis of 1997 data from. Delaware Office of State Planning Coordination (1999). LU/LC characteristics of the Inland Bays watershed from analysis of 1992 data by Mackenzie and McCullough (1999).

Watershed	Built-up	Agriculture	Forest	Wetlands	Other	Area
	(%)	(%)	(%)	(%)	(%)	(km2)
1. Munchy Branch	65.2	27.2	4.5	3.1	0.0	1.3
2. Bundicks Branch	5.6	47.2	40.9	5.2	1.2	17.9
3. Swan Creek	6.9	24.0	58.1	1.2	9.7	13.5
4. Millsboro Pond	12.8	41.5	30.1	11.9	3.7	157.2
5. Blackwater Creek	5.8	70.4	14.6	8.0	1.3	9.0
6. Beaverdam Ditch	1.5	93.0	1.7	2.3	1.4	5.8
7. Love Creek	11.6	54.5	23.2	4.9	5.8	11.6
8. Chapel Branch	11.4	37.9	39.4	6.7	4.7	23.0
9. Unity Branch	6.6	66.7	21.2	4.1	1.3	8.8
10. Iron Branch	4.2	58.7	4.6	30.5	2.0	13.7
11. Wharton Branch	9.3	50.6	12.4	24.2	3.6	24.9
12. Pepper Creek	6.8	48.2	6.5	37.2	1.3	25.3
13. Vines Creek	3.8	33.6	9.7	52.5	0.4	36.1
Inland Bays	13.8	39.2	32.5	7.6	6.9	721.6

SAMPLING AND ANALYTICAL METHODS

Base-flow water samples were collected at each stream-sampling station at approximately bi-weekly intervals from October 1998 to May 2000 (Table 4). Base-flow samples were collected after at least three days with no measurable precipitation based on precipitation data collected at Georgetown, DE and available at http://www.rec.udel.edu/TopLevel/Weather.htm. At each station, a clean one-liter bottle was filled by dipping below the surface layer of the tributary or with a peristaltic pump. In each case, the bottle was rinsed at least three times with the water to be sampled prior to sample collection. An aliquot sample was filtered immediately after collection through Whatman GF/F glass fiber filters for dissolved nutrient analyses and together with the remaining unfiltered sample were stored on ice in the dark until returned to the laboratory. Measurements of water temperature, conductivity, pH, and dissolved oxygen were made at each station at the time of sample collection.

As soon after base-flow sampling as possible and after the return to the laboratory (typically within 5 hours of the end of sample collection), a 10-ml aliquot of the filtered dissolved nutrient sample was ampulated for subsequent determination of dissolved organic carbon (DOC). The remaining filtered sample and the ampules were then frozen until ready for the determination of dissolved constituents. The unfiltered sample was filtered in the laboratory as soon after sampling as possible onto precombusted Whatman GF/F filters for the determination of particulate organic carbon and nitrogen (POC and PON), and onto clean Whatman GF/F filters for particulate phosphorus (PP) and chlorophyll a. Total suspended solids (TSS) were determined by collection on tared 47-mm diameter, 0.4- μ m pore-size Nuclepore ® filter membranes.

Table 4.	Dates of base-flow	sample collection at DNREC and CISNet si	tes.

Fall 1998	Winter 1999	Spring 1999	Summer 1999	Fall 1999	Winter/Spring 2000
29 October 18 November 21 December	12 January 10 February 26 February 9 March	25 March 8 April 19 April 3 May 14 May 27 May 10 June	25 June 8 July 27 July 5 August 25 August 3 September	28 September 13 October 29 October 23 November 20 December	10 February 2 March 3 April 4 May

Once the DOC sample was taken from the filtered aliquot and ampulated, the samples for dissolved nutrient and DOC analysis were kept frozen for up to one year until analyzed. The chlorophyll *a* samples were treated with 90% acetone and stored in a freezer until analyzed, if the analysis could be performed within 24 hours. If not, samples were frozen for up to a month and acetone was added 24 hours before analysis. TSS samples were weighed, dried under a heat lamp, and reweighed within a few days of collection. Samples for PON, POC, and PP were dried and stored for up to a year until analysis. These storage protocols were designed to minimize the degradation of samples prior to analysis. No storage effects were noted in this study.

Storm-water samples were collected at the six DNREC stations (Table 1) using ISCO

6700 automatic sample collectors on eight occasions from May 1999 to April 2000 (Table 5). Storm-water sampling was automatically enabled by an increase in tributary stage height of at least 0.0061 m subsequent to the manual or remote arming of the sampler. Samples were collected immediately on enabling and, subsequently, at intervals of 3 hours for up to 33 hours or until the samples were retrieved (typically 12 samples were collected per event). During warm weather, ice packs were used during sampling to keep the samples cold and to retard biogeochemical reactions that might alter the water chemistry. Samples were collected in clean one-liter bottles and on retrieval, were returned to the laboratory for filtering and analysis. In the laboratory, an aliquot sample was taken and filtered, as described above, for dissolved nutrient analysis.

The water-quality parameters measured on samples are summarized in Table 6. A brief description of the methods follows. Further details are available from the investigators, as necessary. In the field, conductivity was determined using a Cole-Parmer Model 1481-40 conductivity meter calibrated using KCl standards purchased from Oakton Instruments. pH was determined potentiometrically using an Orion 210A pH meter calibrated using commercial NBS-traceable standards. Dissolved oxygen was determined amperometrically using a Yellow Springs Instrument Model YSI58 dissolved oxygen meter calibrated in air. Temperature measurements were taken using the thermistor on the dissolved oxygen meter.

Table 5. Dates and success of storm-water sampling at DNREC sites.

Site	20 May 99	15 July 99	22 Aug. 99	23 Sept. 99	19 Oct. 99	6 Jan. 00	13 Mar. 00	10 Apr. 00
Munchy Branch		Х	X	Х	Х	Х		Х
Bundicks Branch		Х	Х	X	Х	Х	Х	Х
Swan Creek		X		X	Х	Х	Х	X
Millsboro Pond	Χ	X	X	X	Х	Х	Х	X
Blackwater Creek		X	Х		X	X	X	Х
Beaverdam Ditch	Χ	X			Х	Х		Х

Table 6. Water-quality measurements at DNREC and CISNet sites. Field measurements were not made on storm-water samples.

Field Measurements:	Conductivity, Temperature, pH, Dissolved Oxygen			
Laboratory Measurements:	Particulate	Organic Carbon, Organic Nitrogen, Phosphorus, Suspended Solids, Chlorophyll <i>a</i> .		
	Dissolved	Ammonium, Nitrate+Nitrite, Total Dissolved Nitrogen, Phosphate, Total Dissolved Phosphorus, Silicate, Dissolved Organic Carbon		

Samples for particulate organic carbon (POC) and nitrogen (PON), together with the precombusted (500 °C for 2 hours) 13-mm GF/F (glass fiber) filter on which they were collected,

were encapsulated in clean (rinsed in methylene chloride and acetone) tin cups, dried in air, and stored in a desiccator until combusted and analyzed on a Carlo Erba Model EA1108 CHNS analyzer. Between 25 and 75 ml of sample was filtered for PON/POC analysis depending on the turbidity of the sample. The CHNS analyzer was calibrated using weighed samples of ethylenediaminetetraacetic acid (EDTA-- $C_{10}H_{16}O_8N_2 \cdot 2H_2O$) and phenylalanine ($C_9H_{11}O_2N$).

Between 25 and 100 ml of sample, depending on turbidity, was filtered for particulate phosphorus (PP) analysis. Samples, together with the clean GF/F filter on which they were collected, were stored and dried in glass scintillation vials until combusted, dissolved, and subsequently analyzed as dissolved phosphate. Prior to drying, the sample was soaked in 2 ml of 0.017 M MgSO₄ to prevent the formation of insoluble phosphate compounds on combustion at 450 - 500 °C for 2 hours, After cooling, 5 ml of 0.2M HCl were added to each vial, and the samples were heated to 80°C for 30 minutes to dissolve the residue of combustion. The concentration of phosphate was determined colorimetrically in the supranatant using the phospho-molybdenum blue method (Solarzano and Sharp, 1980a).

Total suspended solids (TSS) were determined by filtering water samples through predried (under a heat lamp) and tared Nuclepore ® membrane filters (47-mm diameter, 0.4- μ m pore-size). Up to 150 ml of water sample was filtered through each filter, depending on turbidity. The sample retained on the filter was then re-dried for 2 hours under the heat lamp and weighed.

Up to 100 ml of sample, depending on turbidity, was filtered onto a 25-mm GF/F filter for the determination of chlorophyll *a*. The filter and sample were placed into a glass scintillation vial. The extracted chlorophyll was determined fluorometrically on a Turner AU10 Fluorometer. Commercially purchased chlorophyll *a* was standardized using the spectrophotometric method of Parsons et al. (1984) and subsequently used to calibrate the fluorometric determinations.

Dissolved ammonium (NH₄⁺, abbreviated NH4 in this report), nitrate+nitrite (NO₃⁻+NO₂⁻, abbreviated NO3), and phosphate (ΣPO₄³⁻, abbreviated PO4), were determined by automated colorimetry on filtered samples using an O/I Analytical Flow Solution IV Analyzer. NH4 was determined by the phenol hypochlorite method (Glibert and Loder, 1977; Grasshoff and Johansen, 1972). NO3 concentration was determined by the sulphanilamide/N(1-napthyl) ethylene diamine method after cadmium reduction of NO₃⁻ to NO₂⁻ (Glibert and Loder, 1977). PO4 was determined by the phospho-molybdenum blue method (Strickland and Parsons, 1972). Total dissolved nitrogen (TDN) and phosphorus (TDP) were determined as NO3 and PO4 after oxidation in an autoclave by multiply reprecipitated potassium persulfate (K₂S₂O₈) (Glibert and Loder, 1977; D'Elia et al., 1977; Solarzano and Sharp, 1980b).

Dissolved organic nitrogen and phosphorus (DON and DOP) are determined as the difference between the dissolved total concentrations (TDN and TDP) and inorganic concentrations (DIN = NO3 + NH4 and DIP = PO4).

Dissolved organic carbon (DOC) was determined on the ampulated samples after acidification and bubbling with helium or argon to remove inorganic carbon. Samples were then catalytically combusted in a Shimadzu TOC 5000 and detected by non-dispersive infrared analysis. The instrument was calibrated using aqueous solutions of potassium hydrogen phthalate ($KHC_8H_4O_4$).

All of these methods are routinely used in the CMS laboratories and further details of the analytical methods are available from the investigators, as needed. The estimated precision of

each analysis is given in Table 7. Because of the uncertainties in the component analyses, the precisions of the calculated values of DON and DOP are \pm 2.2 - 11 micromolar (μ M) and \pm 0.03 - 0.07 μ M, respectively. Total nitrogen (TN = TDN + PON), phosphorus (TP = TDP + PP), and organic carbon (TOC = DOC + POC) have uncertainties of \pm 2.1 - 10 μ M, \pm 0.03 - 0.05 μ M, and \pm 15 - 50 μ M, respectively.

Table 7. Typical precision achieved for each analytical procedure used in this report.

Field Measurements					
Conductivity	<u>+</u> 20 μS				
Temperature (T)	<u>+</u> 0.2 °C				
Dissolved	<u>+</u> 0.3				
Oxygen (DO)	mg/L				
pH	<u>+</u> 0.05				

Particulate Constituents				
Organic C (POC)	<u>+</u> 3 - 6 μM			
Organic N	<u>+</u> 0.5 - 1			
(PON)	μM			
Suspended	<u>+</u> 0.2 mg/L			
Solids (TSS)				
P (PP)	<u>+</u> 0.02 μM			
Chlorophyll a	<u>+</u> 0.2 - 5			
	μg/L			

Dissolved Constituents						
Ammonium (NH4)	<u>+</u> 0.2 -1 μM					
Nitrate + Nitrite (NO3)	<u>+</u> 1 - 5 μM					
Total N (TDN)	<u>+</u> 2 - 10 μM					
Phosphate	<u>+</u> 0.02 -0.05					
(DIP=PO4)	μΜ					
Total P (TDP)	<u>+</u> 0.02 -0.05					
	μМ					
Organic	<u>+</u> 15 - 50					
Carbon (DOC)	μМ					

Quality control of the water-quality data was achieved by comparison of measurements to prepared samples and blanks, replicated analysis of selected samples on each day analyses were performed, participation in interlaboratory comparisons (Sharp et al., in press), and by examination of the data after the analyses were completed. In the case of TDN and TDP, analyses were repeated when the difference between these values and the sum of their separately determined inorganic components was significantly less than zero. Other analytical outliers were identified by the examination of trends with time for each parameter at each location and reanalyzed as needed. Direct electronic transmission of data from the analytical source to the database was used whenever possible in order to minimize the opportunity for transmission and reentry errors. Any errors or potential errors identified by users of this database should be reported to the authors of this report for verification and correction. All data in the database from DNREC stations have been examined for potential analytical, transcription, and other errors. All reported calculations are based on these quality-assured chemical data.

HYDROGRAPHIC METHODS

Instrumentation and systems used to measure, record, and compute stream stage height, discharge, and precipitation were operated, maintained, and subjected to QA/QC procedures by the Water Resources Division, U.S. Geological Survey (USGS). Continuous records of discharge were obtained at all of the DNREC stations (Table 1). These stations electronically recorded stage height, and for some stations (Millsboro Pond Overflow, Beaverdam Ditch, and Blackwater Creek), precipitation at 15-minute intervals. USGS staff developed and maintained stage height-discharge rating curves and provided access to their database of computed

instantaneous and mean daily discharge values. With the exception of Vines Creek, spot measurements of discharge were also obtained by the USGS at all of the CISNet stations (Table 2). All of the stream flow and ancillary precipitation data collected by USGS at these stations and discussed in this report are considered provisional and subject to revision at the time of the preparation of this report. The 15-minute stage height-discharge data were used for the determination of storm-water discharge and loadings. The 15-minute measurements were also averaged to give a mean daily discharge for base-flow periods. Mean daily discharges with storm flow removed (see below) were used to determine quarterly and annual loadings due to base flow.

Base-flow separations were done manually for the six continuous record stations using methods described by Gray (1970) and Maidment (1993). Prior hydrograph separation work by Johnston (1976) provided practical guidance for the current study. The basic procedure includes:

- 1. A semi-logarithmic plot of the hydrograph and a precipitation time series were constructed in computer-based plotting software.
- 2. Base-flow periods were identified by choosing periods where there had not been precipitation for at least 3 days. The base-flow hydrograph or recession curve was digitized on screen to be equal to stream flow during these periods. This procedure generates a series of characteristic recession curves for each station.
- 3. For periods during and following precipitation, the base-flow hydrograph was visually estimated. First, an estimated recession curve is extended back under the falling limb of the storm hydrograph to the point of peak flow. Next, an estimated recession curve is extended forward under the rising limb of the storm hydrograph.
- 4. The base-flow curve under the storm hydrograph was then estimated by considering the shape of the storm hydrograph, the preceding and following recession curves, and the precipitation for the storm.
- 5. The difference between total flow and base flow is considered to be a combination of overland and near-stream shallow subsurface flow (e.g., interflow). Separation of overland flow and interflow was not attempted.

These calculated flow components allow computation of nutrient fluxes and volumes of base flow and storm flow during storm periods. These values could be used to identify watersheds with similar hydrologic characteristics and are used with chemistry data for computations of chemical mass loadings and the relationships between stream flow and concentration, which may be useful for estimating loading from unsampled storms.

Daily mass loadings of dissolved and particulate constituents are computed as the product of water discharge and chemical concentrations on the sampling dates. Estimated daily loadings were calculated from the mean daily discharges and the estimated concentrations of constituents and these estimated daily loadings were summed to give quarterly and annual (both for the water year, WY, and the calendar year, CY) loadings for each of the DNREC watersheds. Daily concentrations of chemical constituents were estimated by linear interpolation between the previous and subsequent base-flow samples collected and analyzed at each site. Missing data, if any, were estimated using the same technique. For the period of 1 October 1998 to 28 October 1998 prior to the initiation of sampling, the concentration of N, P, and organic carbon (DOC and

POC) are taken to be that of the initial base-flow sample collected on 29 October 1998.

Total loadings during a storm are computed as the products of constituent concentrations and time-integrated discharge for the 3-hour period, centered on the time that an individual sample was collected during the storm event. For events where sampling did not cover the entire period of the storm and storm-water recession, the calculated loads cover only the sampled interval. Provisional discharge data obtained from the USGS were used in all computations. There may be significant changes in loadings calculated with final discharge values. Storm discharge was computed as the difference between the base-flow discharge for the storm-water period, estimated as above but integrated over the 15-minute discharge data, and the total discharge.

Watershed delineations for areas upstream of sampling stations were prepared manually by USGS personnel (V. Smith and A. Tallman, written communication, 1999) and were based on the 1992 edition 1:24,000-scale USGS topographic maps and associated digital line graph products supplemented by field observations and aerial photograph analyses. Boundaries were electronically captured as shape files by heads-up digitizing in ARCView (ESRI, 2000). GIS-based watershed delineations on a 30-meter digital elevation model (DEM) by Mackenzie et al. (1999) included portions of the watersheds downstream of the sampling sites and thus could not be used in the present study.

Land use area and percentage calculations for the sampled watersheds (Table 3 and Figure 1) were computed on 1997 1-meter resolution data sets covering Sussex County obtained from Mackenzie and McCullough (1999) and the Delaware Office of State Planning Coordination (1999). ArcView v.3.2 (ESRI, 2000) was used to cull the data with the intersect feature of the Geoprocessor extension, and the CALCAPL ave script was used to recalculate areas in the resultant shape files.

There were significant variations in monthly rainfall during the sampling period (Figure 3). The early part of the study, from fall 1998 to summer 1999, was conducted during a period of lower than usual rainfall. This "drought" was punctuated by a wetter than average fall of 1999 that included some major storm events, including the one associated with Hurricane Floyd. By comparison, the latter part of this study, in winter/spring 2000, was conducted during a relatively wet period compared to the average year. The variable rainfall amounts have significant impact on the discharge of water to the Inland Bays and, therefore, the loadings of nutrients to this ecosystem.

RESULTS Base-Flow Discharge

Base-flow loadings were calculated from the provisional data supplied by the USGS. In some cases, incomplete discharge data sets and incomplete quality control hampered the determination of base-flow and storm-water loadings. Where major discrepancies or omissions were found in the discharge database provided to us, we have brought these discrepancies to the attention of USGS and have estimated, if possible, the flow during these periods. Estimation was based on linear extrapolation or correlation with more complete discharge data sets. In addition, modifications of the discharge database (post-November 2000) could not be fully incorporated into this report. The major discrepancies, omissions, or modifications in the USGS discharge database were for the following periods and stations:

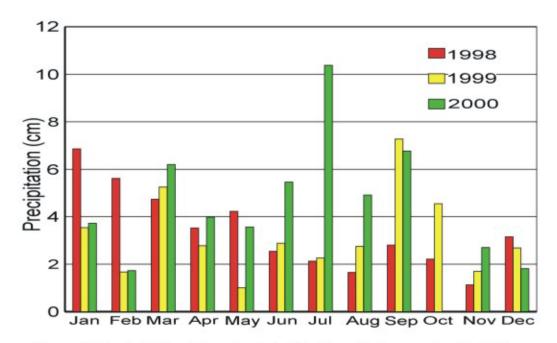


Figure 3. Precipitation data collected at the Cape Henlopen rain site (J. R. Scudlark and M. B. Freeman, personal communication). These data show the 1999 drought, Hurricane Floyd in September 1999, and the wetter than normal summer 2000.

- Modifications of the discharge calculations for Beaverdam Ditch, Blackwater Creek, and Millsboro Pond completed by USGS after 15 December 2000 were not incorporated into this report.
- Omitted data for Bundicks Branch for January- March 2001 were unavailable for incorporation into this report.
- Missing data for Blackwater Creek for the period of October -December 1998 were not included in this report. Current values indicating no flow during this period, in contrast to observations, were used in this report.
- No discharge data were available from the USGS for the April 2000 storm.

Figures 4 - 9 show the concentrations of N, P, organic carbon species, and suspended solids concentrations and base-flow discharge at each of the DNREC sites (Table 1). There is a great deal of variation in the range of concentrations and the seasonal variation in concentration found at these stations. This variation, combined with the seasonal variations in base-flow discharge, led to large differences in the calculated loadings between stations and for different chemical species at each station. A qualitative summary of the observations at each station follows.

Munchy Branch

Munchy Branch is the smallest watershed sampled during this project (1.3 km²) and the only watershed where the predominant land use is "built-up." There is a small pond above the

Munchy Branch sampling site, and regulation of pond discharge and some nearby construction early in the project may have been responsible for some of the variability in discharge observed in fall 1998 and winter 1999 (Figure 4). The base-flow discharge was highest in the winter and lowest during the summer, although the high rainfall in summer 2000 somewhat obscures this pattern. TDN, predominantly in the form of NO3, is consistently high from late fall to early summer, with minimum concentrations in the early fall. PON dominates the total N discharge in the spring and this distribution is consistent with the high concentrations of suspended solids observed in this period.

Dissolved phosphorus (TDP and PO4) concentrations ranged from 0.2 to 2.1 μ M and 0.1 to 0.5 μ M, respectively, during the year with the highest concentrations found in mid-summer. PP concentrations followed a similar pattern except for a peak, similar to that observed for PON, in early summer 1999. During this period, PP was the dominant form of phosphorus in the discharge (up to 5 μ M).

Dissolved organic carbon (DOC) showed no seasonal trend, but rather increased monotonically throughout the sampling period. This may have resulted from the significantly higher rainfall and discharge in the latter part of this study compared to the earlier part. POC concentrations, by comparison, peaked in the summer, when discharge was at its minimum, and remained lower and constant during the rest of the year. As a result of these temporal patterns, DOC loading correlates directly with discharge, and POC loading is inversely correlated with discharge. The concentrations of suspended solids at Munchy Branch showed large variability and no obvious seasonal trend.

Bundicks Branch

Bundicks Branch is a medium-sized watershed (17.9 km²) dominated by approximately equal amounts of unditched cropland and forestland including an extensive forested riparian zone. Historically, this watershed was primarily in dairy production; however, only one such dairy operation remains. This farm has a liquid waste handling process that includes spray irrigation facilities within the watershed. The base-flow discharge at this station was highest during the mid- to late-spring and fairly constant during the summer, fall, and early winter (Figure 5).

Nitrogen discharge was dominated by NO3 with substantial fractions of DON and NH4 only during the late fall and early winter. PON concentrations were variable with relative maxima in both the summer and winter. TDN and NO3 concentrations remained within the relatively narrow ranges of 250 - 450 μM and 250 - 350 μM , respectively. As a result of the relatively small variation in total N, the flux of nitrogen predominantly reflects the variation in discharge with the highest loading in the mid- to late-spring. The concentrations and loadings of PON were higher in the wetter spring of 2000 than they were in the dry spring of 1999 and reflect the differences in suspended solids concentrations between the two years.

Phosphorus in base flow is found in approximately equal fractions, and PO4 and DOP and the concentrations of these fractions co-vary. The highest concentrations are found in mid-summer when discharge is lowest. PP concentrations do not vary substantially through the year. Maximum phosphorus loadings occur during late spring and early summer and minimum loadings during the winter, but substantial loadings occur at all times of the year.

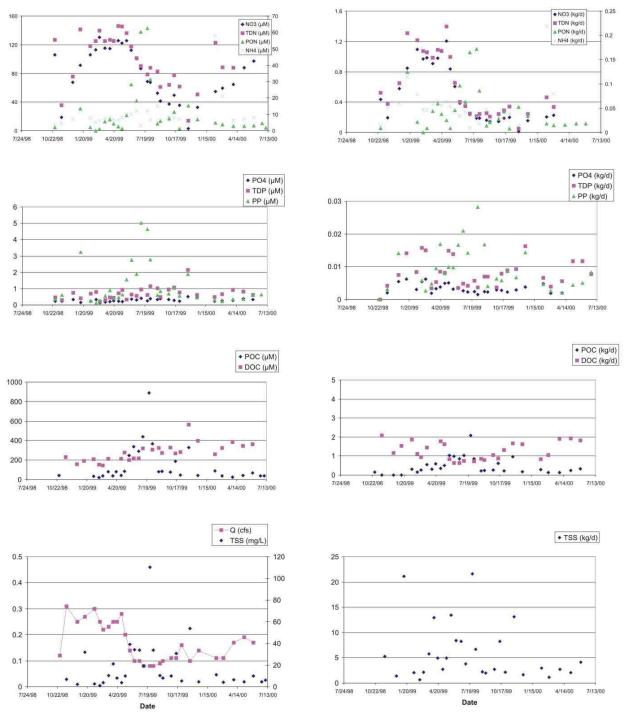


Figure 4. Concentrations (left) and loadings (right) of N, P, and organic C species, and suspended solids in base-flow discharge at Munchy Branch. For charts with two y-axes, NH4, PON, and TSS are plotted on the right axis.

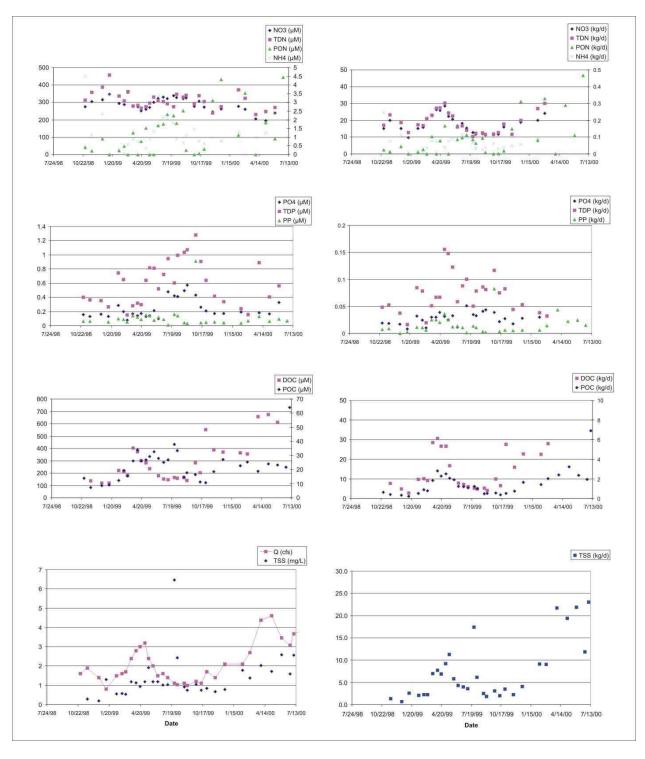


Figure 5. Concentrations (left) and loadings (right) of N, P, and organic C species and suspended solids in base-flow discharge at Bundicks Branch. For charts with two y-axes, NH4, PON, and POC are plotted on the right axis.

Dissolved organic carbon was the predominant form of organic carbon in the Bundicks Branch discharge. Concentrations of DOC were highest in the late winter and early spring, and concentrations ranged between 100 and 700 µM. POC concentrations were lower than DOC but followed a seasonal pattern similar to that of DOC. Loadings of organic C were highest in the late winter and early spring when both discharge and organic C concentration are at their maxima.

Suspended solids followed the pattern of discharge with the highest concentrations co-occurring with the high flow rates. Suspended solids concentrations and loadings were higher in the wetter winter of 2000 than they were in the drier winter of 1999. These higher concentrations are reflected in the higher concentrations of PON, PP, and POC found in winter 2000 than in winter 1999.

Swan Creek

The Swan Creek watershed is another medium-sized watershed (13.5 km²); however; in comparison to Bundicks Branch, it is dominated by forested land uses with agriculture representing a much smaller fraction of the total. Discharge was highest in the late winter and spring and lowest in the summer, although the high rainfall in summer 2000 somewhat obscures this seasonal trend (Figure 6). NO3 represented the dominant form of nitrogen in the discharge throughout most of the year, with the highest concentrations found during the summer and early fall. During the summer, when discharge was at a minimum, PON became an equally important form of nitrogen at this site. As a result of the discharge patterns, however, NO3 was the principal form of nitrogen in the loading, and loading is maximum at the high flow periods in the late winter and spring.

Phosphorus concentrations were quite variable at this station but were generally lower in the fall than at other seasons. The high concentrations of TDP compared to PO4 indicate that a significant fraction of the TDP is in the form of DOP. As with nitrogen, phosphorus loading was highest at periods of high discharge, and particulate phosphorus can represent up to 50% of the TP discharge at these times.

DOC concentrations correlate well with discharge, and concentrations peak in the spring. The concentrations of DOC in the fall 1999 to spring 2000 period were significantly higher than the previous year, reflecting, perhaps, the differences in rainfall and resulting discharge. POC concentrations correlate inversely with discharge and peak in the summer. As a result of these patterns, DOC dominated the flux of organic carbon at this site, and loadings peaked in the spring. Suspended solid concentrations were highest in the summer when discharge was lowest and particulate loading shows no consistent trend with season.

Millsboro Pond

Millsboro Pond is the largest watershed sampled in this study (157.2 km²) and has the largest stream discharge into the Inland Bays. Agricultural land use predominates, and the watershed contains a significant amount of forested land cover. There are a number of ponds in this watershed that tend to moderate both the flow and the nutrient concentrations at the Millsboro discharge site. Discharge at Millsboro Pond was highest in the spring and normally lowest in the summer and fall (Figure 7). However, the high rainfall in September and October 1999 obscures this normal pattern.

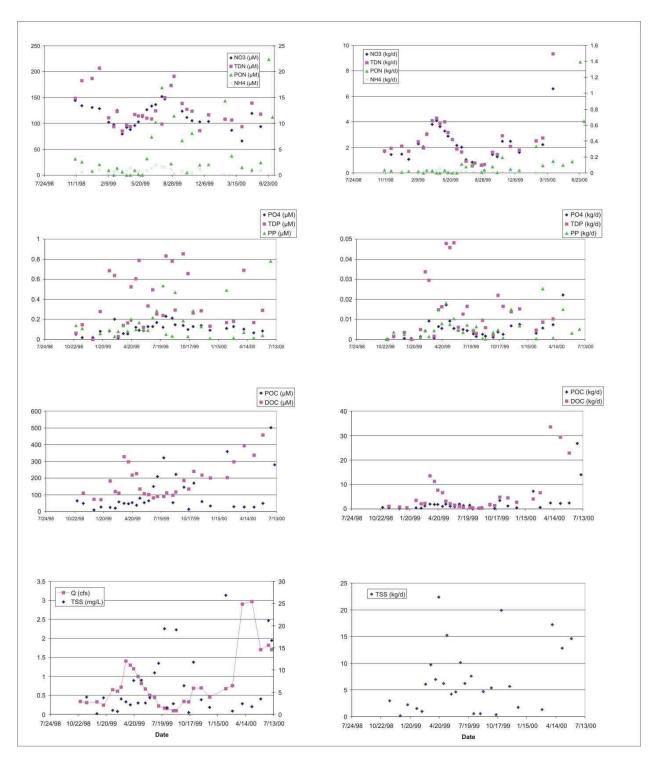


Figure 6. Concentrations (left) and loadings (right) of N, P, and organic C species, and suspended solids in base-flow discharge at Swan Creek. For charts with two y-axes, NH4, PON, and TSS are plotted on the right axis.

TDN and NO3 concentrations were highest in the winter and lowest in summer. DON was a small fraction of the total, and neither NH4 nor PON contribute significantly to the nitrogen load. This pattern, together with the discharge pattern leads to a peak in nitrogen loadings in late winter/early spring that is 10-15 times higher than the summer nitrogen loads.

The concentrations of phosphorus as TDP, PO4, and PP were quite variable and show little seasonal trend. DOP was a significant fraction of the TDP at most times of the year. As a result of the lack of seasonal trend in concentration, the loadings of P correlate well with discharge.

As with Munchy Branch and to a lesser extent with Swan Creek, DOC concentrations increased throughout the sampling period. POC concentrations were significantly lower and declined through the same period until the early summer of 2000. As a result of the lack of seasonal trend, organic carbon loadings correlate well with discharge.

Suspended solid concentrations were generally higher during periods of higher discharge. TSS concentrations in spring 2000 were somewhat less than during the same period in 1999.

Blackwater Creek

Blackwater Creek is a small watershed (9.0 km²) in which agriculture is the dominant land use. The creek drains an extensive ditch network in the watershed. Discharge at this site was focused in the winter and spring with little or no base-flow discharge occurring during the summer and early fall. This pattern was found in the early part of this study, but the large amounts of rainfall in the early fall of 1999 led to discharges during this period higher than those observed in fall 1998 (Figure 8).

Nitrogen was found principally as NO3, and the concentrations are at their highest in the winter and spring and lowest in the summer; these correlate well with discharge. Nitrogen loading occurred predominantly in the winter and spring, and in the form of NO3. PON concentrations became important only during the summer when discharge was at a minimum where this site more closely resembled a pond than a stream.

The concentrations of phosphorus and organic carbon species were highest during the period of low discharge. However, these high concentrations had no impact on loading. The loadings of P and organic C were controlled by discharge and they peaked in the winter/spring 1999. Consistent with the patterns of discharge, they were also high in the fall of 1999.

Total suspended solid concentrations were also generally higher at periods of high discharge. The highest observed concentrations were associated with the periods immediately following the major storms in fall 1999.

Beaverdam Ditch

Beaverdam Ditch is another small agricultural watershed (5.8 km²) similar to Blackwater Creek. Almost all of the watershed (93%) is in agricultural production. The observed discharge pattern is similar to that observed at Blackwater Creek where the seasonal pattern of winter/spring-only discharge was disrupted by the higher than average rainfall and discharge patterns observed in fall 1999 (Figure 9).

The concentrations and loadings of N, P, and organic carbon species, consistent with the similar land use and discharge patterns, followed patterns similar to those found at Blackwater Creek. There were broad periods of nitrogen and phosphorus loading during the late winter and spring. There was a great deal of variability in phosphate concentrations with a peak in PP

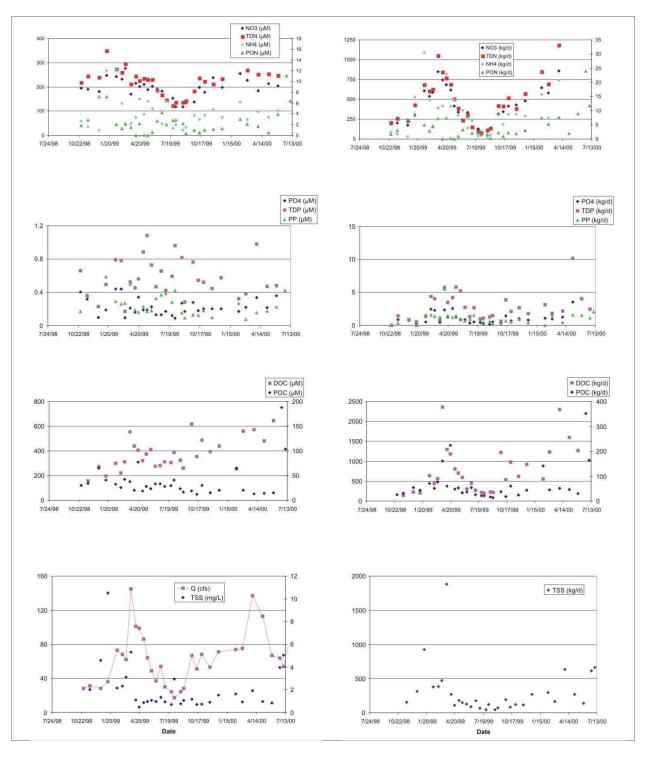


Figure 7. Concentrations (left) and loadings (right) of N, P, and organic C species, and suspended solids in base-flow discharge at Millsboro Pond. For charts with two y-axes, NH4, PON, POC, and TSS are plotted on the right axis.

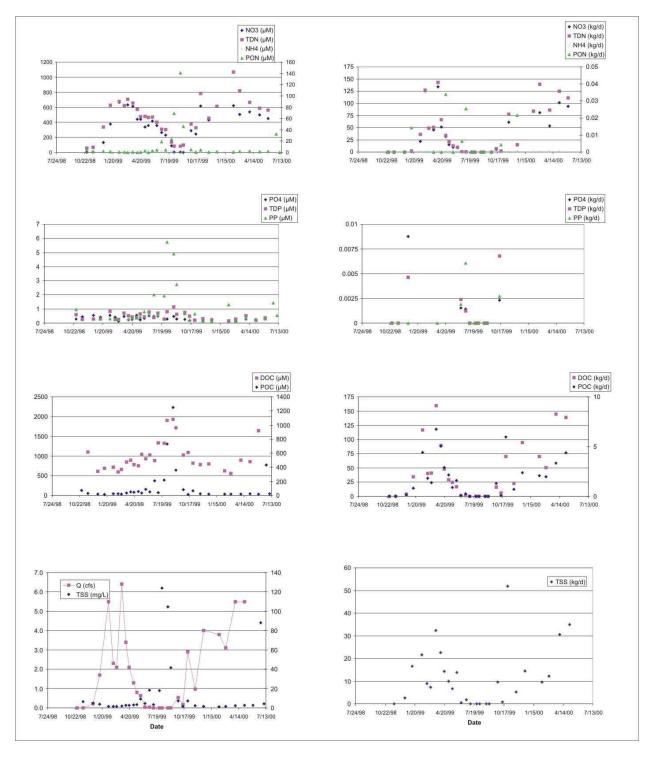


Figure 8. Concentrations (left) and loadings (right) of N, P, and organic C species, and suspended solids in base-flow discharge at Blackwater Creek. For charts with two y-axes, NH4, PON, POC, and TSS are plotted on the right axis.

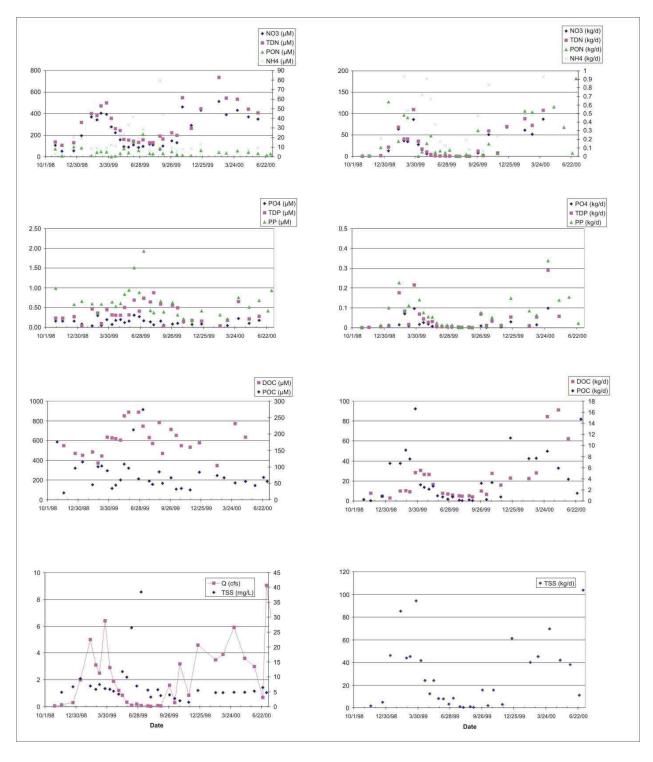


Figure 9. Concentrations (left) and loadings (right) of N, P, and organic C species and suspended solids in base-flow discharge at Beaverdam Ditch. For charts with two y-axes, NH4, PON, POC, and TSS are plotted on the right axis coinciding with the summer low flow period. Organic carbon concentrations, both DOC and POC, showed no obvious seasonal pattern, and, therefore, loadings correlate well with discharge. TSS correlates with discharge.

Storm-Water Discharge

Figures 10 through 15 show typical examples of concentration and loading curves for the sampled watersheds. There are several types of relationships between concentration and discharge observed at the DNREC sampling stations.

The phenomenon of high concentrations of dissolved and particulate constituents at the beginning of a storm with subsequent decline of concentrations is commonly referred to as a "first flush." This phenomenon represents the delivery of soluble and particulate constituents from the land surface into the streams in overland flow, suspension of stream bottom sediments, and redissolution of constituents in stream bottom sediments. The automated storm samplers were set to try to capture the water associated with a "first flush" followed by 11 additional samples at 3 hour increments that were to sample storm flow for the duration of individual storm events. This schedule had relatively good success in capturing the flow at the very beginning of a storm event. However, it may not have fully sampled the first flush of nutrients after the initiation of the storm if the first flush was short in duration and lagged the initiation of the storm discharge. This sampling schedule also had mixed success in sampling entire storm events. The sampling interval was too long for very small storms (where return to base-flow conditions took place in less than one day), and too short for larger storms (where return to base-flow conditions took place in more than 1.5 days).

Millsboro Pond showed no regular and consistent relationships between concentrations of dissolved constituents and discharge (Figure 10). This is most likely due to biogeochemical and sedimentary processes occurring in the ponds immediately upstream of the sampling point and the lack of significant flushing of these impoundments except during the largest storms, larger than those sampled during this project. For example, high NH4 concentrations, thought to be typical of respiration rates in excess of rates of photosynthesis, were observed in July 1999 (Figure 10), but not in later events. There also appeared to be diurnal trends in nutrient concentrations during some storm events, reflecting the importance of within-pond biogeochemistry.

Positive correlations of the concentrations of dissolved constituents with increasing discharge were observed at most sites for most constituents, but only for some storms. Sometimes, the highest observed concentrations lagged behind the times of the peak discharge (Figure 11). On some occasions, there are observed similarities between the patterns of dissolved and particulate concentration during storms. This is consistent with a similar source for both dissolved and particulate nutrient species. Because particulate forms are generally associated with overland flows, this similarity in distribution would suggest that dissolved constituents are also derived from overland runoff.

Concentrations of TDN decreased with increasing storm discharge at Bundicks Branch (7/1999, see Figure 12; also occurred 9/1999, 10/1999, 1/2000) and Munchy Branch (1/2000, see Figure 13; also occurred 9/1999). This indicates that, at these stations, ground water is the primary source of TDN for these watersheds and that storm flow serves to dilute the ground-water contribution. Preliminary work with provisional discharge data found statistically significant but inverse correlations between discharge and TDN concentrations for Bundicks Branch, Swan Creek, Blackwater Creek, and Beaverdam Ditch for some of the storms. However, it is possible that dissolved and particulate loading reflect resuspension of streambottom sediments and associated interstitial water.

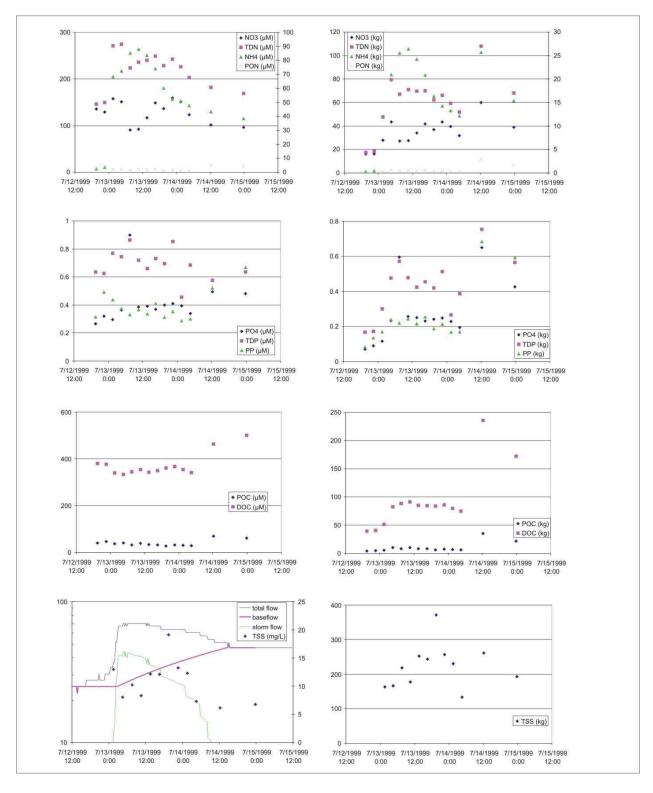


Figure 10. Concentrations and loadings of N, P, and organic C species and suspended solids in Millsboro Pond for a summer storm. For charts with two y-axes, NH4, PON, and TSS are plotted on right axis. Flow in cfs, loads reported for a 3 hour sampling interval.

First flush effects were rarely observed for the dissolved constituents. The lack of observed first flush may be due to the relatively long sampling intervals used in this study. These may have been insufficient to observe first flush effects of very short duration. However, it may also indicate that the source of dissolved constituents is dominantly from ground water and that dilution during storms is the primary process affecting the patterns of loading at the experimental watersheds.

The general term "particulates" will be used to describe particulate forms of nitrogen, phosphorus, carbon, as well as total suspended solids. For most of the stations and storms, concentrations of particulate nitrogen, carbon, and phosphorus appear to follow the same general trends as those of total suspended solids and are positively correlated with discharge. Because of the gentle stream gradients and low flow velocities during base-flow discharge in the sampled watersheds, base flow would not be expected to be a significant source of particulates. Conversely, the higher flow velocities that occur during storm discharge events would be expected to result in higher concentrations of particulates from overland runoff. There are exceptions to this rule, however, as base-flow concentrations of particulates (before and after a storm) are sometimes higher than during the storm. This may be due to a dilution effect in watersheds where particulate transport in storm-water runoff is inhibited.

The first flush of particulates was observed for the storm of 1/2000 (Figures 13 - 15) for all stations except Bundicks Branch and Millsboro Pond. This phenomenon was also observed in Millsboro Pond and Swan Creek for the storm of 9/1999. It is possible, however, that such first flush discharges occurred but that the sampling interval (3 hours) was too long to adequately sample it.

Concentration of particulates may also follow the discharge hydrograph with the highest concentrations occurring at the highest discharges. The storm of 7/1999 showed this for all stations except Millsboro Pond, where discharge is moderated by the impoundments in this watershed. This was observed in Blackwater Creek, Bundicks Branch, and Swan Creek for the storm of 10/1999 (Figure 11). Preliminary work with provisional discharge data found statistically significant correlations between discharge and particulate phosphorus and total suspended solids for Munchy Branch, Bundicks Branch, Blackwater Creek, and Beaverdam Ditch for some of the storm events. The lack of correlation at other times may be due to storm size and the interval between the sampled event and previous storms.

DISCUSSION

Base-Flow Loadings

The chemical data at the six DNREC stations together with the water discharge associated with base flow determined by the above hydrograph separation procedures were used to calculate quarterly and annual loadings from each watershed to the Inland Bays. The concentrations measured on the first sampling date, 29 October 1998, were used for all of the preceding dates during that month, and daily concentrations between sampling dates were calculated by linear extrapolation. Missing measurements were also calculated by the same procedure. The product of the measured and estimated daily concentrations and estimated baseflow discharge rates were then integrated for each quarter of the study (IV98, I99, II99, II99, IV99, and I00), for the 1999 water year (WY99 = 1 October 1998 to 30 September 1999), and for the 1999 calendar year (CY99 = 1 January 1999 to 31 December 1999). These data are

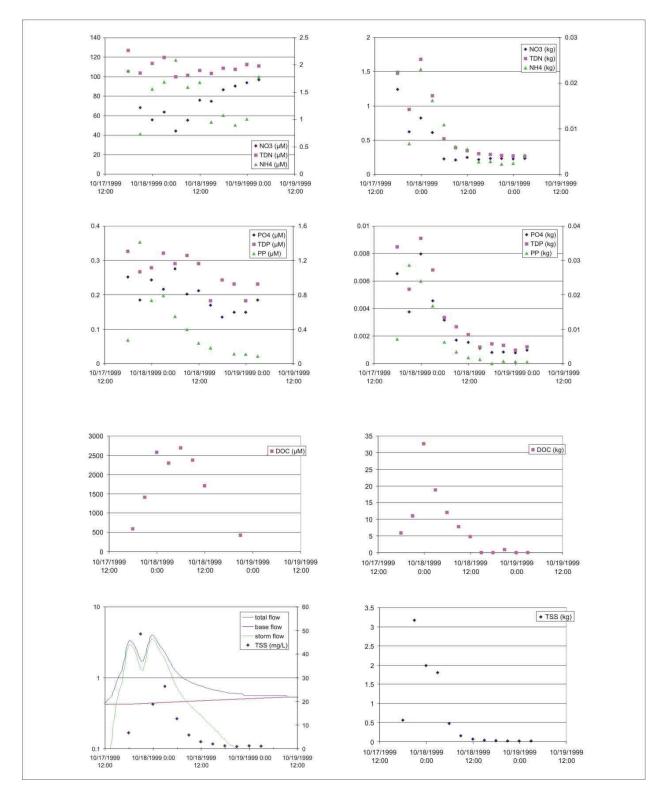


Figure 11. Concentrations (left) and loadings (right) of N, P, and organic C species and suspended solids in Swan Creek for a storm in October 1999. For charts with two y-axes, NH4, PP, and TSS are plotted on right axis. Flow in cfs, loads reported for a 3 hour sampling interval.

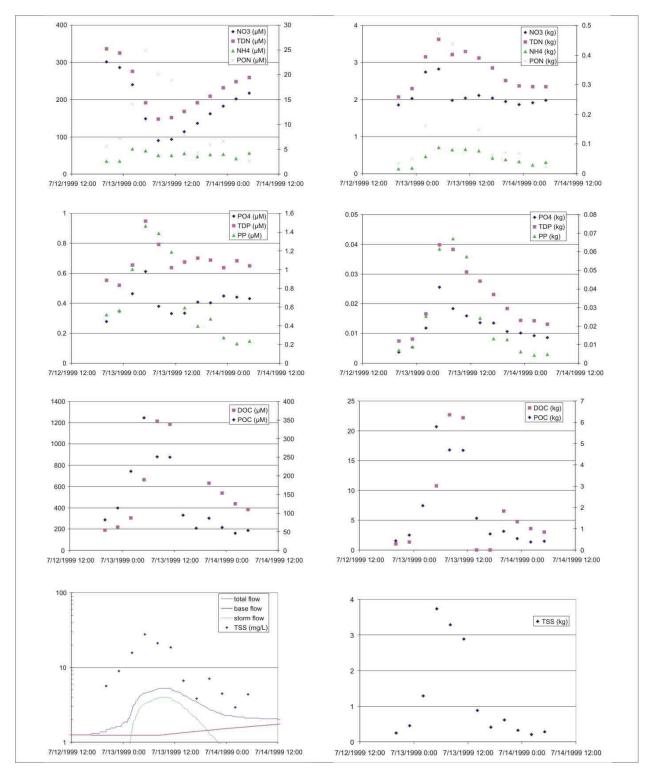


Figure 12. Concentrations (left) and loadings (right) of N, P, and organic C species and suspended solids in Bundicks Branch for a summer storm. For charts with two y-axes, NH4, PON, PP, and POC are plotted on the right axis. Flow in cfs, loads reported for a 3 hour sampling interval.

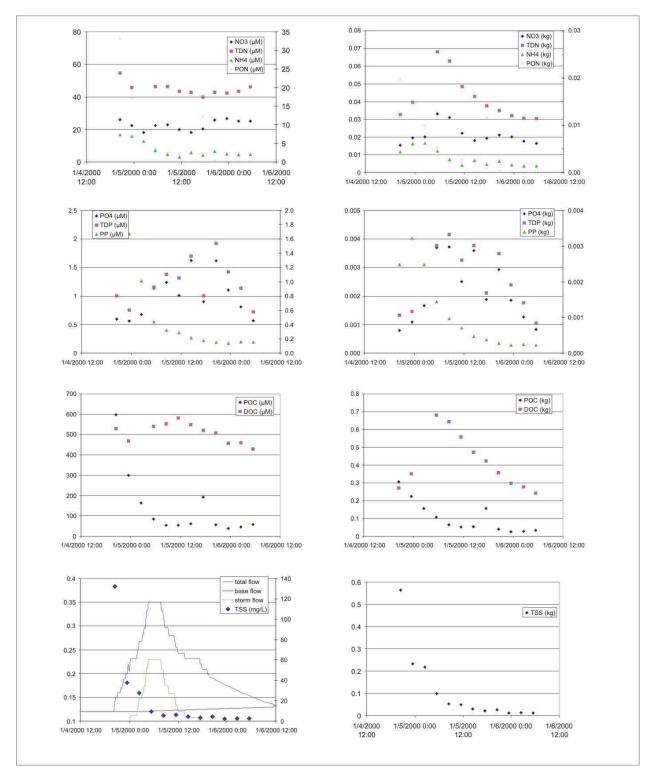


Figure 13. Concentrations (left) and loadings (right) of N, P, and organic C species and suspended solids in Munchy Branch for a storm in January 2000. For charts with two y-axes, NH4, PON, PP, and TSS are plotted on the right axis. Flow in cfs, loads reported for a 3 hour sampling interval.

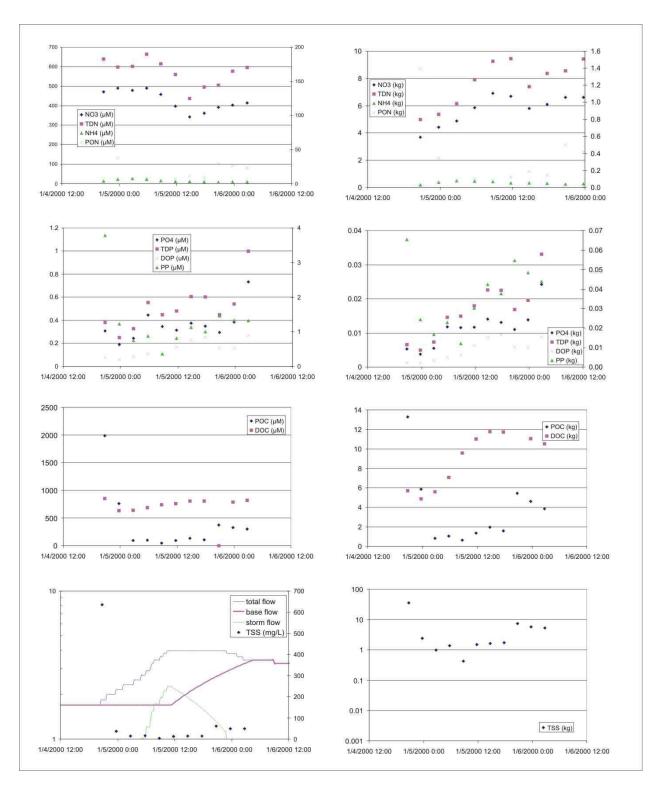


Figure 14. Concentrations (left) and loadings (right) of N, P, and organic C species and suspended solids in Blackwater Creek for a storm in January 2000. For charts with two y-axes, NH4, PON, PP, and TSS are plotted on right axis. Flow in cfs, loads reported for a 3 hour sampling interval.

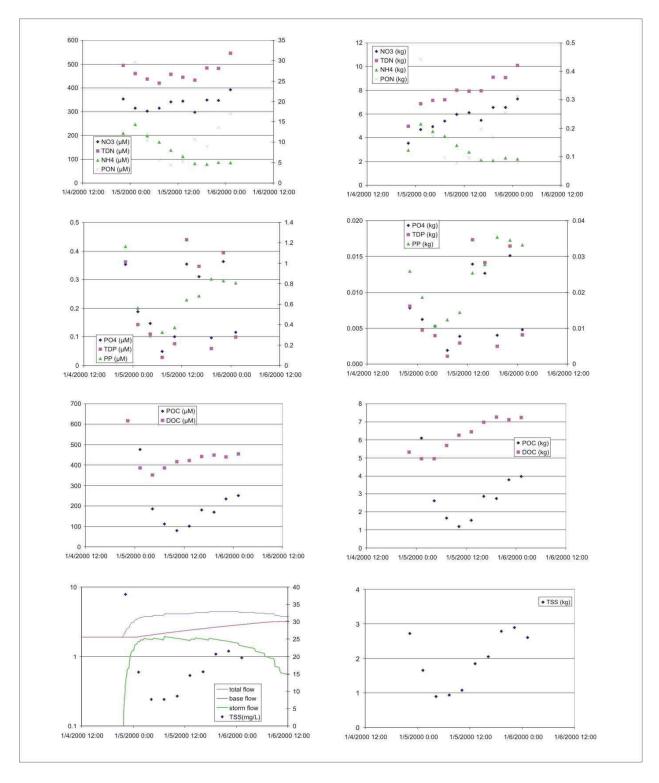


Figure 15. Concentrations (left) and loadings (right) of N, P, and organic C species and suspended solids in Beaverdam Ditch for a storm in January 2000. For charts with two y-axes, NH4, PON, PP, and TSS are plotted on the right axis. Flow in cfs, loads reported for a 3 hour sampling interval.

tabulated in Table 8. The areal loadings are given in Table 9.

There are no simple statistical relationships between the quarterly and annual loadings and land use characteristics because of the small number of stations and the relatively large number of land use characteristics of interest. However, there are some interesting trends in the data (Figure 16, Table 9). For example, Swan Creek had the lowest loading of both dissolved and particulate N, P and organic C of any of the sampled tributaries. Bundicks Branch was a close second for many of these parameters. These two watersheds have the highest fraction of forested land use, and Swan has a lower fraction of agricultural land use than does Bundicks. Both watersheds are located to the north of Indian River Bay and have similar soils and geological settings. Which of these factors are responsible for these low loading rates remains to be determined.

Munchy Branch had the highest areal loading of particulate matter (TSS) of all of the stations sampled and this high loading is reflected in the high areal loading of PON, PP, and POC. This high loading of particulate material may have been the result of the extensive commercial land uses, and associated impervious surfaces, in the watershed.

A rigorous statistical analysis of the relationship between land use and loadings will require the additional analysis of data from the CISNet stations as well as the DNREC stations. These results will be forwarded to DNREC as they become available.

The calculated seasonal loadings (Tables 8 and 9) largely reflect the patterns illustrated in Figures 4 - 9. There is sufficient resolution to calculate monthly loadings of N, P, and OC, but this has not yet been done. The monthly patterns will be more sensitive to recent rainfall than the quarterly loading, but should reflect the patterns discussed above.

Storm-Flow Loadings

During storms, the discharges of nitrogen, phosphorus, and organic carbon result from both base-flow discharges and the additional contributions associated with the storm. The data collected during each storm and at each site were used to calculate the total discharge of these constituents. The total discharge was then divided into the base-flow and storm-flow components based on the estimated base-flow discharges and the concentrations of these constituents during the previous and subsequent base-flow sampling periods, as discussed above. These results are given in Tables 10 (total discharge) and 11 (areally normalized discharges).

The concentrations of dissolved and particulate constituents in storm flow are dependent on many factors that control the mobilization and delivery of the constituents in and to the stream during a storm event. These factors include rainfall amount, intensity and duration, stream flow velocity, amount of soluble and insoluble particulates on the land surface of the watershed prior to the storm, slope and land cover characteristics of the watershed, atmospheric deposition with the storm, ground-water conditions prior to the storm, and others. Because of the large number of potential independent variables and the complex interrelationships between these variables it is not possible at this time to construct statistically valid models of these dependencies. Nonetheless, it is possible to determine overall loading of nitrogen, phosphorus, and organic carbon during storm periods and to divide this discharge into that associated with base flow and that associated with the additional storm loads.

Figure 17 and Table 11 compare unit loadings from storms in July 1999 and January 2000. During individual storm events, it appears that storm flow is two times to 2 orders of magnitude larger than base flow. However, total and unit loads from individual storm events

Table 8. Total base-flow loads (kg) and discharge (m³) per time period specified* for DNREC watersheds (see Table 1). TDN, PON – total dissolved and particulate organic nitrogen, TDP, PP – total dissolved and particulate phosphorus, DOC, POC – dissolved and particulate organic carbon, TSS- total suspended solids, Q – discharge in m³.

Station	Period	TDN	PON	TDP	PP	DOC	POC	TSS	Q
Munchy	IV 98	52	4	0.7	1.4	112	22	281	4.50E+4
Branch	I 99	97	4	0.9	1.7	124	26	576	5.47E+4
	II 99	69	5	0.7	1.4	102	69	762	3.82E+4
	III 99	29	10	0.7	1.9	98	96	789	2.66E+4
	IV 99	26	5	1.4	1.2	186	72	927	3.92E+4
	100	48	2	0.7	0.4	141	24	260	3.63E+4
Sums	WY 99	247	23	3.0	6.5	436	213	2407	1.64E+5
	CY 99	221	24	3.7	6.2	510	263	3054	1.59E+5
Bundicks	IV 98	1595	2	3.7	0.6	513	28	93	3.23E+5
Branch	I 99	1556	2	4.2	0.9	926	66	268	3.23E+5
	II 99	2069	6	8.9	1.8	1590	175	617	5.06E+5
	III 99	1047	5	7.2	1.5	501	72	503	2.41E+5
	IV 99	1475	12	6.2	0.9	1783	81	292	3.74E+5
	100	2228	15	5.5	1.0	2543	142	786	5.05E+5
Sums	WY 99	6268	15	24.0	4.7	3530	341	1481	1.39E+6
	CY 99	6147	24	26.6	5.1	4800	394	1680	1.44E+6
Swan	IV 98	176	2	0.2	0.3	88	27	217	7.44E+4
Creek	I 99	195	1	1.2	0.3	270	54	271	1.20E+5
	II 99	242	2	2.1	0.7	385	117	770	1.64E+5
	III 99	60	4	0.5	0.2	45	68	309	3.00E+4
	IV 99	195	7	1.2	0.6	320	134	701	1.27E+5
	100	217	12	1.5	0.8	514	218	1292	1.48E+5
Sums	WY 99	673	10	4.0	1.5	787	265	1567	3.88E+5
	CY 99	691	15	5.1	1.8	1020	372	2051	4.40E+5
Millsboro	IV 98	1.83E+04	296	78	57	1.28E+4	2.16E+3	1.68E+4	5.57E+6
Pond	I 99	4.98E+4	439	227	155	5.41E+4	5.69E+3	5.79E+4	1.32E+7
	II 99	4.68E+4	256	318	108	6.81E+4	6.43E+3	1.60E+4	1.51E+7
	III 99	9.98E+3	123	91	36	2.18E+4	1.48E+3	5.68E+3	4.83E+6
	IV 99	3.89E+4	184	202	54	6.44E+4	3.11E+3	1.27E+4	1.24E+7
	100	5.99E+4	461	238	81	7.83E+4	6.32E+3	2.20E+4	1.51E+7
Sums	WY 99	1.25E+5	1113	714	356	1.57E+5	1.58E+4	9.63E+4	3.88E+7
	CY 99	1.46E+5	1002	839	354	2.08E+5	1.67E+4	9.23E+4	4.56E+7
Blackwater	IV 98	6.87E+1	0	0.1	0.3	1.15E+2	3	72	1.43E+4
Creek	I 99	5.34E+3	6	9.6	5.4	4.98E+3	184	1276	5.85E+5
	II 99	1.82E+3	4	3.9	3.2	2.60E+3	160	872	2.52E+5
	III 99	2.89E+2	17	1.6	2.8	1.04E+3	140	1228	7.03E+4
	IV 99	4.58E+3	18	4.8	6.2	5.53E+3	255	2062	5.40E+5
	100	9.42E+3	18	8.4	13.7	7.07E+3	202	1372	8.27E+5
Sums	WY 99	7.51E+3	27	15.3	11.7	8.73E+3	486	3447	9.22E+5
	CY 99	1.20E+4	45	20.0	17.6	1.41E+4	738	5438	1.45E+6
Beaverdam	IV 98	174	9	0.7	2.3	585	108	528	9.39E+4
Ditch	I 99	1008	11	1.6	3.3	1051	189	1321	1.82E+5
	II 99	388	8	1.4	2.9	1039	117	1100	1.18E+5
	III 99	235	10	1.5	2.1	757	103	837	9.64E+4
	IV 99	1125	9	1.5	1.9	1467	122	630	2.13E+5
	100	1697	14	1.2	2.3	1206	171	979	2.02E+5
Sums	WY 99	1805	38	5.3	10.6	3432	516	3787	4.90E+5
	CY 99	2756	38	6.1	10.2	4315	531	3889	6.10E+5

*Total loadings for quarters of different lengths IV 98 - 92 days; I 99 - 90 days; II 99 - 91 days; III 99 - 92 days; IV99 - 92 days; I 00 - 91 days. Annual loads are given for water year 99 (WY 99 = 1 Oct. 99-30 Sept. 99) and calendar year 99 (CY 99 = 1 Jan. 99 - 31 Dec. 99)

Table 9.Areal base-flow loads (kg/km²) and discharge (Q, m³/km²) per time period specified* for DNREC watersheds (see Table 1). TDN, PN – total dissolved and particulate organic nitrogen, TDP, PP – total dissolved and particulate phosphorus, DOC, POC – dissolved and particulate organic carbon, TSS- total suspended solids.

Station	Period	TDN	PON	TDP	PP	DOC	POC	TSS	Q
Munchy	IV 98	40	3	0.5	1.1	86	17	216	3.46E+4
Branch	I 99	75	3	0.7	1.3	95	20	443	4.21E+4
	II 99	53	4	0.5	1.1	79	53	586	2.94E+4
	III 99	22	8	0.5	1.4	76	74	607	2.05E+4
	IV 99	20	4	1.1	0.9	143	56	713	3.01E+4
	100	37	2	0.6	0.3	108	19	200	2.79E+4
Sums	WY 99	190	17	2.3	5.0	336	163	1852	1.26E+5
	CY 99	170	18	2.9	4.8	392	202	2349	1.22E+5
Bundicks	IV 98	89	0	0.2	0.0	29	2	5	1.81E+4
Branch	I 99	87	0	0.2	0.1	52	4	15	1.80E+4
	II 99	116	0	0.5	0.1	89	10	34	2.83E+4
	III 99	58	0	0.4	0.1	28	4	28	1.34E+4
	IV 99	82	1	0.3	0.1	100	5	16	2.09E+4
	100	124	1	0.3	0.1	142	8	44	2.82E+4
Sums	WY 99	350	1	1.3	0.3	197	19	83	7.78E+4
_	CY 99	343	1	1.5	0.3	268	22	94	8.06E+4
Swan	IV 98	13	0	0.0	0.0	6	2	16	5.51E+3
Creek	199	14	0	0.1	0.0	20	4	20	8.86E+3
	II 99	18	0	0.2	0.0	28	9	57	1.21E+4
	III 99	4	0	0.0	0.0	3	5	23	2.22E+3
	IV 99 I 00	14 16	1 1	0.1	0.0	24	10	52	9.40E+3
Cume		<u>16</u>	<u>1</u> 1	0.1	0.1	38 58	<u>16</u>	96	1.10E+4
Sums	WY 99 CY 99	50 51	1 1	0.3 0.4	0.1 0.1	56 76	20 28	116 152	2.87E+4 3.26E+4
Millsboro	IV 98	117	2	0.4	0.1	81	14	107	3.54E+4
Pond	I 99	317	3	1.4	1.0	344	36	368	8.41E+4
i ond	II 99	298	2	2.0	0.7	433	41	101	9.64E+4
	III 99	63	1	0.6	0.2	138	9	36	3.07E+4
	IV 99	248	1	1.3	0.3	410	20	81	7.87E+4
	100	381	3	1.5	0.5	498	40	140	9.59E+4
Sums	WY 99	795	7	4.5	2.3	997	100	613	2.47E+5
	CY 99	926	6	5.3	2.3	1325	106	587	2.90E+5
Blackwater	IV 98	8	0	0.0	0.0	13	0	8	1.59E+3
Creek	I 99	593	1	1.1	0.6	554	20	142	6.50E+4
	II 99	202	0	0.4	0.4	289	18	97	2.80E+4
	III 99	32	2	0.2	0.3	115	16	136	7.81E+3
	IV 99	509	2	0.5	0.7	614	28	229	6.00E+4
	100	1046	2	0.9	1.5	786	22	152	9.18E+4
Sums	WY 99	835	3	1.7	1.3	971	54	383	1.02E+5
	CY 99	1336	5	2.2	2.0	1572	82	604	1.61E+5
Beaverdam	IV 98	30	2	0.1	0.4	101	19	91	1.62E+4
Ditch	I 99	174	2	0.3	0.6	181	33	228	3.13E+4
	II 99	67	1	0.2	0.5	179	20	190	2.04E+4
	III 99	40	2 2	0.3	0.4	131	18	144	1.66E+4
	IV 99	194	2	0.3	0.3	253	21	109	3.68E+4
	100	293	2	0.2	0.4	208	29	169	3.48E+4
Sums	WY 99	311	7	0.9	1.8	592	89	653	8.45E+4
	CY 99	475	7	1.1	1.8	744	92	670	1.05E+5

were one or more orders of magnitude smaller than the quarterly base-flow loads (Table 8). Because of the previously cited problems with discharge data, it is not possible to assess the relative magnitudes of all storms and base flow at this time.

Negative stormflow loads (Table 10) are probably a result of uncertainties in estimating base-flow discharge and/or concentrations in base flow during the storm. It is also possible, however, that negative discharge reflects the restriction of discharge from the ground water into the sampled streams (that is the primary source of base flow) when stream elevations rise above ground-water elevations during early parts of storms. With time, base flow resumes when ground water eventually rises higher than stream water elevations in response to recharge and falling stream stage. It is also possible that concentrations of constituents in ground water are overestimated during the storm event. Additional work using stage height to estimate the reduction of the base- flow component will be done.

The reason for the low unit discharge in Swan Creek (Tables 9 and 11; Figures 16 and 17) may be controlled by the underlying geology, which could allow significant amounts of groundwater to bypass the stream system or could reflect the extensive riparian boundary and forest cover in this watershed. The aquifer beneath the area that includes the Swan Creek watershed is highly permeable and unusually thick (Andres, 1992).

Additional analysis of the storm-water discharge results will be done after discharge records have been finalized by USGS. If significant correlations between discharge and nutrient concentrations are found, then this offers promise for estimating and modeling future storm flow loadings. In particular, there is a need to develop and test methods for estimating the unsampled storms at these sites and, perhaps, to infer the storm-water loads for ungaged and unsampled watersheds.

CONCLUSIONS

On the bases of this limited data set alone, there is no simple statistical relationship between land use and land cover and the base-flow discharges of water, nitrogen, phosphorus, suspended solids, and organic carbon. However, this lack of a simple relationship is due to the small number of watersheds and storm events studied and the large number of land use/land cover parameters that describe these watersheds. Continuing studies of an additional group of 7 basins in the Inland Bays watershed, however, may provide the statistical power to properly test for such relationships. This work is in progress as part of the ongoing EPA-funded CISNet project and a newer project funded by the Delaware Water Resources Research Center.

Table 10. Provisional cumulative mass loads (in kg) for storms. TDN, PON – total dissolved and particulate organic nitrogen, TDP, PP – total dissolved and particulate phosphorus, DOC, POC – dissolved and particulate organic carbon, TSS- total suspended solids, Q – discharge in m^3 .

Station	Collection Date	Loading	TDN	PON	TDP	PP	DOC	POC	TSS	Q
Munchy	15-Jul-99	Total	2.04E+00	6.54E-01	7.85E-02	1.46E-01	2.00E+01	9.05E+00	9.02E+00	1.01E+02
Branch		Base	4.64E-01	3.25E-01	1.00E-02	5.81E-02	1.06E+00	2.58E+00	7.40E-01	1.31E+01
		Storm	1.57E+00	3.28E-01	6.85E-02	8.77E-02	1.89E+01	6.47E+00	8.28E+00	8.78E+01
Munchy	23-Sep-99	Total	1.28E+00	6.62E-01	6.40E-02	1.04E-01	1.85E+01	7.62E+00	9.66E+00	1.01E+02
Branch		Base	3.38E-01	3.72E-02	1.00E-02	8.59E-03	1.45E+00	3.67E-01	3.11E-01	1.31E+01
		Storm	9.46E-01	6.25E-01	5.40E-02	9.57E-02	1.70E+01	7.25E+00	9.38E+00	8.76E+01
Munchy	19-Oct-99	Total	1.23E+00		6.86E-02	8.85E-02			4.00E+00	1.29E+02
Branch		Base	3.79E-01	4.28E-02	1.13E-02	1.03E-02	1.23E+00	6.43E-01	1.15E+00	1.28E+01
		Storm	8.47E-01		5.73E-02	7.82E-02			2.85E+00	1.16E+02
Munchy	6-Jan-00	Total	4.36E-01	6.19E-02	2.72E-02	1.17E-02	4.34E+00	1.12E+00	1.24E+00	2.63E+01
Branch		Base	4.34E-01	3.76E-02	7.66E-03	5.39E-03	1.82E+00	2.99E-01	2.01E-01	1.46E+01
		Storm	3.71E-02	2.43E-02	2.02E-02	6.33E-03	2.67E+00	8.18E-01	1.03E+00	1.16E+01
Bundicks	15-Jul-99	Total	3.09E+01	1.90E+00	2.24E-01	2.80E-01	7.37E+01	2.22E+01	1.40E+01	3.95E+02
Branch		Base	2.07E+01	1.65E-01	1.36E-01	8.15E-03	9.40E+00	1.85E+00	1.29E+00	1.82E+02
		Storm	1.02E+01	1.74E+00	8.82E-02	2.72E-01	6.64E+01	2.04E+01	1.29E+01	2.13E+02
Bundicks	23-Sep-99	Total	3.66E+01	3.04E+00	5.03E-01	6.35E-01	3.00E+02	3.84E+01	4.04E+01	7.23E+02
Branch		Base	1.81E+01	3.95E-03	1.63E-01	9.17E-02	1.28E+01	8.63E-01	3.17E-01	1.47E+02
		Storm	1.84E+01	2.91E+00	3.45E-01	5.32E-01	2.87E+02	3.60E+01	3.86E+01	6.27E+02
Bundicks	19-Oct-99	Total	3.44E+01	4.55E+00	4.18E-01	6.46E-01		5.77E+01	3.43E+01	8.01E+02
Branch		Base	1.82E+01	7.62E-03	1.01E-01	5.39E-03	1.46E+01	5.23E-01	3.07E-01	1.35E+02
		Storm	1.63E+01	4.54E+00	3.17E-01	6.41E-01		5.72E+01	3.39E+01	6.66E+02
Bundicks	6-Jan-00	Total	3.15E+01	7.29E-01	2.83E-01	6.60E-02	9.87E+01	1.34E+01	8.17E+00	3.43E+02
Branch		Base	2.61E+01	2.84E-01	5.78E-02	7.30E-03	2.69E+01	1.88E+00	6.69E-01	2.28E+02
		Storm	3.12E+00	4.21E-01	2.20E-01	5.81E-02	6.95E+01	1.14E+01	7.44E+00	1.16E+02
Bundicks	13-Mar-00	Total	3.01E+01	1.40E+00	2.00E-01	1.93E-01	3.96E+01	2.22E+01	2.94E+01	2.64E+02
Branch		Base	2.97E+01	2.43E-01	8.71E-02	1.98E-02	3.89E+01	2.01E+00	1.14E+00	2.39E+02
		Storm	3.46E-01	1.16E+00	1.13E-01	1.73E-01	6.35E-01	2.02E+01	2.82E+01	2.45E+01
Swan	15-Jul-99	Total	3.66E+00	1.60E+00	4.06E-02	7.63E-02		2.50E+01	4.63E+00	5.97E+01
Creek		Base	1.05E+00	1.07E-01	4.94E-03	6.90E-03	6.91E-01	1.81E+00	8.59E-01	2.19E+01
		Storm	2.52E+00	1.49E+00	3.31E-02	6.83E-02		2.31E+01	3.77E+00	6.36E+01
Swan	23-Sep-99	Total	3.67E+00	8.86E-01	3.81E-02	6.65E-02	3.91E+01	1.80E+01	8.07E+00	8.80E+01
Creek		Base	2.26E+00	1.17E-01	2.41E-02	8.35E-03	2.18E+00	2.11E+00	1.01E+00	3.69E+01
		Storm	1.27E+00	3.41E-01	1.22E-02	3.31E-02	3.61E+01	9.19E+00	3.07E+00	5.06E+01
Swan	19-Oct-99	Total	7.56E+00		4.22E-02	9.07E-02			8.96E+00	1.66E+02
Creek		Base	2.87E+00	6.44E-02	2.69E-02	5.42E-03	3.24E+00	1.18E+00	6.40E-01	5.56E+01
		Storm	3.79E+00		1.11E-02	8.03E-02			7.91E+00	1.01E+02
Swan	6-Jan-00	Total	2.86E+00	3.96E-03	1.29E-02	8.37E-04	1.73E+01	6.28E-01	2.37E-01	5.13E+02
Creek		Base	2.34E+00	1.18E-01	6.50E-03	7.01E-03	3.54E+00	2.31E+00	2.34E-01	3.85E+02
		Storm	5.11E-01	-1.14E-01	6.37E-03	-6.17E-03	1.38E+01	-1.68E+00	3.48E-03	1.29E+02
Swan	13-Mar-00	Total	3.31E+00		4.59E-02	2.16E-03	8.15E+00	8.11E-01	7.98E-01	7.61E+01
Creek		Base	3.11E+00	9.06E-02	2.26E-02	2.07E-03	8.51E+00	7.28E-01	2.72E-01	7.28E+01
		Storm	2.01E-01		2.33E-02		-3.65E-01	8.32E-02	5.27E-01	3.23E+00

Table 10. (continued) NOTE: Discharge estimated from ISCO water level record. TDN, PON – total dissolved and particulate organic nitrogen, TDP, PP – total dissolved and particulate phosphorus, DOC, POC – dissolved & particulate organic carbon, TSS- total suspended solids, Q–discharge in m³.

Station	Collection Date	Loading	TDN	PON	TDP	PP	DOC	POC	TSS	Q
Millsboro	15-Jul-99	Total	8.32E+02	9.87E+00	5.79E+00	3.57E+00		1.45E+02	2.67E+03	1.05E+04
Pond		Base	3.44E+02	1.93E+01	3.34E+01	3.29E+01	6.47E+02	7.05E+01	6.49E+01	6.17E+03
		Storm	5.02E+02	4.56E+00	3.31E+00	1.68E+00		8.66E+01	2.61E+03	4.35E+03
Millsboro	23-Sep-99	Total	9.73E+02	8.22E+00	9.20E+00	3.28E+00	4.60E+03	1.07E+02	2.29E+02	1.60E+04
Pond		Base	4.88E+02	1.62E+01	3.49E+01	3.17E+01	1.27E+03	5.57E+01	5.96E+01	6.56E+03
		Storm	3.82E+02	4.87E+00	4.03E+00	2.16E+00	2.60E+03	5.20E+01	4.17E+01	9.41E+03
Millsboro	19-Oct-99	Total	1.25E+03	1.63E+01	6.04E+00	2.88E+00		2.05E+02	8.11E+01	1.47E+04
Pond		Base	6.39E+02	1.80E+00	3.27E+00	8.71E-01	9.30E+02	4.16E+01	2.43E+01	6.80E+03
		Storm	5.35E+02	1.38E+01	2.64E+00	1.79E+00		1.51E+02	6.89E+01	7.69E+03
Millsboro	6-Jan-00	Total	1.14E+03	1.25E+01	2.77E+00	2.40E+00	9.16E+02	1.25E+02	8.95E+01	9.87E+03
Pond		Base	8.51E+02	1.96E+01	3.45E+01	3.20E+01	1.06E+03	1.04E+02	3.63E+01	9.08E+03
		Storm	1.50E+02	5.69E+00	-1.34E+00	1.05E+00	-2.63E+02	1.86E+01	5.41E+01	8.07E+02
Millsboro	13-Mar-00	Total	1.14E+03	2.22E-01	6.65E+00	9.23E-01	8.05E+02	3.21E+01	4.03E+01	1.01E+04
Pond		Base	8.74E+02	6.29E+00	2.76E+00	7.35E-01	1.57E+03	4.98E+01	2.85E+01	8.26E+03
		Storm	2.63E+02	-5.12E+00	3.90E+00	1.88E-01	-5.30E+02	-1.02E+01	1.42E+01	1.87E+03
Blackwater	15-Jul-99	Total	5.25E-02	4.33E-03	2.15E-04	1.08E-03	6.31E-01	3.78E-02	3.73E-02	1.35E+01
Creek		Base	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
		Storm	5.25E-02	4.33E-03	2.15E-04	1.08E-03	6.31E-01	3.78E-02	3.73E-02	1.35E+01
Blackwater	19-Oct-99	Total	2.51E+02	4.01E+01	6.58E+00	6.70E+00		3.72E+02	5.88E+02	1.54E+03
Creek		Base	3.30E+01	1.38E-01	6.21E-02	5.36E-02	5.96E+01	2.00E+00	1.74E+00	1.70E+02
		Storm	2.18E+02	4.00E+01	6.52E+00	6.64E+00		3.70E+02	5.87E+02	1.37E+03
Blackwater	6-Jan-00	Total	8.11E+01	3.50E+00	1.71E-01	3.77E-01	8.40E+01	3.83E+01	6.39E+01	3.51E+02
Creek		Base	7.56E+01	1.15E-01	4.75E-02	1.10E-01	6.46E+01	1.69E+00	9.63E-01	2.44E+02
		Storm	5.47E+00	3.38E+00	1.23E-01	2.67E-01	2.73E+01	3.66E+01	6.29E+01	1.07E+02
Blackwater	13-Mar-00	Total	1.43E+01	5.32E-01	2.34E-02	1.43E-01	2.35E+01	6.59E+00	3.03E+01	6.41E+01
Creek		Base	1.43E+01	3.84E-02	1.53E-02	8.83E-03	1.07E+01	3.42E-01	2.44E-01	4.00E+01
		Storm	-7.92E-02	4.93E-01	8.04E-03	1.34E-01	1.28E+01	6.25E+00	3.01E+01	2.41E+01
Beaverdam	20-May-99	Total	3.68E+00	3.95E-01	1.05E-01			3.78E+00	2.97E+01	2.58E+01
Ditch		Base	2.00E+00	1.30E-01	1.28E-02	2.77E-03	9.26E+00	1.13E+00	8.90E+00	1.69E+01
		Storm	1.68E+00	2.66E-01	9.17E-02			2.65E+00	2.08E+01	8.80E+00
Beaverdam	15-Jul-99	Total	3.54E+00	8.40E-01	5.03E-02	1.80E-01	1.89E+01	5.20E+00	4.26E+00	6.18E+01
Ditch		Base	2.38E+00	2.77E-01	2.48E-02	5.18E-02	9.69E+00	2.83E+00	4.37E+00	3.89E+01
		Storm	9.96E-01	5.44E-01	2.37E-02	1.26E-01	8.46E+00	2.26E+00	-2.85E-01	2.42E+01
Beaverdam	19-Oct-99	Total	3.62E+02		2.35E+00	6.71E+00			2.04E+02	2.87E+03
Ditch	note 1	Base	4.97E+01	1.42E+01	3.11E+01	3.11E+01	7.80E+01	1.54E+01	3.21E+00	3.61E+02
		Storm	2.20E+02		1.26E+00	4.24E+00			1.80E+02	2.20E+03
Beaverdam	6-Jan-00	Total	7.41E+01	1.72E+00	7.10E-02	2.25E-01	5.87E+01	2.50E+01	1.95E+01	3.83E+02
Ditch		Base	6.65E+01	1.46E+01	3.10E+01	3.11E+01	5.49E+01	1.83E+01	4.65E+00	2.36E+02
		Storm	2.15E+01	1.19E+00	4.52E-02	1.40E-01	1.59E+01	1.87E+01	1.58E+01	1.46E+02

Table 11. Provisional areal storm loadings (kg/km 2 .) and discharge (m). TDN, PON – total dissolved and particulate organic nitrogen, TDP, PP – total dissolved and particulate phosphorus, DOC, POC – dissolved and particulate organic carbon, TSS- total suspended solids, Q – discharge in m.

Station	Collection Date	Loading	TDN	PON	TDP	PP	DOC	POC	TSS	Q
Munchy	15-Jul-99	Total	1.57E+00	5.03E-01	6.04E-02	1.12E-01	1.54E+01	6.96E+00	6.94E+00	7.76E-02
Branch		Base	3.57E-01	2.50E-01	7.71E-03	4.47E-02	8.17E-01	1.99E+00	5.69E-01	1.01E-02
		Storm	1.21E+00	2.52E-01	5.27E-02	6.75E-02	1.45E+01	4.98E+00	6.37E+00	6.75E-02
Munchy	23-Sep-99	Total	9.88E-01	5.09E-01	4.93E-02	8.02E-02	1.42E+01	5.86E+00	7.43E+00	7.74E-02
Branch		Base	2.60E-01	2.86E-02	7.69E-03	6.61E-03	1.11E+00	2.82E-01	2.39E-01	1.01E-02
		Storm	7.27E-01	4.81E-01	4.16E-02	7.36E-02	1.31E+01	5.58E+00	7.21E+00	6.74E-02
Munchy	19-Oct-99	Total	9.43E-01		5.28E-02	6.80E-02			3.08E+00	9.94E-02
Branch		Base	2.91E-01	3.29E-02	8.68E-03	7.91E-03	9.46E-01	4.94E-01	8.85E-01	9.88E-03
		Storm	6.52E-01		4.41E-02	6.01E-02			2.19E+00	8.95E-02
Munchy	6-Jan-00	Total	3.35E-01	4.76E-02	2.10E-02	9.02E-03	3.34E+00	8.59E-01	9.51E-01	2.02E-02
Branch		Base	3.34E-01	2.89E-02	5.89E-03	4.15E-03	1.40E+00	2.30E-01	1.55E-01	1.12E-02
		Storm	2.85E-02	1.87E-02	1.55E-02	4.87E-03	2.05E+00	6.29E-01	7.96E-01	8.95E-03
Bundicks	15-Jul-99	Total	1.73E+00	1.06E-01	1.25E-02	1.56E-02	4.12E+00	1.24E+00	7.83E-01	2.20E-02
Branch		Base	1.16E+00	9.23E-03	7.61E-03	4.55E-04	5.25E-01	1.03E-01	7.18E-02	1.02E-02
		Storm	5.68E-01	9.69E-02	4.93E-03	1.52E-02	3.71E+00	1.14E+00	7.18E-01	1.19E-02
Bundicks	23-Sep-99	Total	2.04E+00	1.70E-01	2.81E-02	3.55E-02	1.67E+01	2.15E+00	2.26E+00	4.04E-02
Branch		Base	1.01E+00	2.21E-04	9.10E-03	5.12E-03	7.14E-01	4.82E-02	1.77E-02	8.21E-03
		Storm	1.03E+00	1.63E-01	1.92E-02	2.97E-02	1.60E+01	2.01E+00	2.16E+00	3.50E-02
Bundicks	19-Oct-99	Total	1.92E+00	2.54E-01	2.33E-02	3.61E-02		3.22E+00	1.91E+00	4.48E-02
Branch		Base	1.01E+00	4.26E-04	5.63E-03	3.01E-04	8.16E-01	2.92E-02	1.71E-02	7.55E-03
		Storm	9.09E-01	2.54E-01	1.77E-02	3.58E-02		3.20E+00	1.90E+00	3.72E-02
Bundicks	6-Jan-00	Total	1.76E+00	4.08E-02	1.58E-02	3.69E-03	5.52E+00	7.51E-01	4.56E-01	1.92E-02
Branch		Base	1.46E+00	1.58E-02	3.23E-03	4.08E-04	1.50E+00	1.05E-01	3.74E-02	1.27E-02
		Storm	1.74E-01	2.35E-02	1.23E-02	3.25E-03	3.88E+00	6.36E-01	4.16E-01	6.50E-03
Bundicks	13-Mar-00	Total	1.68E+00	7.84E-02	1.12E-02	1.08E-02	2.21E+00	1.24E+00	1.64E+00	1.47E-02
Branch		Base	1.66E+00	1.36E-02	4.86E-03	1.10E-03	2.18E+00	1.12E-01	6.36E-02	1.34E-02
		Storm	1.93E-02	6.48E-02	6.29E-03	9.69E-03	3.55E-02	1.13E+00	1.58E+00	1.37E-03
Swan	15-Jul-99	Total	2.71E-01	1.18E-01	3.01E-03	5.65E-03		1.85E+00	3.43E-01	4.42E-03
Creek		Base	7.81E-02	7.89E-03	3.66E-04	5.11E-04	5.12E-02	1.34E-01	6.36E-02	1.62E-03
		Storm	1.87E-01	1.10E-01	2.45E-03	5.06E-03		1.71E+00	2.80E-01	4.71E-03
Swan	23-Sep-99	Total	2.72E-01	6.56E-02	2.82E-03	4.93E-03	2.90E+00	1.33E+00	5.98E-01	6.52E-03
Creek		Base	1.68E-01	8.67E-03	1.78E-03	6.18E-04	1.62E-01	1.56E-01	7.46E-02	2.73E-03
		Storm	9.40E-02	2.52E-02	9.02E-04	2.45E-03	2.67E+00	6.81E-01	2.27E-01	3.75E-03
Swan	19-Oct-99	Total	5.60E-01		3.13E-03	6.72E-03		0.00E+00	6.63E-01	1.23E-02
Creek		Base	2.12E-01	4.77E-03	1.99E-03	4.01E-04	2.40E-01	8.76E-02	4.74E-02	4.12E-03
		Storm	2.81E-01		8.19E-04	5.94E-03		0.00E+00	5.86E-01	7.49E-03
Swan	6-Jan-00	Total	2.12E-01	2.93E-04	9.53E-04	6.20E-05	1.28E+00	4.66E-02	1.76E-02	3.80E-02
Creek		Base	1.74E-01	8.74E-03	4.81E-04	5.19E-04	2.62E-01	1.71E-01	1.73E-02	2.85E-02
		Storm	3.78E-02	-8.45E-03	4.72E-04	-4.57E-04	1.02E+00	-1.25E-01	2.58E-04	9.53E-03
Swan	13-Mar-00	Total	2.45E-01	1.79E-03	3.40E-03	1.60E-04	6.03E-01	6.01E-02	5.91E-02	5.63E-03
Creek		Base	2.31E-01	6.71E-03	1.67E-03	1.53E-04	6.30E-01	5.39E-02	2.01E-02	5.39E-03
		Storm	1.49E-02	0.00E+00	1.73E-03	0.00E+00	-2.70E-02	6.16E-03	3.90E-02	2.39E-04

Table 11 (continued). NOTE: Discharge estimated from ISCO water level record. TDN, PON – total dissolved and particulate organic nitrogen, TDP, PP – total dissolved and particulate phosphorus, DOC, POC – dissolved and particulate organic carbon, TSS- total suspended solids, Q – discharge in m.

Station	Collection Date	Loading	TDN	PON	TDP	PP	DOC	POC	TSS	Q
Millsboro	15-Jul-99	Total	5.29E+00	6.28E-02	3.68E-02	2.27E-02	0.00E+00	9.23E-01	1.70E+01	6.70E-02
Pond		Base	2.19E+00	1.23E-01	2.13E-01	2.09E-01	4.12E+00	4.49E-01	4.13E-01	3.93E-02
		Storm	3.19E+00	2.90E-02	2.11E-02	1.07E-02	0.00E+00	5.51E-01	1.66E+01	2.77E-02
Millsboro	23-Sep-99	Total	6.19E+00	5.23E-02	5.85E-02	2.09E-02	2.92E+01	6.79E-01	1.45E+00	1.02E-01
Pond		Base	3.10E+00	1.03E-01	2.22E-01	2.02E-01	8.06E+00	3.54E-01	3.79E-01	4.17E-02
		Storm	2.43E+00	3.10E-02	2.56E-02	1.37E-02	1.66E+01	3.31E-01	2.66E-01	5.98E-02
Millsboro	19-Oct-99	Total	7.98E+00	1.03E-01	3.84E-02	1.83E-02		1.31E+00	5.16E-01	9.33E-02
Pond		Base	4.06E+00	1.15E-02	2.08E-02	5.54E-03	5.92E+00	2.65E-01	1.55E-01	4.33E-02
		Storm	3.40E+00	8.77E-02	1.68E-02	1.14E-02		9.61E-01	4.38E-01	4.89E-02
Millsboro	6-Jan-00	Total	7.28E+00	7.94E-02	1.76E-02	1.53E-02	5.83E+00	7.98E-01	5.69E-01	6.28E-02
Pond		Base	5.41E+00	1.25E-01	2.19E-01	2.04E-01	6.72E+00	6.64E-01	2.31E-01	5.78E-02
		Storm	9.54E-01	3.62E-02	-8.50E-03	6.67E-03	-1.67E+00	1.18E-01	3.44E-01	5.13E-03
Millsboro	13-Mar-00	Total	7.24E+00	1.41E-03	4.23E-02	5.87E-03	5.12E+00	2.04E-01	2.56E-01	6.44E-02
Pond		Base	5.56E+00	4.00E-02	1.75E-02	4.68E-03	9.97E+00	3.17E-01	1.81E-01	5.25E-02
		Storm	1.68E+00	-3.26E-02	2.48E-02	1.20E-03	-3.37E+00	-6.50E-02	9.06E-02	1.19E-02
Blackwater	15-Jul-99	Total	5.84E-03	4.81E-04	2.38E-05	1.20E-04	7.01E-02	4.20E-03	4.15E-03	1.50E-03
Creek		Base	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
		Storm	5.84E-03	4.81E-04	2.38E-05	1.20E-04	7.01E-02	4.20E-03	4.15E-03	1.50E-03
Blackwater	19-Oct-99	Total	2.79E+01	4.46E+00	7.32E-01	7.44E-01		4.14E+01	6.54E+01	1.71E-01
Creek		Base	3.66E+00	1.53E-02	6.90E-03	5.96E-03	6.62E+00	2.23E-01	1.94E-01	1.88E-02
		Storm	2.42E+01	4.45E+00	7.25E-01	7.38E-01		4.11E+01	6.52E+01	1.52E-01
Blackwater	6-Jan-00	Total	9.01E+00	3.89E-01	1.90E-02	4.19E-02	9.33E+00	4.25E+00	7.10E+00	3.90E-02
Creek		Base	8.40E+00	1.28E-02	5.28E-03	1.22E-02	7.17E+00	1.88E-01	1.07E-01	2.71E-02
		Storm	6.08E-01	3.76E-01	1.37E-02	2.97E-02	3.03E+00	4.06E+00	6.99E+00	1.19E-02
Blackwater	13-Mar-00	Total	1.58E+00	5.91E-02	2.60E-03	1.59E-02	2.61E+00	7.32E-01	3.37E+00	7.13E-03
Creek		Base	1.59E+00	4.27E-03	1.70E-03	9.81E-04	1.19E+00	3.81E-02	2.71E-02	4.45E-03
		Storm	-8.80E-03	5.48E-02	8.94E-04	1.49E-02	1.42E+00	6.94E-01	3.34E+00	2.68E-03
Beaverdam	20-May-99	Total	6.34E-01	6.82E-02	1.80E-02	0.00E+00		6.52E-01	5.12E+00	4.44E-03
Ditch	-	Base	3.46E-01	2.23E-02	2.21E-03	4.78E-04	1.60E+00	1.94E-01	1.54E+00	2.92E-03
		Storm	2.89E-01	4.58E-02	1.58E-02	0.00E+00		4.57E-01	3.58E+00	1.52E-03
Beaverdam	15-Jul-99	Total	6.10E-01	1.45E-01	8.67E-03	3.10E-02	3.26E+00	8.97E-01	7.35E-01	1.07E-02
Ditch		Base	4.10E-01	4.77E-02	4.28E-03	8.92E-03	1.67E+00	4.89E-01	7.54E-01	6.70E-03
		Storm	1.72E-01	9.37E-02	4.09E-03	2.17E-02	1.46E+00	3.89E-01	-4.91E-02	4.18E-03
Beaverdam	19-Oct-99	Total	6.24E+01		4.06E-01	1.16E+00			3.51E+01	4.96E-01
Ditch	note 1	Base		2.46E+00			1.34E+01	2.66E+00		
		Storm	3.79E+01			7.31E-01			3.10E+01	
Beaverdam	6-Jan-00	Total		2.96E-01			1.01E+01	4.31E+00		
Ditch		Base					9.46E+00			
		Storm					2.74E+00			

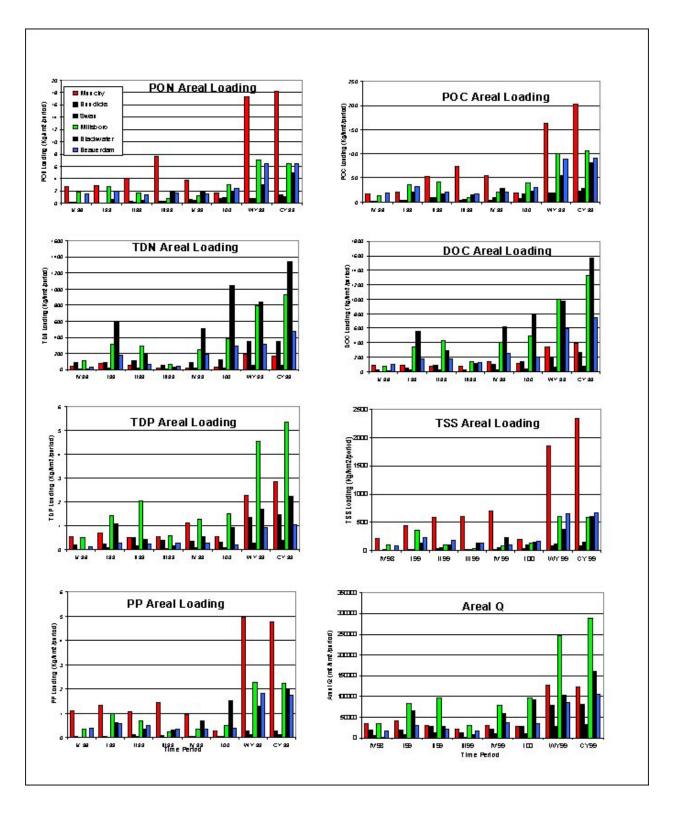


Figure 16. Comparison of quarterly areal base-flow loading rates of N, P, C, and suspended solids. Legend for all charts is in the top left chart.

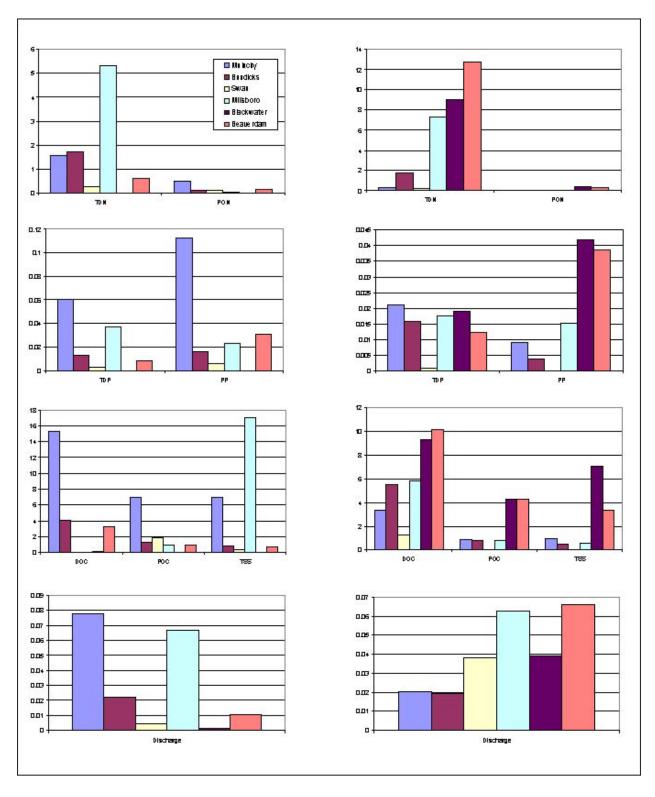


Figure 17. Comparision of areal loadings of N, P, C, and suspended solids and unit discharge for two storms (July 1999 and January 2000). Legend for all charts is in top left chart. Discharge in cfs, loadings in kg/square km.

REFERENCES CITED

- Andres, A. S., 1992, Estimate of nitrate flux to Rehoboth and Indian River Bays, Delaware: Delaware Geological Survey Open File Report No. 35, 36 p.
- Andres, A. S., Savidge, K., Scudlark, J. R., and Ullman, W., 2002, Delaware Inland Bays tributary Total Maximum Daily Load water-quality database: Delaware Geological Survey Digital Data Geological Digital Data Product 02-01.
- Delaware Office of State Planning Coordination, 1999. Gross land use changes in Delaware, 1992 to 1997. http://www.state.de.us/planning/info/lulcdata/change/lulcchng.htm
- D'Elia, C. F., Steudler, P. A., and Corwin, N., 1977, Determination of total nitrogen in aqueous samples using persulfate digestion. Limnology and Oceanography v. 22, p. 760-764.
- ESRI, 2000, ArcView GIS, version 3.2, Redlands, CA, Environmental Systems Research Institute, Inc. Gray, D. M., ed., 1970, Handbook on the principles of hydrology: Port Washington, New York, Water Information Center, Inc.
- Glibert, P. M. and Loder, T. C., 1977, Automated analysis of nutrients in seawater: A manual of techniques. Woods Hole Oceanographic Institution Technical Report WHOI-77-47, 46 p.
- Grasshoff, K. and Johansen, J., 1972, A new sensitive and direct method for the automatic determination of ammonia in seawater: Journal de Conseil, Conseil International pour l'Exploration de la Mer v. 34, p. 516-521.
- Johnston, R. H., 1976, Relation of ground water to surface water in four small basins of the Delaware Coastal Plain: Delaware Geological Survey Report of Investigations No. 24, 56 p.
- Mackenzie, J., Martin, J. H., Pintea, L, Boonmee, B., Gedamu, N., and Thomas, T. C., 1999, Delaware Inland Bays watershed nutrient management project. http://www.udel.edu/FREC/spatlab/>.
- Mackenzie, J., and McCullough, P., 1999, Delaware land-use/land cover transitions 1984 -- 1992 . http://www.udel.edu/FREC/spatlab/>
- Maidment, D.R., ed., 1993, Handbook of hydrology: New York, McGraw-Hill, Inc.
- Parsons, T. R., Maita, Y., and Lalli, C.M., 1984, A manual of chemical and biological methods for seawater analysis: Pergamon Press, New York, 173 p.
- Sharp, J. H., Rinker, K. R., and Savidge, K. B., in press, A preliminary methods comparison for measurement of dissolved organic nitrogen in seawater: Marine Chemistry.
- Solórzano, L., and Sharp, J. H., 1980a, Determination of total dissolved phosphorus and particulate phosphorus in natural waters: Limnology and Oceanography v. 25, p.754-758.
- ____ 1980b, Determination of total dissolved nitrogen in natural waters: Limnology and Oceanography v. 25, p. 751-754.
- Strickland, J. D. H., and Parsons, T. R., 1972, A Practical Handbook of Seawater Analysis, 2nd Edition. Bulletin of the Fisheries Research Board of Canada, 310 p.