

## Ecosystem metabolism in streams of the Catskill Mountains (Delaware and Hudson River watersheds) and Lower Hudson Valley

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**Abstract.** Ecosystem metabolism was measured in 10 streams flowing into New York City drinking-water-supply reservoirs. Six of the streams were located west of Hudson River (WOH) in the Catskill Mountains and 4 were in the Croton River watershed east of Hudson River (EOH). Measurements were made for 3-d periods between June and November in each of 3 y using an open-system O<sub>2</sub> technique with reaeration determined from propane evasion. Chlorophyll *a* concentrations, algal cover types, and nutrient uptake were measured concurrently. Gross primary productivity ranged from 2.02 to 4.32 g O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> in the WOH streams and from 0.23 to 1.13 g O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> in the EOH streams. Community respiration ranged from 3.94 to 8.30 g O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> in the WOH streams and from 1.39 to 6.12 g O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> in the EOH streams. All streams were heterotrophic. The WOH streams were larger and more open than the EOH streams. Metabolism was strongly correlated with instream environmental and water-chemistry variables and riparian shade. Land use was largely forested with some agriculture in the WOH watersheds, and it was forested or urbanized in EOH watersheds. Landuse impacts were confounded by the smaller size and denser shade along EOH streams than along WOH streams.

**Key words:** primary productivity, respiration, algae, New York City, drinking water supply.

Ecosystem metabolism measurements provide data on the processes of primary productivity and respiration, both of which are important to C cycling. Metabolic rates are a function of the biomass of algae and heterotrophic microorganisms and, to a lesser extent, macrophytes, macroinvertebrates, and fish. Rates also are influenced by environmental variables, including light, temperature, water chemistry (including nutrients and toxic contaminants), and hydrodynamics, which in turn may be related to watershed land use. Metabolism has been measured in several mid-Atlantic and New England streams and rivers on the east coast of North America (Hoskin 1959, Flemer

1970, Hall 1972, McDiffet et al. 1972, Fisher and Likens 1973, Fisher and Carpenter 1976, Hornberger et al. 1977, Sumner and Fisher 1979, Hornick et al. 1981, Hill and Webster 1982, Bott et al. 1985, 2006, McTammany et al. 2003), but no data have been published for the tributaries to the New York City (NYC) drinking-water-supply reservoirs that are the subject of this large-scale enhanced water-quality monitoring project (the Project; Blaine et al. 2006).

Most studies of ecosystem condition focus on descriptive variables such as water chemistry or biological community structure (e.g., algae, macroinvertebrates, or fish). The European Water Framework Directive explicitly recognized the importance of ecosystem function in assessing the ecological status of aquatic systems (Vighi et al. 2006), but functional measures are only beginning to be used in assessments of ecosystem health (e.g., Braioni et al. 2001, Young et al. 2004, Meyer et al. 2005, Pascoal et al. 2005). At present, active research is focused on resolving techniques to assess anthropogenic influences on stream function (RIVFUNCTION project: <http://www.ladybio.ups-tlse.fr/rivfunction/>; Gessner and Chauvet 2002). Other researchers in Australia and

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New Zealand (Bunn 1995, Rapport et al. 1998, Bunn et al. 1999, Young and Huryn 1999, Bunn and Davies 2000) have begun to use functional measures such as nutrient uptake and metabolism in stream assessments to gain a more complete picture of ecosystem condition.

Ecosystem functions “that are recognized as satisfying human needs” are considered ecosystem services (Rapport et al. 1998). Fish production and water purification through nutrient sequestration are examples of such services, but it is important to note that these services are linked to primary productivity and heterotrophic activity (respiration) at the base of the food web. In addition, primary productivity and respiration can be critical determinants of the O<sub>2</sub> status of streams and rivers.

Therefore, measurements of ecosystem metabolism were included in our synoptic survey of streams and rivers in the NYC source-water area to provide a robust assessment of ecosystem condition. The synoptic survey was intended to generate an overview of conditions at a number of sites within the study period. Ten streams were ranked on the basis of their rates of ecosystem metabolism (i.e., ecosystem “vigor,” sensu Rapport et al. 1998) and these metabolic processes were related to environmental variables at 2 scales: instream condition and watershed land use. Significant differences in metabolism among streams may be related to water-quality degradation from agricultural activities or urbanization in these watersheds. Our data provide a baseline for ecosystem functions against which future data can be compared.

## Methods

### *Study sites*

Ten study sites were established along streams flowing into NYC drinking-water-supply reservoirs (*integrative* sites in Arscott et al. 2006, Blaine et al. 2006). These sites were on mid- to large-sized streams and: 1) their locations in the watershed integrated the effects of multiple land uses on their biological communities, and 2) a larger array of integrated programmatic elements, including ecosystem functions, were studied in them. Six of the streams were in Catskill Mountain watersheds west of Hudson River (WOH) and 4 were in watersheds east of Hudson River (EOH) (figs 1 and 2 in Arscott et al. 2006). Pertinent site characteristics are reported both in Table 1 and Appendix 1, and additional descriptive detail and landuse statistics can be found in Arscott et al. (2006).

Each study reach was delimited by an upstream injection substation, an upstream sonde (dissolved

O<sub>2</sub>/temperature data logger) substation approximately mid-way through the reach, and a downstream sonde substation. Sites were selected so that conditions affecting reaeration were similar above the upstream and downstream sonde locations. Between-sonde distances were dependent on discharge during the metabolism measurements. 2000 was a high-flow year, but 2001 and 2002 were both low-flow years based on 30 y of record (fig. 3 in Arscott et al. 2006). Discharge, stream width and depth, and water velocity are reported in Newbold et al. (2006).

Our measurements of stream metabolism were made concurrently with nutrient-spiraling experiments, and concentrations of analytes used in our data analyses are those reported in Newbold et al. (2006), except for total alkalinity and specific conductance (reported in Dow et al. 2006), and dissolved organic C (DOC) and biodegradable DOC (BDOC) (reported in Kaplan et al. 2006). Data concerning molecular tracer compounds are reported in Aufdenkampe et al. (2006). Data not reported elsewhere that were used in analyses are presented in Appendix 1. All variables measured in the Project and their abbreviations are listed in appendix 2 in Blaine et al. (2006).

### *Metabolism measurements*

Community metabolism was determined using open-system measurements of dissolved O<sub>2</sub> change. Five sondes (2000: YSI model 600XL [Yellow Springs, Inc., Yellow Springs, Ohio] coupled with Campbell CR-500 data loggers [Campbell, Logan, Utah]; 2001–2002: YSI model 600XLM) were placed in water-saturated towels and calibrated according to the manufacturer’s instructions. The sondes were then placed at a single location in the thalweg of the stream for a 7 to 12 h comparison period before deployment for experimental measurements. We compensated for differences between sondes when analyzing data according to the upstream–downstream approach. Two sondes were deployed to both the upstream and downstream substations. Pairs of sondes were chosen on the basis of similarities of dissolved O<sub>2</sub> readings near the end of the comparison period and probe characteristics (e.g., sensor charge and voltage). The 5<sup>th</sup> sonde was retained for quality assurance/quality control (QA/QC). Dissolved O<sub>2</sub> concentrations and water temperature were measured and logged at 15-min intervals, usually for a 3-d period. Daily QA/QC checks were made by comparing instantaneous readings of dissolved O<sub>2</sub>, % saturation, temperature, specific conductance, and sensor charge of the deployed sondes to the readings on the QA/QC sonde using a YSI 650MDS meter.

TABLE 1. Selected site characteristics, reaeration coefficients ( $K_{O_2}$ ), and ranges of daily minimum and maximum dissolved  $O_2$  % saturation values at integrative sites in 10 streams in New York City drinking-water-supply watersheds. Numbers in parentheses after stream names refer to specific sampling sites (see figs 1 and 2 and table 1 in Arscott et al. 2006 for site locations and names). See Newbold et al. (2006) for discharge, water velocity, stream width and depth. PAR = photosynthetically active radiation. – indicates data not available.

Stream	Measurement dates	Year	Mean PAR (mol quanta/d)	Mean daily temperature ( $^{\circ}C$ )	Between-sonde distance (m)	% tree canopy	Minimum dissolved $O_2$ % saturation	Maximum dissolved $O_2$ % saturation	$K_{O_2}$ (1/d)
West Branch Delaware (5)	26–27 Oct	2000	17.86	11.70	1913	46.1	86.7–87.4	107.9–109.5	–
	17–19 Jul	2001	33.38	21.03	806		64.6–67.8	111.3–122.1	4.55
	9–11 Jul	2002	38.66	20.17	1950		79.9–81.7	117.4–119.6	7.80
Bush Kill (11)	13–15 Jun	2000	27.69	16.84	2040	68.4	87.1–89.0	106.5–107.1	12.28
	26–28 Jun	2001	29.45	17.72	2220		85.9–87.0	104.7–105.7	29.35
	18–20 Jun	2002	29.41	14.24	2214		90.0–90.6	102.8–104.7	19.97
Schoharie (18)	5–6 Oct	2000	3.12	11.68	1275	49.1	92.3–92.9	100.0–102.3	30.05
	31 Jul–2 Aug	2001	40.33	23.55	421		83.4–85.5	114.6–116.0	12.10
	20–22 Aug	2002	23.13	22.36	191		81.0–83.1	115.0–117.6	25.39
Esopus (23)	19–20 Oct	2000	8.01	9.72	1333	51.5	93.4–94.2	100.3–101.0	–
	5–7 Jun	2001	38.20	12.87	1438		94.0–94.5	101.7–102.4	51.44
	4–6 Jun	2002	21.20	13.32	1502		92.8–94.0	98.7–103.5	49.32
Neversink (29)	12–13 Jul	2000	20.48	8.63	1839	53.5	90.8–90.9	97.0–97.9	–
	15–16 Aug	2001	26.40	17.68	741		87.4–88.0	101.2–101.4	24.13
	6–8 Aug	2002	35.91	17.31	730		86.5–86.9	99.8–101.9	21.53
Rondout (30)	20–21 Jul	2000	36.68	13.22	1457	65.9	97.0–97.3	99.1–100.1	24.51
	28–30 Aug	2001	11.23	16.26	378		85.6–86.7	103.4–105.5	29.71
	23–25 Jul	2002	23.67	17.15	374		86.5–87.5	104.2–104.7	37.22
Middle Branch Croton (40)	21–22 Sep	2000	4.98	19.34	500	89.9	89.8–91.0	95.4–97.1	59.16
	23–24 Oct	2001	6.74	14.86	153		87.4–88.5	105.8–106.0	34.66
	27–29 Aug	2002	1.63	20.31	277		92.7–93.3	94.7–103.7	58.68
Muscoot (46)	31 Aug–1 Sep	2000	1.50	20.32	150	92.0	94.4–95.0	101.4–101.8	38.35
	2–4 Oct	2001	0.91	13.94	255		89.7–92.6	100.2–101.5	23.95
	24–26 Sep	2002	1.19	15.80	150		87.1–87.6	94.7–99.5	20.40
Cross (52)	23–25 Aug	2000	9.05	17.46	1337	73.4	92.4–93.8	102.4–103.6	23.60
	9–11 Oct	2001	14.14	9.61	253		87.1–91.4	104.6–106.4	12.92
	10–12 Sep	2002	19.17	17.85	255		89.5–90.3	105.0–107.5	17.32
Kisco (55)	28–29 Sep	2000	1.55	12.22	398	93.1	95.9–96.0	99.2–99.7	19.35
	16–18 Oct	2001	4.39	11.78	376		84.0–85.4	96.0–98.6	12.31
	8–10 Oct	2002	2.16	12.83	366		89.9–90.8	98.7–103.5	9.98

Photosynthetically active radiation (PAR) was measured by securing 2 LI 190SA quantum sensors (LI-COR, Lincoln, Nebraska) to stakes at both the upstream and downstream substations. PAR was measured every 15 s, and 15-min integrals were logged on a LI-COR 1400 data logger. In 2005, the tree canopy at each study site was photographed at 8 to 12 locations, equally spaced along each study reach, using a digital camera (Nikon Coolpix 995) equipped with a fisheye lens (Nikon FC-E8 28 mm). The camera was positioned 0.67 m above the stream water surface at the center of the stream. Each photograph captured the canopy for a distance of ~25 m.

Reaeration coefficients were determined from measurement of propane evasion (after Marzolf et al. 1994, 1998, Young and Huryn 1998). Propane was bubbled into the stream at the injection site through 1.5-m-long gas-diffuser tubes (Aquatic Eco-Systems, Apopka,

Florida), and a  $Br^-$  conservative-tracer solution was injected simultaneously using a peristaltic pump. The injection site was far enough upstream to ensure mixing of sources and full lateral dispersion at the uppermost sampling station.

Samples were collected at 5 substations over the length of the study reach.  $Br^-$  was monitored over the entire injection at the 1<sup>st</sup> substation and at either the 4<sup>th</sup>- or 5<sup>th</sup>-most downstream substation, and 5 propane and 5  $Br^-$  samples were taken when concentrations were at a plateau. Propane and  $Br^-$  samples were collected at the remaining substations only during the plateau. Sampling times were set on the day before the experiment by timing the transit of a pulse of rhodamine WT through the reach. Field blanks were collected at each substation before the start of the injection. A standard curve was prepared by diluting water from the plateau (maximum propane concen-

tration) at the uppermost sampling substation to 50%, 10%, and 1% in site water collected before the injection.

Conservative-tracer samples were collected in 125-mL plastic bottles, and propane samples were collected in 73-mL serum bottles that were stoppered and crimp-sealed in the field. In 2000, bottles were filled by immersing them directly in the stream. In 2001 and 2002, water was collected by immersing a bucket into the flow in an upstream direction and serum bottles were filled by dipping them into the bucket to minimize turbulence during filling. Samples were refrigerated during storage.

Open-system metabolism measures included both benthic and water-column activity. Water-column metabolism was measured separately by filling 10 BOD bottles (6 light and 4 dark) with stream water. Stream water was bubbled with N<sub>2</sub> to reduce the dissolved O<sub>2</sub> saturation to ~70% if values were >85%. Initial dissolved O<sub>2</sub> concentration, temperature, and % saturation were measured using a YSI Model 58 dissolved O<sub>2</sub> meter and probe with stirrer for use with BOD bottles. The bottles were incubated in the stream for 4 to 6 h during which PAR was monitored. Following incubation, dissolved O<sub>2</sub> concentration, temperature, and % saturation were measured again.

#### *Substratum and biomass assessments*

Benthic substrata and plant cover types were combined in measurements in 2000, but they were categorized separately in 2001 and 2002. Twenty transects were set between upstream and downstream sondes, and 10 equidistant lateral points were designated along each transect. At each point, stream depth was measured, and predominant types of substrata and attached biomass (cover type) were assessed using a viewing bucket. Substratum categories followed those of Hynes (1970). Cover types were categorized by macroscopic appearance as: filamentous green algae, filamentous diatoms, diatoms (brown velvet appearance), black cover (a slime scraped from rocks that appeared black), tufts (short filamentous algae, either immature or abraded), fuzz (silt enmeshed in tufts), and silt. Microscopic examination documented the presence of diatoms in the black-cover, fuzz, and silt cover types.

Replicate samples (2–5) for periphyton chlorophyll *a* and organic matter were collected for cover types that made up ≥10% of the encounters in the mapping effort. Soft substrata were sampled by inserting a plastic tube (11.25-cm inner diameter) into the streambed and suctioning the enclosed surface sediments with a meat baster. Samples of periphyton on rocks were scraped, brushed, and washed into a jar. The

planar surface area of the upper rock surface was traced onto a piece of paper for area quantification using image analysis techniques (see below). Samples were held on ice until return from the field. That evening, samples were centrifuged (7000 × *g*, 15–30 min) and recovered pellets were frozen. If supernatant fluids of silt samples remained turbid, the fines were collected on GF/F filters that were subsequently frozen. Nearly all samples were analyzed for chlorophyll *a* within 3 to 4 wk.

#### *Laboratory analyses*

Br<sup>-</sup> was analyzed by ion chromatography (Model DX-500, Dionex, Sunnyvale, California; Newbold et al. 2006).

In preparation for propane analyses, 2 syringe needles were inserted through the septum of the serum bottle, and 10 mL of water were displaced by injecting air into the bottle to produce a head space. Bottles were shaken horizontally for 3 h at room temperature to equilibrate propane between the water and head space. Propane content was determined on 50-μL samples of head-space gas using capillary gas chromatography as detailed in Bott et al. (2006). Standard curves displayed excellent linearity (*R*<sup>2</sup> values of 0.96–0.99) and tight replication (CV of replicates averaged 7.5% over all concentrations and streams). Propane peaks at the farthest downstream substation ranged between <10% and ~60% of the 1<sup>st</sup> substation values. Absolute concentrations were not critical to assessing reaeration because the reaeration coefficient was computed based on proportional loss over distance.

Chlorophyll-containing pellets were thawed in the laboratory, and chlorophyll *a* was extracted overnight in acetone (made basic with MgCO<sub>3</sub> or NH<sub>4</sub>OH added to the reagent bottle) at -20°C. Following centrifugation (15 min, 10,000 × *g*, 4°C), the absorbances of the supernatant fluids were determined spectrophotometrically at 665 nm and 750 nm (for turbidity) before and after acidification with 2 drops of 1 N HCl. Extractions were repeated on samples until chlorophyll *a* absorbance was either 10% of the value obtained from the 1<sup>st</sup> extraction or <0.1 absorbance units at 665 nm. Samples were iced and handled under low light. Concentrations were determined using the equations of Lorenzen (1967, APHA 1992), which include correction for pheophytin. Following extraction, the pellets were dried at 60°C, weighed, ashed (450°C for 6 h), cooled, and reweighed for an analysis of organic matter content as ash-free dry mass AFDM).

Rock outlines were digitized and planar surface area was determined using public domain Image J 1.34

software (US National Institutes of Health; <http://rsbweb.nih.gov>). Tree canopy photos were processed using Image-Pro Plus 5.0 software. Color photos were segmented to black and white images of sky and tree canopy plus streambank. The proportion of total area accounted for by the canopy category was determined using the Image J 1.34 software. The canopy values from the 8 to 12 photos were averaged to generate a mean % canopy cover for each stream.

#### Data analyses

Biomass and metabolism data for Rondout in 2000 and Kisco in 2002 are presented in tables and figures but were eliminated from the calculations of means and statistical tests as outliers. In 2000, Rondout had been severely scoured ~1 wk before the field work. In 2002, Kisco experienced an anomalous increase in specific conductance from ~490 to 570  $\mu\text{S}/\text{cm}$  beginning ~12 h after measurements began and lasting for ~36 h, followed by a drop to 520  $\mu\text{S}/\text{cm}$ . This anomaly presumably was caused by a time-variable discharge of unknown origin.

In 2000, chlorophyll *a* concentrations were obtained for the most important cover types, which included ~90% of cover types in all streams except Muscoot, Neversink, and Cross, where 65 to 80% of the cover types were sampled. In 2001, chlorophyll *a* concentrations were obtained for >87% of cover types in all streams but Kisco, where 83% of the cover types were sampled. In 2002, chlorophyll *a* analyses were obtained for >91% of the cover types encountered in Esopus, Neversink, Rondout, and Cross; >81% of the cover types in Bush Kill, Schoharie, and Muscoot; >74% of the cover types in West Branch Delaware and Kisco; and 65% of cover types in Middle Branch Croton. Periphyton chlorophyll *a* concentrations were matched with the estimated % of total reach area consisting of that cover type to generate a weighted periphyton chlorophyll *a* concentration/ $\text{m}^2$  (standing stock). Total chlorophyll *a* standing stocks were generated by adding macrophyte (West Branch Delaware) and moss (Rondout, Neversink, and Middle Branch Croton) chlorophyll *a* to periphyton chlorophyll *a*. The 2002 estimate of macrophyte chlorophyll *a* in the West Branch Delaware was based on chlorophyll *a* concentrations obtained for macrophytes in 2001 applied to occurrence data collected in 2002. Organic matter data were treated similarly to generate a weighted estimate for each stream reach.

The loss of propane with downstream distance was determined by nonlinear regression of the [propane: $\text{Br}^-$ ] ratio against downstream distance (SAS/STAT, version 9; SAS Institute, Cary, North Carolina)

using an exponential model (Wanninkhof et al. 1990). The dilution-corrected proportion of propane lost/ $\text{m}$  was multiplied by water velocity, 1.39 (to correct for molecular size, Rathbun et al. 1978), and 60 (s/min) to generate  $K_{\text{O}_2}$  (1/min). Both water velocity through the reach and mean depth of the reach were derived from a computer model of  $\text{Br}^-$  concentrations using OTIS-P as described in Newbold et al. (2006). Reaeration also was computed from geomorphic variables entered into a surface renewal model (SRM; Owens et al. 1964) and an energy dissipation model (Tsivoglou and Neal 1976, APHA 1992).

$\text{O}_2$  data usually were analyzed using the 2-station (upstream–downstream) approach (after Owens 1974). Reaeration coefficients were corrected to ambient temperatures based on Elmore and West (1961). The hourly rate of change of dissolved  $\text{O}_2$  concentration (Odum 1956) corrected for reaeration was computed at each 15-min interval over a 24-h diel period. The average hourly rate of community respiration during darkness ( $\text{PAR} < 2 \mu\text{mol quanta m}^{-2} \text{s}^{-1}$ ) was extrapolated to 24 h ( $\text{CR}_{24}$ ). Gross primary productivity (GPP) was computed by adding photoperiod respiration to net  $\text{O}_2$  change during the photoperiod. Net daily metabolism (NDM) was computed as the difference between GPP and  $\text{CR}_{24}$  ( $\text{NDM} = \text{GPP} - \text{CR}_{24}$ ). Reaeration coefficients from propane evasion were used for all analyses except that coefficients based on the SRM approach were used for Esopus, Neversink, and West Branch Delaware in 2000. These exceptions presumably introduced little error because GPP data obtained with reaeration estimates from the SRM procedure at other sites that year agreed closely with data obtained with reaeration estimates based on propane evasion (propane/SRM =  $0.97 \pm 0.66$ ,  $\bar{x} \pm \text{SD}$ ,  $n = 16$ ), as did respiration data (propane/SRM =  $1.07 \pm 0.59$ ,  $n = 14$ ). In 3 instances (Kisco 2000, Rondout 2000, and 1 d in 2002 for Middle Branch Croton River), single-station analysis was applied to downstream data because the upstream probe failed or exhibited drift in readings.

Mean  $\text{O}_2$  change in dark bottles was added to the net  $\text{O}_2$  change in each light bottle to yield an estimate of water-column GPP, the average of which was compared to whole-system metabolism for the corresponding time period.

A photosynthesis–irradiation (PI) curve was prepared for each stream each year by regressing change in dissolved  $\text{O}_2$  (PS) against average PAR (instantaneous light intensity, *I*) every 15 min during the period of increasing PAR intensity from sunrise to mid-day. A hyperbolic tangent function (Jassby and Platt 1976)

$$\text{PS} = \beta' + \text{PS}_{\text{max}} \times \tanh([\alpha \times \text{PAR}]/\text{PS}_{\text{max}})$$

where  $\alpha$  is a constant (initial slope of the regression),  $\beta'$  is analogous to community respiration (used to position the curve correctly in each analysis), and  $PS_{\max}$  is the maximum rate of photosynthesis in the absence of photoinhibition was fit to the data, except in a few instances (noted in Table 3) when photoinhibition was clearly apparent in the data. Those data were analyzed using an exponential model with a photoinhibition term (Platt et al. 1980):

$$PS = \beta' + PS_{\max} \times (1 - \exp[-\alpha \times PAR/PS_{\max}]) \times \exp(-\phi \times PAR/PS_{\max})$$

where  $\phi$  is a term describing photoinhibition. Values for  $PS_{\max}$ ,  $\alpha$ , and saturation intensity ( $I_s$ ) were determined. Usually data from all days were combined in a single regression for the year but, in a few instances (Rondout in 2000; Cross, Kisco, and Schorarie in 2001; Cross and Muscote in 2002), values were obtained from individual daily curves and then averaged, either because the range of intensities varied substantially between days or because different models were used on different days. In addition to data from Rondout (2000) and Kisco (2002), data from the Neversink (2000) were excluded as outliers from the PI curve analyses because PAR values were extremely low in comparison to other years.

GPP was normalized for total daily PAR and for PAR after adjusting for saturation because photosynthesis is a saturation phenomenon. The adjustment was made by substituting  $I_s$  for each stream and year for PAR intensities that exceeded  $I_s$ , and daily PAR was recomputed ( $PAR_{\text{sat adj}}$ ). In essence, this procedure excluded surplus radiation above the  $I_s$ . Streams were then ranked according to  $GPP/PAR$  and  $GPP/PAR_{\text{sat adj}}$ .

All statistical analyses were done using  $\log_{10}(x)$ -transformed or  $\arcsine\sqrt{(x)}$ -transformed (for %) 3-y means with a constant added before transformation when needed. Differences between sites were determined from analyses of variance (ANOVAs) followed by Tukey's tests when ANOVAs were significant ( $p \leq 0.05$ ). Multiple linear regression analyses (MLR) were used to assess which combinations of variables explained the most variance in metabolism variables and biomass. The stepwise forward selection procedure was used (Stat View version 4.02; Abacus Concepts, Berkeley, California) to model biomass or metabolism variables as a function of instream environmental variables, chlorophyll *a* and biomass (for metabolism regressions), and nutrient-uptake metabolic variables (Newbold et al. 2006) (all specified in Tables 2 and 5). Residuals from each regression were examined for correlations with watershed landscape

variables (% land uses: residential, commercial, industrial, other urban, cropland, orchard, farmstead, grassland, brush, mixed brush-grassland, deciduous forest, coniferous forest, mixed forest, water, wetland, commercial + industrial, coniferous + mixed forest, farmstead + cropland, grassland + mixed forest, total forest; and road density, population density, watershed area, mean annual watershed-area-normalized State Pollution Discharge Elimination System [SPDE] effluent volume discharge [point-source discharge]; appendix 2 of Blaine et al. 2006, table 2 of Arscott et al. 2006), BDOC and DOC (Kaplan et al. 2006), specific conductance (Dow et al. 2006), and Hilsenhoff Biotic Index, Ephemeroptera, Plecoptera, Trichoptera (EPT) richness, total macroinvertebrate richness, and percent model affinity (Kratzer et al. 2006). Residual variances from the MLR analyses also were tested for correlations with the following molecular tracers (see table 1 of Aufdenkampe et al. 2006 for abbreviations): bCOP, EPI, BAP, CAF, HHCB, AHTN, FLU, PHE, ANT, 2MP, 1MP, FLR, PYR, BAA, CHR, BBF, BKF, CHOL, aCOP, bONE, aONE, SNOL, fragrance materials, volatile, soot, and total polyaromatic hydrocarbons (PAH), and fecal steroids.

#### *Ordination analyses of metabolism, land use, and instream variables*

Redundancy analysis (RDA, Jongman et al. 1995) and variance partitioning (Borcard et al. 1992) methods were used to determine the relative contributions of instream environmental variables and watershed landscape variables to an RDA model explaining differences in 8 metabolism/chlorophyll *a* biomass variables among the 10 study sites. The manual forward selection procedure included in CANOCO (version 4.0; Microcomputer Power, Ithaca, New York; ter Braak and Šmilauer 1998) was used in 2 separate iterations to select watershed landscape variables and instream variables to include in further analyses. Watershed landscape variables were summarized at 3 spatial scales: 1) watershed (defined by watershed boundaries), 2) riparian (defined by 30-m buffers around each side of all streams or water bodies in the stream network upstream of each sampling site), and 3) reach (30-m riparian buffers for a distance of 1 km upstream from each sampling site) (Arscott et al. 2006). Instream variables included physical measures of PAR, water temperature and velocity, discharge, channel width and depth, % fine sediments (sand, silt, and clay), % cobble and boulder, hydraulic exchange coefficient (mm/s), and transient storage ( $A_s/A$ ) (Newbold et al. 2006); chemical constituents sampled during the metabolism experiments ( $NH_4-N$ ,  $NO_3-N$ , soluble

Kjeldahl N [SKN], total Kjeldahl N [TKN], dissolved organic N [DON], particulate N [PN], soluble reactive P [SRP], total P [TP], particulate P [PP], and glucose; see Newbold et al. 2006 for definitions and analytical techniques); certain molecular tracers (Aufdenkampe et al. 2006); DOC concentrations (Kaplan et al. 2006); and specific conductance and total alkalinity (TA) collected during summer baseflow sampling (Dow et al. 2006). Variables that contributed significantly ( $p < 0.10$  after 1000 Monte Carlo permutations) were retained to build partial RDA models necessary for variance partitioning analysis. Individual years were used for each site, but Kisco 2002 and Rondout 2000 data were excluded (reasons given above).

Variance partitioning (Borcard et al. 1992) was used to decompose the total variability in metabolism and chlorophyll *a* biomass variables that could be attributed to either watershed landscape variables, instream variables, or their interaction. This analysis was done by defining the suite of variables from one category (watershed landscape or instream variables) as covariables and recomputing each RDA to generate partial RDAs based on the variables in the other category.

The last step in this multivariate approach was a Co-Inertia Analysis (CIA), an unconstrained direct gradient analysis of the metabolism–environment relationship (Dolédec and Chessel 1994). CIA first computes separate ordinations of each of the data tables. In this case, metabolism and environmental variables (selected using techniques described above) were examined via separate Principal Components Analyses (PCA). CIA then matches the 2 ordinations, thereby maximizing the covariance between the tables and providing correlation coefficients between metabolism PCA factors and environment PCA factors. Output from the matching process illustrates the costructure of each table and gives an ordination of metabolism and environmental vectors and a distribution of sites defined by both metabolism and environment scores in 2-dimensional space. Statistical significance of the costructure between metabolism and environmental matrices was assessed by a Monte Carlo random permutation test with 1000 random matches of the 2 tables. The CIA was done using ADE-4 software (ADE-4, 2001, University of Lyon, Lyon, France; Thioulouse et al. 1997).

## Results

### *Benthic substrata and cover types*

Cobble made up 53% to 76% of the streambed material in the WOH streams and 19% to 52% of the streambed in EOH streams. EOH streams, especially Cross and Kisco, had the largest % sand and silt. Of the

WOH streams, Neversink had the greatest proportion of soft substrata. Some EOH streams (Middle Branch Croton and Kisco) had unexpectedly high % boulders (higher than percentages in some WOH streams).

Algal cover types varied among streams and years. In 2001 and 2002, diatoms and filamentous diatoms were predominant in Bush Kill, Esopus, and West Branch Delaware, where they made up ~50% of encounters. In 2000, filamentous green algae made up ~70% of encounters in the Schoharie but, in 2001, diatoms made up nearly the same % (although *Spirogyra* sp. also occurred). In 2002, other categories predominated in Schoharie. *Ulothrix* sp. was common in Neversink in 2001, and *Cladophora* sp. was common in Bush Kill in all years. Both *Cladophora* and *Rhizoclonium* were common in Rondout in 2001, but their cover was lower the next year. *Oscillatoria* sp. (Cyanobacteria) mats were observed in Neversink in 2002. Three-year mean values of % filamentous green algae ranged from <1% (Muscoot) to 11% (Esopus) in all streams but West Branch Delaware (15.6%) and Schoharie (29%), and the 2-y mean for Rondout was 26%. The 3-y means for total % filamentous algae (including filamentous diatoms) were 29%, 26%, 20%, and 18% in the Schoharie, Rondout, Bush Kill, and West Branch Delaware, respectively, and between 1% and 11% elsewhere. Bare substrata occurred most often in Cross, Esopus, and Bush Kill.

Macrophytes occasionally formed significant growths, e.g., *Callitriche* sp. in Rondout (2002) and *Ranunculus* sp. in the Neversink, but macrophytes were encountered most noticeably every year in West Branch Delaware. *Podostemum* sp., *Ranunculus* sp., and *Potamogeton* (probably *praelongus*) sp. were predominant in West Branch Delaware in 2001 and 2002, and *Anacharis* sp. was prevalent in 2000. Mosses occurred in Middle Branch Croton (3%) during 2002, but they made up a slightly larger % (~6%) of encounters in both Neversink and Rondout. Leaf packs were noted in Muscoot, Cross, and Kisco because these streams were studied late in the field season.

### *Chlorophyll a and organic matter*

Periphyton chlorophyll *a* standing stock for each stream and year (Fig. 1A) ranged from <10 (Kisco 2000) to >160 mg/m<sup>2</sup> (Muscoot 2002). Chlorophyll *a* standing stocks in EOH streams were higher during 2001 and 2002 (low-flow years) than in 2000 (ANOVA and Tukey's tests,  $p < 0.05$ ), but this result was less pronounced in the larger WOH streams ( $p > 0.05$ ). Three-year mean periphyton chlorophyll *a* standing stocks ranged from 30 (Neversink) to 102 mg/m<sup>2</sup> (Muscoot) (Fig. 1B), and standing stocks overlapped in

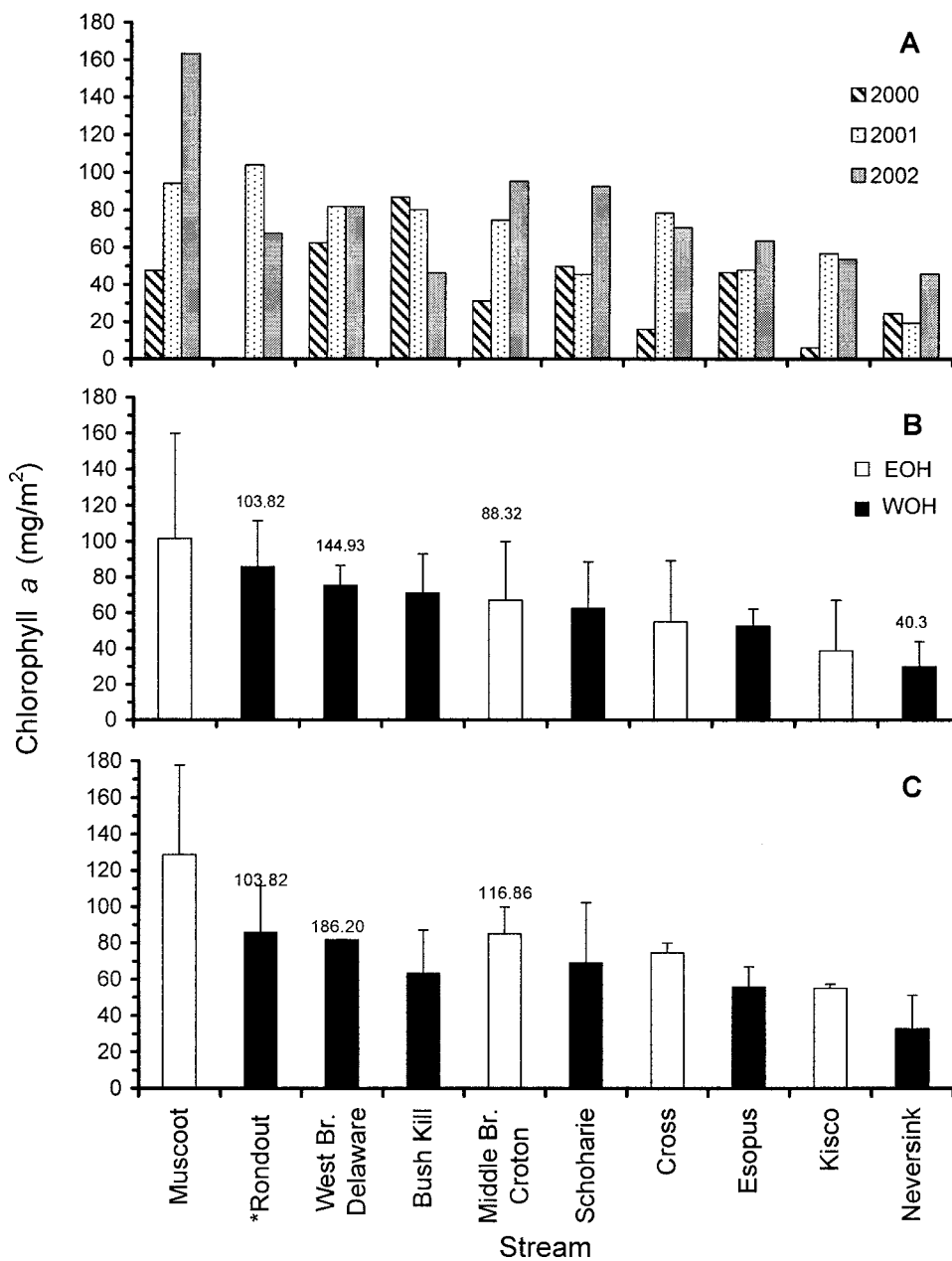


FIG. 1. Annual (A), 3-y mean (+1 SD) (B), and low-flow-year mean (+1 SD) (C) periphyton chlorophyll *a* standing stocks in 10 streams in New York City drinking-water-supply watersheds. Numbers in B and C are chlorophyll *a* standing stocks when macrophyte and moss chlorophyll were included in the stream total. Streams are ranked according to the 3-y mean chlorophyll *a* standing stock. See Table 1 for site numbers. EOH = east of Hudson River, WOH = west of Hudson River, Br. = branch. \* indicates Rondout (2000) values omitted (see text for explanation).

EOH and WOH streams with no significant differences among streams (ANOVA,  $p > 0.05$ ). During the low-flow years differences among streams were not significant (ANOVA,  $p > 0.05$ ; Fig. 1C).

Total chlorophyll *a* standing stock in West Branch Delaware was 186 mg/m<sup>2</sup> for the 2 low-flow years (when macrophyte cover was >10%), a substantial increase over the periphyton chlorophyll value (82

mg/m<sup>2</sup>; Fig. 1B, C). Increases in chlorophyll *a* standing stock from macrophytes and mosses during low-flow years were smaller elsewhere. Three-year mean total chlorophyll *a* standing stocks in the EOH and WOH regions overlapped with no significant differences among streams (ANOVA,  $p > 0.05$ ; Fig. 1B). However, low-flow-year mean total chlorophyll *a* standing stocks were significantly greater in West Branch Delaware,

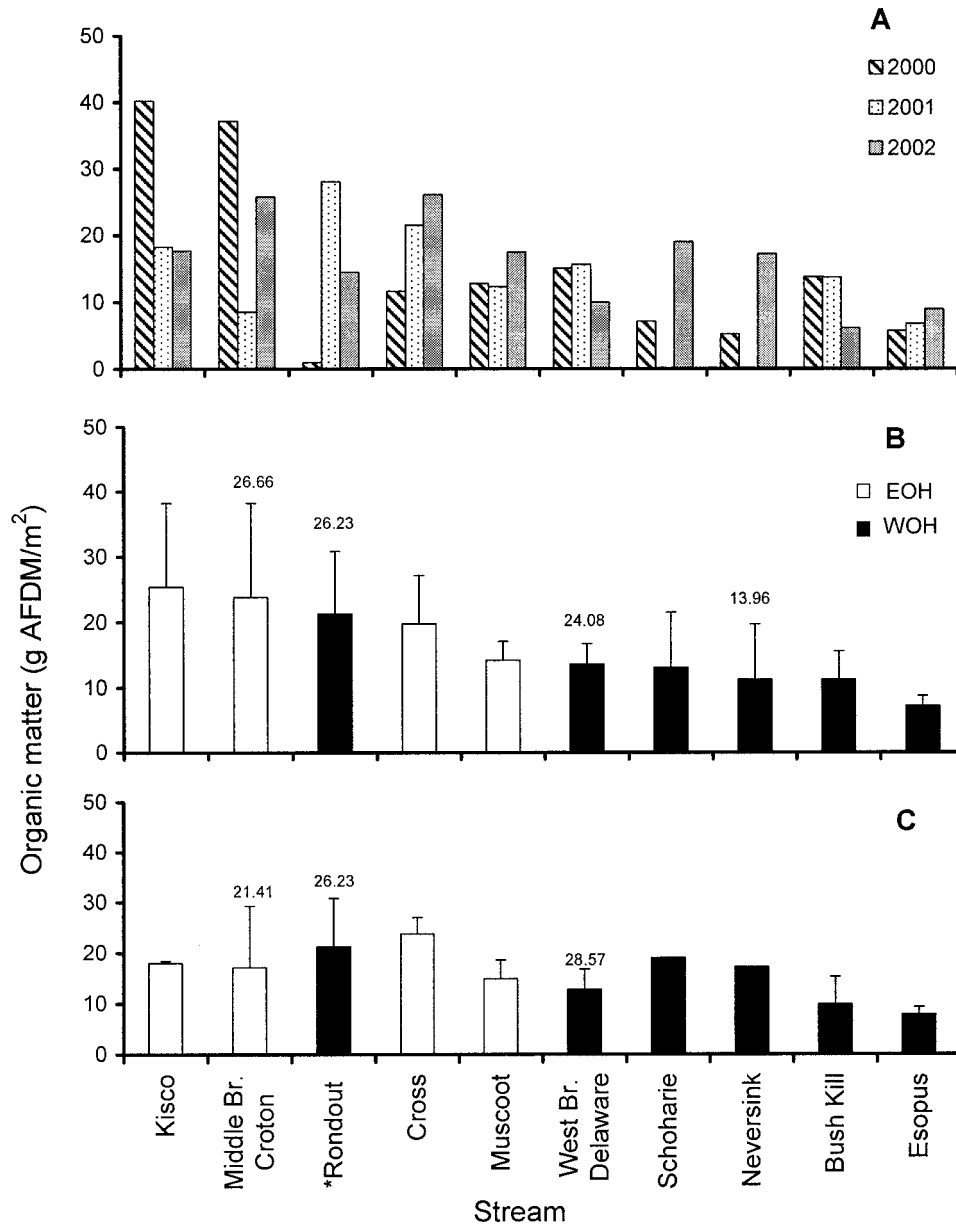


FIG. 2. Annual (A), 3-y mean (+1 SD) (B), and low-flow-year mean (+1 SD) (C) periphyton organic matter standing stocks in 10 streams in New York City drinking-water-supply watersheds. Numbers in B and C are organic matter standing stocks when macrophyte and moss organic matter were included in the stream total. Streams are ranked according to the 3-y mean organic matter standing stock. See Table 1 for site numbers. EOH = east of Hudson River, WOH = west of Hudson River, Br. = branch, AFDM = ash-free dry mass. \* indicates Rondout (2000) values omitted (see text for explanation).

Muscoot, and Middle Branch Croton than in Neversink (ANOVA and Tukey's test,  $p \leq 0.05$ ; Fig. 1C).

Periphyton organic matter standing stock ranged from  $\sim 6$  to  $\sim 40$  g/m<sup>2</sup> (Fig. 2A). Three-year means were similarly high in Kisco and Middle Branch Croton and lowest in Esopus (Fig. 2B). During low-flow years, organic matter standing stocks tended to be lower in Esopus, Bush Kill, and West Branch Delaware ( $< 13$  g/m<sup>2</sup>) than other streams, where

values ranged from 15 to 24 g/m<sup>2</sup> (Fig. 2C), but 3-y mean and low-flow-year mean periphyton organic matter standing stocks did not differ significantly among streams (ANOVA,  $p > 0.05$ ; Fig. 2B, C). Total organic matter standing stocks were higher in West Branch Delaware, Rondout, Middle Branch Croton, and Kisco than in Esopus (ANOVA and Tukey's test,  $p \leq 0.05$ ; Fig. 2B). However, during low-flow years, standing stocks for only West Branch Delaware and

TABLE 2. Multiple linear regression (MLR) models for weighted periphyton chlorophyll (chl) *a* ( $p = 0.0004$ ) and organic matter (OM) content ( $p = 0.026$ ) as functions of environmental (physicochemical: this study, Dow et al. 2006, Kaplan et al. 2006, Newbold et al. 2006; biological: Kratzer et al. 2006) and metabolic (this study, Newbold et al. 2006) variables in 10 streams in New York City drinking-water-supply watersheds. Coefficients are given for significant ( $p < 0.05$ ) correlations among residual variances from the MLR analyses and watershed landscape variables (Arscott et al. 2006) and concentrations of molecular tracers (Aufdenkampe et al. 2006).  $\beta$  = standardized partial regression coefficient, PAR = photosynthetically active radiation, GPP/PAR<sub>sat adj</sub> = gross primary production normalized for saturating photosynthetically active radiation, 1MP = 1-methyl phenanthrene, 2MP = 2-methyl phenanthrene, PYR = pyrene, vol PAHs = volatile polycyclic aromatic hydrocarbons, C<sub>bkgd</sub> = background concentration, SKN = soluble Kjeldahl N, TKN = total Kjeldahl N, PN = particulate N, TN = total N, DON = dissolved organic N, PP = particulate P, TP = total P, TSS = total suspended solids, VSS = volatile suspended solids,  $V_f$  = uptake velocity, NDM = net daily metabolism, CR<sub>24</sub> = 24-h community respiration.

Dependent variable	MLR models				Correlations of residuals		
	Coefficient	Independent variable	$\beta$	Cumulative adjusted $R^2$	Variable	$r$	$p$
$\log_{10}$ (periphyton chl <i>a</i> ) <sup>a</sup>	0.825	$\log_{10}$ (GPP/PAR <sub>sat adj</sub> )	0.932	0.303	2MP	0.690	0.025
	0.348	$\log_{10}$ (TN)	0.782	0.862	1MP	0.676	0.029
	1.539				PYR	0.659	0.036
					Vol PAHs	0.672	0.031
$\log_{10}$ (OM) <sup>b</sup>	0.255	$\log_{10}(\sum \text{clay} + \text{silt} + \text{sand})$	0.695	0.419	% orchard	0.678	0.029
	0.925						

<sup>a</sup> Additional variables used in the chl *a* analysis were PAR, temperature, % tree canopy closure (Table 1), C<sub>bkgd</sub> of NH<sub>4</sub>-N, NO<sub>3</sub>-N, TDN, PN, DON, SKN, TKN, SRP, TDP, PP, and TP,  $V_f$ -NH<sub>4</sub>,  $V_f$ -SRP, water velocity, discharge, stream width, water depth, (Newbold et al. 2006), total alkalinity (Dow et al. 2006), (clay + silt + sand), (cobble + boulder) (Appendix 1)

<sup>b</sup> Variables used in the OM analysis were those used in the chl *a* analysis plus  $V_f$  and C<sub>bkgd</sub> of glucose and arabinose (Newbold et al. 2006), NDM, GPP, and CR<sub>24</sub>

Rondout were greater than in Esopus (ANOVA and Tukey's test,  $p \leq 0.05$ ; Fig. 2C).

Periphyton chlorophyll *a* standing stock was not significantly correlated with 3-y mean background concentrations (C<sub>bkgd</sub>) and uptake velocities ( $V_f$ ) of NH<sub>4</sub>, SRP, arabinose, or glucose (Newbold et al. 2006), and C<sub>bkgd</sub> of NO<sub>3</sub>-N, SKN, TKN, SRP, TDP, TP, total and volatile suspended solids (TSS and WSS, respectively), TA, total N (TN), TDN, PP, PN, DON, PAR, or temperature ( $p > 0.05$ ). However, total chlorophyll *a* standing stock was significantly and positively correlated with temperature ( $r = 0.664$ ,  $p = 0.034$ ) and marginally correlated with NO<sub>3</sub>-N ( $r = 0.626$ ,  $p = 0.052$ ), a possible N source for algae and heterotrophs. Periphyton organic matter standing stock was significantly and positively correlated with glucose ( $r = 0.689$ ,  $p = 0.025$ ), but total organic matter standing stock was not significantly correlated with any other variable. Total chlorophyll *a* standing stock was significantly and positively correlated with cholesterol ( $r = 0.652$ ,  $p = 0.040$ ) and total fecal steroids ( $r = 0.632$ ,  $p = 0.049$ ), 2 of the molecular tracers monitored by Aufdenkampe et al. (2006), suggesting positive association with sewage contamination, but neither periphyton organic matter nor total organic matter standing stock were correlated with molecular tracer compounds ( $p > 0.05$ ).

MLR analysis generated a model that explained >85% of the variance in periphyton chlorophyll *a*

standing stock on the basis of GPP/PAR<sub>sat adj</sub> and TN (Table 2). Residuals from this model were correlated with several molecular tracer compounds, but not with any of the watershed landscape variables (Table 2). MLR analysis generated a model that explained ~42% of the variance in periphyton organic matter standing stock on the basis of substratum type. Residuals from this model were correlated with % orchard land use (Arscott et al. 2006).

### Metabolism

Metabolism measurements were made on 75 d over the 3-y period. GPP (3-y means) ranged from ~0.2 to 4 g O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> (Fig. 3). Mean GPP was lower in all EOH streams than in WOH streams. GPP was significantly greater in Bush Kill, Esopus, Rondout, and West Branch Delaware than in Kisco, and GPP was significantly greater in Bush Kill and Esopus than in Muscoot (ANOVA and Tukey's test:  $p \leq 0.05$ ). During low-flow years, GPP was greater in Esopus, Bush Kill, Neversink, and Rondout than in Muscoot and Kisco (ANOVA and Tukey's test:  $p \leq 0.05$ ).

GPP was significantly negatively correlated with several water-chemistry variables including SKN, TKN, TDP, glucose, DON, TA, and specific conductance (Appendix 2). These correlations reflect both the greater TA and specific conductance in EOH streams (Dow et al. 2006) and the potential for high rates of

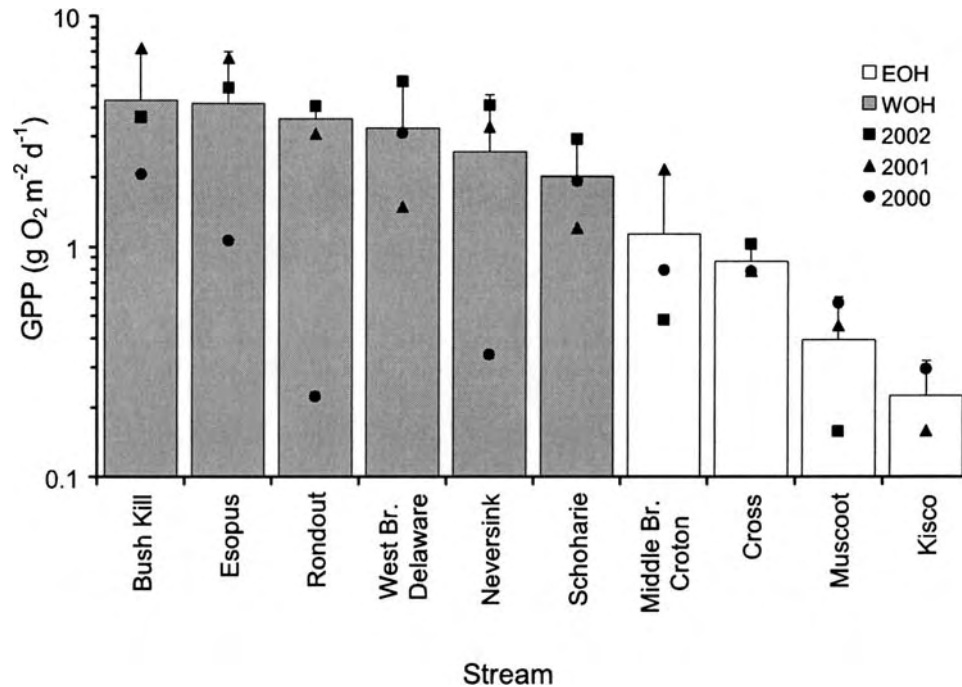


FIG. 3. Log plot of gross primary productivity (GPP) in 10 streams in New York City drinking-water-supply watersheds. Bars show the 3-y mean (+1 SD), and symbols indicate annual means. EOH = east of Hudson River, WOH = west of Hudson River, Br. = branch.

photosynthesis to reduce nutrient concentrations. GPP was positively correlated with PAR, several indicators of stream size,  $CR_{24}$ , and the  $V_f$  of  $NH_4$ . GPP was negatively correlated with several watershed landscape variables indicative of urbanization (e.g., 2000 population density, % residential land use), which was greater in EOH watersheds, and positively correlated with watershed area and % forested land use (hereafter = sum of % coniferous + % deciduous + % mixed forest), both of which were greater in WOH watersheds (figs 6A and 7A in Arscott et al. 2006). GPP was significantly negatively correlated with several molecular tracers: HHCB and AHTN (both fragrance materials; see table 1 in Aufdenkampe et al. 2006, appendix 2 in Blaine et al. 2006 for tracer names and abbreviations) and 6 hydrocarbons that tended to be greater in streams with greater human impact (fig. 7 in Aufdenkampe et al. 2006).

Saturation curves were obtained in nearly every PI analysis (Table 3). Year-to-year variability was considerable as shown by large standard deviations of derived parameters. Net  $O_2$  production did not occur ( $PS_{max}$  was negative) in some streams. Three-year mean  $PS_{max}$  and  $I_5$  were greater in WOH streams than in EOH streams, but  $\alpha$  values were similar between regions. The only significant difference between streams was that  $PS_{max}$  was greater in West Branch

Delaware, Bush Kill, Esopus, and Rondout than in Neversink (ANOVA:  $p = 0.01$ , Tukey's test:  $p < 0.05$ ).

Rankings of streams changed slightly depending on whether sites were ranked on the basis of GPP normalized for total daily PAR ( $GPP/PAR$ ) or GPP normalized for saturating PAR ( $GPP/PAR_{sat\ adj}$ ) (Fig. 4A, B). Among other small shifts, Rondout and Bush Kill ranked higher on the basis of  $GPP/PAR_{sat\ adj}$  than on the basis of  $GPP/PAR$ , whereas Muscoot and Middle Branch Croton ranked lower on the basis of  $GPP/PAR_{sat\ adj}$  than on the basis of  $GPP/PAR$ . However, differences among streams were not significant (ANOVA,  $p > 0.05$ ) regardless of how GPP was normalized.

Water-column metabolism accounted for only a minor % (usually  $< 3.5\%$ ) of total ecosystem metabolism in most streams (Table 4). The exceptions were Cross and West Branch Delaware where mean values were 9.37% and 5.91%, respectively. Elevated values occurred during 1 y of study in Bush Kill (11.3% in 2000), Cross (27.8% in 2000), Middle Branch Croton (6.4% in 2000), and Kisco (11.3% in 2001), but the only stream in which high values occurred more than once was West Branch Delaware (7.8% in 2001 and 9.8% in 2002). Overall, system metabolic activity could be attributed primarily to the benthic community.

$CR_{24}$  ranged from  $\sim 1$  to  $\sim 8$   $g\ O_2\ m^{-2}\ d^{-1}$  with highest values in Bush Kill, Neversink, and Esopus

TABLE 3. Parameters derived from photosynthesis–irradiation relationships for 10 streams in New York City drinking-water-supply watersheds. Net O<sub>2</sub> change was analyzed using the hyperbolic tangent model for all stream/year combinations except Cross (2000, 2001, 11 September 2002), Middle Branch Croton (2002), and Schoharie (2002) for which the exponential model with a photoinhibition term was used (see text for model details). EOH = east of Hudson River, WOH = west of Hudson River, PAR = photosynthetically active radiation, PS<sub>max</sub> = maximum rate of photosynthesis in the absence of photoinhibition,  $\alpha$  = regression slope,  $\beta'$  = analog for community respiration (used to position the curve correctly in each analysis), and I<sub>s</sub> = saturation intensity.

Stream	Region	PS <sub>max</sub> ( $\mu\text{g O}_2 \text{ m}^{-2} \text{ s}^{-1}$ )		$\alpha$ ( $\text{g O}_2/\text{mol quanta PAR}$ )		$\beta'$ ( $\mu\text{g O}_2 \text{ m}^{-2} \text{ s}^{-1}$ )		I <sub>s</sub> ( $\mu\text{mol quanta m}^{-2} \text{ s}^{-1}$ )	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
West Branch Delaware	WOH	67.74	33.78	0.310	0.109	-35.93	10.80	251	164
Bush Kill		73.85	33.87	0.473	0.108	-53.11	22.72	170	105
Schoharie		9.62	59.06	0.581	0.380	-29.99	22.91	74	14
Esopus		74.33	47.57	0.415	0.271	-57.61	33.18	267	205
Neversink		-78.28	3.06	0.244	0.064	-95.44	17.76	334	101
Rondout	EOH	84.72	15.32	0.629	0.177	-23.61	16.58	144	65
Middle Branch Croton		-12.78	84.22	0.667	0.333	-67.89	20.78	106	42
Muscoot		-19.29	10.01	0.773	0.443	-27.63	5.88	26	5
Cross		24.04	2.50	0.311	0.190	-21.04	4.18	126	93
Kisco		4.14	11.43	0.153	0.059	-7.92	6.72	49	19
<b>WOH region</b>		<b>38.66</b>	<b>63.24</b>	<b>0.442</b>	<b>0.15</b>	<b>-49.28</b>	<b>26.17</b>	<b>207</b>	<b>95</b>
<b>EOH region</b>		<b>-0.97</b>	<b>19.38</b>	<b>0.476</b>	<b>0.292</b>	<b>-31.12</b>	<b>25.85</b>	<b>77</b>	<b>47</b>

(Fig. 5). Except for Middle Branch Croton, EOH streams ranked lower than WOH streams on the basis of CR<sub>24</sub>, as they did for GPP. Mean CR<sub>24</sub> was significantly greater in Bush Kill, Neversink, and Esopus than in Kisco (ANOVA and Tukey's test:  $p \leq 0.05$ ). During low-flow years, CR<sub>24</sub> was significantly greater in Esopus, Bush Kill, and Neversink than in Kisco, and CR<sub>24</sub> was significantly greater in Esopus than in Muscoot (ANOVA and Tukey's test,  $p \leq 0.05$ ).

CR<sub>24</sub> was not correlated with temperature, presumably because the range of temperatures was relatively narrow during the study. CR<sub>24</sub> was negatively correlated with glucose and with periphyton organic matter, both of which were greater in EOH streams, and positively correlated with discharge, PAR, and total and ultrafine (<10  $\mu\text{m}$ ) suspended solids (Appendix 2). In addition, CR<sub>24</sub> was correlated positively with GPP and  $V_f$  values for NH<sub>4</sub>, glucose, and arabinose. Greater nutrient use is consistent with higher respiration rates. CR<sub>24</sub> was negatively correlated with indicators of human impact, such as population density and % urban land use, and positively correlated with % forested land use. CR<sub>24</sub> also was negatively correlated with the molecular tracers HHCB and AHTN, and with several PAH tracers. These correlations were consistent with lower respiration rates in streams where human impacts were concentrated.

Overall, metabolism in every study stream was dominated by respiration, indicating a net consumption of energy at the times measurements were made (Fig. 6A). NDM values were negative for all streams in all years except that NDM was slightly positive in

Rondout (2001) perhaps because Rondout was still recovering from the storm scour of 2000. However, by 2002, metabolism in Rondout also was dominated by respiration. With the exception of Middle Branch Croton and Rondout, NDM values were more negative in WOH streams, where CR<sub>24</sub> was higher, than in EOH streams. Nevertheless, neither 3-y mean nor low-flow year NDM values differed among streams (ANOVAs,  $p > 0.05$ ).

The highest mean GPP/CR<sub>24</sub> ratio occurred in Rondout (0.92), whereas the remaining streams had ratios  $\leq 0.6$  and 3 EOH streams had ratios of only  $\sim 0.2$  (Fig. 6B). GPP/CR<sub>24</sub> was significantly higher in Rondout than in Kisco, Middle Branch Croton, and Muscoot, and GPP/CR<sub>24</sub> was significantly higher in West Branch Delaware than in Muscoot (ANOVA and Tukey's test,  $p < 0.05$ ). GPP/CR<sub>24</sub> for low-flow years was significantly higher in Rondout, Schoharie, and West Branch Delaware than in Muscoot, and GPP/CR<sub>24</sub> was significantly higher in Rondout than in Middle Branch Croton (ANOVA and Tukey's test,  $p < 0.05$ ).

NDM was correlated with only 2 environmental and 1 metabolism variables (Appendix 2). GPP/CR<sub>24</sub> was positively correlated with PAR and negatively correlated with SKN, TKN, glucose, DON, and TA (Appendix 2), all of which were greater in EOH streams than in WOH streams. GPP/CR<sub>24</sub> was negatively correlated with watershed landscape variables related to urbanization and positively correlated with watershed area and % total forested land use (Appendix 2).

MLR generated a model that explained  $\sim 95\%$  of the variance in GPP on the basis of PAR,  $V_f$ -NH<sub>4</sub>,

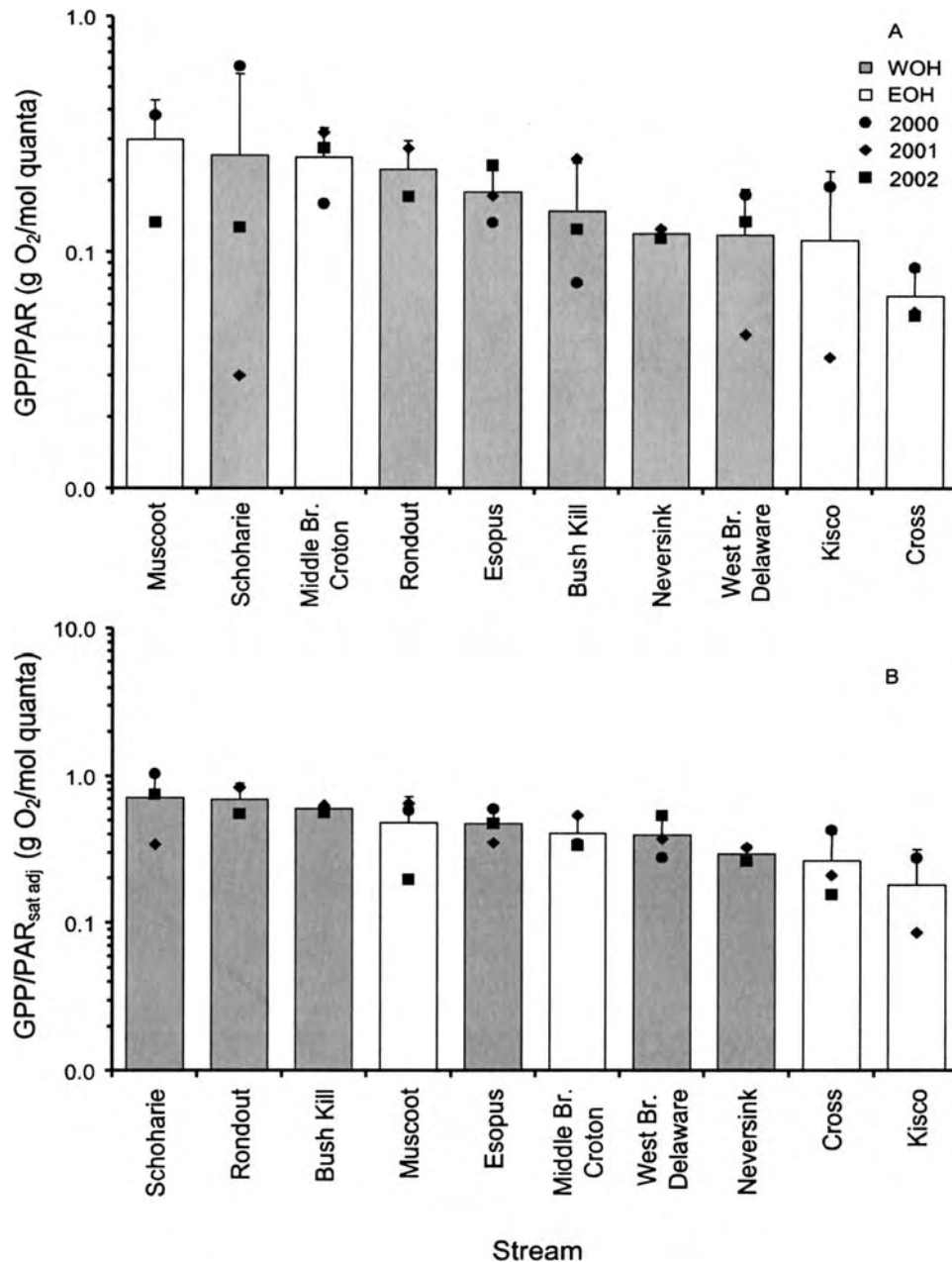


FIG. 4. Log plots of gross primary productivity (GPP) normalized for total daily photosynthetically active radiation (PAR) (GPP/ PAR) (A) and for saturating PAR ( $GPP/PAR_{sat\ adj}$ ; see text for explanation) (B) in 10 streams in New York City drinking-water-supply watersheds. Bars show the 3-y mean ( $\pm 1$  SD), and symbols indicate annual means. EOH = east of Hudson River, WOH = west of Hudson River, Br. = branch.

periphyton chlorophyll *a* standing stock, and substratum composition (Table 5) and a model that explained ~83% of the variance in the absolute value of CR<sub>24</sub> on the basis of  $V_f$ -NH<sub>4</sub> and periphyton organic matter standing stock. MLR generated a model that explained ~83% of the variance in NDM on the basis of periphyton chlorophyll *a* standing stock,  $V_f$ -arabinose, and mean water temperature and a model that explained 95% of the variance in GPP/CR<sub>24</sub> on the

basis of chlorophyll *a* standing stock, PAR, and concentrations of glucose and TKN. The residuals from the NDM equation were positively correlated with caffeine concentrations (Aufdenkampe et al. 2006).

#### Ordination analyses

*RDA model and variance partitioning.*—Four watershed landscape variables and 6 instream variables

TABLE 4. Water-column metabolism as a fraction of total ecosystem metabolism in 10 streams in New York City drinking-water-supply watersheds. GPP = gross primary productivity.

Stream	Water-column GPP (g O <sub>2</sub> m <sup>-2</sup> h <sup>-1</sup> )		Whole-stream GPP (g O <sub>2</sub> m <sup>-2</sup> h <sup>-1</sup> )		Water-column GPP/ whole-stream GPP (%)	
	Mean	SD	Mean	SD	Mean	SD
West Branch Delaware	0.0233	0.0280	0.2820	0.2444	5.91	5.06
Bush Kill	0.0032	0.0081	0.3923	0.3024	3.49	6.75
Schoharie	0.0004	0.0004	0.2206	0.0921	0.18	0.12
Esopus	-0.0023	0.0017	0.4094	0.2404	-0.49	0.21
Neversink	0.0002	0.0012	0.2393	0.1803	1.43	2.69
Rondout	-0.0004	0.0014	0.3652	0.0723	-0.08	0.37
Middle Branch Croton	0.0033	0.0033	0.1627	0.1113	3.04	3.11
Muscocot	0.0003	0.0007	0.0577	0.0301	0.67	1.20
Cross	0.0080	0.0131	0.0868	0.0271	9.37	15.98
Kisco	0.0002	0.0008	0.0333	0.0219	3.42	6.86

contributed significantly (Monte Carlo permutation test,  $p < 0.1$ ) to an RDA model explaining the variances of metabolism and periphyton standing stock variables. All canonical eigenvalues (axes) together accounted for 71.9% of the unconstrained variance in metabolism variables with 31.5% and 22.4% loading on axis 1 and 2, respectively. Percent residential land use and instream PAR during the metabolism experiments provided the greatest explanatory power among the watershed landscape and instream variables, respectively. In general, instream

variables explained more of the constrained variance (47%) than watershed landscape variables (28%). The interaction between the watershed landscape and instream variables also was an important source of explained variance (25% of constrained variance).

CIA.—The first 2 factors of a PCA using 8 metabolic and periphyton standing stock variables measured from 10 sites in 3 y (30 sites – 2 outliers removed = 28 sites) accounted for 69.2% of the variance in the data matrix (F1 = 38.5%, F2 = 30.7%; Fig. 7A). The 1<sup>st</sup> 2 factors of the PCA using 10 environmental variables

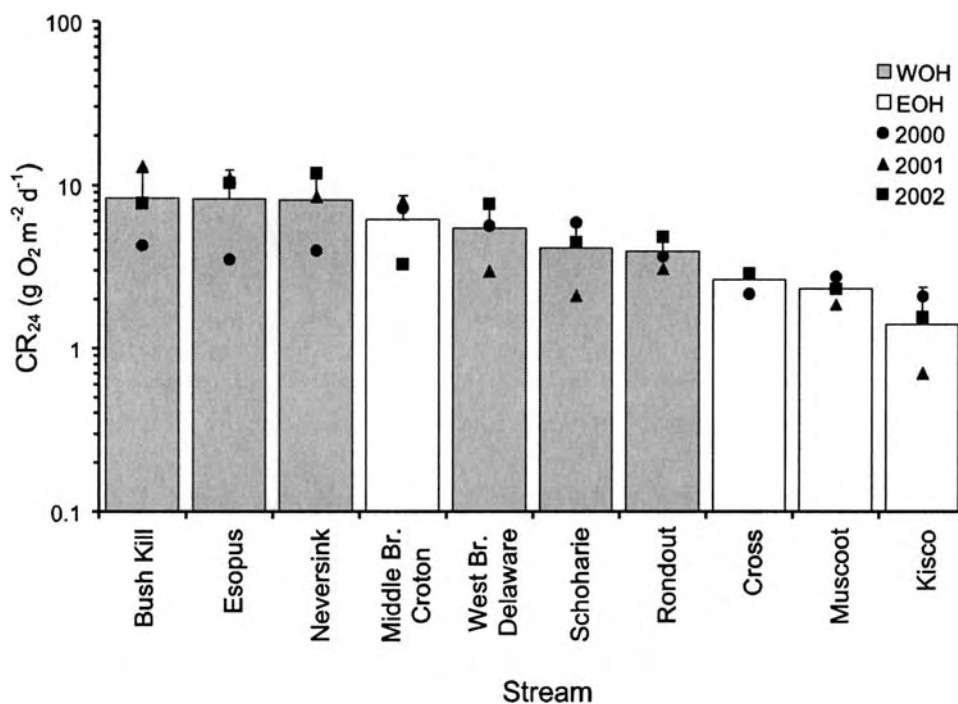


FIG. 5. Log plot of 24-h community respiration ( $CR_{24}$ ) in 10 streams in New York City drinking-water-supply watersheds. Bars show the 3-y mean (+1 SD), and symbols indicate annual means. EOH = east of Hudson River, WOH = west of Hudson River, Br. = branch.

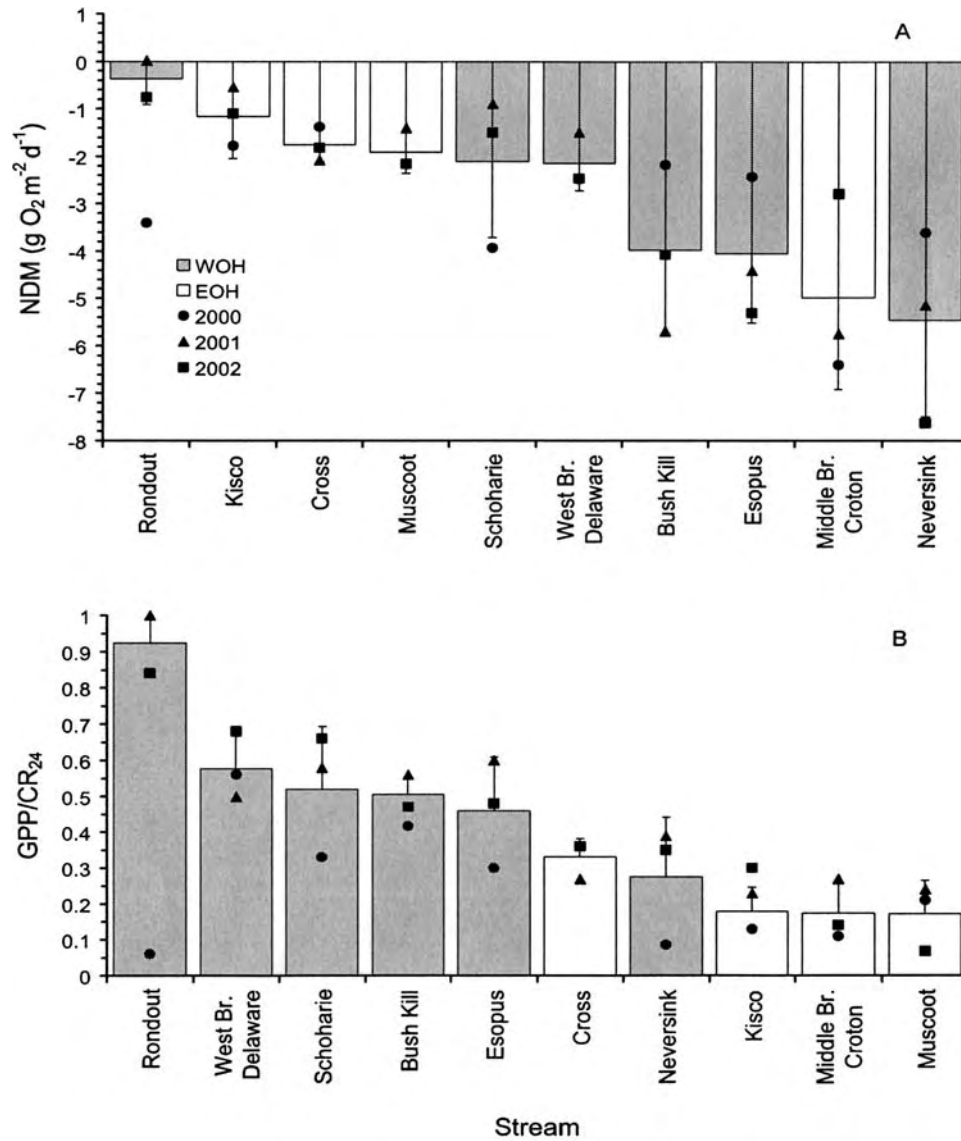


FIG. 6. Balance of gross primary productivity (GPP) and community respiration (CR<sub>24</sub>) expressed as net daily metabolism (GPP - CR<sub>24</sub> = NDM) (A) and as a ratio (GPP/CR<sub>24</sub>) (B) in 10 streams in New York City drinking-water-supply watersheds. Bars show the 3-y mean (±1 SD), and symbols indicate annual means. EOH = east of Hudson River, WOH = west of Hudson River, Br. = branch.

describing the same sites accounted for 55.7% of the variance in the data matrix (F1 = 34.9%, F2 = 20.8%; Fig. 7B). The CIA maximized the covariance between these 2 PCAs, such that 93% of the covariance between the analyses was projected on F1 and F2. A Monte Carlo permutation test (iterated 1000 times) yielded no randomly extracted covariance projections that were better than the solution originally obtained (*p* < 0.001). The correlation coefficients between metabolism and environment ordinations were *r* = 0.85 and *r* = 0.63 for F1 and F2 axes, respectively.

Higher rates of GPP and CR<sub>24</sub> and higher GPP/CR<sub>24</sub> ratios were associated with the positive F1 dimension, and higher periphyton standing stocks were associated

with the positive F2 dimension (Fig. 7A). Environmental vectors associated with the F1 dimension were PAR, watershed-scale % residential land use, and stream DOC concentrations (Fig. 7B). Mean stream temperature, number of point-source discharges, reach-scale % farmstead and % cropland land use (as 1k-FMCR in Fig. 7A), and watershed-scale % coniferous forest together defined the environmental F2 axis (Fig. 7B; see appendix 2 in Blaine et al. 2006 for variable abbreviations).

In general, EOH sites were distinctly different than WOH sites based on both metabolism and environmental variables (Fig. 7C). EOH sites had lower rates of metabolism, higher % residential land use, and

TABLE 5. Multiple linear regression (MLR) models for gross primary productivity (GPP;  $p = 0.0004$ ), 24-h community respiration ( $CR_{24}$ ;  $p = 0.0009$ ), net daily metabolism (NDM;  $p = 0.0028$ ), and GPP/ $CR_{24}$  ( $p = 0.0005$ ) as functions of environmental (physicochemical: this study, Dow et al. 2006, Kaplan et al. 2006, Newbold et al. 2006; biological: Kratzer et al. 2006) and periphyton biomass (this study) variables in 10 streams in New York City drinking-water-supply watersheds. Coefficients are given for significant ( $p < 0.05$ ) correlations among residual variances from the MLR analyses and watershed landscape variables (Arscott et al. 2006) and concentrations of molecular tracers (Aufdenkampe et al. 2006).  $\beta$  = standardized partial regression coefficient,  $V_f$  = nutrient uptake velocity, PAR = photosynthetically active radiation, TKN = total Kjeldahl N concentration, OM = weighted periphyton organic matter, chl  $a$  = weighted periphyton chlorophyll  $a$ ,  $C_{bkgd}$  = background concentration.

Dependent variable	MLR models				Correlations of residuals		
	Coefficient	Independent variable	$\beta$	Cumulative adjusted $R^2$	Variable	$r$	$p$
$\log_{10}(\text{GPP})^a$	0.592	$\log_{10}(\text{PAR})$	0.654	0.745			
	0.931	$\log_{10}(\sum \text{cobble} + \text{boulders})$	0.256	0.854			
	0.610	$\log_{10}(\text{chl } a)$	0.216	0.912			
	0.772	$\log_{10}(V_f - \text{NH}_4)$	0.264	0.954			
	-2.273						
$\log_{10}(\text{CR}_{24})^b$	1.212	$\log_{10}(V_f - \text{NH}_4)$	0.705	0.681			
	-0.628	$\log_{10}(\text{OM})$	-0.413	0.829			
	2.897						
$\log_{10}(\text{NDM} + 11)^b$	-0.509	$\log_{10}(V_f - \text{arabinose})$	-0.826	0.428	Caffeine	0.82	0.002
	0.481	$\log_{10}(\text{chl } a)$	0.798	0.627			
	-0.754	$\log_{10}(\text{temperature})$	-0.544	0.834			
	0.086						
$\log_{10}(\text{GPP}/\text{CR}_{24})^b$	0.452	$\log_{10}(\text{PAR})$	0.839	0.558			
	1.000	$\log_{10}(\text{chl } a)$	0.631	0.753			
	-0.412	$\log_{10}(\text{TKN})$	-0.616	0.850			
	0.351	$\log_{10}(\text{glucose})$	0.488	0.949			
	-3.464						

<sup>a</sup> Additional variables used in the GPP analysis were those used in the chlorophyll analysis (see Table 2 footnote) with the deletion of GPP/ $\text{PAR}_{\text{sat adj}}$  and the inclusion of weighted periphyton and total chl  $a$  and OM, and seston particulate P and N

<sup>b</sup> Additional variables included in the  $CR_{24}$ , NDM, and P/R analyses included  $V_f$  and  $C_{bkgd}$  concentrations of arabinose and glucose

higher DOC concentrations than WOH sites. WOH sites had higher rates of metabolism, higher GPP/ $CR_{24}$ , higher watershed-scale % forested land use, and larger and more open-canopied streams with greater PAR than EOH sites. Periphyton and total chlorophyll  $a$  standing stocks and stream temperatures were lower in 2000 than in other years at many sites, probably because of higher-than-average rainfall during 2000 (Dow et al. 2006). Sites were arrayed on the basis of environmental variables from those with closed canopies (EOH) to those with open canopies (WOH) and, within each region, the least-impacted sites tended to occur to the right of each cluster. Sites were arrayed similarly on the basis of metabolism variables but with slightly less clarity. Interannual variability in flow tended to be reflected in separation of sites on the basis of high- vs low-flow years.

## Discussion

### *Rates of metabolism in mid-Atlantic to New England streams*

Metabolic rates measured in our study were within the range of values obtained between mid-April and

October using an open-system technique in other streams of similar size on the east coast of the US between North Carolina and New Hampshire (Table 6). Rates of GPP were similar among the larger streams ( $\geq 15$  m wide; discharge  $\geq 0.75$  m<sup>3</sup>/s) despite differences in latitude, perhaps because incident PAR saturated photosynthesis in all of them. GPP in WOH and EOH streams was similar to GPP in meadow and forested reaches, respectively, of 6 Piedmont streams in southeastern Pennsylvania (Bott et al. 2006) in which paired reaches on each stream differed only in riparian-zone management.

The primary control on GPP in many streams appears to be riparian-zone vegetation (Bunn and Davies 2000), and a closed tree canopy during the warm season reduces GPP (Young and Huryn 1999, Hill and Dimick 2002). Study streams were smaller and tree-canopy densities were greater in the EOH region (90–93% closed canopies for all streams except Cross [73%]) than in the WOH region (56–68% closed canopies), resulting in lower PAR at EOH sites than at WOH sites. Light obviously influences GPP, but the high rates of GPP reported in Table 6 tended to occur in reaches impacted by wastewater effluents (e.g.,

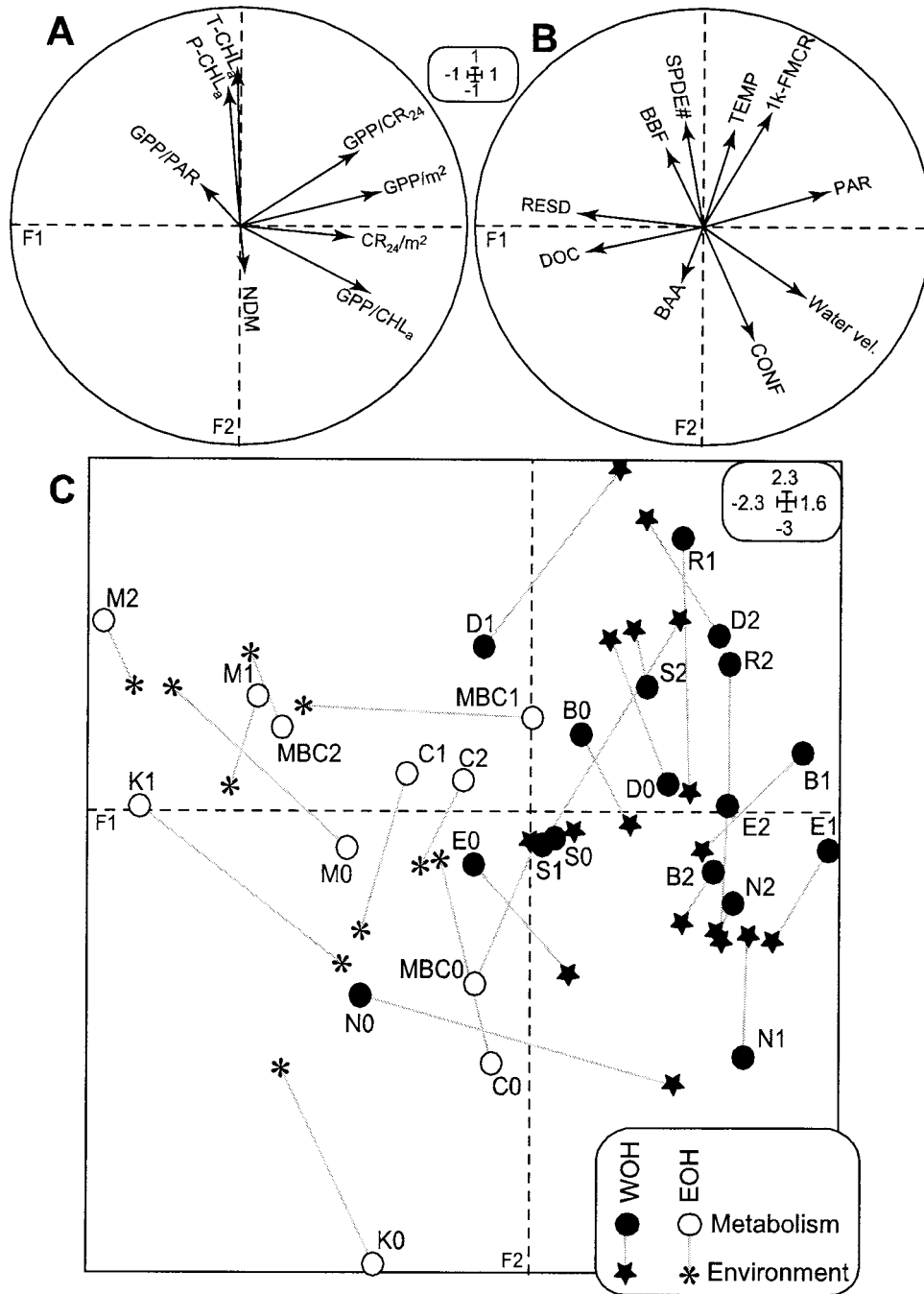


FIG. 7. Results from Co-inertia Analysis showing the ordination of metabolism (A) and environmental (B) vectors, and a distribution of sites/year defined by both metabolism and environment scores in 2-dimensional space (C). Each site/year is plotted twice, once on the basis of metabolism scores and once on the basis of environmental scores, and the symbols are linked by lines. WOH = west of Hudson River, EOH = east of Hudson River sites, B = Bush Kill, D = West Branch Delaware River, E = Esopus Creek, N = Neversink River, R = Rondout Creek, S = Schoharie Creek, C = Cross River, K = Kisco River, M = Muscoot River, MBC = Middle Branch Croton River. Sampling years are indicated as a single digit after the site letter code. 0 = 2000, 1 = 2001, 2 = 2002. GPP = gross primary productivity, CR<sub>24</sub> = 24-h community respiration, T-CHL = total chlorophyll *a*, P-CHL = periphyton chlorophyll *a*, NDM = net daily metabolism, PAR = photosynthetically active radiation. See appendix 2 in Blaine et al. (2006) for environmental variable abbreviations (except 1k-FMCR = reach-scale % farmstead + % cropland; water vel = water velocity). Panel insets show axis scales.

Raritan River, New Jersey; Flemer 1970) and lowest rates occurred in low-nutrient systems (e.g., Baker River, New Hampshire, Hornberger et al. 1977; mountain streams in Virginia and North Carolina, Hoskin 1959).  $CR_{24}$  tended to be lower in EOH streams than in the streams used for comparison, but  $CR_{24}$  was similar among WOH streams and the other streams in Table 6.

#### *Factors controlling stream metabolism and algal biomass*

Most ecosystem metabolism occurred on or in the streambed with little activity attributable to the water column. The greater water-column activity in Bush Kill, Cross, Middle Branch Croton, and Neversink during 2000 than during 2001 and 2002 (low-flow years), may have been associated with particulates scoured from the streambed or introduced into the stream during storms in 2000. In contrast, greater water-column activity in Kisco and West Branch Delaware during one or both of the low-flow years may have reflected development of phytoplankton communities. Year-to-year differences in the West Branch Delaware and Neversink may have been related, in part, to seasonality because sampling times differed between normal and low-flow years. Macrophytes were most common in West Branch Delaware, the stream most heavily impacted by agriculture, but GPP in the West Branch Delaware was similar to GPP elsewhere, at least at the time of our study. In agreement with our study, macrophytes contributed less to ecosystem primary productivity than benthic algae in some other systems, e.g., the Fort River, Massachusetts (Fisher and Carpenter 1976), and the Jackson River, Virginia (TLB, unpublished data).

Instream and riparian-influenced physical, chemical, and biological variables accounted for most variability in GPP and  $CR_{24}$ . In the MLR analyses, NDM was the only metabolism variable with residual variance that was correlated with watershed landscape variables or molecular tracers, and those correlations pointed to fecal pollution of human origin as an influence on metabolism. The residuals from the MLR models for chlorophyll *a* and organic matter standing stocks were correlated with some hydrocarbon tracers and with % orchard land use, respectively. The tracers were indicative of combustion and petroleum sources. The correlation with orchards was unexpected, but may have been related to chemicals associated with that land use (Phillips et al. 2002).

The significant negative correlations of GPP, GPP/PAR, and GPP/PAR<sub>sat adj</sub> with the fragrance materials HHCB and AHTN and several PAHs were consistent with the finding of lower productivity in the subur-

banized EOH streams. Muscoot had the highest chlorophyll *a* standing stock among the EOH streams and had high concentrations of most nutrients, but GPP was low in the Muscoot. On the other hand, GPP/PAR was relatively high in Muscoot (Fig. 4A), so its low GPP might be attributable to low light intensities. Kisco had the 2<sup>nd</sup> highest concentrations of many nutrients (NO<sub>3</sub>-N, SRP, TDP) but ranked lowest in GPP, even after normalization for both PAR and chlorophyll *a* standing stock in 2001, suggesting impairment of metabolic function for other reasons.

$CR_{24}$  generally was higher in WOH streams than in EOH streams, but  $CR_{24}$  in the Middle Branch Croton (located EOH) was within the range for WOH streams. Hyporheic respiration can make a significant contribution to total system respiration in some streams (Grimm and Fisher 1984, Mulholland et al. 1997). However, streams in our study with high  $CR_{24}$  (including Middle Branch Croton) tended to have low transient storage volume (Newbold et al. 2006), a measure of the extent of the hyporheic zone. Thus, it is unlikely that hyporheic respiration made a significant contribution to total system respiration in Middle Branch Croton. It is more likely that the elevated respiration rates in Middle Branch Croton were related to leaf-pack accumulations at the time of some of our measurements.

$CR_{24}$  was strongly correlated with the  $V_f$ -values of NH<sub>4</sub>, glucose, and arabinose (Newbold et al. 2006). In contrast, Meyer et al. (2005) found a correlation of NH<sub>4</sub> uptake only with total metabolism (GPP + CR). It was surprising that  $CR_{24}$  was not higher in EOH streams, given that baseflow concentrations of glucose and BDOC tended to be high there (Kaplan et al. 2006). Like GPP,  $CR_{24}$  may have been impaired by pollution in some of the EOH streams.

Respiration exceeded photosynthesis in all of our study streams, including the open-canopied WOH streams. The nearly 2-y return of Rondout to a heterotrophic condition following the scour event of 2000 may exemplify the recovery trajectory of metabolism from severe storm disturbance in a mid-sized stream. Thus, stream energy budgets were dependent on inputs of allochthonous organic matter, a result that is consistent with data for numerous other streams. Note, however, that a heterotrophic status does not mean that algae are unimportant in the food web because macroinvertebrates may preferentially ingest algae over more abundant detrital foods (e.g., Bunn et al. 1999, Finlay et al. 2002, McCutchan and Lewis 2002).

#### *Potential effects of contaminants on metabolism*

Contamination by toxic compounds is a likely explanation for impaired function in the Kisco River,

TABLE 6. Comparison of mean ( $\pm 1$  SD when available) values for gross primary productivity (GPP) and community respiration (CR) in similarly sized streams in the eastern US from Massachusetts to North Carolina. Metabolic rates were determined using an open-system method during warm weather (usually late June–October). Data reported in the original publications were converted to  $O_2$  units using a photosynthetic quotient of 1.2 or a respiratory quotient of 0.85. Data reported as net primary productivity (NPP) were converted to GPP using a NPP/GPP ratio of 0.536 (McTammany et al. 2003). – indicates data not available.

Stream	State	GPP ( $g\ O_2\ m^{-2}\ d^{-1}$ )	CR ( $g\ O_2\ m^{-2}\ d^{-1}$ )	Width (m)	Discharge ( $m^3/s$ )	Reference	Comments
West Branch Delaware River	New York	3.26 $\pm$ 1.85	5.41 $\pm$ 2.34	19.56	1.87	This study	14% agriculture (22% including pasture); 62% forest
Bush Kill	New York	4.32 $\pm$ 2.67	8.30 $\pm$ 4.39	12.99	1.67	This study	2% agriculture (3.5% including pasture); 86% forest
Esopus Creek	New York	4.17 $\pm$ 2.83	8.22 $\pm$ 4.11	20.65	3.20	This study	<1% agriculture; 95% forest
Schoharie Creek	New York	2.02 $\pm$ 0.86	4.13 $\pm$ 1.90	22.47	0.46	This study	<1% agriculture (2% including pasture); 89% forest
Neversink River	New York	2.58 $\pm$ 1.98	8.05 $\pm$ 3.90	18.65	1.30	This study	<1% agriculture; 97% forest
Rondout Creek	New York	3.57 $\pm$ 0.69	3.94 $\pm$ 1.23	17.19	2.12	This study	<1% agriculture; 97% forest
Middle Branch Croton River	New York	1.13 $\pm$ 0.97	6.12 $\pm$ 2.52	7.83	0.14	This study	16% urban; 63% forest
Muscoot River	New York	0.39 $\pm$ 0.21	2.31 $\pm$ 0.45	6.76	0.06	This study	26% urban; 45% forest
Cross River	New York	0.86 $\pm$ 0.14	2.63 $\pm$ 0.41	6.18	0.11	This study	11% urban; 66% forest
Kisco River	New York	0.23 $\pm$ 0.10	1.39 $\pm$ 0.98	9.24	0.24	This study	22% urban; 60% forest
Fort River	Massachusetts	2.61 $\pm$ 1.51	4.67 $\pm$ 2.47	14	0.28	Fisher and Carpenter 1976	Agriculture and forest, mild residential development, forested riparian zone
Raritan River site 1	New Jersey	4.1 $\pm$ 1.3	4.4 $\pm$ 0.5	15	0.4	Flemer 1970	Control reach
Raritan River site 2	New Jersey	11.3 $\pm$ 4.3	9.1 $\pm$ 2.5	19	1.0	Flemer 1970	Activated sludge treatment plant discharge, forested riparian zone
Raritan River site 3	New Jersey	11.9 $\pm$ 7.0	9.1 $\pm$ 1.5	14	0.8	Flemer 1970	Activated sludge treatment plant discharge, forested riparian zone
Pennsylvania Piedmont streams (forested riparian zone) <sup>§</sup>							
Birch Run	Pennsylvania	0.62 $\pm$ 0.27 <sup>a</sup>	5.45 $\pm$ 5.41	6.27	0.076	Bott et al. 2006	
Buck and Doe Run	Pennsylvania	1.47 $\pm$ 0.33 <sup>b</sup>	3.05 $\pm$ 0.62	15.91	0.744	Bott et al. 2006	
Doe Run at Wisters	Pennsylvania	1.65 $\pm$ 0.51 <sup>c</sup>	4.92 $\pm$ 3.61	7.26	0.176	Bott et al. 2006	
Birch Run at Fishers	Pennsylvania	1.02 $\pm$ 0.14 <sup>d</sup>	3.30 $\pm$ 2.03	5.29	0.120	Bott et al. 2006	
Pocopson Creek	Pennsylvania	1.78 $\pm$ 1.94 <sup>c</sup>	2.68 $\pm$ 2.19	7.78	0.139	Bott et al. 2006	
White Clay Creek	Pennsylvania	1.85 $\pm$ 1.61 <sup>e</sup>	3.12 $\pm$ 1.37	4.97	0.081	Bott et al. 2006	
Pennsylvania Piedmont streams (meadow reaches) <sup>§</sup>							
Birch Run	Pennsylvania	3.57 $\pm$ 1.16 <sup>a</sup>	4.28 $\pm$ 1.99	2.03	0.066	Bott et al. 2006	
Buck and Doe Run	Pennsylvania	4.97 $\pm$ 1.04 <sup>b</sup>	8.33 $\pm$ 0.99	11.43	0.535	Bott et al. 2006	
Doe Run at Wisters	Pennsylvania	5.29 $\pm$ 1.12 <sup>c</sup>	5.06 $\pm$ 1.35	5.73	0.168	Bott et al. 2006	
Birch Run at Fishers	Pennsylvania	2.15 $\pm$ 2.02 <sup>f</sup>	3.06 $\pm$ 1.35	4.05	0.144	Bott et al. 2006	
Pocopson Creek	Pennsylvania	2.60 $\pm$ 0.34 <sup>c</sup>	3.89 $\pm$ 0.84	4.79	0.136	Bott et al. 2006	
White Clay Creek	Pennsylvania	2.01 $\pm$ 1.06 <sup>e</sup>	2.78 $\pm$ 1.28	2.95	0.076	Bott et al. 2006	
Sandy Creek	North Carolina	1.32	4.10	–	–	Hoskin 1959	0.3 m deep, unpolluted, drains forest and fields
Eno River	North Carolina	2.40	5.63	–	–	Hoskin 1959	–
Little River	North Carolina	1.28	5.56	–	–	Hoskin 1959	–
Sinking Creek	Virginia	9.36	17.20	–	–	Hoskin 1959	Limestone, agriculture, valley farms
Stirrup-Iron Creek	Virginia	0.52	1.88	–	–	Hoskin 1959	Igneous rocks
Little River	North Carolina	1.24	5.27	–	–	Hoskin 1959	–

TABLE 6. Continued.

Stream	State	GPP (g O <sub>2</sub> m <sup>-2</sup> d <sup>-1</sup> )	CR (g O <sub>2</sub> m <sup>-2</sup> d <sup>-1</sup> )	Width Discharge (m <sup>3</sup> /s)	Reference	Comments
Mechums River	Virginia	1.45 ± 1.19	2.87 ± 1.40	16	Hornberger et al. 1977	Downstream of town and agriculture; point-source and nonpoint-source discharges
South Fork Rivanna River	Virginia	2.13 ± 1.07	3.40 ± 1.37	26	Hornberger et al. 1977	Downstream of reservoir
Rivanna River	Virginia	2.11 ± 1.17	5.13 ± 3.34	36	Hornberger et al. 1977	Downstream of Charlottesville, sewage treatment plant impacts
South River	Virginia	2.03 ± 0.89	5.31 ± 4.55	11	Hornberger et al. 1977	Agricultural basin
Rappahannoch River	Virginia	6.08 ± 2.86	7.32 ± 2.26	180	Hornberger et al. 1977	Relatively unimpacted, largely forested
Baker River	New Hampshire	0.45 ± 0.17	1.92 ± 0.60	18	Hornberger et al. 1977	Clean, low-nutrient system
Little Tennessee River site 1	North Carolina	1.15	4.3	18.3	McIlammany et al. 2003	Forested
Little Tennessee River site 2	North Carolina	1.21	3.07	17.2	McIlammany et al. 2003	Forested
Little Tennessee River site 3	North Carolina	2.59	3.35	46.3	McIlammany et al. 2003	Agricultural basin, forested riparian zone
Little Tennessee River site 4	North Carolina	3.57	3.76	40.5	McIlammany et al. 2003	Agricultural basin, forested riparian zone

<sup>a</sup> Mean ± 1 SD of 2 estimates, 6 to 7 d each

<sup>b</sup> Mean ± 1 SD over 6 d

<sup>c</sup> Mean ± 1 SD of 2 estimates, 6 d each

<sup>d</sup> Mean ± 1 SD of 2 estimates, 7 and 9 d each

<sup>e</sup> Mean ± 1 SD of 4 estimates, 1 to 7 d each

<sup>f</sup> Mean ± 1 SD of 2 estimates, 2 and 7 d each

<sup>g</sup> Light agriculture in watershed, no direct agricultural impacts

where mean baseflow concentrations of the 5 most toxic PAHs, benzo(a)pyrene (BAP), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(a)anthracene (BAA), and chrysene (CHR) were high ( $>0.002 \mu\text{g/L}$ ). In 2002, concentrations of these PAHs in Kisco were the highest concentrations measured anywhere in the Project ( $>0.1 \mu\text{g/L}$ ; Aufdenkampe et al. 2006), with the concentration of BAA exceeding the chronic toxicity guidance value ( $0.03 \mu\text{g/L}$ ) and approaching the acute toxicity value ( $0.23 \mu\text{g/L}$ ) set by New York State (NYS DEC 1998). PAH concentrations were below concentrations shown to impact algae in laboratory experiments, but only a few such studies have been conducted, and those studies were with individually tested compounds (Warshawsky et al. 1995, Halling-Sorensen et al. 1996, Dijkman et al. 1997, Marwood et al. 1999).

Molecular tracers that are indicators of sewage contamination (i.e., caffeine, fragrance materials, and fecal steroids) also were consistently high in Kisco (Aufdenkampe et al. 2006). Although nontoxic, these tracers are likely to be proxies for unmeasured compounds (e.g., metals, pesticides, herbicides) with known toxicity (Kolpin et al. 2002, Glassmeyer et al. 2005). In fact, Phillips and Bode (2004) found that concentrations of 4 insecticides (diazinon, carbaryl, malathion, and chlorpyrifos) and the herbicide 2,4-D exceeded guidelines for protection of aquatic life in some Kisco samples, although none violated standards for human health. Highest concentrations (and most exceedences) occurred in stormflow samples (Phillips and Bode 2004). During the limited time when we were actually making measurements in Kisco, we twice observed evidence of significant point-source pulses: 1<sup>st</sup> with the specific conductance step (490 to 570  $\mu\text{S/cm}$ ) during our 2002 metabolism experiment (see above) and 2<sup>nd</sup> during a storm on 9 September 2004 in which pH went from 7.1 to 2.9 for 4 h before returning to 7.1 and specific conductance changed from  $\sim 110$  to  $>600 \mu\text{S/cm}$  and back (AKA, unpublished data).

Molecular tracer sampling did not coincide with metabolism studies and data suggests that water-column concentrations of potential toxics in Kisco were highly variable in time, but most toxic compounds have high partitioning coefficients ( $\log K_{\text{OW}}$ ) and bioaccumulation factors (e.g.,  $\log K_{\text{OW}} = 6.44$  for BAP, BBF, and BKF and  $\log K_{\text{OW}} = 5.84$  for fluoranthene and CHR; DelVento and Dachs 2002). A contaminant with  $\log K_{\text{OW}}$  between 5 and 7 poses greater risk of bioconcentration or biomagnification than a compound with  $\log K_{\text{OW}} < 5$  (Baird et al. 2001). Thus, these compounds were likely to be at higher and more constant concentrations in the benthos, where their potential effects on stream metabolism would be

greatest. Measured concentrations of toxics were not high enough to depress metabolism conclusively, but the sum of stresses imposed by measured compounds and unmeasured toxics, including photodegradation products (Warshawsky et al. 1995, Huang et al. 1997, Marwood et al. 1999) interacting with other environmental variables, certainly could have depressed metabolism.

We emphasize that Kisco ranked high in toxicity, but it was not the most contaminated of the 60 sites included in the Project (Arcscott et al. 2006, Aufdenkampe et al. 2006). In addition, other sites in our study may have been influenced by toxics to a lesser extent. Insecticides, herbicides, and fungicides have been detected in Middle Branch Croton (Phillips and Bode 2004). Among WOH streams, Neversink had low  $\text{GPP}/\text{PAR}_{\text{sat adj}}$  consistent with its low chlorophyll *a* standing stocks, and Rondout and Bush Kill had higher  $\text{GPP}/\text{PAR}_{\text{sat adj}}$  values, consistent with relatively high chlorophyll *a* standing stocks. However, West Branch Delaware was anomalous, with high chlorophyll *a* standing stocks but low  $\text{GPP}/\text{PAR}_{\text{sat adj}}$ , perhaps because of chemical impacts. Concentrations of the 5 most toxic PAHs discussed above were higher in West Branch Delaware than in other WOH streams, and these contaminants may have depressed metabolism. In addition, herbicide (atrazine, metolachlor) concentrations were highest in reservoirs receiving drainage from the West Branch Delaware, East Branch Delaware (which includes Bush Kill), and Schoharie watersheds where % agricultural land uses (includes all agricultural land uses listed in table 2 of Dow et al. 2006) were greatest among the study watersheds (Phillips et al. 2000). Atrazine was toxic to algae in laboratory bioassays (Fairchild et al. 1998), although grazing (Muñoz et al. 2001) and light history (Guasch and Sabater 1998) influenced its effects on periphyton. Laursen and Carlton (1999) reported depression of microbial respiration, denitrification, and nitrification in stream sediments by exposure to atrazine. The effective atrazine concentrations in these studies were orders of magnitude greater than concentrations reported in New York field sites, but available data are for receiving reservoirs rather than the tributary streams studied here.

#### *Watershed land use and metabolism*

King et al. (2005) noted that watershed land use is linked indirectly to the stream biota by a “dizzying array” of near-stream and instream factors. CIA pointed to some connections between metabolic and biomass variables and land use. For example,  $\text{GPP}$ ,  $\text{CR}_{24}$ , and  $\text{GPP}/\text{CR}_{24}$  were negatively related to %

residential land use, and chlorophyll *a* standing stocks were positively related to point-source discharge. However, stream size and degree of tree canopy closure are confounding factors in attempts to detect the influence of land use on metabolism in our study because urbanized land use predominated along smaller streams with closed tree canopies, whereas agricultural and forested land uses predominated along larger streams with greater light exposure.

The negative correlations between GPP and landuse variables related to urbanization and positive correlations with % forested land use obtained in our study differ from the results of Meyer et al. (2005), who found no correlations between metabolism variables and indicators of urbanization. These contrasting results were surprising because our EOH study sites had lower percentages of urban characteristics than the sites studied by Meyer et al. (2005). In fact, our sites are probably better described as suburban than urban. The effect of watershed disturbance on metabolism was investigated in 2 other studies (landuse conversion to pasture in Young and Huryn 1999, clearing of vegetation and compaction of soils in Houser et al. 2005). GPP declined in each case, results that were attributed to production of an unstable streambed by eroded soils and to turbidity during storms.

Wilcock (1986) reported that dissolved O<sub>2</sub> saturation values were lower in agriculturally influenced streams compared to nonimpacted streams. Consistent with that observation, West Branch Delaware, the most agriculturally influenced stream studied here, had the widest range of dissolved O<sub>2</sub> saturation values, although extremes were dampened when studies were done in October at temperatures that were nearly 10°C cooler than those occurring during mid-summer. Schoharie also had a fairly wide range of dissolved O<sub>2</sub> saturation values. The Schoharie watershed had less agricultural land use than the West Branch Delaware watershed but had an equally open canopy and a substantially greater proportion of the local land area classified as agricultural (Arscott et al. 2006).

#### *Evaluation of stream condition—structural and functional measures*

Maximum chlorophyll *a* standing stocks probably occurred prior to leafout in some of our study streams, especially those with greatest canopy closure, and lower periphyton standing stocks probably were encountered during our summer sampling than would have been found in early spring. Chlorophyll *a* standing stock was measured for periphyton samples scraped from rocks during spring macroinvertebrate sampling (JKJ, unpublished data). These values are not

strictly comparable to those in our study. However, for purposes of discussion, the chlorophyll *a* standing stock values for our summer samples were 52 to 83% of values obtained in the spring samples in 7 of the 10 streams. Summer values were 16% of spring values in Kisco, 121% of spring values in Rondout, and 139% of spring values in Cross.

Periphyton chlorophyll *a* standing stocks of 100–150 mg/m<sup>2</sup> were considered indicative of nuisance algal growths by Horner et al. (1983) and Welch et al. (1988). Using that criterion, only one stream, the Muscoot, had nuisance periphyton growth. In British Columbia (Nordin 1985) and New Zealand (Zuur 1992) streams, periphyton chlorophyll *a* standing stocks of 50 mg/m<sup>2</sup> are considered protective of recreational uses and standing stocks of 100 mg/m<sup>2</sup> are considered protective of other forms of aquatic life. Dodds (2002) proposed categorizing streams as oligotrophic, mesotrophic, or eutrophic on the basis of chlorophyll *a* standing stocks of <20 mg/m<sup>2</sup>, 20 to 70 mg/m<sup>2</sup>, and >70 mg/m<sup>2</sup>, respectively. Based on 3-y mean chlorophyll *a* standing stocks in our streams, none of our study streams would be considered oligotrophic; Muscoot, Rondout, West Branch Delaware, and Bush Kill would be considered eutrophic, and the remaining streams would be considered mesotrophic.

The range of metabolic values measured in 8 of the 10 streams studied here typify rates expected in streams with minimal or slight impacts, as characterized by macroinvertebrate multimetric index scores (Kratzer et al. 2006). The exceptions were Kisco and Muscoot where urban/suburban infrastructure and measured toxicity were greatest, but even they were not the most seriously compromised streams in the framework of the larger Project (Arscott et al. 2006).

The rates measured in our study provide the first snapshots of algal biomass production and C processing in these streams. Assessments of the impact of improvements to septic systems and institution of best management practices on the landscape on streams draining these critical watersheds can now be based on ecosystem functions, including nutrient spiraling (Newbold et al. 2006), primary productivity, and respiration, in addition to responses of macroinvertebrates communities or water chemistry.

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APPENDIX 1. Mean ( $\pm 1$  SD) values for stream water-chemistry variables not reported elsewhere in this series that were used in data analyses. SKN = soluble Kjeldahl N, TKN = total Kjeldahl N, PN = particulate N, TN = total N, DON = dissolved organic N, PP = particulate P, TP = total P, TSS = total suspended solids, VSS = volatile suspended solids, TSS<sub>10</sub> = ultrafine TSS <10  $\mu\text{m}$ , VSS<sub>10</sub> = ultrafine VSS <10  $\mu\text{m}$ . – indicates only 1 value collected, no SD calculated. All concentrations in mg/L.

Stream	SKN	TKN	PN	TN	DON	PP	TP	TSS	VSS	TSS <sub>10</sub>	VSS <sub>10</sub>
West Branch	0.160	0.246	0.086	1.153	0.145	0.014	0.031	5.503	1.450	0.742	0.135
Delaware (5)	(0.033)	(0.080)	(0.048)	(0.140)	(0.032)	(0.005)	(0.007)	(4.019)	(0.911)	(0.554)	(0.093)
Bush Kill (11)	0.077	0.112	0.035	0.227	0.066	0.002	0.014	2.841	0.829	0.201	0.069
	(0.012)	(0.026)	(0.016)	(0.060)	(0.011)	(0.001)	(0.002)	(0.269)	(0.053)	(0.061)	(0.017)
Schoharie (18)	0.058	0.080	0.023	0.168	0.049	0.001	0.003	1.056	0.547	0.166	0.063
	(0.019)	(0.029)	(0.020)	(0.057)	(0.018)	(0.001)	(0.001)	(0.029)	(0.054)	(0.074)	(0.021)
Esopus (23)	0.047	0.076	0.029	0.183	0.037	0.002	0.008	7.208	3.267	0.339	0.108
	(0.025)	(0.035)	(0.020)	(0.105)	(0.027)	(0.001)	(0.001)	(7.924)	(4.582)	(0.218)	(0.077)
Neversink (29)	0.047	0.094	0.047	0.223	0.040	0.001	0.004	1.379	0.555	0.641	0.207
	(0.049)	(0.105)	(0.056)	(0.171)	(0.048)	(0.001)	(0.004)	(1.516)	(0.394)	(0.798)	(0.231)
Rondout (30)	0.031	0.060	0.028	0.281	0.026	0.001	0.005	0.609	0.348	0.209	0.062
	(0.001)	(0.009)	(0.010)	(0.058)	(0.001)	(0.001)	(<0.001)	–	–	(0.033)	(0.003)
Middle Branch	0.427	0.665	0.238	0.922	0.418	0.033	0.051	5.631	2.599	0.767	0.389
Croton (40)	(0.040)	(0.293)	(0.282)	(0.365)	(0.035)	(0.031)	(0.031)	(5.690)	(2.381)	(1.016)	(0.571)
Muscoot (46)	0.443	0.431	0.001	1.587	0.433	0.008	0.048	1.117	0.614	0.204	0.074
	(0.010)	(0.010)	(0.000)	(0.136)	(0.010)	(0.001)	(0.015)	(0.542)	(0.183)	(0.097)	(0.028)
Cross (52)	0.272	0.396	0.124	0.506	0.264	0.015	0.027	0.672	0.403	0.165	0.060
	(0.046)	(0.201)	(0.155)	(0.307)	(0.048)	(0.018)	(0.071)	(0.815)	(0.470)	(0.176)	(0.062)
Kisco (55)	0.293	0.312	0.023	0.589	0.280	0.008	0.030	0.675	0.446	0.110	0.045
	(0.002)	(0.036)	(0.031)	(0.064)	(0.001)	(0.008)	(0.004)	(0.014)	(0.265)	(0.095)	(0.033)

APPENDIX 2. Individual correlations of metabolic variables with instream physicochemical variables, other metabolic variables, watershed landuse variables, and molecular tracers. Names and abbreviations of molecular tracers are given in Aufdenkampe et al. (2006). Other abbreviations as in Table 2 and Appendix 1. Population density is for year 2000, Cond = specific conductance, OM = weighted periphyton organic matter, chl *a* = weighted periphyton chlorophyll *a*.

Metabolic variable	Environmental variables		Other metabolic variables		Watershed land use		Molecular tracers					
	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i> value				
GPP	PAR	0.880	<0.001	$V_f$ -NH <sub>4</sub>	0.828	0.002	Population density	-0.783	<0.001	BAP	-0.657	0.037
	SKN	-0.782	0.005	CR <sub>24</sub>	0.869	<0.001	Watershed area	0.745	0.011	HHCB	-0.754	0.009
	TKN	-0.704	0.021				% residential	-0.891	<0.001	AHTN	-0.634	0.048
	TDP	-0.637	0.046				% commercial	-0.884	<0.001	FLR	-0.68	0.028
	Glucose	-0.828	0.002				% industrial	-0.672	0.031	BAA	-0.636	0.047
	DON	-0.786	0.005				% other urban	-0.763	0.008	CHR	-0.674	0.031
	TA	-0.785	0.005				% deciduous forest	0.777	0.006	BBF	-0.654	0.038
	Water velocity	0.822	0.002				% mixed forest	0.750	0.010	BKF	-0.658	0.037
	Discharge	0.847	0.001				% wetland	-0.856	<0.001			
	Width	0.748	0.010				Road density	-0.863	<0.001			
	Depth	0.758	0.009									
	Cond	-0.825	0.002									
	CR <sub>24</sub>	PAR	0.695	0.023	$V_f$ - NH <sub>4</sub>	0.847	0.001	Population density	-0.701	0.022	BAP	-0.652
Periphyton OM		-0.655	0.038	$V_f$ - arabinose	0.684	0.027	% residential	-0.683	0.027	HHCB	-0.741	0.012
Glucose		-0.740	0.012	$V_f$ -glucose	0.703	0.021	% commercial	-0.770	0.007	AHTN	-0.700	0.022
TSS		0.716	0.017	GPP	0.869	<0.001	% deciduous forest	0.675	0.030	FLR	-0.732	0.014
TSS <sub>10</sub>		0.669	0.033				% mixed forest	0.666	0.033	BAA	-0.634	0.048
Water velocity		0.711	0.019				% wetland	-0.690	0.025	CHR	-0.662	0.035
Discharge		0.663	0.035				Road density	-0.694	0.024	BBF	-0.652	0.039
Cond		-0.647	0.041							BKF	-0.648	0.041
										soot PAHs	-0.641	0.045
										soot PAHs	-0.634	0.048
GPP/PAR	chl <i>a</i>	0.666	0.033						PAHs	-0.657	0.037	
GPP/ PAR <sub>aat adj</sub>	chl <i>a</i>	0.664	0.034						BAP	-0.660	0.036	
	Glucose	-0.751	0.010						ANT	-0.761	0.008	
	Σ (clay + silt + sand)	-0.660	0.036						FLR	-0.756	0.009	
									BAA	-0.677	0.029	
									CHR	-0.673	0.031	
									BBF	-0.668	0.033	
									BKF	-0.668	0.033	
									soot PAHs	-0.697	0.028	
									PAHs	-0.640	0.045	
NDM	TSS <sub>10</sub>	-0.668	0.033	$V_f$ -arabinose	-0.701	0.021						
	VSS <sub>10</sub>	-0.790	0.005									
GPP/CR <sub>24</sub>	PAR	0.779	0.006				Population density	-0.753	0.010			
	SKN	-0.775	0.006				Watershed area	0.704	0.021			
	TKN	-0.755	0.009				% residential	-0.807	0.003			
	Glucose	-0.641	0.043				% commercial	-0.681	0.028			
	DON	-0.773	0.007				% other urban	-0.668	0.033			
	TA	-0.675	0.030				% wetland	-0.749	0.010			
							% commercial + industrial	-0.675	0.030			
						Road density	-0.742	0.012				
						% total forested	0.634	0.048				