Organic matter transport in New York City drinking-water-supply watersheds

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Abstract. Organic matter (OM) in streams that provide drinking water is a potential energy source for bacterial regrowth in distribution systems and a precursor for disinfection byproducts. Baseflow concentrations of OM were measured over a 3-y period in 60 streams divided evenly between water-supply regions east and west of the Hudson River (EOH or WOH) in New York State. A baseline of OM concentrations in the 2 regions was generated, and land use/cover variables were related to those baseline concentrations. Dissolved organic C (DOC), biodegradable DOC (BDOC), and particulate OM (POM) reflected regional differences in land use and point-source discharges. Three-year mean concentrations for these variables and for total organic C (TOC) were significantly lower in the WOH than in the EOH by factors of 1.5 to 2.3. Size fractionation of POM showed similarities between regions with >70% of particles in the 0.5- to 10-µm size class. DOC made up most of the TOC in both regions, and DOC:POC ratios ranged from 1.7 to 54.4. Stepwise multiple linear regressions revealed that agriculture and forest land uses explained most of the variation in OM concentrations in the WOH, whereas wetlands and point-source discharges, primarily associated with wastewater treatment plants, explained most of the variation in OM concentrations in the EOH. Despite the potential problems from OM for drinking water quality, OM is a natural and important component of stream ecosystems, so its total elimination from watersheds is neither advisable nor possible. Our data from watersheds in the WOH region with high percentages (>97%) of forested land use and from small to mid-sized watersheds in the EOH with no point-source discharges provide lower limits for OM concentrations and targets for best management practices.

Key words: organic matter, dissolved organic carbon, biodegradable dissolved organic carbon, particulate organic carbon, land use, land cover.

Each year, the rivers of the world export $\sim 1 \times 10^{12}$ kg of organic matter (OM) to the oceans (Spitzy and Ittekkot 1991). Most of this OM consists of dissolved organic molecules and dead particulate matter (Wetzel 1995). Collectively, these pools of detrital OM are an important energy source for microorganisms and macroinvertebrates, fueling stream ecosystem metabolism and contributing to stream food webs (sensu Pomeroy 1974, Hall et al. 2000). The concentrations of OM suspended in transport result from the sum of terrestrial and instream inputs and their transforma-

tions in the stream. Inputs of terrestrial OM to streams connect aquatic ecosystems with their watersheds (Hynes 1975), whereas the transport of OM in stream water provides a longitudinal linkage between upstream and downstream reaches and an energy subsidy for downstream community metabolism (Newbold et al. 1982, Webster et al. 1999, Dawson et al. 2001, Kaplan and Newbold 2003).

OM in drinking-water supplies provides precursors for disinfection by-products (DBP) and C and energy sources for bacterial regrowth. DBPs include carcinogens and mutagens generated from reactions of OM with chemical oxidants, such as trihalomethanes and haloacetic acids, following chlorination (Chow et al. 2003) and ketones following ozonation (Matsuda et al. 1992). Biodegradable constituents in the OM pool can promote the growth of heterotrophic bacteria in water-distribution systems and subsequent deterioration of water quality (Escobar et al. 2001, Laurent et al. 2005).

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The US Environmental Protection Agency National Primary Drinking Water Regulations establish maximum contaminant levels for both DBP concentrations and densities of bacteria. Modifications to disinfectant dosing can lead to conflicts in the attempts to reduce chemical and microbiological risks (e.g., high disinfectant levels increase chemical risks but lower microbiological risks and vice versa), but the control of OM is an approach that can reduce both risks simultaneously.

Land use affects stream water concentrations of dissolved and particulate OM, with modifications caused by soil type, climate, and season. (In our paper, land use implies both land use and land cover.) Wetlands are recognized as sources of dissolved organic C (DOC) (Gergel et al. 1999, Elder et al. 2000, Hillman et al. 2004), and forests or forested riparian zones are more retentive than agricultural lands of suspended solids (Johnson et al. 1997, Correll et al. 1999, Jones et al. 2001, Dodds and Whiles 2004), particulate organic C (POC) (Neill et al. 2001, Quinn and Stroud 2002, Thomas et al. 2004), and DOC (Williams et al. 2001, Quinn and Stroud 2002). The effects of watershed urbanization are more equivocal and may increase (Duncan 1999), decrease (Dodds and Whiles 2004), or have no significant impact (Jones et al. 2001) on suspended solids. A tentative link has been found between increased DOC concentrations and urban density and drainage infrastructure (Hatt et al. 2004).

OM was sampled at 60 sites throughout the New York City drinking-water-supply watersheds and concentration patterns were analyzed to: 1) establish regional baseflow concentrations of OM, 2) estimate the magnitudes of temporal and spatial variability in those concentrations, and 3) identify which factors associated with anthropogenic modifications of land use at the watershed scale affect OM concentrations. One rationale for establishing such a baseline is that it can be used in the future to assess the efficacy of best management practices designed to improve source-water quality. Therefore, the concentrations of DOC, biodegradable DOC (BDOC), total suspended solids (TSS), particulate OM (POM), and the size distributions of TSS and POM particles were measured. In addition, the concentrations of the various suspended and dissolved organic C constituents were related to instream processes and land use.

Methods

Study area and sampling regime

The greater New York City (NYC) metropolitan area receives nearly all of its drinking water via an aqueduct system connecting streams and reservoirs north and west of the city. The Croton River headwaters and tributaries to the Kensico Reservoir contribute ~10% to the total volume supplied and are located in the east of Hudson River (EOH) region and just north of the city. The remaining 90% is supplied from headwater streams and reservoirs located in the west of Hudson River (WOH) region ~160 km northwest of the NYC metropolitan area (see fig. 1 in Blaine et al. 2006).

In spring 2000, 30 EOH and 30 WOH stream sites located upstream of the NYC reservoirs were selected for a large-scale enhanced water-quality monitoring project (the Project) conducted by Stroud Water Research Center between 2000 and 2002. Site characteristics are described in detail and their locations are shown in figs 1 and 2 of Arscott et al. (2006). Low population densities, agriculture, and forests typically characterize the WOH region. The EOH region has more natural wetland areas, but also is more impacted by urban/suburban development than the WOH region (Arscott et al. 2006).

DOC, BDOC, TSS, and POM were measured annually at each site during summer baseflow for 3 y. Baseflow conditions were defined operationally (see appendix in Arscott et al. 2006 for details) as relatively constant stream flow, changing <10% over the 24 h preceding sampling, based on either co-located or nearby real-time USGS gauging stations. If gauges did not co-occur with a site, discharge was estimated from discharge–watershed-area regression equations developed independently for groups of watersheds within each region.

Seston.—One seston sample was collected from each site for TSS and POM analyses. A gasoline-powered pump was used to fill ten 5-L polyethylene bottles from the thalweg. One 5-L bottle was reserved for subsequent analysis of TSS. The remaining water, ~45 L, was separated in the field into 3 fractions (<10 μm, 10–20 μm, and >20 μm) by filtering a known volume through a stacked series of 20-μm and 10-μm mesh Nytex® sieves. The material collected on the 20-μm and 10-μm Nytex® sieves was transferred to 250-mL polyethylene bottles by spraying the mesh with deionized water and collecting the transfer water with a funnel. Approximately 5 L of the filtrate that passed through the stacked sieves were saved for further processing. Samples were chilled at 4°C in coolers and processed within 7 d from the time of collection.

Seston samples were filtered to collect different size fractions on OM-free, tared, glass-fiber filters (Whatman GF/F). Filters were dried at 60°C for 48 h for TSS determinations based on dry mass/L. Filters were combusted at 500°C for 2 h, and POM was calculated as ash-free dry mass/L based on the difference

between dry mass (TSS) and ash mass. POM was converted to particulate organic C (POC) when calculating C exports and DOC:POC ratios based on the assumption that POC = 0.45[POM] (Gjessing 1976, Hedges et al. 1986).

Total and biodegradable DOC.—Single samples for DOC and BDOC were collected in glassware that was rendered organic C free by combustion at 500°C for 6 h. Samples were protected from the atmosphere by sealing the collection vessels with persulfate-cleaned Teflon-backed silicone septa (Kaplan 1994). Samples were collected in 500-mL borosilicate bottles that were rinsed twice with site water, filled, capped, and placed in the dark on ice. Within 48 h, the samples were filtered into three 40-mL borosilicate vials for DOC and ten 40-mL borosilicate vials for BDOC analysis. Filtration to remove particles was done with precombusted glass-fiber filters (Whatman GF/F), an acetal-resin syringe-type filter holder, and a polypropylene syringe. Five of the vials for BDOC analyses were fixed with azide to stop any microbial activity, and the DOC concentrations in the water were measured within 1 wk. The other 5 vials were incubated for 28 d at room temperature in the dark to allow the bacterial inoculum in the filtered water to grow and metabolize the BDOC. The water in the vials was then refiltered and DOC concentrations were measured (Kaplan et al. 1994). DOC analyses were done by the Pt-catalyzed persulfate oxidation method using a model 700 or 1010 TOC analyzer (O. I. Analytical, College Station, Texas; Kaplan 1992). Azide blanks were determined for DOC contributions before taking the azide solution into the field, with an acceptance criterion of <0.1 mg C/L. On average, DOC contributions from the azide were 0.023 ± 0.022 mg C/L (mean ± SD, $n = 19$). BDOC was calculated as the difference in DOC of water samples before and after incubation and was not corrected for azide blanks.

Supplemental data

Data generated by other scientists involved in the Project were used in the analyses of DOC, BDOC, and POM patterns. Site characterizations, including land use, population density (summarized at the watershed scale), and annual mean watershed-area-normalized point-source discharges were generated in the landscape template developed to describe study sites (Arscott et al. 2006). Densities of benthic chlorophyll *a* were determined as part of the macroinvertebrate studies (Kratzer et al. 2006), and concentrations of fragrances associated with detergents, fecal steroids, and caffeine were analyzed within a larger study of molecular tracers (Aufdenkampe et al. 2006).

Data analyses

The use of single samples made it possible to achieve a broad spatial coverage of the water-supply watersheds, while field duplicates, collected as part of the quality-assurance plan, provided estimates of precision, expressed as relative % difference (DOC: 2.2 ± 2.7%, $n = 16$; BDOC: 30 ± 37%, $n = 12$; TSS: 23 ± 31%, $n = 9$; POM: 29 ± 32%, $n = 9$).

Data were managed and analyzed with SAS running on a Windows 2000 server (SAS/STAT, version 9.1, SAS Institute, Cary, North Carolina). Statistical significance of all tests was set at $p < 0.05$. Concentration and point-source discharge data were $\log_{10}(x)$ transformed, % data were arcsine square-root(x) transformed, and geometric means were calculated for the molecular tracer data prior to analyses.

OM constituent (DOC, BDOC, POM, and TOC) concentrations were compared between regions and among watersheds within regions using analysis of variance (ANOVA). When means differed significantly, Tukey's Studentized Range test was used to determine which means differed.

Paired *t*-tests were used to examine upstream–downstream trends in concentrations of OM constituents over all 3 y for samples collected within a few days of each other at all sites aligned along the main stems of rivers associated with terminal reservoirs. Because the comparisons were between adjacent sites along the main stems and not multiple comparisons over the entire watershed, *p*-values were not Bonferroni adjusted. The coefficients of variation (CV) associated with the 3-y mean summer baseflow concentrations were used to examine interannual variability of each OM constituent at each site. The influence of baseflow discharge on interannual variability of concentrations of OM constituents was examined using analysis of covariance (ANCOVA).

Spearman Rank Correlations were used to determine whether concentrations of OM constituents were related to landuse variables or to other water-chemistry variables (from the supplemental data sets, see above). Outliers were identified using DFFITS (to identify outliers from their influence on fitted values; Myers 1990). Stepwise multiple linear regressions (MLR) were used to determine the influence of landuse and other water-chemistry variables on concentrations of organic C constituents. Adjusted R^2 values were used in calculating the total R^2 for the MLRs.

Results

Spatial patterns

Regions.—The 3-y mean baseflow concentrations of TOC in the EOH exceeded those in the WOH by 2.3×

TABLE 1. Mean (±1 SD) dissolved organic C (DOC), bioavailable DOC (BDOC), particulate organic matter (POM), and total organic C (TOC = DOC + 0.45[POM]) sampled annually between 2000 and 2002 during summer baseflow in watersheds in the east of Hudson River (EOH) and west of Hudson River (WOH) regions of New York City's drinking-water supply. The number of sites in each region/watershed is shown in parentheses. TSS = total suspended solids, MNC = Muscoot and other sites north of Croton Reservoir, WBC = West Branch Croton River, EMC = East and Middle Branch Croton River, TCS = Titicus, Cross, and Stone Hill rivers, KSC = Kensico Reservoir and other sites south of Croton Reservoir, WBD = West Branch Delaware River, EBD = East Branch Delaware River, SCH = Schoharie River, ESP = Esopus Creek, NVR = Neversink River and Rondout Creek. Significant differences between regions are indicated in bold font. Among watersheds within regions, means with different letters within columns are significantly different ($p < 0.05$).

Region/ watershed	DOC (mg/L)	BDOC		POM		TOC (mg/L)
		(mg/L)	(%DOC)	(mg/L)	(%TSS)	
EOH (30)	**3.50 ± 1.75**	0.43 ± 0.52	**10.3 ± 5.1**	**1.70 ± 1.80**	36.6 ± 8.5	**4.27 ± 2.23**
WOH (30)	**1.53 ± 0.49**	0.29 ± 0.13	**18.3 ± 4.2**	**0.81 ± 0.34**	36.4 ± 11.4	**1.89 ± 0.57**
EOH						
MNC (7)	4.82 ± 2.61	0.83 ± 0.99	13.0 ± 8.2	2.00 ± 2.83[AC]	40.3 ± 7.5	5.71 ± 3.29
WBC (6)	3.43 ± 1.64	0.38 ± 0.19	11.3 ± 4.7	2.52 ± 1.55[A]	35.8 ± 12.1	4.57 ± 2.11
EMC (8)	3.21 ± 1.16	0.33 ± 0.20	9.3 ± 3.6	2.11 ± 1.49[A]	34.9 ± 8.9	4.17 ± 1.68
TCS (4)	2.83 ± 0.91	0.27 ± 0.12	8.7 ± 2.3	0.58 ± 0.28[A]	37.0 ± 7.2	3.09 ± 1.00
KSC (5)	2.75 ± 1.12	0.25 ± 0.14	8.6 ± 3.7	0.53 ± 0.34[BC]	34.9 ± 6.8	2.99 ± 1.20
WOH						
WBD (9)	2.04 ± 0.38[A]	0.40 ± 0.11[A]	20.2 ± 4.1	0.94 ± 0.33	35.1 ± 5.8	2.46 ± 0.47[A]
EBD (6)	1.53 ± 0.37[AB]	0.33 ± 0.14[AB]	20.7 ± 4.6	0.82 ± 0.33	38.3 ± 3.7	1.89 ± 0.52[AB]
SCH (6)	1.37 ± 0.27[B]	0.22 ± 0.07[BC]	16.3 ± 3.5	0.67 ± 0.37	34.5 ± 4.5	1.66 ± 0.34[B]
ESP (5)	1.11 ± 0.39[B]	0.19 ± 0.04[BC]	16.6 ± 3.7	0.93 ± 0.46	24.1 ± 8.8	1.53 ± 0.44[B]
NVR (4)	1.14 ± 0.22[B]	0.17 ± 0.01[C]	15.7 ± 2.2	0.60 ± 0.16	54.8 ± 16.8	1.41 ± 0.27[B]

(Table 1). TOC concentrations were significantly greater in the EOH than in the WOH region (ANOVA: $p < 0.01$). DOC concentrations exceeded POC concentrations (DOC:POC > 1) at every site. The range of ratios was considerably broader in the EOH region (1.7–54.4) than the WOH region (2.8–9.4), and the mean ratio was significantly higher in the EOH than in the WOH region (ANOVA: $p < 0.01$; EOH: 12.0 ± 10.3, WOH: 5.9 ± 1.8).

Despite considerable overlap among some watersheds, DOC concentrations differed significantly between regions (ANOVA: $p < 0.01$; Table 1, Fig. 1A, B). The 5 sites with the highest DOC concentrations were all from the EOH region (sites 36 in the West Branch Croton watershed, 44 in the East and Middle Branch Croton watershed, 43, 49, and 58 in the Muscoot and other sites north of Croton Reservoir watershed; Fig. 1A), whereas the 5 sites with the lowest DOC concentrations were all from the WOH region (sites 19 in the Schoharie Creek watershed, 22, 23, and 24 in the Esopus Creek watershed, and 30 in the Neversink River and Rondout Creek watershed; Fig. 1B).

BDOC concentrations <0.3 mg/L were observed for ~50% of the EOH sites (Fig. 2A) and ~67% of the WOH sites (Fig. 2B), and BDOC concentrations did not differ between regions (Table 1). However, the % of DOC consisting of BDOC was significantly higher in

the WOH region than in the EOH region (ANOVA: $p < 0.01$; Table 1).

Most of the TSS particles were in the 0.5- to 10-μm size range (EOH: 67 ± 17%, range = 28–91%; WOH: 73 ± 12%, range = 50–96%), as was most POM (EOH: 71 ± 15%, range = 36–92%; WOH: 77 ± 11%, range = 48–94%). The % of TSS consisting of POM did not differ between regions (Table 1). POM concentrations <1 mg/L were observed at ~50% of the EOH (Fig. 3A) sites and ~77% of the WOH sites (Fig. 3B). Four of the 5 sites with the lowest POM concentrations were in the EOH region, but mean POM concentrations at 8 sites in the EOH region were >2 mg/L. POM concentrations were significantly higher in the EOH region than in the WOH region (ANOVA: $p < 0.03$; Table 1).

Among watersheds.—Concentrations of OM constituents were more similar among watersheds in the EOH region than in the WOH region (Table 1). TOC, DOC, and BDOC concentrations and the % of DOC consisting of BDOC declined among EOH watersheds along the sequence: Muscoot River and other sites north of Croton Resevoir (MNC) > West Branch Croton River (WBC) > East and Middle Branch Croton Reservoir (EMC) > Titicus, Cross, and Stone Hill rivers (TCS) > Kensico Reservoir and other sites south of Croton Reservoir (KSC) (Table 1). The only significant differences among watersheds were for
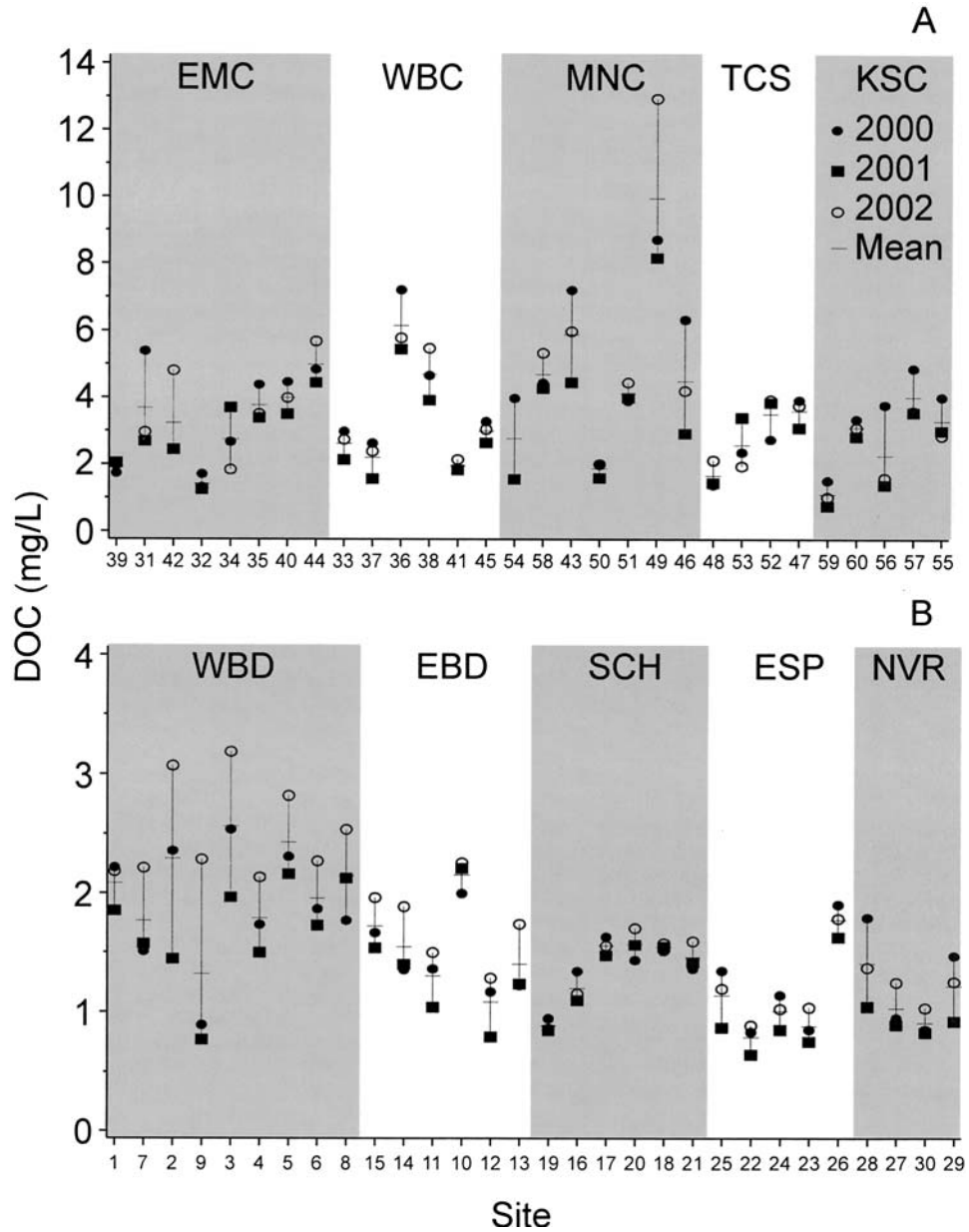
FIG. 1. Baseflow concentrations and the 3-y mean of dissolved organic C (DOC) in watersheds of the east of Hudson River (EOH; A) and west of Hudson River (WOH; B) regions of the New York City drinking-water supply for the years 2000, 2001, and 2002. See Table 1 for watershed abbreviations. Sites are ordered by increasing watershed area from left to right.

concentrations of POM, which were significantly higher in WBC, EMC, and TCS than in KSC (ANOVA, Tukey's test: $p < 0.05$; Table 1). The 5 sites (32, 39, 48, 50, and 59) with the lowest mean DOC concentrations were distributed among all of the EOH watersheds except WBC (Fig. 1A). These sites also had low concentrations of BDOC (≤ 0.2 mg/L; Fig. 2A) and POM (< 1.5 mg/L; Fig. 3A). The 5 sites were further characterized by small- to mid-sized watershed areas (0.2–17.7 km^2), but broad ranges of population density

(22.4–646 ind./km^2) and % wetland land cover (0.6–6.3%) (Arscott et al. 2006). Another common element for all 5 sites was the absence of known point-source discharges under the State Pollution Discharge Elimination System (SPDE) (typically wastewater treatment plant effluents; Arscott et al. 2006).

Concentrations of OM constituents in the WOH region generally declined among watersheds along the sequence: West Branch Delaware (WBD) > East Branch Delaware (EBD) > Schoharie (SCH) > Esopus
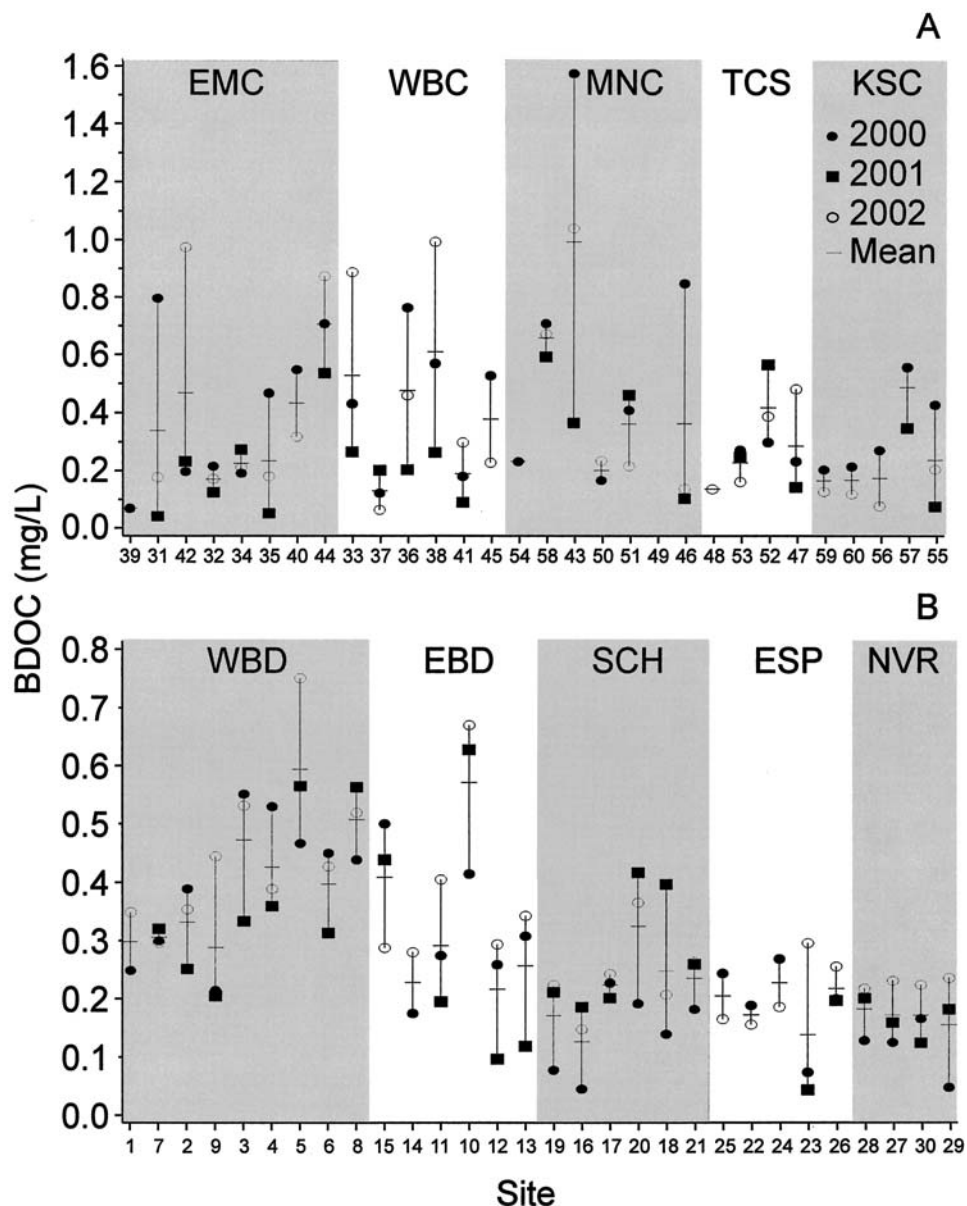
FIG. 2. Baseflow concentrations and the 3-y mean of biodegradable dissolved organic C (BDOC) in watersheds of the east of Hudson River (EOH; A) and west of Hudson River (WOH; B) regions of the New York City drinking-water supply for the years 2000, 2001, and 2002. See Table 1 for watershed abbreviations. Sites are ordered by increasing watershed area from left to right.

(ESP) > Neversink River and Rondout Creek (NVR) (Table 1). TOC, DOC (Fig. 1B), and BDOC (Fig. 2B) concentrations were significantly higher in WBD than in SCH, ESP, or NVR (ANOVA, Tukey's test, $p < 0.05$; Table 1), and POM concentrations did not differ among watersheds (ANOVA, Tukey's test: $p > 0.05$; Table 1, Fig. 3B). This sequence of declining OM constituent concentrations among the WOH watersheds corresponded to increases in % forest land use (Spearman Rank Correlation: $r = -1.0$, $p < 0.01$) along the same sequence of watersheds: 65.1% (WBD) <

82.4% (EBD) < 89.1% (SCH) < 96.6% (ESP) < 97.2% (NVR) (Arscott et al. 2006).

Within-watershed spatial and temporal patterns

Upstream–downstream changes in organic C concentrations.—Study watersheds in the WOH region were associated with terminal reservoirs, and a subset of sites in each watershed was aligned along the main stem of the river. These data were examined for longitudinal (upstream to downstream) trends in
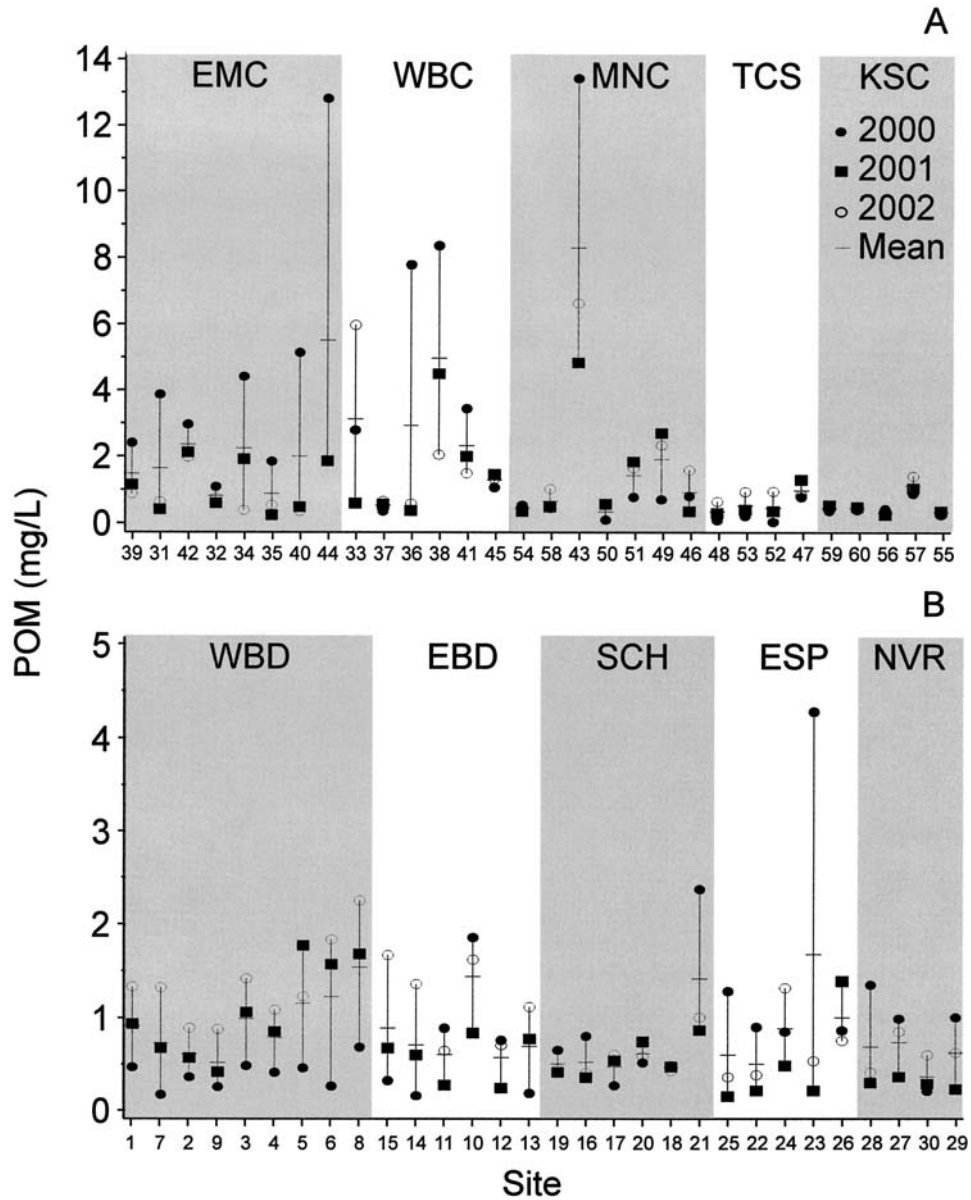
FIG. 3. Baseflow concentrations and the 3-y mean of particulate organic matter (POM) in watersheds of the east of Hudson River (EOH; A) and west of Hudson River (WOH; B) regions of the New York City drinking-water supply for the years 2000, 2001, and 2002. See Table 1 for watershed abbreviations. Sites are ordered by increasing watershed area from left to right.

concentrations and fluxes (concentration × discharge) of OM moving toward the reservoirs when baseflow samples from the main stem were collected on the same day or within a few days of each other. Despite consistent upstream–downstream differences at some sites over all 3 y, few upstream–downstream comparisons were significant.

Only one upstream–downstream mainstem comparison was made in the EOH region. DOC, BDOC, and POM decreased between sites 55 and 57 on the Kisco (paired t-tests: $p < 0.02$, $p = 0.06$, $p < 0.03$, respectively; see fig. 2 and table 1 in Arscott et al. 2006 for site

numbers and locations). In the WOH region, DOC increased in the downstream direction in all 3 y in the West Branch Delaware between sites 1 and 3 (paired t-test: $p = 0.22$) and in the Esopus between sites 22 and 23 (paired t-test: $p = 0.14$) and sites 23 and 26 (paired t-test: $p < 0.01$). Two other upstream–downstream DOC concentration patterns seen in all 3 y involved mixing of tributary inputs. In the East Branch Delaware, DOC concentrations decreased between sites 10 and 13 (paired t-test: $p < 0.03$), a pattern that probably reflected dilution of DOC at site 13 caused by the entry of water with low DOC concentrations from the

Dry Brook tributary (site 12) and from groundwater. In the Neversink, DOC concentrations were always higher in the East Branch Neversink (site 28) than in the West Branch Neversink (site 27) yielding intermediate DOC concentrations in the Neversink below the confluence (site 29; paired t-tests: $p = 0.25$). DOC flux increased in the downstream direction for all pairs of mainstem sites in all watersheds in the WOH region, including those sites without consistent increases in downstream concentration. No consistent longitudinal concentration patterns were observed for BDOC, but BDOC flux increased downstream in the East Branch Delaware based on data from the 2 y when samples were collected on the same dates.

POM increased in the downstream direction in all 3 y in the Schoharie between site 18 and site 21 (paired t-test: $p = 0.18$). POM concentration and watershed area were significantly positively correlated ($r = 0.68$, $p < 0.01$) when all watersheds in the WOH region with >78% forest land cover were considered. POM flux increased in the downstream direction in all watersheds except the West Branch Delaware. DOC dominated the TOC concentration pool at all sites, and the TOC flux pattern was reflected in the DOC flux pattern, even when POM flux did not increase downstream.

Interannual variability in organic C concentrations.—Mean CVs for analyte concentrations were 23% for DOC (range: 7–62%), 50% for BDOC (range: 1–119%), and 61% for POM (range: 15–145%) in the EOH region, and 17% for DOC (range: 2–64%), 33% for BDOC (range: 4–02%), and 57% for POM (range: 7–135%) in the WOH region. DOC concentrations decreased between years 1 and 2 and increased between years 2 and 3 at several sites, and these variations were directly related to changes in baseflow discharge (ANCOVA: $p < 0.01$). Discharge and DOC concentrations were strongly positively correlated in the EOH ($r > 0.83$ at 33% of EOH sites, $r > 0.94$ at 27% of EOH sites) and in the WOH ($r > 0.83$ at 80% of WOH sites, $r > 0.94$ at 50% of WOH sites).

Relationships among OM constituents and land use and supplemental variables

EOH.—Point-source discharges (SPDE effluents) were 4.5× to 10.2× greater at sites 43, 49, and 58 than at the site receiving the 4th-highest discharge and were ≥30× to 69× greater than at the other 8 EOH sites receiving point-source discharges; 17 EOH sites received no point-source discharges. These large disparities in point-source discharges across the EOH region strongly influenced the correlations between OM constituents and molecular tracers specific to human wastewater (fragrance materials and caffeine) and fecal matter (total fecal steroids) (Aufdenkampe et al. 2006). When data from all 30 EOH sites were considered, DOC and BDOC were positively correlated with fragrance materials (DOC: $r = 0.58$, $p < 0.01$; BDOC: $r = 0.69$, $p < 0.01$), caffeine (DOC: $r = 0.54$, $p < 0.01$; BDOC: $r = 0.70$, $p < 0.01$), and total fecal steroids (DOC: $r = 0.67$, $p < 0.01$; BDOC: $r = 0.70$, $p < 0.01$; Fig. 4A), and POM was positively correlated with fecal steroids ($r = 0.56$, $p < 0.01$; Fig. 4B). However, when the values for sites 43, 49, and 58 were excluded, only the correlations of fecal steroids with DOC, BDOC, or POM were significant. The 3-y mean fecal steroid concentration was ~4× greater at site 49 than at all other sites and was an outlier in the data set based on an analysis of its influence on the fitted value in the regressions of fecal steroids and OM constituents (DFFITS, Myers 1990). Therefore, the data from site 49 were excluded from the regressions of fecal steroids with DOC, BDOC, and POM. Percent wetland was positively correlated with DOC ($r = 0.61$, $p < 0.01$) and BDOC ($r = 0.63$, $p < 0.01$; Fig. 4C), but correlations between OM constituents and benthic chlorophyll a (Kratzer et al. 2006) were not significant.

Point-source discharges and % wetland explained most of the variance in DOC and BDOC concentrations in MLR models using all 30 sites and point-source discharge, and % mixed forest explained most of the variance in POM concentrations (Table 2). However, the models were sensitive to the effects of point-source discharges at sites 43, 49, and 58, and when these sites were removed from the analysis, % wetland explained 36% of the variance in DOC concentrations, % wetland and % industry explained 61% of the variance in BDOC concentrations, and % mixed forest and % orchard explained 46% of the variance in POM concentrations.

WOH.—The 3-y mean concentrations of DOC, BDOC, and TSS were strongly and positively correlated with fragrance materials (DOC: $r = 0.37$, $p < 0.05$; BDOC: $r = 0.53$, $p < 0.01$; TSS: $r = 0.39$, $p < 0.04$). DOC, BDOC, and POM were strongly positively correlated with concentrations of caffeine (DOC: $r = 0.52$, $p < 0.01$; BDOC: $r = 0.58$, $p < 0.01$; POM: $r = 0.40$, $p < 0.03$) and total fecal steroids (DOC: $r = 0.76$, $p < 0.01$; BDOC: $r = 0.89$, $p < 0.01$; POM: $r = 0.56$, $p < 0.01$; TSS: $r = 0.50$, $p < 0.01$; Fig. 5A). DOC and BDOC were positively correlated with % agriculture (a combination of farmstead, cropland, and grassland) (DOC: $r = 0.79$, $p < 0.01$; BDOC: $r = 0.78$, $p < 0.01$; Fig. 5B), and the 9 sites with the highest % agriculture were located in the West Branch Delaware. DOC and BDOC also were correlated with density of benthic chlorophyll a (DOC: $r = 0.44$, $p < 0.02$; BDOC: $r = 0.61$, $p < 0.01$; Fig. 5C).
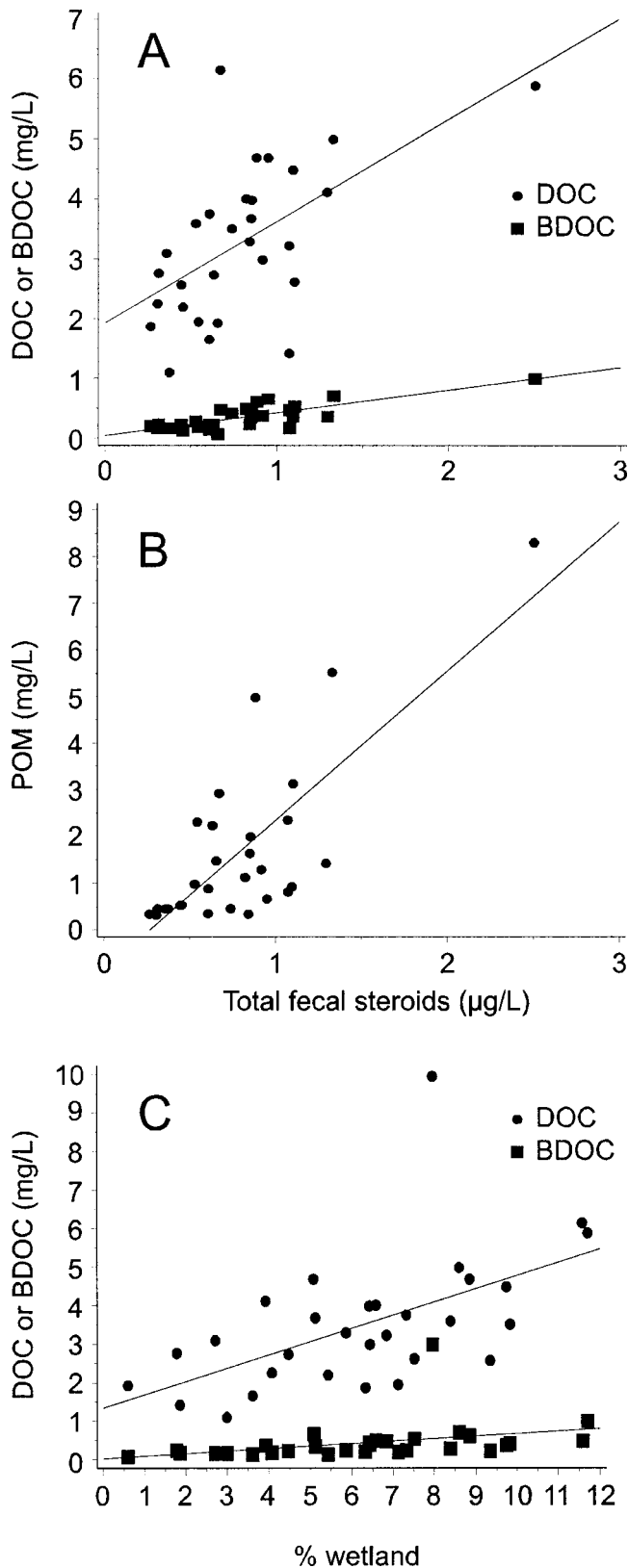
Chlorophyll *a*, in turn, was correlated with nutrient concentrations (total P: $r = 0.68$, $p < 0.01$; free + organically bound NH_3-N: $r = 0.65$, $p < 0.01$), and watershed area ($r = 0.45$, $p < 0.01$).

An MLR with % grasslands (+ effect), % deciduous forest (−), and % orchards (+) explained 72% of the variance in DOC concentrations, whereas an MLR with % grassland (+), % orchard (+), and % industry (+) explained 76% of the variance in BDOC concentrations (Table 2). An MLR with point-source discharge (+) and % mixed forest (−) explained 32% of the variance in POM concentrations (Table 2).

Discussion

Baseflow sampling

The broad spatial coverage and 3-y time frame of our monitoring efforts within a large, yet constrained, geographic region combined with landuse data provided an in-depth perspective on the quantity and character of OM transported by these streams under baseflow conditions. Our study was not intended to generate annual export budgets of OM for the watersheds. In fact, such an objective would have required focusing on fluxes that occurred during storms (Hinton et al. 1997, Buffam et al. 2001). Instead, our study was done under baseflow conditions to provide a baseline of OM concentrations measured under conditions that were easier to replicate than stormflow conditions. Thus, our study was designed to facilitate comparisons with surveys to be done in the future.

Baseflow can account for as much as 67% of the total runoff in upland watersheds in the Mid-Atlantic region (Olmsted and Hely 1962). The application of a hydrograph separation technique to 50 USGS-gauged streams draining the major watersheds in the EOH and WOH regions revealed that baseflow accounted for 58% to 65% of the total discharge during the 2000 to 2002 study period (C. L. Dow, Stroud Water Research Center, personal communication). OM fluxes are influenced by increases in TOC concentrations and changes in TOC quality during storm flows. However,

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FIG. 4. Relationship between dissolved organic C (DOC) and biodegradable DOC (BDOC) concentrations and total fecal steroid concentrations (A), between particulate organic matter (POM) and total fecal steroid concentrations (B), and between DOC and BDOC and % wetland land use (C) at sites in the east of Hudson River (EOH) region of the New York City drinking-water supply. Site 49 was excluded from panels (A) and (B) ($n = 29$), but not from panel (C) ($n = 30$) (see text for details).

TABLE 2. Partial R^2 values and direction of slopes (+/−) for significant predictive watershed landuse variables ($p < 0.05$) from stepwise multiple linear regression models explaining concentrations of dissolved organic C (DOC), biodegradable DOC (BDOC), and particulate organic matter (POM) among 30 east of Hudson River (EOH) and 30 west of Hudson River (WOH) sites in New York City drinking-water-supply watersheds. Total R^2 values reported are the adjusted R^2 values to compensate for the number of predictors used. SPDE = mean annual watershed-area-normalized State Pollution Discharge Elimination System effluent volume = point-source discharge. Blanks indicate that the landscape characteristic was not a significant predictor in the model.

Landscape characteristic	DOC	BDOC	POM
EOH			
SPDE	0.38 (+)	0.43 (+)	0.25 (+)
% wetland	0.17 (+)	0.19 (+)	
% commercial			
% cropland		0.06 (+)	
% mixed brushland			
% mixed forest			0.26 (+)
Total R^2	**0.52**	**0.64**	**0.46**
WOH			
% grassland	0.65 (+)	0.61 (+)	
% industry		0.12 (+)	
% deciduous forest	0.06 (−)		
% orchard	0.04 (+)	0.06 (+)	
% mixed forest			0.18 (−)
SPDE			0.17 (+)
Total R^2	**0.72**	**0.76**	**0.32**

the contribution of baseflow to total discharge and the fact that weather patterns in the region keep streams under baseflow conditions more often than stormflow conditions suggest that samples collected under baseflow conditions provide an appropriate reflection of landuse impacts on OM components of water quality.

Composition of OM

Our findings that TOC concentrations at baseflow were dominated by DOC and that POM in seston was dominated by fine particles across both regions were consistent with observations from watersheds across wide areas of temperate North America, including the Cascade Mountains of Oregon (Naiman and Sedell 1979), the Boreal biome of eastern Canada (Naiman 1982), the southern Appalachian Mountains (Wallace et al. 1982), sections of Pennsylvania, Michigan, Idaho, and Oregon (Minshall et al. 1983), and southwestern British Columbia (Kiffney and Bull 2000). Streams in which POC dominates the TOC pool have been studied, but th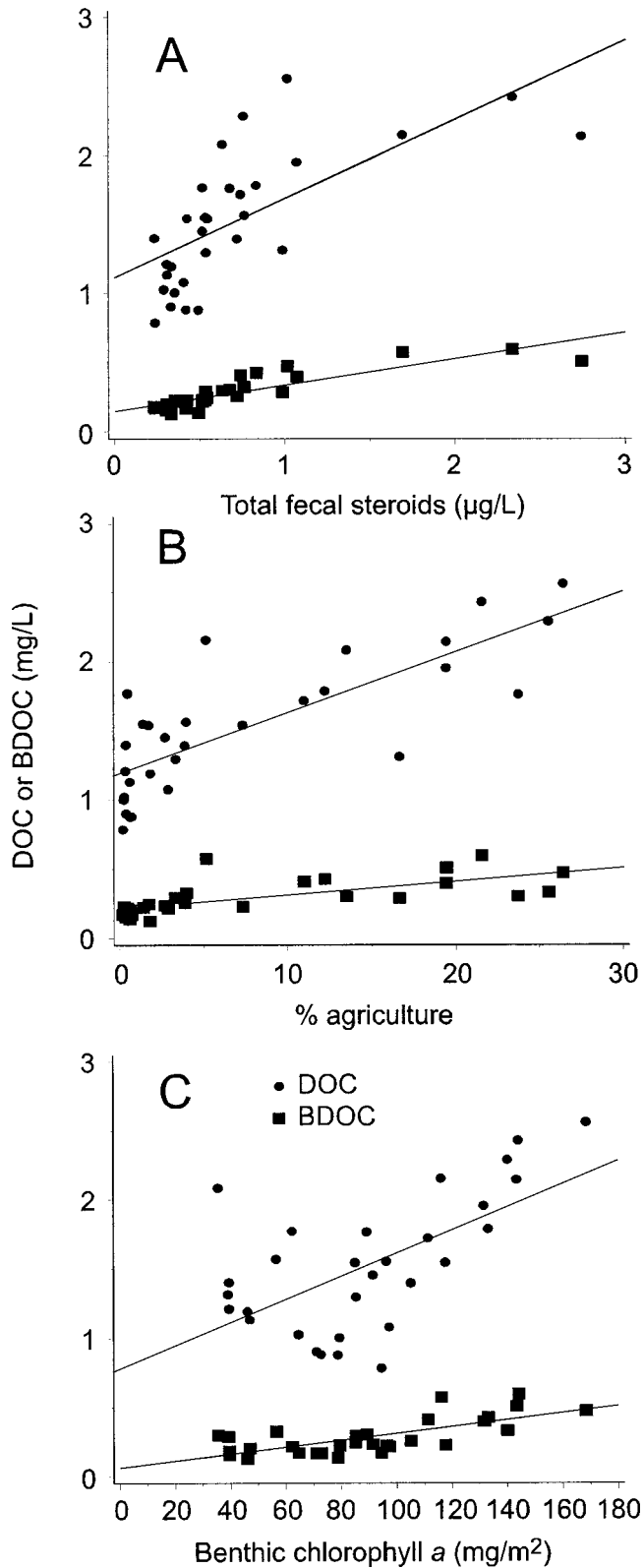ese studies included measurements made during storms when POC may increase proportionately more than DOC (Golladay 1997, Kaiser et al. 2004), streams in the headwaters of protected forested watersheds that are influenced by low-DOC groundwaters and receive large inputs of forest litter (Comiskey 1978), or large turbid rivers, such as the Brazos or Missouri Rivers, that consistently transport high concentrations of suspended sediments (Malcolm and Durum 1976).

POM size classes in our study included a 0.5- to 10-μm size class, which falls within the range of ultrafine particulate OM (Minshall et al. 1983). Our observation that >70% of POM in both regions was in this size class emphasizes the quantitative importance of the smallest organic particles in the seston of low- to mid-order streams. The consistent importance of this size class across the wide variety of streams and land uses suggests that similar instream physical transport and retention processes, rather than variations in sources, controlled the size distributions of organic particles in suspension.

The 0.5- to 10-μm size class overlaps with the size of protozoan pathogens such as *Cryptosporidium*, which has been identified in storm samples from the WOH and EOH regions (Jiang et al. 2005) and is a particular concern in drinking water. However, *Cryptosporidium* is a specialized form of POM, and without data specific to the transport behavior of these spores relative to bulk POM, our POM data should not be considered representative of *Cryptosporidium* transport behavior.

Spatial and temporal patterns in DOC composition

Increases in DOC concentrations with distance downstream, as observed for some sites in the West Branch Delaware and Esopus watersheds, have been reported previously for small headwater streams dominated by low DOC concentrations from groundwater sources (Kaplan et al. 1980, Wallace et al. 1982, Tate and Meyer 1983). Increases in POM concentrations with stream size also have been reported (Whiles and Dodds 2002). A more general finding for DOC, based on data for 31 streams (Mulholland 1997), was that DOM concentrations and DOM flux increased as a function of watershed area or stream order. This pattern suggests that DOM is sufficiently refractory to accumulate in larger streams, and it further suggests that DOM is derived primarily from the terrestrial environment (allochthonous C) because much of the autochthonous DOM in streams is biologically labile (Kaplan and Bott 1982). However, DOC concentrations did not change systematically with distance downstream in the Tagliamento River system in Italy, where

FIG. 5. Relationship between dissolved organic C (DOC) and biodegradable DOC (BDOC) concentrations and total fecal steroid concentrations (A), % agriculture land use (B), and benthic chlorophyll a densities (C) at sites in the west of Hudson (WOH) region of the New York City drinking-water supply ($n = 30$).

much of the DOC was recalcitrant soil-derived C (Kaiser et al. 2004). The concentrations of BDOC in our study indicated that most DOC was refractory, despite the fact that a significant fraction of the DOC was biodegradable.

Rates of ecosystem metabolism indicate that massive microbial degradation of DOC occurs in streams and rivers (Cole and Caraco 2001, Mayorga et al. 2005), including metabolism within the hyporheic zone (Sobczak and Findlay 2002). The slow metabolism of a large recalcitrant DOC pool is considered instrumental in providing metabolic stability within stream ecosystems (Wetzel 2003). However, the processes that continually produce, transform, and consume DOC molecules in transport complicate attempts to understand the dynamics of DOC concentrations in streams and rivers without direct measurements of uptake rates.

Allochthonous sources of OM dominate the pool of OM transported in most streams in the Eastern Deciduous Forest biome (Webster and Meyer 1997). However, autochthonous sources of DOC certainly can contribute significantly to TOC in forest streams during seasons when the forest canopy is open (Kaplan and Bott 1982), in desert streams where adequate sunlight and infrequent storms allow algal biomass to accumulate (Jones et al. 1996), and in forest streams when logging opens the forest canopy and facilitates chlorophyll a accrual (Kiffney et al. 2000). In our study, the positive correlations between benthic chlorophyll a and DOC and BDOC concentrations suggest a significant role for autochthonous DOC in the WOH watersheds. Nutrient concentrations at agriculturally impacted sites in the WOH region probably contributed to the higher benthic chlorophyll a density in the WOH than in the EOH region. The significant positive correlation between chlorophyll a (as a surrogate for algal biomass) and watershed area (as a surrogate for stream width) supports the idea from the River Continuum Concept that higher densities of benthic algae develop as the canopies of mid-order streams widen beyond the shading influence of their riparian forests (Vannote et al. 1980).

Increased DOC concentrations with increased stream discharge during storms or snowmelt is a common phenomenon and is assumed to result from

the alteration of flow paths for water entering streams (McDowell and Likens 1988). A negative correlation of DOC concentration and discharge reported for headwater streams in British Columbia appears to have been heavily influenced by dry-season benthic algal biomass accumulations and high levels of DOC concentrations from exudates (Kiffney et al. 2000). Our data, which reveal a positive correlation between DOC concentrations and rates of baseflow discharge, suggest that changes from high to low baseflow conditions were accompanied by subtle shifts in flow paths along hydrologic gradients. A long-term trend of increasing DOC concentration has been observed in the Hudson River (Burns et al. 2005, Findlay 2005), but the first year of our study was the wettest, so the relationship between baseflow discharge and DOC concentrations may have been sufficient to overcome any contravening effects of this long-term trend. However, to the extent that the phenomenon observed in the Hudson River is representative of phenomena occurring within the watersheds of the WOH and EOH regions, this trend could adversely impact the quality of the NYC water supply.

Landuse effects on OM

Percent agriculture land use in the WOH region and point-source discharge and % wetland land use in the EOH region were the primary landuse characteristics that influenced concentrations of OM in the study streams. In the WOH, relationships between OM concentrations and benthic chlorophyll *a*, fragrance materials, caffeine, and fecal steroids support these landuse results. Densities of algal biomass are influenced by levels of light and nutrients, both of which may be higher when a watershed is used for agriculture rather than covered by forest. Fragrance materials and caffeine are clear signals of sources related to human activities, although the fecal steroids could be from humans, domesticated animals, or wildlife. In the EOH region, the particularly strong correlations between DOC and BDOC and caffeine, fragrance materials, and fecal steroids identify organically enriched point-source discharge as a contributor to the organic loading (Westerhoff and Anning 2000, Kolpin et al. 2002, Glassmeyer et al. 2005). Anthropogenic inputs of organic C from industrial development or orchards supplemented the natural background concentrations of organic C from wetlands, even when sites with high point-source discharges were removed from the data set.

The strong contribution of wetlands to BDOC concentrations in the EOH region is particularly interesting because organic C accumulates in wetlands, whereas BDOC usually is consumed and not exported. This apparent disparity (i.e., the suggestion that wetlands are a source of BDOC) could mean that partial photochemical oxidation of DOC (Mopper and Kieber 2002, Latch and McNeill 2006) may transform some recalcitrant DOC molecules into biologically labile DOC (BDOC) once it leaves the wetlands and is transported downstream. Support for this explanation comes from the observation that photolysis products of recalcitrant DOC from *Typha latifolia* and *Juncus effusus* stimulated production of bacteria from the Talladega Wetland Ecosystem (Wetzel et al. 1995), but this area of inquiry would benefit from direct experimentation.

DOC from point sources (Sirivedhin and Gray 2005) and peat soils (Fleck et al. 2004) have been identified as potential DBP precursors, as have biologically labile algal exudates (Nguyen et al. 2005). The literature on the relative importance of DOC sources to DBP formation is equivocal. For example, an analysis of 17 different Alaskan water supplies found that phenolic compounds in DOC were the primary contributors to DBPs (White et al. 2003), whereas a study of wastewater effluents and surface waters found that DBP formation potential was negatively correlated to the phenolic signature of the DOC (Sirivedhin and Gray 2005). Thus, whether the wetland influence (EOH) or the algal influence (WOH) on stream DOC have any particular significance to DBP formation potential is unclear, but these factors probably do contribute to the higher % of DOC consisting of BDOC in the WOH than in the EOH.

DOC in drinking water

A survey of DOC and BDOC in US drinking-water sources revealed median concentrations of DOC (2.27 mg/L) and BDOC (296 µg/L) in 53 surface-water supplies (Kaplan et al. 1994). The median concentrations of DOC (1.50 mg/L) and BDOC (241 µg/L) in the WOH were below the concentrations reported in the US drinking water survey, whereas median concentrations for DOC (3.26 mg/L) and BDOC (312 µg/L) in the EOH region were higher than ~76% (DOC) and ~64% (BDOC) of the concentrations reported in the survey (Kaplan et al. 1994). Sobczak and Findlay (2002) reported DOC concentrations from streams in forested sites in the Catskill region and the Hudson River valley that were comparable to the concentrations in the EOH and WOH regions. Sobczak and Findlay (2002) also measured BDOC in batch cultures. They reported a lower % of DOC consisting of BDOC but a higher % of DOC lost along hyporheic flow paths

than in streams in our study (except for the Neversink, which showed no uptake of DOC).

From a drinking-water-treatment perspective, low organic C concentrations are desirable because of the influence of organic C on DBP concentrations and bacterial regrowth. Moreover, organic C can influence other aspects of drinking-water quality, including the aesthetics of taste and pollutant transport. For example, microorganisms such as Cyanobacteria and *Streptomyces* can produce geosmin and 2-methyliso-borneol, organic compounds known to impart undesirable taste and odor to water supplies (Suffet et al. 1999, Hockelmann and Juttner 2005). DOC alters the availability of hydrophobic pollutants (Caron and Suffet 1989) and heavy metals such as Cd, Cu, Cr (Guggenberger et al. 1994), and Hg (Wallschlager et al. 1996), and facilitates movement of these metals from watershed soils into streams and reservoirs (Shafer et al. 1997). OM associated with particles can adsorb nutrients and contribute to eutrophication of downstream reservoirs, and particulate matter in streams increases turbidity, which can limit instream primary production and reduce habitat quality for stream invertebrates (Wood and Armitage 1997) and spawning fishes (Waters 1995). However, organic C also is a natural and important component of stream ecosystem function. Our data from watersheds in the WOH region with high % forest (Esopus: 96.6% forested, Neversink River and Rondout Creek: 97.2% forested) and from sites in the EOH that are in small to moderately sized watersheds with no point-source discharges (e.g., sites 32 and 59) probably provide lower limits for OM levels that can be achieved through best management practices in the 2 regions.

In conclusion, our spatially extensive study of OM concentrations under baseflow conditions revealed distinct regional differences that were related to differences in land use. In the absence of human activities, differences in DOC concentrations between the regions were expected because % wetland is higher in the EOH than in the WOH region, and wetlands influenced DOC and BDOC concentrations in the EOH region. Agriculture appeared to increase concentrations of DOC and BDOC in the West Branch Delaware watershed and clearly distinguished the West Branch Delaware watershed from other watersheds in the WOH region where agriculture was not as widespread. High levels of point-source discharges at 3 sites in the Muscoot and other sites north of Croton Reservoir strongly influenced DOC, BDOC, and POM in the EOH, but human activity was a predictor of BDOC even with these sites removed from the data set. BDOC is a source of energy and organic C building blocks for heterotrophic microbial metabolism and is

the organic analog to the inorganic nutrients (N and P) that are most commonly associated with water-quality assessments (Carpenter et al. 1998, Neill et al. 2001). In both the WOH and EOH regions, OM concentrations were related to the human activities in the watersheds, and this relationship suggests that continuing efforts to improve water quality by addressing human impacts at the watershed scale are appropriate.

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