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SYNTHESIS AND EMERGING IDEAS

Nitrogen attenuation in the Connecticut River, northeastern USA; a comparison of mass balance and N_2 production modeling approaches

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Abstract Two methods were used to measure in-stream nitrogen loss in the Connecticut River during studies conducted in April and August 2005. A mass balance on nitrogen inputs and output for two study reaches (55 and 66 km), at spring high flow and at summer low flow, was computed on the basis of total nitrogen concentrations and measured river discharges in the Connecticut River and its tributaries. In a 10.3 km subreach of the northern 66 km reach, concentrations of dissolved N_2 were also measured during summer low flow and compared to modeled N_2 concentrations (based on temperature and atmospheric gas exchange rates) to determine the measured "excess" N_2 that indicates denitrification. Mass balance results showed no in-stream nitrogen loss in either reach during April 2005, and no nitrogen loss in the southern 55 km study reach during August 2005. In the northern 66 km reach during August 2005, however, nitrogen output was 18% less than the total nitrogen inputs to the reach. N_2 sampling results gave an estimated rate of N_2 production that would remove 3.3% of the nitrogen load in the river over the 10.3 km northern sub-reach. The nitrogen losses measured in the northern reach in August 2005 may represent an approximate upper limit for nitrogen attenuation in the Connecticut River because denitrification processes are most active during warm summer temperatures and because the study was performed during the annual low-flow period when total nitrogen loads are small.

Keywords Nitrogen · Denitrification · Mass balance · Connecticut River

Introduction

The Connecticut River is a significant source of nitrogen to Long Island Sound, where high nitrogen loads cause seasonal hypoxia. To respond to this problem with effective strategies for reducing nitrogen loads in the Connecticut River, it is important to determine the rate and location of nitrogen loss during downstream transport to the Sound. Recent research has investigated the sources and transport of nitrogen in the Connecticut River basin (Deacon et al. 2006), but the extent to which nitrogen is lost during transport remains unclear (Moore et al. 2004; Seitzinger et al. 2002). The objective of the present study, therefore, was to assess the degree and variability of nitrogen attenuation in the Connecticut

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River by making measurements in two reaches of the river during two different seasonal flow regimes (spring and summer).

Previous research efforts have used a variety of approaches to measure nitrogen loss, mostly in smaller streams. Some methods, such as acetylene inhibition (Pfenning and McMahon 1996) and isotope tracing (Bohlke et al. 2004), have attempted to directly measure the rate of nitrogen cycling processes (e.g. denitrification). Other methods, such as mass balance (Burns 1998; Campbell et al. 2000) and dissolved N_2 measurements (McCutchan et al. 2003; Laursen and Seitzinger 2002), have inferred processes indirectly by identifying changes in the mass or concentration of end products (e.g. NO_3 and/or N_2). For larger watersheds, the mass balance approach is usually applied only in combination with nitrogen-input models (Castro et al. 2003). In the present study on the Connecticut River, the methods of mass balance and N_2 measurements were used independently to estimate the rates of in-stream nitrogen loss. For the mass balance, the need for nitrogen input modeling was avoided through intensive sampling and streamflow measurements.

Materials and methods

Study area

The Connecticut River has a drainage area of 29,140 km^2, and descends 730 m over its 660 km course. The river is regulated for electricity generation, with six hydroelectric stations and two storage reservoirs. The Connecticut River watershed is about 80% forested, 9% agricultural land, 5% urban, and 6% wetlands or barren (Deacon et al. 2006). Two reaches of the Connecticut River were selected for the mass-balance measurements of nitrogen loads. The northern reach, on the New Hampshire-Vermont border, was 66 km in length and the southern reach, in Massachusetts, had a length of 55 km (Fig. 1).

During 3 years of monthly sampling at three sites on the Connecticut River, total nitrogen concentrations ranged from 0.24 to 1.0 mg l^{-1} (median 0.50 mg l^{-1}) (Deacon et al. 2006). During the spring and summer 2005 sampling of the present study, concentrations of total nitrogen in the Connecticut River ranged from 0.39 to 0.82 mg l^{-1}. Nitrate concentrations ranged from 0.17 to 0.28 mg l^{-1}, ammonia ranged from 0.02 to 0.03 mg l^{-1}, and total ammonia plus organic nitrogen ranged from 0.23 to 0.62 mg l^{-1}.

For the N_2-production modeling approach, a 10.3 km subreach of the Connecticut River within the northern study reach was selected (Fig. 1). This section of river is a natural channel without impoundments, and had no significant tributaries that may affect the measured N_2 concentrations in the river.

Mass balance

Sample collection and analysis

The mass balance measurements were made during spring runoff in April 2005 and again during summer low flow in August 2005. These periods represented two approximate endpoints of the system—spring being the time when the largest portion of annual nitrogen loads are transported downriver at high velocity and cold water temperatures, and summer being the time of the lowest river velocities and discharge (Fig. 2) and the warmest water temperatures.

The study reaches were sampled using a Lagrangian approach (Moody 1993) during dry weather and relatively stable flow conditions. In summer, sampling was timed to avoid the largest flow changes from hydro-power dam releases to the extent possible. Total travel times through the study reaches were estimated to range from approximately 11 h (at spring high flow) to 50 h (at summer low flow) based on a previous dye-tracing study (Smith 2002) and historical velocity-discharge measurements at stream gaging stations.

Each study reach had a U.S. Geological Survey (USGS) streamflow gaging station at the upstream and downstream end, and on several tributaries, so that discharge could be easily determined for computing nitrogen loads (Fig. 1). In addition to the upstream and downstream ends of the Connecticut River study reaches, all major tributaries within each reach were sampled, resulting in a sampling coverage of >95% of the contributing drainage area. Manual streamflow measurements were made at the time of sampling on ungaged tributaries. Three municipal wastewater treatment plants in the northern study reach, which discharge directly to the Connecticut

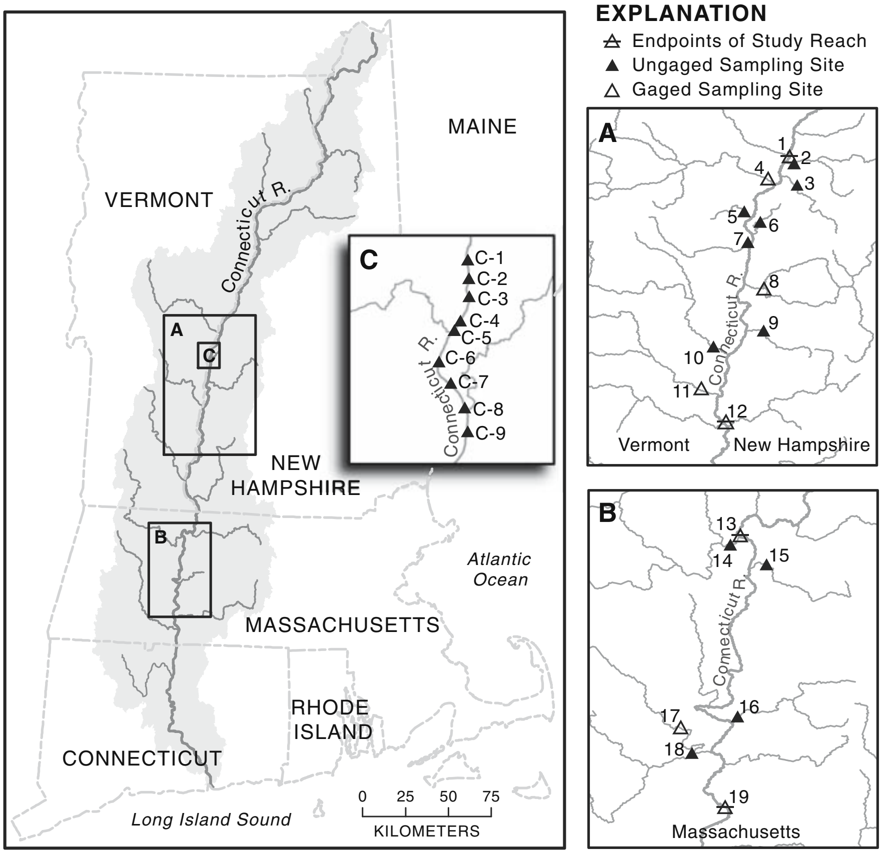

Fig. 1 Location map of study area. Region A shows the northern 66 km mass-balance reach, region B shows the southern 55 km mass-balance reach, and region C shows the study reach for N_2 modeling

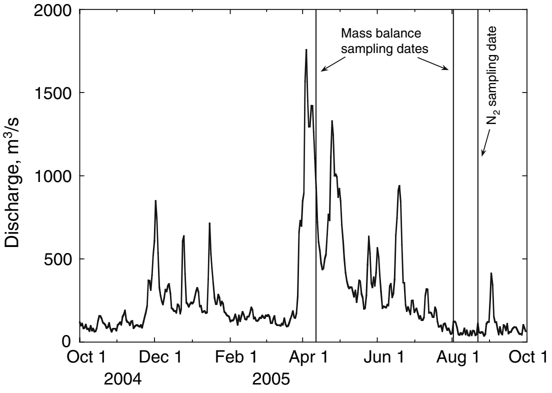

Fig. 2 Plot of daily mean discharge in water-year 2005 for the Connecticut River at North Walpole, NH (site 12 in Table 1), showing sample-collection dates for the nitrogen mass balance and N_2 modeling studies

River (or at the mouth of a tributary), were also sampled during each study period. Stream discharge was measured using procedures described in Rantz (1982).

The small unsampled drainage area (<5%) contributing to each study reach consisted of land immediately bordering the Connecticut River within the reach, or on very small tributaries. We assumed that discharge from these areas was ground-water seepage, and used the average nitrogen concentration of 7 streambank seeps sampled in the two study reaches to represent ground water. Ground-water discharge was computed from maps of seasonal ground-water recharge for the region (Flynn and Tasker 2004) or, in summer (when small-stream discharge is almost entirely ground-water seepage), from the average discharge per unit area of the smallest measured tributaries.

All water samples were collected and processed according to procedures described in Wilde et al. (1999), using depth- and width-integrated sampling. All samples were analyzed for ammonia, nitrate, total ammonia plus organic nitrogen (unfiltered), orthophosphate, total phosphorus (unfiltered), and chloride. Samples were analyzed by the USGS National Water Quality Laboratory (NWQL) in

Denver, CO, following the methods described in Fishman and Friedman (1989) and Patton and Truitt (2000). Total nitrogen was calculated from the sum of nitrate and total ammonia plus organic nitrogen (which includes all particulate nitrogen).

Mass balance computations

To determine nitrogen loss in each study reach by mass balance computations, the nitrogen output (concentration multiplied by streamflow) was compared to the sum of all measured and estimated nitrogen inputs to the reach. Estimated inputs include the ground-water contribution (described above) and a channel storage term (described below).

Due to diurnal variations in streamflow during spring snowmelt, and flow regulation in summer for hydroelectric power generation, the measured outflow of water from each study reach does not exactly match the sum of the inflows, as some water (and nitrogen) is taken into or released from channel storage. Thus, the difference between the outflow and total inflows during each sampling event became the 'channel storage' term in the mass-balance equation, equal to the rate of change of water stored in the reach (Tables 1 and 2). The nitrogen concentration of stored water was assumed to equal the flow-weighted average of the sampled inputs. The resulting change in nitrogen storage within the channel (positive or negative) was subtracted from the total nitrogen input to adjust the total input for mass-balance comparison with the nitrogen output (Fig. 3). Chloride, a conservative species, was also measured in each sample to verify that a mass balance was achieved during the sampling on each study reach.

N_2 sample collection and analysis

Field sampling for N_2

The 10.3 km subreach of the northern study area was sampled in August 2005, during a period of steady low flow between daily hydro-power releases from the Wilder Dam, located 15 km upstream. A LaGrangian sampling scheme was used to collect water samples for dissolved gas analyses (N_2:Ar) at 6 locations in the study reach. Temperature was recorded continuously using a StowAway® temperature logger (Onset Computer Corporation, Bourne, MA) suspended from the boat at a depth of 0.5 m. Samples were collected at mean depth in the area of greatest discharge (thalweg) using a peristaltic pump, filling 60-ml Biological Oxygen Demand (BOD) bottles. The tube was inserted to fill BOD bottles from the bottom. During bottle filling, two volumes were allowed to overflow, preventing contamination of water samples by atmospheric N_2. Samples were preserved by pipetting a small volume of saturated $ZnCl_2$ solution into each bottle (final concentration 0.5% vol/vol) immediately before inserting the ground glass stopper. Samples were then submerged in a cooler containing river water, to which a small amount of ice was added to keep the temperature approximately 1–2°C below in situ river temperature (which was approximately 24°C, and varied less than 1°C during sampling). Samples were stored at 22°C prior to analysis.

In previous studies, denitrification has been modeled at the sub-reach scale (i.e. between successive sampling points) (Laursen and Seitzinger 2002, 2004). For the Connecticut River, the approach was modified to increase sensitivity (which increases as the time interval for transport increases; Laursen and Seitzinger 2005) by treating the entire reach as a single entity (transit time 4.2 h). The rate of denitrification that resulted in the best fit to measured changes in N_2 concentrations between location C-3 and location C-9 was determined by modeling. Location C-1 was excluded, as dissolved gas values from this location were not consistent with those from the remaining locations, possibly due to poor mixing of river water at this deep, low-velocity location.

Determining atmospheric gas exchange

Atmospheric exchange of N_2 and Ar were determined by co-injecting two conservative tracers, one nonvolatile (sodium bromide) and one volatile (sulfur hexafluoride, SF_6). A similar dual-tracer approach (using two volatile tracers) has been used to determine CO_2 transfer rates in the Hudson River (Clark et al. 1994). Sodium bromide and SF_6 solutions, prepared in buckets, were poured into the river at a falls at the head of the reach (above location C-1). The rapids and constriction of flow into a narrow rock

Table 1 Water and nitrogen inputs and outputs from the Connecticut River study reaches on April 12, 2005

Site no.	Site name	Discharge (m^3 s^{-1})	Chloride (kg h^{-1})	Ammonia (kg h^{-1})	Ammonia + Organic N (kg h^{-1})	Nitrate (kg h^{-1})	Total nitrogen load (kg h^{-1})
Northern reach							
1	Connecticut River inflow	657	13,615	47.3	868	487	1355
2	Mascoma River	25.3	1178	0.91	22.7	9.2	31.9
3	Bloods Brook	2.38	85.2	0.15	0.89	1.5	2.35
4	Ottauquechee River	73.1	2207	4.47	57.1	64.2	121
5	Lulls Brook	2.79	75.1	0.10	1.46	1.9	3.35
6	Blow-me-down Brook	2.29	69.8	0.05	1.07	1.8	2.91
7	Mill Brook	5.52	128	0.20	1.01	3.5	4.53
8	Sugar River	38.8	2370	3.21	29.5	14.5	44.0
9	Little Sugar River	2.60	54.8	0.09	1.27	0.9	2.21
10	Black River	53.2	1916	3.07	47.5	32.6	80.1
11	Williams River	11.3	445	0.33	4.84	8.5	13.4
	Ground water discharge	21.2	1949	1.13	19.0	65.9	84.9
	Wastewater outfalls	0.174	133	1.51	1.73	7.01	8.73
	Total input	896	24,227	62.5	1056	699	1755
	Channel storage[a]	43.2	1170	3.02	51.0	33.7	84.7
	Adjusted input (-storage)	852	23,057	59.5	1005	665	1670
12	Connecticut River output	852	21,776	61.4	1037	638	1676
	Output − Input (%Δ)	0.0%	−5.6%	3.1%	3.2%	−4.0%	0.3%
	95% confidence range	±13%	±14%	±19%	±19%	±14%	±17%
Southern reach							
13	Connecticut River inflow	943	29,401	67.9	2122	662	2784
14	Deerfield River	95.7	3006	1.72	36.5	79.9	116.5
15	Sawmill River	2.16	84.1	0.08	4.86	1.06	5.92
16	Fort River	2.45	191	0.10	6.77	1.82	8.59
17	Mill River	3.68	198	0.13	3.98	3.30	7.28
18	Manhan River	5.78	323	0.27	1.66	8.96	10.6
	Ground water discharge	20.2	1860	1.08	18.2	62.9	81.1
	Total input	1073	35,062	71.3	2194	820	3014
	Channel storage[a]	−67.1	−2192	−4.46	−137	−51.3	−188
	Adjusted Input (-storage)	1140	37,254	75.7	2331	871	3202
19	Connecticut River output	1140	37,126	94.0	2461	867	3328
	Output − Input (%Δ)	0.0%	−0.3%	24.2%	5.6%	−0.5%	3.9%
	95% confidence range	±13%	±13%	±16%	±18%	±13%	±17%

[a] Channel storage is the difference between the total inflow to, and outflow from, each reach; this is a rate of change in the volume of water stored in the reach (m^3 s^{-1})

channel at these falls produced thorough mixing of the river, so that complete mixing of SF_6 and bromide occurred before location C-1.

Samples were collected at the 9 downstream locations (Fig. 1) for SF_6 and bromide. SF_6 samples were collected in 1-l glass bottles via peristaltic pump following the same procedure as the N_2 samples, and were capped without headspace and stored at ambient air temperature away from direct sunlight. Bromide samples were collected in 250-ml polyethylene bottles via peristaltic pump, filtered, and stored at ambient air temperature. Samples were collected near

Table 2 Water and nitrogen inputs and outputs from the Connecticut River study reaches on August 2–3, 2005

Site No.	Site name	Discharge ($m^3\ s^{-1}$)	Chloride ($kg\ h^{-1}$)	Ammonia ($kg\ h^{-1}$)	Ammonia + Organic N ($kg\ h^{-1}$)	Nitrate ($kg\ h^{-1}$)	Total nitrogen load ($kg\ h^{-1}$)
Northern reach							
1	Connecticut River inflow	41.3	1707	4.17	36.5	24.9	61.3
2	Mascoma River	0.583	82.1	0.01	0.51	0.11	0.62
3	Bloods Brook	0.062	6.38	0.00	0.03	0.02	0.06
4	Ottauquechee River	1.25	110	0.65	1.79	0.36	2.14
5	Lulls Brook	0.083	7.43	0.00	0.02	0.13	0.15
6	Blow-me-down Brook	0.041	3.66	0.00	0.04	0.00	0.04
7	Mill Brook	0.045	2.13	0.00	0.02	0.02	0.04
8	Sugar River	2.24	275	0.17	2.46	1.32	3.78
9	Little Sugar River	0.065	1.86	0.00	0.03	0.08	0.11
10	Black River	1.13	202	0.07	1.04	2.12	3.16
11	Williams River	0.538	57.6	0.02	0.51	1.51	2.02
	Ground water discharge	0.680	63	0.04	0.61	2.12	2.73
	Wastewater outfalls	0.085	34.1	0.05	0.65	7.00	7.65
	Total input	48.1	2552	5.19	44.2	39.6	83.8
	Channel storage[a]	1.98	105	0.21	1.82	1.63	3.45
	Adjusted Input (-storage)	46.2	2447	4.98	42.35	38.01	80.4
12	Connecticut River output	46.2	2274	2.49	37.7	27.8	65.5
	Output − Input (%Δ)	0.0%	−7.1%	−49.9%	−10.9%	−27.0%	−18.5%
	95% confidence range	±13%	±15%	±29%	±21%	±16%	±14%
Southern reach							
13	Connecticut River inflow	144	7008	9.32	151	122	273
14	Deerfield River	23.2	922	1.67	16.1	33.4	49.5
15	Sawmill River	0.940	38.2	0.02	0.67	0.57	1.24
16	Fort River	0.555	48.1	0.04	0.62	0.61	1.23
17	Mill River	0.623	37.0	0.02	0.37	0.67	1.04
18	Manhan River	0.728	58.4	0.07	0.51	1.63	2.14
	Ground water discharge	0.651	60	0.03	0.59	2.03	2.61
	Total input	171	8172	11.2	170	161	331
	Channel storage[a]	11.5	553	0.76	11.5	10.9	22.4
	Adjusted Input (-storage)	159	7619	10.4	158	150	308
19	Connecticut River output	159	7669	9.18	161	158	320
	Output − Input (%Δ)	0.0%	0.7%	−11.9%	2.0%	5.4%	3.7%
	95% confidence range	±14%	±16%	±22%	±21%	±16%	±16%

[a] Channel storage is the difference between the total inflow to, and outflow from, each reach; this is a rate of change in the volume of water stored in the reach ($m^3 s^{-1}$)

the centroid of the bromide and SF_6 plumes, as estimated by the surface velocity and specific conductance (bromide influence) of river water.

Both the SF_6 and bromide tracers were diluted during downstream transport due to mixing, but only SF_6 was affected by exchange with the atmosphere. The changes in bromide concentration were used to correct SF_6 for dilution; thus the rate of SF_6 loss to the atmosphere could be determined. The SF_6 transfer rate was used to calculate gas transfer rates for N_2 and Ar by relating gas transfer rates to molecular diffusion coefficients for the gases (Laursen and

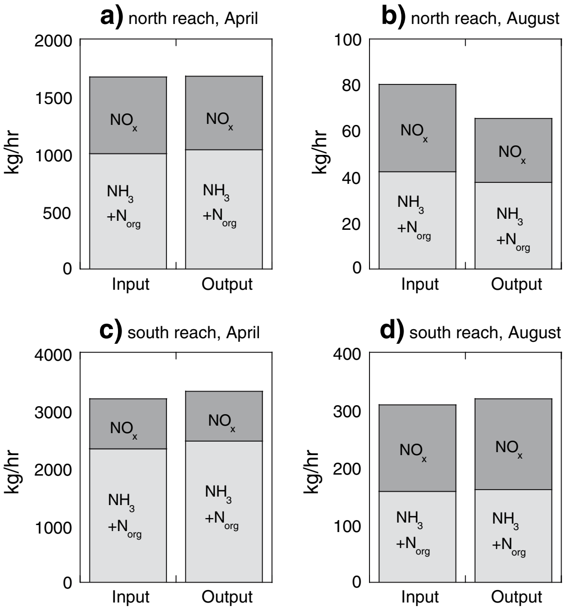

Fig. 3 Bar graphs of total nitrogen input and output from the two Connecticut River study reaches in April and August 2005. (**a**) northern reach, April 12, 2005; (**b**) northern reach, August 8–10, 2005; (**c**) southern reach, April 13, 2005; (**d**) southern reach, August 2–3, 2005

Seitzinger 2002). The atmospheric exchange of N_2 across the air-water interface (F) was calculated as the product of the first-order gas transfer rates (K), the mean water column depth (h), and the difference between the mean gas concentration in the water column (C_{mean}) and the atmospheric equilibrium concentration (C_{equil}) according to:

$$F = hK\left(C_{mean} - C_{equil}\right) \qquad (1)$$

assuming that the water column was well-mixed (homogeneous).

Sample analysis and modeling of denitrification

Analysis of N_2:Ar samples

Dissolved N_2:Ar was measured using a Membrane Inlet Mass Spectrometry (MIMS) system at Horn Point Laboratory, University of Maryland Center for Environmental Science, following previously described analytical and standardization procedures (Kana et al. 1994, 1998). Because replicate samples generally had a lower percent standard deviation among gas ratio measurements (<0.05%) than among direct gas measurements (<0.10%), changes in dissolved N_2 were calculated from the change in N_2:Ar through time during downstream transport. The Ar concentration at location C-3 was calculated directly from the mass spectrometry signal for $m/z = 40$, and the downstream Ar concentration at location C-9 was modeled based on a calculated Ar transfer rate.

Analysis of SF_6 and bromide

Samples were analyzed for SF_6 at the USGS Chlorofluorocarbon Lab in Reston, VA (gas chromatography with electron capture detection; Busenberg and Plummer 2000) and for bromide at the USGS NWQL (ion chromatography; Fishman and Friedman 1989).

Modeling denitrification

Denitrification was determined by comparing changes in the measured dissolved N_2 concentration with modeled N_2 concentrations for a parcel of water as it moved downstream. The model predicts downstream changes in N_2 concentration as a function of atmospheric exchange and channel morphology (mean width and depth), and allows for changes in K_{N_2} and equilibrium N_2 concentrations due to temperature changes at each 1-min time step (Laursen and Seitzinger 2002). N_2 production is then determined by excess N_2—that is, the measured change in dissolved N_2 that cannot be accounted for by atmospheric exchange. We assumed that this N_2 production was the result of denitrification. However, denitrification rates estimated by this approach are, strictly, net N removal by conversion to N_2 (i.e. denitrification minus N_2-fixation).

Error analysis

Mass balance computations

Confidence limits (uncertainties) on the nitrogen mass balance results were determined by propagating the estimated errors in the measured discharge and concentration values (Appendix A) through the mass-balance computations. The uncertainty in the nitrogen mass input and output for each study reach, following the error-propagation principles described by Taylor (1982) and simplifying terms, is given as:

$$\delta N_t = \sqrt{\sum \left[(\delta Q_i/Q_i)^2 + \left((\delta N_{k_i})^2 + (\delta NO_{x_i})^2 \right) \Big/ (N_{k_i} + NO_{x_i})^2 \right] [Q_i (N_{k_i} + NO_{x_i})]^2} \quad (2)$$

where:

δ = Uncertainty in associated term
N_t = Total nitrogen mass (input or output)
Q_i = Discharge at sampling site *i*
N_{k_i} = Ammonia + organic N concentration at site *i*
NO_{x_i} = Nitrate concentration at site *i*

The uncertainty in the nitrogen loss (or gain) for each study reach is then given as:

$$\Delta N_\Delta = \sqrt{(\delta N_i)^2 + (\delta N_o)^2} \quad (3)$$

where:

N_Δ = Change in nitrogen mass (output − input)
N_i = Total nitrogen mass input
N_o = Total nitrogen mass output

N_2 analysis and modeling

To estimate the uncertainty in the modeled denitrification rate, the model was run for all combinations of recalculated gas transfer rates, uncertainty in measured gas concentrations, and uncertainty in channel depth (Appendix A). All error terms were assumed to be additive. These multiple model runs, each finding the denitrification rate that resulted in the best fit to the data, were used to determine the maximum error in the estimated values. Therefore, while the range in modeled denitrification rates is nominally ±1 standard deviation, in reality the results are more conservative.

Results

Mass balance

A mass balance on the discharge measurements made for the Connecticut River and its tributaries during the April and August 2005 studies (Tables 1 and 2) shows that, except for the southern reach in summer, the water terms balance to within 5%. As noted previously, an exact balance would not be expected in summer due to increasing or decreasing channel storage resulting from flow regulation for hydroelectric power generation. After adjusting for changes in channel storage, chloride mass flux balanced within 1% for the southern reach, and within 7% (net loss) for the northern reach (Tables 1 and 2). Because chloride behaves conservatively, a precise measure of all inputs and outputs should, in theory, balance exactly. Thus, chloride (and possibly streamflow) inputs may have been slightly overestimated in the northern reach.

The total nitrogen inputs and outputs balance to within 4% (±17% at 95% confidence) in both the north and south study reaches during April 2005 (Table 1), as well as in the southern reach during August 2005 (Table 2, Fig. 3). In the northern reach in August 2005, however, the nitrogen mass output was measured to be 18.5% less than the total nitrogen inputs (±14% at 95% confidence) (Table 2, Fig. 3), indicating that in-stream nitrogen loss was occurring.

The error terms for both reaches during the April 2005 study period (±17%), and for the southern reach in summer (±16%), are substantially larger than the measured nitrogen gain (0.3–3.9%) in these reaches. This indicates that, within the limits of 95% confidence, we cannot state that nitrogen was either being lost or gained over the study reaches. For the northern reach in summer, however, we have 95% confidence that nitrogen was being lost (4.5% to 32.5% loss).

Gas exchange rates

The SF_6 concentration, corrected for dilution, decreased to 66% of initial concentration over the 3.5 h transit from C-1 to C-6. Below C-6, SF_6 was too dilute to reliably include in the model of SF_6 loss. The first-order transfer rate of SF_6 (K_{SF6}) calculated

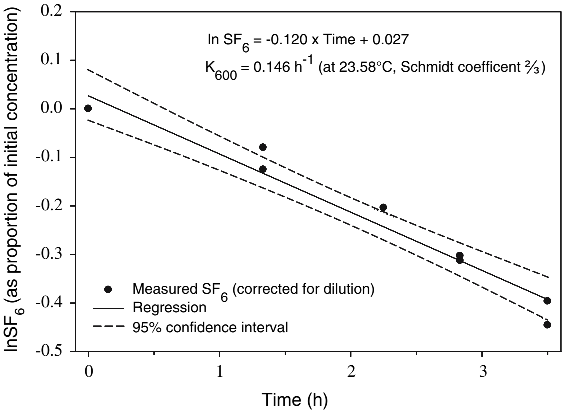

Fig. 4 Change in SF_6 concentration during downstream transport used to calculate gas exchange rates. SF_6 concentration is expressed as a natural-log transformed proportion of initial. Values are corrected for dilution on the basis of change in concentration of co-injected conservative tracer (bromide)

over the reach C-1 to C-6 was 0.120 h^{-1} (Fig. 4). Based on SF_6 loss, K_{600} was calculated as 0.146 h^{-1}, assuming average depth of 1.34 m, average temperature of 23.58°C, and a Schmidt number coefficient (n) of ⅔ (Appendix B).

N_2 modeling

The sampling and modeling of dissolved N_2 in the 10.3 km subreach of the northern study area showed that denitrification was occurring at a rate of 198 μmol N m^{-2} h^{-1} (average of population of estimates) with a 95% confidence interval of 169 to 228 μmol N m^{-2} h^{-1} (Table 3). If this N_2 production rate is multiplied by the approximate bed-surface area of the study reach (length times average channel width), the total denitrification rate for the reach is found to be approximately 2.8 kg h^{-1}. This rate of denitrification would consume approximately 3.3% of the total nitrogen load in the river at low flow (83.8 kg h^{-1}; Table 2) over the 10.3 km reach. If the denitrification rate were constant (unlikely) across the entire 66 km northern study reach, approximately 21% (±3.1% at 95% confidence) of the total low-flow nitrogen load in the Connecticut River would be removed. For comparison, an 18% (±14%) loss of nitrogen in the northern 66 km reach in summer was determined by the mass balance method. These results suggest that denitrification may be the major mechanism of nitrogen removal in the study reach, although further field tests to narrow the uncertainty margin in the results would add confidence to this thesis.

Discussion

The mass balance of nitrogen inputs and outputs from the two study reaches during April 2005—showing no significant nitrogen loss—was expected because the rapid transport and cold water temperatures during this high-flow season provide little opportunity for biological processes to remove nitrogen from the water column. The different results between the two study reaches in August 2005 (measured nitrogen loss in only the northern reach), however, was less expected. This finding may be due to the presence of hydroelectric power dams on the Connecticut River, which significantly alter the natural character of the channel. Dams are present at the head and foot of both study reaches, but a greater length of deep, impounded water extends across the southern reach than the northern study reach which, by contrast, has substantially more shallow, gravelly pool-and-riffle sequences. It is possible that, by allowing greater interaction of the water column with a biologically active substrate, these shallow channel sections in the north provide an opportunity for attenuation of in-stream nitrogen that does not exist in the southern reach. As noted by Alexander et al. (2000), nitrogen removal by denitrification and settling is generally less in deeper channels where streamwater has less contact with benthic sediment.

The uncertainty analysis on the nitrogen mass balances, however, shows the possibility that there may be no appreciable difference in nitrogen removal between the north and south reaches, as the 95% confidence ranges of nitrogen loss overlap. An alternate perspective is that the error analysis does show a 95% certainty that nitrogen is removed in the northern reach in summer, but no such certainty elsewhere. The N_2 results also lend confidence to the summer nitrogen removal rates estimated by mass balance on the northern reach. A nitrogen removal rate between 169 and 228 μmol N m^{-2} h^{-1}, computed from the N_2 measurements at 95% certainty, would remove 18% to 24% of the nitrogen load in the river over the 66 km northern reach; this compares

Table 3 Model output for a variety of assumptions concerning uncertainty in N2:Ar, initial Ar, Schmidt number coefficient, and channel depth

N2:Ar for modeling[a]	Ar for modeling[b]	Depth[c]	Rate (μmol N m^{-2} h^{-1})	
			$n = 2/3$[d]	$n = 1/2$[e]
Measured values	Measured	Measured	255	214
		Measured +5%	225	145
		Measured −5%	286	244
Measured values	Measured + 1 stdev	Measured	225	164
		Measured +5%	172	154
		Measured −5%	278	
Measured values	Measured − 1 stdev	Measured	298	276
		Measured +5%	291	249
		Measured −5%	306	284
Measured value + 0.3 stdev (location 3) Measured value − 0.3 stdev (location 9)	Measured	Measured	249	207
		Measured +5%	218	138
		Measured −5%	280	238
Measured value − 0.3 stdev (location 3) Measured value + 0.3 stdev (location 9)	Measured	Measured	262	220
		Measured +5%	232	152
		Measured -5%	292	251
Measured value + 0.3 stdev (location 3) Measured value − 0.3 stdev (location 9)	Measured + 1 stdev	Measured	54	0
		Measured +5%	0	−120
		Measured −5%	114	54
Measured value − 0.3 stdev (location 3) Measured value + 0.3 stdev (location 9)	Measured + 1 stdev	Measured	67	8
		Measured +5%	18	−107
		Measured −5%	126	67
Measured value + 0.3 stdev (location 3) Measured value − 0.3 stdev (location 9)	Measured – 1 stdev	Measured	292	270
		Measured +5%	284	242
		Measured −5%	300	278
Measured value − 0.3 stdev (location 3) Measured value + 0.3 stdev (location 9)	Measured − 1 stdev	Measured	305	283
		Measured +5%	297	256
		Measured −5%	313	290

[a] Measured values for N_2:Ar were 38.358 for location 3 and 38.435 for location 9; 0.3 standard deviates = 0.005 (standard deviation of replicates = 0.019)

[b] The measured value of Ar at location 3 was 12.825, with a standard deviation of 0.041

[c] Average depth for all transects = 1.34 m

[d] The value for k_{600} was 19.56 cm h^{-1} $\left(n = 2/3\right)$

[e] The value for k_{600} was 18.63 cm h^{-1} $(n = 1/2)$

favorably with the mass-balance results showing 18% (±14%) nitrogen loss.

The nitrogen loss rates measured in the northern reach in August 2005 likely represent an upper limit for the Connecticut River, because: (1) low velocities (long residence times) and warm temperatures during summer low flow may maximize the opportunity for biological activity to remove nitrogen from the water column, and (2) the nitrogen load in the river is greater at times of higher streamflow; therefore, the measured nitrogen-loss rate would remove a smaller portion of the total nitrogen load under most flow conditions.

The zero to 18% nitrogen loss measured in the Connecticut River in spring and summer 2005, both as a percent of nitrogen load and as a total loss, were within the range found in other studies. Using a mass balance approach in a small watershed (55 km^2), Burns (1998) found only a 3% loss of in-stream nitrate over a 1 km reach during spring high flow, and up to 24% loss in summer. Using the acetylene block technique to measure denitrification in many sediment samples from a large river system in Australia, Bartkow and Udy (2004) estimated that 3% to 15% of riverine nitrogen was lost in-stream, with denitrification rates mostly less than 150 μmol N m^{-2} h^{-1}, but as high as 950 μmol N m^{-2} h^{-1}. The denitrification rate of 198 μmol N m^{-2} h^{-1} measured in the Connecticut River in August 2005 was comparable to rates measured in a number of small to mid-sized rivers draining predominantly forested catchments (Laursen and Seitzinger 2005). Higher rates of denitrification were measured by McCutchan et al. (2003) on the agriculture- and urban-influenced South Platte River in Colorado, where 86% of in-stream nitrogen could be removed in one day. Similarly, on the very large (6300 km length), agricultural-impacted Changjiang River in China, denitrification was found to occur at the high rate of >5,000 μmol N m^{-2} h^{-1} (Yan et al. 2004).

Field measurements and watershed modeling both show that nitrogen loss rates can vary by two orders of magnitude within a single river system (Toms et al. 1975; Alexander et al. 2000). Thus, watershed models with stream- or reach-specific capabilities that can integrate this variability may prove useful for predicting nitrogen loss in the Connecticut drainage network. One empirical model of annual riverine nitrogen retention, RivR-N, suggests that nitrogen retention is greater (as a percent of nitrogen load) in small-order streams than in larger reaches (Seitzinger et al. 2002). Applied to the Connecticut River drainage basin, RivR-N predicted approximately 65% of total nitrogen inputs to be removed during riverine transport, with a reach-specific removal of approximately 15% in fourth-order reaches (such as the 66 km northern study reach). Another model, SPARROW, has also been applied to the Connecticut River as part of a nitrogen transport study for New England watersheds (Moore et al. 2004). The SPARROW results also showed that, on an annual basis, nitrogen loss was more likely to be significant in small streams than in large rivers having a mean discharge greater than 2.83 m^3 s^{-1} (100 ft^3 s^{-1}).

Whereas previous field studies of nitrogen attenuation have largely been confined to small watersheds or predominantly agricultural basins, the Connecticut River study provides additional data on the significance of in-stream nitrogen loss in a large, mostly forested watershed. The results support the indication by RivR-N that processing of nitrogen (primarily denitrification in low-order streams) within the Connecticut River drainage network could remove a significant portion of nitrogen during transport to Long Island Sound. The study results and the SPARROW model, however, both suggest that little nitrogen removal occurs in the large main stem of the Connecticut River on an annual basis. Thus, the impact on Long Island Sound by nitrogen sources in the Connecticut River watershed may be largely determined by the seasonal distribution of the source input (e.g. snowmelt) and the travel distance on low-order tributaries of the Connecticut River.

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Appendix A—Uncertainty analysis computations

Mass balance

Uncertainties in the mass balance measurements at each sampling site consisted of potential errors in the flow measurements, and analytical errors in determining the concentrations of nitrate and total ammonia plus organic nitrogen (which are summed to compute the total nitrogen concentrations). Because the rivers were well mixed, and samples were collected using depth- and width-integrated sampling (discharge weighted), sampling error was assumed to be negligible relative to the discharge and analytical uncertainties. For the ground-water component of the nitrogen input to each study reach, however, the standard deviations of nitrate and total ammonia plus organic nitrogen among the seven ground-water seep samples were used to determine the uncertainty in the ground-water nitrogen concentration.

Discharge records at the USGS streamflow gaging stations used in the study were rated "good," which the USGS defines as within 10% of the true value at 95% confidence (Kiah et al. 2005). Manual discharge measurements were rated "fair" (or better), which the USGS defines as within 15% of the true value at 95% confidence (Sauer and Meyer 1992). Analytical uncertainty was approximately 5% at 95% confidence for nitrate (Antweiler et al. 1993), and approximately 10% at 95% confidence for total ammonia plus organic nitrogen (Patton and Truitt 2000).

The uncertainties in the source terms (such as analytical error) were combined as the square root of the sum of their squares for each computation step, where the relative (percent) errors were squared and summed when terms were multiplied, and the absolute errors were squared and summed when terms were added (Taylor 1982).

N2 analysis and modeling

Uncertainty in gas transfer rates is derived from the scatter in SF_6:Br data and the uncertainty in the Schmidt number coefficient used to calculate N_2 transfer rates from SF_6 transfer rates (see Laursen and Seitzinger 2002). To compute the upper and lower confidence limits of N_2 transfer rates, the maximum and minimum slopes of the regression line of SF_6:Br versus time were calculated using ±1 standard deviation (Fig. 4). N_2 gas transfer rates were then re-calculated using the maximum and minimum SF_6 transfer rates derived from these slopes, with Schmidt number coefficients of $^2\!/_3$ (for flat surfaces, no waves) and $^1\!/_2$ (wavy surfaces not broken by white caps) (Jähne et al. 1987). A Schmidt number coefficient of $^2\!/_3$ was used for the baseline model, whereas a Schmidt number coefficient of $^1\!/_2$ represented maximum error.

N_2 concentrations at locations C-3 and C-9 (used as model inputs) were calculated for all possible scenarios among the two sources of error—uncertainty in Ar and uncertainty in N_2:Ar. Argon was modeled using measured Ar (at location C-3) ±1 standard deviation (0.04 for replicate samples). The standard deviation associated with replicate N_2:Ar measurement was ±0.019. N_2 concentrations were calculated at locations C-3 and C-9 as ±0.27 standard deviates. The probability of actual N_2:Ar being within +0.27 standard deviate of measured N_2:Ar at location C-3 while, simultaneously, actual N_2:Ar being within −0.27 standard deviate of measured N_2:Ar at location C-9, was approximately 70% (probability associated with 1 standard deviation). Channel depth is well constrained by the many transect measurements made along the study reach; for modeling purposes, however, uncertainty in average channel depth was assumed to be ±5%.

Appendix B—Sample calculations for gas transfer rates

1. $K_{SF6} = 0.120\ h^{-1}$ (regression of ln-transformed, bromide-corrected SF_6 concentrations versus time (Fig. 4)).
2. Average temperature over reach (locations C-1 to C-6) = 23.58°C
3. Schmidt number for SF_6 @ 23.58°C = 808*
4. $K_{600} = K_{SF6} \times (600/808)^{-n}$
5. $K_{600} = 0.146\ h^{-1}\left(n = {}^2\!/_3\right), = 0.139\ h^{-1}\left(n = {}^1\!/_2\right)$. K_{600} values are used to calculate N_2 and Ar transfer rates at each time step given in situ temperature. For example, @ 20°C:
6. $K_{N2} = K_{600} \times (580/600)^{-n}$ (Schmidt number for N_2 @ 20°C = 580)*
7. $K_{N2} = 0.134\ h^{-1}\left(n = {}^2\!/_3\right), = 0.126\ h^{-1}\left(n = {}^1\!/_2\right)$
8. $K_{Ar} = K_{600} \times (518/600)^{-n}$ (Schmidt number for Ar @ 20°C = 518)*
9. $K_{Ar} = 0.144\ h^{-1}\left(n = {}^2\!/_3\right), = 0.133\ h^{-1}\left(n = {}^1\!/_2\right)$

* Calculated based on Wanninkhof (1992).

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