

Seasonal and Spatial Patterns of Nitrate and Silica Concentrations in Canajoharie Creek, New York

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ABSTRACT

The impact of nonpoint-source pollution on surface waters in agricultural watersheds is an emerging environmental issue. As part of the U.S. Geological Survey National Water Quality Assessment program in the Hudson River Basin, Canajoharie Creek was monitored for seasonal and spatial patterns of nutrient chemistry from March 1993 to January 1996. Nitrate and silica concentrations in Canajoharie Creek suggest that seasonal and spatial variations of these nutrients are dominated by biological processes, particularly uptake by phytoplankton. Observed concentration patterns were more typical of those observed in much larger, low-gradient streams. The median nitrate and silica concentrations in Canajoharie Creek were significantly lower from April through November than during winter. Concentrations of both constituents declined downstream from the headwaters during base-flow conditions in June 1995. Groundwater and surface water chemistry data support biological causes for downstream decreases in silica. The strong correlation between nitrate and silica in samples collected along the mainstem suggests that most of the nitrate decrease is due to uptake by diatoms. Downstream patterns of chlorophyll-*a* in phytoplankton strongly suggest the conversion of in-stream nutrients to algal biomass. Data collected from Canajoharie Creek outlet during the northeast drought of 1995 indicate that silica concentrations in May had possibly declined to a level that adversely affected the diatom community. This decline in the diatom population and subsequent resurgence is inferred from a sharp rise in silica concentrations between May and July and a reversal of this trend from mid-July through October without associated changes in hydrology.

AMONG all algae, only the Chrysophyta genera and in particular the diatoms utilize silica as an essential element for growth (Reynolds, 1984). Diatoms are nearly ubiquitous in distribution (Cox, 1991), often dominate the composition of river phytoplankton (Allan, 1995), and are among the most abundant of living things on earth (Needham and Lloyd, 1916). The role of diatoms in lowering silica concentrations in streams seasonally has been well documented. Swale (1969), Wang and Evans (1969), Lack (1971), Edwards (1974), and Casey et al. (1981) all noted summer declines in dissolved silica concentrations and attributed the declines to silica uptake by diatoms. Few studies, however, have focused on the seasonal and spatial relation between silica and nitrate in streams.

This paper describes the influence of diatoms on seasonal and spatial patterns of nitrate, silica, and other

nutrients in Canajoharie Creek, which drains a small agricultural watershed in the Hudson River Basin in central New York. It also (i) compares nutrient concentrations in Canajoharie Creek during low-flow conditions with those at 44 other stream sites across the basin, (ii) compares 2 yr of at least monthly nutrient data from Canajoharie Creek with corresponding data from 11 other sites in the basin, and (iii) describes a possible shift from conditions that favored diatoms to those favoring other forms of algae during the northeast drought of 1995.

WATERSHED DESCRIPTION

The Canajoharie Creek watershed (155 km²) is in the Mohawk River subbasin of the Hudson River Basin (Fig. 1) and lies entirely within the Mohawk Valley ecoregion (Reschke, 1990). About two-thirds of the watershed is in agricultural use (U.S. Geological Survey, 1986). Watershed elevation ranges from 640 to 195 m with a mean annual precipitation of about 100 cm (Randall, 1996). Canajoharie Creek is 27 km long and a 4th order stream at its watershed outlet. Brimstone Creek, the largest tributary to Canajoharie Creek, joins the mainstem 9 km above the watershed outlet.

Holocene alluvium in the central part of the watershed forms an unconfined aquifer that is in contact with much of Canajoharie Creek (Fig. 1). Most of this aquifer is overlain by agricultural land containing row crops, dairy cattle, and hay fields. A glaciolacustrine clay unit underlies the unconfined aquifer and confines a sand aquifer that discharges to Canajoharie Creek in isolated locations. The recharge areas for these aquifers are undefined. Recharge to the unconfined aquifer is probably derived from a combination of direct infiltration of precipitation, upland runoff, losing upstream reaches of Canajoharie Creek, and occasional infiltration of Canajoharie Creek floodwaters through the banks of agricultural drainage ditches. Riparian areas adjacent to Canajoharie Creek are almost entirely agricultural and commonly lack buffer strips.

METHODS

Surface Water Data

For purposes of this study, the watershed outlet was considered to be a point 8.6 km upstream of the Village of Canajoharie, where Canajoharie Creek joins the Mohawk River. This location was chosen to avoid any effects of the village on water chemistry and to ensure accessibility to the creek. A U.S. Geological Survey (USGS) streamflow gauging station at the outlet recorded stage at 15-min intervals, and these data were used to calculate discharge during the sampling period through standard USGS methods and procedures (Rantz, 1982).

Surface water samples were collected at the watershed out-

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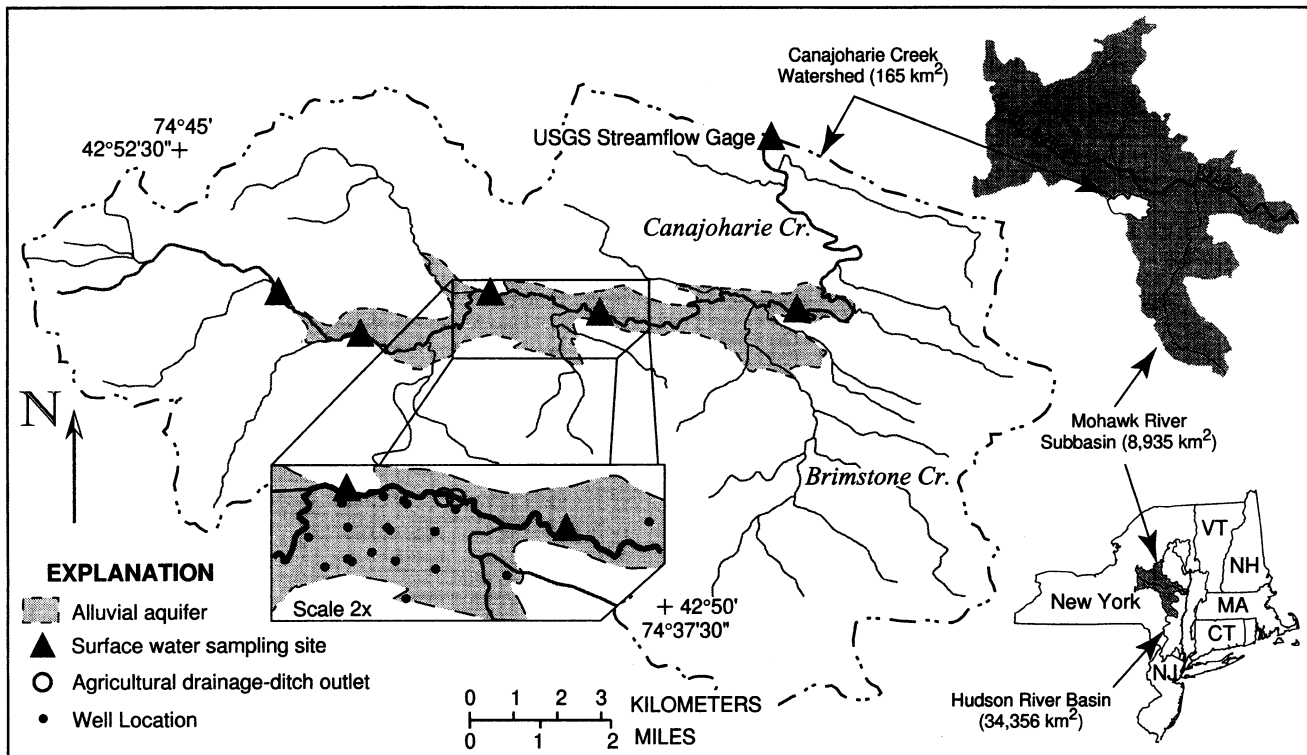


Fig. 1. Extent of the unconfined aquifer and locations of sampling sites in Canajoharie Creek watershed.

let at least monthly (weekly during the late spring and early summer) from March 1993 through January 1996 and analyzed for nutrients, dissolved organic carbon (DOC), suspended organic carbon (SOC), and major dissolved ions. Depth-integrated, equal-width-increment surface water samples were collected with a DH81 or D77 (depending on flow conditions) water sampling apparatus (Shelton, 1994). All samples were collected in Teflon bottles, processed according to established USGS guidelines (Shelton, 1994), and shipped in ice for analyses at the USGS National Water Quality Laboratory (NWQL) according to procedures described by Wershaw et al. (1987), Fishman and Friedman (1989), and Fishman (1993). Analytical methods for specific nutrient analytes are described in Table 1. Total organic N concentrations were calculated as the difference between dissolved ammonium and total organic N plus ammonium.

Additional surface water samples were collected at six sites along the Canajoharie Creek mainstem and from two agricultural drainage ditch outlets (Fig. 1) during 19 to 22 June 1995

Table 1. Analytical methods used for nutrient analyses of water samples from Hudson River Basin, 1993-1995.

Analyte	Analytical method
Silica, dissolved	Colorimetry—molybdate blue†
Nitrate plus nitrite, dissolved	Colorimetry—cadmium reduction-diazotization†
Ammonia plus total organic N	Colorimetry—block digester-salicylate-hypochlorite†
Ammonia, dissolved	Colorimetry†
Carbon, dissolved organic (DOC)	Wet oxidation‡
Carbon, suspended organic (SOC)	Wet oxidation‡
Orthophosphate	Colorimetry—phosphomolybdate§

† Fishman and Friedman, 1989.

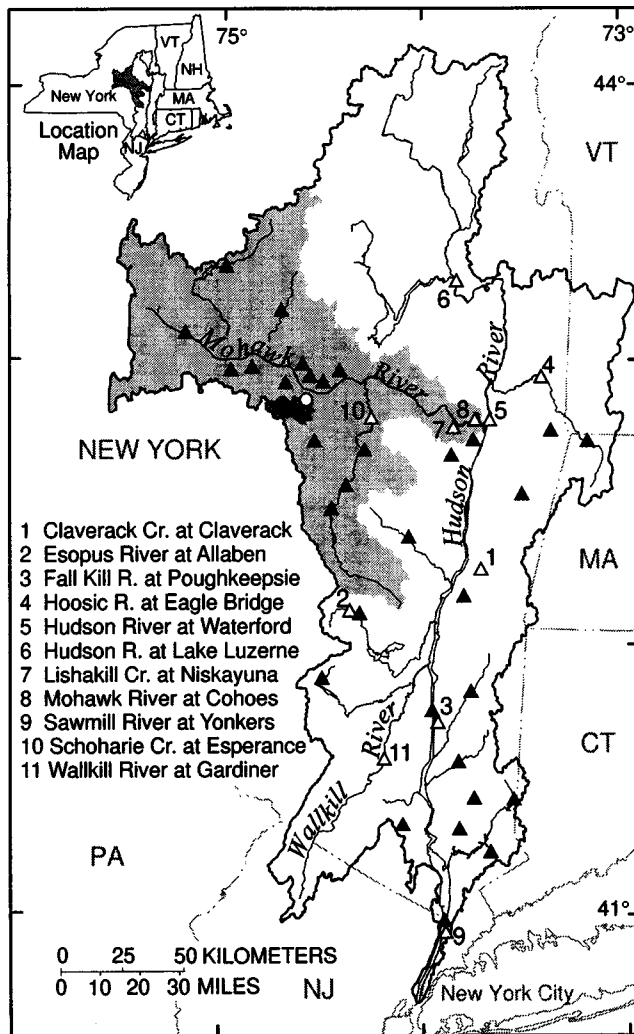
‡ Wershaw et al., 1987.

§ Fishman, 1993.

and analyzed for the same analytes as those from the watershed outlet. Phytoplankton were collected at all six mainstem sites, and periphyton samples were collected at five mainstem sites for analysis for chlorophyll-a, a commonly used indicator of algal biomass (Delong and Brusven, 1992; Morin and Cattaneo, 1992; Stevenson and Lowe, 1986). Phytoplankton samples were collected and processed onsite according to established USGS methods (Shelton, 1994) and analyzed at the NWQL by methods described in Britton and Greeson (1987). Periphyton samples were scraped from a 2.85-cm² area on each of three representative rocks in riffle areas at each of five locations (Porter et al., 1993).

Nutrient-concentration data collected from the Canajoharie Creek outlet during low flow in August 1993 were compared with those collected from 44 other stream sites in the Hudson River Basin (Fig. 2) during that period; these data are reported in Firda et al. (1993). In addition, nutrient concentrations at Canajoharie Creek outlet from April 1993 through March 1995 were compared with the concentrations at 11 other watershed outlets across the Hudson River Basin during the same period; these data are reported in Firda et al. (1993, 1994, 1995). Samples at Canajoharie Creek and 2 other watershed outlets were collected more frequently (i.e., >1/mo) during the spring and early summer than at the other eight sites. Only the sample collected closest to the 15th of the month was used in the analysis for months with multiple samples to make these data sets more comparable.

The methods used for statistical analysis in this paper depend on whether the data analyzed are censored (i.e., reported as less than the detection limit). For constituents that are frequently censored, such as nitrate, parametric methods of statistical analysis are not appropriate because the distribution of censored data are commonly not normal (Helsel and Hirsch, 1992); in such instances, the Spearman-rho correlation coefficient was used to test correlations. For those constituents not censored, a parametric Pearson's *r* correlation coefficient was



- 1 Claverack Cr. at Claverack
- 2 Esopus River at Allaben
- 3 Fall Kill R. at Poughkeepsie
- 4 Hoosic R. at Eagle Bridge
- 5 Hudson River at Waterford
- 6 Hudson R. at Lake Luzerne
- 7 Lishakill Cr. at Niskayuna
- 8 Mohawk River at Cohoes
- 9 Sawmill River at Yonkers
- 10 Schoharie Cr. at Esperance
- 11 Walkkill River at Gardiner

EXPLANATION

- Mohawk River Subbasin
- Canajoharie Creek Watershed
- ▲ August 1993 Low-Flow Sites
- ▲• August 1993 Low-Flow Sites and Sites with Monthly Data (4/93 - 3/95)
- Canajoharie Creek

Fig. 2. Locations of sampling sites used in nutrient-chemistry comparisons.

calculated. For each case, the coefficient is reported as either the Spearman-rho or the Pearson's r^2 . Seasonal comparisons of median concentrations of nitrate and silica are based on the nonparametric Wilcoxon signed-rank test.

Groundwater Data

Nineteen monitoring wells were installed in the part of the watershed that contains the greatest proportion of agricultural land (Fig. 1), which is also an area of significant groundwater discharge to Canajoharie Creek. Wells were installed according to methods described in Lapham et al. (1995). Seventeen of the 19 wells were on a 110-ha corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] farm, one was on a dairy farm, and one was in a hay field. Fifteen of the 19 wells were screened in the unconfined aquifer; two of these wells were sampled three times (September 1993, June and August 1994),

two wells were sampled in June and August 1994, two were sampled in September 1993 and June 1994, and the remaining 11 were sampled once (August 1994). The other four wells were screened in the confined aquifer; one was sampled three times (September 1993, June and August 1994), one was sampled in July 1994, and two were sampled in August 1994. Water samples were collected according to methods described in Koterba et al. (1995) and analyzed for nutrients and major ions at the NWQL by methods described in Wershaw et al. (1987), Fishman and Friedman (1989), and Fishman (1993). Methods used for specific analytes are described in Table 1.

RESULTS

Seasonal Patterns of Nutrient Concentrations at the Watershed Outlet

Nitrate concentrations at the Canajoharie Creek watershed outlet (1993–1995) are depicted in Fig. 3. Because most of the nitrite + nitrate consisted of nitrate, nitrite + nitrate is presented as nitrate in the following figures and discussion. The maximum measured nitrate concentration was 3.3 mg/L as N and occurred during a storm in October 1995. Median nitrate concentrations were 1.2 mg/L as N from December through March, and near the detection limit of 0.05 mg/L as N during the rest of the year.

Dissolved silica concentrations generally paralleled those of nitrate (Fig. 3). A Spearman-rho analysis of data collected during 1993 to 1994 indicates that dissolved silica concentration was significantly positively related to nitrate concentration ($\rho = 0.63$ and $p < 0.001$). If one sample collected in June 1994 under baseflow conditions with an anomalously high silica concentration (9.6 mg/L) is excluded from this analysis, the relation is even stronger ($\rho = 0.74$ and $p < 0.001$). Silica concentrations ranged from 4 to 5 mg/L as SiO_2 during winter to <1.0 mg/L as SiO_2 during the summers of 1993 and 1994. Silica concentrations during the drought in the summer of 1995 departed from the pattern of 1993 and 1994 and steadily increased from mid-May through mid-July, although nitrate concentrations remained below detection limits. A Spearman-rho analysis of data collected during the summer of 1995 indicates no statistically significant correlation between dissolved silica and nitrate concentrations.

Concentrations of ammonium, total organic N (Fig. 3), SOC (not shown), and DOC (not shown) did not display clear seasonal trends. During the drought of 1995, the concentrations of total organic N increased (similarly to those of dissolved silica) to levels only previously observed during storm runoff events. Orthophosphate was detected only in samples collected during winter or associated with a runoff-producing storm (Fig. 3), except for two samples collected near the height of the drought of 1995 (June through early July) during the rise in both total organic N and silica concentrations.

Spatial Patterns of Nutrient Concentrations in Surface Water

Nitrate and silica concentrations in Canajoharie Creek decreased from upstream to downstream sites

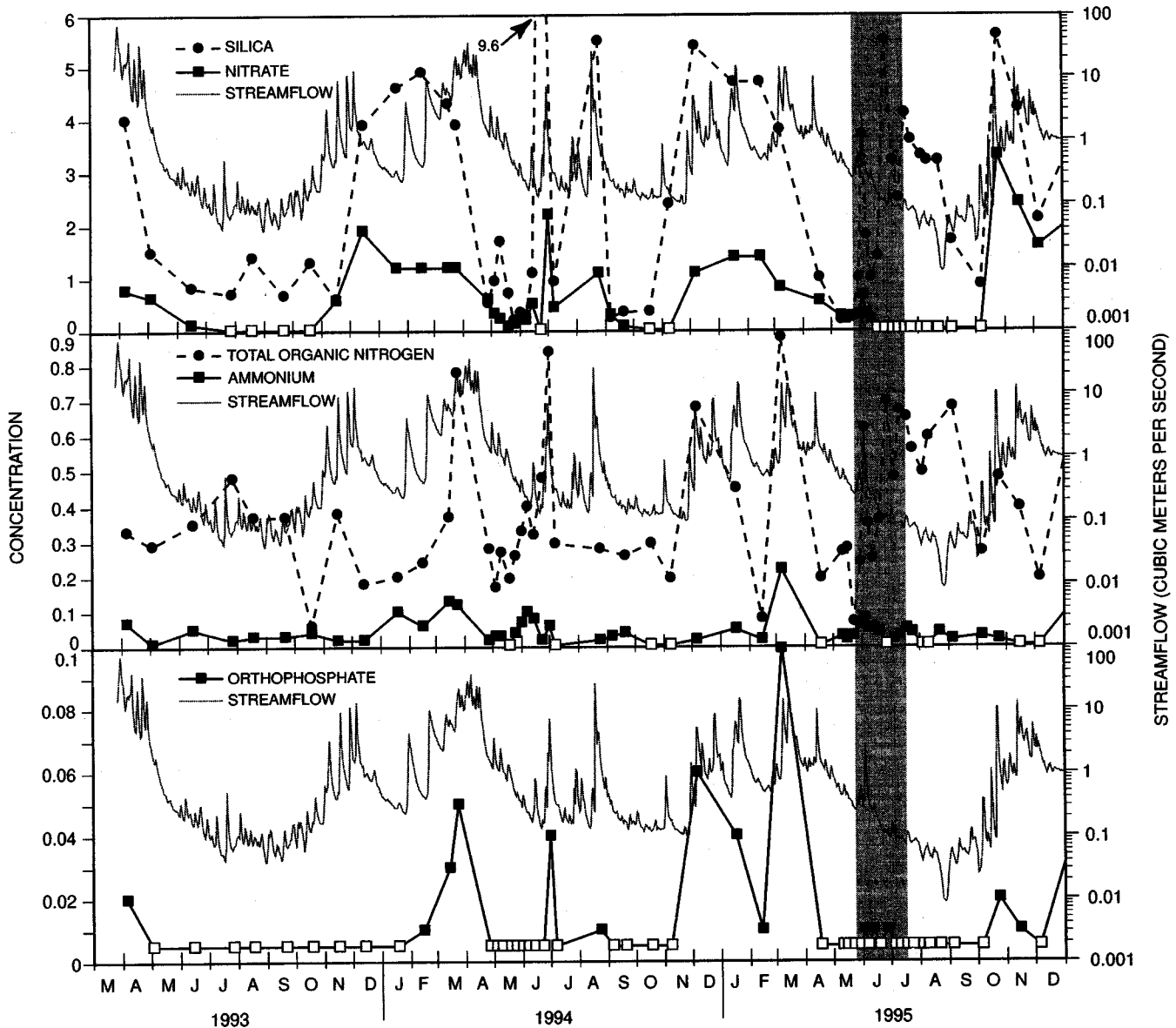


Fig. 3. Analytes and streamflow discharge at the outlet of Canajoharie Creek, April 1993 to December 1995. Open symbol indicates analyte was below detection. Gray bar highlights period when drought may have adversely affected the diatom community.

in June 1995 and, based on a Pearson's analysis, are significantly positively correlated with each other (Pearson $r^2 = 0.93$, $p < 0.001$) (Fig. 4). Log-transformed concentrations of chlorophyll-a in phytoplankton in mainstem samples are inversely correlated with concentrations of silica and nitrate (Pearson's $r^2 = 0.87$ and 0.91 , respectively; $p = 0.006$ and $p = 0.003$, respectively) (Fig. 5). Measured chlorophyll-a concentrations in periphyton were highest at a site 14.5 km above the watershed outlet (Fig. 6), which is also 0.7 km downstream from an agricultural drainage ditch whose discharge nearly doubled the mainstem nitrate load. Chlorophyll-a concentrations in periphyton decreased with nitrate and silica concentrations downstream from this site.

Groundwater

Nitrate concentrations in water from the 15 wells screened in the unconfined aquifer ranged from <0.05

to 19 mg/L as N. A median concentration of 4.4 mg/L as N for these wells was calculated from (i) the average nitrate concentration for each well and (ii) a value of one-half the detection limit for samples with concentrations below the detection limit. Nitrate concentrations in samples from five wells screened in the unconfined aquifer within 10 m of Canajoharie Creek ranged from <0.05 to 6.5 mg/L as N, with a median value of 5.1 mg/L as N. Nitrate concentrations in the six samples from the four wells screened in the confined aquifer were below the detection limit of 0.05 mg/L as N.

Temporal and Spatial Nutrient Trends in Other Hudson River Basin Watersheds

Concentrations of five constituents in samples collected during low-flow conditions at the Canajoharie Creek outlet site and at 44 other stream sites in August 1993 are shown in box plots in Fig. 7A. Of these sites,

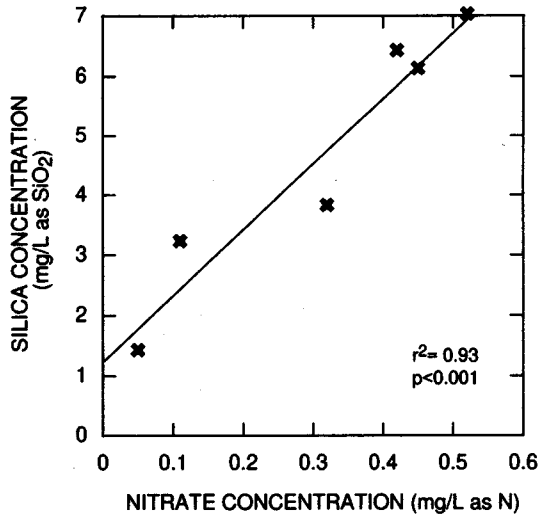
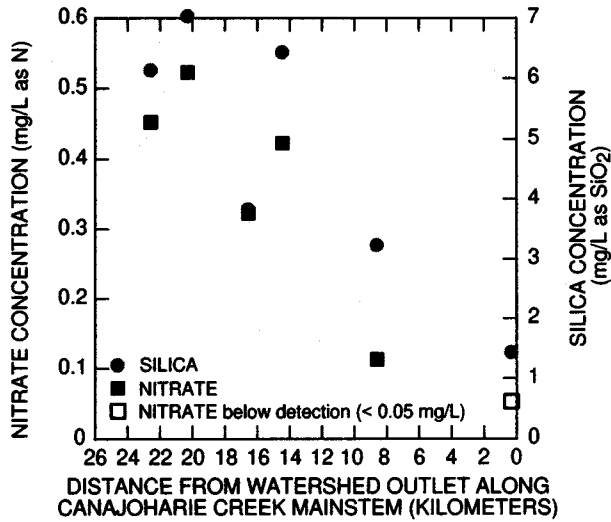


Fig. 4. Concentrations of nitrate and silica along Canajoharie Creek mainstem (top) and relation between nitrate and silica concentrations (bottom), June 1995.

Canajoharie Creek had the third-lowest concentration of silica and no detectable orthophosphate or nitrate. The SOC concentration at Canajoharie was well above the median for the 44 sites and was similar to the concentrations in the lower Hudson River (the two sites sampled in the tidal part of the Hudson River). The total organic N concentration at Canajoharie was greater than the 90th percentile value for the 44 sites and was exceeded only by the concentration at Wallkill River, a large watershed that is 55% agricultural, and at two watersheds that are >84% urban. Similarly, concentrations were lower at the Canajoharie Creek outlet than at (i) 13 of the 44 sites below watersheds that are at least 35% agricultural (Fig. 7B), and (ii) a regional subset of 16 sites within the Mohawk River Valley (Fig. 7C). Among the agricultural sites, only the Wallkill River had a lower silica concentration (1.1 mg/L as SiO₂), and higher concentrations of SOC (2.6 mg/L) and total organic N (0.58 mg/L as N), than Canajoharie Creek.

Median concentrations of silica and nitrate in samples collected at Canajoharie Creek during the nonwinter

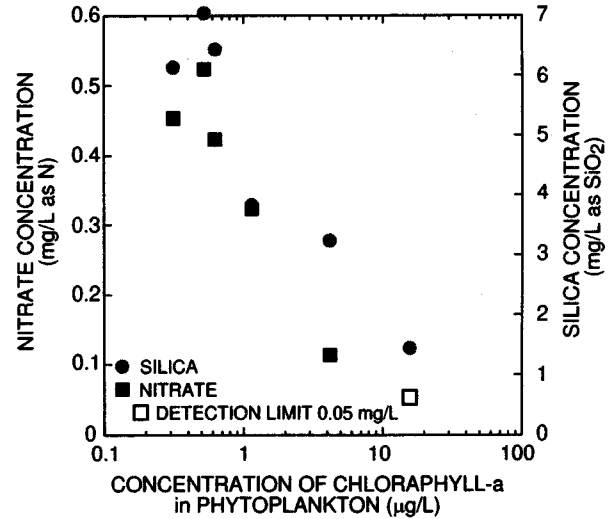


Fig. 5. Nitrate and silica concentrations in relation to chlorophyll-a concentration in phytoplankton samples collected along Canajoharie Creek mainstem, June 1995.

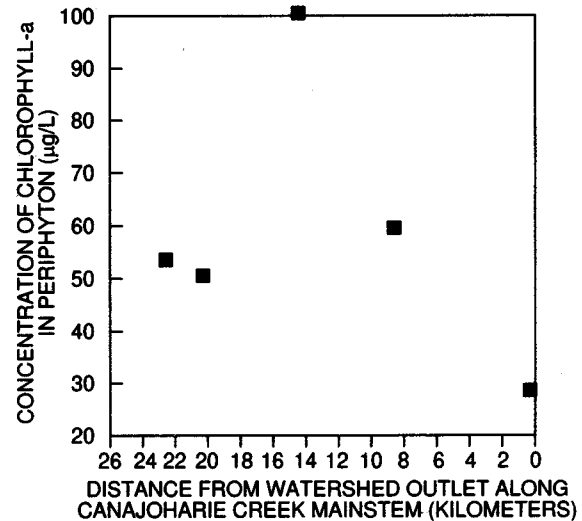


Fig. 6. Chlorophyll-a concentration in periphyton along Canajoharie Creek mainstem, June 1995.

periods (0.72 and 0.09 mg/L, respectively) were significantly lower (Wilcoxon signed-rank test, $p = 0.01$, and $p < 0.01$, respectively) than those collected during the winter or during storms (4.7 and 1.2 mg/L, respectively). Temporal data during the same period collected at 11 other Hudson River Basin watershed outlets indicate that several sites have significant seasonal differences in either silica or nitrate, but only two sites (on Esopus Creek and Wallkill River) had the magnitude of seasonal differences in both constituents similar to that observed at Canajoharie Creek (Table 2). Although the seasonal differences in median silica concentrations at Esopus Creek are statistically significant, the absolute difference in concentration is small.

DISCUSSION

Seasonal and spatial patterns in silica concentrations in Canajoharie Creek appear to be dominated by biolog-

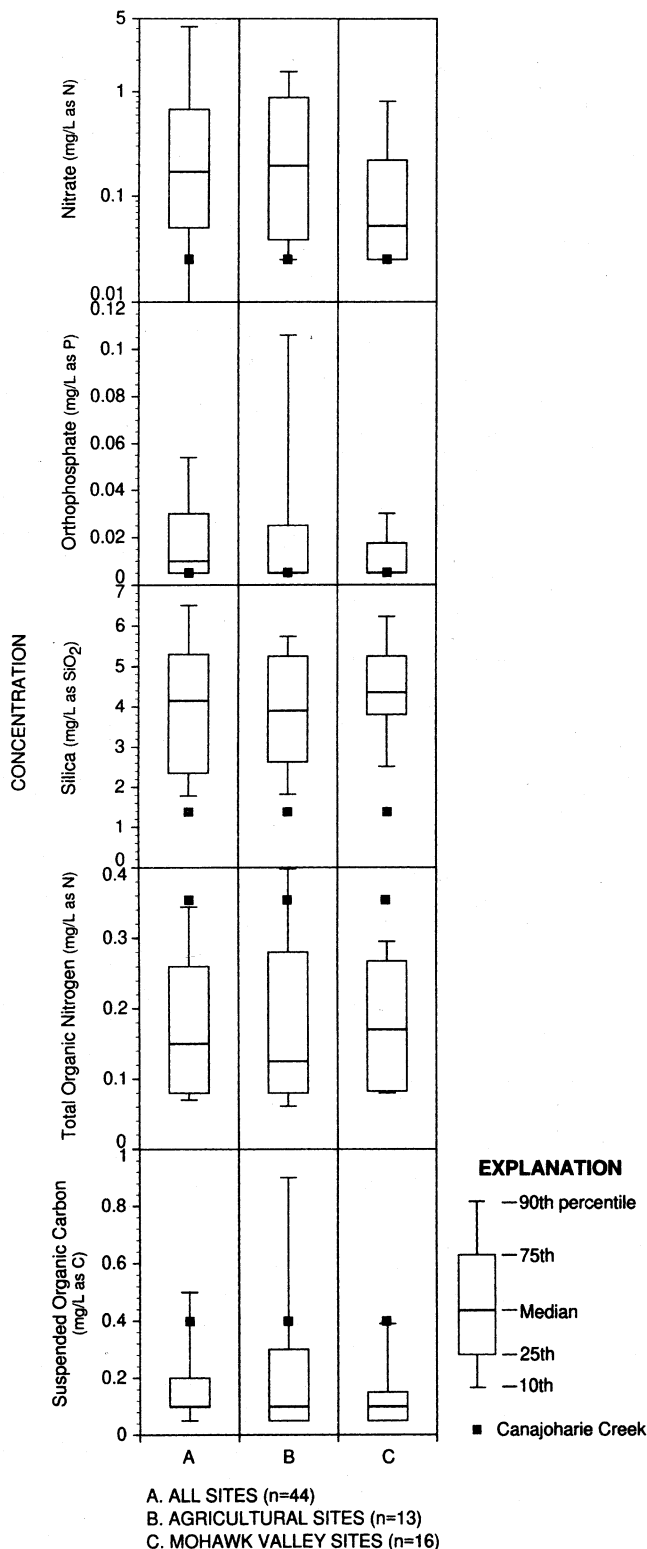


Fig. 7. Concentrations of selected constituents at Canajoharie Creek outlet during low flow (August 1993) in relation to concentrations during the same period at (A) all sites sampled in the Hudson River Basin, (B) sites below watersheds with 35% or more agricultural land, and (C) sites in the Mohawk River subbasin.

ical processes. The silica concentrations during winter at the watershed outlet were about 10 times greater than those observed during summer. This increase is probably not due to a winter increase in the amount of groundwater discharging from the confined aquifer to Canajoharie Creek, because that water is nitrate-free and, thus, would be expected to decrease the concentrations of surface water nitrate—contrary to observations. Furthermore, the difference in hydraulic head values between the confined and unconfined aquifers (Fig. 8) suggests that the creek contains a greater proportion of shallow groundwater during winter than at other times. Summer base-flow silica concentrations at the watershed outlet and along the mainstem of Canajoharie Creek in June 1995 were well below those measured in adjacent shallow wells (4.6–12 mg/L SiO_2) and deep wells (11–12 mg/L as SiO_2); thus, dilution is ruled out as a cause for the silica decline observed in base-flow samples. Inorganic precipitation of silica in the stream cannot explain the downstream or seasonal concentration decline because silica is generally conservative at observed surface water pH values (Drever, 1988).

Seasonal fluctuations of nitrate concentration in surface water are commonly attributed to seasonal differences in groundwater flow paths and to the reduced uptake of N by plants during winter (Neill, 1989); however, the relation between nitrate and silica concentrations in Canajoharie Creek over time and space suggests that diatoms are a major factor in the changes in nitrate concentrations. Diatoms (which utilize silica, nitrate, and phosphate as nutrients) tend to out compete cyanobacteria and green algae for nutrients when silica is not growth limiting (Sommer, 1988). Diatom abundance could explain both the seasonal and spatial variability of silica in Canajoharie Creek, whereby algal uptake along the length of the creek during the summer of 1993 and 1994 decreases silica concentrations at the watershed outlet, and a downstream increase in algal biomass causes a decrease in inorganic nutrient concentrations. Neither denitrification in the hyporheic zone nor an increasing proportion of denitrified groundwater during summer can be ruled out as factors contributing to the observed summer decline in nitrate concentrations, but the uptake of silica by some biologic process (probably diatoms), implies that at least some of the nitrate also must be taken up by this process.

Higher concentrations of ammonium plus total organic N and SOC at Canajoharie Creek in August 1993 than at other watershed outlets—and low or undetectable concentrations of nitrate, silica, and orthophosphate at the Canajoharie outlet—suggest higher rates of primary production and/or greater algal biomass and/or greater availability of nutrients at the Canajoharie site than at these other sites. Although the high concentrations of total organic N and SOC at Canajoharie Creek could be due to nutrient uptake by algal groups other than diatoms, the extremely low concentration of silica in Canajoharie Creek suggests that diatoms are a large component of the algal community.

The chemical data from August 1993, and 2 yr of chemical data from 11 watershed outlets from April

Table 2. Median seasonal concentrations of nitrate and silica in streamwater samples from 12 sites across Hudson River Basin, New York, 1993–1995. (Site locations shown in Fig. 2. Concentrations are mg/L; numbers in parentheses are *n* values.)

Site	Nitrate as N			Silica as SiO ₂		
	December–March (incl. stormflow)	April–November	Significance	December–March (incl. stormflow)	April–November	Significance
Canajoharie Creek near Canajoharie	1.2 (10)	0.09 (13)	**	4.7 (9)	0.72 (13)	**
Claverack Creek at Claverack	0.9 (8)	1.00 (16)		6.3 (7)	5.1 (16)	**
Esopus River at Allaben	0.29 (8)	0.07 (16)	**	2.8 (7)	2.4 (16)	**
Fall Kill River at Poughkeepsie	0.56 (8)	0.25 (16)	**	6.6 (7)	7.15 (16)	
Hoosic River at Eagle Bridge	0.55 (13)	0.43 (11)		4.2 (12)	2.3 (11)	**
Hudson River at Waterford	0.44 (8)	0.48 (14)		4.8 (7)	4.75 (14)	
Hudson River at Lake Luzerne	0.23 (10)	0.14 (14)	*	6.1 (9)	4.9 (14)	*
Lishkill Creek at Niskayuna	0.51 (12)	0.30 (12)	*	8.1 (12)	6.9 (12)	*
Mohawk River at Cohoes	0.66 (12)	0.61 (9)	*	4.9 (11)	3.3 (9)	**
Sawmill River at Yonkers	1.2 (11)	0.68 (13)	*	10.0 (10)	9.1 (13)	
Schoharie Creek at Esperance	0.58 (9)	0.35 (15)		3.95 (8)	2.2 (15)	*
Wallkill River at Gardiner	1.1 (12)	0.47 (12)	**	6.3 (11)	2.5 (12)	***

*, **, ****P* < 0.05, < 0.01, and < 0.001, respectively.

1993 through March 1995, indicate that nutrient dynamics of Canajoharie Creek at the outlet site are more similar to larger, low-gradient rivers such as the Wallkill, Mohawk, and Hudson Rivers (Fig. 2) than to other streams of its size and watershed land use. Seasonal patterns of nitrate and silica concentrations in Canajoharie Creek are most similar to those in the Wallkill River, even though the drainage area of the Wallkill is about 10 times larger.

The uniqueness of nutrient patterns in Canajoharie Creek in relation to those of other watersheds of comparable size is consistent with the concept that in-stream biological processes are largely regulated by the geomorphic character of the stream system (Vannote et al., 1980). For example, the gradient of Canajoharie Creek (for much of its length) is extremely low, relative to other streams in watersheds of similar size, and below its junction with Brimstone Creek, it is characterized by deep, meandering runs and long pools. Among the 14 low-flow sites in watersheds that are at least 35% agricultural, the stream gradient of Canajoharie Creek and the Wallkill River ranked just above the 25th and

10th percentiles, respectively (Fig. 9). Although stream gradient alone does not determine the presence or absence of diatoms or other algae, a low stream gradient allows a longer opportunity for uptake than a high gradient (Allan, 1995); it also allows less scouring of algal communities during high-flow conditions.

Biological Indicators of Nutrient Conversion

The strong correlation between silica and nitrate concentrations in June 1995 mainstem base-flow samples (Fig. 4 and 5) suggests that most of the downstream decrease in nitrate concentration is, at least for that period, controlled by diatoms. Although it is tempting to relate the silica and nitrate molar ratio observed in these samples to what might be expected in resident diatoms, a standard ratio for all diatoms is not available because of the wide variability of this ratio among diatom species (S. Kilham, 1996, personal communication). It must also be kept in mind that what we measured were effectively the *leftovers* or what was not taken up by the entire algal community, which likely includes a variety of diatom species. The corresponding down-

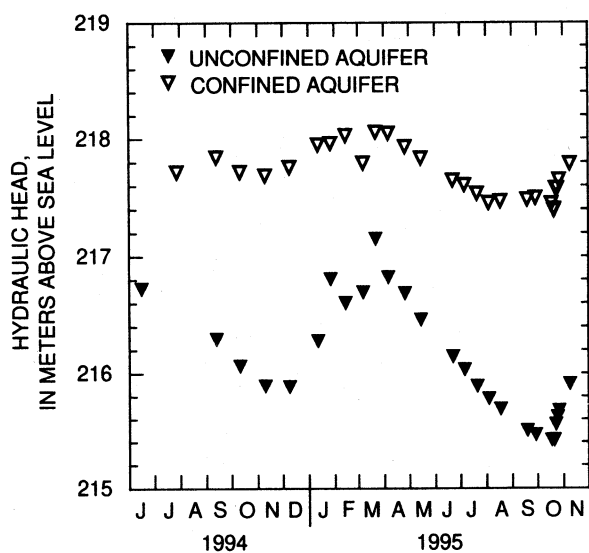


Fig. 8. Hydraulic head in selected wells screened in the confined and unconfined aquifers, June 1994 to November 1995.

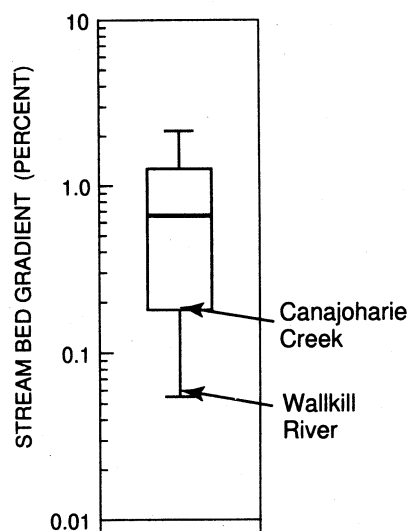


Fig. 9. Distribution of streambed gradients at Canajoharie Creek, Wallkill River, and 11 other agricultural watershed sites sampled in August 1993 in the Hudson River Basin.

stream increase in chlorophyll-a concentration in phytoplankton (an index of phytoplankton biomass), further suggests that observed nitrate and silica concentrations were significantly affected by diatoms. The sharp increase in the phytoplankton biomass at the site furthest downstream, however, could also result partly from the more open canopy and the change in channel morphology from shallow runs and riffles to deep runs and pools.

Although the concentrations of chlorophyll-a in periphyton do not directly support the hypothesis of conversion of nitrate and silica to algal biomass, the periphyton community is clearly responding to the nitrate input from the agricultural drainage ditch at 11.4 km (Fig. 1). The overall lack of correlation with nitrate and silica may reflect the effect of some other growth-limiting factor on the periphyton community, such as available light.

Drought of 1995

The seasonal patterns of silica and nitrate concentration and the relation between silica and nitrate concentrations observed at the watershed outlet during the height of the 1995 drought differed sharply from those observed in 1993 and 1994, possibly as a result of a decline in the predominance of diatoms in nutrient processing. Discharge at the watershed outlet was <0.15 m³/s from mid-June through early October, and rainfall was 38% below normal for the year by the end of August (National Climatic Data Center, 1996, written communication). Silica concentrations increased from 0.24 to 4.1 mg/L as SiO₂ from late May to mid-July, then declined through October, and nitrate concentrations remained below the detection limit of 0.05 mg/L as N from mid-June into October. The sustained low nitrate concentrations are generally due to some combination of diminished shallow (unconfined aquifer) groundwater discharge to Canajoharie Creek and uptake of available nitrate by algae and riparian plants. Similarly, the early increase in silica concentrations is generally due to deep groundwater discharge to the creek, decreased uptake by diatoms, and possibly dissolution of dead diatoms.

The greater decline in unconfined aquifer water levels than in the confined aquifer during the drought (Fig. 8) caused a proportional increase in the deep groundwater component of streamflow discharging to the creek. Over the course of the drought, this process alone would tend to increase silica concentrations and decrease nitrate concentrations in the stream, but the decline in silica concentrations after the mid-July peak cannot be attributed to any known hydrologic or abiotic factors and, without a biologic uptake mechanism, would have continued to rise, or at least remain elevated, as the drought continued. If uptake by diatoms could reduce the in-stream silica concentrations by 80% (from 4.1 to 0.86 mg/L as SiO₂) from mid-July to October, a period in which deep groundwater and silica were entering the creek in their largest proportions, this mechanism could not have been operating effectively during the sharp rise in silica concentrations before the mid-July peak.

The drought could have initially caused a large enough change in nutrient conditions to adversely affect the diatom community via, for example, exceedingly low concentrations of available silica, or some factor(s) that favored green algae or macrophytes over diatoms. The resulting decrease in silica uptake by diatoms, combined with an increase in available silica from deep groundwater or diatom dissolution, could have restored conditions necessary for diatoms to out-compete green algae and macrophytes for nitrate and subsequently remove large amounts of silica from the creek.

If a decline in the diatom population between mid-May and mid-July 1995 did occur, the similar trends in increasing total organic N and silica concentrations during this period (Fig. 3) suggest the organic N is associated with either the dying diatom population and/or organic waste from an emerging algal community replacing the diatoms. Similarly, detectable concentrations of orthophosphate during this period in two base flow samples suggests either the dissolution of P from dying diatoms and/or a shift in the nutrient requirements of the emerging algal community.

Peaks of total organic N concentrations during winter months probably are not the result of biological nitrate processing during winter, but instead reflect the movement of organic N with suspended sediment during winter storms. Peaks of nitrate and silica during storm events may reflect flushing of these constituents from soil and/or shallow groundwater.

Further examination of nutrient dynamics in the Canajoharie Creek watershed and its comparison with other watersheds would benefit from investigation of algal-community composition and structure, as well as the incorporation of additional watershed and geomorphic data.

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