

CATCHMENT-SCALE VARIATION IN THE NITRATE CONCENTRATIONS OF GROUNDWATER SEEPS IN THE CATSKILL MOUNTAINS, NEW YORK, U.S.A.

A. JOSHUA WEST¹, STUART E. G. FINDLAY^{2*}, DOUGLAS A. BURNS³,
KATHLEEN C. WEATHERS² and GARY M. LOVETT²

¹ *Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, England;*

² *Institute of Ecosystem Studies, P.O. Box AB, Millbrook, NY 12545, U.S.A.;* ³ *United States Geological Survey, 425 Jordan Rd., Troy, NY 12180, U.S.A.*

(* author for correspondence, e-mail: FindlayS@ecostudies.org)

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Abstract. Forested headwater streams in the Catskill Mountains of New York show significant among-catchment variability in mean annual nitrate (NO_3^-) concentrations. Large contributions from deep groundwater with high NO_3^- concentrations have been invoked to explain high NO_3^- concentrations in stream water during the growing season. To determine whether variable contributions of groundwater could explain among-catchment differences in streamwater, we measured NO_3^- concentrations in 58 groundwater seeps distributed across six catchments known to have different annual average streamwater concentrations. Seeps were identified based on release from bedrock fractures and bedding planes and had consistently lower temperatures than adjacent streamwaters. Nitrate concentrations in seeps ranged from near detection limits (0.005 mg NO_3^- -N/L) to 0.75 mg NO_3^- -N/L. Within individual catchments, groundwater residence time does not seem to strongly affect NO_3^- concentrations because in three out of four catchments there were non-significant correlations between seep silica (SiO_2) concentrations, a proxy for residence time, and seep NO_3^- concentrations. Across catchments, there was a significant but weak negative relationship between NO_3^- and SiO_2 concentrations. The large range in NO_3^- concentrations of seeps across catchments suggests: 1) the principal process generating among-catchment differences in streamwater NO_3^- concentrations must influence water before it enters the groundwater flow system and 2) this process must act at large spatial scales because among-catchment variability is much greater than intra-catchment variability. Differences in the quantity of groundwater contribution to stream baseflow are not sufficient to account for differences in streamwater NO_3^- concentrations among catchments in the Catskill Mountains.

Keywords: catchment-scale variability, groundwater, nitrate, seep, streamwater

1. Introduction

Understanding the processes that control the cycling of nitrogen (N) through terrestrial and aquatic ecosystems is important because N is often a limiting nutrient and a potential cause of forest decline (Schulze, 1989). Also, N release from terrestrial ecosystems can lead to deteriorating water quality in streams and downstream water bodies (Smil, 1997). Better understanding of controls on N release is



particularly important in the Catskill mountain region of New York because of high rates of N deposition in this region (Ollinger *et al.*, 1993; Weathers *et al.*, 2000) that serves as the major source of drinking water for metropolitan New York (Iwan, 1987).

In the northeast United States, the chief source of N to upland, forested ecosystems is atmospheric deposition (Vitousek *et al.*, 1997) and rates of N deposition have increased dramatically in the last 100 years as a result of fossil fuel combustion, primarily from automobiles (Berner and Berner, 1996). In the past two decades, many streams receiving high N inputs from deposition have shown significant increases in NO_3^- concentrations (e.g. Murdoch and Stoddard, 1993; Driscoll and van Dreason, 1993; Aber *et al.*, 1998). An ecosystem is considered saturated with N when the supply exceeds the capacity for assimilation, and excess NO_3^- leaches into streamwater. Stoddard (1994) suggested that the degree of N saturation can be assessed by comparing the mean concentration and seasonal pattern of NO_3^- concentrations in streamwater with more saturated systems that show higher concentrations during the growing season.

The effects of specific factors and processes such as forest structure, altitude and aspect, plant uptake and microbial immobilization that can influence the movement of NO_3^- from the atmosphere to the forest and eventually into streamwater are reasonably well understood in isolation (e.g. Lovett, 1994; Weathers and Likens, 1997; Currie and Nadelhoffer, 1999; Weathers *et al.*, 2000). What remains unclear are the interactions and controlling factors at the basin scale that ultimately determine how or when ecosystems receiving different nitrogen inputs will display changes in nitrogen export.

Streams in the Catskills show significant long-term increases in NO_3^- concentration (Murdoch and Stoddard, 1993) as well as dramatic (17-fold) among-catchment differences in mean stream NO_3^- concentrations (Lovett *et al.*, 2000a). Several hypotheses including flowpath effects (Jordan *et al.*, 1997), terrestrial vegetation (Lovett *et al.*, 2000a) and in-stream retention (Valett *et al.*, 1996) have been proposed to explain temporal and spatial variability in stream NO_3^- . The influence of hydrology on watershed chemistry has been extensively studied, and differences in hydrologic flowpaths have been shown to be an important factor regulating base cation and nitrogen transport in many catchments (Hendershot *et al.*, 1992; Ross *et al.*, 1994; Schaeffer and Driscoll, 1993; Pierson and Taylor, 1994; Creed and Band, 1998). Recently, Burns *et al.* (1998) showed that differences in groundwater contribution can maintain high NO_3^- concentrations in some Catskill streams even during the growing season. They argue that recharge of groundwater during late fall and early spring allows water with high NO_3^- concentrations to move through the rooting zone during this period of low biotic uptake. Further, they show that high summertime NO_3^- concentrations in three streams can be explained by inputs of seep water with high- NO_3^- concentrations; and thus, high NO_3^- concentrations in streamwater during the growing season are not necessarily symptomatic of nitrogen saturation.

We hypothesize that this mechanism that maintains high NO_3^- concentrations in streamwater during the growing season may also be effective in explaining among-catchment differences in streamwater NO_3^- concentrations. If groundwater seeps in the Catskills have consistently high NO_3^- concentrations, then among-stream variations in groundwater contribution may account for some of the observed among-catchment difference in streamwater NO_3^- concentration. If deep groundwaters do not have consistently high NO_3^- concentrations then among-catchment differences in groundwater contribution are less helpful in explaining differences in streamwater NO_3^- concentrations.

We tested whether groundwaters had consistently high NO_3^- concentrations by directly sampling deep water emerging at bedrock fractures and bedding planes in six different catchments chosen to span the known range in mean Catskill streamwater NO_3^- concentration.

2. Material and Methods

The Catskill region is an uplifted plateau with mountains carved by erosion. The bedrock is primarily flat-lying sandstone, shale and conglomerate of Devonian age, covered by glacial till and shallow Inceptisol soils (Murdoch and Stoddard, 1992). Vegetation at lower elevations is dominated by mixed oak forests which grade into northern hardwood forests above 500 m. Spruce-fir forests are present on some of the higher mountains above 1100 m. The focus of this study is on six Catskill catchments: Kanape Brook, Grog Kill, Biscuit Brook, Winnisook Brook, Hollow Tree Brook, and Mill Brook. Catchments were selected to span the documented range in headwater stream NO_3^- concentrations; two of the six streams were known to have high year-round NO_3^- concentrations, two were selected with intermediate, and two had relatively low NO_3^- concentrations (Table I). These streams drain primarily unmanaged forest land that is either part of the New York State Catskill Forest Preserve or owned by private land-holders. Four of these streams have multiple primary tributaries; all sampling was done in first-order reaches in the completely forested headwaters.

Groundwater seeps along these streams were identified and water samples collected during summer low-flow conditions. Seeps were selected based on observed flow during the dry summer months, their characteristic vegetation (primarily the *Laportea canadensis* nettles and the *Chrysosplenium saxifrage*), and a water temperature at their source consistently lower than that of the streamwater. Streamwater samples were collected at four to six sites along the length of each stream.

The six sets of seeps and associated streamwater were each sampled once. One of the catchments (Biscuit Brook) has been sampled as part of previous studies by the United States Geological Survey (USGS), and we sampled seeps in this catchment twice to examine potential temporal variability in seep chemistry. Sampling was done on a different day for each catchment, but all were sampled within a

TABLE I

Mean NO_3^- concentration (SD) for the six streams selected to represent high, medium and low NO_3^- concentration. Values are means of three years of quarterly sampling ($n = 12$ for each)

Stream Name	Mean NO_3^- -N (mg N/L)	Catchment area (ha)	Catchment base elevation (m)
Grog Kill (GK)	0.04 (0.03)	441	271
Kanape Brook (KA)	0.14 (0.09)	766	334
Winnisook Brook (WI)	0.30 (0.12)	230	811
Biscuit Brook (BB)	0.31 (0.14)	992	619
Mill Brook (MB)	0.50 (0.21)	279	674
Hollow Tree Brook (HT)	0.50 (0.07)	492	457

five-week period of low flow during the summer of 1997 (mid-June to late July). Biscuit Brook discharge is continuously monitored by the USGS and mean discharge for the seven separate sampling dates was 1.5 ± 0.9 (SD) cfs. Samples were syringe-filtered on site through $0.9 \mu\text{m}$ glass fiber filters into acid washed 125 mL polyethylene bottles, and refrigerated at 4°C until the time of analysis. Samples were analyzed within 1–3 weeks of collection and tests in our laboratory show NO_3^- concentrations are stable for at least six weeks. Samples were analyzed for NO_3^- by automated wet chemical colorimetry (Alpkem Autoanalyzer) and for SiO_2 by inductively coupled plasma emission spectroscopy (ICP).

Among-catchment differences in seep NO_3^- concentrations were assessed with analyses of variance using within-catchment variation of seep NO_3^- as the error term. Potential relationships between seep chemistry and relative position of seeps in the catchment were assessed by calculating nonparametric Spearman's correlation coefficients.

3. Results and Discussion

3.1. CONFIRMATION OF SEEPS

Temperatures of seep water ($10.9 \pm 2.5^\circ$, $n = 22$) were significantly ($p = 0.005$, $F_{1,46} = 8.8$) lower than nearby surface waters ($14.0 \pm 4.3^\circ$, $n = 26$) suggesting recent emergence from deep flowpaths. In addition to temperature, SiO_2 has been used as an indicator of groundwater residence time (Hinton *et al.*, 1994). There were significant positive correlations between seep SiO_2 concentrations and relative downstream position (Figure 1) in three out of four cases where seeps were

distributed over at least a 1 km length down the catchment. Two of the six catchments could not be used in this analysis because of either a small number of seeps ($n = 3$ seeps near Kanape Brook) or because all seeps occurred at roughly the same elevation (Mill Brook). This pattern of increasing SiO_2 concentrations with decreasing elevation in each catchment suggests seep waters collected near the base of the catchment had been in contact with bedrock for increasingly longer times.

Most of the seeps we sampled in Biscuit Brook and in the Winnisook drainage were the same sites sampled by Burns *et al.* (1998) who used similar evidence to argue that these seeps represent deep flowpaths rather than shallow groundwater or soil water that had recently entered bedrock fractures. Mean NO_3^- concentrations for Biscuit Brook seeps we sampled in summer of 1997 were within the range of the more extensive sampling spanning three years conducted by Burns *et al.* (1998). Nitrate concentrations in Biscuit Brook seeps on the two separate sampling dates in 1997 (mid-June = 0.35 ± 0.13 (SD) mg NO_3^- -N/L and mid-July = 0.41 ± 0.11) were not significantly different from each other (t -test, $p = 0.17$).

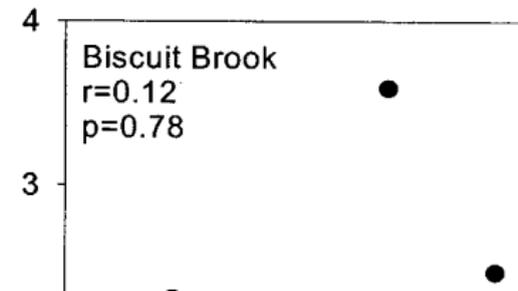
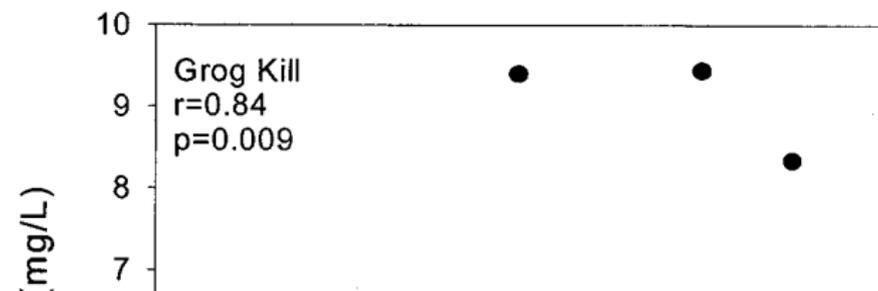
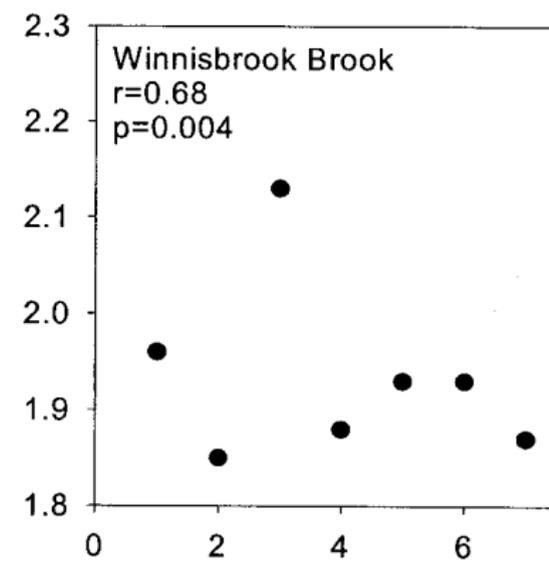
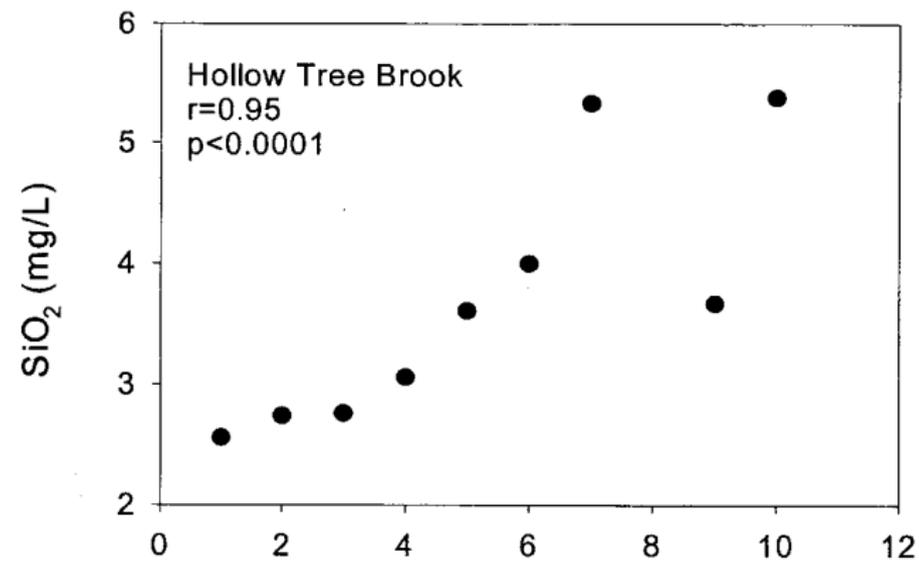
3.2. SEEP NO_3^- CONCENTRATIONS

The concentration of NO_3^- in the seep water we sampled showed large variability from one catchment to another, but relatively little variability within individual catchments (Figure 2). Differences in seep NO_3^- concentrations across catchments were highly significant (ANOVA, $F_{5,52} = 54.0$, $p < 10^{-6}$) demonstrating that among-catchment variability was much greater than smaller-scale variability within individual catchments. In fact, the NO_3^- concentrations in the seeps span the entire range of NO_3^- concentrations found in the group of streams sampled (c.f. Table I). Clearly, groundwater seeps cannot be characterized as having consistently high NO_3^- when compared across different catchments. Instead, there is significant spatial heterogeneity in the NO_3^- concentrations of seep water that spans the same range as does streamwater NO_3^- concentrations.

3.3. CONTROLS ON NO_3^-

Residence time in the groundwater flow system may contribute to within- and among-catchment variability in seep NO_3^- concentration. The down-catchment increase in SiO_2 (e.g. Figure 1) suggests increased residence time (c.f. Hinton *et al.*, 1994) for water emerging as seeps near the base of the catchment. Within those catchments showing a downslope increase in seep silicate concentration (Hollow Tree, Grog Kill and Winnisook, Figure 1) we found no significant downslope changes in seep NO_3^- concentrations (Spearman's rank correlation) for Hollow Tree Brook and Winnisook Brook ($p = 0.47$ and 0.7 , respectively) and a significant negative relationship ($p = 0.035$, $r = -0.74$) for Grog Kill.

Comparing mean concentrations among catchments reveals a statistically significant ($p = 0.001$) but weak ($r = -0.42$) negative correlation between seep SiO_2 and seep NO_3^- concentrations (Figure 3A) and for streamwater SiO_2 and streamwater



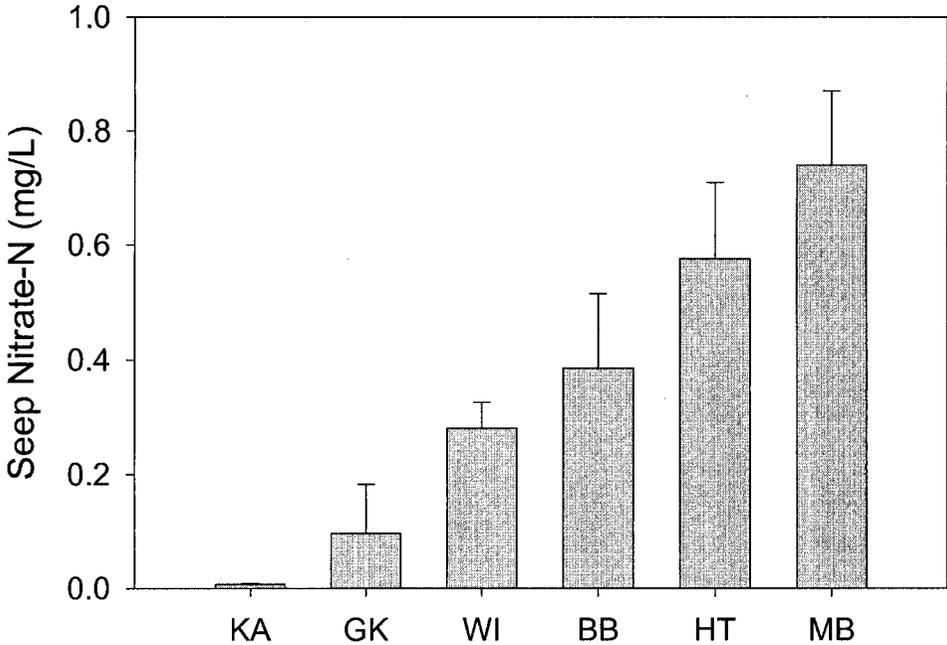


Figure 2. Mean NO_3^- -N concentration (+1 SD) in seep waters sampled in the six catchments. KA = Kanape Brook (number of seeps = 3); GK = Grog Kill (8); WI = Winnisook Brook (16); Biscuit Brook (9); Hollow Tree Brook (12); Mill Brook (10).

NO_3^- concentrations ($p < 0.001$, $r = -0.52$; Figure 3B). This inverse relationship is largely driven by the high SiO_2 concentrations in the two streams with low NO_3^- concentrations (Kanape Brook and Grog Kill) selected for study. Given the low explanatory power of the SiO_2 - NO_3^- relationship among catchments and the lack of a consistent downslope pattern in NO_3^- concentrations within catchments, it is unlikely that residence time of groundwater within or among catchments is significantly affecting measured NO_3^- at the points of seep emergence or delivery to the stream channel.

The narrow range in NO_3^- concentrations for all the seeps within any single catchment relative to among-catchment variability, suggests that the mechanism responsible for variations in NO_3^- concentrations must operate at a large spatial scale. Nitrogen deposition to the region is fairly uniform (Lovett *et al.*, 2000a) yet there is significant variability in seep and stream NO_3^- concentrations among catchments. Therefore, whatever is causing this variability must operate at a spatial scale of 100 or more ha, the minimum size of these catchments. We did not observe significant variability in the NO_3^- concentrations of seeps along the course of each stream, which would be expected if the primary mechanism controlling variations in seep NO_3^- concentrations operated at a relatively small scale. For instance, small areas of saturated soil strongly influence dissolved organic carbon and NO_3^- concentrations

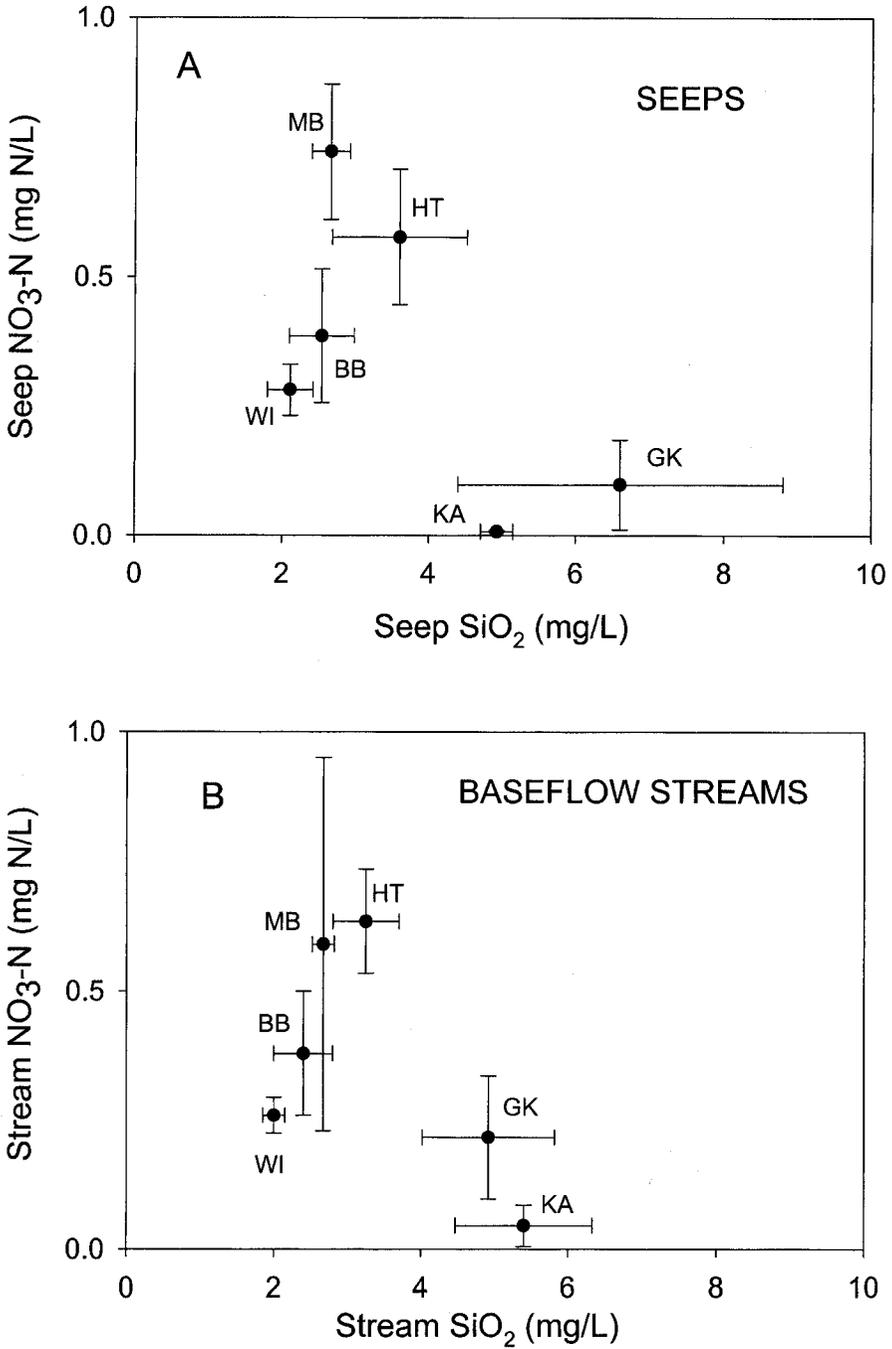


Figure 3. Correlation between (A) mean seep NO₃⁻ concentration and mean seep SiO₂ concentration for the six catchments sampled during summer 1997, and (B) mean stream NO₃⁻ concentration and mean stream SiO₂ concentration. Error bars are ± 1 SD.

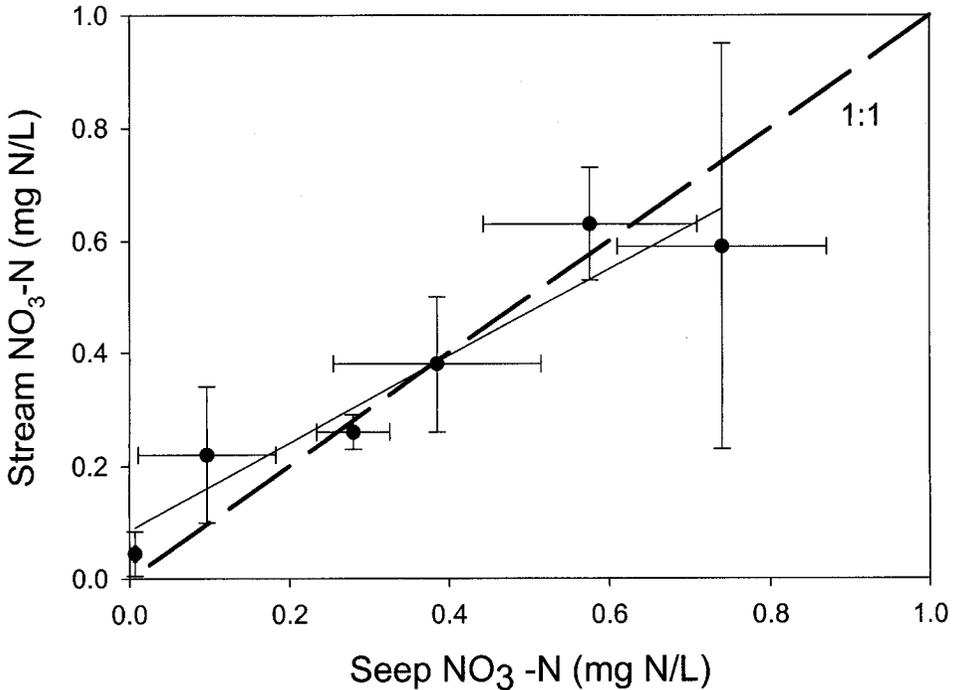


Figure 4. Relationship between seep NO_3^- concentrations and stream NO_3^- concentrations during summer 1997. The solid line is the regression ($p < 0.05$, $r^2 = 0.91$) between seep and stream NO_3^- concentrations and the dashed line is a 1:1 line. Error bars are ± 1 SD.

during storm events and over seasonal changes in hydrology (Boyer *et al.*, 1997; Creed *et al.*, 1996). However, during baseflow in our streams, such heterogeneity is small relative to among-catchment differences in groundwater NO_3^- concentration.

There is a strong correspondence between seep and streamwater NO_3^- concentrations at the time of sampling (Figure 4), which is to be expected because these samples were collected during baseflow when deep groundwater is the major contributor to streamflow. The similarity between seep NO_3^- concentrations and baseflow stream NO_3^- concentrations implies that in-stream processes do not consume or generate large amounts of NO_3^- , at least during summer baseflow conditions when the samples were collected. Differential instream uptake or release of NO_3^- within the stream channel would alter the 1:1 relationship between the NO_3^- concentrations of source (seep) water and the output (stream) water. The relative importance of terrestrial flowpath versus in-stream effects on nutrient concentrations has been examined with a variety of observational, modeling and mass balance approaches (Creed *et al.*, 1996; Valett *et al.*, 1996; Mulholland and Hill, 1997; Burns, 1998). Not surprisingly, catchment hydrology, near-stream flowpaths and in-stream biotic processes have all been shown to influence the final streamwater concentration of NO_3^- .

The data collected during this study, however, suggest a factor or set of factors that operate at the catchment (or larger) scale that affects the NO_3^- concentrations of seep water, and therefore, baseflow streamwater. We propose a hypothetical model whereby the NO_3^- concentrations of groundwater emanating as seeps are a reflection of the N cycling processes in catchment soils. The relative quantity of NO_3^- available in soil for leaching into infiltrating water that recharges these seeps during the spring and fall varies significantly among catchments. The catchments with lowest stream NO_3^- concentrations are dominated by oak forests and oak stands have low rates of nitrification (Lovett *et al.*, 2000b). Therefore, oak dominated areas have lower quantities of NO_3^- available for leaching from surface soils into groundwaters and ultimately into seeps. The presence of oak may be indicative of repeated disturbance in the past (Kudish, 2000), thus there may be an interaction between forest history and vegetation composition in controlling NO_3^- leaching. In any event, we hypothesize that the strongest controls on the NO_3^- concentrations in seep and stream water are the result of differences in disturbance and vegetation factors which manifest themselves as differences in NO_3^- generation in catchment soils. We are in the process of collecting more information about these catchments to test this hypothetical model.

4. Conclusions

Our results suggest a catchment-scale process capable of influencing deep groundwater NO_3^- concentrations. Differences among catchments in forest harvesting history, land use, disturbance or tree species composition may act at the appropriate scale, but we do not yet have the necessary data nor can we demonstrate the actual mechanistic link to adequately test these potential controlling factors. Within particular catchments or stream reaches, input of groundwater with high NO_3^- concentration will play an important role in controlling the seasonal changes in NO_3^- concentration in the streams, as described by Burns *et al.* (1998). However, seep water does not have consistently high NO_3^- concentrations and so, variations in groundwater input cannot be the sole explanation for inter-catchment variability in streamwater NO_3^- concentrations. Any model attempting to explain the variability in NO_3^- concentrations from one Catskill stream to another must also explain the variability in the NO_3^- concentrations of seep water from one catchment to another.

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