Water Quality Monitoring in the Source Water Areas for New York City: An Integrative Watershed Approach

A Report on Year 4 (2003) Monitoring Activities

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Table of Contents

Table of common abbreviations used in this report.

Abbreviation	Description
1MP	1-methyl phenanthrene
2MP	2-methyl phenanthrene
aCOP	Cholestanol
AFDM	Ash Free Dry Mass
AHTN	Tonalide
ALKL	Alkalinity
ANOVA	Analysis of Variance
ANT	Anthracene
aONE	Cholestanone
BAA	Benzo(a)anthracene
BAP	Benzo(a)pyrene
BBF	Benzo(b)fluoranthrene
bCOP	coprostanol
BDOC	Biodegradable Dissolved Organic Carbon
BKF	Benzo(k)fluoranthene
BMP	Best Management Practice
BOD	Biological Oxygen Demand
BOM	Benthic Organic Matter
Ca	Calcium
CAF	Caffeine
CCS	Continuing Calibration Standards
CHOL	Cholesterol
CHR	Chrysene
Cl	Chloride
cm	centimeter
CO_2	Carbon Dioxide
CoIA	Co-Inertia Analysis
COND	Specific Conductance
CR24	Community Respiration
CV	Coefficient of Variation
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
DON	Dissolved Organic Nitrogen
eCOP	24-ethyl-coprostanol
EOH	East of Hudson Watersheds (a.k.a., Croton-Kensico System)
EPI	Epicoprastanol
EPT	Ephemeroptera, Plecoptera, and Trichoptera
FB	Field Blank
FD	Field Duplicate
FLR	Fluoranthene
FLU	Fluorene
FM	Fragrance Materials
FS	Fecal Steroids
GF/F	Glass Fiber Filters
GIS	Geographic Information System
GPP	Gross Primary Productivity
GPS	Global Positioning System
h	hour
H/LPAH	High-to-Low Molecular Ration for PAHs
HBI	Hilsenhoff Biotic Index
HDPE	High Density Polyethylene
HEV	Hydraulic Uptake Velocity
HHCB	Galaxolide
HMW	High Molecular Weight
ID	inner diameter
ISCO	Automated field water sampling device

Abbreviation	Description
K	Potassium
L	Liter
LB	Lab Blank
LCS	Laboratory Control Standard
LMW	Low Molecular Weight
MDL	Method Detection Limit
Mg	Magnesium
min	minute
mL	milliliter
MLR	Multiple Linear Regression
MS	Matrix Spike
Na	Sodium
NDM	Net Daily Metabolism
NH_4-N	Ammonium Nitrogen
NO_3-N	Nitrate Nitrogen
NUTW	Whole water (unfiltered) nutrient sample
NY DEC	New York State Department of Environmental Conservation
NYC	New York City
NYCDEP	New York City Department of Environmental Protection
NYS DOH	New York State Department of Health
NYSDEC	New York State Department of Environmental Conservation
OD	Optical Density
OM	Organic Matter
OTIS	One Dimensional Transport In Streams
PAH	Polycyclic Aromatic Hydrocarbons
PAR	Photosynthetically Active Radiation
PCA	Principal Components Analysis
PD	Percent Difference
PHE	Phenanthrene
PMA	Percent Model Affinity
PYR	Pyrene
QA/QC	Quality Assurance Quality Control
QAPP	Quality Assurance Project Plan
RPD	Relative Percent Difference
SAS	Statistical Software Package in use at Stroud
SD	Standard Deviation
sec	second
SKN	Soluble Kjeldahl Nitrogen
SNOL	24-ethylcholestanol
SO_4	Sulfate
SOP	Standard Operating Procedure
SPDES	State Pollutant Discharge Elimination System
SRM	Surface Reaeration Model
SRP	Soluble Reactive Phosphorus
SWRC	Stroud Water Research Center
TDP	Total Dissolved Phosphorus
TKN	Total Kjeldahl Nitrogen
TM	Thematic Mapper
TP	Total Phosphorus
TSS	Total Suspended Solids
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
v_f	Uptake Velocity
VSS	Volatile Suspended Solids
WOH	West of Hudson Watersheds (a.k.a., Catskill-Delaware)
WQS	Water Quality Score (Macroinvertebrate based)
WWTP	Waste Water Treatment Plant

Chapter 1 - Introduction

The drinking water industry in the United States and abroad now recognizes that protecting the sources of fresh water is a critical component of any long-term plan for a drinking water system. With this recognition has come a new understanding of the central role that watersheds – and their aquatic ecosystems – play in the filtration/treatment process that is necessary to provide clean, safe drinking water to the public in the most cost-effective way. Source water protection requires managing these water supply watersheds and ecosystems. Consequently, a successful management plan for New York City's drinking water must be based on a solid understanding of the streams and the watersheds they drain in order to make source watershed protection a reality.

Watersheds and their ecosystems have three critical functions: (i) they are the ultimate sources of water; (ii) they are major sources of naturally occurring and anthropogenic constituents (physical, chemical, and biological) in water; and (iii) they are primary natural processors of water-borne constituents. Because past, present, and future land-use activities in source water areas affect each of these functions, successful source water protection requires an "Integrated Watershed Approach" to assess sources, impacts, and processes relavent to the streams and reservoirs of the source area.

A monitoring program for drinking water source areas should focus primarily on constituents of natural and anthropogenic origin (hereafter contaminants) that can, at certain concentrations, contaminate water and render it unsuitable for human consumption and/or unable to support wildlife. An integrated watershed approach to contaminant dynamics in the NYC source area needs to recognize four basic elements: Source, Transport, Ecosystem Impairment, and Symptom. The existing monitoring programs, like most other source water programs, include strong elements of Transport (levels of contaminants in the source water and distribution system, consisting of streams, rivers, reservoirs, and distribution pipes) and Symptom (turbidity, oxygen deficits, taste and odor, disinfection byproduct formation potential, etc.). These elements are driven by local, state, and federal regulations and by operational needs (understanding ambient quality of water for treatment purposes). This program, which focuses on elements of Ecosystem Impairment and Source, is intended to enhance on-going efforts by introducing both new study variables and a different scale (spatial and temporal) for certain study variables.

Each contaminant in the NYC system has a source. Identifying the historical and current sources of the principal contaminants in the various watersheds and sub-watersheds is critical to developing long-term plans for current remediation and future protection and development. This requires an intensive and coordinated spatial and temporal sampling program as well as sophisticated analytical

techniques that can distinguish among the various possible sources of contaminants within each of the NYC source watersheds.

Each contaminant is capable of causing some impairment to streams, rivers, and reservoirs of the NYC water supply system. This impairment can cause a change in the structural and/or functional properties of the ecosystem which renders it unable to effectively or efficiently utilize, process, metabolize, or otherwise sequester materials, including contaminants entering from the watershed.

Careful assessment of contaminant sources in watersheds supplying NYC drinking water and of key structural and functional properties of streams, rivers, and reservoirs in the NYC distribution system will provide: (i) a basis for measuring spatial variation in the source of contaminants and their impacts on ecosystem functioning and biological communities; (ii) a basis for measuring temporal/spatial change in both the source of contaminants and their impacts on stream, river, and reservoir functionality; and (iii) a stronger scientific basis for the overall management plan for the NYC source water area.

The principal objectives of this monitoring program have been:

1. To provide dependent variables for statistical analyses relating aquatic ecosystem structure and function to land use, best management practice (BMP) implementation, and other watershed inputs or factors.

2. To provide chemical and biological indicators for evaluating the occurrence and source of selected aquatic contaminants.

3. To provide a baseline data set of population, community and ecosystem-level variables and molecular indicators of contaminants to assess changes in water quality and aquatic ecosystem structure and function in response to on-going and/or future shifts in land use/cover. For example, (i) quantitative measures of stream ecosystem structure/function can be used in a before-after analytical framework; or (ii) measurements made across sites help define the true range of conditions throughout these watersheds. This range can them be compared to future changes to understand improvements or degradations at specific points in a watershed.

Data from Source and Ecosystem Impairment monitoring will put into perspective: (i) the magnitude and complexity of contaminant/source issues throughout the NYC source water area and (ii) the current status of ecosystem health within the NYC source water system (i.e., where the ability to process excess nutrients in watersheds is in good to excellent condition and where that ability has been compromised). In addition, these data will provide a baseline for measuring success of on-going remediation efforts in NYC source water areas and will be helpful in

designing/implementing future remediation or conservation efforts (e.g., BMP, stream restoration, zoning) as part of an overall NYC management plan.

This monitoring program was designed to complement existing programs of the New York State Department of Environmental Conservation (NYS DEC), New York City Department of Environmental Protection (NYC DEP), United States Environmental Protection Agency (US EPA), and the New York State Department of Health (NYS DOH), as well as programs under the direction of -- and/or in cooperation with -- the various counties in the study area. Several of the principal study elements in this program were not monitored by any of the above groups at the outset of this endeavor. While one or more groups are monitoring some elements (or parts of an element) they are doing so with lower spatial intensity and, in some cases, less accuracy or precision. Although the Stroud Center's program was designed to have some overlap of study site locations with NYS DEC and NYC DEP programs, to allow data generated from each program to supplement and add perspective to one another, this program is an independent effort designed to enhance overall monitoring in these source areas.

This report details year 4 (2003; Phase II year 1) of this project. A technical overview of the study design and study site descriptions (Chapter 2) is followed by separate chapters on specific tasks of the program: Nutrients, Ions, and Particulates in Transport (Chapter 3); Molecular Tracers Analysis (Chapter 4); Macroinvertebrate Community Structure and Function (Chapter 5); Dissolved Organic Carbon (DOC) and Biodegradable Dissolved Organic Carbon (BDOC) Dynamics (Chapter 6); Nitrogen (N), Phosphorus (P), and DOC Spiraling (Chapter 7); Net Stream Metabolism (Chapter 8); and Algal Productivity (Chapter 9).

Each chapter contains an overview of field and laboratory methods along with a results and discussion of data from year four research/monitoring activities. A summary of quality assurance/quality control (QA/QC) efforts for the fourth year of monitoring is also included in the Appendix. Data discussion focuses on year four and describes how data within each task characterized individual study sites, subwatersheds, and the two regions (East and West of the Hudson River) that comprise the NYC source water areas. Integration across monitoring tasks and comparison to Phase I results, to the extent possible, are also discussed.

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Chapter 2 - Technical Design

Overview

This project was designed as a six-year study divided into two discrete three-year phases; Phase I from 2000 to 2002 and Phase II from 2003-2005. Drinking water source areas are located in primary locations referred to as East of Hudson (EOH; a.k.a., Croton/Kensico System) watersheds and West of Hudson (WOH; a.k.a., Catskill/Delaware System) watersheds (Figs. 2.1 and 2.2).

During Phase I, annual studies of various project elements at 60 stream and 8 reservoir stations were performed. Each element was studied at a specified portion of study sites. These activities were replicated in Phase II but occurred at new locations throughout the source watersheds. The scientific strength of this program is a result of the kinds and number of elements measured, spatial scope of the study (108 stream and 14 reservoir stations visited over 6 years) and its replication over time.

In Phase I, 60 stream (30 EOH, 30 WOH) and eight reservoir (2 EOH, 6 WOH) sampling stations were established (Phase I reports online: http://www.stroudcenter.org/research/newyorkproject.htm) to provide complete spatial coverage of source watersheds. For Phase II, 48 new (differing from Phase I) stream stations were established, and monitoring at 12 of the Phase I stations has continued (Tables 2.1 through 2.4; 27 EOH, 33 WOH stations). Continued monitoring at the 12 Phase-I stations during Phase II tie these phases together for a continuous temporal perspective. Reservoir monitoring stations in Phase II occur in seven (7) reservoirs (Figs. 2.5 and 2.6). Four stations were located in new reservoirs, two within reservoirs studied in Phase I but with new substation locations, and one within a Phase I reservoir at the same Phase I substations (Figs. 2.3 and 2.4, Table 2.5 and 2.6). All of theses stations will be subject to annual monitoring reported herein for three years (through 2005).

Selection of new sampling stations was based on a combination of (i) “areas of concern” revealed during Phase I, (ii) desire to broaden spatial coverage within source watersheds, and (iii) the need to measure, quantify, and determine more sources and effects of contaminants in watersheds and the present condition and ability of existing ecosystems to process both natural and unnatural (contaminants) watershed inputs. In general, new stream sites were located on other important tributaries to primary reservoirs in the system or further upstream in the watershed from Phase I stations.

Phase I stream sampling stations were distributed among the major sub-basins of the principal source watersheds (designated as 50 "targeted" and 10 "integrative" sampling stations depending on the project elements being measured at each

station). Criteria for selecting Phase I study sites were as follows: (1) land use (forested — upland and riparian; agriculture — row crop, dairy, and beef; suburban — septic and sewage treatment, road runoff, fertilization, pesticides; urban — waste water treatment plants, urban runoff); (2) Gauged stream flow (USGS records); (3) NYC DEP / NY DEC / EPA study or demonstration sites; (4) NYC DEP / NY DEC / EPA / County background data; (5) BMP's in progress, BMP implementation, or BMP pending implementation; (6) Feasibility in studying various elements of our monitoring program.

Selection of Phase II study sites was a combination of the above but relied more heavily on providing information that would supplement Phase I results. For example, Phase I integrative sites in EOH watersheds lacked a "least-impaired" site, while integrative sites in the WOH watersheds lacked an impacted site. Integrative stations occurred sufficiently downstream in a watershed to integrate effects of land use and other factors on a given project element or task under study over a large portion of the watershed. Further, at "Integrative" stations monitoring activities included detailed study of nutrient spiraling and stream metabolism (see Chapters 7 and 8, respectively). In some instances 'downstream' distance was constrained by feasibility of one or more of the study elements. For Phase II, we selected sites that potentially "filled" these gaps along measured "impact gradients". For "targeted" stations, site selection included new sites in major tributaries not sampled in Phase I. "Targeted" stations occurred on streams of varying size and monitoring activities were limited to measurement of nutrients, major ions, and organic particles in transport, molecular tracers, dissolved organic carbon dynamics, and macroinvertebrate communities (see Chapters 3-6). Also, in a few instances new "targeted" sites were selected to be upstream of potential negative impacts to water quality in "degraded" Phase I sites to help identify "areas of concern". Finally, several "targeted" sites were selected to broaden the spatial extent of this program (i.e., moving even further upstream).

Overall project design was intended to: (i) expand understanding of sources of principal contaminants in "source water" watersheds of NYC; (ii) provide new information about present structure and function of the aquatic ecosystems comprising the "system"; and (iii) use that information as (a) a measure of anthropogenic stress, (b) an estimate of "functional capacity" of these ecosystems to absorb, sequester, or otherwise process natural inputs and contaminants, and (c) a baseline to determine future improvement and/or deterioration in watershed conditions. This work plan was designed to have elements complement and build on one another. Some project elements (e.g., grab samples of water chemistry) were instantaneous with regard to condition over time. Some elements (e.g., macroinvertebrates) contain information about water quality/habitat condition over time. Some (e.g., N, P, DOC spiraling, and stream metabolism) were integrative in a spatial sense. This programs strength lies in its breadth of study elements and its high degree of integration (same sites/timing/personnel).

This project is a spatially intense, broad synoptic survey repeated annually, rather than a highly targeted survey with high repetition that has limited spatial scope. All major watersheds throughout the study area were subjected to this monitoring regime, rather than one or two watersheds representing a small portion of the study area. This broad synoptic approach avoids two serious problems associated with a spatially limited, temporally intense approach: (1) pseudoreplication - where multiple samples taken from a given stream throughout the year still only represent one stream and one watershed; and (2) serial autocorrelation - where repeated measures of the same variable during the year tend to be correlated with one another or are non-independent (e.g., baseline chemistry, macroinvertebrates). This applies to both baseflow and stormflow sampling. For example, the project focuses on between-stream variability rather than between-storm variability for a given stream.

Phase II Study Site Descriptions

Study sites were separated into two groups: 50 "targeted" and 10 "integrative" sampling stations (see above for definitions; Figs. 2.1 and 2.2). Several of the specific task components involved all 60 sites, while a few tasks incorporated only the integrative sites. Seven reservoirs were also studied for certain project elements (Figures 2.3 and 2.4). Stream and reservoir stations were located using a Trimble GPS Pathfinder ™ ProXR receiver unit (Tables 2.3, 2.4, and 2.6). Figures 2.1 and 2.2 illustrate Phase II stream stations and Figures 2.3 and 2.4 illustrate Phase II reservoir stations and substations (Phase I sites were also included).

Land cover, population, and wastewater treatment/discharge facilities varied greatly among the 60 stream and seven reservoir watersheds (Table 2.1, 2.2, and 2.5). Land cover data for WOH stations were derived by the NYC DEP from 1 or 2 Landsat Thematic Mapper (TM) scenes per major watershed (as defined by the reservoirs) spanning 1992 and 1993. For EOH stations, land cover data were derived from five Landsat TM scenes in combination with Landsat Multispectral Scanner data from two dates, all spanning the period 1987 to 1993. East of Hudson data were originally from University of Massachusetts but were modified and distributed by the NYC DEP. Land cover data were compiled for each study watershed, as defined by station locations. Watershed boundaries were derived from an existing NYC DEP coverage of subwatershed delineations for the region, with some modifications necessary to match the mouth of a given subwatershed boundary with the location of a particular study site. The study sites were located using a GPS as previously described. The EOH land cover grid did not exactly match the overall EOH delineated watershed boundary coverage. Therefore, when combining the two data sources, the non-overlapping portions resulted in a “no-data” classification affecting a total of 20 EOH watersheds. The no-data classification ranged from 0.1 to 12.5 % of the total watershed area in these watersheds with a median value of 0.8 %.

Wetland data were derived from the U.S. Fish and Wildlife Service's National Wetlands Inventory and were processed (including field checks) for the WOH and EOH regions by the NYC DEP. Wetland data for the WOH region were based on high-altitude aerial photography taken between 1982 and 1987; EOH data were based on photography taken between 1984 and 1987. Classification of wetland types was based on Cowardin et al. (1979). Polygon wetland features were compiled for each study watershed as described for land cover data. Only the "palustrine" wetland class – those wetlands commonly referred to as swamp, marsh, bog, etc., and including small ponds – was compiled for study watersheds.

Population density data were compiled from total population counts from the 2000 census using census blocks within each county (Tables 2.1, 2.2, and 2.5). Census blocks are the smallest unit for which census data are available (Census 2000 Geographic terms and concepts; http://www.census.gov/geo/www/census2k.html). Census 2000 Geographic Census data, including population counts, were retrieved as Census 2000 TIGER/Line data through the Environmental Systems Research Institute, Inc. (ESRI) web page at http://www.esri.com/data/download/census2000_tigerline/index.html. Watershed boundaries were used to determine what proportion of each census block fell within a given study site watershed. The fraction of the census block area falling within a given watershed was multiplied by the total population count for that census block. This product of fractional census block area and corresponding population count was summed for all census blocks falling within a watershed and then divided by the watershed area to arrive at a watershed population density estimate.

A GIS point coverage of waste water treatment plants (WWTP) with 2002 permits through the State Pollutant Discharge Elimination System (SPDES) was supplied by the NYC DEP. The coverage was used to determine the number of active (i.e., discharging) plants located upstream of each stream and reservoir station (Tables 2.1, 2.2, and 2.5).

Although geology, soil, and related physiographic information have not been compiled for these study sites, a brief discussion is necessary to highlight the variation in physiographic conditions across the NYC watershed area and the effect this variation has on in-stream conditions. Factors such as geology and geochemistry, topography, and soil type create unique regional conditions that influence macroinvertebrate community assemblages across latitudinal and longitudinal gradients (see 2000 Journal of the N. Amer. Benthol. Soc. 19(3) for an entire issue devoted to landscape classifications and aquatic biota and bioassessments). The Omernik (1987) classification of ecoregions, which was developed to explain water chemistry patterns across the United States based on geology, physiography, soil type, and vegetation, places EOH and WOH watersheds in different ecoregions (WOH = North Central Appalachians and Northern Appalachian Plateau and Uplands; EOH = Northeastern Highlands and

Northeastern Coastal Zone). Further, physiographic divisions defined by Fenneman and Johnson (1946) place WOH watersheds in the Appalachian Plateaus and EOH watersheds in the New England region. Finally, bedrock geology (Isachsen et al. 2000) is vastly different and more complex in EOH than in WOH and is probably a major factor influencing K, Mg, Na, Ca, and some trace metals (Al and Fe).

Phase II versus Phase I landscape comparison

Correlation PCA (Fig. 2.5) between eight watershed specific, GIS derived variables (land cover percentages [agriculture, forest, impervious surface, wetland, water], population density from 2000, the number of active SPDES permitted dischargers, and watershed area) and 60 Phase I and 48 new Phase II sites illustrated the landscape differences among study sites and similarities between Phase I and II site characteristics. The analysis explained 57.2 % of the variance in the data-matrix on the first two axes (factor 1 = 33.7 %, F2 = 23.5 %). The first factor was primarily composed of population density (28.5 % of F1 definition), percent impervious surface (23.5 %), percent wetland (19.9 %), and percent water (12.5 %). The second factor was primarily composed of percent forest (48.3 %) and percent agriculture (36.2 %). Watershed area and number of active SPDES permitted dischargers contributed most to the 3rd axis (not shown; 27.6 % and 46.6%, respectively).

East of Hudson sites (solid squares) clustered separately from WOH sites (x's) and revealed distinctly different anthropogenic impact gradients in these watersheds using these variables. East of Hudson sites ranged from nearly 95% forest (Table 2.1) with little impervious surface, agricultural land, no permitted dischargers, and low population density (relative to other EOH watersheds) to sites with high impervious surface cover, higher wetland cover, high population density, and a greater number of permitted dischargers. Agriculture played a minor role in EOH site characteristics. West of Hudson sites were typically located in larger watersheds (Table 2.1 and 2.2). West of Hudson sites ranged from nearly 100% forested with very low population density and zero permitted dischargers to sites dominated by agricultural lands (Table 2.2). Impervious surfaces, wetland area, population density, and the number of permitted dischargers in WOH watersheds were all considerably lower than what was quantified for EOH watersheds.

This analysis illustrated (a) that site selection for Phase II sites resulted in site characteristics consistent with Phase I study sites and (b) that objectives in site selection were met with regard to landscape variables. For example, a primary objective for Phase II site selection in WOH watersheds was to increase the number of stream sites (particularly "integrative" sites) that had potential for greater anthropogenic impact and sites in EOH watersheds should be selected to help round out the "least" impacted sites. Phase II Integrative sites 3 and 9 in the WOH occur towards the "agricultural" end and site 34 in the EOH occurs towards the "forest" end of the landscape gradient. Further, EOH sites 124-126 and 129 help better

define forest dominated streams and WOH sites 103, 105, 151, and 153 help further define agriculturally dominated streams.

Stormflow

Stormflow sampling occurred at three of the 60 baseflow monitoring sites: W. Br. Delaware River at Hawleys (6); Neversink River near Claryville (29); and the Kisco River near Stanwood (55). A USGS gauging station is co-located with the monitoring site on the Kisco River (USGS ID 01374987), and a USGS station is located approximately 1.5 km downstream of the site on the Neversink River (USGS ID 01435000). Since there were no significant tributaries entering the Neversink between the monitoring site and the gauging station, this USGS gauging station was considered to be representative of discharge at site 29. For the third monitoring site, the W. Br. Delaware River at Hawleys, a USGS gauging station was located several miles downstream in Walton (USGS ID 01423000). Storm discharge was estimated for this site using the USGS gauging station located in Walton and watershed area relationships(see text below).

Due to equipment failures (e.g., dead batteries; trigger mechonism dislodged by debris), attempts to collect two samples during at least one storm at each monitoring site in the fall of 2003 yielded only one successfully sampled event (Fig. 2.6). On 23 September at the W. Br. Delaware River at Hawleys site (6) a storm event resulted in a peak discharge of ~60 $m^3 s^{-1}$. This storm amounted to a 10-fold increase in flow within 12 hours. The two samples during stormflow represented high turbidity at a discharge of ~57.1 $m^3 s^{-1}$ and high flow at 60 $m^3 s^{-1}$. Discharge values for these samples were estimated using the measured discharge at the Walton gauge multiplied by the ratio of the watershed area at the monitoring site to the watershed area for the USGS gauging station at Walton. A MiniTroll stage recorder, which records relative stage height, was located at the monitoring site on the W.Br. Delaware. The stage hydrograph from the MiniTroll unit was compared to the discharge hydrograph for the USGS gauging station in Walton to assess the offset in timing between peak stage at the monitoring site and peak discharge at the Walton gauge. The offset in peak flow times was also applied to the high turbidity discharge estimate. Because instantaneous flow data were collected at 15-minute intervals at each of the gauging stations, discharge taken at the interval closest to the actual sampling time of each sample was used. These instantaneous discharge data were considered provisional data by the USGS and were not subjected to final review or approval by the USGS. Water chemistry results for stormflow are presented in Chapter 3.

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Omernik, J.M. 1987. Aquatic ecoregions of the coterminous United States. Annals of the Association of American Geographers. 77:118-125.

Table 2.1: Station names and descriptive information of 27 East of Hudson stream sites. T or I = "Targeted" or "Integrative" sites; Winter/Storm = "Winter-baseflow (WB)" or "Stormflow (S)" sampling sites; Area = watershed area, and "Active SPDES" = number of active SPDES licensed dischargers. Pop. Density = # people per km^2.

Site	Full Name/Description	T or I	Winter/ Storm	Area km^2	Active SPDES	Pop. Density	Land Cover Percentages (%) [1]				
							Agric	Imperv.	Forest	Wetland	Water
34	Haviland Hollow Br. at Haviland Hollow [T]	I	WB	25.1	0	56	3.5	0.9	94.6	4.5	0.6
46	Muscoot River nr Baldwin Place [I, WB]	I	WB	35.1	6	392	9.9	13.6	65.1	9.5	10.1
52	Cross River in Ward Pound Ridge Resv. [I, WB]	I	WB	44.5	1	131	7.4	5.9	82.1	9.3	4.5
55	Kisco River nr Stanwood [I, WB, S]	T	WB/S	45.5	1	380	8.3	21.0	69.9	5.4	0.6
124	Unnamed trib. of E. Br. Croton R. nr Pawling	T	No	4.0	0	68	10.0	2.6	81.7	2.5	2.5
125	Quaker Brook at W.G. Merrit County Park	T	WB	17.9	0	29	2.1	0.2	96.6	4.1	0.7
126	Stump Pond Stream nr Pawling	T	No	12.9	2	92	3.1	3.5	89.7	8.5	2.3
127	Black Pond Brook at Meads Corner	T	No	9.5	0	45	2.9	0.9	86.0	11.5	7.9
129	Unnamed trib. of E. Br. Croton River	T	No	6.1	0	110	5.5	8.1	86.0	2.8	0.2
130	Titicus River near Salem Center	I	WB	31.2	0	206	15.0	14.1	67.6	9.2	2.2
131	Titicus River near North Salem	T	No	24.0	0	245	9.7	15.4	70.5	10.7	2.8
132	Bog Brook nr Sears Corner	T	No	5.6	3	126	6.2	15.0	78.4	8.2	0.4
133	Unnamed trib. of Muscoot R. at Mahopac Falls	T	WB	16.1	1	332	7.0	11.4	61.4	6.1	19.4
134	Plum Brook at Shenorock	T	No	5.9	2	563	5.5	21.2	71.2	3.5	2.1
137	Unnamed trib. of Muscoot Res. nr Goldens Br.	T	No	5.4	1	212	7.7	17.5	72.5	6.6	2.3
138	Cross River nr Katonah	T	No	77.9	4	110	8.2	7.2	77.1	8.0	7.4
139	Muscoot River nr Whitehall Corners	I	WB	84.5	10	404	11.1	20.2	60.1	7.3	8.0
140	Hunter Brook nr Yorktown.	T	No	7.1	0	529	8.2	26.3	63.3	2.2	0.1
141	Unnamed trib. of Croton Res. nr Croton Heights	T	No	3.2	0	200	3.4	13.1	83.5	0.9	0.0
142	Kisco River nr Bedford	T	WB	15.0	0	95	9.5	8.3	81.2	6.4	0.9
143	Unnamed tributary to Cross River nr Cross R.	T	No	5.7	1	131	15.2	4.8	79.9	11.4	0.1
145	Broad Brook nr Bedford Hills	T	WB	13.4	3	204	14.6	17.0	67.8	4.2	0.2
146	Stone Hill River nr Bedford	T	No	19.4	0	98	3.5	3.5	89.6	10.8	2.6
147	Unnamed trib. of Kensico Res. at Mt Pleasant	T	No	4.0	0	229	6.4	10.2	68.9	4.7	2.0
148	Unnamed trib. of Kensico Res. nr Thornwood	T	WB	1.0	0	439	6.5	27.7	55.5	0.0	0.0
149	Waccabuc River at Boutonville	T	No	27.8	1	159	8.6	8.0	77.5	9.0	5.8
150	E. Br. Croton River at Brewster	T	WB	194.5	9	124	11.2	7.8	76.8	8.7	3.6

Superscripts at the end of some "Full Name/Description's" indicate the phase I status of a site: T = Targeted, I = Integrative, WB = Winter-baseflow, and S = storm sampling.

[1] – land cover percentages may sum to >100% as wetlands were quantified from different source.

Table 2.2: Station names and descriptive information for the 33 West of Hudson stream sites. T or I = "Targeted" or "Integrative" sites; Winter/Storm = "Winter-baseflow (WB)" or "Stormflow (S)" sampling sites; Area = watershed area, and "Active SPDES" = number of active SPDES licensed dischargers. Pop. Density = # people per km^2.

Site	Full Name/Description	T or I	Winter/ Storm	Area km^2	Active SPDES	Pop. Density	Land Cover Percentages (%) [1]				
							Agric	Imperv.	Forest	Wetland	Water
3	W. Br. Delaware R. at South Kortright [I, WB]	I	WB	122.7	2	22	55.1	0.6	43.6	1.3	0.7
6	W. Br. Delaware R. at Hawleys [I, WB, S]	T	WB/S	663.9	5	10	42.5	0.4	56.5	1.1	0.7
9	Trout Creek nr Trout Creek [I, WB]	I	WB	53.3	1	11	48.5	0.6	48.5	1.2	2.4
10	E. Br. Delaware R. nr Arkville [I, WB]	I	WB	181.6	2	8	30.3	0.2	69.3	1.0	0.2
15	Tremper Kill nr Andes [I, WB]	I	WB	77.8	0	8	35.7	0.2	63.5	1.3	0.6
23	Esopus Creek nr Allaben [I, WB]	T	WB	178.0	1	3	2.9	0.0	96.9	0.5	0.2
26	Esopus Creek nr Mount Tremper [T]	T	WB	438.7	2	6	2.6	0.0	97.1	0.5	0.2
29	Neversink River nr Claryville [I, WB, S]	I	WB/S	165.9	0	2	0.7	0.1	98.5	0.4	0.7
101	Rose Brook nr South Kortright	T	No	38.1	0	4	34.6	0.1	65.3	0.4	0.0
102	Coulter Brook nr Bovina Center	T	WB	12.5	0	4	13.6	0.0	86.4	0.2	0.0
103	Elk Creek at East Delhi	T	WB	39.7	0	11	52.7	0.4	46.5	1.1	0.4
104	Planter Brook at Fraser	T	No	36.5	0	8	37.8	0.1	62.0	1.6	0.1
105	East Brook nr Walton	T	WB	62.1	0	7	46.0	0.1	53.5	0.9	0.4
106	Dryden Brook nr Beerston	T	No	24.8	0	6	18.7	0.0	81.2	0.7	0.1
107	E. Br. Delaware at Roxbury	T	WB	34.2	1	7	25.2	0.3	74.5	1.5	0.0
108	Scudders Run nr Roxbury Run	T	WB	2.4	1	17	3.4	0.0	96.5	1.2	0.1
109	Batavia Kill nr Kellys Corner	T	No	49.6	0	9	32.9	0.0	67.1	0.5	0.0
110	Vly Creek nr Fleischmanns	T	No	55.1	0	4	18.8	0.0	81.1	0.5	0.0
111	Dry Brook nr Mapledale	T	No	44.0	0	1	3.3	0.0	96.5	0.4	0.1
112	Mill Brook nr Grant Mills	T	No	64.5	0	2	11.7	0.0	88.3	0.3	0.0
113	Coles Clove nr Downsville	T	No	35.9	0	3	31.2	0.0	68.6	0.8	0.2
114	Holiday Brook nr Downsville	T	No	12.1	0	2	15.1	0.0	84.6	0.5	0.3
115	Schoharie Creek near Elka Park	T	No	41.3	3	4	4.3	0.0	95.5	1.4	0.1
116	East Kill near East Jewett	T	No	39.0	1	4	3.9	0.0	95.2	1.0	0.9
117	Batavia Kill near Windham	T	No	132.5	6	14	18.4	0.7	80.5	1.4	0.3
118	Bear Kill nr Grand Gorge	T	WB	66.9	1	15	37.9	0.4	61.2	1.4	0.5
119	Birch Creek at Big Indian	T	No	32.2	1	14	4.2	0.0	95.6	0.2	0.2
120	Bushnellsville Creek at Shandaken	T	WB	28.8	0	5	1.8	0.0	98.2	0.1	0.0
121	Warner Creek nr Chichester	T	No	23.4	0	5	0.5	0.0	99.5	0.6	0.0
122	W. Br. Neversink River above Frost Valley	T	No	22.1	0	2	0.0	0.0	100.0	0.1	0.0
123	Rondout Creek near Peekamoose	T	No	45.6	0	2	0.3	0.0	99.7	0.1	0.0
151	Betty Brook nr South Kortright	T	WB	23.6	2	9	41.0	0.0	58.2	2.5	0.8
153	Loomis Brook nr Trout Creek.	T	No	31.7	0	11	44.9	0.4	53.7	0.8	1.0

Superscripts at the end of some "Full Name/Description's" indicate the phase I status of a site: T = Targeted, I = Integrative, WB = Winter-baseflow, and S = storm sampling.

[1] – land cover percentages may sum to >100% as wetlands were quantified from different source.

Table 2.3: Location information for the 27 East of Hudson stream sites. Each site (except 150; from map) was located using a Trimble GPS Pathfinder TM ProXR receiver unit, with real-time correction (Datum = WGS 84). See Table 2.1 for site names and descriptive information.

Site	Latitude	Longitude	Maximum Position Dilution of Precision	Horizontal Precision (95% CI) m
	Degrees – Minutes - Seconds			
34	41.49438077	-73.54641599	3.5	1.217
46	41.33265904	-73.76496965	4.5	1.037
52	41.26028843	-73.60198649	4.4	0.860
55	41.22898049	-73.74356273	2.5	1.281
124	41.54005559	-73.61557599	5.3	1.443
125	41.49874968	-73.53383643	4.7	1.122
126	41.50820788	-73.68247079	2.9	0.881
127	41.48360034	-73.76890208	3.1	0.953
129	41.42346001	-73.55755546	5.2	0.963
130	41.32768298	-73.58078559	5.5	0.887
131	41.33487622	-73.55814227	4.1	1.152
132	41.42927864	-73.58463644	6.0	1.202
133	41.37483505	-73.76203475	2.3	0.723
134	41.33612911	-73.73477869	4.5	1.655
137	41.28965343	-73.65908981	4.2	0.915
138	41.26682982	-73.66836286	3.1	1.022
139	41.27257487	-73.74575572	5.8	2.170
140	41.29094958	-73.83465386	2.3	0.602
141	41.24316019	-73.81795596	4.8	1.203
142	41.19248383	-73.72695417	4.8	0.929
143	41.27460174	-73.61832933	3.1	0.932
145	41.24776891	-73.67044354	5.3	1.093
146	41.21572580	-73.63194603	5.1	1.161
147	41.12490180	-73.74346656	24.8	3.505
148	41.10273616	-73.75709573	4.3	1.376
149	41.25844110	-73.56610994	2.3	0.804
150	41.40277778	-73.59305556	NA	NA

Table 2.4: Location information for the 33 West of Hudson stream sites. Each site was located using a Trimble GPS Pathfinder TM ProXR receiver unit, with real-time correction (Datum = WGS 84). See Table 2.2 for site names and descriptive information.

Site	Latitude	Longitude	Maximum Position Dilution of Precision	Horizontal Precision (95% CI) m
	Degrees – Minutes - Seconds			
3	42.34367436	-74.71979975	2.2	0.656
6	42.17548414	-75.01828999	4.2	0.924
9	42.17376864	-75.27943302	2.2	1.082
10	42.16987985	-74.61151354	2.4	0.651
15	42.12610104	-74.81170240	2.6	0.688
23	42.11731029	-74.37679339	2.4	0.572
26	42.03961869	-74.28169149	5.2	1.512
29	41.90174954	-74.58072348	3.0	0.752
101	42.33553867	-74.73917211	2.9	0.768
102	42.25703301	-74.77161393	3.5	0.947
103	42.29949546	-74.89223927	4.3	1.122
104	42.24288046	-74.96426207	7.3	1.911
105	42.18096091	-75.10621802	8.3	1.510
106	42.11789180	-75.24962674	12.2	0.861
107	42.29375686	-74.55917861	3.6	0.876
108	42.23393721	-74.59036309	2.8	0.643
109	42.18139839	-74.59126882	5.0	1.239
110	42.17068580	-74.51546992	4.7	1.185
111	42.10767973	-74.56120015	5.8	1.172
112	42.10617040	-74.73026838	5.7	0.879
113	42.12910492	-74.89832297	5.0	1.066
114	42.06546841	-74.87722641	3.3	0.769
115	42.17198754	-74.14987465	2.4	0.605
116	42.24242108	-74.17846641	3.4	0.834
117	42.29337212	-74.30532935	3.3	0.738
118	42.33792438	-74.45102525	4.0	0.927
119	42.10938420	-74.45181128	6.1	0.938
120	42.12109310	-74.39868066	3.1	0.837
121	42.10009907	-74.29540223	8.8	0.985
122	41.99047876	-74.49263600	5.6	1.066
123	41.91630759	-74.43564844	4.4	1.013
151	42.34512936	-74.73337798	3.3	0.919
153	42.15946134	-75.27729896	11.6	1.235

Table 2.5: Station names, substation locations, and descriptive information for the seven reservoir sites. "Active SPDES" = number of active SPDES licensed dischargers. Pop. Density = # people per km². See table 1 for notes on land cover.

Site	Station Name –	Surface Area (ha)	Wtsh Area (km²)	Active SPDES	Pop. Density	Land Cover Percentages (%) Agric	Imperv.	Forest	Wetlands	Water
East of Hudson Reservoirs										
155	Muscoot Reservoir	295	196	23	253	8.2	17.0	71.0	15.5	3.5
156	Amawalk Reservoir	224	51	9	361	11.2	14.5	61.6	8.0	11.8
157	Titicus Reservoir	276	63	0	136	13.4	10.5	69.6	8.3	5.9
158	Cross River Reservoir	363	78	4	110	8.2	7.2	77.1	8.2	7.4
West of Hudson Reservoirs										
65	Neversink Reservoir	599	238	0	4	2.2	0.2	94.4	0.7	3.2
66	Pepacton Reservoir	2096	961	7	8	20.5	0.1	76.9	0.6	2.6
67	Cannonsville Reservoir	1849	1178	7	15	37.7	0.6	59.2	1.0	2.6

Table 2.6: Location data for reservoir substations. Sites were located using a Trimble GPS Pathfinder ™ ProXR receiver unit, with realtime correction (Datum = WGS 84).

Site	Reservoir	Substation Number	Latitude	Longitude	Maximum Position Dilution of Precision	Horizontal Precision (95% CI)
			degrees, minutes, seconds			
155	Muscoot	1	41° 16' 41" N	73° 41' 27" W	2.0	0.4
		2	41° 16' 05" N	73° 41' 30" W	3.1	0.7
		3	41° 16' 18" N	73° 42' 48" W	2.7	0.5
156	Amawalk	1	41° 19' 03" N	73° 44' 31" W	3.0	0.5
		2	41° 18' 45" N	73° 44' 23" W	4.8	0.8
		3	41° 17' 47" N	73° 44' 51" W	6.0	0.9
157	Titicus	1	41° 19' 52" N	73° 36' 47" W	4.8	0.8
		2	41° 19' 53" N	73° 37' 40" W	3.6	0.6
		3	41° 19' 39" N	73° 38' 32" W	3.9	0.6
158	Cross River	1	41° 15' 10" N	73° 37' 18" W	2.4	0.3
		2	41° 15' 14" N	73° 37' 55" W	4.1	0.9
		3	41° 15' 45" N	73° 39' 17" W	4.3	0.5
65	Neversink	1	41° 50' 19" N	74° 38' 53" W	2.3	0.3
		2	41° 49' 53" N	74° 39' 52" W	1.8	0.3
		3	41° 50' 52" N	74° 40' 09" W	1.7	0.3
66	Pepacton	1	42° 05' 13" N	74° 48' 05" W	2.6	0.4
		3	42° 04' 54" N	74° 52' 30" W	2.1	0.4
		4	42° 06' 04" N	74° 49' 39" W	2.8	0.3
		5	42° 04' 27" N	74° 50' 14" W	2.2	0.3
		6	42° 04' 30" N	74° 53' 15" W	2.4	0.3
		7	42° 06' 07" N	74° 54' 05" W	2.2	0.3
67	Cannonsville	3	42° 06' 07" N	75° 17' 51" W	3.1	0.4
		4	42° 05' 52" N	75° 19' 07" W	2.2	0.4
		5	42° 07' 25" N	75° 18' 25" W	4.3	0

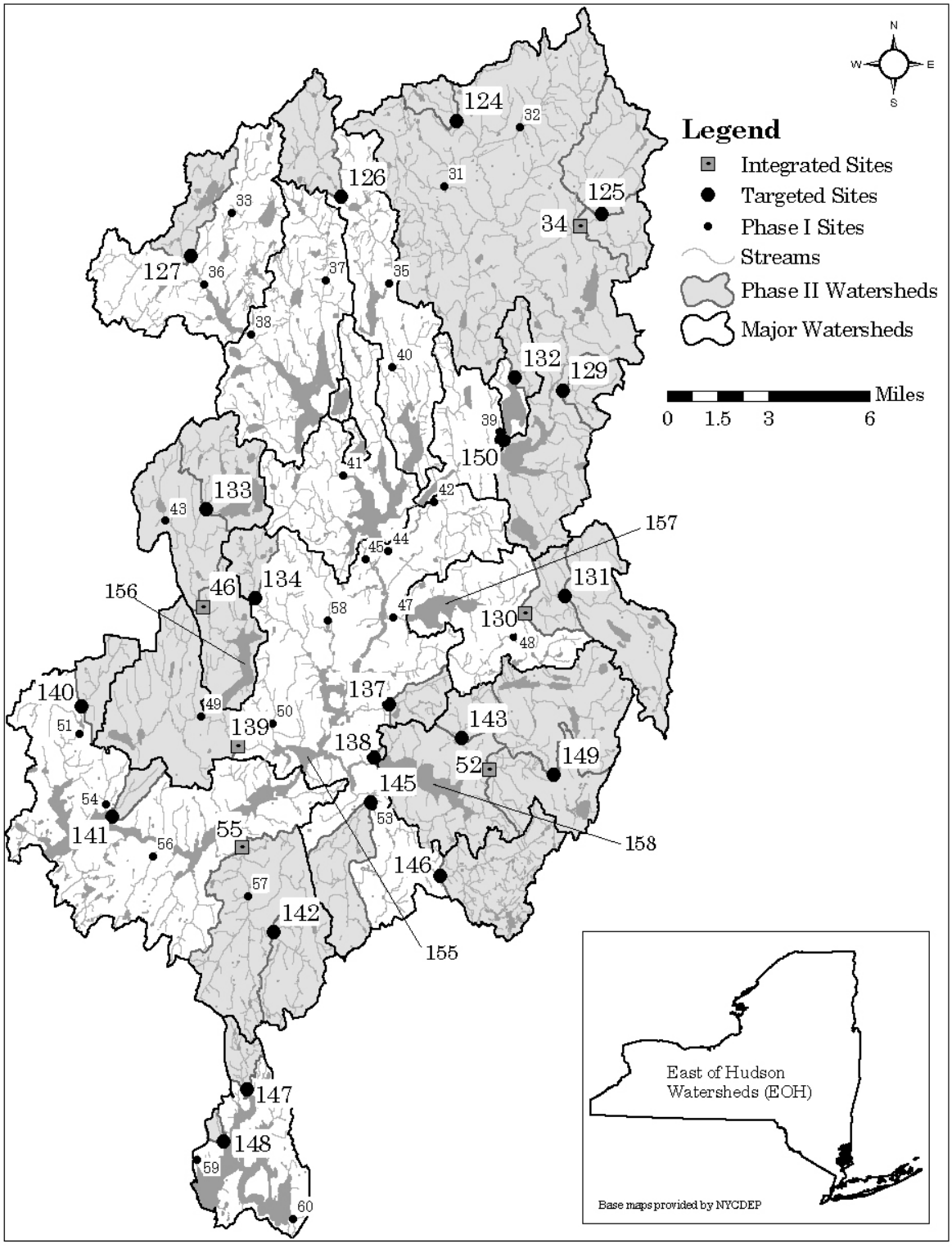

Figure 2.1: Location of Phase II sampling sites in the East of Hudson Watersheds (a.k.a. Croton/Kensico System). Study sites names and descriptive information is found in Tables 2.1 and 2.3, by site number.

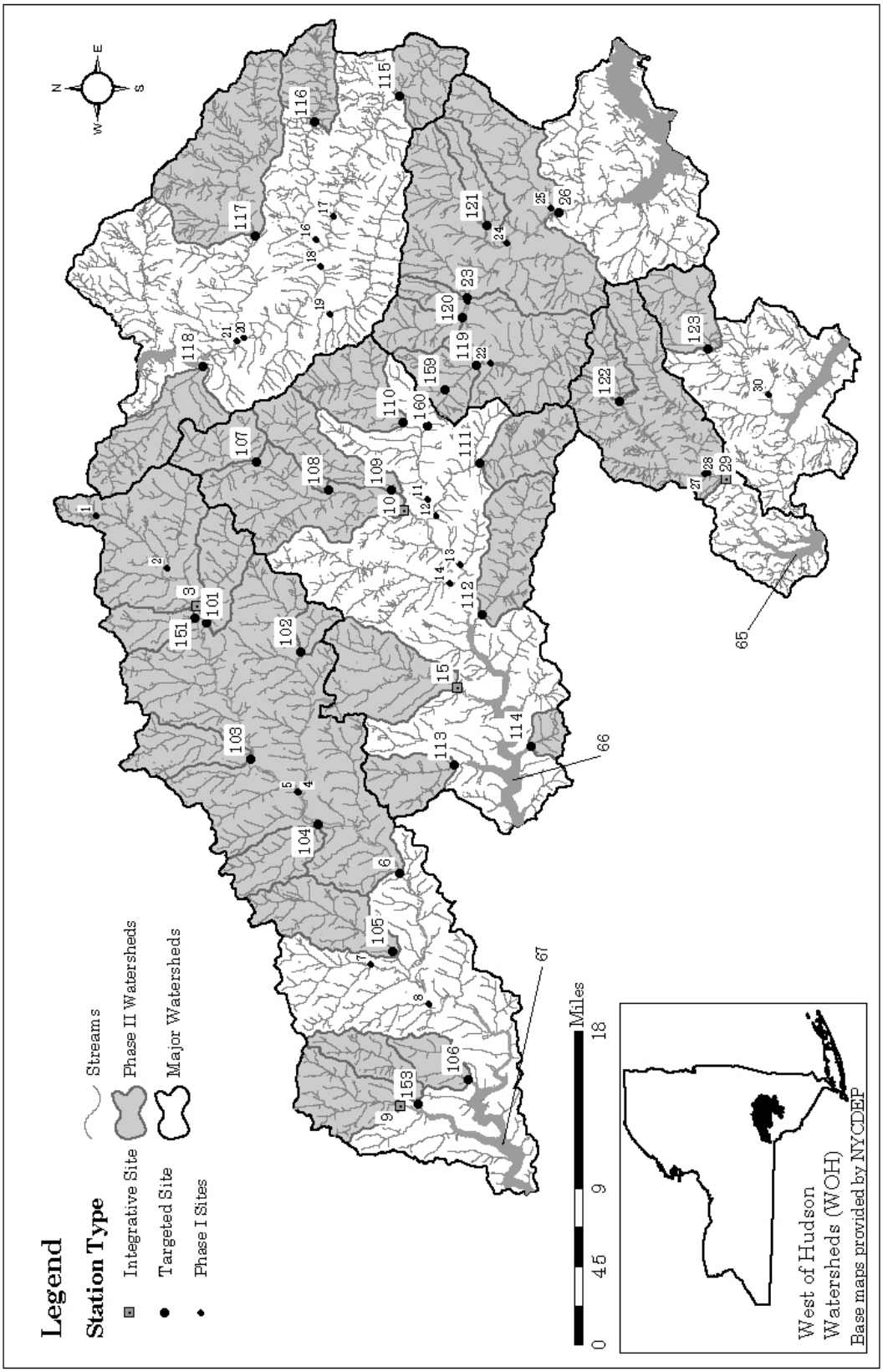

Figure 2.2: Location of Phase II sampling sites in West of Hudson watersheds (a.k.a. Delaware/Catskills System). Study site names and descriptive information are found in Tables 2.2 and 2.4, by site number.

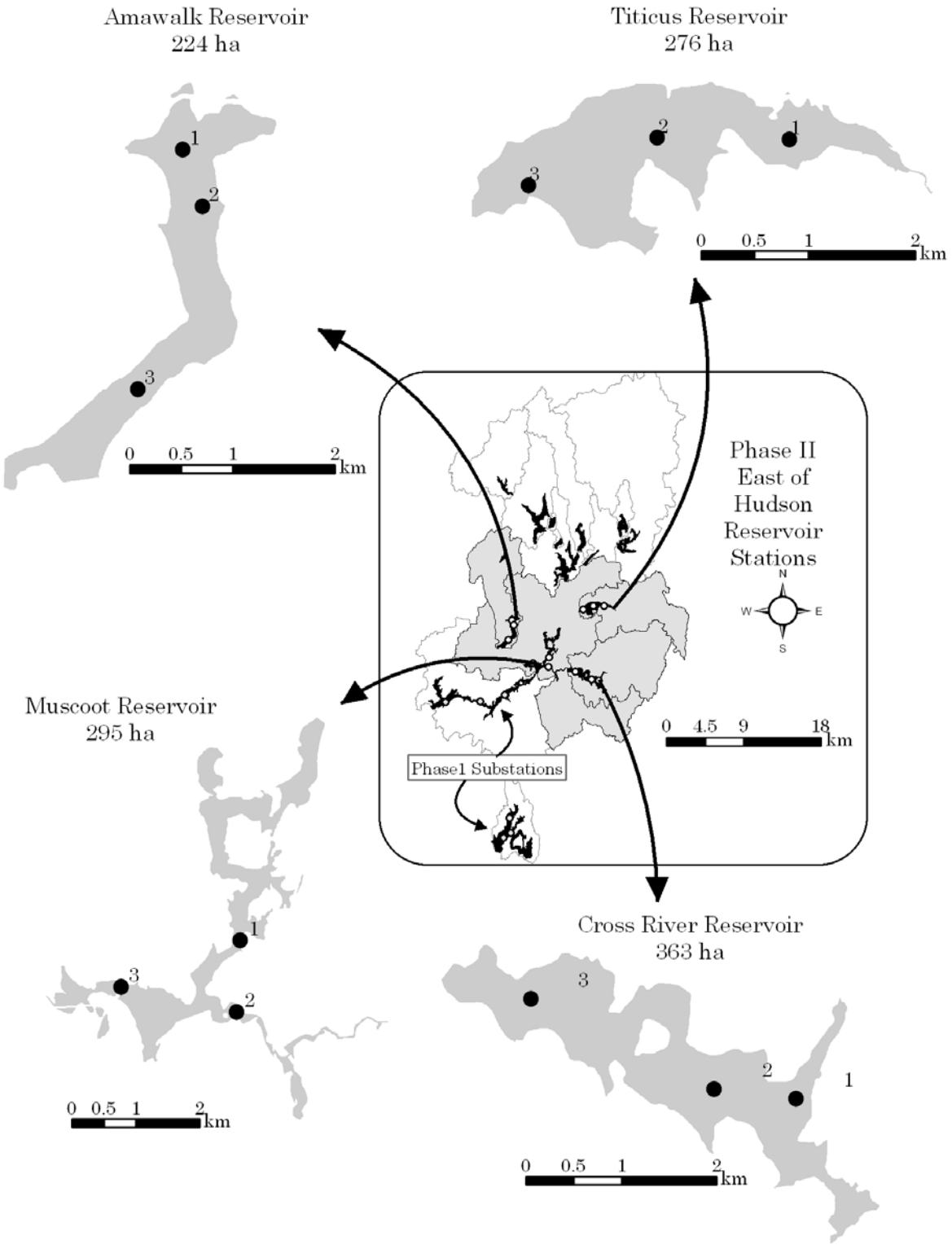

Figure 2.3: Location of reservoir sampling stations (each reservoir) and substations (actual sample locations) within each reservoir for the East of Hudson Reservoirs. Solid circles represent Phase II substations and Phase I substations are represented by open circles in in-lay map.

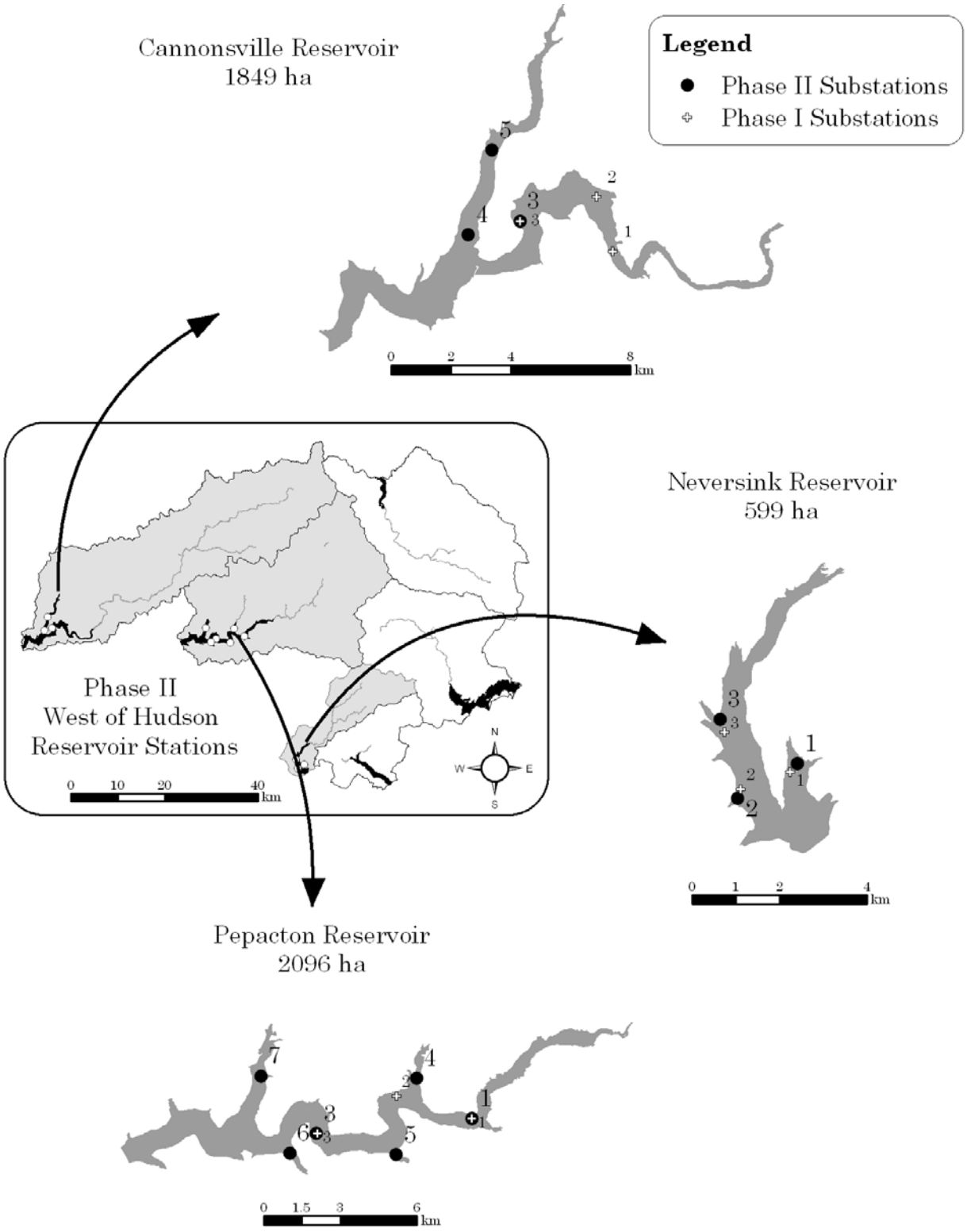

Figure 2.4: Location of reservoir sampling stations (each reservoir) and substations (actual sample locations) within each reservoir for the West of Hudson Reservoirs. Solid circles represent Phase II substations and white crosses represent Phase I substations.

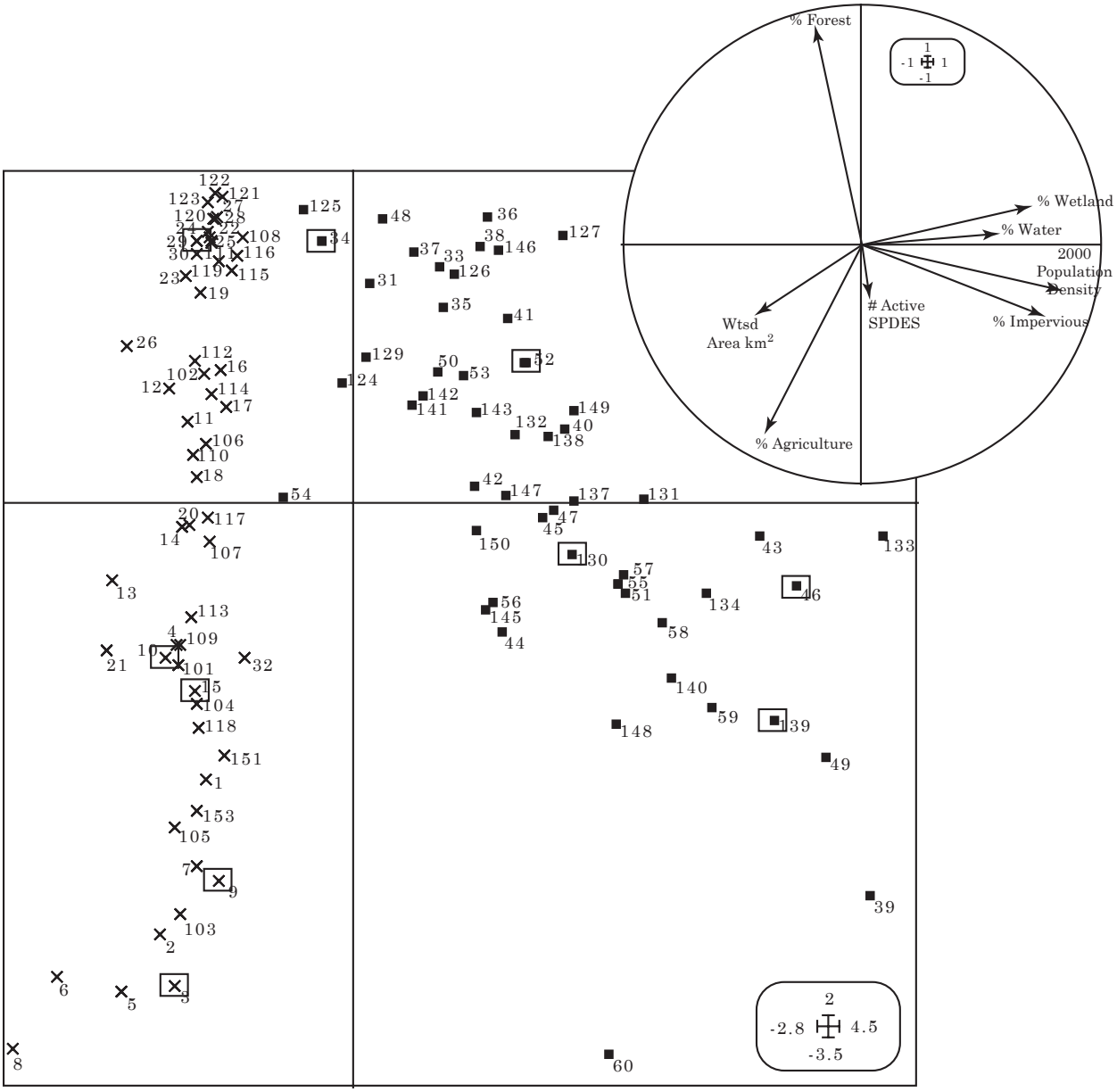

Figure 2.5: A Correlation Principal Components Analysis (PCA) for landscape variables (percent agriculture, forest, impervious surface, wetland, and water; 2000 population density, number of active SPDES permitted dischargers, and watershed area) at each stream study site (108 total sites from Phase I and II). Solid squares are EOH sites and x's are WOH sites. Site description/numbers are reported in Tables 2.1-2.4. Open squares around various site points identify integrative sites.

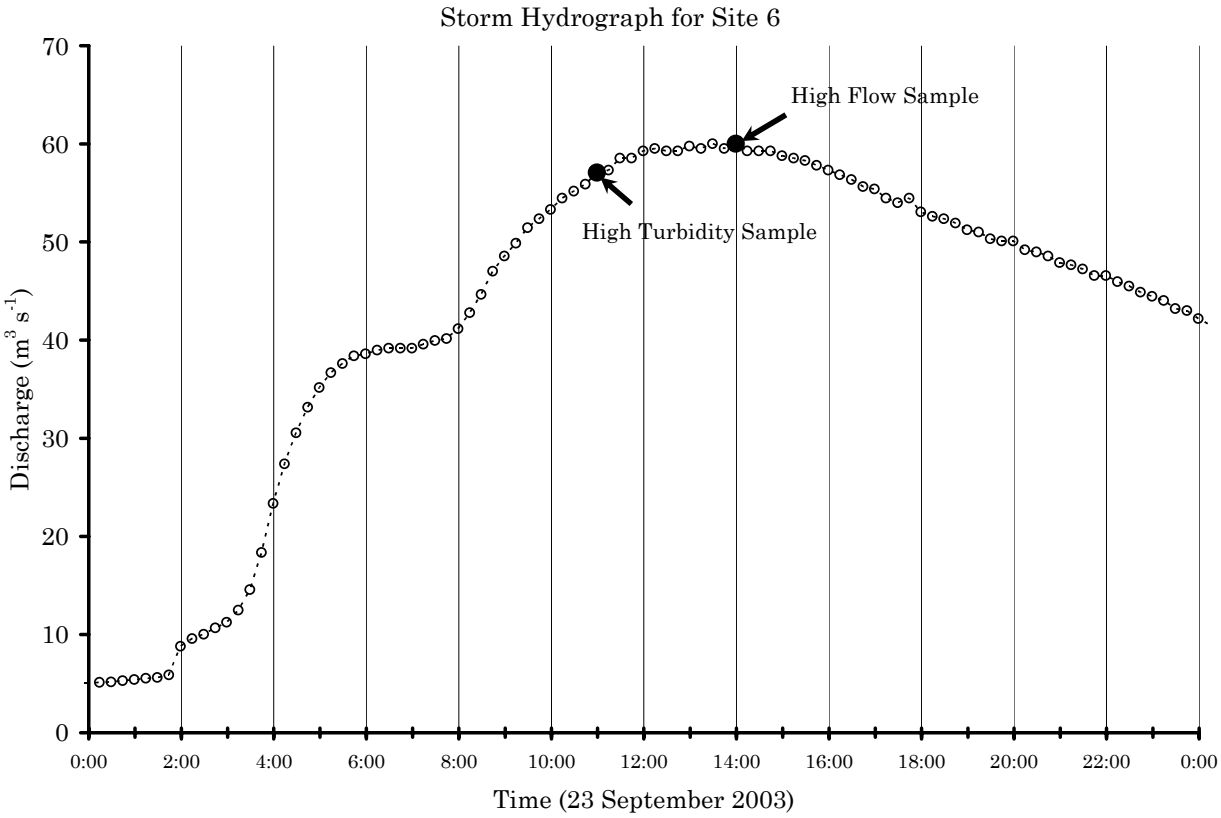

Figure 2.6: Storm hydrograph showing sampling times for the two samples (high turbidity and high flow samples) for a storm on 23 September 2003 at the West Branch of the Delaware River near Hawleys (site 6). Discharge estimated from USGS instantaneous (provisional) discharge data for the W. Br. Delaware at Walton (USGS ID 01423000) gauging station was corrected to estimate flow at site 6 using watershed area to discharge relationships (see text for details)

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Chapter 3 - Nutrients, Major Ions, and Suspended Particles in Transport

Research Task

Concentrations of nutrients and major ions transported in streams can be significant indicators of ecosystem impairment, particularly when monitored over a significant period of time and across landscapes of complex land-use patterns. They also provide important supplementary data for the other aspects of this monitoring project. These stream constituents provide an assessment of inorganic and nutrient water quality relative to differences in existing watershed characteristics and can be used to quantify and predict changes in water quality in response to changes in land use. Nutrients, major ions, and suspended particles were measured during baseflow conditions at 48 new and 12 existing (i.e., Phase I) sites located throughout the NYC drinking-water source watersheds and during a significant run-off event at one of our three stormflow sampling sites (Figs 2.1, 2.2, and 2.6).

Suspended particles monitored included both organic and inorganic particles. Organic particle dynamics can be indicative of upstream processing of organic matter, stream linkage (i.e., the upstream to downstream transfer of organic energy), and carbon loading to downstream reservoirs. The objectives for the suspended solids portion of this task were to characterize the concentrations and transport of inorganic and organic particles during baseflow conditions at targeted and integrative sampling stations, and to describe, to a first approximation, the response of organic particle transport to runoff events at three of the ten integrative sampling sites. A summary of year four monitoring data is presented herein, including observations concerning the spatial and temporal variation of suspended particles throughout the study region.

Methods

Baseflow

Samples analyzed for nutrients, major ions, and suspended particles for each of the 60 study sites east and west of the Hudson River (EOH and WOH, respectively) were collected between August and October. Nutrient and major ion baseflow sampling was coordinated with the molecular tracer and dissolved organic carbon (DOC)/biodegradable DOC (BDOC) tasks (Chapters 4 and 6). If a river appeared unusually turbid, or otherwise displayed signs of high flow (based on available USGS real-time gauging stations at or within the vicinity of the sampling sites), at the time scheduled for sampling, the site was (re)sampled at a later date.

A stream grab sample (500-1000 mL) for nutrients and major ions was taken from the thalweg of each stream using acid-washed 1-L Nalgene® bottles. Samples were

chilled to ~4°C in coolers until they could be processed. An Orion® field pH meter, and a YSI® conductivity/temperature meter were used to measure pH, conductivity, and temperature *in situ*. Immediately upon return from the field, the 500-1000 mL grab sample from each site was split into 5-6 samples for subsequent analyses of nutrients and major ions.

One aliquot was frozen for subsequent analysis of total kjeldahl nitrogen (TKN - semi-automated phenate block digester method) and total phosphorus (TP - EPA method # 365.1 & 365.5). Another aliquot was refrigerated at 4°C for subsequent alkalinity analysis (EPA method # 310.1). An additional split for alkalinity analysis was collected for WOH sites, as we anticipated low alkalinities, which require a modified titration analysis using an increased sample volume (Rounds and Wilde 2001; USGS methodology). The remaining water was then filtered through a cellulose nitrate membrane (0.45 μm) filter, split among three 100-mL samples into 125-mL polyethylene bottles and stored for later analysis of dissolved nutrients, anions, and cations. One filtered split was frozen for subsequent analysis of soluble kjeldahl nitrogen (SKN - semi-automated phenate block digester method), nitrate and nitrite (NO_3-N & NO_2-N, EPA method # 353.2), ammonium (NH_4-N, EPA method # 350.1), soluble reactive phosphorus (SRP, EPA methods # 365.1), and total dissolved phosphorus (TDP, EPA methods # 365.5). The second filtered split was refrigerated at 4°C for analysis of chloride (Cl, EPA method # 375.4) and sulfate (SO_4, EPA method # 325.3). The final filtered split was acid-fixed with 0.2 μL HNO_3/mL for later analysis of Ca, K, Na, and Mg (EPA method # 200.7). All nutrient and major ion analyses were performed by the Patrick Center for Environmental Research at the Academy of Natural Sciences of Philadelphia.

Triplicate 5-L samples of water for suspended particle analyses were collected at 60% depth from the thalweg, capped and returned to the laboratory in a cooler. Samples were chilled to ~4°C until they could be processed (within 7 days from the time of collection). In the laboratory, each sample was measured in a graduated cylinder, and as much water as would go through a GF/F filter was filtered onto an ashed, tared, GF/F filter for total suspended solids (TSS). Filters were analyzed for TSS by drying at 60°C for ~48 hours to obtain dry weight and volatile suspended solids (VSS) by muffling at 500°C for ~2 hours for ash weight. The dry weight per L is the TSS fraction (mg/L), while the difference between the dry weight and the ash weight per L, the ash-free dry mass (AFDM) per L, is the VSS fraction (mg/L).

Stormflow

Concentrations of nutrients, major ions, and suspended solids in transport (as well as molecular tracers [Chapter 4], and DOC and BDOC [Chapter 6]) were quantified during a single storm that occurred on September 23, 2003, at site 6, W. Br. Delaware River at Hawleys (Fig. 2.6).

The sampling site was instrumented with two ISCO automated samplers, the first of which was set to trigger following a 10-15 cm rise in stage. The second ISCO was triggered by the completion of sampling by the first ISCO. Once triggered, the ISCOs sampled hourly in duplicate for a total 6 h. When a run-off event was imminent, changes in stream discharge and stage height at or near each site were monitored using real-time updates of stream-specific gauging stations on the USGS internet sites. There was no USGS gauging station in close proximity to the storm sampling site at the W. Branch of the Delaware River, so this site was equipped with a single water-level recorder (pressure transducer) to record actual changes in stage height.

The first sample from each duplicate pair of hourly samples (n=12) was used for the analyses in this task, and the second in each pair (n=12) was used for molecular tracer analyses. Two sets of duplicate samples were analyzed for this storm; one sample corresponded to peak flow (±1 h), as determined by provisional hydrograph data provided by the USGS (or pressure transducer data) and the other corresponded to peak TSS transport (±1 h) selected by visual comparison of sample turbidity. After completing the filtration, ~50 mL of the filtrate from each sample was used for DOC analysis. After thorough shaking of the original sample, the unfiltered nutrient and alkalinity sample splits were collected, as described above. The remaining sample volume was processed for total and volatile suspended solids also as described above (again following thorough shaking). The filtrate from the DOC processing was subsequently re-filtered through a cellulose nitrate membrane (0.45 µm) filter and split among three 125-mL HDPE bottles for dissolved nutrients and major ions, as described above. The resulting (5-6) 100-mL sample splits were filtered, fixed, and stored as necessary for subsequent analysis of whole and dissolved nutrients (SKN, TKN, TP, NO_3-N & NO_2-N, NH_4-N, SRP, TDP), anions (Cl, SO_4), cations (Ca, K, Na, Mg), and alkalinity. Samples were collected and stored on ice within 6-12 hours of sample collection by the ISCO automated sampler.

QA/QC

The QA/QC procedures of the Patrick Center for Environmental Research laboratory for all sample analyses for this project included analysis of lab blanks, duplicated samples, matrix spikes, reference or lab control standards (LCS), and continuing calibration standards (CCS). Laboratory quality control for suspended particles was evaluated using lab blanks (LB) of deionized water and a laboratory control sample (LCS) of resuspended stock particles collected from the benthos of White Clay Creek (certified to 16.7% OM by Lancaster Laboratory, PA). Each day of sample processing included the filtration of 1 to 2 LBs (~1 L) and 1 to 2 LCS (~90-100 mL of freshly resuspended particles) onto organic-free, tared (~0.7 µm) GF/F filters and processing as above.

Baseflow. A field duplicate (FD) or field blank (FB) sample was collected at one predetermined site during each week of baseflow sampling. This schedule resulted

in four field-duplicated samples and three field blanks. QA/QC sites were randomly selected prior to the onset of the sampling season, with FD and FB sampling alternating from week to week. Major ion/nutrient field-duplicated samples were collected simultaneously and in close proximity to each other in the water column, and analyzed as a discrete sample. Conductivity, pH, and temperature, which were measured *in situ,* were also field-duplicated (each measurement was made twice). For suspended particles, field duplicates were collected simultaneously by filling three additional 5-L bottles while field blanks involved 4 L of deionized water, following the same protocol used to filter and analyze stream samples. Ion/nutrient field blanks were taken by transferring deionized water into the 1-L grab sample bottles at each of the three randomly selected QA/QC sites. Conductivity, temperature, and pH of the field blank samples were measured at the time of collection, although pH of the deionized water had little significance.

Stormflow. Collection of field blanks and duplicates under changing stormflow could not be practicably obtained with precision and accuracy assured. Thus, field blanks (or "equipment rinsate blanks") and field duplicates were collected during baseflow by collecting a volume of deionized water through the ISCO sampling apparatus immediately following routine equipment maintenance. A single QA/QC sample (FD and FB) was collected following the storm sample collected on September 23, 2003.

Ion Balance. A cation/anion balance and the difference between measured and calculated conductivity were used as additional consistency checks for baseflow and stormflow inorganic chemistry data. All concentrations were converted from mg/L to μeq/L for the ion balance calculation. DOC concentrations, which were often used to estimate the organic anion contribution to the ion balance, were not included. The equivalent concentrations were summed separately for the cations and anions, with the final ion balance expressed as a percent difference (PD):

(PD[ion]) = ((cations – anions)/(cations + anions)) * 100

Conductivity Check. An additional data consistency check was performed using measured and calculated conductivity. Conductivity was calculated by summing the product of ion concentration (converted to μM) and associated equivalent conductivities. This sum was then adjusted for ionic strength at finite concentrations (APHA, 1992). As with the ion balance calculations, the conductivity calculation did not include the organic anion contribution (estimated from DOC concentrations). Agreement between measured and calculated conductivity was assessed through a percent difference:

PD[cond] = ((meas. conductivity – calc. conductivity)/meas. conductivity)*100

Results and Discussion

QA/QC

A full field and laboratory QA/QC summary is included in Appendix A3 of this report. It indicates that there were no QA/QC issues within the laboratory effort and that no serious issues arose from the field QA/QC. There were several continuing calibration sample exceedances for N and P species and SO_4, however, all of these exceedances were for low-concentration samples (i.e., near stated detection limits) where relative (e.g., percent) recoveries can be inflated (as compared to absolute differences) and were therefore not considered to be an issue. A single field QA/QC exceedance occurred for K in the storm field duplicate. Given that there were no issues with the baseflow duplicates for K, or any of the other constituents within the storm duplicates, this single exceedance did not warrant further consideration.

Fifty-five laboratory blanks (LB) were analyzed for whole-sample TSS and VSS. TSS and VSS concentrations in these blanks averaged 0.14 to 0.22 mg/L, respectively. All of the TSS blanks met the acceptance criterion of a 1.2 mg/L detection limit, and 50 of the 55 VSS blanks met the acceptance criterion of the 0.22 mg/L detection limit. Fourty-four laboratory control standards were analyzed and had a mean recovery of 99.8% for TSS and 98.8% for VSS. One of the 44 TSS LCS samples exceeded the acceptance criterion of 80 to 120% accuracy, while 4 of the 44 VSS LCS samples exceeded the acceptance criterion.

All of the baseflow field blanks (FB) for suspended particles processed during the year 4 field season met the QC criterion of less than 2x detection limit, with a mean TSS of 0 and a range of -0.009 to 0.196 mg/L and VSS mean of 0.11 mg/L (range 0.069 to 0.194 mg/L). The one exceedance for a FB was the VSS associated with storm sampling. However, the FB value of 0.7 mg /L was considerably below the stormflow values for VSS of 12 and 18 mg/L VSS. All of the field duplicates also met the acceptance criterion with a mean relative percent difference (RPD) of 3.21% for TSS and 6.35%for VSS of the baseflow samples, and 3.22% for TSS and 9.52% for VSS of the stormflow sample.

The ion balance and conductivity checks demonstrated strong consistency between cation and anion sums and measured versus-calculated conductivity, respectively. The mean PD[ion] for baseflow samples was 2.0% (±2.2%) and for stormflow samples the mean was -1.2%(±0.70%). None of the baseflow or stormflow PD[ion] values exceeded 10%. The mean PD[cond] across baseflow samples was 7.6% (±4.6%) and for stormflow samples the mean was 4.6% (±1.4%). Only one baseflow sample (site 46 at 22%) and no stormflow samples exceeded a PD[cond] value of 20%.

Baseflow ionic, nutrient, and suspended particle water chemistry

General Relationships and Patterns. Cation and anion sums for 2003 continued to demonstrate the clear regional differences in baseflow chemistry between EOH and WOH sites (Fig. 3.1) as was evident from Phase I results . In general, ionic composition, which indicates the amount of dissolved solids in stream water, was two to four times greater for EOH sites relative to WOH sites. Notable exceptions were sites 34 (Haviland Hollow), 125 (Quaker Brook at W.G. Merrit County Park - upstream of site 34) and 127 (Black Pond Brook at Meads Corner). Site 127, which is in the West Branch Croton watershed, is upstream of any influence from the Delaware Aquaduct water that empties into the West Branch Reservoir.

There were slight differences between WOH and EOH sites for suspended solids. TSS averaged 2.059 mg/L for the EOH (range 0.260 to 7.612 mg/L) and 2.229 mg/L (range 0.249 to 6.442 mg/L) for the WOH sites (Figure 3.2). VSS averaged 0.888 mg/L (range 0.185 to 2.491 mg/L) for the EOH and 0.573 mg/L (range 0.217to 1.473 mg/L) for the WOH sites (Fig. 3.2). The average organic matter content was 48.2% for the EOH (range 24.6 to 82.5%) and 32.4% for the WOH (range 11.7 to 87.5%) (Fig. 3.3).

The primary factor in separating the stream sites based on relative baseflow chemistry was total ionic composition as determined by separate Principal Components Analyses (PCA) on baseflow major ion and nutrient concentrations for each region (Figs. 3.4 and 3.5) including both Phase I and Phase II sites. Three-year means were used to represent analyte concentrations at Phase I sites. The PCA loading plots (Figs. 3.4a and 3.5a) show that along the first PCA axis, the influence of each input variable was relatively similar, although for the EOH results, some of the N species (NH_4-N, TKN, SKN, OrgN) were not as important in separating sites as the remaining analytes (at least along this first axis). It should be noted that the EOH PCA was run without including three sites from Phase I that had very high nutrient concentrations: Hallocks Mill Brook (49), Secor Brook (43), and an unnamed tributary to the New Croton Reservoir near Lake Purdy (58). The WOH PCA results suggest that the Phase II sites, as a group, have relatively lower ionic composition and relatively higher nutrient concentrations. This observation stems from the relative position of Phase II site scores in Fig. 3c, where more Phase II sites then Phase I sites plot in the lower two quadrants of the figure. Based on the loadings in Fig. 3a, the lower two quadrants would reflect lower ionic concentration and higher nutrient concentrations (the arrows in Fig. 3a indicate direction of influence for the given variable). The EOH PCA results suggest that Phase II sites encompass the conditions found for Phase I sites in terms of inorganic water quality factors driving separation of sites. It must be emphasized that since these results only reflect the first year of Phase II work, no definitive conclusions or observations should be drawn regarding Phase II-to-Phase I site comparisons.

Potential anthropogenic influences on baseflow chemistry. Multiple linear regression was used to explore relationships between individual measures of water chemistry for samples collected in 2003 and selected watershed characteristic variables (Table 3.1). While water chemistry is a response variable to the influences of upstream watershed landscape conditions, cause-and-effect can not be inferred from these models. A stepwise variable selection process was used to determine significant watershed characteristic variables at a significance cut-off of 0.05. The watershed characteristics brought into the stepwise routine as independent variables were the percentages of impervious surface (IMP), agriculture (AGR), and wetlands (WET), along with average annual WWTP annual flow for 2002 normalized for watershed area (log_{10}-transformed with 0.1 added to all values), and total persons based on the 2000 Census (log_{10}-transformed). Separate regressions were run for EOH and WOH sites. Regressions within each of these defined regions were run for the following suite of analytes: chloride (Cl), sulfate (SO_4), calcium (Ca), potassium (K), magnesium (Mg), sodium (Na), particulate N &P (PN, PP), total dissolved N & P (TDN, TDP), alkalinity (ALKL), conductivity (COND) and pH. Water chemistry data were log_{10}-transformed with 0.01 added to the PN and PP values to avoid taking the log of zero.

Of all the models run, only one was not significant – the PN model for EOH sites. For many of these models, a great deal of variability in stream chemistry was explained by one or more of the five watershed characteristic variables as reflected in the high R^2 values. Overall though, WOH models tended to have stronger relationships between stream chemistry and watershed characteristics based on R^2 values. Watershed characteristics that drove the observed relationships were impervious area for anions, both EOH and WOH, and cations for EOH; agriculture was the dominant predictor of cation chemistry and to a limited extent nutrients for WOH sites. Impervious area was a significant predictor of EOH site conductivity, but with an R^2=0.44 the relationship was not very strong. Agriculture was the dominant predictor of conductivity for WOH sites.

Stormflow inorganic and nutrient water quality.

Ionic, nutrient, suspended particles, and DOC values for the single storm collected at the West Branch Delaware site are provided in Table 3.2. Baseflow values, collected August 19, 2003, are also provided for comparison. Discharge during this storm event increased approximately 10-fold (Fig. 2.6 – Chapter 2). In general, dissolved solid concentrations decreased with this storm event, as reflected in the conductivity values, with suspended particles increasing. Of the four storms sampled at this site (3 storms were sampled in Phase I), this storm event represented the largest storm (in terms of overall discharge and change in discharge from pre-storm baseflow) collected at this site.

Literature Cited

American Public Health Association (APHA). 1992. Standard methods for the examination of water and wastewater. 18th edition. American Water Works Association, Water Environment Federation, Washington, DC. pp. 2-44.

Rounds, S. A., and F. D. Wilde. 2001. Chapter 6.6 Alkalinity and acid neutralizing capacity. Pages 50 *in* National field manual for the collection of water-quality data: U.S. Geological Survey techniques of water-resources investigations, book 9. USGS Information Services, Denver, CO.

Table 3.1: Multiple linear regression results (partial and full R^2 values) for the model of an individual water quality parameter (2003 values) regressed against the selected watershed characteristics (WWTP volume and total persons were log_{10}-transformed). A stepwise procedure was used to select/reject independent variables based on an α=0.05. Water quality units are mg/L except for pH, conductivity (µS/cm), and alkalinity (µeq/L); all concentration data were log_{10} transformed (0.01 added to PN, PP values).

		Regression partial R^2					
ANALYTE	REGION	IMP	AGR	WET	WWTP VOLUME 2002 (cm)	TOTAL PERSONS (2000)	R^2
ANION							
CL	EOH	0.39					0.39
CL	WOH	0.47			0.13	0.05	0.66
SO4	EOH	0.11		0.45			0.56
SO4	WOH	0.45	0.09		0.07		0.60
CATION							
CA	EOH	0.42					0.42
CA	WOH		0.54		0.17		0.71
K	EOH	0.51	0.12				0.62
K	WOH		0.87		0.04		0.91
MG	EOH	0.60					0.60
MG	WOH		0.71		0.09		0.80
NA	EOH	0.35					0.35
NA	WOH	0.52			0.12	0.05	0.69
NUTRIENTS							
PN	EOH						--
PN	WOH			0.24	0.10		0.34
TDN	EOH	0.66					0.66
TDN	WOH		0.68		0.06		0.74
PP	EOH			0.09		0.47	0.56
PP	WOH			0.43			0.43
TDP	EOH	0.40		0.09			0.50
TDP	WOH		0.58		0.05		0.63
OTHER							
ALKL	EOH	0.31	0.11				0.42
ALKL	WOH		0.51		0.09		0.60
COND	EOH	0.44					0.44
COND	WOH	0.03	0.56		0.21		0.80
PH	EOH		0.22	0.21			0.43
PH	WOH		0.30				0.30

Table 3.2: Stormflow data for the West Branch Delaware River at Hawleys (site id 6) site collected on September 23, 2003. Summer baseflow data are shown for comparison. Flow data and relative position of samples on the storm hydrograph can be found in Chapter 2 (Figure 2.6).

Analyte	Baseflow data	High Turbidity	High Flow
Sample Date	19AUG03	23SEP03	23SEP03
pH	8.3	7.3	7.2
Conductivity (uS/cm)	107	73	68
Alkalinity (ueq/L)	543	370	345
Chloride (mg/L)	10	7.3	6.3
Sulfate (mg/L)	6.7	5.5	5
Magnesium (mg/L)	2.3	1.5	1.4
Calcium (mg/L)	11	6.9	6.1
Sodium (mg/L)	6.8	4.1	3.6
Potassium (mg/L)	1.1	2.4	2.4
Nitrate-N (mg/L)	0.5	0.4	0.3
Ammonia-N (mg/L)	0.01	0.003	0.01
Soluble Kjeldahl N (mg/L)	0.2	0.3	0.4
Organic-N (mg/L)	0.2	0.3	0.4
Soluble reactive phosphorus (mg/L)	0.02	0.04	0.05
Total Dissolved P (mg/L)	0.02	0.05	0.06
Kjeldahl N (mg/L)	0.2	1	1.1
Total P (mg/L)	0.02	0.2	0.2
Total suspended solids (mg/L)	3.6	130	89
Volatile suspended solids (mg/L)	0.9	18	12
Percent organic matter (%)	26	14	14
DOC (ug/L)	2173	1399	1789

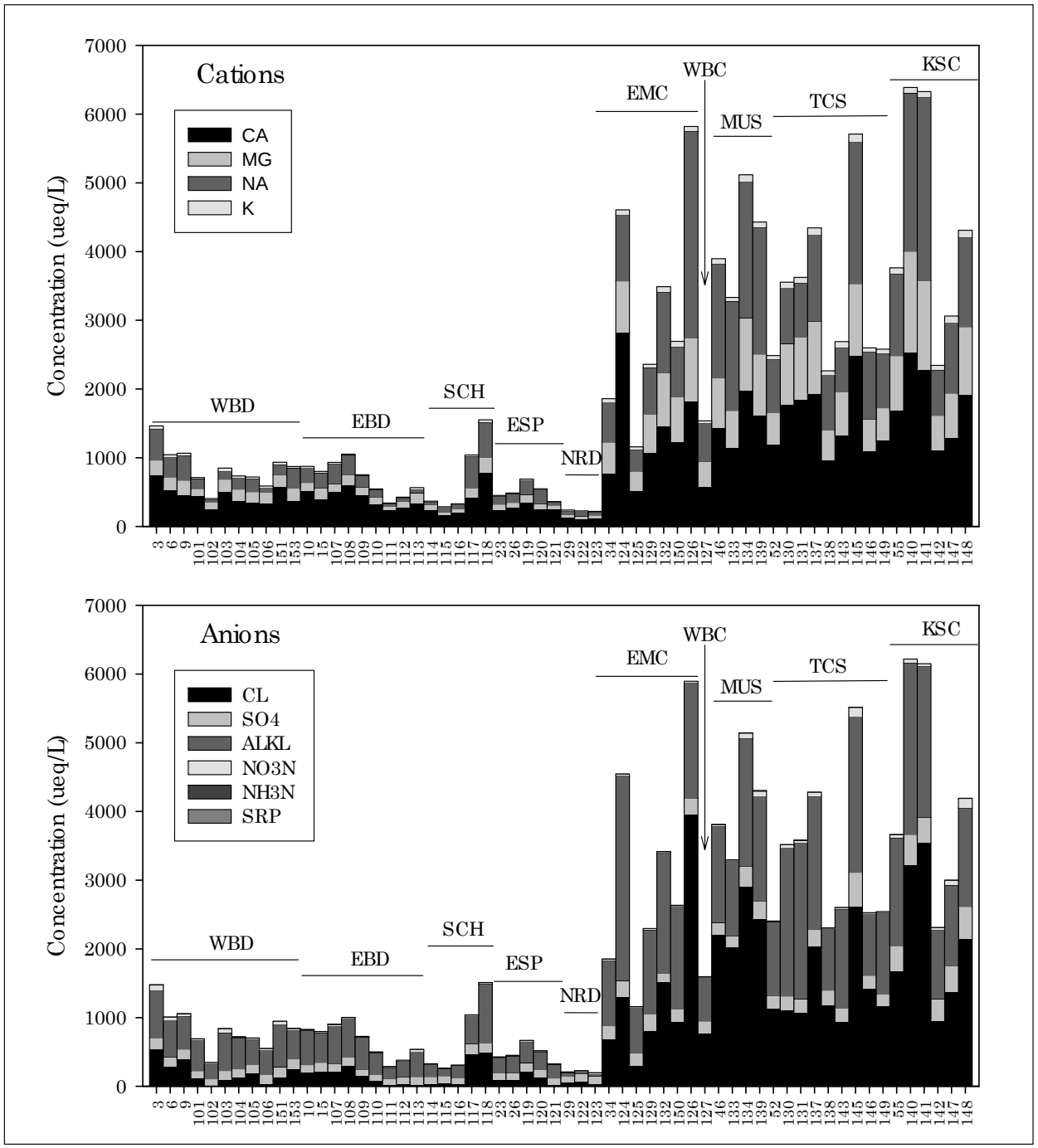

Figure 3.1: Major cation and anion summaries for all 60 stream monitoring sites for the 2003 sampling year. Subwatershed designations are: Neversink River and Rondout Creek (NRD); Esopus Creek (ESP); Schoharie Creek (SCH); E. Br. Delaware River (EBD); and W. Br. Delaware River (WBD). E. & M. Br. Croton R. (EMC); W. Br.Croton R. (WBC); Muscoot R. (MUC); Titicus, Cross, and Stone Hill Rivers (TCS); and Kensico Resv. & Lower New Croton Resv. (KSC).

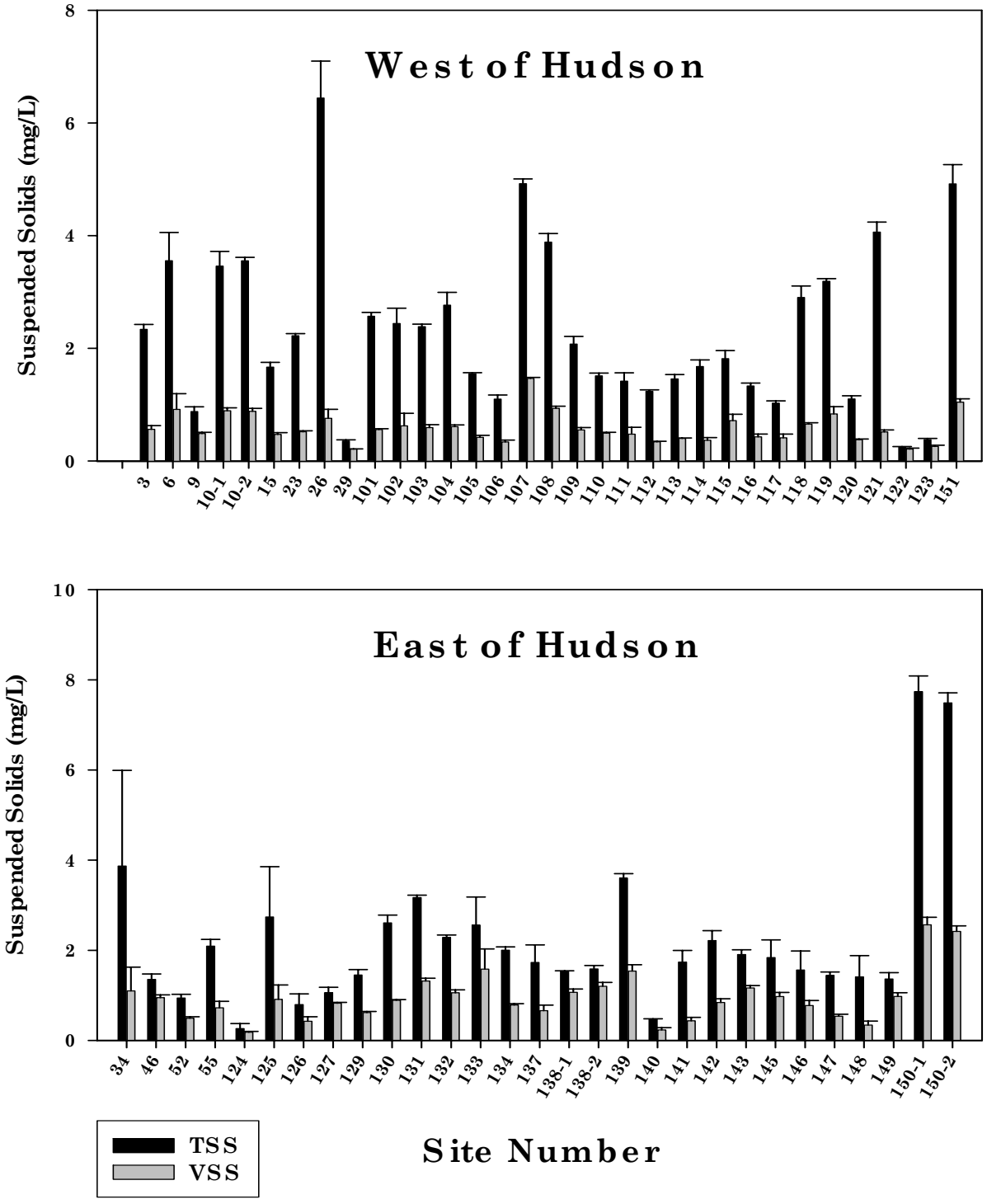

Figure 3.2: Whole sample Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) from samples collected at EOH and WOH sites in 2003. Error bars (standard deviation) reflect variability among three replicate samples collected per site.

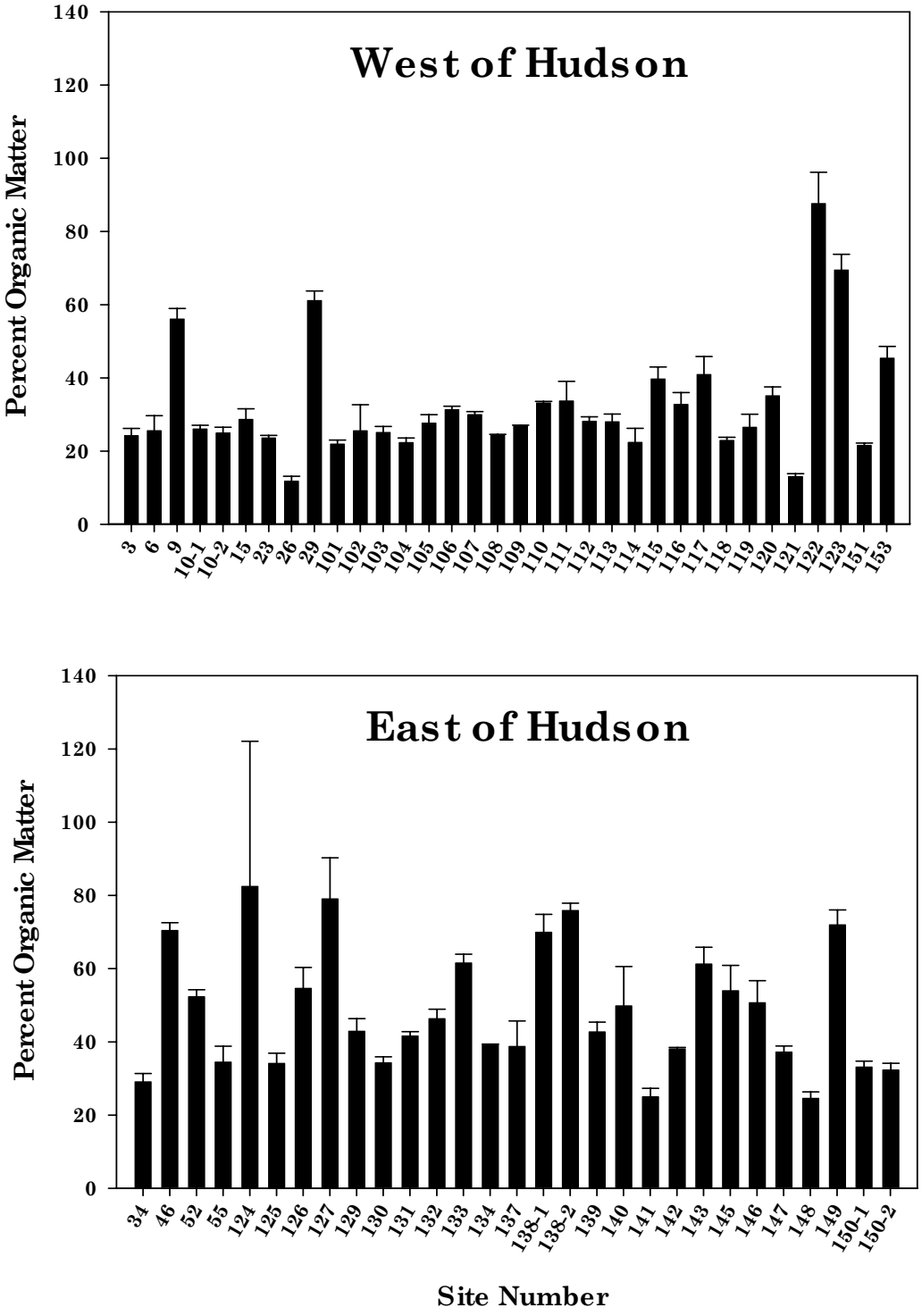

Figure 3.3: Percent organic matter (as VSS/TSS*100) for the 2003 sampling effort at all EOH and WOH sites. Error bars (standard deviation) reflect variability among three replicate samples collected per site.

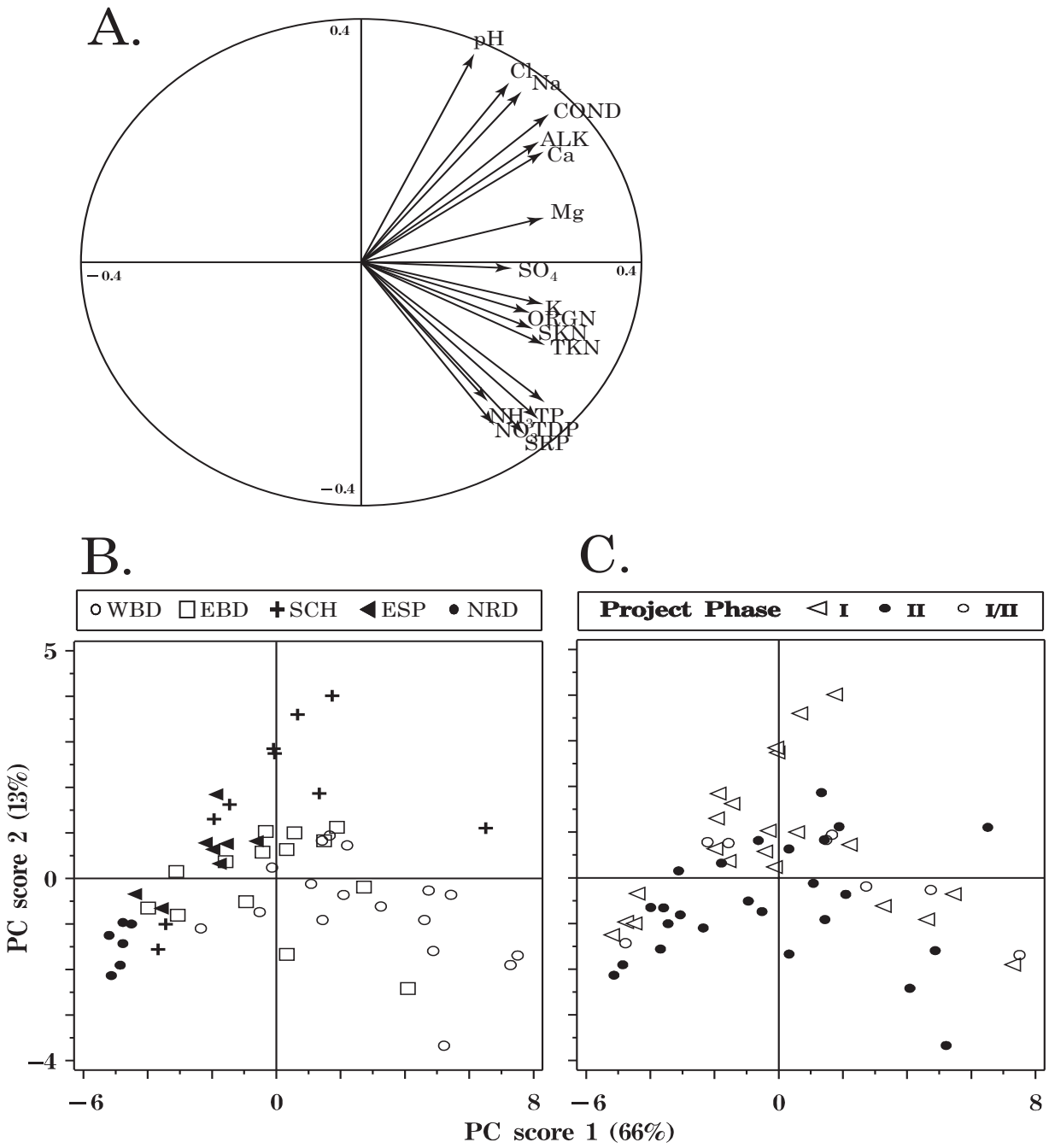

Figure 3.4: First and second principal component scores (results separate by watershed [B]; and sampling time whether in Phase I, II or both [C]) and loadings (A) from a PCA of inorganic chemistry for the 33 WOH sites. All input variables were log –transformed. Site variability explained by the first two PC scores is provided in the axis labels. Subwatershed designations are: Neversink River and Rondout Creek (NRD); Esopus Creek (ESP); Schoharie Creek (SCH); E. Br. Delaware River (EBD); and W. Br. Delaware River (WBD).

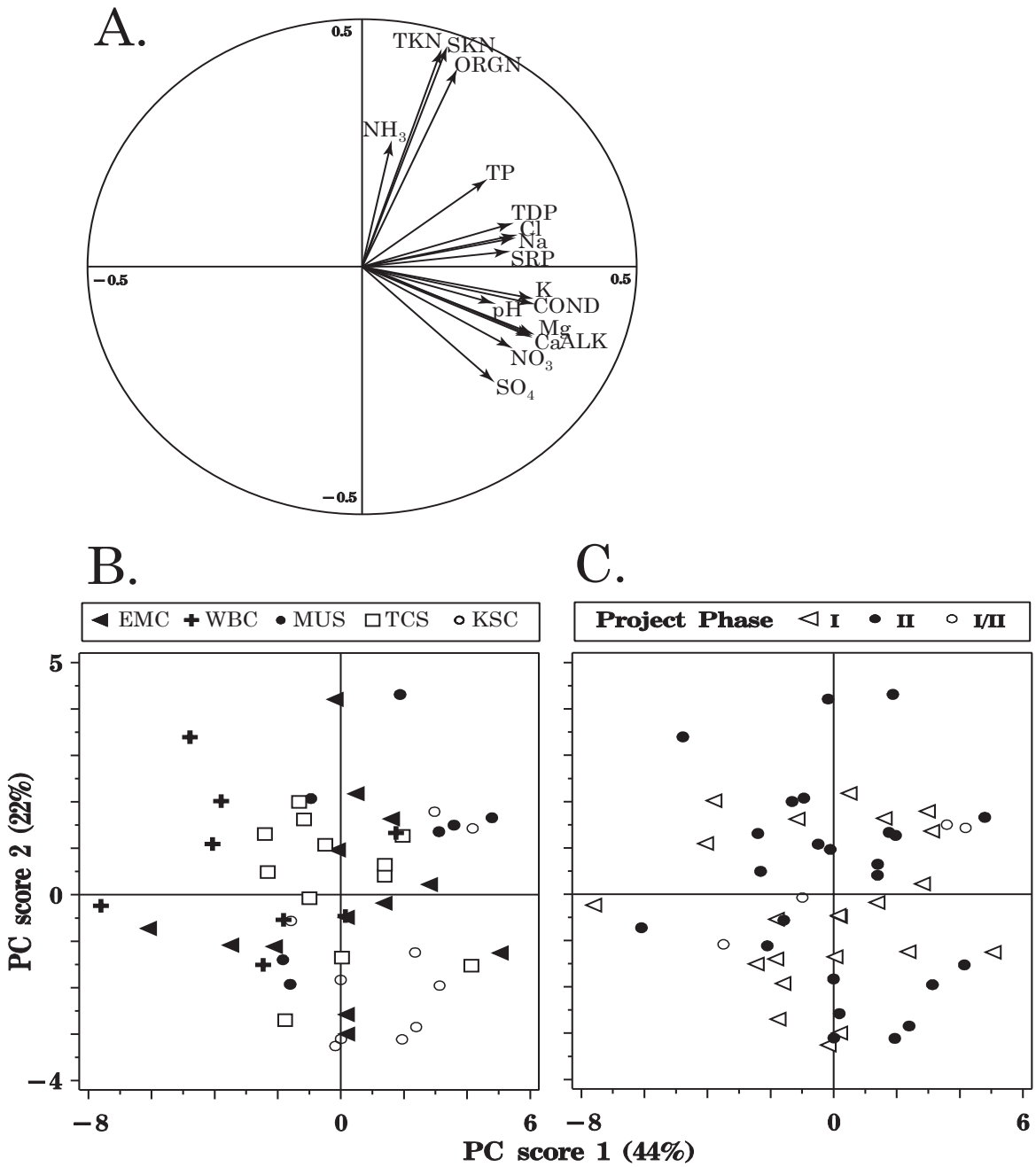

Figure 3.5: First and second principal component scores (results separate by watershed [B]; and sampling time whether in Phase I, II or both [C]) and loadings (A) from a PCA of inorganic chemistry for the 27 EOH sites. All input variables were log –transformed. Site variability explained by the first two PC scores is provided in the axis labels. Subwatershed designations are: Kenisco Resv and Lower New Croton Resv (KSC); Titicus , Cross, and Stone Hill Rivers (TSC); Muscoot River (MUS); E. and M. Br. Croton Rivers (EMC); and W. Br. Croton River (WBC). Phase I sites Hallocks Mill Brook (49), Secor Brook (43), and an unnamed tributary to the New Croton Reservoir near Lake Purdy (58) were not included in the analysis.

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Chapter 4 - Molecular Tracers in Transport

Introduction

Degradation of water quality can occur from a variety of point and non-point sources of natural and anthropogenic contamination, such as sewage (from septic leakage or waste water treatment plants (WWTP) effluent), atmospheric deposition, road and agricultural runoff, and wildlife. The range of contaminants includes nutrients, heavy metals, pesticides, other toxic organic compounds, and pathogens. In order to best maintain the quality of drinking water resources, targeted efforts to reduce or eliminate primary contamination sources first require the accurate identification and quantification of all contaminant sources that contribute to water quality impairment. The use of molecular tracers to identify sources of contaminants is an emerging technique that qualitatively links the presence of components unique to these sources with contaminants of concern (Leeming *et al.* 1996; Simonich *et al.* 2000; Standley *et al.* 2000; Kolpin *et al.* 2002; Buerge *et al.* 2003).

We have chosen a suite of 25 organic compounds that act as robust proxies for a variety of contamination sources (Table 4.1). These compounds include twelve polycyclic aromatic hydrocarbons (PAH), two fragrance materials (FM), caffeine (CAF) and seven fecal steroids (FS). Polycyclic aromatic hydrocarbons are found in raw and refined petroleum and coal products and are also formed during the combustion of vegetation, wood, waste, coal and petroleum. Thus PAHs have both natural and anthropogenic sources. The compounds that we quantify here were fluorene (FLU), phenanthrene (PHE), anthracene (ANT), 2-methyl phenanthrene (2MP), 1-methyl phenanthrene (1MP), fluoranthene (FLR), pyrene (PYR), benzo(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), and benzo(a)pyrene (BAP). Fragrance materials are anthropogenic compounds used in a variety of consumer products such as soaps, detergents and lotions. Thus, FMs enter the environment primarily through greywater sewage (Simonich *et al.* 2000). The compounds that we quantify here were tonalide (7-acetyl-1,1,3,4,4,6,-hexamethyl-1,2,3,4-tetrahydronaphthalene, AHTN) and galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[γ]-2-benzopyran, HHCB). Both AHTN and HHCB are non-biodegradable, making them particularly suited for tracers studies (Simonich *et al.* 2002). Caffeine is a natural compound that occurs in certain tropical plants, including tea and coffee, and is added to numerous food products and pharmaceuticals. In temperate climates, the primary source of caffeine to watersheds is via the urine of those who consume caffeine-containing products (Buerge *et al.* 2003). Fecal steroids are natural compounds that are produced in the intestines of birds and mammals. Ratios of certain steroids to others allow for the discrimination between human fecal material and that of other animals (Leeming *et al.* 1996). The steroids we quantify for this study were coprostanol (5β-cholestan-3β-ol, bCOP), *epi*coprostanol (5β-cholestan-3α-

ol, EPI), cholesterol (cholest-5-en-3β-ol, CHOL), cholestanol (5α-cholestan-3β-ol, aCOP), coprostanone (5β-cholestan-3-one, bONE), cholestanone (5α-cholestan-3-one, aONE), 24-ethyl-coprostanol (24-ethyl-5β-cholestan-3β-ol, eCOP), 24-ethyl-*epi*coprostanol (24-ethyl-5β-cholestan-3α-ol, eEPI), 24-ethyl-cholesterol (24-ethyl-cholest-5-en-3β-ol, eCHO), and 24-ethylcholestanol (24-ethyl-5α-cholestan-3β-ol, SNOL).

Research Task

Monitoring for molecular tracer content in samples collected from New York City drinking water source watersheds was conducted at each of 60 stream sampling stations (see Chapt. 2 and Tables 2.1-2.4 and Figs. 2.1-2.2) during summer baseflow conditions to determine the relative influence of contaminant sources on water quality. In addition, molecular tracers were analyzed in samples collected during winter baseflow conditions at 28 sites targeted to provide information on background levels, winter recreation area influences, and the effect of low temperatures on sewage treatment efficiency. However, as we have done in previous years (with the exception of the Phase I report), winter baseflow data for this project year will be presented in next year's report. Stormflow samples were collected at one "integrative" sampling station to determine changes in source composition, as determined by molecular tracer fingerprints, with storm runoff.

The molecular tracer investigation targets two of the projects primary objectives, as listed in the Quality Assurance Project Plan (QAPP). First, molecular tracers are designed to act as indicators for evaluating the occurrence and source of selected aquatic chemical contaminants. Second, the three-year data set will be utilized as a baseline for assessing changes in water quality in response to changes in land use and best management practice (BMP) implementations.

Methods

Detailed descriptions of our field and laboratory methods were provided in the Quality Assurance Project Plan (QAPP) for Project Year 4 and the Standard Operating Procedures attached therein. What follows is a brief description of these methods.

Field

During summer and winter baseflow collections, 8 L water samples were collected for tracer analysis in pre-cleaned glass jars. At the same time, samples were collected for all other baseflow analyses (i.e., nutrients, major ions, TSS, DOC, etc. see Chapters 3 & 6). Stormflow samples were collected using ISCO samplers fitted with pre-cleaned glass receiving bottles. The ISCO samplers were set to begin sampling with a small rise (approximately 10 to 15 cm) of stream water and took

two 1-liter samples every hour for up to 12 hours. A subset of two paired 1-L samples for each stream – representing high flow (HF) and high turbidity (HT) – were chosen for analysis. Selection of the two samples were based on examining the storm hydrograph available from a nearby USGS gauging station collecting near real-time data or from a co-located stage recorder (In-Situ, Inc., Mini-Troll). Peak particulate concentrations were determined visually. High flow samples were removed from the ISCO apparatus within 18 hours of collection and then handled in the same manner as baseflow water samples. Water samples were stored in a cool and dark place and extracted within 7 days.

All glass sampling equipment and sample jars were precleaned of organic contaminants baking in a kiln at 480°C for 4 hours. Metal and Teflon sampling equipment was cleaned with solvent rinses, as was any field equipment that needed to be reused between sites. The probe and collection tubing on ISCO samplers were cleaned weekly with 0.1 N HCl, 0.1 N NaOH, and deionized water.

Field blanks and duplicates were each collected at three sites during summer baseflow sampling (5% of sites) and two sites during winter baseflow sampling. One set of field blanks and duplicates was collected through the ISCO sampler during stormflow collections.

Laboratory

Molecular tracers were extracted from all samples by liquid-solid extraction onto an Empore™ disk, using protocols similar to EPA approved alternate test method 608 ATM 3M0222 or to EPA Method 3535. In 2003, we used a protocol that had been modified slightly over that used previously in order to increase reproducibility, recovery and sensitivity, as was described in an addendum to our Year 4 QAPP. In addition, for summer 2003 baseflow samples, we analyzed concentrations of tracers associated with the dissolved phase separately from those in the particulate phase.

In brief, sample water was filtered through a glass fiber filter stacked on top of an Empore™ C-18 solid phase extraction (SPE) disk. Particulate tracer compounds were extracted from the filter by sonic extraction and dissolved tracers were eluted from the Empore disk with solvents. Surrogate recovery standards – perdeuterated phenanthrene (PHE-D10), perdeuterated chrysene (CHR-D12), perdeuterated perylene (PER-D12), perdeuterated caffeine (CAF-D9) and perdeuterated cholesterol (CHO-D6) – were added to the surface of both the filter and the disk, after they were separated but prior to extraction. Dissolved and particulate extracts were then back-extracted in a separatory funnel with an aqueous salt solution to remove impurities, mixed with anhydrous sodium sulfate to remove moisture, rotoevaporated, and transferred to auto-injector vials. Concentrated sample extracts were derivitized with BSTFA (N,*O*-bis(trimethylsilyl)trifluoroacetamide) with 1% TMCS (Trimethylchlorosilane) in order to analyze fecal sterols, which contain alcohol groups. These derivitized sample extracts were analyzed for each of the

molecular tracers compounds by capillary gas chromatography – mass spectrometry (GC/MS) in selective ion monitoring (SIM) mode, using a J&W DB1701 column (30 m, 0.25 mm i.d., 250 μm coating) on an Agilent 6890 series GC interfaced with a 5973n series MS.

Laboratory blanks and duplicates, and matrix spike samples, were prepared in conjunction with all sites having field blanks and duplicates (3 sites during summer baseflow sampling and two sites during winter baseflow sampling).

Quantification

As described in our Phase I report, we now quantify molecular tracer data with an automated data quantification system. In brief, after confirmation by the analyst, compound peak areas for standards and samples were exported from the Agilent GC-MS "ChemStation" chromatography software directly into our central server. We then manipulate this raw data within the server with SAS-based scripts to produce the final data. Thus, decisions – regarding how to fit the calibration curve, when to drop outlying standards, whether or not peak identity is adequately confirmed, etc. – were all made uniformly for 2003 data using the same objective criteria used in the previous three years.

All data presented here were surrogate-corrected with the extraction recoveries measured within each sample for each surrogate standard, which were associated with tracer compounds as follows (see Table 4.1): perdeuterated phenanthrene (D_{10}-PHE) for FLU, PHE, ANT, 2MP, and 1MP; perdeuterated chrysene (D_{12}-CHR) for FLR, PYR, BAA, and CHR; the average recovery of D_{10}-PHE and D_{12}-CHR for HHCB and AHTN; perdeuterated perylene for BBF, BKF, and BAP, perdeuterated caffeine (D_9-CAF) for CAF and perdeuterated cholesterol (D_6-CHO) for all fecal steroids.

Results

Summer Baseflow

Total concentrations of PAHs in summer base flow samples varied by up to two orders of magnitude between sites (Fig 4.1, 4.2). For the ten sites that were also sampled during the first three years of this project (Phase I), concentrations measured in 2003 were consistently lower, by as much as an order of magnitude, lower than the geometric mean from Phase I (Fig. 4.1, 4.2). In general, total PAH concentrations were higher at east of Hudson (EOH) sites relative to west of Hudson (WOH) sites, such that 25 of the 27 EOH sites were in the top 37 most contaminted sites (Fig. 4.1a). Concentrations of both low-molecular weight, volatile PAHs and high-molecular weight "soot" PAHs appear to generally follow similar patterns between sites as total PAHs (Fig. 4.1), as do concentrations of individual

PAHs (Fig. 4.2). However, inter-site variations in the volatile PAHs were not as great as that observed in the soot PAHs (Fig. 4.1-4.2), with the former varying by less than one order of magnitude and the latter by two orders of magnitude. This pattern was not observed in Phase I data (SWRC 2003). For volatile PAHs, concentrations in the dissolved phase generally exceed concentrations contained in suspended particles, whereas the reverse appeared to be true, although not as consistently, for soot PAHs (Fig. 4.1).

Molecular tracers do not necessarily need to be toxic compounds. However, ten of the twelve PAHs analyzed for this project were listed by the EPA as Priority Toxic Pollutants and five of these were known human carcinogens (EPA 2002a, EPA 2002b). These five most toxic PAHs (BAA, CHR, BAP, BBF, BKF) have been given exceptionally low "National Recommended Water Quality Criteria for Human Health" of 0.0038 µg/L for the consumption of the water or 0.018 µg/L for the consumption of organisms living in the water (EPA 2002b). Similarly, NY State Department of Environmental Conservation (NYSDEC) has set water quality guidance values of 0.002 µg/L for these same compounds (BAA, CHR, BAP, BBF, BKF) for ambient waters directly feeding water supplies, 0.0012 µg/L for BAP in waters used for fish consumption, and 0.03 µg/L for BAA as a flag of chronic toxicity to aquatic life (NYSDEC 1998). In contrast to results from Phase I (SWRC 2003), only six sites exhibited concentrations that exceeded the lower limit of the EPA criteria in at least one of these compounds and only one site had a compound that exceed the higher limit (Fig. 4.2). Although these are non-regulatory guidance values that are not enforceable, and none of the sites are near water supply intakes, these guidance values are useful to place measured PAH concentrations in the context of potential human and ecosystem toxicity. In all but one case (BAP at site 125), these high concentrations were driven by high concentrations of PAHs in stream water particles.

The ratios of certain PAH compounds to others have been used to identify both petroleum sources, such as spills of kerosene, diesel oil, lubricating oil and crude oil (Yunker *et al.* 2002; Zakaria *et al.* 2002), and combustion sources, such as automotive exhaust, smelter emissions, coal burning emissions and wood smoke (Dickhut *et al.* 2000; Yunker *et al.* 2002). Two of the most useful of these ratios are that of ANT/(ANT+PHE) and FLR/(FLR+PYR), where low values suggest petroleum sources and high values combustion sources (Fig. 4.3ab). The petroleum/combustion transition point for ANT/(ANT+PHE) is considered to be 0.1. For FLR/(FLR+PYR) the transition is less clear, and values between 0.4 and 0.5 are considered to indicate mixed sources (Yunker *et al.* 2002). Another useful source indicator is the ratio of high molecular weight (HMW) PAH compounds to low molecular weight (LMW) PAH compounds (H/L_{PAH})(Fig. 4.3c). In general, LMW, volatile PAHs strongly predominate over HMW PAHs in crude oil and most refined petroleum products (with the exception of asphalt) (Zakaria *et al.* 2002), whereas HMW PAHs are the primary constituents of soot (Countway *et al.* 2003). Ratios above approximately 0.5 appear to indicate combustion sources.

In general, PAH source indicator ratios generally high. For our 2003 data, only six sites exhibited ANT/(ANT+PHE) ratios (of total PAHs) less than 0.2 and only one site exhibited a FLR/(FLR+PYR) ratio less than 0.4. H/L_{PAH} ratios were more split, with 16 of 60 sites having values below 0.5. H/L_{PAH} ratios in particles were generally much higher than those found in the dissolved phase.

Caffeine concentrations spanned almost four orders of magnitude between sites (Fig. 4.4a). In all but three cases, concentrations in the dissolved phase were higher than those associated with particles. Concentrations were lower in 2003 than Phase I geometric means for six of the ten sites also sampled in Phase I.

Fragrance materials showed generally uniform concentrations between sites (Fig. 4.4a). Similar to caffeine, concentrations in the dissolved phase were generally higher than those associated with particles.

Total fecal steroid concentrations were substantially less concentrated in 2003 relative to Phase I samples (Fig. 4.5a). These lower concentrations were noteworthy because of the exceptional interannual consistency observed for sites in Phase I. Coprostanol concentrations showed a very similar pattern to that of total fecal steroids (Fig. 4.5b). The primary exception is that concentrations of bCOP ranged over five orders of magnitude, whereas total fecal steroids only ranged two orders of magnitude. Because bCOP is the dominant FS found for humans and is a minor FS component for all other animals (Leeming *et al.* 1996), concentrations of bCOP in surface waters tend to directly correlate with human sewage inputs (Leeming and Nichols 1996). Thus, linear relationships between bCOP and bacterial indicators of sewage contamination (fecal streptococci and thermotolerant coliforms), allow for the translation of bCOP concentrations into fecal bacterial counts. Using the relationships in Leeming and Nichols (1996), three sites (107, 109 and 110) consistently contained more than 0.1 μg/L of bCOP corresponding to 35 enterococci (a subset of fecal streptococci) and 300 thermotolerant coliforms per 100 mL of water. Unlike caffeine and fragrance materials, fecal steroids appeared evenly distributed between particulates and the dissolved phase.

Similar to PAHs, ratios of fecal steroids can help distinguish potential sources (Fig. 4.6). The ratio bCOP/(bCOP+aCOP) has been used to demonstrate a predominance of fecal contamination from humans relative to that from livestock and wildlife (Grimalt *et al.* 1990; O'Leary *et al.* 1999). O'Leary et al. (1999) suggested that values of this ratio >0.3 are a clear indication of human fecal contamination and values between 0.2 and 0.3 suggest mixed sources. The ratio bCOP/(bCOP+EPI) has also been used to distinguish human sewage from other fecal contamination sources, with values > 0.5 attributable only to humans (Leeming *et al.* 1998). Last, because cholesterol is widely found in all organisms, bCOP/CHO has also been used to trace human sewage contamination (Mudge and Seguel 1999).

For our 2003 data, values of fecal steroid ratios were high for a number of sites. Seven sites have bCOP/(bCOP+aCOP) ratios over 0.5 and 26 sites have ratios over 0.2. Ratios of bCOP/CHO mirror these patterns, and 40 sites exhibit bCOP/(bCOP+EPI) values greater than 0.5.

Stormflow

Due to technical difficulties related to the overabundance of storms, we were ironically only able to collect one acceptable set of samples from one storm at one site (6) during 2003. Peak discharge (60 m^3/s) was larger during this storm than any of the other three that we had sampled at that site (15, 40 and 10 m^3/s respectively) (Fig. 2.6), and as a result total suspended sediment (TSS) concentrations (130 mg/L at high turbidity and 89 mg/L at high flow) were almost three times higher than previously observed (Table 3.1). This situation offers a unique opportunity to examine processes, given that tracer concentrations were quantified for the dissolved and particulate phases for this 2003 sampling.

Concentrations of both dissolved and particulate PAHs increased by about one order of magnitude during this storm (Fig. 4.7a). However, the ratio of high to low molecular weight PAHs and the ANT/(ANT+PHE) ratios during this storm did not differ substantially from base flow values (Fig. 4.7). This was in contrast to observations of increasing ratios in two of the three previously sampled storms.

Caffeine and fragrance material concentrations exhibited a larger increase during this storm than for previously observed storms, by more than one order of magnitude relative to baseflow (Fig. 4.8). Concentrations of each peaked during the high-turbidity rising limb of the hydrograph, despite the fact that more than 90% of the caffeine and more than half of the fragrances were found in the dissolved phase. Coupled by the fact that these stormflow concentrations were comparable or less than baseflow concentrations measured previously, suggests that these compounds get flushed from the watershed.

The sum of fecal steroids and coprostanol also exhibited larger increases during this storm than observed previously (Fig. 4.9), whereas concentrations were in the same range as previous observations, with generally very reproducible values between events (Fig. 4.9a). Coprostanol, on the other hand, only showed storm related increases in concentrations at the Neversink (site 29) (Fig. 4.9b). bCOP/(bCOP+aCOP) and bCOP/CHO ratios both increase during the storm, suggesting that the increased fluxes of fecal steroids into the river were primarily from human sources.

Discussion

Sources

Polycyclic aromatic hydrocarbons have three groups of sources that can be distinguished from one another based on compound distributions and ratios. These were: (1) petroleum products – such as kerosene, diesel oil, lubricating oil and crude oil – which were characterized by lower ratios of less stable to more stable isomers (i.e., ANT/(ANT+PHE) or FLR/(FLR+PYR)) and by lower ratios of high to low molecular weight PAHs (H/L_{PAH}) (Yunker *et al.* 2002; Zakaria *et al.* 2002); (2) combustion byproducts – such as automotive exhaust, smelter emissions, coal burning emissions and wood smoke – which are characterized by higher ratios of less stable to more stable isomers and by higher H/L_{PAH} ratios (Dickhut *et al.* 2000; Yunker *et al.* 2002); and (3) asphalt, which is characterized by low ratios of less stable to more stable isomers (similar to petroleum products) and by higher H/L_{PAH} ratios (similar to combustion byproducts) (Yunker *et al.* 2002).

At 2003 sites, high ratios of ANT/(ANT+PHE), FLR/(FLR+PYR) and H/L_{PAH} (Fig. 4.3) indicate that combustion emissions appear to dominate over petroleum spills as the primary source of PAHs to most of the stream sites (Fig. 4.3ab). However, these patterns appear to be less pronounced than those observed for Phase I sites during 2000 to 2002 (Fig. 4.3). In fact, H/L_{PAH} ratios in particular suggest that petroleum products could have been an important source of PAHs at nearly a third of all sites. However, total concentrations of PAHs from any source were substantially reduced relative to Phase I findings (Fig. 4.1-4.2). These observations can possibly be explained by the high levels of precipitation throughout the summer of 2003. Higher water flows would preferentially dilute PAH components from sources that have a constant flux (i.e., soot from automobiles and coal-fired power plants), whereas flushing of pavement and sewage systems by heavy rains would tend increase the fluxes (per unit watershed area) of petroleum products into streams and rivers. This flushing would increase the relative proportions of petroleum sources while at the same time concentrations might still decrease due to dilution.

Caution should be taken, however, when interpreting subtle differences in H/L_{PAH} ratios because of the substantial enrichment of high molecular weight PAHs in particles. Clearly, in-stream variations in flow that change the concentrations of suspended particulates can in turn have a strong affect on these ratios. At the same time, the high correlation between dissolved and particulate concentrations ($r^2 = 0.39$, $p < 10^{-7}$) demonstrates that differences in turbidity at base flow would not greatly affect inter-site comparisons.

Therefore, measured PAH concentrations and ratios at NY sites suggest that PAHs were introduced to stream waters via a combination of combustion sources (via soot deposition from local or distant locations) along with contributions from asphalt

from road runoff. Although spills of petroleum products appear to be a negligible source in general, their relative contributions may increase during exceedingly wet years. However, preferential evaporative losses of the more volatile and bioavailable low molecular weight PAHs during transport and storage in the environment could transform petroleum products to give a low ANT/(ANT+PHE) and high H/L_{PAH} signature similar to that of asphalt (Countway *et al.* 2003).

Fragrance materials, HHCB and AHTN, and caffeine are introduced to streams and rivers by relatively unambiguous sources. Fragrance materials are anthropogenic compounds introduced to the environment primarily in domestic greywater sewage. Because of the low biodegradability of these polycyclic compounds, they are transported relatively conservatively though sewage treatment and down streams (Simonich *et al.* 2002; Artola-Garicano *et al.* 2003). However, because of the hydrophobicity of HHCB and AHTN (LOG_{10} of their octanol-water partition coefficients are 5.9 and 5.7 respectively), it has been suggested that their concentrations are often a function of total suspended solid concentrations in sewage treatment plant effluent (Simonich *et al.* 2002; Artola-Garicano *et al.* 2003). Our data, showing that most of these fragrances were found in the dissolved phase (Fig. 4.4), suggest the opposite and explain why the concentrations of fragrance materials were closely correlated with caffeine, which is very hydrophilic (SWRC 2003).

The only source of caffeine to streams and rivers in temperate climates is the urine of humans (and sometimes domestic animals). Although removed more effectively than HHCB and AHTN by waste water treatment processes, caffeine still displays relatively low rates of biodegradation in the environment and is transported though waterways relatively efficiently (Buerge *et al.* 2003). However, caffeine has much lower particle affinity (LOG_{10} of octanol-water partition coefficients are -0.7, 5.7, 5.9 for caffeine, AHTN and HHCB respectively) and is thus much less affected by the dynamics of the particulate phase. In addition, these low particle affinities suggest that caffeine is much more likely to enter streams from leaking septic systems via ground water inputs.

Fecal steroids have three primary potential sources to streams and rivers; human sewage, agricultural wastes from domestic animals, and wildlife (mammals and birds). These sources can generally be differentiated because animal species excrete fecal steroids in characteristic patterns (Leeming *et al.* 1996). The most striking of these patterns is that human fecal material has extremely high concentrations of coprostanol (bCOP) relative to other steroids, whereas coprostanol is a minor component of the fecal steroids of other animals (Leeming *et al.* 1996). Although fecal steroids are known have high particle affinity, little is known about the biodegradation rates or residence times of fecal steroids in the environment.

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Table 4.1: Compounds chosen as molecular tracers, abbreviations used in this report, and ions (mass-to-charge ratios) selected for quantitation and confirmation of each compound using Selected Ion Monitoring (SIM) mode with our Gas Chromatography-Mass Spectrometry (GC-MS) system.

Compound	Abbreviation	Quant. Ion	1st Confirm. Ion	2nd Confirm. Ion	3rd Confirm. Ion
Internal Standards					
p-terphenyl-D14	TERd14	244	212	160	122
5α-cholestane	aCHO	217	357	372	149
PAH					
fluorene	FLU	166	82	139	
phenanthrene	PHE	178	89	152	76
anthracene	ANT	178	89	152	76
2-methyl phenanthrene	2MP	192	165	94	
1-methyl phenanthrene	1MP	192	165	94	
fluoranthene	FLR	202	101	88	174
pyrene	PYR	202	101	88	174
benz(a)anthracene	BAA	228	114	101	200
chrysene	CHR	228	113	101	200
benzo(b)fluoranthene	BBF	252	126	113	224
benzo(k)fluoranthene	BKF	252	126	113	224
benzo(a)pyrene	BAP	252	126	113	224
phenanthrene-D10 (surrogate)	PHEd10	188	94	160	80
chrysene-D12 (surrogate)	CHRd12	240	120	106	208
perylene-D12 (surrogate)	PERd12	264	132	118	232
Fragrances					
tonalide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[γ]-2-benzopyran)	HHCB	243	258	213	
galaxolide (7-acetyl-1,1,3,4,4,6,-hexamethyl-1,2,3,4-tetrahydronaphthalene)	AHTN	243	258	213	159
Caffeine					
caffeine	CAF	194	109	82	67
caffeine-D9 (surrogate)	CAFd9	203	115	88	70
Steroids					
coprostanol (5β-cholestan-3β-ol)	bCOP	370	355	215	257
epi-coprostanol (5β-cholestan-3α-ol)	EPI	370	215	355	257
cholesterol (cholest-5-en-3β-ol)	CHOL	368	129	329	458
cholestanol (5α-cholestan-3β-ol)	aCOP	215	460	445	335

Compound	Abbreviation	Quant. Ion	1st Confirm. Ion	2nd Confirm. Ion	3rd Confirm. Ion
24-ethyl-coprostanol (24-ethyl-5β-cholestan-3β-ol)	eCOP	398	383	215	257
24-ethyl-*epi*coprostanol (24-ethyl-5β-cholestan-3α-ol)	eEPI	398	383	215	257
cholestanone (5α-cholestan-3-one)	aONE	231	386	371	
coprostanone (5β-cholestan-3-one	bONE	231	386	371	316
24-ethyl-cholesterol (24-ethyl-cholest-5-en-3β-ol)	eCHO	129	357	486	396
24-ethyl-cholestanol (24-ethyl-5α-cholestan-3β-ol)	SNOL	215	488	473	383
cholesterol-D6 (surrogate)	CHOLd6	374	131	333	464

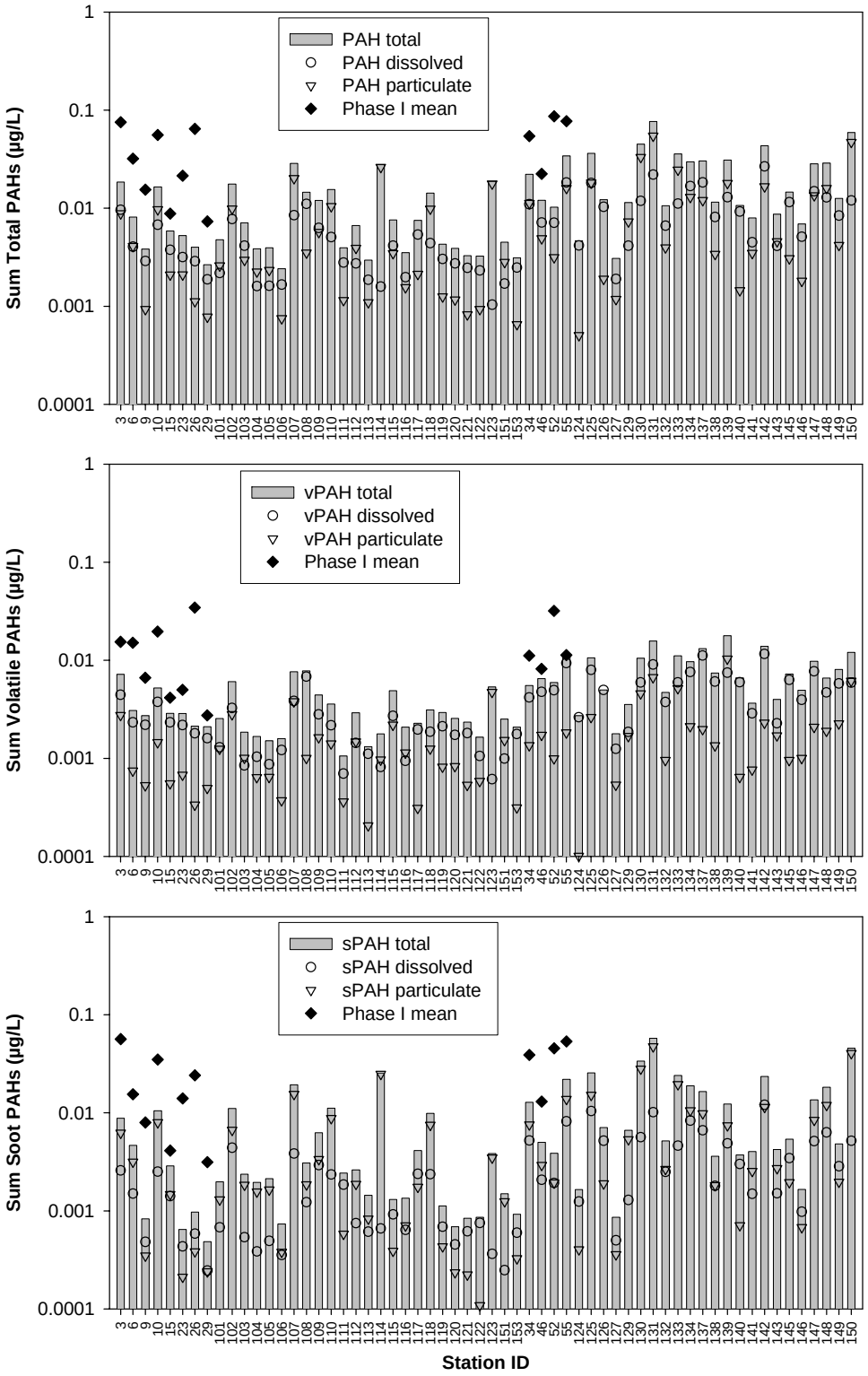

Figure 4.1: Summer baseflow stream water concentrations at all sites for the **A**) sum of all measured PAH compounds (1MP, 2MP, ANT, BAA, BAP, BBF, BKF, CHR, FLR, FLU, PHE, PYR), **B**) sum of volatile PAH compounds (1MP, 2MP, FLU, PHE), and **C**) sum of high molecular weight PAH compounds (BAA, BAP, BBF, BKF, CHR, FLR, PYR). Phase I data are presented as geometric means.

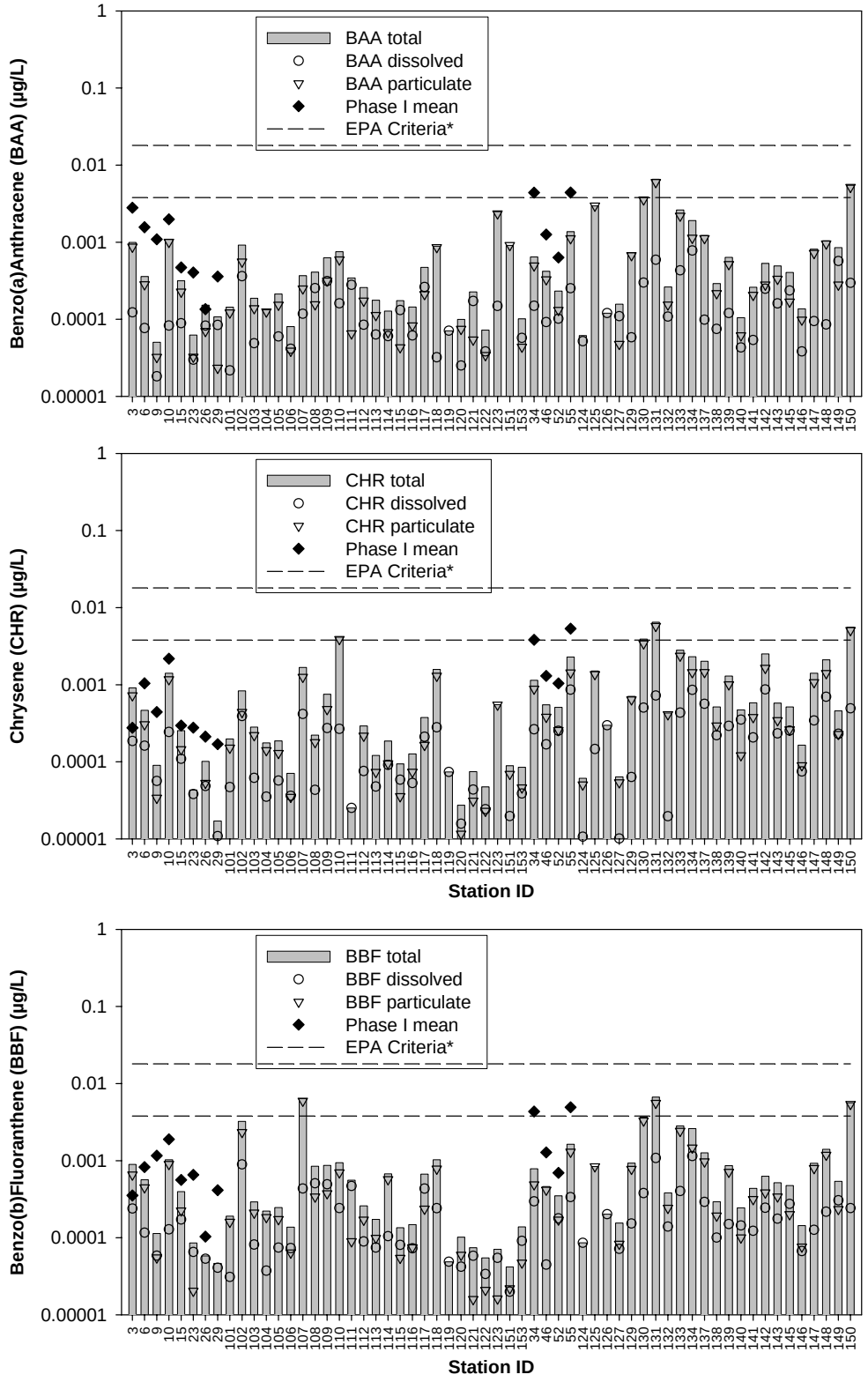

Figure 4.2: Summer baseflow stream water concentrations at all sites for the five most toxic measured PAH compounds: **A**) Benzo(a)Anthracene (BAA), **B**) Chrysene (CHR), **C**) Benzo(b)Fluoranthene (BBF), and continued on next page **D**) Benzo(k)Fluoranthene (BKF), **E**) Benzo(a)Pyrene (BAP).

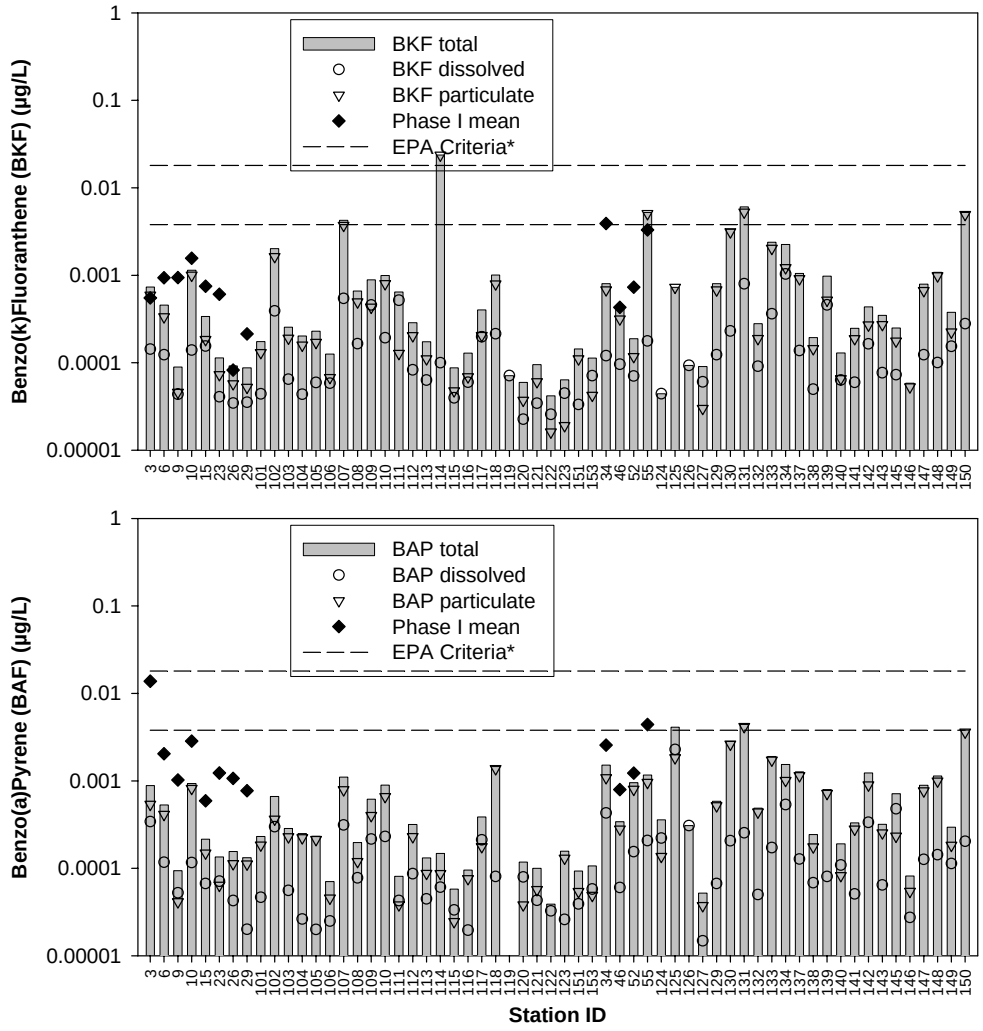

Figure 4.2 continued: These five most toxic PAH compounds are all classified as probable human carcinogens in US EPA's "2002 Edition of the Drinking Water Standards and Health Advisories" (EPA 822-R-02-038). "EPA Criteria" refer to ambient water quality criteria outlined by the US EPA in their report entitled "National Recommended Water Quality Criteria: 2002" (EPA-822-R-02-047), which supercede previous criteria compilations including the "Blue Book," 'Red Book," "Gold Book" and EPA's last compilation published in April 1999. The lower line represents the threshold concentration above which human health risks have been identified for the consumption of the water, and the upper line represents the threshold concentration for above which human health risks have been identified for the consumption of organisms living in the water. Phase I data are presented as geometric means.

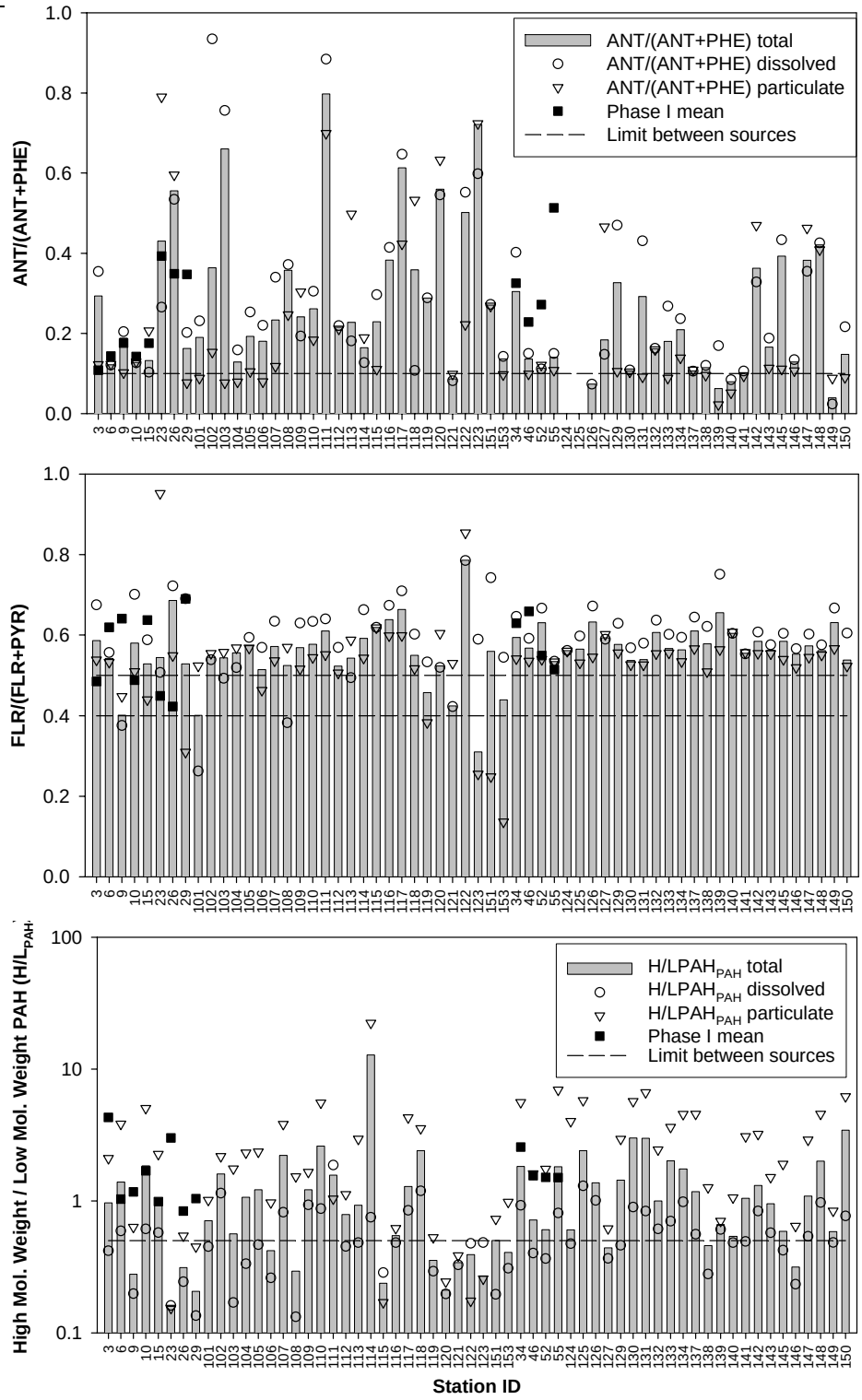

Figure 4.3: Summer baseflow PAH ratios useful as source indicators: **A**) high values of ANT/(ANT+PHE) indicate combustion sources dominate over petroleum sources, **B**) as do high values of FLR/(FLR+PYR), and C) a predominance of high versus low molecular weight PAHs indicates combustion sources or asphalt versus fresh petroleum.

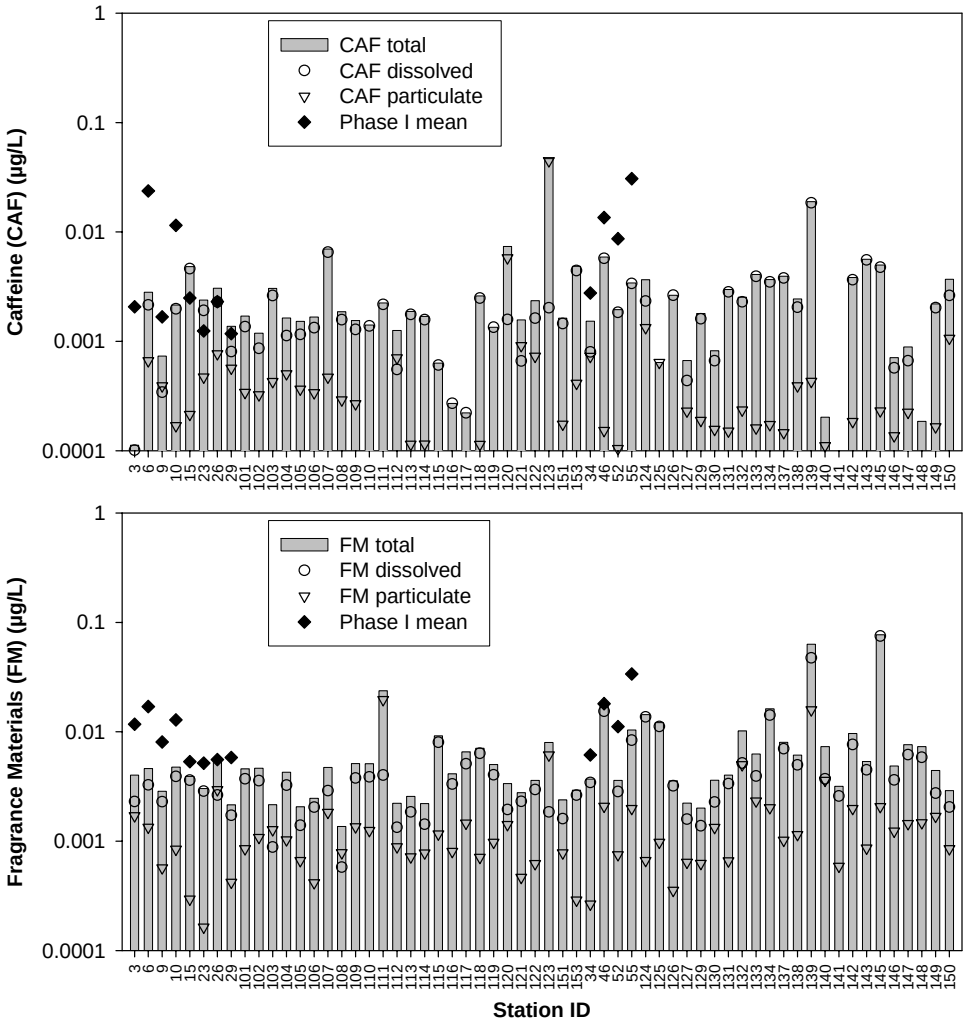

Figure 4.4: Summer baseflow stream water concentrations at all sites for tracers of sewage inputs: **A**) Caffeine (CAF), and **B**) the sum of the two Fragrance Materials (FM) tonalide (AHTN) and galaxolide (HHCB).

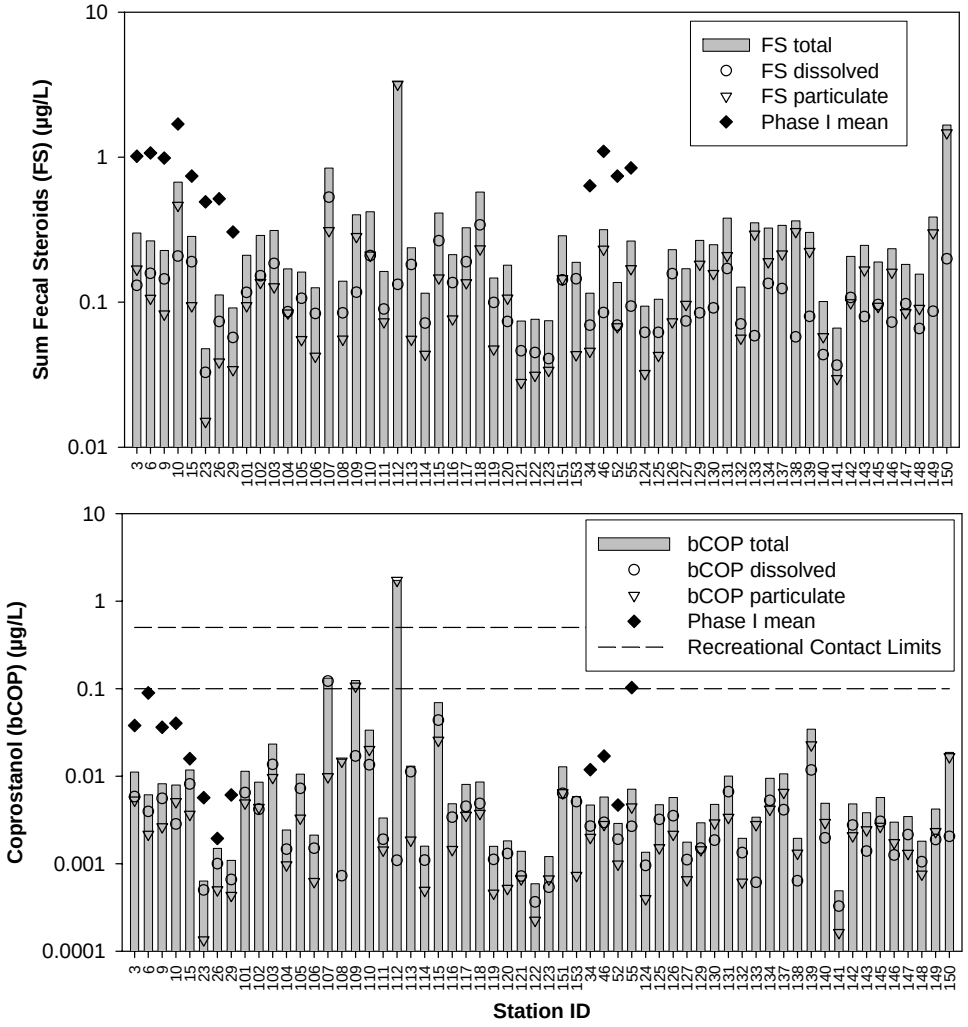

Figure 4.5: Summer baseflow stream water concentrations at all sites for tracers of fecal inputs: **A**) the sum of all measured Fecal Steroids (FS) (aCOP, aONE, bCOP, bONE, CHO, EPI, SNOL), and **B**) coprostanol (bCOP), which is a specific indicator of human fecal material. "Recreational Contact Limits" refer to concentrations of coprostanol that have been demonstrated to correspond to fecal bacteria concentrations of: 1) 35 enterococci (a subset of fecal streptococci) per 100 mL and 300 thermotolerant coliforms per 100 mL for the lower line, and 2) 200 enterococci per 100 mL and 1100 thermotolerant coliforms per 100 mL for the upper line, as per Leeming and Nichols (1996).

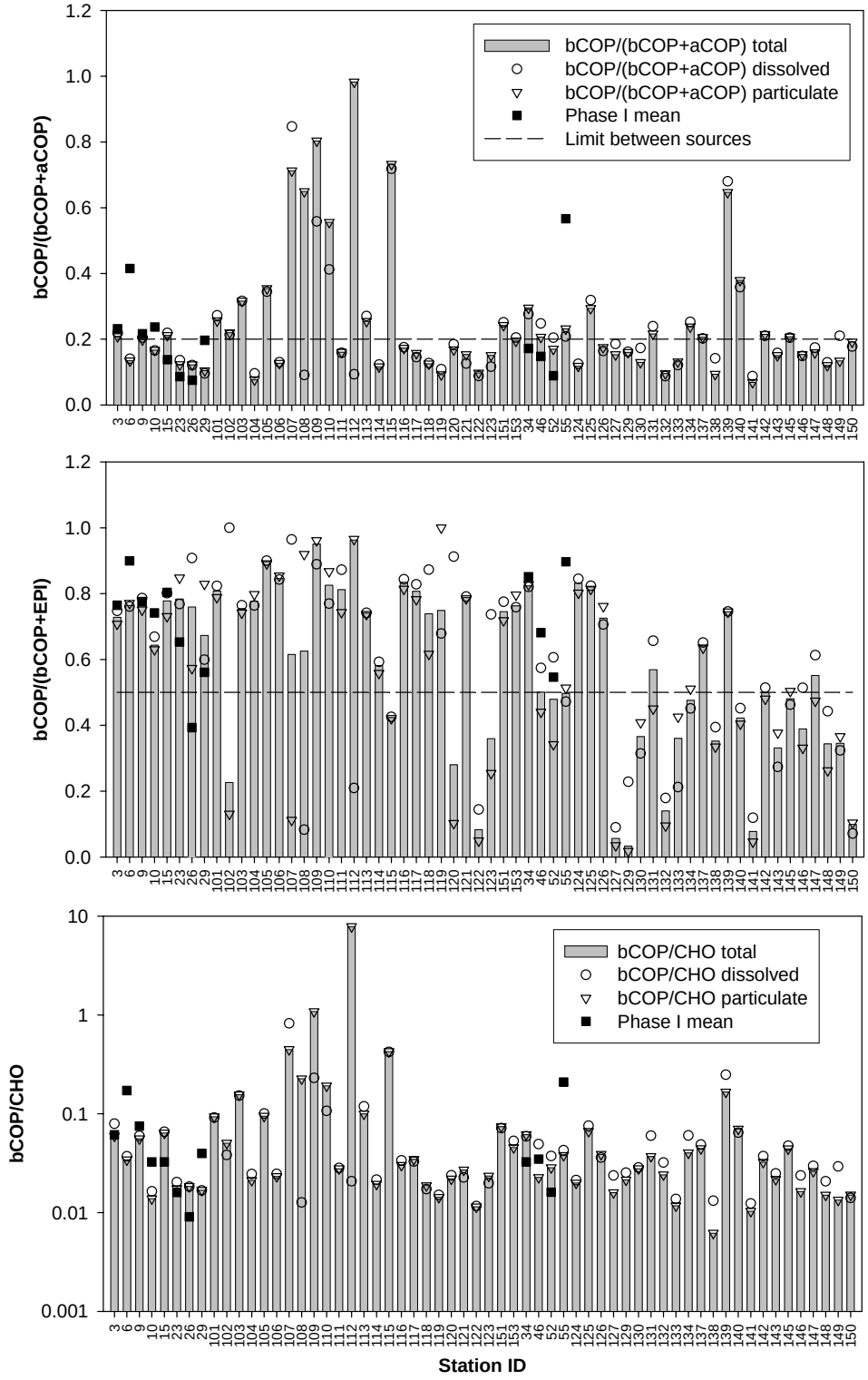

Figure 4.6: Summer baseflow fecal steroid ratios useful as indicators of human fecal sources. High values of **A**) bCOP/(bCOP+aCOP) >0.2, **B**) bCOP/(bCOP+EPI) > 0.5, and **C**) bCOP/CHO all demonstrate a predominance of fecal contamination from humans relative to that from livestock and wildlife.

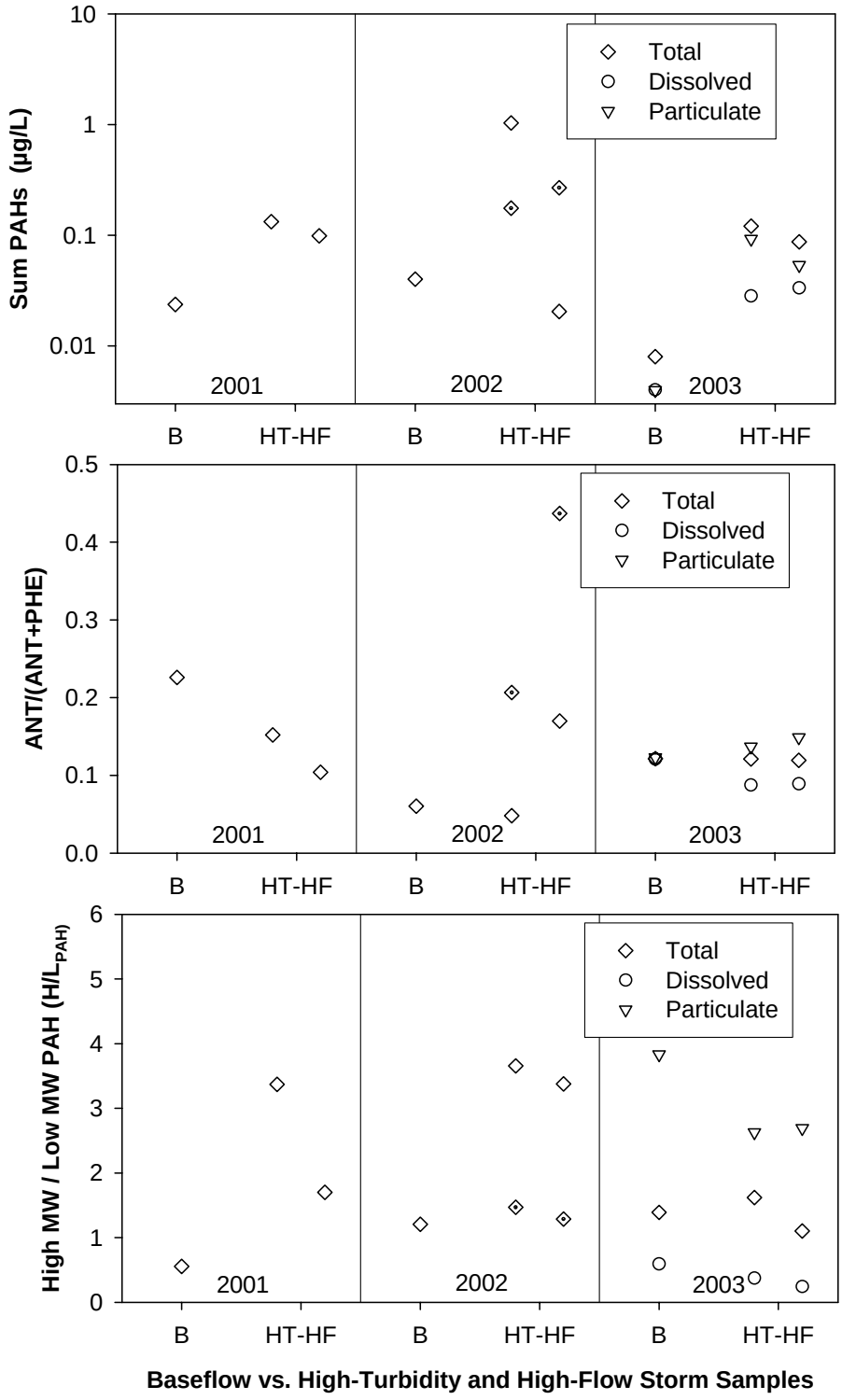

Figure 4.7: Comparison of summer baseflow (B) to high-tubidity (HT) and high-flow (HF) storm samples for **A**) sum of PAH concentrations, **B**) ANT/(ANT+PHE) ratios, and **C**) ratios of high to low molecular weight PAHs (H/LPAH). Dotted diamonds in 2002 represent the second, smaller storm collected in that year.

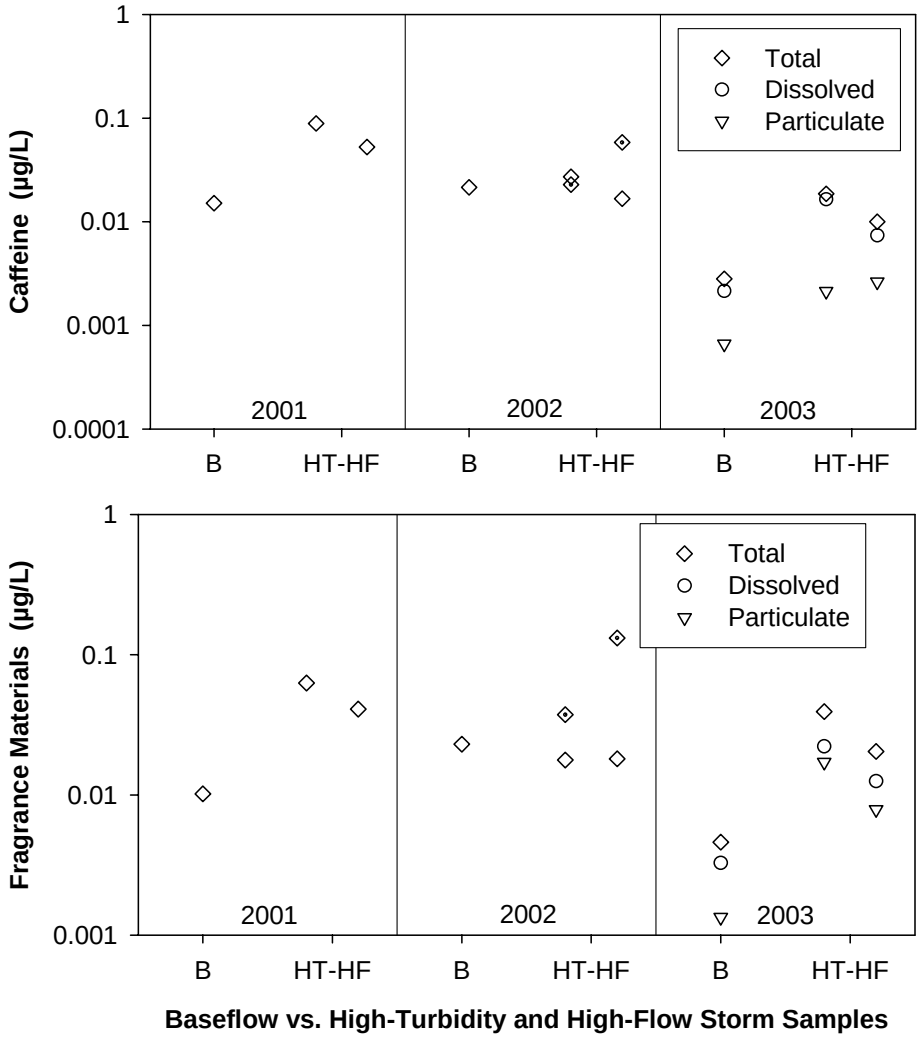

Figure 4.8: Comparison of summer baseflow (B) to high-tubidity (HT) and high-flow (HF) storm samples for **A**) caffeine concentrations, and **B**) concentrations of fragrance materials (FM).

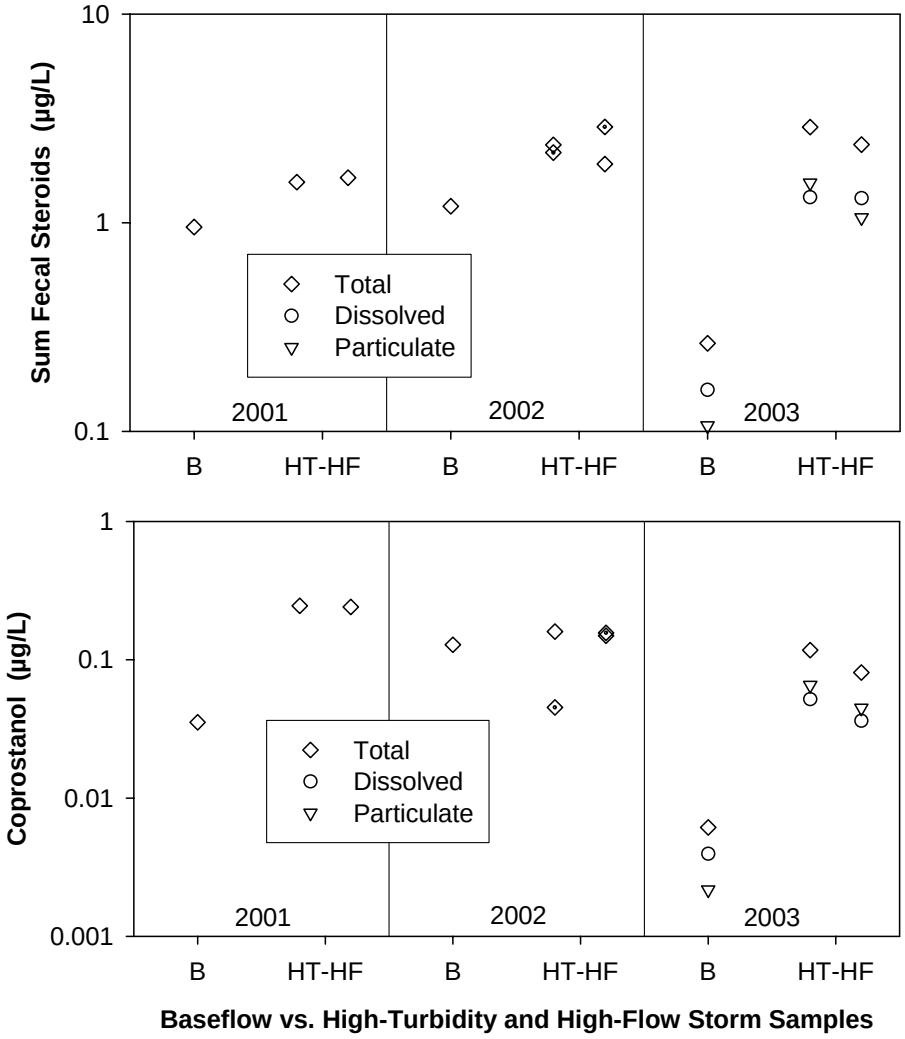

Figure 4.9: Comparison of summer baseflow (B) to high-tubidity (HT) and high-flow (HF) storm samples for **A**) sum of fecal steroid (FS) concentrations, and **B**) coprostanol (bCOP) concentrations.

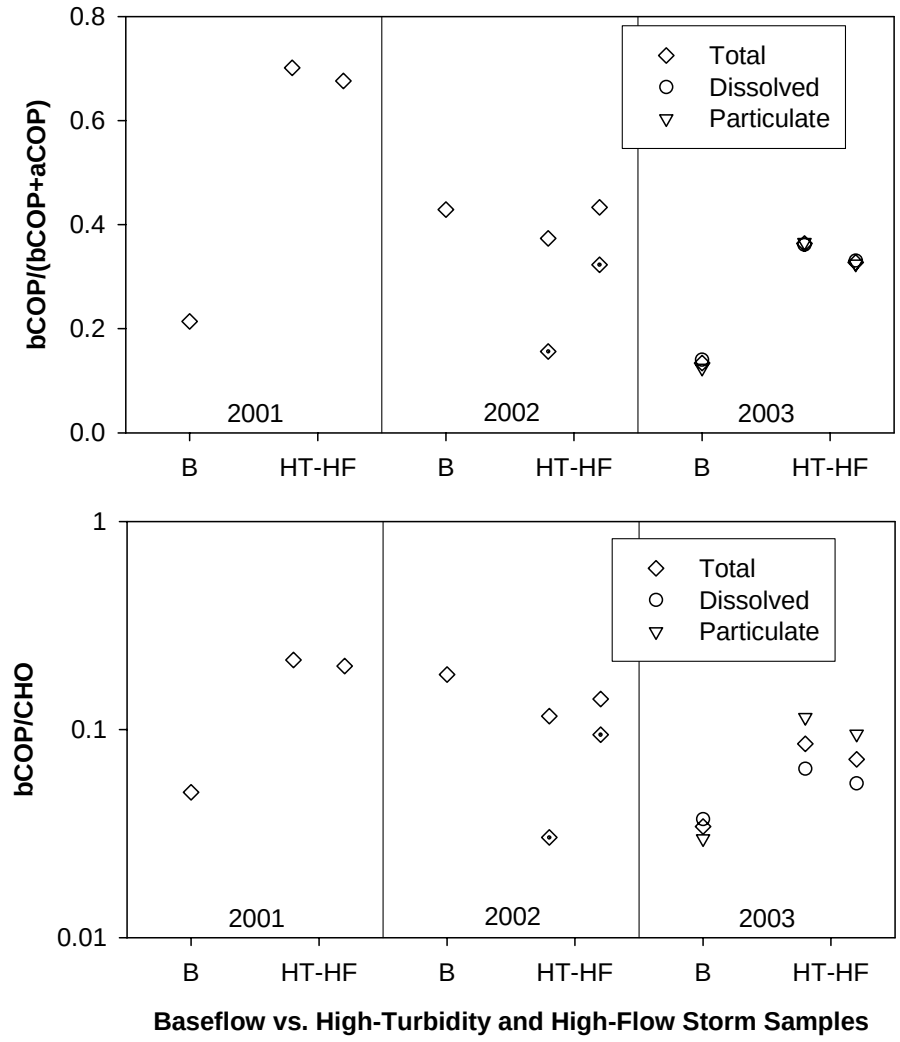

Figure 4.10: Comparison of summer baseflow (B) to high-tubidity (HT) and high-flow (HF) storm samples for **A**) bCOP/(bCOP+aCOP) ratios, and **B**) bCOP/CHO ratios.

Chapter 5 - Macroinvertebrate Communities

Introduction

This portion of the NY Watersheds study uses naturally occurring benthic (i.e., bottom-dwelling) macroinvertebrate populations in the streams and rivers of the NY Watersheds to assess whether statistically significant and ecologically meaningful differences in environmental quality occur. Benthic macroinvertebrates such as insects, worms, and molluscs are the preferred group of aquatic organisms monitored in water quality assessment programs (Hellawell 1986) because: (1) they provide an extended temporal perspective (relative to traditional water samples that are collected periodically) because they have limited mobility and relatively long life spans (e.g., a few months for some chironomid midges to a year or more for some insects and molluscs); (2) the group has measurable responses to a wide variety of environmental changes and stresses; (3) they are an important link in the aquatic food web, converting plant and microbial matter into animal tissue that is then available to fish; and (4) they are abundant and their responses can be easily analyzed statistically (Weber 1973). Thus, the presence or conspicuous absence of certain macroinvertebrate species at a site is a meaningful record of environmental conditions during the recent past, including ephemeral events that might be missed by assessment programs that rely only on periodic sampling of water chemistry. Most stream ecosystems have relatively diverse macroinvertebrate assemblages with species from a number of different orders [e.g., mayflies (Ephemeroptera), caddisflies (Trichoptera), stoneflies (Plecoptera), beetles (Coleoptera), true flies (Diptera)]. Likewise, the common trophic groups (i.e., herbivores, detritivores, predators) are represented by a number of different species. Various abiotic factors (e.g., hydrology, substrate, temperature, oxygen, pH) and biotic factors (e.g., food quality and quantity, interactions with competitors or predators) have molded, through natural selection, a unique set of optimum environmental requirements for each species. These environmental requirements contribute significantly to the distribution and abundance of these organisms within and among natural stream ecosystems, and influence their response to environmental perturbation.

Aquatic macroinvertebrate species characteristic of the streams and rivers of New York can be typically divided into three subsets based on their period of major growth and activity: (1) species with their principal larval growth during fall - winter - spring and whose adults (in the case of aquatic insects) emerge during spring or early summer (e.g., *Ephemerella*, *Eurylophella*, *Ameletus*, many stoneflies, some *Hydropsyche* and *Cheumatopsyche*, *Prosimulium*); (2) species with their principal larval growth and adult emergence during summer (e.g., *Tricorythodes*, some *Simulium*); and (3) species with one or more cohorts per year that include significant larval growth during fall - winter - spring as well as during summer (*Baetis*, *Centroptilum*, some *Hydropsyche* and *Cheumatopsyche*, *Chimarra*, many chironomids). Early spring sampling in this program focuses on collecting species

near the end of the fall-winter-spring growth cycle, which is when individuals for many species are largest and often easier to identify. In addition, because they have been actively growing and developing the streams since at least the previous September, the presence/absence, absolute abundance, physiological state, etc. of larvae collected in spring integrates both habitat and water quality conditions in a given stream or river over the previous 6-9 months. Thus, the macroinvertebrates collected in spring provide a strong "temporal perspective" during an important and significant portion of the year.

Methods

Field Collection of Macroinvertebrate Samples

Macroinvertebrates were collected at 60 locations distributed throughout the watersheds (see Figures 2.1 and 2.2) between 5 May and 16 May 2003. The sampling protocol was designed to characterize riffle-inhabiting macroinvertebrates in a reach that included several riffles (i.e., for additional habitat and biotic diversity) rather than the approach of characterizing macroinvertebrates from a single riffle or part of a riffle. Reach length varied among streams and rivers, but generally included 20-50 m of riffle. Random sampling locations were chosen based on their longitudinal (e.g., along the length of the study reach) and lateral positions. For example, a sampling location in a stream might be designated as 17-25, which would represent 17 m upstream and 25% across the stream from the bank. The sampling protocol called for a total of four composite samples representing 16 samples to be collected at each site. At 8 of 60 sites (Table 5.1), riffle habitat was limited and we modified the sampling design by collecting fewer samples (i.e., 4 or 8 versus 16).

Benthic macroinvertebrates were collected in riffle habitats with a Surber sampler (1 ft^2 or 0.093 m^2; 0.250-mm mesh) using a quantitative composite sampling regime that was modified from Stroud SOP S-04-09. Sampling started at the downstream end of the sampling area and proceeded in an upstream direction. The operator identified the location of each sampling area based on the longitudinal and lateral position. If boulders or large woody debris interfered with sampling at the designated sampling location, the location was moved slightly until there was no obstruction. If it was impossible to obtain a good sample from this location, an alternative sampling site that was also randomly chosen was used for this sample.

To collect the macroinvertebrate sample, the back edge of the Surber sampler is set on the stream bottom so that there is a tight seal across the substrate to prevent animals from escaping under the sampler. The square bottom frame is then laid out on the stream bottom to delimit the 1 ft^2 sample area. Rocks that were under the frame were included in the sample if more than half of the rock was inside the frame; if more than half of the rock was outside of the frame it was not included in

the sample. Larger rocks (> 65 mm in longest dimension) were removed individually, and scrubbed with a soft bristled brush under the water in front of the net. Scrubbing removes most attached organisms while the water current moving through the sampler carries these dislodged organisms into the sample net. Each scrubbed rock was placed in a plastic bucket (held by a second person) for subsequent counting. The minimum rock counted and/or measured is > 65 mm on the longest axis. Large rocks that could not be moved were scrubbed in place. After all rocks were scrubbed and removed, the enclosed benthic area was rapidly stirred and agitated for at least 20 seconds to suspend any residual organisms in the water column and subsequently into the sample net. The sampler was then removed from the bottom and stream water splashed onto the outside of the net in order to wash clinging animals into the bottom of the net. Each sample was randomly assigned to one of four composite samples so the net for a sample was inverted and the contents washed into a plastic bucket designated for that composite sample.

Composite samples resulted from combining four 1 ft^2 samples (if possible) into one composite sample (i.e., containing macroinvertebrates from 4 ft^2) and then subsampling the combined samples in the field such that a subsample equaled one sample (i.e., macroinvertebrates representative of 1 ft^2). After all samples (usually 16) had been collected and combined into four composite samples, each composite sample was split into subsamples (each representing 1 ft^2), with one of the subsamples being preserved and brought back to the laboratory for analysis. Each composite sample was washed into a large sample splitter that was placed in a large plastic trash can half filled with water. The mixture of macroinvertebrates, detritus, and sediments was homogenized and resuspended by stirring, agitating, and pushing water into the subsampler. The material then resettled across the bottom of the subsampler while slowly drawing the subsampler out of the barrel. If the material did not appear evenly distributed, the resuspension and settling process was repeated. The net (0.250-mm mesh)-covered bottom was separated from the rest of the subsampler, and the + shaped plastic separator was pushed into the sample material, dividing the material into four equal parts. A spatula and scissors was used to separate subsamples and transfer a subsample to a labeled sample jar filled with 5% buffered formalin, which was then transported to the laboratory. If the composite sample contained four samples, then 1/4th of the composite material represented macroinvertebrates from 1 ft^2. If only eight samples were collected, then each composite sample contained the contents of two samples (i.e., macroinvertebrates from 2 ft^2), and the composite sample was split into two subsamples (each representing 1 ft^2).

Sample compositing has advantages because it can increase both accuracy and precision relative to standard (non-compositing) macroinvertebrate sampling. For example, compositing increases the accuracy of the desired description by increasing the number of samples collected and therefore the area sampled in these riffles without increasing the number of samples processed. At the same time,

compositing homogenizes spatial variation when these samples were combined, which reduces variance among samples in statistical analyses.

Associated with each sample, water depth was measured to the nearest cm and current velocity was estimated with a current meter set at a point 0.6 of the distance from the bottom to the water surface. The number of large rocks (> 65 mm in longest dimension) that had been in that sample was also recorded. Periphyton biomass (as chlorophyll a and ash free dry mass) was measured for each composite sample by collecting a small algae-covered stone (3-5 cm in diameter) near where each sample were collected and placing it in labeled plastic Tupperware containers associated with each composite sample (i.e., 2 or 4 rocks per composite sample). The plastic Tupperware containers were stored on dry ice (in field) or in a freezer (in laboratory) until chlorophyll a and ash free dry mass analyses were completed in the laboratory (< 30 d for chlorophyll a).

Laboratory Processing of Macroinvertebrate Samples

Benthic materials (i.e., macroinvertebrates and detritus) were transferred from the sample jar into a 0.250-mm mesh sieve and rinsed thoroughly with water to remove fine particles. Because macroinvertebrates were abundant (hundreds to thousands per sample), each sample was split into four subsamples, and then one of those subsamples was split into four subsamples (i.e., 1/16th of a sample). Actual subsample size processed varied among samples (1/16, 1/8, 3/16, 1/4) and reflected the number of macroinvertebrate per sample. Our target was to identify 100-300 macroinvertebrates per subsample. Macroinvertebrates were separated from detritus by taking a small portion from the subsample and placing it in a plastic sorting tray partially filled with 80% ethanol. This material was then carefully examined with the aid of a dissecting microscope (12 X magnification). All macroinvertebrates were removed from the detrital material collected in the subsample, and the detrital material was transferred to an aluminum weigh boat (see Benthic Organic Matter below).

Aquatic insects were generally identified to genus or species; other macroinvertebrates (e.g., crustacea, mites, flatworms, oligochaetes, and nematodes) were commonly left at higher taxonomic levels (e.g., order, family). Specimens that were damaged or extremely small were identified to the taxonomic levels possible, but these were higher than species and even genus. Chironomids were subsampled before identification, and the number examined represented the percentage of chironomids in that sample. For example, if a sample contained 300 macroinvertebrates and 40% of them were chironomids, then 40 chironomids were identified to genus/species and these identifications were applied proportionally to the remaining 80 chironomids. Identified macroinvertebrates were placed in vials containing 80% ethanol and a permanent label containing the appropriate information (project name, project number, study site, sampling device, sample number sample date, name of individual who sorted and identified sample).

Macroinvertebrate specimens (sorted and unsorted material) were archived by the Stroud Center for at least 10 years after the collection date. After verification, selected voucher specimens may be incorporated into the permanent macroinvertebrate collection at the Stroud Center.

Periphyton chlorophyll a and biomass were estimated for rocks collected in association with each composite sample. For chlorophyll a analyses, rocks were extracted overnight in alkaline acetone and optical densities determined at 665 nm and 750 nm (for turbidity) before and after acidification with a drop of 1 N HCL. Optical densities were used to determine chlorophyll a concentrations with correction for phaeophytin (Lorenzen 1967). These rocks were then scrubbed with small brushes to remove attached organic material (i.e., the biofilm of algae, fungi, and bacteria). This organic material was captured on a pre-ashed GF/F filter, dried at 60 °C for >48 h, weighed (dry mass of organic and inorganic matter on rock surfaces), ashed at 550°C for 5 hours, and then weighed again (dry mass of inorganic materials). Weight loss during ashing represents the organic content of the periphyton expressed as mg or g AFDM/m^2. Periphyton chlorophyll *a* and biomass are measures of the biofilm that represents macroinvertebrate food attached to rocks

Benthic Organic Matter (BOM) is also a measure of macroinvertebrate food, but in the form of medium and coarse organic particles (i.e., captured by a 0.250 mm mesh sieve) intermixed among rocks and finer substrates in the stream bed. BOM was estimated as the detrital material associated with each processed subsample. After the macroinvertebrates were removed, the wet detritus (organic and inorganic material) was transferred to an aluminum weigh boat and dried at 60 °C for >48 h. The sample was weighed (dry mass of organic and inorganic materials), ashed at 550°C for 5 hours, and then weighed again (dry mass of inorganic materials). Weight loss during ashing represents BOM expressed as mg or g AFDM/m^2.

QA/QC of Macroinvertebrate Data

Errors for macroinvertebrate data were measured three ways: sorting errors, identification/count errors, and identification accuracy. Sorting error (or efficiency) was measured on 12 samples (the number of samples required by the QA/QC Plan) by resorting through the processed detrital material looking for macroinvertebrates that were not found in the first sort. Sorting error was reported as the number of individuals found expressed as a percentage of the total number of macroinvertebrates found for a sample). Error in macroinvertebrates identifications and counts was estimated by reexamining the specimens identified in 12 samples (the number of samples required by the QA/QC Plan). Errors arose due to incorrect identifications or counts or placing an individual in the wrong vial. Error in macroinvertebrate identification or count was reported as the number of mistakes expressed as a percentage of the total number of macroinvertebrates identified. Finally, identification accuracy was assessed by sending voucher specimens for each

genus and/or species to be verified at the Aquatic Resource Center, Inc, 545 Cathy Jo Circle, Nashville, TN 37211.

All macroinvertebrate and associated data was compiled into SAS data sets. The contents of these data sets were then compared with original laboratory or field data sheets, with 100% of the data being proofread and any discrepancies being corrected.

Status of Macroinvertebrate Samples

All 240 macroinvertebrate samples collected in 2003 have been processed, and identifications have been completed.

QA/QC review of the macroinvertebrate data was carried out as the samples were processed and thus has been completed. Sorting error ranged from 0% and 12% (Table 5.2), with no samples exceeding the 15% limit defined in the QA/QC Plan. The overall sorting error rate across the 12 samples was 5.3%, which was below the 15% limit defined in the QA/QC Plan. Error in macroinvertebrate identification or count ranged from 0 to 5.4% (Table 5.3), with none of the samples exceeding the 10% limit defined in the QA/QC Plan. The overall error in identifications or counts across the 12 samples was 0.9%, which was well below the 10% limit defined in the QA/QC Plan. Finally, the voucher specimens have been sent to the Aquatic Resource Center, and we expect their assessment within a month. Any serious discrepancies (i.e., species-level differences) will be resolved by our senior entomologist (25 years of experience).

All macroinvertebrate and associated data was compiled into SAS datasets, with 100% of the data being proofread and corrected. Statistical analyses programs that compare macroinvertebrate assemblages among stations have been developed and some initial results are provided below. The results presented in this progress report address the metrics that are used to calculate the NY Water Quality Score (NY DEC 2002). This includes:

Total Richness	Total Richness summarizes species responses (as presence/absence but not abundance) of all taxa, including pollution-sensitive and pollution-tolerant taxa. It is reported as the mean number of aquatic macroinvertebrate species found in each subsample. Total Richness generally decreases in response to moderate to severe pollution. Total Richness is often split into EPT Richness and Chironomid Richness.
EPT Richness	EPT Richness is reported as the mean number of Ephemeroptera, Plecoptera, and Trichoptera species found in each subsample. These three insect orders

	contain many pollution-sensitive taxa; thus, this metric summarizes responses of mostly pollution-sensitive taxa. EPT Richness generally decreases in response to moderate to severe pollution.
HBI	Hilsenhoff Biotic Index (MBI) - Analyses involving abundance (i.e., density) or presence/absence (richness) are only able to incorporate pollution tolerance information indirectly, through the interpretation of results for individual taxa or groups of taxa. Biotic indexes combine abundance data and pollution tolerance values for each taxon to form a weighted average for the aquatic macroinvertebrates at that site. A biotic index is estimated with data from each sample, and summarized as a mean per sample. Tolerance values (values range from 0 to 10, with 10 being most tolerant and 0 being least tolerant of pollution) for the Hilsenhoff Biotic Index were obtained from two sources: NY QA/QC 2002, and unpublished data obtained from US EPA
PMA	Percent Model Affinity - PMA compares the observed distribution of individuals among seven orders with a hypothetical macroinvertebrate community representing an unimpacted macroinvertebrate assemblage. The model community consists of 40% Ephemeroptera, 5% Plecoptera, 10% Trichoptera, 10% Coleoptera, 20% Chironomidae, 5% Oligochaeta, 10% Other Taxa. The PMA is calculated by comparing values for each taxonomic group from the model and observed communities, and taking the sum of the smaller of the two values from each taxonomic group.
WQS	Water Quality Score - The values for each of the four metrics (Total Richness, EPT Richness, HBI, and PMA are converted to a WQS (range = 0-10) using the Biological Assessment Profile in NY DEC (2002). The WQS for the site is the mean of the WQSs for the four individual indexes. Based on data collected with a kick sampler (0.8 x 0.9 mm-mesh) between July and September, a WQS of 7.5-10 indicates no impact, 5.0-7.5 indicates slight impact, 2.5-5.0 indicates moderate impact, and 0.0-2.5 indicates severe impact. The applicability of this system to other sampling designs (e.g., different sampling efforts or different seasons) remains unknown.

Total Richness, EPT Richness, and HBI all have a long history in water quality monitoring. PMA is less commonly used. While numerous multimetric indexes have been developed for stream macroinvertebrate assemblages and are widely used in water quality monitoring, the Biological Assessment Profile used to calculate a Water Quality Score and to assess water quality impact have been developed specifically for New York streams by NY DEC.

Because the total number of individuals identified differed greatly among our samples and always exceeded the 100 individuals that are standard in the NY DEC protocol, we used a rarefaction process to produce standardized samples. Standardized samples were created by randomly resampling (without replacement) 100 individuals from each raw sample, and individual measures of community structure (i.e., Total Species Richness, EPT Richness, HBI, PMA) were calculated from this standardized sample. The resampling process was repeated 1000 times for each sample, and the means of the 1000 values were used to calculate the WQS for that sample.

Modifications to the QA/QC Plan for 2004

Overall, the field and laboratory protocols outlined in the 2003 QA/QC Plan worked well, and we do not suggest any changes to the QA/QC Plan for 2004 at this time. Other modifications (e.g., the addition of sites) may become apparent after the sites have been sampled and data have been analyzed.

Results and Discussion

Range of conditions across sites in 2003

Macroinvertebrate communities sampled in 2003 varied greatly across the New York City drinking water watersheds. The range of conditions was similar to that observed in Phase I (years 1-3) of this study. Biological metrics (i.e., Species Richness, EPT Richness, HBI, PMA, and WQS) indicated that the macroinvertebrate communities at the 60 sites represented a continuum of conditions from relatively high water and habitat quality to relatively low water and habitat quality (see Table 5.4 for values for each site).

Water Quality Score ranged from a high of 9.3 at Site 111 (Dry Brook nr Mapledale) to a low of 3.5 at Site 55 (Kisco R. nr Stanwood) (Table 5.4, Figure 5.1). Over half of the sites (34 of 60) had a WQS characteristic of no impact, 14 sites had a WQS characteristic of slight impact, and 12 sites had a WQS characteristic of moderate impact. The 10 sites with the highest WQS were all WOH sites, while the 10 sites with the lowest WQS were all EOH sites (Table 5.5). A similar pattern was observed for each of the four components of the WQS [i.e., Species Richness (Figure 5.2); EPT Richness (Figure 5.3); HBI (Figure 5.4); PMA (Figure 5.5)], where the majority of

the sites with the highest scores were WOH, while the sites with the lowest scores were generally EOH.

The degree and frequency of impairment were less among sites in the WOH region. Twenty-five of the 33 WOH sites had WQSs of 7.5 or higher, indicating no impact. Eight WOH sites fell in the slightly impacted range (7.5<WQS>5). No WOH sites had WQSs in the moderate or severely impacted ranges (WQS<5). The five sites in the WOH with the highest WQS were (in descending order): Site 111 - Dry Brook nr Mapledale, Site 121 - Warner Cr. nr Chichester, Site 15 - Tremper Kill nr Andes, Site 106 - Dryden Br. nr Beerston, and Site 153 - Loomis Br. nr Trout Creek (Table 5.6). Sites with lowest WQS in the WOH were (in ascending order): Site 117 - Batavia Kill nr Windham, Site 26 - Esopus Cr. nr Mount Tremper, Site 107 - E. Br. Delware R. at Roxbury, Site 118 - Bear Kill nr Grand Gorge, and Site 3 - W. Br. Delaware R. at South Kortright (Table 5.6). Nine sites in the EOH region were classified as non-impacted with WQSs at or above 7.5, six EOH sites were in the slightly impacted range (7.5<WQS>5), and 12 in the moderately impacted range (5<WQS>2.5). No sites were classified as severely degraded in the EOH. The five EOH sites with the highest WQS were (in descending order): Site 52 - Cross R. in W.P.R. Reservation, Site 146 - Stone Hill R. nr Bedford, Site 149 - Waccabuc R. at Boutonville, Site 125 - Quaker Br. at Merrit County Park, and Site 34 - Haviland Hollow Br. at Haviland Hollow (Table 5.7). The five EOH sites with the lowest WQS were (in ascending order): Site 55 - Kisco R. nr Stanwood, Site 148 - trib. of Kensico Res. nr Thornwood, Site 130 - Titicus R. nr Salem Center, Site 133 - trib. of Muscoot R. at Mahopac Falls, and Site 138 - Cross R. nr Katonah (Table 5.7).

Total macroinvertebrate densities in 2003 ranged from 4,932/m^2 at Site 115 (Schoharie Creek nr Elka Park) to 79,656/m^2 at Site 130 (Titicus R. nr Salem Center) (Table 5.8). Total densities ranged from 11,376/m^2 to 79,656/m^2 among moderately impacted sites, 6,410/m^2 to 51,398/m^2 among sites classified as slightly impacted and 4,932/m^2 to 71,613/m^2 among sites classified as non-impacted. Density for several major taxonomic groups correlated significantly with WQS (Table 5.9). Total Ephemeroptera density (r=0.62), EPT density (r=0.42), Trichoptera density (0.47), and Coleoptera density (0.43) had significant positive relationships with WQS. Total Oligochaeta density (r=-0.54), noninsect density (which were primarily Oligochaeta; r=-0.44), and Diptera density (r=-0.42) had significant negative relationships with WQS. We did not find significant relationships between total Plecoptera density and WQS and total insect density and WQS. Sites with lower WQSs tended to have higher numbers of macroinvertebrates, resulting in a slight negative relationship between total macroinvertebrate density and WQS (r=-0.28).

Integrative Sites in 2003

The integrative sites in Phase II included nine sites continued from Phase I (i.e., Sites 3, 9, 10, 15, 29, 34, 46, 52) and two new sites (i.e., Sites 139 and 130). The integrative sites were representative of the range of conditions among all 60 Phase

II sites (Figure 5.6): six sites were classified as non-impacted (WQS at Site 15=9.2, Site 52=8.3, Site 10=8.3, Site 9=8.2, Site 34=8.0, and Site 29=7.5), three were classified as slightly impacted (WQS at Site 3=6.8, Site 139=6.2, and Site 46=5.3), and one was classified as moderately impacted (WQS at Site 130=4.0).

Phase II Sites compared to Phase I sites

Figure 5.7 shows the range of WQSs for WOH sites in Phase II 2003 combined with average WQSs for WOH sites in Phase I 2000-2002. Phase II included a few WOH sites toward the more impacted end of the range of WQSs (i.e., Sites 116, 118, 107, and 117). However, none of these sites were classified in the moderately or severely impacted categories. Thus, the WOH sites represent only part of the conditions represented in the EOH. EOH Phase II sites also spanned the range of the average WQSs from Phase I (2000- 2002) (Figure 5.8). Several new EOH sites in 2003 were non-impacted sites (i.e., Sites 125, 146, 149, 124, 127, 129, and 126). However, none of these sites scored as well as the best WOH sites.

The gray bars in Figures 5.7 and 5.8 are WQSs from the 12 sites (Sites 3, 6, 9, 10, 15, 23, 26, 29, 34, 46, 52, 55) that were common to both Phase I and II of this 6-year project. These sites represent the range of conditions seen in both the EOH and WOH regions in 2003. Overall, these sites address three of the four water quality classification categories: non-impact, slight impact, and moderate impact (no sites scored in the severe impact category in 2003). WQSs from 2003 overlapped or were within the range of scores found at most of the 12 sites in 2000 to 2002 (Figure 5.9). The 2003 WQS was lower than the previous three years at Site 9 (Trout Creek at Trout Creek) and Site 55 (Kisco R. nr Stanwood). The Trout Creek site was classified as non-impacted for all four years. The Kisco R. site was classified as slightly impacted in 2001 (WQS=6.3) and 2002 (WQS=5.0), but moderately impacted in 2000 (WQS=4.6) and 2003 (WQS=3.5). At Site 15 (Tremper Kill nr Andes), the 2003 WQS (=9.2) was higher than in previous years and has been increasing each year since 2000. Interannual variability in WQS is especially evident at Site 46 (Muscoot R. nr Baldwin Place). The WQS was 5.2 in 2000, 6.7 in 2001, 3.3 in 2002, and 5.3 in 2003.

Comparisons to reference conditions and within watershed comparisons

Reference conditions were defined as the three sites with the highest WQS in EOH and the WOH (top 10% of sites in each region). The three WOH reference sites were: Site 111 - Dry Brook nr Mapledale (WQS=9.3), Site 121 - Warner Creek nr Chichester (WQS=9.3), and Site 15 - Tremper Kill nr Andes (WQS=9.2). The three EOH reference sites were: Site 52 - Cross River in Ward Pound Ridge Resv (WQS=8.3), Site 146 - Stone Hill River nr Bedford (WQS=8.1), and Site 149 - Waccabuc River at Boutonville (WQS=8.1). These sites were compared with sites in each watershed (ANOVA with Tukey's means comparison test, see Figure 5.10 for Tukey's results by watershed). These reference sites and analyses were specific for

the 2003 analyses and may change as additional years of data will give more statistical power and add more information on the natural interannual variation within and between sites.

The *a priori* hypothesis in these analyses was that the macroinvertebrate assemblages at potentially impacted sites would not differ from the macroinvertebrate assemblages at Sites 111, 121, and 15 in the WOH and Sites 52, 146, and 149 in the EOH. Evidence of a negative impact was defined as a difference in the macroinvertebrate assemblage that resulted in a significantly lower WQS at a potentially impacted site relative to all three reference sites. This difference in the macroinvertebrate assemblage may reflect lower Total Richness, lower EPT Richness (i.e., primarily pollution-sensitive species), higher HBI (i.e., lower relative abundance of pollution-sensitive groups such as mayflies), and/or a reduction in the Percent Model Affinity (i.e., the similarity of the macroinvertebrate community structure relative to the model community). In our interpretation of the quantitative data, differences between a potentially impacted site and the reference sites must be parallel. Differences that were significant for only one or two of the reference sites were not considered evidence of environmental change potentially because these differences did not exceed natural variation observed among three reference sites.

In the WOH, 16 of 33 sites (48%) had WQSs that were statistically lower than at all three reference sites. And, in the EOH, 18 of 27 sites (67%) had WQSs that were statistically lower than at the three reference sites. The larger proportion of EOH sites with WQSs less than reference sites illustrates the greater range in WQSs in the EOH region. WQSs in the slightly and moderately impacted categories were usually significantly less than all three reference sites. In several cases, sites classified in the non-impacted category had a WQS that was statistically lower than at the reference sites (i.e., Sites 122 and 29 in the Neversink Watershed, Sites 119, 120, and 23 in the Ashokan Watershed, Sites 110, 109, 108, 112, 10, 114, and 113 in the Pepacton Watershed, and Sites 101, 151, and 6 in the Cannonsville Watershed).

WOH Watersheds in 2003

All WOH watersheds had sites with WQSs that were significantly lower than at the three reference sites, and with the exception of the Rondout watershed, all watersheds had sites within that watershed that differed from each other. Frequently one site within each watershed had a WQS that was significantly lower than at all other sites in the watershed.

Cannonsville Watershed – In the Cannonsville watershed, Site 101 - Rose Brook nr South Kortright (WQS=7.9), Site 151 - Betty Brook nr South Kortright (WQS=7.7), Site 6 - W. Br. Delware R. at Hawleys (WQS=7.7), and Site 3 - W. Br. Delaware R. at South Kortright (WQS=6.8) had WQSs that were lower than at the three reference sites. In addition, four sites in the Cannonsville had WQSs that were

lower than at the other sites in the watershed. The WQS at Site 3 was lower than most other Cannonsville watershed sites (Site 101, Site 9 - Trout Creek nr Trout Creek, Site 103 - Elk Creek at East Delhi, Site 104 - Planter Brook at Fraser, Site 102 - Coulter Brook nr Bovina Center, Site 105 - East Brook nr Walton, Site 153 - Loomis Brook nr Trout Creek; and Site 106 - Dryden Brook nr Beerston). Site 6 was lower than four Cannonsville sites (102, 105, 153, and 106). Site 151 (Betty Brook nr South Kortright) was lower than Sites 105, 153, and 106, and Site 101 was lower than Sites 153 and 106. All Cannonsville sites except for Site 3 were classified as non-impacted; Site 3 was classified as slight impact.

Pepacton Watershed – Reference Sites 15 and 111 are in the Pepacton watershed. WQSs at the Pepacton sites ranged from 9.3 at Site 111 to 6.2 at Site 107 (E. Br. Delaware at Roxbury). Relative to the three reference sites, WQSs were significantly lower at Site 107 and Site 113 (Coles Clove nr Downsville). The WQS at Site 107 was lower than at all other Pepacton Watershed sites, and Site 107 the only site in the Pepacton classified as slightly impacted.

Schoharie Watershed – Of the four sites in the Schoharie watershed, Site 117 - Batavia Kill nr Windham, Site 118 - Bear Kill nr Grand Gorge, and Site 116 - East Kill nr Jewett Center had WQSs that were lower than at the reference sites. Site 115 (Schoharie Creek nr Elka Park) did not differ from the reference sites. The WQS for Site 117 (=5.1) was lower than for all other Schoharie sites, and was the lowest WQS in the WOH. The WQS at Site 115 fell in the non-impacted category, while Sites 116, 117, and 118 were all classified slightly impacted.

Ashokan Watershed – Except for Site 121, which was designated as one of the three WOH reference sites, all Ashokan watershed sites had WQSs that were statistically lower than at the reference sites,. Sites that were lower were 26 (Esopus Creek nr Mount Tremper), 119 (Birch Creek at Big Indian), 120 (Bushnellsville Creek at Shandaken), and 23 (Esopus Creek nr Allaben). Site 26 had a lower WQS than all other Ashokan sites. Macroinvertebrate assemblages were classified as moderately impacted at Site 26 (WQS=5.9), slightly impacted at Site 23 (WQS=7.0), and non-impacted at the other Ashokan sites.

Neversink Watershed – Two sites were sampled in the Neversink watershed: Site 122 - W. Br. Neversink above Frost Valley and Site 29 - Neversink R. nr Claryville. Both of these sites had WQSs that were lower than at the reference sites, and the WQS at Site 29 (WQS=7.5) was lower than at Site 122 (WQS=8.2). Both Neversink sites were non-impacted.

Rondout Watershed – Only one site (Site 123 - Rondout Creek nr Peekamoose) was sampled in the Rondout watershed. The WQS at Site 123 (=7.3) was significantly lower than at the three reference sites, and would classify the site as slightly impacted.

EOH Watersheds in 2003

Four of the six EOH watersheds had sites with WQSs that were lower than at the reference sites. In two of these watersheds, WQSs at all sites were lower than at the reference sites.

Middle & West Br. Croton Watershed – One site (Site 126 - Stump Pond Stream nr Pawling) in the Middle Br. Croton watershed was sampled in 2003, and it was not different from the three reference sites. One site (Site 127 - Black Pond Brook at Meads Corner) was also sampled in the West Br. Croton watershed in 2003, and that also was not different from the reference sites.

E. Br. Croton Watershed – In the E. Br. Croton watershed, WQSs at Sites 132 (Bog Brook nr Sears Corner) and 150 (E. Br. Croton River at Brewster) were less than at the reference sites. Site 150 was less than all other E. Br. Croton sites and Site 132 was less than Site 125 (Quaker Brook at W.G. Merrit Count Park). Site 150 was classified as moderately impacted and Site 132 as slightly impacted. The remaining E. Br. Croton sites (Site 125, Site 34 - Haviland Hollow Br. At Haviland Hollow, Site 129 - Unnamed trib. of the Croton R., Site 124 - Unnamed trib. of E. Br. Croton R. nr Pawling) were classified as non-impacted.

East and South of the Croton Watershed –A total of 12 sites were sampled in the East and South of the Croton Watershed, and this included all three EOH reference sites (i.e., Sites 52, 146, and 149). All nine non-reference sites (Site 143 - Unnamed trib. to Cross R. nr Cross R., Site 141 - Unnamed trib. of Croton Res. Nr Croton Heights, Site 131 - Titicus R. nr North Salem, Site 137 - Unnamed trib. of Muscoot Res. Nr Goldens Br., Site 145 - Broad Brook nr Bedford Hills, Site 142 - Kisco R. nr Bedford, Site 138 - Cross R. nr Katonah, Site 130 - Titicus R. nr Salem Center, and Site 55 - Kisco R. nr Stanwood) had WQSs that were lower than at the reference sites. There were also differences among the nine non-reference sites. The WQS for Site 55 was lower than for Sites 142, 145, 137, 131, 141, and 143, and was the lowest observed among EOH sites in 2003. The WQS for Site 143 was higher than for the other non-reference sites in the East and South of the Croton watershed. Site 143 (WQS= 6.3) was classified as slightly impacted. The other seven sites ranged from the border between slightly and moderately impacted (WQS=5.1 at Site 141) to moderately impacted (WQS=3.5 at Site 55).

North of the Croton Watershed – All five sites in the North of the Croton watershed had WQSs that were lower than at the reference sites (i.e., Site 139 - Muscoot R. nr Whitehall Corners, Site 46 - Muscoot R. nr Baldwin Place, Site 134 - Plum Brook at Shenorock, Site 140 - Hunter Brook nr Yorktown, and Site 133 - Unnamed trib. of Muscoot R. at Mahopac Falls). The WQS for Site 133 was lower than at Sites 46 and 139. Sites 46 and 139 were classified as slightly impacted, whereas Site 133 was classified as moderately impacted. However, Site 46 was not significantly different from other moderately impacted Sites 134 and 140.

Kensico R. Watershed – WQSs at the two Kensico R. Watershed sites (Site 147 - Unnamed trib. of Kensico Res. at Mt Pleasant and Site 148 - Unnamed trib. of Kensico Res. nr Thornwood) were lower than at the reference sites. In addition, Site 148 was lower than Site 147. Site 147 (WQS=5.6) was classified as slightly impacted and Site 148 (WQS=3.7) was classified as moderately impacted.

WQS related to landscape variables

Principal Components Analysis (Figure 2.5) separated WOH and EOH sites based on a suite of landscape variables (i.e., watershed area, percent forest cover, number of active SPDES permits, etc.), thus revealing markedly different anthropogenic impact gradients. EOH sites fell out along a high population density/percent impervious cover to high percent forest gradient. WOH sites oriented vertically with Factor 2, explained largely by percent agriculture and percent forest cover. To examine whether macroinvertebrate assemblages might be responding to these gradients, we ran simple linear regressions between WQS and the landscape variables describing these gradients. Among EOH sites, there was a significant negative relationship between WQS and population density ($r=0.62$, $p=0.0005$; Figure 5.11) and between WQS and percent impervious ($r=0.71$, $p<0.0001$; Figure 5.12). Among WOH sites, however, WQS was not related to percent agriculture ($r=0.08$, $p=0.64$; Figure 5.13), nor to percent forest ($r=0.08$, $p=0.67$; Figure 5.14).

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Table 5.1: Macroinvertebrate sampling sites where the sampling protocol was modified in response to field conditions.

Site #	Site Description	Samples Collected
Site 6	W. B. of Delaware Riv. at South Kortright	4 random samples
Site 55	Kisco River nr. Stamwood	8 random samples
Site 126	Stump Pond Stream nr. Pawling	8 random samples
Site 143	Unnamed trib. To Cross River	4 random samples
Site 148	Unnamed trib. To Kensico Res.	8 random samples
Site 149	Waccabuc River	8 random samples
Site 132	Bog Brook	8 random samples
Site 110	Vly Creek	8 random samples

Table 5.2: Macroinvertebrate sorting errors found by resorting a processed sample from 2003.

			number of macroinvertebrates		
Station	MI #	ID #	in initial sort	in resort	% missed
10	2	30310	219	21	8.80%
34	3	30007	199	14	6.60%
46	3	30015	207	3	1.40%
110	4	30424	177	24	12.00%
124	4	30040	319	18	5.30%
125	4	30048	154	7	4.30%
132	4	30104	160	0	0.00%
139	3	30159	161	11	6.40%
140	1	30165	271	23	7.80%
142	2	30182	196	14	6.70%
145	3	30207	178	0	0.00%
151	3	30255	289	11	3.70%
Overall					5.30%

Table 5.3: Errors in non-midge macroinvertebrate identifications and counts from QA/QC 2003.

Station	MI #	ID #	% incorrect
10	2	30310	1.80%
34	3	30007	0.00%
46	3	30015	0.00%
110	4	30424	1.00%
124	4	30040	0.00%
125	4	30048	1.00%
132	4	30104	0.00%
139	3	30159	0.00%
140	1	30165	1.00%
142	2	30182	5.40%
145	3	30207	0.00%
151	3	30255	0.00%
Overall			0.90%

Table 5.4: Aquatic macroinvertebrate assemblages from 2003 described with mean (± 1 SE) values for four individual biometrics [Total Richness, EPT Richness, Hilsenhoff Biotic Index (HBI), and Percent Model Affinity (PMA)], which were combined in the multimetric index [Water Quality Score (WQS)].

Site	Total Richness	EPT Richness	HBI	PMA	WQS
3	33.0±1.0	8.0±0.3	5.55±0.07	51±1	6.8±0.1
6	31.2±1.4	9.8±1.4	4.72±0.15	64±5	7.7±0.5
9	30.6±0.8	11.8±0.2	4.29±0.16	69±5	8.2±0.2
10	35.7±0.5	11.7±0.3	5.10±0.12	70±3	8.3±0.1
15	37.6±0.7	15.9±0.8	3.51±0.11	74±1	9.2±0.1
23	28.6±1.8	8.4±0.8	4.82±0.11	56±1	7.0±0.3
26	24.7±1.7	6.8±0.9	5.52±0.08	48±2	5.9±0.3
29	31.3±2.4	9.7±0.3	4.28±0.14	57±3	7.5±0.2
34	28.7±1.7	9.8±0.7	3.90±0.13	73±1	8.0±0.2
46	18.6±1.3	6.5±1.0	5.62±0.50	45±1	5.3±0.3
52	32.2±1.7	11.5±0.8	4.30±0.16	73±3	8.3±0.3
55	12.8±0.3	2.3±0.3	6.45±0.14	34±1	3.5±0.1
101	28.6±1.6	10.2±0.8	4.16±0.24	72±4	7.9±0.3
102	33.5±1.4	12.0±0.9	3.92±0.06	82±2	8.8±0.2
103	33.9±0.5	11.0±0.6	4.39±0.20	69±3	8.3±0.2
104	30.6±1.8	12.8±1.0	4.42±0.09	78±2	8.5±0.2
105	31.1±1.9	13.5±0.6	3.34±0.11	81±2	9.0±0.1
106	31.4±1.0	15.0±0.6	3.37±0.12	82±1	9.2±0.1
107	25.9±1.2	6.6±1.1	5.33±0.14	51±2	6.2±0.3
108	30.8±1.9	13.5±1.1	3.88±0.29	64±2	8.3±0.3
109	32.6±1.1	12.9±1.0	4.01±0.27	68±3	8.5±0.2
110	32.1±2.2	12.7±0.9	3.39±0.32	76±5	8.8±0.4
111	36.1±1.1	15.4±0.7	2.95±0.08	73±4	9.3±0.2
112	35.1±1.3	12.3±0.6	4.25±0.32	63±4	8.3±0.3
113	27.1±1.5	11.4±1.3	4.10±0.09	63±2	7.7±0.3
114	30.6±1.5	11.2±1.0	4.74±0.27	70±4	8.0±0.3
115	37.5±2.6	14.4±0.8	4.30±0.12	69±1	8.7±0.1
116	25.5±1.2	9.7±0.7	4.55±0.10	53±3	6.9±0.2
117	20.2±1.1	5.0±0.3	5.23±0.05	40±2	5.1±0.1
118	29.2±2.2	7.9±0.8	5.43±0.03	52±2	6.6±0.2
119	31.8±1.8	10.4±0.8	4.71±0.08	61±2	7.7±0.3
120	28.7±0.3	10.3±0.6	4.47±0.10	62±4	7.6±0.2
121	39.9±2.3	17.7±0.5	3.84±0.07	80±1	9.3±0.0
122	32.8±1.9	11.9±0.7	3.68±0.15	60±2	8.2±0.2
123	25.9±2.1	8.2±1.2	3.70±0.13	61±2	7.3±0.4
124	22.4±0.9	9.6±0.5	3.07±0.17	73±3	7.7±0.1
125	29.0±1.0	12.0±0.5	3.72±0.21	63±3	8.1±0.2
126	26.9±0.8	8.8±0.3	3.81±0.14	67±4	7.6±0.1
127	24.0±2.2	10.9±1.1	3.17±0.12	63±1	7.7±0.3
129	26.8±1.5	9.5±0.3	4.36±0.16	75±2	7.7±0.1
130	13.4±1.4	3.5±0.2	5.88±0.05	37±1	4.0±0.1
131	20.8±0.5	4.6±0.4	6.05±0.06	42±1	4.9±0.1
132	22.9±1.0	7.0±0.5	4.86±0.10	85±1	7.2±0.1

Site	Total Richness	EPT Richness	HBI	PMA	WQS
133	16.9±1.5	2.1±0.3	6.03±0.29	38±2	4.1±0.2
134	13.7±1.1	3.8±0.4	5.11±0.14	43±3	4.6±0.2
137	16.6±0.9	3.9±0.4	6.03±0.48	45±2	4.6±0.2
138	21.5±1.6	2.1±0.6	6.34±0.07	39±1	4.2±0.3
139	18.7±1.4	5.3±0.7	4.34±0.19	63±2	6.2±0.3
140	18.0±1.4	3.1±0.4	6.21±0.12	38±1	4.3±0.1
141	18.6±1.0	5.8±0.7	5.52±0.15	43±2	5.1±0.3
142	18.8±1.2	4.1±0.2	6.06±0.10	38±2	4.5±0.1
143	25.8±0.9	7.2±0.9	5.59±0.08	53±2	6.3±0.2
145	19.2±1.9	2.6±0.4	5.82±0.05	41±2	4.6±0.3
146	29.1±1.4	11.4±0.5	3.94±0.19	67±1	8.1±0.2
147	17.7±0.8	5.6±0.4	4.61±0.16	50±1	5.6±0.1
148	13.0±2.0	2.3±0.3	5.48±0.14	32±1	3.7±0.2
149	32.8±0.8	11.1±0.6	4.50±0.10	65±2	8.1±0.2
150	19.6±1.1	3.4±0.3	6.06±0.05	42±1	4.6±0.1
151	34.9±2.3	10.9±0.4	4.91±0.09	59±2	7.7±0.2
153	30.0±1.0	14.4±0.4	2.98±0.20	80±1	9.1±0.2

Table 5.5: Ten sites where macroinvertebrates indicated the highest and lowest stream quality based on Water Quality Score (WQS) in 2003.

Site #	Site Description	WQS	Site #	Site Description	WQS
Highest Quality (descending order)			Lowest Quality (ascending order)		
111	Dry Brook nr Mapledale	9.3	55	Kisco R. nr Stanwood	3.5
121	Warner Cr. nr Chichester	9.3	148	trib. Kensico Res. nr Thorn.	3.7
15	Tremper Kill nr Andes	9.2	130	Titicus R. nr Salem Center	4
106	Dryden Br. nr Beerston	9.2	133	trib. Muscoot @ Mahopac Fls	4.1
153	Loomis Br. nr Trout Creek	9.1	138	Cross R. nr Katonah	4.2
105	East Br. nr Walton	9	140	Hunter Br. nr Yorktown	4.3
110	Vly Cr. nr Fleishmanns	8.8	142	Kisco R. nr Bedford	4.5
102	Coulter Br. nr Bovina Center	8.8	145	Broad Br. nr Bedford Falls	4.6
115	Schoharie Cr. nr Elka Park	8.7	137	trib. Muscoot R. Whitehall	4.6
104	Planter Brook @ Fraser	8.5	134	Plum Br. @ Shenorock	4.6

Table 5.6: Five WOH sites where macroinvertebrates indicated the highest and lowest stream quality based on Water Quality Score (WQS) in 2003.

Site #	Site Description	WQS	Site #	Site Description	WQS
Highest Quality (descending order)			Lowest Quality (ascending order)		
111	Dry Brook nr Mapledale	9.3	117	Batavia Kill nr Windham	5.1
121	Warner Cr. nr Chichester	9.3	26	Esopus Cr. nr Mt Tremper	5.9
15	Tremper Kill nr Andes	9.2	107	E. Br. Delaware R.@Roxbury	6.2
106	Dryden Br. nr Beerston	9.2	118	Bear Kill nr Grand Gorge	6.6
153	Loomis Br. nr Trout Creek	9.1	3	W.Br.Dela. R.@S.Kortright	6.8

Table 5.7: Five EOH sites where macroinvertebrates indicated the highest and lowest stream quality based on Water Quality Score (WQS) in 2003.

Site #	Site Description	WQS	Site #	Site Description	WQS
	Highest Quality (descending order)			Lowest Quality (ascending order)	
52	Cross R. in W. P. R. Resv	8.3	55	Kisco R. nr Stanwood	3.5
146	Stone Hill R. nr Bedford	8.1	148	trib. Kensico Res. nr Thorn.	3.7
149	Waccabuc R. @ Boutonville	8.1	130	Titicus R. nr Salem Center	4
125	Quaker Br.@Merrit Cnty Park	8.1	133	trib. Muscoot@Mahopac Fls	4.1
34	Haviland Holl. Br.@Havil. Holl	8	138	Cross R. nr Katonah	4.2

Table 5.8: Density (individuals/m²) of selected groups of aquatic macroinvertebrates from 60 sites in the NYC drinking water watersheds. Column labels are underlined: Total Macroinvertebrate density, Total Insect density, EPT density, Ephemeroptera density, Plecoptera density, Trichoptera density, Diptera density, Coleoptera density, Total Noninsect density, Oligochaeta density.

Site	Total	Insects	EPT	E	P	T	D	C	Noninsects	O
3	37466±15093	30545±12021	4692±2121	2517±986	92±84	2083±1168	24606±9537	1247±463	6921±3098	5027±2282
6	71613±7144	61376±5562	14796±3754	8516±2955	1376±544	4903±708	36774±3480	9806±978	10237±3034	2409±854
9	31584±4506	27570±4023	9792±1953	7283±1549	602±258	1907±391	15613±2296	2165±654	4014±731	817±163
10	30839±2300	25505±1881	8172±165	5505±544	602±149	2065±351	14667±1773	2667±381	5333±461	3398±550
15	20876±2183	16778±1495	9146±837	5296±833	311±122	3538±343	6731±619	859±112	4097±693	546±73
23	25534±2996	22308±2211	6308±959	4975±760	86±86	1247±343	15785±1244	215±49	3226±865	473±125
26	25097±2124	16932±1080	3233±697	2308±514	43±43	882±239	13699±796	0±0	8165±1048	2710±468
29	21699±3094	19935±2750	5763±1307	3484±1019	516±241	1763±218	14000±1522	172±61	1763±513	129±74
34	12173±3399	10932±3185	4465±1108	2427±745	1126±452	912±163	5097±1652	1301±440	1242±328	519±219
46	30108±3247	20323±2447	11161±1610	2108±284	6796±1813	2258±740	8946±1126	172±70	9785±2297	9699±2371
52	19392±4619	14384±2685	7451±1697	3428±327	2145±879	1878±820	5560±464	1313±598	5008±2013	2582±872
55	50753±5960	36129±4426	2151±555	430±111	946±318	774±248	33591±4177	387±177	14624±3670	13032±4094
101	22452±6052	20701±5457	9437±3420	8060±2731	912±391	465±306	10323±2136	942±143	1751±701	262±153
102	16480±2314	15297±2339	8867±1208	7384±971	409±62	1075±293	6179±1250	229±54	1183±73	158±38
103	36559±3485	31785±2218	11398±1419	7699±1068	1634±318	2065±70	18323±1155	2065±932	4774±1368	1591±463
104	12366±1142	9749±928	5649±279	4065±86	502±111	1082±178	3907±786	194±59	2616±251	2014±344
105	8910±1027	6910±850	3976±396	2619±211	303±35	1054±168	2556±407	369±103	2000±276	259±29
106	13699±1962	12731±1874	6308±1459	4975±1177	559±286	774±98	6072±530	351±122	968±198	50±18
107	36387±6501	22194±4660	4430±814	2581±530	473±275	1376±497	16215±3548	1548±539	14194±2145	3140±838
108	5345±55	5061±56	2556±216	850±52	1343±276	363±63	2182±243	307±24	284±98	

Table 5.8: Continued.

Site	Total	Insects	EPT	E	P	T	D	C	Noninsects	O
109	13948±3864	12230±3688	5335±2185	3441±1360	718±427	1176±454	6591±1423	292±146	1718±242	252±106
110	6354±825	6097±718	2981±531	2127±204	214±50	640±294	3019±514	90±47	257±116	47±18
111	18602±4464	16656±3738	9376±1833	5366±1046	172±93	3839±1033	7237±1926	43±25	1946±749	344±140
112	17161±2813	12158±1462	5004±614	2860±341	330±14	1814±291	7018±1541	136±54	5004±1458	1828±612
113	12043±3061	11252±2881	5729±1968	3338±1065	482±213	1910±723	5299±2174	224±93	791±239	138±64
114	12516±3098	10290±2486	4710±1026	3774±832	355±62	581±218	5301±1549	280±94	2226±709	1613±583
115	4932±1523	3870±1281	2050±648	1105±349	223±79	723±232	1719±725	90±37	1062±336	299±108
116	10011±1257	9401±1146	2484±505	2050±434	125±35	308±99	6910±869	7±7	609±144	25±15
117	6410±2624	5945±2494	748±210	610±180	64±33	74±34	5141±2328	49±21	466±140	94±34
118	19535±1038	17336±676	3948±191	2976±213	604±125	368±101	12822±817	516±79	2199±493	1808±479
119	15220±4840	13052±4206	4989±1402	3957±1174	298±93	734±300	7880±3162	184±58	2168±644	252±128
120	21785±5251	19978±4541	6237±1208	4516±950	172±0	1548±349	13656±3514	65±41	1806±722	753±449
121	5211±819	4472±672	2319±337	1471±207	323±52	525±112	2031±330	115±23	740±175	261±45
122	15326±2471	13491±1892	3978±262	1269±128	1032±160	1677±125	8530±1465	982±444	1835±687	100±82
123	51398±20476	46495±18889	9634±2524	5075±1409	1892±549	2667±796	26710±11059	10151±5507	4903±1592	1935±1131
124	9401±1942	8886±1832	6175±1342	3279±781	2470±668	425±83	1612±370	1099±188	514±181	113±78
125	12962±3455	11907±3236	5073±1140	2249±774	2179±542	645±211	6145±2020	688±223	1056±326	287±74
126	5967±681	5756±715	2214±363	1219±271	554±115	442±149	1487±277	1980±272	211±37	36±36
127	21763±4538	18215±3397	10839±2129	3849±909	5656±1063	1333±226	4731±654	2581±1137	3548±1995	731±503
129	27129±7693	24849±7190	11129±2928	7333±2179	3237±816	559±147	10882±3695	2839±856	2280±550	1634±436
130	79656±17662	69892±14305	7785±2091	2065±592	5290±1658	430±149	61419±12604	688±290	9763±3390	7355±2969

Table 5.8: Continued.

Site	Total	Insects	EPT	E	P	T	D	C	Noninsects	O
131	35183±5663	23082±2936	4358±592	1477±92	1591±559	1290±165	18495±2292	229±162	12100±2800	11384±2529
132	26796±3646	24136±3199	14136±1872	11161±1700	2229±441	746±157	5197±803	4774±641	2659±1056	839±469
133	11376±1592	7951±1038	368±88	39±23	11±11	318±89	7471±962	90±58	3426±1392	3056±1316
134	50882±10121	44559±8793	19068±3509	4602±1002	14208±2817	258±165	25434±5539	57±57	6323±1646	5792±1778
137	62968±12526	42065±11588	17161±7097	4258±780	12516±6526	387±191	24860±5351	0±0	20903±6042	20731±6103
138	12533±2200	8282±1645	416±100	14±14	53±19	348±104	7867±1647	0±0	4251±603	1135±392
139	8282±961	6422±904	2674±420	1557±332	14±14	1102±211	3712±488	36±22	1860±400	628±26
140	13219±1214	8638±868	595±124	315±86	136±102	143±29	7792±879	158±59	4581±734	4151±732
141	17591±3103	14179±2423	2853±705	939±302	1577±330	337±135	10853±1576	473±250	3412±794	3039±648
142	12495±2820	9651±2074	785±204	382±80	237±108	167±64	8618±1846	247±179	2844±899	2452±759
143	29004±5611	22328±4078	5161±807	344±122	2532±864	2285±652	15005±2645	2119±838	6675±1656	817±309
145	22810±4713	18480±3779	1262±582	186±64	573±193	502±356	16731±3033	487±195	4330±1122	3154±898
146	12075±978	9609±649	6233±430	1753±185	2846±428	1634±224	2659±114	616±237	2466±620	505±122
147	12423±2216	9760±1363	4108±753	308±133	3516±623	283±97	4022±514	1616±450	2663±1147	1957±1034
148	24989±4281	23032±4379	1204±281	0±0	559±147	645±247	21806±4115	22±22	1957±399	1527±419
149	12507±832	11090±885	5481±249	1047±214	2019±336	2416±391	3517±359	2043±695	1417±226	483±141
150	39570±6533	34581±5869	4043±1402	344±140	0±0	3699±1359	30538±4542	0±0	4989±831	2452±435
151	30452±7407	27591±6590	6839±1704	3828±1105	602±127	2409±714	19656±4525	1054±395	2860±887	1355±479
153	23606±3491	21627±3167	12645±1438	10065±1252	559±163	2022±718	8774±1862	158±122	1978±367	753±220

Table 5.9: Significance (*p*) of correlation coefficients (r) describing the relationship between the WQS and 10 density measures (log(x+1) transformation). Column labels are underlined: Total Macroinvertebrate density, Total Insect density, EPT density, Ephemeroptera density, Plecoptera density, Trichoptera density, Diptera density, Coleoptera density, Total Noninsect density, Oligochaeta density.

	Total	Insect	EPT	E	P	T	D	C	Noninsect	O
r	-0.28	-0.22	0.42	0.62	0.17	0.47	-0.42	0.43	-0.44	-0.54
p	0.02	0.09	<0.001	<0.0001	0.2	<0.001	<0.001	<0.001	<0.001	<0.0001

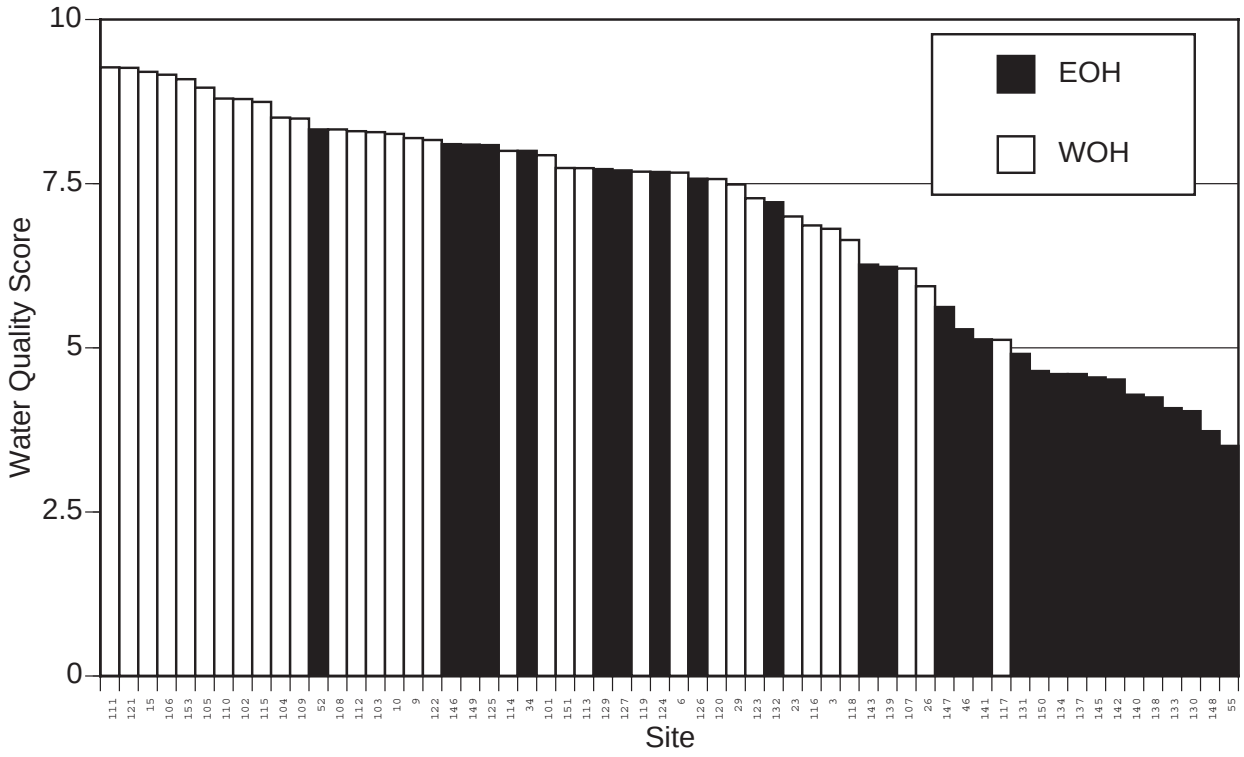

Figure 5.1. WQSs at all 60 Sites in 2003. White bars represent WOH sites and black bars represent EOH sites. Sites are arranged from highest to lowest WQS.

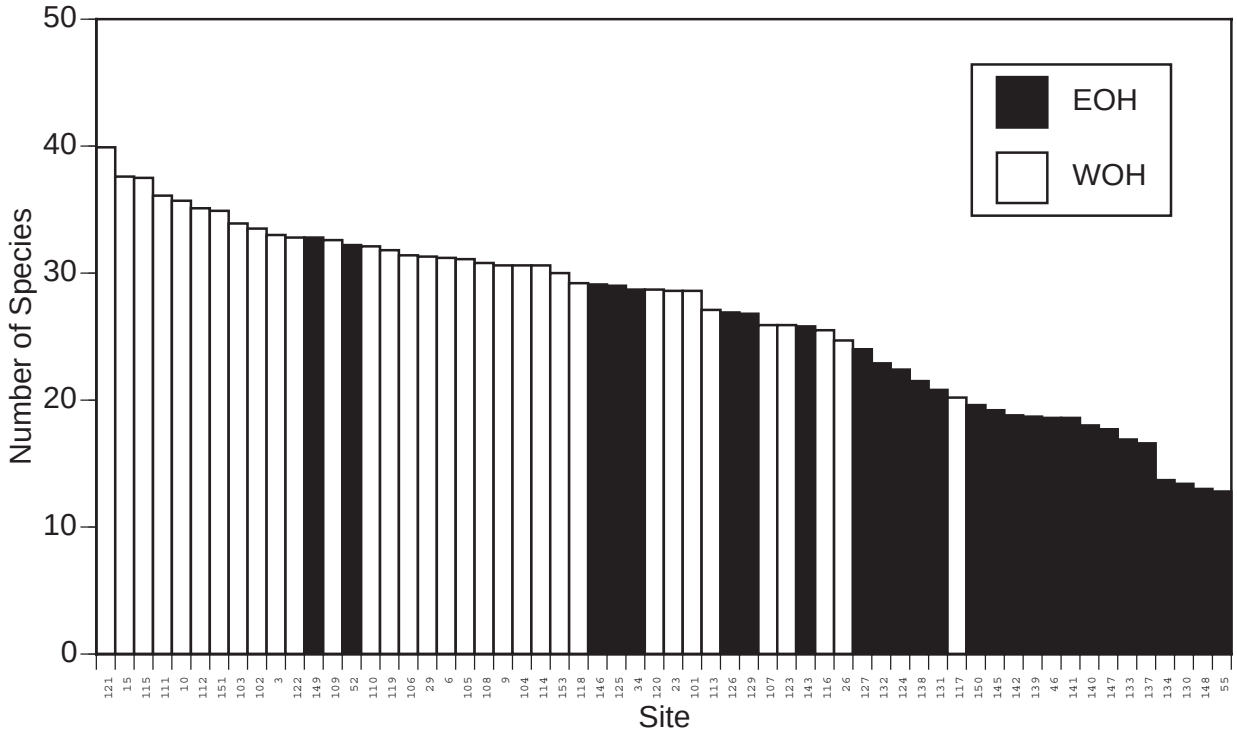

Figure 5.2. Total species richness for all 60 sites in 2003. White bars represent WOH sites and black bars represent EOH sites. Sites are arranged from highest to lowest species richness.

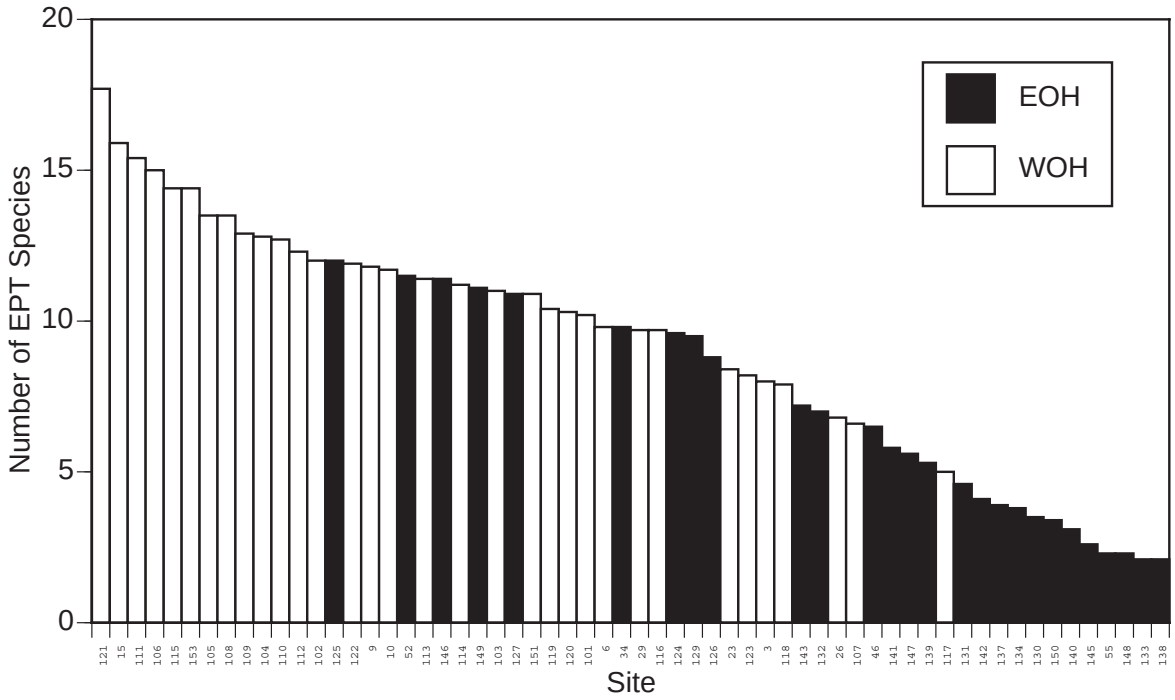

Figure 5.3. Number of EPT species at all 60 sites in 2003. White bars represent WOH sites and black bars represent EOH sites. Sites are arranged from highest to lowest EPT richness.

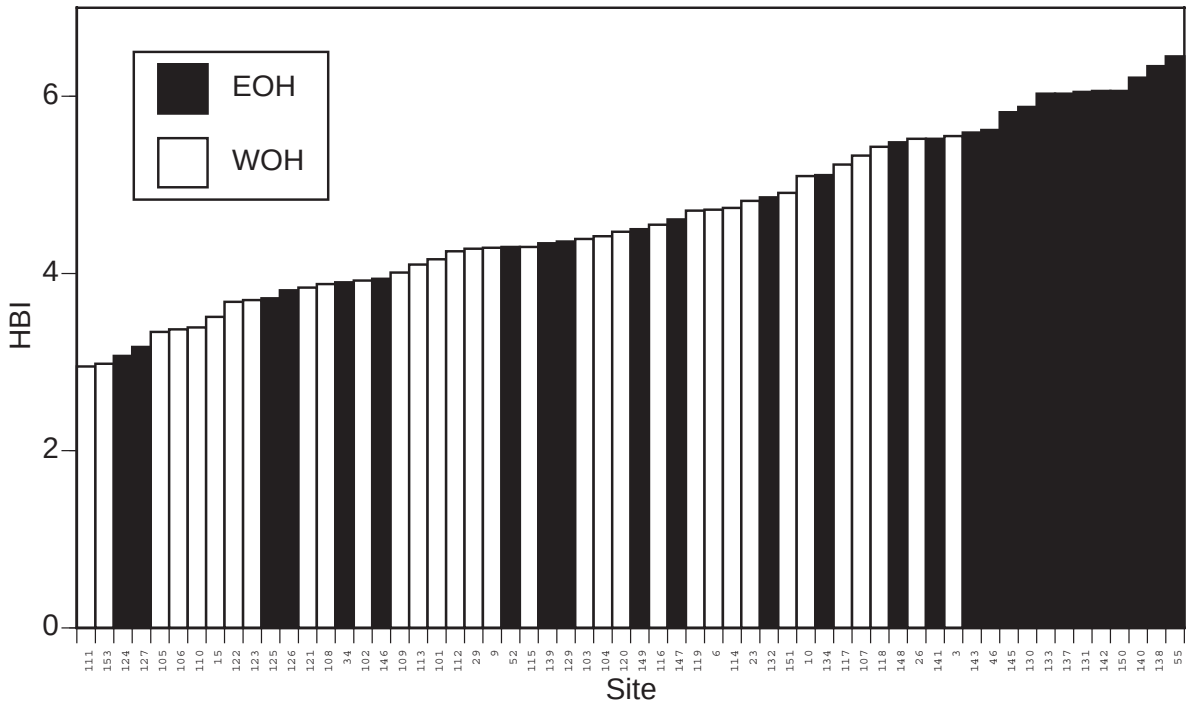

Figure 5.4. Hilsenhoff Biotic Index scores for all 60 sites in 2003. White bars represent WOH sites and black bars represent EOH sites. Sites are arranged from lowest HBI score to highest HBI score.

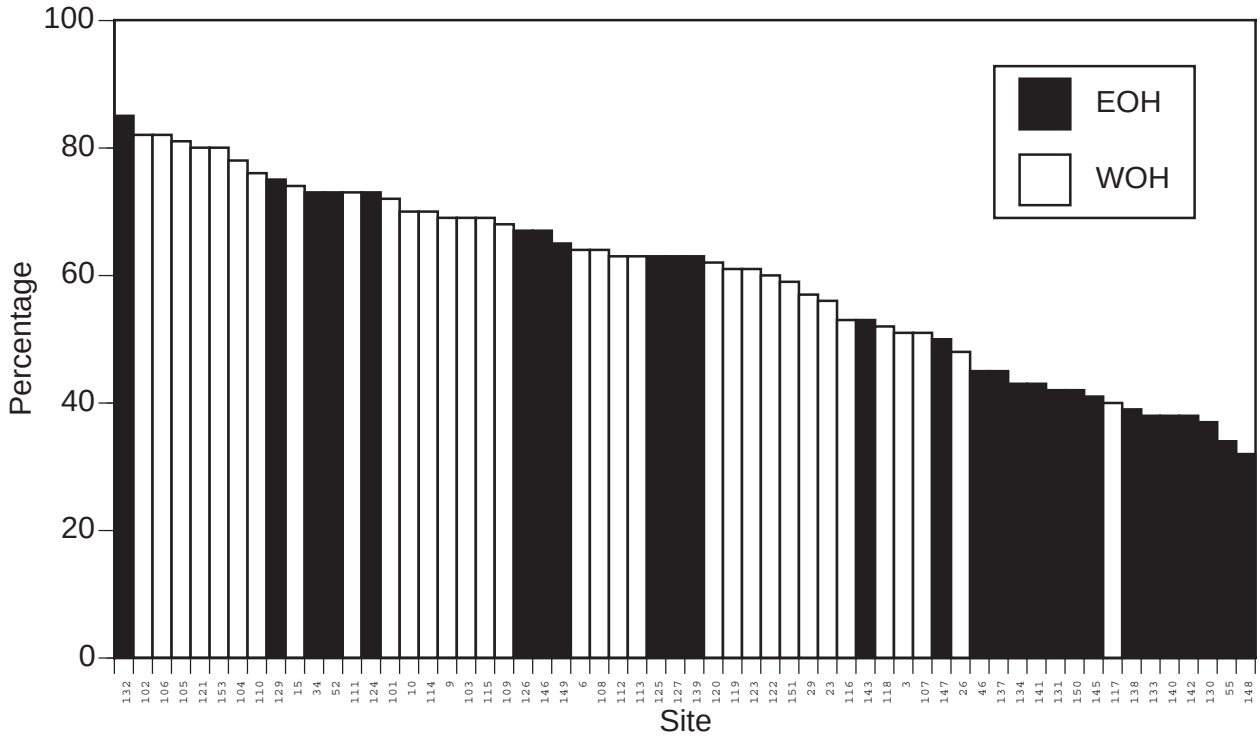

Figure 5.5. Percent Model Affinity values for all 60 sites in 2003. White bars represent WOH sites and black bars represent EOH sites.

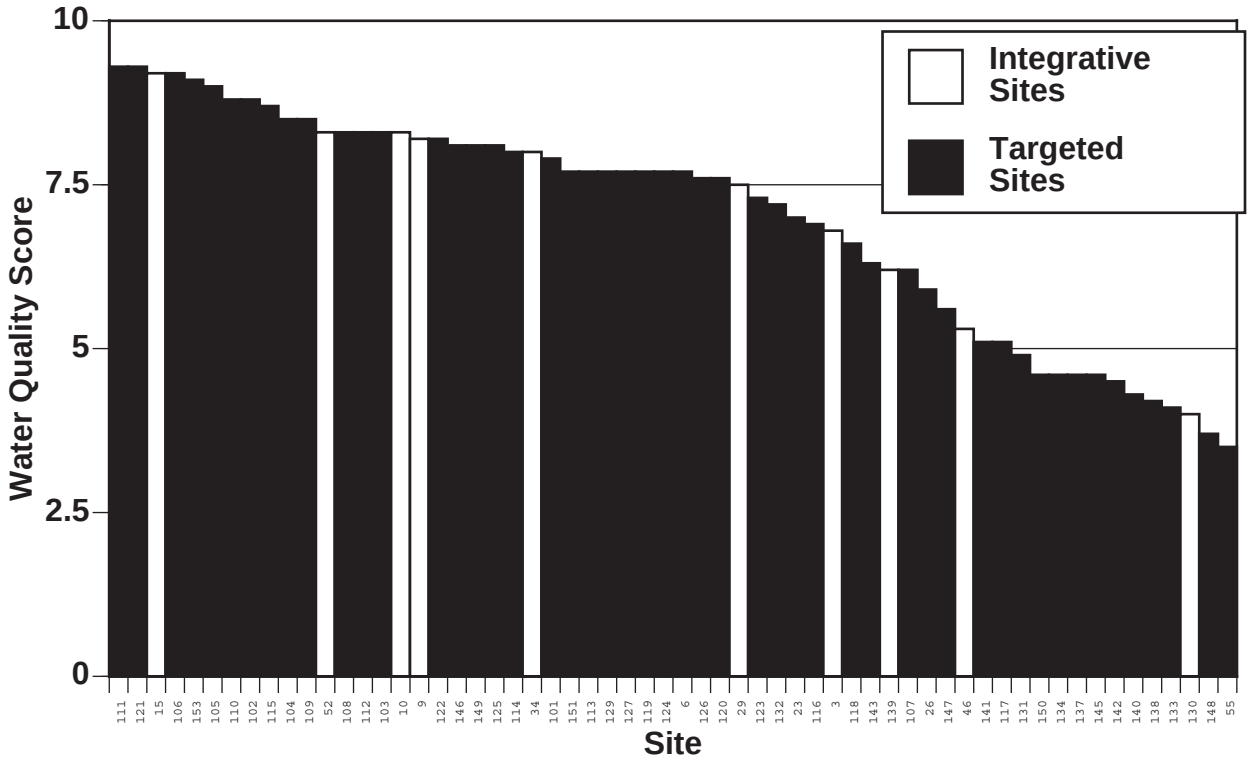

Figure 5.6: 2003 WQSs for Integrative (white) and targeted (black) sites.

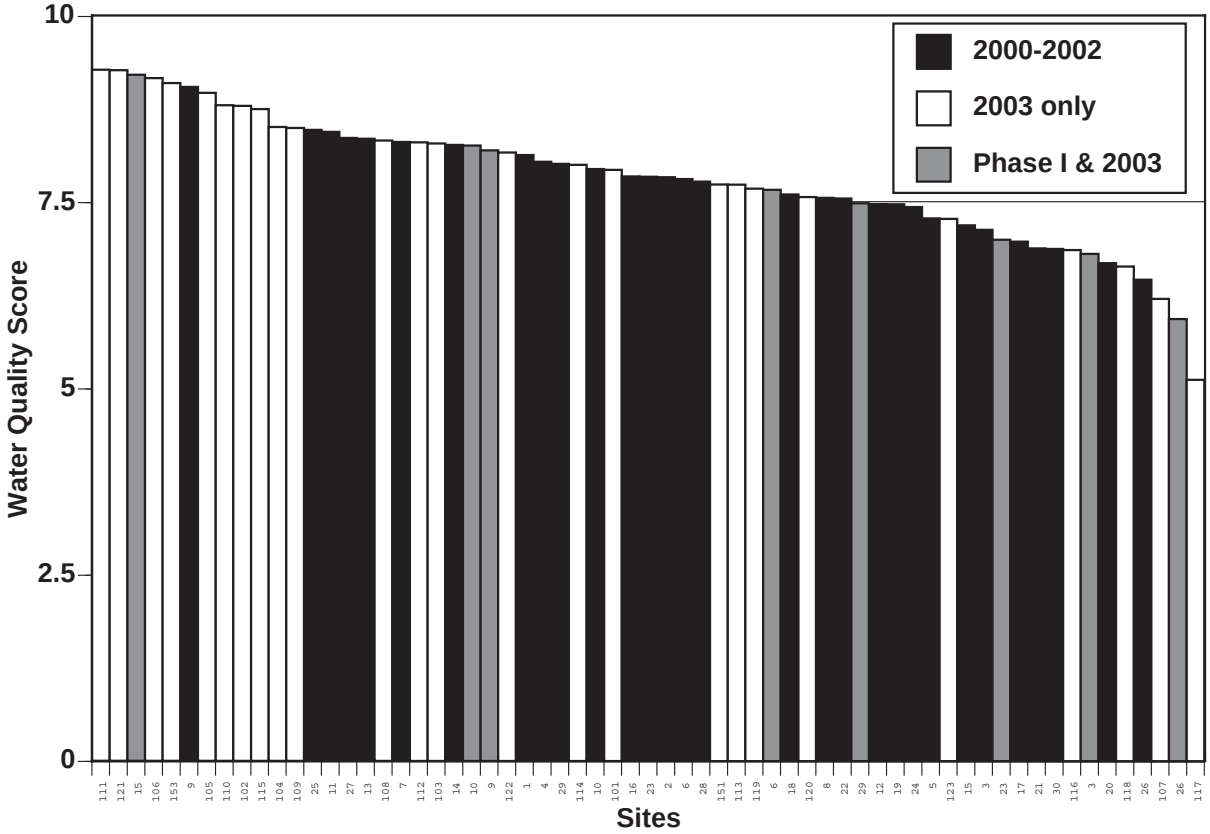

Figure 5.7: Average WQS for 2000 to 2002 (in black) and 2003 (in white) WOH sites. Gray bars represent Phase I site WQS in 2003.

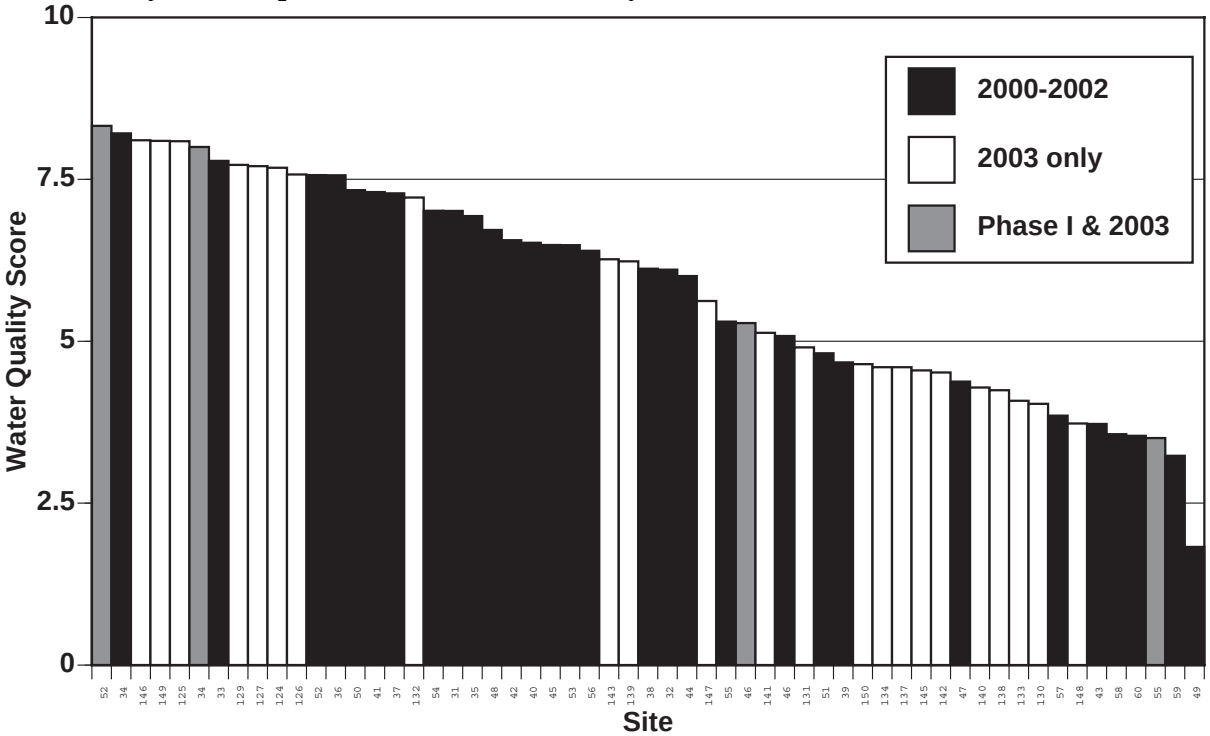

Figure 5.8: Average WQS for 2000 to 2002 (in black) and 2003 (in white) for EOH sites. Gray bars indicate Phase I site WQS in 2003.

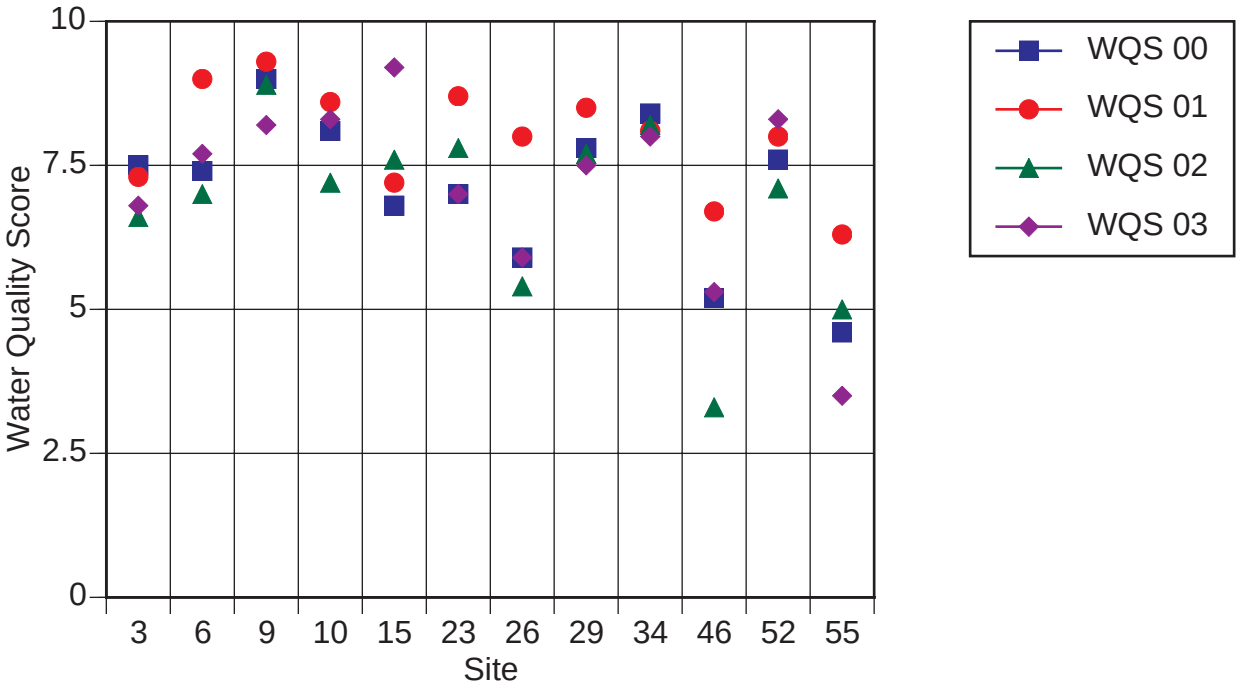

Figure 5.9. 2000 to 2003 WQS at the 12 sites in common to Phases I and II.

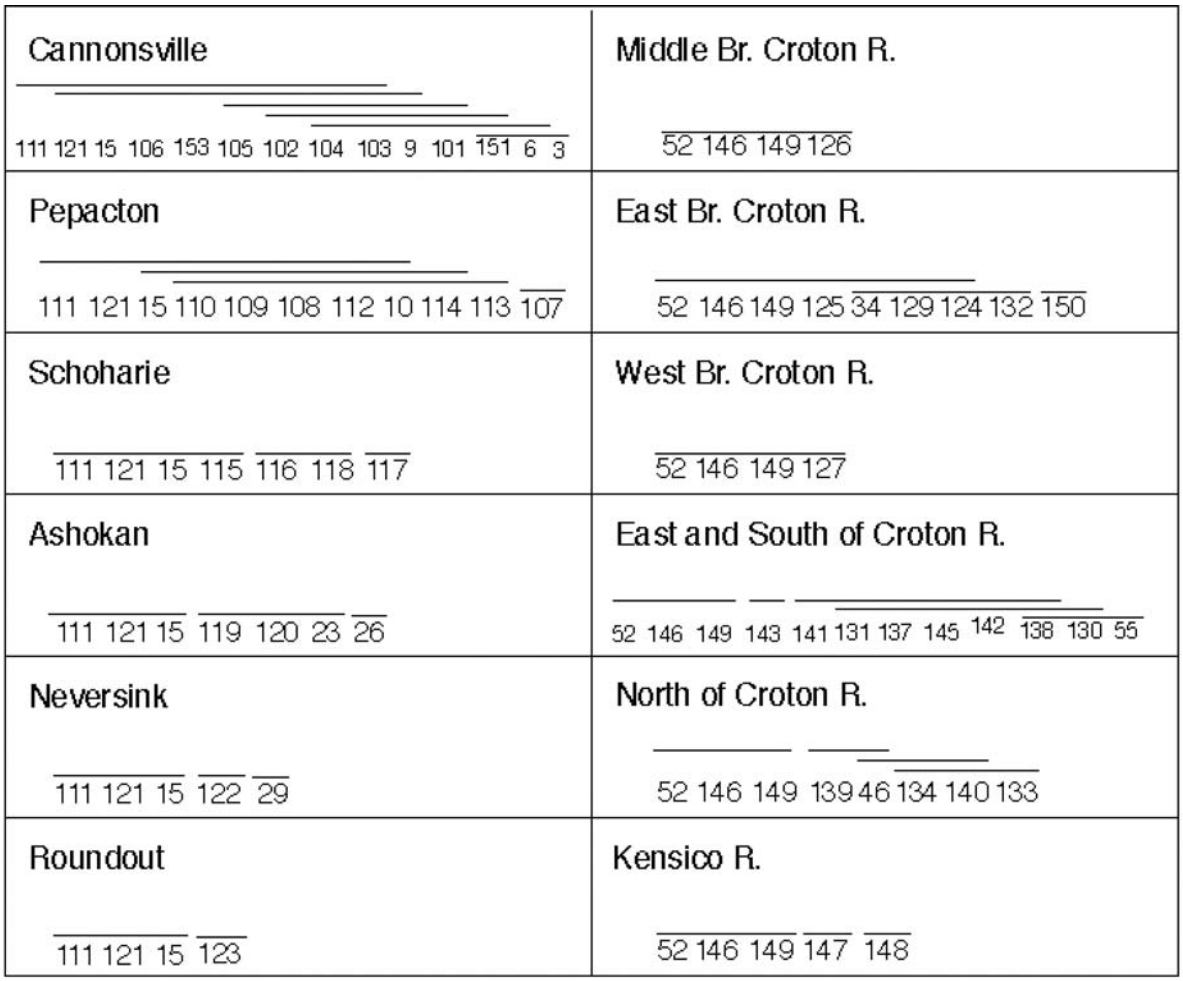

Figure 5.10. Results of Tukey's test comparing reference sites to sites within the respective watershed. Stations under the same line were not significantly different.

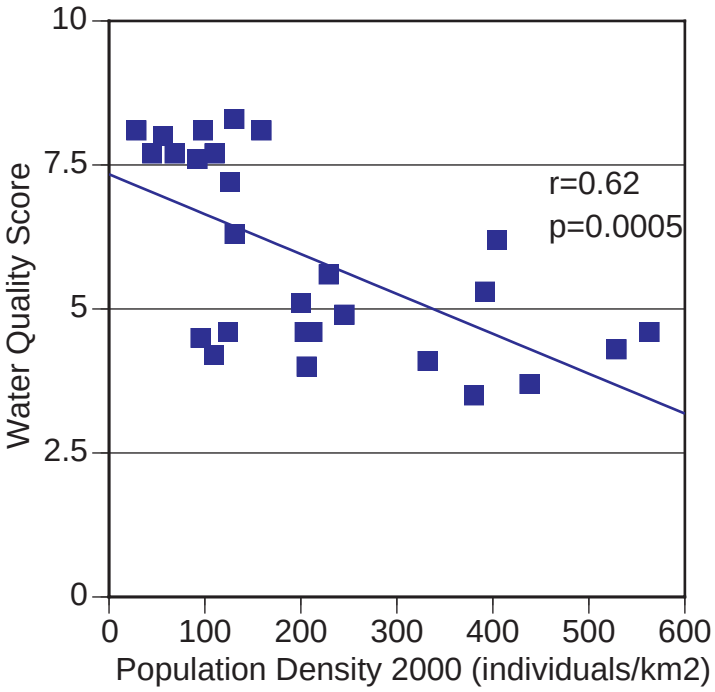

Figure 5.11. Relationship between WQS and population density in the EOH.

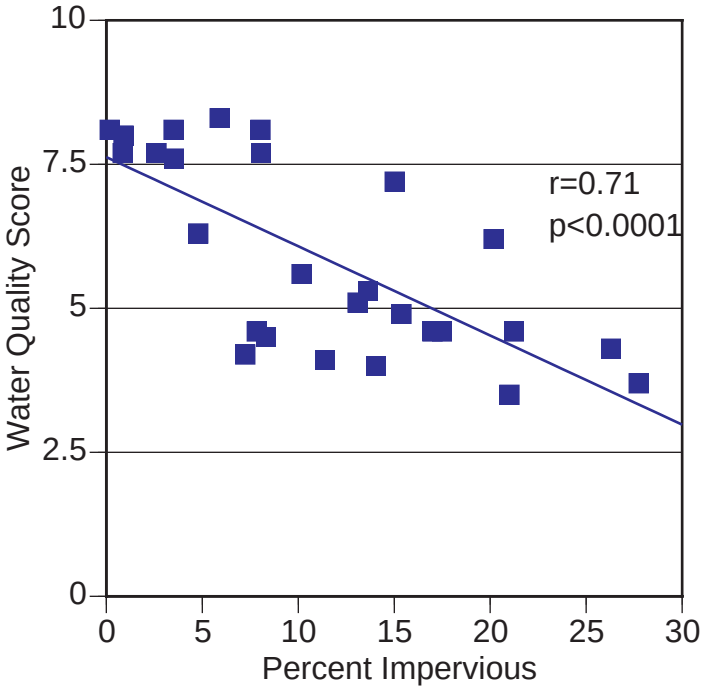

Figure 5.12. Relationship between WQS and percent impervious cover in the EOH.

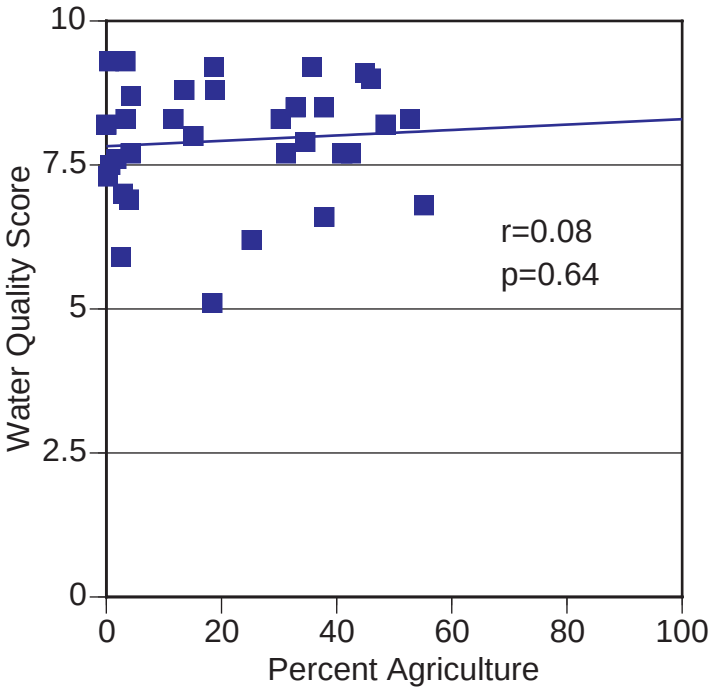

Figure 5.13. Relationship between WQS and percent agriculture cover in the WOH.

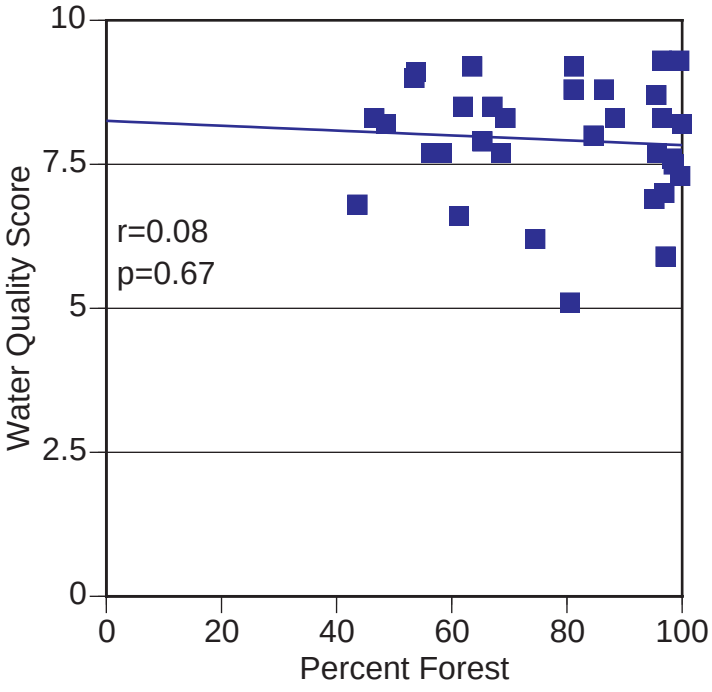

Figure 5.14. Relationship between WQS and percent forest cover in the WOH.

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Chapter 6 - DOC and BDOC Dynamics

Research Task

Dissolved organic carbon (DOC) is the sum of all reduced carbon molecules dissolved in water and represents the largest pool of detrital carbon in stream ecosystems (Wetzel 2001). Heterotrophic bacteria utilize DOC as a source of energy and C, and DOC in transport provides a metabolic link between upstream and downstream segments. DOC concentrations provide a bulk indicator of organic pollution and are also indicative of terrestrial processing of organic matter. In the absence of extensive wetlands, bogs or swamps, baseflow concentrations of DOC in undisturbed watersheds generally range from approximately 1 to 3 mg C/L (1000 to 3000 µg/L) (Thurman 1984). Higher concentrations suggest sources of organic pollution such as point sources from sewage treatment plant discharges and eutrophic, algal-rich farm ponds, or non-point source runoff from urban or rural landscapes. The biodegradable DOC fraction (BDOC) consists of organic molecules that heterotrophic bacteria can utilize as a source of energy and carbon (Servais and Ventresque 1989). Within the context of drinking water quality, DOC is of interest because molecules within a subset of the DOC pool constitute the precursors of disinfection byproducts, DOC constituents, at very low concentrations, can generate taste and odor problems, and BDOC constitutes the nutritional resources that can contribute to biological regrowth within water distribution systems (Escobar et al. 2001) when carbon is the limiting nutrient.

Data generated in this research task were particularly relevant to research objectives 1 and 3, indicating how well best management practice (BMP) implementation is controlling sources of DOC and BDOC and how well the ecosystem conserves and processes organic matter. These data provide baseline targets for BMP and insights into potential land uses that contribute DOC and BDOC, including natural sources such as wetlands. Additionally, these DOC and BDOC data provide supporting information to help interpret the tracer, spiraling, and metabolism studies.

Methods

Samples for DOC were collected and processed with particular attention to avoiding contamination (Kaplan 1994) and analyzed by Pt-catalyzed persulfate oxidation (Kaplan 1992). Briefly, all glassware used for water collection was rendered organic-carbon (C) free by combustion at 500°C for six hours, and samples were protected from the atmosphere by sealing the collection vessels with persulfate-cleaned Teflon-backed silicone-septa. Baseflow stream samples were collected in 500-mL borosilicate bottles that were rinsed twice with site water, filled, capped, and placed on ice in the dark. Within 36 hours, the samples were filtered into 40-9mL borosilicate vials. Filtration to remove particles was performed with precombusted

glass fiber filters (Whatman GF/F), an acetal-resin syringe type filter holder, and a peristaltic pump.

Analysis was performed with either an OI 700 or an OI 1010 analyzer. The OI 700 acidifies the sample to convert all inorganic carbon to CO_2, sparges the sample with ultrapure N_2 (taken from the headspace in a liquid nitrogen tank) and allows the CO_2 to escape to the atmosphere. Next sodium persulfate is added and the sample is heated to 100°C to convert the DOC to CO_2. A second sparging removes the CO_2, which is trapped on a molecular sieve cooled to room temperature. Finally, the molecular sieve is heated to 200°C to release the CO_2 in a sharp peak, and the C-concentration is measured with a non-dispersive infrared detector (NDIR). The OI 1010 operates slightly differently, as it does not have a molecular sieve, and the sparge gases were continuously fed through the NDIR. An extensive comparison of the OI 700 and OI 1010 analyzers, including groundwaters and surface waters from 102 geographically dispersed watersheds showed no differences between the instruments (Kaplan 2000); we are aware that the older instrument (OI 700) is capable of greater analytical precision than the newer instrument (Kaplan, unpublished data).

The BDOC method relies on the measurement of DOC in water samples before and after incubation for 28 days at room temperature in the dark (Kaplan et al. 1994). In the BDOC method, 10 organic-C free 40-mL vials are filled with subsamples of the filtered water from each site. DOC concentrations in five of the vials were measured immediately and the other five vials were incubated to allow the bacterial inoculum contained in the filtered water to grow and metabolize the BDOC. After 28 days, the samples in the five vials were refiltered using a syringe and syringe type filter holder, and analyzed for DOC. BDOC was calculated as the difference between the initial and final DOC concentrations.

Results

QA/QC

QA/QC for year 4 include laboratory measurements of standards and blanks, and baseflow field sampling of duplicates and blanks. QA/QC summary data are presented in Appendix A.6.

Laboratory QA/QC procedures involved the analysis of standards prepared by potassium hydrogen phthalate (KHP), blanks of deionized water, analytical replicates, and spikes of samples with concentrated KHP. Periodic checks of our laboratory standards were performed with a Demand standard purchased from QC SPEX. The Demand standard is an organic-C molecule (glucose) that can be used for assessment of DOC analyses or biochemical oxygen demand (BOD) analyses.

All analyses of DOC, including field samples, standards, and blanks were performed in duplicate. A total of 367 KHP standards were measured with an average recovery of 99.5% (range 90.5 to 106.8%). Duplicate analyses of the KHP standards had a relative percent difference (RPD) that averaged 1.08% (range 0.66 to 9.97%). When lab blanks were analyzed for RPD, the values ranged from 0 to 127.27% (61.2% +/- 41.1%, mean +/- standard deviation). The concentration of the lab blanks ranged from 17 to 224 ug C/L, well below the lowest DOC concentration for a field sample (1030 ug C/L).

Matrix spikes consisted of amending a field sample with a concentrated stock solution of KHP. Typically 380 µL of a 200 mg C/L standard were added to approximately 38 mL of sample. We used one of the five field replicates for the matrix spike and compared that concentration to the mean of the four remaining, unspiked field replicates. Overall, the three matrix spikes for the second year sampling ranged from 93.4 to 106.8% (100.3 +/- 6.7%, mean +/- standard deviation).

Field QA/QC procedures involved field duplicates and field blanks. For the 60 field sites sampled in the fourth year, we performed seven field duplicates and six field blanks. A field duplicate consisted of taking a second 500 mL water sample in a separate borosilicate bottle and treating the duplicate in the same manner as all other samples. The field blank consisted of filling a 500 mL borosilicate bottle with deionized water and then processing this sample along with all other samples. Between each sample, the filtration apparatus was rinsed with deionized water, and the field blank typically was processed in the middle of the field samples collected on a given day. The DOC field duplicates for baseflow, stormflow, and reservoir samples expressed as relative percent difference, ranged from 0.26 to 1.47%. The field blanks for baseflow ranged from 0.013 to 0.080 mg C/L, and the field blank for stormflow was 0.399 mg C/L.

Field Data

Overview of Entire Study Region –Baseflow Sampling

The year 4 data set of baseflow concentrations substantiates clear differences in DOC concentrations that were observed between the east of Hudson (EOH) sites and the WOH sites. The average DOC concentration WOH was 1934 µg C/L, and the range was 1030 to 3714 µg C/L. Only 6 of the WOH sites had average concentrations above 2500 µg C/L, and half of the sites had DOC concentrations that were less than 1500 µg C/L (Fig. 6.1). The average DOC concentration EOH was 4178 µg C/L, the range was 1407 to 9897 µg C/L, and 6 sites had concentrations below 2500 µg C/L (Fig. 6.2). The average BDOC concentrations for EOH and WOH sites also differed, with mean concentrations at EOH sites 1.5-fold higher (237 µg C/L WOH, 354 µg C/L EOH). BDOC as a percent of DOC in the WOH sites averaged 12.7% (range 2.7 to 31.1%) and in the EOH sites averaged 8.4% (range 1.3 to 16.7%).

The extremes within the DOC data set show that the five sites with the lowest concentrations were all from the WOH and the five sites with the highest concentrations were all from the EOH. The five lowest DOC concentrations include site 106, Dryden Brook nr Beerston (1131 μg C/L), site 112, Mill Brook nr Grant Mills (1114 μg C/L), site 119, Birch Creek at Big Indian (1076 μg C/L), site 120, Bushnellsville Breek at Shandaken (1030 μg C/L), and site 123, Rondout Creek near Peekamoose (1156 μg C/L). The five highest DOC concentrations include site 132, Bog Brook nr Sears Corner (5786 μg C/L), site 46, Muscoot River nr Baldwin Place (6035 μg C/L), site 149, Waccabuc River at Boutonville (6066 μg C/L), site 150, E. Branch Croton River at Brewster (6559 μg C/L), and site 127, Black Pond Brook at Meads Corner (9897 μg C/L).

Step-wise multiple linear regressions were used to identify land-use variables that could predict DOC and BDOC concentrations. All concentration data were log transformed to improve linearity and equality of variance. The percentage of watersheds in wetlands was a significant predictor of DOC concentrations in both the WOH ($r^2 = 0.58$) and the EOH ($r^2 = 0.75$) sites (Tables 6.1, 6.2). When data from both WOH and EOH were considered together, percent agriculture was also a significant predictor of DOC concentration, explaining an additional 2.3% of the variance (total $r^2 = 0.77$). BDOC concentrations were predicted by the percent impervious surfaces in the WOH ($r^2 = 0.17$) and the EOH ($r^2 = 0.17$) sites.

Discussion

The five WOH sites with the lowest DOC concentrations (106, 112, 119, 120, and 123) provide a good baseline target for BMP implementation. All the sites were located in medium sized watersheds, had population densities of 2 to 14 people/km^2, extensive forest cover (81.2 to 100%), no detectable impervious cover, and few active sewage treatment plants with 2003 permits through the State Pollutant Discharge Elimination System (SPDES). Even these high quality watersheds had measurable concentrations of BDOC (113 to 212 μg C/L range; approximately 10% to 20% of the DOC), as BDOC production is a natural function of healthy ecosystems. This helps place possible limits or boundaries to BMP expectations. Sites on the EOH with low (< 2500 μg C/L) DOC concentrations (sites 124, 125, 140, 141, 147, 148,) were smaller watersheds with few wetlands, no reported SPDES discharges, but a range of impervious surface cover (0.2 to 27.7%).

The five EOH sites with the highest DOC concentrations (46, 127,132, 149, and 150) reflect the impacts of wetland processes, as the watersheds had 8.2 to 11.5 % wetland cover. Other potential sources of DOC associated with human activities, such as impervious surfaces (range 0.9 to 15%) and active SPDES sites (range 0 to 9) were not consistently present across these sites, and at this point, contributions, if any, from these sources to individual watersheds were not know.

The year 4 data set complements and reinforces the information obtained during Phase I of this investigation. The DOC and BDOC concentrations for the 12 sites carried over from Phase I fell within the range of the prior 3-year data set. A difference between the year 4 and the Phase I analysis, however, is that for Phase I, three land use characteristics were significant predictors of DOC concentration: wetlands, sewage treatment plant effluents, and impervious surfaces, with wetlands explaining 62% of the variance, and three land-use variables – sewage treatment plant effluent, % impervious area, and agricultural activity – explained a total of 44% of the BDOC variance with sewage discharge explaining 28% of the variance. This was not the case for this first year of Phase II investigations. Wetlands have been identified as an important source of DOC (Mulholland 1979; Hemond 1990), and while this DOC has a high humic content which is generally considered refractory to biological decomposition, others have shown that humic-C in stream is biologically labile (Volk et al. 1997). Impervious surfaces have also been identified as a source of DOC (Jordan et al. 2000; Wallace et al. 2002), though these studies were not peer reviewed and do not address the issues of DOC quality (i.e., BDOC concentrations).

There are relatively few published reports of DOC and BDOC concentrations in watersheds that supply drinking water. One study that measured concentrations in 80 watersheds across the continental United States where drinking water treatment plants are supplied by surface waters reported DOC concentrations of 800 to 5000 μg C/L (mean 2300 μg C/L) and BDOC concentrations of 100 to 1000 μg C/L (mean 300 μg C/L) (Kaplan et al. 1994). For the most part, the data reported for the 60 study sites fall within these ranges.

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Table 6.1: Summary of the separate stepwise multiple linear regression results for DOC and BDOC concentrations (log_{10} transformed) versus %wetlands and %impervious area for WOH sites. Results are shown for those independent variables that remained in the final model (i.e., significant at $p = 0.05$). Multicolinearity among the independent variables was not a factor.

Variable	Coefficient estimate	Partial R^2	F Value	p-value
Year 4 Mean DOC (log10 transformed - µg C/L) West of Hudson				
Intercept	3.079			
% wetlands	0.218	0.58	42.79	<0.0001
Year 4 Mean BDOC (log10 transformed - µg C/L) West of Hudson				
Intercept	2.296			
% impervious area	0.396	0.168	6.24	0.018

Table 6.2: Summary of the separate stepwise multiple linear regression results for DOC and BDOC concentrations (log_{10} transformed) versus %wetlands, %impervious area, %row-crop agriculture, and WWTP outflows. Results are shown for those independent variables that remained in the final model (i.e., significant at $p = 0.05$). Multicolinearity among the independent variables was not a factor.

Variable	Coefficient estimate	Partial R^2	F Value	p-value
Year 4 Mean DOC (log10 transformed - µg C/L) East of Hudson				
Intercept	3.257			
% wetlands	0.050	0.75	74.06	<0.0001
Year 4 Mean BDOC (log10 transformed - µg C/L) East of Hudson				
Intercept	2.296			
% impervious area	0.396	0.168	6.24	0.018

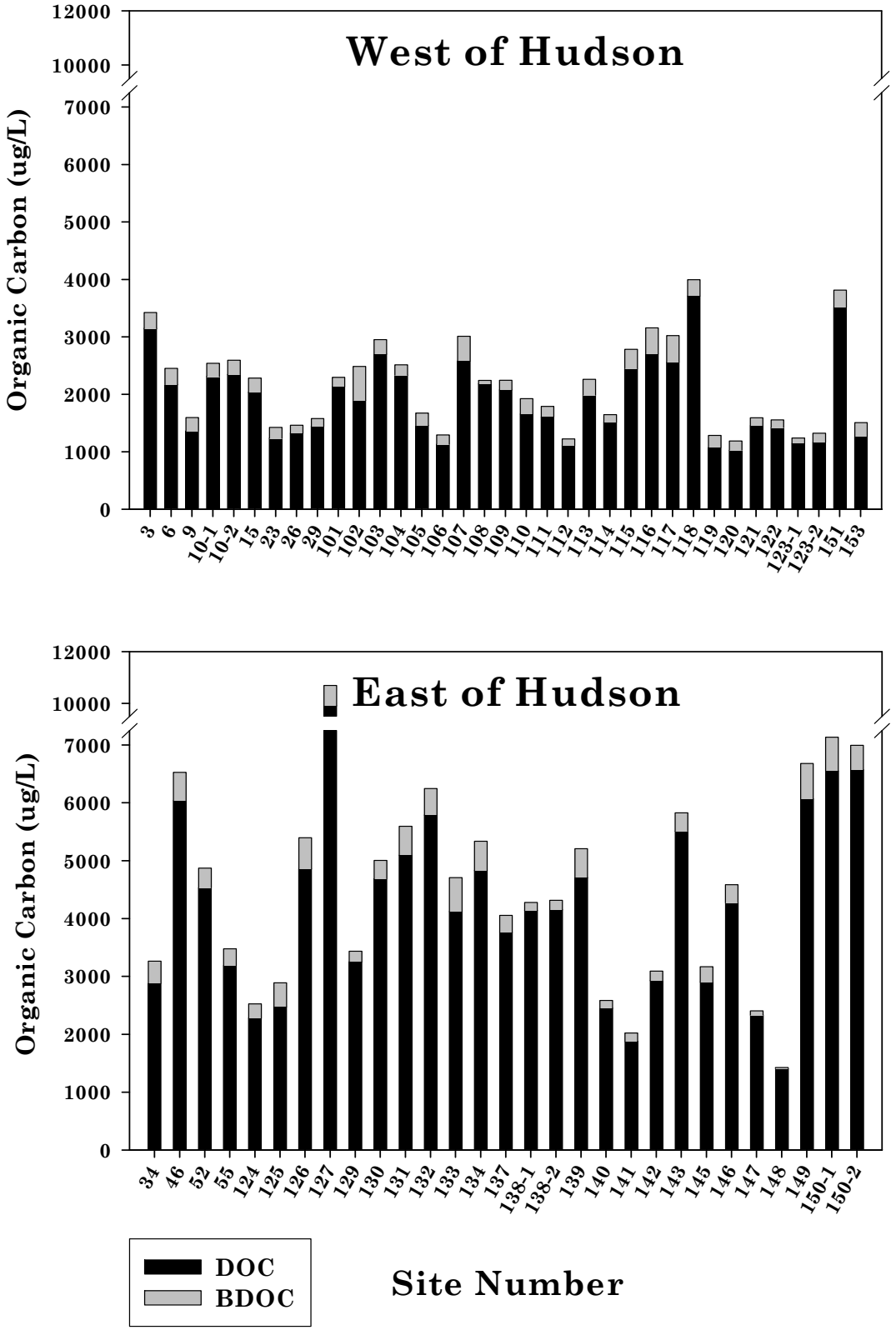

Figure 6.1: Baseflow DOC and BDOC concentrations measured at the 60 EOH and WOH stream sampling sites for Year 4.

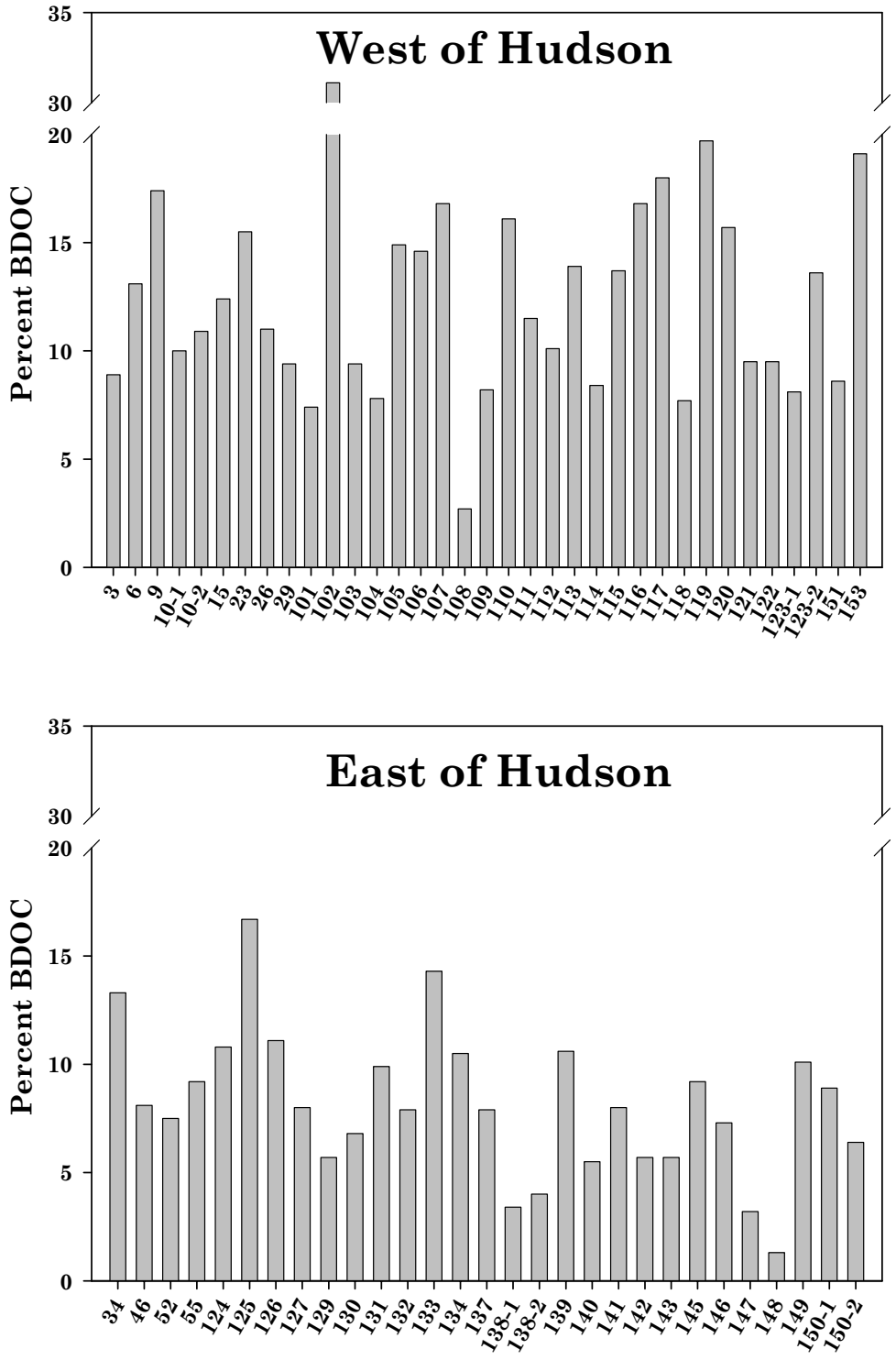

Figure 6.2: Baseflow BDOC concentrations expressed as a percentage of DOC concentrations measured at the 60 EOH and WOH stream sampling sites for Year 4.

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Chapter 7 - Nitrogen (N), Phosphorus (P), and Dissolved Organic Carbon (DOC) Spiraling

Research Task

Phosphorus and nitrogen entering the streams that feed the NYC reservoirs are likely to be taken up and recycled at least once and probably several times within the stream ecosystem prior to reaching the reservoirs. Because this cycling occurs simultaneously with downstream transport it is sometimes referred to as "spiraling". The "spiraling length" represents the distance over which the average nutrient atom travels as it completes one cycle of utilization from a dissolved available form, passes through one or more metabolic transformations and is returned to a dissolved available form. Quantitatively, it is the ratio of the downstream flux of nutrient to the uptake of nutrient per unit length of stream. More intense utilization of the nutrient, along with more effective retention of particulate forms, shortens the spiraling length so that an individual nutrient atom completes more cycles in its passage through a stream-river network. Dissolved organic carbon (DOC) undergoes similar spiraling except that its utilization eventually results in oxidation, and the spiraling length in this case refers to the distance traveled until oxidation.

The significance of spiraling to the NYC watersheds relates both to the function of the stream ecosystem itself, as well as implications for downstream ecosystems (the reservoirs) and resulting water quality. For the stream ecosystem, spiraling reflects the degree of metabolic activity within the system, the ability of the system to retain nutrients, and the relative utilization rates (hence degree of nutrient limitation) among different nutrients. Spiraling length also describes the scale on which upstream processes are linked to downstream processes. Thus spiraling represents a fundamental measure of stream ecosystem function. Ecosystem impairment is likely to increase spiraling length (reduce the cycling intensity), through reduced uptake, excessive loading, or decreased retentive ability of the ecosystem. An exception to this rule would occur when the increased loading of a single nutrient stimulates uptake of a second nutrient, whose spiraling length would shorten.

The processing or spiraling of nutrients may have a variety of implications to downstream ecosystems. Uptake may sequester nutrients for long periods resulting in seasonal alterations of downstream nutrient loads. Processing may also alter the partitioning of the nutrient forms (inorganic/organic, dissolved/particulate) with attendant implications to the availability of the nutrient reaching the downstream system. In the case of nitrogen, significant in-stream removal may occur through denitrification. In the case of DOC, more intense utilization within the stream ecosystem directly reduces the downstream loading.

The measurement of uptake length will provide a first step in addressing the role of spiraling as an indicator of ecosystem function and as a potential influence on downstream water quality. A complete evaluation of spiraling length requires use of isotopic tracers, but previous studies have shown that the uptake that can be observed by incrementing the background nutrient concentrations by small amounts provides a reasonable first approximation to the uptake length (or distance traveled in the available form). Past studies have also shown that uptake length is normally >90% of the total spiraling length (Newbold 1992), a result that can be evaluated from the fractions of dissolved and particulate nutrient in the water column.

This section reports the uptake length of inorganic nitrogen (NH_4^+), inorganic phosphorus (PO_4^{-3}), and organic carbon (glucose and arabinose) in streams derived from whole-stream injections of standard solutions of N, P, and C along with a conservative tracer (bromide). Peak concentrations of the added nutrients were in the μM range, and the carbohydrates were in the nM range. Concentrations of each constituent were measured at five stations downstream and the data fitted to a one-dimensional advection-dispersion model augmented to include transient storage. The task was performed at each of the 10 integrative stations between July and November 2003.

In 2003, which represents the first year of Phase II and the fourth year of the project, seven sites were studied for the first time. Three sites have been continued from Phase I. These were station #52 (Cross River in Ward Pound Ridge Reserve), #46 (Muscoot River, near Baldwin), and #29 (Neversink River near Claryville). The year 2003 was unusually wet, with relatively high baseflows. Flows during the nutrient injections at the three sites that were continued from Phase I were 2-6 times higher than the highest flows sampled in the respective streams during Phase I.

Methods

Uptake lengths for dissolved phosphate, ammonium, glucose, and arabinose were determined by whole-stream solute injections, following the general approach described by the Stream Solute Workshop (1990).

One injection was made at or near each of the 10 "integrative" sampling stations. Each injection involved simultaneous addition of a conservative tracer (sodium bromide), PO_4^{-3}, NH_4^+, glucose, and arabinose at rates designed to achieve maximum concentration (after mixing) in the stream of 30 μg/L PO_4^{-3}, 30 μg/L NH_4^+, and 0.20 μM for the carbohydrates. Amendments were metered in at a constant rate, using a peristaltic pump for time periods ranging from 70 to 120 minutes, depending on flow and channel characteristics. These injections were conducted

simultaneously with propane injections made for the purpose of assessing gas exchange rates (Chapter 8).

On the day prior to an injection, preliminary measurements were made of streamflow and travel times. Streamflow was measured by wading cross sections (or from a bridge), and measuring depth and velocity (Swoffer current meter) at 10-20 intervals. Time of travel was estimated from the introduction of a pulse of rhodamine dye, which was tracked visually. From these measurements the following design parameters for the actual injection were determined: (i) quantity of conservative tracer, phosphorus, nitrogen, and carbon to be injected; (ii) duration of injection; (iii) concentrations and metering rates for the injection solutions; (iv) longitudinal locations of five sampling stations downstream from injections; (v) schedule for collection of water samples from each station. The design objective was to achieve target concentrations (with thorough lateral mixing) of all constituents by the upstream most sampling station, to minimize longitudinal variation in the peak concentration of the conservative tracer, and to observe approximately 60% uptake of each nutrient within the study reach. Unless a Year-1 sampling station was reused, an uptake mass transfer coefficient of 5×10^{-5} m/s was used to locate downstream stations. A spreadsheet-based model was used to calculate the design parameters. Where rhodamine dye was not used for time of travel, all design parameters were calculated from a time of travel prediction model derived from Year-1 parameters.

Immediately prior to the beginning of an injection, background water samples for nutrient concentrations were taken at each downstream sampling station. Subsequent samples were taken according to the sampling schedule relative to initiation of the injection. Five water samples for assay of N, P, glucose, and arabinose, in addition to the conservative tracer, were taken from each station within the period of plateau concentration, or in the period of maximal concentrations. Samples for N and P assay were field-filtered through a rinsed, Whatman® 0.45 µm cellulose nitrate membrane filter and frozen within 24 h of collection for analysis within 60 days. Samples for glucose and arabinose assay were sterile-filtered (0.2 µm HT Tuffryn Acrodisc®) and frozen within 24 h for analysis within 2 months. At the upstream-most and downstream-most sampling stations additional water samples for the conservative tracer were collected to describe the complete passage of the injection pulse. Additionally, samples were collected at the injection site and at the downstream-most sampling station before, during, and after the injection for supplemental water chemistry analyses (NO_3-N, SKN, TKN, TDP, and TP) to monitor changes in other N and P species throughout the injections.

Uptake length for ammonium, phosphate, and carbohydrates was estimated from the average concentration elevation, $\Delta c(x)=c(x)-c_b(x)$ where $c(x)$ is the average concentration of the added nutrient sampled during the plateau at a distance x meters downstream into the reach; and $c_b(x)$ is the background (i.e., un-amended)

concentration at distance x of the nutrient measured immediately prior to injection. To adjust for longitudinal dilution and dispersion, we calculated the ratio, r, of the concentration elevation to that of the bromide (the conservative tracer): i.e., $r=\Delta c/\Delta [Br^-]$. The uptake length, S, for the respective nutrient was calculated as the inverse of the longitudinal loss-rate, k_l, which, in turn was estimated by non-linear regression from the relation $r(x)=r_0 \exp(-k_l x)$, where r_0 is the concentration ratio elevation at x=0. The mass transfer coefficient for uptake, v_f, or "uptake velocity" was then calculated as $v_f = k_l d$, where v_w is the reach-average water velocity, and d is the reach-average depth.

This approach to estimating the uptake velocity assumes that uptake increases linearly with the concentration, c(x), of the nutrient throughout the varying concentration exposures of the injection, i.e., that the v_f measured at elevated $c(x)$ is the same as v_f at background concentration. It is likely, however, that some decline in v_f occurs at higher concentrations as biological uptake approaches saturation, so that, in this respect, the estimates of v_f should be considered as lower-bound approximations. The potential error introduced by possible non-linearity in uptake was held to a minimum by limiting the injection concentrations to ~0.030 mg/L above background, for ammonium and phosphate, and to 0.2 μM above background for carbohydrates.

In 2003 the ammonium concentrations measured at Station #139 (Muscoot R. near Whitehall Corners) were anomalous. Background ammonium concentrations measured prior to the injection ranged from 0.27 to 0.41 mg/L, with a mean of 0.33 mg/L (Table 7.3). This background was far higher than all other backgrounds measured during the total of 40 injections conducted for this project, which typically have been near the detection limit of 0.01 mg/L and in no case has exceeded 0.050 mg/L. The background also greatly exceeded the design concentration elevation, $\Delta c(x=0)$ of 0.030 μg/L for the injection. The injection was conducted without modification because the results of these analyses were not available until several weeks later. The plateau concentrations for the injection ranged from 0.09 to 0.22 mg/L, which was lower than the backgrounds but considerably higher than the design elevation. It is suspected that there was a transitory upstream input of ammonium that occurred on the day of the injection which declined somewhat between the time the background concentrations were sampled and the plateau measurements were taken. Interestingly, the measured ammonium concentrations declined longitudinally both in absolute concentration and after correction for by the bromide concentrations. The data were analyzed as though the observed ammonium had been experimentally injected, but using an assumed background of 0.010 mg/L. The non-linear regression explained 99% of the variance. Note that although the suspected input may have been declining, the experimental sampling was precisely timed to follow a downstream pulse, so that the temporal variation of the input would not have compromised the estimate. As discussed above, the relatively high concentrations would be expected to reduce the estimated uptake velocity. However,

the non-resulting estimate of 0.34 mm/s was within the range of the estimates from other streams. We therefore report this estimate for the ammonium uptake, but note that it was made under unusual circumstances.

Conservative tracer (bromide) data were analyzed by fitting the concentration-time curves to a one-dimensional advection-dispersion model that includes a transient storage component (OTIS-P, Runkel 1998). Streamflow, a fixed parameter, was calculated from corrected injection pump rate and duration and area under the empirically derived bromide curves at the downstream station. Where sufficient empirical data were not available to complete the tail of the curves, the tail was extrapolated and the estimated area under this portion of the curve was included in the flow calculation. The model yields estimates of the longitudinal dispersion, cross-sectional stream area, the hydraulic exchange velocity (the rate of vertical mixing into the stream bed), and the transient storage volume (the hyporheic zone or region of stream sediments in active exchange with the water). The parameters were estimated iteratively by the OTIS-P model, which uses a non-linear least squares estimation procedure.

The carbohydrates, glucose and arabinose, were analyzed by HPLC with pulsed amperometric detection (Dionex 500) using a protocol recently improved for resolution, sensitivity, and precision (Cheng and Kaplan 2001). These modifications have resulted in improved baseline stability, allowing detection limits of less than or equal to 0.4 nM for monosaccharides, average coefficient of variation of 1.3% for a 100 nM standard, and recovery between 92 and 109% for individual monosaccharides in stream water amended with standards.

Bromide was analyzed by ion chromatography with conductivity detection (Dionex 500).

Results and Discussion

QA/QC

Quality Assurance/Quality Control results are summarized in Appendix 7, Tables 7.1-7.4. Among field and laboratory blanks, exceedances occurred only for bromide (4%) and glucose (30% laboratory, 63%.field). While the high frequency of exceedances for glucose is a concern and will be addressed in a review and modification of field and laboratory procedures, it is unlikely that they influenced the estimates of glucose uptake for two reasons. First, the mean concentration of blanks (10 nM field, 5 nM), and even the highest blank concentrations (26 nM field, and 55 nM lab), were well below the 200 nM that is injected to the stream for uptake measurements. Second, it appears that the source of the blank contamination was related to the blank preparation, and was not indicative of the quality of the actual samples. Background samples (taken from the each station prior to injection, Table 7.4) were consistent within streams and, for 4 streams,

were below 10 nM. The mean within-site standard deviation of background samples was 4.0 nM, whereas the standard deviation among field blanks was 7.8 nM and among laboratory blanks was 12 nM. The highest background concentration among 47 measured was 38 nM, whereas two laboratory blanks out of 40 exceeded this concentration, at 55 and 56 nM respectively.

All field and laboratory duplicates were satisfactory. Among matrix spikes, 3 out of 65 bromide spike recoveries exceeded the accuracy limits of 90-110%. Two of these, at 88%, were near the limit, while the third, at 71%, reflected a sample-specific malfunction of the auto-sampler for the ion chromatograph. Any sample subject to a similar malfunction would have been easily identified and discarded. All laboratory control standards were satisfactory.

Field Data Summary.

Significant uptake was measured for each of the nutrients at each of the ten stations (Table 7.1). Uptake lengths for all nutrients were positively correlated with streamflow, water depth, and water velocity (Spearman's rank correlation coefficient, r, ranged from 0.76 to 0.95, $P<0.05$, $n=10$). These associations represent the expected influence of scale on the relationship between downstream transport of the nutrients and transfer to the streambed.

Uptake length for phosphate ranged from 847 m to 12,270 m. These lengths imply that phosphorus is intensively cycled and undergoes several cycles, or spirals, during passage through a reach of a given order. Ammonium uptake length ranged from 114 m to 4805 m and was in all cases shorter than the respective phosphate uptake length. Glucose uptake length ranged from 325 m to 6349 m, and arabinose from 685 to 15,291 m. The uptake length of arabinose correlated closely ($r=0.99$) with that of glucose, but was, on the average, 2.1 times longer. The uptake lengths for all four nutrients were significantly correlated among each other ($r= 0.78$ to 0.99, $P<0.01$). These inter-correlations reflect both the scaling effects of river velocity and depth as well as rates of transfer across the water/sediment interface.

Uptake velocity, v_f, (Table 7.2) expresses the nutrient utilization rate as a mass transfer coefficient from which the scale-effects of stream size (specifically depth and velocity) on uptake length have been removed. As a consequence, the uptake velocity is not expected to correlate with measures of stream size (Table 7.3), and in previous years no significant correlations of v_f for any of the nutrients with flow, current velocity, depth, or width have been observed ($P>0.10$). In 2003 this pattern continued, except that the uptake velocity of phosphate correlated with water velocity and flow, as further discussed below.

Phosphate uptake velocity ranged from 0.012 to 0.039 mm/s (Table 7.2), with a mean of 0.018 (±0.008, standard deviation) mm/s, identical to the mean for all streams measured in Phase I. The v_f for phosphate correlated negatively with

background concentrations (Table 7.4) of total nitrogen (TN, r=-0.75, P<0.05) and total dissolved nitrogen (TDN, r=-0.75, P<0.05), but in contrast to previous years the correlation with background SRP (r=-0.55), was not significant (P=0.11). Nonetheless, the 2003 uptake velocities fall generally within the pattern established in Phase I, except that in 2003 v_f 's measured at higher SRP concentrations may have been somewhat higher than in 2000-2003 (Fig. 7.1).

As noted above, the uptake velocity of phosphate correlated with current velocity (r=0.73, P=0.016) and with flow (r=0.64, P=0.048). This correlation, although not expected as a consequence of scale, is consistent with an influence of water velocity on the rate of mass transfer phosphorus to the streambed through a benthic boundary layer (Borchard et al. 1994). In Phase I no such correlation was found, but it is possible that the effect became apparent only in 2003 because of higher water velocities: the median water velocity of the streams sampled in 2003 was 0.29 m/s as opposed to 0.16 for Phase I. However, as Fig. 7.2 illustrates, this hypothesis cannot explain a number of high v_f 's observed at relatively low current velocities during 2000-2002.

Uptake velocity of ammonium ranged from 0.032 to 0.133 mm/s, with a mean of 0.064 (±0.032) mm/s, which is near the Phase-I mean of 0.058 mm/s. Ammonium uptake velocity was not correlated with the background concentrations of any of the measured forms of phosphorus or nitrogen. The Phase I studies, by contrast yielded a clear negative relationship between background dissolved inorganic nitrogen and ammonium uptake velocity. As illustrated in Fig. 7.3, most of the ammonium v_f 's measured in 2003 were consistent with the Phase I pattern, and the lack of correlation is primarily attributable to an unusually high value from the Titicus River (site #130).

The ammonium uptake velocity measured at the Titicus River of 0.133 mm/s was the highest measured at any of the Phase-I or Phase-II sites to date. Suspended solids may have contributed to the high ammonium uptake at Titicus. Both TSS (3.97 mg/L) and VSS (1.30 mg/L) were the highest concentrations measured during the nutrient injections in 2003. In the Phase I analysis, it was found that high concentrations of TSS were associated with high ammonium uptake velocities (Fig. 7.4). However, in 2003 two other streams with TSS and VSS values only slightly lower than those in the Titicus R. yielded relatively low ammonium v_f 's. Another factor that might be related to the high ammonium uptake is SRP, which at 0.039 mg/L was the highest measured in 2003. High phosphorus might have stimulated the uptake of ammonium. However, in 2000-2002 we did not observe stimulation of uptake by high phosphorus; the streams with the highest SRP concentrations (Kisco R. and Muscoot R.) had the lowest ammonium uptake velocities.

The uptake velocities of ammonium and phosphate measured in 2003 did not correlate with each other (r=0.48, P=17). In the Phase I studies these two variables were correlated.

The mean glucose uptake velocity was 0.072 ±0.028 mm/s, which is higher than the mean of 0.58±0.033 mm/s measured in Phase I. The mean uptake velocity for arabinose was 0.025±0.009 mm/s, also higher than the respective Phase I mean, which was 0.021±0.010. Glucose and arabinose uptake velocities were correlated with each other (r=0.76, p=0.01), but not with either ammonium or phosphate uptake velocities. The inter-correlation of glucose and arabinose uptake was similar to that observed in Phase I (r=0.87). There were no significant correlations of uptake velocity for either glucose or arabinose with their respective background concentrations (Table 7.11), indicating these carbohydrates did not occur in sufficient concentrations to saturate uptake.

The hydraulic exchange velocity (HEV) ranged from 0.01 to 0.079 mm/s with a mean of 0.042 mm/s, considerably higher than the mean of 0.025 mm/s from Phase I. The mean HEV was higher then the mean uptake velocities of phosphate and arabinose but lower than those of ammonium and glucose. However, there were no significant correlations between HEV and the uptake velocity for any of the four nutrients. Transient storage volumes ranged from 6.5 to 23% of water-column volume. The mean was13%, or slightly lower than the Phase I mean of 15.

Phase I Sites

Three sites, #52 (Cross River), #46 (Muscoot River near Baldwin Place), and #29 (Neversink River near Claryville), were continued from Phase I. None of the uptake velocities measured in 2004 fell below the range established in Phase I but several measurements were above the range. Specifically, the uptake velocities for ammonium, phosphate and glucose at site #46, Muscoot R., were higher than any of the respective 2000-2002 measurements for that site; uptake velocity for phosphate at site #29, Neversink R., was higher than in 2000-2002; and uptake of both arabinose and glucose was higher at the Cross River than in 2000-2002. As noted previously, the flows in 2003 greatly exceeded those during the Phase-I injections, and the increased velocities may have played a role. The higher uptake velocities at the Musoot R. were of particular interest because these were among the lowest measured in Phase I, and the low uptake velocities were tentatively associated with high nutrient concentrations. The high flows of 2003 did not reduce nutrient concentrations at the Muscoot and, in fact ammonium concentration was higher than in previous years.

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Table 7.1: Uptake lengths (m) estimated from nutrient injections in 2003. 95% Confidence intervals are listed parenthetically.

Stream	Station #	Date	Ammonium	Phosphate	Arabinose	Glucose
Cross R.	52	2-Jul-03	784	3451	1425	584
			(715, 867)	(3111, 3873)	(1366, 1489)	(545, 630)
Haviland Hollow	34	26-Jun-03	1554	3015	2180	825
			(1323, 1882)	(2793, 3275)	(2006, 2387)	(766, 894)
E. Br. Delaware R., Arkville	10	16-Oct-03	2666	12270	10858	2978
			(2347, 3085)	(10384, 14970)	(10020, 11862)	(2682, 3347)
Tremperkill	15	1-Oct-03	1864	8244	5038	1645
			(1705, 2056)	(7047, 9930)	(4464, 5780)	(1477, 1855)
Muscoot R., Baldwin	46	11-Jun-03	1224	4281	1290	459
			(1086, 1403)	(3056, 7138)	(1246, 1337)	(395, 548)
Muscoot R., Whitehall*	139	16-Jul-03	1945	4822	4132	1152
			(1766, 2165)	(4329, 5441)	(3860, 4446)	(1001, 1356)
Neversink R.	29	12-Nov-03	4805	8000	15291	6349
			(4241, 5543)	(7273, 8897)	(13351, 17857)	(5149, 8278)
Titicus	130	30-Jul-03	114	847	685	325
			(64, 502)	(714, 1042)	(667, 705)	(299, 355)
W. Br. Delaware R., Kortright	3	28-Aug-03	1378	5168	2844	1096
			(1223, 1579)	(4310, 6456)	(2573, 3179)	(998, 1215)
Trout Creek	9	13-Aug-03	1147	3660	2933	968
			(1035, 1287)	(3175, 4323)	(2581, 3398)	(789, 1253)

* - Ammonium uptake estimate at Muscoot R. Whitehall was inferred from apparent upstream ammonium source that exceeded experimental input.

Table 7.2: Uptake velocity, v_f, (mm/s) estimated from nutrient injections in 2003.

Stream	Station #	Date	Ammonium	Phosphate	Arabinose	Glucose
Cross R.	52	02-Jul-03	0.052	0.012	0.029	0.070
Haviland Hollow	34	26-Jun-03	0.035	0.018	0.025	0.067
E. Br. Del. R., A.	10	16-Oct-03	0.096	0.021	0.024	0.086
Tremperkill	15	01-Oct-03	0.085	0.019	0.032	0.097
Muscoot R., B.	46	11-Jun-03	0.051	0.015	0.049	0.136
Muscoot R., W.C.*	139	16-Jul-03	0.034	0.014	0.016	0.058
Neversink R.	29	12-Nov-03	0.065	0.039	0.020	0.049
Titicus	130	30-Jul-03	0.133	0.018	0.022	0.047
W. Br. Del. R., K.	3	28-Aug-03	0.044	0.012	0.022	0.056
Trout Creek	9	13-Aug-03	0.043	0.013	0.017	0.051
Mean			0.064	0.018	0.025	0.072
Std. Deviation			0.032	0.008	0.009	0.028

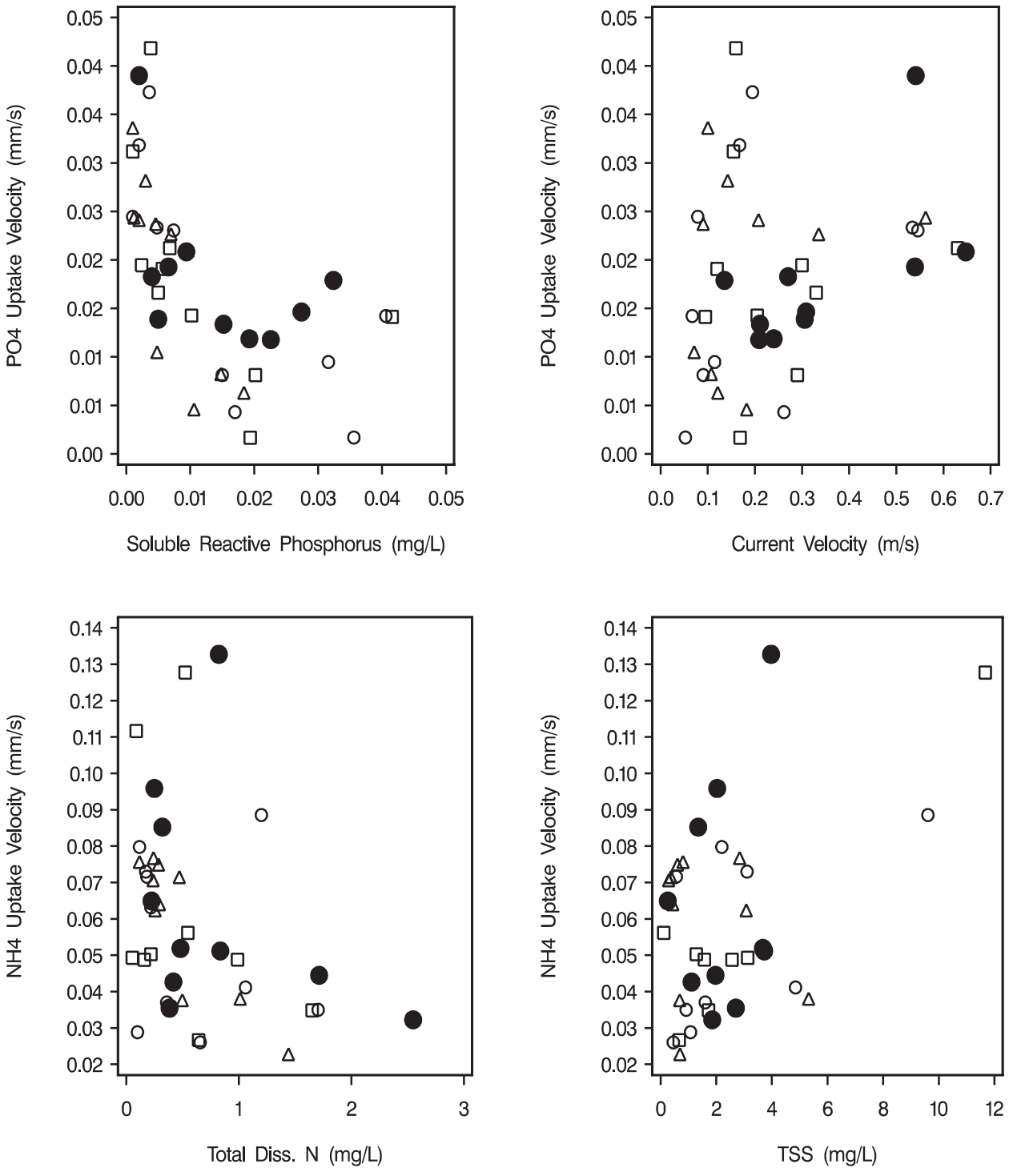
* - Ammonium uptake estimate at Muscoot R. Whitehall was inferred from apparent upstream ammonium source that exceeded experimental input.

Table 7.3: Channel and flow characteristics measured during nutrient injections.

Stream	Station #	Average Water Velocity (m/s)	Average Streamflow (m^3/s)	Average Width (m)	Average Depth (m)	Longitudinal Dispersion (m^2/s)	Transient Storage Volume (A_S/A)	Hydraulic Exchange Velocity (mm/s)
Cross R.	52	0.209	0.34	8.4	0.19	1.51	0.08	0.016
Haviland Hollow	34	0.271	0.42	7.7	0.2	2.25	0.06	0.01
E. Br. Del. R., A.	10	0.647	3.81	14.9	0.39	4.55	0.2	0.079
Tremperkill	15	0.54	1.92	12.1	0.29	5.79	0.07	0.029
Muscoot R., B.	46	0.309	0.63	10.1	0.2	1.99	0.07	0.026
Muscoot R., W.C.	139	0.306	0.69	10.2	0.22	1.21	0.08	0.074
Neversink R.	29	0.541	7.67	24.6	0.58	18.65	0.08	0.029
Titicus	130	0.136	0.1	6.6	0.11	0.12	0.23	0.063
W. Br. Del. R., K.	3	0.24	0.67	11	0.26	2.07	0.18	0.043
Trout Creek	9	0.211	0.39	8	0.23	1.56	0.22	0.053

Table 7.4: Background nutrient concentrations measured during nutrient injections.

Stream	Site #	Date 2003	NH_4-N mg/L	NO_3-N mg/L	SKN mg/L	TKN mg/L	PN mg/L	SRP mg/L	TDP mg/L	TP mg/L	PP mg/L	Arabinose nM	Glucose nM	DOC mg/L	BDOC mg/L	TSS mg/L	VSS mg/L
Cross R.	52	2-Jul	0.012	0.212	0.269	0.299	0.03	0.023	0.021	0.028	0.007	<2	3.4	3.15	0.28	3.68	1.16
Haviland Hollow	34	26-Jun	0.02	0.213	0.172	0.176	0.004	0.004	<0.01	0.011	0.004	<2	5.69	1.36	0.24	2.71	1.24
E.B. Del., A.	10	16-Oct	<0.010	0.1	0.15	0.188	0.038	0.009	0.015	0.023	0.008	<2	24.36	1.57	0.17	2.03	0.84
Tremperkill	15	1-Oct	<0.010	0.216	0.105	0.132	0.028	0.007	0.01	0.015	0.005	<2	8.39	2.04	0.25	1.35	0.52
Muscoot R., B.	46	11-Jun	0.041	0.403	0.433	0.492	0.059	0.027	0.029	0.046	0.017	<2	14.54	1.45	0.14	3.73	1.21
Muscoot R., W.C.	139	16-Jul	0.325	1.855	0.695	0.653	0	0.005	0.016	0.011	0	<2	28.29	2.88	0.38	1.86	0.74
Neversink R.	29	12-Nov	<0.010	0.179	<0.1	<0.1	0	<0.003	<0.01	<0.01	0.001	<2	5.42	6.04	0.49	<1.2	<0.22
Titicus	130	30-Jul	0.016	0.56	0.263	0.32	0.058	0.032	0.039	0.048	0.009	<2	6.77	4.53	0.34	3.97	1.3
W. B. Del., K.	3	28-Aug	0.013	1.45	0.264	0.327	0.063	0.019	0.023	0.033	0.01	<2	12.32	4.69	0.32	1.97	0.74
Trout Creek	9	13-Aug	0.014	0.294	0.125	0.149	0.024	0.015	0.015	0.021	0.006	<2	17.44	4.7	0.5	<1.2	0.51



Figures 7.1-7.4: Uptake velocities, v_f, of phosphate and ammonium measured in 2003 (black dots) plotted with measurements from 2000 (squares), 2001 (triangles), and 2002 (circles).

Chapter 8 - Stream Metabolism

Purpose and Significance

At the 10 integrative study sites (Figs. 2.1 & 2.2), metabolism measurements provide data on ecosystem processes of primary productivity and community respiration. Primary productivity is the rate of synthesis of plant biomass, and respiration is an index of the utilization of reduced chemical energy, including the metabolic costs of photosynthesis. In our study streams, algal productivity predominates primary productivity. Goals of these studies were to rank study sites according to intensity of these metabolic processes and to relate findings to environmental variables. We expect that these ecosystem functions will be related principally to the biomasses of algae, heterotrophic microorganisms, and (to a lesser extent) macrophytes and macroinvertebrates as well as to environmental variables of light, temperature, and dissolved and particulate nutrients. Some of those environmental variables, in turn, are related to watershed uses and sources of contaminants. Changes in process rates or in the balance of these functions over time would indicate changes in watershed activities and signal that investigative work on upstream tributaries and the watershed is needed to determine causative factors. These measures of ecosystem function add an additional dimension beyond descriptive variables (e.g., nutrient concentrations, invertebrate densities) to our research program.

Three streams studied in Phase I, the Cross, Neversink, and Muscoot (at Baldwin) were retained as study sites for Phase II. Seven new streams were added, West Br. Delaware at South Kortright, Trout Creek, Muscoot (at Whitehall), East Br. Delaware, Titicus, and Haviland Hollow for reasons outlined in Chapter 2.

Methods

Field procedures

Community metabolism was determined using open-system measurements of dissolved O_2 change. Pairs of sondes (YSI model 600XLM, Yellow Springs Inc., Yellow Springs, OH) were deployed at the upstream and downstream ends of each study reach to measure dissolved O_2 and temperature, usually for three-day periods. The EPA-approved 600XLM sonde, coupled with a rapid pulse dissolved O_2 probe, has a manufacturer-certified precision of 0.01 mg/L and an accuracy of ± 0.2 mg/L. Temperature was monitored with a manufacturer-specified precision of 0.01°C and an accuracy of ± 0.15°C. The study reaches were those referred to in the nutrient spiraling studies and were delimited by a top (injection) substation, an upstream sonde substation usually ~ mid-way through the reach, and a downstream sonde substation. On the Neversink and Muscoot (Whitehall), upstream sondes were positioned closer to the top of the reach because discharges

were exceedingly high. Conditions affecting reaeration were similar above the upstream and the downstream sondes. On the three streams carried forward from Phase I, distances between upstream and downstream sondes in 2003, were from 2 to nearly 5 times longer than in 2001 and 2002 (low flow years). The distance on the Neversink (1754 m) was close to that in 2000 (1839 m), which was another year with higher flows, and on the Cross the distance in 2003 (673 m) was about half that in 2000 (1337 m). The distance on the Muscoot (Baldwin) (708 m) was much greater than in 2000 (150 m). Reach lengths were long because the streams were impacted by frequent high flows during the very rainy summer - fall period of 2003.

At the field site, sondes (including one designated as QA/QC) were placed in water-saturated Turkish towels (M. Lizzote, YSI, personal communication) and calibrated according to the manufacturer's instructions. The sondes then were placed at a single location in the thalweg of the study stream for an overnight (7-12 h) period prior to deployment. Differences between sondes were used when analyzing data to calculate offsets that were applied to the upstream-downstream approach. Two sondes each then were transferred to the upstream and downstream substations, with pairings based on the similarities of dissolved O_2 concentrations toward the end of the field calibration period and probe characteristics (e.g., DO charge and voltage). Dissolved O_2 concentrations and water temperature were measured and logged at 15-min. intervals. Daily QA/QC checks were made by securing the QA/QC sonde to the stake holding the data sondes and after a 0.5 h equilibration period taking instantaneous readings of dissolved O_2, % saturation, temperature, conductivity, and DO charge for each data sonde that were then checked against the QA/QC sonde using a YSI 650MDS meter.

Above-water photosynthetically active radiation (PAR) at each site was measured at 15 sec intervals using two quantum sensors (Li-Cor, Lincoln, NE) secured to the stakes holding the sondes. Each 15-min average was logged on a Li-COR 1400 data logger.

Reaeration coefficients were determined empirically from a propane evasion experiment (Marzolf et al. 1994, Young and Huryn 1998, Marzolf et al. 1998) performed once during each measurement period. On the day prior to the experiment, the time of travel of water through the study reach was estimated using rhodamine WT. Data were used to assign sampling times for the propane evasion experiment. For that experiment, conducted simultaneously with the nutrient spiraling studies, propane was bubbled into the stream using gas diffuser tubes at the injection site (a point ~ 50 - 175 m upstream from the uppermost sampling substation). A conservative tracer solution of bromide was injected simultaneously a few cm upstream of the propane using a peristaltic pump. Sources were mixed by the bubbling propane and turbulence during transit from the injection point to the uppermost sampling substation. Five sampling substations were set over the length of the study reach. The entire injection was monitored for

bromide at the top substation and at either the fourth or fifth downstream substation (with 5 propane samples taken at 2-10-min intervals when concentrations were at the plateau). Only plateau samples were collected for both propane and bromide at the remaining substations. Field blanks were collected at each substation prior to the start of the injection. For each field injection, a standard curve of propane concentration was prepared by diluting water from the plateau (maximum propane concentration) at the uppermost sampling substation to three lower percentages (50%, 10%, 1%) in site water collected prior to the injection. Conservative tracer samples were collected in 125-mL plastic bottles. Propane samples were collected in heavy-walled 75-mL glass serum bottles that were rubber-stoppered and crimp-sealed in the field. Water samples were collected by immersing a bucket into the flow in an upstream direction and then filling the sample bottles from the bucket. This approach reduced turbulence during sampling. Propane bottles were completely filled (no head space) and were stored under refrigeration.

Open-system metabolism measures include both benthic and water column activity. Water column metabolism was measured separately at each site as follows. Ten BOD bottles (six light and four dark) were filled with stream water. Initial DO concentration, temperature, and percent saturation were measured in each bottle using a YSI Model 58 DO meter and probe with stirrer suitable for use with BOD bottles. Water used for incubation in the bottles was sparged with N_2 gas to lower the percent saturation to ~70% if initial saturation values were greater than 85%. The bottles were then incubated in the stream for a 4 - 6 h period. PAR was monitored during the incubation. At the end of the incubation period the dissolved O_2 concentrations were again determined.

Types of streambed substrata and periphyton in each reach were characterized by a mapping effort. Twenty transects were set at intervals between the top and bottom sondes. At each transect the width of the river was measured, and 10 - 12 equidistant lateral sampling points were set. At each point, river depth was measured and the appearance of both the bed (substratum) and biomass attached to the substratum (referred to as "cover type") were characterized using a viewing bucket. Our substrata categories follow those of Hynes (1970), except that our pebble category included material he classified as gravel.

Benthic samples for chlorophyll *a* and organic mass analyses were collected from substrata constituting 10% or more of the cover types encountered during the mapping effort. Samples of soft substrata were collected by inserting a plastic tube (100 cm^2 ID) into the riverbed to isolate a portion of sediment and removing surface sediments with a meat baster. Samples of periphyton on rocks were scraped, brushed, and washed into a jar. Samples were held on ice until return to the laboratory. The planar surface area of the rock was traced onto a piece of paper.

Laboratory analyses

Bromide was analyzed by ion chromatography (see Chapter 7). For propane analyses, 10 mL of water were displaced by injecting air into the crimp-sealed serum bottle to produce a head space. Bottles were shaken for 3 h at room temperature to equilibrate propane between the water and head space. Samples (50 μL) of head space gases were analyzed using a capillary gas chromatograph with flame ionization detector and helium carrier gas. Propane concentrations (determined from the standard curve) were ~100% at each top substation and ranged between <10 % and ~60% of that at the most downstream substation. Absolute concentrations are not critical to assessing reaeration; proportional loss over distance is used to compute the coefficient.

Samples for chlorophyll analyses were centrifuged at the field laboratory and frozen until extraction. Samples were extracted overnight in acetone (made basic by adding a pinch of $MgCO_3$ to the reagent bottle). The next day, samples were centrifuged for 10 - 20 min at 10,000x *g* at 4°C and the optical densities of the supernatant fluids were determined at 665 nm and 750 nm (for turbidity) before and after acidification with 0.1 N HCl. Acetone was removed and samples were re-extracted with additional acetone until the extract yielded a chlorophyll absorbance that was either 10-15% of the optical density (OD) for the first extract of that sample or <0.1 absorbance units at 665 nm. Chlorophyll samples were iced and handled under low light during analyses. Concentrations were determined using the equations of Lorenzen (1967, APHA 1992) with correction for pheophytin. A subset of the scraped rocks were frozen and brought to the laboratory for chlorophyll analyses in order to determine how completely the rock was scraped. Prior to analysis, the bottom side of the rock (marked in the field) was flamed with a blowtorch (while the top was immersed in water). Since rocks may tumble in the field this step reduced the chance of including chlorophyll from the bottom of the rock in the estimate of rock-associated unscraped chlorophyll. The ratio of scraped to total chlorophyll (scraped and unscraped) is an estimate of how completely we scraped the rocks in the field.

The spectrophotometer was recalibrated at the beginning of the field season by Perkin-Elmer. Samples from the Muscoot (Baldwin), Haviland Hollow, Cross, and some samples from the Muscoot (Whitehall) were run on that spectrophotometer. A new spectrophotometer, also calibrated by Perkin-Elmer, was used for the samples from the remaining sites.

Matrix spikes for chlorophyll were performed as follows. In the laboratory, samples from a subset of rocks were divided into three aliquots of equal wet weight. The chlorophyll in two subsamples was determined and used as lab duplicates. The mean concentration was used as a guide for the appropriate addition of chlorophyll standard to generate a matrix spike for the third subsample.

Following extraction the sample was dried at 60 °C, weighed, ashed (500 °C for 4 h), cooled, and reweighed for an analysis of organic matter content (ash free dry mass). The Mettler balance used in the analysis was calibrated at the beginning of the field season.

Rock outlines were digitized and planar surface area was determined using the public domain NIH Image software (developed at the U.S. National Institutes of Health and available on the Internet at http://rsb.info.nih.gov/nih-image/).

Data analysis

Chlorophyll concentrations were measured for the most important cover types, which, in 2003 accrued to 87 - 99% of the algal types in Haviland Hollow, Cross, Muscoot (Whitehall Corners), Neversink, Trout Cr., and Tremper Kill. The coverage was lower (74 - 81%) in the Muscoot (Baldwin), Titicus, East Br. Delaware, and W. Br. Delaware (S. Kortright). Chlorophyll concentrations were matched with the percentage of total reach area of that cover type to generate a weighted chlorophyll concentration/m^2. Values for organic matter content were treated similarly to generate a weighted estimated for the reach.

Propane data from each sampling station were normalized for bromide concentration and regressed against downstream distance using non-linear regression (SAS, Institute, Cary, NC) (after Wanninkhof et al. 1990). The derivative represents the proportion of propane (corrected for dilution) lost/m, which when multiplied by water velocity, 1.39 (to correct for molecular size) and 60 (sec/min) yields a K_{O2}. Water velocity through the reach and mean depth of the reach were derived from the computer modeling of bromide concentrations using the OTIS-P model as described in Chapter 7. As a back-up to the propane technique, reaeration was also computed from geomorphic variables entered into a surface reaeration model (Owens 1974) and an energy dissipation model (Tsivoglou and Neal 1976, APHA et al. 1992).

Oxygen data for metabolism estimates were analyzed using the two-station (upstream - downstream) approach (Owens 1974) using SAS software. The rate of change of DO concentration (Odum 1956) corrected for reaeration was computed at each 15-min interval over a 24 h diel period. The average hourly rate of community respiration during darkness (corrected for reaeration) was extrapolated to 24 h (CR_{24}). Gross Primary Productivity (GPP) was computed by adding daytime respiration to net oxygen change during the photoperiod. Net daily metabolism was computed as the difference between GPP and CR_{24} (NDM = GPP - CR_{24}). In addition, data were analyzed using the single-station approach applied to the individual upstream and downstream data sets.

The separate measurements of water column metabolism were analyzed as follows. Changes in dark bottles were added to net oxygen changes in the light bottles to

yield an estimate of GPP in the water column. Whole system metabolism for the corresponding time period was determined by integration of the area under the diel rate of change curve using the overnight respiration rate extrapolated through the daylight hours as a baseline.

Differences between streams were determined using ANOVA and Tukeys test (p=0.05) on log-transformed data with a constant added before the transformation when appropriate. Reported correlations were based on untransformed variables.

QA/QC Results

Pertinent QA/QC data are presented in Appendices 8.1 through 8.9.

Chlorophyll *a*

Rock scrapings were analyzed for chlorophyll content within 28 days except for the samples from the West Br. Delaware (S. Kortright) and Titicus, which were analyzed at 30 and 35 days, respectively. The common unit for comparing samples, blanks, and laboratory control standards is µg chlorophyll *a*/sample. Blanks had negligible absorbance and OD at 665 nm for them averaged 0.001 ± 0.003 (x ± SD, n=136) whereas the OD_{665} for the first extract of river samples was 0.740 ± 0.475. The OD_{665} of 95% of the most dilute extracts (Ext. 5) was > 0.023 whereas the absorbance of 95% of the blanks was < 0.007, approximately a 3-fold difference in cutoff between blanks and most-dilute samples. The consistently low blanks confirm that there is little chance for between-sample contamination and indicate that the spectrophotometer was working properly. However, blanks do not enter into the calculation of chlorophyll concentrations in samples, which are based on turbidity corrected changes in OD at 665 nm.

Measured chlorophyll concentrations in standards run along with river samples averaged 101.9 ± 13.7% of the expected chlorophyll concentration (40 µg/sample). Only 5 of the 83 standards had measured values that exceeded the added concentration by more than 20%. Standards do not enter into our calculation of chlorophyll concentrations in samples.

We addressed the question of accuracy of field procedures by determining how completely rocks were scraped. For this, 80 rocks were analyzed for the amount of chlorophyll remaining on them after the periphyton was scraped. Chlorophyll was extracted within the 28-day holding except for a few rocks analyzed on day 30 and 35. Fifty-eight percent of the rocks were scraped with 80% or better efficiency (Fig. 8.1). Only 8.75% of the rocks (or 7 rocks) were scraped with less than 50% efficiency and the cover types on those rocks tended to be designated “black”, “bare” or “green algae”. As noted in Phase I, rocks with moss and some species of filamentous algae, e.g., *Cladophora*, are difficult to scrape completely. It also is more difficult to

scrupulously scrape rocks with low chlorophyll amounts on them, labeled "bare" cover type. However, the total chlorophyll per unit area on the bare rocks is usually comparatively low.

The precision of chlorophyll *a* determinations in the laboratory was based on the analysis of laboratory duplicates. The average RPD for laboratory dups was 8.54%. Only 2 out of 14 samples exceeded the target RPD of 20%.

Matrix spikes were added to 19 samples with an overall recovery of 80.14 ± 26.23% of the added chlorophyll. Three samples had extremely low recoveries. In two of these instances we surmise that this is explained by a missing dilution factor. Based on the amounts of chlorophyll added as a spike, a dilution would have been required to generate the optical densities recorded in the first extract, based on data for other samples with similar additions of spike. Recoveries for those samples (Tag Nos. 36108 and 36113) increased from 14.98% to 58.22% and from 33.63% to 97.79% respectively when we included a 1:2 dilution in the computation but we have not adjusted the data without stronger evidence. If the three samples are excluded from the percent recovery computation, the recovery of the matrix spikes was 90.04 ± 12.16%. This suggests good recovery of the spike overall. Note, however, that in computing environmental concentrations the sequential extraction procedure we employ assures nearly complete recovery of chlorophyll and improves the accuracy of data from field samples.

Propane

No samples exceeded the 21-day holding period. Field duplicates were collected at two or three substations on each river during the propane injections. Relative percent differences averaged 8.4 ± 7.0 (x ± SD, n=27) and were well within the acceptable limit (50%) for all determinations, and < 20% RPD for all but three pairs. In addition to this precision, our propane data are in a time series that makes it easier to identify outliers at any sampling location. Absolute propane concentrations are not required to estimate reaeration, but propane values for samples collected at the top (Substation 1), middle (Substation 3), and bottom (Substation 5) of the reach were compared with data for propane blanks and standards. Values at the most downstream station were usually from 2- to 3- fold higher than the blanks (up to 11-fold greater on Trout Creek), and were in the range of the blanks only on the Neversink. Values at the most downstream station were usually close to the 10% concentration measured in the standard curve for that stream.

Dissolved oxygen

The calibration of the data sondes was checked daily against the QA/QC sonde. Of 99 such QA/QC checks the data sondes were within 96-104% of the reading of the QA/QC sonde. Overall the mean percent difference between data sondes and the QA/QC sonde was 1.24 ± 1.15 % (x ± SD, n=99). In contrast, the overall mean

percent difference between data sondes and Winkler DO titrations was 10.8 ± 3.9 % (x ± SD, n= 54). We calibrate the sondes against air but made Winkler determinations of dissolved oxygen to allow documentation of our data against historical records or Winkler-based data from other sources.

Results and Conclusions

Benthic substrata and cover types

Benthic substrata in each study stream are shown in Fig. 8.2. Cobble was the predominant substrate type encountered in all WOH rivers, comprising from 67 to 80 % of bed material. The percentage of cobble encountered in EOH streams was lower, ranging from 33% to 53%. Of the WOH rivers, Trout Creek and the Neversink had the greatest proportions of soft substrata (sand, silt, and clay), amounting to 18.9 and 12.7% respectively, and the remaining WOH streams ranged between 5.3 and 8.8%. The EOH streams, except for the Titicus (5.2%), had larger percentages of soft substrata ranging between 15.2 (Haviland Hollow) and 35% (Cross River). Two EOH streams, Haviland Hollow and the Muscoot (Baldwin), were visited twice during the season because heavy rains prevented completion of work on the first visit. We used this to assess the RPD of different substrate categories between visits. All but two of the RPDs were < 27%, and were lower for the Muscoot than Haviland Hollow (Table 8.1).

Major categories of plant cover types (macroscopic appearance through the viewing bucket) were filamentous green algae, filamentous diatoms, diatoms (brown velvet appearance), black cover (a slime scraped from black colored rocks), tufts (filamentous algae or moss either in an immature state or following scour often overlain with silt), and fuzz (silt enmeshed in a biological growth resulting in an appearance similar to a peach skin). Microscopic examination documented the presence of diatoms in the black covers, fuzz, and silt cover types.

The percentage encounters of different cover types in each stream are shown in Fig. 8.3. Diatoms and filamentous diatoms were the predominant algal cover type in the East Br. Delaware. Diatoms were also important in the Tremper Kill and Neversink. Filamentous green algae (with or without diatoms or silt) made up ~45% of the encounters in the West Br. Delaware (S. Kortright). Filamentous algae were also important in Trout Creek and the Muscoot (Baldwin). Bare substrata were encountered at a significant number of points in the Muscoot (Baldwin), Neversink, Haviland Hollow, Cross, and Muscoot (Whitehall Corners). Black cover was noted most often in the Titicus. Mosses made up fairly large proportions (≥25%) of the encounters at Haviland Hollow and Muscoot (Whitehall Corners), but macrophytes never accounted for significant biomass in the streams studied this year. Silt with associated diatoms was an important cover type in Trout Creek, where the stream gradient was low, and had lesser but measurable accumulations at both stations on

the Muscoot and the East Br. Delaware (Arkville and Tremper Kill).

Chlorophyll *a* and organic matter

Benthic algal chlorophyll *a* data are presented in Fig. 8.4. Chlorophyll data were based on samples from >85% of cover types for all streams but West Br. Delaware (S. Kortright) (80.5%), East Br. Delaware (79.5%), Titicus (77%), and Muscoot (Baldwin) (74%). Chlorophyll values ranged from <20 mg/m^2 (Neversink) to >150 mg/m^2 (E. Br. Delaware), with diatoms making the largest contributions in the sites with the three highest contributions. WOH streams were at the extremes of chlorophyll concentrations with EOH streams in between. Concentrations (all reported as mg/m^2) were above 90 in the Tremper Kill (94), West Br. Delaware (S. Kortright) (116), and East Br. Delaware (158), which had the highest concentration. Concentrations were lowest in the Neversink (11). Concentrations in the remaining streams were intermediate, ranging from 30 (Muscoot Baldwin) to 56 (Titicus).

Ash free dry mass of benthic organic matter associated with periphyton were greatest in Trout Cr. (17.6 g/m^2) and least in the Neversink (2 g/m^2). Intermediate streams ranged in values from 6.3 to ~12.9 g/m^2. Streams ranked in a different order than for chlorophyll *a* (Fig. 8.5).

Periphyton chlorophyll correlated positively only with SRP ($r=0.718$, $p = 0.02$) out of all the environmental variables. Total organic matter (AFDM) correlated negatively with CR_{24} ($r=-0.652$, $p=0.04$) and positively with NDM ($r=0.685$, $p=0.03$), which was expressed as a negative number.

Metabolism

Measures were made between 10 June 2003 (Muscoot, Baldwin) and 13 November 2003 (Neversink). Discharge in the Neversink was especially high at the time of our visit and it snowed on the first day of work. The East Br. Delaware was studied on a cloudy week with occasional showers. There was a major storm during the work on the Muscoot (Baldwin) but low light at the Haviland Hollow site is due primarily to shade.

All metabolism estimates for 2003 were based on the two-station method with reaeration determined from propane evasion. Mean values for GPP ranged from ~0.52 – 4 g $O_2 \cdot m^{-2} \cdot day^{-1}$ (Fig. 8.6, Table 8.2). As in Phase I, EOH streams tended to rank lower than WOH streams, possibly a function of lower light levels at many of those sites. The Muscoot (Whitehall) was an exception and ranked in the middle of WOH sites according to mean GPP/m^2. That site is below the Amawalk Reservoir and also received input from Hallocks Mill tributary. Ammonia concentrations were extraordinarily high compared to the other sites (0.325 mg/L vs. 0.001 – 0.041 mg/L elsewhere). Haviland Hollow was a very shaded site, as was the Muscoot (Baldwin),

and PAR presumably constrained photosynthesis there. There was no significant difference in GPP between Haviland Hollow, Muscoot (Baldwin), and Titicus, but they were all significantly lower than all the other sites (ANOVA, Scheffé MRT, $p \leq 0.05$ on log transformed data).

GPP was normalized for the incident PAR received each day. Photosynthesis has been reported to saturate at PAR intensities between 200 and 400 μmol quanta·m^{-2}·sec^{-1} (Hill 1996). We are in the processes of analyzing photosynthesis-irradiation curves for each daily measurement, but for now the upper end of that range (400 μmol quanta·m^{-2}·sec^{-1}) was extrapolated to a total daily PAR saturation value assuming a 12-h photoperiod, which generated a value of 17.28 mol quanta/day. Analysis of Phase I data indicated that photosynthesis saturated at 17.95 mol quanta/day at WOH sites, which is very close to the computed value but at a much lower intensity (5.13 mol quanta/day) at the EOH sites. We used 17.28 as the saturation intensity for all sites in the analysis described below.

Sites were ranked according to GPP normalized for total daily PAR (GPP/PAR_{tot}, Fig. 8.7, top panel) and for GPP normalized for saturating PAR (GPP/PAR_{sat} Fig. 8.7, bottom panel), which was computed by substituting 17.28 for any PAR value greater than it. Using the saturation intensity changed the ranking of only the East and West Branches (S. Kortright) of the Delaware. The GPP/PAR_{tot} ratio for the Muscoot (Baldwin) was significantly greater than in the West Br. Delaware, Trout Creek, Muscoot (Whitehall), and Haviland Hollow; the Titicus was greater than Trout Creek, Muscoot (Whitehall), and Haviland Hollow and the Neversink was greater than Haviland Hollow (ANOVA, Scheffé MRT, $p \leq 0.05$ on log transformed data).

Water column metabolism was measured in each stream using light and dark bottle incubations. Data are summarized in Table 8.3. Water column metabolism was a negligible proportion of total ecosystem metabolism in every stream and thus system activity can be related primarily to benthic periphyton. Oxygen changes even in light bottles were negative in most streams, indicating that activity was dominated by respiration at the time of our studies. Water column GPP was measurable only in the Cross and Tremper Kill. This may indicate a preponderance of bacteria and a low algal standing crop in the water column owing to the frequent high flows that occurred in nearly all streams during 2003.

Mean daily respiration (CR_{24}) produced the rankings of streams shown in Fig. 8.8. Mean values ranged from 3 to 11.5 g O_2·m^{-2}· day^{-1}. Highest respiration occurred in the Neversink and lowest respiration in the Titicus, but EOH and WOH streams were intermixed in the ranking. Average CR_{24} in the Neversink was significantly greater than in all other streams (ANOVA, Scheffé MRT, $p \leq 0.05$ on log transformed absolute values). Respiration in Tremper Kill was greater than in Trout Creek, Cross, East Br. Delaware, Haviland Hollow, and Titicus. Respiration in Muscoot (Baldwin) was greater than in Cross, East Br. Delaware, Haviland Hollow, and

Titicus and respiration in Muscoot (Whitehall), West Br. Delaware, Trout Creek, and Cross was greater than in East Br. Delaware, Haviland Hollow, and Titicus. Respiration in Tremper Kill was greater than in Trout Creek, Cross, East Br. Delaware, Haviland Hollow, and Titicus.

Net daily metabolism (NDM) indicated that all of the study streams were heterotrophic, i.e., respiration exceeded photosynthesis, implying a net consumption of energy at the times measurements were made (Fig 8.9). Because of the high respiration rate in the Neversink, NDM was most negative there and the value was significantly lower than in all the other streams (ANOVA, Scheffé MRT, $p \leq 0.05$ on NDM values + a constant [26]). Differences among the other streams were not statistically significant.

The rates of GPP and CR_{24} were examined on a relative basis using the P/R ratio [GPP/CR_{24}] which produced the rankings shown in Fig. 8.10. The highest mean P/R ratio, was 0.65 (East Br. Delaware). While the lowest P/R ratio occurred in the Neversink (0.10), in contrast to the NDM, on this relative basis the Muscoot (Baldwin) and Haviland Hollow were not much different, and the Tremper Kill (at 0.25) was only slightly higher. The remaining streams had ratios between 0.36 and 0.58. The Muscoot (Baldwin), Neversink, and Haviland Hollow had some of the lowest light levels and the Neversink some of the lowest nutrient levels, thus limiting the amount of photosynthesis relative to respiration.

GPP was positively correlated with PAR ($r = 0.883$, $p<0.001$), CR_{24} negatively with temperature ($r=-0.752$, $p=0.01$), presumably because streams with greatest respiration were studied later in the season, and NDM positively with temperature ($r=0.735$, $p=0.013$) because NDM was expressed as a negative number. GPP/PAR_{tot} and GPP/PAR_{sat} were each positively correlated with total P and particulate P ($r=0.643$, $p=0.05$, and $r=0.632$, $p=0.05$ respectively for PAR_{tot}) and $r=0.659$, $p=0.04$, and $r=0.644$, $p=0.05$ respectively for PAR_{sat}.

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Table 8.1. Relative percent difference (RPD) in Substratum between two visits to two study sites, Muscoot (Baldwin) and Haviland Hollow.

	Muscoot (Baldwin)			Haviland Hollow		
Category	Visit 1	Visit 2	RPD	Visit 1	Visit 2	RPD
Substratum (as %)						
Cobble	37.1	40.9	9.7	24.8	34.2	31.9
Boulder	25	21	17.4	41.3	32.5	23.8
Pebble	14.8	17.3	15.6	14	18.1	25.5
Sand	20.6	17.3	17.4	11.3	14.8	26.8
Clay	1.3	1.6	20.7	3.1	0.4	154.3
Wood	1.3	1.2	8.0			
Silt		0.8		0.4		
Bedrock				4.8		
Grass				0.4		

Table 8.2. Ecosystem metabolism at integrative stations in study streams determined by the 2-station (upstream-downstream) method. Reaeration determined by the propane evasion method.

River	Date	g $O_2 \cdot m^{-2} \cdot day^{-1}$			PAR (mole q $\cdot m^{-2}$ day^{-1})	Mean Temperature (°C)	GPP/PAR
		GPP	CR_{24}	NDM			
Muscoot (Baldwin)	10-Jun	1.3710	9.2773	-7.9063	3.50	17.79	0.3917
	11-Jun	0.9512	9.4889	-8.5377	0.90	17.60	1.0569
	12-Jun	1.0082	9.5571	-8.5489	0.95	18.49	1.0613
Mean		**1.1101**	**9.4411**	**-8.3310**	**1.78**	**17.96**	**0.8366**
SD		**0.2277**	**0.1459**	**0.3678**	**1.49**	**0.47**	**0.3853**
Titicus	29-Jul	0.9546	3.0411	-2.0865	2.22	20.69	0.4300
	30-Jul	1.2663	2.8209	-1.5546	1.67	20.11	0.7583
	31-Jul	1.2704	2.5719	-1.3015	1.64	19.47	0.7746
Mean		**1.1638**	**2.8113**	**-1.6475**	**1.84**	**20.09**	**0.6543**
SD		**0.1812**	**0.2347**	**0.4007**	**0.33**	**0.61**	**0.1944**
Neversink	11-Nov	2.0955	22.2705	-20.1750	2.60	4.21	0.8060
	12-Nov	3.1085	23.2581	-20.1496	7.77	6.07	0.4001
	13-Nov	2.1991	26.5338	-24.3347	7.86	6.15	0.2798
Mean		**2.4677**	**24.0208**	**-21.5531**	**6.08**	**5.48**	**0.4953**
SD		**0.5574**	**2.2316**	**2.4090**	**3.01**	**1.10**	**0.2757**
Cross River	1-Jul	1.8408	4.5975	-2.7567	8.63	20.22	0.2133
	2-Jul	2.2407	4.7498	-2.5091	7.89	20.21	0.2840
	3-Jul	1.8592	4.9485	-3.0893	5.93	20.03	0.3135
Mean		**1.9802**	**4.7653**	**-2.7850**	**7.48**	**20.15**	**0.2703**
SD		**0.2258**	**0.1760**	**0.2911**	**1.40**	**0.11**	**0.0515**
Tremper Kill	30-Sep	2.5245	11.8150	-9.2905	10.77	11.24	0.2344
	1-Oct	2.6427	11.9591	-9.3164	10.87	11.04	0.2431
	2-Oct	2.3097	12.6689	-10.3592	8.96	9.53	0.2578
Mean		**2.4923**	**12.1477**	**-9.6554**	**10.20**	**10.60**	**0.2451**
SD		**0.1688**	**0.4571**	**0.6097**	**1.08**	**0.93**	**0.0118**
East Br. Delaware (Arkville)	14-Oct	3.1955	4.7793	-1.5838	12.05	11.48	0.2652
	15-Oct	1.2180	3.5384	-2.3204	5.15	10.94	0.2365
	16-Oct	1.8408	1.9827	-0.1419	9.76	8.78	0.1886
Mean		**2.0848**	**3.4335**	**-1.3487**	**8.99**	**10.40**	**0.2301**
SD		**1.0111**	**1.4012**	**1.1081**	**3.51**	**1.43**	**0.0387**
West Br. Delaware (S. Kortright	26-Aug	4.1601	6.8892	-2.7291	16.14	17.90	0.2578
	27-Aug	3.7559	7.2315	-3.4756	22.43	18.66	0.1674
	28-Aug	4.1397	6.7713	-2.6316	25.41	17.26	0.1629
Mean		**4.0186**	**6.9640**	**-2.9454**	**21.33**	**17.94**	**0.1960**
SD		**0.2277**	**0.2390**	**0.4617**	**4.73**	**0.70**	**0.0535**
Trout Creek	12-Aug	3.2555	6.0045	-2.7490	15.44	19.14	0.2108
	13-Aug	3.3771	6.0153	-2.6382	21.91	20.02	0.1541
	14-Aug	4.0557	6.3526	-2.2969	27.16	20.18	0.1493
Mean		**3.5628**	**6.1241**	**-2.5614**	**21.50**	**19.78**	**0.1714**
SD		**0.4312**	**0.1979**	**0.2356**	**5.87**	**0.56**	**0.0342**

River	Date	g $O_2 \cdot m^{-2} \cdot day^{-1}$			PAR (mole q $\cdot m^{-2}$ day^{-1})	Mean Temperature (°C)	GPP/PAR
		GPP	CR_{24}	NDM			
Muscoot (Whitehall)	15-Jul	2.9586	6.8069	-3.8483	24.65	14.25	0.1200
	16-Jul	1.8804	7.5029	-5.6225	8.59	13.79	0.2189
	17-Jul	2.7765	6.8826	-4.1061	21.29	14.59	0.1304
Mean		**2.5385**	**7.0641**	**-4.5256**	**18.18**	**14.21**	**0.1564**
SD		**0.5772**	**0.3819**	**0.9586**	**8.47**	**0.40**	**0.0543**
Haviland Hollow	24-Jun	0.4294	3.1441	-2.7147	4.72	19.16	0.0910
	25-Jun	0.5246	3.2647	-2.7401	4.93	19.86	0.1064
	26-Jun	0.6172	3.6817	-3.0645	4.78	20.99	0.1291
Mean		**0.5237**	**3.3635**	**-2.8398**	**4.81**	**20.00**	**0.1088**
SD		**0.0939**	**0.2821**	**0.1950**	**0.11**	**0.92**	**0.0192**

Table 8.3. Water column metabolism as a fraction of total ecosystem metabolism in study streams, Year 4, 2003.

Stream	Date of Measure	Surface PAR (mol quanta/h)	Water Column GPP ($g \cdot m^{-2} \cdot h^{-1}$)	Whole Stream GPP ($g \cdot m^{-2} \cdot h^{-1}$)	Water column GPP/ Whole stream GPP (as %)
Cross	2-Jul	0.92	0.0005	0.2296	0.22
East Br. Delaware	16-Oct	1.04	-0.0012	0.0145	-8.3
Haviland Hollow	26-Jun	1.02	-0.002	0.0728	-2.75
Muscoot (Baldwin)	11-Jun	0.08	-0.0007	0.0817	-0.86
Muscoot (Whitehall)	17-Jul	1.05	-0.001	0.3187	-0.31
Neversink	12-Nov	1.11	-0.0035	0.3948	-0.89
Titicus	30-Jul	0.22	-0.0008	0.1469	-0.54
Tremper Kill	1-Oct	1.34	0.0006	0.3267	0.18
Trout Creek	13-Aug	2.65	-0.0021	0.35	-0.6
W. Br. Delaware (S. Kortright)	28-Aug	4.2	-0.0023	0.4387	-0.52

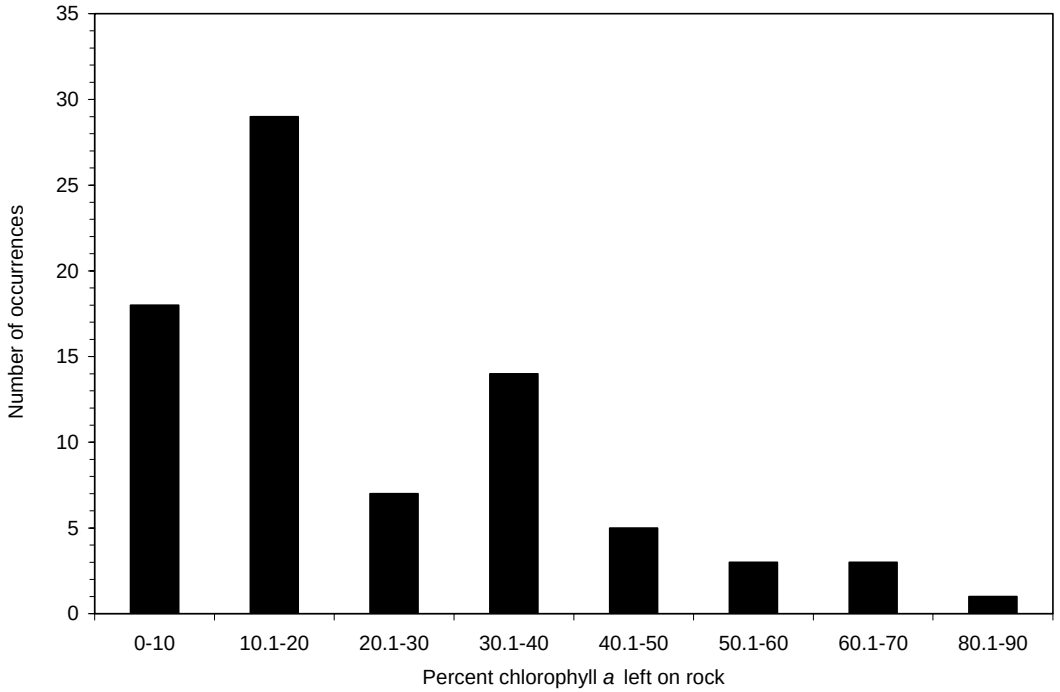

Figure 8.1: Frequency distribution of percent chlorophyll a left on rocks after being scraped, 2003.

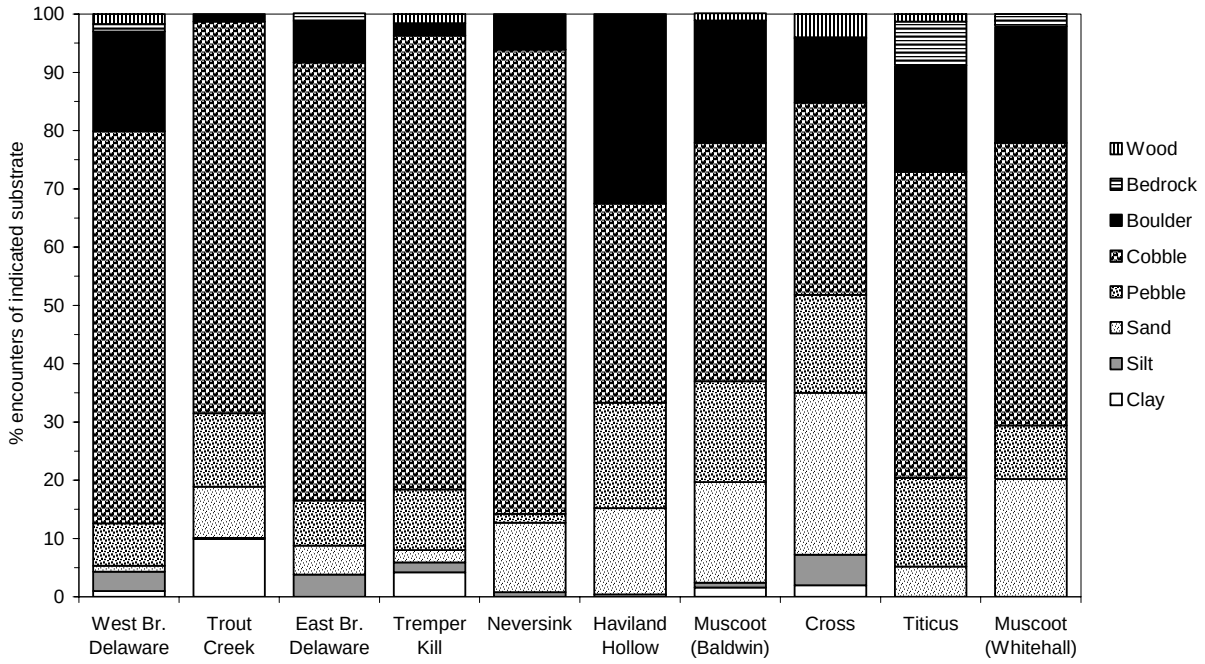

Figure 8.2: Substrate types encountered in study reaches, 2003. Site locations: West Br. Delaware - S. Kortright (3); Trout Creek - Trout Creek (9); East Br. Delaware - Arkville (10); Tremper Kill - Andes (15); Neversink - Claryville (29); Haviland Hollow - Haviland Hollow (34); Muscoot - Baldwin Place (46); Cross - Ward Pound (52); Titicus - Salem Center (130); Muscoot - Whitehall Corners (139).

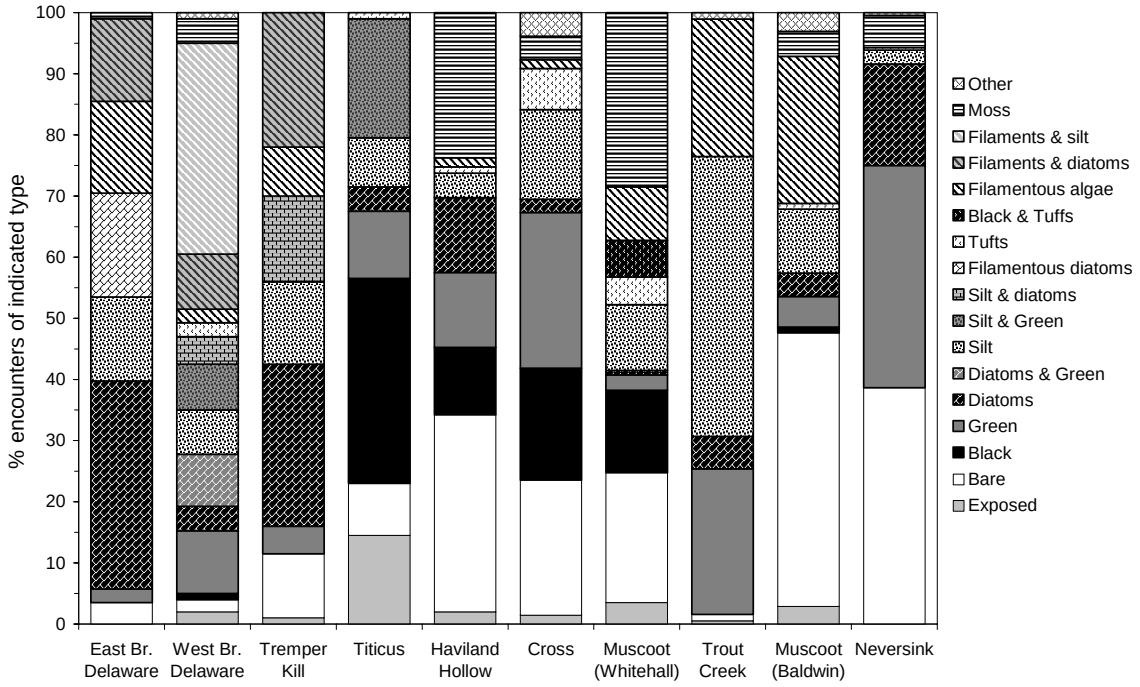

Figure 8.3: Cover types encountered in study reaches, 2003. Specific site locations are noted in Fig. 8.2.

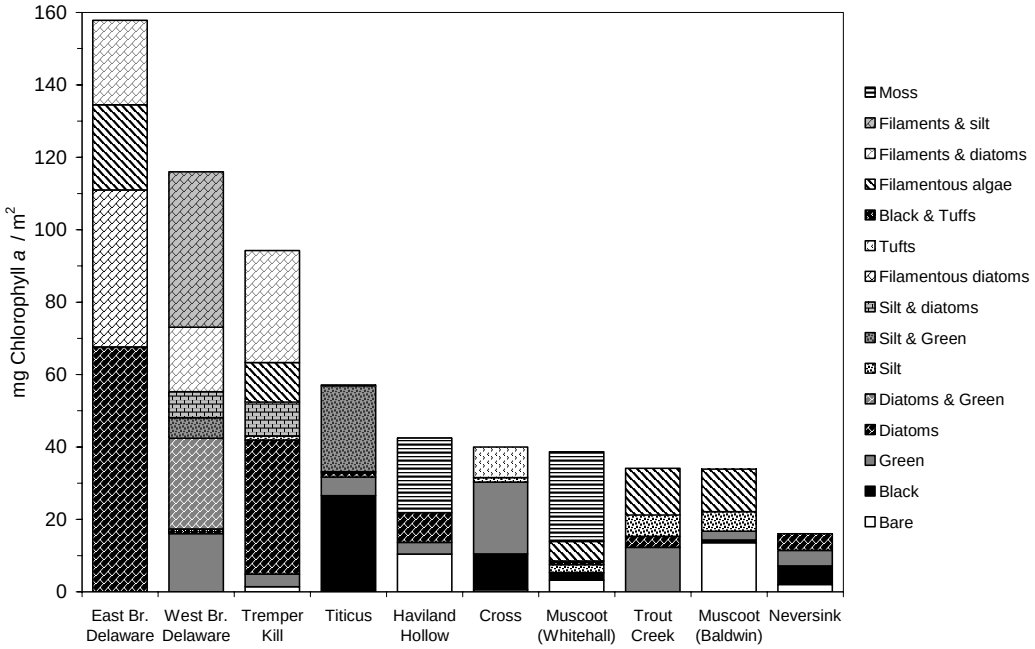

Figure 8.4: Benthic algal chlorophyll *a* concentrations weighted by cover type, 2003. Specific site locations are noted in Fig. 8.2.

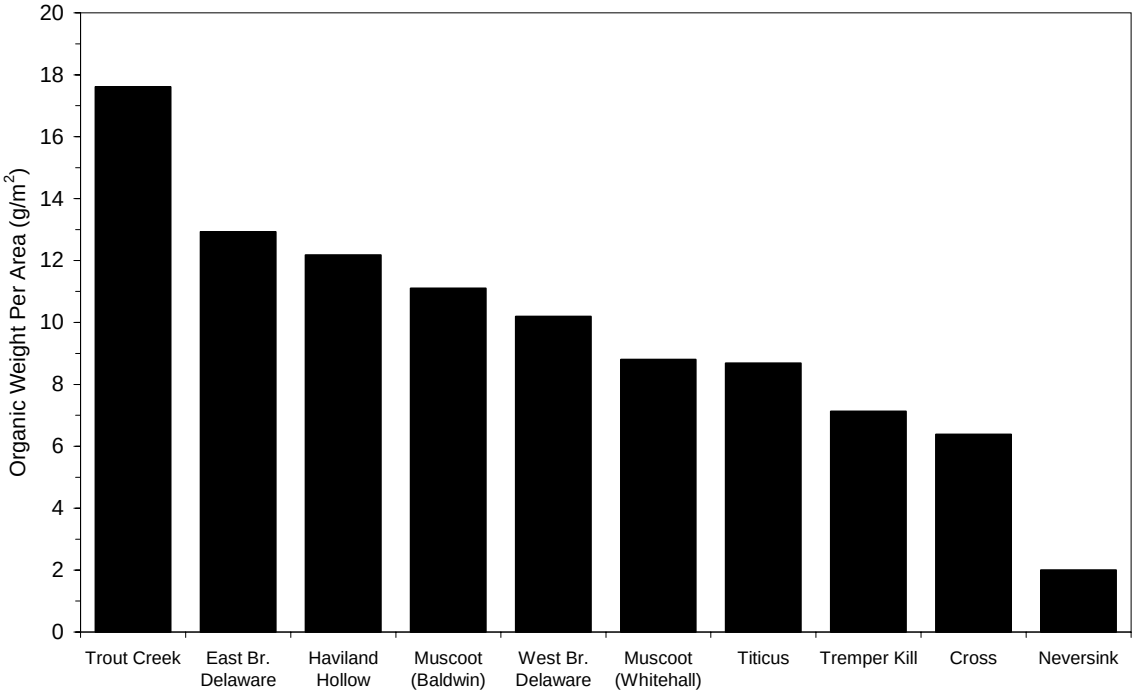

Figure 8.5: Benthic organic matter concentrations associated with periphyton in study reaches, 2003. Specific site locations are noted in Fig. 8.2.

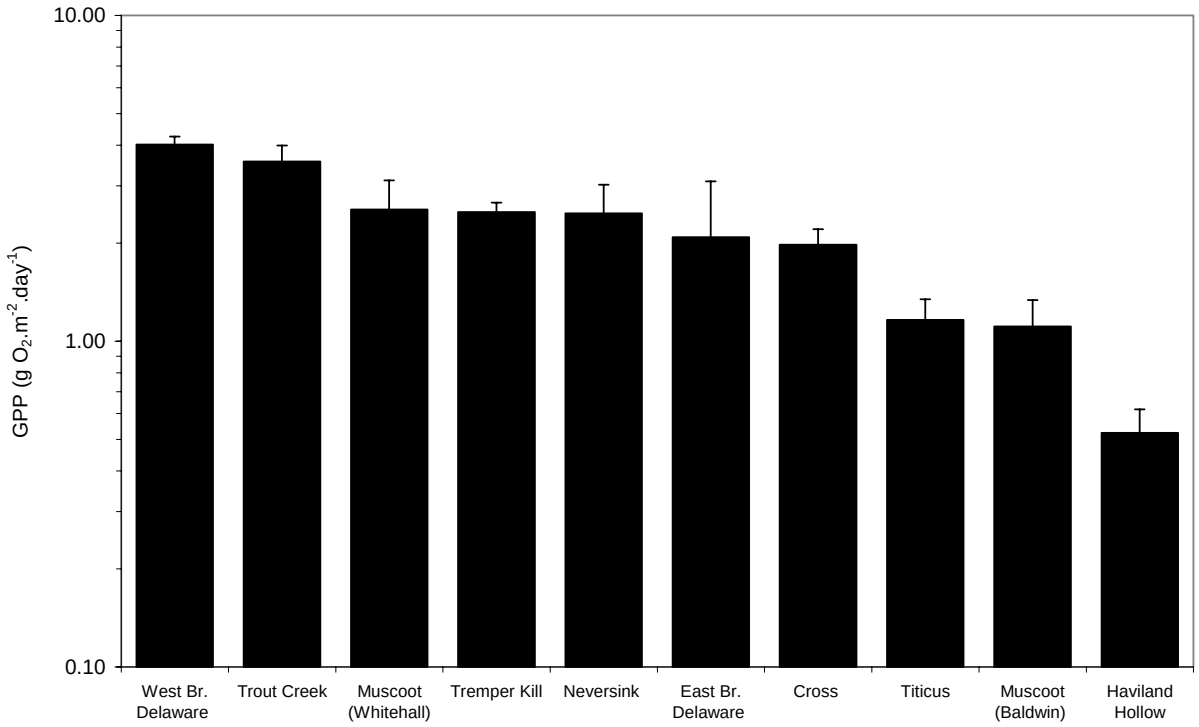

Figure 8.6: Gross Primary Productivity (GPP) in study streams, 2003. Note the log transformation of the y-axis. Specific site locations are noted in Fig. 8.2.

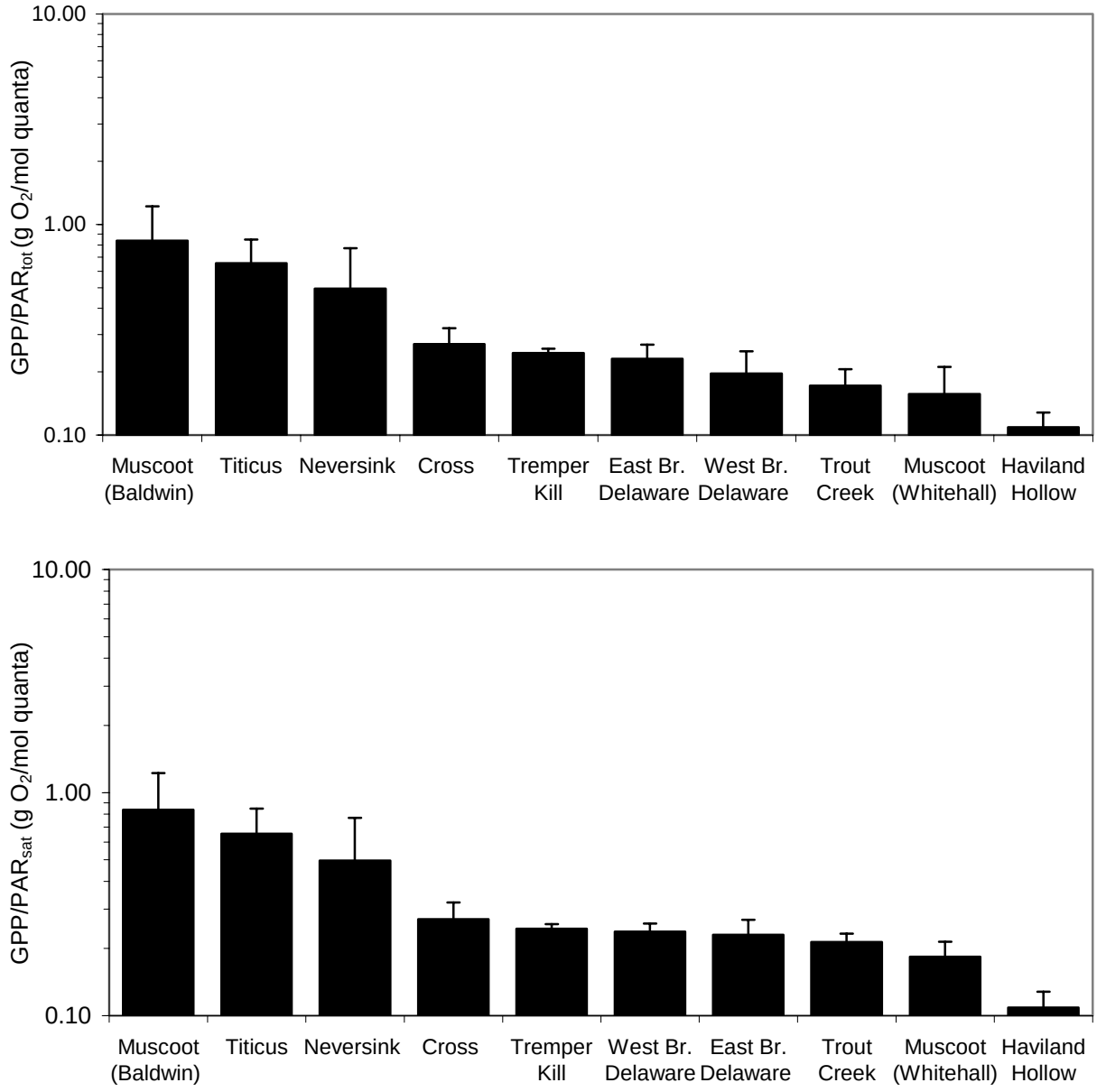

Figure 8.7: Gross Primary Productivity (GPP) per unit light (gO_2/mol quanta) using field data (top panel) or field data with the substitution of 17.28 mol quanta as a saturation intensity for values greater than that value (bottom panel), 2003. Note log transformation of the y-axis. Specific site locations are noted in Fig. 8.2.

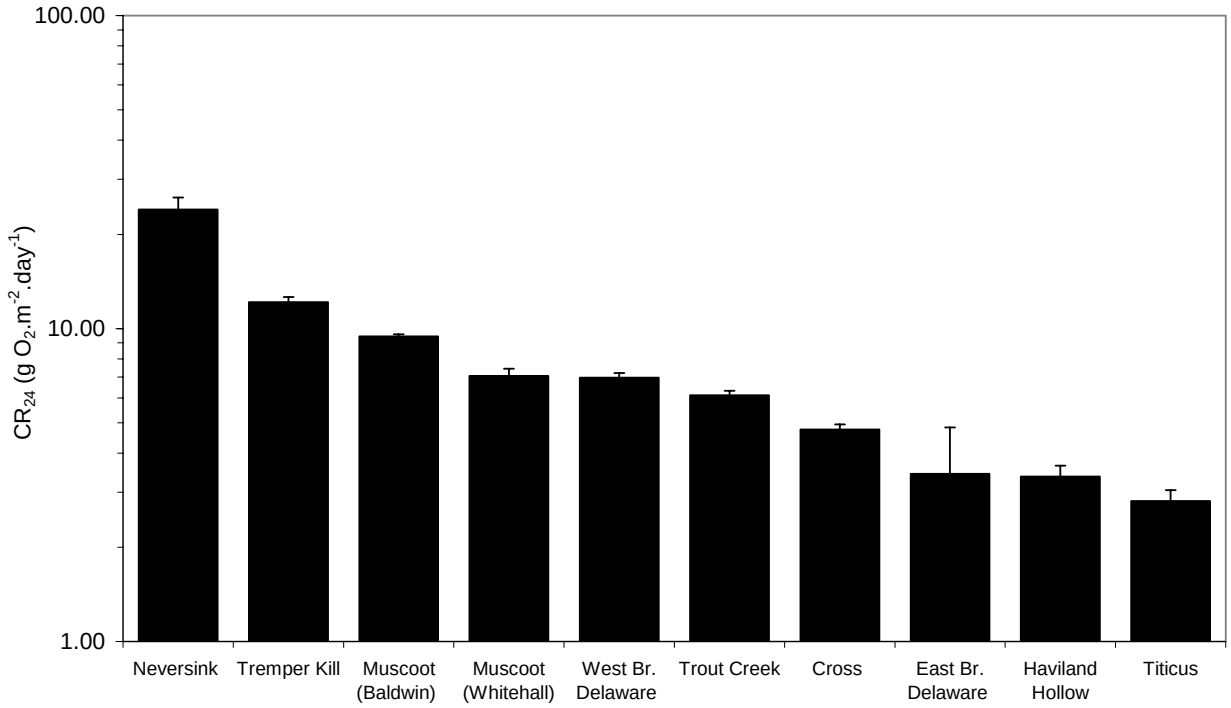

Figure 8.8: Community respiration (CR24) in study streams, 2003. Note the log transformation of the y-axis. Specific site locations are noted in Fig. 8.2.

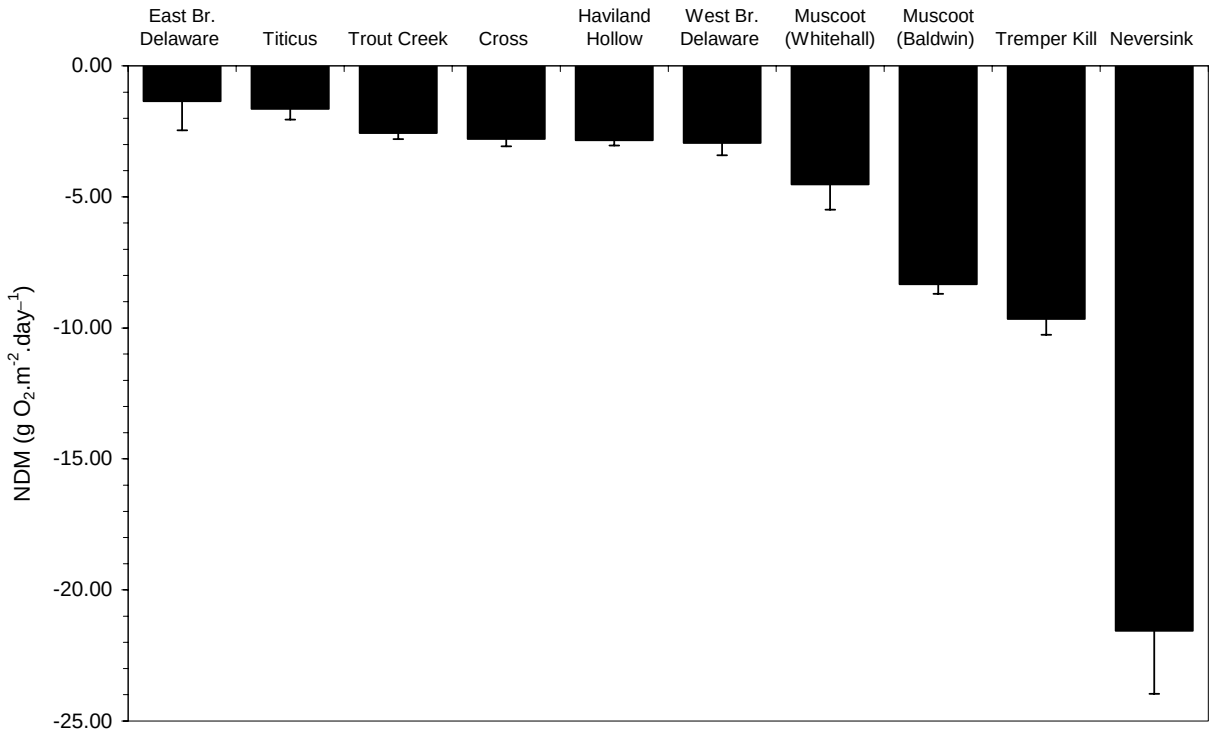

Figure 8.9: Net daily metabolism (NDM) in study streams, 2003. Specific site locations are noted in Fig. 8.2.

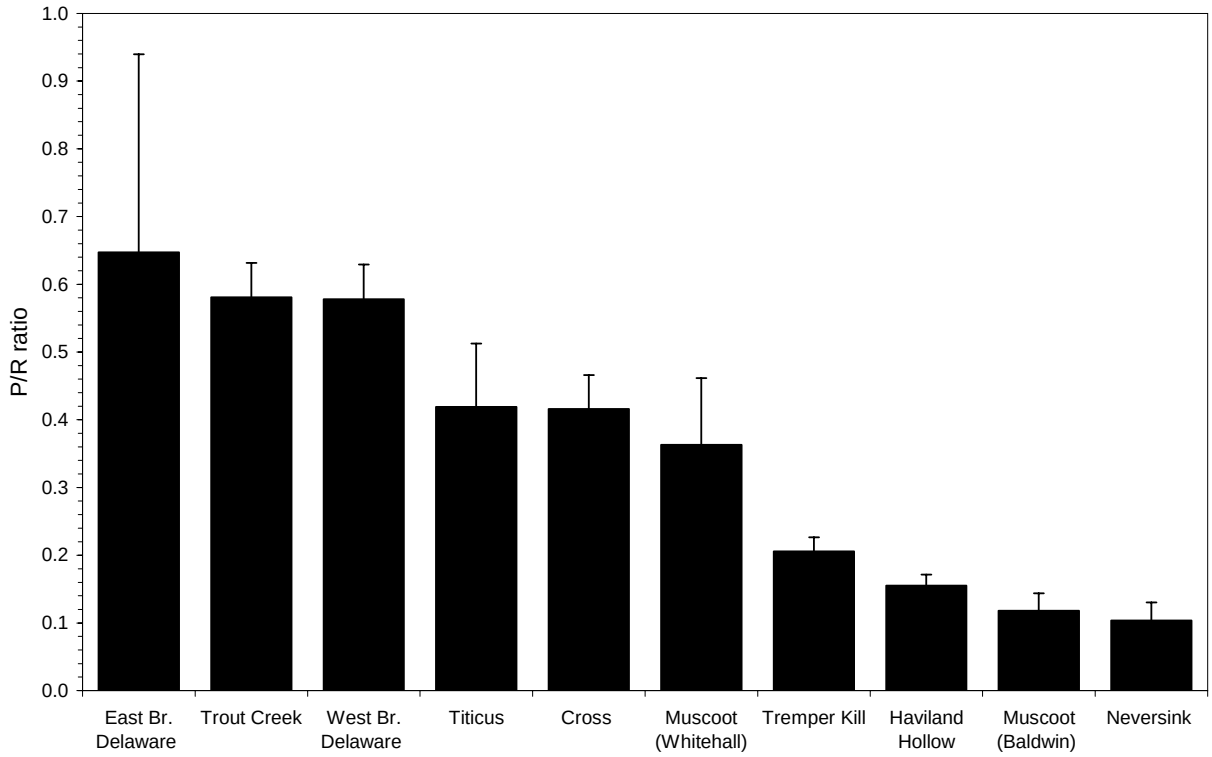

Figure 8.10: P/R (GPP/CR24) ratios in study streams. Specific site locations are noted in Fig. 8.2.

Chapter 9 - Reservoir Primary Productivity

Purpose and Significance

Our goals in this research were to (1) quantify algal biomass and productivity in study reservoirs, (2) continue comparisons of biomass and productivity among reservoirs, and (3) assess potential links between algal responses, the physical chemical characteristics of reservoirs, and potential watershed sources of nutrients. Reservoir condition is assessed on the basis of primary productivity and chlorophyll *a* concentrations because these variables are directly related to the amount of particulate matter in the reservoirs. In Phase II of this project we have (1) expanded spatial coverage to include four new reservoirs, the Amawalk, Titicus, Muscoot, and Cross, by terminating studies on the Ashokan, Rondout, Schoharie, Kensico, and New Croton, (2) intensified work on the Pepacton to six stations, and (3) continue study of the Neversink and Cannonsville reservoirs which were extremes of low and high productivity, respectively in Phase I. Data from Phase II also will contribute to the accumulating data set for biomass, productivity, and related environmental variables that will serve as a baseline of reservoir condition. Just as with the influent tributary streams, changes in response variables over time will be evaluated with regard to changes in watershed use.

Methods

Field procedures

On the day prior to productivity measurements, an anchored buoy was placed at each of three sampling locations (substations, subst.) on the reservoir. The location of each substation was fixed using GPS. The EOH and WOH reservoir substations were presented in Figs. 2.3 and 2.4, respectively, and GPS coordinates are recorded in Table 2.6.

The depth of the photic zone was determined at each substation by measuring photosynthetically active radiation (PAR) at successive 0.5 m depths through the water column using a spherical underwater quantum sensor and LI-Model 1400 light meter (Li-Cor, Lincoln, NB) coupled with simultaneous measures of above-water PAR made with a quantum sensor for use in air. Measurements were made as close to mid-day as possible. Depths at which underwater PAR was 50%, 25%, 10% and 1% of above-water PAR were determined. At the same time, data were collected to construct dissolved O_2 and temperature profiles from surface to the bottom, using a YSI model 5739 probe coupled with a model 58 meter (Yellow Springs Instruments, Yellow Springs, OH).

The next day primary productivity was measured at each substation based on dissolved O_2 changes in light and dark bottles. Incubations were conducted during the 4.5 -6 hrs around solar noon on days when objects cast a distinct shadow. Water was collected using Van Dorn samplers from just under the water surface and at depths of 50%, 25%, 10% and 1% incident light. Water (15 - 18 L) from a given depth was pooled in an 18 L bucket and sparged with N_2 gas for approximately 6 min. to lower dissolved oxygen from saturation (often >95%) to a value usually between 60 and 70% saturation. Because there was no measurable change in pH on sparging, we assumed that the concentration of dissolved CO_2 (which is highly water-soluble) was not affected. Water from the lowest depths usually did not require sparging. The BOD bottles (2 light and 1 dark) used for incubations were rinsed 3 times with bucket water and then immersed in the bucket in order to cool them to ambient water temperature thus avoiding oxygen bubble formation from supersaturation on the walls of bottles at a warm air temperature. The bottles were then filled through a hose in the side of the bucket approximately 5 cm from the bottom with care to avoid introducing bubbles, stoppered, and transferred to a holding bath of surface water in a shaded location on the boat. Water temperature, dissolved O_2 concentration, and percent oxygen saturation were measured on each bottle using a YSI Model 58 meter and model 5905 probe with stirrer suitable for use with BOD bottles. Each bottle then was topped off with sparged water from the tub (0.5 – 1 mL at most) and placed in a holding bath. The process was repeated with water collected from each depth. After the bottles from all depths at a substation were prepared, they were placed in Plexiglas holders and suspended horizontally in the reservoir at the depth from which the water had been collected. The entire process was repeated at each substation. After incubation, we retrieved the bottles and again measured dissolved O_2 concentration and saturation and water temperature. During each incubation period we measured above-water PAR from the boat deck.

As the BOD bottles were filled with water from each depth, a 2 L sample of water from the tub was collected for chlorophyll *a* analysis. Those samples were immediately placed on ice, filtered onto GF/F filters within 24 h, and filters were stored frozen until extraction. Field blanks (2 L of nanopure water) were filtered through the filtering apparatus. The filter was treated as a chlorophyll sample.

Surface water samples for chemistry determinations also were collected from the tub and filtered through precombusted Gelman GF/F filters (250 mL for inorganic analyses and 40 mL for dissolved organic carbon, DOC). Inorganic samples were placed on ice until they could be frozen in the laboratory; DOC samples were fixed with azide and refrigerated. Other samples of tub water were collected directly into 125 mL bottles (leaving no head space), placed on ice, and refrigerated for total alkalinity determinations.

Between use on each reservoir, BOD bottles were treated to prevent microbial wall growth. Bottles were filled with a 30% bleach solution, held for 15 min., rinsed with copious amounts of water and allowed to air dry.

The PAR sensors were re-calibrated by the manufacturer prior to the start of the 2002 field season and carry a stated accuracy of ± 3-5% traceable to the U.S. National Institute of Standards and Technology with calibration guaranteed for 2 years. The spectrophotometer used for chlorophyll analyses and balances used for weighing were calibrated at the start of the field season. A new UV-visible spectrophotometer was calibrated by Perkin Elmer and placed into use during the field season.

Laboratory analyses

Chlorophyll was analyzed both spectrophotometrically (Lorenzen 1967) and fluorometrically (EPA Method 445, Arar and Collins 1997). The frozen filters were snipped and macerated for 30 sec. in 9 mL of a 90% acetone/10% saturated $MgCO_3$ solution (1 g $MgCO_3$/100 ml H_2O; APHA 1997) at 4°C. The samples were returned to the freezer for 16 - 24 h in darkness for extraction of chlorophyll. After extraction, the filters were compressed using a Teflon pestle and the supernatant fluid was transferred to a centrifuge tube. The samples were centrifuged at 8,000 x *g* for 20 min. at 4°C. The supernatant fluid was then transferred to a test tube in an ice bath and covered with aluminum foil; the pellet along with the filter was held in the freezer for re-extraction if necessary. All manipulations were performed in subdued light to avoid photobleaching of pigments. An aliquot (3.5 mL) of the supernatant fluid was transferred to a cuvette for spectrophotometric determination of absorbances at 750 nm and 665 nm before and after acidification with 2 drops of 1N HCl. The remainder (5.5 mL) was analyzed fluorometrically by making an appropriate dilution (between 1:2 and 1:10) in a 9 mL cuvette and measuring fluorescence intensity before and after acidification in a Turner Model 10-AU fluorometer. Samples were extracted repeatedly if OD_{665} before acidification either was > 0.1 absorbance units or > 10% of the absorbance in the initial extraction. This insured complete extraction of each sample. At the beginning of the field season laboratory control standards were prepared by adding 40 µg of chlorophyll *a* (Sigma, St. Louis, MO) from a concentrated stock solution to 3.5 mL final volume of mL acetone (total volume). Beginning in September we prepared a large volume of the standard (40 µg/3.5 mL) and delivered 3.5 mL of that solution to the cuvette as the laboratory control standard. This gave better reproducibility. A solid standard calibrated against a spectrophotometrically-determined chlorophyll standard was used for fluorometric assays.

Water chemistry determinations were performed according to procedures documented in Chapters 3 and 6.

Data analysis

Oxygen changes in the light bottles at each depth were converted to an estimate of Gross Primary Productivity (GPP) by adding the change in the dark bottle at that depth to the net oxygen change in each light bottle. Data are presented on an area-specific basis by integrating over the depth of the photic zone. Similarly, chlorophyll concentrations determined on a volumetric basis were integrated over the depth of the photic zone to generate a value-per-unit surface area.

Statistical procedures were performed on log-transformed data. Differences between sites were determined using ANOVA and Scheffé multiple range tests (p=0.05).

QA/QC

Pertinent QA/QC data are presented in Appendices 9.1 through 9.7.

Chlorophyll a

All reservoir chlorophyll samples were analyzed spectrophotometrically within 28 days. Fluorometric analyses were completed within 28 days except for the Pepacton reservoir samples subst. 1, 4, 5 (40 days) and subst. 3, 6 and 7 (33 days) because the fluorometer required recalibration prior to their analyses.

The results of spectrophotometric analyses showed that the mean chlorophyll concentrations in 119 first and 73 second extracts of samples were 178-fold and 47-fold greater, respectively, than the mean chlorophyll concentrations in the lab blanks. The mean value for absorbance of the lab blanks was 0.000, while the means for the 73 second extracts of samples were 0.043. Ninety-five percent of blanks had absorbances <0.007, whereas 95% of the second extracts had absorbances >0.014, a 2-fold difference. Our data were not blank-corrected, but blanks assure that between-sample contamination was negligible and (along with lab control standards) that the spectrophotometer was working correctly. Field blanks, which serve as a check for cross-contamination at the filtering step, had a mean chlorophyll concentration of 1.7% of the mean concentration in samples. Thus, data were not compromised by cross-contamination between samples.

Fluorometric analyses showed that the mean chlorophyll concentrations in the first and second extracts of samples were 19,455-fold and 4,598-fold greater, respectively, than the mean chlorophyll concentrations in the lab blanks. The mean fluorescence emission of the lab blanks was 0.819, while the means for the 129 second extracts of samples was 476.7 and of 11 third extracts was 179.6. Ninety-five percent of blanks had emissions <4.7, whereas 95% of the second extracts had absorbances >129, a 27-fold difference. As for spectrophotometric determinations, the blanks assure that between-sample contamination was negligible and (along

with lab control standards) that the fluorometer was working correctly. Field blanks had a mean chlorophyll concentration of 1.8% of the mean concentration in samples when analyzed fluorometrically.

We had to replace the spectrophotometer after the analyses for one reservoir (Cross) had been completed. Fluorometric chlorophyll analyses for the Cross were 98 ± 13 percent of the spectrophotometer values (mean ± SD, n=17). However, the fluorometric analyses of the other reservoir chlorophylls yielded concentrations that were 145 ± 43 percent (mean ± SD, n=119 samples) of those obtained from analyses using the new spectrophotometer. The results reported here were based on the fluorometric analyses.

Comparison of fluorometric to spectrophotometric analyses of chlorophyll concentrations expressed per m^2 of reservoir surface yielded fluorometric concentrations that ranged from 0.94 (Cross) to 1.73 (Pepacton) of those obtained spectrophotometerically (Table 9.1). Data were similar for the Muscoot and Titicus reservoirs, but about 50% higher for the Neversink, Cannonsville and Amawalk.

Laboratory control standards were analyzed with each set of extractions. This year the concentration of each chlorophyll stock vial was determined at the time the vials were prepared and the measured concentrations at the time of use were compared to those initial concentrations. The mean measured value was 37.69 ± 2.20 μg (mean ± SD, n=20) and the percent measured of that added averaged 99.31 ± 4.19 % overall. We prepared a dilute standard (40 μg/3.5 ml) for use in later work. The CVs of repeated delivery from two such dilute stocks were lower (1.3%, 2.7%) than when a concentrated stock was diluted in the cuvette (6.5%).

The relative percent difference (RPD) between field duplicate chlorophyll samples analyzed fluorometrically averaged 14.74 ± 10.70 (n=16 paired samples), with a median RPD of approximately 11.23, which is well within the precision specified in the QAPP document (Stroud 2003). The range in RPD, was from 2.55% to 33.91% and all values but one were <30%.

The stability of the fluorometer was checked before and after each use using solid standards that had been calibrated to a chlorophyll standard. The RPD of the readings in fluorescence units of the solid standards on days of analyses and fluorescence units at calibration averaged 0.9% and 1.37% for the low standard and 1.19% and 1.09% for the high standard following calibrations 1 and 2, respectively.

Dissolved Oxygen

We use all the changes in dissolved O_2 in reporting metabolism data for the reservoirs. We have used the manufacturer's specification of an accuracy of ± 0.1

mg/L for the Model 58 meter/probe combination and noted in the data tables the substations and depths where changes in dissolved oxygen □ 0.2 mg/L occurred.

Duplicate incubations were conducted with separate water samples collected either from the surface or the 50% depth at one or more substations on each reservoir. GPP and respiration were computed as oxygen change/L per unit time. The RPD between duplicates in GPP/h was < 20% in 10 instances and between 20% and 26% in 3 instances. However, RPDs were > 60% in the Muscoot where there were clumps of floating algae and suspended flocs that were likely to have been unevenly distributed in the bottles and at subst. 1 on the Pepacton, where fine particles occurred, although an uneven distribution was not expected. If those two comparisons were excluded the RPD for GPP/h for the remaining 13 comparisons averaged 12.65%. The RPD in respiration between duplicates was also high for the Muscoot (64.8%), at subst. 3 on the Titicus (130.9%) and at subst. 1 on the Neversink (44.7%). However, the average RPD for CR/h for the remaining 12 comparisons averaged 11.6 ± 10.1 % (mean ± SD, n=12).

The three surface water incubations within the Cannonsville, Cross, Titicus, and Neversink reservoirs generated CVs for GPP/PAR that ranged between 14.1% and 42.8% (Table 9.2). Higher values occurred on the Amawalk (257.8%), Muscoot (60.8%) and Pepacton (112.5%). The grand mean of GPP/PAR expressed per unit volume had a CV of 57.0% over reservoirs. Thus, the within-reservoir variability was less than the between-reservoir variability for four of the seven studied. Study sites on some reservoirs, particularly the Cannonsville and Pepacton, would maximize variability because they were selected in order to maximize chances of observing local influences.

Nutrient Chemistry

Concentrations of NH_4-N, NO_3-N, SRP, and TDP were determined for each reservoir. Blanks never exceeded twice the detection limit. Laboratory duplicates were always within the 20% limit for quality control. The mean % recovery in matrix spikes was within the range of 95% to 105% for all analytes but TDP, which had a mean percent recovery that was too high. Quality control data for DOC are presented in Chapter 6. Field duplicates were obtained only for total alkalinity determinations. Data exceeded the 20% QC standard in one instance. Field duplicates were inadvertently not collected for nutrients, but field duplicate samples collected during Phase I met QA/QC requirements. The oversight will be corrected at the step of label preparation for field work so that this does not occur again.

Physical – Chemical Profiles

Temperature and dissolved O_2 profiles for each reservoir are shown in Figs. 9.1 - 9.8. Light profiles showed that the depth of the photic zone in the EOH reservoirs ranged from 3.5 m (Muscoot) to 6 m (Cross, Amawalk). In the WOH reservoirs the depths ranged from 6 m (Cannonsville) to 10 m (Neversink). In this high-flow year the thermocline in WOH reservoirs tended to be deep (11-16 m) and exhibit gradual temperature change. In contrast, in the Cross and Amawalk the thermocline began at 2 and 6 m, respectively, and covered only 5-6 m. The thermocline in the Muscoot was poorly defined and was only evidenced at subst. 2 in the Titicus (which was studied late in the season). Oxygen saturation values in the Amawalk and Titicus reservoirs were demonstrably clinograde, with saturation values and dissolved O_2 concentrations approaching zero in the hypolimnion at more than one substation (Lampert and Sommer 1997). This also occurred at Cannonsville subst. 3 and Cross subst. 2. The other reservoirs had orthograde profiles with considerably higher hypolimnetic dissolved O_2 concentrations and saturation values. As noted in other years, it is possible that organic matter settled to the thermocline in the Pepacton reservoir where it was undergoing decomposition because dissolved O_2 concentrations were lower at that depth.

Depth of the photic zone (depth to 1% surface PAR) at each substation ranged from 3.75 m (Muscoot, subst. 1) to 12.25 m (Neversink subst. 1). The photic zone was deepest in the Neversink (10.25 – 12.25 m) and Pepacton (8.0 – 9.5 m) reservoirs. The shallowest extent occurred in the Muscoot (3.75 – 4.5 m) and Titicus reservoirs (5.25 – 6.25 m). The depths of the photic zones were 6 – 6.25 m in the Cross, 7 – 8.5 m in the Amawalk, and 7.0 – 7.5 m in the Cannonsville.

Field notes indicated that there were fine particles (perhaps pollen) in the Neversink at all substations and that the water had a slightly greenish tint. Fine suspended matter was noted in the Cross reservoir, especially at subst. 2, and microscopic examination indicated that diatoms were numerous. Fine suspended material was present at Cannonsville subst. 5 and at subst. 4 clumps of larger particles occurred as well. At subst. 3, there were very fine green particles but they were less abundant than at subst. 4. Fine suspended particles were noted at all substations in the Amawalk, Titicus, and Pepacton reservoirs, but it was noted that water clarity was good in the Pepacton. In the Muscoot, water clarity was considered poor at subst. 1 where floating and suspended "inky" green material was noted. This occurred to a lesser extent at subst. 3. At subst. 2, only suspended fines were noted.

Algal Biomass and Primary Productivity

Chlorophyll a

Reservoirs were sampled between July 10 (Cross) and October 23 (Titicus). Photic zone chlorophyll concentrations ranged from 12 to ~150 mg/m^2 and reservoirs

ranked according to the mean chlorophyll concentration as shown in Fig. 9.9. The reservoir with the highest chlorophyll concentration was the Cannonsville, while the Neversink had the lowest concentration. Those values were significantly greater and lower, respectively, than data for the remaining reservoirs (ANOVA and Scheffe MRT on log transformed data, $p<0.05$). Concentrations in the Cannonsville and Pepacton reservoirs, but not in the Neversink, were higher than the mean values for Phase 1 when spectrophotometrically derived concentrations were compared. The 2003 value (all data reported as mg/m^2) for the Cannonsville was 91.4 viz. a viz. the Phase I mean of 74.6 and for the Pepacton the 2003 value was 42.19 viz. a viz. a Phase I mean of 21.3. However, recall that some different substations were studied on those reservoirs. The mean for the Neversink was lower in 2003 (10.18) than in Phase I (24.3), but substation locations were essentially the same with only slight relocation to accommodate increased depth in 2003.

Some within-reservoir trends in chlorophyll concentration were noted. Concentrations in the Cannonsville were highest at substations 3 and 5. Subst. 3 was studied other years as the furthest downstream station in the W. Br. Delaware arm of the reservoir (Fig. 9.10). Subst. 5 was furthest up the Trout Creek arm of the reservoir. Concentrations tended to increase through the Pepacton reservoir, being ~25% greater at subst. 7 than at subst. 1 (compare Fig. 2.4 and Fig. 9.10). Concentrations at subst. 1 in the Muscoot were considerably higher than at subst. 2. Concentrations decreased from subst. 1 through subst. 3 in the Titicus and Cross reservoirs.

Primary productivity

As in Phase I, the highest Gross Primary Productivity (GPP) occurred in the Cannonsville reservoir even though two substations were changed (Fig. 9.11). Lowest GPP occurred in the Neversink. Productivity values for Pepacton (subst. 3, 6. and 7), Cross, Titicus and Neversink reservoirs were affected to some degree by low light levels because of rain showers (Pepacton, Cross), a thunderstorm (Neversink), or seasonality (Titicus). Those reservoirs ranked lowest in GPP. Even with the rainstorm the total accumulated light for the Cross was fairly close to that on reservoirs studied on storm-free days because the study was conducted in early July. The patterns of solar radiation on the days of those studies are shown in Fig. 9.12. Rains occurred later in the day after incubations were begun under promising sky conditions. Parenthetically, the 2003 field season was exceptionally wet and scheduling was particularly difficult. When GPP was normalized for PAR the low intensity during incubation on the Pepacton subst. 3, 6, and 7 generated a mean value higher than the Cannonsville (Fig. 9.13) and elevated the Titicus to just below the Cannonsville. The Neversink remained low but the Cross had the lowest rank.

We examined the possibility of ranking the reservoirs based on surface incubations. We assumed that photosynthesis would be saturated at a surface light intensity

between 200 and 400 µmol quanta·m^{-2}·s^{-1}, or a 1 hr integrated value of 0.72 and 1.44 mol quanta/m^2. Regressing surface incubations normalized for chlorophyll *a* against PAR generated a non-significant regression with a slightly negative slope, suggesting that photoinhibition could be occurring at higher light intensities. We have observed this in some of our work over the years. Thus, we abandoned that approach for ranking the reservoirs.

The areal specific GPP data is somewhat better aligned with the chlorophyll data and probably provides the most appropriate ranking. Overall, Cannonsville ranked highest and Neversink the lowest in both chlorophyll and productivity. The Pepacton, Amawalk and Muscoot followed the Cannonsville, but had roughly half the biomass or activity of the Cannonsville, but clearly data from the remainder of Phase II is needed to appropriately rank these reservoirs.

Patterns within reservoirs

Primary productivity data for each reservoir are summarized in Table 9.3 along with chlorophyll concentrations and pertinent environmental data. Data are presented for each substation, with an overall mean for each reservoir, and the reservoirs are ordered in each table on the basis of GPP/mol quanta PAR. While we used all data to compute GPP, the depths for which changes in dissolved O_2 in the light bottles – or in both light and dark bottles – exceeded the error bounds of the probe are indicated in the table.

Both GPP/PAR and chlorophyll *a* were greater in the Cannonsville at subst. 3 and 5 than at subst. 4, although the difference in productivity was small between subst. 4 and 5. This suggests the continuing influence of the W. Br. Delaware during this high flow year at subst. 3, and perhaps an impact of Trout Creek at subst. 5. Concentrations of NO_3 were higher there. In the Pepacton reservoir chlorophyll concentrations did not differ greatly between stations, but showed an increasing trend between subst. 1 and 7. There was a distinct decreasing concentration gradient in NO_3 over the same substations. On a given day of measurement, GPP/PAR ranked in the substation order as: 7>6>3, and 5>4=1, gradients that were consistent with the trend in chlorophyll. Chlorophyll and productivity were higher at subst. 1 in the Muscoot (although productivity was also high at subst. 3) compared to subst. 2. There was an increasing gradient in both NO_3 and NH_4 over the same distance. Productivity and chlorophyll were slightly higher at subst. 1 on the Cross than at subst. 2 and 3. Nitrogen gradients were similar. Gradients in the Amawalk or Titicus reservoirs were not very pronounced, except for nitrogen concentrations in the Amawalk.

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Table 9.1: Comparison of chlorophyll *a* concentrations from each reservoir substation analyzed spectrophotometrically and fluorometrically.

Reservoir	Substation	Spectrophoto-metric analysis (mg Chl *a*/m²)	Fluorometric analysis (mg Chl *a*/m²)	Fluorometric assay / spectrophotometric assay
Neversink	1	11.1	16.01	1.44
6-Aug-03	2	9.11	12.39	1.36
	3	10.34	14.47	1.40
	Mean			1.40
	Std Dev			0.04
Pepacton	1	43.81	56.84	1.30
24-Sep-03	4	46.3	60.5	1.31
	5	38.61	63.91	1.66
25-Sep-03	3	32.14	70.63	2.20
	6	27.25	61.13	2.24
	7	42.11	70.64	1.68
	Mean			1.73
	Std Dev			0.41
Cannonsville	3	100.88	150.09	1.49
20-Aug-03	4	81.4	124.19	1.53
	5	91.89	148.27	1.61
	Mean			1.54
	Std Dev			0.06
Muscoot	1	62.23	61.81	0.99
8-Oct-03	2	35.43	37.62	1.06
	3	36.84	40.85	1.11
	Mean			1.05
	Std Dev			0.06
Amawalk	1	39.62	50.44	1.27
10-Sep-03	2	29.16	56.98	1.95
	3	31.22	50.49	1.62
	Mean			1.61
	Std Dev			0.34
Titcus	1	50.87	49.81	0.98
23-Oct-03	2	38.36	41.95	1.09
	3	35.55	39.15	1.10
	Mean			1.06
	Std Dev			0.07
Cross River	1	57.87	55.27	0.96
10-Jul-03	2	56.09	46.49	0.83
	3	43.87	44.73	1.02
	Mean			0.94
	Std Dev			0.10

Table 9.2. Comparison of surface water incubations within each reservoir and between reservoirs.

Reservoir / Date	Location	Data Quality	Volumetric GPP/h ($g \cdot m^{-3} \cdot h^{-1}$)	Surface PAR Hr. ave.	Volumetric GPP/PAR
Muscoot	1	a	0.3022	3.01	0.1003
8-Oct-03	2	b	0.0865	3.20	0.0270
	3	b	0.1584	2.87	0.0551
	Mean		0.1823	3.03	0.0608
	St. dev.		0.1098	0.16	0.0370
	CV		60.24	5.38	60.81
Cannonsville	3		0.0521	3.29	0.0158
20-Aug-03	4	c	0.0641	4.08	0.0157
	5	c	0.0532	4.36	0.0122
	Mean		0.0565	3.91	0.0146
	St. dev.		0.0066	0.56	0.0021
	CV		11.72	14.22	14.12
Cross River	1		0.0518	3.11	0.0167
10-Jul-03	2		0.0622	3.16	0.0197
	3	c	0.0544	3.98	0.0137
	Mean		0.0561	3.42	0.0167
	St. dev.		0.0054	0.49	0.0030
	CV		9.68	14.26	18.05
Titicus	1	b	0.0761	1.27	0.0599
23-Oct-03	2	b	0.0496	1.33	0.0374
	3		0.0367	1.15	0.0319
	Mean		0.0541	1.25	0.0431
	St. dev.		0.0201	0.09	0.0149
	CV		37.10	7.15	34.47
Pepacton	1	c	0.0295	3.51	0.0084
24-25-Sep-03	3	b	0.0578	1.66	0.0347
	4		0.0344	3.89	0.0089
	5		0.0236	3.59	0.0066
	6		0.0467	1.12	0.0418
	7	b	0.0773	0.71	0.1089
	Mean		0.0449	2.41	0.0349
	St. dev.		0.0201	1.41	0.0392
	CV		44.76	58.29	112.54

			Volumetric GPP/h		
Amawalk	1	b	0.0800	4.39	0.0182
10-Sep-03	2		0.0678	4.59	0.0148
	3	c	-0.0499	3.82	-0.0131
	Mean		0.0327	4.26	0.0067
	St. dev.		0.0718	0.40	0.0172
	CV		219.73	9.32	257.87
Neversink	1		0.0163	1.50	0.0109
6-Aug-03	2		0.0155	1.64	0.0095
	3		0.0270	1.34	0.0201
	Mean		0.0196	1.49	0.0135
	St. dev.		0.0064	0.15	0.0058
	CV		32.61	9.88	42.81
	Grand Mean		0.0637	2.8243	0.0272
	St. Dev.		0.0406	0.4546	0.0155
	CV		63.70	16.09	57.00

a: change ≥ 0.2 mg/L for light bottle
b: change ≥ 0.2 mg/L for dark bottle
c: change ≥ 0.2 mg/L for both light and dark bottles

Table 9.3: Summary of gross primary productivity (GPP) per unit area over the photic zone, GPP normalized for incident PAR, chlorophyll *a* and nutrients for each reservoir, Year 4 data. Data shown are those for each reservoir location with the mean and standard deviation for the reservoir.

Reservoir Date	Station	Depth of photic zone (m)	Data change ≥ 0.2 mg/L for LB or both at depths:	Photic zone temp. range (°C)	GPP (g O_2 m^{-2} h^{-1})	Surface PAR (mol quanta m^{-2} h^{-1})	GPP/ mol quanta PAR	Chlorophyll *a* (mg/m^2)	NO_3-N (mg/L)	NH_3-N (mg/L)	TDP (mg/L)	o-PO_4-P (mg/L)	DOC (mg/L)	Total Alkalinity (mg $CaCO_3$/L)
Cannonsville	3	7	2,3,4	27.0-22.6	0.938	3.21	0.291	150.09	0.008	0.012	0.005	0.003	2.59	4.9, 4.8
20-Aug-03	4	7.5	2,3,4	26.2-22.9	0.838	4.05	0.207	124.19	0.016	0.012	0.004	0.002	2.57, 2.59	
	5	7	2,3,4	25.6-22.9	0.929	4.34	0.214	148.27	0.027	0.010	0.003	0.002	2.61	4.7, 4.6
	Mean	**7.17**			**0.902**	**3.87**	**0.238**	**140.85**	**0.017**	**0.011**	**0.004**	**0.002**	**2.59**	**4.75**
	St. Dev.	**0.29**			**0.055**	**0.59**	**0.047**	**14.45**	**0.010**	**0.001**	**0.001**	**0.001**	**0.02**	**0.13**
Amawalk	1	7	1,2,3,4	22.7-20.3	0.5947	4.38	0.1359	50.44	0.012	0.0024	0.004	0	—[a]	25.8, 20.7
10-Sep-03	2	7.25	2,3,4	22.9-19.2	0.4802	4.55	0.1056	56.98	0.003	0.0009	0.004	0	—[a]	
	3	8.5	2,3	23.3-17.6	0.5028	3.78	0.1329	50.49	0.003	0.0009	0.004	0	—[a]	21.1, 21.0
	Mean	**7.58**			**0.526**	**4.23**	**0.125**	**52.64**	**0.006**	**0.001**	**0.004**	**0.000**		**22.15**
	St. Dev.	**0.80**			**0.061**	**0.40**	**0.017**	**3.76**	**0.005**	**0.001**	**0.000**	**0.000**		**2.44**
Muscoot	1	3.75	1,2,3,4	15.7-15.4	0.5251	3.01	0.1742	61.81	0.151	0.026	0.005	0.001	4.44	20.7, 19.4
8-Oct-03	2	4	1,2,3,4	16.7-15.6	0.3286	3.18	0.1034	37.62	0.167	0.033	0.006	0.001	4.53	
	3	4.5	1,2,3,4	17.4-15.1	0.5215	2.83	0.1837	40.85	0.234	0.086	0.007	0.002	4.69	23, 27.5
	Mean	**4.08**			**0.458**	**3.01**	**0.154**	**46.76**	**0.184**	**0.048**	**0.006**	**0.001**	**4.55**	**22.65**
	St. Dev.	**0.38**			**0.112**	**0.17**	**0.044**	**13.13**	**0.044**	**0.033**	**0.001**	**0.001**	**0.13**	**3.56**
Pepacton	1	8	1,2,5	18.8-18.2	0.364	3.52	0.103	56.84	0.026	0.002	0.004	0	2.39	3.8, 4.1
24-Sep-03	4	8	2,3	19.5-18.8	0.386	3.87	0.100	60.50	0.012	0.001	0.004	0	2.17	
	5	8.5	2,3	19.7-19.0	0.498	3.56	0.140	63.91	0.029	0.001	0.003	0	2.03	3.8, 4
25-Sep-03	3	9.25	1,2	19.2-18.8	0.342	1.62	0.211	70.63	0.013	0.001	0.003	0	2.20	3.8, 3.9
	6	9.5	2	19.3-18.5	0.264	1.09	0.240	61.13	0.010	0.001	0.003	0	2.21	
	7	9	1	19.2-19.1	0.256	0.70	0.365	70.64	0.005	0.001	0.004	0	2.07	3.8, 4
	Mean	**8.71**			**0.352**	**2.39**	**0.193**	**63.94**	**0.016**	**0.001**	**0.004**	**0.000**	**2.18**	**3.90**
	St. Dev.	**0.64**			**0.089**	**1.41**	**0.102**	**5.65**	**0.009**	**0.000**	**0.001**	**0.000**	**0.13**	**0.12**
Cross River	1	6.25		25.5-20.0	0.253	3.15	0.080	55.27	0.015	0.017	0.006	0.002	4.84	12.4, 11.8
10-Jul-03	2	6.25		25.5-18.5	0.199	3.21	0.062	46.49	0.005	0.008	0.005	0.001	4.53, 4.51	
	3	6		24.8-19.3	0.227	3.95	0.058	44.73	0.004	0.008	0.006	0.002	4.59	11.7, 12.1
	Mean	**6.17**			**0.227**	**3.44**	**0.067**	**48.83**	**0.008**	**0.011**	**0.006**	**0.002**	**4.62**	**12.00**
	St. Dev.	**0.14**			**0.027**	**0.45**	**0.012**	**5.65**	**0.006**	**0.005**	**0.001**	**0.001**	**0.15**	**0.32**
Titicus	1	5.25	1,2	11.9-11.1	0.243	1.26	0.192	49.81	0.01	0.01	0.009	0.003	4.80	127.5, 128.7
23-Oct-03	2	5.75	1,2,3	11.9-11.7	0.196	1.31	0.150	41.95	0.016	0.016	0.008	0.003	4.67	
	3	6.25	2	11.9-11.7	0.224	1.13	0.197	39.15	0.018	0.016	0.006	0.002	4.57	106.9, 88.3
	Mean	**5.75**			**0.221**	**1.23**	**0.180**	**43.64**	**0.015**	**0.014**	**0.008**	**0.003**	**4.68**	**112.85**
	St. Dev.	**0.50**			**0.024**	**0.09**	**0.026**	**5.53**	**0.004**	**0.003**	**0.002**	**0.001**	**0.12**	**19.18**
Neversink	1	12.25		23.6-18.0	0.149	1.50	0.099	16.01	0.073	0.005	0	0.001	1.82	0.8, 0.7
6-Aug-03	2	11		23.7-19.2	0.101	1.66	0.061	12.39	0.069	0.005	0	0	1.73, 1.73	
	3	10.25		24.3-20.4	0.210	1.36	0.156	14.47	0.069	0.005	0.015	0	1.81	0.7, 0.7
	Mean	**11.17**			**0.154**	**1.51**	**0.105**	**14.29**	**0.070**	**0.005**	**0.005**	**0.000**	**1.77**	**0.73**
	St. Dev.	**1.01**			**0.055**	**0.15**	**0.048**	**1.82**	**0.002**	**0.000**	**0.009**	**0.001**	**0.05**	**0.05**

[a] samples lost

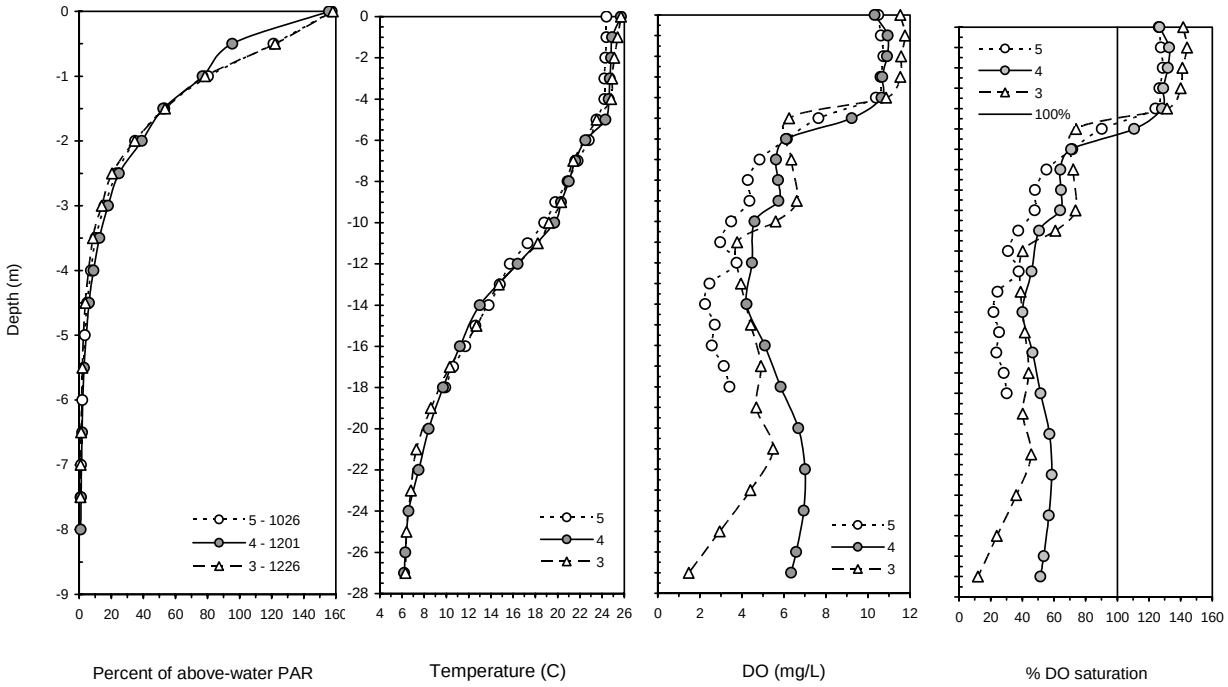

Figure 9.1: Profiles of light, temperature, and dissolved oxygen in Cannonsville Reservoir, 19 August 2003.

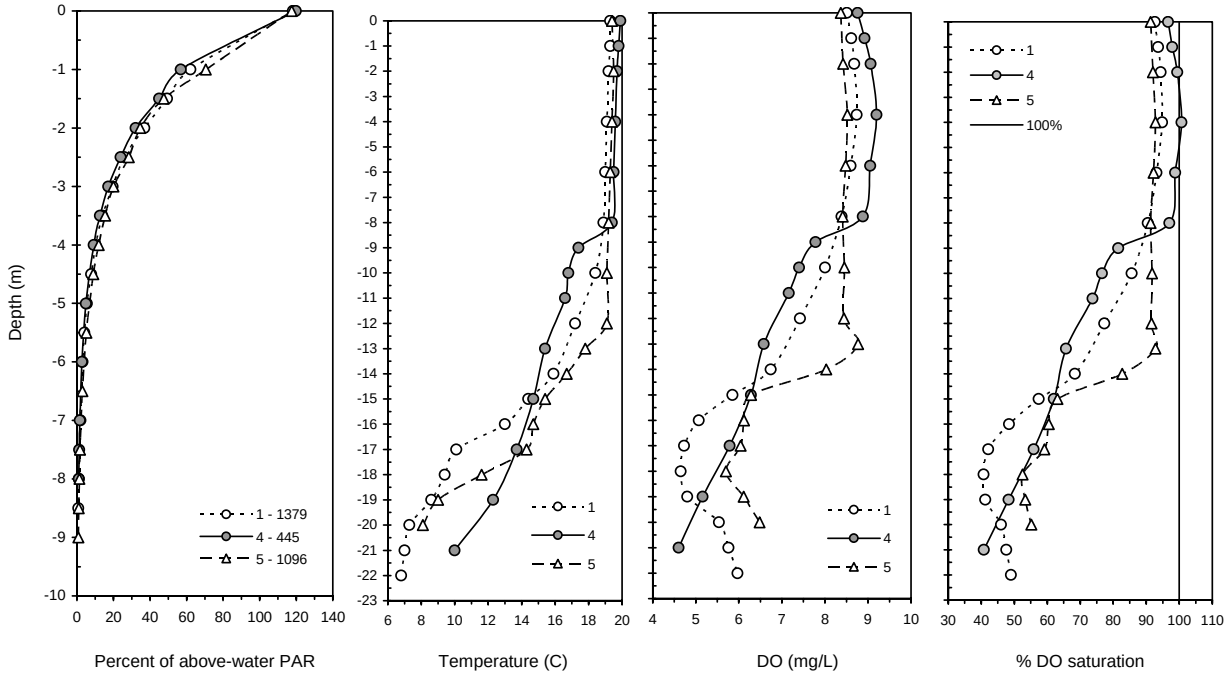

Figure 9.2: Profiles of light, temperature, and dissolved oxygen in Pepacton Reservoir, Stations 1, 4, 5 on 23 September 2003.

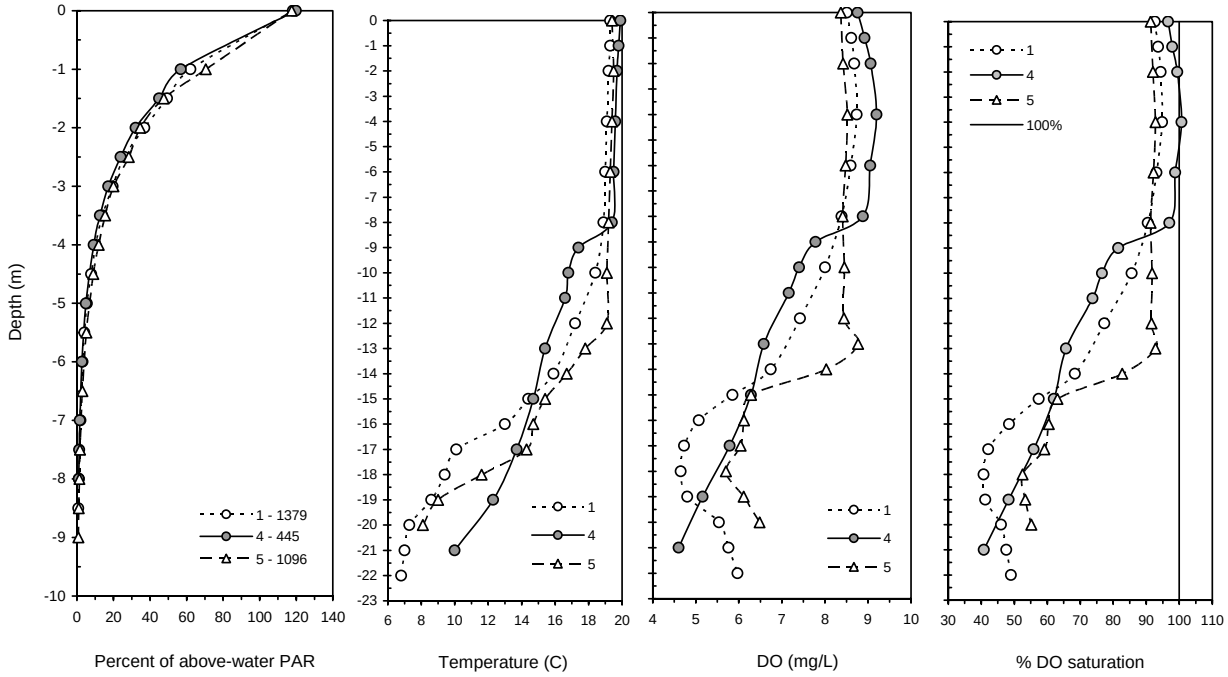

Figure 9.3: Profiles of light, temperature, and dissolved oxygen in Pepacton Reservoir, Stations 3, 6, 7 on 24 September 2003.

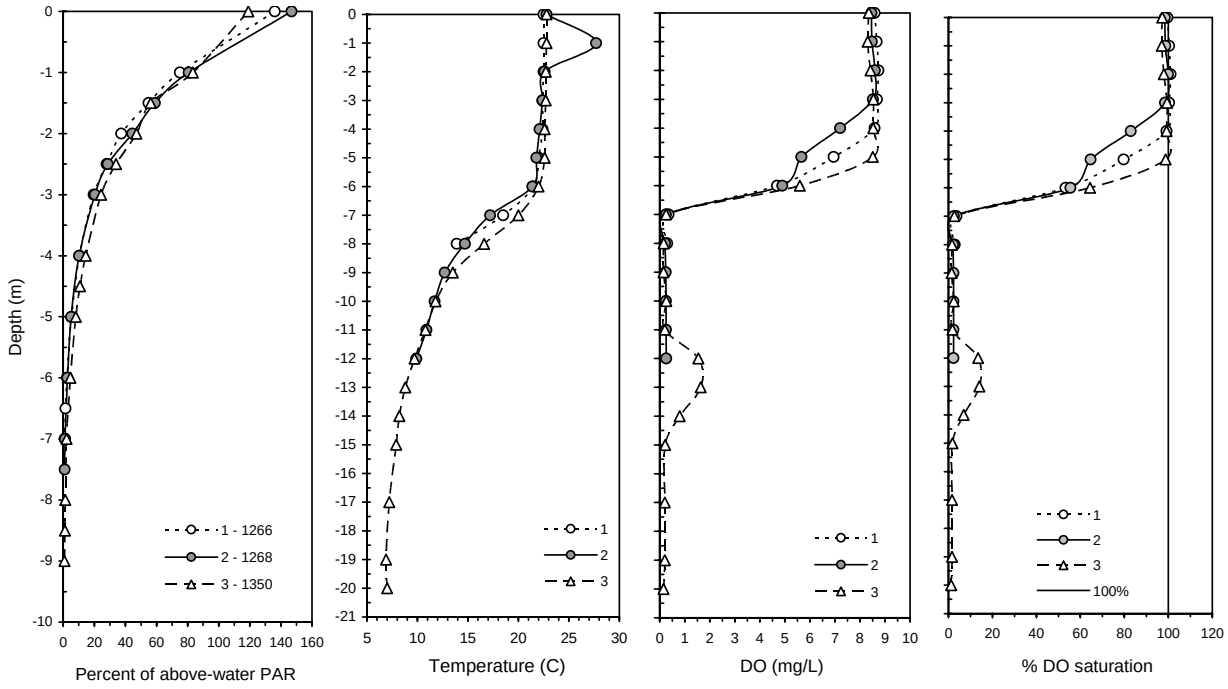

Figure 9.4: Profiles of light, temperature, and dissolved oxygen in Amawalk Reservoir on 9 September 2003.

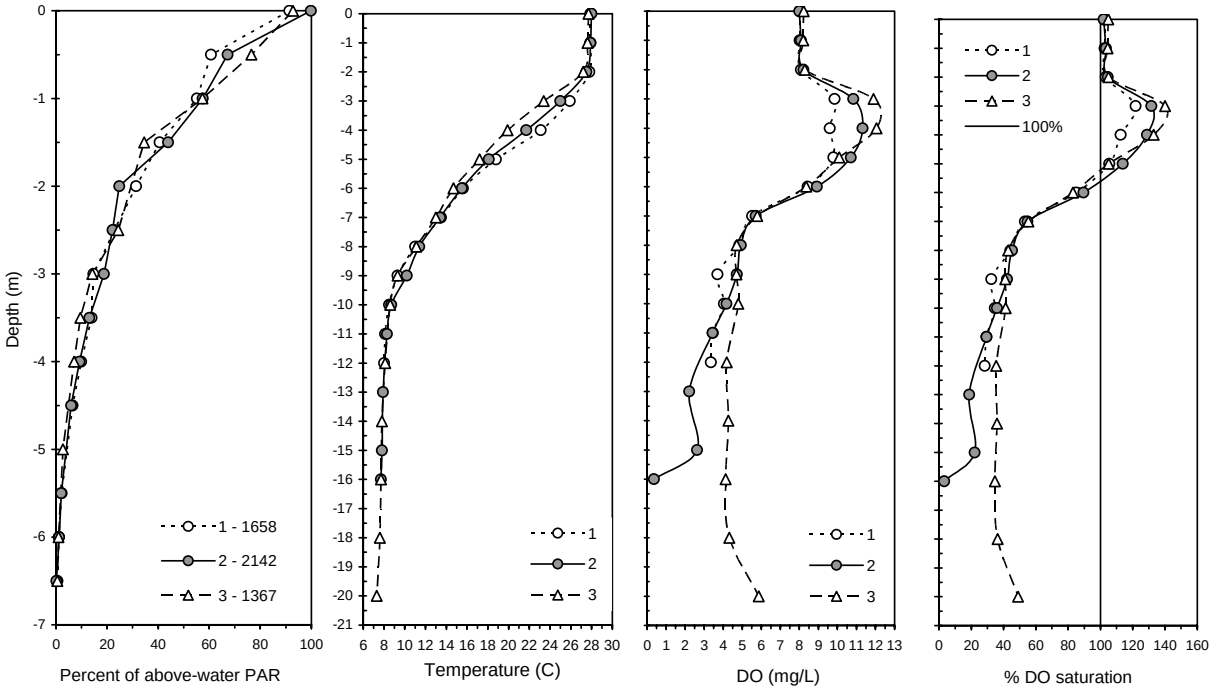

Figure 9.5: Profiles of light, temperature, and dissolved oxygen in Cross River Reservoir on 8 July 2003.

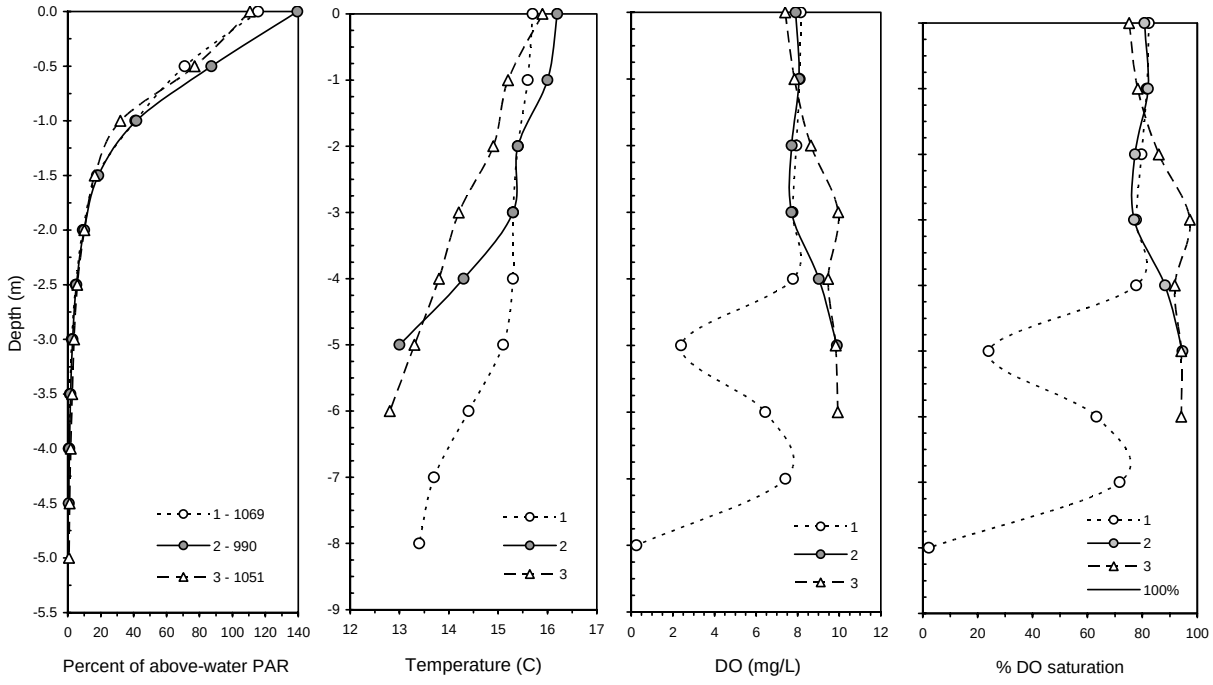

Figure 9.6: Profiles of light, temperature, and dissolved oxygen in Muscoot Reservoir on 7 October 2003.

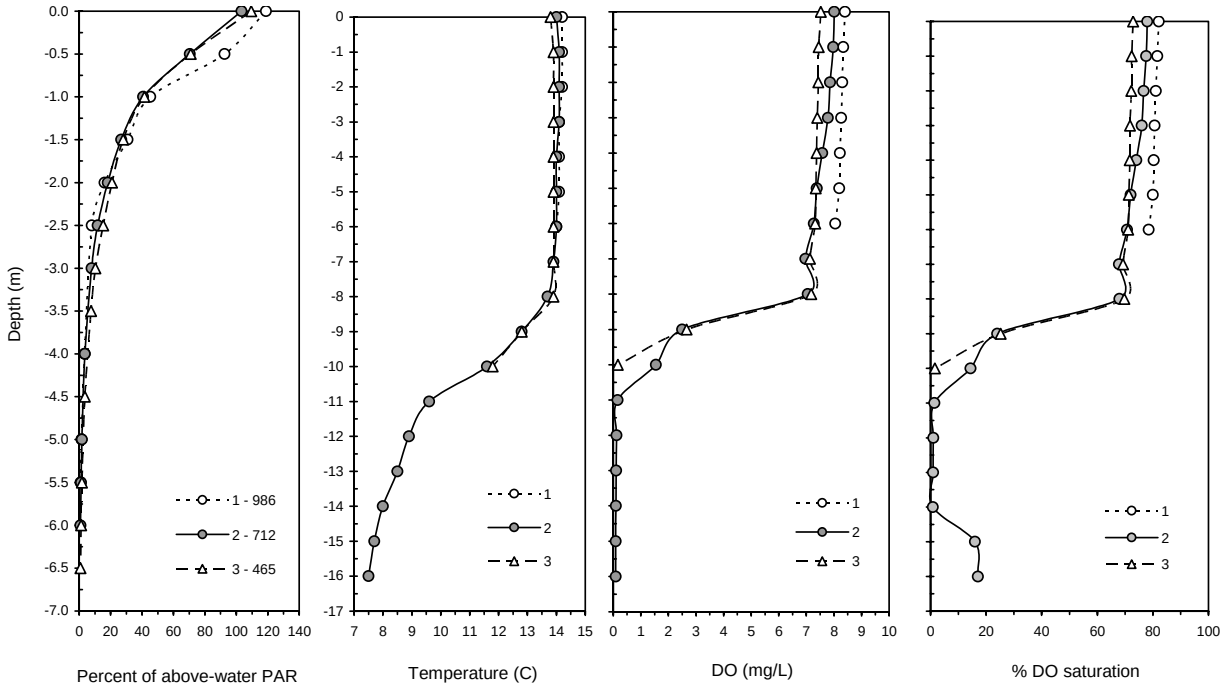

Figure 9.7: Profiles of light, temperature, and dissolved oxygen in Titicus Reservoir on 21-22 October 2003.

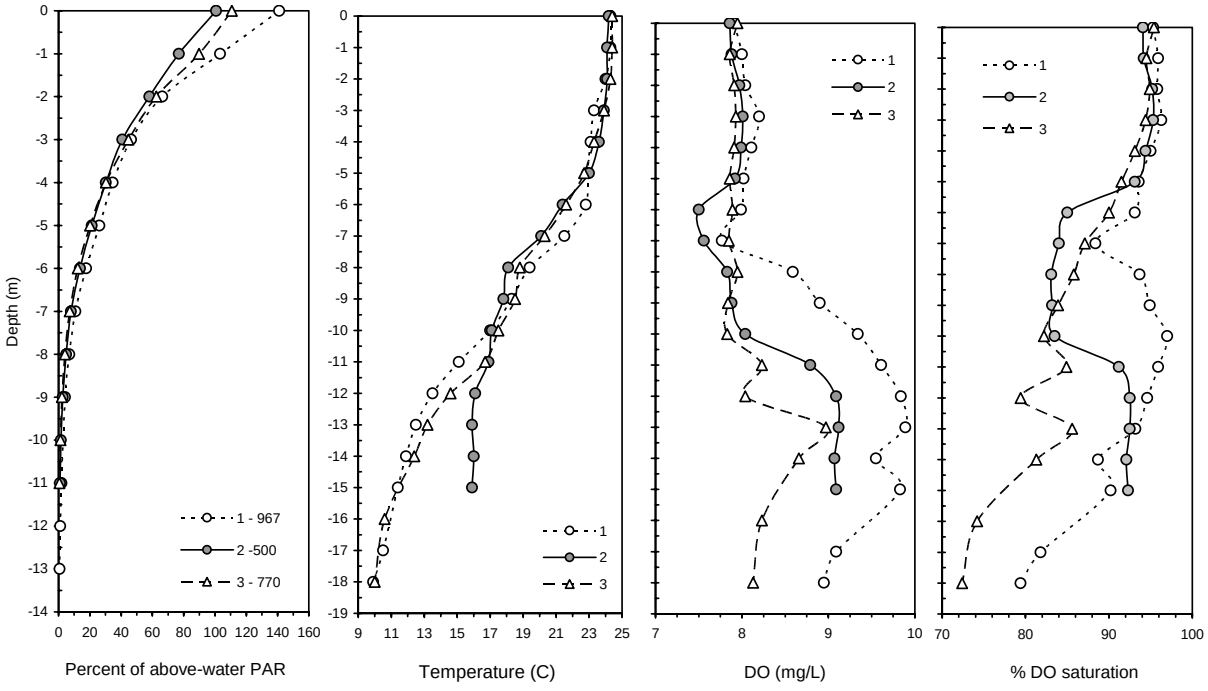

Figure 9.8: Profiles of light, temperature, and dissolved oxygen in Neversink Reservoir on 5 August 2003.

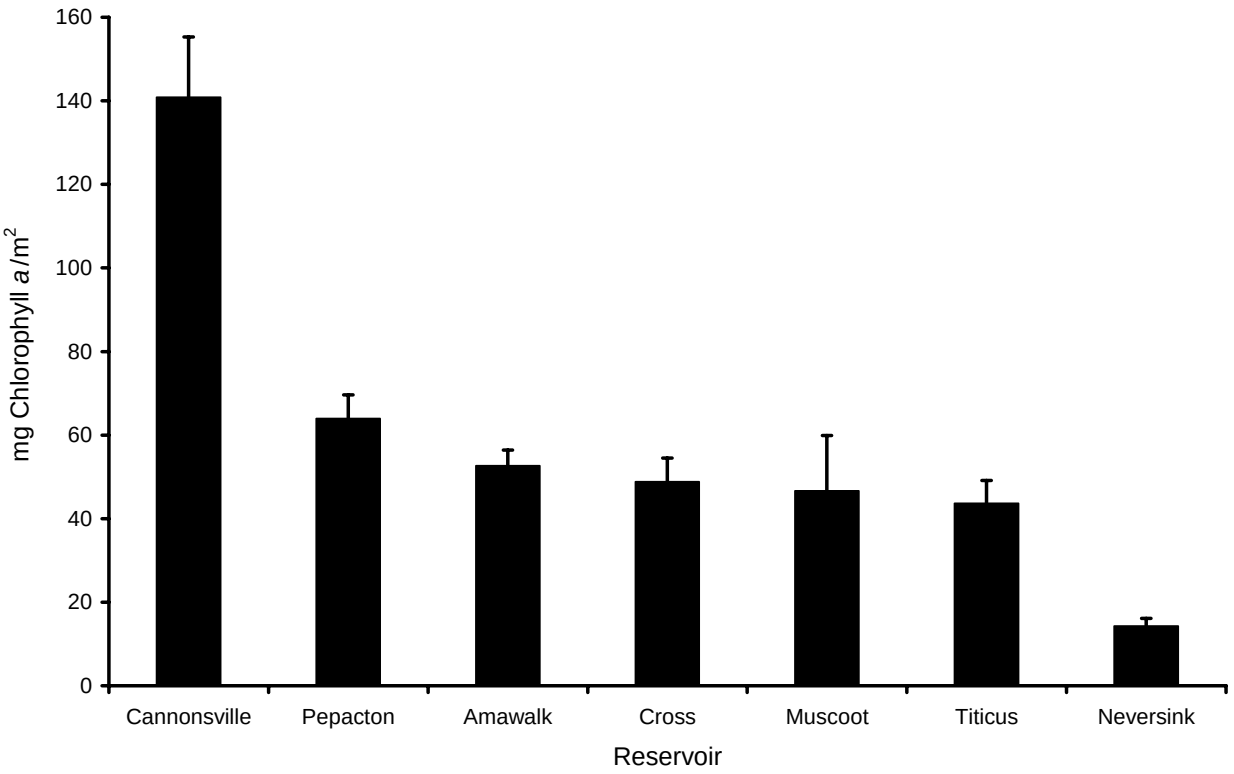

Figure 9.9: Reservoir chlorophyll *a* concentrations (mean ± SD, n=3), 2003 field season.

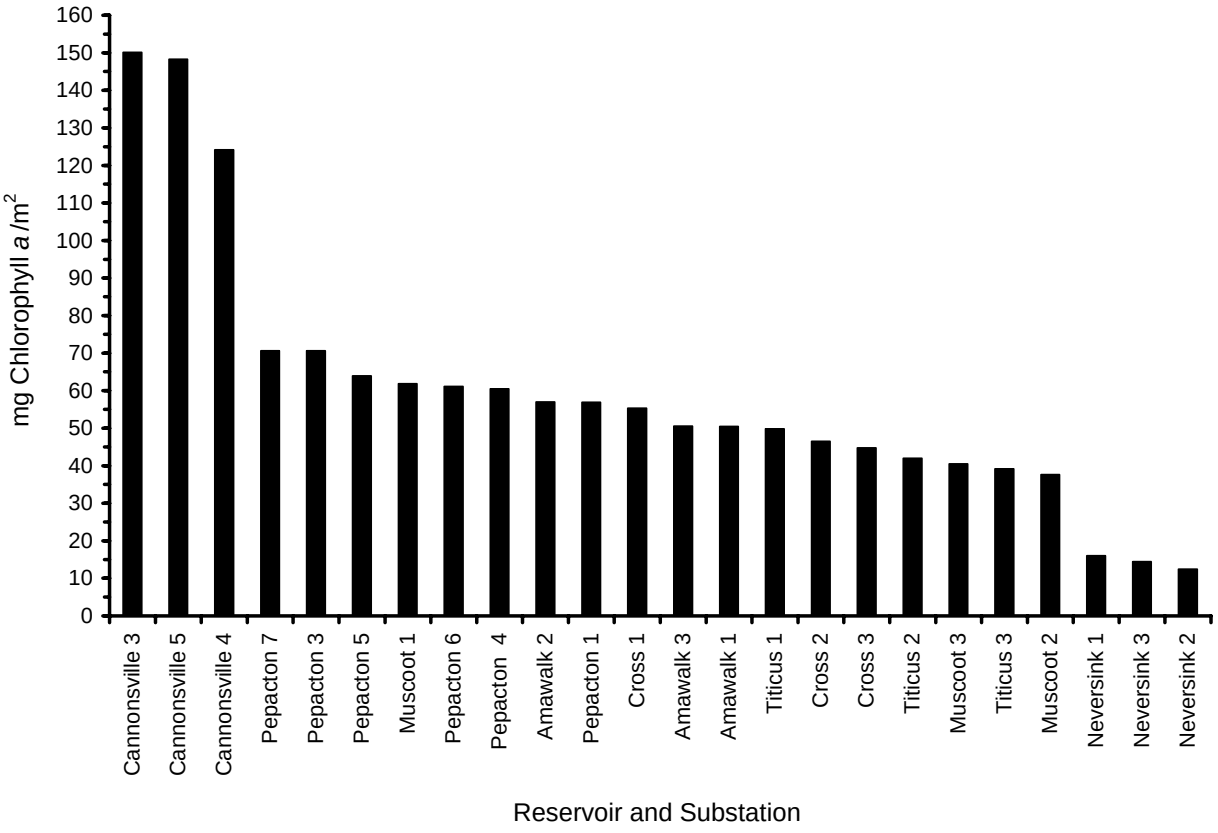

Figure 9.10: Chlorophyll *a* concentrations of each reservoir substation, 2003 field season.

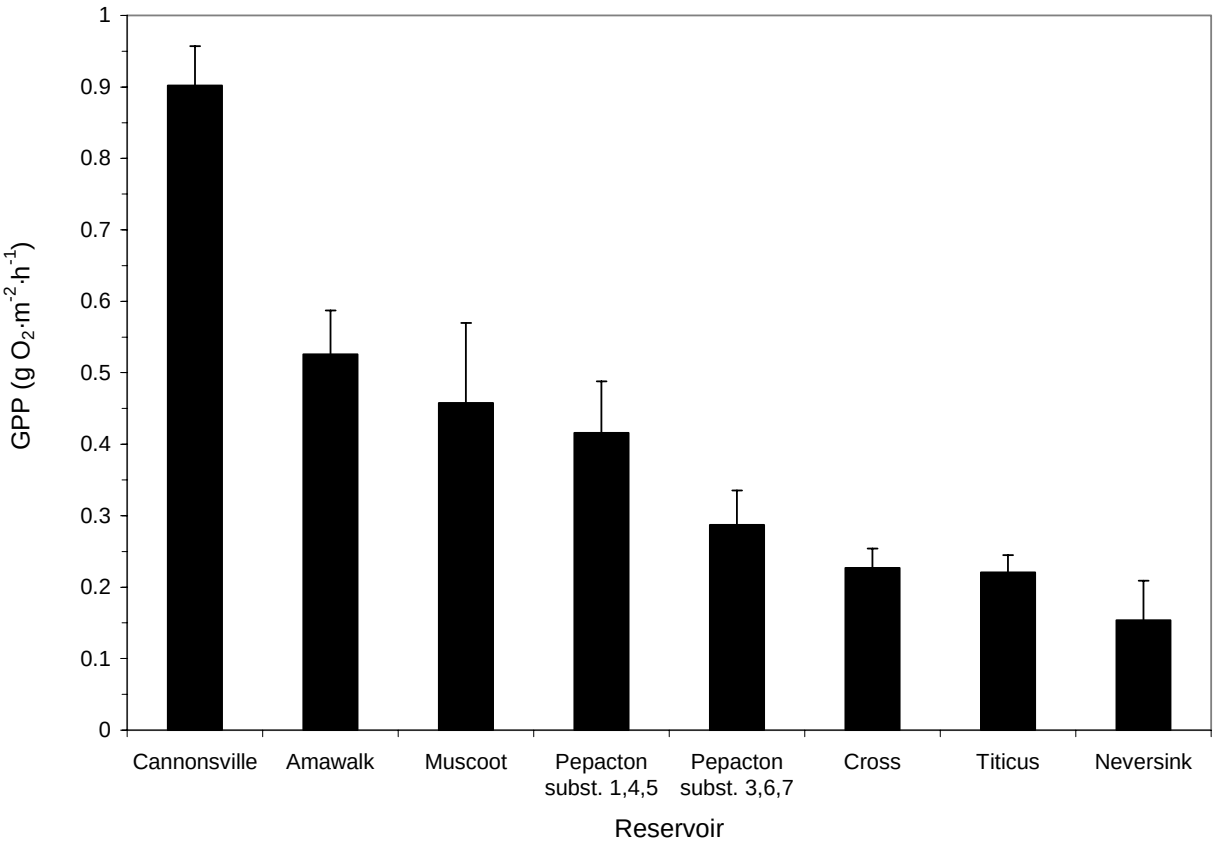

Figure 9.11: Gross primary productivity in each reservoir, 2003 field season. Data shown are mean ± SD, n=3. The incubations on the Pepacton were conducted on different days and are shown separately.

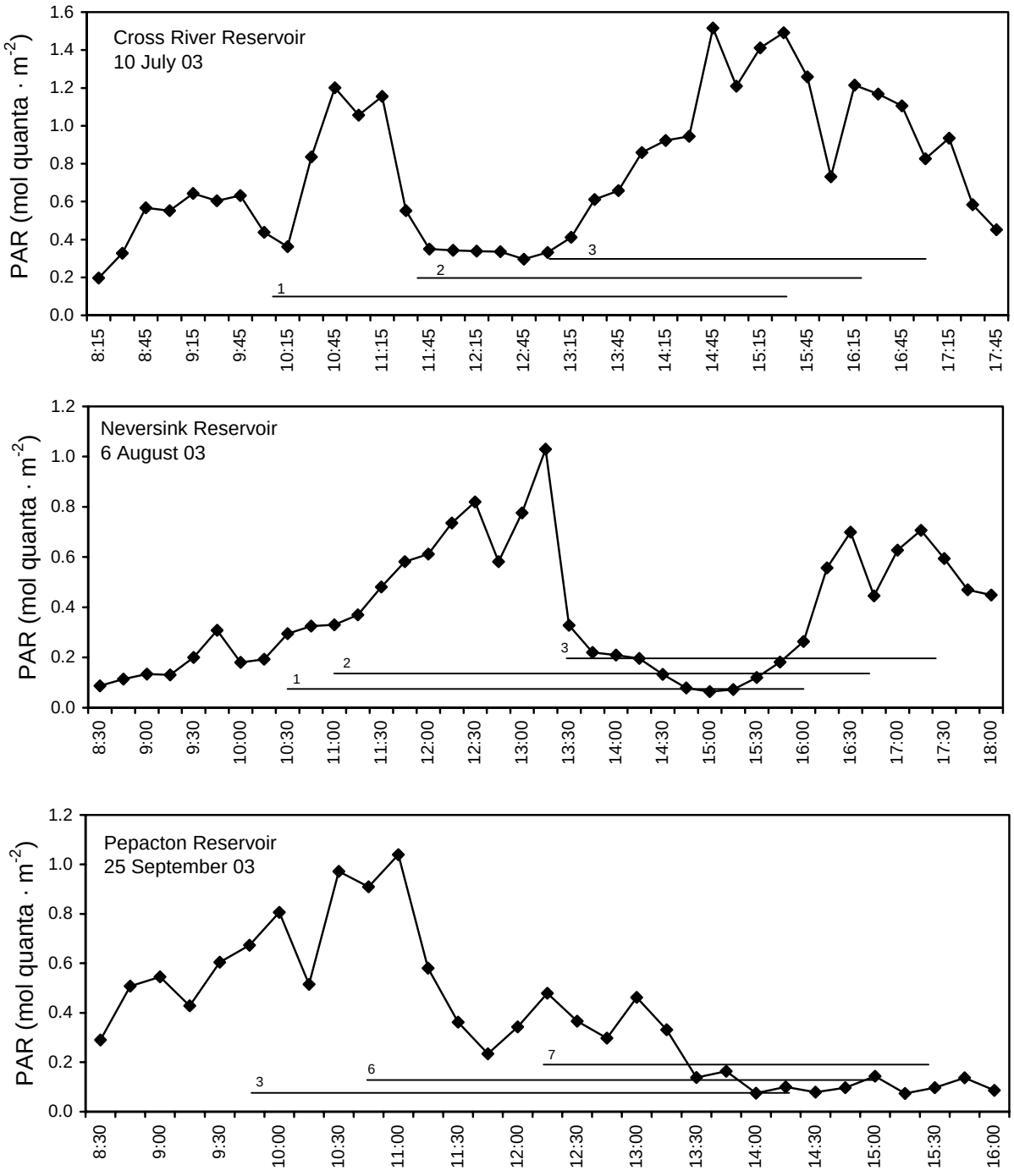

Figure 9.12: Patterns of solar radiation (15 min. intervals) during incubations on the Cross, Neversink and Pepacton Reservoirs. Incubation times at each substation are shown as horizontal lines.

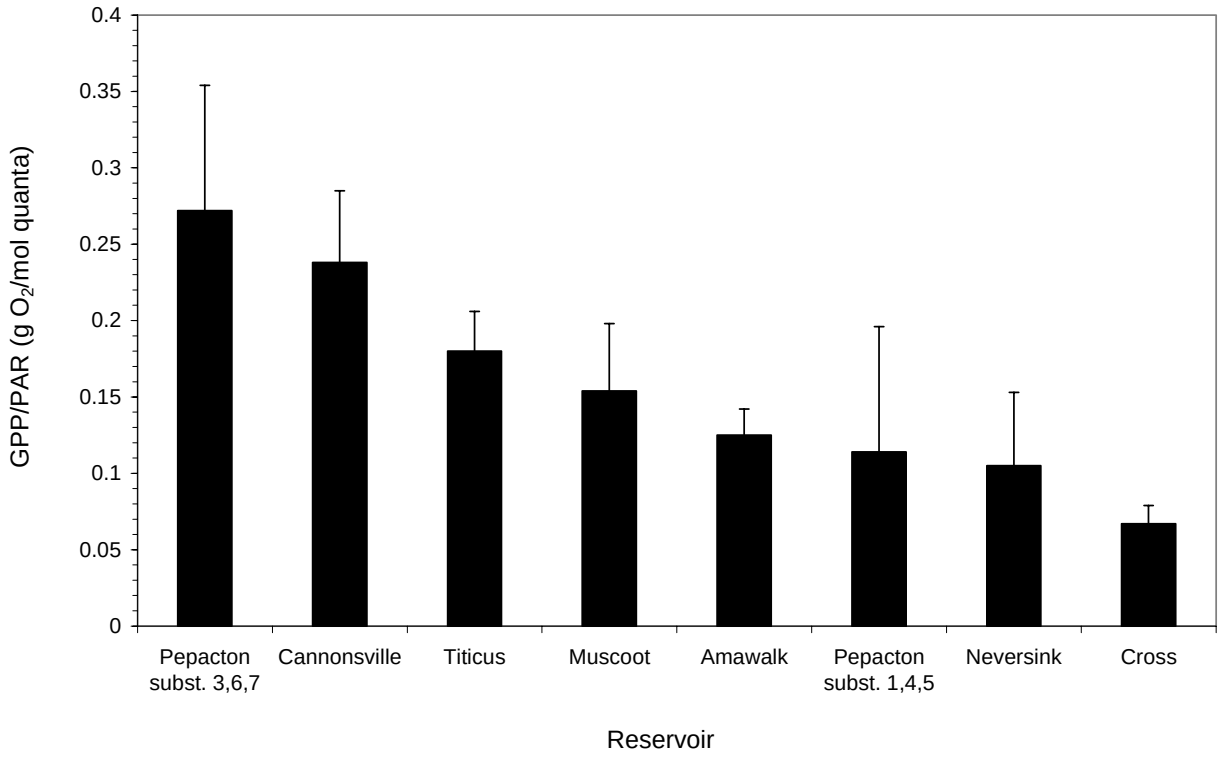

Figure 9.13: GPP normalized for PAR during the incubation period, 2003 field season.

Appendix 3 – QA/QC summary data for Nutrients, Major Ions, and Particulates in Transport (Chapter 3)

2003 QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MAJOR IONS/NUTRIENTS
DATA SUMMARIES

METHOD DETECTION LIMITS (MDL), QUALITY CONTROL CRITERIA (AS EXCEEDANCE LIMITS):
(Units = mg/L; Alkalinity (ALKL) reported as ueq/L CaCO3)

CMPD	MDL (2000-2003)	Precision (RPD specific)	Accuracy (%)
PH	-	20	75-125
ALKL (ueq/L)	-	20	75-125
COND (uS/cm)	-	20	75-125
CA (mg/L)	0.1	20	75-125
MG (mg/L)	0.1	20	75-125
NA (mg/L)	1.5	20	75-125
K (mg/L)	0.4	20	75-125
CL (mg/L)	1	20	75-125
SO4 (mg/L)	2	20	75-125
NH3N (mg/L)	0.01	20	75-125
NO3N (mg/L)	0.02	20	75-125
SKN (mg/L)	0.1	20	75-125
TKN (mg/L)	0.1	20	75-125
SRP (mg/L)	0.00	20	75-125
TDP (mg/L)	0.01	20	75-125
TP (mg/L)	0.01	20	75-125

ADDITIONAL DEFINITIONS AND NOTES:

1. Sample blank (field and laboratory) exceedances are assessed at concentrations > 2*MDL value
2. Precision assessed using either the Relative Percent Difference (RPD) value or the Absolute Difference between duplicate values
   - When the mean concentration of a duplicate set of samples is < the quantity of (1/stated precision limit * MDL) then the appropriate precision assessment is the absolute difference with a corresponding exceedance criterion equal to the MDL.

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2003 QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MAJOR IONS/NUTRIENTS
Summary data for: Field (FB) & Lab (LB) Blanks Year: 2003

- Sample Type: SB=Summer Baseflow; ST=Stormflow
- Laboratory QA/QC results include baseflow and stormflow sample analyses.

		SB				ST			
QAQC	Cmpd	Mean	Stdev	Obs	#flag	Mean	Stdev	Obs	#flag
FB	PH	.	.	.	.	4.90	.	1	0
FB	ALKL (ueq/L)	-4.4	12.9	3	0	1.83	.	1	0
FB	COND (uS/cm)	.	.	.	.	7.30	.	1	0
FB	CA (mg/L)	0.067	0.023	3	0	0.040	.	1	0
FB	MG (mg/L)	0	0	3	0	0	.	1	0
FB	NA (mg/L)	0.057	0.023	3	0	0.18	.	1	0
FB	K (mg/L)	0.037	0.012	3	0	0.67	.	1	0
FB	CL (mg/L)	0	0	3	0	0.50	.	1	0
FB	SO4 (mg/L)	0.60	0.40	3	0	0.80	.	1	0
FB	NH3N (mg/L)	0.0020	0.0010	3	0	0.0050	.	1	0
FB	NO3N (mg/L)	0.0020	0.0010	3	0	0.011	.	1	0
FB	ORGN (mg/L)	0.013	0.0080	3	0	0.0070	.	1	0
FB	SKN (mg/L)	0.015	0.0080	3	0	0.012	.	1	0
FB	TKN (mg/L)	0.011	0.011	3	0	0.012	.	1	0
FB	SRP (mg/L)	0.0010	0.0010	3	0	0.0020	.	1	0
FB	TDP (mg/L)	0.0020	0.0010	2	0	0.0040	.	1	0
FB	TP (mg/L)	0.0010	0.0010	3	0	0.0040	.	1	0
LB	CA (mg/L)	0.0073	0.016	11	0	.	.	.	.
LB	MG (mg/L)	0	0	10	0	.	.	.	.
LB	NA (mg/L)	0.043	0.020	9	0	.	.	.	.
LB	K (mg/L)	0.034	0.0088	9	0	.	.	.	.
LB	CL (mg/L)	0.026	0.056	19	0	.	.	.	.
LB	SO4 (mg/L)	0.38	0.23	16	0	.	.	.	.
LB	NH3N (mg/L)	0.0042	0.0026	43	0	.	.	.	.
LB	NO3N (mg/L)	0.0023	0.0016	29	0	.	.	.	.
LB	SKN&TKN (mg/L)	0.024	0.019	38	0	.	.	.	.
LB	SRP (mg/L)	0.00078	0.00055	49	0	.	.	.	.
LB	TDP&TP (mg/L)	0.0013	0.00074	35	0	.	.	.	.

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion of 2*MDL
(Method Detection Limit - see page 168 for values)

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2003 QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MAJOR IONS/NUTRIENTS
Summary data for: Field (FD) & Lab (LD) Duplicates Year: 2003

- Sample Type: SB=Summer Baseflow; ST=Stormflow
- Precision Evaluation Type: RPD=Relative Percent Difference; ABD DIFF=Absolute value of the difference
- Laboratory QA/QC results include baseflow and stormflow sample analyses.

			----------RPD (%)---------				-----ABS DIFF (conc.)-----			
Type	QAQC	Cmpd	Mean	Stdev	Obs	#flag	Mean	Stdev	Obs	#flag
SB	FD	PH	.	.	0	0	0.015	0.0070	2	0
SB	FD	ALKL (ueq/L)	1.77	2.56	4	0	.	.	0	0
SB	FD	COND (uS/cm)	0.16	0.11	2	0	.	.	0	0
SB	FD	CA (mg/L)	2.14	4.09	4	0	.	.	0	0
SB	FD	MG (mg/L)	1.14	1.42	4	0	.	.	0	0
SB	FD	NA (mg/L)	0.43	0.31	2	0	0.015	0.021	2	0
SB	FD	K (mg/L)	0	.	1	0	0.027	0.031	3	0
SB	FD	CL (mg/L)	2.59	2.59	3	0	0.30	.	1	0
SB	FD	SO4 (mg/L)	0.96	.	1	0	0.47	0.72	3	0
SB	FD	NH3N (mg/L)	1.20	.	1	0	0.0020	0.0020	3	0
SB	FD	NO3N (mg/L)	1.15	0.58	2	0	0.0020	0.0030	2	0
SB	FD	ORGN (mg/L)	16.8	17.5	4	2	.	.	0	0
SB	FD	SKN (mg/L)	.	.	0	0	0.017	0.0070	4	0
SB	FD	TKN (mg/L)	5.98	.	1	0	0.011	0.010	3	0
SB	FD	SRP (mg/L)	11.8	.	1	0	0	0	3	0
SB	FD	TDP (mg/L)	.	.	0	0	0.0010	0.0010	4	0
SB	FD	TP (mg/L)	.	.	0	0	0.0010	0.0010	4	0
SB/ST	LD	CA (mg/L)	0.30	0.31	8	0	.	.	0	0
SB/ST	LD	MG (mg/L)	0.51	1.06	8	0	.	.	0	0
SB/ST	LD	NA (mg/L)	0.16	0.23	2	0	0.014	0.019	5	0
SB/ST	LD	K (mg/L)	0	.	1	0	0	0	6	0
SB/ST	LD	CL (mg/L)	1.26	1.36	5	0	0	.	1	0
SB/ST	LD	SO4 (mg/L)	1.56	0.89	2	0	0.40	0.30	8	0
SB/ST	LD	NH3N (mg/L)	1.56	2.21	2	0	0.00089	0.00070	27	0
SB/ST	LD	NO3N (mg/L)	0.64	0.69	7	0	0.00050	0.00084	6	0
SB/ST	LD	SKN&TKN (mg/L)	1.89	2.67	2	0	0.012	0.0099	21	0
SB/ST	LD	SRP (mg/L)	1.14	1.92	16	0	0.00022	0.00043	18	0
ST	FD	PH	.	.	0	0	0.020	.	1	0
ST	FD	ALKL (ueq/L)	5.71	.	1	0	.	.	0	0
ST	FD	COND (uS/cm)	2.62	.	1	0	.	.	0	0
ST	FD	CA (mg/L)	0.84	.	1	0	.	.	0	0
ST	FD	MG (mg/L)	0	.	1	0	.	.	0	0
ST	FD	NA (mg/L)	.	.	0	0	0.15	.	1	0
ST	FD	K (mg/L)	.	.	0	0	0.66	.	1	1
ST	FD	CL (mg/L)	14.0	.	1	0	.	.	0	0
ST	FD	SO4 (mg/L)	.	.	0	0	0.40	.	1	0
ST	FD	NH3N (mg/L)	.	.	0	0	0.0010	.	1	0
ST	FD	NO3N (mg/L)	0.48	.	1	0	.	.	0	0
ST	FD	ORGN (mg/L)	6.61	.	1	0	.	.	0	0
ST	FD	SKN (mg/L)	.	.	0	0	0.0090	.	1	0
ST	FD	TKN (mg/L)	.	.	0	0	0.014	.	1	0
ST	FD	SRP (mg/L)	6.45	.	1	0	.	.	0	0
ST	FD	TDP (mg/L)	.	.	0	0	0.0010	.	1	0
ST	FD	TP (mg/L)	.	.	0	0	0.0010	.	1	0

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion (see page 168 for values).

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2003 QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MAJOR IONS/NUTRIENTS
Summary data for: Matrix Spikes (as percent recovery)

- Sample Type: SB=Summer Baseflow; ST=Stormflow
- Laboratory QA/QC results include baseflow and stormflow sample analyses.

Year	Cmpd	Mean	Stdev	Obs	#flag
2003	CA (mg/L)	104.1	3.76	8	0
2003	MG (mg/L)	102.6	1.30	8	0
2003	NA (mg/L)	98.7	3.30	7	0
2003	K (mg/L)	97.3	4.54	7	0
2003	CL (mg/L)	105.2	3.53	9	0
2003	SO4 (mg/L)	99.2	8.82	10	0
2003	NH3N (mg/L)	98.8	3.59	30	0
2003	NO3N (mg/L)	99.8	2.73	13	0
2003	SKN&TKN (mg/L)	97.3	4.22	22	0
2003	SRP (mg/L)	98.6	2.74	34	0
2003	TDP&TP (mg/L)	98.7	2.84	23	0

Notes:
(1) #flag indicates the number of samples whose percent recovery exceeded the defined QC criterion (see page 168 for values).

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2003 QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MAJOR IONS/NUTRIENTS
Summary data for: Laboratory Control Standards (as percent recovery)

- Sample Type: SB=Summer Baseflow; ST=Stormflow
- Laboratory QA/QC results include baseflow and stormflow sample analyses.

Year	Cmpd	Mean	Stdev	Obs	#flag
2003	CA (mg/L)	104.3	1.89	4	0
2003	MG (mg/L)	97.3	1.50	4	0
2003	NA (mg/L)	101.3	3.59	4	0
2003	K (mg/L)	105.5	4.43	4	0
2003	CL (mg/L)	98.9	3.84	18	0
2003	SO4 (mg/L)	100.3	4.99	10	0
2003	NH3N (mg/L)	106.1	3.54	22	0
2003	NO3N (mg/L)	103.0	1.56	22	0
2003	SKN&TKN (mg/L)	98.2	2.09	22	0
2003	SRP (mg/L)	101.2	2.14	22	0
2003	TDP&TP (mg/L)	96.8	2.13	24	0

Notes:
(1) #flag indicates the number of samples whose percent recovery exceeded the defined QC criterion (see page 168 for values).

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2003 QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MAJOR IONS/NUTRIENTS
Summary data for: Continuing Calibration Standards (as percent recovery)

- Sample Type: SB=Summer Baseflow; ST=Stormflow
- Laboratory QA/QC results include baseflow and stormflow sample analyses.

Year	Cmpd	Mean	Stdev	Obs	#flag
2003	CA (mg/L)	105.7	4.77	12	0
2003	MG (mg/L)	98.9	4.01	13	0
2003	NA (mg/L)	103.0	1.80	9	0
2003	K (mg/L)	104.7	3.71	10	0
2003	SO4 (mg/L)	88.8	14.4	25	5
2003	NH3N (mg/L)	100.2	12.6	68	4
2003	NO3N (mg/L)	104.7	8.03	54	1
2003	SKN&TKN (mg/L)	102.7	11.4	61	5
2003	SRP (mg/L)	103.3	15.0	75	12
2003	TDP&TP (mg/L)	103.3	12.6	55	3

Notes:
(1) #flag indicates the number of samples whose percent recovery exceeded the defined QC criterion (see page 168 for values).

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Produced on 30MAR04:12:21

2003 QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MAJOR IONS/NUTRIENTS
Summary data for: Conductivity Checks and Cation/Anion Balance (as percent differences)

- Sample Type: SB=Summer Baseflow; ST=Stormflow
- Conductivity Check as the difference between measured and calculating conductivity divided by measured conductivity
- Cation/Anion Balance as the sum of anions subtracted from the sum of cations divided by the sum of all ions (units = ueq/L)

Year	Task	Mean	Stdev	Min	Max	N obs
CONDUCTIVITY CHECK (uS/cm)						
2003	SB	7.59	4.61	-22.0	13.8	61
2003	ST	4.59	1.41	2.96	5.52	3
CATION/ANION BALANCE (ueq/L)						
2003	SB	1.94	2.16	-1.9	8.89	65
2003	ST	-1.2	0.70	-2.1	-0.5	4

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Appendix 4 – QA/QC summary data for Molecular Tracers in Transport (Chapter 4)

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
DATA SUMMARY BY SAMPLING SEASON

METHOD DETECTION LIMITS (MDL), QUALITY CONTROL CRITERIA (AS EXCEEDANCE LIMITS):

CMPD	MDL (2002-2003) (ug/L)	Precision (RPD specific) (%)	Accuracy (MS specific) (ug/L)
FLU	0.0099	30	30-150
PHE	0.015	30	30-150
ANT	0.017	30	30-150
2MP	0.036	30	30-150
1MP	0.024	30	30-150
FLR	0.025	30	30-150
PYR	0.042	30	30-150
BAA	0.0030	30	30-150
CHR	0.0033	30	30-150
BBF	0.015	30	30-150
BKF	0.0083	30	30-150
BAP	0.010	30	30-150
2MN	.	30	30-150
HHCB	0.0090	50	25-175
AHTN	0.014	50	25-175
CAF	0.0055	30	30-150
bCOP	0.016	50	25-175
EPI	0.0039	50	25-175
CHOL	.	50	25-175
aCOP	0.0042	50	25-175
eCOP	.	50	25-175
eEPI	.	50	25-175
bONE	0.0059	75	25-175
aONE	0.0056	75	25-175
eCHO	.	50	25-175
SNOL	0.0065	75	25-175

ADDITIONAL DEFINITIONS AND NOTES:

1. Sample blank (field and laboratory) exceedances are assessed at concentrations > 2*MDL value
2. Precision assessed using either the Relative Percent Difference (RPD) value or the Absolute Difference between duplicate values
   - When the mean concentration of a duplicate set of samples is < the quantity of (1/stated precision limit * MDL) then the appropriate precision assessment is the absolute difference with a corresponding exceedance criterion equal to the MDL.
   - Precision summaries presented in the Molecular Tracer QAQC appendix include all duplicate pairs for the absolute difference summaries, while only those duplicate pairs whose mean concentration is greater than the criterion defined above are included in the RPD summaries.

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QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Field (FB) & Lab (LB) Blanks Year: 2003 Compound Group: PAH/Fragrances/Caffeine

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.

			SB (ug/L)				ST (ug/L)			
QAQC	Cmpd	Type	Mean	Stdev	Obs	#flag	Mean	Stdev	Obs	#flag
FB	FLU	D	0.00049	0.00042	3	0	0.0070	0.0072	2	0
FB	FLU	P	0.00013	0.00009	3	0	0.0041	0.0054	2	0
FB	FLU	SUM	0.00062	0.00037	3	0	0.011	0.013	2	1
FB	PHE	D	0.0011	0.0012	3	0	0.0046	0.0015	2	0
FB	PHE	P	0.00092	0.00050	3	0	0.0014	0.00020	2	0
FB	PHE	SUM	0.0021	0.00093	3	0	0.0060	0.0017	2	0
FB	ANT	D	0.00019	0.00017	3	0	0.00021	0.00008	2	0
FB	ANT	P	0.00014	0.00013	3	0	0.00021	0.00030	2	0
FB	ANT	SUM	0.00033	0.00023	3	0	0.00042	0.00038	2	0
FB	2MP	D	0.00049	0.00042	3	0	0.00063	0.00021	2	0
FB	2MP	P	0.00027	0.00037	3	0	0.00028	0.00039	2	0
FB	2MP	SUM	0.00076	0.00041	3	0	0.00091	0.00061	2	0
FB	1MP	D	0.00029	0.00034	3	0	0.0024	0.0024	2	0
FB	1MP	P	0.00014	0.00018	3	0	0.00025	0.00022	2	0
FB	1MP	SUM	0.00042	0.00033	3	0	0.0026	0.0022	2	0
FB	FLR	D	0.00023	0.00011	3	0	0.0017	0.0017	2	0
FB	FLR	P	0.00016	0.00021	3	0	0.00051	0.00042	2	0
FB	FLR	SUM	0.00039	0.00014	3	0	0.0023	0.0013	2	0
FB	PYR	D	0.00030	0.00023	3	0	0.00041	0.00002	2	0
FB	PYR	P	0.00016	0.00020	3	0	0.00013	0.00019	2	0
FB	PYR	SUM	0.00046	0.00014	3	0	0.00055	0.00021	2	0
FB	BAA	D	0.00011	0.00006	3	0	0.00032	0.00006	2	0
FB	BAA	P	0.00008	0.00005	3	0	0.00060	0.00028	2	0
FB	BAA	SUM	0.00018	0.00010	3	0	0.00092	0.00023	2	0
FB	CHR	D	0.00010	0.00008	3	0	0.00018	0.00007	2	0
FB	CHR	P	0.00009	0.00002	3	0	0.00015	0.00001	2	0
FB	CHR	SUM	0.00019	0.00010	3	0	0.00033	0.00006	2	0
FB	BBF	D	0.00021	0.00015	3	0	0.00042	0.00059	2	0
FB	BBF	P	0.00020	0.00027	3	0	0	0	2	0
FB	BBF	SUM	0.00040	0.00017	3	0	0.00042	0.00059	2	0
FB	BKF	D	0.0037	0.0061	3	0	0.00035	0.00050	2	0
FB	BKF	P	0.00024	0.00029	3	0	0	0	2	0
FB	BKF	SUM	0.0039	0.0064	3	0	0.00035	0.00050	2	0
FB	BAP	D	0.00007	0.00004	3	0	0.00035	0.00011	2	0
FB	BAP	P	0.00015	0.00019	3	0	0	0	2	0
FB	BAP	SUM	0.00022	0.00016	3	0	0.00035	0.00011	2	0
FB	2MN	D	0.00042	0.00057	3	0	0.0016	0.0015	2	0
FB	2MN	P	0.00006	0.00003	3	0	0.00072	0.00052	2	0
FB	2MN	SUM	0.00048	0.00059	3	0	0.0023	0.0021	2	0
FB	PHEd10	D	0.019	0.00065	3	0	0.078	0.0010	2	0
FB	PHEd10	P	0.019	0.00065	3	0	0.078	0.0010	2	0
FB	PHEd10	SUM	0.038	0.0013	3	0	0.16	0.0020	2	0
FB	CHR-D	D	0.018	0.00063	3	0	0.075	0.00099	2	0
FB	CHR-D	P	0.018	0.00063	3	0	0.075	0.00099	2	0
FB	CHR-D	SUM	0.037	0.0013	3	0	0.15	0.0020	2	0
FB	PERd12	D	0.023	0.00079	3	0	0.095	0.0012	2	0
FB	PERd12	P	0.023	0.00079	3	0	0.095	0.0012	2	0
FB	PERd12	SUM	0.046	0.0016	3	0	0.19	0.0025	2	0

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion of 2*MDL
(Method Detection Limit - see page 175 for values)

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Field (FB) & Lab (LB) Blanks Year: 2003 Compound Group: PAH/Fragrances/Caffeine

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.

			SB/ST (ug/L)			
QAQC	Cmpd	Type	Mean	Stdev	Obs	#flag
LB	FLU	D	0.00022	0.00008	2	0
LB	FLU	P	0.00004	0.00002	2	0
LB	FLU	SUM	0.00026	0.00009	2	0
LB	PHE	D	0.0013	0.00028	2	0
LB	PHE	P	0.00070	0.00065	2	0
LB	PHE	SUM	0.0019	0.00092	2	0
LB	ANT	D	0.00065	0.00047	2	0
LB	ANT	P	0.00047	0.00014	2	0
LB	ANT	SUM	0.0011	0.00061	2	0
LB	2MP	D	0.0011	0.00006	2	0
LB	2MP	P	0.00038	0.00024	2	0
LB	2MP	SUM	0.0015	0.00018	2	0
LB	1MP	D	0.00052	0.00019	2	0
LB	1MP	P	0.00039	0.00040	2	0
LB	1MP	SUM	0.00092	0.00059	2	0
LB	FLR	D	0.00045	0.00007	2	0
LB	FLR	P	0.00032	0.00035	2	0
LB	FLR	SUM	0.00077	0.00042	2	0
LB	PYR	D	0.00057	0.00030	2	0
LB	PYR	P	0.00030	0.00035	2	0
LB	PYR	SUM	0.00086	0.00065	2	0
LB	BAA	D	0.00018	0.00012	2	0
LB	BAA	P	0.00019	0.00024	2	0
LB	BAA	SUM	0.00037	0.00012	2	0
LB	CHR	D	0.00012	0.00002	2	0
LB	CHR	P	0.00012	0.00015	2	0
LB	CHR	SUM	0.00024	0.00017	2	0
LB	BBF	D	0.00031	0.00026	2	0
LB	BBF	P	0.00007	0.00010	2	0
LB	BBF	SUM	0.00038	0.00036	2	0
LB	BKF	D	0.00028	0.00033	2	0
LB	BKF	P	0.00003	0.00005	2	0
LB	BKF	SUM	0.00032	0.00038	2	0
LB	BAP	D	0.00042	0.00055	2	0
LB	BAP	P	0.00007	0.00005	2	0
LB	BAP	SUM	0.00050	0.00060	2	0
LB	2MN	D	0.00079	0.00011	2	0
LB	2MN	P	0.00072	0.00047	2	0
LB	2MN	SUM	0.0015	0.00058	2	0
LB	PHEd10	D	0.019	0.0016	2	0
LB	PHEd10	P	0.019	0.0016	2	0
LB	PHEd10	SUM	0.039	0.0033	2	0
LB	CHR-D	D	0.019	0.0016	2	0
LB	CHR-D	P	0.019	0.0016	2	0
LB	CHR-D	SUM	0.038	0.0032	2	0
LB	PERd12	D	0.024	0.0020	2	0
LB	PERd12	P	0.024	0.0020	2	0
LB	PERd12	SUM	0.047	0.0040	2	0

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion of 2*MDL
(Method Detection Limit - see page 175 for values)

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Field (FB) & Lab (LB) Blanks Year: 2003 Compound Group: Fecal Sterols

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.

			SB (ug/L)				ST (ug/L)			
QAQC	Cmpd	Type	Mean	Stdev	Obs	#flag	Mean	Stdev	Obs	#flag
FB	HHCB	D	0.0030	0.0030	3	0	0.0067	0.0054	2	0
FB	HHCB	P	0.0012	0.0010	3	0	0.0098	0.0023	2	0
FB	HHCB	SUM	0.0042	0.0025	3	0	0.017	0.0077	2	1
FB	AHTN	D	0.0013	0.00031	3	0	0.0081	0.0073	2	0
FB	AHTN	P	0.00070	0.00086	3	0	0.0016	0.00067	2	0
FB	AHTN	SUM	0.0020	0.0011	3	0	0.0097	0.0066	2	0
FB	CAF	D	0.0012	0.00079	3	0	0.0039	0.0035	2	0
FB	CAF	P	0.00094	0.00084	3	0	0.0050	0.0036	2	0
FB	CAF	SUM	0.0022	0.0015	3	0	0.0089	0.00011	2	0
FB	CAFd9	D	0.025	0.00083	3	0	0.10	0.0013	2	0
FB	CAFd9	P	0.025	0.00083	3	0	0.10	0.0013	2	0
FB	CAFd9	SUM	0.049	0.0017	3	0	0.20	0.0026	2	0
FB	bCOP	D	0.00074	0.0012	3	0	0.00066	0.00094	2	0
FB	bCOP	P	0.00019	0.00030	3	0	0	0	2	0
FB	bCOP	SUM	0.00093	0.0015	3	0	0.00066	0.00094	2	0
FB	EPI	D	0.00081	0.0013	3	0	0.070	0.094	2	1
FB	EPI	P	0.00007	0.00008	3	0	0.0031	0.0044	2	0
FB	EPI	SUM	0.00088	0.0012	3	0	0.073	0.090	2	2
FB	CHOL	D	0.0066	0.0027	3	0	0.046	0.0041	2	0
FB	CHOL	P	0.012	0.012	3	0	0.022	0.0035	2	0
FB	CHOL	SUM	0.019	0.010	3	0	0.067	0.00054	2	0
FB	aCOP	D	0.00020	0.00025	3	0	0.0013	0.00014	2	0
FB	aCOP	P	0.00093	0.0014	3	0	0.00014	0.00020	2	0
FB	aCOP	SUM	0.0011	0.0014	3	0	0.0015	0.00006	2	0
FB	eCOP	D	0.00001	0.00003	3	0	0.00011	0.00016	2	0
FB	eCOP	P	0.00002	0.00004	3	0	0	0	2	0
FB	eCOP	SUM	0.00004	0.00007	3	0	0.00011	0.00016	2	0
FB	eEPI	D	0.00002	0.00004	3	0	0.00055	0.00077	2	0
FB	eEPI	P	0.00002	0.00004	3	0	0	0	2	0
FB	eEPI	SUM	0.00004	0.00007	3	0	0.00055	0.00077	2	0
FB	bONE	D	0.00003	0.00006	3	0	0.00017	0.00024	2	0
FB	bONE	P	0.00016	0.00025	3	0	0	0	2	0
FB	bONE	SUM	0.00019	0.00031	3	0	0.00017	0.00024	2	0
FB	aONE	D	0.00011	0.00009	3	0	0.00028	0.00039	2	0
FB	aONE	P	0.00005	0.00008	3	0	0	0	2	0
FB	aONE	SUM	0.00016	0.00015	3	0	0.00028	0.00039	2	0
FB	eCHO	D	0.0048	0.0040	3	0	0.021	0.011	2	0
FB	eCHO	P	0.0056	0.0055	3	0	0.0085	0.0063	2	0
FB	eCHO	SUM	0.010	0.0056	3	0	0.030	0.017	2	0
FB	SNOL	D	0.00081	0.00095	3	0	0.0028	0.0039	2	0
FB	SNOL	P	0.00090	0.0011	3	0	0	0	2	0
FB	SNOL	SUM	0.0017	0.0012	3	0	0.0028	0.0039	2	0
FB	CHOLd6	D	0.021	0.00072	3	0	0.087	0.0011	2	0
FB	CHOLd6	P	0.021	0.00072	3	0	0.087	0.0011	2	0
FB	CHOLd6	SUM	0.043	0.0014	3	0	0.17	0.0023	2	0

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion of 2*MDL
(Method Detection Limit - see page 175 for values)

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Field (FB) & Lab (LB) Blanks Year: 2003 Compound Group: Fecal Sterols

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.

			SB/ST (ug/L)			
QAQC	Cmpd	Type	Mean	Stdev	Obs	#flag
LB	HHCB	D	0.0035	0.00040	2	0
LB	HHCB	P	0.0011	0.00086	2	0
LB	HHCB	SUM	0.0047	0.0013	2	0
LB	AHTN	D	0.0023	0.00008	2	0
LB	AHTN	P	0.00054	0.00021	2	0
LB	AHTN	SUM	0.0029	0.00013	2	0
LB	CAF	D	0.00076	0.00085	2	0
LB	CAF	P	0.00035	0.00030	2	0
LB	CAF	SUM	0.0011	0.0011	2	0
LB	CAFd9	D	0.025	0.0021	2	0
LB	CAFd9	P	0.025	0.0021	2	0
LB	CAFd9	SUM	0.050	0.0042	2	0
LB	bCOP	D	0.00063	0.00089	2	0
LB	bCOP	P	0.00054	0.00076	2	0
LB	bCOP	SUM	0.0012	0.0016	2	0
LB	EPI	D	0.00084	0.00027	2	0
LB	EPI	P	0.00014	0.00020	2	0
LB	EPI	SUM	0.00098	0.00007	2	0
LB	CHOL	D	0.0069	0.0037	2	0
LB	CHOL	P	0.0080	0.0025	2	0
LB	CHOL	SUM	0.015	0.0062	2	0
LB	aCOP	D	0.00037	0.00009	2	0
LB	aCOP	P	0.00021	0.00005	2	0
LB	aCOP	SUM	0.00059	0.00015	2	0
LB	eCOP	D	0	0	2	0
LB	eCOP	P	0	0	2	0
LB	eCOP	SUM	0	0	2	0
LB	eEPI	D	0	0	2	0
LB	eEPI	P	0	0	2	0
LB	eEPI	SUM	0	0	2	0
LB	bONE	D	0.00045	0.00062	2	0
LB	bONE	P	0.00002	0.00003	2	0
LB	bONE	SUM	0.00047	0.00059	2	0
LB	aONE	D	0.00033	0.00046	2	0
LB	aONE	P	0.00000	0.00001	2	0
LB	aONE	SUM	0.00033	0.00047	2	0
LB	eCHO	D	0.016	0.018	2	0
LB	eCHO	P	0.00064	0.00051	2	0
LB	eCHO	SUM	0.016	0.017	2	0
LB	SNOL	D	0.00083	0.00068	2	0
LB	SNOL	P	0.00014	0.00020	2	0
LB	SNOL	SUM	0.00098	0.00089	2	0
LB	CHOLd6	D	0.022	0.0018	2	0
LB	CHOLd6	P	0.022	0.0018	2	0
LB	CHOLd6	SUM	0.043	0.0037	2	0

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion of 2*MDL
(Method Detection Limit - see page 175 for values)

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Field (FD) & Lab (LD) Duplicates Year: 2003 Compound Group: PAH/Fragrances/Caffeine Type: SB

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.
- Precision Evaluation Type: RPD=Relative Percent Difference; ABD DIFF=Absolute value of the difference

			RPD (%)				ABS DIFF (ug/L)			
QAQC	Cmpd	Type	Mean	Stdev	Obs	#flag	Mean	Stdev	Obs	#flag
FD	FLU	D	.	.	0	0	0.00016	0.00013	3	0
FD	FLU	P	.	.	0	0	0.00030	0.00047	3	0
FD	FLU	SUM	.	.	0	0	0.00043	0.00062	3	0
FD	PHE	D	.	.	0	0	0.00013	0.00017	3	0
FD	PHE	P	.	.	0	0	0.0022	0.0037	3	0
FD	PHE	SUM	.	.	0	0	0.0023	0.0037	3	0
FD	ANT	D	.	.	0	0	0.00017	0.00008	3	0
FD	ANT	P	.	.	0	0	0.0058	0.0100	3	1
FD	ANT	SUM	.	.	0	0	0.0060	0.0099	3	1
FD	2MP	D	.	.	0	0	0.00013	0.00013	3	0
FD	2MP	P	.	.	0	0	0.00010	0.00002	3	0
FD	2MP	SUM	.	.	0	0	0.00009	0.00008	3	0
FD	1MP	D	.	.	0	0	0.00007	0.00006	3	0
FD	1MP	P	.	.	0	0	0.00020	0.00028	3	0
FD	1MP	SUM	.	.	0	0	0.00026	0.00028	3	0
FD	FLR	D	.	.	0	0	0.00009	0.00005	3	0
FD	FLR	P	.	.	0	0	0.00017	0.00013	3	0
FD	FLR	SUM	.	.	0	0	0.00016	0.00010	3	0
FD	PYR	D	.	.	0	0	0.00010	0.00006	3	0
FD	PYR	P	.	.	0	0	0.00030	0.00029	3	0
FD	PYR	SUM	.	.	0	0	0.00026	0.00036	3	0
FD	BAA	D	.	.	0	0	0.00002	0.00002	3	0
FD	BAA	P	.	.	0	0	0.00009	0.00007	3	0
FD	BAA	SUM	.	.	0	0	0.00011	0.00007	3	0
FD	CHR	D	.	.	0	0	0.00005	0.00004	3	0
FD	CHR	P	.	.	0	0	0.00038	0.00060	3	0
FD	CHR	SUM	.	.	0	0	0.00038	0.00059	3	0
FD	BBF	D	.	.	0	0	0.00002	0.00001	3	0
FD	BBF	P	.	.	0	0	0.00004	0.00003	3	0
FD	BBF	SUM	.	.	0	0	0.00005	0.00004	3	0
FD	BKF	D	.	.	0	0	0.00003	0.00004	3	0
FD	BKF	P	.	.	0	0	0.00001	0.00001	3	0
FD	BKF	SUM	.	.	0	0	0.00003	0.00004	3	0
FD	BAP	D	.	.	0	0	0.00006	0.00008	3	0
FD	BAP	P	.	.	0	0	0.0016	0.0027	3	0
FD	BAP	SUM	.	.	0	0	0.0015	0.0026	3	0
FD	2MN	D	93.3	92.6	3	3	.	.	0	0
FD	2MN	P	142.1	100.1	3	2	.	.	0	0
FD	2MN	SUM	126.7	107.7	3	2	.	.	0	0
FD	PHEd10	D	1.73	1.14	3	0	.	.	0	0
FD	PHEd10	P	1.73	1.14	3	0	.	.	0	0
FD	PHEd10	SUM	1.73	1.14	3	0	.	.	0	0
FD	CHR-D	D	1.73	1.14	3	0	.	.	0	0
FD	CHR-D	P	1.73	1.14	3	0	.	.	0	0
FD	CHR-D	SUM	1.73	1.14	3	0	.	.	0	0
FD	PERd12	D	1.73	1.14	3	0	.	.	0	0
FD	PERd12	P	1.73	1.14	3	0	.	.	0	0
FD	PERd12	SUM	1.73	1.14	3	0	.	.	0	0

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion
(see page 175 for values).

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Field (FD) & Lab (LD) Duplicates Year: 2003 Compound Group: PAH/Fragrances/Caffeine Type: ST

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.
- Precision Evaluation Type: RPD=Relative Percent Difference; ABD DIFF=Absolute value of the difference

			----------RPD (%)---------				------ABS DIFF (ug/L)-----			
QAQC	Cmpd	Type	Mean	Stdev	Obs	#flag	Mean	Stdev	Obs	#flag
FD	FLU	D	.	.	0	0	0.00044	.	1	0
FD	FLU	P	.	.	0	0	0.00089	.	1	0
FD	FLU	SUM	.	.	0	0	0.00044	.	1	0
FD	PHE	D	.	.	0	0	0.00018	.	1	0
FD	PHE	P	.	.	0	0	0.0011	.	1	0
FD	PHE	SUM	.	.	0	0	0.00092	.	1	0
FD	ANT	D	.	.	0	0	0.00026	.	1	0
FD	ANT	P	.	.	0	0	0.00032	.	1	0
FD	ANT	SUM	.	.	0	0	0.00058	.	1	0
FD	2MP	D	.	.	0	0	0.00053	.	1	0
FD	2MP	P	.	.	0	0	0.0012	.	1	0
FD	2MP	SUM	.	.	0	0	0.00070	.	1	0
FD	1MP	D	.	.	0	0	0.00003	.	1	0
FD	1MP	P	.	.	0	0	0.00032	.	1	0
FD	1MP	SUM	.	.	0	0	0.00029	.	1	0
FD	FLR	D	.	.	0	0	0.00062	.	1	0
FD	FLR	P	.	.	0	0	0.00051	.	1	0
FD	FLR	SUM	.	.	0	0	0.0011	.	1	0
FD	PYR	D	.	.	0	0	0.00007	.	1	0
FD	PYR	P	.	.	0	0	0.00061	.	1	0
FD	PYR	SUM	.	.	0	0	0.00053	.	1	0
FD	BAA	D	.	.	0	0	0.00024	.	1	0
FD	BAA	P	.	.	0	0	0.00022	.	1	0
FD	BAA	SUM	.	.	0	0	0.00001	.	1	0
FD	CHR	D	.	.	0	0	0.00007	.	1	0
FD	CHR	P	.	.	0	0	0.00022	.	1	0
FD	CHR	SUM	.	.	0	0	0.00029	.	1	0
FD	BBF	D	.	.	0	0	0.00004	.	1	0
FD	BBF	P	.	.	0	0	0.00046	.	1	0
FD	BBF	SUM	.	.	0	0	0.00041	.	1	0
FD	BKF	D	.	.	0	0	0.00009	.	1	0
FD	BKF	P	.	.	0	0	0.00038	.	1	0
FD	BKF	SUM	.	.	0	0	0.00030	.	1	0
FD	BAP	D	.	.	0	0	0.00014	.	1	0
FD	BAP	P	.	.	0	0	0.00048	.	1	0
FD	BAP	SUM	.	.	0	0	0.00062	.	1	0
FD	2MN	D	85.1	.	1	1	.	.	0	0
FD	2MN	P	7.01	.	1	0	.	.	0	0
FD	2MN	SUM	49.8	.	1	1	.	.	0	0
FD	PHEd10	D	0.10	.	1	0	.	.	0	0
FD	PHEd10	P	0.10	.	1	0	.	.	0	0
FD	PHEd10	SUM	0.10	.	1	0	.	.	0	0
FD	CHR-D	D	0.10	.	1	0	.	.	0	0
FD	CHR-D	P	0.10	.	1	0	.	.	0	0
FD	CHR-D	SUM	0.10	.	1	0	.	.	0	0
FD	PERd12	D	0.10	.	1	0	.	.	0	0
FD	PERd12	P	0.10	.	1	0	.	.	0	0
FD	PERd12	SUM	0.10	.	1	0	.	.	0	0

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion
(see page 175 for values).

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Field (FD) & Lab (LD) Duplicates Year: 2003 Compound Group: Fecal Sterols Type: SB

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.
- Precision Evaluation Type: RPD=Relative Percent Difference; ABD DIFF=Absolute value of the difference

			RPD (%)				ABS DIFF (ug/L)			
QAQC	Cmpd	Type	Mean	Stdev	Obs	#flag	Mean	Stdev	Obs	#flag
FD	HHCB	D	.	.	0	0	0.0016	0.0015	3	0
FD	HHCB	P	.	.	0	0	0.0034	0.0057	3	1
FD	HHCB	SUM	.	.	0	0	0.0043	0.0044	3	1
FD	AHTN	D	.	.	0	0	0.0011	0.0016	3	0
FD	AHTN	P	.	.	0	0	0.00055	0.00094	3	0
FD	AHTN	SUM	.	.	0	0	0.0016	0.0014	3	0
FD	CAF	D	.	.	0	0	0.00073	0.00071	3	0
FD	CAF	P	196.4	.	1	1	0.00022	0.00013	2	0
FD	CAF	SUM	184.8	.	1	1	0.00048	0.00023	2	0
FD	CAFd9	D	1.73	1.14	3	0	.	.	0	0
FD	CAFd9	P	1.73	1.14	3	0	.	.	0	0
FD	CAFd9	SUM	1.73	1.14	3	0	.	.	0	0
FD	bCOP	D	.	.	0	0	0.00052	0.00064	3	0
FD	bCOP	P	.	.	0	0	0.00067	0.00046	3	0
FD	bCOP	SUM	.	.	0	0	0.00100	0.0010	3	0
FD	EPI	D	.	.	0	0	0.00038	0.00032	3	0
FD	EPI	P	.	.	0	0	0.0017	0.0017	3	0
FD	EPI	SUM	.	.	0	0	0.0021	0.0014	3	0
FD	CHOL	D	29.3	31.2	3	1	.	.	0	0
FD	CHOL	P	21.4	11.3	3	0	.	.	0	0
FD	CHOL	SUM	22.1	9.70	3	0	.	.	0	0
FD	aCOP	D	46.5	.	1	0	0.0010	0.0013	2	0
FD	aCOP	P	18.4	1.08	2	0	0.00055	.	1	0
FD	aCOP	SUM	21.2	11.0	2	0	0.0025	.	1	0
FD	eCOP	D	40.9	.	1	0	.	.	0	0
FD	eCOP	P	12.9	13.9	2	0	.	.	0	0
FD	eCOP	SUM	16.0	18.3	2	0	.	.	0	0
FD	eEPI	D	60.7	.	1	1	.	.	0	0
FD	eEPI	P	25.7	12.0	2	0	.	.	0	0
FD	eEPI	SUM	30.2	18.3	2	0	.	.	0	0
FD	bONE	D	.	.	0	0	0.00081	0.00090	3	0
FD	bONE	P	.	.	0	0	0.00056	0.00048	3	0
FD	bONE	SUM	.	.	0	0	0.0014	0.00096	3	0
FD	aONE	D	.	.	0	0	0.00045	0.00046	3	0
FD	aONE	P	.	.	0	0	0.00048	0.00030	3	0
FD	aONE	SUM	.	.	0	0	0.00067	0.00059	3	0
FD	eCHO	D	21.9	27.6	3	1	.	.	0	0
FD	eCHO	P	33.3	8.56	3	0	.	.	0	0
FD	eCHO	SUM	28.3	7.59	3	0	.	.	0	0
FD	SNOL	D	41.8	.	1	0	0.00055	0.00004	2	0
FD	SNOL	P	20.9	3.94	2	0	0.0022	.	1	0
FD	SNOL	SUM	20.3	13.6	2	0	0.0016	.	1	0
FD	CHOLd6	D	1.73	1.14	3	0	.	.	0	0
FD	CHOLd6	P	1.73	1.14	3	0	.	.	0	0
FD	CHOLd6	SUM	1.73	1.14	3	0	.	.	0	0

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion
(see page 175 for values).

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Field (FD) & Lab (LD) Duplicates Year: 2003 Compound Group: Fecal Sterols Type: ST

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.
- Precision Evaluation Type: RPD=Relative Percent Difference; ABD DIFF=Absolute value of the difference

			----------RPD (%)---------				------ABS DIFF (ug/L)-----			
QAQC	Cmpd	Type	Mean	Stdev	Obs	#flag	Mean	Stdev	Obs	#flag
FD	HHCB	D	.	.	0	0	0.0023	.	1	0
FD	HHCB	P	.	.	0	0	0.00083	.	1	0
FD	HHCB	SUM	7.78	.	1	0	.	.	0	0
FD	AHTN	D	.	.	0	0	0.0019	.	1	0
FD	AHTN	P	.	.	0	0	0.00039	.	1	0
FD	AHTN	SUM	.	.	0	0	0.0023	.	1	0
FD	CAF	D	.	.	0	0	0.0036	.	1	0
FD	CAF	P	.	.	0	0	0.00022	.	1	0
FD	CAF	SUM	.	.	0	0	0.0033	.	1	0
FD	CAFd9	D	0.10	.	1	0	.	.	0	0
FD	CAFd9	P	0.10	.	1	0	.	.	0	0
FD	CAFd9	SUM	0.10	.	1	0	.	.	0	0
FD	bCOP	D	.	.	0	0	0.0030	.	1	0
FD	bCOP	P	.	.	0	0	0.0011	.	1	0
FD	bCOP	SUM	5.78	.	1	0	.	.	0	0
FD	EPI	D	14.4	.	1	0	.	.	0	0
FD	EPI	P	2.72	.	1	0	.	.	0	0
FD	EPI	SUM	8.06	.	1	0	.	.	0	0
FD	CHOL	D	16.0	.	1	0	.	.	0	0
FD	CHOL	P	8.77	.	1	0	.	.	0	0
FD	CHOL	SUM	3.93	.	1	0	.	.	0	0
FD	aCOP	D	20.1	.	1	0	.	.	0	0
FD	aCOP	P	6.59	.	1	0	.	.	0	0
FD	aCOP	SUM	5.55	.	1	0	.	.	0	0
FD	eCOP	D	12.4	.	1	0	.	.	0	0
FD	eCOP	P	17.9	.	1	0	.	.	0	0
FD	eCOP	SUM	5.11	.	1	0	.	.	0	0
FD	eEPI	D	28.9	.	1	0	.	.	0	0
FD	eEPI	P	4.28	.	1	0	.	.	0	0
FD	eEPI	SUM	7.72	.	1	0	.	.	0	0
FD	bONE	D	.	.	0	0	0	.	1	0
FD	bONE	P	1.56	.	1	0	.	.	0	0
FD	bONE	SUM	1.56	.	1	0	.	.	0	0
FD	aONE	D	.	.	0	0	0.0050	.	1	0
FD	aONE	P	.	.	0	0	0.00038	.	1	0
FD	aONE	SUM	54.6	.	1	0	.	.	0	0
FD	eCHO	D	13.4	.	1	0	.	.	0	0
FD	eCHO	P	9.96	.	1	0	.	.	0	0
FD	eCHO	SUM	0.55	.	1	0	.	.	0	0
FD	SNOL	D	31.5	.	1	0	.	.	0	0
FD	SNOL	P	8.73	.	1	0	.	.	0	0
FD	SNOL	SUM	9.09	.	1	0	.	.	0	0
FD	CHOLd6	D	0.10	.	1	0	.	.	0	0
FD	CHOLd6	P	0.10	.	1	0	.	.	0	0
FD	CHOLd6	SUM	0.10	.	1	0	.	.	0	0

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion
(see page 175 for values).

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Matrix Spikes (as percent recovery) Year: 2003

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.
- Matrix spikes cover both baseflow and stormflow sampling

			-------SB/ST (ug/L)-------			
Tracer Group	Cmpd	Type	Mean	Stdev	Obs	#flag
PAH/Fragrances/Caffeine	FLU	D	87.8	27.8	3	0
PAH/Fragrances/Caffeine	FLU	P	48.1	50.0	3	1
PAH/Fragrances/Caffeine	FLU	SUM	68.0	26.9	3	0
PAH/Fragrances/Caffeine	PHE	D	76.5	7.30	3	0
PAH/Fragrances/Caffeine	PHE	P	68.2	26.5	3	0
PAH/Fragrances/Caffeine	PHE	SUM	72.3	12.4	3	0
PAH/Fragrances/Caffeine	ANT	D	65.0	3.68	3	0
PAH/Fragrances/Caffeine	ANT	P	66.6	21.1	3	0
PAH/Fragrances/Caffeine	ANT	SUM	65.8	9.54	3	0
PAH/Fragrances/Caffeine	2MP	D	87.1	6.08	3	0
PAH/Fragrances/Caffeine	2MP	P	99.5	4.01	3	0
PAH/Fragrances/Caffeine	2MP	SUM	93.3	3.83	3	0
PAH/Fragrances/Caffeine	1MP	D	81.0	2.06	3	0
PAH/Fragrances/Caffeine	1MP	P	100.8	5.14	3	0
PAH/Fragrances/Caffeine	1MP	SUM	90.9	3.16	3	0
PAH/Fragrances/Caffeine	FLR	D	83.8	4.98	3	0
PAH/Fragrances/Caffeine	FLR	P	87.2	3.78	3	0
PAH/Fragrances/Caffeine	FLR	SUM	85.5	0.78	3	0
PAH/Fragrances/Caffeine	PYR	D	90.1	6.06	3	0
PAH/Fragrances/Caffeine	PYR	P	102.1	14.2	3	0
PAH/Fragrances/Caffeine	PYR	SUM	96.1	9.28	3	0
PAH/Fragrances/Caffeine	BAA	D	97.2	8.18	3	0
PAH/Fragrances/Caffeine	BAA	P	90.6	16.3	3	0
PAH/Fragrances/Caffeine	BAA	SUM	93.9	4.50	3	0
PAH/Fragrances/Caffeine	CHR	D	88.5	3.70	3	0
PAH/Fragrances/Caffeine	CHR	P	87.5	18.0	3	0
PAH/Fragrances/Caffeine	CHR	SUM	88.0	10.3	3	0
PAH/Fragrances/Caffeine	BBF	D	105.3	3.24	3	0
PAH/Fragrances/Caffeine	BBF	P	108.5	21.6	3	0
PAH/Fragrances/Caffeine	BBF	SUM	106.9	12.1	3	0
PAH/Fragrances/Caffeine	BKF	D	96.3	4.30	3	0
PAH/Fragrances/Caffeine	BKF	P	109.1	25.9	3	0
PAH/Fragrances/Caffeine	BKF	SUM	102.7	13.6	3	0
PAH/Fragrances/Caffeine	BAP	D	105.9	1.23	3	0
PAH/Fragrances/Caffeine	BAP	P	84.9	35.1	3	0
PAH/Fragrances/Caffeine	BAP	SUM	95.4	17.4	3	0

Notes:
(1) #flag indicates the number of samples whose percent recovery exceeded the defined QC criterion (see page 175 for values).

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Matrix Spikes (as percent recovery) Year: 2003

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.
- Matrix spikes cover both baseflow and stormflow sampling

			-------SB/ST (ug/L)-------			
Tracer Group	Cmpd	Type	Mean	Stdev	Obs	#flag
Fecal Sterols	HHCB	D	79.2	26.2	3	0
Fecal Sterols	HHCB	P	58.9	74.3	3	1
Fecal Sterols	HHCB	SUM	69.0	24.1	3	0
Fecal Sterols	AHTN	D	98.2	36.0	3	0
Fecal Sterols	AHTN	P	99.7	21.3	3	0
Fecal Sterols	AHTN	SUM	98.9	23.3	3	0
Fecal Sterols	CAF	D	85.8	1.69	3	0
Fecal Sterols	CAF	P	-158.3	451.5	3	1
Fecal Sterols	CAF	SUM	-36.2	226.4	3	1
Fecal Sterols	bCOP	D	89.9	6.78	3	0
Fecal Sterols	bCOP	P	63.1	14.3	3	0
Fecal Sterols	bCOP	SUM	76.5	7.11	3	0
Fecal Sterols	EPI	D	144.7	71.8	3	1
Fecal Sterols	EPI	P	222.3	134.1	3	2
Fecal Sterols	EPI	SUM	183.5	54.9	3	2
Fecal Sterols	CHOL	D	243.9	156.9	3	2
Fecal Sterols	CHOL	P	-769.4	1115.5	3	3
Fecal Sterols	CHOL	SUM	-262.7	522.4	3	1
Fecal Sterols	aCOP	D	127.8	61.1	3	1
Fecal Sterols	aCOP	P	26.5	26.6	3	1
Fecal Sterols	aCOP	SUM	77.2	34.4	3	0
Fecal Sterols	bONE	D	120.0	15.9	3	0
Fecal Sterols	bONE	P	77.7	34.8	3	0
Fecal Sterols	bONE	SUM	98.8	22.8	3	0
Fecal Sterols	aONE	D	111.8	9.48	3	0
Fecal Sterols	aONE	P	72.9	16.4	3	0
Fecal Sterols	aONE	SUM	92.4	11.8	3	0
Fecal Sterols	eCHO	D	261.6	97.0	3	2
Fecal Sterols	eCHO	P	-547.0	446.9	3	3
Fecal Sterols	eCHO	SUM	-142.7	175.9	3	2
Fecal Sterols	SNOL	D	108.7	30.6	3	0
Fecal Sterols	SNOL	P	30.8	27.4	3	1
Fecal Sterols	SNOL	SUM	69.8	7.09	3	0

Notes:
(1) #flag indicates the number of samples whose percent recovery exceeded the defined QC criterion
(see page 175 for values).

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Matrix Spike Duplicates Year: 2003 Compound Group: PAH/Fragrances/Caffeine

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.
- Precision Evaluation Type: RPD=Relative Percent Difference; ABD DIFF=Absolute value of the difference

		----------RPD (%)---------				------ABS DIFF (ug/L)-----			
Cmpd	Type	Mean	Stdev	Obs	#flag	Mean	Stdev	Obs	#flag
FLU	D	.	.	0	0	0.0021	0.0033	3	0
FLU	P	.	.	0	0	0.0023	0.0039	3	0
FLU	SUM	.	.	0	0	0.0044	0.0072	3	1
PHE	D	.	.	0	0	0.00082	0.00084	3	0
PHE	P	.	.	0	0	0.0034	0.0046	3	0
PHE	SUM	.	.	0	0	0.0042	0.0040	3	0
ANT	D	.	.	0	0	0.0011	0.0016	3	0
ANT	P	.	.	0	0	0.0023	0.0033	3	0
ANT	SUM	.	.	0	0	0.0035	0.0049	3	0
2MP	D	.	.	0	0	0.0010	0.0016	3	0
2MP	P	.	.	0	0	0.0018	0.0015	3	0
2MP	SUM	.	.	0	0	0.0026	0.0032	3	0
1MP	D	.	.	0	0	0.0011	0.0013	3	0
1MP	P	.	.	0	0	0.0018	0.0017	3	0
1MP	SUM	.	.	0	0	0.0026	0.0032	3	0
FLR	D	.	.	0	0	0.00063	0.00037	3	0
FLR	P	.	.	0	0	0.00059	0.00045	3	0
FLR	SUM	.	.	0	0	0.00062	0.00077	3	0
PYR	D	.	.	0	0	0.00049	0.00046	3	0
PYR	P	.	.	0	0	0.0014	0.0010	3	0
PYR	SUM	.	.	0	0	0.0017	0.0011	3	0
BAA	D	2.49	2.97	2	0	0.00030	.	1	0
BAA	P	5.76	1.17	2	0	0.0017	.	1	0
BAA	SUM	6.18	2.19	3	0	.	.	0	0
CHR	D	.	.	0	0	0.00011	0.00010	3	0
CHR	P	.	.	0	0	0.00062	0.00087	3	0
CHR	SUM	4.19	4.93	3	0	.	.	0	0
BBF	D	.	.	0	0	0.00032	0.00031	3	0
BBF	P	.	.	0	0	0.00020	0.00031	3	0
BBF	SUM	.	.	0	0	0.00049	0.00063	3	0
BKF	D	.	.	0	0	0.00033	0.00030	3	0
BKF	P	.	.	0	0	0.00075	0.0010	3	0
BKF	SUM	.	.	0	0	0.00085	0.0011	3	0
BAP	D	.	.	0	0	0.00022	0.00020	3	0
BAP	P	.	.	0	0	0.00013	0.00003	3	0
BAP	SUM	.	.	0	0	0.00029	0.00028	3	0

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Matrix Spike Duplicates Year: 2003 Compound Group: Fecal Sterols

- Data are sorted by compound retention times
- SB=Summer Baseflow; ST=Stormflow - Sample Type: D=Dissolved; P=Particulate; SUM=Diss.+Part.
- Precision Evaluation Type: RPD=Relative Percent Difference; ABD DIFF=Absolute value of the difference

		----------RPD (%)---------				------ABS DIFF (ug/L)-----			
Cmpd	Type	Mean	Stdev	Obs	#flag	Mean	Stdev	Obs	#flag
HHCB	D	.	.	0	0	0.00030	0.00015	3	0
HHCB	P	.	.	0	0	0.0016	0.0013	3	0
HHCB	SUM	3.35	.	1	0	0.0018	0.0014	2	0
AHTN	D	.	.	0	0	0.00034	0.00030	3	0
AHTN	P	.	.	0	0	0.0012	0.00092	3	0
AHTN	SUM	.	.	0	0	0.0013	0.00044	3	0
CAF	D	.	.	0	0	0.00059	0.00051	3	0
CAF	P	.	.	0	0	0.00060	0.00044	3	0
CAF	SUM	4.56	2.17	3	0	.	.	0	0
bCOP	D	.	.	0	0	0.00040	0.00042	3	0
bCOP	P	.	.	0	0	0.0019	0.0014	3	0
bCOP	SUM	.	.	0	0	0.0020	0.00090	3	0
EPI	D	17.0	18.1	2	0	0.00080	.	1	0
EPI	P	30.6	18.1	3	1	.	.	0	0
EPI	SUM	26.3	20.0	3	0	.	.	0	0
CHOL	D	6.64	7.83	3	0	.	.	0	0
CHOL	P	25.5	20.3	3	0	.	.	0	0
CHOL	SUM	13.7	11.6	3	0	.	.	0	0
aCOP	D	5.37	4.86	3	0	.	.	0	0
aCOP	P	20.6	20.3	3	0	.	.	0	0
aCOP	SUM	7.81	7.96	3	0	.	.	0	0
bONE	D	3.04	4.77	3	0	.	.	0	0
bONE	P	21.4	27.0	3	0	.	.	0	0
bONE	SUM	8.11	11.6	3	0	.	.	0	0
aONE	D	9.35	10.4	3	0	.	.	0	0
aONE	P	22.3	25.3	3	0	.	.	0	0
aONE	SUM	10.8	9.10	3	0	.	.	0	0
eCHO	D	8.60	4.79	3	0	.	.	0	0
eCHO	P	42.5	31.1	3	2	.	.	0	0
eCHO	SUM	22.3	19.4	3	0	.	.	0	0
SNOL	D	6.91	9.51	3	0	.	.	0	0
SNOL	P	23.5	25.1	3	0	.	.	0	0
SNOL	SUM	7.84	11.7	3	0	.	.	0	0

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR MOLECULAR TRACERS - 2003.
Summary data for: Standard Reference Material

- Data are sorted by compound retention times

SRM lot#	Year	Cmpd	Cert value (ug/L)	Mean	Stdev	Obs	#flag
QCO121_057	2003	FLU	139 (68.5- 209)	43.1	.	1	1
QCO121_057	2003	PHE	142 (55.6- 228)	161.6	.	1	0
QCO121_057	2003	FLR	133 (65.4- 201)	113.0	.	1	0
QCO121_057	2003	PYR	134 (53.4- 215)	118.0	.	1	0
QCO121_057	2003	BAA	126 (71.7- 180)	109.3	.	1	0

Notes:
(1) #flag indicates the number of SRM samples outside of acceptance limits
(as defined by range given in the 'Cert value (ug/L)' field).

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\tracers2003\NYC_TRCRS03_QAQC_APPENDIX_C.LST
Produced on 07SEP04:12:23

Appendix 6 – QA/QC summary data for DOC and BDOC Dynamics (Chapter 6)

2003 QUALITY ASSURANCE/QUALITY CONTROL DATA FOR DOC/BDOC.
Summary data for all FIELD QA/QC data

- Sample Type: SB=Summer Baseflow; ST=Stormflow
- QAQC Sample Type: FB = Field Blank (ug/L), FD - Field Duplicate (Relative Percent Difference)
- Method Detection Limit (MDL) = 50 ug/L; Precision QC Limit = 15% (applicable to RPD); Accuracy = 85 to 115%.

QAQC_Type	Sample_Type	Year	DOC_Sample_Type	Mean (ug/L)	Stdev	#obs	#flag
FB	SB	2003	DOC	39.7	25.0	5	0
FB	SB	2003	DOC(day28)	42.0	16.1	5	0
FB	ST	2003	DOC	339	.	1	1
FD	SB	2003	DOC	0.71	0.53	7	0
FD	SB	2003	DOC(day28)	2.63	3.99	7	0
FD	ST	2003	DOC	.	.	0	0

ADDITIONAL DEFINITIONS AND NOTES:
1. Sample blank (field and laboratory) exceedances are assessed at concentrations > 2*MDL value
2. Precision assessed using the Relative Percent Difference (RPD) value.
3. #flag indicates the number of samples whose concentration exceeded the defined QC criterion of 2*MDL (Method Detection Limit - see above for values)

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\doc2003\DOC03_QAQC_APPENDIX_C.LST
Produced on 30MAR04:12:34

2003 QUALITY ASSURANCE/QUALITY CONTROL DATA FOR DOC/BDOC.
Summary data for all LAB QA/QC data

- Lab QAQC samples include baseflow and stormflow sampling efforts
- QAQC Sample Type: LB = LAB Blank (ug/L), LCS - Lab Control Standard (ug/L & %recovery)
  MS = Matrix Spike (ug/L), LD = Lab Duplicate (Relative Percent Diff. & Absolute Diff.)
- Method Detection Limit (MDL) = 50 ug/L; Precision QC Limit = 15% (applicable to RPD); Accuracy = 85 to 115%.

QAQC_Type	Year	Mean (ug/L)	Stdev	#obs	#flag	--% Recovery-- --(LCS only)-- Mean	Stdev
LB	2003	62.1	37.1	187	25		
LCS	2003	2052	46.0	367	0	99.5	2.72

			----------RPD (%)----------				------Abs. Diff. (ug/L)-------			
QAQC_Type	Year	Type*	Mean	Stdev	#obs	#flag	Mean	Stdev	#obs	#flag
LD	2003	KHP	1.08	1.30	340	0	22.2	26.5	340	35
LD	2003	NANO	61.2	41.1	187	152	31.9	18.8	187	27

ADDITIONAL DEFINITIONS AND NOTES:
1. Sample blank (field and laboratory) exceedances are assessed at concentrations > 2*MDL value
2. Precision assessed using the Relative Percent Difference (RPD) value.
3. #flag indicates the number of samples whose concentration exceeded the defined QC criterion of 2*MDL (Method Detection Limit - see above for values)

* 'Type' for lab duplicates applies to the specific group of samples summarized

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\doc2003\DOC03_QAQC_APPENDIX_C.LST
Produced on 30MAR04:12:34

Appendix 7 – QA/QC summary data for Nitrogen, Phosphorus, and Dissolved Organic Carbon Spiraling (Chapter 7)

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR NUTRIENT & CARBOHYDRATE SPIRALING - 2003.

METHOD DETECTION LIMITS (MDL), QUALITY CONTROL CRITERIA (AS EXCEEDANCE LIMITS):

CMPD	MDL (2003)	Precision (% RPD specific)	Accuracy (%)
BR (mg/L)	0.01	10	90-110
ARAB (nM)	2	20	75-125
GLUC (nM)	2	20	75-125
NH3N (mg/L)	0.01	20	75-125
NO3N (mg/L)	0.02	20	75-125
SKN (mg/L)	0.1	20	75-125
TKN (mg/L)	0.1	20	75-125
SRP (mg/L)	0.00	20	75-125
TDP (mg/L)	0.01	20	75-125
TP (mg/L)	0.01	20	75-125

ADDITIONAL DEFINITIONS AND NOTES:

1. Sample blank (field and laboratory) exceedances are assessed at concentrations > 2*MDL value
2. Precision assessed using either the Relative Percent Difference (RPD) value or the Absolute Difference between duplicate values
   - When the mean concentration of a duplicate set of samples is < the quantity of (1/stated precision limit * MDL) then the appropriate precision assessment is the absolute difference with a corresponding exceedance criterion equal to the MDL.

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\spiraling2003\INJECT_03_QAQC_APPENDIX_C.LST
Produced on 29MAR04:10:12

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR NUTRIENT & CARBOHYDRATE SPIRALING - 2003.
Summary data for: Field (FB) & Lab (LB) Blanks

QAQC	Year	Cmpd	Mean	Stdev	Obs	#flag
FB	2003	BR (mg/L)	0.006	0.004	59	1
FB	2003	GLUC (nM)	10	7.8	16	10
FB	2003	NH3N (mg/L)	0.004	0.003	39	0
FB	2003	SRP (mg/L)	0.0009	0.0008	39	0
LB	2003	BR (mg/L)	0.002	0.006	86	4
LB	2003	ARAB (nM)	0.08	0.5	40	0
LB	2003	GLUC (nM)	5.3	12	40	12
LB	2003	NH3N (mg/L)	0.004	0.003	69	0
LB	2003	NO3N (mg/L)	0.003	0.002	38	0
LB	2003	SKN&TKN (mg/L)	0.02	0.02	46	0
LB	2003	SRP (mg/L)	0.0008	0.0007	72	0
LB	2003	TDP&TP (mg/L)	0.001	0.0008	44	0

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion of 2*MDL
(Method Detection Limit - see page 191 for values)

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\spiraling2003\INJECT_03_QAQC_APPENDIX_C.LST
Produced on 29MAR04:10:12

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR NUTRIENT & CARBOHYDRATE SPIRALING - 2003.
Summary data for: Field (FD) & Lab (LD) Duplicates

- Precision Evaluation Type: RPD=Relative Percent Difference; ABD DIFF=Absolute value of the difference

			----------RPD (%)---------				------ABS DIFF (ug/L)-----			
QAQC	Year	Cmpd	Mean	Stdev	Obs	#flag	Mean	Stdev	Obs	#flag
FD	2003	BR (mg/L)	0.8	0.9	30	0	0.002	0.002	19	0
FD	2003	GLUC (nM)	9.2	13	30	2	.	.	0	0
FD	2003	NH3N (mg/L)	4.6	4.7	5	0	0.001	0.001	25	0
FD	2003	SRP (mg/L)	2.2	2.4	28	0	0.0005	0.0007	2	0
LD	2003	BR (mg/L)	1.0	1.0	63	0	0.0008	0.0004	2	0
LD	2003	ARAB (nM)	2.6	2.2	39	0	.	.	0	0
LD	2003	GLUC (nM)	7.6	12	39	3	.	.	0	0
LD	2003	NH3N (mg/L)	0.8	1.1	7	0	0.0009	0.0007	40	0
LD	2003	NO3N (mg/L)	0.5	0.4	10	0	0.0004	0.0008	7	0
LD	2003	SKN&TKN (mg/L)	3.1	2.8	4	0	0.010	0.008	23	0
LD	2003	SRP (mg/L)	1.0	1.6	29	0	0.0002	0.0004	21	0
LD	2003	TDP&TP (mg/L)	.	.	0	0	0.0004	0.0006	28	0

Notes:
(1) #flag indicates the number of samples whose concentration exceeded the defined QC criterion (see page 191 for values).

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\spiraling2003\INJECT_03_QAQC_APPENDIX_C.LST
Produced on 29MAR04:10:12

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR NUTRIENT & CARBOHYDRATE SPIRALING - 2003.
Summary data for: Matrix Spikes (as percent recovery)

Year	Cmpd	Mean	Stdev	Obs	#flag
2003	BR (mg/L)	97	5.6	65	3
2003	ARAB (nM)	103	6.3	39	0
2003	GLUC (nM)	101	9.0	39	0
2003	NH3N (mg/L)	98	3.4	48	0
2003	NO3N (mg/L)	99	2.4	17	0
2003	SKN&TKN (mg/L)	98	4.6	26	0
2003	SRP (mg/L)	98	2.9	50	0
2003	TDP&TP (mg/L)	99	2.6	28	0

Notes:
(1) #flag indicates the number of samples whose percent recovery exceeded the defined QC criterion (see page 191 for values).

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\spiralings2003\INJECT_03_QAQC_APPENDIX_C.LST
Produced on 29MAR04:10:12

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR NUTRIENT & CARBOHYDRATE SPIRALING - 2003.
Summary data for: Laboratory Control Standards (as percent recovery)

Year	Cmpd	Mean	Stdev	Obs	#flag
2003	BR (mg/L)	97	2.7	115	0
2003	ARAB (nM)	100	6.1	24	0
2003	GLUC (nM)	95	7.3	24	0
2003	NH3N (mg/L)	106	3.4	38	0
2003	NO3N (mg/L)	102	1.9	32	0
2003	SKN&TKN (mg/L)	99	1.8	30	0
2003	SRP (mg/L)	102	2.8	35	0
2003	TDP&TP (mg/L)	97	1.8	36	0

Notes:
(1) #flag indicates the number of samples whose percent recovery exceeded the defined QC criterion (see page 191 for values).

Appendix source: \\StroudSAS\research\nywatershed\nywatershed2003\spiralings2003\INJECT_03_QAQC_APPENDIX_C.LST
Produced on 29MAR04:10:12

Appendix 8 – QA/QC summary data for Stream Metabolism (Chapter 8)

Appendix A.8.1. Comparison of concentrations and initial absorbance values in chlorophyll samples, standards and blanks. Data document that (1) absorbances of the most dilute samples were greater than blanks, (2) cross-contamination between samples was not a problem (i.e., blanks were low), and (3) the spectrophotometer was functioning properly (standards were near the desired concentration of 40 µg/sample). Note that samples were extracted repeatedly until the OD_{665b} was either <10% of the initial absorbance for that sample or < 0.1 absorbance units.

Appendix Table 8.1: Summary of chlorophyll *a* concentrations and initial (before acidification) absorbances at 665 nm in samples of river periphyton, blanks and standards, Year 4 data, 2003.

	Chlorophyll *a* (µg/sample)					OD_{665B}				
	n	x	SD	5th Percentile	95th Percentile	n	x	SD	5th Percentile	95th Percentile
Sample extracts	244	260.34	297.84	15.08	945.96	649	0.399	0.448	0.028	1.342
Ext. 1	244	204.03	209.98	12.03	672.794	244	0.740	0.475	0.125	1.662
Ext. 2	234	48.66	91.35	2.81	205.367	234	0.258	0.325	0.027	1.026
Ext. 3	132	14.55	24.06	2.00	67.199	132	0.107	0.139	0.020	0.388
Ext. 4	33	11.76	11.29	2.49	33.439	33	0.103	0.092	0.036	0.374
Ext. 5	6	7.58	4.94	2.57	13.993	6	0.066	0.028	0.023	0.097
Blanks	136	0.060	0.060	-0.094	0.187	136	0.001	0.003	-0.004	0.0066
Standards	86	36.58	7.70	24.65	49.40	86	0.858	0.164	0.745	1.011

All samples processed within 28 day holding period.

Appendix A.8.2. Accuracy of standards analyzed with stream samples. Note that standards do not enter into the computation of the chlorophyll concentration in a sample, which is obtained by entering sample absorbances into the equation of Lorenzen (Limnol. Oceanogr. 12:343-346, 1967). Standards ensured technician accuracy and spectrophotometer performance.

Appendix Table 8.2: Reproducibility of preparing and quantifying chlorophyll in standards run with river periphyton chlorophyll analyses, Year 4 data, 2003.

Date of analysis	LCS No.	Vial #	Added µg/sample	Measured Chlorophyll a (µg/sample)	Relative % difference (Lab Dups 1&2)	Percent measured/ added
11-Jun-03	1	4	38.36	51.74	23.89	134.87
11-Jun-03	2	4	38.36	40.70		106.09
13-Jun-03	1	5	38.36	39.57	3.94	103.16
13-Jun-03	2	5	38.36	41.16		107.31
13-Jun-03	3	6	38.36	45.00		117.31
13-Jun-03	4	6	38.36	42.29		110.24
13-Jun-03	5	6	38.36	52.11		135.84
17-Jun-03	1	5	38.36	43.60	12.47	113.65
17-Jun-03	2	5	38.36	49.40		128.77
18-Jun-03	1	6	38.36	38.26	3.84	99.75
18-Jun-03	2	6	38.36	39.76		103.65
18-Jun-03	3	7	38.36	39.95		104.14
18-Jun-03	4	7	38.36	37.70		98.29
25-Jun-03	1	8	33.59	35.36	1.31	105.28
25-Jun-03	2	8	33.59	35.83		106.67
26-Jun-03	1	8	33.59	36.77	7.94	109.46
26-Jun-03	2	8	33.59	33.96		101.10
27-Jun-03	1	9	35.64	35.93	0.52	100.80
27-Jun-03	2	9	35.64	35.74		100.27
01-Jul-03	1	9	35.64	34.80	3.56	97.65
01-Jul-03	2	9	35.64	33.59		94.24
03-Jul-03	1	9	35.64	36.39	0.51	102.11
03-Jul-03	2	9	35.64	36.58		102.64
08-Jul-03	1	10	36.95	37.05	1.25	100.26
08-Jul-03	2	10	36.95	37.52		101.53
09-Jul-03	1	10	36.95	35.83		96.97
10-Jul-03	1	10	36.95	33.31	1.67	90.14
10-Jul-03	2	10	36.95	33.87		91.66
11-Jul-03	1	11	36.30	34.24	4.18	94.33
11-Jul-03	2	11	36.30	32.84		90.46
12-Jul-03	1	11	36.30	34.33	3.22	94.59
12-Jul-03	2	11	36.30	35.46		97.68
14-Jul-03	1	11	36.30	35.08		96.65
22-Jul-03	1	12	35.36	35.27	4.89	99.75
22-Jul-03	2	13	36.11	33.59		93.01
23-Jul-03	1	13	36.11	35.46	5.14	98.19
23-Jul-03	2	13	36.11	33.68		93.27

Date of analysis	LCS No.	Vial #	Added µg/sample	Measured Chlorophyll a (µg/sample)	Relative % difference (Lab Dups 1&2)	Percent measured/ added
24-Jul-03	1	13	36.11	34.71		96.12
25-Jul-03	1	13	36.11	30.97		85.76
06-Aug-03	1	14	35.74	34.50	3.95	96.54
06-Aug-03	2	14	35.74	33.17		92.80
08-Aug-03	1	14	35.74	24.65		68.98
21-Aug-03	1	15	35.83	33.53	3.84	93.58
21-Aug-03	2	15	35.83	32.27		90.06
22-Aug-03	1	17	35.64	32.21		90.38
26-Aug-03	1	17	35.64	31.53		88.46
29-Aug-03	1	18	36.86	33.62		91.22
03-Sep-03	1	19	36.49	36.63	3.91	100.37
03-Sep-03	2	19	36.49	35.22		96.53
03-Sep-03	3	19	36.49	43.54		119.32
09-Sep-03	1	19	36.49	37.20	0.55	101.94
09-Sep-03	2	19	36.49	37.40		102.50
16-Sep-03	1	20	36.30	37.29	9.99	102.73
16-Sep-03	2	20	36.30	41.21		113.53
17-Sep-03	1	20	36.30	31.81	7.77	87.63
17-Sep-03	2	21	34.52	34.38		99.60
18-Sep-03	1	21	34.52	34.05	37.60	98.65
18-Sep-03	2	21	34.52	23.28		67.43
23-Sep-03	1	21	34.52	51.87	24.61	150.25
23-Sep-03	2	21	34.52	40.50		117.32
25-Sep-03	1	21	34.52	39.34		113.96
25-Sep-03	1	21	34.52	45.78		132.61
09-Oct-03	1	dilute1	38.77	38.02	1.29	98.07
09-Oct-03	2	dilute1	38.77	37.53		96.81
12-Oct-03	1	dilute1	38.77	37.81		97.51
14-Oct-03	1	dilute1	38.77	37.44		96.57
14-Oct-03	1	dilute1	38.77	37.76	0.77	97.39
14-Oct-03	2	dilute1	38.77	37.47		96.64
15-Oct-03	1	dilute1	38.77	38.25	0.29	98.65
15-Oct-03	2	dilute1	38.77	38.36		98.94
17-Oct-03	1	dilute1	38.77	37.55	0.87	96.86
17-Oct-03	2	dilute1	38.77	37.88		97.71
20-Oct-03	1	dilute1	38.77	37.94		97.85
22-Oct-03	1	dilute1	38.77	39.90		102.92
22-Oct-03	1	dilute2	40.17	40.17		100.01
27-Oct-03	1	dilute2	40.17	39.36		97.98
28-Oct-03	1	dilute2	40.17	41.36		102.96
09-Dec-03	1	dilute3	36.55	34.99	4.37	95.73
09-Dec-03	2	dilute3	36.55	36.55		100.00
10-Dec-03	1	dilute3	36.55	38.25	0.34	104.63
10-Dec-03	2	dilute3	36.55	38.11		104.27
11-Dec-03	1	dilute3	36.55	35.07		95.96

Date of analysis	LCS No.	Vial #	Added µg/sample	Measured Chlorophyll a (µg/sample)	Relative % difference (Lab Dups 1&2)	Percent measured/ added
	Conc. Vials mean			37.01	7.42	101.94
			sd	5.49	9.24	14.06
			n	62	23	
			Dilute1			
			mean	37.99	0.81	97.99
			sd	0.67	0.41	1.73
			n	12	4	
			Dilute2			
			mean	40.30		100.32
			sd	1.01		2.51
			n	3		
			Dilute3			
			mean	36.59	2.36	100.12
			sd	1.58	2.85	4.31
			n	5	2	
			Grand			
			Mean	37.25	6.15	101.19
			SD	4.84	8.59	12.34
			n	82	29	

Appendix A.8.3. Chlorophyll lab duplicate samples. Laboratory duplicates were prepared by dividing field samples into three aliquots of equal weight. Laboratory duplicates served as a check on analytical procedures. Factors affecting reproducibility between lab duplicates include the amounts of filamentous algae and water in a sample and their distribution during the process of subsampling in the laboratory. Laboratory duplicates exceeded 20% RPD only twice and averaged 8.54% overall.

Appendix Table 8.3: Precision of chlorophyll *a* determinations in samples of river periphyton assessed from the relative % difference of lab duplicates, Year 4 data, 2003.

Stream	Tag No.	Lab Dup.	Chlorophyll *a* (µg/sample)	Average Lab Dups	Relative % difference Lab Dups	
Muscoot at Baldwin	36025	1	151.96	147.35	6.26	
6/10/2003	36025	2	142.74			
	36038	1	53.33	55.33	7.25	
	36038	2	57.34			
Haviland Hollow	36070	1	147.15	169.00	25.86	*
6/25/2003	36070	2	190.85			
	36071	1	132.71	132.71	0.00	
	36071	2	132.71			
	36073	1	210.10	205.29	4.69	
	36073	2	200.48			
Cross River	36081	1	280.26	280.26	0.00	
7/1/2003	36081	2	280.26			
	36082	1	255.41	249.79	4.49	
	36082	2	244.18			
	36091	1	12.83	12.63	3.17	
	36091	2	12.43			
Muscoot below Amawalk Resvr.	36108	1	121.09	117.88	5.44	
7/15/2003	36108	2	114.67			
	36113	1	50.52	53.73	11.94	
	36113	2	56.93			
West Br. Delaware at Trout Creek	36143	1	35.00	37.97	15.63	
8/12/2003	36143	2	40.94			
	36154	1	67.60	67.96	1.06	
	36154	2	68.32			
West Br. Delaware at S. Kortright	36167	1	373.93	399.57	12.83	
8/26/2003	36167	2	425.21			
	36169	1	183.39	204.83	20.93	*
	36169	2	226.26			
				Mean	8.54	
				SD	7.90	

* Exceeds 20% limit for RPD.

Appendix A.8.4. We assessed the accuracy of the method by determining how thoroughly rocks were scraped on a subset of 80 rocks. Periphyton scrapings and the rock both were analyzed for chlorophyll *a*. Overall, 85% of the rocks were scraped with 60 – 98 % efficiency. This year, we demarcated the scraped area and flame the unscraped portion of the rock so that the assessment of rock-associated chlorophyll includes only the scraped area of the rock.

Appendix Table 8.4: Recovery of chlorophyll from rocks in study streams, Year 4 data, 2003.

Stream	Chlorophyll (µg in scrapings)	Chlorophyll (µg on rock)	Total Chlorophyll (µg)	Rock area (cm^2)	Total Chlorophyll ($\mu g/cm^2$)	% Recovered in scrapings	% Left on rock	Cover type		Days held
Muscoot (Whitehall)	8.02	68.16	76.18	36.02	2.11	10.53	89.47	Black	BK	7
Muscoot (Whitehall)	32.08	60.14	92.22	40.40	2.28	34.78	65.22	Black & tufts	BK+T	7
Haviland Hollow	19.25	32.08	51.32	32.49	1.58	37.50	62.50	Bare	B	16
Haviland Hollow	55.33	92.22	147.55	39.12	3.77	37.50	62.50	Black	BK	16
Muscoot (Baldwin)	60.54	74.84	135.39	23.35	5.80	44.72	55.28	Green	G	21
Neversink	46.67	56.45	103.12	38.33	2.69	45.26	54.74	Green	G	28
Haviland Hollow	273.45	328.78	602.23	63.67	9.46	45.41	54.59	Diatoms	D	16
Tremper Kill	269.64	263.56	533.20	43.50	12.26	50.57	49.43	Diatoms	D	7
Muscoot (Baldwin)	133.52	120.29	253.80	52.71	4.82	52.61	47.39	Filamentous algae	FA	21
Haviland Hollow	42.10	37.42	79.52	23.27	3.42	52.94	47.06	Green	G	16
Muscoot (Baldwin)	303.92	240.57	544.49	83.95	6.49	55.82	44.18	Bare	B	21
Muscoot (Baldwin)	270.64	213.84	484.48	57.15	8.48	55.86	44.14	Filamentous algae	FA	21
Tremper Kill	596.05	376.09	972.14	51.06	19.04	61.31	38.69	Diatoms	D	7
Muscoot (Baldwin)	402.95	253.94	656.89	50.08	13.12	61.34	38.66	Black	BK	21
Cross	47.71	28.07	75.78	29.22	2.59	62.96	37.04	Black	BK	15
Titicus	379.66	221.99	601.65	32.25	18.66	63.10	36.90	Silt & green	S+G	35
Muscoot (Baldwin)	333.19	189.78	522.97	45.56	11.48	63.71	36.29	Filamentous algae	FA	21
Haviland Hollow	199.67	112.27	311.94	71.86	4.34	64.01	35.99	Bare	B	16
Cross	371.68	208.49	580.17	72.10	8.05	64.06	35.94	Green	G	15
Titicus	193.30	103.45	296.74	48.40	6.13	65.14	34.86	Diatoms	D	35
Haviland Hollow	202.88	108.26	311.14	47.05	6.61	65.21	34.79	Bare	B	16
Muscoot (Whitehall)	37.69	20.05	57.74	26.67	2.16	65.28	34.72	Black	BK	7
Cross	499.58	252.60	752.18	79.30	9.49	66.42	33.58	Green	G	15
Cross	153.16	74.84	228.01	89.63	2.54	67.17	32.83	Silt	S	15
E. Br. Delaware	573.88	277.19	851.07	57.07	14.91	67.43	32.57	Diatoms	D	14
Haviland Hollow	164.79	77.52	242.31	38.31	6.32	68.01	31.99	Black	BK	16
Titicus	123.13	49.40	172.53	75.75	2.28	71.37	28.63	Diatoms	D	35
Muscoot (Whitehall)	52.12	18.71	70.83	41.71	1.70	73.58	26.42	Black & tufts	BK+T	7
Trout Creek	188.41	61.48	249.89	25.69	9.73	75.40	24.60	Filamentous algae	FA	17
Titicus	220.64	68.96	289.61	44.15	6.56	76.19	23.81	Silt & green	S+G	35
W. Br. Delaware (S. Kortright)	401.87	113.87	515.74	45.36	11.37	77.92	22.08	Silt & filam. algae	S+FA	30
Muscoot (Baldwin)	130.31	36.09	166.39	35.46	4.69	78.31	21.69	Green	G	21
Cross	382.91	96.23	479.14	32.99	14.52	79.92	20.08	Tufts	T	15
Muscoot (Whitehall)	358.05	85.54	443.58	76.88	5.77	80.72	19.28	Filamentous algae	FA	7
Muscoot (Whitehall)	71.37	16.04	87.41	47.00	1.86	81.65	18.35	Bare	B	7
Cross	1271.01	284.67	1555.69	51.94	29.95	81.70	18.30	Tufts	T	15
Titicus	477.77	106.44	584.21	55.02	10.62	81.78	18.22	Black	BK	35
Cross	560.53	120.29	680.81	74.79	9.10	82.33	17.67	Green	G	15
Neversink	172.85	36.31	209.16	56.50	3.70	82.64	17.36	Diatoms	D	28
Tremper Kill	30.55	6.42	36.97	36.86	1.00	82.65	17.35	Silt	S	7
Muscoot (Baldwin)	63.75	13.37	77.12	35.97	2.14	82.67	17.33	Filamentous algae	FA	21
Trout Creek	415.06	86.07	501.13	86.42	5.80	82.82	17.18	Filamentous algae	FA	17
W. Br. Delaware (S. Kortright)	250.51	49.32	299.83	33.20	9.03	83.55	16.45	Silt & green	S+G	30
Haviland Hollow	265.43	52.12	317.55	99.98	3.18	83.59	16.41	Green	G	16
E. Br. Delaware	594.93	109.06	703.99	38.01	18.52	84.51	15.49	Filamentous algae	FA	14
Muscoot (Baldwin)	212.90	37.42	250.33	67.36	3.72	85.05	14.95	Bare	B	21
Neversink	41.26	7.16	48.42	25.31	1.91	85.21	14.79	Bare	B	28
Muscoot (Baldwin)	280.67	46.78	327.44	63.48	5.16	85.71	14.29	Bare	B	21
Titicus	584.30	94.22	678.53	42.25	16.06	86.11	13.89	Black	BK	35
Tremper Kill	1678.86	245.38	1924.24	78.13	24.63	87.25	12.75	Filamentous algae	FA	7

Appendix Table 8.4: (continued).

Stream	Chlorophyll (µg in scrapings)	Chlorophyll (µg on rock)	Total Chlorophyll (µg)	Rock area (cm^2)	Total Chlorophyll ($\mu g/cm^2$)	% Recovered in scrapings	% Left on rock	Cover type	Days held
W. Br. Delaware (S. Kortright)	821.07	119.62	940.68	82.63	11.38	87.28	12.72	Silt & filam. algae	30
Tremper Kill	1294.31	183.64	1477.94	126.74	11.66	87.57	12.43	Diatoms	7
Trout Creek	539.80	76.45	616.25	96.82	6.36	87.59	12.41	Diatoms	17
Titicus	288.40	39.96	328.36	47.61	6.90	87.83	12.17	Green	35
Muscoot (Whitehall)	58.94	8.02	66.96	27.61	2.43	88.02	11.98	Black	7
Haviland Hollow	184.04	24.06	208.09	35.00	5.95	88.44	11.56	Bare	16
Trout Creek	537.59	67.36	604.95	56.28	10.75	88.87	11.13	Diatoms	17
Haviland Hollow	245.38	29.40	274.78	38.72	7.10	89.30	10.70	Diatoms	16
Tremper Kill	733.30	87.14	820.44	59.37	13.82	89.38	10.62	Diatoms	7
E. Br. Delaware	629.21	72.44	701.65	37.18	18.87	89.68	10.32	Filam. algae & diatoms	14
W. Br. Delaware (S. Kortright)	1105.02	125.63	1230.65	91.25	13.49	89.79	10.21	Silt & diatoms	30
Tremper Kill	1693.29	192.06	1885.35	103.02	18.30	89.81	10.19	Filam. algae & diatoms	7
Titicus	1059.79	114.62	1174.41	54.03	21.74	90.24	9.76	Silt & green	35
Trout Creek	567.58	54.53	622.11	96.95	6.42	91.23	8.77	Filamentous algae	17
Neversink	144.22	13.15	157.37	50.75	3.10	91.64	8.36	Diatoms	28
Haviland Hollow	309.53	28.07	337.60	31.92	10.58	91.69	8.31	Diatoms	16
Tremper Kill	945.96	83.80	1029.76	58.10	17.72	91.86	8.14	Filam. algae & diatoms	7
Muscoot (Whitehall)	92.62	8.02	100.64	34.97	2.88	92.03	7.97	Black & tufts	7
W. Br. Delaware (S. Kortright)	1579.62	130.44	1710.07	78.27	21.85	92.37	7.63	Silt & filam. algae	30
Neversink	76.74	6.31	83.05	85.84	0.97	92.40	7.60	Green	28
E. Br. Delaware	1716.75	109.38	1826.13	44.69	40.86	94.01	5.99	Diatoms	14
W. Br. Delaware (S. Kortright)	800.98	50.52	851.50	35.90	23.72	94.07	5.93	Diatoms & green	30
Tremper Kill	1200.36	75.38	1275.74	58.61	21.77	94.09	5.91	Diatoms	7
Trout Creek	389.88	20.05	409.93	42.05	9.75	95.11	4.89	Green	17
W. Br. Delaware (S. Kortright)	837.54	36.49	874.03	22.85	38.25	95.83	4.17	Diatoms & green	30
E. Br. Delaware	1184.21	48.92	1233.12	67.18	18.36	96.03	3.97	Filam. algae & diatoms	14
E. Br. Delaware	857.75	19.65	877.40	76.45	11.48	97.76	2.24	Diatoms	14
Muscoot (Baldwin)	430.62	9.36	439.98	49.43	8.90	97.87	2.13	Filamentous algae	21
Haviland Hollow	410.57	5.35	415.92	70.59	5.89	98.71	1.29	Moss	16
Neversink	8.62	0.00	8.62	41.05	0.21	100.00	0.00	Bare	28

Appendix Table 8.4: (continued).

Stream	Chlorophyll (µg in scrapings)	Chlorophyll (µg on rock)	Total Chlorophyll (µg)	Rock area (cm^2)	Total Chlorophyll ($\mu g/cm^2$)	% Recovered in scrapings	% Left on rock	Cover type				Days held
First Visit												
Muscoot (Baldwin)	164.79	360.86	525.65	85.96	6.12	31.35	68.65	Bare		B		22
Haviland Hollow	166.39	312.74	479.14	99.98	4.79	34.73	65.27	Bare		B		22
Muscoot (Baldwin)	22.85	40.10	62.95	62.96	1.00	36.31	63.69	Bare		B		22
Muscoot (Baldwin)	129.91	219.19	349.09	36.72	9.51	37.21	62.79	Bare		B		22
Haviland Hollow	214.11	320.76	534.87	42.17	12.68	40.03	59.97	Black	BK			22
Muscoot (Baldwin)	400.95	593.41	994.36	95.69	10.39	40.32	59.68	Filamentous algae			FA	22
Muscoot (Baldwin)	107.86	140.33	248.19	75.17	3.30	43.46	56.54	Bare		B		22
Haviland Hollow	46.51	56.13	102.64	36.28	2.83	45.31	54.69	Bare		B		22
Haviland Hollow	143.54	137.66	281.20	33.66	8.35	51.05	48.95	Green		G		22
Haviland Hollow	121.89	90.88	212.77	29.84	7.13	57.29	42.71	Diatoms			D	22
Muscoot (Baldwin)	90.61	64.15	154.77	49.83	3.11	58.55	41.45	Filamentous algae			FA	22
Haviland Hollow	28.47	18.04	46.51	20.98	2.22	61.21	38.79	Bare		B		22
Muscoot (Baldwin)	70.17	33.41	103.58	76.39	1.36	67.74	32.26	Bare		B		22
Haviland Hollow	121.89	53.46	175.35	44.46	3.94	69.51	30.49	Black	BK			22
Muscoot (Baldwin)	565.34	240.57	805.91	130.69	6.17	70.15	29.85	Filamentous algae			FA	22
Haviland Hollow	146.75	61.48	208.23	31.87	6.53	70.47	29.53	Diatoms			D	22
Haviland Hollow	45.71	18.71	64.42	16.59	3.88	70.95	29.05	Green		G		22
Muscoot (Baldwin)	605.84	213.84	819.68	93.86	8.73	73.91	26.09	Filamentous algae			FA	22
Muscoot (Baldwin)	181.63	60.14	241.77	42.97	5.63	75.12	24.88	Filamentous algae			FA	22
Haviland Hollow	325.97	96.23	422.20	30.31	13.93	77.21	22.79	Diatoms			D	22
Muscoot (Baldwin)	177.22	13.37	190.58	53.30	3.58	92.99	7.01	Filamentous algae			FA	22

Appendix A.8.5. Data indicate full recovery of chlorophyll from the samples. Note however that since we use a sequential extraction procedure and sum the chlorophyll in each extract, we ensure detection of all chlorophyll in the sample.

Appendix Table 8.5: Accuracy of determining chlorophyll *a* in samples of river periphyton assessed from recovery of chlorophyll from spiked samples, Year 4 data, 2003.

Stream	Tag No.	Lab Dup.	Matrix Spike	Chlorophyll *a* (µg/sample)	Average Lab Dups	Matrix spike (µg/sample)	% Recovery
Muscoot (Baldwin)	36000	1		204.48	207.09		
3-Jun-03		2		209.70			
		3	1	715.29		621.27	81.80
	36004	1		33.68	38.09		
		2		42.50			
		3	2	140.73		114.27	89.82
	36015	1		45.31	51.52		
		2		57.74			
		3	3	210.50		154.57	102.85
Muscoot (Baldwin)	36025	1		151.96	147.35		
10-Jun-03		2		142.74			
		3	4	588.19		442.05	99.73
	36038	1		53.33	55.33		
		2		57.34			
		3	5	228.14		165.99	104.11
Haviland Hollow	36046	1		3.21	2.81		
17-Jun-03		2		2.41			
		3	6	8.02		8.42	61.90
	36056	1		21.65	21.05		
		2		20.45			
		3	7	77.78		63.15	89.84
Haviland Hollow	36070	1		147.15	169.00		
25-Jun-03		2		190.85			
		3	8	615.06		507.00	87.98
	36071	1		132.71	132.71		
		2		132.71			
		3	9	542.89		398.14	103.02
	36073	1		210.10	205.29		
		2		200.48			
		3	10	637.11		615.86	70.12
Cross	36081	1		280.26	280.26		
1-Jul-03		2		280.26			
		3	11	1027.64		840.79	88.89
	36082	1		255.41	249.79		
		2		244.18			
		3	12	904.94		749.38	87.43
	36091	1		12.83	12.63		
		2		12.43			
		3	13	25.26		37.89	33.33

Stream	Tag No.	Lab Dup.	Matrix Spike	Chlorophyll *a* (µg/sample)	Average Lab Dups	Matrix spike (µg/sample)	% Recovery
Muscoot (Whitehall)	36108	1		121.09	117.88		
16-Jul-03		2		114.67			
		3	14	170.84		353.64	14.98
	36113	1		50.52	53.73		
		2		56.93			
		3	15	107.94		161.18	33.63
Trout Creek	36143	1		35.00	37.97		
13-Aug-03		2		40.94			
		3	16	159.82		113.91	106.97
	36154	1		67.60	67.96		
		2		68.32			
		3	17	244.90		203.88	86.78
W. Br. Delaware (S.	36167	1		373.93	399.57		
Kortright)		2		425.21			
28-Aug-03		3	18	1430.83		1198.70	86.03
	36169	1		183.39	204.83		
		2		226.26			
		3	19	778.89		614.48	93.42
						Mean	80.14
						SD	26.23
						Mean with 3 outliers removed	90.04
						SD	12.16

Appendix A.8.6. Field duplicates for propane data showed tight correspondence in subsamples for propane analyses.

Appendix Table 8.6: Relative percent difference in propane concentrations (expressed as percent of maximum) on each stream, Year 4 data, 2003. The measure on field duplicate samples provides an estimate of precision of the measures.

Stream	Date	Substation	Propane (%)		Relative percent difference (%)	
			Field Dup 1	Field Dup 2		
Muscoot (Baldwin)	11-Jun-03	2	69.492	59.437	15.6	
		4	17.233	15.531	10.4	
		5	11.058	9.768	12.4	
Haviland Hollow	26-Jun-03	2	81.887	80.556	1.6	
		4	13.535	12.342	9.2	
		5	8.389	9.142	8.6	
Cross	2-Jul-03	2	63.035	57.737	8.8	
		4	10.667	13.282	21.8	*
		5	10.595	9.491	11.0	
Muscoot (Whitehall)	16-Jul-03	2	73.494	71.242	3.1	
		4	RDF	32.421		
		5	16.868	20.603	19.9	
Titicus	30-Jul-03	2	28.831	28.887	0.2	
		4	5.829	5.799	0.5	
		5	4.034	3.216	22.6	*
Trout Creek	13-Aug-03	2	78.496	80.003	1.9	
		4	57.925	55.814	3.7	
		5	49.444	48.622	1.7	
W. Br. Delaware (S. Kortright)	28-Aug-03	2	62.354	57.086	8.8	
		4	24.601	24.285	1.3	
		5	20.01	17.598	12.8	
Tremper Kill	1-Oct-03	2	75.485	80.947	7.0	
		4	45.657	46.864	2.6	
		5	24.015	29.904	21.8	*
E. Br. Delaware	16-Oct-03	2	5.98	6.329	5.7	
		4	4.581	4.31	6.1	
		5	4.151	4.132	0.5	
Neversink	12-Nov-03	2	69.252	74.286	7.0	
		4	1.607	BDL		
Mean					8.4	
SD					7.0	
Median					7.0	

* Data were outside the limit for field duplicate samples.

RDF - Sample damaged in field, not analyzed.

BDL - Below detection limits.

Appendix A.8.7. Propane data for samples from the most downstream station in all streams but the Neversink were at least twice the blank value.

Appendix Table 8.7: Propane peak areas for samples at different substations, for blanks, and for standards, Year 4 data, 2003.

Stream	Propane peak area ($x10^3$)								
	Samples			Blanks	Standards				
	Subst. 1 x±SD	Subst. 3 x±SD	Subst. 5 x±SD	x±SD	1% x±SD	10% x±SD	50% x±SD	100% x±SD	R^2 Lin. Reg.
Muscoot (Baldwin)	50.7 ± 6.6	25.4 ± 2.3	11.1 ± 0.6	4.7 ± 1.4	7.5 ± 0.4	12.3 ± 0.4	26.7 ± 1.3	49.8 ± 0.7	0.997
Haviland Hollow	43.9 ± 1.9	29.6 ± 1.1	7.1 ± 0.4	3.4 ± 0.2	3.7 ± 0.2	7.8 ± 0.9	22.9 ± 1.5	42.9 ± 1.7	1.000
Cross	42.0 ± 9.4	10.8 ± 0.8	6.8 ± 0.5	2.7 ± 0.3	2.5 ± 0.7	6.2 ± 0.7	22.9 ± 0.4	43.8 ± 1.0	1.000
Muscoot (Whitehall)	39.6 ± 1.2	22.2 ± 0.5	9.6 ± 0.6	2.6 ± 0.7	3.6 ± 0.5	6.6 ± 0.6	20.3 ± 1.1	38.5 ± 0.7	1.000
Titicus	184.0 ± 10.6	20.5 ± 0.8	10.0 ± 1.1	2.8 ± 0.8	6.3 ± 0.3	21.6 ± 0.4	91.3 ± 0.5	186.4 ± 2.8	0.999
Trout Creek	55.6 ± 6.0	41.8 ± 1.7	30.6 ± 1.3	2.6 ± 0.3	3.8 ± 0.1	7.8 ± 0.3	29.0 ± 0.6	57.0 ± 1.3	0.999
W. Br. Delaware	51.5 ± 1.9	22.8 ± 0.7	12.9 ± 0.5	2.6 ± 0.4	3.9 ± 0.4	8.6 ± 0.8	28.5 ± 2.4	52.4 ± 2.0	1.000
Tremper Kill	13.4 ± 0.9	8.0 ± 0.2	5.9 ± 0.5	2.1 ± 0.1	2.4 ± 0.3	3.8 ± 0.4	7.2 ± 0.2	13.7 ± 0.4	0.991
E. Br. Delaware	7.6 ± 0.3	5.6 ± 0.0	4.1 ± 0.2	2.3 ± 0.1	2.3 ± 0.0	2.9 ± 0.2	5.1 ± 0.4	7.6 ± 0.2	0.998
Neversink	6.4 ± 0.1	3.0 ± 0.5	2.3 ± 0.1	2.1 ± 0.0	2.4 ± 0.1	2.9 ± 0.6	4.5 ± 0.8	6.7 ± 0.6	0.999

Appendix A.8.8. There were 99 checks of data sondes against the QA/QC sonde. Overall data sondes closely agreed with the QA/QC sonde with a 0.124 mg/L difference and 1.23 RPD. The relationship between an individual data sonde and the QA/QC sonde usually constant throughout the measurement period, i.e., drift was minimal. Checks of data sondes against Winkler dissolved O_2 determinations showed the concentrations determined by the sondes differed 1.026 ± 0.351 mg/L (x ± SD, n=54) and 10.82 RPD. Thus, sondes were calibrated against air according to the manufacturers directions. Winkler titrations were performed to allow comparison of our data with other data sets based on that method.

Appendix Table 8.8: Summary of daily QA/QC checks of data sondes against QA/QC sonds and dta sondes against winklers for each stream, Year 4, 2003.

		Deployed - QAQC Sonde					Deployed - Winkler				
		Abs. Difference, mgDO/L		% Difference		n	Abs. Difference, mgDO/L		% Difference		n
Stream	Dates	Mean	SD	Mean	SD		Mean	SD	Mean	SD	
Muscoot (Baldwin)	10-12Jun03	0.022	0.017	0.256	0.197	9	0.827	0.015	9.440	0.158	3
Haviland Hollow	24-27Jun03	0.126	0.039	1.500	0.461	9	0.768	0.218	8.526	2.304	6
Cross	01-04Jul03	0.042	0.036	0.479	0.408	8	0.888	0.183	10.199	1.897	8
Muscoot (Whitehall)	15-18Jul03	0.150	0.180	1.491	1.826	12	1.243	0.149	12.633	1.718	6
Titicus	29Jul-01Aug03	0.142	0.124	1.576	1.396	16	1.225	0.224	14.160	2.200	8
Trout Creek	12-15Aug03	0.215	0.094	2.370	1.075	6	1.555	0.740	16.352	6.068	4
W. Br. Delaware	26-29Aug03	0.102	0.113	0.930	1.014	6	1.320	0.184	14.490	4.221	4
Tremper Kill	30Sep-03Oct03	0.157	0.080	1.479	0.764	6	0.843	0.166	7.694	1.004	4
E. Br. Delaware	14-17Oct03	0.109	0.112	0.937	0.950	11	0.886	0.249	8.086	1.528	7
Neversink	11-14Nov03	0.158	0.110	1.290	0.869	16	0.725	0.058	5.801	0.437	4
											5
Grand Means		0.124		1.236		99	1.026		10.817		4
SD		0.115		1.149			0.351		3.884		

Appendix 9 – QA/QC summary data for Reservoir Primary Productivity (Chapter 9)

Appendix 9.1.a. & b. Comparison of concentrations and initial absorbance values in chlorophyll samples and blanks to document that (1) the most dilute samples had absorbencies greater than blanks and (2) that cross-contamination between samples was not a problem (i.e., field and laboratory blanks were low). Field blanks test for cross contamination at the filtration step, and laboratory blanks at the assay step.

Appendix Table 9.1.a: Summary of chlorophyll *a* concentrations and initial (i.e., before acidification) absorbances at 665 nm in spectrophotometrically-read reservoir samples and blanks, Year 4 data.

	New Spectrophotometer									
	Chlorophyll *a* (µg/sample)					OD_{665B}				
	n	x	SD	5th Percentile	95th Percentile	n	x	SD	5th Percentile	95th Percentile
Sample extracts[a]	119	10.970	11.386	1.721	20.339	211	0.092	0.068	0.022	0.216
Ext. 1	119	9.377	8.562	1.721	17.064	133	0.121	0.066	0.044	0.224
Ext. 2	73	2.469	2.699	0.767	3.911	76	0.043	0.036	0.014	0.097
Ext. 3	2	4.715	3.837	2.002	7.428	2	0.075	0.046	0.042	0.107
Lab Blanks	37	0.0528	0.03878	0.000	0.0936	37	0.000	0.003	-0.003	0.007
Field Blanks	7	0.1871	0.21141	-0.0374	0.5426	8	0.008	0.003	0.004	0.014

Appendix Table 9.1.b: Summary of chlorophyll *a* concentrations and initial (i.e., before acidification) fluorescence in fluorometrically-read reservoir samples and blanks, Year 4 data.

	Fluorometer									
	Chlorophyll *a* (µg/sample)					R_b				
	n	x	SD	5th Percentile	95th Percentile	n	x	SD	5th Percentile	95th Percentile
Sample extracts[a]	136	14.401	11.370	2.477	34.355	296	503.48	220.23	129	891
Ext. 1	136	11.673	9.391	1.930	29.794	150	551.37	181.49	252	902
Ext. 2	129	2.759	1.771	0.517	5.104	135	476.65	238.53	129	851
Ext. 3	11	1.386	2.368	0.427	8.300	11	179.64	134.77	101	547
Lab Blanks	39	0.0006	0.0018	-0.0001	0.0052	39	0.819	1.331	0.163	4.680
Field Blanks	8	0.2612	0.3498	0.0028	1.0116	10	22.21	28.04	3.47	81.80

[a] The *n* for OD_{665B} and R_b represents each initial absorbance/fluorescence reading. The *n* for chlorophyll *a* represents the chlorophyll *a* in extracts 2 and 3 added to the amount in extract 1 to generate the total chlorophyll *a* for that sample. Therefore, the final *n* cannot exceed the n for extract 1.

Appendix 9.2. Comparison of chlorophyll concentration from spectrophotometric and fluorometric analyses, individual samples. Data document higher concentrations from fluorometric analyses for all but the Cross reservoir.

Appendix Table 9.2: Comparison of spectrophotomer and fluorometer analyses for concentrations in individual samples.

Station Name	Reservoir Station	Sample No.	Spec Chl *a* concentraion (ug/L)	Fluor Chl *a* concentraion (ug/L)	Fluor Chl *a*/ Spec Chl *a*	QAQC	Comments
Cross River	1	36400	6.175	6.042	97.85	FD1-2	Old spec
	1	36401	4.210	4.743	112.65	FD2-2	
	1	36402	4.210	4.398	104.47		
	1	36403	4.678	4.573	97.76		
	1	36404	8.046	6.979	86.75		
	1	36405	24.324	23.742	97.61		
	2	36406	4.584	5.627	122.75		
	2	36407	4.678	4.450	95.12		
	2	36408	4.678	4.150	88.71		
	2	36409	8.326	5.629	67.60		
	2	36410	21.705	18.542	85.43		
	3	36411	4.678	5.408	115.60		
	3	36412	5.426	5.284	97.38	FD1-2	
	3	36413	4.958	5.025	101.34	FD2-2	
	3	36414	4.678	3.967	84.80		
	3	36415	5.052	5.128	101.51		
	3	36416	16.279	17.178	105.52		
Neversink	1	36440	1.328	1.851	139.34	FD1-2	New Spec
	1	36441	1.020	1.374	134.78	FD2-2	
	1	36442	0.861	1.375	159.71		
	1	36443	0.907	1.215	133.90		
	1	36444	0.767	1.238	161.44		
	1	36445	1.001	1.252	125.04		
	2	36446	0.870	1.205	138.44		
	2	36447	0.833	1.242	149.17		
	2	36448	1.067	1.565	146.70		
	2	36449	0.674	0.958	142.25		
	2	36450	0.814	0.822	100.96		
	3	36451	1.403	2.127	151.54		
	3	36452	1.160	1.635	140.91	FD1-2	
	3	36453	1.076	1.457	135.43	FD2-2	
	3	36454	1.132	1.561	137.87		
	3	36455	1.001	1.321	132.00		
	3	36456	0.477	0.718	150.48		
Cannonsville	5	36480	9.599	14.941	155.66	FD1-2	New Spec
	5	36481	11.807	17.400	147.38	FD2-2	
	5	36482	11.245	19.111	169.94		
	5	36483	11.881	19.516	164.26		
	5	36484	23.707	36.661	154.64		
	5	36485	1.909	4.804	251.72		
	4	36486	9.393	15.470	164.70		

Station Name	Reservoir Station	Sample No.	Spec Chl *a* concentraion (ug/L)	Fluor Chl *a* concentraion (ug/L)	Fluor Chl *a*/ Spec Chl *a*	QAQC	Comments
Cannonsville	4	36487	12.293	19.190	156.10		New Spec
	4	36488	15.231	22.989	150.94		
	4	36489	13.715	21.041	153.41		
	4	36490	3.237	4.152	128.26		
	3	36491	8.204	11.866	144.64		
	3	36492	18.201	24.545	134.86	FD1-2	
	3	36493	12.069	23.425	194.10	FD2-2	
	3	36494	15.044	26.321	174.96		
	3	36495	24.306	34.581	142.27		
	3	36496	2.582	2.332	90.29		
Amawalk	1	36520	5.248	6.987	133.13	FD1-2	New Spec
	1	36521	5.501	6.424	116.78	FD2-2	
	1	36522	5.464	6.530	119.52		
	1	36523	5.828	7.164	122.91		
	1	36524	5.389	7.024	130.35		
	1	36525	6.231	8.328	133.66		
	2	36526	3.340	6.013	180.02		
	2	36527	4.444	6.905	155.38		
	2	36528	2.559	6.017	235.13		
	2	36529	4.017	6.732	167.58		
	2	36530	5.052	12.495	247.33		
	3	36531	3.087	5.569	180.39		
	3	36532	4.219	6.361	150.77	FD1-2	
	3	36533	3.948	5.988	151.67	FD2-2	
	3	36534	4.081	6.081	149.00		
	3	36535	4.534	7.289	160.77		
	3	36536	2.030	3.834	188.88		
Pepacton	1	36560	4.912	6.680	136.01	FD1-2	New Spec
	1	36561	5.043	6.991	138.65	FD2-2	
	1	36562	6.025	6.173	102.46		
	1	36563	5.468	8.872	162.27		
	1	36564	5.445	6.580	120.85		
	1	36565	5.361	7.307	136.30		
	4	36566	5.520	7.913	143.36		
	4	36567	7.391	8.376	113.33		
	4	36568	6.755	9.885	146.34		
	4	36569	6.371	8.197	128.65		
	4	36570	3.403	4.476	131.53		
	5	36571	3.200	5.571	174.11		
	5	36572	3.546	7.410	209.00	FD1-2	
	5	36573	4.612	7.602	164.82	FD2-2	
	5	36574	5.492	7.347	133.78		
	5	36575	4.369	7.861	179.93		
	5	36576	4.902	7.893	161.01		
	3	36600	5.936	6.341	106.82	FD1-2	
	3	36601	4.182	8.037	192.18	FD2-2	
	3	36602	3.490	8.264	236.83		

Station Name	Reservoir Station	Sample No.	Spec Chl *a* concentraion (ug/L)	Fluor Chl *a* concentraion (ug/L)	Fluor Chl *a*/ Spec Chl *a*	QAQC	Comments
Pepacton	3	36603	4.176	8.002	191.64		New Spec
	3	36604	3.667	9.138	249.18		
	3	36605	2.161	5.012	231.92		
	6	36606	3.228	6.864	212.65		
	6	36607	3.826	6.018	157.27		
	6	36608	4.388	6.912	157.52		
	6	36609	2.404	7.813	324.97		
	6	36610	1.806	4.354	241.12		
	7	36611	4.472	7.590	169.73		
	7	36612	4.285	8.372	195.39	FD1-2	
	7	36613	3.162	7.502	237.25	FD2-2	
	7	36614	5.482	8.707	158.83		
	7	36615	5.239	7.754	148.00		
	7	36616	4.079	7.422	181.97		
Muscoot	1	36640	90.732	83.873	92.44	FD1-2	New Spec
	1	36641	48.064	50.647	105.37	FD2-2	
	1	36642	12.795	9.768	76.35		
	1	36643	10.535	9.555	90.71		
	1	36644	11.420	13.342	116.83		
	1	36645	8.395	8.952	106.64		
	2	36646	10.934	13.368	122.26		
	2	36647	11.492	4.791	41.69		
	2	36648	10.721	12.193	113.73		
	2	36649	8.570	10.766	125.62		
	2	36650	5.663	7.194	127.02		
	3	36651	11.214	13.007	115.99		
	3	36652	12.215	13.337	109.19		
	3	36653	10.811	12.198	112.83		
	3	36654	11.316	12.466	110.16		
	3	36655	8.198	9.194	112.14		
	3	36656	3.224	3.289	102.04		
Titicus	1	36680	6.240	6.696	107.31	FD1-2	New Spec
	1	36681	8.504	8.863	104.22	FD2-2	
	1	36682	9.655	9.920	102.75		
	1	36683	11.021	7.710	69.96		
	1	36684	10.169	10.455	102.81		
	1	36685	9.037	9.757	107.96		
	2	36686	5.754	5.938	103.20		
	2	36687	6.970	7.019	100.71		
	2	36688	6.437	5.946	92.38		
	2	36689	6.811	7.199	105.70		
	2	36690	6.699	8.827	131.78		
	3	36691	6.147	6.540	106.41		
	3	36692	5.379	6.022	111.94	FD1-2	
	3	36693	5.576	4.904	87.96	FD2-2	
	3	36694	5.669	6.050	106.71		
	3	36695	5.716	6.608	115.61		

Station Name	Reservoir Station	Sample No.	Spec Chl *a* concentraion (ug/L)	Fluor Chl *a* concentraion (ug/L)	Fluor Chl *a*/ Spec Chl *a*	QAQC	Comments
Titicus	3	36696	5.632	6.262	111.20		New Spec
		Old Spec Mean	8.040	7.698	97.815		
		Std Dev.	6.356	5.958	13.078		
		n	17	17	17		
		New Spec Mean	7.204	9.402	144.593		
		Std Dev.	9.679	10.049	43.092		
		n	119	119	119		
		Total Mean	7.309	9.189	138.746		
		Std Dev.	9.314	9.633	43.411		
		n	136	136	136		

Appendix 9.3. Accuracy of standards analyzed with reservoir chlorophyll samples. Standards do not enter into the computation of chlorophyll concentrations for they were obtained by entering sample absorbances or fluorescence values into equations. Standards ensure technician accuracy and that the fluorometer and spectrophotometer were functioning properly (i.e., standards were near the desired concentration of 40 µg/sample).

Appendix Table 9.3: Reproducibility of preparing and quantifying chlorophyll in standards run with reservoir chlorophyll analyses, Year 4 data, 2003.

Date of analysis	LCS No.	Vial #	Added µg/sample	Measured Chlorophyll *a (µg/sample)*	Percent measured/added
15-Jul-03	1	12	35.36	33.87	95.78
15-Jul-03	2	12	35.36	36.86	104.24
16-Jul-03	1	12	35.36	34.90	98.69
16-Jul-03	2	12	35.36	33.31	94.19
2-Sep-03	1	18	36.86	37.15	100.79
2-Sep-03	2	18	36.86	35.06	95.10
12-Sep-03	1	19	36.49	35.60	97.55
12-Sep-03	2	19	36.49	40.41	110.73
15-Sep-03	1	20	36.3	38.95	107.29
30-Sep-03	1	dilute1	38.77	38.77	100.00
30-Sep-03	2	dilute1	38.77	38.15	98.41
2-Oct-03	1	dilute1	38.77	38.01	98.04
12-Oct-03	1	dilute1	38.77	37.65	97.10
14-Oct-03	1	dilute1	38.77	37.44	96.57
22-Oct-03	1	dilute2	40.17	37.50	93.35
23-Oct-03	1	dilute2	40.17	39.69	98.80
30-Oct-03	1	dilute2	40.17	40.11	99.84
30-Oct-03	2	dilute2	40.17	40.13	99.89
15-Nov-03	1	dilute2	40.17	39.84	99.17
16-Nov-03	1	dilute2	40.17	40.41	100.59
			Conc. vials Mean	36.23	100.49
			SD	2.34	5.79
			n	9	
			Dilute1 Mean	38.00	99.58
			SD	0.51	4.24
			n	5	
			Dilute2 Mean	39.61	98.60
			SD	1.06	2.65
			n	6	
			Grand Mean	37.69	99.31
			SD	2.20	4.19
			n	20	

Appendix 9.4. Field duplicate samples for chlorophyll determinations were within 15% of each other.

Appendix Table 9.4: Precision of chlorophyll a determinations in reservoir samples assessed from the relative % difference of field duplicates (Dups.). Fluorometer data only.

Reservoir	Date	Station	Tag No.	Field Dups.	Chlorophyll *a* (µg/sample)	Relative % Difference Field Dups.	
Cross River	10-Jul-03	1	36400	1	12.08	24.09	*
			36401	2	9.49		
		3	36412	1	10.57	5.03	
			36413	2	10.05		
Neversink	6-Aug-03	1	36440	1	3.70	29.56	*
			36441	2	2.75		
		3	36452	1	3.27	11.49	
			36453	2	2.91		
Cannonsville	20-Aug-03	5	36480	1	14.94	15.21	
			36481	2	17.40		
		3	36492	1	27.00	4.03	
			36493	2	28.11		
Amawalk	10-Sep-03	1	36520	1	13.97	8.39	
			36521	2	12.85		
		3	36532	1	6.49	8.03	
			36533	2	5.99		
Pepacton	24-Sep-03	1	36560	1	13.36	4.55	
			36561	2	13.98		
		5	36572	1	14.82	2.55	
			36573	2	15.20		
	25-Sep-03	3	36600	1	11.41	33.91	*
			36601	2	16.07		
		7	36612	1	16.74	10.96	
			36613	2	15.00		
Muscoot	8-Oct-03	1	36640	1	93.94	25.18	*
			36641	2	72.93		
		3	36652	1	18.94	4.25	
			36653	2	19.76		
Titicus	23-Oct-03	1	36680	1	13.39	27.85	*
			36681	2	17.73		
		3	36692	1	12.04	20.45	*
			36693	2	9.81		
					Mean	14.74	
					SD	10.70	
					Median	11.23	

* Exceeds 20% limit for RPD.

Appendix 9.5. Solid standards held their calibration for long periods of time assuring fluorometer stability.

Appendix Table 9.5: Relative % difference (RPD) between solid secondary standard (SSS) at calibration and during fluorometric analysis.

Calibration Date	Solid Secondary Standard	FSU at calibration (FSU_{cal})	Analysis date	FSU on Analysis date (FSU_{anal})	RPD of FSU_{anal} vs. FSU_{cal}
7-Jul-03	HIGH	206.5	15-Jul-03	195	5.72852
			15-Jul-03	205	0.72904
			16-Jul-03	207	0.24184
			16-Jul-03	206	0.24242
			02-Sep-03	205	0.72904
			02-Sep-03	205	0.72904
			03-Sep-03	205	0.72904
			03-Sep-03	206	0.24242
			11-Sep-03	205	0.72904
			11-Sep-03	207	0.24184
			15-Sep-03	205	0.72904
			15-Sep-03	205	0.72904
			30-Sep-03	204	1.21803
			30-Sep-03	207	0.24184
			02-Oct-03	207	0.24184
			02-Oct-03	207	0.24184
			07-Oct-03	206	0.24242
			07-Oct-03	211	2.15569
			Mean	205.44	0.90
			SD	3.03	1.30
	LOW	38.4	15-Jul-03	38.1	0.78431
			15-Jul-03	38.2	0.52219
			16-Jul-03	38.2	0.52219
			16-Jul-03	37.9	1.31062
			02-Sep-03	37.8	1.5748
			02-Sep-03	38.4	0
			03-Sep-03	38	1.04712
			03-Sep-03	37.7	1.83968
			11-Sep-03	38.2	0.52219
			11-Sep-03	37.9	1.31062
			15-Sep-03	37.9	1.31062
			15-Sep-03	37.2	3.1746
			30-Sep-03	37.7	1.83968
			30-Sep-03	38.6	0.51948
			02-Oct-03	37.7	1.83968
			07-Oct-03	37.7	1.83968
			07-Oct-03	38.3	0.26076
			Mean	37.97	1.19
			SD	0.33	0.79

Calibration Date	Solid Secondary Standard	FSU at calibration (FSU_{cal})	Analysis date	FSU on Analysis date (FSU_{anal})	RPD of FSU_{anal} vs. FSU_{cal}
28-Oct-03	HIGH	213.5	28-Oct-03	215	0.70012
			29-Oct-03	197	8.03898
			29-Oct-03	207	3.09156
			29-Oct-03	215	0.70012
			29-Oct-03	217	1.62602
			30-Oct-03	213	0.23447
			03-Nov-03	215	0.70012
			03-Nov-03	215	0.70012
			03-Nov-03	212	0.70505
			03-Nov-03	213	0.23447
			04-Nov-03	217	1.62602
			04-Nov-03	216	1.16414
			15-Nov-03	215	0.70012
			15-Nov-03	214	0.23392
			18-Nov-03	212	0.70505
			18-Nov-03	215	0.70012
			Mean	213.00	1.37
			SD	4.90	1.92
	LOW	39.45	28-Oct-03	39.6	0.37951
			29-Oct-03	39.7	0.63171
			29-Oct-03	40	1.38452
			29-Oct-03	39.9	1.13422
			29-Oct-03	38.7	1.91939
			30-Oct-03	39.7	0.63171
			03-Nov-03	40.2	1.88324
			03-Nov-03	39.6	0.37951
			03-Nov-03	40	1.38452
			03-Nov-03	40.3	2.13166
			04-Nov-03	40	1.38452
			04-Nov-03	39.7	0.63171
			15-Nov-03	39.9	1.13422
			15-Nov-03	39.4	0.12682
			18-Nov-03	40	1.38452
			18-Nov-03	39.8	0.88328
			Mean	39.78	1.09
			SD	0.37	0.60

Appendix 9.6. The RPD (relative percent difference) for GPP in samples collected from the same reservoir substation averaged 19.5% with most values < 30%. The RPD for respiration in samples collected from the same substation averaged 25.3% with most values < 30%.

Appendix Table 9.6: Variability in dissolved O_2 change associated with replicate bottles filled with water from the same location.

Reservoir and Subsite	Date	Depth (m)	GPP/h (g DO $m^{-3} \cdot h^{-1}$)	Volumetric GPP/h		Volumetric CR/h (g DO $m^{-3} \cdot h^{-1}$)	Data quality*	RPD	
				Mean	SD			GPP/h	CR/h
Neversink (1)	6-Aug-03	0	0.0185	0.0157	0.0039	-0.0148		7.64	-44.68
			0.0129						
		0 dup	0.015	0.017	0.0027	-0.0094			
			0.0189						
Neversink (3)		2.75	0.0217	0.0228	0.0017	-0.0168		8.98	-11.74
			0.024						
		2.75 dup	0.0224	0.025	0.0036	-0.0149			
			0.0275						
Muscoot (1)	8-Oct-03	0	0.4035	0.4033	0.0003	-0.0493	a	66.91	-64.81
			0.4031				a		
		0 dup	0.2153	0.2011	0.0201	-0.0252	b		
			0.1869				b		
Muscoot (3)		0.75	0.2048	0.2087	0.0056	-0.0211	b	18.94	-1.75
			0.2126				b		
		0.75 dup	0.1676	0.1726	0.007	-0.0208	b		
			0.1776				b		
Cross River (1)	10-Jul-03	0	0.0397	0.0486	0.0127	-0.0251		12.33	-5.9
			0.0576						
		0 dup	0.0531	0.055	0.0027	-0.0237			
			0.0569						
Amawalk (1)	10-Sep-03	0	0.086	0.0759	0.0144	-0.0258	b	10.46	-24.44
			0.0657				b		
		0 dup	0.0733	0.0842	0.0155	-0.0202	b		
			0.0952				b		

Appendix Table 9.6 (continued):

Reservoir and Subsite	Date	Depth (m)	GPP/h ($g\ DO \cdot m^{-3} \cdot h^{-1}$)	Volumetric GPP/h		Volumetric CR/h ($g\ DO \cdot m^{-3} \cdot h^{-1}$)	Data quality*	RPD	
				Mean	SD			GPP/h	CR/h
Amawalk (3)	10-Sep-03	1.75	0.1012	0.1015	0.0005	-0.0197	b	2.09	-4.18
			0.1018				b		
		1.75 dup	0.0984	0.0994	0.0013	-0.0205	b		
			0.1003				b		
Cannonsville (5)	20-Aug-03	0	0.05	0.0471	0.0041	-0.0577	c	23.16	-1.29
			0.0442				c		
		0 dup	0.0663	0.0594	0.0097	-0.0584	c		
			0.0525				c		
Cannonsville (3)		1.5	0.1751	0.1784	0.0046	-0.0432	b	7.61	-1.68
			0.1817				b		
		1.5 dup	0.1944	0.1925	0.0027	-0.0425	b		
			0.1906				b		
Titicus (1)	23-Oct-03	0	0.064	0.0662	0.003	-0.0259		26.08	-5.99
			0.0683				b		
		0 dup	0.0879	0.086	0.0026	-0.0244	b		
			0.0842				b		
Titicus (3)		1	0.0637	0.0624	0.0018	-0.0105	b	4.51	-130.92
			0.0612				b		
		1 dup	0.0733	0.0653	0.0113	-0.0022	b		
			0.0573				b		
Pepacton (1)	24-Sep-03	0	0.0276	0.0205	0.01	-0.0571	c	60.89	-8.08
			0.0135				a		
		0 dup	0.042	0.0385	0.0049	-0.0526	c		
			0.035				c		
Pepacton (5)		1.5	0.0788	0.0807	0.0027	-0.0148	b	0.27	-23.62
			0.0826				b		
		1.5 dup	0.0836	0.0805	0.0043	-0.0187	b		
			0.0775				b		

Appendix Table 9.6 (continued):

Reservoir and Subsite	Date	Depth (m)	GPP/h (g DO $\cdot m^{-3} \cdot h^{-1}$)	Volumetric GPP/h		Volumetric CR/h (g DO $\cdot m^{-3} \cdot h^{-1}$)	Data quality*	RPD	
				Mean	SD			GPP/h	CR/h
Pepacton (3)	25-Sep-03	0	0.044	0.0504	0.0091	-0.0087		25.36	-24.76
			0.0569				b		
		0 dup	0.0671	0.0651	0.0029	-0.0112	b		
			0.063				b		
Pepacton (7)		1.75	0.0419	0.0421	0.0002	-0.0119		17	-26.1
			0.0422						
		1.75 dup	0.0307	0.0355	0.0068	-0.0092			
			0.0403						

* a: Change in dissolved O_2 > 0.2 mg/L for NPP & CR, b: Change in dissolved O_2 > 0.2 mg/L for NPP, c: Change in dissolved O_2 > 0.2 mg/L for CR.

Appendix 9.7. The QC summaries associated with inorganic chemistry assays of reservoir samples indicated no problems with blanks or lab duplicate samples. Recoveries of matrix spikes were close to 100% but for TDP. Replication of field duplicate samples for total alkalinity was within specifications except for one exceedence.

Appendix Table 9.7: QC summary of alkalinity field duplicates and field blanks, and nutrient laboratory blanks, duplicates and spikes performed with reservoir samples, Year 4 data, 2003.

	Alkalinity	NH_4N	NO_3N	SRP	TDP
	mg $CaCO_3$/L		mg/L		
Field duplicates*					
# of samples	16				
# of duplicate pairs for RPD calc.	8				
Mean RPD	9.38				
Max. RPD	21.94				
# of samples >20% RPD	1				
# of duplicate pairs for Abs Diff calc.	8				
Mean Abs Diff	0.14				
Max. Abs Diff	0.3				
# of samples > DL	0				
Blanks					
# of samples		38	27	39	22
Mean		0.004	0.004	0.001	0.001
SD		0.003	0.002	0.001	0.001
QC detection limit (DL)		0.011	0.02	0.003	0.01
# exceeding 2x(DL)		0	0	0	0
Laboratory duplicates*					
# of samples		10	10	10	10
# of duplicate pairs for RPD calc.		0	0	0	0
Mean RPD					
Max. RPD					
# of samples >20% RPD					
# of duplicate pairs for Abs Diff calc.		5	5	5	5
Mean Abs Diff		0.0006	0.0004	0.0004	0.0008
Max. Abs Diff		0.001	0.001	0.001	0.002
# of samples > DL		0	0	0	0
Matrix spike recovery					
# of samples		5	5	5	5
Mean % Recovery		96.36	98.89	98.18	127.68
SD		1.53	0.54	2.61	69.25

* If the mean of a pair of duplicate samples was < 5 times the DL then the absolute difference was used to evaluate the duplicate precision. Values were flagged if the absolute difference of a duplicate pair was > the DL.