

## Upland Disturbance Affects Headwater Stream Nutrients and Suspended Sediments during Baseflow and Stormflow

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### ABSTRACT

Because catchment characteristics determine sediment and nutrient inputs to streams, upland disturbance can affect stream chemistry. Catchments at the Fort Benning Military Installation (near Columbus, Georgia) experience a range of upland disturbance intensities due to spatial variability in the intensity of military training. We used this disturbance gradient to investigate the effects of upland soil and vegetation disturbance on stream chemistry. During baseflow, mean total suspended sediment (TSS) concentration and mean inorganic suspended sediment (ISS) concentration increased with catchment disturbance intensity (TSS:  $R^2 = 0.7$ ,  $p = 0.005$ , range = 4.0–10.1 mg L<sup>-1</sup>; ISS:  $R^2 = 0.71$ ,  $p = 0.004$ , range = 2.04–7.3 mg L<sup>-1</sup>); dissolved organic carbon (DOC) concentration ( $R^2 = 0.79$ ,  $p = 0.001$ , range = 1.5–4.1 mg L<sup>-1</sup>) and soluble reactive phosphorus (SRP) concentration ( $R^2 = 0.75$ ,  $p = 0.008$ , range = 1.9–6.2 μg L<sup>-1</sup>) decreased with increasing disturbance intensity; and ammonia (NH<sub>4</sub><sup>+</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), and dissolved inorganic nitrogen (DIN) concentrations were unrelated to disturbance intensity. The increase in TSS and ISS during storms was positively correlated with disturbance ( $R^2 = 0.78$  and  $0.78$ ,  $p = 0.01$  and  $0.01$ , respectively); mean maximum change in SRP during storms increased with disturbance ( $r = 0.7$ ,  $p = 0.04$ ); and mean maximum change in NO<sub>3</sub><sup>-</sup> during storms was marginally correlated with disturbance ( $r = 0.58$ ,  $p = 0.06$ ). Soil characteristics were significant predictors of baseflow DOC, SRP, and Ca<sup>2+</sup>, but were not correlated with suspended sediment fractions, any nitrogen species, or pH. Despite the largely intact riparian zones of these headwater streams, upland soil and vegetation disturbances had clear effects on stream chemistry during baseflow and stormflow conditions.

HEADWATER STREAMS are important sites of nutrient processing (Peterson et al., 2001) and are strongly influenced by their surrounding catchment, which is their primary source of organic material, nutrients, and sediment (Hynes, 1975; Vannote et al., 1980). Geology, land use, and other catchment characteristics affect the rate at which these substances are delivered to streams (Omernik, 1976; Richards et al., 1996). Because of the ubiquity of anthropogenic landscape modification (Hannah et al., 1994; Vitousek et al., 1997), it is important to understand the impacts of anthropogenic catchment disturbance on stream ecosystems.

Concentrations of nutrients and suspended sediments in headwater streams are controlled by a variety of an-

thropogenic and natural factors. Natural variation in inputs of substances to streams is observed due to seasonal differences in precipitation and evapotranspiration, and differences among catchments in geology, soil, and vegetation. Urban and agricultural land use often increase the inputs of sediments and nutrients (e.g., Allan et al., 1997; Strayer et al., 2003). Deforestation can dramatically increase sediment runoff (e.g., Gurtz et al., 1980; Kreutzweiser and Capell, 2001) and increase the export of nutrients, particularly nitrogen, to streams (e.g., Likens et al., 1970; Harr and Fredriksen, 1988; Martin et al., 2000). The effects of catchment disturbance can be particularly strong during storm events (Webster et al., 1990).

The effects of disturbance within the riparian zone and the role of the riparian zone in mitigating some impacts of land use have been well-studied (e.g., Lowrance et al., 1984; Gregory et al., 1991; Osborne and Kovacic, 1993; Richards et al., 1996), and several intensive studies of the impacts of whole catchment deforestation have been conducted (Likens et al., 1970; Gurtz et al., 1980; Webster et al., 1992). However, the effects of localized, intense soil and vegetation disturbance in upland areas (i.e., upgradient from the riparian floodplain) are not well understood and they are the focus of this study.

Military reservations are well suited for studies of the impact of catchment disturbance on streams because of the broad range of disturbance intensities within these reservations and the proximity of highly disturbed and relatively undisturbed catchments. Military reservations are often regional islands of high quality habitat (Cohn, 1996), but, in areas dedicated to training exercises, intense soil and vegetation disturbance often occur (e.g., Quist et al., 2003). As a result, these reservations contain a wide range of anthropogenic disturbance intensities within a small region of relatively homogenous soils, vegetation, and geology. At the Fort Benning Military Installation, upland soil and vegetation disturbance has been shown to affect stream bed stability, the abundance of coarse woody debris and benthic organic matter, and stream metabolism (Houser et al., 2005; Maloney et al., 2005). In this study, we report the results from a set of streams spanning a gradient of disturbance at the Fort Benning Military Installation that illustrate the impact of upland soil and vegetation disturbance on stream chemistry, particularly nutrient and

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**Abbreviations:** BC1 and BC2, tributaries of Bonham Creek; DIN, dissolved inorganic nitrogen (NH<sub>4</sub><sup>+</sup> + NO<sub>3</sub><sup>-</sup>); DOC, dissolved organic carbon; HB, Hollis Branch Creek; ISS, inorganic suspended sediment; KM1 and KM2, tributaries of Kings Mill Creek; LC, Lois Creek; LPK, tributary of Little Pine Knot Creek; OSS, organic suspended sediment; SB2, SB3, and SB4, tributaries of Sally Branch; SRP, soluble reactive phosphorus; TSS, total suspended sediment.

**Table 1. Physical characteristics of the study stream reaches. Width, depth, flow, and velocity values are means and standard deviations based on measurements made during quarterly NaCl injections conducted from the summer of 2001 through the summer of 2003.**

Stream†	Width	Mean depth	Flow	Velocity	Catchment area	Mean slope	Disturbance intensity
	m		L s <sup>-1</sup>	m s <sup>-1</sup>	ha	%	% catchment
KM2	1.64 (0.39)	0.15 (0.10)	16.58 (19.55)	0.04 (0.03)	231	5.2 (2.8)	1.8
BC2	0.97 (0.08)	0.11 (0.03)	4.85 (2.70)	0.05 (0.02)	74.9	5.5 (3.0)	3.2
LC	1.85 (0.20)	0.12 (0.03)	16.64 (14.36)	0.07 (0.04)	332	5.5 (2.8)	3.7
KM1	1.91 (0.22)	0.13 (0.04)	25.61 (13.67)	0.1 (0.02)	369	3.9 (2.7)	4.6
HB	1.77 (0.15)	0.11 (0.03)	18.67 (14.9)	0.09 (0.04)	215	5.7 (2.9)	6.6
SB2	1.54 (0.14)	0.06 (0.02)	14.65 (6.14)	0.15 (0.03)	123	6.2 (3.2)	8.1
BC1	1.33 (0.15)	0.14 (0.03)	0.826 (3.91)	0.04 (0.01)	210	4.8 (3.0)	10.5
SB3	1.00 (0.13)	0.05 (0.03)	6.15 (4.03)	0.11 (0.03)	71.7	7.1 (3.6)	10.5
LPK	0.77 (0.09)	0.04 (0.02)	3.13 (1.45)	0.10 (0.02)	33.1	7.8 (4.0)	11.3
SB4	1.31 (0.47)	0.04 (0.02)	6.60 (3.94)	0.12 (0.03)	100	7.7 (3.9)	13.7

† BC1 and BC2, tributaries of Bonham Creek; HB, Hollis Branch Creek; KM1 and KM2, tributaries of Kings Mill Creek; LC, Lois Creek; LPK, tributary of Little Pine Knot Creek; SB2, SB3, and SB4, tributaries of Sally Branch.

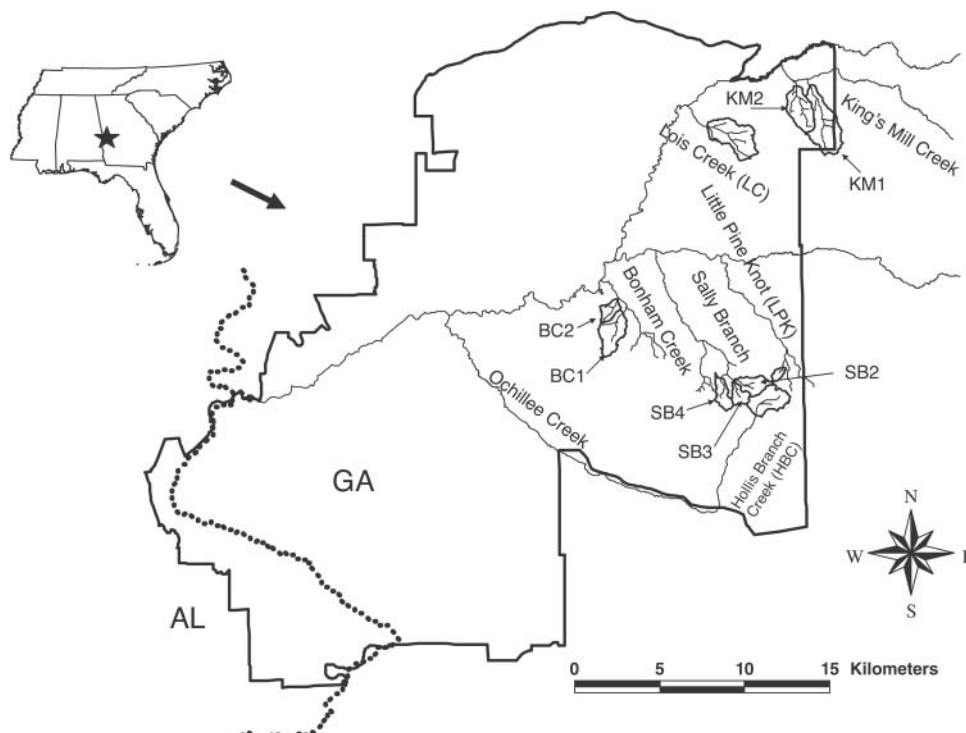
suspended sediment concentrations, during baseflow and stormflow conditions.

## MATERIALS AND METHODS

### Study Site

Ten second- to third-order streams on the Fort Benning Military Installation and within the Chattahoochee River Drainage of west-central Georgia were selected for study (Table 1; Fig. 1). Until purchased by the U.S. military in 1918 and 1941–1942, the land use was primarily row crop agriculture and pasture. Subsequently, the forest has regrown and, within the undisturbed areas on the base, land cover now consists primarily of oak–hickory–pine and southern mixed forest, with underlying sandy or sandy clay loam soils (Omernik, 1987). Dominant soil series found within catchments were Troup, Lakeland, Nankin, and Cowarts soils. Troup soils are deep,

excessively drained, moderately permeable loamy, kaolinitic, thermic Grossarenic Kandiudults. Lakeland soils are very deep, excessively drained, rapidly to very rapidly permeable, thermic coated Typic Quartzipsamments. Nankin soils are very deep, well drained, moderately slowly permeable, fine, kaolinitic, thermic Typic Kanhapludults. Dominant hydric soils included Bibb and Chastain soils. Bibb soils are very deep, poorly drained, moderately permeable coarse-loamy, siliceous, active, acid, thermic Typic Fluvaquents. Chastain soils are very deep, poorly drained, fine, mixed, semiactive, acid, thermic Fluvaquentic Endoaqupts. The surficial geology of Fort Benning Military Installation generally consists of Eutaw, Cusseta Sand, and Blufftown formations with a few, small areas of Tuscaloosa formation. In general, these formations are similar, and in some places, Eutaw can be difficult to differentiate from Blufftown (Eargle, 1955) and Cusseta Sand (Veatch and Stephenson, 1911). The dominant lithology of all four formations includes sand and clay. In addition,



**Fig. 1. Map showing the 10 study catchments located on the Fort Benning Military Installation near Columbus, Georgia. Study catchments include two tributaries of Bonham Creek (BC1, BC2), three tributaries of Sally Branch Creek (SB2, SB3, and SB4); two tributaries of Kings Mill Creek (KM1, KM2); one tributary of Little Pine Knot Creek (LPK); Hollis Branch Creek (HB); and Lois Creek (LC).**



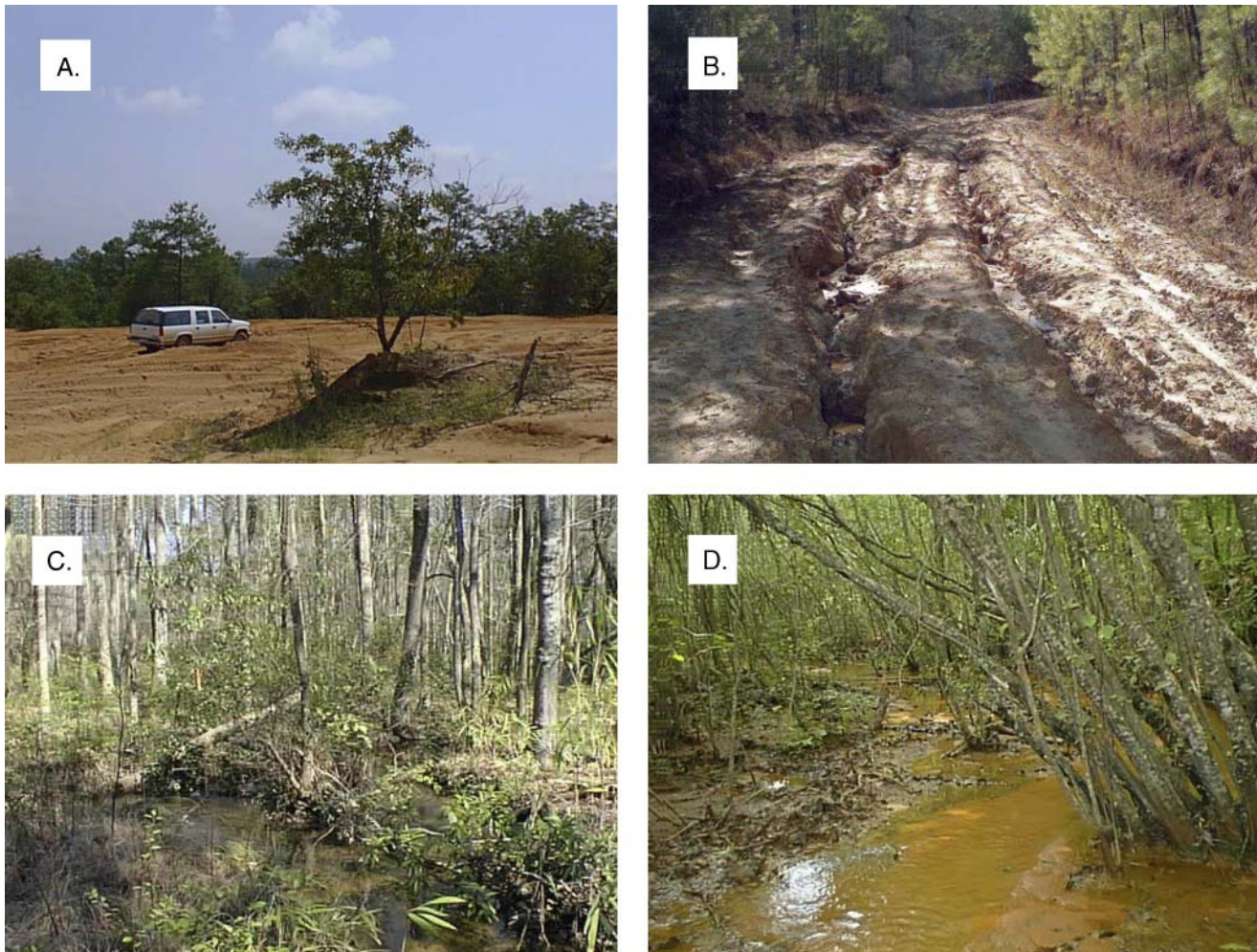
gravel may be present in Tuscaloosa (Veatch, 1909), marl in Blufftown, and lignite in Eutaw formations (Hilgard, 1860; Veatch, 1909). Certain areas of the reservation are frequently used for military training involving infantry and mechanized heavy equipment (e.g., tracked vehicles such as tanks). As a result, some catchments have localized areas with high soil and vegetation disturbance resulting in bare ground, compaction of surface soils, and high rates of erosion (Fig. 2A, 2B) and this disturbance causes visible differences among streams in high and low disturbance catchments (Fig. 2C, 2D). Other catchments have remained essentially undisturbed for the last 60 to 80 yr.

The streams included in the study are typical low-gradient, sandy, Southeastern Plains streams (Folley, 1992) with intact riparian canopies and mostly forested catchments. The riparian forest is almost entirely deciduous resulting in little shading of the streams during winter and spring. Leaf emergence usually occurs in late March or early April and leaf abscission usually occurs in early November. Thus, from late spring through early autumn the riparian trees provided a closed canopy and the streams were generally well shaded. Though precipitation (averaging approximately 1000 mm annually) is distributed evenly throughout the year, stream discharge exhibits seasonal patterns. High rates of evapotrans-

piration during the growing season result in lower stream discharge in summer and fall relative to winter and spring. The following abbreviations are used to identify the streams included in this study: two tributaries of Bonham Creek (BC1, BC2), three tributaries of Sally Branch (SB2, SB3, and SB4); two tributaries of Kings Mill Creek (KM1, KM2); one tributary of Little Pine Knot Creek (LPK); Hollis Branch Creek (HB); and Lois Creek (LC) (Fig. 1).

### Disturbance Intensity

Disturbance intensity for each catchment was quantified by Maloney et al. (2005) and the methods are briefly reviewed here. Land use and basic soil types of the study catchments were quantified using geographic information system (GIS) datasets (streams, 1:24 000, 1993; soils, 1:20 000, 1998; and roads, 10 m, 1995), available digital orthophotography (1:5000, July 1999), digital elevation models (DEMs, 1:24 000, grid size 10 m, 1993), and Landsat imagery (28.5 m, July and December 1999) provided by Fort Benning personnel and available on the U.S. Department of Defense SERDP Environmental Management Program data repository (<http://sempdata.wes.army.mil/>; verified 12 Oct. 2005). Catchment soils were characterized as the percentage of the catchment with soil in each



**Fig. 2.** Photographs of disturbed upland areas and stream study sites from the Fort Benning Military Installation. (A) Heavily disturbed upland area. (B) Unpaved road with eroded gullies. (C) Stream site from a low disturbance catchment (Lois Creek, LC). (D) Stream site from a high disturbance catchment (Sally Branch tributary, SB4).

of three categories (see Study Site for detailed soil descriptions): sand (Ailey loamy coarse sand and Lakeland sand soils), sandy clay loams (Nankin sandy clay loam soils), and loamy sands (dominated by Troup loamy sand, Cowarts and Ailey soils). Catchment area and mean catchment slope were calculated using the Arcview extension ATtILA (Ebert and Wade, 2000) and available DEMs (10-m resolution). Disturbance intensity was defined as the percent of unpaved road area and other areas of bare ground on slopes of >5% in each catchment. At Fort Benning, much of the bare ground was created by military training using tracked vehicles. Unpaved roads are mostly roads and trails used by tracked military vehicles. The areas of soil and vegetation disturbance were located in upland areas away from the perennial streams, but most were hydrologically connected during storms via ephemeral drainages discharging to the perennial stream. Of the 249 Fort Benning catchments, 245 have disturbance intensities between 0 and 17% (K. Maloney, unpublished data). The 10 catchments included in this study spanned much of this disturbance gradient with disturbance intensities ranging from 1.8 to 13.7% (Table 1).

### Field Methods

Baseflow chemistry grab samples were taken from the thalweg with care to avoid suspending stream sediments. Samples were collected once or twice quarterly under baseflow conditions (defined as at least 2 d after peaks in stream discharge due to storms). Spring, summer, autumn, and winter sampling was conducted in April or May; July or August; October, November, or December; and January or February, respectively.

Stormflow chemistry samples were collected using Isco (Lincoln, NE) autosamplers (Model 6700) equipped with water depth and ultrasonic flow velocity sensors (Model 710) and configured to collect a maximum of 24 samples during a storm. The sampler intake and depth/velocity sensor were positioned in the thalweg of each stream. The Isco sampler was programmed to begin sampling when the depth sensor detected an increase in depth greater than 1.5 to 3.5 cm depending on the stream and season. Samples were collected every 30 or 60 min (depending on the stream and season) for the duration of the period that stream depth remained elevated or until 24 samples were collected. Discharge during storms was calculated by the Isco sampler using the water depth and velocity data recorded at 15-min intervals and data describing stream channel shape (which was measured and entered during Isco sampler deployment). Stormflow chemistry samples were collected across a number of storms and seasons for each stream. Because of equipment limitations, the autosamplers were deployed in a maximum of five streams at a time and moved to the remaining streams immediately thereafter. The streams included in the first and second sampling groups were varied to the extent possible within the constraints of military-base access restrictions. Because all streams were not sampled simultaneously and some storms would cause sufficient change in depth to trigger the autosamplers in only a subset of the sampled streams, the number of storm events sampled differs among streams.

Stream discharge was determined at the time of baseflow sample collection by salt dilution gauging using a continuous NaCl injection. Background conductivity ( $\gamma_b$ ) was recorded before the injection. During the injection, a concentrated NaCl solution was delivered to the stream at a constant rate using an FMI model QBC pump (Fluid Metering, Syosset, NY). Conductivity was recorded every 30 s until steady-state conditions were reached. Stream discharge ( $Q$ ,  $L s^{-1}$ ) was calculated as

$Q = (C_{NaCl}R_{inj})/(\gamma_{ss} - \gamma_b)$ , where  $\gamma_b$  is the background conductivity ( $\mu S cm^{-1}$ ),  $\gamma_{ss}$  is the steady state injection conductivity ( $\mu S cm^{-1}$ ),  $C_{NaCl}$  is the conductivity of the NaCl injection solution ( $\mu S cm^{-1}$ ), and  $R_{inj}$  is the injection rate ( $L s^{-1}$ ). Stream width was the average of wetted width measurements taken every 5 m along 50- to 100-m reaches of each stream.

### Chemical Analysis

Suspended sediment (total, inorganic, and organic) concentrations were determined gravimetrically on samples filtered through pre-combusted and tared glass fiber filters (Whatman [Maidstone, UK] GFF, 0.7- $\mu m$  effective pore size) and total suspended sediment mass ( $TSS_{mass}$ ) was determined using an electronic balance after drying ( $80^\circ C$ ). Sample volumes of 100 to 700 mL were filtered depending on sample concentrations. Inorganic suspended sediment mass ( $ISS_{mass}$ ) was determined by combusting ( $500^\circ C$  for 12 h), rewetting to restore the water of hydration, drying, and reweighing. Organic suspended sediment mass ( $OSS_{mass}$ ) was determined by difference ( $OSS_{mass} = TSS_{mass} - ISS_{mass}$ ; American Public Health Association, 1992).

Samples for dissolved N and P analyses were frozen after filtration (Whatman GFF filters). Soluble reactive phosphorus (SRP) concentration was determined by the ascorbic acid-molybdenum blue method (American Public Health Association, 1992) using a 10-cm spectrophotometer cell to achieve low detection limits. Ammonium concentration ( $NH_4^+$ ) was determined by phenate colorimetry (American Public Health Association, 1992) and nitrite-nitrate by Cu-Cd reduction followed by azo dye colorimetry (American Public Health Association, 1992), both using a Bran+Lubbe (Delavan, WI) autoanalyzer (TRAACS Model 800 or AA3). Because stream water was always relatively high in dissolved oxygen concentration ( $>6 mg L^{-1}$ ) and because spot checks revealed minimal nitrite ( $<2 \mu g N L^{-1}$ ), hereafter we refer to nitrite-nitrate concentration as nitrate concentration ( $NO_3^-$ ). Dissolved organic carbon (DOC) concentration was determined by high temperature combustion using a Shimadzu (Kyoto, Japan) Model 5000 TOC analyzer. Total soluble silica concentration (Si) was measured in filter samples by inductively coupled plasma emission spectroscopy (TJA Model 9000; American Public Health Association, 1992). Samples for major cations were acidified after filtration (0.5%  $HNO_3$ ) and dissolved calcium concentration ( $Ca^{2+}$ ) and dissolved magnesium concentration ( $Mg^{2+}$ ) were determined by inductively coupled plasma emission spectrometry. Samples for chloride and sulfate analysis were refrigerated after filtration and analyzed by ion chromatography.

### Statistical Analysis

A number of statistical analyses were used to understand the factors affecting stream chemistry. Seasonal differences in stream concentration were analyzed using the Scheffé test for multiple comparisons (GLM procedure; SAS Institute, 2000). Multiple regression was used to test for the effects of disturbance and soil characteristics on stream chemistry. The baseflow chemistry data was transformed (by logarithm or square root) where necessary to normalize residuals or stabilize variance. Spearman rank correlation was used to test for correlations among soil characteristics and disturbance. Because the stormflow chemistry data could not be transformed to produce approximately normal residuals and homogeneity of variance in regression against disturbance, Spearman rank correlational analysis was used for analysis of the effects of disturbance and soil characteristics on storm chemistry.



## RESULTS

### Baseflow Chemistry: Seasonal Patterns

There were moderate seasonal differences in stream discharge and concentrations of suspended sediment, dissolved organic carbon (DOC), and soluble reactive phosphorus (SRP). Baseflow stream discharge was highest in spring and lowest in summer and autumn (Fig. 3A). Spring discharge was significantly higher than all other seasons. Differences in discharge among the other seasons were not significant. Minimum total (TSS), inorganic (ISS), and organic (OSS) suspended sediment concentrations occurred in winter (Fig. 3B–3D), which was a period of intermediate discharge in these streams. The TSS and ISS were significantly higher

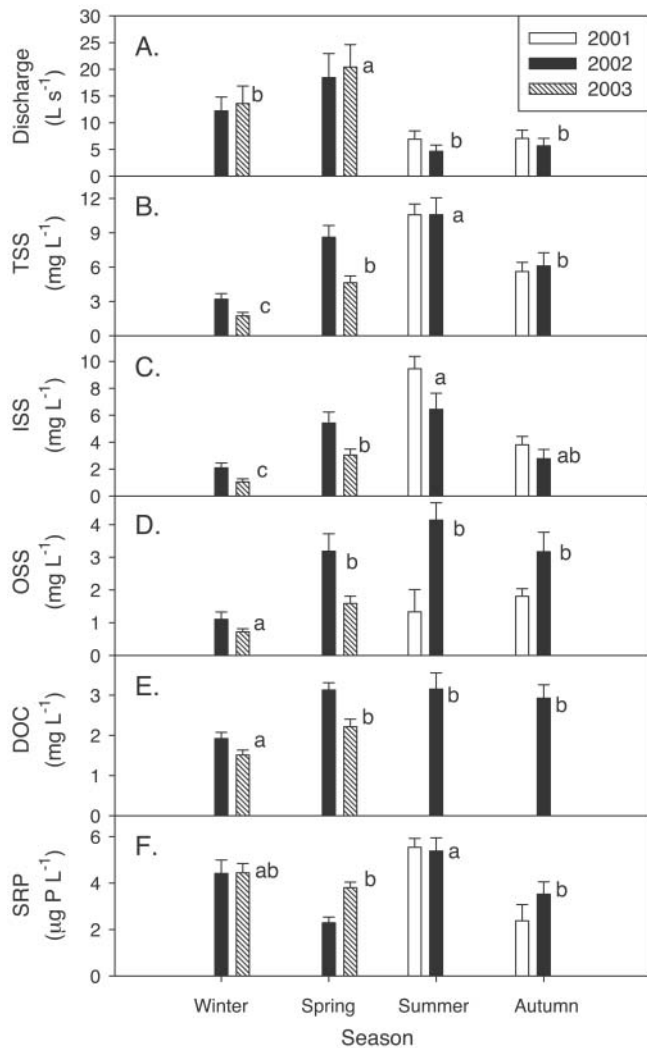
in summer, the period of minimum discharge, than in other seasons. There was not a significant difference in OSS among spring, summer, and autumn. Similar to OSS, minimum DOC occurred in winter and there were no significant differences among spring, summer, and autumn DOC (Fig. 3E). Summer SRP was significantly higher than spring and autumn; winter SRP was not significantly different from any other season (Fig. 3F). There were no significant differences among season mean concentrations of ammonia ( $\text{NH}_4^+$ ; range = 7.2–20.0  $\mu\text{g N L}^{-1}$ ), nitrate ( $\text{NO}_3^-$ ; range = 17.0–29.2  $\mu\text{g N L}^{-1}$ ), conductivity (range = 17.0–24.8  $\mu\text{S cm}^{-1}$ ), or pH (range = 5.1–5.4).

### Baseflow Chemistry: Effects of Disturbance

Stream chemistry was significantly influenced by catchment disturbance intensity. Disturbance was a significant predictor of TSS during baseflow (Table 2). Mean TSS ranged from  $4.0 \pm 0.9 \text{ mg L}^{-1}$  in the least disturbed catchments to as high as  $10.1 \pm 1.3 \text{ mg L}^{-1}$  in the second most disturbed catchments (Fig. 4A). In low disturbance catchments (disturbance intensity < 7% catchment area), mean TSS was less than  $6 \text{ mg L}^{-1}$ . In high disturbance catchments (disturbance intensity > 7% catchment area) mean TSS was generally greater than  $6 \text{ mg L}^{-1}$  and was more variable among streams. BC1 was an exception to this pattern. BC1 drained a catchment that had a notably broader, flatter floodplain than most of the other study catchments and this broad floodplain may have provided greater protection from the impacts of disturbance. BC1 was included in all figures, but was omitted from all statistical analyses.

The pattern in baseflow ISS across the disturbance gradient was similar to that seen for TSS. There was a significant increase in ISS with increasing disturbance intensity (Table 2), and BC1 was an outlier (Fig. 4B). At sites with disturbance intensities less than 7% of the catchment, mean ISS ranged from  $2.0 \pm 0.5$  to  $3.8 \pm 0.9 \text{ mg L}^{-1}$ , whereas for streams in catchments with disturbance intensities greater than 7%, mean ISS ranged from  $5.6 \pm 0.9$  to  $7.3 \pm 1.3 \text{ mg L}^{-1}$ . As was the case with TSS, there was increased variability in ISS among streams with increasing disturbance intensity. Mean OSS ranged from  $1.1 \pm 0.3$  to  $4.0 \pm 0.7 \text{ mg L}^{-1}$  and there was not a significant correlation with disturbance intensity (Table 3).

The effect of disturbance intensity on dissolved nutrients varied among constituents. Nitrate and  $\text{NH}_4^+$  did not increase significantly with disturbance intensity (Table 2). However, three streams with moderately high disturbance intensities had the highest  $\text{NO}_3^-$  and the stream with the highest disturbance intensity had the highest  $\text{NH}_4^+$  (Table 3). There was a marginally significant ( $p = 0.06$ ,  $R^2 = 0.4$ ) increase in DIN with increasing disturbance due to the uniformly low concentrations of inorganic N in the streams with low disturbance intensities (Table 2; Fig. 5A). Soluble reactive phosphorus declined significantly from  $6.2 \pm 0.7 \mu\text{g L}^{-1}$  in the least disturbed catchment to  $2.6 \pm 0.3 \mu\text{g L}^{-1}$  in the most disturbed catchment (Fig. 5B). The DOC declined



**Fig. 3.** Seasonal mean discharge and suspended sediment concentrations during baseflow sampling across all streams. (A) Discharge, (B) total suspended sediment (TSS), (C) inorganic suspended sediment (ISS), (D) organic suspended sediment (OSS), (E) dissolved organic carbon (DOC), and (F) soluble reactive phosphorus (SRP). Separate bars are shown for each year. Error bars are one standard error. Letters indicate where significant differences exist among seasons ( $p < 0.05$ ; Scheffé adjustment for multiple comparisons). Years were pooled for the statistical analysis. Sample size ranges from 18 to 21 depending on year and season.

**Table 2. Regression analysis results for stream mean baseflow concentrations of water chemistry variables vs. disturbance intensity and soil characteristics ( $N = 9$  for all regressions).**

Dependent variable†	Independent variable	Estimate $\pm$ SE	$R^2$	$p$
Square root (TSS)	disturbance intensity	$0.09 \pm 0.02$	<b>0.70</b>	<b>0.005</b>
Square root (OSS)	disturbance intensity		NS‡	
log(ISS)	disturbance intensity	$0.08 \pm 0.02$	<b>0.71</b>	<b>0.004</b>
Square root (DOC)	disturbance intensity	$-0.06 \pm 0.0090$	<b>0.79</b>	<b>0.001</b>
	% sandy soil	$0.003 \pm 0.001$	<b>0.08</b>	<b>0.09</b>
Square root (SRP)	disturbance intensity	$-0.06 \pm 0.02$	<b>0.75</b>	<b>0.008</b>
	% loamy sand	$0.005 \pm 0.002$	<b>0.11</b>	<b>0.07</b>
log( $\text{NH}_4^+$ )	disturbance intensity	$0.07 \pm 0.04$	<b>0.32</b>	<b>0.1</b>
log( $\text{NO}_3^-$ )	disturbance intensity		NS	
log(DIN)	disturbance intensity	$0.1 \pm 0.05$	<b>0.4</b>	<b>0.06</b>
$\text{H}^+$	disturbance intensity	$-1.3 \times 10^{-6} \pm 2.8 \times 10^{-7}$	<b>0.75</b>	<b>0.003</b>
log( $\text{Ca}^{2+}$ )	disturbance intensity		NS	
	% loamy sand	$-0.01 \pm 0.004$	<b>0.56</b>	<b>0.01</b>
	% sandy clay loam	$0.04 \pm 0.02$	<b>0.22</b>	<b>0.04</b>
log(conductivity)	disturbance intensity		NS	
$\text{Cl}^-$	disturbance intensity		NS	
Square root (Si)	disturbance intensity	$-0.03 \pm 0.01$	<b>0.53</b>	<b>0.03</b>

† DIN, dissolved inorganic nitrogen; DOC, dissolved organic carbon; ISS, inorganic suspended sediment; OSS, organic suspended sediment; SRP, soluble reactive phosphorus; TSS, total suspended sediment.

‡ Not significant.

significantly from  $4.1 \pm 0.7 \text{ mg L}^{-1}$  in the least disturbed catchment to  $1.5 \pm 0.2 \text{ mg L}^{-1}$  in the most disturbed catchment (Fig. 5C; Table 2).

There was a significant increase in pH with increasing disturbance intensity (Fig. 5D; Table 2) and pH was significantly correlated ( $r = 0.77$ ,  $p = 0.02$ ) with  $\text{Ca}^{2+}$  which also increased with disturbance ( $r = 0.67$ ,  $p = 0.05$ ). Although DOC was negatively correlated with disturbance, it was not significantly correlated with pH and its inclusion in a multiple regression model did not improve the prediction of pH. As was seen for suspended sediment, BC1 was an outlier in the relationship between pH and disturbance exhibiting pH levels similar to streams in lower disturbance catchments.

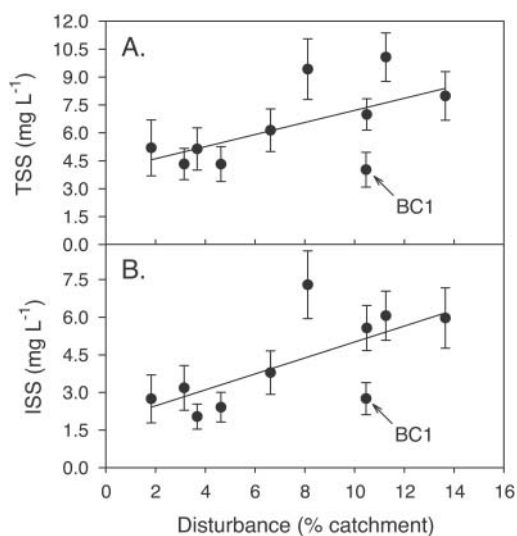
Silica decreased significantly as disturbance intensity increased (Table 2). In the three least disturbed

catchments Si was greater than  $4 \text{ mg L}^{-1}$ , whereas in the more disturbed catchments Si was less than  $3.7 \text{ mg L}^{-1}$  (Fig. 5E). There was no significant relationship between disturbance intensity and conductivity, chloride ( $\text{Cl}^-$ ) concentration, or sulfate ( $\text{SO}_4^{2-}$ ) concentration (Table 3).

Stepwise regression analysis was used to investigate whether adding soil descriptors significantly improved the regression models for the above stream chemistry constituents or affected the proportion of variability explained by disturbance (Table 2). Disturbance was not significantly correlated with soil description (% sand:  $r = 0.4$ ,  $p = 0.3$ ; % loamy sand:  $r = -0.5$ ,  $p = 0.17$ ; % sandy clay loam:  $r = 0.4$ ,  $p = 0.3$ ; spearman rank correlation). Most catchments were dominated by two soil categories: sandy soils or loamy sands. Only SB4 and SB2 had greater than 4% sandy clay loam. Adding soil descriptors to the analysis did not significantly improve the regression models for any of the suspended sediment fractions, any nitrogen species, or pH. Catchment soil type was a significant predictor for DOC, SRP, and  $\text{Ca}^{2+}$ . However, for DOC and SRP, disturbance explained much more variance than did soil type (Table 2). Percent loamy sand and percent sandy clay loam both were significant predictors of  $\text{Ca}^{2+}$  and when these variables were included in the regression model, disturbance was not significant.

### Concentration–Discharge Relationships during Storm Events

Discharge, suspended sediment, and solute concentration patterns during a storm in January 2003 are presented in Fig. 6 for two streams, one draining a relatively low disturbance catchment and the other draining a relatively high disturbance catchment. These patterns are typical of other storms. With the exception of  $\text{Cl}^-$ , all concentrations increased during storms, relative to pre-storm values. The increases in TSS, ISS, DOC, and  $\text{NO}_3^-$  during stormflow were distinct and larger in the more highly disturbed stream (Fig. 6C–6H). In contrast, stormflow SRP was variable and concentrations



**Fig. 4. Relationship between disturbance and baseflow concentrations of (A) total suspended sediment (TSS) and (B) inorganic suspended sediment (ISS). Error bars are one standard error. Trend lines are shown for significant relationships ( $p < 0.05$ ). Regressions statistics are shown in Table 2. Stream BC1 (tributary of Bonham Creek) was excluded from statistical analyses (see Results).**

**Table 3. Mean ( $\pm$ standard error) baseflow concentrations for selected stream chemistry variables.**

Stream <sup>†</sup>	N	OSS <sup>‡</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Conductivity	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
		mg L <sup>-1</sup>	$\mu\text{g N L}^{-1}$	$\mu\text{g N L}^{-1}$	$\mu\text{S cm}^{-1}$	mg L <sup>-1</sup>	mg L <sup>-1</sup>
KM2	16	2.5 $\pm$ 0.80	3.8 $\pm$ 0.65	10.4 $\pm$ 2.0	21.5 $\pm$ 1.1	2.1 $\pm$ 0.11	2.6 $\pm$ 0.39
BC2	15	1.1 $\pm$ 0.30	22.6 $\pm$ 3.2	8.7 $\pm$ 2.0	22.2 $\pm$ 0.92	2.2 $\pm$ 0.13	2.6 $\pm$ 0.31
LC	16	3.0 $\pm$ 0.79	9.1 $\pm$ 3.0	12.6 $\pm$ 2.4	17.6 $\pm$ 1.1	1.5 $\pm$ 0.077	2.1 $\pm$ 0.29
KM1	16	1.9 $\pm$ 0.49	11.8 $\pm$ 1.4	4.3 $\pm$ 0.74	14.3 $\pm$ 0.63	1.5 $\pm$ 0.052	1.0 $\pm$ 0.13
HB	15	2.4 $\pm$ 0.38	56.0 $\pm$ 5.3	12.2 $\pm$ 3.6	15.9 $\pm$ 0.70	1.7 $\pm$ 0.041	1.3 $\pm$ 0.16
SB2	16	2.1 $\pm$ 0.42	40.0 $\pm$ 3.2	8.2 $\pm$ 1.0	20.3 $\pm$ 1.4	1.6 $\pm$ 0.078	2.7 $\pm$ 0.50
BC1	16	1.2 $\pm$ 0.33	4.5 $\pm$ 2.0	6.5 $\pm$ 1.4	25.0 $\pm$ 0.59	1.5 $\pm$ 0.71	4.8 $\pm$ 0.37
SB3	16	1.4 $\pm$ 0.34	15.4 $\pm$ 4.9	8.2 $\pm$ 1.6	26.2 $\pm$ 1.5	1.7 $\pm$ 0.079	3.7 $\pm$ 0.50
LPK	15	4.0 $\pm$ 0.66	52.2 $\pm$ 6.8	15.6 $\pm$ 3.7	13.9 $\pm$ 0.25	1.6 $\pm$ 0.060	0.85 $\pm$ 0.11
SB4	16	2.0 $\pm$ 0.50	21.9 $\pm$ 3.5	28.4 $\pm$ 2.8	23.1 $\pm$ 1.88	1.7 $\pm$ 0.066	3.6 $\pm$ 0.65

<sup>†</sup> BC1 and BC2, tributaries of Bonham Creek; HB, Hollis Branch Creek; KM1 and KM2, tributaries of Kings Mill Creek; LC, Lois Creek; LPK, tributary of Little Pine Knot Creek; SB2, SB3, and SB4, tributaries of Sally Branch.

<sup>‡</sup> Organic suspended sediment.

were at times lower than pre-storm values (Fig. 6E, 6F). Ammonia generally exhibited little change during storm-flow (Fig. 6G, 6H). Sulfate concentration declined initially and then increased as discharge peaked and declined (Fig. 6I, 6J).

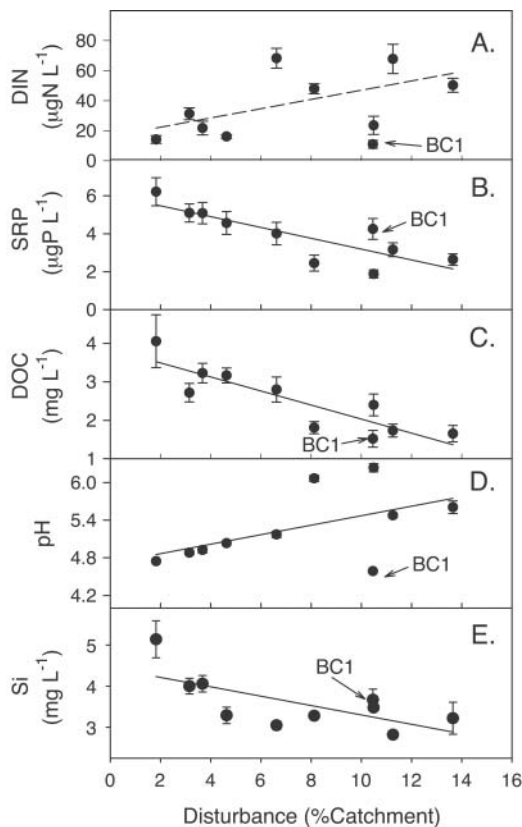
Differences between concentrations on the rising and falling limb of a storm hydrograph can provide information concerning the sources of various dissolved and

particulate substances. Evans and Davies (1998) proposed the following model:

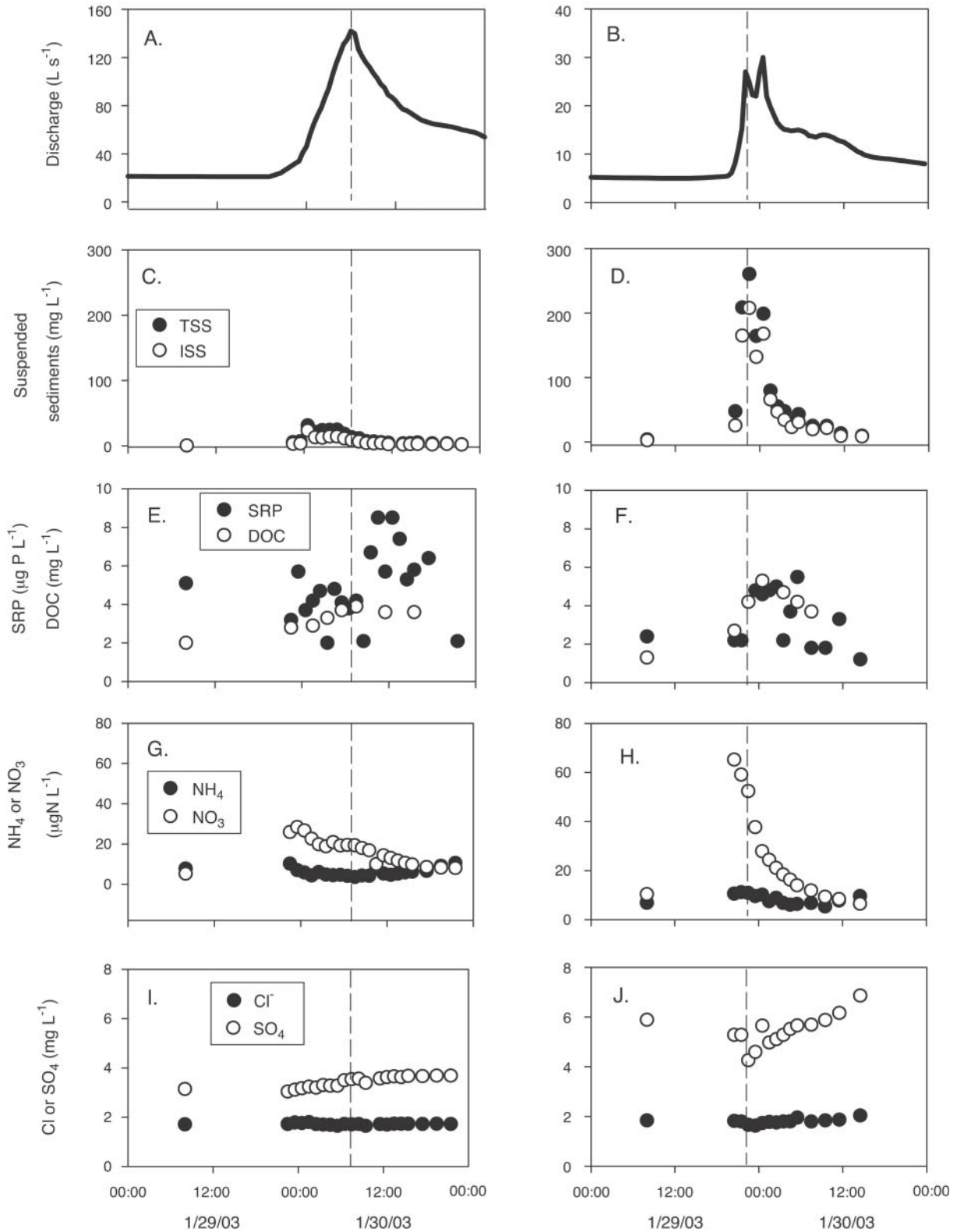
- During baseflow, stream concentrations reflect ground water concentrations.
- On the rising limb of the hydrograph, stream concentrations reflect surface event water and mobilization from nearby sources.
- On the falling limb, stream concentrations reflect catchment soil water.

A clockwise hysteresis in the plot of concentration vs. discharge occurs when solute concentrations are higher on the rising limb of the storm hydrograph (e.g., Fig. 7A), and suggests that solute concentrations in surface event water exceed soil water concentrations. An anti-clockwise hysteresis occurs when solute concentrations are higher on the falling limb of the storm hydrograph (e.g., Fig. 7B), and suggests that solute concentrations in soil water exceed surface event water. Indeterminate shapes occur when neither limb of the hydrograph exhibits consistently higher solute concentrations. These inferences are generalities as there is often considerable variability in the shape of these plots among storm events in any given stream (Johnson and East, 1982; McDiffett et al., 1989), but they remain informative.

There was no apparent effect of disturbance on the shape of the concentration–discharge plots in this study, but differences among stream chemistry constituents were observed (Table 4). Total suspended sediment exhibited higher concentrations on the rising limb of the hydrograph (clockwise) in 21 of the 22 storms where an unambiguous shape was observed in the concentration vs. discharge plot (Fig. 7A; Table 4). Sulfate exhibited the opposite pattern with concentrations being higher on the descending limb of the hydrograph (anti-clockwise) in 18 of the 19 storms where an unambiguous shape was observed (Fig. 7B; Table 4). The DOC data are more limited, but showed higher concentrations on the falling limb of the hydrograph (anti-clockwise) in 9 of the 11 storms where an unambiguous shape was seen (Table 4). Nitrate exhibited higher concentrations on the rising limb of the hydrograph in 17 of the 20 storms where a clear pattern was observed (Fig. 7C; Table 4). Soluble reactive phosphorus and NH<sub>4</sub><sup>+</sup> rarely showed an obvious pattern in concentration–discharge diagrams.

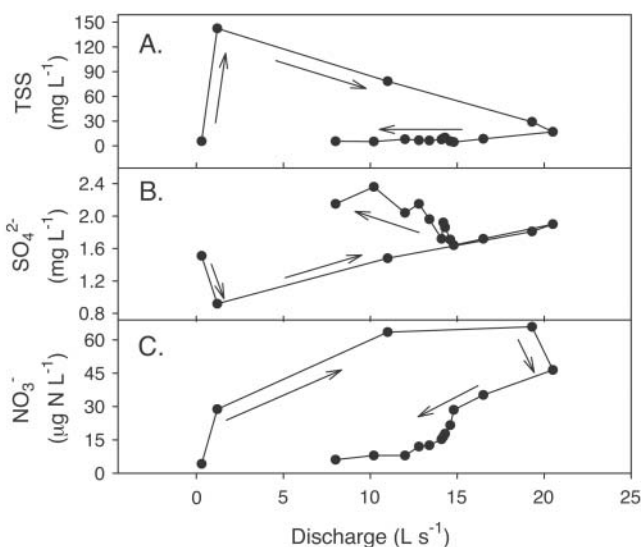


**Fig. 5. Relationship between disturbance and baseflow concentrations of (A) dissolved inorganic nitrogen (DIN), (B) soluble reactive phosphorus (SRP), (C) dissolved organic carbon (DOC), (D) pH, and (E) dissolved silica (Si). Error bars are one standard error; error bars are not visible in (D) because they do not extend beyond data points. Dashed trend line shown for marginally significant regression ( $p = 0.06$ ); solid trend lines are shown for significant ( $p < 0.05$ ) regressions. Regression statistics are shown in Table 2. Stream BC1 (tributary of Bonham Creek) was excluded from statistical analyses (see Results).**



**Fig. 6.** Discharge and suspended sediment and solute concentrations in two streams during a storm 29–30 January 2003. The left column shows data from Lois Creek (LC), which drains a relatively low disturbance catchment, and the right column shows data from a tributary of Sally Branch (SB3), which drains a relatively high disturbance catchment (see Table 1). The points to the left and separated from the others in (C)–(J) represent pre-storm values determined from samples collected about 1 d before the storm. Rainfall totaled 33 mm during the period from 2000 h 29 September to 1600 h 30 September as measured at a site within 10 km of each stream. Dashed line marks peak discharge for the storms. Note that y axis scale differs between left and right columns for discharge [(A) and (B)].





**Fig. 7.** Example concentration vs. discharge plots for (A) total suspended sediment (TSS), (B)  $\text{SO}_4^{2-}$ , and (C)  $\text{NO}_3^-$ . Data are from Tributary 2 of Kings Mill Creek (KM2) on 11 July 2002. Arrows point from beginning to end of storm.

Soluble reactive phosphorus was indeterminate in 26 out of 32 storms and  $\text{NH}_4^+$  was indeterminate in 18 out of 32 and evenly divided between clockwise and anti-clockwise for the remainder (Table 4).

**Stormflow Chemistry: Effects of Disturbance**

The impact of disturbance on stream chemistry parameters during storm events was evaluated using the maximum change in concentration during storms (i.e., the difference between baseflow concentration measured before the storm and maximum concentration observed during a storm). In all cases where there were significant changes in concentration during storms, the concentration increased.

The increase in TSS, ISS, and OSS during storm events was positively correlated with catchment disturbance. In catchments with a disturbance intensity of <7%, the mean maximum change in TSS ranged from

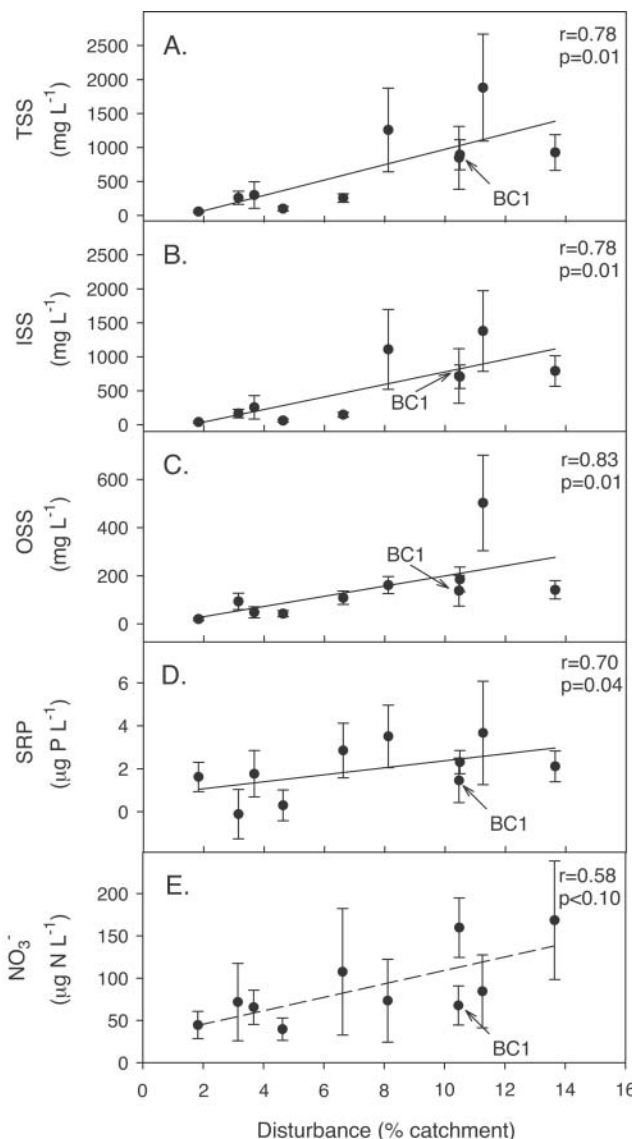
**Table 4.** Summary table of concentration† vs. discharge plots showing the number of storm events that were classified as clockwise, anti-clockwise, or indeterminate. High disturbance streams are those with disturbance intensities greater than 7% of the catchment, and low disturbance streams are those with disturbance intensities less than 7% of the catchment.

Direction	TSS	SRP	$\text{NH}_4^+$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	DOC
<b>High disturbance level</b>						
Clockwise	11	1	4	11	1	1
Anti-clockwise	1	3	3	0	12	3
Indeterminate	7	15	12	8	6	2
Total number of storm events	19.00	19.00	19.00	19.00	19.00	6.00
<b>Low disturbance level</b>						
Clockwise	10	0	4	6	0	1
Anti-clockwise	0	2	3	3	6	6
Indeterminate	3	11	6	4	7	0
Total number of storm events	13.00	13.00	13.00	13.00	13.00	7.00

† DOC, dissolved organic carbon; SRP, soluble reactive phosphorus; TSS, total suspended sediment.

57 to 300  $\text{mg L}^{-1}$  (Fig. 8A). In catchments with a disturbance intensity of >7%, mean maximum change in TSS ranged from 847 to 1881  $\text{mg L}^{-1}$ . In contrast to the patterns under baseflow conditions, BC1 did not appear to be an outlier in the relationship between the magnitude of storm TSS or ISS increase and disturbance intensity. The variability in maximum change in TSS among storms within streams was greater for streams with disturbance intensities of >7% than in streams with lower disturbance intensities.

The pattern in TSS appeared to be driven by the ISS fraction of suspended sediments which showed essen-



**Fig. 8.** Relationship between maximum change in concentration during a storm (= maximum storm concentration – baseflow concentration) and disturbance for (A) total suspended sediment (TSS), (B) inorganic suspended sediment (ISS), (C) organic suspended sediment (OSS) (note different scale of the y axis), (D) soluble reactive phosphorus (SRP), and (E) nitrate ( $\text{NO}_3^-$ ). Data points are stream averages. Error bars are one standard error. Spearman rank correlational analysis results are given in each panel. Stream BC1 (tributary of Bonham Creek) was excluded from statistical analyses (see Results).

tially the same pattern as TSS. In catchments with a disturbance intensity of <7%, the mean maximum change in ISS ranged from 38 to 255 mg L<sup>-1</sup> (Fig. 8B). In catchments with a disturbance intensity of >7%, mean maximum change in ISS ranged from 707 to 1378 mg L<sup>-1</sup>. Again, the variability in maximum change in ISS among storms was considerably greater in streams draining the more highly disturbed catchments.

The mean maximum change in OSS during storm events was also positively correlated with catchment disturbance (Fig. 8C). However, the change in OSS was small compared to the change in ISS reflecting the fact that most of the suspended sediments in transport during storms were inorganic. Unlike TSS and ISS, OSS did not show an obvious break point between streams in catchments above and below 7% catchment disturbance. The stream in the second most disturbed catchment exhibited a much higher mean maximum change in OSS than any other stream.

The effect of disturbance on stormflow nutrients varied among constituents. Mean maximum change in SRP increased significantly with disturbance (Fig. 8D). The increase in mean maximum change in NO<sub>3</sub><sup>-</sup> with disturbance intensity was only marginally significant (Fig. 8E), and the variability within each site was high. Maximum change in SRP and NO<sub>3</sub><sup>-</sup> did not show the breakpoint near 7% disturbance intensity that was seen for maximum change in TSS or ISS. The maximum changes observed in storms for DOC, NH<sub>4</sub><sup>+</sup>, and DIN were not significantly related to disturbance.

The maximum increases in concentrations during storms was correlated with catchment soil characteristics only for DOC and NO<sub>3</sub><sup>-</sup>. Change in NO<sub>3</sub><sup>-</sup> was negatively correlated ( $r = -0.67$ ,  $p = 0.05$ ) with percent loamy sand and exhibited a marginally significant correlation with percent sandy clay loam ( $r = 0.63$ ,  $p = 0.06$ ). Dissolved organic carbon was positively correlated with percent sand ( $r = 0.68$ ,  $p = 0.04$ ) and negatively correlated with percent loamy sand ( $r = -0.68$ ,  $p = 0.04$ ).

## DISCUSSION

We studied a specific disturbance type (upland soil and vegetation disturbance that results in bare ground and highly disturbed soils) in relative isolation of other disturbance factors. In contrast to whole catchment deforestation studies, we examined the impact of a moderate range of disturbance intensity (1.8 to 13.7% of the catchment) in catchments with largely undisturbed riparian zones. However, the disturbance intensity in the areas we defined as disturbed was likely more severe than is typical in most types of deforestation (e.g., timber harvest). Disturbance intensity affected stream chemistry and the magnitude of the disturbance effect varied widely among constituents. Variation in catchment soil characteristics was limited among our study catchments and had only moderate effects on a few stream constituents.

The strongest stream response to increased upland soil and vegetation disturbance intensity was an increase in suspended sediment concentration during baseflow

and stormflow conditions (Fig. 4, 8). We believe that the effect of disturbance on suspended sediments during baseflow is probably due to the unstable substratum that characterizes the streambeds of these disturbed streams (Maloney et al., 2005). We hypothesize that storm events frequently import eroded sediments to the stream and these sediments form an unstable bed that results in relatively high baseflow concentrations of suspended solids. The magnitude of the increases in TSS and ISS during storms and their variability increased with disturbance intensity, and there appears to be a distinct difference between catchments with disturbance intensities of <7% compared to those with disturbance intensities of >7%. In streams in low disturbance catchments, maximum changes in TSS and ISS during storms were low regardless of magnitude of storm. In more highly disturbed catchments, maximum changes in TSS and ISS were much more variable, most likely due to effects of variations in storm size and antecedent conditions on suspended sediment concentrations in these catchments. However, normalizing storm TSS and ISS concentration increases to peak storm discharge did not improve the relationships with disturbance intensity. A contributing factor to these patterns in suspended sediment concentrations during storm events may have been the impact of disturbance on stream hydrology. Maloney et al. (2005) showed that in many of these streams, the hydrologic response to storms (flashiness) was more rapid in the highly disturbed catchments.

These results agree with others who have observed increased suspended sediment concentrations in response to deforestation and logging road construction (e.g., Likens et al., 1970; Gurtz et al., 1980; Harr and Fredriksen, 1988; Kreutzweiser and Capell, 2001; MacDonald et al., 2003; but see Bhat et al., 2005). Our results differ from studies that have shown that riparian buffers can protect streams from suspended sediment inputs (e.g., Martin et al., 2000; MacDonald et al., 2003). We found higher suspended solids concentrations in catchments with extensive vegetation and soil disturbance suggesting that the eroded particles were effectively transported to the stream. We believe this transport occurred through the formation of ephemeral stream channels that connect the upland disturbed sites to the perennial stream channel. Once in stream channels and floodplains, redistribution and transport of catchment soil often continues for many years (Brown and Krygier, 1971). Swift (1988) found that 80% of the eroded soil from a forest clearcut remained in the stream channel after 2.5 yr. In the current study, the stream sediments in the disturbed catchments are easily resuspended and higher suspended sediment concentrations are observed even during baseflow conditions.

In addition to increases in total suspended sediment concentrations, catchment disturbance often causes an increase in the inorganic fraction of suspended sediments (e.g., Likens et al., 1970; Bormann et al., 1974; Webster et al., 1992). In the current study, the increase in suspended sediment concentrations with disturbance was dominated by the inorganic fraction. There was not a significant increase in baseflow organic suspended

sediments with disturbance intensity. The clay- and sand-dominated soils in these catchments do not appear to be an important source of organic material.

There was a strong negative correlation between DOC and disturbance intensity (Fig. 5C). Similar declines in total organic carbon concentrations with increased catchment disturbance by military training were found by Bhat et al. (2005) in a group of larger, more disturbed streams at Fort Benning Military Installation. There are several possible explanations for this pattern. Disturbed sites have reduced organic matter content in the upland catchment soils (Garten et al., 2003) perhaps indicating a lower reservoir of leachable organic matter for output to the streams in disturbed catchments. In-stream DOC sources can be important in determining stream DOC (Bormann et al., 1974; Schiff et al., 1990; Webster et al., 1992). The potential in-stream sources of DOC, such as benthic organic matter and coarse woody debris, are reduced in our disturbed streams (Maloney et al., 2005). A third possible cause of lower DOC in the more highly disturbed catchments is the high concentration of inorganic sediments in the disturbed streams that may result in increased DOC adsorption in these streams. Clays are known to have high sorption potential for DOC (Jardine et al., 1989) and the sediments of the more highly disturbed streams generally have higher content of clay-size particles (Maloney et al., 2005). Other studies have found forest cutting to result in an increase in DOC export initially (Hobbie and Likens, 1973); however, after this initial increase, DOC exports have been shown to fall to intensities below those found in undisturbed catchments (Meyer and Tate, 1983). The initial disturbance of the current study watersheds occurred before the current study. An initial increase in DOC may have occurred that was not observed by the current study.

There was a strong negative correlation between SRP and disturbance intensity (Fig. 5B). This finding contrasts with others who have found no relationship between dissolved phosphorus and land use or ecosystem disturbance (Prairie and Kalff, 1988; Hury et al., 2002). Soluble reactive phosphorus is strongly adsorbed to inorganic particles, particularly clays (Meyer, 1979; Hill, 1982; Wood et al., 1984), and it is possible that higher concentrations of inorganic suspended and streambed sediments in the more disturbed streams result in higher rates of SRP adsorption resulting in lower streamwater SRP. It is important to note that this type of adsorption is potentially reversible and does not represent removal from the system. An alternative possible mechanism is reduced in-stream sources of SRP (remineralization of organic P) in highly disturbed streams due to reduced abundance of coarse woody debris and benthic organic matter. However, previous work suggests that the opposite trend in SRP should result from decreases in coarse woody debris and benthic organic matter because these materials can be major sites of phosphate uptake (Munn and Meyer, 1990). A third possible cause of reduced SRP is reduced inputs from highly disturbed catchments. The reduced abundance of organic matter in the soils in disturbed catchments (Garten et al., 2003)

may result in reduced leaching of SRP to soil water and ultimately to the stream.

There were no strong patterns in baseflow concentrations for nitrogen species across the gradient of catchment disturbance (Table 3). This contrasts with studies that have shown  $\text{NO}_3^-$  to exhibit a strong response to catchment deforestation or other disturbances (e.g., Likens et al., 1970; Bormann et al., 1974; Harr and Fredriksen, 1988; Martin et al., 2000; Hury et al., 2002; Yeakley et al., 2003). The current study examined the effects of chronic upland disturbance. It is possible that initial increases in  $\text{NO}_3^-$  would have occurred before the current study. Retention and denitrification in the intact riparian zone of these streams may also reduce the export of  $\text{NO}_3^-$  to the streams such that differences in transport from the upland areas to the riparian are not reflected in stream concentrations (Peterjohn and Correll, 1984; Hill, 1996; Hill et al., 2000).

The effect of catchment disturbance on storm increases in nutrient concentrations was considerably weaker than was observed for suspended sediments (Fig. 8). The increase in SRP during storms was significantly higher in disturbed catchment streams, and the relationship between increase in  $\text{NO}_3^-$  during storms and disturbance intensity was marginally significant. The increase in storm SRP with increasing disturbance intensity was opposite the effect disturbance intensity had on baseflow SRP. The reasons for the difference in disturbance effects on SRP patterns during baseflow and stormflow conditions may be related to disturbance effects on catchment soils and inorganic sediments in the streams. Under baseflow conditions, soils and streambed sediments may be a sink for SRP via sorption to inorganic particles. However, erosion and suspension of inorganic sediments in runoff during storms may result in net desorption of P. For  $\text{NO}_3^-$ , larger storm increases in concentration with higher intensities of catchment disturbance are consistent with other studies showing higher  $\text{NO}_3^-$  concentrations and exports with disturbance (e.g., Likens et al., 1970). Because  $\text{NO}_3^-$  in rainfall is likely much higher than  $\text{NO}_3^-$  in streamwater in the current study streams, the greater storm concentration increases suggest the possibility of lower rates of retention of atmospheric N deposition in the more disturbed catchments, perhaps due to lower retention by vegetation and soil microbes in the denuded areas of these catchments.

There was a strong positive correlation between pH and disturbance (Fig. 5D), but the mechanisms that caused this relationship are not clear. Catchment deforestation has been found to significantly increase  $\text{H}^+$  export, resulting in a decrease in stream pH (Likens et al., 1970; Martin et al., 2000; Yeakley et al., 2003). We see the opposite pattern here among catchments with an increase in pH with disturbance intensity. High DOC concentrations often result in lower pH, but among these streams the relationship between DOC and pH was not significant. pH was not significantly correlated with soil characteristics. However, pH was significantly correlated with  $\text{Ca}^{2+}$  which was significantly correlated with catchment soil characteristics. Thus, the strong



positive correlation between pH and disturbance may be the result of both disturbance effects and soil characteristics. Surficial geology appeared to be unimportant in the pattern of pH concentration among streams; there was no correlation between the fraction of a catchment underlain by the Blufftown formation, the only calcareous formation that occurs in these catchments, and pH.

There was no apparent effect of catchment disturbance on baseflow conductivity  $\text{Cl}^-$  or  $\text{SO}_4^{2-}$  (Table 3). This contrasts with the findings of a number of catchment deforestation studies. Sulfate concentration generally decreases in response to catchment deforestation (Likens et al., 1970; Martin et al., 2000; Yeakley et al., 2003), whereas conductivity and  $\text{Cl}^-$  have been shown to increase (Likens et al., 1970). Silica significantly decreased with disturbance intensity in our study (Fig. 5E), suggesting that there may be differences in subsurface flow path or decreases in soil-water residence time that resulted in reduced Si weathering in the disturbed catchments.

### Discharge versus Concentration during Storm Events

We observed distinct shapes in the concentration vs. discharge plots for some stream chemistry constituents (Fig. 7; Table 4), but there were no apparent effects of disturbance intensity on these shapes. Suspended sediment concentrations were almost always higher on the rising limb of the hydrograph and peak suspended sediment concentrations usually preceded peak discharge (Fig. 6C, 6D, 7A). This suggests that surface runoff and mobilization from nearby areas is the dominant source of suspended sediments. Although the disturbed upland areas are likely the ultimate source of the excess suspended sediment in these streams, sediment that has been transported to the ephemeral stream channels or into the stream itself appears to be responsible for the initial large increase during most storms.

Dissolved organic carbon always increased during storm events, and DOC was generally higher on the falling limb of the storm hydrograph (anti-clockwise; Fig. 6E, 6F; Table 4), suggesting that soil water is an important source of DOC during storms. This supports the hypothesis that the reduced organic material in the soils of disturbed catchments is at least partly responsible for the significant decline in DOC in these streams as disturbance intensity increases. Others have observed higher DOC on the rising limb of the hydrograph in mountain streams (McDowell and Fisher, 1976; Meyer and Tate, 1983), suggesting that there are differences in sources of DOC among upland and lowland streams. Interpretation of the concentration vs. discharge patterns for DOC in the current study may be complicated by the possible effects of higher DOC adsorption during the rising limb of the hydrograph due to high inorganic suspended sediment concentrations.

Stormflow  $\text{NO}_3^-$  was generally higher on the rising limb of the hydrograph (Fig. 6G, 6H, 7C) suggesting that surface runoff (transport of rainfall  $\text{NO}_3^-$  or leaching of

accumulated  $\text{NO}_3^-$  from surface soils) or riparian zone soils are major sources. A similar pattern was observed by McDiffett et al. (1989), but Buffam et al. (2001) observed the opposite, anti-clockwise pattern with higher  $\text{NO}_3^-$  occurring on the falling limb of the hydrograph. Buffam et al. (2001) attributed this pattern to the  $\text{NO}_3^-$  buildup in unsaturated soils throughout the catchment which was flushed to streams during the storm.

Soluble reactive phosphorus and  $\text{NH}_4^+$  were highly variable during storms and did not exhibit consistent differences between concentrations on the rising and falling limb of the hydrograph (Fig. 6E–6H). As has been observed in other studies (Evans and Davies, 1998),  $\text{SO}_4^{2-}$  was consistently higher on the falling limb of the hydrograph suggesting a catchment soil water source (Fig. 6I, 6J, 7B).

## CONCLUSIONS

Upland soil and vegetation disturbance had clear effects on suspended sediments, nutrients, and other aspects of stream chemistry. A relatively simple disturbance metric, the proportion of a catchment composed of bare ground on slopes greater than 5% and unpaved roads, explained significant proportions of the variability for a group of stream chemistry parameters. The dominant effect of military training disturbance to upland vegetation and soils on streams was a large increase in inorganic suspended sediment transport. The increase was particularly evident during storms, but a significant effect existed during baseflow conditions as well. The increase in inorganic suspended sediments may have contributed to some of the other chemistry patterns that were observed, reducing baseflow SRP and DOC due to adsorption. These results illustrate that in regions with highly erodible soils, upland soil and vegetation disturbance can affect streams despite intact riparian zones.

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