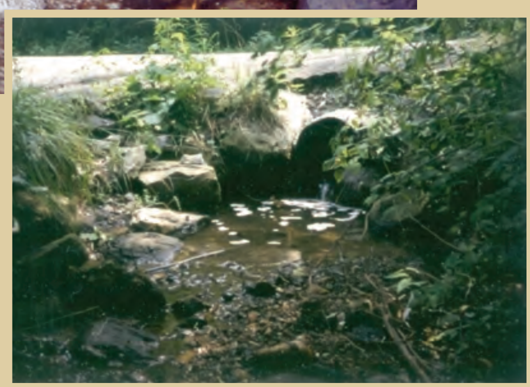
Prepared in cooperation with
State University of New York Research Foundation for the
New York City Department of Environmental Protection

Nutrients, Dissolved Organic Carbon, Color, and Disinfection Byproducts in Base Flow And Stormflow in Streams of the Croton Watershed, Westchester and Putnam Counties, New York, 2000–02



Open-File Report 2009–1054

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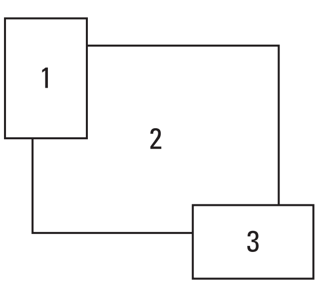
Cover.



1. Cross River tributary at Ward Pound Ridge Reservation, Cross River, Westchester County, New York
2. Sample site YRK, with passive sampler, control structure, and staff/crest gages, Yorktown, Westchester County, New York
3. Tributary of Lake Carmel, Lake Carmel, Westchester County, New York

Nutrients, Dissolved Organic Carbon, Color, and Disinfection Byproducts in Base Flow and Stormflow in Streams of the Croton Watershed, Westchester and Putnam Counties, New York, 2000–02

By Paul M. Heisig

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Preface

This report provides results from a 1999–2002 investigation that was part of an overall evaluation of the Croton Watershed, which includes 12 reservoirs in Westchester and Putnam Counties, N.Y., that provide about 10 percent of New York City's water supply. The City was weighing a decision on whether or not to construct a water-filtration plant for this water supply. The investigation, the Croton Terrestrial Processes Project, was carried out by the State University of New York School of Environmental Science and Forestry, the Upstate Freshwater Institute, and the U.S. Geological Survey.

The project had two major work components:

(1) determination of tributary loading to the reservoirs in support of a parallel study of the Croton Watershed reservoirs conducted by the Upstate Freshwater Institute, and

(2) investigation of the effects of suburban development (land use, wastewater disposal, riparian wetlands) on runoff generation and water quality, including both an intensive study of the watershed (Burns and others, 2005), and a "broadbrush" study (this report) that documented water-quality conditions at a variety of land-use/drainage-efficiency settings across the Croton Watershed.

Most results from the overall project were written up and provided directly to the New York City Department of Environmental Protection (NYCDEP) and were not published. These reports are on file at NYCDEP and with the respective authors.

Selected reference:

Burns, D.A., Vitvar, Tomas, McDonnell, Jeffrey, Hassett, James, Duncan, Jonathan, and Kendall, Carol, 2005, Effects of suburban development on runoff generation in the Croton River basin, New York, USA: Journal of Hydrology, v. 311, no. 4, p. 266–281.

[1]The following section describes the overall project goals, work components, and investigators.

[1] Hassett, J.M., 2003, Croton terrestrial processes project—final report, volume 1, chapter 2, project goals and organization: New York City Department of Environmental Protection, 24 p.

2.0 Project Goals and Organization

2.1 Introduction

The Project represented a complex series of tasks motivated by science questions and management issues. The science questions, as stated in the contract are:

1. What are the sources of N, P, TOC, DOC, color and disinfection by-product (DBP) precursors?
2. Can the sources be partitioned as to relative importance by land use, land cover, topography, or other geographic variables?
3. How are these constituents transported to the nearest stream course?

4. What transformations do these constituents undergo before reaching a reservoir?

The contract listed several more specific questions:

- What are the sources of runoff in the catchment?
- What are the residence times of water entering the stream and how does this relate to the stream water chemistry?
- What are the flowpaths of water to the stream and how do they control stream color, DOC, DBP precursors, N biogeochemistry and P transport?
- How does landuse affect water and solute export to the stream and ultimately the reservoir?

A series of interrelated tasks were generated to manage data gathering efforts. In keeping with the scientific nature of the effort, the tasks were stated as hypotheses, to wit:

A2.1 Characterization of Nutrient and Color Can Be Predicted Using a Basin-Wide Source Assessment

A2.2 Characterization of Organic Carbon Sources and Their DBP Formation Potential Can Be Predicted Using a Basin-Wide Assessment for DBPs

A2.3 DOC Flushing and Draining and N Transformations Can Be Predicted by the Topographic Index and Catchment Position

A2.4 Wetland Zones are "Hot Spots" for Contributions of Elevated DOC and Increase "Color" to Streams

A2.5 Water Residence Time and Its Control on Solute Contact Time and Water Color

A2.6 Runoff Production Mechanisms and Flowpaths are Different in the 3 Selected Watersheds - These Different Mechanisms Control the Export of Nutrients at the Watershed Scale

A2.7 Geographic Sources of Water Can Be Determined Using End Member Mixing and Isotope Hydrograph Separation Techniques

A2.8 The Field Data Can Be Linked into a Series of GIS-Based Series of Models, Each Sharing Common Data, to be Used by the DEP to Investigate a Variety of Management Scenarios.

The field and modeling efforts were closely linked, as shown in Table 3-1.

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Table 2-1. Review of Tasks Implemented in Croton Terrestrial Processes Study

Task	Process(es)	Field Work	Model Issues
Tasks A1.1 and A1.2. Loadings from tributaries to reservoirs	Transport via first and second order streams, and rivers draining upstream reservoirs	Nutrients, color, HAA formation potential, THM formation potential, flows	Loadings needed for reservoir analysis, but loadings converted to export coefficients and used to extend information from Tasks A2.1 and A2.2
A2.1 Characterization of Nutrient and Color Sources Can Be Predicted Using a Basin-Wide Source Assessment	Transport via first and second order streams	Nutrients, color, land uses, base flow, storm flow at broad brush sites	Export coefficients, regression techniques, synthesis of land uses
A2.2 Characterization of Organic Carbon Sources and Their DBP Formation Potential Can Be Predicted Using a Basin-Wide Source Assessment	Transport via first and second order streams	Nutrients, color, land uses, base flow, storm flow, HAA formation potential, THM formation potential at broad brush sites	Export coefficients, regression techniques, synthesis of land uses
A2.3 DOC Flushing and Draining and N Transformations Can Be Predicted by the Topographic Index and Catchment Position	DOC and N transported to stream via rising water table in response to storm events, seasonal high water table, snow melt.	Throughfall samplers, soil solution samplers (i.e., lysimeters), water table observation wells, piezometers. DOC and N series measured during baseflow and storm runoff at basin outlet and places within the basin.	2-m and 10-m maps used to calculate topographic index (i.e., $\ln(A/\tan\beta)$). TOPMODEL used to predict areas of recharge to stream via groundwater or saturation excess overland flow.
A2.4 Wetland Zones are “Hot Spots” for Contributions of Elevated DOC and Increase “Color” to Streams	Wetlands generate DOC and “color”, presumably as a result of carbon cycling in wetlands. Color and DOC may be transported via either baseflow or stormflow.	Synoptic surveys (water quality at streams draining wetland sites during baseflow), piezometers, ‘peepers’, baseflow and storm flow sampling from selected wetlands.	Geochemical mixing models (such as ARGUS, MINEQL, etc.).

Table 2-1. Review of Tasks Implemented in Croton Terrestrial Processes Study

Task	Process(es)	Field Work	Model Issues
A2.5 Water Residence Time and its Control on Solute Contact Time and Water Color	Older water contributes a different chemical and isotopic signature to streamflow as compared to newer or event water. Age of water at different points in the watershed determined by stable isotopes.	Precipitation, groundwater (from wells and piezometers), sequential rainfall, ISCO sampling of stream during runoff events.	Information compared to model output, particularly TOPMODEL as it relates to predictions of flowpaths.
A2.6 Runoff Production Mechanisms are Different in the 3 Selected Watersheds – These Different Mechanisms Control the Export of Nutrients at the Watershed Scale	Urbanization causes a shift in runoff from saturation excess overland flow to infiltration excess overland flow, creating a change in timing of runoff and transport of nutrients.	Precipitation, runoff, soil properties (i.e., infiltration rates determined using ring infiltrometers, saturated hydraulic conductivities, etc.), chemical signatures, contribution of groundwater/event water to runoff.	Water balance (measured vs. predicted) for the three intensive sites. Parameters to fit data from three sites (i.e., per cent impervious cover to explain differences in runoff timing; infiltration excess overland flow to explain chemical signatures of water).
A2.7 Geographic Sources of Water Can Be Determined Using End Member Mixing Analysis and Isotope Hydrograph Separation Techniques	Urbanization causes a shift that favors large contributions to stream runoff from impervious parts of the watershed.	Precipitation, groundwater (from wells and piezometers), surface runoff samplers, sequential rainfall, ISCO sampling of stream during runoff events.	Data from mixing analyses used to help parameterize models as to predicted versus observed concentration-discharge relationships.

2.2 Personnel

Table 2-2 identifies the Principal Investigators associated with each task.

Table 2-2. Principal Investigators Associated with Project Tasks

Task	Principal Investigator(s)	Affiliation
Project Management	James M. Hassett	SUNY-ESF
Tasks A1.1 and A1.2. Loadings from tributaries to reservoirs	James Hassett Steven Effler Paul Heisig	SUNY-ESF Upstate Freshwater Inst. US Geological Survey
A2.1 Characterization of Nutrient and Color Sources Can Be Predicted Using a Basin-Wide Source Assessment	Paul Heisig	US Geological Survey
A2.2 Characterization of Organic Carbon Sources and Their DBP Formation Potential Can Be Predicted Using a Basin-Wide Source Assessment	Paul Heisig	US Geological Survey
A2.3 DOC Flushing and Draining and N Transformations Can Be Predicted by the Topographic Index and Catchment Position	Myron Mitchell Douglas Burns Jeffrey McDonnell	SUNY-ESF US Geological Survey Oregon State University

Table 2-2. Principal Investigators Associated with Project Tasks

Task	Principal Investigator(s)	Affiliation
A2.4 Wetland Zones are "Hot Spots" for Contributions of Elevated DOC and Increase "Color" to Streams	Donald Siegel	Syracuse University
A2.5 Water Residence Time and its Control on Solute Contact Time and Water Color	Myron Mitchell Douglas Burns Jeffrey McDonnell	SUNY-ESF US Geological Survey Oregon State University
A2.6 Runoff Production Mechanisms are Different in the 3 Selected Watersheds – These Different Mechanisms Control the Export of Nutrients at the Watershed Scale	Myron Mitchell Douglas Burns Jeffrey McDonnell	SUNY-ESF US Geological Survey Oregon State University
A2.7 Geographic Sources of Water Can Be Determined Using End Member Mixing Analysis and Isotope Hydrograph Separation Techniques	Myron Mitchell Douglas Burns Jeffrey McDonnell	SUNY-ESF US Geological Survey Oregon State University
A2.8 The Field Data Can Be Linked into a Series of GIS-Based Series of Models, Each Sharing Common Data, to be Used by the DEP to Investigate a Variety of Management Scenarios.	Theodore Endreny	SUNY-ESF

2.3 Project Duration

Various issues caused the original conception as to project duration to be modified. The project occurred in three distinct phases. The reservoir component began first, with field sampling beginning in April 1999, and continued during the limnological season (i.e., April - November) until the end of 2001. The tasks associated with the reservoir component are described in the final report for that component (UFI, 2003); selected sections of the tributary loading studies (Tasks A1.1 and A1.2) are reported here as well (see Section 3).

The 'broadbrush' tasks (Tasks A2.1 and 2.2) began in June 2000, the wetlands studies (Task A2.4) began during May 2000. The intensive site tasks (A2.3, 2.5-7) began in August 2001 and ended in August 2002. Some instruments in some of the intensive sites were installed earlier, and thus some data were gathered for more than the one year originally envisioned. The modeling tasks (A2.8, 3.1) lasted throughout the duration of the study. The general duration of each task is shown in Figure 2-1; note that the broadbrush and wetlands tasks were extended to provide some overlap with the intensive site studies.

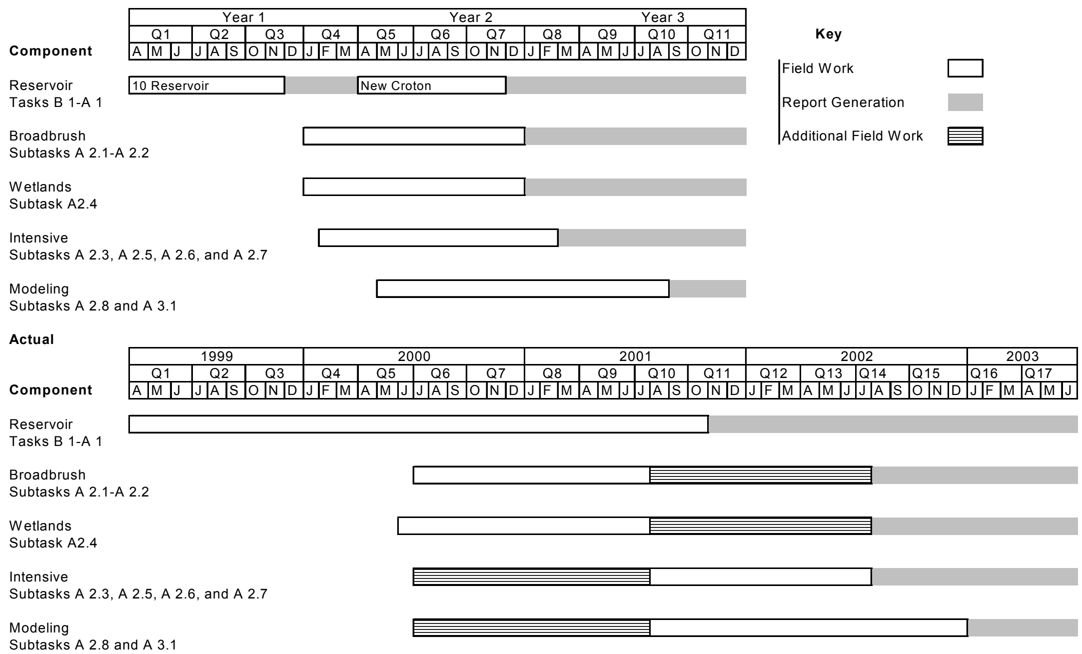

Figure 2-1. Duration of tasks as planned in the contract (top half) and as actually implemented (bottom half). The additional field work was conducted so as to provide some overlap among the tasks to allow for comparisions under similar hydrologic conditions.

2.4 Sampling Locations and Hydrologic Conditions

2.4.1 Sampling Locations

Figure 2-2 shows the general location of the sampling sites for the Terrestrial Process tasks in the context of the Croton system. The sites for the different tasks represent a broad range of land uses within the Croton watershed, as will be discussed subsequently.

2.4.2 General Hydrologic Conditions

As noted above, the tasks were conducted in phases as dictated by several factors; e.g., status of contract issues, sub-contracts, site permissions, etc. Figure 2-3 shows the annual hydrograph (by water year) for Angle Fly Brook (USGS ID 01371976), a gaged stream in operation over the course of the study. The figures show sampling events for the tasks identifed above, and provide a general view of the hydrologic conditions extant in the Croton watershed during the study. Of particular note are the low flows reflecting the drought conditions which prevailed from summer 2001 into 2002, which corresponded to the intensive site sampling.

It should be noted that a sampling event as indicated on Figure 2-3 represented sampling from several sites, as indicated on Figure 2-2. Further, some of

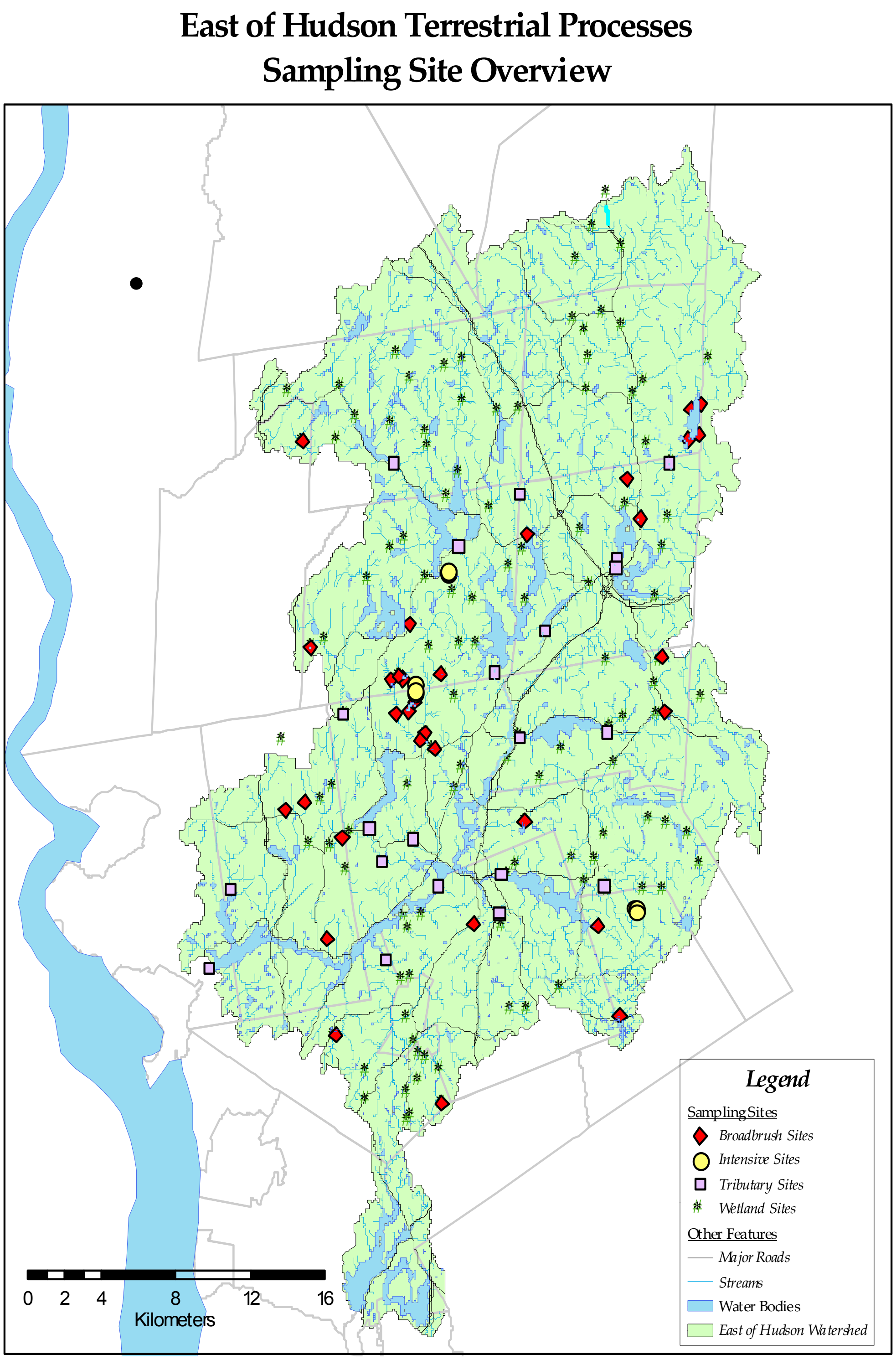

Figure 2-2. Sampling sites locations indicated by task. Each sampling site was sampled numerous times for a range of water quality constituents during the course of the Croton Terrestrial Process Study.

x

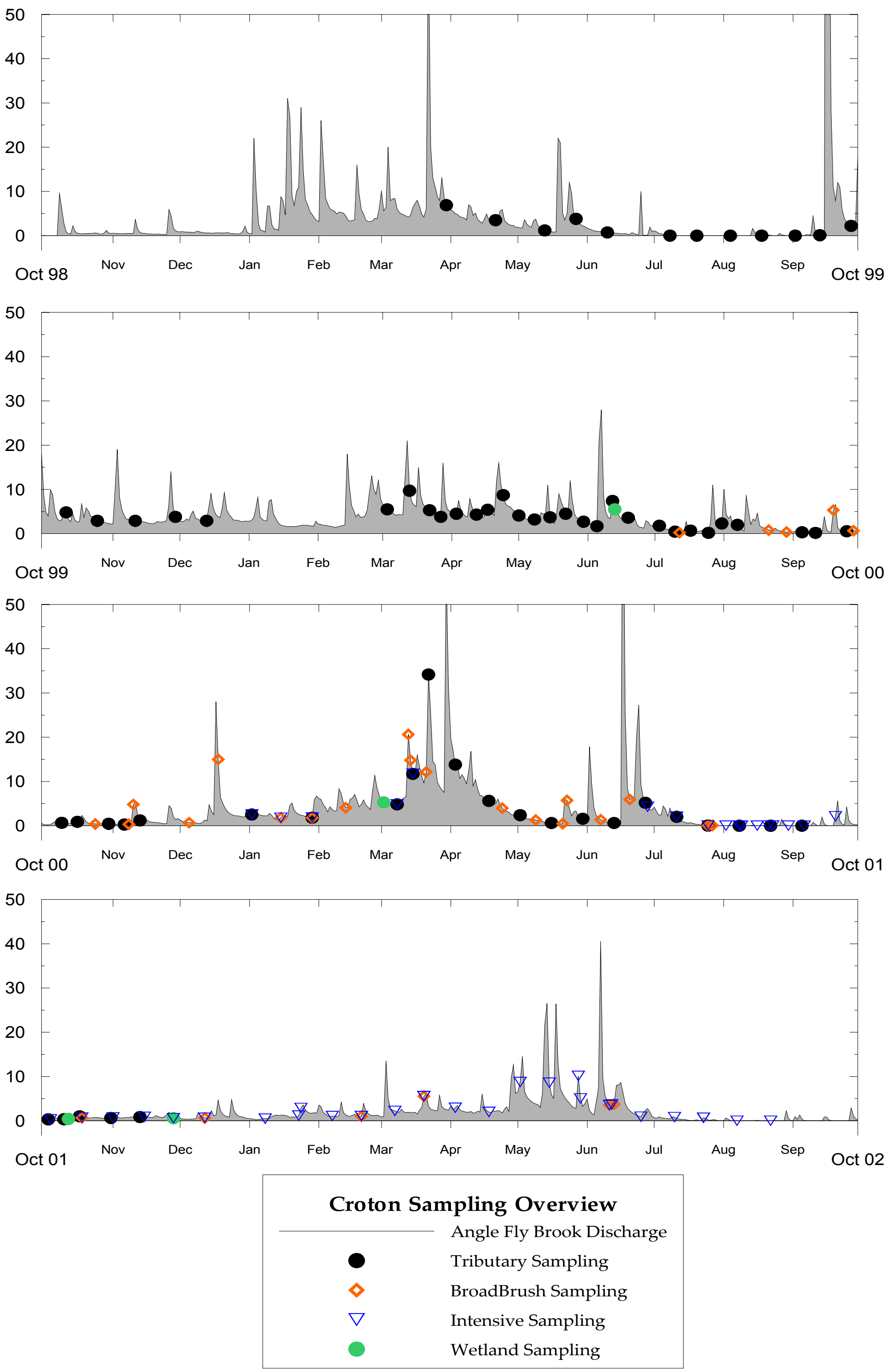

Figure 2-3. Flow (cfs) at USGS gage on Angle Fly Brook related to sampling events. See Figure 2-2 for sampling locations. Note the severe drought conditions associated with the onset of Intensive Site Sampling.

the sampling efforts, i.e., storm sampling, represented multiple samples from the same location over a short period of time.

2.4.3 Field and Laboratory Methods

The field and laboratory methods utilized in support of the investigations were documented in the Croton Project Quality Assurance Plan submitted to the NYC Department of Environmental Protection prior to the onset of field work. Methods will be described, as appropriate, in succeeding sections. In general, samples were collected in accorcance with the project protocols, sent to one of five labs, with results returned to the Principal Investigator and project database.

The tasks were designed and implemented in support of different objectives, and therefore the analytical requirements varied slightly from task to task. In addition, budget factors caused some analyses to be shifted from one lab to another. The next table shows the analyses performed in support of the tasks.

Table 2-3. Laboratory Analyses Conducted in Support of Croton Terrestrial Process Study Tasks

Task	Analyses	Comment
Tasks A1.1 and A1.2. Loadings from tributaries to reservoirs	Nutrients (N and P species) Color (DOC, g440, UV254, Mn, Fe, etc.)	Data and analyses submitted as a part of the final report for Component B of the Croton Project. Some information extracted and presented as a part if this report.
A2.1 and A2.2 Characterization of Nutrient and Color Sources and Organic Carbon Sources and Their DBP Formation Potential Can Be Predicted Using a Basin-Wide Source Assessment	Nutrients (N and P species) Color (DOC, g440, UV254, Mn, Fe, etc.) Disinfection by-product precursors	Full suite of analyses for one year. A subset of the analyses were performed during the extended second year.
A2.4 Wetland Zones are “Hot Spots” for Contributions of Elevated DOC and Increase “Color” to Streams	Geochemistry (Ca, Mg, Cl, etc.) Limited nutrient (N species) Color (DOC, g440, UV254, Mn, Fe, Fluorescence. etc.)	Synoptic sampling events independent of other tasks.
Intensive sites (A2.3, 2.5-7)	Geochemistry (Ca, Mg, Cl, etc. Nutrients (N and P species) DOC, Disinfection by-product precursors (outlet and selected storm samples)	Overlap with Tasks A2.1 and 2.2 in that samples at outlet were part of the basin-wide source assessment.

Table 2-4 shows the number of analyses performed in support of the Terrestrial Processes tasks. The table does not include data for the tributary loading tasks nor the various ‘speciality’ studies, e.g., the wetlands synoptic surveys, the deep water study conducted in B28, etc. and thus represents a conservative estimate of the overall analytical effort.

Table 2-4. Approximate Number of Laboratory Analyses Done in Support of Croton Terrestrial Process Study Tasks

Lab	Analyte	# Analyses	Analyte	# Analyses
Geochemistry, Syracuse University	Ca	1975	Mg	1963
	Si	1976	Al	761
	Fe	1976	K	1976
	Sr	1976	S	1975
Biogeochemistry, SUNY-ESF	pH	2020	Cl	1942
	NH_4	1988	Br	1791
	Na	1925	NO_3	1940
	K	1926	SO_4	1943
	Ca	1926	Total N	1975
	Mg	1926	DOC	1930
	Total Al	1926		
Upstate Freshwater Institute	NH_4	687	Dissolved Fe	468
	NOx	704	Dissolved Mn	469
	TDN	677	Total Mn	521
	SRP	590	Filtered Color	779
	TDP	866	Total Color	669
	TP	2172	g440	597
	DIC	39	UV254	689
	DOC	1173	Chlorophyll	312
	POC	465	Chlorophyll	507
	SiO_2	544	TSS	208
Environmental Chemistry, SUNY-ESF	Filtered:		Total:	
	Chloroform	1073	Chloroform	1073
	DCB	1086	DCB	1099
	DBC	1086	DBC	1099
	Bromoform	1086	Bromoform	1099
	TTHMfp	1012	TTHMfp	1018
	CAA	1031	CAA	1081
	BAA	1024	BAA	1067
	DCAA	1031	DCAA	1081
	TCAA	1031	TCAA	1081
	BCAA	1030	BCAA	1081
	BDCAA	1031	BDCAA	1081
	DBAA	1024	DBAA	1067
	CDBAA	1024	CDBAA	1067
	TBAA	1024	TBAA	1067
USGS Stable Isotope Lab	^{18}O		^{2}H	

Table 2-4. Approximate Number of Laboratory Analyses Done in Support of Croton Terrestrial Process Study Tasks

Lab	Analyte	# Analyses	Analyte	# Analyses
Notes: DOC = Dissolved organic carbon; NOx = nitrate + nitrite; TDN = Total dissolved nitrogen; TDP = Total dissolved phosphate; TP = Total phosphate; DIC = Dissolved inorganic carbon; POC = Particulate organic carbon; TSS = Total suspended solids; Chloroform = Trichloromethane; DCB = Dichlorobromomethane; DBC = Dibromochloromethane; Bromoform = Tribromomethane; TTHMfp = Total trihalomethane formation potential; CAA = Chloroacetic acid; BAA = Bromoactetic acid; DCAA = Dichloroacetic acid; TCAA = Trichloroacetic acid; BCAA = Bromochloroacetic acid; BDCAA = Bromodichloroacetic acid; DBAA = Dibromoacetic acid; CDBAA = Chlorodibromoacetic acid; TBAA = Tribromoacetic acid.				

Table 2-5. Review of Laboratory Methods and Detection Limits

Analyte	Method	Method Detection Limit
Organic Carbon, dissolved (DOC)	Combustion-Infrared MethodSM18 (5310 B.)	0.1 mg/l
Inorganic Carbon, dissolved (DIC)	UV persulfate SM18 (5310 C.)	0.1 mg/l
Solids, Total Suspended (TSS)	Gravimetric SM18 (2540 D.)	1.0 mg/l
Hydrogen Ion (pH)	Electromertic SM18 (4500-H+ B.)	
Phosphorus, Total (TP)	Manual single reagent (ascorbic acid) Persulfate digestion SM18 (4500-P.B. 5)	0.6 ug/l
Alkalinity	Electrometric SM18 (2320-B.)	20.0 mg/l
Ammonia (as N)	Automated Phenate EPA (350.1)	10.0 ug/l
Nitrate + Nitrite (NO_x as N)	Automated Cadmium reduction EPA (353.2)	10.0 ug/l
Orthophosphate (as P)	Manual single reagent (ascorbic acid) SM18 (4500-P E.)	0.3 ug/l
Sulfide	Iodometric SM18 (4500-S2-)	1.0 mg/l
Temperature	SM18 (2550 B.)	
Color	Platinum Cobalt, HACH 455nm automated non acidified SM18 (2120 B.)	2 CU
Dissolved Silica (Si)	Molydbosilicate Method SM18 (4500-Si D.)	0.4 mg/l
Iron, total & dissolved Fe-T; Fe-D)	Atomic Absorption Spectrometric, acidified/non digested SM18 (3111B or 3113B)	0.1 ug/l
Manganese, total & dissolved (Mn-T; Mn-D)	Atomic Absorption Spectrometric, acidified/non digested SM18 (3111B or 3113B)	0.1 ug/l
Turbidity	Nephelometric, SM18 (2130 B.)	0.1 NTU
Chlorophyll	Spectrophotometric Parsons et. al. 1984	

Table 2-5. Review of Laboratory Methods and Detection Limits

Analyte	Method	Method Detection Limit
Total Dissolved Nitrogen (TDN)	1999 - Persulfate-boric acid digestion Ebina, 1983, cadmium reduction (EPA 353.2) or 2000 Pyrochemolu-minscence ANTEK	10 ug/l
Particulate Organic Nitrogen (PON)	Concentration onto a glass fiber filter/ digestion/distillation SM18 (4500-Norg C.)	
Particulate Organic Carbon (POC)	Concentration onto a glass fiber filter/ acid fuming/ SM18 (5310B.) using "boat attachment" for DC 190	
Particulate Phosphorous (PP)	Concentration onto a membrane filter, then as total phosphorus SM18 (4500-P.B. 5)	
g440	Spectrophotometric Davies-Colley and Vant (1987)	0.02/m
UV 254		
Chloride	Ion chromatography. Laboratory Analyses for Surface Water Chemistry. EPA 600/4-87/026.	0.01 mg/l
Sulfate	Ion chromatography. Laboratory Analyses for Surface Water Chemistry. EPA 600/4-87/026.	0.005 mg/l
Nitrate (NO_3^-)	Ion chromatography. Laboratory Analyses for Surface Water Chemistry. EPA 600/4-87/026.	0.05 mg/l
Trihalomethanes (THM)	EPA Method 502.2 (modifications noted in text)	Chloroform: 0.54 ug/l Dichlorobromoform: 0.40 ug/l Dibromochloroform: 0.58 ug/l Bromoform: 0.40 ug/l
Haloacetic Acids: (HAA)	EPA Method 552.2	Chloroacetic Acid: 0.60 ug/l Bromoacetic Acid: 0.20 ug/l Dichloroacetic Acid: 0.24 ug/l Trichloroacetic Acid: 0.20 ug/l Bromochloroacetic Acid: 0.25 ug/l Dibromoacetic Acid: 0.40 ug/l
Chloroform (Trichloromethane)	EPA Method 502.2(modifications noted in text)	0.54 ug/l
Dichlorobromoform (DCB)	EPA Method 502.2(modifications noted intext)	0.40 ug/l
Dibromochloroform (DBC)	EPA Method 502.2(modifications noted in text)	0.58 ug/l
Bromoform (Tribromomethane)	EPA Method 502.2(modifications noted intext)	0.40 ug/l
Chloroacetic Acid (CAA)	EPA Method 552.2	0.60 ug/l
Bromoacetic Acid (BAA)	EPA Method 552.2	0.20 ug/l
Dichloroacetic Acid (DCAA)	EPA Method 552.2	0.24 ug/l
Trichloroacetic Acid (TCAA)	EPA Method 552.2	0.25 ug/l

Table 2-5. Review of Laboratory Methods and Detection Limits

Analyte	Method	Method Detection Limit
Bromochloroacetic AcidBCAA)	EPA Method 552.2	0.25 ug/l
Dibromoacetic Acid (DBAA)	EPA Method 552.2	0.40 ug/l
Na	Spectrospan DCP-III	~20 ug/L
K	Spectrospan DCP-III	~20 ug/L
Ca	Spectrospan DCP-III	~20 ug/L
Mg	Spectrospan DCP-III	~20 ug/L

2.5 Quality Assurance

The quality control/quality assurance programs in place in each of the five laboratories were described in the Croton Project Quality Assurance Plan. Additional QA/QC methods were employed as the data was transferred from the labs to the PIs and the project database. The PIs reviewed the data as related to their tasks and communicated with the lab directors to resolve any apparent issues.

The data were rescrutinized as they were transferred into the project database. In particular, the information conveyed from the field via the Chain of Custody forms was compared to the data from the labs. As described later, each sampling event was assigned a unique ID for the database; this allowed a comparison of lab results (with their own IDs) to the chain of custody information to further resolve questions as to sample identification, etc.

The data in the final database were further scutinized. The distribution of values for each analyte was examined for outliers. Given the preceding quality control checks, a conservative approach was taken. When necessary, the database manager communicated further with the lab director(s). In all, far fewer than 1% of the data were questioned at this point, and most values remained in the data set.

The fact that there was some overlap in the analyses conducted by the labs allowed for one final data check. Linear regressions were run, regressing an analyte from one lab versus the values for the same analyte from the second lab. Regressions both forced through the intercept, and with intercept estimated, were run. The following table shows the results of these comparisons for the regressions forced through the intercept. It should be noted that the .

Table 2-6.

Analyte	Labs	n	Correlation coefficient	Equation
Dissolved organic carbon	UFI Mitchell	533	0.972	DOC(M) = 0.982 DOC(U)

Table 2-6.

Analyte	Labs	n	Correlation coefficient	Equation
Na	Mitchell Siegel	1565	0.971	Na(S) = 1.027 Na (M)
K	Mitchell Siegel	1567	0.958	K(S) = 1.056 K (M)
Mg	Mitchell Siegel	1554	0.988	Mg (S) = 1.002 Mg (M)
Ca	Mitchell Siegel	1566	0.982	Ca(S) = 0.994 Ca (M)
Si	UFI Siegel	241	0.986	Si (S) = 0.994 Si (U)

Contents

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Nutrients, Dissolved Organic Carbon, Color, and Disinfection Byproducts in Base Flow and Stormflow in Streams of the Croton Watershed, Westchester and Putnam Counties, New York, 2000–02[1]

By Paul M. Heisig

Abstract

The Croton Watershed is unique among New York City's water-supply watersheds because it has the highest percentages of suburban development (52 percent) and wetland area (6 percent). As the City moves toward filtration of this water supply, there is a need to document water-quality contributions from both human and natural sources within the watershed that can inform watershed-management decisions.

Streamwater samples from 24 small (0.1 to 1.5 mi^2) subbasins and three wastewater-treatment plants (2000–02) were used to document the seasonal concentrations, values, and formation potentials of selected nutrients, dissolved organic carbon (DOC), color, and disinfection byproducts (DBPs) during stormflow and base-flow conditions. The subbasins were categorized by three types of drainage efficiency and a range of land uses and housing densities.

Analyte concentrations in subbasin streams differed in response to the subbasin charateristics. Nutrient concentrations were lowest in undeveloped, forested subbasins that were well drained and increased with all types of development, which included residential, urban commercial/industrial, golf-course, and horse-farm land uses. These concentrations were further modified by subbasin drainage efficiency. DOC, in contrast, was highly dependent on drainage efficiency. Color intensity and DBP formation potentials were, in turn, associated with DOC and thus showed a similar response to drainage efficiency. Every constituent exhibited seasonal changes in concentration.

Nutrients. Total (unfiltered) phosphorus (TP), soluble reactive phosphorus (SRP), and nitrate were associated primarily with residential development, urban, golf-course, and horse-farm land uses. Base-flow and stormflow concentrations of the TP, SRP, and nitrate generally increased with increasing housing density. TP and SRP concentrations were nearly an order of magnitude higher in stormflow than in base flow, whereas nitrate concentrations showed little difference between these flow conditions. Organic nitrogen concentrations (calculated as the difference between concentrations of total dissolved N and of all other N species) was the dominant form of nitrogen in undeveloped and moderately to poorly drained subbasins.

High TP concentrations in stormflows (800–1,750 µg/L) were associated with well drained and moderately drained residential subbasins with high- and medium-density housing and with the moderately drained golf-course subbasin. Areas with medium to high housing densities favor TP transport because they provide extensive impervious surfaces, storm sewers, and local relief, which together can rapidly route stormwater to streams. SRP concentrations were highest in the same types of subbasins as TP, but also in sewered residential and horse-farm subbasins. The ratio of SRP to TP was typically a smaller in stormflow than in base flow. Base-flow TP and SRP concentrations were highest during the warm-weather months (May to October). The highest nitrate concentrations (3.0–4.5 mg/L) were associated with the urban subbasin and the three well drained, high-density residential subbasins. The two moderately drained lake subbasins and the two poorly drained (colored-water wetland) subbasins had consistently low nitrate concentrations despite low and medium housing densities. Nitrate concentrations were generally highest during the winter months and lowest during the autumn leaf-fall period. Organic N concentrations were highest during the leaf-fall period.

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[1] Citation of unpublished report:
Heisig, P.M., 2008, Croton terrestrial processes project—final report, volume 1, chapter 4, broad brush study: New York City Department of Environmental Protection, 105 p., online only.

Dissolved Organic Carbon. DOC concentration was consistently highest in the two poorly drained (colored-water-wetland) subbasins and lowest in the well drained subbasins. Base-flow DOC concentration increased with decreasing drainage efficiency, except in the well drained sewered subbasin with high-density housing, where slightly elevated DOC concentrations throughout the year may indicate leakage from a nearby sewer main. Seasonal changes in stormflow DOC concentration were pronounced in all subbasins. An early November storm (after leaf fall) resulted in DOC concentrations that, in many subbasins, were two to three times greater than the next highest storm DOC concentration.

Color. Color (Pt-Co) was closely associated with elevated DOC concentration in the two poorly drained (colored-water-wetland) subbasins. These subbasins had base-flow medians 7 to 15 times higher than the base-flow medians in all of the well drained subbasins and half of the moderately drained subbasins. Color was also closely associated with stormflows: median stormflow intensities at most well drained and uncolored-water-wetland subbasins were about twice the base-flow intensities. Seasonal variations in color were evident in base flow and stormflow. Most residential subbasins with low median base-flow Pt-Co color showed late-fall peaks of nearly 30 Pt-Co color units (during and immediately after leaf off) and relatively stable Pt-Co color during the remainder of the year. Stormflow intensities followed the same pattern; the autumn color peaks were proportionally larger than the corresponding DOC peaks compared to other times of year, which suggests that DOC derived from autumn leaf litter is a better color source than at other times of year.

Disinfection Byproducts. Formation potentials of DBPs increased in base flow with decreasing drainage efficiency. Formation potentials of trihalomethane (THM) species and haloacetic acid (HAA) species, respectively, were added to determine total THMs and total HAAs. Chlorine-containing forms of THMs and HAAs produced in formation potential tests were much more common than bromine-containing forms. The bromine-containing forms, however, were associated with residential and golf-course land uses. THMs produced in formation potential tests were dominated by a single form (chloroform), whereas three forms of HAAs were common (monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA).

DBP formation potentials increased in base flow with decreasing drainage efficiency. THM and HAA formation potentials exhibited autumn (leaf fall) and late spring base-flow peaks; HAAs were higher in fall, and THMs were higher in spring. Stormflow THM and HAA formation potentials were typically high, irrespective of land use or drainage efficiency.

The major source of precursor material for DBPs in most subbasins is terrestrial DOC. Specific ultraviolet absorbance (SUVA) values in samples from subbasins with lakes indicate that the DOC is a mixture of both aquatic and terrestrial sources.

No universal surrogate for all DBPs (THMs and HAAs) was identified from DOC, UV-254, gelbstoff 440, or platinum-cobalt (Pt-Co) color. Samples were grouped by flow condition (stormflow or base flow) and by the presence or absence of recent leaf litter. The best surrogates for THMs differed from those for HAAs. The best surrogates for THMs were UV-254 and DOC, whereas the best surrogate for HAAs differed among the sample groups. THM-to-surrogate relations were generally stronger than HAA-to-surrogate relations probably because THMs have a single dominant form, whereas HAAs have three dominant forms which differed in concentration among subbasin categories.

Wastewater Effluent. The quality of wastewater effluent from three wastewater-treatment plants (tertiary treatment) differed with treatment process and plant upgrades. Nitrate and ammonium were the only constituents with concentrations that exceeded concentrations observed in streamflow samples. DBP formation potentials were low overall, but there were elevated concentrations of some brominated forms and of the HAA form monochloroacetic acid.

4.1 Introduction

A network of streamflow-sampling sites ("broad-brush" sites) was established in cooperation with the Research Foundation of the State of New York for the New York City Department of Environmental Protection (NYCDEP) in 24 small subbasins and at 3 wastewater-treatment plants within New York City's Croton watershed (fig. 1) to provide a basinwide assessment of selected nutrients, dissolved organic carbon (DOC), color, and disinfection byproducts (DBPs) during 2000–02. The 24 subbasins were selected to reflect the range of drainage conditions and land uses within the 374-mi^2 watershed. All subbasins are drained by first- and second-order streams. The use of small drainage areas (< 1.5 mi^2) allowed accurate determination of drainage-efficiency, land-use, and housing-density characteristics.

4.1.1 Subbasin Selection

Subbasins were selected to represent the full range of drainage efficiencies, land-use types, and housing densities. The subbasins are listed by these characteristics and sampling frequency in table 1.

The three levels of drainage efficiency were designated as (1) **well drained** subbasins that contain little if any impounded water or wetland area (11 subbasins), (2) **moderately drained** subbasins with a lake or an uncolored-water wetland between the sampling point and the primary subbasin land use (11 subbasins), and (3) **poorly drained** subbasins with a colored-water wetland between the sampling point and the primary subbasin land use (2 subbasins). Wetlands were divided into two groups on the basis of base-flow Pt-Co color—uncolored water appeared clear upon visual inspection, whereas colored water was tea-colored, high in DOC, and defined by at least three base-flow samples with color intensities greater than 100 Pt-Co color units (PCU). The two wetland streams that had colored base flow (RIC, MAO; table 1) are along the north-central and northwestern edges of the Croton Watershed (fig. 1).

The drainage efficiencies represent a range of residence times and chemical environments for streamwaters. Residence times in well drained subbasins, where base flow and stormflow move rapidly, tend to be shorter than in subbasins with lakes or wetlands; lakes and wetlands also allow certain chemical constituents such as nutrients to be transformed, taken up, or produced through chemical and biological processes involving bacteria, algae, and macrophytes. Nitrogen species can be transformed, and sorption/desorption of phosphorus on sediments can be facilitated by bacterially mediated redox processes. The reader is referred to Allen (p. 283–303, 1995) for a review of nutrient dynamics in running waters.

Land use (other than forested) within the Croton watershed is primarily residential. Most houses are served by septic systems and domestic wells. The 11 well drained subbasins represent a wide range of housing density (a gradient of development from 0 to over 1,000 houses per mi^2), whereas the housing density in the 13 subbasins with a lake or a wetland ranges from low to medium (table 1). Residences in 22 of the 24 subbasins are served by individual septic systems; the other two subbasins in the southwestern part of the watershed are served by sanitary sewers. Sanitary sewering is intended to protect the quality of shallow ground water by exporting wastewater, rather than allowing it to infiltrate into the water table and streams, but leakage from sewer mains can potentially introduce contamination and have the opposite result. The two sewered subbasins —one with medium housing density (GRA) and one with high housing density (YRK)—were chosen for comparison of water quality with the unsewered subbasins.

Three land uses other than forested and residential were represented by single subbasins: a golf course, a horse farm, and an urban commercial/ industrial area (table 1). The latter land use was difficult to isolate within a subbasin because it is typically close to residential and other types of land use such as parks and transportation corridors. One subbasin with a mixture of these land uses (BED) was selected and designated as "urban" (table 1).

Three wastewater-treatment plants (WWTPs) of different size were selected to supplement the subbasin network with effluent samples. The treatment plants and their 2001 average daily outflow, in millions of gallons per day (MGD) were the Town of Yorktown (Hallock Mills) plant (HAL, 1.5 MGD), the Village of Mahopac plant (MAH, 0.13 MGD), and the Clocktower Commons plant, also known as the Tracy plant, which serves a commercial/ business complex (CLK, 0.01 MGD). All facilities provide tertiary treatment (phosphorus removal), although the oldest facility (Town of Yorktown) frequently violated standards for ammonia in effluent. The Yorktown plant utilizes trickling filters and the Mahopac and Clocktower plants use rotating biological contactors (K. Kane, New York City Department of Enivronmental Protection, oral commun., 2003).

4.1.2 Sampling Frequency

Streamflows in the 24 subbasins were sampled at one of three frequencies—high, medium, or low (table 1). This classification denotes whether or not stormflows were sampled and the frequency of sampling in addition to base-flow samples.

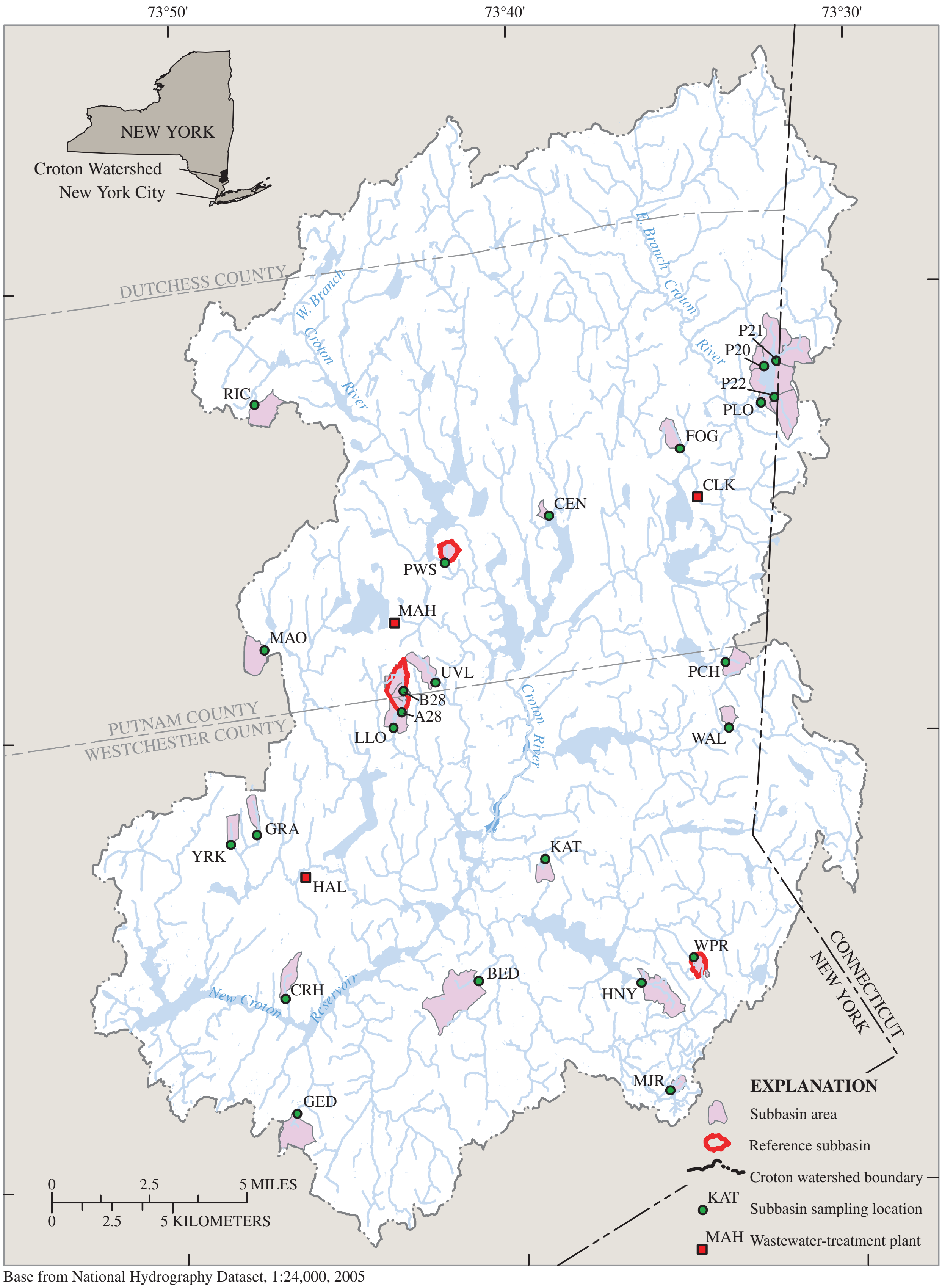

Figure 1. Croton Watershed boundaries and hydrography, showing stream-network subbasins and sampling sites, southeastern N.Y.

Table 1. Drainage efficiency, land use, housing density, and sampling frequency for 24 subbasins and three wastewater-treatment plant sites in the Croton Watershed, southeastern, N.Y.

[Med., medium. Boldface denotes reference site. Locations are shown in fig. 1.]

Drainage efficiency	A. Well drained subbasins (no surface-water impoundment immediately above sampling point)							B. Moderately drained subbasins (with a lake)		C. Moderately drained subbasins with uncolored water (with a wetland)[1]				D. Poorly drained subbasins with colored water (with a wetland)[1]		Waste-water-treat-ment plants
Land use and sewering	Forest	Residential Unsewered	Residential Unsewered	Residential Unsewered	Residential Sewered	Urban[2]	Horse farm	Resi-dential	Golf course	Forest	Residential Unsewered	Residential Unsewered	Residential Sewered	Residential unsewered	Residential unsewered	
Housing density[3]	Zero	Low	Med.	High	High	Med.	Low	Med.	Zero	Zero	Low	Med.	Med.	Low	Med.	
Subbasin name and sampling frequency[4]	**WPR (H)**	CRH (L)	P21 (L) VL (M)	P20 (L) P22 (L) **A28 (L)** B28 (H)	YRK (M)	BED (L)	WAL (M)	PLO (M) LLO (L) KAT (M)	CEN [5] (M)	HNY (L)	FOG (L) MJR (M) PCH (L) GED (M)	**PWS (H)**	GRA (L)	RIC (M)	MAO (L)	HAL (Q) CLK (Q) MAH (Q)

[1] Subbasins containing wetlands were categorized according to base-flow color (tea colored to uncolored). Uncolored-water wetlands had base-flow color values below 100 color units; colored-water wetlands had at least one base-flow color value above 100 color units.

[2] Urban land use includes extensive residential housing, including apartments and condominiums, transportation corridors (highways and railroads), commercial corridors, light industrial areas, a park with athletic fields, and a headwater-area lake.

[3] Housing density, in houses per square mile:

Zero 0
Low 1–250
Medium 251–599
High 600–1020.

[4] Sampling frequency:

L = low storm-recession and base-flow sampling,
M = moderate passive (rising-limb) samplers for storms, also storm-recession and base-flow sampling,
H = high routine base-flow sampling and automatic stormflow sampling,
Q = quarterly wastewater-treatment effluent.

[5] Subbasin CEN (with golf course) receives additional storm runoff from a section of two-lane highway.

Base-flow samples were collected monthly at all 24 sites during the first year of study (July 2000–July 2001), and thus are directly comparable with one another. Stormflow was sampled sporadically at different sites from November 2000 to July 2002.

The three subbasins in which sampling was high-frequency or “intensive” (WPR, B28, PWS, fig. 1, table 1) were instrumented with streamflow gages and automatic samplers to obtain stormflow samples in addition to monthly base-flow samples. These subbasins, which are the focus of other chapters in this report, were also instrumented with piezometers, lysimeters, and weather stations. Selection of the three subbasins was designed to provide the most detailed understanding of the occurrence and concentrations of nutrients, DOC, color, and DBPs in streamwater across the gradient of residential development (zero, medium, and high housing density). The subbasins with medium- and high-density housing were served by septic systems.

Eight subbasins were selected for moderate-frequency sampling (table 1) and sampled periodically for rising-limb and (or) falling-limb (recession) stormflow samples, in addition to regular base-flow samples. Rising-limb stormflow samples were collected with passive samplers and (or) temporarily deployed automatic samplers. These subbasins represented a range of housing densities and drainange efficiencies as well as sewered-residential, golf-course, and horse-farm land uses (table 1).

Low-frequency sampling at the remaining 13 subbasins included only monthly base flow and occasional stormflow-recession samples. These subbasins included all drainage efficiencies and sewered and unsewered residential land use.

Effluent samples were collected quarterly at the three wastewater-treatment plants. Samples at the Mahopac plant were collected between 8:30 a.m. and 1:00 p.m. Samples from the Yorktown and Clocktower Commons plants were sampled between 11:30 a.m. and 2:30 p.m.

4.1.3 Representativeness of Stormflow Samples

The stormflow data collected from the subbasins are not equally representative of *maximum* or *median* stormflow concentrations because of the different sampling frequencies. Stormflow data from the frequently sampled subbasins provide the most reliable definition of maximum concentrations that may be expected from storms at different times of year; however, median concentrations are affected by differences in the number and types of storm samples collected (rising limb, peak, steeply falling limb, recession). Data from the sites with medium- and low-frequency sampling provide an incomplete picture of concentrations; thus, the medians (table 2, appendix 1) should be interpreted as minimum stormflow concentration estimates. Flow conditions and the number of stormflow samples collected are given for each drainage efficiency and land-use category (tables 3–9) so that the reader can assess whether or not the data are indicative of maximum concentrations.

Detailed data from the three frequently sampled subbasins are helpful for interpretion of data from the less frequently sampled subbasins. For example, the stormflow-concentration data from the two developed, frequently sampled subbasins (PWS, B28) typically show a peak in total phosphorus (TP) concentration during the rising-limb and peak flows on storm hydrographs and a peak in DOC concentration during recession flows. Thus, rising-limb data from passive samplers provide reliable estimates of maximum TP concentrations and poor estimates of maximum DOC concentrations, whereas recession samples provide the opposite.

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Table 2. Median values of selected constituents in base flow and stormflow for each drainage efficiency and land-use category, and housing density in the stream network, Croton Watershed, southeastern New York, 2000–02.

[PCU, platinum-cobalt color units]

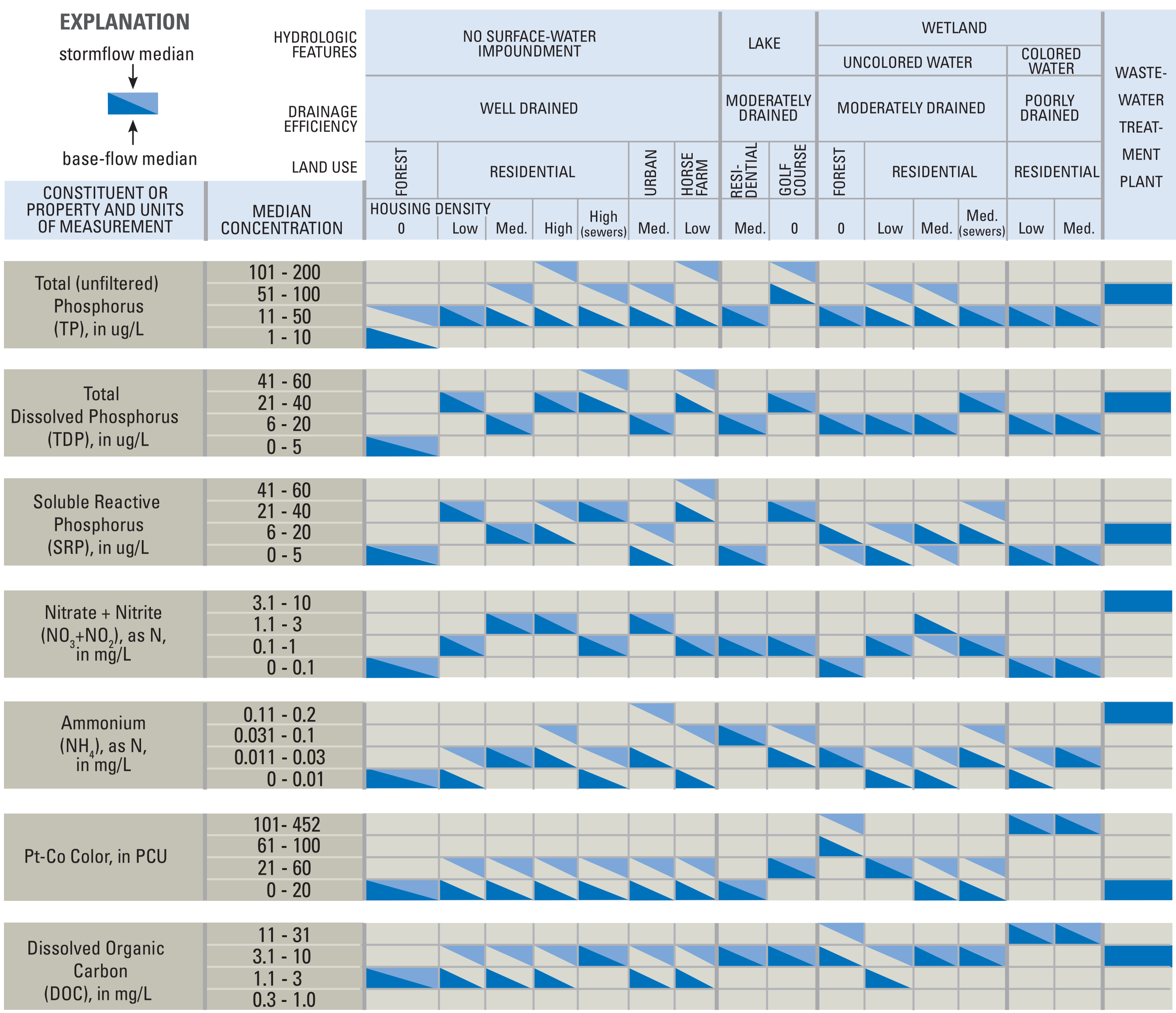
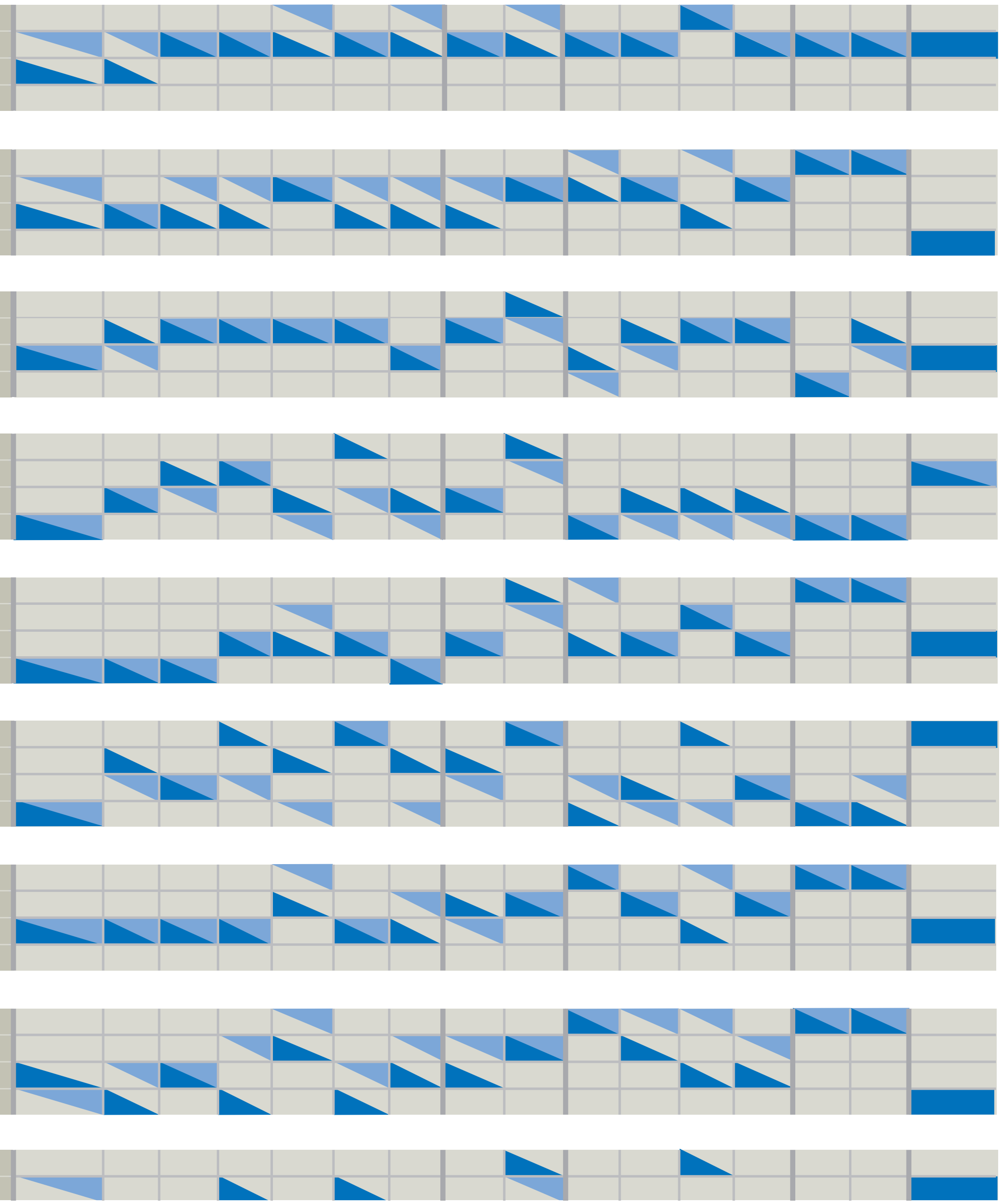


Table 2. Median values of selected constituents in base flow and stormflow for each drainage efficiency and land-use category, and housing density in the stream network, Croton Watershed, southeastern New York, 2000–02.

[PCU, platinum-cobalt color units]

Particulate Organic Carbon (POC), in mg/L	11 - 100
	3.1 - 10
	1.1 - 3
	0.2 - 1
Unfiltered Trihalomethanes, (THM) formation potential, in ug/L	501 - 1,000
	251 - 500
	101 - 250
	0 - 100
Unfiltered Bromodichloromethane formation potential, in ug/L	41 - 60
	21 - 40
	11 - 20
	5 - 10
Unfiltered Dibromochloromethane formation potential, in ug/L	6.1 - 10
	3.1 - 6
	1.1 - 3
	0.1 - 1
Unfiltered Haloacetic Acids (HAA) formation potential, in ug/L	601 - 1100
	401 - 600
	251 - 400
	150 - 250
Unfiltered Monochloroacetic Acid (MCAA) formation potential, in ug/L	101 - 300
	71 - 100
	41 - 70
	8 - 40
Unfiltered Dichloroacetic Acid (DCAA) formation potential, in ug/L	101 - 300
	61 - 100
	31 - 60
	10 - 30
Unfiltered Trichloroacetic Acid (TCAA) formation potential, in ug/L	201 - 700
	101 - 200
	71 - 100
	30 - 70
Unfiltered Dibromoacetic Acid	0.81 - 2.9
	0.41 - 0.8



4.2 Concentrations of Selected Constituents Categorized by Drainage Efficiency and Land Use

The following sections describe the occurrence and concentration of seven selected constituents at the 27 sampling sites—three nutrients, DOC, color, and two disinfection byproducts (DBPs)—from July 2000 through July 2001. The nutrients discussed are total (unfiltered) phosphorus (TP), soluble reactive phosphorus (SRP), and nitrate+nitrite (herein referred to as nitrate). Total dissolved phosphorus (TDP) is omitted from this discussion because it is approximately equivalent to SRP, as indicated by median concentrations in table 2. The two DBPs discussed are formation potentials, rather than naturally occurring concentrations of total trihalomethanes and total haloacetic acids. Additional constituents that are included in table 2 and appendix 1 but are not discussed in detail include ammonium, particulate organic carbon (POC), the THM species bromodichloromethane and dibromochloromethane, and the HAA species monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), and dibromoacetic acid (DBAA).

Base-flow water quality in three *reference* subbasins with a range of housing densities (zero, medium, and high) was compared to the base-flow water quality in all other subbasins. Two of the subbasins had high-sampling frequencies (WPR and PWS) and one subbasin (A28) had a low-sample frequency. WPR is a well drained, forested subbasin with no residential development and PWS is a moderately drained subbasin with an uncolored-water wetland and medium-density housing. Subbasin A28, a low-sampling frequency subbasin, is well drained and has high density housing. It was chosen to represent subbasins with high housing densities instead of the B28 (high sampling frequency) subbasin because the B28 sampling location was moved two times during the study. The B28 subbasin is located within the A28 subbasin.

Results for each constituent are described in the following sequence:

- Summary of base-flow and stormflow medians (highest and lowest) by drainage efficiency, land use, and housing density, and median and maximum concentrations in WWTP effluent (with reference to table 2).
- Seasonal base-flow concentrations at the three reference subbasins compared with all other subbasins. In this section, the subbasins are divided into eight groups (A through H) on the basis of drainage efficiency, land use, housing density, and wastewater disposal (septic systems or sanitary sewers). The first group described for each constituent consists of the three reference sites.
- Stormflow-concentration summary for the range of drainage efficiencies and land uses. Maximum stormflow concentrations and seasonal changes are discussed, and comparisons with base-flow concentrations are made (tables 3–9).

4.2.1 Total (Unfiltered) Phosphorus (TP)

Anthropogenic sources of phosphorus in the Croton Watershed include

- human wastewater, which may be disposed through septic systems or routed through sanitary sewers to wastewater-treatment plants;
- fertilizers, which are applied to some residential lawns and to golf courses; and
- animal wastes, such as manure from horse farms.

Median concentrations (table 2) indicate that TP is highest in drainage-efficiency and land-use categories similar to those with elevated SRP (well to moderately drained residential with medium to high housing density and golf course subbasins), but that elevated TP concentrations were closely associated with stormflow (sorbed onto particulates).

4.2.1.1 Summary: Median Concentrations in Base Flow, Stormflow, and Wastewater-Treatment Plant (WWTP) Effluent

Base-Flow Medians: Total base-flow TP medians ranged from 11 to 50 µg/L in all drainage-efficiency and land-use categories except for high concentrations (~75 µg/L) in samples collected from the moderately drained golf-course subbasin (CEN) and low concentrations (1–10 µg/L) at the well drained, forested subbasin (WPR).

Stormflow Medians: TP stormflow medians were equal to or higher than base-flow medians because phosphorus that is sorbed to particulate matter is typically transported during storms. The highest stormflow medians (101–200 µg/L) were in the following drainage and land-use categories:

- well drained, with high density housing (P20, P22, 28A, B28);
- well drained, with horse farm (WAL); and
- moderately drained (lake), with golf course (CEN).

Stormflow medians in samples collected from well drained subbasins with medium and high housing densities ranged from 51 to 200 µg/L, values which consistently exceeded base-flow medians (11–50 µg/L). Rapid movement of stormwater over impervious surfaces and into storm drains in these subbasins favors transport of particulates, and the elevated concentrations in streams during storms indicate the presence of phosphorus source(s) at the land surface. Stormflow medians from moderately and poorly drained subbasins with either lakes or wetlands were within the same concentration ranges as the base-flow medians—the longer stormwater residence times in these subbasins probably allow some particulate matter to settle out. The high stormflow concentrations in the golf-course subbasin, despite its moderate drainage efficiency, probably reflect (1) the strength of the phosphorus source and (2) limited stormwater retention by small ponds rather than a sizeable lake.

WWTP Effluent: The wastewater effluent TP median for all WWTP samples was within the 51–100 µg/L range (table 2). These concentrations are well below the range (200–1,000 µg/L) of SPDES (State Pollution Discharge Elimination System) permitted discharge concentrations at these plants (Kimberlee Kane, New York City Department of Environmental Protection, written commun., 2006). Individual WWTP median and maximum concentrations were as follows:

- Yorktown (HAL): median = 63 µg/L, maximum = 133 µg/L;
- Clocktower Commons (CLK): median = 138 µg/L, maximum = 154 µg/L; and
- Mahopac (MAH): median = 66 µg/L, maximum = 125 µg/L.

4.2.1.2 Base-Flow Concentrations, by Drainage Efficiency and Land-Use Category

The highest base-flow TP concentrations ranged from 100 to 300 µg/L and were associated with the following drainage and land-use categories:

- well drained, with high-density housing and sanitary sewers (YRK) (fig. 2G);
- moderately drained (lake), with medium-density housing (PLO, LLO) (fig. 2E);
- moderately drained (wetland, with uncolored water), with medium-density housing and sanitary sewers (GRA) (fig. 2G); and
- moderately drained (lake), with golf-course (CEN) (fig. 2H).

The forested (undeveloped) subbasin (WPR) had the lowest base-flow TP concentrations—all were less than 20 µg/L (fig. 2A).

Base-flow TP concentrations showed high-concentration spikes most commonly during the autumn and spring, when high base flows can transport particulates. Seasonal changes in base-flow TP concentrations were low during the cold months and high during the warm months.

A. Reference Subbasins: well drained, forested; moderately drained (uncolored-water wetland) with medium-density housing; and well drained subbasin with high-density housing

Maximum base-flow TP concentrations (fig. 2A) were

- 18 µg/L, well drained, forested (WPR), September;
- 70 µg/L, moderately drained (uncolored-water wetland), medium-density housing (PWS), April; and
- 114 µg/L, well drained, high-density housing (A28), October.

The reference subbasins indicated an overall increase in base-flow TP concentration with increasing housing density, but the relation is not as well defined as for base-flow SRP (fig.3A). Concentration spikes (70–120 µg/L) in TP in the samples collected from the subbasins with high and medium housing density occurred during the transition from elevated warm-weather concentrations to low, cold-weather concentrations. The forested subbasin did not show any spikes in base-flow concentration.

B. Well drained subbasins with high- to low-density housing

Maximum base-flow TP concentrations (fig. 2B) were

- 58 µg/L, low-density housing (UVL; June) (CRH; September);
- 99 µg/L, medium-density housing (P21), November; and
- 126 µg/L, high-density housing (P22), July.

TP concentrations in samples collected in the well drained residential subbasins showed less seasonal variability, in general, than the reference subbasins. Base-flow concentrations from May through October were similar to those in reference subbasins, but the concentrations from December through April were generally higher. All well drained residential subbasins had higher base-flow TP concentrations than the moderately drained (uncolored-water wetland) reference subbasin with medium housing density (PWS) from December through March. The relation between TP concentration and housing density among the well drained residential subbasins was weaker than among the reference subbasins, as had also been noted for SRP. Maximum base-flow TP concentrations were similar (except for P22) to those at the reference subbasins, but base-flow TP concentrations at several subbasins with medium- and high-density housing decreased, rather than increased, during the autumn and spring.

C. Moderately drained (uncolored-water-wetland) subbasins with forest or low-density housing

Maximum base-flow TP concentrations (fig. 2C) were

- 47 µg/L, forested (HNY), July;
- 87 µg/L, low-density housing (MJR), October.

The presence of uncolored-water wetlands in subbasins with low-density housing appeared to have little effect on base-flow TP concentrations, apart from smaller, later (from late April to early May) spring concentration peaks than in the well drained subbasins. This delay was probably a result of the lower drainage efficiency in these subbasins than in the well drained subbasins. TP concentrations in samples from all subbasins within this group were higher than those from the well drained, forested subbasin (WPR), except during the winter months. The two subbasins with the highest housing densities (180, 208 houses/mi^2) in this drainage-efficiency and land-use category had peak concentrations comparable to samples from the well drained subbasins with high- or medium-density housing.

D. Poorly drained (colored-water-wetland) subbasins with low- and medium-density housing

Maximum base-flow TP concentrations (fig. 2D) were

- 40 µg/L, low-density housing (RIC), May;
- 69 µg/L, medium-density housing (MAO), May.

Base-flow TP concentrations in samples collected in the two subbasins with colored-water wetlands were low in winter, peaked in spring, and remained intermediate through summer and autumn, with no autumn peak. (Autumn and winter data were available only for subbasin RIC.) Base-flow TP concentrations in the poorly drained subbasin with medium-density housing matched that of the reference subbasin with medium-density housing from May through August. Base-flow TP concentrations in samples collected from the subbasin with low-density housing were about 15 to 30 µg/L lower than in samples collected from the subbasin with medium-density housing in the spring and early summer and about 0 to 10 µg/L lower during late summer.

E. Moderately drained (lake) subbasins with medium-density housing

The maximum base-flow TP concentrations (fig. 2E) were

- 260 µg/L, (PLO), September;
- 140 µg/L, (LLO), April.

Base-flow TP concentrations in samples collected from these subbasins were among the highest in the study and exceeded most concentrations in the reference subbasin with high-density housing. The timing and presence of autumn and spring peaks differed between the lake subbasins and also from the high-density reference subbasin. High TP concentrations in the middle to late summer and early autumn at the lake outlets (especially at subbasin PLO) represent discharge of turbid, algae-laden lake water following intense growth during spring and summer. TP reached its maximum concentration (260 µg/L) at subbasin PLO during this time. Concentrations in samples collected from lake subbasins PLO and LLO (fig. 1) were typically higher than in the reference subbasin with high-density housing, except during the late October peak, when base-flow TP in samples collected from both lake subbasins declined. This decline suggests that high late-fall base flows from streams into the lakes temporarily diluted the TP concentrations within the lakes. The spring peak was absent at subbasin PLO, but reached 140 µg/L at subbasin LLO (fig. 1, 2E).

F. Well drained urban subbasin with medium-density housing, transportation corridors, and commercial/industrial land

The maximum base-flow TP concentration (fig. 2F) was

- 47 µg/L, (BED), June.

Base-flow TP concentrations in samples collected from the urban subbasin (BED) were characterized as relatively stable (20–50 µg/L), with a minor September rise, a December low, and a gradual increase to a maximum in early June. Concentrations were similar to those at the reference subbasin with high-density housing except for the lack of peaks in the autumn and spring. This subbasin contains a headwater lake, which explains its similarity in pattern and concentration to the lake subbasin LLO described above.

G. Sewered subbasins: well drained with high-density housing and moderately drained (uncolored-water wetland) with medium-density housing

Maximum base-flow TP concentrations (fig. 2G) were

- 284 µg/L, well drained, high-density housing (YRK), July;
- 156 µg/L, moderately drained (uncolored-water wetland), medium-density housing (GRA), December.

Base-flow TP concentrations in samples collected from the two sewered subbasins (YRK, GRA) were higher than those at the reference subbasin with high-density housing except when streamflow was diluted during the autumn and spring peak periods. Base-flow concentrations in samples collected from the sewered subbasins reached peaks in early December (GRA) and in July (YRK) when TP concentrations in samples collected from most other subbasins were moderate to low. Concentrations of TP in samples collected from these two subbasins showed seasonal TP patterns, and concentrations were similar to those in several well drained subbasins with high- and medium-density housing (fig. 2B). However, those subbasins did not show the same dilution of TP concentrations in the spring and autumn peaks. Dilution at these times indicates that at least part of the TP in samples collected from sewered subbasins did not originate from the same source as TP in the unsewered subbasins.

H. Moderately drained (lake) subbasin with golf course (CEN) and well drained subbasin with horse farm (WAL)

Maximum base-flow TP concentrations (fig. 2H) were

- 143 µg/L, moderately drained (lake), with golf course (CEN), May;
- 65 µg/L, well drained, with horse farm (WAL), October.

Base-flow TP concentrations in samples collected from the golf-course subbasin exceeded those from the reference subbasin with high-density housing in all samples except those collected during late October. Most concentrations from the golf-course subbasin ranged from about 40 to 100 µg/L. The late May peak concentration from the golf-course subbasin is consistent with a P source from fertilizer application.

TP concentrations in most samples collected from the horse-farm subbasin equaled or exceeded those from the reference subbasin with high-density housing. The major exceptions were in samples collected during the autumn and spring peaks. TP concentrations increased during the autumn peak period and decreased (became diluted) during the spring peak period.

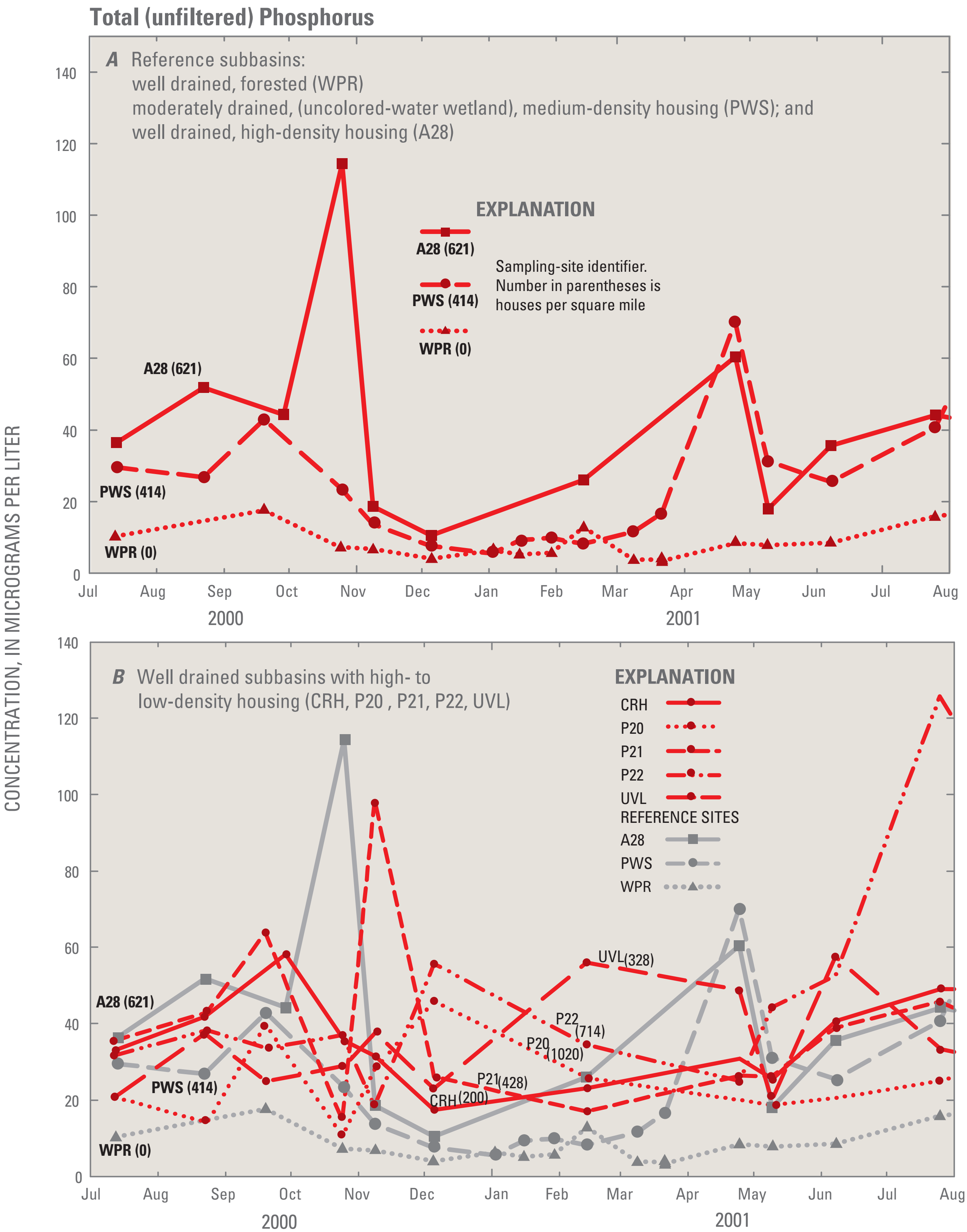


Figure 2. Base-flow total (unfiltered) phosphorus concentrations from July 2000 to July 2001, Croton Watershed, *(A)* reference subbasins, well drained, forested (WPR); moderately drained, medium-density housing (PWS); well drained, high density housing (A28); and *(B)* well drained subbasins, unsewered, high- to low-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

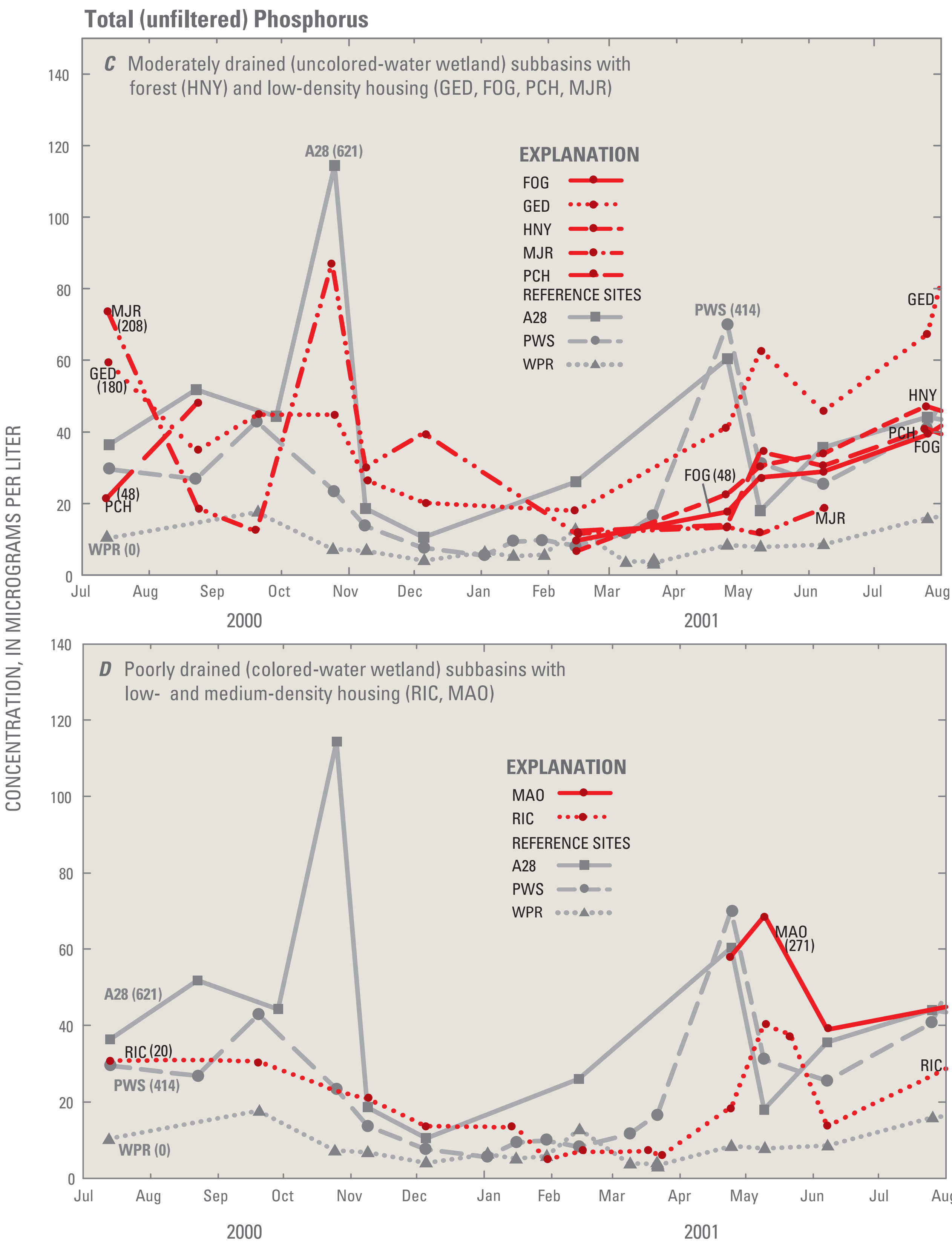


Figure 2. Base-flow total (unfiltered) phosphorus concentrations from July 2000 to July 2001, Croton Watershed, *(C)* moderately drained subbasins, uncolored-water wetland, low-density housing, and *(D)* poorly drained, colored-water wetland subbasins, low- and medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

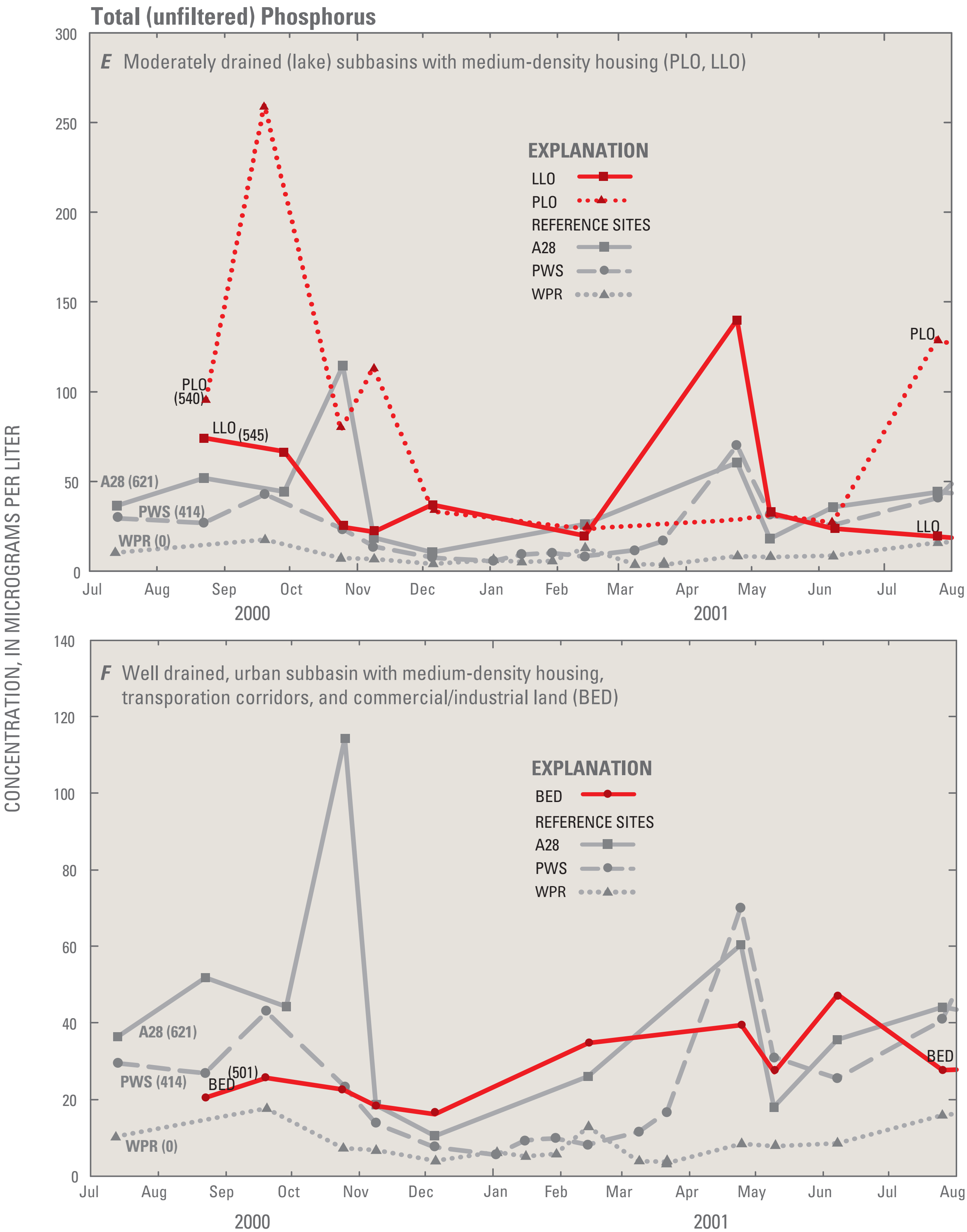


Figure 2. Base-flow total (unfiltered) phosphorus concentrations from July 2000 to July 2001, Croton Watershed, *(E)* moderately drained subbasins with lakes, medium-density housing, and *(F)* well drained, urban subbasin, medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

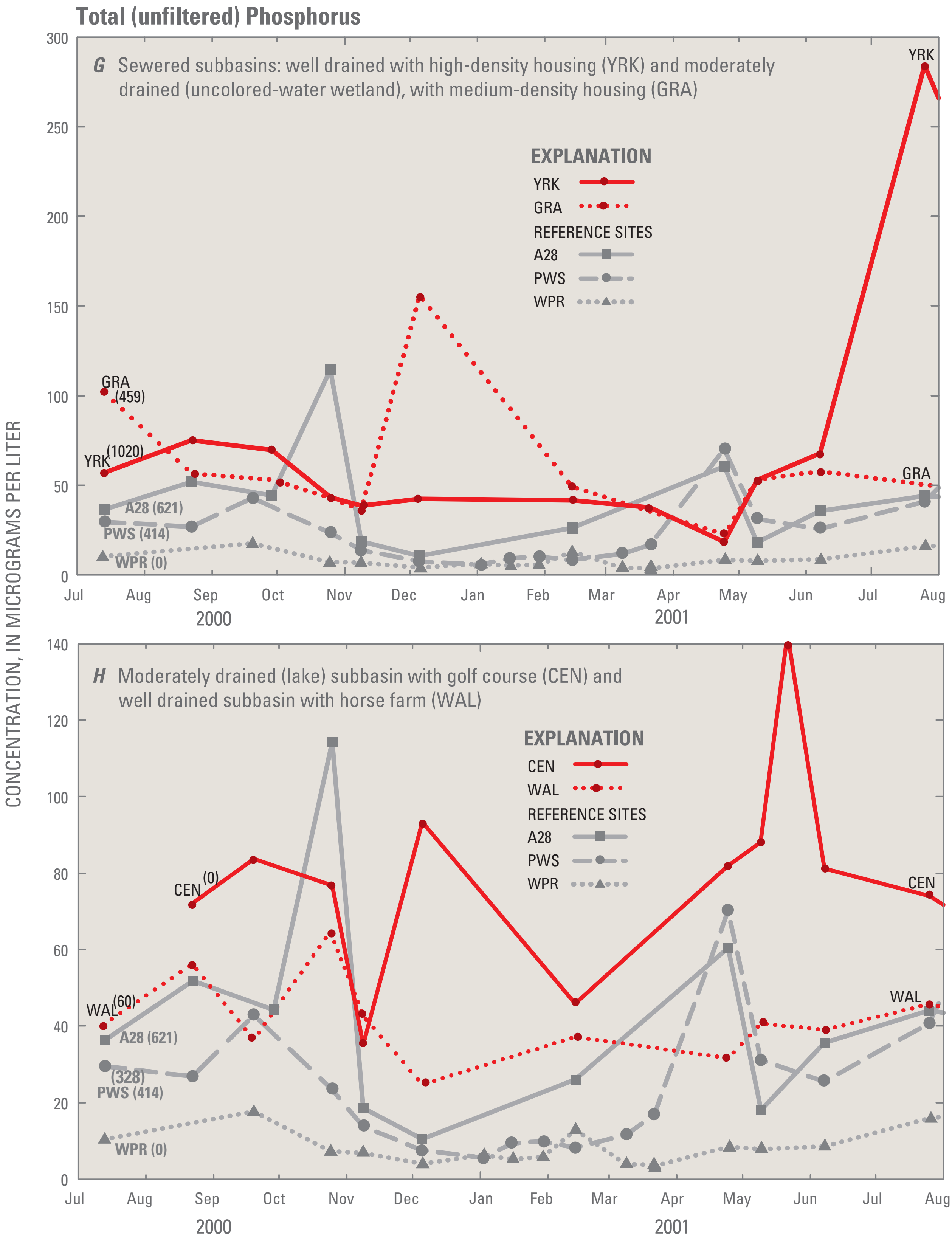


Figure 2. Base-flow total (unfiltered) phosphorus concentrations from July 2000 to July 2001, Croton Watershed, *(G)* sewered subbasins, well drained, high-density housing (YRK), moderately drained, uncolored-water wetland, medium-density housing (GRA), and *(H)* moderately drained subbasin, lake and golf course (CEN), well-drained subbasin with horse farm (WAL). Housing density, in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

4.2.1.3 Stormflow Concentrations

TP concentrations in stormflow were strongly affected by land use and drainage efficiency (table 3). Maximum stormflow concentrations in the well drained subbasins were at least tenfold higher than base-flow concentrations. Maximum TP concentrations in stormflows ranged from about 100 µg/L in subbasins that are forested, undeveloped or have low-density housing to 1,000 µg/L in subbasins with medium-density housing to 1,200–1,800 µg/L in subbasins with high-density housing. Maximum stormflow concentrations in subbasins with medium-density housing and wetlands or lakes generally did not exceed 200 µg/L.

High stormflow concentrations (around 1,000 µg/L) were measured in samples from two other subbasin categories, (1) well drained, high-density housing with sanitary sewers, and (2) moderately drained (small ponds) with a golf course.

The positive relation between maximum TP concentration and housing density is associated with (1) the presence of P sources (fertilizer and organic material from lawns) and (2) good drainage (storm drains and high relief that provide for rapid stormwater transport out of the subbasin). These features characterize most residential subbasins with high- and medium-density housing in the Croton Watershed. Sewering did not appear to decrease stormflow TP concentration (1,148 µg/L maximum) in the well drained subbasin with high-density housing (YRK) from which fewer samples were collected and which had lower relief than the unsewered reference subbasin with high-density housing. The relatively low stormflow TP concentrations in poorly drained subbasins suggest that low streamflow velocities and long subbasin residence times inhibit the transport of TP-bearing particulate matter.

Stormflow TP concentrations from all well drained subbasins typically exceeded or equaled the base-flow TP concentrations just before or just after a storm event (table 3). This comparison indicates that the increased TP concentrations are derived from sources associated with surface runoff. Stormflow concentrations at the most poorly drained subbasins were variable in comparison with TP concentrations in base-flow samples collected before and after storm events.

4.2.2 Soluble Reactive Phosphorus (SRP)

Manmade phosphorus sources in the Croton watershed were described in the preceding (TP) section. Soluble reactive phosphorus is a measure of readily bioavailable phosphorus and is appproximately equivalent to orthophosphate.

4.2.2.1 Summary: Median Concentrations in Base Flow, Stormflow, and WWTP Effluent

Base-Flow Medians: Median base-flow and stormflow concentrations of SRP are given by concentration range and drainage-efficiency and land-use category in table 2. Concentration differences among stream network subbasins are consistent with the phosphorus sources listed in the TP section.

The highest base-flow median SRP concentrations (21–40 µg/L) were in the following subbasin categories

- Well drained, with low-density housing (CRH);
- Well drained, with high-density housing and sanitary sewers (YRK);
- Well drained, with horse farm (WAL; and
- Moderately drained (lake), with golf course (CEN).

The lowest base-flow median SRP concentrations (~5 µg/L) were from the following drainage and land-use categories:

- Well drained, forested (WPR);
- Moderately drained (lake), with medium-density housing (PLO, LLO);
- Moderately drained (uncolored-water wetland), with low-density housing (FOG,MJR,PCH,GED);
- Well drained, urban (BED); and
- Poorly drained (colored-water wetland), with low- and medium-density housing (RIC, MAO).

Table 3. Seasonal stormflow concentrations of total unfiltered phosphorus (TP) in the stream network by subbasin category, Croton Watershed, southeastern, N.Y., 2000–02.

[mi^2, square miles; All values are in micrograms per liter]

Land use and drainage efficiency category	Number of samples	Flow conditions sampled[1]	For each half-month period: ***max*** = Highest stormflow concentrations; ***rel.*** = Relation of stormflow concentrations to baseflow concentration[2]	Jan		Feb		Mar		May		Jun		Jul		Nov		Dec	
Forested (zero housing)																			
Well drained	37	r, p, f, re	*max*				95		33		39	71			63	46			9
			rel.				≥		≥		≥	≥			≥	≥			≥
Moderately drained, Wetland, uncolored water	2	re	*max*					9			44								
			rel.					≤			≤								
Residential (by housing density)																			
Low-density (<250 houses mi^{-1})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	5	f, re	*max*					49			60					66		14	44
			rel.					>			>					>		<	>
Moderately drained Wetland, uncolored water	30	r, f, re	*max*					110			189	55				138			60
			rel.					>			<=>	<=>				>			<=>
Poorly drained Wetland, colored water	27	r, p, f, re	*max*				62		157		38					48			4
			rel.				≥		≥		<					≤			<
Medium-density (251-600 houses mi^{-2})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	9	p, f, re	*max*					19	98		201					557		22	70
			rel.					≤	>		≥					≥		<=>	>
Well drained Urban	5	f, re	*max*					71			81					195		25	40
			rel.					>			>					>		>	>
Moderately drained Wetland, uncolored water	58	r, p, f, re	*max*		17			18	182		788	283	1070		674	186		44	18
			rel.		>			>	≥		≥	≥	≥		≥	≥		>	≥
Moderately drained Wetland, uncolored water, sewered	5	f, re	*max*								107					121			40
			rel.								>					>			<
Poorly drained Wetland, colored water	4	f, re	*max*								43					24		88	42
			rel.								=					=		>	>
Moderately drained Lake	23	r, p, f, re	*max*					35			106					153		114	587
			rel.					<=>			≥					≥		≥	≥
High-density (>600 houses mi^{-2})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	138	r, p, f, re	*max*		1078		1219		1223		323	1752			627	1280			
			rel.		≥		≥		≥		≥	≥			≥	≥			
Well drained Sewered	21	r, p, f, re	*max*					1148	172		159	565				965			98
			rel.					>	≥		>	≥				>			<=>
Golf Course				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Moderately drained Lake (small ponds)	12	r, p, f, re	*max*					479			127		701			937			394
			rel.					>			=		>			>			>
Horse Farm				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	11	r, f, re	*max*					180			123	472				180		143	
			rel.					>			>	>				>		>	

[1]Flow conditions in storm hydrograph
- r, rising limb
- p, peak
- f, steeply falling limb
- re, recession

[2]Relation of stormflow concentration to base-flow concentration
- = equal to
- > greater than
- ≥ greater than or equal to
- < less than
- ≤ less than or equal to
- <=> variable

Stormflow medians: Median stormflow concentrations of SRP were higher than the corresponding base-flow medians in four of the drainage and land-use categories, and three of the four are well drained subbasins. The highest stormflow medians were associated with the following concentration ranges and subbasin categories:

- (41–60 µg/L)
  –well drained, with horse farm (WAL);
- (21–40 µg/L)
  –well drained, with low-density housing (CRH);
  –well drained, with high-density housing (P20, P22, A28,B28);
  –well drained, with high-density housing and sanitary sewers (YRK);
  –moderately drained (lake), with golf course (CEN); and
  –moderately drained (uncolored-water wetland), with medium-density housing and sanitary sewers (GRA).

The elevated median concentration at the well drained subbasin with low-density housing may reflect contributions from large fertilized lawns or perhaps undocumented livestock.

The *lowest* median stormflow concentrations (~5 µg/L) were similar to those of base flow:

- Well drained, forested (WPR);
- Moderately drained (lake), with medium-density housing (PLO, LLO);
- Moderately drained (uncolored-water wetland) forested (HNY); and
- Poorly drained (colored-water wetland) with low and medium-density housing (RIC, MAO).

Median SRP concentrations in stormflow were much lower than the concentrations of TP (table 2) because SRP is bioavailable and subject to sorption on particulate matter. Its presence in streamwater appears to be favored by two factors,

(1) short residence times as surface water (well drained subbasins), and

(2) P sources near the streams such that uptake or sorption is minimized.

WTTP effluent: The median SRP concentration in effluents from three wastewater-treatment plants ranged from 6–20 µg/L (table 2). Concentrations varied at each facility and among the facilities over the course of sampling. Individual WWTP median and maximum concentrations were as follows:

- Yorktown (HAL) median = 2.3 µg/L, maximum = 16.3 µg/L;
- Clocktower Commons (CLK) median = 50 µg/L, maximum = 87 µg/L; and
- Mahopac (MAH) median = 35 µg/L, maximum = 82.6 µg/L.

4.2.2.2 Base-Flow Concentrations, by Drainage Efficiency and Land-Use Category

The *highest* base-flow SRP concentrations were between 50–60 µg/L in subbasins with

- Well drained, high-density housing with sanitary sewers;
- Moderately drained (lake), with medium-density housing; and
- Moderately drained (lake), with golf course.

The forested, undeveloped subbasin had the lowest base-flow SRP concentrations — all were less than 5 µg/L.

Seasonal changes in base-flow SRP concentrations were evident at most subbasins. The highest concentrations occurred during low base-flow conditions from June through late October or early November, and the lowest concentrations coincided with high base flows from November or December through May.

A. Reference Subbasins: well drained, forested; moderately drained (uncolored-water wetland) with medium-density housing; and well drained subbasin with high-density housing

Overall increases in base-flow SRP concentration with increasing housing density were evident at the three reference subbasins. This relation was most obvious from June through October, when SRP concentrations were at their seasonal high (WPR = 0–5 µg/L; PWS ~20 µg/L; A28 = 30–40 µg/L; fig. 3A). The relation was less clearly defined during seasonal transitions

(November, May), but then resumed at lower concentrations from December through April (WPR= 1–2 µg/L; PWS= 2–6 µg/L; A28=3–10 µg/L).

B. Well drained subbasins with high- to low-density housing

Maximum base-flow SRP concentrations (fig 3B) were

- 42 µg/L, low-density housing (CRH), July;
- 29 µg/L, medium-density housing (P21), July; and
- 43 µg/L, high-density housing (P22), June.

Most SRP concentrations were within the range of the three reference subbasins, but the relation between SRP concentration and housing density was weaker among these subbasins than the reference subbasins. Samples from the subbasin with low-density housing (CRH) had anomalously high SRP concentrations. Concentrations equal to or greater than those at the subbasin with high-density housing, especially from December through April, may reflect high fertilizer usage, undocumented livestock, or failing septic systems (see golf-course and horse-farm subbasin data, and sewered subbasin data discussed in sections H and G below).

C. Moderately drained (uncolored-water wetland) subbasins with forest or low-density housing

Maximum base-flow SRP concentrations (fig. 3C) were

- 25 µg/L, forested (HNY), July;
- 25 µg/L, low-density housing (GED), July.

Uncolored-water wetlands appear to have little effect on SRP concentrations in subbasins with low-density housing. Most concentrations were less than 25 µg/L— below those in the reference subbasin (PWS) with medium-density housing. Housing density was not a reliable predictor of SRP in base flow among these subbasins, as the lowest and highest concentrations were in samples from subbasins with similar housing density (180 and 208 houses per mi^2, respectively). Samples from the forested subbasin (HNY) had low SRP concentrations from December through May that were similar to those at the well drained, forested reference subbasin (WPR), and higher concentrations from June through November that were comparable to those in the moderately drained (uncolored water wetland) subbasins with low-density housing.

D. Poorly drained (colored-water wetland) subbasins with low- and medium-density housing

Maximum base-flow SRP concentrations (fig. 3D) were

- 9 µg/L, low-density housing (RIC), September;
- 18 µg/L, medium-density housing (MAO), April.

SRP concentrations and seasonal variations in samples collected from the poorly drained subbasin (colored-water wetland) with low-density housing (RIC) were similar to those in uncolored-water wetlands. SRP concentrations in samples from the poorly drained subbasin with medium-density housing were as low as in the well drained, forested reference subbasin (WPR), except in late April and early May when concentrations rose to 10 to 20 µg/L.

E. Moderately drained (lake) subbasins with medium-density housing

Maximum base-flow SRP concentrations (3E) were

- 61 µg/L, (PLO), October;
- 13 µg/L, (LLO), October (limited number of samples).

Seasonal changes in SRP concentrations differed from those at the moderately drained reference subbasin with medium-density housing (PWS). Samples from the lake subbasins showed large seasonal fluctuations—sample concentrations from December through April were as low as at the reference forested subbasin (WPR), whereas those from May to November were variable but reached as high as 60 µg/L during leaf fall in late October.

F. Well drained urban subbasin with medium-density housing, transportation corridors, and commercial/industrial land

The maximum base-flow concentration (fig. 3F) was

- 11 µg/L (BED), in May.

This subbasin was characterized by low SRP concentrations in base flow with subdued seasonal fluctuatons. SRP concentrations were typically less than 10 µg/L—consistently above those at the forested reference subbasin (WPR) and below those at the reference subbasin with medium-density housing (PWS), except from late April through early May when the concentrations were equal.

G. Sewered subbasins: well drained with high-density housing and moderately drained (uncolored-water wetland) with medium-density housing

Maximum base-flow SRP concentrations (fig. 3G) were

- 56 µg/L, well drained, high-density housing (YRK), August;
- 34 µg/L, moderately drained (uncolored-water wetland), medium-density housing (GRA), June.

Samples from the two sewered subbasins (YRK, GRA) had higher SRP concentrations than the corresponding reference subbasins (A28, PWS). High SRP concentrations in samples from the sewered subbasins may reflect (1) high-end housing densities within their respective medium- and high-density classes (higher than the reference subbasins) or (2) leakage from sanitary sewers that parallel the streams.

H. Moderately drained (lake) subbasin with golf course (CEN) and well drained subbasin with horse farm (WAL)

Maximum base-flow SRP concentrations (fig. 3H) were

- 57 µg/L, moderately drained (lake), with golf course (CEN), July;
- 30 µg/L, well drained, with horse farm (WAL), June.

Subbasins with a golf course or horse farm had zero- or low-density housing but derived SRP from fertilizer and animal-waste sources. SRP concentrations in the golf-course subbasin exceeded all but one of those in the reference subbasin with high-density housing (A28) by as much as 20 µg/L. SRP concentrations in stream samples from the horse-farm subbasin were between those at the reference subbasins with medium (PWS) and high (A28) housing densities from June through October but exceeded those reference subbasins from December through April.

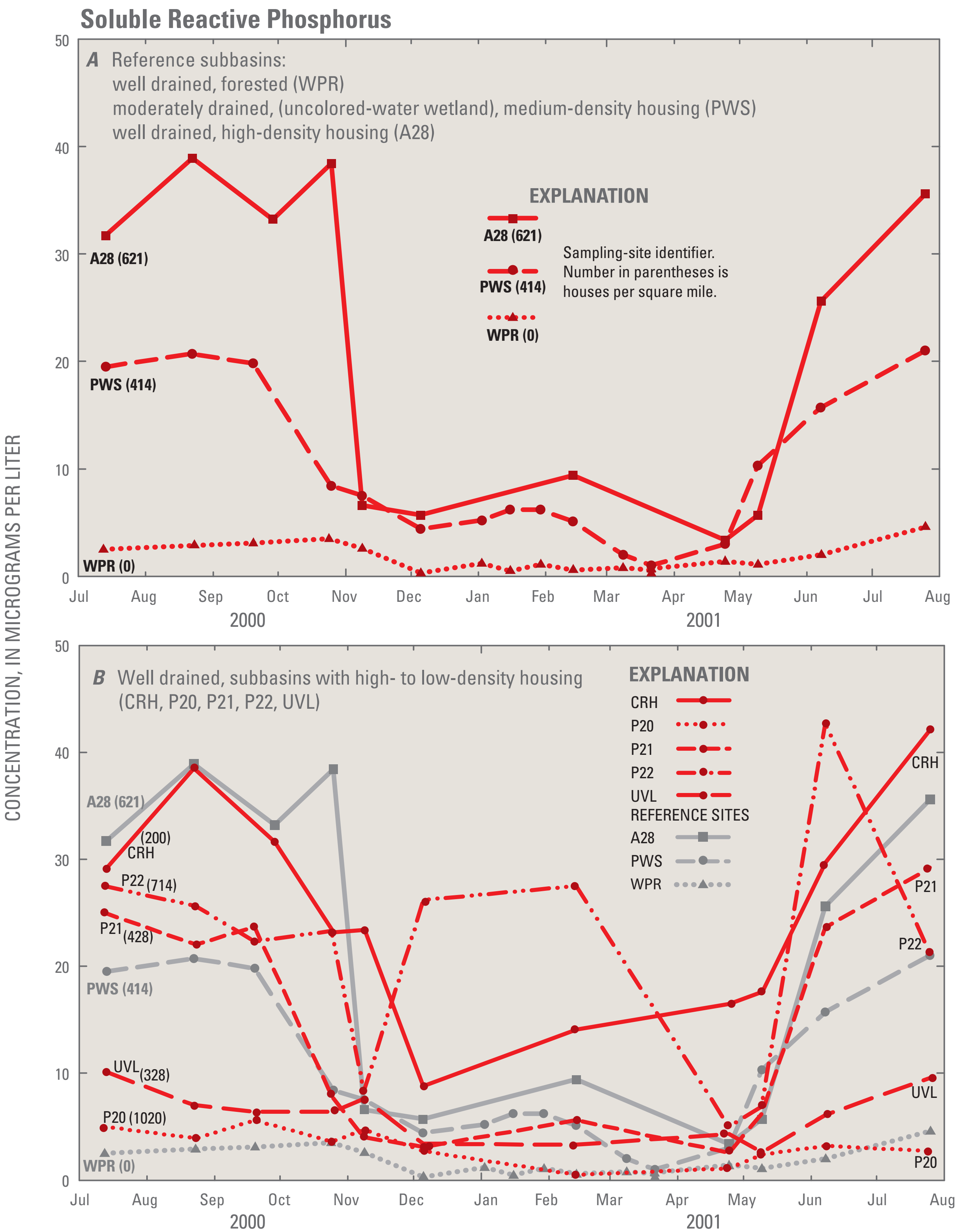


Figure 3. Base-flow soluble reactive phosphorus concentrations from July 2000 to July 2001, Croton Watershed, *(A)* reference subbasins, well drained, forested (WPR); moderately drained, uncolored-water wetland (PWS); medium-density housing, well drained, high density housing (A28), and *(B)* well drained subbasins, high- to low-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

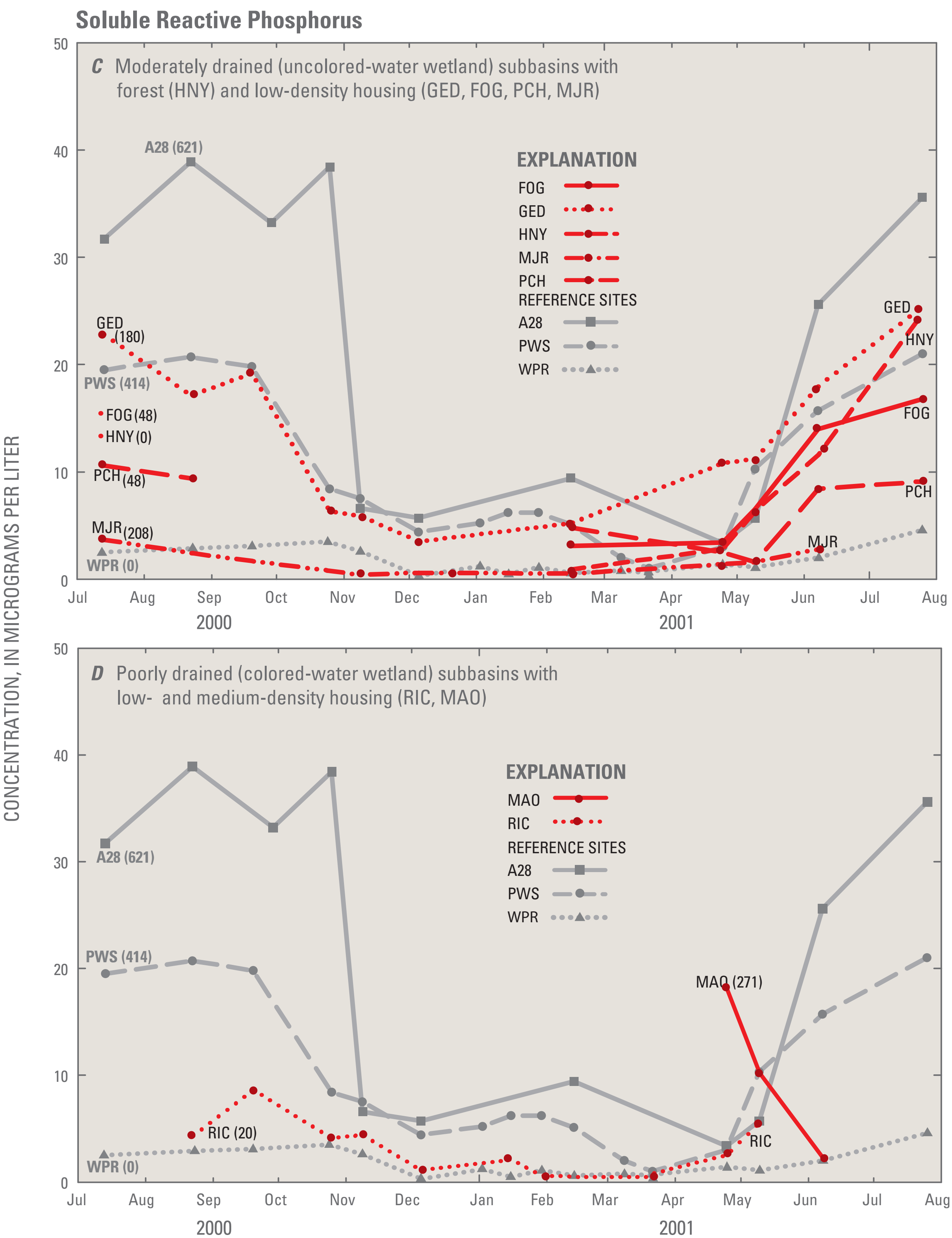


Figure 3. Base-flow soluble reactive phosphorus concentrations from July 2000 to July 2001, Croton Watershed, *(C)* moderately drained, uncolored-water wetland subbasins, forest and low-density housing, and *(D)* poorly drained, colored-water wetland subbasins with low- and medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig.1; sampling frequency shown in table 1.)

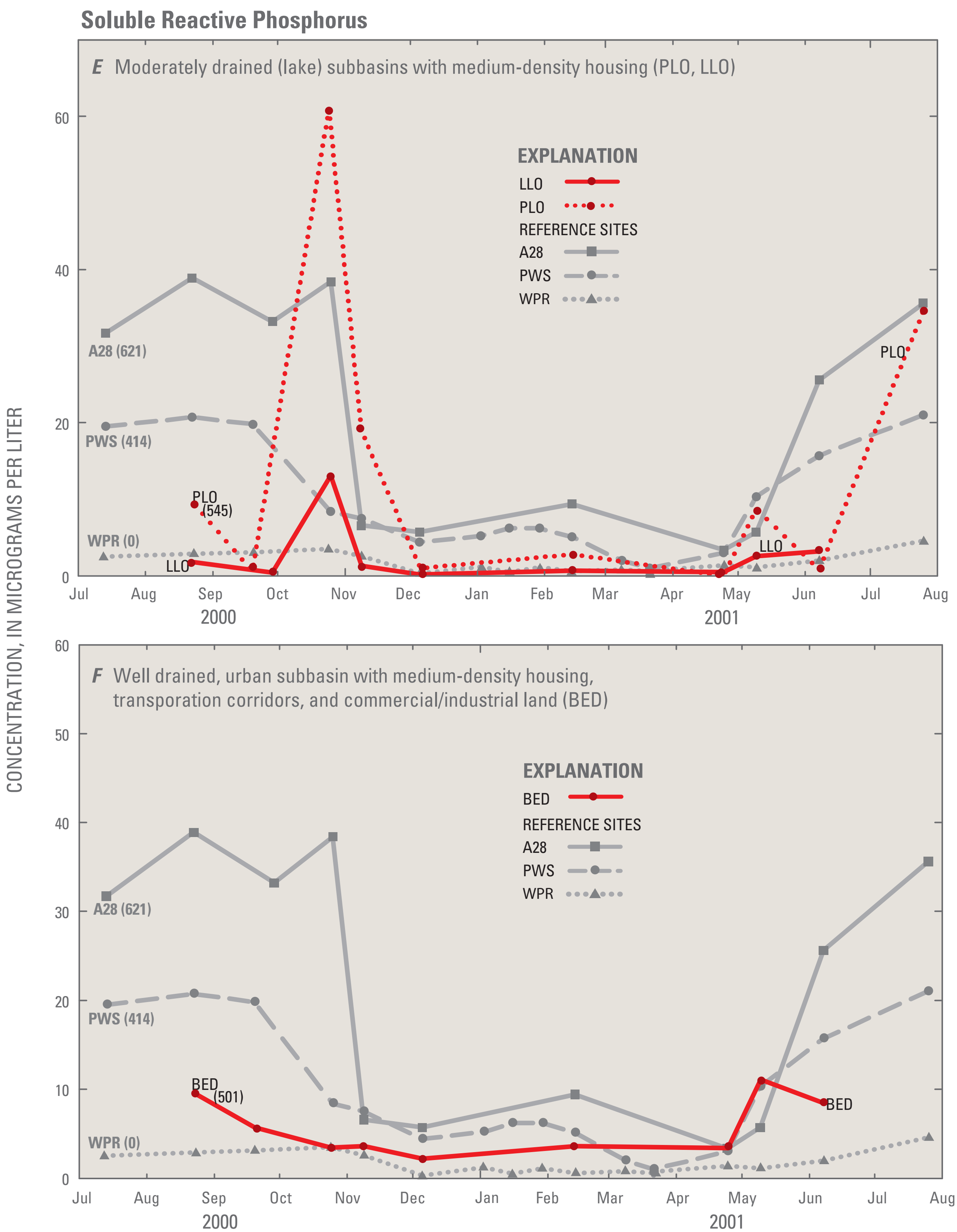


Figure 3. Base-flow soluble reactive phosphorus concentrations from July 2000 to July 2001, Croton Watershed, *(E)* moderately drained (lake) subbasins, medium-density housing, and *(F)* well drained, urban subbasin, medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

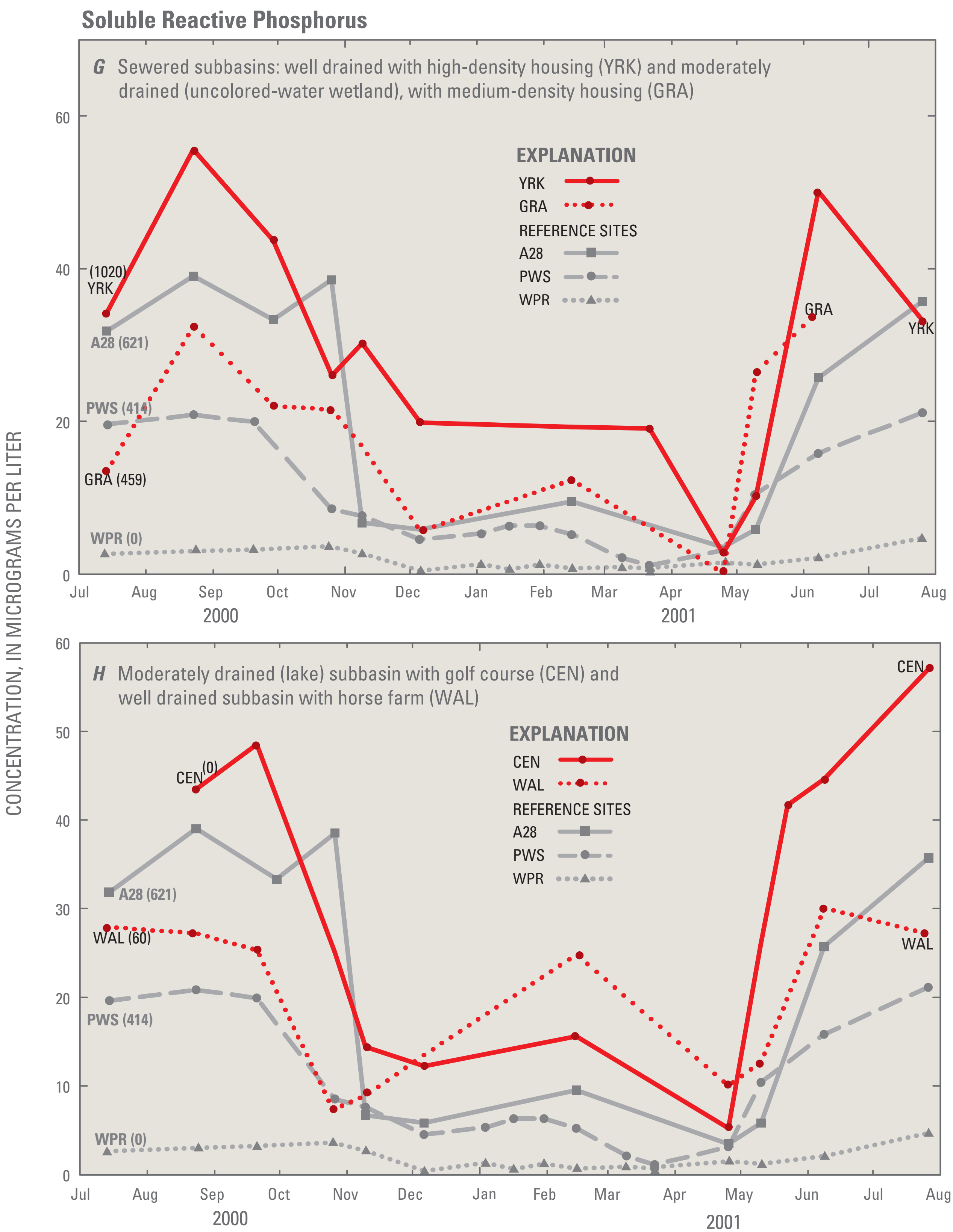


Figure 3. Base-flow soluble reactive phosphorus concentrations from July 2000 to July 2001, Croton Watershed, *(G)* sewered subbasins, well drained, high-density housing (YRK), moderately drained, uncolored-water wetland, medium-density housing (GRA), and *(H)* moderately drained subbasin, lake and golf course (CEN), well-drained subbasin with horse farm (WAL). Housing density, in houses per square mile, is denoted in parentheses after the subbasin site ID. (Locations are shown in fig. 1, sampling frequency shown in table 1.)

4.2.2.3 Stormflow Concentrations

SRP concentrations in stormflows were strongly affected by the degree and type of development within a subbasin (table 4). Stormflow concentrations were highest (100–350 µg/L) in well drained subbasins with high-density housing (sewered and unsewered) and at the golf-course and horse-farm subbasins.

Maximum stormflow concentrations in residential, well drained subbasins generally doubled with each step in the housing density classification (low<medium<high; table 4). The responses of stream stormflow concentrations to increases in housing density in sewered subbasins were similar to those in unsewered basins. Stormflow concentrations in samples from residential subbasins with uncolored-water wetlands or a lake were also similar to those in the corresponding well drained subbasins within the same housing-density category. Stormflow concentrations from colored-water-wetland subasins (the most poorly drained) were from 50 to 90 percent lower than those from well drained subbasins within the same housing-density category, and were about the same as those from the forested, undeveloped subbasins.

SRP concentrations in stormflow samples from well drained, subbasins with residential housing typically equaled or exceeded the base-flow concentrations in samples collected nearest in time to the storm event (before or after); this indicates that some SRP increases are derived from sources associated with surface runoff. Stormflow concentrations in samples from the most poorly drained (colored-water wetland) subbasins and in the forested (undeveloped) subbasins differed little from the base-flow concentrations collected just before or after the storm event.

Differences in base-flow and stormflow SRP concentrations varied seasonally. The largest differences between stormflow and base-flow concentrations were in samples collected during early-November (especially) and late-December storms. The smallest differences were in samples collected during spring storms, probably because a succession of springtime storms may result in dilution of phosphorus sources.

The highest stormflow SRP concentrations occurred during an early November storm, which followed the leaf-fall period and the autumn application of lawn fertilizers. This storm generated the first- or second-highest SRP concentration at nearly every subbasin. Otherwise, the second highest stormflow concentrations occurred in late May or late December.

4.2.3 Nitrate

Nitrate was the most common form of nitrogen in streams that drain well to moderately drained subbasins with medium to high housing densities or horse farm land use. Dissolved organic nitrogen was dominant in subbasins with little residential development, or with elevated DOC concentrations (lakes or colored-water wetlands). Nitrate+nitrite (as N) was measured in the laboratory, but since nitrate is the dominant form, the term “nitrate” is used herein instead of nitrate+nitrite. Sources of nitrogen associated with human activity in the Croton Watershed include (1) domestic wastewater, which may be discharged to septic systems or routed through sanitary sewers to wastewater-treatment plants, (2) fertilizers, which are applied to some residential lawns and to golf courses, and (3) animal wastes, such as manure from horse farms.

4.2.3.1 Summary: Median Concentrations (as N) in Base Flow, Stormflow, and WWTP Effluent

Base-Flow and Stormflow Medians: Nearly all median base-flow concentrations in each subbasin category were within the same concentration range as the stormflow medians (table 2); this indicates that the nitrate sources affect the concentrations in ground-water discharge (base flow) and surface-water runoff similarly. The *highest* median nitrate concentrations (between 1.1–3.0 mg/L, table 2.) in streamwaters (baseflow and stormflow) were associated with well drained subbasins with medium- and high-density housing and urban land use. Extended surface-water-residence times and elevated DOC in poorly or moderately drained (wetland) subbasins were associated with lower base-flow and stormflow nitrate concentrations than those in the well drained subbasins. Median base-flow and stormflow nitrate concentrations in the two colored-water-wetland subbasins (low and medium housing density) were below the detection limit (0.01 mg/L). Only base-flow nitrate concentrations at the moderately drained (uncolored-water wetland) subbasin with medium-density housing (PWS) were in the same range as nitrate concentrations in the well drained subbasins with medium- or high-density housing.

WWTP Effluent: Effluent samples from the three wastewater-treatment plants had a median concentration range of 3.1–10 mg/L, as N (table 2), which exceeded nitrate concentrations in all subbasin categories. Median and maximum nitrate concentrations at the individual WWTPs were as follows:

- Yorktown (HAL) median = 2.04 mg/L, maximum = 3.52 mg/L;
- Clocktower Commons (CLK) median = 8.85 mg/L, maximum = 16.00 mg/L; and
- Mahopac (MAH) median = 11.57 mg/L, maximum = 15.40 mg/L.

Nitrate concentrations at the Yorktown WWTP were lower than the other WWTPs because most effluent nitrogen is in the form of ammonia (median = 20.0 mg/L as N). The median ammonia concentration for CLK and MAH was 0.02 mg/L.

Table 4. Seasonal stormflow concentrations of soluble reactive phosphorus (SRP) in the stream network, by subbasin category, Croton Watershed, southeastern, N.Y., 2000–02.

[mi^2, square miles; All values are in micrograms per liter]

Land use and drainage efficiency category	Number of samples	Flow conditions sampled[1]	For each Half-month period: *max* = Highest stormflow concentrations; *rel.* = Relation of stormflow concentrations to baseflow concentration[2]																
Forested				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	13	r, p, f, re	*max*					1	1		5					58			1
			rel.					=	=		≥					>			=
Moderately drained Wetland-uncolored water	2	re	*max*					1			7								
			rel.					=			=								
Residential (by housing density)																			
Low-density (<250 houses mi^{-1})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	4	f, re	*max*					6			22					36			29
			rel.					<			=					>			>
Moderately drained Wetland-uncolored water	28	r, f, re	*max*					32			14					33			7
			rel.					≥			<=>					≥			>
Poorly drained Wetland-colored water	14	r, f, re	*max*						1		5					16			1
			rel.						=		=					≥			=
Medium-density (251-600 houses mi^{-2})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	9	p, f, re	*max*					31	7		25					64			14
			rel.					≥	≥		≥					≥			≥
Well drained, Urban	4	f, re	*max*					6			13					77			8
			rel.					>			>					>			>
Moderately drained Wetland-uncolored water	26	r, p, f, re	*max*					8	4		10		19		25	23			5
			rel.					>	>		≥		=		≤	≥			>
Moderately drained Wetland-uncolored water, sewered	4	f, re	*max*					19			32					71			17
			rel.					>			=					>			>
Poorly drained Wetland-colored water	3	r, p, f, re	*max*								2					2			7
			rel.								<					=			>
Moderately drained Lake	21	f, re	*max*					4			15					76			49
			rel.					=			≥					<=>			≥
High-density (>600 houses mi^{-2})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	25	r, p, f, re	*max*					30	53		201					165			45
			rel.					≥	≥		<=>					>			<=>
Well drained Sewered	18	r, p, f, re	*max*					44	56		91					214			45
			rel.					≥	≥		>					<=>			=
Golf Course				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Moderately drained Lake (small ponds)	12	r, p, f, re	*max*					30			32		165			341			79
			rel.					>			=		<=>			>			>
Horse Farm				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	8	r, f, re	*max*					52			80					132			90
			rel.					≥			>					>			>

[1]Flow conditions - storm hydrograph
- r, rising limb
- p, peak
- f, steeply falling limb
- re, recession

[2]Relation of stormflow concentration to base-flow concentration
- = equal to
- > greater than
- ≥ greater than or equal to
- < less than
- ≤ less than or equal to
- <=> variable

4.2.3.2 Base-Flow Concentrations, by Drainage Efficiency and Land-Use Category

Base-flow nitrate concentrations followed a similar seasonal pattern at most well drained and moderately drained (uncolored-water-wetland) subbasins (fig. 4A–H). The lowest concentrations occurred after leaf-fall in mid-autumn, the highest concentrations occurred in winter, a secondary low occurred in mid-spring, and mid-range concentrations occurred in summer. Nitrate concentrations in base-flow samples were lowest in the well drained, forested subbasin (WPR), and concentrations generally increased with housing density, although some subbasins with low-density housing had elevated concentrations. Samples from the two sewered subbasins (YRK, GRA) typically had lower nitrate concentrations than their unsewered counterparts, and the well drained subbasin with horse-farm land use had base-flow concentrations similar to those in subbasins with low-density housing. Base-flow samples from the urban subbasin (BED) had high nitrate concentrations with minimal seasonal variation.

Moderately drained (lake) subbasins and, in particular, poorly drained (colored-water-wetland) subbasins had different seasonal patterns of base-flow nitrate concentration than the other subbasins and had among the lowest nitrate concentrations in the study (dissolved organic nitrogen was the dominant form of nitrogen). Lake subbasins with medium-density housing showed a seasonal pattern of nitrate concentration opposite of that in well drained subbasins, with peak base-flow concentrations in mid-autumn and mid-spring. The golf-course subbasin (CEN), which has small ponds, had only a partial set of sample data but had among the lowest base-flow nitrate concentrations. Nitrate concentrations in stream samples at the two poorly drained subbasins with colored-water wetlands (RIC, MAO) were near or below the detection limit most of the year, except for a single peak in mid-autumn at the subbasin with medium-density housing (MAO).

A. Reference Subbasins: well drained, forested; moderately drained (uncolored-water wetland) with medium-density housing; and well drained subbasin with high-density housing

Maximum base-flow nitrate concentrations (fig. 4A) were

- 0.11 mg/L, well drained, forested (WPR), early January;
- 2.62 mg/L, moderately drained, medium density housing (PWS) late July; and
- 2.68 mg/L, well drained, high-density housing (A28), early February.

The strongest seasonal pattern of base-flow nitrate concentration was at the reference subbasin with high-density housing (A28). Lowest concentrations were in late October and early November, during and immediately after leaf fall, when stream DOC was elevated (along with dissolved organic nitrogen). A minor secondary minimum occurred in late April and early May. The highest concentrations were in winter, when biological activity was at a minimum. Mid-range concentrations were observed from late spring through early autumn.

Nitrate concentrations in base flow from the forested reference subbasin (WPR) were among the lowest of all subbasins, but showed a seasonal nitrate concentration pattern similar to that of the reference subbasin with high-density housing.

The subbasin with medium-density housing (PWS) showed far less seasonal variability in base-flow nitrate concentration (smaller decrease in fall, and lack of a winter peak) than the reference subbasin with high-density housing (fig. 4A) but had the highest concentrations of the three reference sites all year, except during the winter peak when the well drained subbasin with high-density housing (A28) had the highest base-flow nitrate concentrations. The base-flow concentrations at the subbasin with medium-density housing were anomalous in that they were more stable and higher than those in all the other moderately drained (uncolored-water wetland) subbasins and most well drained subbasins.

B. Well drained subbasins with high- to low-density housing

Maximum base-flow nitrate concentrations were

- 2.02 mg/L, low-density housing (CRH) February;
- 2.66 mg/L, medium-density housing (UVL), February; and
- 3.73 mg/L, high-density housing (P20), February.

The seasonal pattern observed at these subbasins was the same as at the reference subbasin with high-density housing (A28), although the fluctuations at one subbasin (P21) were subdued. Base-flow nitrate concentrations generally increased with increasing housing density.

C. Moderately drained (uncolored-water-wetland) subbasins with forest or low-density housing

Maximum base-flow nitrate concentrations were

- 0.62 mg/L, forested (HNY), early July;
- 1.68 mg/L, low-density housing (GED), February.

Seasonal patterns in base-flow nitrate concentrations in these two categories were similar to those at the two well drained reference subbasins, but the autumn decreases were less pronounced, and the spring decreases were more pronounced.

Base-flow nitrate at the moderately drained forested subbasin (HNY) was similar to that at the well drained forested subbasin (WPR), except for the first sample in July, which had the maximum concentration (see above), and for the lack of a winter peak. Base-flow nitrate increased with housing density among the moderately drained low-density housing subbasins, except at subbasin MJR, which consistently had low nitrate concentrations (fig. 4C).

D. Poorly drained (colored-water-wetland) subbasins with low- and medium-density housing

Maximum base-flow nitrate concentrations were

- 0.04 mg/L, low-density housing (RIC), late March;
- 0.94 mg/L, medium-density housing (MAO), late October.

All nitrate concentrations in these samples were near or below the detection limit (0.01 mg/L), with the exception of the late October sample from the subbasin with medium-density housing (MAO). This peak was unusual because it coincided with concentration lows at the well drained and uncolored-water-wetland subbasins.

The low nitrate concentrations from these subbasins, compared to well drained subbasins, are probably a result of denitrification (nitrate loss) under local anoxic conditions associated with high DOC concentrations and abundant organic matter in these subbasins.

E. Moderately drained (lake) subbasins with medium-density housing

The maximum base-flow nitrate concentration, 1.15 mg/L, was measured in a sample from subbasin PLO in late October. Base-flow nitrate concentrations were typically low—0.2 to 0.4 mg/L—except during late October and late April peaks, when samples from both subbasins reached about 1 mg/L (fig. 4E). The October peak coincided with the base-flow nitrate peak at the poorly drained (colored-water wetland) subbasin with medium-density housing (MAO) and with concentration lows at the well drained subbasins and the moderately drained (uncolored-water) wetland subbasins.

F. Well drained urban subbasin with medium-density housing, transportation corridors, and commercial/industrial land

The maximum subbasin BED base-flow nitrate concentration (fig. 4F) was 3.24 mg/L, in late October.

All concentrations exceeded those at the three reference subbasins and did not vary by more than 0.5 mg/L during the year. No winter peak was identified, but a small late-October peak coincided those at the moderately drained (lake) subbasins with medium-density housing and at the two poorly drained (colored-water wetland) subbasins. Subbasin BED contains a headwater lake.

G. Sewered subbasins: well drained with high-density housing and moderately drained (uncolored-water wetland) with medium-density housing

Maximum base-flow nitrate concentrations (fig. 4G) were

- 1.57 mg/L, well drained, with high-density housing and sanitary sewers (YRK), late July;
- 1.54 mg/L, moderately drained (uncolored water wetland) with medium-density housing and sanitary sewers (GRA), early February.

Base-flow nitrate concentrations in sewered subbasins, and their seasonal patterns, were similar to one another as well as to those in well drained and uncolored-water-wetland subbasins with low- and medium-density housing. Nitrate concentrations were generally lower than in subbasins with similar housing densities, which suggests that sanitary sewering does decrease the amount of nitrate reaching the stream. This observation is the opposite of what was observed for SRP. SRP may be higher in these subbasins because sewerlines following stream courses offer minimal contact with soils prior to entering streams if leakage occurs. Longer ground-water flowpaths from septic systems distributed throughout a watershed result in much greater contact times for soil material to sorb wastewater phosphorus. Alternatively, relatively small stream concentrations of nitrate may not indicate low concentrations entering the stream but perhaps uptake of nitrate by algal growth or other biological activity in the stream.

The high nitrate concentration in base flow of late July 2001 in the sewered subbasin with high-density housing coincided with high TP concentration and unfiltered trihalomethane (THM) formation potentials. These data may indicate wastewater contribution to the stream.

H. Moderately drained (lake) subbasin with golf course (CEN) and well drained subbasin with horse farm (WAL)

Maximum base-flow nitrate concentrations (fig. 4H) were

- 0.28 mg/L, moderately drained (lake), with golf course (CEN), early December;
- 1.17 mg/L, well drained, with horse farm (WAL), late July.

Base-flow nitrate concentrations in samples from the golf-course subbasin (CEN) were lower than in most other subbasins; the lowest concentrations were measured in summertime samples. No winter or early spring data were available, but the concentrations were probably highest at this time of year, as observed in many other subbasins.

Base-flow nitrate concentrations in the horse-farm subbasin were equivalent to those in the four subbasins with moderate drainage (uncolored-water wetlands) and low-density housing, although the lack of winter peak concentrations was most similar to that of the reference subbasin (PWS) with moderate drainage (uncolored-water wetland) and medium density housing.

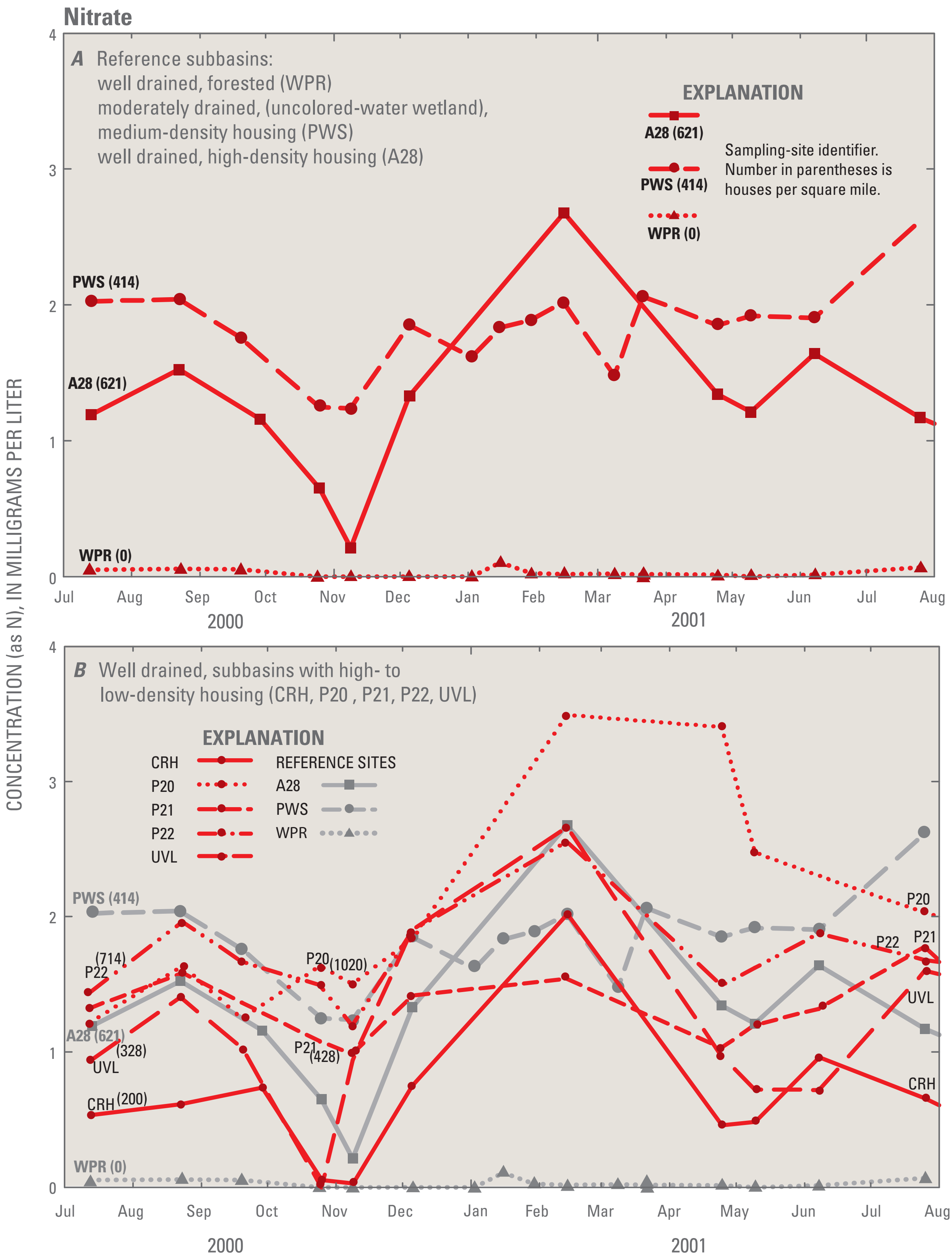


Figure 4. Base-flow nitrate concentrations (as N) from July 2000 to July 2001, Croton Watershed, *(A)* reference subbasins, well drained forested (WPR); moderately drained (uncolored -water wetland), medium-density housing (PWS); well drained, high-density housing (A28), and *(B)* well drained subbasins, high- to low-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

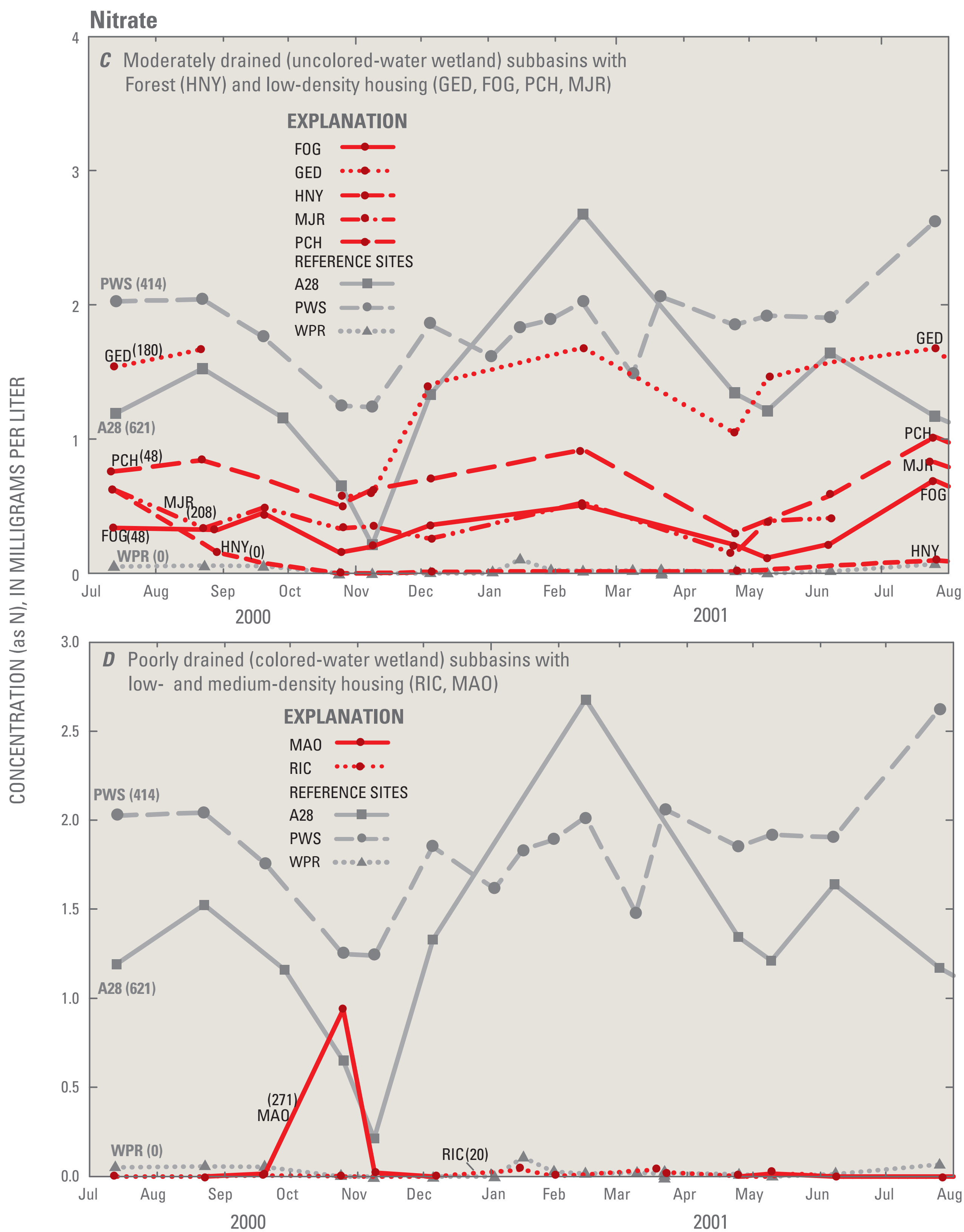


Figure 4. Base-flow nitrate (as N) concentrations from July 2000 to July 2001, Croton Watershed, *(C)* moderately drained, uncolored-water wetland subbasins, low-density housing, and *(D)* poorly drained, colored-water wetland subbasins, low- and medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

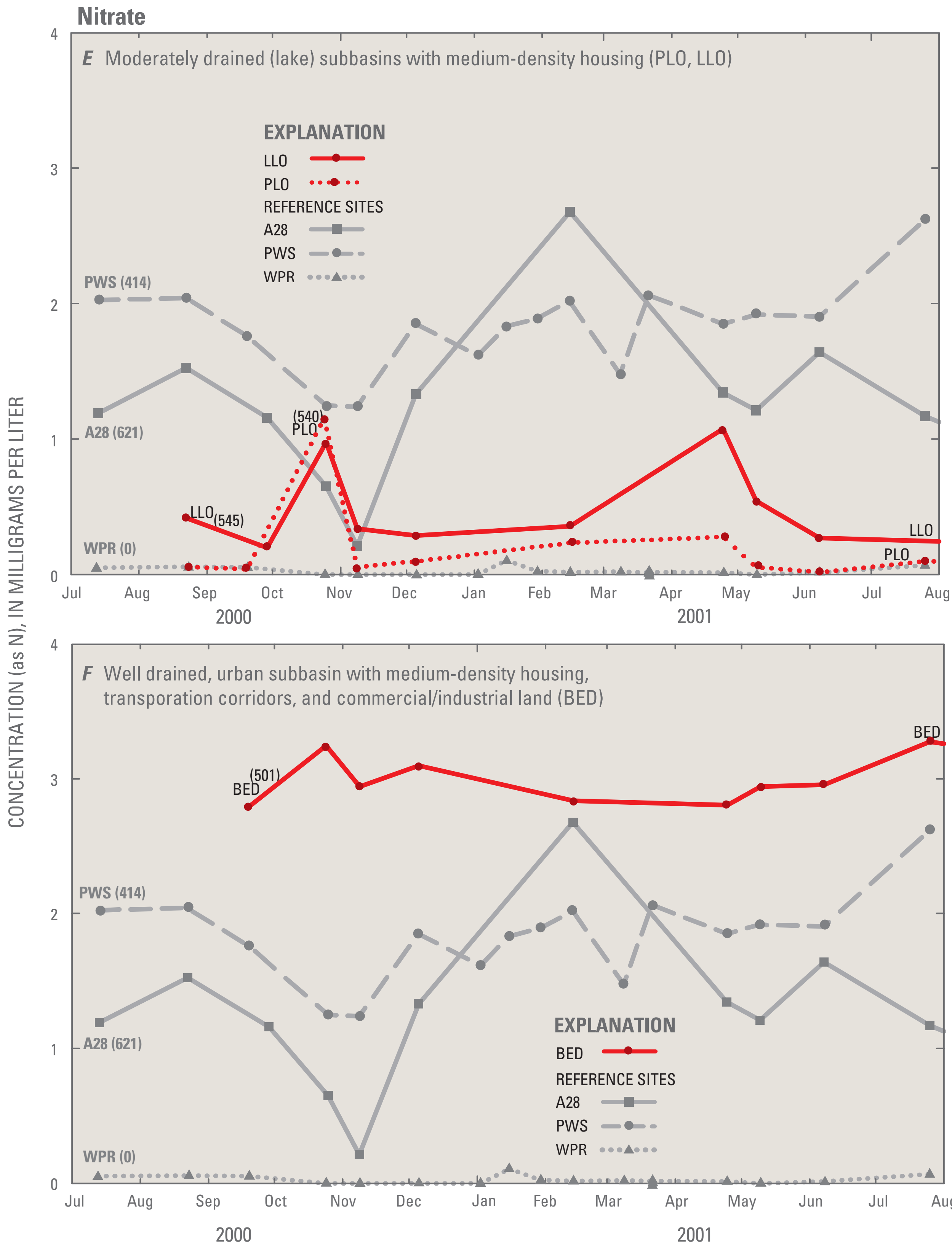


Figure 4. Base-flow nitrate (as N) concentrations from July 2000 to July 2001, Croton Watershed, *(E)* moderately-drained subbasins with lakes and medium-density housing, and *(F)* well drained, urban subbasin, medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

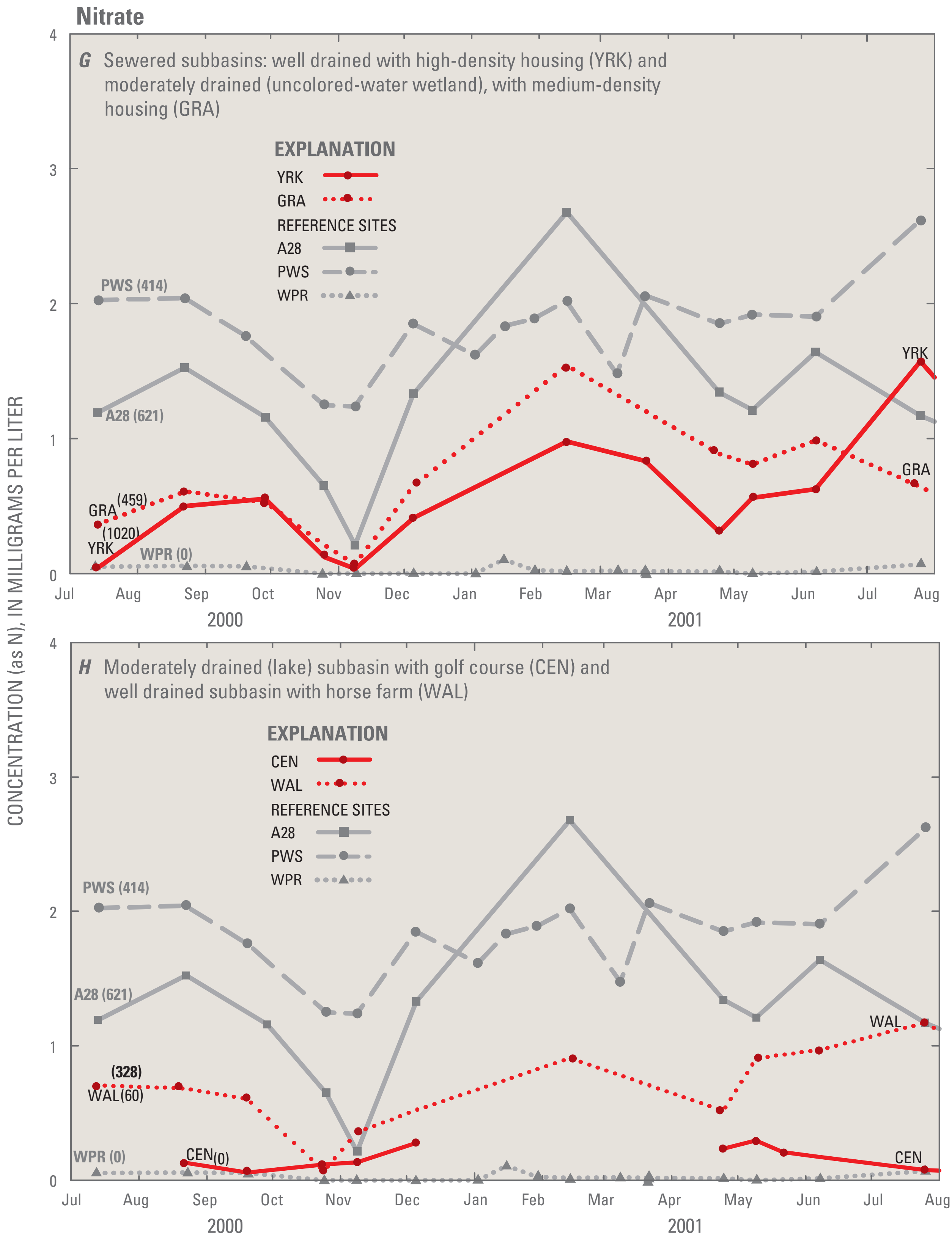


Figure 4. Base-flow nitrate (as N) concentrations from July 2000 to July 2001, Croton Watershed, *(G)* sewered subbasins, well drained, high-density housing (YRK), moderately drained (uncolored-water wetland), medium-density housing (GRA), and *(H)* moderately-drained (lake) subbasin, golf course (CEN), well-drained subbasin, horse farm (WAL). Housing density in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

4.2.3.3 Stormflow Concentrations

Nearly every form of land use resulted in higher stormflow nitrate concentrations than were detected in the two forested (undeveloped) subbasins (WPR, HNY; table 5A) —stormflow nitrate concentrations at those subbasins did not exceed 0.3 mg/L. The highest stormflow nitrate concentrations were in samples from well drained subbasins with residential development. Concentrations increased with increasing housing density, and were typically highest in the winter, when biological activity was at a minimum (tables 5A, 5B).

The highest individual stormflow nitrate concentrations from this study were the 4.56 and 3.51 mg/L (tables 5A, 5B).

Decreases in subbasin drainage efficiency—from well drained to moderately drained (uncolored-water wetlands and lakes) to poorly drained (colored-water wetlands)—corresponded to decreases in stormflow nitrate concentration. Decreased drainage efficiency corresponds to general increases in water residence time, biological activity, and DOC concentration. Stormflow nitrate concentrations in uncolored-water wetland or lake subbasins with low- and medium-density housing were about one-half of those in the corresponding well drained subbasins during the December 2000 storm. Stormflow nitrate concentrations in colored-water wetlands with low- and medium-density housing were as low as those in the two forested subbasins, except during March and November storms, when they reached about 1 mg/L.

Stormflow nitrate concentrations in sanitary sewered subbasins were generally less than those in the corresponding unsewered subbasins. Stormflow nitrate concentrations in the urban subbasin (BED) had among the most consistent elevated stormflow nitrate concentrations (maximum: 2.96 mg/L, in early December).

The subbasins with golf-course (CEN) and horse-farm (WAL) land uses were not among the highest sources of stormflow nitrate. Stormflow samples from the golf-course subbasin (CEN) had high storm concentrations of 0.70 mg/L (March) and 1.00 mg/L (early November); the remainder of the storm samples had concentrations about half as high. The horse-farm subbasin (WAL) had a maximum stormflow nitrate concentration of 1.75 mg/L (late December) but maintained concentrations of 0.65 to 1.08 mg/L in other storm samples.

4.2.4 Dissolved Organic Carbon (DOC)

DOC is closely associated with natural sources of organic matter, such as in wetlands, where water may have long contact time with decaying organic matter. In response, DOC concentrations progressively increase from well drained to moderately drained (uncolored-water wetland or lake) to poorly drained (colored-water wetland) subbasins (table 2). Domestic wastewater is a secondary source of DOC.

4.2.4.1 Summary: Median Concentrations in Base Flow, Stormflow, and WWTP Effluent

Base-Flow and Stormflow Medians: Median base-flow DOC concentrations increased with each decrease in subbasin drainage efficiency (well drained to moderately drained to poorly drained), which implies that natural DOC sources are the primary control on concentration. DOC concentrations in stormflows were within a higher range (table 2) than base-flow concentrations in most (10 of the 11) well drained subbasins; the exception was in samples from the sewered subbasin with high-density housing (YRK)–base-flow DOC concentrations were generally about 1 mg/L higher than at the high-density housing reference subbbasin (perhaps indicative of sewer leakage). Base-flow and stormflow DOC concentrations fell within the same concentration range at most moderately drained and all poorly drained subbasins (table 2).

WWTP Effluent: Effluent from the wastewater-treatment plants had a moderately high median DOC concentration—between 3.1 and 10 mg/L (table 2). Individual WWTP median and maximum concentrations were as follows:

- Yorktown (HAL) median = 8.94 mg/L, maximum = 10.51 mg/L;
- Clocktower Commons (CLK) median = 5.05 mg/L, maximum = 7.31 mg/L; and
- Mahopac (MAH) median = 5.69 mg/L, maximum = 7.58 mg/L.

4.2.4.2 Base-Flow Concentrations, by Drainage Efficiency and Land-Use Category

Base-flow DOC was characterized by a consistent seasonal pattern in most of the residential well drained and moderately drained (uncolored-water wetland) subbasins. The pattern consisted of a mid-autumn peak following the leaf-fall period, moderate to low winter concentrations, mid- to late spring peak(s), and relatively low summer concentrations until August, when DOC concentrations could approach those of the mid-autumn peak (fig. 5, A–H). DOC concentrations typically were lowest in the well drained residential subbasins. DOC concentrations in the two sewered subbasins (YRK, GRA) consistently exceeded

Table 5A. Seasonal stormflow concentrations of nitrate as N in the stream network by subbasin category, Croton Watershed, southeastern, N.Y., 2000–02.

[mi2, square miles; All values are in milligrams per liter.]

Drainage/land-use category	Number of samples	Flow conditions sampled[1]	For each half-month period: *max* = Highest stormflow concentrations; *rel.* = Relation of stormflow concentrations to baseflow concentration[2]																
Forested (zero housing)				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	13	r, p, f, re	*max*					0.02	0.02		<0.01					0.18		<0.01	0.03
			rel.					≤	≤		=					>		=	>
Moderately drained Wetland, uncolored water	2	f, re	*max*													0.24			0.03
			rel.													>			>
Residential (by housing density)																			
Low-density (<250 houses mi^{-1})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	5	f, re	*max*					1.48			0.33					0.32		0.19	2.87
			rel.					>			<					<=>		<=>	<=>
Moderately drained Wetland, uncolored water	34	r, f, re	*max*					1.56			0.85				0.72	0.52		0.87	1.46
			rel.					>			≤				≤	≤		≥	≥
Poorly drained Wetland, colored water	13	r, f, re	*max*					0.04	1.15		0.01					1.10			0.16
			rel.					≥	≥		=					≥			>
Medium-density (251-600 houses mi^{-2})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	9	p, f, re	*max*					2.20	1.56		0.91					1.33		1.48	3.51
			rel.					≤	≤		≤					≤		<=>	<=>
Well drained Urban	5	f, re	*max*					2.51			1.53					0.94		2.96	2.76
			rel.					<			<					<		≤	≤
Moderately drained Wetland, uncolored water	33	r, p, f, re	*max*					1.68	1.82		1.54		1.13		2.91	1.06		1.29	1.71
			rel.					≥	≤		≤		≤		≥	<		<	<=>
Moderately drained Wetland, uncolored water, sewered	5	f, re	*max*					1.66			0.39					0.57		0.12	1.96
			rel.					>			<					>		<=>	<=>
Poorly drained Wetland, colored water	5	f, re	*max*								<0.01					0.03			0.17
			rel.								=					≥			≥
Moderately drained Lake	23	r, p, f, re	*max*					0.85			0.47					0.12		0.28	0.21
			rel.					≥			=					=		=	=
High-density (>600 houses mi^{-2})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	27	r, p, f, re	*max*					3.47	3.34		3.44					1.18		0.98	4.56
			rel.					<=>	<=>		<=>					=		<=>	<=>
Well drained Sewered	20	r, p, f, re	*max*					0.87	1.04		0.49					0.45		0.16	1.33
			rel.					<=>	<=>		≤					>		≥	≥
Golf Course				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Moderately drained Lake (small ponds)	11	r, p, f, re	*max*					0.70			0.23		0.50			1.00			0.49
			rel.					≥			=		≥			>			>
Horse Farm				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	8	r, f, re	*max*					0.96			0.77					1.08		0.65	1.75
			rel.					≥			=					>		≥	≥

[1]Flow conditions in storm hydrograph
- r, rising limb
- p, peak
- f, steeply falling limb
- re, recession

[2]Relation of stormflow concentration to base-flow concentration
- = equal to
- > greater than
- ≥ greater than or equal to
- < less than
- ≤ less than or equal to
- <=> variable

Table 5B. Comparison of maximum nitrate (as N) concentrations in stormflows among well drained subbasins with different housing densities for December and March storms, stream network, Croton Watershed, southeastern N. Y., 2000–02.

[mg/L, milligrams per liter]

Storm date	Well drained residential subbasin, nitrate concentration (mg/L as N)		
	Low-density housing	Medium-density housing	High-density housing
December 2000	2.87	3.51	4.56
March 2001	1.48	2.20	3.47

those in the unsewered basins; the greatest concentration differences were seen during late-summer low flows. Increases in DOC concentrations during low base-flow periods suggest a ground-water source that may be derived from sanitary-sewer leakage.

Seasonal DOC patterns in base-flow samples from lake subbasins with medium-density housing were nearly the opposite of those in the well drained and moderately drained (uncolored-water wetland) subbasins—concentrations remained high through most of the year, reflecting lake discharge but were diluted during the autumn and spring and to a lesser extent in winter. The range of DOC concentrations in samples from lake subbasins was similar to that in uncolored-water-wetland subbasins.

The moderately drained (lake) subbasin with golf-course (CEN) and the poorly drained (colored-water wetland) subbasin with low-density housing (RIC) had similar annual patterns, but concentrations at the colored-water subbasin were about 5 times higher. Both subbasins showed a decrease in concentration from September through April, and additional decreases during the autumn peak that could have resulted from DOC dilution in the increased base flows. The two subbasins differed, however, in that the spring DOC peak at the golf-course subbasin represented the highest DOC concentrations of the year, whereas the peak at the colored-water subbasin was relatively minor.

A. Reference Subbasins: well drained, forested; moderately drained (uncolored-water wetland) with medium-density housing; and well drained subbasin with high-density housing

Maximum base-flow DOC concentrations (fig 5A) were

- 2.7 mg/L, well drained, forested (WPR), late October;
- 3.6 mg/L, moderately drained (uncolored-water wetland), medium-density housing (PWS), late April; and
- 2.9 mg/L, well drained, high-density housing (A28), early June, and 2.8 mg/L, late October and early November, following leaf fall.

The well drained forested (WPR) and high-density housing (A28) reference subbasins were characterized by high concentrations in late summer, mid-autumn, and late spring and by relatively stable concentrations (1–2 mg/L) over the remainder of the year.

The moderately drained (uncolored water wetland) reference subbasin with medium-density housing (PWS) had, in addition to the periods of high DOC described above, an additional mid-spring base-flow DOC peak with the highest DOC concentration of the year among the three reference sites.

B. Well drained subbasins with high- to low-density housing

Late summer, fall, and spring base-flow DOC peaks at these subbasins coincided with those of the reference subbasins, with similar concentrations, except for the mid-spring base-flow peak at the reference subbasin with medium-density housing. DOC concentrations in base flow were generally higher than those at the forested reference subbasin and lower than base-flow DOC concentrations at the high-density housing reference subbasin. Most base-flow DOC concentrations were between 1 and 3 mg/L and showed little association with housing density.

C. Moderately drained (uncolored-water wetland) subbasins with forest or low-density housing

Maximum base-flow DOC concentrations (fig. 5C) were

- 9.2 mg/L, forested (HNY), early June;
- 6.5 mg/L, low-density housing (FOG), late October.

Base-flow samples from subbasins with uncolored-water wetlands typically had higher DOC concentrations than those from the reference subbasins. Concentrations in the forested subbasin were usually between 4 and 8 mg/L, and those in the subbasins with low-density housing were between 1 and 6 mg/L.

Seasonal base-flow DOC variation at the subbasins with low-density housing was similar to that at the two well drained reference subbasins. The forested subbasin showed high DOC concentrations sporadically from mid-summer to late autumn that sometimes exceeded concentrations of the autumn leaf-fall peak.

DOC concentration showed to little association with housing density.

D. Poorly drained (colored-water wetland) subbasins with low- and medium-density housing

Maximum base-flow DOC concentrations (fig. 5D) were

- 31.2 mg/L, poorly drained (colored-water wetland) with low-density housing (RIC) August (highest base-flow DOC concentration of the study) ;
- 23.8 mg/L, poorly drained (colored-water wetland) with medium-density housing (MAO), August.

High DOC concentrations at subbasin RIC were sustained from July through early December, except for one sample in late October. The spring base-flow peak in DOC concentration was lower than the high concentrations of late summer. Low concentrations of about 5 mg/L were measured in subbasin RIC samples from February and March (fig. 5D).

E. Moderately drained (lake) subbasins with medium-density housing

The maximum base-flow DOC concentration in this category was 7.6 mg/L from subbasin PLO, in August (fig. 5E).

DOC concentrations from these two subbasins (PLO, LLO) with a lake were typically double those of the reference subbasins.

The seasonal DOC concentration pattern was opposite that measured in samples from the well drained basins; concentrations decreased during the autumn and spring base-flow DOC concentration peaks at the reference subbasins (fig. 5E). This contrasting base-flow DOC pattern at the lake subbasins may reflect discharge of algae-laden water much of the year with dilution during high autumn and spring base-flows.

F. Well drained urban subbasin with medium-density housing, transportation corridors, and commercial/industrial land

The maximum DOC concentration in this subbasin (BED) was 3.8 mg/L, in August (fig. 5F).

Concentrations were typically about 2 mg/L, and autumn and spring peaks were minor. The concentration pattern was most similar, in general, to that of the lake subbasins described above. This subbasin has a headwater lake.

G. Sewered subbasins: well drained with high-density housing and moderately drained (uncolored-water wetland) with medium-density housing

Maximum base-flow DOC concentrations (fig. 5G) were

- 4.8 mg/L, well drained, with high-density housing (YRK), early July;
- 4.6 mg/L, moderately drained, with medium-density housing (GRA), August.

Elevated low-flow DOC concentrations at the two sewered subbasins in July may be indicative of leakage from sewer mains. Base-flow DOC concentrations at these subbasins (YRK, GRA) were about 1 mg/L higher than those at the reference subbasins. DOC concentrations at the two sewered subbasins were usually within 1 mg/L of each other, although samples from the subbasin with high-density housing (YRK) were typically higher in DOC than at the subbasin with medium-density housing (GRA).

H. Moderately drained (lake) subbasin with golf course (CEN) and well drained subbasin with horse farm (WAL)

Maximum base-flow DOC concentrations (fig. 5H) were

- 8.3 mg/L, moderately drained (lake), with golf course (CEN) late May;
- 6.9 mg/L, well drained, with horse farm (WAL), late October.

Most base-flow DOC concentrations in samples collected from the golf-course subbasin were between 2 and 8 mg/L and exceeded those in all three reference basins, except for the late-April sample. DOC at the golf-course subbasin declined about 0.5 mg/L during the autumn peak at the reference subbasins.

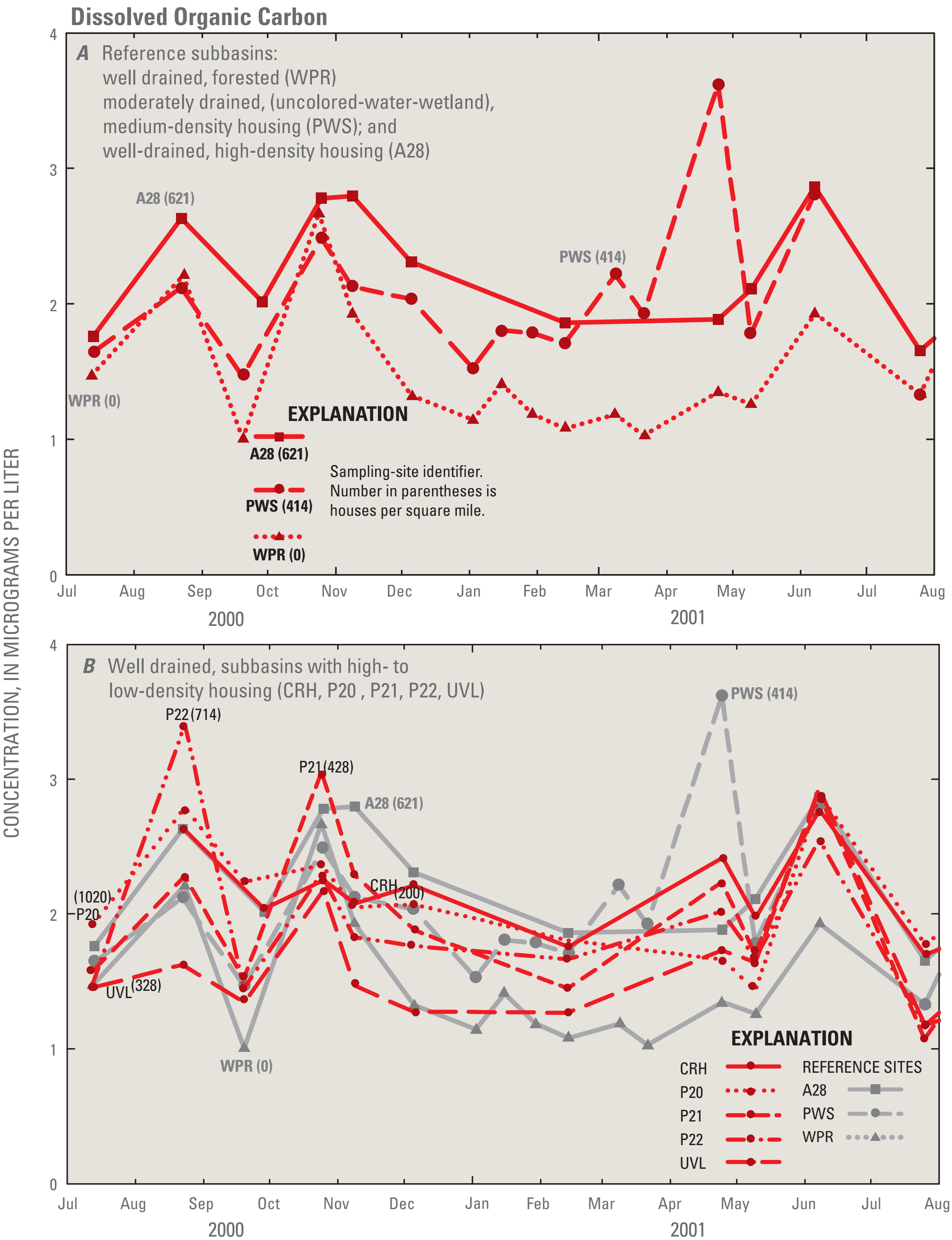


Figure 5. Base-flow dissolved organic carbon concentrations from July 2000 to July 2001, Croton Watershed, *(A)* reference subbasins, well drained, forested (WPR); moderately drained, uncolored water wetland, medium-density housing (PWS); well-drained, high-density housing (A28), and *(B)* well drained subbasins, high- to low-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

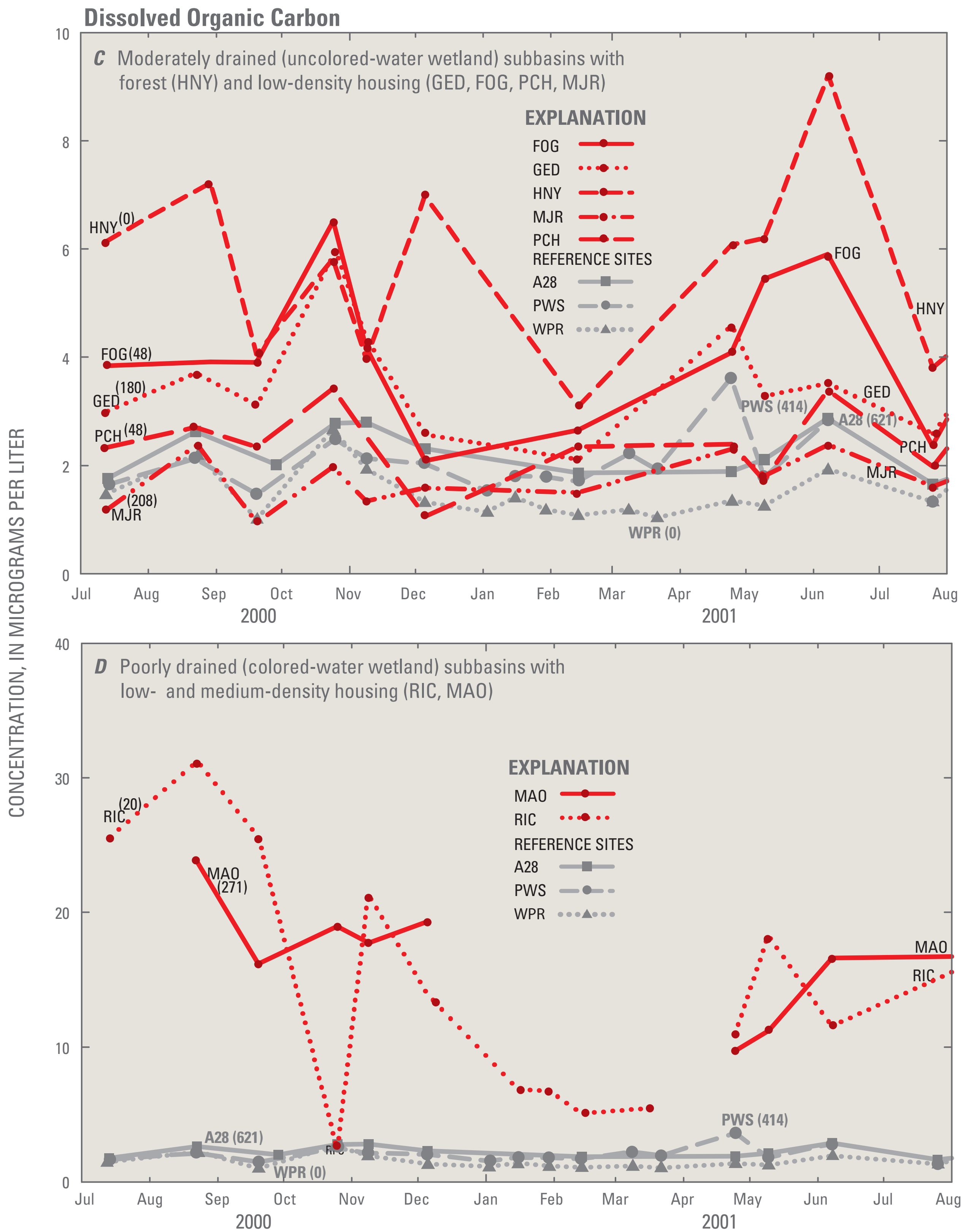


Figure 5. Base-flow dissolved organic carbon concentrations from July 2000 to July 2001, Croton Watershed, *(C)* moderately drained, uncolored-water wetland subbasins with forest and low-density housing, and *(D)* poorly drained, colored-water wetland subbasins with low- and medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

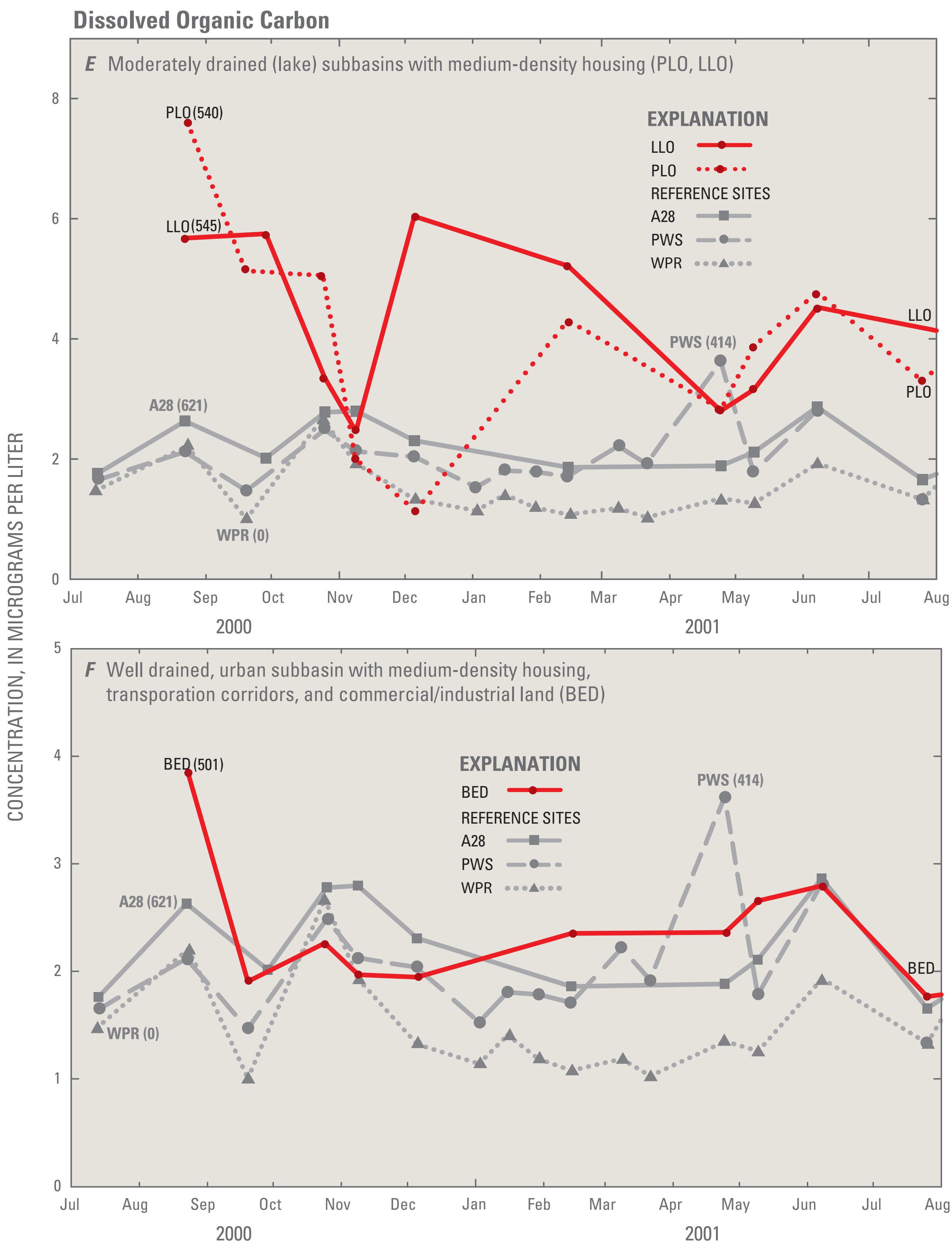


Figure 5. Base-flow dissolved organic carbon concentrations from July 2000 to July 2001, Croton Watershed, *(E)* moderately-drained subbasins with lakes and medium-density housing, and *(F)* well drained, urban subbasin, medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

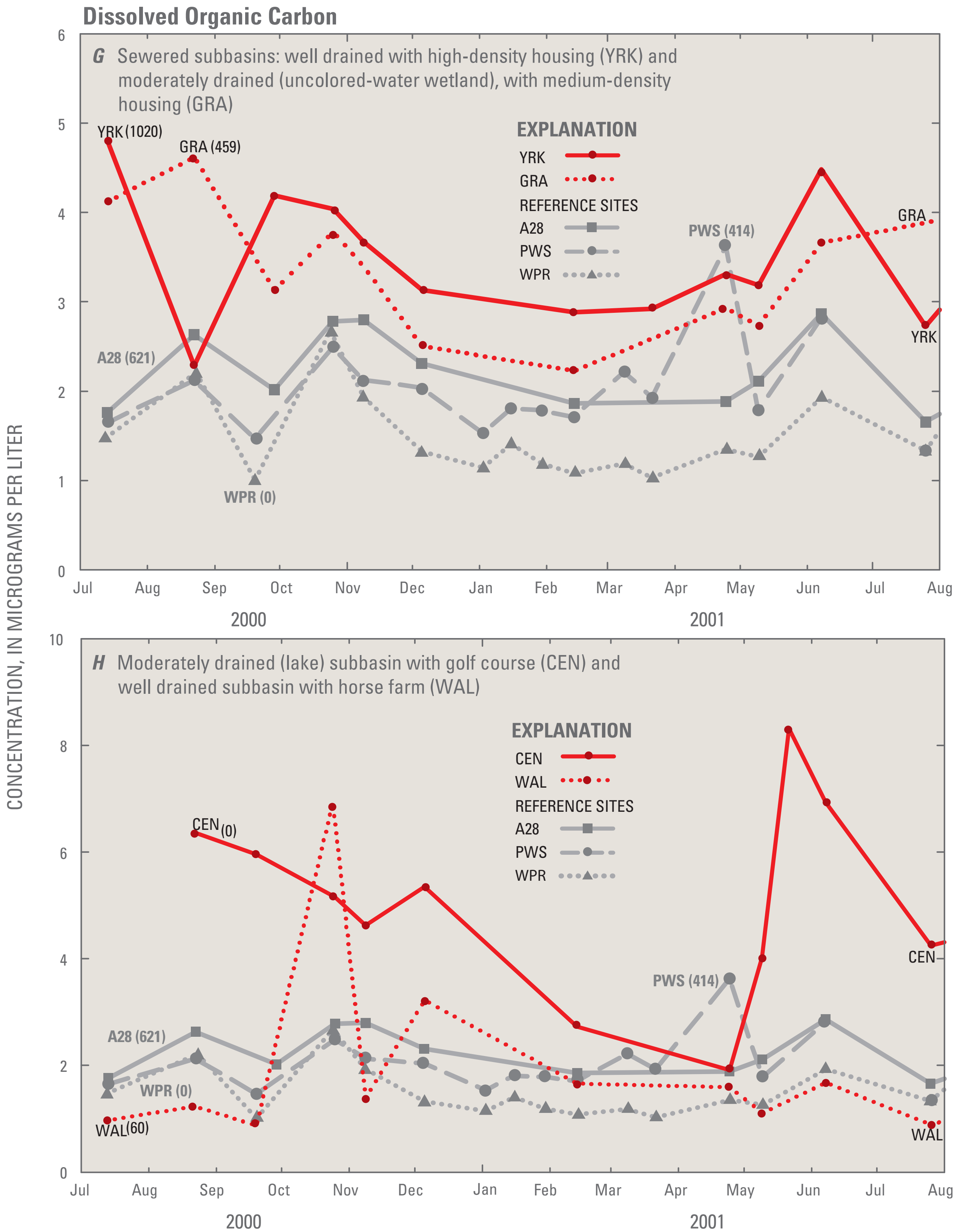


Figure 5. Base-flow dissolved organic carbon concentrations from July 2000 to July 2001, Croton Watershed, *(G)* sewered subbasins, well drained, high-density housing (YRK), moderately drained, uncolored-water wetland, medium-density housing (GRA), and *(H)* moderately-drained subbasin, lake and golf course (CEN), well-drained subbasin, horse farm (WAL) . Housing density in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

DOC concentrations in the well drained horse-farm subbasin were generally within the range of the reference subbasins, except during an autumn peak of 6.9 mg/L that exceeded concentrations in all other well drained basins. The horse-farm subbasin had a minor early December peak and virtually no spring peak.

4.2.4.3 Stormflow Concentrations

Stormflow DOC concentrations were strongly associated with season and drainage efficiency (table 6). The highest concentration (30.1 mg/L) and the greatest number of stormflow DOC concentrations greater than 5 mg/L occurred in early November, after leaf fall. Stormflow concentrations in all drainage and land-use categories (table 6) exceeded 10 mg/L during this storm; this reflects the presence of leaf litter throughout the watershed at this time of year. DOC increases in response to a late-May storm were nearly as widespread as in the autumn storm (>5 mg/L at all subbasins except the forested reference subbasin (WPR)), but most concentrations did not exceed 10 mg/L. A late-December storm resulted in maximum concentrations greater than 5 mg/L in about half of the drainage and land-use categories.

The only other stormflow concentrations greater than 5 mg/L occurred in early and late March and in early December, but only at subbasins with favorable drainage or land use. DOC measurements greater than 5 mg/L were most closely associated with colored-water wetlands. Subbasins with lakes, uncolored-water wetlands, or high-density housing with sanitary sewers had at least one high DOC measurement in March or early December.

Stormflow DOC concentrations exceeded or equaled base-flow DOC in nearly all samples from the same subbasin. The primary exception was in early December; maximum stormflow DOC concentrations at many subbasins were similar to, or less than base-flow DOC concentrations (table 6).

4.2.5 Color (Pt/Co)

Color in streamwater sampled in this study is closely associated with the presence of natural sources of organic matter, such as (1) wetlands, where water may have long contact time with decaying organic matter, and (2) throughout the watershed, through the addition of leaf litter during and immediately after leaf fall (late October to early November). Color intensity typically increases with increasing DOC, although different DOC sources (terrestrial, wetland, lake) may have different color characteristics (intensity, hue).

4.2.5.1 Summary: Median Intensities in Base Flow, Stormflow, and WWTP Effluent

Base-Flow and Stormflow Medians: Median color intensity in stormflows exceeded those in base flows in all subbasins except those with colored-water wetlands, lakes, or forested, undeveloped land use; base-flow intensities in these subbasins were comparable to, or higher than, stormflow intensities (table 2). Color also increased with decreases in subbasin drainage efficiency.

The well drained, forested subbasin (WPR) had low color intensity in base-flow and stormflow samples (0–20 Pt-Co color units (PCU), table 2), in contrast with the other well drained subbasins. This difference may reflect the greater direct surface runoff to streams in subbasins with residential development than in forested subbasins. Subbasins in the uncolored-water wetlands group differed in their color intensity, presumably in response to subbasin differences in drainage efficiency and wetland size. Subbasins with lakes and medium-density housing had relatively low (0–20 PCU) stormflow and base-flow color intensity. Water from these subbasins commonly had a greenish tinge from intense algal growth in the lakes, which was either filtered out before analysis or did not affect the color measurement. The highest median color intensities (> 100 PCU) were in subbasins with colored-water wetlands (table 2).

WWTP effluent: Effluent from the wastewater-treatment plants had a low median color intensity—between 0 and 20 PCU (table 2).

Median and maximum color at the individual WWTPs were as follows:

- Yorktown (HAL) median = 9.5 PCU, maximum = 15 PCU;
- Clocktower Commons (CLK) median = 11 PCU, maximum = 23 PCU; and
- Mahopac (MAH) median = 7 PCU, maximum = 10 PCU.

Table 6. Seasonal stormflow concentrations of dissolved organic carbon (DOC) in the stream network by subbasin category, Croton Watershed, southeastern, N.Y., 2000–02.

[mi^2, square miles; All values are in milligrams per liter.]

Land use and drainage efficiency category	Number of samples	Flow conditions sampled[1]	For each half-month period: *max* = Highest stormflow concentrations; *rel.* = Relation of stormflow concentrations to baseflow concentration[2]																
Forested (zero housing)				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	13	r, p, f, re	*max*					2.0	2.3		4.6					23.7		2.0	2.5
			rel.					≥	>		>					>		≤	>
Moderately drained Wetland, uncolored water	4	f, re	*max*					3.7			10.4					21.4			11.5
			rel.					>			>					>			>
Residential (by housing density)																			
Low-density (<250 houses mi^{-1})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	5	f, re	*max*					2.8			6.5					18.3		1.9	3.8
			rel.					>			>					>		<	>
Moderately drained Wetland, uncolored water	33	r, f, re	*max*					4.2			10.2				4.1	28.2		3.8	8.2
			rel.					>			>				>	>		>	>
Poorly drained Wetland, colored water	14	r, f, re	*max*					5.3	5.5		20.5					27.9			13.1
			rel.					>	<=>		>					>			<
Medium-density (251-600 houses mi^{-2})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	9	p, f, re	*max*					3.1			6.6					17.1		1.6	4.4
			rel.					≥≥			>					>		<=>	>
Well drained Urban	5	f, re	*max*					2.6			4.5					16.3		2.1	3.5
			rel.					>			>					>		>	>
Moderately drained Wetland, uncolored water	32	r, p, f, re	*max*					4.8	4.8		7.9		9.2		5.2	24.9		3.0	3.9
			rel.					≥≥	>		>		>		>	>		<=>	>
Moderately drained Wetland, uncolored water, sewered	5	f, re	*max*					2.6			7.7					21.2		3.5	4.9
			rel.					>			>					>		>	>
Poorly drained Wetland, colored water	5	f, re	*max*								10.6					30.1		16.9	14.3
			rel.								<					>		<	<
Moderately drained Lake	22	r, p, f, re	*max*					4.2			7.9					22.6		5.5	6.4
			rel.					<			≥≥					>		<=>	>
High-density (>600 houses mi^{-2})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	27	r, p, f, re	*max*					3.5	3.8		7.5					22.8		2.6	4.2
			rel.					>	>		>					>		>	>
Well drained Sewered	19	r, p, f, re	*max*					5.6	6.3		11.0					25.5		4.6	10.1
			rel.					>	≥		>					>		>	>
Golf Course				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Moderately drained Lake (small ponds)	11	r, p, f, re	*max*					3.7			5.6		11.8			14.5			5.9
			rel.					>			<		>			>			>
Horse Farm				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	8	r, f, re	*max*					3.6			7.3					11.0		1.5	4.0
			rel.					>			>					>		<	>

[1]Flow conditions in storm hydrograph
- r, rising limb
- p, peak
- f, steeply falling limb
- re, recession

[2]Relation of stormflow concentration to base-flow concentration
- = equal to
- > greater than
- ≥≥ greater than or equal to
- < less than
- ≤≤ less than or equal to
- <=> variable

4.2.5.2 Base-Flow Intensities, by Drainage Efficiency and Land-Use Category

A seasonal pattern in base-flow color was observed in sample data from most of the well drained and moderately drained subbasins. The pattern consisted of a mid-autumn peak following the leaf-fall period, a mid-spring peak, and relatively low and stable intensities for the remainder of the year. The autumn peak was generally higher than the mid-spring peak. The two sewered subbasins had less pronounced color peaks and higher summer color intensities than the other unsewered, well drained subbasins. The well drained urban subbasin (BED) was the only subbasin with a winter color peak. The moderately drained (lake) subbasin with medium-density housing (PLO) began its autumn peak in September, which coincided with high DOC and TP concentrations.

The annual base-flow color pattern of the golf-course subbasin (CEN) was similar to that of the poorly drained (colored-water wetland) subbasin with low-density housing (RIC), but the intensities at the colored-water wetland subbasin were about 10 times higher. Both subbasins showed a large spring peak and generally high summer intensity but differed in that the golf-course subbasin (CEN) showed dilution (decreasing intensity) during the autumn peak period while color at the colored-water-wetland subbasin showed no response.

A. Reference Subbasins: well drained, forested; moderately drained (uncolored-water wetland) with medium-density housing; and well drained subbasin with high-density housing

Maximum base-flow color intensities (fig. 6A) were

- 31 PCU, well drained, forested (WPR), late October, following leaf fall;
- 25 PCU, moderately drained (uncolored water wetland), medium-density housing (PWS), late April; and
- 31 PCU, well drained, high-density housing (A28), late October to early November.

Base-flow color remained relatively stable (5 to 15 PCU) among the three reference subbasins through the remainder of the year, although the forested subbasin had one secondary peak in January.

B. Well drained subbasins with high- to low-density housing

These subbasins showed the same autumn and spring base-flow color peaks as the three reference subbasins; color intensities were equal to or less than those at the reference subbasins. Most autumn base-flow color peaks were between 10 and 20 PCU and were higher than the corresponding spring peaks. Most base-flow color intensities were between 5 and 15 PCU.

Maximum base-flow color intensities (fig. 6B) were

- 15 PCU, low-density housing (CRH), late April;
- 29 PCU, medium-density housing (P21), late October; and
- 20 PCU, high-density housing (P22), late October.

C. Moderately drained (uncolored-water wetland) subbasins with forest or low-density housing

Maximum base-flow color intensities (fig. 6C) were

- 114 PCU, forested (HNY), early June;
- 79 PCU, low-density housing (FOG), late October.

Color intensities in base-flow samples collected from these subbasins were typically higher than those in the reference subbasins—the forested subbasin (HNY) color intensities were usually between 35 and 90 PCU, and those in the subbasins with low-density housing were between 15 and 50 PCU.

Seasonal color variation was similar to that at the well drained reference subbasins—autumn and spring peaks—but the spring peaks were later and lasted until June in the more poorly drained subbasins with uncolored water wetlands.

Housing density (between 48 and 208 houses per mi^2) among these subbasins showed little relation to color.

D. Poorly drained (colored-water wetland) subbasins with low- and medium-density housing

Maximum base-flow color intensities (fig. 6D) were

- 369 PCU, low-density housing (RIC), July (the highest base-flow color value in the study) ;
- 209 PCU, medium-density housing (MAO), December (there was no flow in July).

Samples from RIC showed a well-defined peak in May, but high intensities (greater than 200 PCU) were sustained from July through early November.

The lowest base-flow color intensities at both subbasins were between 50 and 70 PCU from January through March at RIC and in May at MAO (incomplete record).

E. Moderately drained (lake) subbasins with medium-density housing

The maximum base-flow color intensity (fig. 6E) was 27 PCU, in late September, at subbasin PLO. All color intensities from samples collected at the lake subbasins were within the range of the reference subbasins; the main differences were an early start of the autumn peak at PLO (late September through late October) and a minor peak in February at subbasin (LLO).

F. Well drained urban subbasin with medium-density housing, transportation corridors, and commercial/industrial land

The maximum base-flow color intensity was 21 PCU, in February (fig.6F). Secondary autumn and spring color peaks were between 10 and 15 PCU. Most color intensities were below or equal to those of the reference subbasins, except for the high intensity measurement in February.

G. Sewered subbasins: well drained with high-density housing and moderately drained (uncolored-water wetland) with medium-density housing

Maximum base-flow color intensities (fig. 6G) were

- 22 PCU, well drained with high-density housing and sanitary sewers (YRK), in late October;
- 24 PCU, moderately drained (uncolored-water wetland) with medium-density housing and sanitary sewers (GRA), in May.

Color intensities in base-flow samples from sewered subbasins were similar to those in the reference basins from September through February but were higher from March through August. Color intensities in July were roughly double those from the reference subbasins. Autumn and spring peaks were smaller in magnitude than those at most reference basins. Base-flow color intensities in samples from the sewered subbasins were similar—always within 4 PCU of each other.

H. Moderately drained (lake) subbasin with golf course (CEN) and well drained subbasin with horse farm (WAL)

Maximum base-flow color intensities (fig. 6H) were

- 55 PCU, moderately drained (lake) subbasin with golf-course (CEN), late May;
- 28 PCU, well drained subbasin with horse-farm (WAL), late October.

Most of the color intensities in samples from the golf-course subbasin were between 10 and 35 PCU and exceeded those in all reference basins except during the autumn and spring peaks. The autumn base-flow color peak in the reference subbasins coincided with a drop in color intensity in the golf-course subbasin. The late May peak at the golf-course subbasin may be a spring peak delayed by several small ponds that slow drainage from this subbasin.

Base-flow color intensities in the well drained horse-farm subbasin were within the color intensity range of samples from the reference subbasins. An autumn color peak matched the color peaks in the forested and high-density housing reference subbasins, but no spring color peak in base flow samples was observed.

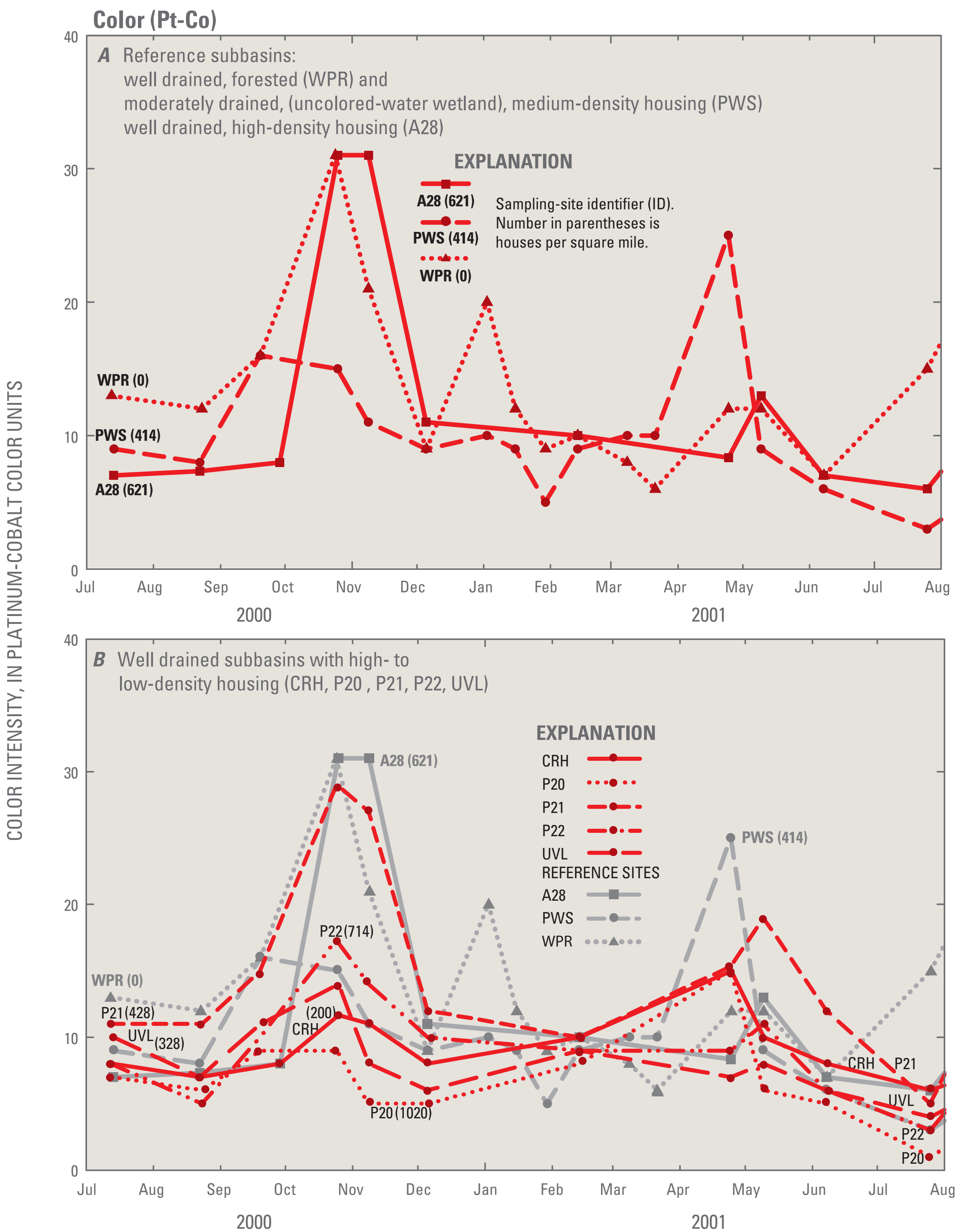


Figure 6. Base-flow Pt-Co color intensities from July 2000 to July 2001, Croton Watershed, *(A)* reference subbasins, well drained, forested (WPR); moderately drained, uncolored-water wetland, medium-density housing (PWS); well drained, high-density housing (A28), and *(B)* well-drained subbasins, high- to low-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

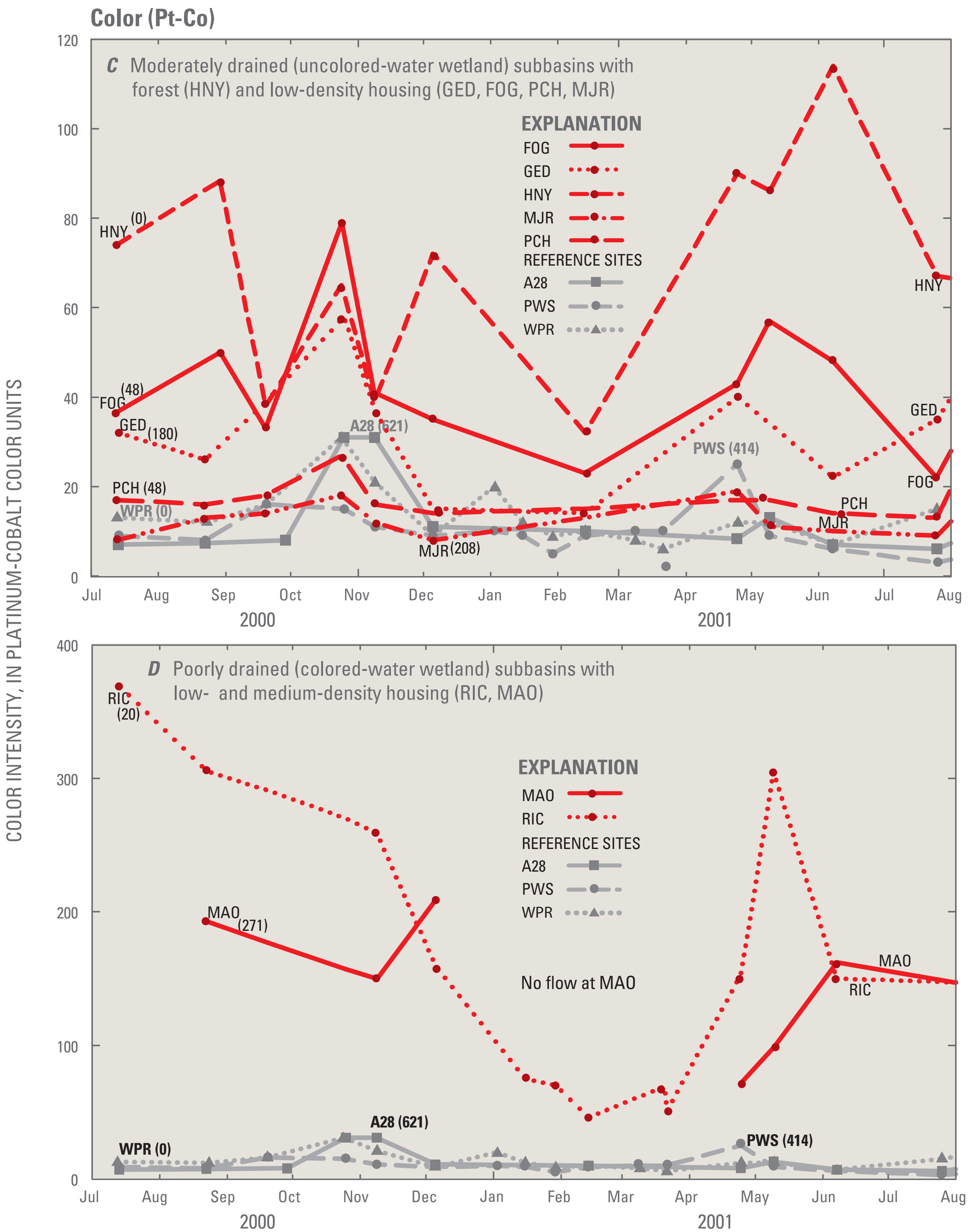


Figure 6. Base-flow color intensities from July 2000 to July 2001, Croton Watershed, *(C)* moderately drained, uncolored-water wetland subbasins with low-density housing, and *(D)* poorly drained, colored-water wetland subbasins with low- and medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

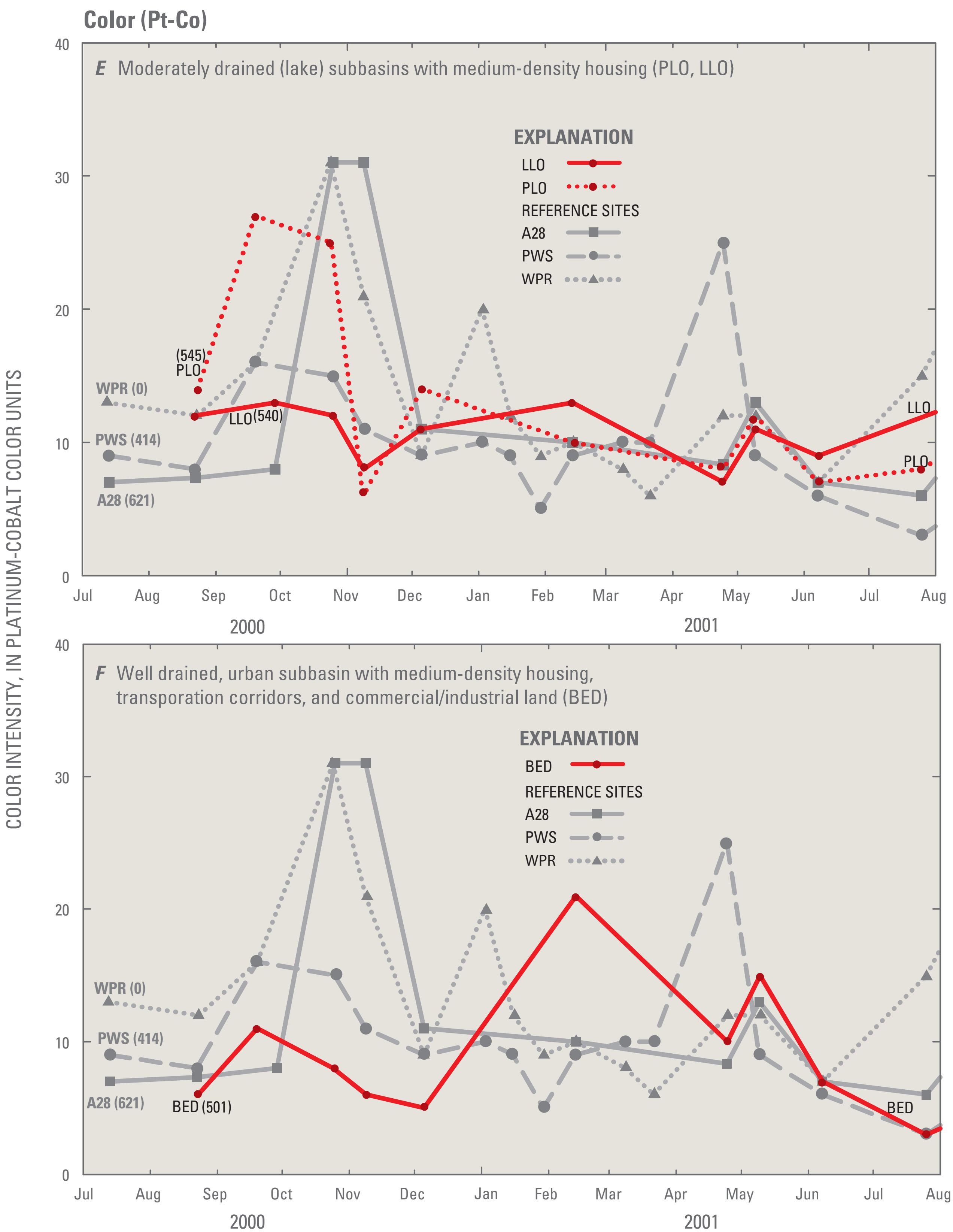


Figure 6. Base-flow color intensities from July 2000 to July 2001, Croton Watershed, *(E)* moderately-drained subbasins with lakes and medium-density housing, and *(F)* well drained, urban subbasin, medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

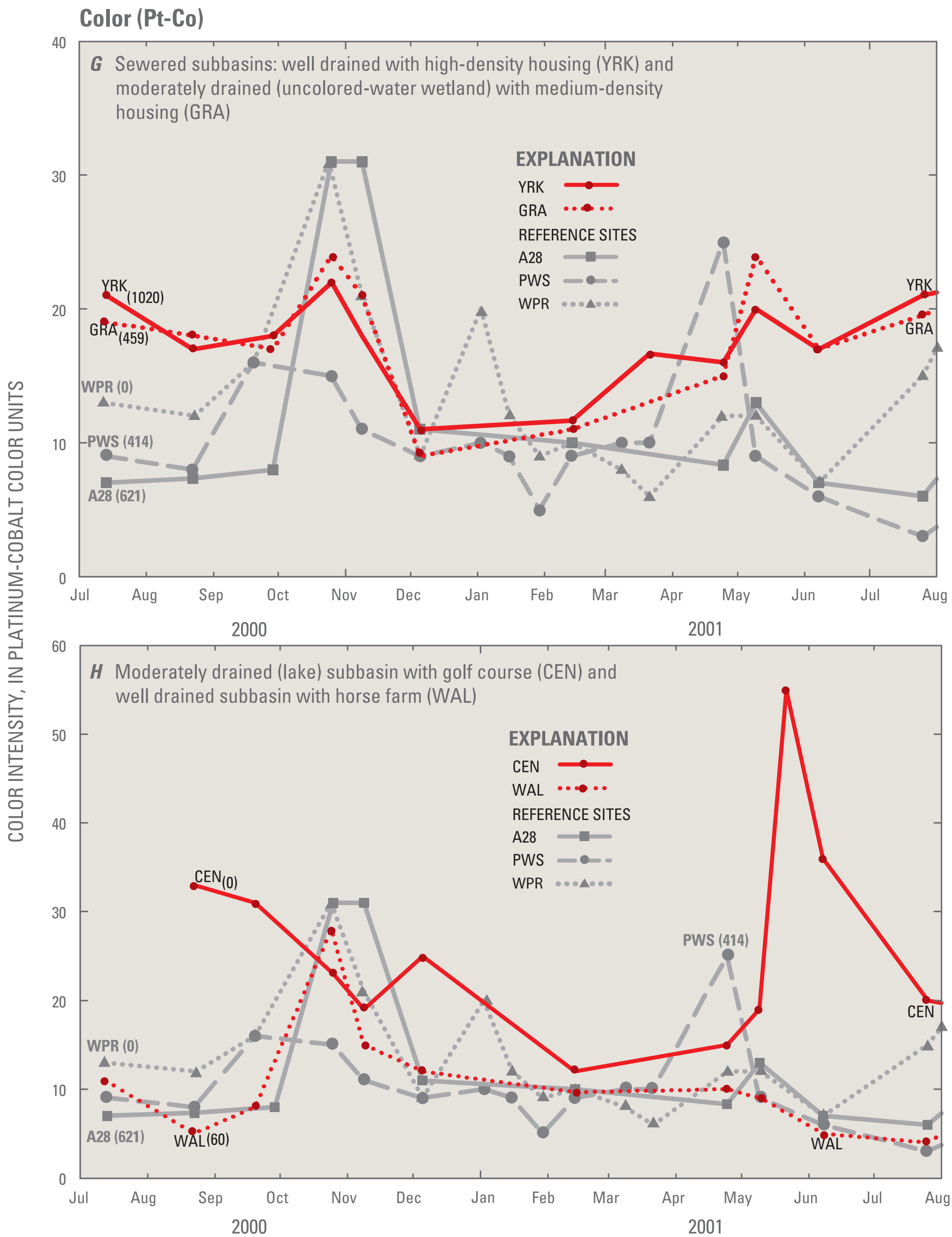


Figure 6. Base-flow color intensities from July 2000 to July 2001, Croton Watershed, *(G)* sewered subbasins, well drained, high-density housing (YRK), moderately drained, uncolored-water wetland, medium-density housing (GRA), and *(H)* moderately-drained subbasin, lake and golf course (CEN), well drained, horse farm (WAL). Housing density, in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

4.2.5.3 Stormflow Color Intensities

Stormflow color intensities were strongly associated with season, drainage efficiency, and, to a lesser extent, land use (table 7). The highest value (452 PCU) and the greatest number of color measurements greater than 100 PCU were measured in early November, after leaf fall. All residential subbasins (all drainage efficiencies), and the forested, uncolored-water-wetland subbasin (HNY) exceeded 100 PCU. The only subbasins with intensities below 100 PCU were the well drained, forested reference subbasin (99 PCU) and the golf-course and horse-farm subbasins (81 and 80 PCU, respectively).

The only other stormflow intensities greater than 100 PCU occurred in late spring and in late December but only at subbasins with favorable drainage efficiencies and land uses: (1) moderately drained (uncolored-water wetland), forested (HNY), (2) moderately drained (uncolored-water wetland), low-density housing (FOG, MJR, PCH, GED), and (3) poorly drained (colored-water wetland), low-density housing (RIC).

Stormflow color intensities from the Croton subbasins were elevated with respect to the National Secondary Drinking-Water Regulation for color (15 PCU), which applies to the entry point of distribution systems rather than measurements within the watersheds. However, it is notable that 82 of the 88 maximum stormflow intensities (93 percent) listed in table 7 exceeded the regulation. Four of the 6 color intensities that were equal to or less than 15 PCU were from the well drained, forested subbasin (WPR).

Stormflow color exceeded or equaled base-flow color in nearly all subbasins. The primary exceptions were in December when water from the two subbasins with colored-water wetlands, which have high base-flow color intensities, were diluted by stormflow.

4.2.6 Unfiltered Trihalomethane (THM) Formation Potential in Filtered Samples

THMs are formed when DOC reacts with chlorine used for disinfection. Only certain fractions of DOC react with chlorine and these fractions are called precursors. The sources of the precursors include terrestrial and aquatic natural organic matter and domestic wastewater. THMs are measured in water samples after adding chlorine under controlled laboratory conditions. The resulting concentrations of THMs are called formation potentials (FP), as they are not actual streamwater concentrations.

4.2.6.1 Summary: Median Formation Potentials in Base Flow, Stormflow, and WWTP Effluent

Base-Flow and Stormflow Medians: Median THM formation potentials showed a progressive increase with decreasing drainage efficiency (table 2). The highest formation potentials were generated in samples from the two colored-water-wetland subbasins; base flow and stormflow THM formation potentials were within the same formation potential interval (501–1,000 μg/L; table 2). The lowest base-flow THM formation potentials were generated in water samples from the well drained subbasins. These formation potentials were lower than most stormflow medians, which suggests that THM precursors are more strongly associated with surface-runoff sources than with the ground-water sources. Housing density was not associated with median unfiltered THM formation potentials within the formation potential ranges used in table 2. The sewered subbasin with high-density housing (YRK), however, had higher values than the unsewered well drained subbasins. The pattern of unfiltered THM median formation potentials in table 2 is most similar to that of DOC.

WWTP effluent: Effluent from all of the wastewater-treatment plants had an overall unfiltered median formation potential of 247 μg/L.

Individual WWTP median and maximum formation potentials were as follows:

- Yorktown (HAL) median = 42 μg/L, maximum = 66 μg/L;
- Clocktower Commons (CLK) median = 247 μg/L, maximum = 311 μg/L; and
- Mahopac (MAH) median = 249 μg/L; maximum = 435 μg/L.

Low unfiltered THM formation potentials at the Yorktown (HAL) WWTP are attributed to the reaction of chlorine, used for disinfection, with ammonia (ammonium ion) in the effluent to form chloramines preferentially over THM species (U.S. Environmental Protection Agency, http://www.epa.gov/ncea/pdfs/water/chloramine/dwchloramine.pdf/, last accessed 5 September, 2007). Effluent ammonium concentrations at this WWTP ranged from 10 to 21 mg/L as N; ammonium concentrations at the other plants did not exceed 0.35 mg/L as N.

Table 7. Seasonal stormflow color intensity (Pt-Co) in the stream network by subbasin category, Croton Watershed, southeastern, N.Y., 2000–02.

[mi², square miles. All values are in PCU, platinum-cobalt units.]

For each half-month period: *max* = Highest stormflow intensities; *rel.* = Relation of stormflow intensities to baseflow intensities[2]

Land use and drainage efficiency category	Number of samples	Flow conditions sampled[1]		Jan		Feb		Mar		May		Jun		Jul		Nov		Dec	
Forested (zero housing)																			
Well drained	18	r, p, f, re	*max*					12	14		46	48			43	99		12	15
			rel.					≥	>		>	>			>	>		>	>
Moderately drained Wetland, uncolored water	4	f, re	*max*					46			163					261			159
			rel.					>			>					>			>
Residential (by housing density)																			
Low-density (<250 houses mi⁻¹)				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	5	f, re	*max*					32			63					149		10	24
			rel.					>			>					>		>	>
Moderately drained Wetland, uncolored water	28	r, f, re	*max*					41			108	66			29	452		26	106
			rel.					>			>	>			>	>		>	>
Poorly drained Wetland, colored water	6	f, re	*max*					64	55		279					309			142
			rel.					<	>		<=>					>			<
Medium-density (251-600 houses mi⁻²)				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	9	p, f, re	*max*					15			74					159		17	39
			rel.					>			>					>		>	>
Well drained Urban	5	f, re	*max*					35			40					161		10	20
			rel.					>			>					>		>	>
Moderately drained Wetland, uncolored water	34	r, p, f, re	*max*					18	38		63	126	72		33	151		18	18
			rel.					>	>		>	≥	>		>	>		>	>
Moderately drained Wetland, uncolored water, sewered	5	f, re	*max*					19			73					125		22	25
			rel.					>			>					>		>	>
Poorly drained Wetland, colored water	5	f, re	*max*								70					140		76	195
			rel.								<					<		<	<
Moderately drained Lake	21	r, p, f, re	*max*					10			93					386		20	13
			rel.					<			≥					≥		<	≤
High-density (>600 houses mi⁻²)				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	76	r, p, f, re	*max*					18	30		75	135			85	186		18	23
			rel.					≥	≥		>	<=>			≥	>		>	>
Well drained Sewered	18	r, p, f, re	*max*					65	61		114	53					265	20	30
			rel.					>	≥		>	>					>	>	>
Golf Course				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Moderately drained Lake (small ponds)	10	r, p, f, re	*max*					33			39		91			81			51
			rel.					>			<=>		>			>			>
Horse Farm				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	10	r, f, re	*max*					29			63	65				80		23	28
			rel.					>			>	<=>				>		>	>

[1]Flow conditions in storm hydrograph
- r, rising limb
- p, peak
- f, steeply falling limb
- re, recession

[2]Relation of stormflow intensities to base-flow intensities
- = equal to
- > greater than
- ≥ greater than or equal to
- < less than
- ≤ less than or equal to
- <=> variable

4.2.6.2 Base-Flow Unfiltered Trihalomethane Formation Potential, by Drainage Efficiency and Land-Use Category

A seasonal THM formation-potential pattern in baseflow was observed in most subbasins but was most pronounced in subbasins with high DOC concentrations—subbasins with colored-water and uncolored-water wetlands. The pattern consisted of a small autumn base-flow THM peak, low winter formation potentials, a larger spring THM peak or the start of increasing formation potentials that continued into the summer. One exception to this base-flow THM pattern was observed in samples from the well drained, sewered subbasin with high-density housing (YRK), which had a large THM peak (about 1,200 µg/L) in late July that coincided with high nitrate and TP concentrations. Formation potentials of base-flow samples from well drained residential subbasins were typically lower than those at the residential subbasins with a lake (PLO, LLO), the sewered subbasin with uncolored-water wetland (GRA), and the golf-course subbasin (CEN).

A. Reference Subbasins: well drained, forested; moderately drained (uncolored-water wetland) with medium-density housing; and well drained subbasin with high-density housing

Maximum base-flow unfiltered THM formation potentials (fig. 7A) were

- 356 µg/L, well drained, forested (WPR), late July;
- 260 µg/L, well drained, with high-density housing (A28), late July; and
- 545 µg/L, moderately drained, with medium-density housing (PWS), early June.

The seasonal pattern at the reference sites consisted of:

(1) Low autumn peaks and variable spring peaks,

(2) Variable summer formation potentials (low in 2000 and high in 2001), and

(3) Lowest formation potentials from December through February.

Formation potentials of base-flow samples in the forested subbasin (WPR) and the well drained subbasin with high-density housing (A28) were generally between 75 and 200 µg/L and within 50 µg/L of each other all year, except in late July 2001 when the formation potentials of samples from the forested subbasin (WPR) peaked. Formation potentials of samples from the moderately drained subbasin with medium-density housing (PWS) were similar to those from the other reference subbasins from July 2000 through February 2001, but then increased into the 200–550 µg/L range from March through July 2001, with the exception of one early May 2001 sample.

B. Well drained subbasins with high- to low-density housing

Most base-flow samples from this subbasin group followed the same seasonal THM formation potential pattern and range of formation potentials as samples from the forested and high-density-housing reference subbasins (fig. 7B). Elevated spring formation potentials (330–340 µg/L) in samples from subbasin P21 approached those at the reference subbasin with medium density housing (PWS).

C. Moderately drained (uncolored-water wetland) subbasins with forest or low-density housing

Maximum base-flow unfiltered THM formation potentials (fig. 7C) were

- 930 µg/L, forested (HNY), early June;
- 835 µg/L, low-density housing (FOG), late April.

Formation potentials in all uncolored-water-wetland subbasins exceeded those in nearly all reference-subbasin samples and varied as follows:

- 150–450 µg/L; July 2000 to February 2001;
- 150–900 µg/L; March 2001 to July 2001.

Seasonal patterns of base-flow formation potentials were similar to those at the two well drained reference subbasins, except for the autumn and spring peaks, which were as much as 200 and 400 µg/L higher, respectively, than the highest reference subbasin formation potentials. Differences in housing density within the low-density housing range showed no association with THM formation potential.

D. Poorly drained (colored-water wetland) subbasins with low- and medium-density housing

Maximum base-flow unfiltered THM formation potentials in these two subbasins (fig. 7D) were

- 2,262 μg/L, low-density housing (RIC), early May;
- 1,299 μg/L, medium-density housing (MAO), early June.

The lowest base-flow unfiltered formation potentials were between 340 and 380 μg/L. All formation potentials from samples collected from these two subbasins exceeded the formation potentials of samples from the reference-subbasins with similar housing densities.

Fall THM peaks in base flow occurred in late September, and spring peaks occurred in late May and early June. The contrast between well-defined spring peaks in the low-density residential subbasin (RIC) and the broad, high peaks in the subbasin with medium-density housing (MAO) suggest poorer drainage at MAO than at RIC.

E. Moderately drained (lake) subbasins with medium-density housing

The maximum base-flow unfiltered THM formation potential (fig. 7E) was

- 510 μg/L in late July 2001 (PLO).

Formation potentials of base-flow samples from September 2000 through February 2001 were equal to or as much as 100 μg/L higher than those at the three reference subbasins. Spring–summer 2001 formation potentials of base-flow samples were elevated and similar to those at the reference subbasin with medium-density housing (PWS).

F. Well drained urban subbasin with medium-density housing, transportation corridors, and commercial/industrial land

The maximum base-flow unfiltered THM formation potential (fig. 7F) was

- 261 μg/L in late October.

Most formation potentials of base-flow samples were about the same as those from the three reference subbasins, except for the autumn peak, which was about 50 μg/L higher.

G. Sewered subbasins: well drained with high-density housing and moderately drained (uncolored-water wetland) with medium-density housing

Maximum base-flow unfiltered THM formation potentials (fig. 7G) were

- 1,228 μg/L, well drained, with high-density housing (YRK), late July;
- 589 μg/L, moderately drained, (uncolored-water wetland) with medium-density housing (GRA), late April.

Formation potentials of samples from these two sewered subbasins were typically about 100 μg/L higher than at the three reference subbasins but followed the same seasonal pattern. The high formation potential of the late July 2001 sample at subbasin YRK coincided with high TP and nitrate concentrations.

H. Moderately drained (lake) subbasin with golf course and well drained subbasin with horse farm (WAL)

Maximum base-flow unfiltered THM formation potentials (fig. 7H) were

- 702 μg/L, golf-course subbasin (CEN), early June;
- 374 μg/L, horse-farm subbasin (WAL), late July.

All (partial record) golf-course subbasin (CEN) formation potentials of base-flow samples exceeded those at the three reference subbasins and ranged from 200 to 400 μg/L from August 2000 through late April 2001 and from 400 to 700 μg/L from May to July 2001. The autumn THM base-flow peak at the three reference subbasins coincided with a decrease in formation potential in samples from the golf-course subbasin. Sample coverage was insufficient to confirm the presence or absence of an early spring peak.

THM formation potentials of base-flow samples from the horse-farm subbasin (WAL) were typically within or slightly below the formation potential range of base-flow samples from the three reference subbasins. The low autumn- and spring-peak formation potentials at this subbasin were consistently below those measured in base-flow samples from the reference subbasins.

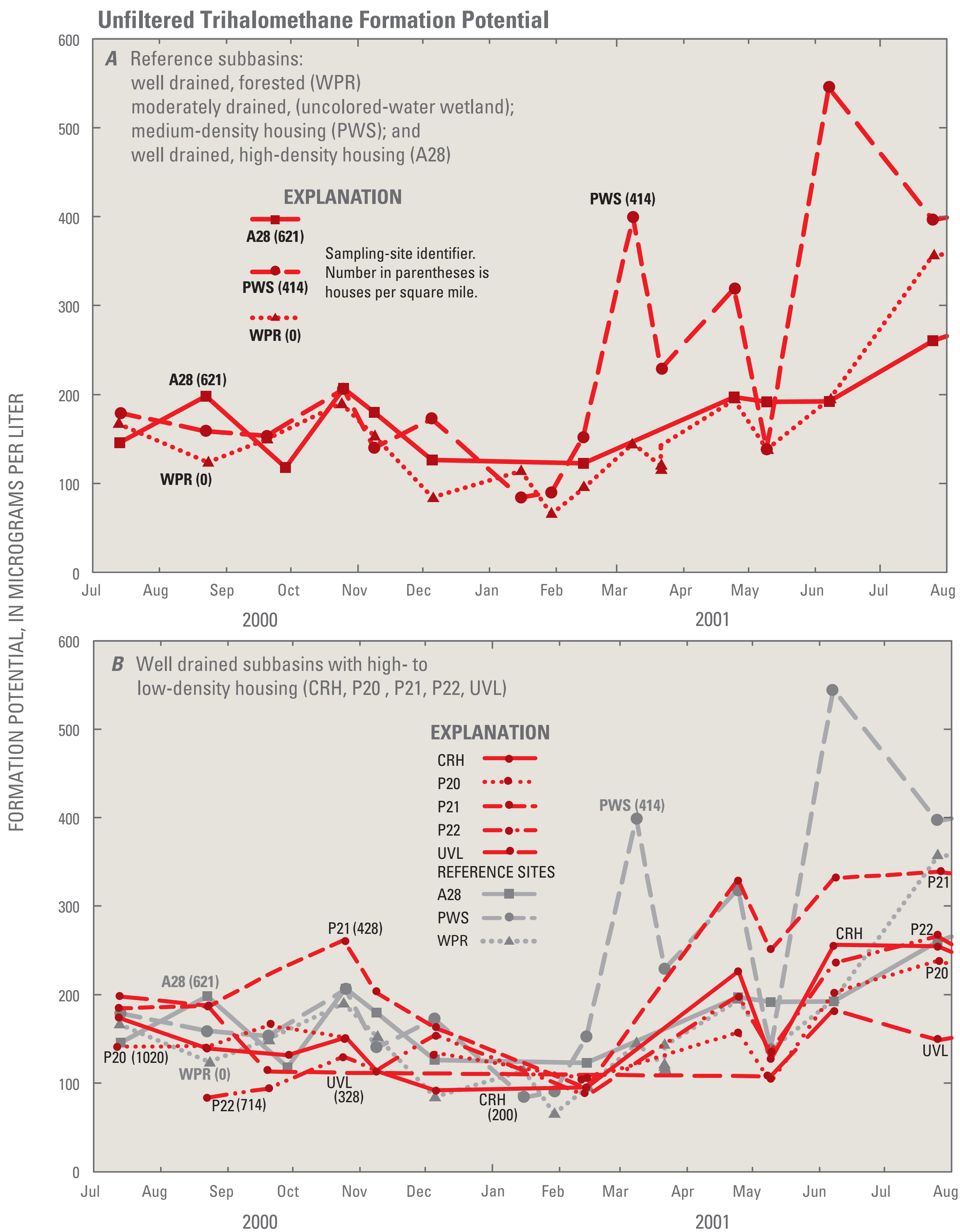


Figure 7. Base-flow unfiltered trihalomethane formation potentials from July 2000 to July 2001, Croton Watershed, *(A)* reference subbasins, well drained, forested (WPR); moderately drained, uncolored-water wetland, medium-density housing (PWS); well drained, high-density housing (A28), and *(B)* well-drained subbasins, high- to low-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

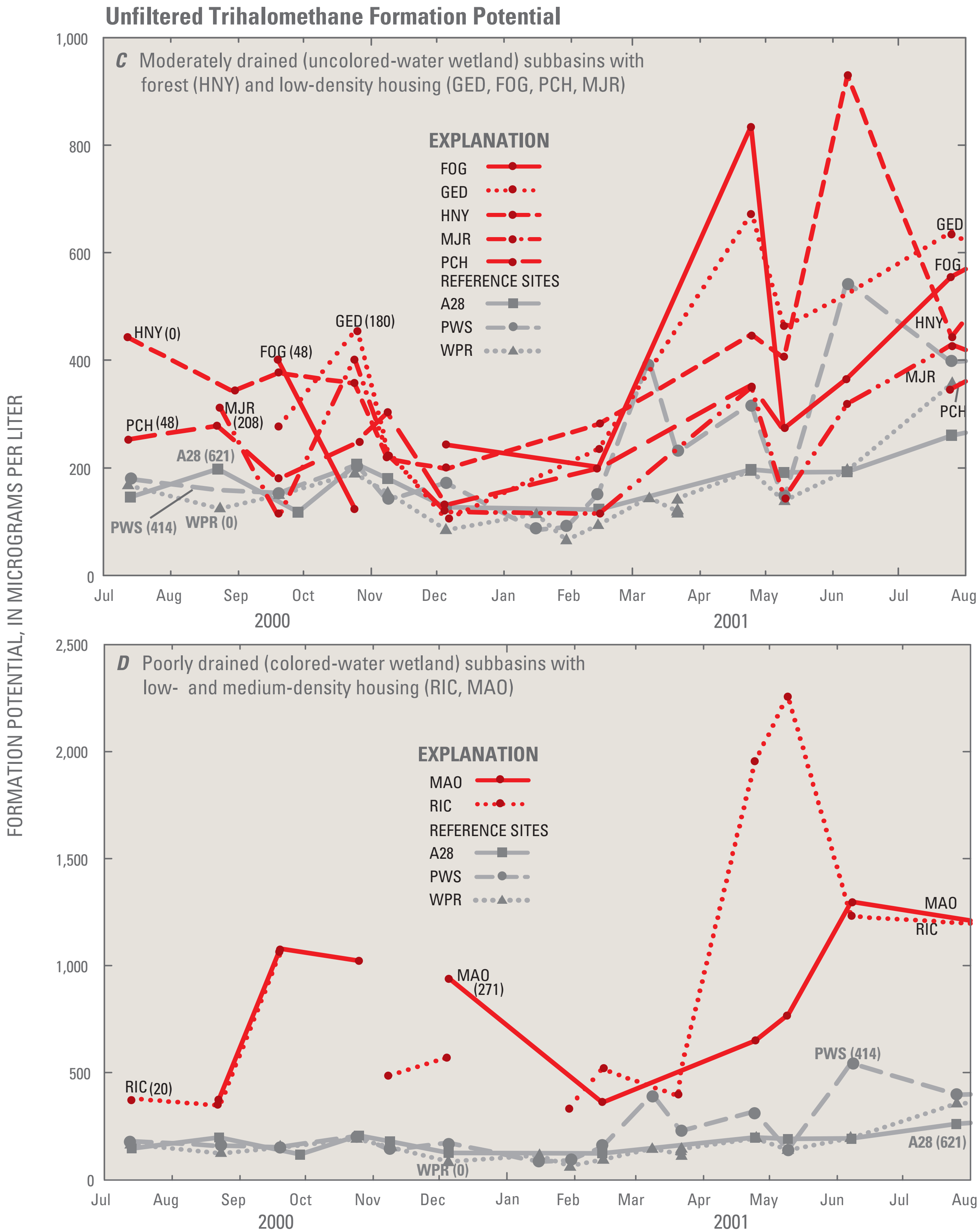


Figure 7. Base-flow unfiltered trihalomethane formation potentials from July 2000 to July 2001, Croton Watershed, *(C)* moderately drained, uncolored-water wetland subbasins with low-density housing, and *(D)* poorly drained, colored-water wetland subbasins with low- and medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

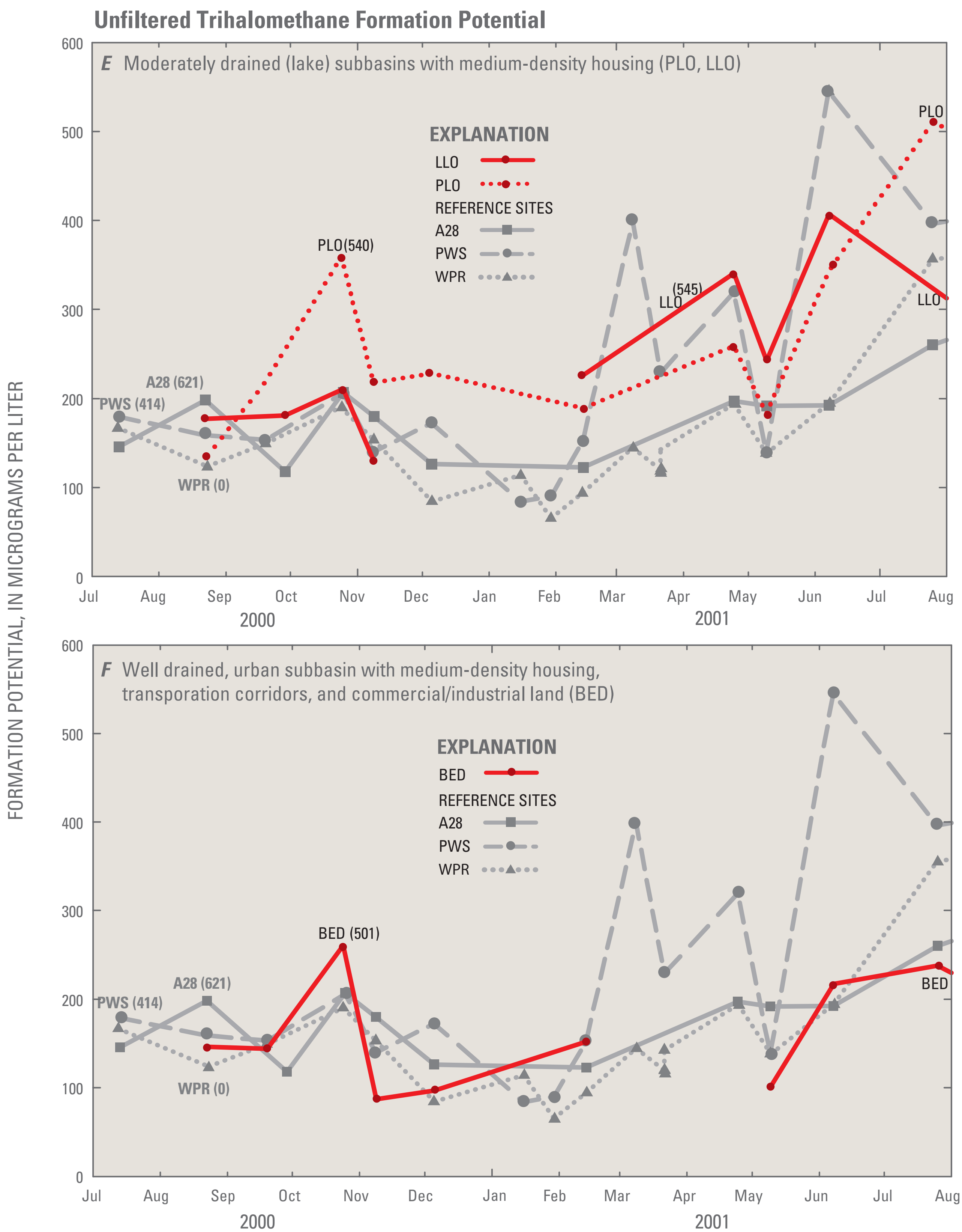


Figure 7. Base-flow unfiltered trihalomethane formation potentials from July 2000 to July 2001, Croton Watershed, *(E)* moderately drained, subbasins with lakes and medium-density housing, and *(F)* well drained, urban subbasin, medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

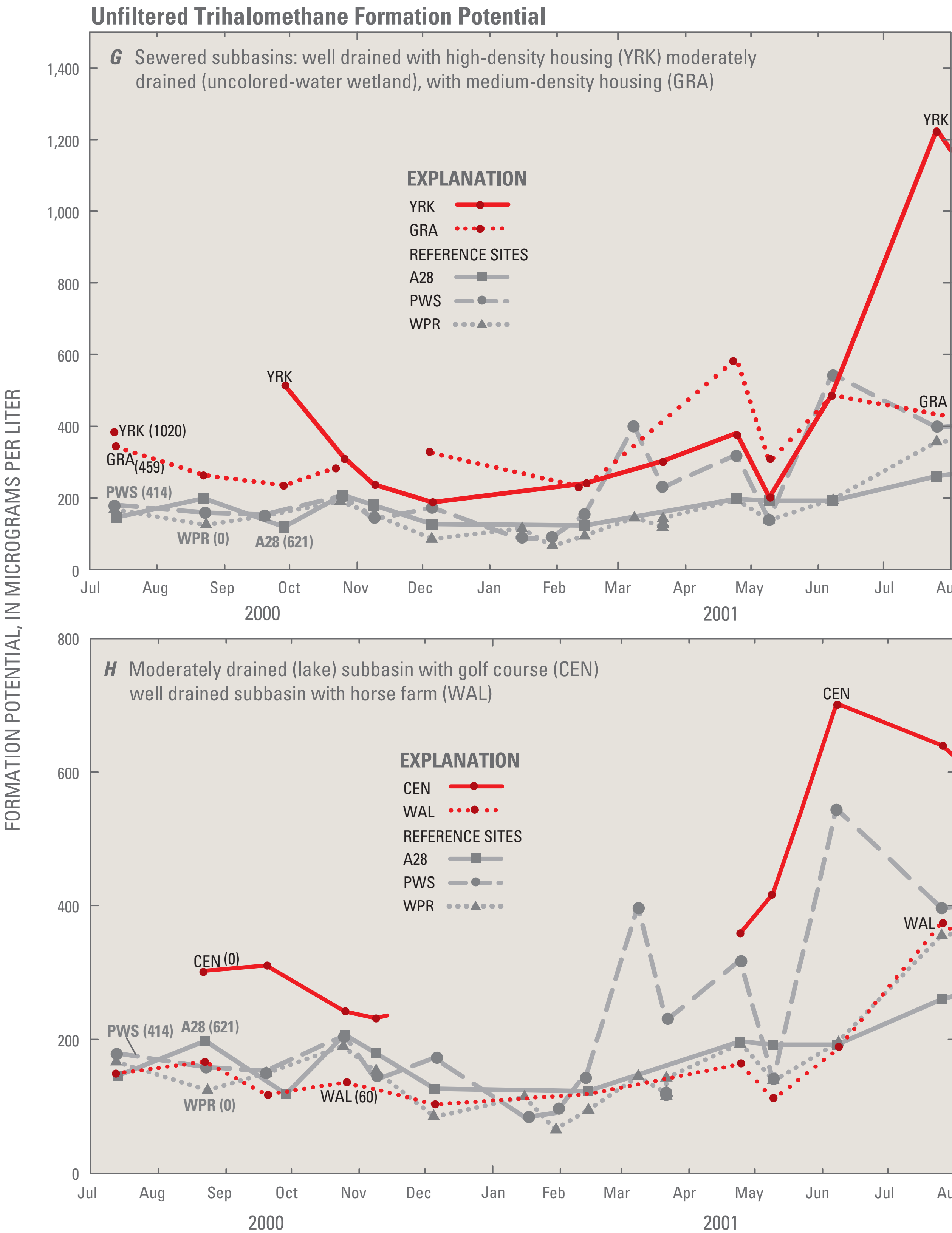


Figure 7. Base-flow unfiltered trihalomethane formation potentials from July 2000 to July 2001, Croton Watershed, *(G)* sewered subbasins: well drained, high-density housing (YRK) and uncolored-water wetland, medium-density housing (GRA), and *(H)* moderately-drained subbasin, lake, golf course (CEN), well drained subbasin, horse farm (WAL). Housing density, in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

4.2.6.3 Stormflow Unfiltered Trihalomethane Formation Potentials

Stormflow formation potentials were affected by drainage efficiency, housing density, and season (table 8). The change in drainage efficiency from well drained to poorly drained corresponded to THM formation-potential changes in stormflow from no difference to as much as a six-fold increase among subbasins with low- and medium-density housing. This relation was evident in all but the late May storm, in which formation potentials in samples were similar among subbasins with different drainage efficiencies. No comparison of the effects of drainage efficiency in subbasins with high housing density could be made because all four of these subbasins were well drained. The seasonal patterns of stormflow THM formation potentials consisted of widespread high formation potentials in storms from May through November; the two highest stormflow THM formation potentials (1,735 and 1,600 µg/L) occurred during a late July storm in the well drained, forested and well drained, high-density housing subbasins. The most dilute stormflow with respect to THM formation potential occurred during March and December storms.

Housing density also had a positive effect on stormflow THM formation potentials. From March through July stormflows, THM formation potential commonly increased (by about 50 to 300 µg/L) with increasing housing-density among subbasins with the same drainage efficiency. November and December stormflow formation potentials differed less among housing-density categories, presumably because leachate from leaf litter was present throughout the study area.

Sewers positively affected unfiltered THM formation potentials but only in March and late-December storms when THM formation potentials of samples from the two sewered subbasins (YRK, GRA) were the same to as much as 4 times higher than those in corresponding unsewered subbasins.

Stormflow unfiltered THM formation potentials in samples from the golf-course (CEN) and horse-farm (WAL) subbasins were in the intermediate range (300 and 650 µg/L) during most storms, with one or two high formation potentials (>1,000 µg/L) in June and December.

Stormflow THM formation potentials in samples from most subbasins exceeded THM formation potentials in base-flow samples collected before or after the storms. This indicates that surface runoff is a major source of unfiltered THM formation potential. The storm of early March 2001 was the only storm in which formation potentials in most subbasins were more dilute than, or equal to, the formation potentials in base-flow samples before or after the storm.

4.2.7 Unfiltered Haloacetic Acid (HAA) Formation Potential

Haloacetic acids (HAAs) are formed when DOC reacts with chlorine used for disinfection. Only certain fractions of DOC react with chlorine and these fractions are called precursors. The sources of the precursors include terrestrial or aquatic natural organic matter or domestic wastewater. HAAs are measured in water samples after adding chlorine under controlled laboratory conditions. The resulting concentrations of HAAs are called formation potentials (FP), as they are **not** actual streamwater concentrations.

4.2.7.1 Summary: Median Formation Potentials in Base Flow, Stormflow, and WWTP Effluent

Base-Flow and Stormflow Medians: HAA median formation potentials, like those of trihalomethanes, increased with decreasing drainage efficiency (table 2). Median formation potentials were highest in colored-water-wetland subbasins (601–1,100 µg/L) and lowest in well drained subbasins (150–250 µg/L). The unfiltered HAA-formation potential patterns differed from those of unfiltered THM formation potentials in that stormflow medians were in the same range as the base-flow medians in nearly all subbasin categories, which indicates that ground-water sources are of similar magnitude to surface-runoff sources. Housing density showed little correlation with median HAA formation potentials; only the sewered subbasin with high-density housing and the urban subbasin plotted one interval higher than the other well drained subbasins in table 2. The subbasin with the highest base-flow HAA formation potentials outside of the colored-water-wetland subbasins was the golf-course subbasin (CEN).

WWTP effluent: Effluent from the wastewater-treatment plants had a moderate median HAA formation potential between 251 and 400 µg/L (table 2). Individual WWTP median and maximum unfiltered HAA formation potentials were as follows:

- Yorktown (HAL) median = 122 µg/L, maximum = 236 µg/L;
- Clocktower Commons (CLK) median = 424 µg/L, maximum = 617 µg/L; and
- Mahopac (MAH) median = 433 µg/L, maximum = 633 µg/L.

Low HAA formation potentials at the Yorktown (HAL) WWTP, like low THM formation potentials, are attributed to the reaction of chlorine, used for disinfection, with ammonia (ammonium ion) in the effluent to form chloramines preferentially

Table 8. Seasonal stormflow unfiltered trihalomethane (THM) formation potentials in the stream network by subbasin category, Croton Watershed, southeastern, N.Y., 2000-02.

[mi^2, square miles. All values are in micrograms per liter]

Land use and drainage efficiency category	Number of samples	Flow conditions sampled[1]	For each half-month period: *max* = Highest stormflow formation potential; *rel.* = Relation of stormflow formation potentials to baseflow formation potentials[2]																
Forested (zero housing)				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	26	r, p, f, re	*max*				398	115	322		769	374			1600	286		171	152
			rel.				<=>	<	>		≥	>			>	>		>	>
Moderately drained Wetland, uncolored water	3	f, re	*max*					695			1001					960			
			rel.					=			=					≥			
Residential (by housing density)																			
Low-density (<250 houses mi[-1])				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	4	f, re	*max*					212			754							136	251
			rel.					=			=							=	=
Moderately drained Wetland, uncolored water	29	r, f, re	*max*					549			1381	600			713	985		483	845
			rel.					≤			≥	=			>	≥		>	>
Poorly drained Wetland, colored water	19	r, p, f, re	*max*				1376	536	378		865					1281			1348
			rel.				<=>	=	≤		<					>			>
Medium-density (251-600 houses mi[-2])				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	7	p, f, re	*max*					300			1012					262		219	216
			rel.					<=>			>					>		>	>
Well drained Urban	5	f, re	*max*					273			483					624		168	171
			rel.					>			>					>		>	>
Moderately drained Wetland, uncolored water	50	r, p, f, re	*max*		491		497	450	662		1263	981	1282		1057	1015		313	250
			rel.		>		=	≤	>		>	≥	>		>	>		>	>
Moderately drained Wetland, uncolored water, sewered	5	f, re	*max*					339			837					241		383	512
			rel.					>			>					<		>	>
Poorly drained Wetland, colored water	6	f, re	*max*					364			966					1043		803	1234
			rel.					<			=					≤		<	>
Moderately drained Lake	23	r, p, f, re	*max*					370			501					945		396	378
			rel.					≤			≥					>		>	<=>
High-density (>600 houses mi[-2])				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	89	r, p, f, re	*max*		499		683	432	290		825	1392			1735	1022		316	217
			rel.		>		≥	>	>		=	<=>			≥	>		>	≥
Well drained Sewered	19	r, p, f, re	*max*					637	1162		914	974				1051			764
			rel.					<=>	<=>		>	>				>			≥
Golf Course				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Moderately drained Lake (small ponds)	11	r, p, f, re	*max*					423			647		1288			306			524
			rel.					<=>			≥		≥			>			>
Horse Farm				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	10	r, f, re	*max*					335			640	968				372		194	1525
			rel.					≤			≥	>				>		>	≥

[1]Flow conditions in storm hydrograph
- r, rising limb
- p, peak
- f, steeply falling limb
- re, recession

[2]Relation of stormflow concentration to base-flow concentration
- = equal to
- > greater than
- ≥ greater than or equal to
- < less than
- ≤ less than or equal to
- <=> variable

over HAA species. Effluent ammonium concentrations at this WWTP ranged from 10 to 21 mg/L as N, and were much higher than at the other plants, where concentrations did not exceed 0.35 mg/L as N (U.S. Environmental Protection Agency, http://www.epa.gov/ncea/pdfs/water/chloramine/dwchloramine.pdf/, last accessed September 5, 2007).

4.2.7.2 Base-Flow Formation Potentials, by Drainage Efficiency and Land-Use Category

The unfiltered HAA formation-potential pattern from base-flow samples at most subbasins consisted of a small autumn peak, moderate winter formation potentials, low formation potentials (from dilution) during the spring, a rebound to wintertime formation potentials (or minor peak) in June, and low formation potentials in July and August (fig. 8A–H). Evaluation of seasonal patterns at the colored-water-wetland subbasins was not possible because of the small number of analyses.

HAA formation potentials of base-flow samples from most subbasin categories (except those with colored-water wetlands or the golf course) were within the range of formation potentials of samples from the three reference subbasins. Uncolored-water-wetland subbasins had only slightly higher base-flow HAA formation potentials than the well drained subbasins. Also, formation potentials were consistently higher in the reference subbasin with medium-density housing and an uncolored-water wetland (PWS) than in the low-density-housing subbasins with uncolored-water wetlands; this may indicate that HAA formation potentials increase with increasing housing density among moderately drained subbasins. HAA formation potentials in samples from the golf-course subbasin (CEN) consistently exceeded those in the moderately drained reference subbasin (PWS) during late spring to summer and especially during the autumn peak (943 µg/L).

A. Reference Subbasins: well drained, forested; moderately drained (uncolored-water wetland) with medium-density housing; and well drained subbasin with high-density housing

Maximum base-flow unfiltered HAA formation potentials (fig.8A) were

- 302 µg/L, well drained, forested (WPR), late October;
- 802 µg/L, moderately drained, medium-density housing (PWS), early December; and
- 512 µg/L, well drained, high-density housing (A28), early November.

All three reference subbasins were characterized by an autumn peak in unfiltered HAA formation potential and springtime dilution (although the autumn peak at the medium-density housing subbasin (PWS) extended into early winter). Autumn HAA formation potential peaks in base-flow samples at the other two subbasins did not extend beyond early November.

The base-flow HAA formation potentials among the reference subbasins were similar to one another for most of the year. Apart from the autumn peak period, formation potentials in samples from the forested subbasin (WPR) ranged from 100 to 200 µg/L, samples from the high housing-density subbasin (A28) ranged from 200 to 400 µg/L, and samples from the medium housing-density subbasin ranged from 200 to 600 µg/L. The reason(s) for the differences among subbasins is unclear. The decreases in late-winter and early-spring HAA formation potentials in samples from the medium housing-density subbasin (PWS) were much larger than at the other two subbasins.

B. Well drained subbasins with high- to low-density housing

HAA formation potentials in base-flow samples from well drained subbasins with low-, medium-, and high-density housing (fig. 8B) were generally within the range of HAA formation potentials in samples from the forested and high-density housing reference subbasins (WPR, A28). One exception was a HAA formation-potential peak in samples from two high-density housing subbasins (P22, P20) in early December (1,114 µg/L and 529 µg/L, respectively), which corresponded to a HAA peak in samples from subbasin PWS (moderate drainage efficiency, medium-density housing).

C. Moderately drained (uncolored-water-wetland) subbasins with forest or low-density housing

Maximum base-flow unfiltered HAA formation potentials (fig. 8C) were

- 635 µg/L, forested, late October;
- 569 µg/L, low-density housing (PCH), early November.

Unfiltered HAA formation potentials in most of the uncolored-water-wetland subbasins were similar to those in the forested and high housing-density reference subbasins (WPR, A28), and well below those at the medium housing-density reference subbasin (PWS). There was no consistent response of HAA formation potential to differences in housing density (0–208 houses/mi^2) within this group of subbasins.

D. Poorly drained (colored-water-wetland) subbasins with low- and medium-density housing

Sample coverage for unfiltered HAA formation potentials was limited, but samples from these subbasins had the highest base-flow formation potentials (fig. 8D) in the stream network:

- 1,766 µg/L, medium-density housing (MAO), early June;
- 1,117 µg/L, low-density housing (RIC), late October.

HAA formation potentials in most other samples from these subbasins were similar to those in the moderately drained medium-housing density reference subbasin (PWS).

E. Moderately drained (lake) subbasins with medium-density housing

Unfiltered HAA formation potentials at the moderately drained (lake) subbasins with medium-density housing (fig. 8E) were generally within the same range as those at the forested (WPR) and high-density housing (A28) reference subbasins.

F. Well drained urban subbasin with medium-density housing, transportation corridors, and commercial/industrial land

The maximum unfiltered HAA formation potential in this subbasin (BED) was 628 µg/L, in early December (fig. 8F), similar to peak values at reference subbasin PWS and the well drained, high-density housing subbasins P22 and P20. Base-flow HAA formation potentials were most similar to the reference subbasin with high-density housing (A28), except for the peak formation potential described above.

G. Sewered subbasins: well drained with high-density housing and moderately drained (uncolored-water wetland) with medium-density housing

Maximum base-flow unfiltered HAA formation potentials (fig. 8G) were

- 488 µg/L, well drained, with high-density housing (YRK), late February;
- 479 µg/L, moderately drained, with medium-density housing (GRA), early June.

Most HAA formation potentials of samples from sewered subbasins were within 100 µg/L of each other. Formation potentials in both sewered subbasins were similar to those in the reference subbasin with high-density housing (A28), but differed widely (about 200 µg/L) from sample to sample.

H. Moderately drained (lake) subbasin with golf course (CEN) and well drained subbasin with horse farm (WAL)

Maximum base-flow unfiltered HAA formation potentials (fig. 8H) were

- 943 µg/L, moderately drained (lake), with golf-course (CEN), late October;
- 425 µg/L, well drained, with horse-farm (WAL), late October.

Data from the golf-course subbasin (CEN) were limited, but HAA formation potentials of many samples were elevated in relation to those at the reference subbasin with medium-density housing (PWS). HAA formation potentials in samples from subbasin CEN differed from those from subbasin PWS in that the autumn peak was earlier and well defined rather than broad.

HAA formation potentials of samples collected from the horse-farm subbasin were all within the range of those from the forested reference subbasin (WPR) and the reference subbasin with high-density housing (A28), except for the July 2001 sample, which was about 100 µg/L greater than that at subbasin A28.

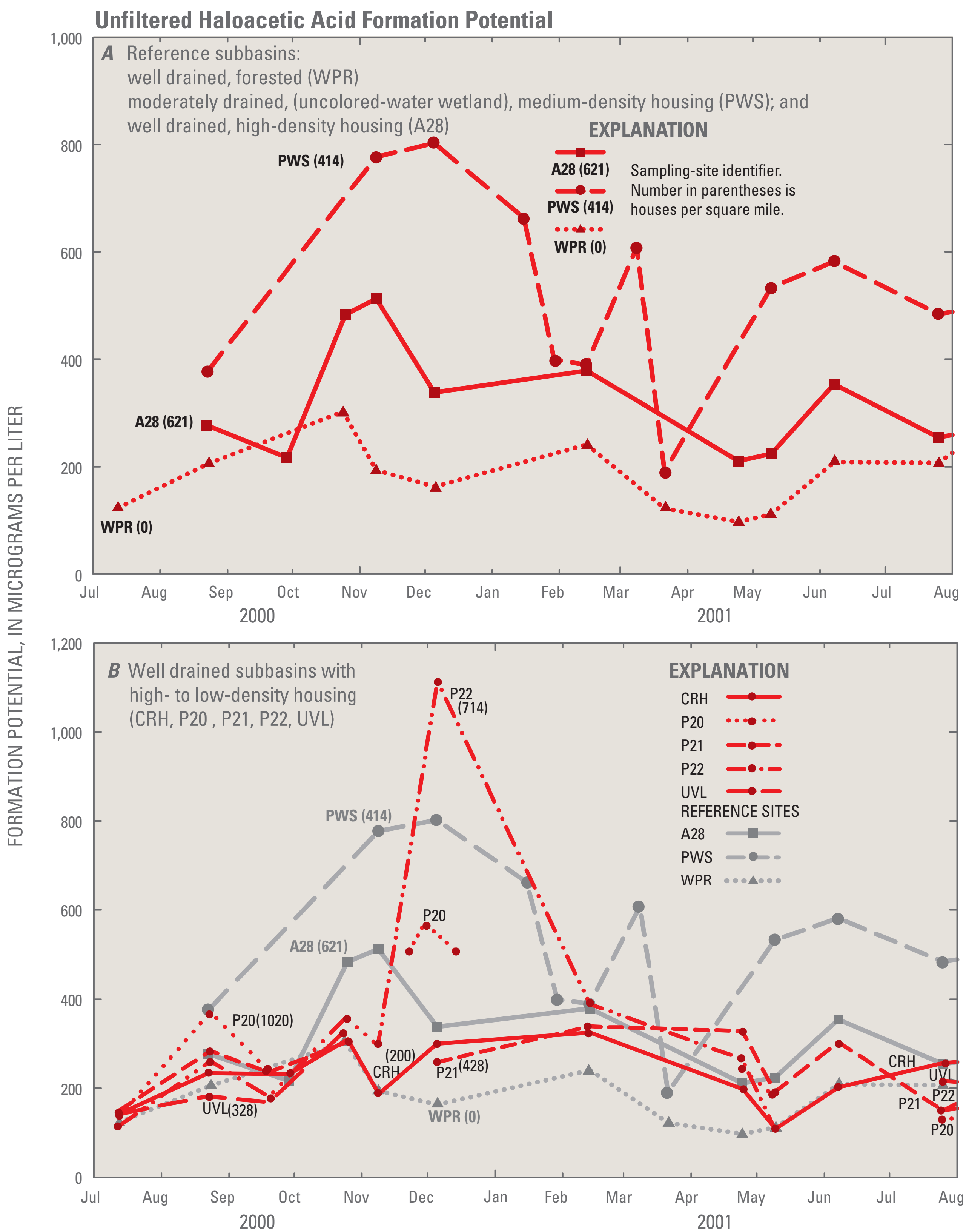


Figure 8. Base-flow unfiltered haloacetic acid formation potentials from July 2000 to July 2001, Croton Watershed, *(A)* reference subbasins, well drained, forested (WPR); moderately drained, uncolored-water wetland, medium-density housing (PWS); well drained, high-density housing (A28), and *(B)* well-drained subbasins, high- to low-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

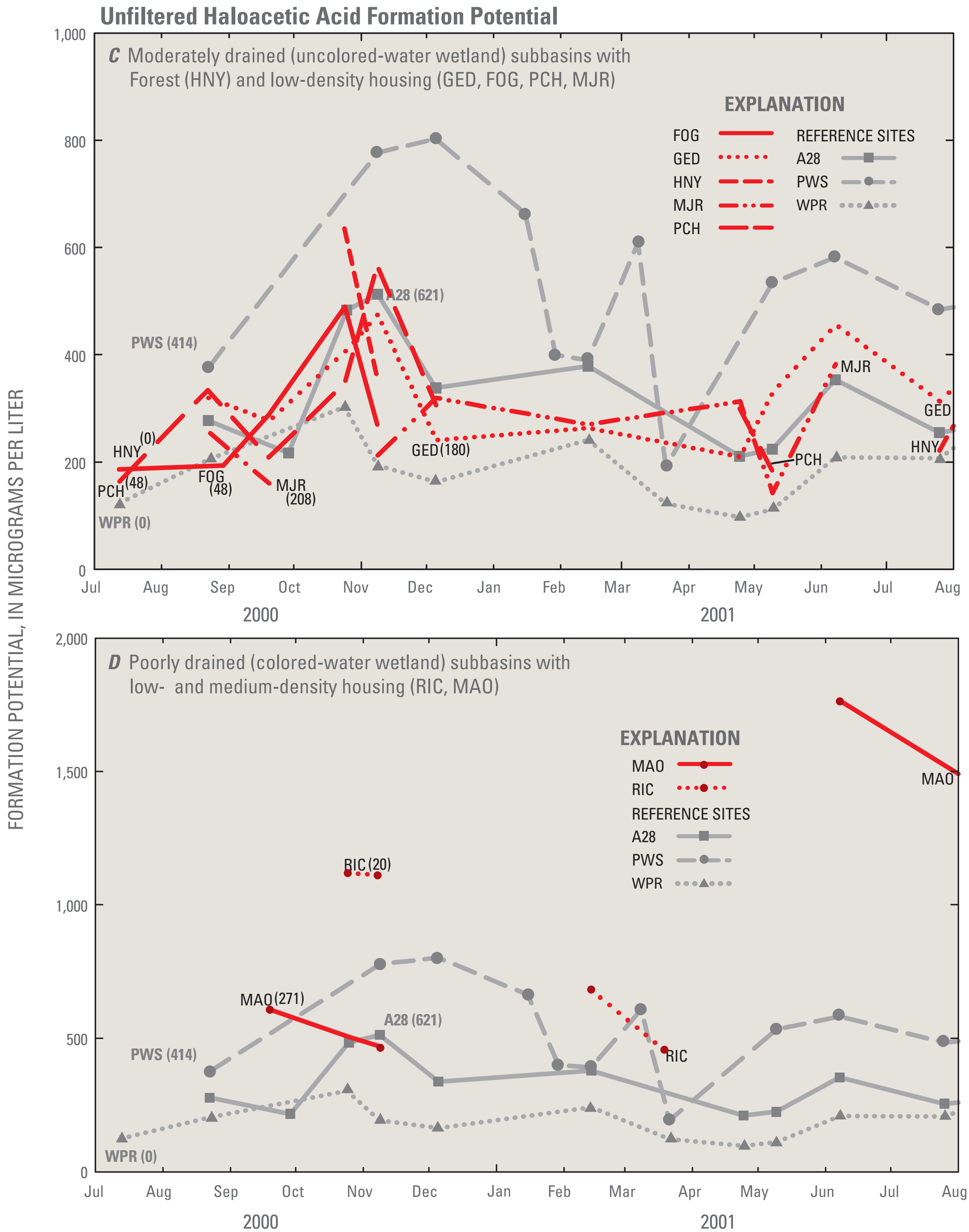


Figure 8. Base-flow unfiltered haloacetic acid formation potentials from July 2000 to July 2001, Croton Watershed, *(C)* moderately drained, uncolored-water wetland subbasins with low-density housing, and *(D)* poorly drained, colored-water wetland subbasins with low- and medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

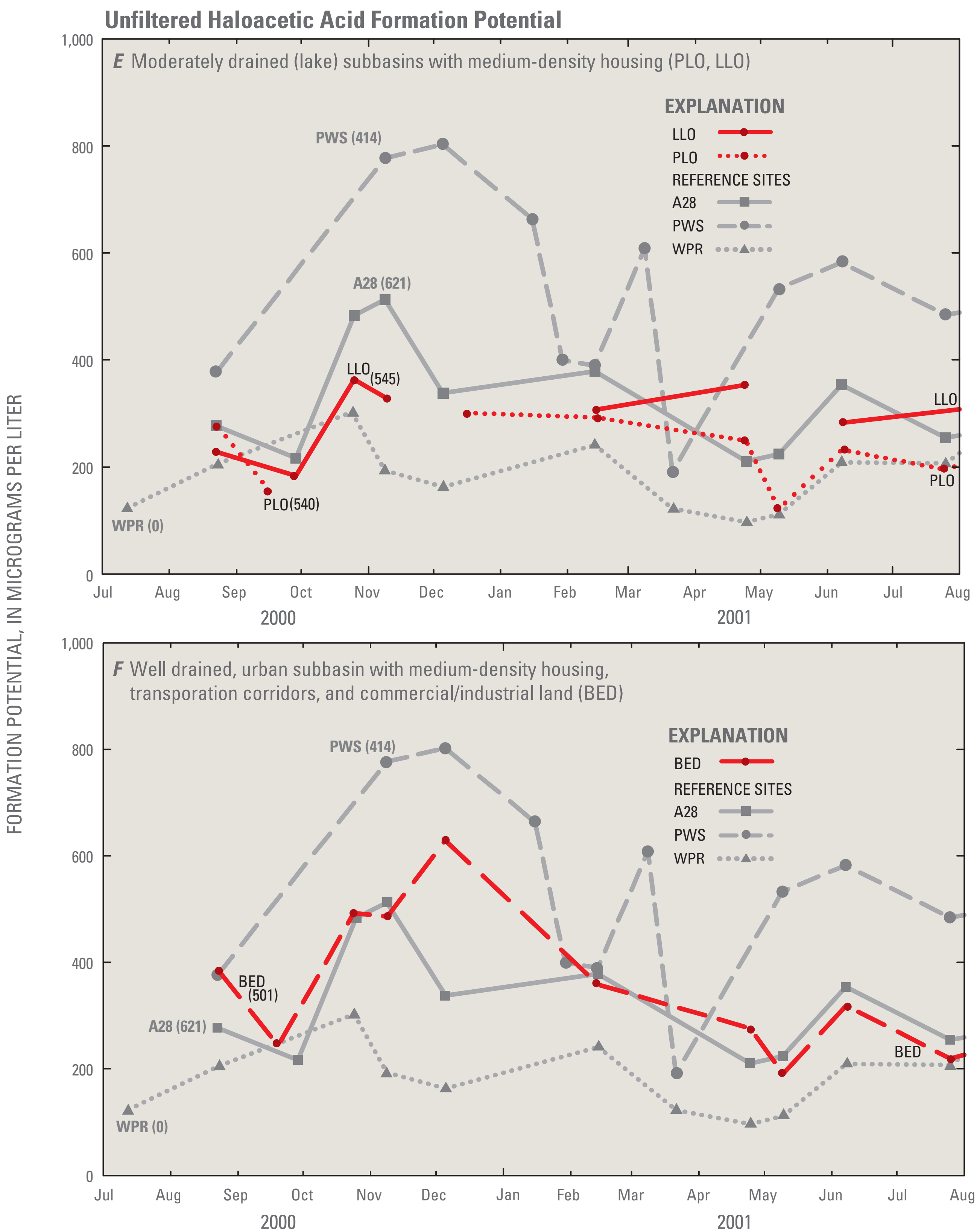


Figure 8. Base-flow unfiltered haloacetic acid formation potentials from July 2000 to July 2001, Croton Watershed, *(E)* moderately-drained subbasins with lakes and medium-density housing, and *(F)* well drained, urban subbasin, medium-density housing. Housing density, in houses per square mile, is denoted in parentheses after the subbasin site name. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

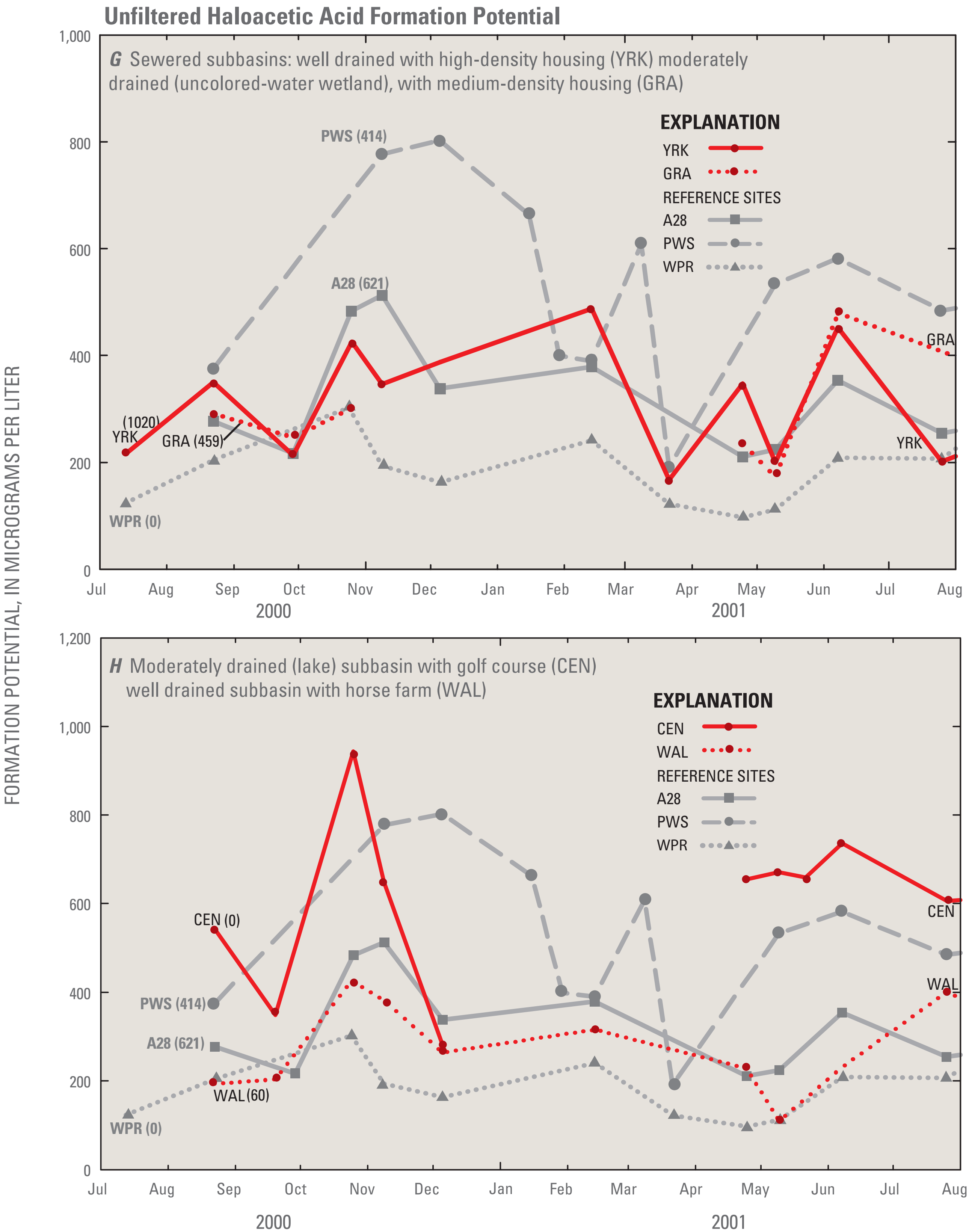


Figure 8. Base-flow unfiltered haloacetic acid formation potentials from July 2000 to July 2001, Croton Watershed, *(G)* sewered subbasins, well drained, high-density housing (YRK), moderately drained uncolored-water wetland, medium-density housing (GRA), and *(H)* moderately-drained subbasin, lake, golf course (CEN), well drained subbasin, horse farm (WAL) . Housing density, in houses per square mile, is denoted in parentheses after the subbasin ID. (Locations are shown in fig. 1; sampling frequency shown in table 1.)

4.2.7.3 Stormflow Formation Potentials

The highest HAA formation potentials in stormflow samples were typically associated with late May, June, July, and late December storms, whereas the lowest maximum stormflow formation potentials were measured in samples from March and early-December storms (table 9). Unfiltered HAA formation potentials were affected by drainage efficiency and land use. All but two of the moderately or poorly drained subbasins (with wetland or lake) had at least one stormflow formation potential greater than 800 µg/L; the two that did not had few storm samples. High stormflow HAA formation potentials were most common (2 or 3 instances) in samples from subbasins with colored- and uncolored-water wetlands with low-density housing and uncolored-water wetlands with medium-density housing (PWS). Well drained subbasins with forested, low-density housing, or urban land use had the lowest maximum stormflow HAA formation potentials. Well drained subbasins with high-density (sewered and unsewered) housing had two or more stormflow formation potentials that exceeded 800 µg/L.

The golf-course (CEN) and horse-farm (WAL) subbasins each had one stormflow HAA formation potential that exceeded 800 µg/L. The highest stormflow formation potential in the horse-farm subbasin was in early June, when stormflow formation potentials at other subbasins were also generally elevated. The golf-course subbasin, in contrast, reached its highest stormflow formation potential in early March, when maximum stormflow formation potentials for most other subbasins were low. Maximum stormflow HAA formation potentials at the golf-course subbasin in other months were greater than 400 µg/L, while those in the horse-farm subbasin were all less than 400 µg/L.

Associations between stormflow and base-flow HAA formation potentials were mixed. In most subbasins, stormflow formation potentials were greater than base-flow formation potentials in late March, May, June, July, and early November, and were lower than base-flow formation potentials in early March and December.

Table 9. Seasonal stormflow unfiltered haloacetic acid (HAA) formations potentials in the stream network by subbasin category, Croton Watershed, southeastern, N.Y., 2000-02.

[mi^2, square miles; All values are in micrograms per liter.]

For each half-month period: *max* = Highest stormflow formation portentials; *rel.* = Relation of stormflow formation portentials to baseflow formation portentials[2]

Land use and drainage efficiency category	Number of samples	Flow conditions sampled[1]		Jan		Feb		Mar		May		Jun		Jul		Nov		Dec	
Forested (zero housing)																			
Well drained	14	r, p, f, re	*max*				178				400	305				508		124	226
			rel.				≥				≥	>				>		<	≥
Moderately drained Wetland, uncolored water	1	f	*max*													707			
			rel.													>			
Residential (by housing density)																			
Low-density (<250 houses mi^{-1})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	4	f, re	*max*					131			547							113	299
			rel.					<			>							<	=
Moderately drained Wetland, uncolored water	24	r, f, re	*max*					709			1573	549			280	1130		311	
			rel.					≥			≥	≥			>	>		≥	
Poorly drained Wetland, colored water	7	r, f, re	*max*								1368					536			1168
			rel.								>					<			>
Medium-density (251-600 houses mi^{-2})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	7	p, f, re	*max*								960					179		194	314
			rel.								≥					<		≤	≤
Well drained Urban	5	f, re	*max*					202			438					567		238	354
			rel.					<			>					>		<	<
Moderately drained Wetland, uncolored water	44	r, p, f, re	*max*				313	514	892		1116	792	645		930	690		400	383
			rel.				<	<	>		≥	≥	≥		≥	<		≤	≤
Moderately drained Wetland, uncolored water, sewered	5	f, re	*max*					136			678					396		258	252
			rel.					<			>					>		<	<
Poorly drained Wetland, colored water	5	f, re	*max*					396			654					652		687	1024
			rel.					<			<					>		>	>
Moderately drained Lake	21	r, p, f, re	*max*					328			693					670		219	1585
			rel.					≤			≥					≥		<	≥
High-density (>600 houses mi^{-2})				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	85	r, p, f, re	*max*		914		418	362	443		489	1368			3566	841		389	351
			rel.		<=>		≥	<	≥		=	<=>			≥	<=>		≤	≤
Well drained Sewered	16	r, p, f, re	*max*					444	1191		1025	1049							839
			rel.					≥	≥		>	≥							<=>
Golf Course				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Moderately drained Lake (small ponds)	10	r, p, f, re	*max*					926			492		416			647			569
			rel.					<=>			<		<			=			>
Horse Farm				*Jan*		*Feb*		*Mar*		*May*		*Jun*		*Jul*		*Nov*		*Dec*	
Well drained	7	r, f, re	*max*					232			378	892				289		111	
			rel.					<			>	≥				<		<	

[1]Flow conditions in storm hydrograph
- r, rising limb
- p, peak
- f, steeply falling limb
- re, recession

[2]Relation of stormflow concentration to base-flow concentration
- = equal to
- > greater than
- ≥ greater than or equal to
- < less than
- ≤ less than or equal to
- <=> variable

4.3 General and Species Specific Associations of Nutrients and Disinfection-Byproduct Formation Potentials with Subbasin Drainage Efficiency, Land Use, Flow Conditions, and Season

4.3.1 General Occurrence of Nutrients and Disinfection-Byproduct Formation Potentials

Associations of concentrations of nutrients and formation potentials of DBPs with land use and drainage efficiency were more common with base-flow samples than with stormflow samples. This result indicates that ground-water contributions of nutrients and DBP precursors to streamflow reflect more subtle variations in subbasin drainage efficiency and land use than stormflow contributions.

The lowest nutrient concentrations and DBP formation potentials in base flow were associated with the well drained, forested (undeveloped) subbasin (fig. 9). Nutrient levels increased with land uses other than forested that included increasingly dense residential development served by septic systems or sanitary sewers, golf courses, and horse farms. Poor drainage efficiency in subbasins typically corresponded with low nutrient levels or, for nitrogen species, a shift to organic nitrogen. In contrast, concentrations of DBPs were highest in samples collected from subbasins with the poorest drainage efficiency and highest DOC concentrations. Land-use effects on concentrations of DBPs were limited. THM formation potentials at the well drained, sewered subbasin with high-density housing were consistently higher than those at the unsewered subbasin with high-density housing. HAA formation potentials were most elevated at the subbasin with golf-course land use, and to a lesser extent at sewered and unsewered subbasins with high housing densities.

Differences in median stormflow concentrations of nutrients and formation potentials of DBPs with their respective base-flow concentrations varied among the constitiuents measured (table 2, fig. 9) in well- and moderately drained subbasins. Stormflow and base-flow concentrations and formation potentials differed least in poorly drained subbasins. Concentrations and formation potentials of total (unfiltered) phosphorus, SRP, ammonium, unfiltered THMs, and unfiltered trichloroacetic acid (TCAA) were most consistently higher in stormflow than in base flow. Surface runoff is thus an important source of these constituents. Constituents most consistently higher in base flow than in stormflow, and presumably associated with ground-water sources, included DBP subspecies: bromodichloromethane, dibromochloromethane, monochloroacetic acid, and dibromoacetic acid. Constituents with similar median concentrations or no dominant association with stormflow or base flow across drainage-efficiency and land-use categories included nitrate, unfiltered HAA and dichloroacetic acid.

4.3.2 Phosphorus and Nitrogen Occurrence and Relative Proportions of Species

Phosphorus and nitrogen, despite having low concentrations in well-drained forested areas and similar anthropogenic sources, have distinct differences in their dominant species among the drainage-efficiency and land-use categories. Total (unfiltered) phosphorus concentration represents all particulate and dissolved forms of phosphorus, whereas SRP is the bioavailable form of dissolved phosphorus. The difference between TP and SRP essentially represents particulate phosphorus (depicted graphically in fig. 9) because the difference between total dissolved phosphorus and SRP is small. Nitrogen species were measured in the dissolved phase (nitrate, ammonium, total dissolved nitrogen). Dissolved organic nitrogen was calculated by subtracting nitrate and ammonium from total dissolved nitrogen.

4.3.2.1 Total (Unfiltered) Phosphorus and Soluble Reactive Phosphorus

Elevated phosphorus concentrations in base flow and stormflow are associated with all forms of development investigated in this study. Concentrations generally increased with housing density whether subbasin areas were served by septic systems or sanitary sewers.

TP and SRP showed strong seasonal variations in base flow and stormflow. Base-flow concentrations of both analytes were low from late November through late April and highest during May through October. TP concentrations were also characterized by base-flow peaks during late October –early November (the leaf fall period) and during late April–May. Stormflow concentrations of TP and SRP matched the base-flow peaks, with highest concentrations during the autumn leaf-fall peak. One exception was high stormflow TP concentrations throughout the year in the well drained subbasin with high-density housing and septic systems (table 3).

The proportion of SRP to TP concentrations in base flow was highest in well drained subbasins with high-density housing (with septic systems or sanitary sewers), horse farms, and golf courses (fig. 9). SRP to TP proportions in moderately drained

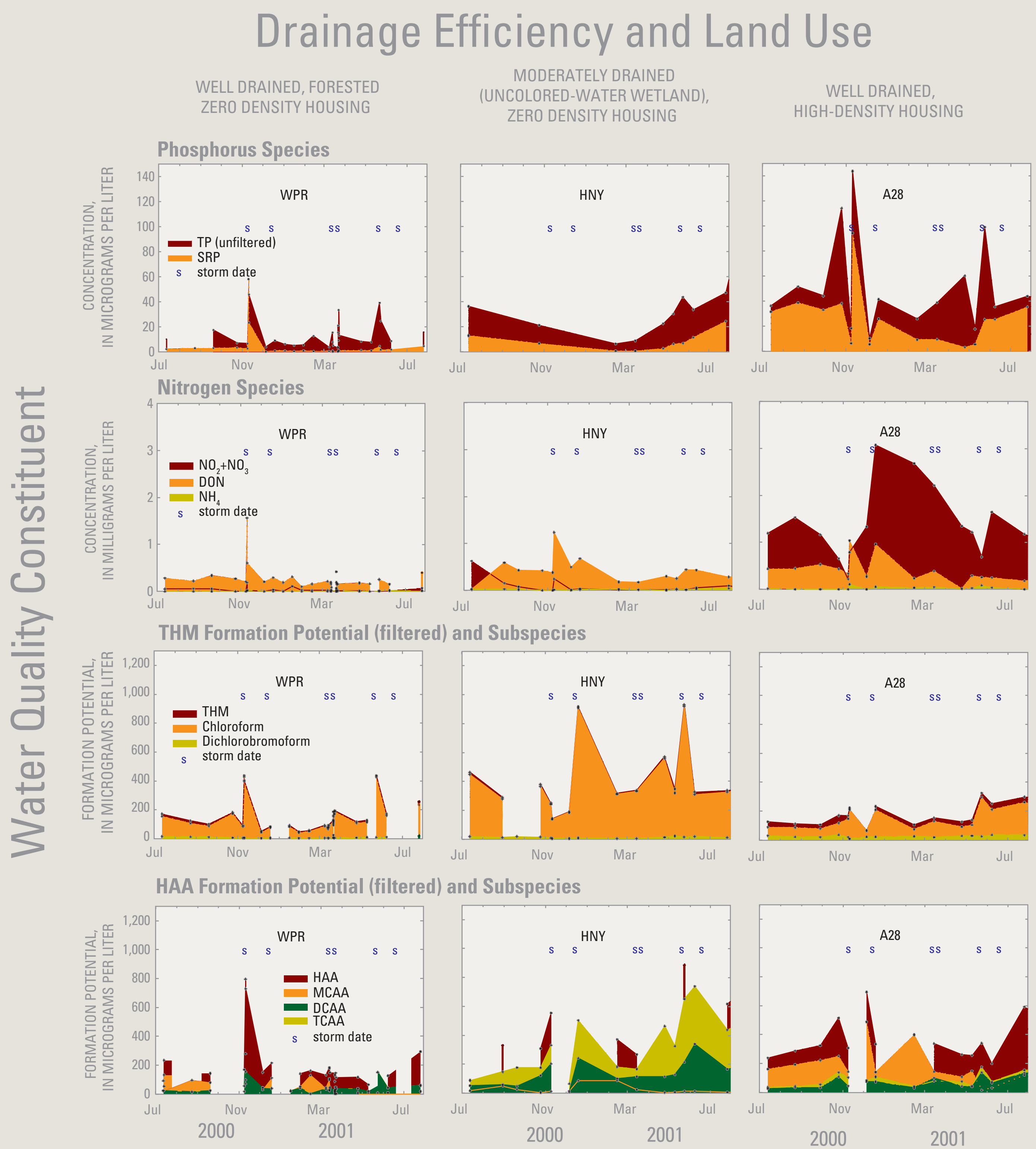
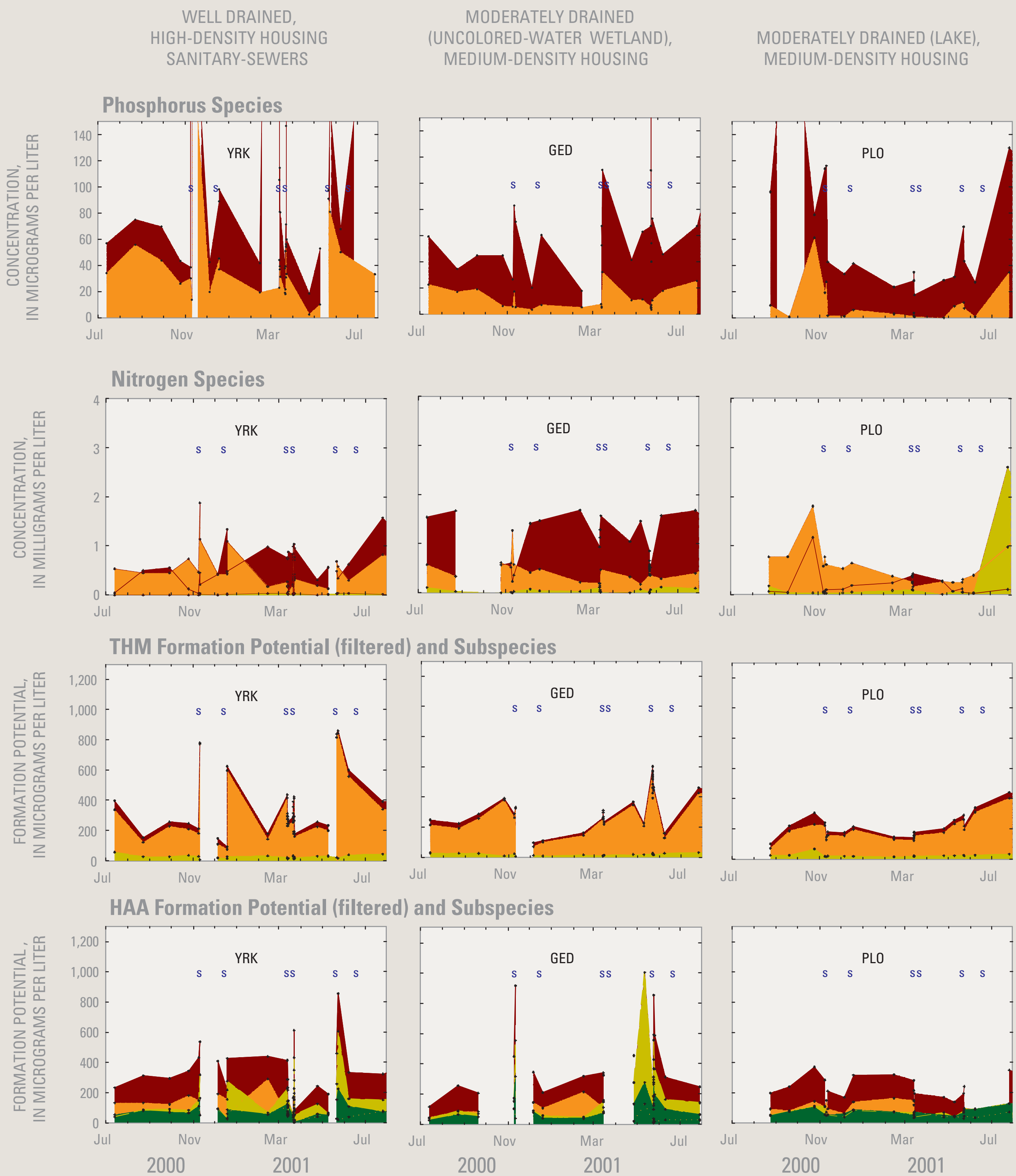


Figure 9. Relation of nutrients and disinfection byproducts to land use and drainage efficiency at representative subbasins from July 2000 to July 2001, Croton Watershed, southeastern New York. Three-letter identifier on each plot indicates the representative subbbasin selected (table 1). Plots include all samples (of base flow and stormflow) collected in each subbasin. Sampling frequency differs among subbasins. (THM, trihalomethane; HAA, haloacetic acid; MCAA, monochloroacetic acid; TCAA, trichloroacetic acid; BCAA, bromochloroacetic acid)

Download figure 9 as a single PDF at **http://pubs.usgs.gov/ofr/2009/1054/ofr2009-1054.figure9.pdf**



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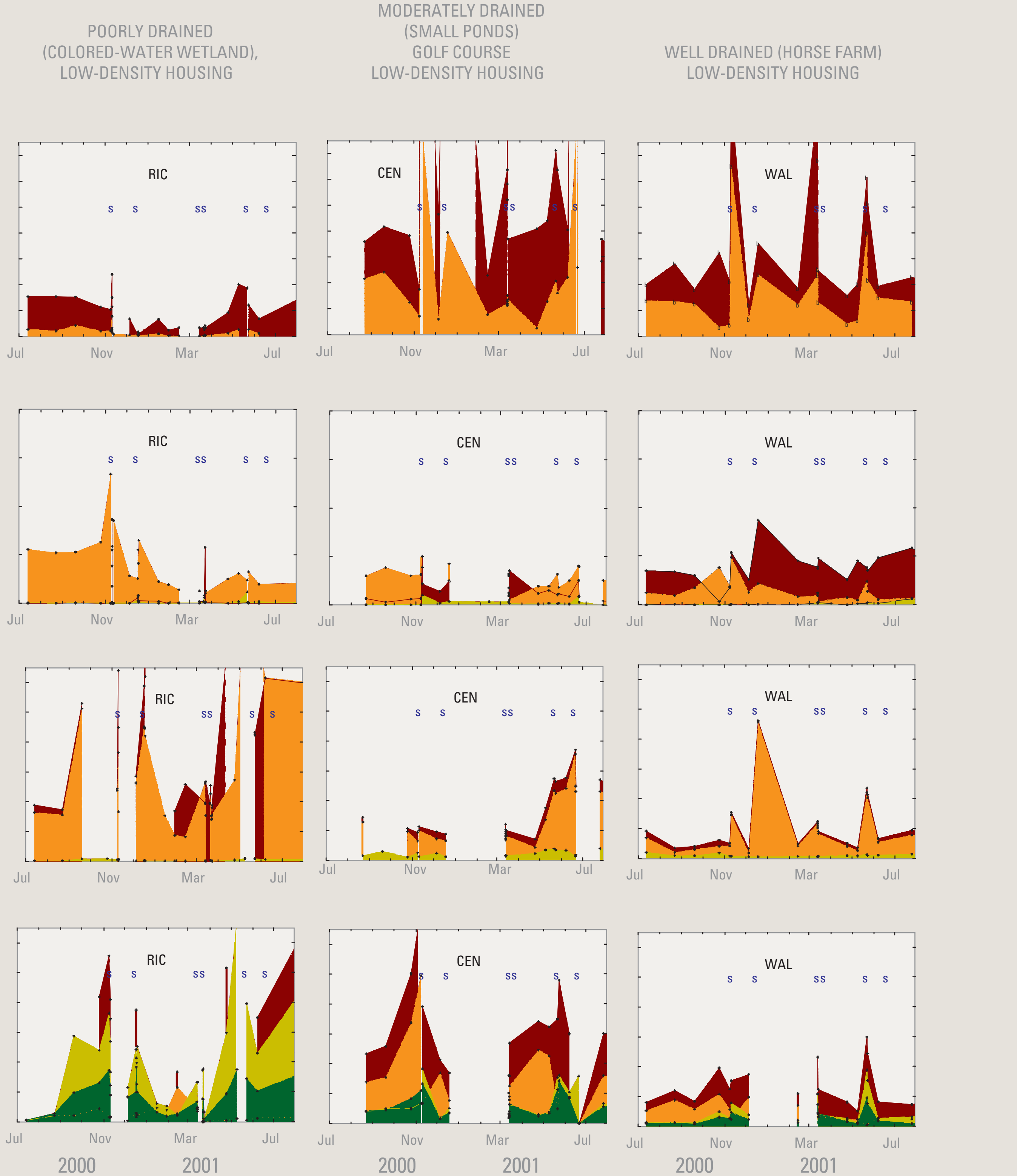

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subbasins with lakes or uncolored-water wetlands and medium-density housing were intermediate. The lowest proportions of SRP to TP were measured in the subbasins with zero- to low-density housing, irrespective of drainage efficiency (well drained to poorly drained).

Stormflow SRP to TP proportions were generally smaller than in base flow because the particulate-matter component of TP is increased by storm runoff. The highest SRP–TP proportions were associated with late autumn storms in all subbasins (tables 3, 4). The highest proportions during the remainder of the year were measured in sanitary-sewered subbasins, well drained subbasins with medium- to high-housing densities, and the golf-course and horse-farm subbasins.

4.3.2.2 Nitrate, Ammonium, and Dissloved Organic Nitrogen

Nitrogen speciation and concentrations were affected by both subbasin drainage efficiency and land use (fig. 9). The lowest concentrations of all three dissolved nitrogen species were associated with the well drained, forested subbasin. The highest concentrations of dissolved nitrogen species were associated with medium- to high-density residential development with septic systems or sanitary sewers in well drained to moderately drained subbasins, the horse-farm subbasin, and poorly drained (colored-water wetland) subbasins.

The dominant forms of nitrogen in a given subbasin were dependent on land use, drainage efficiency, and season. Concentrations of these species changed most consistently during the leaf-fall period (late October to early November) when dissolved organic N increased and nitrate, if present, decreased (fig. 9). Dissolved organic N was the predominant species in forested, undeveloped subbasins regardless of drainage efficiency, although concentrations were highest in the poorly drained subbasins. One exception was the predominance of nitrate in late autumn and spring stormflow samples from the poorly drained, colored-water-wetland subbasin (RIC, fig.9). Nitrate was dominant in base flow from the well drained subbasin with high-density housing, the moderately drained (uncolored-water wetland) subbasin with low-density housing, and in the well drained horse-farm subbasin (fig. 9). Samples collected at the lake outlet from the moderately drained (lake) subbasin with medium-density housing had elevated organic N and nitrate in an autumn peak and elevated ammonium and organic N in a summer peak (fig. 9). Elevated DOC concentrations (accompanied by low oxygen conditions) generally favor the reduced forms of dissolved N (ammonium, organic N) in moderately drained (lake) and poorly drained subbasins.

4.3.3 THM and HAA Species Produced by Formation-Potential Chlorination of Streamwater Samples—Identification and Occurrence

THMs and HAAs differed in the number of dominant forms produced in streamwater samples chlorinated during the formation-potential analyses. THMs and HAAs are similar in the predominance of chlorine-containing forms over bromine-containing forms and the dissolved (filtered) fraction over the particulate fraction (figs. 10, 11). Chlorine-containing forms of DBPs are widespread, whereas bromine-containing forms are most closely associated with residential development and golf-course land use (fig. 2, appendices 1J, 1O, 1P).

Chloroform typically accounts for about 80 to 98 percent of THM formation potentials; the remainder (fig. 10) consists of the three bromine-containing forms: bromodichloromethane (~10–40 μg/L), dibromochloromethane (~1–4 μg/L), and bromoform (~1–4 μg/L).

HAAs, unlike THMs, are largely a composite of the formation potentials of three chlorine-based forms—monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA); the bromine-containing forms typically are found in formation potentials less than 10 μg/L (fig. 11). Each of the three major (chlorine) HAA components responded differently to drainage efficiency, land use, and flow conditions (fig. 11, table 2, appendix 1). In general, MCAA formation potentials were higher in base flow than in stormflow (fig. 11) and were highest in well drained and moderately drained (lake) subbasins with residential development, and in the golf-course subbasin (table 2, fig. 9). MCAA formation potentials were lowest in most wetland subbasins (appendix 1L, fig. 9). DCAA formation potentials increased with increasing DOC concentration and decreasing drainage efficiency, such that the highest concentrations were associated with the colored-water wetland subasins. Stormflow and base-flow DCAA medians were similar to one another within most subbasin categories (table 2). TCAA formation potentials, like those of DCAA, increased with decreasing drainage efficiency, but TCAA differed from DCAA in that stormflow formation potentials were typically higher than base-flow formation potentials (table 2). Median formation potentials of stormflow and base-flow TCAA were similar in the two colored-water-wetland subbasins, the forested, uncolored-water-wetland subbasin, and the golf-course subbasin.

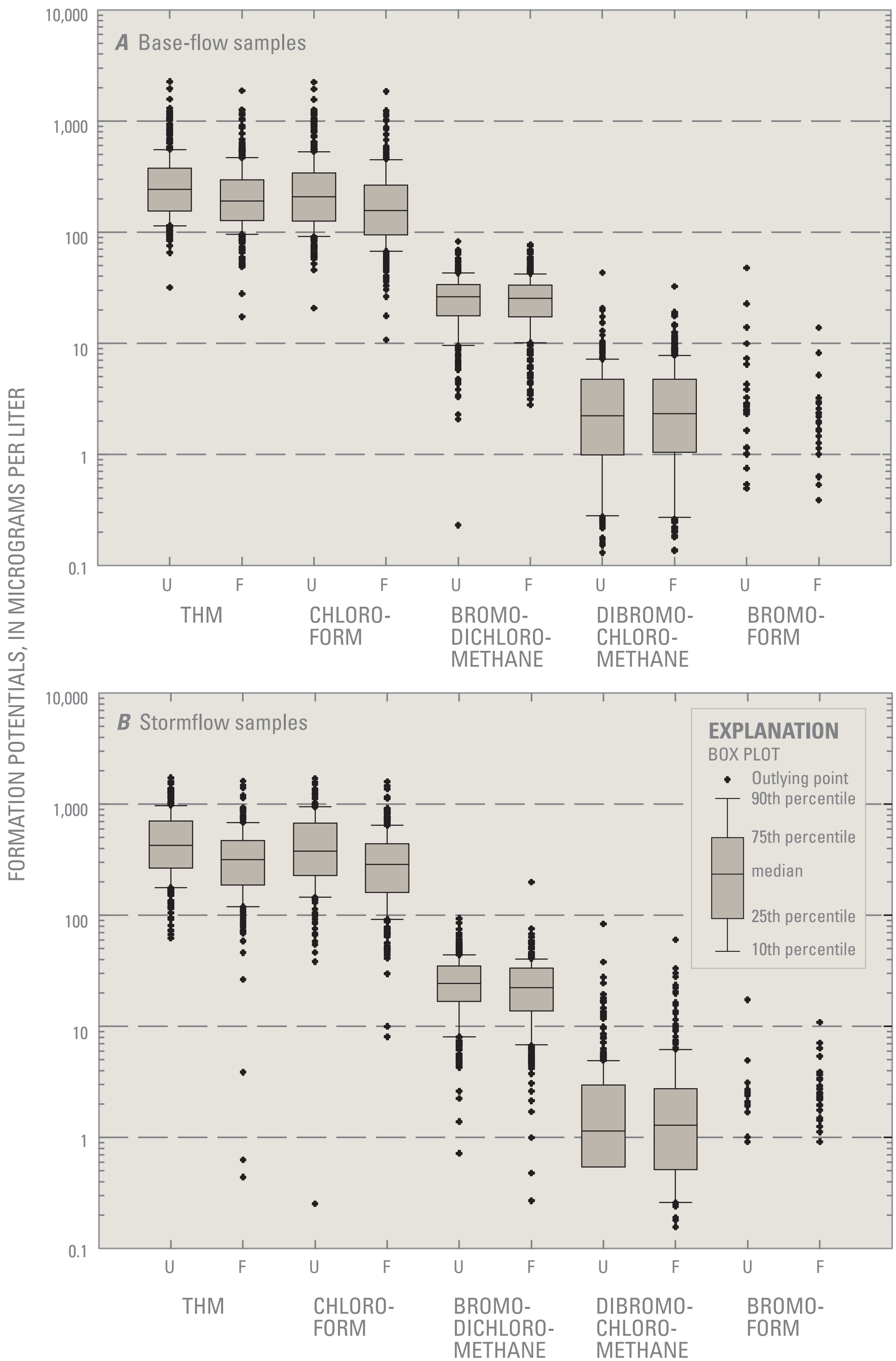

Fig. 10. Formation potentials of unfiltered (U) and filtered (F) trihalomethane (THM) species in *(A)* base-flow and *(B)* stormflow samples from the stream network, Croton Watershed, southeastern New York, 2000–02.

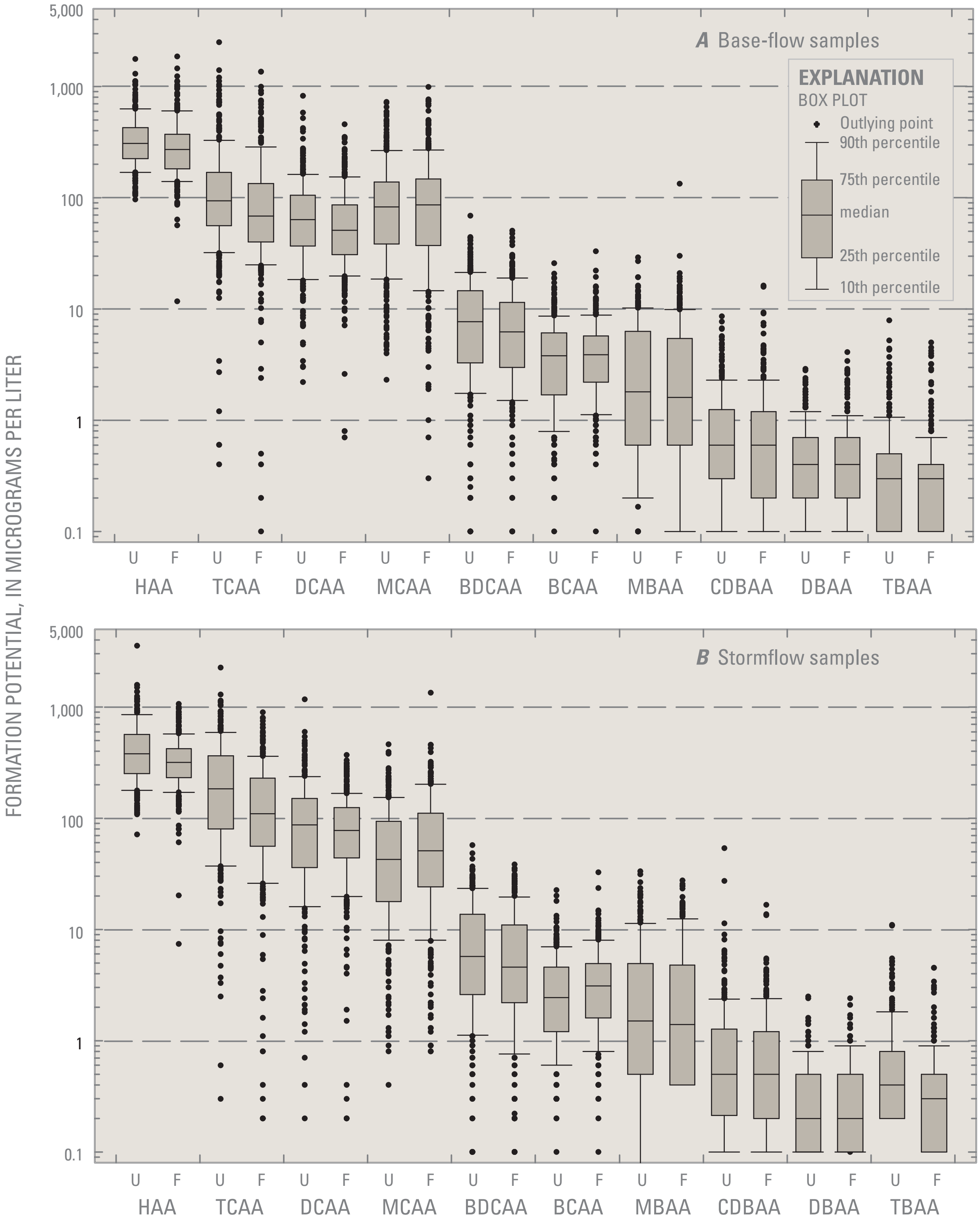

Figure 11. Formation potentials of unfiltered (U) and filtered (F) haloacetic acid (HAA) species in *(A)* base-flow, and *(B)* stormflow samples from the stream network, Croton Watershed, southeastern, New York, 2000–02. (HAA, haloacetic acid; TCAA, trichloroacetic acid; DCAA, dichloroacetic acid; MCAA, monochloroacetic acid; BDCAA, bromodichloroacetic acid; BCAA, bromochloroacetic acid; MBAA, monobromoacetic acid; CDBAA, chlorodibromoacetic acid; DBAA, dibromoacetic acid; TBAA, tribromoacetic acid)

4.3.4 THM and HAA Occurrence with Respect to Flow Conditions, Subbasin Drainage Efficiency, and Land Use

THM and HAA formation potentials responded similarly to flow conditions and to subbasin drainage efficiency and land use. Base-flow formation potentials were responsive to drainage efficiency and, to a limited extent, land use. Peak stormflow formation potentials were most responsive to the source of water (storm runoff) rather than drainage efficiency or land use.

4.3.4.1 Base Flow

Elevated THM and HAA formation potentials in base-flow samples were associated with poor subbasin drainage efficiency. Housing density had no obvious association with THM formation potential in base flow, and a general positive association with HAA formation potential. Moderately elevated formation potentials of both constituents were associated with the golf-course subbasin (table 2, appendices 1I, 1K).

Base-flow DBP formation potentials were characterized by two seasonal peaks. THM formation potentials were highest in late spring and early summer, with a secondary autumn peak (late October–early November). HAA formation potentials exhibited the same peaks except that formation potentials were highest in the autumn peak, with a secondary peak in late spring and summer. High DBP formation potentials during the autumn leaf-fall period indicate that leaf-litter leachate is a precursor for HAAs, and to a lesser extent, THMs.

4.3.4.2 Stormflow

Stormflow THM and HAA formation potentials were typically higher and less dependent on drainage efficiency or land use than base-flow formation potentials (table 2, apppendices 1I, 1K). Maximum stormflow THM formation potentials were 1,000 µg/L in most subbasins (table 8). Only the poorly drained, colored-water-wetland subbasins had base-flow formation potentials of similar or greater magnitude (fig. 7D). The range of HAA formation potentials in stormflow was similar to that of THM formation potential (figs. 10, 11), but about 25 percent fewer maximum storm formation potentials exceeded 800 µg/L, and the variability of formation potentials among subbasins during May and November storms was greater (table 9). HAA stormflow and base-flow median formation potentials were generally more similar than those of THMs in nearly all subbasin categories (table 2).

4.4 Sources of DOC and Potential Surrogate Analytes for Estimation of Disinfection-Byproduct Formation Potentials

Understanding the spatial and temporal formation potential of DBPs in streamflow in the Croton Watershed is critical for watershed management. This section characterizes DOC sources and explores potential surrogates for disinfection byproducts.

The identification of constituents or properties that correlate with DBP formation potentials, called “surrogates”, and that are relatively easy to measaure is desirable because of the cost and time required for formation-potential determinations of DBPs. Analysis of such surrogates might provide a more cost-effective means of DBP assessment than direct measurement of DBP formation potentials. Numerous analyses of DBP formation potential, DOC concentration, ultraviolet absorption at 254 nm (UV-254), Pt-Co color, and gelbstoff 440 (g440) in samples of streamwater from all subbasin categories during base-flow and stormflow conditions provided a basis for identifying the occurrence, sources, and possible surrogates for DBPs within the Croton Watershed.

4.4.1 Characterization of DOC Sources

Specific ultraviolet absorbance (SUVA), the ratio of UV-254 absorbance to DOC concentration, was used as an indicator of DOC source material. The SUVA units given in this section are reported as absorbance per cm of cell length per mg/L of DOC (L/(mg carbon·cm)), as reported by Marzec and others (2002). UV-254 measurements are indicative of the aromatic carbon content of a water sample (Aiken and Cotsaris, 1995). Allochthonous DOC, derived from land surface (terrestrial sources), is characterized by SUVA values greater than 0.020 L/(mg carbon·cm) (Buffle, 1988), whereas SUVA values of 0.04 to 0.05 L/(mg carbon·cm) have been interpreted to indicate mostly humic material (Edzwald, 1993). Autochthonous DOC, derived from aquatic sources, has been characterized for algal exudates (0.020 L/(mg carbon·cm), from UV-254/TOC, (total organic carbon (TOC)), Goel and others, 1995) and for aquatic refractory natural organic matter (0.0017 L/(mg carbon·cm), Buffle, 1988). Thus, aquatic sources typically have SUVA values of 0.020 L/(mg carbon·cm) or lower, and the values for terrestrial sources typically exceed 0.020 L/(mg carbon·cm).

SUVA values from the 27 sampling sites indicate that the DOC in these streams is primarily of terrestrial (allochthonous) origin. SUVA values were grouped by flow condition (base flow and stormflow) and by presence or absence of recent leaf litter. The period of recent leaf litter was designated as from mid-October through December; the period from January through mid-October represented the absence of recent leaf litter.

SUVA values from base flows during the absence of recent leaf litter provided the best indication of SUVA differences among subbasin categories (fig. 12); SUVA values from stormflows during the leaf-litter periods provided a widespread SUVA signal of organic soil material and leaf litter that can mask local differences within the Croton Watershed. Samples from most subbasin categories had base-flow median SUVA values of 0.050 to 0.070 L/(mg carbon·cm) for the January to mid-October period; the exceptions were the lake subbasins with medium-density housing (around 0.040 L/(mg carbon·cm)) and uncolored-water-wetland subbasins with zero or low-density housing (0.075 to 0.100 L/(mg carbon·cm), fig.12A). Low SUVA values from lake subbasins with medium-density housing are consistent with a mixture of algal exudates from the productive lakes and terrestrial organic matter from the watershed soils. The high SUVA values from the uncolored-water-wetland subbasins with zero- and low-density housing may reflect the wetland-vegetation component of SUVA and short water-residence times in the subbasins. Low SUVA values in the two colored-water-wetland subbasins, relative to the SUVA values in the subbasins just described, indicate lower aromatic carbon content in waters with presumably long residence times. DOC concentrations in samples from the colored-water-wetland subbasins were the highest in the study area.

Base-flow SUVA medians from several subbasins were lower (less than 0.060 L/(mg carbon·cm)) during the period from mid-October through December (recent leaf-litter period) than from January through mid-October, whereas SUVA in lake subbasins was highest (about 0.45 L/(mg carbon·cm)) during the recent leaf-litter period. This observation suggests that the SUVA value for leachate from recent leaf litter is between these two values.

SUVA values measured in stormflow samples from January through mid-October were similar to those in base flow for the same period, except that the highest individual measurement was made in the colored-water-wetland subbasin with low housing density (RIC) (fig. 12B). The range of SUVA medians in base flow among the subbasin categories (0.038 to 0.078 L/(mg carbon·cm)) was wider and higher than the range of medians observed in stormflow samples. The narrow range of median stormflow SUVA values at well drained subbasins was generally within the upper range of base-flow median SUVA. The high median SUVA range in stormflow values indicates greater UV-254 absorbance (higher aromatic content) per mg/L DOC in soil organic matter (stormflow sources) than in ground-water discharge (base-flow sources).

Stormflow SUVA values from samples collected during the leaf-litter period (mid-October through December) are similar to the values from the samples collected during the absence of leaf litter from January through mid-October stormflow samples,

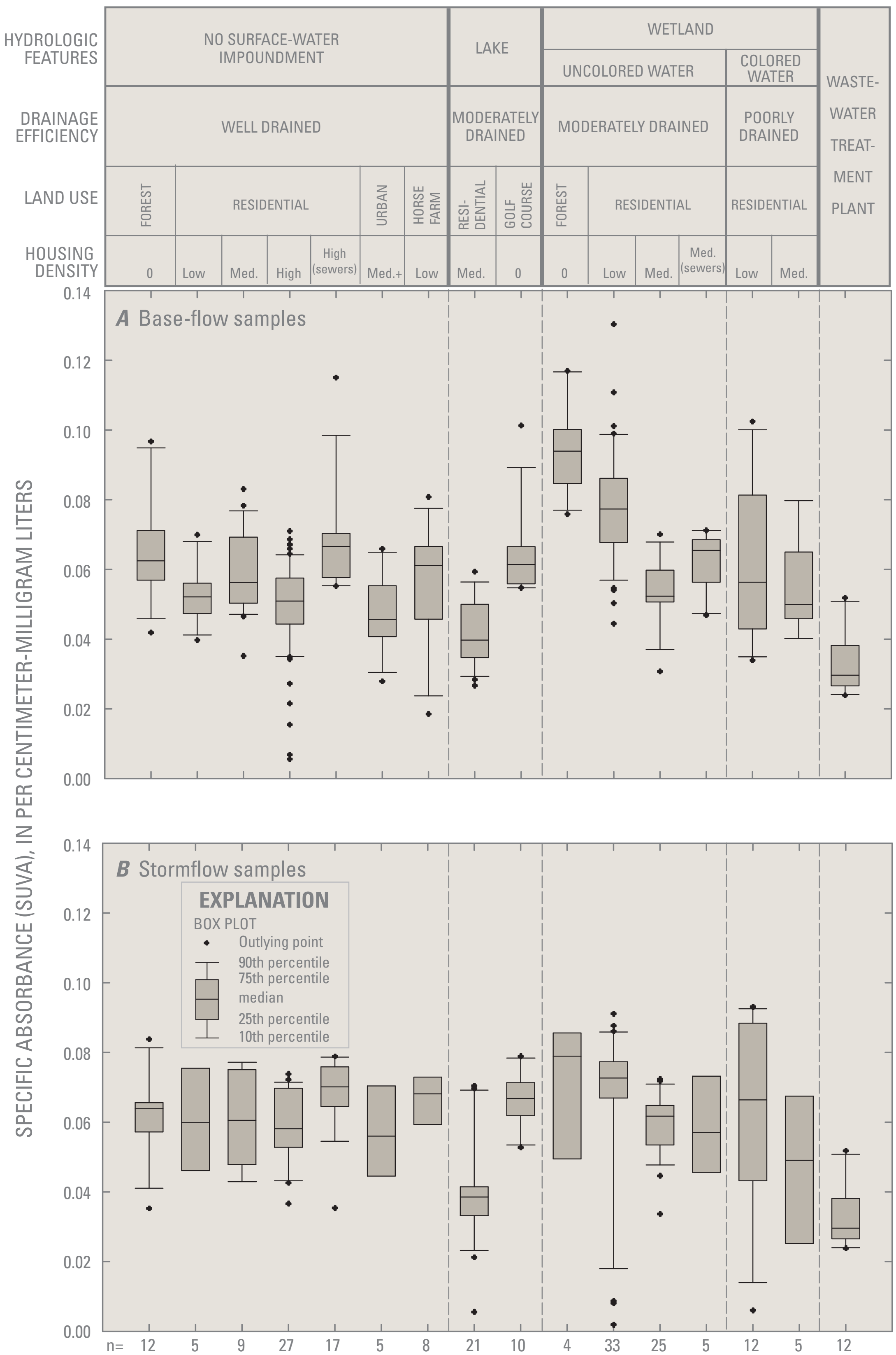

Figure 12. Specific absorbance (SUVA) for January to mid-October, when recent leaf litter was absent from the study area, *(A)* base-flow and *(B)* stormflow samples from the stream network, Croton Watershed, southeastern, New York, 2000–02. Grouped by drainage efficiency, land use, and housing density.

but the median SUVA range for the recent leaf litter period for most subbasin categories is narrower and lower (0.050 to 0.060 L/(mg carbon·cm)). This stormflow SUVA difference between the recent leaf-litter period (mid-October through December) and the period when recent leaf litter was absent (January through mid-October) is consistent with that of the base-flow samples described above.

4.4.2 Surrogates for DBPs

Identification of surrogates for DBP formation potentials (THMs and HAAs) is desirable because of the time and expense of formation-potential analyses. A previous evaluation of THM surrogates (UV-254 and DOC) for large Croton Watershed tributaries (by individual tributary) indicated inconsistent linear-regression r^2 values (Marzec and others, 2002). The lowest r^2 values were generally associated with poorly drained stream basins (with wetlands or large lakes). No differentiation of sample data (by flow conditions or season, for example) was possible because the number of samples from each tributary was small (n = 12 or less). The large number of samples collected from the stream network during this study provided an opportunity to incorporate the effects of season and flow conditions in the evaluation of surrogates for THMs and HAAs.

Candidate surrogate constituents included DOC, UV-254, gelbstoff 440, and color (Pt-Co). Scatterplots of all analyses of filtered THM or HAA formation potential and the concentrations, values, or intensity of any of the potential surrogates show low but generally positive correlations (not shown). The low correlations reflect the combined effects of variations in season, flow condition, drainage efficiency, and land use on formation potential, as documented in previous sections of this chapter. (Gelbstoff 440 is the measure of UV absorption at 440 nanometers.)

Surrogates for DBPs are most useful if they can be applied to large data sets. The stream sample data were therefore divided into the largest groups that might be indicative of different DOC sources and DBP precursors. Narrow groupings with sufficiently wide DOC ranges (for example, uncolored-water wetlands under specific flow conditions and season or time interval) may yield improved correlations, but their applicability across the Croton Watershed is limited.

The sample data were grouped by general flow condition (base flow or stormflow) and by the presence or absence of recent leaf litter, which represents an important annual addition of DOC to the subbasin streamflow. The recent-leaf-litter group represented the period from mid-October through the end of December; the second group (the absence of recent leaf litter) represented the remainder of the year (January through mid-October). Thus, four groups representing four sets of conditions were compared with four potential surrogates for THMs (fig. 13) and HAAs (fig. 14). The linear-regression r^2 values for each pairing are listed in table 10. The results indicate that no single constituent is a suitable surrogate for THM and HAA formation potentials and that flow and leaf-litter conditions preclude identification of a single surrogate for either THMs or HAAs.

Base-flow data were more narrowly defined than stormflow data used in the regressions (table 10). All base-flow evaluations omitted lake-subbasin data because DOC from aquatic sources responded differently to measures of color than DOC from terrestrial sources. Culvert-discharge water samples from sites B28E and B28W also were omitted because they were essentially ground-water drains affected by septic effluent. Stormflow data from all subbasins except CEN (golf course; during the non leaf-litter period) were included because stormflow DOC was more consistent in its THM yield (THM/DOC) across drainage-efficiency and land-use categories.

The DOC concentrations used in the regressions differed between THMs and HAAs. Base-flow THM and surrogate relations were calculated for DOC $\leq$ 5 mg/L because the strongest relations, and most of the samples, were within that concentration range. The character of DOC and of some of the other potential surrogates changed, which decreased THM yield at the high DOC concentrations associated with wetland subbasins. The base-flow HAA and surrogate comparisons were based on the full range of DOC concentrations because there was little or no relation within the 0–5 mg/L DOC range.

The best surrogates for THMs were UV-254 and DOC, with r^2 values as high as 0.70 (table 10, fig. 13). UV-254 was best for base-flow conditions regardless of leaf-litter status, whereas DOC was best for January to mid-October (absence of recent leaf litter) stormflows. No THM surrogate was found for stormflow samples for mid-October through December (recent leaf litter period).

Each of the evaluated surrogates for HAAs had the highest or second highest r^2 value (0.40–0.74) for one of the sample groups, with UV-254 always among the highest (table 10, fig. 14). The r^2 values for possible HAA surrogates were generally lower than those for THMs. These values are probably lower because HAAs occur as three major species, whereas THMs have only one major species. The strongest HAA-surrogate relations were associated with stormflow conditions.

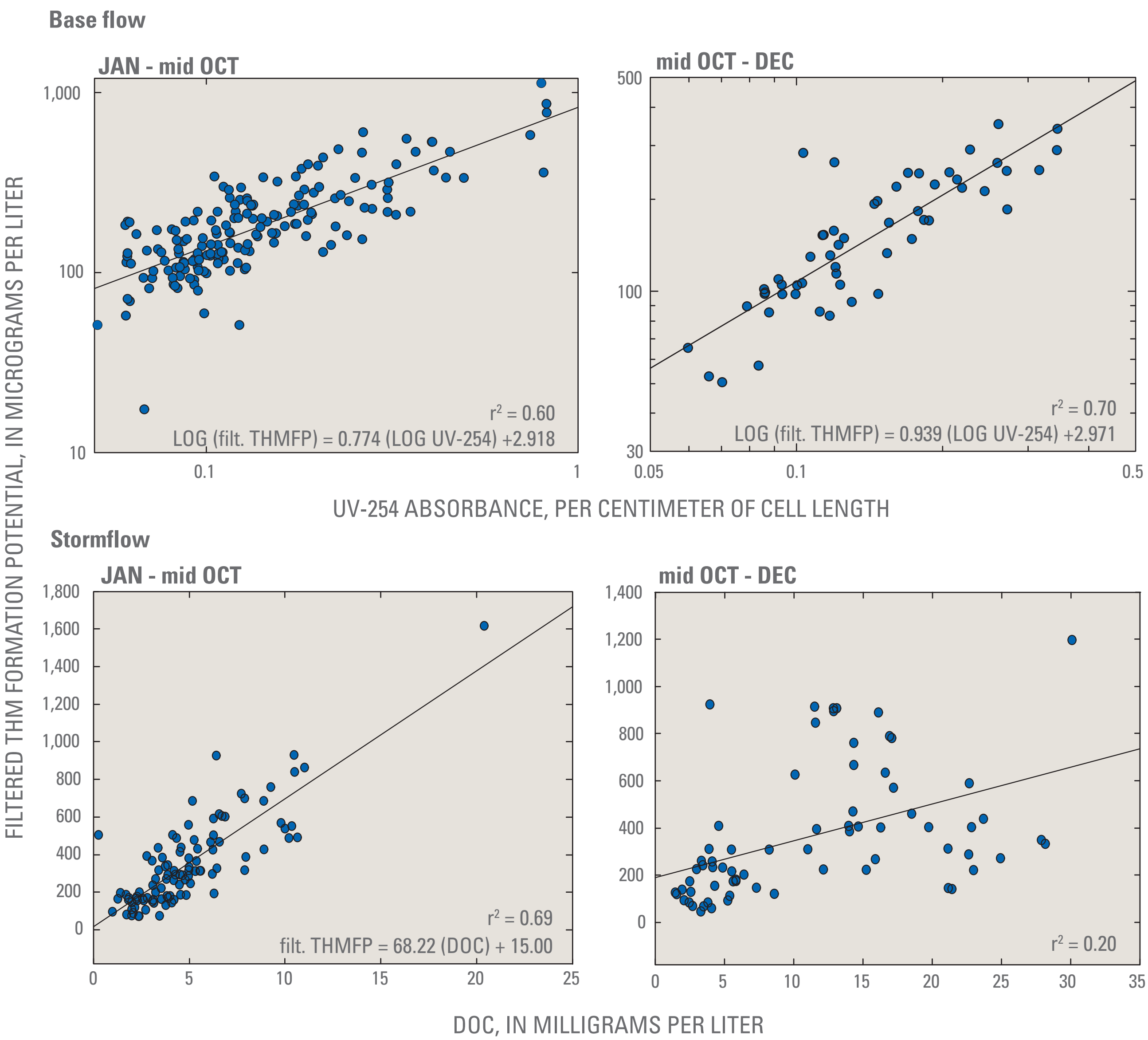

Figure 13. Best filtered THM formation potential surrogates (DOC and UV-254) for streamwater, differentiated by flow conditions (base flow, stormflow) and by the absence or presence of recent leaf litter (Jan. to mid-Oct., mid-Oct. to Dec; respectively), stream network, Croton Watershed, southeastern New York, 2000–02. (DOC, dissolved organic carbon; THM, trihalomethane.)

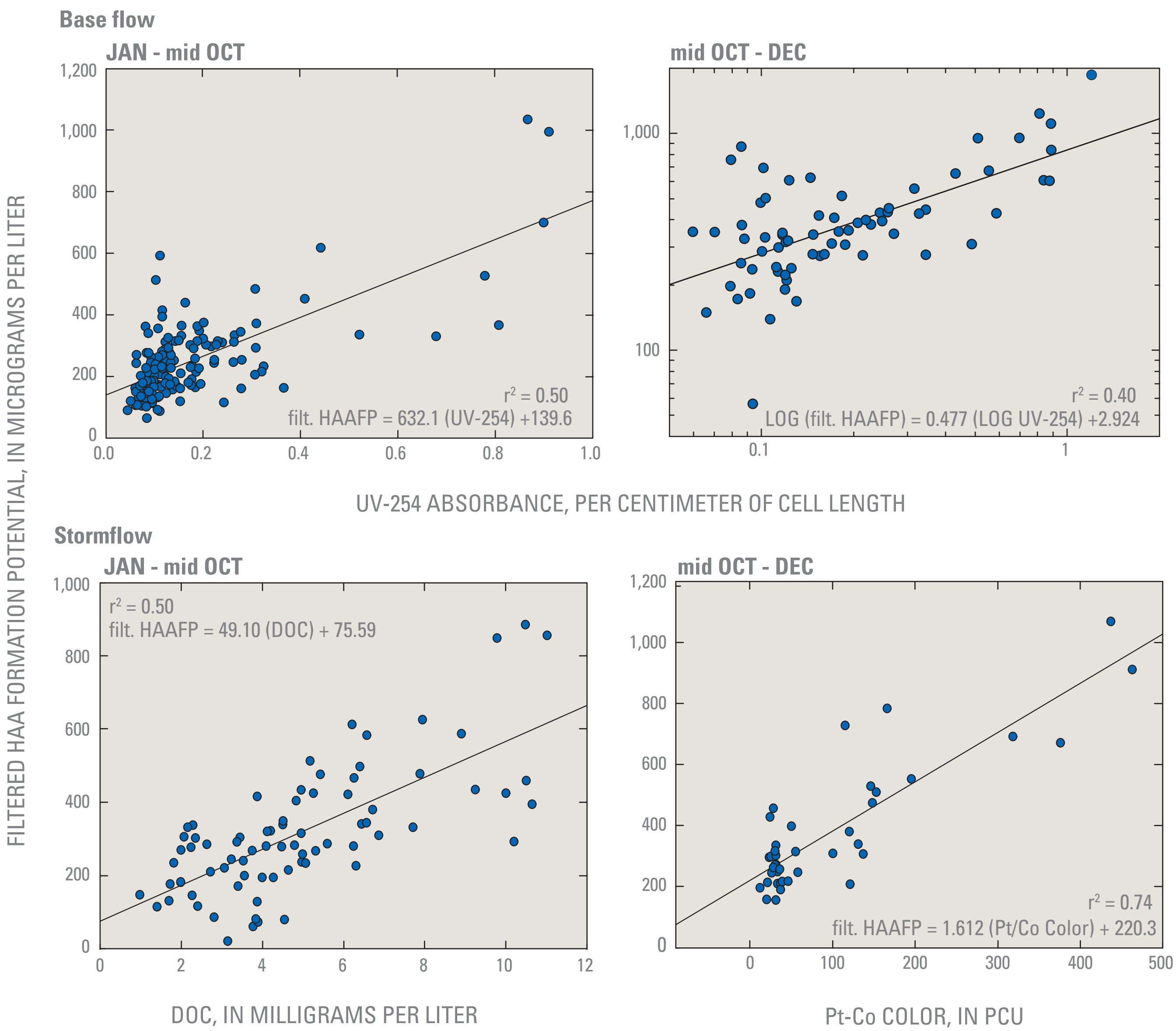

Figure 14. Best filtered HAA formation portential surrogates (DOC, UV-254, and Pt-Co color) for streamwater, differentiated by flow conditions (base-flow, stormflow) and by the absence or presence of recent leaf litter (Jan. to mid-Oct., mid-Oct. to Dec, respectively), stream network, Croton Watershed, southeastern New York, 2000–02. (DOC, dissolved organic carbon; HAA, haloacetic acid; PCU, platinum-cobalt color units)

Table 10. Regression r^2 values for filtered trihalomethane (THM) formation potential and filtered haloacetic acid (HAA) formation potential as functions of four surrogates in base-flow and stormflow samples from the stream network, Croton Watershed, southeastern, N.Y., 2000–02.

[Italicized values are based on log values. mg/L, milligrams per liter; cm, centimeter; UV-254, ultraviolet absorbance at 254 nanometers wavelength; g440, gelbstoff; PCU, platinum-cobalt color units; DOC, dissolved organic carbon]

Flow component	Sampling period	Remarks	r^2 values			
			Dissolved organic carbon (mg/L)	UV-254 (per cm)	g440 (per meter)	Pt-Co color (PCU)
Trihalomethane (THM) formation potential						
Base flow	Jan to mid-Oct	DOC ≤ 5 mg/L All lake subbasins omitted	*0.31*	*0.60*	*0.44*	*0.31*
	Mid-Oct to Dec	DOC ≤ 5 mg/L All lake subbasins omitted	*0.57*	*0.70*	*0.47*	*0.38*
Stormflow	Jan to mid-Oct	Subbasin CEN omitted	0.69	0.65	0.63	0.64
	Mid-Oct to Dec	None	0.20	0.24	0.04	0.08
Haloacetic acid (HAA) formation potential						
Base flow	Jan to mid-Oct	All lake subbasins omitted	0.48	0.50	0.43	0.46
	Mid-Oct to Dec	All lake subbasins omitted	*0.41*	*0.40*	*0.10*	*0.28*
Stormflow	Jan to mid-Oct	Subbasin CEN omitted	0.51	0.48	0.51	0.45
	Mid-Oct to Dec	None	0.54	0.65	0.57	0.74

4.5 Summary

A broad-brush network of 24 small streams in the Croton Reservoir Watershed was selected for evaluation of the effects of subbasin drainage efficiency and land use on surface-water quality (nutrients, DOC, color (Pt-Co), DBPs). Three wastewater-treatment plants also were sampled quarterly for 1 year. Drainage efficiency ranged from well drained subbasins, with short surface-water residence times and low DOC concentrations, to poorly drained subbasins with high DOC concentrations, low dissolved oxygen, and longer surface-water residence times. Land uses included forested (undeveloped), unsewered residential, sanitary-sewered residential, urban, golf-course, and horse-farm.

The occurrences of nutrients, DOC, color, and DBPs in streamflow from the broad-brush network were largely related to subbasin drainage efficiency and/or land use. Nutrient concentrations were associated with residential, golf-course, and horse-farm land use but were modified by drainage efficiency. DOC concentrations, however, were most highly dependent on subbasin drainage efficiency. Because color and DBPs were associated with DOC, these constituents were similarly dependent on drainage efficiency.

DBP analyses included overall formation potentials of trihalomethanes (THMs) and haloacetic acids (HAAs) determined from the sum of formation potentials of their respective component species. THMs were dominated by a single form (chloroform). HAAs, in contrast, were largely a composite of the formation potentials of the three forms of haloacetic acid (MCAA, DCAA, TCAA). These compounds were affected to differing degrees by drainage efficiency, land use, and flow conditions.

4.5.1 Total (Unfiltered) Phosphorus

Base-flow TP concentrations in most subbasins showed a general seasonal pattern of higher concentrations from June to October and lower concentrations from December to March, except for elevated concentrations in the late autumn and spring at most well to moderately drained subbasins without lakes. The highest concentration was measured in the sewered subbasin with high-density housing (284 µg/L) during low streamflows in the summer. This concentration may be related to leakage from a nearby sanitary-sewer main. The seasonal patterns for the lake subbasins with medium-density housing differed from those for the other subbasins; they showed broad late-summer to mid-fall peaks (and a spring peak at one subbasin), which corresponded with algae-laden discharge from the eutrophic lakes.

Maximum TP concentrations in stormflow (800 to 1,750 µg/L) were about five times greater than in base flow. Elevated TP concentrations in stormflows were associated with well drained and moderately drained (with lake or uncolored-water wetlands) subbasins with high- and medium-density housing and with the golf-course (with lake) subbasin. Maximum stormflow TP increased tenfold in samples collected from subbasins with zero and low-density housing to those with medium- and high-density housing. Subbasins with medium- to high-density housing favor TP transport because they contain large impervious surface areas, storm sewers, and local relief, all of which contribute to rapid routing of stormwater to streams. The most likely source of TP from land surface is lawn fertilizer.

4.5.2 Soluble Reactive Phosphorus

Median base-flow SRP concentrations were highest (30–60 µg/L) in samples collected from subbasins with residential development, a golf course, or a horse farm. Concentrations generally increased with increasing housing density, although high concentrations of SRP were measured in samples from one subbasin with low-density housing. Nearly all subbasins showed a seasonal pattern in SRP concentrations that was similar to of the pattern for TP but without autumn or spring peaks. The three subbasins with medium-density housing and lakes showed broad, late-summer to mid-fall SRP concentration peaks similar to those for TP.

Maximum stormflow SRP concentrations (100–340 µg/L) were highest among well drained subbasins with high-density housing (sewered and unsewered), a golf course, or a horse farm, and doubled from low- to medium-density housing and again from medium- to high-density housing in both sewered and unsewered subbasins. Stormflow concentrations were 2 to 10 times higher in late autumn (after leaf fall) and in late spring than in late winter and early spring.

SRP was typically a smaller percentage of TP in stormflow than in base flow because stormflows transport more particulate matter. SRP concentrations were highest, relative to TP in base flow and stormflow in well to moderately drained subbasins with high-density housing (sewered and unsewered), a golf course, or a horse farm.

4.5.3 Nitrate

Nitrate differed from the phosphorus analytes in that nitrate concentrations in stormflow and base flow were similar to one another. Maximum concentrations (3.0 to 4.5 mg/L) were associated with well drained urban and high-density housing subbasins. Concentrations of nitrate in stormflows and base flows increased progressively with increasing housing density in well drained and moderately drained (uncolored-water-wetland) subbasins. Seasonal variations in nitrate concentration in stormflows also were similar to those in base flows; concentrations were lowest after leaf fall (middle through late autumn), highest in winter, low in spring (possibly through dilution), and intermediate in summer and early autumn. Concentrations of nitrate were low in samples collected from subbasins with a lake or colored-water wetland despite low and medium housing densities. The dominant nitrogen form in these subbasins and in undeveloped subbasins was organic nitrogen. Organic nitrogen concentrations typically peaked during the leaf-fall period and, in some instances, exceeded nitrate concentrations.

4.5.4 Dissolved Organic Carbon

Positive correlations between DOC concentration and (1) measures of color and UV absorbance and (2) DBPs indicate that naturally occurring DOC is the primary source material for those parameters. DOC was consistently highest in poorly drained, colored-water-wetland subbasins and lowest in well drained subbasins.

Base-flow DOC concentration progressively increased with decreasing drainage efficiency, except in the well drained sewered subbasin with high-density housing, in which DOC concentrations were slightly elevated throughout the year. Leakage from sewer mains may contribute DOC to the stream. Seasonal changes in base-flow DOC differed with drainage efficiency. Concentrations were low in well drained subbasins and most uncolored-water-wetland subbasins during the winter and early spring, and concentration peaks of similar magnitude were observed during late spring, late summer, and the leaf-fall period in late autumn. The variation in seasonal DOC concentrations in streamflow in lake subbasins with medium-density housing was the opposite of that just described. DOC concentrations in the two colored-water-wetland subbasins were lowest in winter and early spring and highest in summer, and peaked during low-flow conditions in August.

DOC concentrations were typically higher in stormflows than in base flows. DOC concentrations in well drained subbasins increased during storms to values similar to those in uncolored-water-wetland and lake subbasins. The highest stormflow DOC concentrations were nearly always in the two colored-water-wetland subbasins. Seasonal changes in stormflow DOC were pronounced. An early-November storm (after leaf fall) produced streamflow DOC concentrations in many subbasins that were two or three times greater than the next highest storm concentrations. Storms during December or late spring produced the next highest stormflow DOC concentrations.

4.5.5 Color (Pt-Co)

Color was closely associated with elevated DOC concentrations in the poorly drained subbasins, which include the colored-water-wetland subbasins and two uncolored-water-wetland subbasins. Base-flow median intensities were about 150 PCU in subbasins with colored-water wetlands but between 10 and 20 PCU in well drained and most moderately drained subbasins. Color intensities were not high in the two moderately drained (lake) subbasins with medium-density housing despite elevated DOC concentrations (commonly higher than 3 mg/L). This discrepancy is attributed to the contributions of algae-derived DOC from the lakes to streamwater; this DOC has different color characteristics than terrestrial DOC.

Color was also closely associated with stormflows. Median stormflow color intensities at most subbasins were about double of those measured during base-flow conditions. Smaller stormflow and base-flow differences were typical in the undeveloped forested, the colored-water-wetland, and the lake subbasins with medium-density housing.

Seasonal variation in color was evident in base flow and stormflow. Late-autumn peaks were as high as about 30 PCU (during and immediately after leaf fall) and typically lower in late spring in most residential subbasins with low base-flow median color intensities. Color intensities during the remainder of the year were relatively stable. Stormflow intensities followed the same pattern. The high autumn color peak corresponded to an autumn DOC peak that was lower than the spring peak; this indicates that DOC derived from recent leaf litter was more intensely colored than DOC at other times of year. DOC and color were otherwise highly associated.

High base-flow color intensities in subbasins with wetlands and high DOC concentrations had a different seasonal pattern in which color intensities were typically highest from April through November and lowest from December through March.

4.5.6 Trihalomethane Formation Potential

Total THM formation potentials increased as subbasin drainage efficiency decreased (and DOC increased). The highest THM formation potentials were typically associated with stormflow samples. THM formation potentials in stormflow ranged widely, but peak formation potentials were similar, irrespective of land use or drainage efficiency. Concentrations in stormflow samples from the poorly drained subbasins, however, were consistently high.

Base-flow THM formation potentials showed limited response to land use. Housing density did not appear to affect THM formation potentials in samples collected from well drained subbasins, although values for the sanitary-sewered well drained subbasin with high-density housing were typically about 100 μg/L higher than those for unsewered subbasins with similar housing density. Values for the golf-course subbasin (with small lakes) were also generally 50 to 100 μg/L higher than in most well drained subbasins. Late-spring and early-summer formation potentials in samples collected from the golf-course subbasin, however, were 200 to 400 μg/L higher than in samples from the well drained subbasins. The seasonal variation in base-flow THM values for most subbasins entailed low winter formation potentials, spring and autumn peaks, and moderate to high summer formation potentials. Spring and autumn peaks in well drained subbasins were low, but in poorly drained (colored-water-wetland) subbasins spring peaks were generally largest.

Median stormflow total THM formation potentials exceeded 200 μg/L in samples collected from all subbasins. Stormflow THM maximum formation potentials were highest (~1,000 μg/L) in storms between May and November at most subbasins.

4.5.7 Haloacetic Acid Formation Potential

HAA formation potentials were less affected by drainage efficiency than THMs and were more responsive to land use. Median HAA formation potentials were highest in the samples collected from the two colored-water-wetland subbasins and the golf-course subbasin (400–1,100 μg/L) and were lowest in samples collected from well drained subbasins with either forest, a horse farm, or low- and medium-density housing (150–250 μg/L). Formation potentials were intermediate (250–600 μg/L) in subbasins with high-density housing, an urban setting, and uncolored-water wetlands.

Base-flow HAA formation potentials for all subbasins except those with colored-water wetlands or a golf course were within the formation-potential range of the three reference subbasins. Seasonal patterns were characterized by a main peak in autumn, moderate formation potentials in winter, and low formation potentials (by dilution) in spring, followed by rebound in late spring and summer. The low HAA formation potentials caused by dilution in spring contrast with the spring peak formation potentials of total THMs.

Stormflow formation potentials were maximum (~ 1,000–1,700 μg/L) from May through July with some high values in November and December, but only in samples from the lake subbasins with medium-density housing and the colored-water-wetland subbasins. In contrast, high THM formation potentials in November were common for many subbasins.

4.5.8 DBP Sources and Surrogates

Terrestrial DOC is the major source of precursor material for DBPs. SUVA values indicate a mixture of aquatic and terrestrial DOC in lakes. Recent leaf litter appears to have a lower SUVA value than terrestrial DOC from other times of the year.

The chlorine-containing forms of DBPs were much more common than bromine-containing forms. Bromine-containing forms are mostly associated with residential development and golf-course land use. THMs are dominated by a single form (chloroform), whereas HAAs include three common forms (MCAA, DCAA, TCAA).

No universal surrogate for DBPs, THMs, or HAAs was identified from comparisons with DOC, UV-254, gelbstoff 440, or Pt-Co color. Samples were grouped by stormflow or base flow and by the presence or absence of recent leaf litter. The best surrogates for THMs were not the same as those for HAA, and both differed among the flow and leaf-litter sample groups. The best surrogates for THMs were UV-254 and DOC, whereas the best HAA surrogate differed among the four flow and leaf-litter sample groups. THM-surrogate relations were generally stronger than HAA-surrogate relations; stronger THM-surrogate relations may be attributed to the single dominant THM form as opposed to the three dominant HAA forms that differed in occurrence among the drainage-efficiency and land-use categories.

4.5.9 WWTP Effluent

Effluent concentrations/values from three wastewater-treatment plants (tertiary treatment) differed with treatment process and plant upgrades. A general characterization of effluent includes (1) phosphorus concentrations within the same range as in stormflows in most streams, (2) nitrate and ammonium concentrations higher than those in nearly all streams, (3) low color intensities, (4) DOC concentrations similar to those in stormflow, and (5) low DBP formation potentials overall, with elevated formation potentials of some brominated forms and MCAA.

4.6 Acknowledgments

The author would like to acknowledge Jill Piskorz for all of her work: stream sampling and coordination of field crews and sample delivery, as well as database management. The fieldwork and coordination efforts of Donald Cuomo are also acknowledged, as well as stream-survey work by Steve Wolosoff and Richard Burkett.

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4.8 Appendix

Appendix 1. Boxplots of selected constituents in stream base flow and stormflow, by subbasin drainage efficiency, land use, and housing density in streams in the Croton Watershed, southeastern, New York, 2000–02

Concentrations:

A. Total unfiltered phosphorus (TP)

B. Total dissolved phosphorus (TDP)

C. Soluble reactive phosphorus (SRP)

D. Nitrate+nitrite, as N

E. Ammonium, as N

F. Dissolved organic carbon (DOC)

G. Particulate organic carbon (POC)

H. Color

Formation potentials:

I. Unfiltered trihalomethane (THM)

J. Unfiltered bromodichloromethane

K. Unfiltered haloacetic acid (HAA)

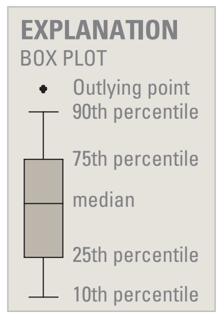
L. Unfiltered monochloroacetic acid

M. Unfiltered dichloroacetic acid

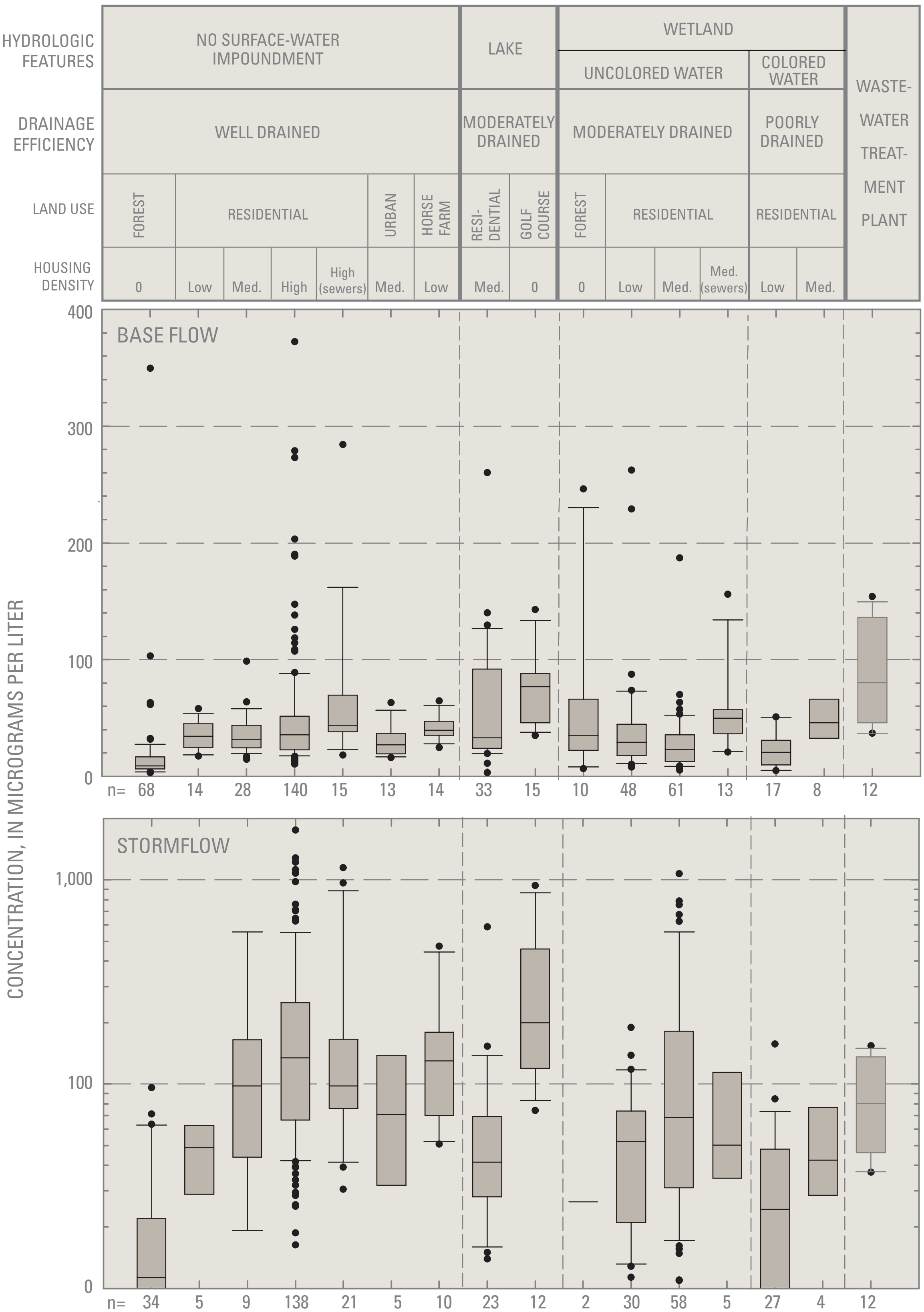
N. Unfiltered trichloroacetic acid

O. Unfiltered bromodichloroacetic acid

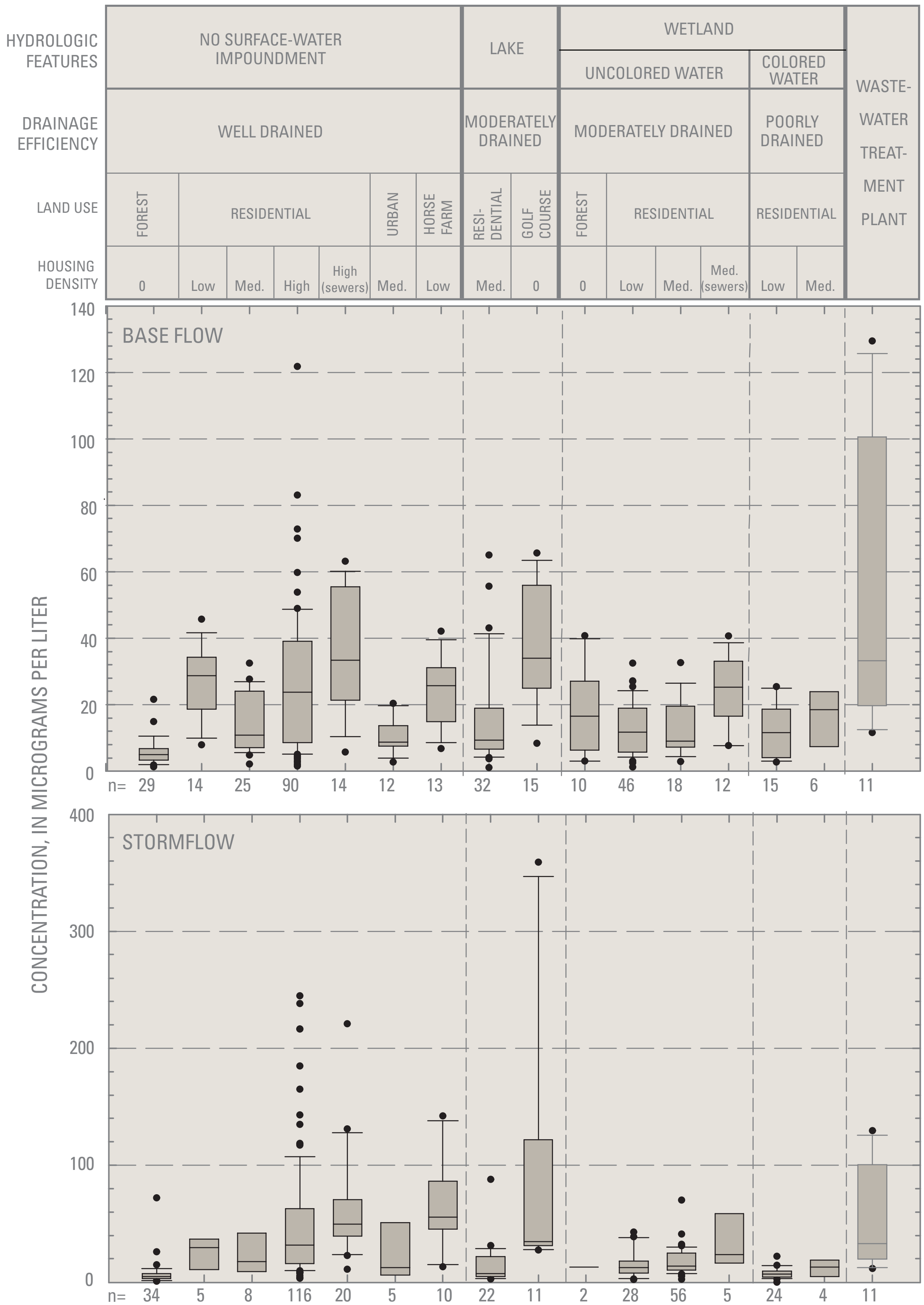
P. Unfiltered dibromochloroacetic acid



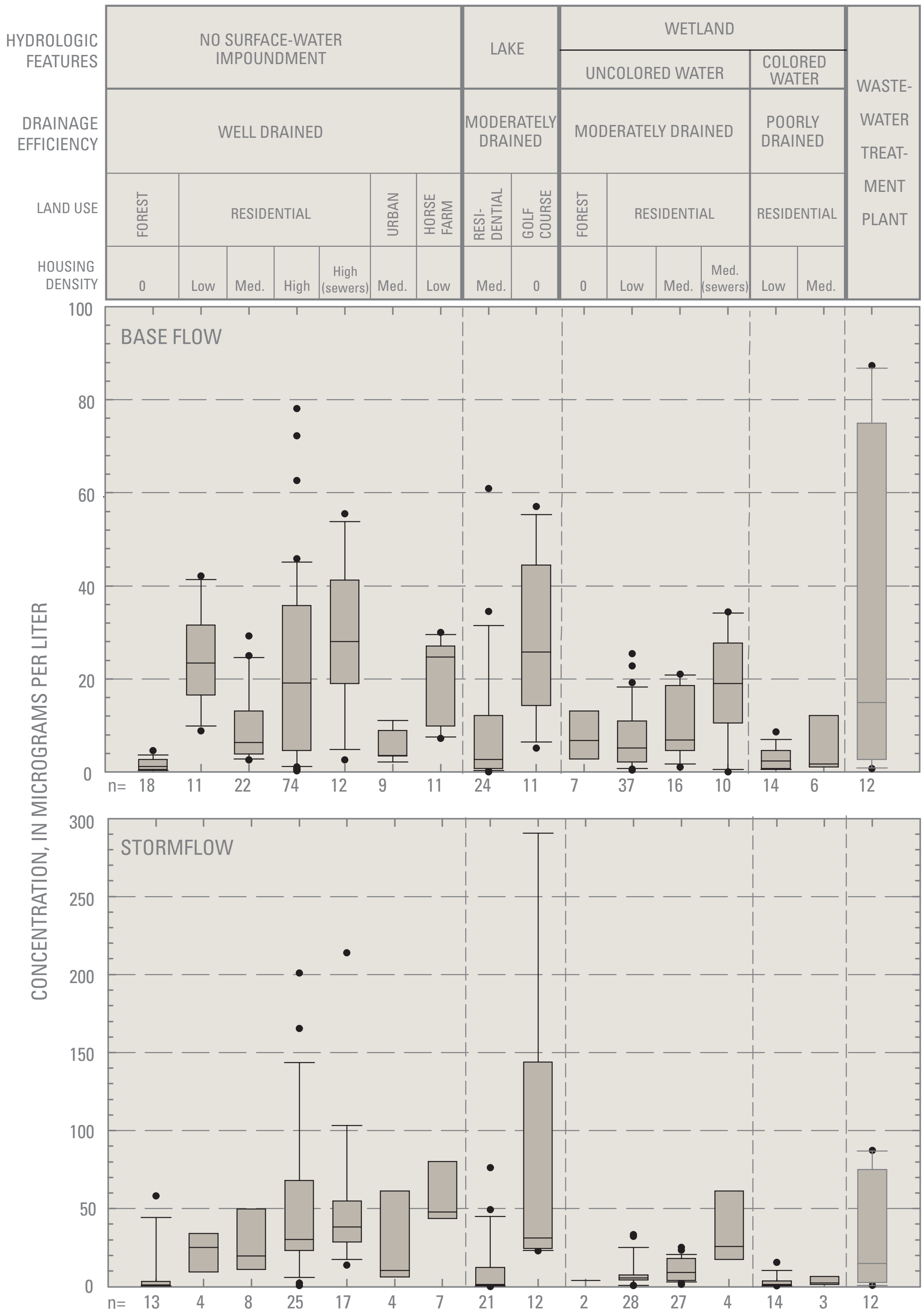
Explanation applies to appendixes 1A–1P



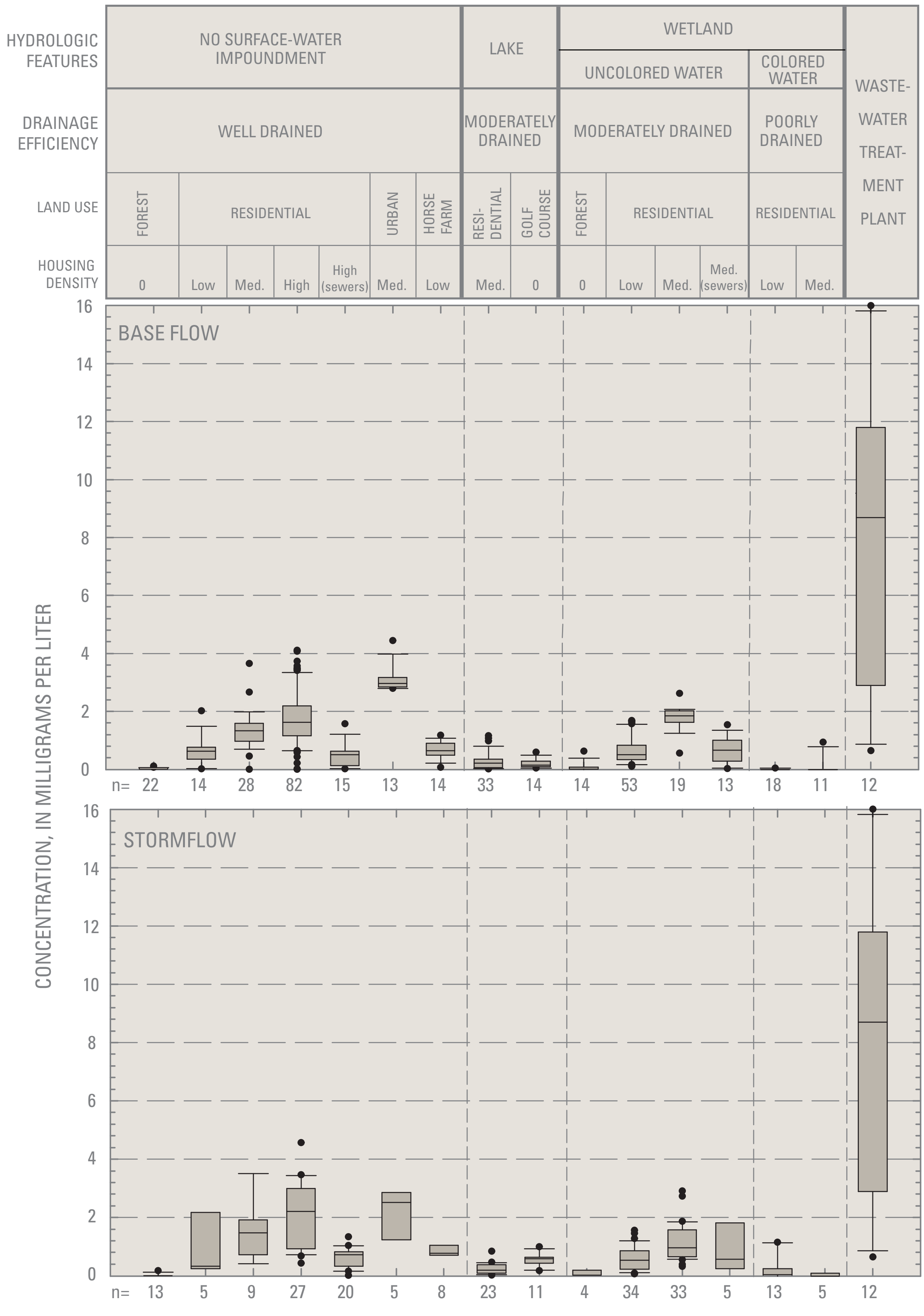
Appendix 1A. Total unfiltered phosphorus (TP) in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



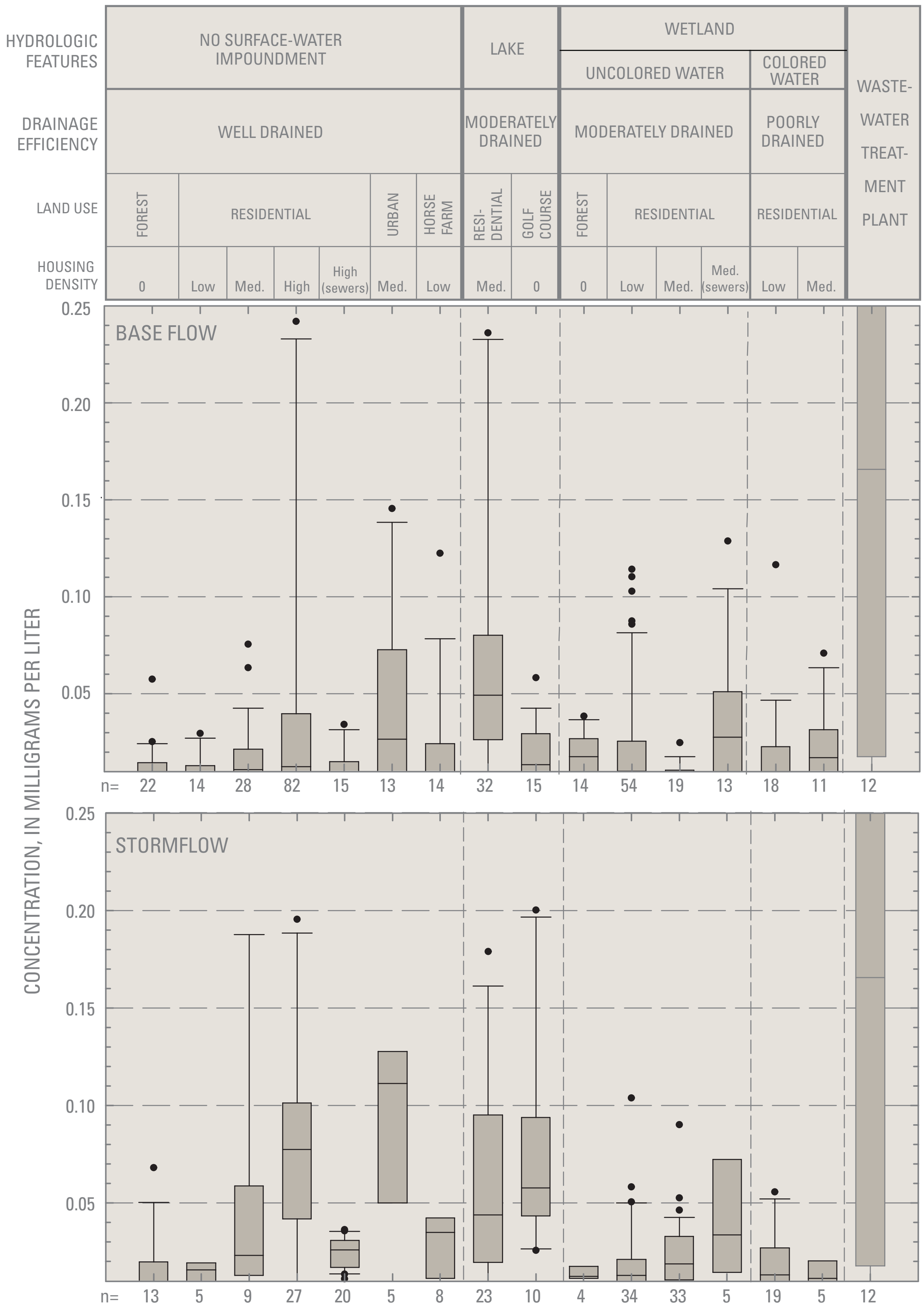
Appendix 1B. Total dissolved phosphorus (TDP) in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



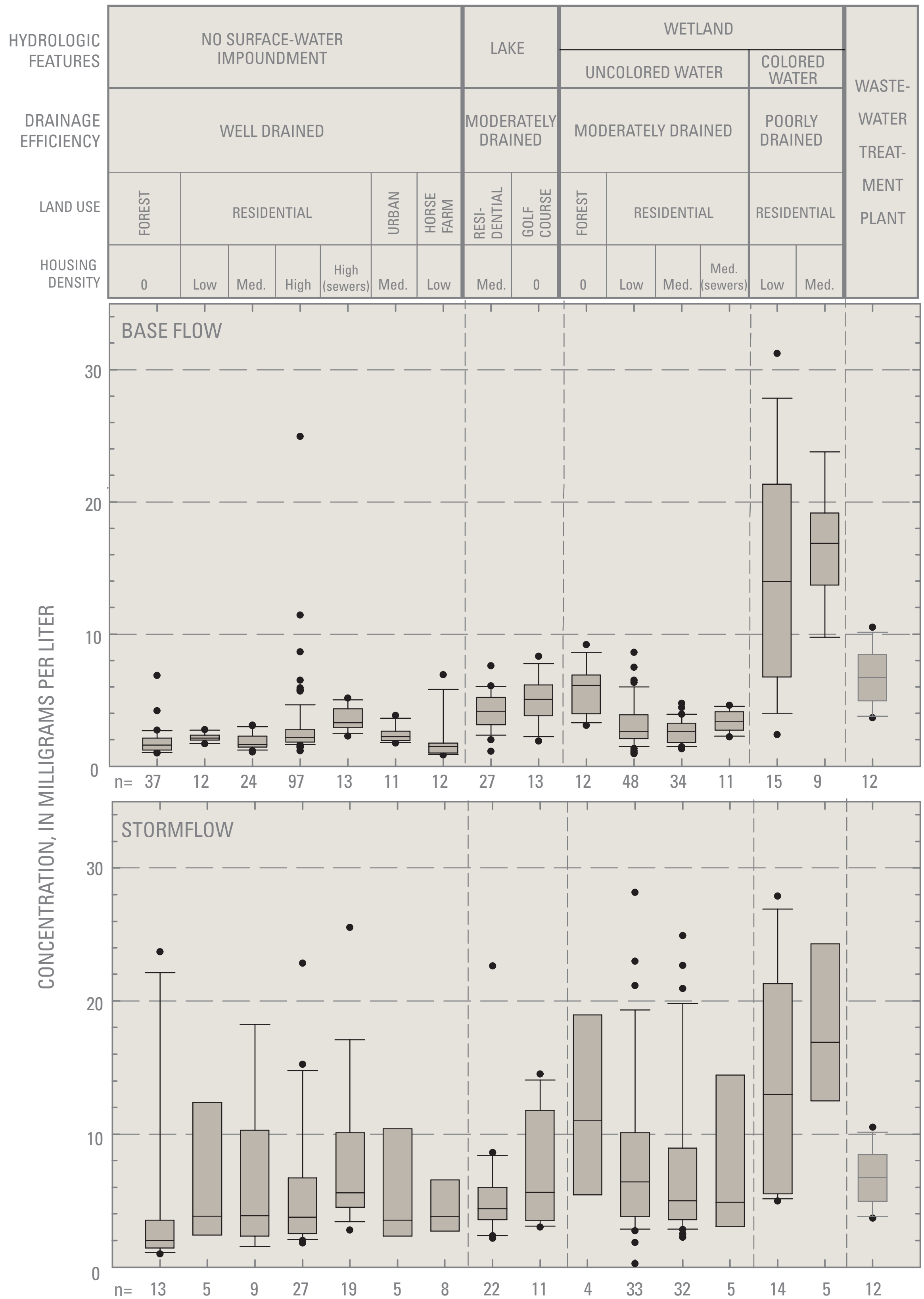
Appendix 1C. Soluble reactive phosphorus (SRP) in base flow and stormflow from the stream network and wastewater-treatment plants grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02



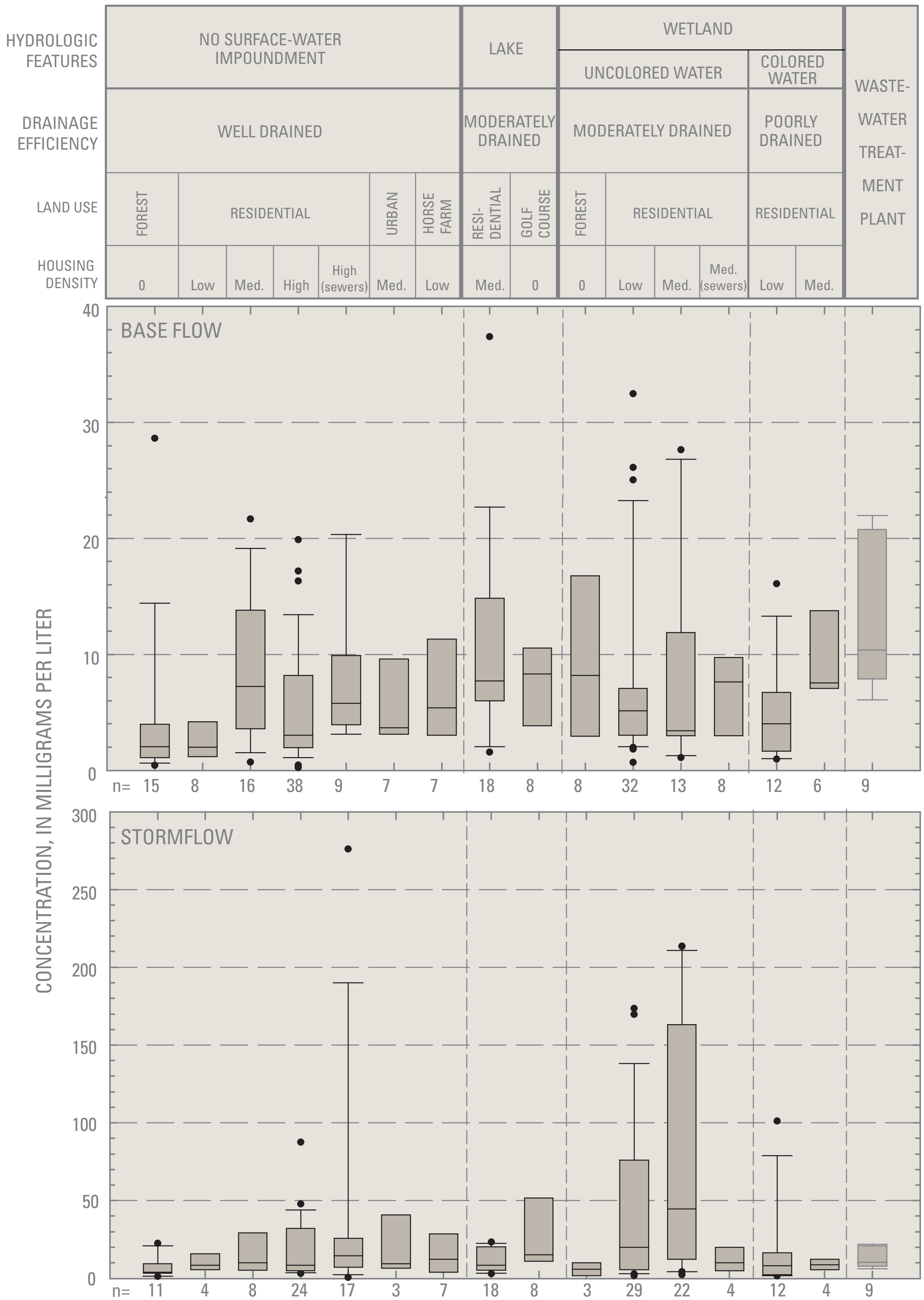
Appendix 1D. Nitrate + nitrite, as N, in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



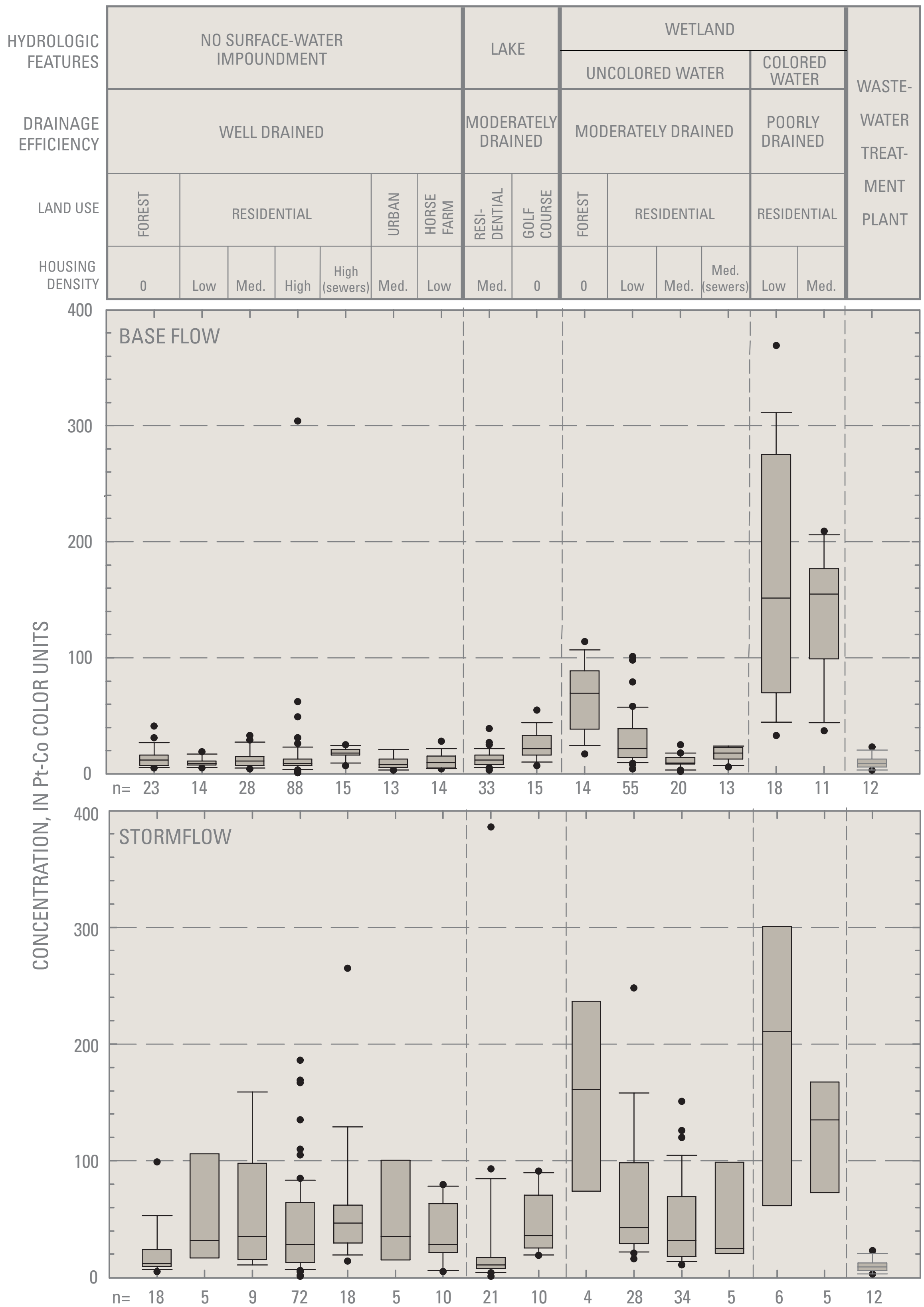
Appendix 1E. Ammonium, as N, in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



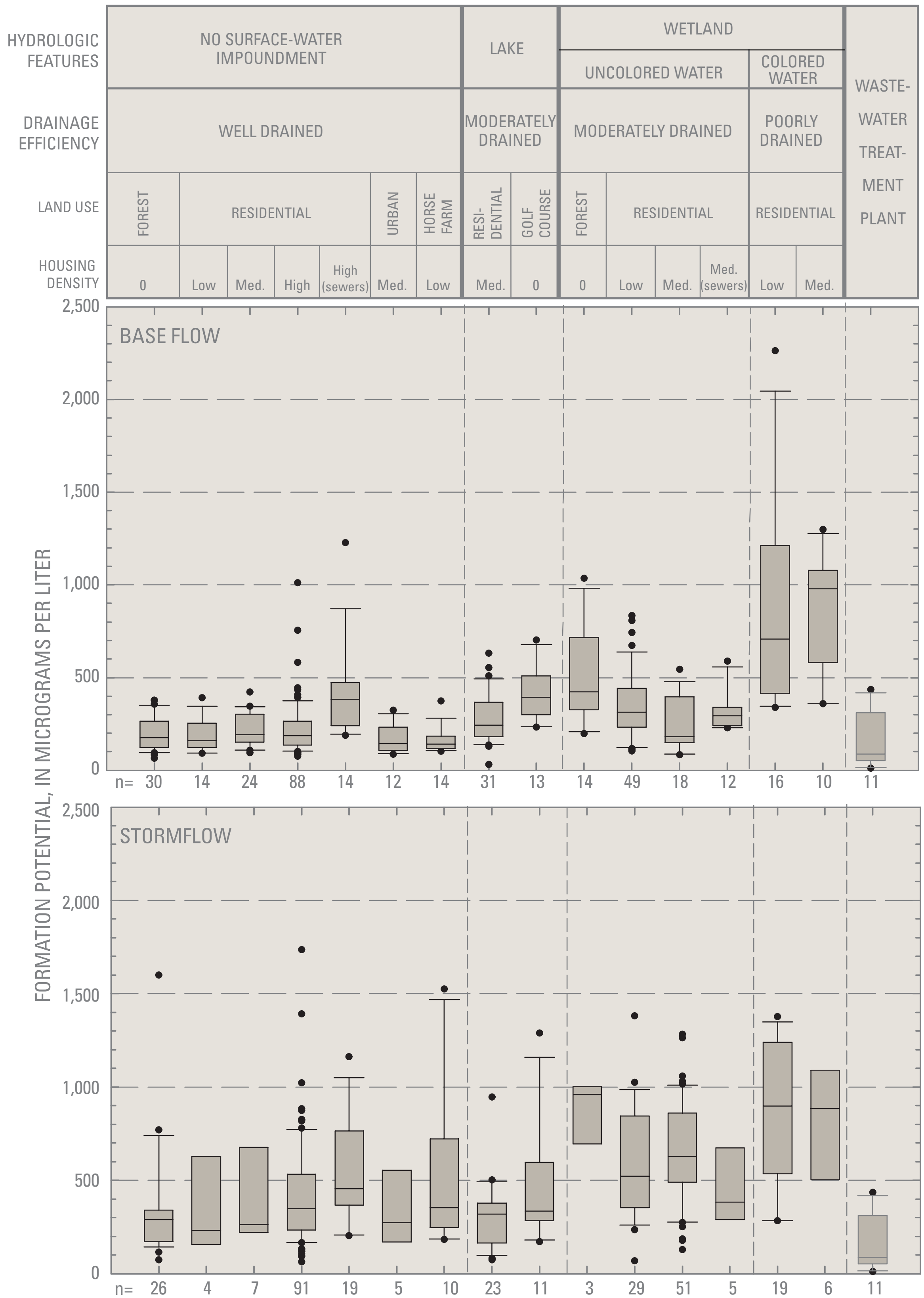
Appendix 1F. Dissolved organic carbon (DOC) in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed southeastern New York, 2000–02.



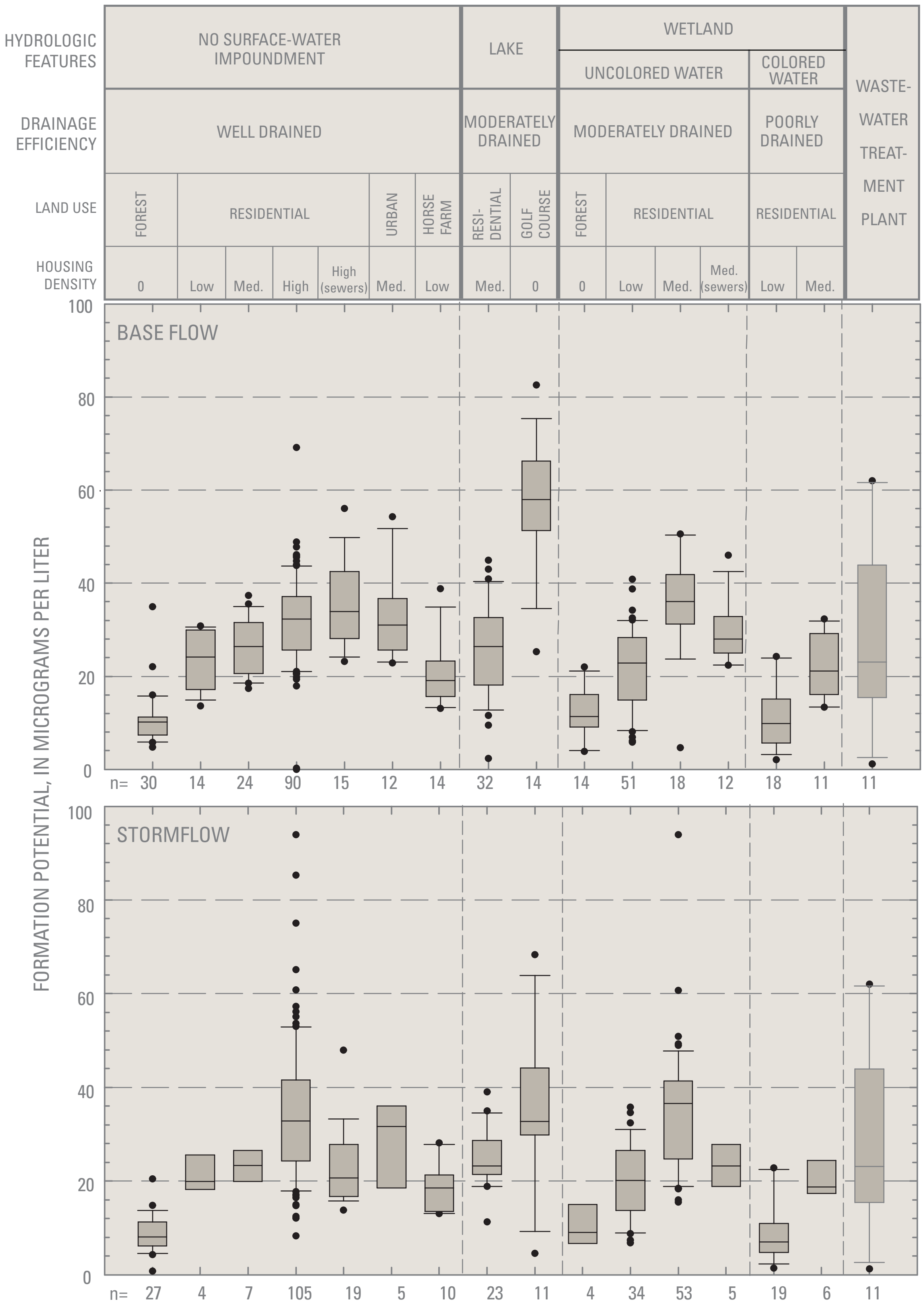
Appendix 1G. Particulate organic carbon (POC) in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



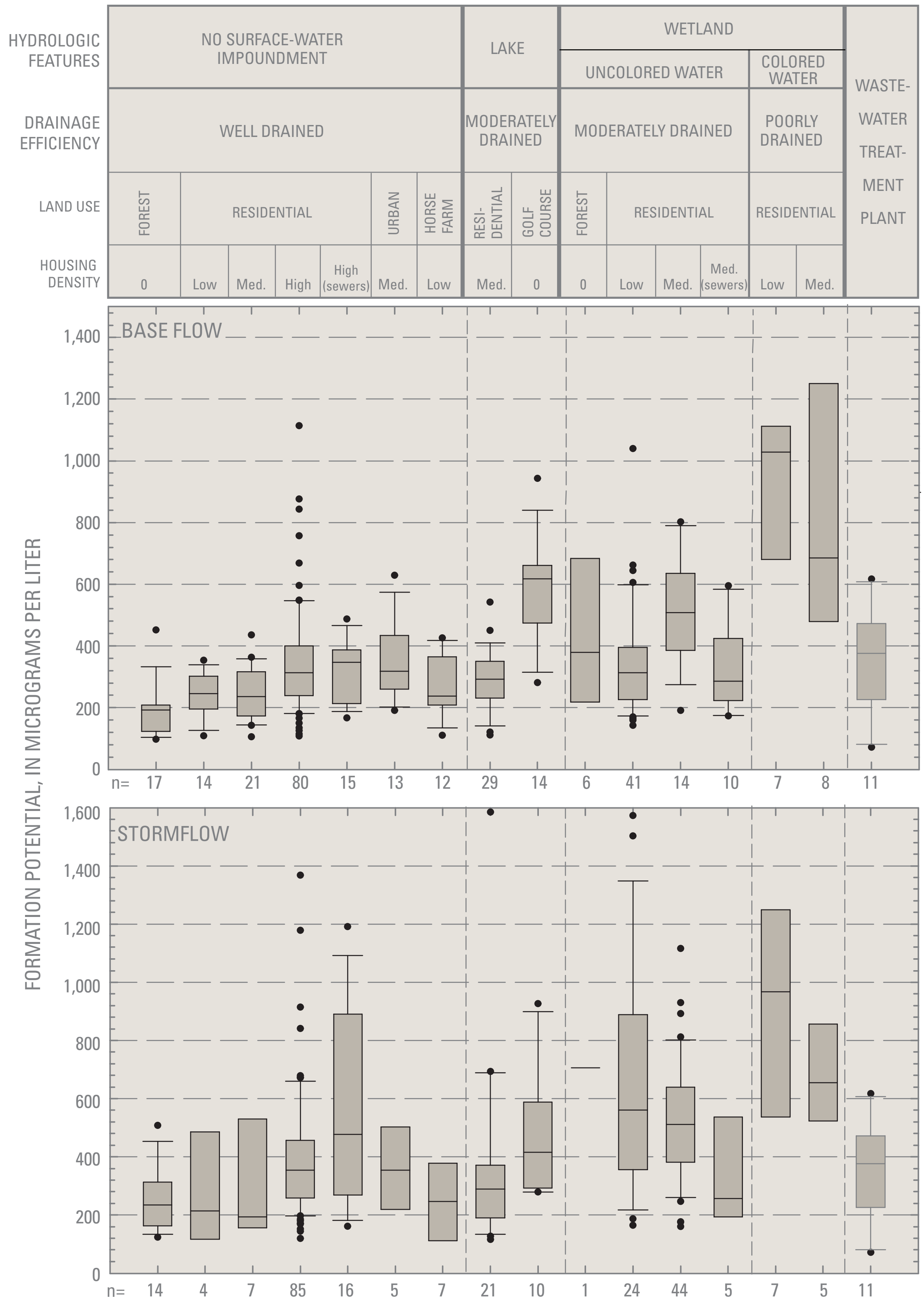
Appendix 1H. Color (Pt-Co) in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



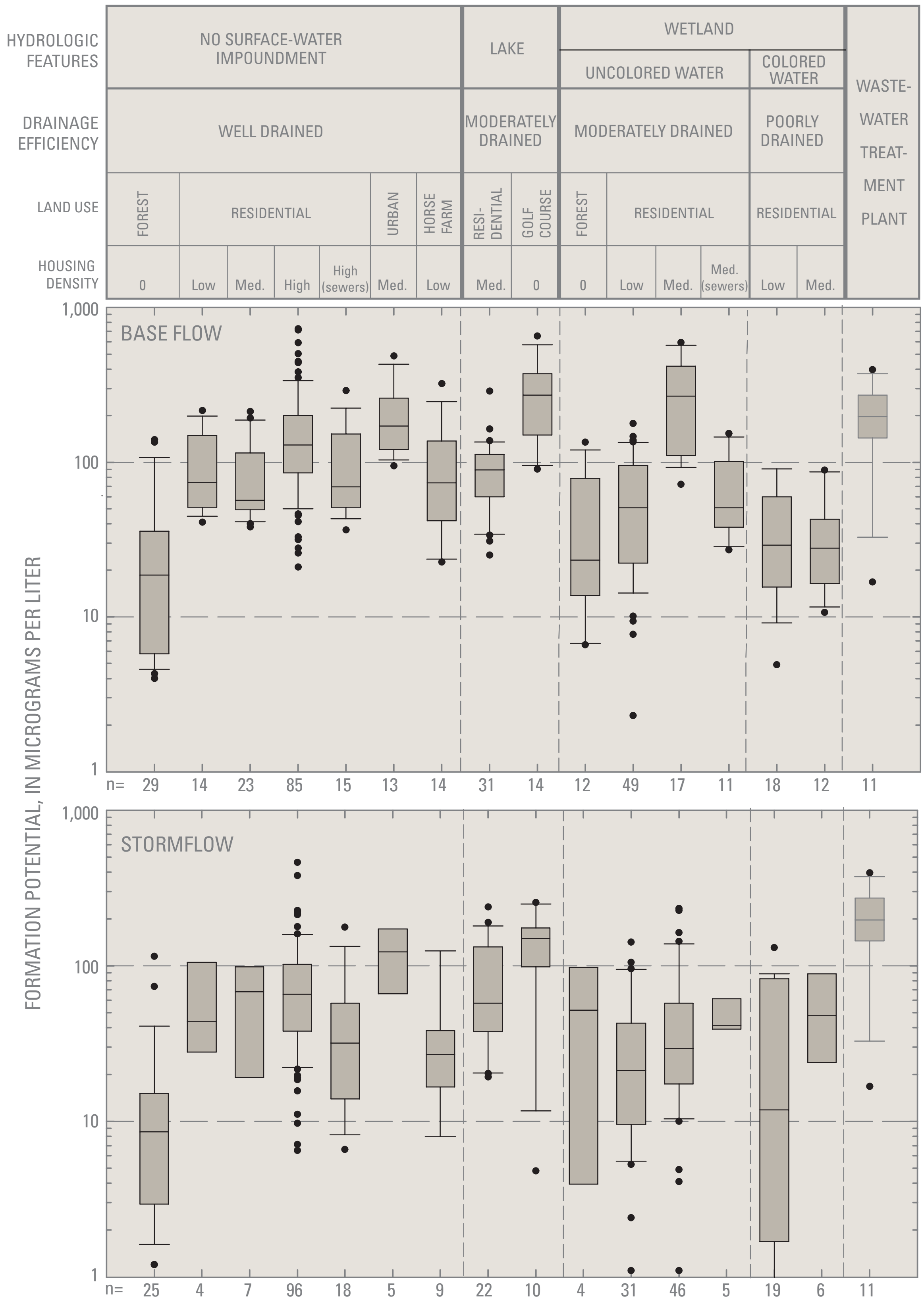
Appendix 1I. Unfiltered trihalomethane (THM) formation potential in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



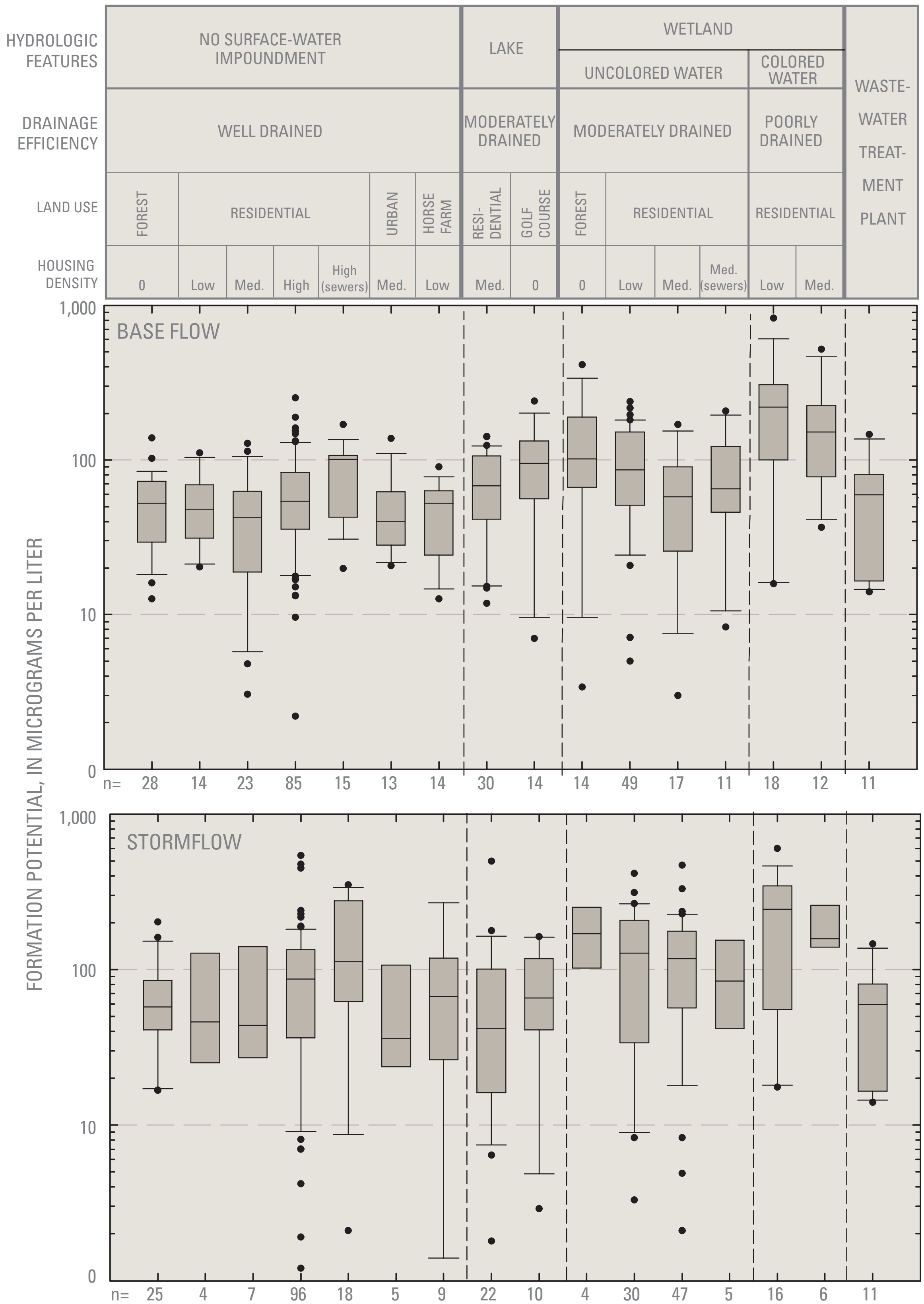
Appendix 1J. Unfilitered bromodichloromethane formation potential in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



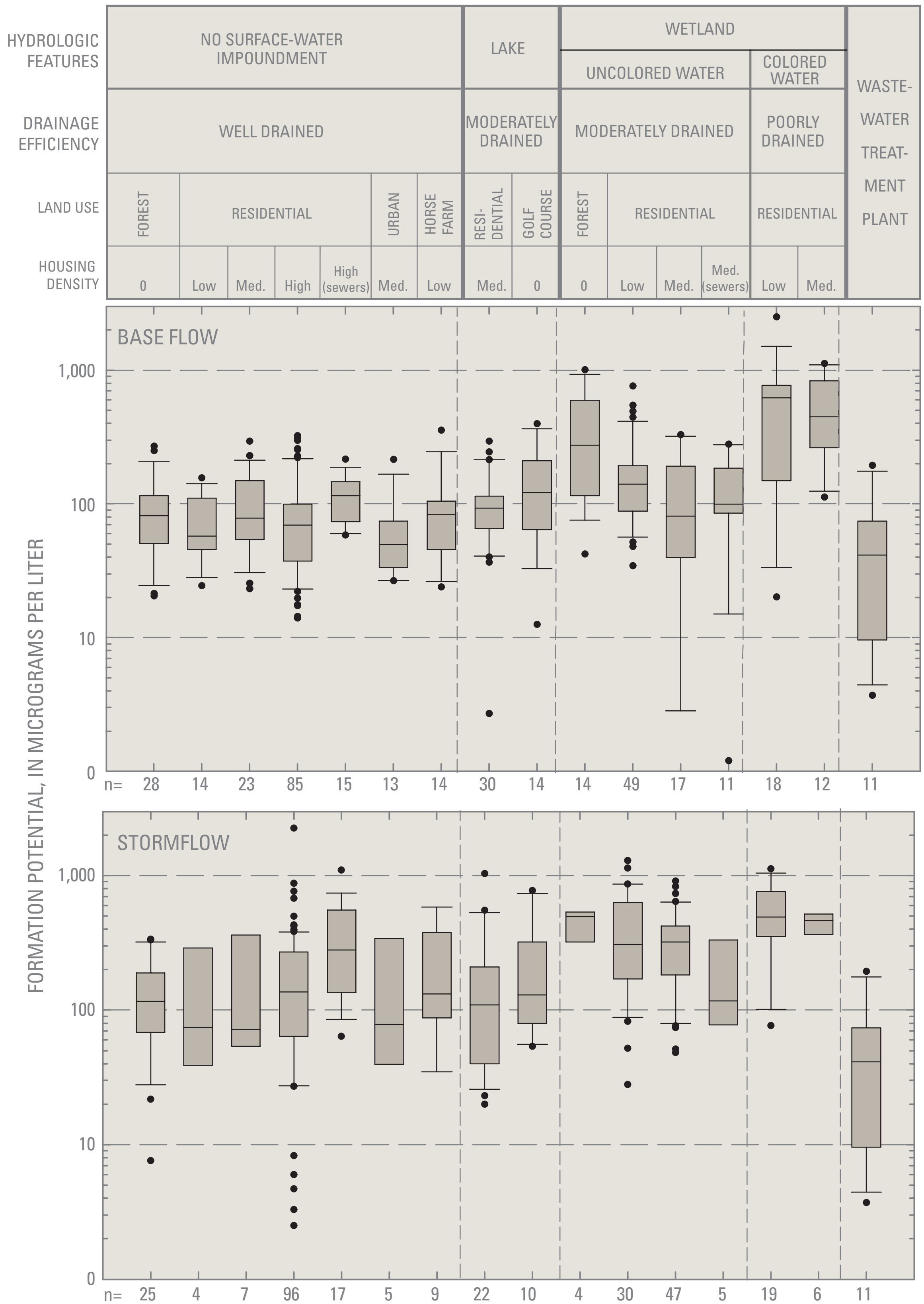
Appendix 1K. Unfiltered haloacetic acid (HAA) formation potential in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



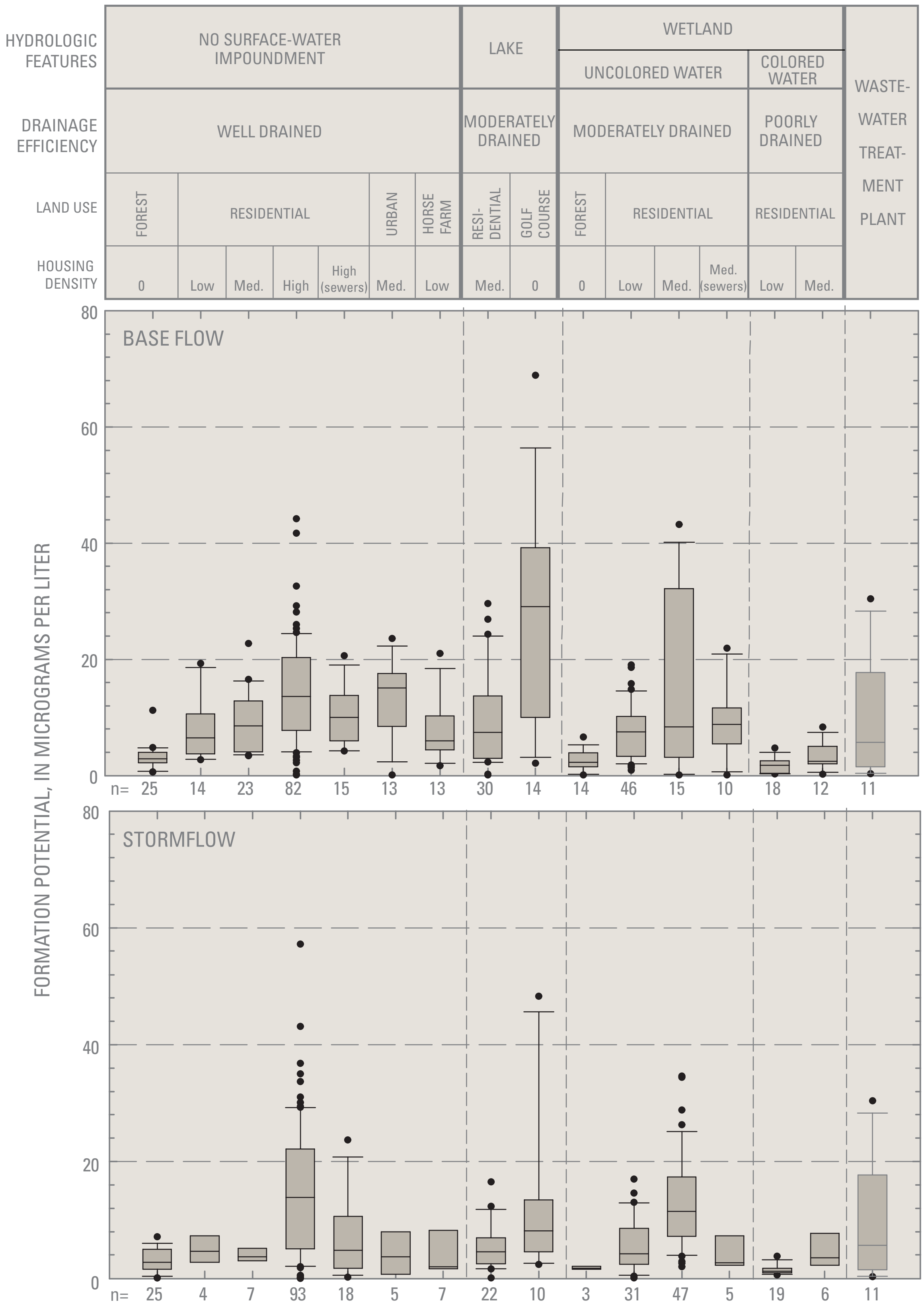
Appendix 1L. Unfiltered monochloroacetic acid (MCAA) formation potential in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



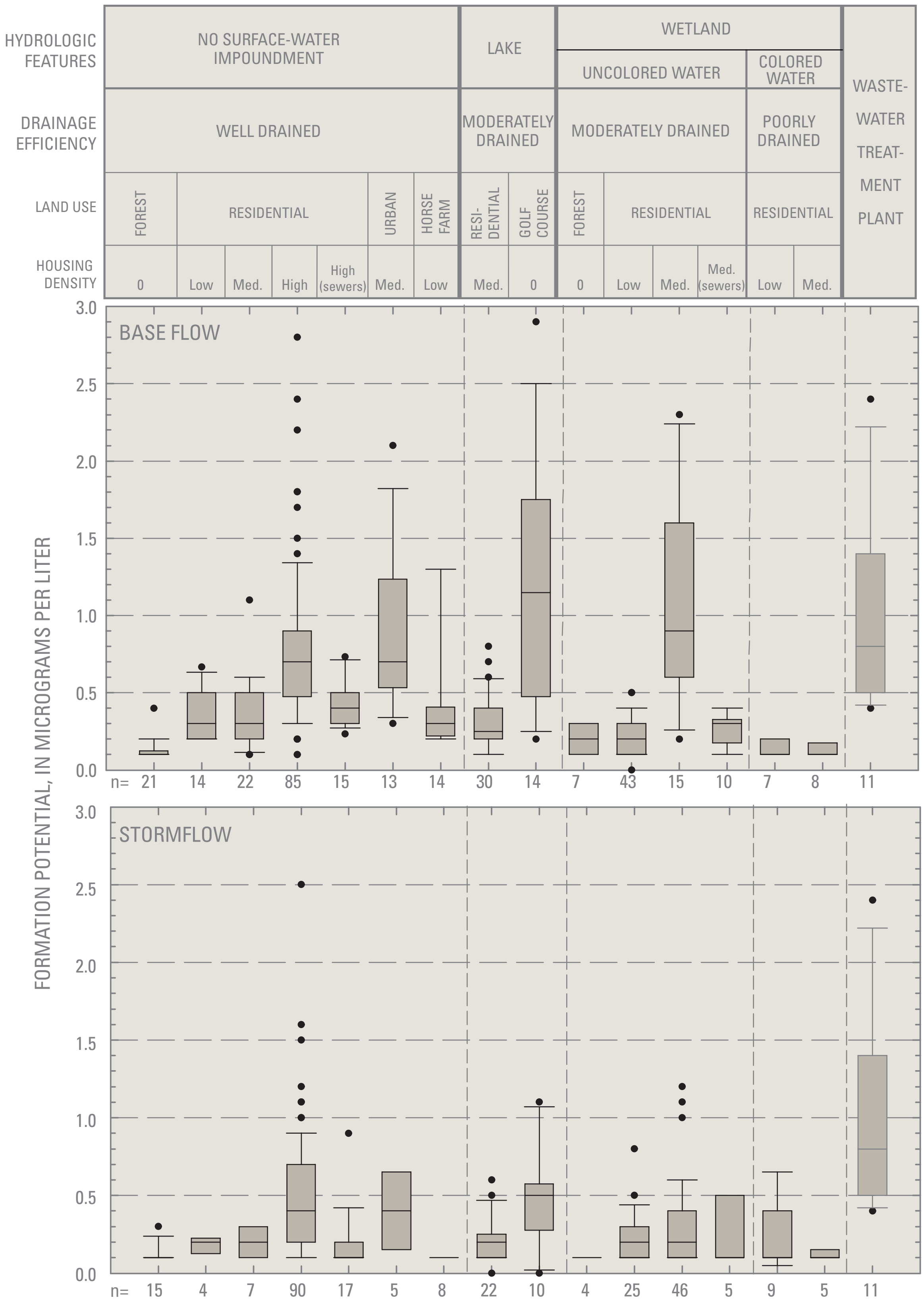
Appendix 1M. Unfiltered dichloroacetic acid (DCAA) formation potential in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



Appendix 1N. Unfiltered trichloroacetic acid (TCAA) formation potential in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



Appendix 1 O. Unfiltered bromodichloroacetic acid (BDCAA) formation potential in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.



Appendix 1P. Unfiltered dibromochloroacetic acid (DBCAA) formation potential in base flow and stormflow from the stream network and wastewater-treatment plants, grouped by drainage efficiency, land use, and housing density, Croton Watershed, southeastern New York, 2000–02.

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