Baseflow and peakflow chemical responses to experimental applications of ammonium sulphate to forested watersheds in north-central West Virginia, USA

Pamela J. Edwards,* Frederica Wood and James N. Kochenderfer
Northeastern Research Station, U.S. Forest Service, Parsons, West Virginia, USA

Abstract:

Stream water was analysed to determine how induced watershed acidification changed the chemistry of peakflow and baseflow and to compare the relative timing of these changes. Two watersheds in north-central West Virginia, WS3 and WS9, were subjected to three applications of ammonium sulphate fertilizer per year to induce acidification. A third watershed, WS4, was the control. Samples were collected for 8 years from WS9 and for 9 years from WS3. Prior to analyses, concentration data were flow adjusted, and the influence of natural background changes was removed by accounting for the chemical responses measured from WS4. This yielded residual values that were evaluated using robust locally weighted regression and Mann–Kendall tests. On WS3, analyte responses during baseflow and peakflow were similar, although peakflow responses occurred soon after the first treatment whereas baseflow responses lagged 1–2 years. This lag in baseflow responses corresponded well with the mean transit time of baseflow on WS3. Anion adsorption on WS3 apparently delayed increases in SO_4 leaching, but resulted in enhanced early leaching losses of Cl and NO_3. Leaching of Ca and Mg was strongly tied, both by timing and stoichiometrically, to NO_3 and SO_4 leaching. *F*-factors for WS3 baseflow and peakflow indicated that the catchment was insensitive to acid neutralizing capacity reductions both before and during treatment, although NO_3 played a large role in reducing the treatment period *F*-factor. By contrast, the addition of fertilizer to WS9 created an acid sensitive system in both baseflow and peakflow. On WS9, baseflow and peakflow responses also were similar to each other, but there was no time lag after treatment for baseflow. Changes in concentrations generally were not as great on WS9 as on WS3, and several ions showed no significant changes, particularly for peakflow. The lesser response to treatment on WS9 is attributed to the past abusive farming and site preparation before larch planting that resulted in poor soil fertility, erosion, and consequently, physical and chemical similarities between upper and lower soil layers. Even with fertilizer-induced NO_3 and SO_4 leaching increases, base cations were in low supplies and, therefore, unavailable to leach via charge pairing. The absence of a time lag in treatment responses for WS9 baseflow indicates that it has substantially different flow paths than WS3. The different hydrologies on these nearby watersheds illustrates the importance of understanding watershed hydrology when establishing a monitoring programme to detect ecosystem change. Published in 2002 by John Wiley & Sons, Ltd.

KEY WORDS   baseflow; peakflow; stream chemistry; watershed acidification; flow paths

INTRODUCTION

Identifying long-term stream chemistry changes owing to acidic deposition has been difficult because few relevant long-term data bases exist (Stoddard, 1991). The inherent chemical differences associated with various stream-flow regimes or with the seasonality of flows further confounds trend detection because these variations must be considered in the monitoring programme or data interpretation (Brewin *et al.*, 1996). If both baseflow and stormflow have not been sampled in the long-term, presence and timing of stream water acidification is

difficult to document, because in many areas acidification may be expressed initially as episodic fluctuations and only later become chronic (Herlihy *et al*., 1993).

In this study we analysed the temporal baseflow and peakflow chemistries of two watersheds that were acidified artificially for 8 and 9 years. Comparisons of peakflow and baseflow responses between and within these watersheds illustrate different responses to acidification owing to the watersheds' different hydrologies and initial watershed conditions. These results demonstrate the need for sampling strategies that consider flow regime and local watershed characteristics to identify ecosystem changes in a timely manner.

METHODS

Study sites

Three watersheds in the mid-Appalachian Mountains of north-central West Virginia were used in this study (Figure 1). Two of the watersheds, WS3 and WS4, are located adjacent to one another on the Fernow Experimental Forest near the town of Parsons. The third watershed, WS9, is located approximately 10 km west of Parsons in the Monongahela National Forest. Watershed WS4 was used as a reference or control watershed whereas WS3 and WS9 were treated repeatedly to induce acidification.

Precipitation on all three watersheds is distributed fairly evenly throughout the year. Resulting stream discharge is measured continuously with 120° V-notch weirs in combination with FW-1 water-level recorders equipped with 7-day strip charts. Watersheds WS3 and WS4 are very similar physically (Table I) and hydrologically (Table I and Figure 2). Mean baseflow residency times in WS3 and WS4 are almost equal
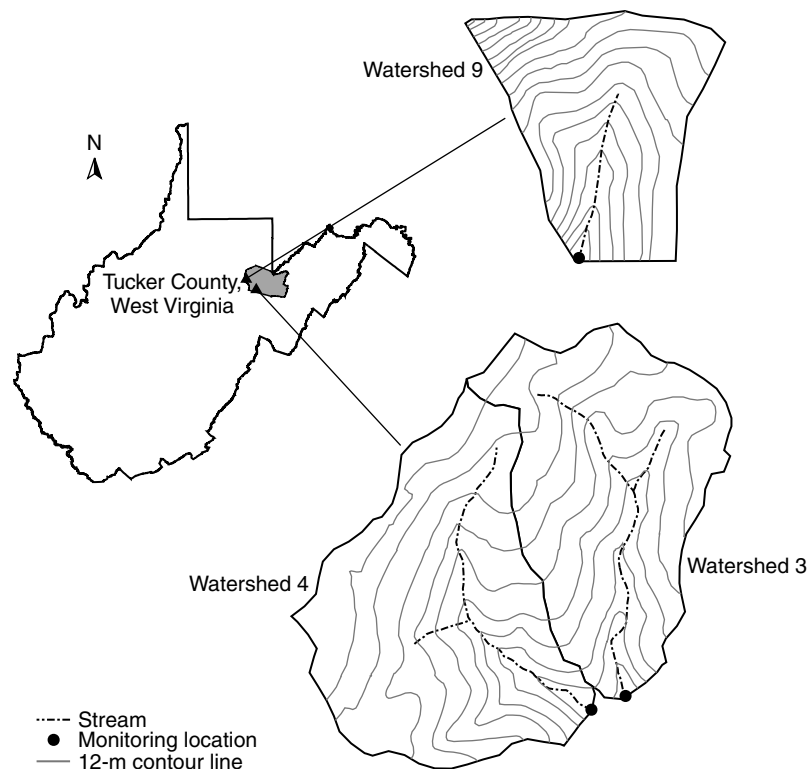

Figure 1. Locations of the experimental watersheds in Tucker County, West Virginia and maps of watersheds 3, 4 and 9. Watersheds WS3 and 4 are illustrated at a smaller scale (1 : 8500) than WS9 (1 : 4000)

Table I. Characteristics of the watersheds; stream flow and precipitation values are means with standard deviations in parentheses

Characteristic	WS9	WS3	WS4
Watershed area (ha)	11·6	34·3	38·9
Minimum elevation (m)	744	735	750
Maximum elevation (m)	878	860	870
Dominant overstory	*Larix leptolepis*	*Prunus serotina*	*Quercus rubra*
vegetation	*Quercus rubra*[a]	*Acer rubrum*	*Fagus grandifolia*
	Prunus serotina[a]	*Betula lenta*	*Acer rubrum*
Overstory age (years)	14[b]	28	90
Average watershed slope (%)	15	20	25
Watershed aspect	South	South	South–South-east
Annual stream flow (mm)			
1951–1997	739 (192)	668 (144)	648 (138)
1986–1997	798 (182)	659 (169)	668 (170)
Mean daily stream flow (mm)			
1951–1997	2·204 (3·770)	1·828 (3·223)	1·773 (3·214)
1986–1997	2·186 (3·784)	1·805 (3·192)	1·829 (3·228)
Annual precipitation (mm)			
1951–1997	1606 (269)	1483 (166)	1463 (163)
1986–1997	1728 (288)	1497 (199)	1468 (203)
Baseflow transit time (year)	n.a.	1·6	1·4

[a] In buffer strip.
[b] Age of *Larix*.

(DeWalle *et al*., 1997), about 1·6 and 1·4 years, respectively (Table I). The frequency of occurrence of the highest 60% of mean daily stream flow on WS3 and WS4 also are nearly identical (Figure 2). Watershed WS9 is smaller than the other two watersheds, but receives significantly greater mean annual precipitation than WS4 ($p = 0.02$). The flow-duration curve for WS9 is shifted to the left of both WS3 and WS4, but is very similar in shape to WS4 through most range of flows (Figure 2). Thus, although WS9 has less area, for any given per cent of time that flow is exceeded, the actual discharge from WS9 is greater than from WS4 (Figure 2). This relationship also is reflected in the higher, although not significantly higher ($p = 0.08$), mean stream flow on WS9 compared to WS4 (Table I).

The watersheds differ markedly in land-use history and now support substantially different vegetation (Table I). Watersheds WS3 and WS4 were cut heavily around 1910. At that time, unharvested species were primarily sugar maple (*Acer saccharum* Marsh.) and northern red oak (*Quercus rubra* L.); the surviving residuals on WS4 are now about 200 years old (Edwards and Helvey, 1991). In the 1940s, an unknown volume of dead American chestnut (*Castanea dentata* (Marsh.) Borkh.) was salvage logged on WS4, but most if not all of this volume is believed to have been located along the watershed's upper boundary because there are no skid trails in the catchment. Since that time, disturbance to WS4 has been minimal.

Watershed WS3 was reharvested between July 1969 and May 1970. Except for a 3-ha buffer strip surrounding the stream, all stems with diameter >2·54 cm were clear-cut. In November 1972, the buffer strip was clear-cut and all of the treetops and woody debris in the channel and within 2·4 m from the channel on both sides of the stream were removed by hand. This included woody material deposited in the channel prior to harvesting. No equipment was permitted in the buffer strip for harvesting or channel clearing (Kochenderfer and Edwards, 1991). The entire watershed regenerated to native vegetation; overstory regeneration (Table I) originated from both stump sprouts and seeds.

Watershed WS9 was cleared in the 1800s for farming. By the 1920s, the farm on WS9 was abandoned owing to soil infertility created by the combination of excessive topsoil erosion and nutrient depletion from poor
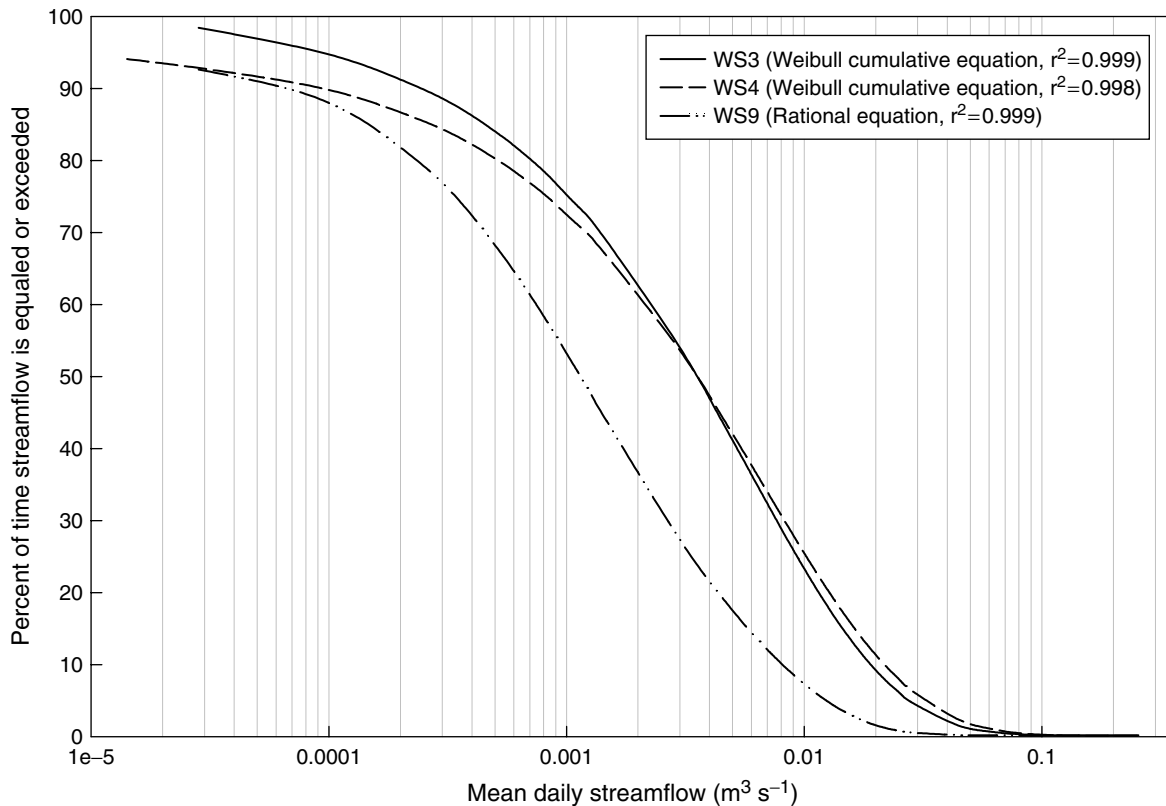
Figure 2. Flow-duration curves developed from historic data (1951–1997)

farm practices. Soon after abandonment, WS9 entered into USDA (United States Department of Agriculture) Forest Service ownership (Lima *et al.*, 1978). The poor-quality hardwood stand that had regenerated (Lima *et al.*, 1978) was clear-cut in 1983, except for a 1·42-ha buffer strip around the stream (approximately 20 m wide on both sides of the stream). Following harvesting, the watershed was raked by bulldozer, and brush and treetops were pushed into rows along the contour. Excluding the unharvested buffer strip, the watershed was planted to 2-year-old Japanese larch (*Larix leptolepis* Seib. and Zucc.) in the spring of 1984 at a spacing of 1·8 × 1·8 m (Kochenderfer and Helvey, 1989). Dominant vegetation in the main portion of the watershed remains *L. leptolepis*, which are now about 8 m tall; older mixed hardwoods (Table I) grow in the buffer strip.

On all three watersheds, the dominant soil type is Calvin channery silt loam (loamy-skeletal, mixed, mesic Typic Dystrochrept) underlain with fractured sandstones and shales of the Hampshire Group (Losche and Beverage, 1967). Soils generally are <1 m in depth. Pretreatment soil chemistry data are given in Table II.

Watershed treatment and sample collection

In the late 1980s, acidification treatments were initiated on WS3 and WS9. Most of the treatment years on the two watersheds overlapped, although the duration of treatments on WS9 was shorter than on WS3. Treatment on WS9 began in April 1987 and was terminated in July 1994. Treatment on WS3 began in January 1989 and continues.

Acidification was induced on both catchments by applying granular ammonium sulphate fertilizer (Table III) to the entire watershed area. Both the ammonium (NH_4) and sulphate (SO_4) ions in the fertilizer contribute

Table II. Pretreatment soil chemistry means and standard deviations (in parentheses) for the watersheds

Analyte	Horizon[a]	WS9	WS3	WS4
pH	A	4·56	4·48	3·95
	B	4·56	4·51	4·55
Exchangeable Ca (cmol kg^{-1})	A	0·64(0·57)	4·79(8·72)	0·49(0·22)
	B	0·39(0·38)	0·07(0·08)	0·09(0·05)
Exchangeable Mg (cmol kg^{-1})	A	0·17(0·12)	0·59(0·88)	0·23(0·10)
	B	0·10(0·04)	0·02(0·02)	0·07(0·04)
Exchangeable Na (cmol kg^{-1})	A	0·03(0·01)	0·07(0·09)	0·08(0·11)
	B	0·02(0·01)	0·02(0·03)	0·02(0·01)
Exchangeable K (cmol kg^{-1})	A	0·28(0·08)	0·34(0·19)	0·20(0·06)
	B	0·17(0·04)	0·08(0·06)	0·09(0·01)
Exchangeable Al (cmol kg^{-1})	A	4·23(0·85)	1·39(1·81)	8·70(3·79)
	B	4·63(1·24)	1·48(2·28)	—
Cation exchange capacity (cmol kg^{-1})	A	6·50(0·99)	11·77(7·86)	9·35(3·41)
	B	6·96(3·25)	6·20(1·47)	5·99(1·54)
Total C (%)	A	3·3(1·3)	9·1(5·4)	11·2(5·3)
	B	1·1(0·7)	1·9(2·3)	4·6(2·7)

[a] WS9 sampled at 0–15 cm and 15–46 cm rather than by horizon

to acidification. Once the fertilizer dissolves in the soil, the NH_4 and SO_4 ions dissociate. The NH_4 ions then undergo fairly rapid nitrification in these watersheds (Gilliam *et al.*, 1996), which liberates hydrogen ions. These liberated protons displace base cations, if available, on soil exchange sites. The dissociated SO_4 and resulting NO_3 (from nitrification) from the fertilizer additions charge pair with these base cations and leach through the soil to stream and groundwater systems. As base cations become less available or in highly acidic soils, the hydrogen ions liberated during nitrification of NH_4 also displace aluminum (Al) rather than base cations. This acidic cation similarly charge pairs and leaches from the soil with SO_4 and NO_3. Over time, reductions and losses of buffering capacities result owing to hydrogen ion accumulation in the soil, and base cation and Al leaching with mobile anions (Reuss and Johnson, 1986; Mitchell *et al.*, 1992).

Three fertilizer applications per year were made at approximately double ambient bulk N and S deposition inputs as estimated from throughfall concentrations (Helvey and Kunkle, 1986). Because ambient inputs vary seasonally, rates of applied ammonium sulphate were varied by season, with WS3 and WS9 generally treated in the spring, summer and autumn (usually March, July, and November) of each year. Spring and autumn applications of 34 kg fertilizer per ha (7·1 kg N ha^{-1} and 8·1 kg S ha^{-1}) were approximately double the deposition rates for January to April and September to December, respectively. Summer applications of 101 kg fertilizer per ha (21·3 kg N ha^{-1} and 24·4 kg S ha^{-1}) were approximately double the deposition rates

Table III. Fertilizer assay results

Analyte	Concentration (µg g^{-1})	Annual application (kg ha^{-1})
Calcium	729·3	0·12
Magnesium	20·18	0·11
Potassium	1606	0·27
Sodium	111·5	0·02
Phosphorus	442·9	0·07
Nitrogen	20·79%	35·14%
Sulfur	21·89%	36·99%

between May and August. The first two applications on WS9 were made by manually applying pre-weighed amounts of fertilizer to the entire watershed after it was gridded into small areas of known acreage. All other applications on both watersheds were made by helicopter.

Stream-flow samples were collected during baseflow and stormflow and were analysed for pH, calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), NO_3, SO_4 and chloride (Cl) using EPA-approved protocols at the Forest Service's Timber and Watershed Laboratory in Parsons. Sample handling, processing and analytical techniques are detailed in Edwards and Wood (1993). Chloride contamination in some standards was a problem prior to 1988, so Cl data prior to that time are not presented or used in analyses. Concentrations of all analytes except pH were expressed as $\mu eq\ L^{-1}$.

Weekly stream grab samples were collected every Monday (WS9) or Tuesday (WS3 and WS4) from a fixed point immediately upstream from each weir when flows were sufficient from 1987 to 1997. Samples that were not from any portion of a storm hydrograph were extracted to create the baseflow chemistry data set.

Stormflow samples from discrete runoff events were collected using ISCO model 2700 automatic samplers. The ISCOs were actuated manually because manual actuation was more reliable than stage actuation for these small streams. To assure sample collection near or at peakflow on these flashy streams, growing-season samples were collected at 15-min intervals from May through to October on the rising limb of the hydrograph and for several samples after peakflow. During the dormant season when soil moisture deficits are low or negligible and hydrological responses are longer, samples were collected at 30- or 60-min intervals.

From the stormflow data set we created a data set composed of chemistry results only from peakflow samples. As stormflow samples were collected on preset intervals, a sample generally was not collected exactly at peakflow for each storm event. Therefore, the sample collected nearest to the time of peakflow was used to represent peakflow conditions. All analytes (including pH expressed as H), except NO_3, reached peak concentrations near the time of peakflow; NO_3 generally peaked later (Edwards *et al.*, 2001).

The WS9 stormflow data set includes data from 1987 to 1997, although WS9 treatment was terminated in July 1994. Stormflow sampling of WS3 and WS4 began in 1988, about 1 year before treatment began. Stormflow sampling ended in 1995 on WS3 and in 1997 on WS4. The number of storms sampled per year and peakflow characteristics are given in Table IV. Sample storms were predominantly moderate- to large-size events because smaller events generally did not result in measurable flow or chemical changes. The overall mean peakflows for each watershed ('All' row in Table IV) were within the largest 10% of storms for the years sampled. However, the minimum peakflows for individual years were as low as the 1% quantile and the maximums were as high as the 100% quantile for those years.

Statistical analyses

In this paper, changes to chemical concentrations at baseflow and peakflow owing to acidification treatments are compared within and between watersheds over time. Because the data are irregularly spaced time-series, parametric time-series analyses could not be performed. Consequently, non-parametric data analyses are used.

Robust locally weighted (RLW) regression, also referred to as Lowess or Loess (Cleveland, 1979; Cleveland and Devlin, 1988) was used to display temporal trends in the data. Locfit software (Loader, 1998) with the robust option was used to develop the trend lines. The RLW regression does not provide estimates of regression coefficients, but it does provide a way to evaluate trends by focusing on the fitted curve (Loader, 1998), with no concern as to whether assumptions inherent in least squares regression were violated. The RLW regression is particularly suited for identifying directional changes in trends. As we wanted to identify trends rather than develop prediction equations, RLW regression met our objectives well.

Because we wanted to isolate treatment effects, we first removed the effects of flow on chemistry. Flow adjustment provides another benefit. It helps reduce the seasonality of concentration data (Hipel and McLeod, 1994), thereby reducing the need for seasonal trend analysis, and increasing the sample size and statistical power of non-seasonal trend analysis.

Flow and chemistry data (except pH) were transformed by taking the logarithm to the base 10 (i.e. $\log_{10}$) of both variables. We used the $\log_{10}$ transformation rather than the natural logarithm because pH already is

Table IV. Stormflow sampling characteristics; peakflow units are $m^3\ s^{-1}$

Watershed	Year	Number of Storms	Peakflow			
			Mean	SD	Minimum	Maximum
WS9	1987	7	0·0137	0·0109	0·0012	0·0235
	1988	8	0·0152	0·0127	0·0019	0·0392
	1989	6	0·0299	0·0356	0·0108	0·1023
	1990	5	0·0311	0·0207	0·0078	0·0580
	1991	4	0·0209	0·0067	0·0133	0·0277
	1992	5	0·0250	0·0211	0·0099	0·0622
	1993	6	0·0253	0·0264	0·0009	0·0689
	1994	4	0·0700	0·0834	0·0203	0·1941
	1995	2	0·0162	0·0111	0·0084	0·0241
	1997	1	0·0352	—	—	—
	All	48	0·0263	0·0315	0·0009	0·1941
WS3	1988	6	0·0454	0·0258	0·0064	0·0807
	1989	8	0·0806	0·0380	0·0389	0·1464
	1990	10	0·0519	0·0596	0·0063	0·2104
	1991	6	0·0267	0·0258	0·0013	0·0630
	1992	8	0·0411	0·0413	0·0012	0·1023
	1993	7	0·0707	0·0594	0·0067	0·1725
	1994	5	0·1406	0·1900	0·0161	0·4768
	1995	2	0·0457	0·0403	0·0172	0·0742
	All	52	0·0618	0·0736	0·0012	0·4768
WS4	1988	4	0·0551	0·0322	0·0129	0·0865
	1989	9	0·0924	0·0413	0·0436	0·1580
	1990	11	0·0600	0·0606	0·0074	0·2268
	1991	6	0·0280	0·0279	0·0014	0·0724
	1992	6	0·0643	0·0517	0·0038	0·1470
	1993	4	0·0689	0·0570	0·0120	0·1371
	1994	5	0·1560	0·2029	0·0293	0·5157
	1995	2	0·0565	0·0442	0·0252	0·0877
	1997	1	0·0930	—	—	—
	All	48	0·0735	0·0801	0·0014	0·5157

expressed as a $\log_{10}$ value. The data then were adjusted for flow by plotting the transformed chemistry data (*y*-axis) against the transformed flow data and fitting an RLW regression trend-line through the data (Figure 3a and b) (Hipel and McLeod, 1994). To avoid oversmoothing the trend line, procedures suggested by Cleveland (1994, pp. 171–175) were used. Residuals were calculated between the trend line and each observation. These residuals represent the flow-adjusted (transformed) concentrations; when plotted against time, they illustrate how flow-adjusted concentrations varied owing to background conditions alone (Figure 3c) and as a result of background + treatment conditions (Figure 3d).

Flow adjusting in this manner tends to underestimate treatment-induced effects because the entire treatment period is used along with the pretreatment data for flow adjustment. If there is a temporal treatment trend, some of it may be attributed to flow rather than treatment (Alley, 1988). However, the underestimation will be less than by an analogous flow-adjustment procedure using simple linear regression, because RLW regression is less sensitive than parametric regression to extreme values (which treatment can induce).

An alternative approach for avoiding underestimation is paired watershed analysis (Hewlett, 1982a), but this procedure was inappropriate for these data because meaningful regression equations predicting treatment watershed concentrations from WS4 concentrations could not be developed for the pretreatment data. Consequently, as is necessary when using residual-value flow adjustment procedures, we
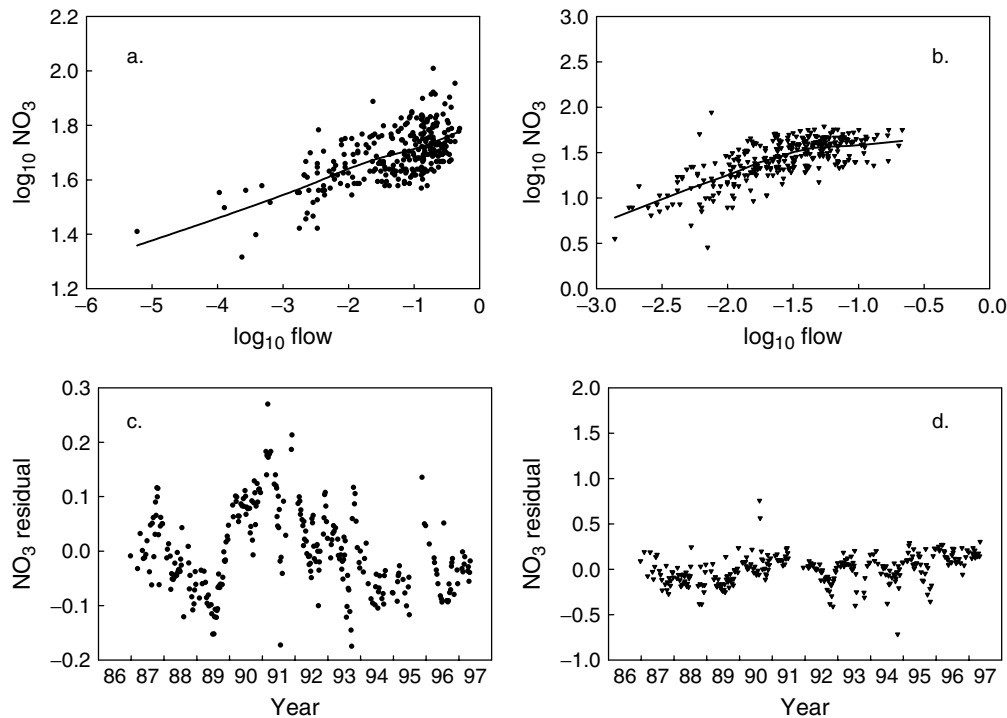
Figure 3. Example of flow adjusting for WS4 (a and c) and for WS9 (b and d). Robust locally weighted regression lines are fitted through $\log_{10}$ transformations of NO_3 (µeq L^{-1}) versus flow (ft^3 s^{-1}) (a and b). Calculated as the difference between observed values and the local regression line in a and b, residuals are plotted against time (c and d)

acknowledge that our analyses generally underestimated the trends attributable to treatment on WS3 and WS9.

To further account for background changes in concentrations, for each corresponding treatment: control watershed data pair, the residual values for WS4 were subtracted from the residual values for WS3 and WS9. These differences plotted against time represent the changes in baseflow and peakflow concentrations that were attributable solely to the treatments on WS3 and WS9. In the example in Figure 3, the WS4 residual values (Figure 3c) subtracted from the WS9 residual values (Figure 3d) would yield the changes resulting from treatment shown later (see Figure 6c). The RLW regression lines again were fitted through these difference values graphed against time (e.g. Figure 6c) to display treatment-induced response trends. Subsequent analyses and discussions involve only these latter residual difference values, which hereafter are referred to as peakflow and baseflow concentrations, even though they are unitless because they are determined from residuals.

The full baseflow and peakflow data sets (i.e. $n = 272$, 290 and 312 for baseflow for WS3, WS4 and WS9, respectively, and $n = 52$, 48 and 48 for peakflow for WS3, WS4 and WS9, respectively) were used in the development of initial concentration versus flow trend lines and residual calculations (e.g. Figure 3a–d) because the full data sets allowed for the best description of flow and concentration relationships. However, residual differences (WS3 − WS4 and WS9 − WS4) were calculated only for samples for which both baseflow or peakflow samples were available for the same day/storm from the WS9−WS4 or WS3−WS4 pairs. For this procedure, $n = 251$ for WS3−WS4 and $n = 230$ for WS9−WS4 baseflow, and $n = 43$ for WS3−WS4 and $n = 32$ for WS9−WS4 peakflow.

Mann–Kendall tests (Mann, 1945) were used to test whether the residual difference (WS3−WS4 and WS9−WS4) data (i.e. not the trend lines themselves) increased or decreased significantly over time. Where an RLW trend line changed direction, a separate Mann–Kendall test statistic was calculated for data on both

sides of that change, as recommended by Hipel and McLeod (1994). Sen slope estimates (Sen, 1968) were calculated to identify the direction (positive or negative) and compare the rates of change of the trends.

Residual analyses allow one to separate and examine trends in chemical responses attributable only to treatment. Additional analyses using raw concentration data (μeq L^{-1}) also were performed. Although these analyses do not isolate treatment effects, they provide an understanding of how overall chemical relationships changed over time.

F-factor values (Henrikson, 1982) were calculated for the period 1982 to 1986 and for 1989 to 1994. F-factors essentially represent the proportional change in concentrations of base cations associated with changes in acid anions, when they change in the same direction. This relationship effectively evaluates the sensitivity of the acid neutralizing capacity (ANC) of the system (Sullivan et al., 1990). Thus, F-factors for 1982 to 1986 represent the proportional change that occurred prior to treatment and represent baseline conditions to which F-factors calculated for the treatment period (1989 to 1994) can be compared.

Although F-factor calculations often use SO_4 concentrations alone as the acid anion, NO_3 concentrations can be added if this ion constitutes a large proportion of total acid anion contributions (Sullivan et al., 1990). Because NO_3 concentrations increased as a result of fertilization and including NO_3 allowed evaluation of its importance to sensitivity to acidification prior to and during treatment, we calculated F-factors using SO_4 alone

$$F_S = \Delta \sum C_B \Big/ \Delta C_{SO_4}$$

and in combination with NO_3

$$F_A = \Delta \sum C_B \Big/ \Delta \sum C_A$$

where $\sum C_B$ is sum of the mean Ca, Mg, K and Na concentrations, C_{SO_4} is the mean SO_4 concentration, and $\sum C_A$ is the sum of the mean SO_4 and NO_3 concentrations. Sea-salt corrections (Sullivan et al., 1990) were not made because Cl inputs from precipitation in this area are negligible (Webb et al., 1997).

Linear regression relationships between individual base cations (y) and acid anions (x) also were determined to examine stoichiometric changes in ion responses. Changes in base cations (μeq L^{-1}) resulting from per unit changes (μeq L^{-1}) in acid anions can be determined from the resulting slopes, and analysis of changes in R^2 values before and during treatment provide insight into changing ion relationships as a result of treatment. For pretreatment, the values were determined from weekly samples, which do not necessarily represent pure baseflow results, but they are principally composed of baseflow.

RESULTS

WS3 baseflow versus peakflow chemistry

Comparisons of WS3 baseflow and peakflow trend lines show similar types of response (Figures 4 and 5). All concentrations except peakflow Na and pre-1991 peakflow SO_4 increased significantly, while pH decreased significantly due to treatment. A major difference between the two hydrological regimes was the timing of initial response to treatment. Baseflow concentrations required a longer time to elicit a response to treatment (Figure 4) than peakflow (Figure 5), which is reflected in the generally larger slope values for peakflows. However, once baseflow began to respond to treatment on WS3, the trend continued through to the end of data collection.

Although the Mann–Kendall tests indicate increasing NO_3, Ca and Mg concentrations in baseflow over the entire period of record, trend lines indicate that these analytes did not begin to increase until nearly 1990 (Figures 4c, 4e and 4f, respectively), about 1 year after the first treatment. Baseflow pH began declining about the same time (Figure 4a). Baseflow SO_4 began to increase in late 1990 to early 1991 (Figure 4b). Potassium
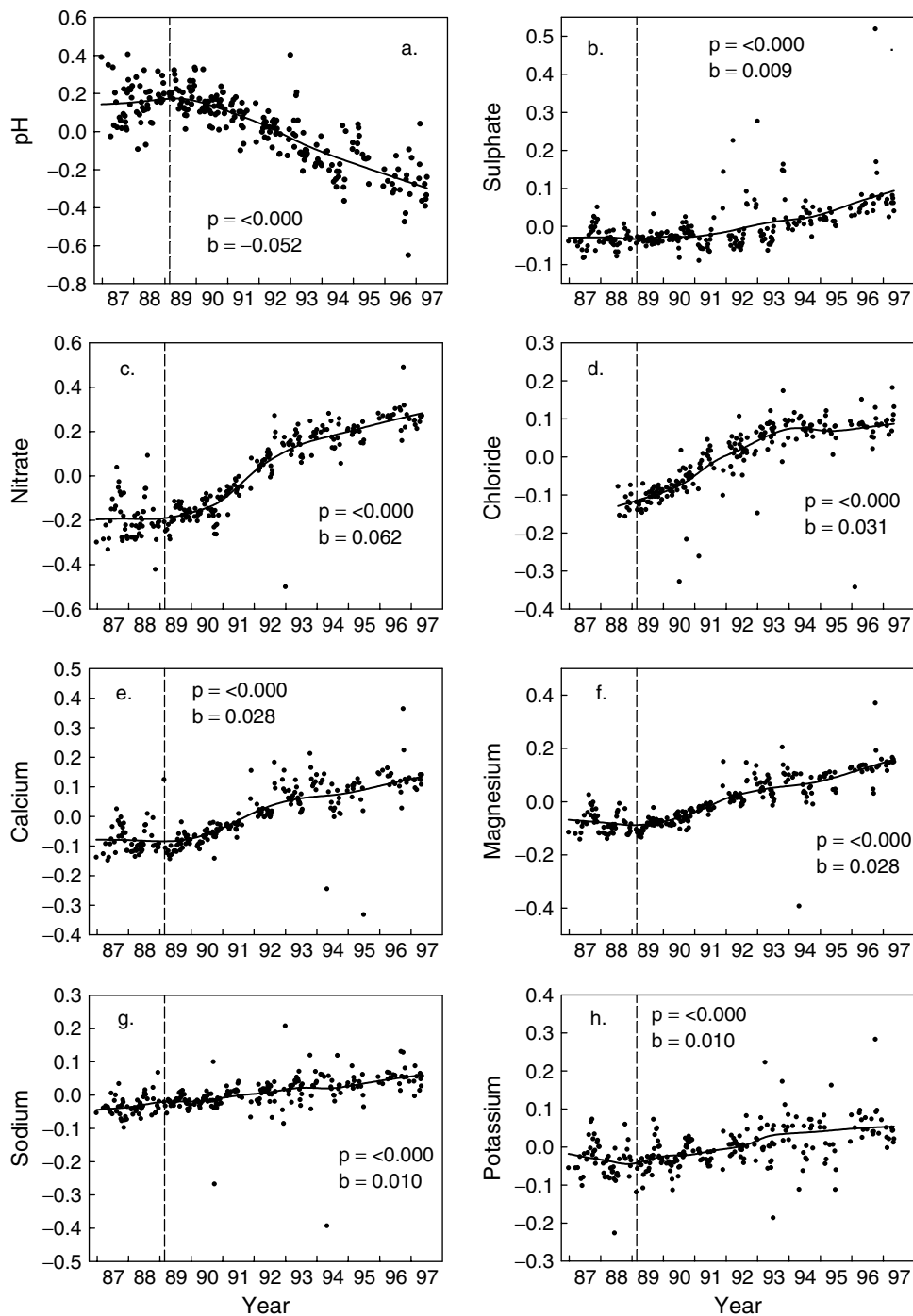
Figure 4. Residuals representing log-transformed baseflow concentration changes over time on WS3 as a result only of the acidification treatment: (a) pH; (b) SO$_4$; (c) NO$_3$; (d) Cl; (e) Ca; (f) Mg; (g) Na; (h) K. Trend lines were developed using robust locally weighted regression. The p-value is the Mann–Kendall probability of a significant monotonic trend over time, and b is the Sen slope estimate of the trend. Treatment began in 1989 (dashed line)
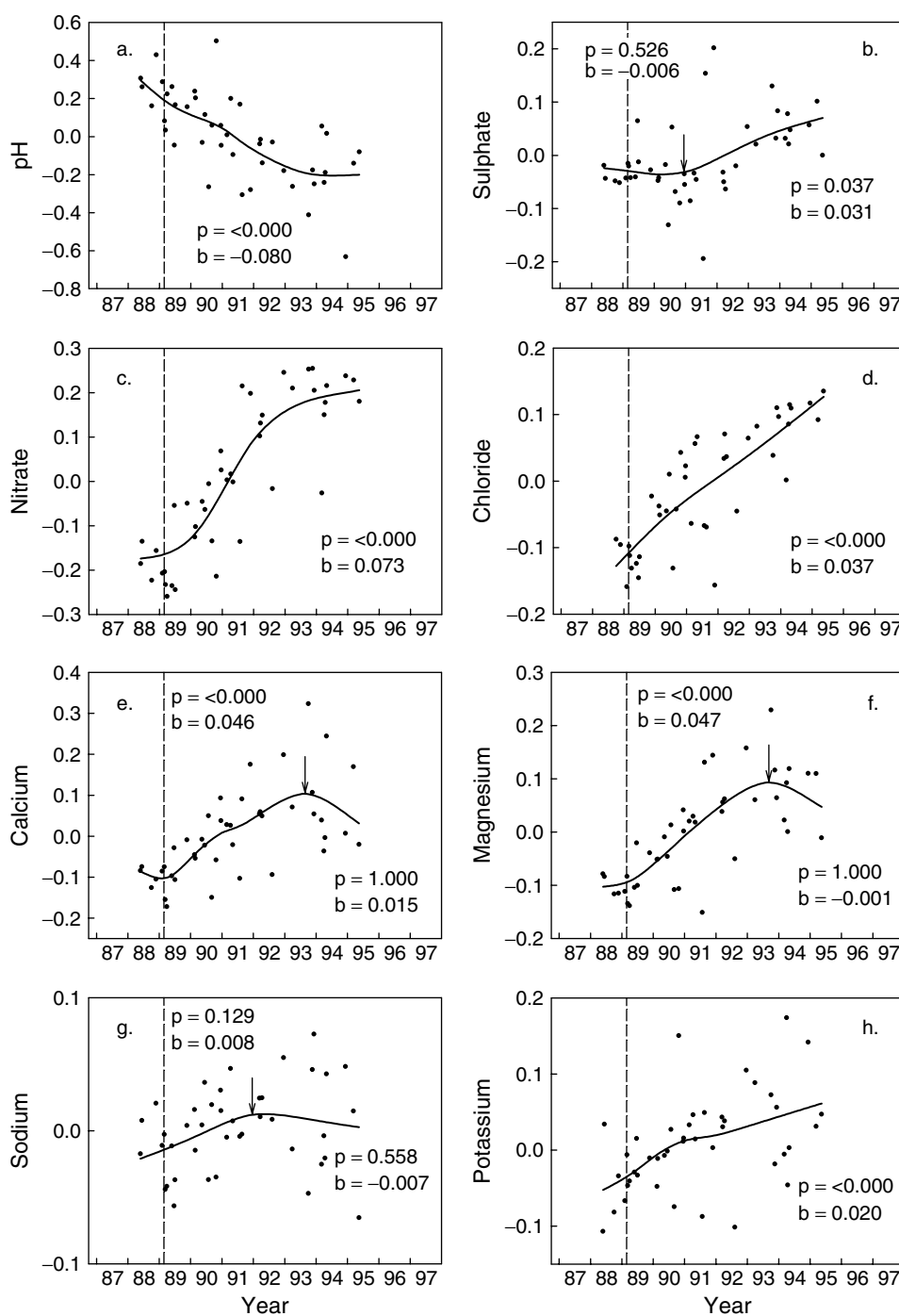
Figure 5. Residuals representing log-transformed peakflow concentration changes over time on WS3 as a result only of the acidification treatment: (a) pH; (b) SO$_4$; (c) NO$_3$; (d) Cl; (e) Ca; (f) Mg; (g) Na; (h) K. Trend lines were developed using robust locally weighted regression. The *p*-value is the Mann–Kendall probability of a significant monotonic trend over time, and *b* is the Sen slope estimate of the trend. An arrow indicates where the RLW trend-line changed directions and trend and slope tests were performed on data on either side of the arrow. Treatment began in 1989 (dashed line)

had initial increases in the first year of treatment and then largely levelled off until late 1991 to early 1992 (Figure 4h). Concentrations of Cl and Na in baseflow also increased when treatment began (Figures 4d and 4g); these two ions are present only in low concentrations in these soils.

All WS3 peakflow concentrations, except SO_4, responded almost immediately to treatment (Figure 5). Peakflow SO_4 concentration trended downward slightly (Figure 5b) but not significantly during the first year of treatment. Peakflow Ca and Mg concentrations for WS3 increased significantly initially (Figures 5e and 5f), but declined beginning about mid-1993. Concentrations of Na increased, although not significantly, through early 1992 and then decreased (Figure 5g).

The downturn in peakflow Ca, Mg and Na concentrations was not significant during these latter years. This non-significance coupled with the limited number of storms sampled after the downturn and substantial spread of data during that period make it impossible to verify a decreasing trend without additional data or other supporting evidence.

WS9 baseflow versus peakflow chemistry

Baseflow and peakflow chemical responses on WS9 were similar (Figures 6 and 7), but rates of chemical change for both flow regimes generally were not as great as for WS3. Baseflow K and peakflow Cl, SO_4, Ca and K were not significantly affected by fertilization (Figures 6 and 7). For those baseflow constituents that did show a significant upward or downward trend, concentration changes occurred almost immediately after the first treatment (Figure 6a–h). Although no matched storm samples were collected during the first year of treatment on WS9 (i.e. from the same storm for both WS9 and WS4), several unmatched storms were sampled on WS9 that year. These storms, adjusted only for flow, indicate that WS9 peakflow concentrations, particularly Ca, Mg, pH and SO_4, responded almost immediately to the acidification treatment (unpublished data). The same trends observed for WS9 during fertilization continued after treatment was terminated in July 1994 (Figures 6 and 7).

WS3 versus WS9 baseflow chemistry

Fertilization affected baseflow concentrations more on WS3 (Figure 4) than on WS9 (Figure 6), as indicated by the typically steeper slopes of the trend lines for WS3. Base cations Ca, Mg and Na were affected more on WS3 than on WS9, even though concentrations changed significantly over time on both catchments (Figures 4 and 6). Sodium decreased on WS9 (Figure 6g), but increased on WS3 (Figure 4g). Concentrations of K increased slightly but significantly on WS3, but did not change on WS9 over time (Figures 4h and 6h). Interestingly, Ca and Mg, which are the base cations present in highest raw concentrations in stream water (i.e. not flow or background adjusted) on WS3 (Adams *et al*., 1997), did not increase immediately in baseflow with the initiation of treatment, but only after a full year of fertilizer applications (Figures 4e and 4f). By contrast, although the rates of increase of Ca and Mg on WS9 were not as great, they increased after a single treatment (Figures 6e and 6f). Average raw concentrations of Ca and Mg on WS9 were at least 30% less than those for WS3 (unpublished data).

Concentration increases for NO_3 were significant on WS3 (Figure 4c) but the increasing trend was not immediate. Concentrations of NO_3 increased slightly about a year after the first treatment but the greatest increases in the trend line slope did not occur until early 1991. In 1991 and thereafter, NO_3 increases in WS3 baseflow were substantial (Figure 4c). On WS9, NO_3 concentrations trended upward slightly but significantly following the first treatment (Figure 6c); the overall response rate was not as great on WS9 as on WS3, particularly after 1990. The NO_3 slope for WS3 was about twice as large as for WS9 (Figures 4c and 6c, respectively).

Initial SO_4 concentrations in WS9 baseflow (Figure 6b) responded immediately but began to decline in early 1991. This decline continued at a slow but significant rate through the end of the study. By contrast, SO_4 concentrations in WS3 baseflow remained steady until about mid-1990, at which time they began to climb steadily (Figure 4b).
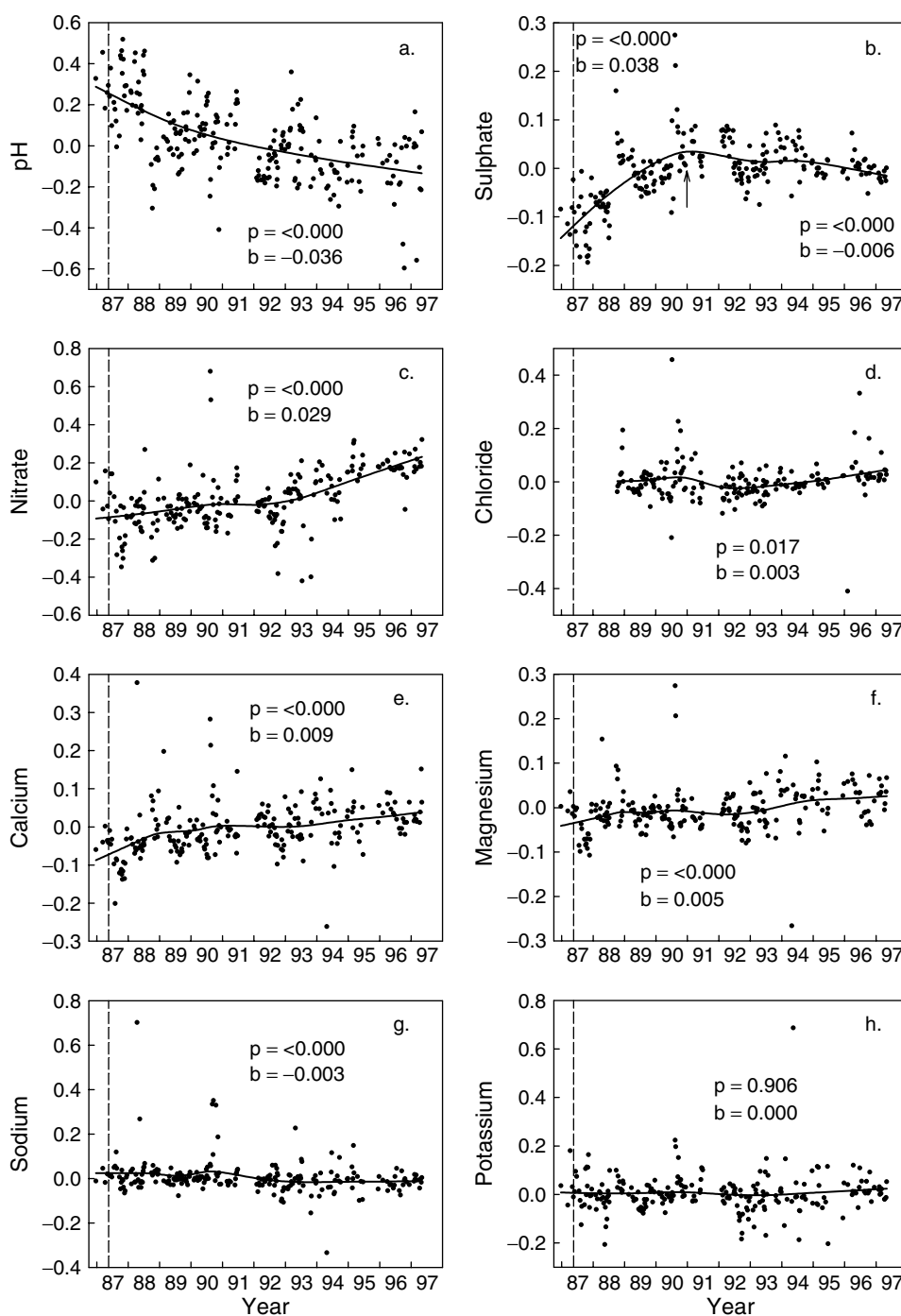
Figure 6. Residuals representing log-transformed baseflow concentration changes over time on WS9 as a result only of the acidification treatment: (a) pH; (b) SO$_4$; (c) NO$_3$; (d) Cl; (e) Ca; (f) Mg; (g) Na; (h) K. Trend lines were developed using robust locally weighted regression. The p-value is the Mann-Kendall probability of a significant monotonic trend over time, and b is the Sen slope estimate of the trend. An arrow indicates where the RLW trend-line changed directions and trend and slope tests were performed on data on either side of the arrow. Treatment began in 1987 (dashed line)

On WS9, pH began to decline with the initiation of treatment (Figure 6a). By contrast, pH on WS3 did not decline until early 1990 (Figure 4a). Raw pH values for baseflow in both watersheds were similar ($\cong 5 \cdot 5$) by 1997.

WS3 versus WS9 peakflow chemistry

Peakflow chemical responses between the two watersheds differed (Figures 5 and 7). On WS3, concentrations of Ca, Mg, K, NO_3 and Cl increased significantly; pH decreased throughout most or all of the study (Figure 5). Concentrations of SO_4 changed little on WS3 until 1991, when it increased steadily and significantly (Figure 5b). On WS9, only Mg and NO_3 concentrations showed strong and fairly consistent increasing trends during peakflow (Figures 7f and 7c). The pH decreased but the decrease is significant only when the entire data set is considered (Figure 7a). When it is separated at 1992, the point at which the trend line flattens out, slopes for neither portion of data changed significantly. Sodium decreased significantly (Figure 7g). Other analytes changed little with time (Cl) or changed directions (Ca, K, SO_4), often about mid-study (Figure 7).

The upturn in the WS9 trend lines for Ca and Na in the last 2 years of the study (Figure 7e and g) is believed to be driven largely by the data point for the final and only storm collected in 1996 and 1997. Without this single observation, the Ca pattern for WS9 peakflow would be more similar to that of SO_4 or K (Figures 7b and 7h) and the Na pattern would have been consistently downward. Even though RLW regression reduces the influence of individual observations on the trend line (Hipel and McLeod, 1994), with no storm samples in 1996 this single 1997 storm strongly influenced the direction of the trend lines at the end of the study. Consequently, these final upward trends in Ca and Na may be erroneous and should be viewed cautiously.

F-factor and regression analyses

F-factors for WS3 and WS9 baseflow before treatment were >1 (Table V), indicating that the ANC of neither stream was sensitive to acidification. F-factors <0·4 indicate acid sensitive systems (Sullivan *et al.*, 1990). However, treatment additions of S and N substantially affected watershed sensitivity to acidification, particularly on WS9. Watershed WS9 baseflow F_S and F_A were $\cong 0 \cdot 1$ (Table V). During treatment, WS3 baseflow $F_S \cong 2 \cdot 5$ compared with $F_A \cong 0 \cdot 6$. Thus, NO_3 played a large role in acidification processes in WS3, even though the catchment remained insensitive to acidification through 1994 ($F_A \cong 0 \cdot 6$).

For WS3, the treatment resulted in similar ANC sensitivities for baseflow ($F_A \cong 0 \cdot 56$) and peakflow ($F_A \cong 0 \cdot 6$) (Table V). On WS3, NO_3 continued to be an important contributor to acidification at peakflow (Table V); F_A was about three times lower ($\cong 0 \cdot 6$) compared with F_S ($\cong 1 \cdot 7$).

On WS9, the addition of NO_3 to the peakflow F-factor calculation resulted in a lower F-factor than with only SO_4 for peakflow, but the difference between F_S and F_A was not nearly as great as for WS3. However, the addition of NO_3 to the F-factor calculation resulted in a value ($F_A \cong 0 \cdot 4$) that was low enough to indicate that WS9 has reached a point at which acidic inputs now have a high potential to result in ANC reductions at peakflow.

The linear regression results confirm the F-factor analysis finding that NO_3 was much less important in acidification processes on WS3 and WS9 before treatment than during treatment. Although most of the WS3 cation : anion relationships were significant ($p \leq 0 \cdot 05$), the R^2 values before treatment were fairly low (all <0·4, and most $\leq 0 \cdot 09$) for each cation : anion regression pair (Table VI). By contrast, many regression pairs for baseflow and peakflow had much higher R^2 values during treatment, particularly those involving Ca and Mg with SO_4 and NO_3. Thus, the linear responsiveness of base cations to acid anions increased dramatically as a result of treatment on both watersheds.
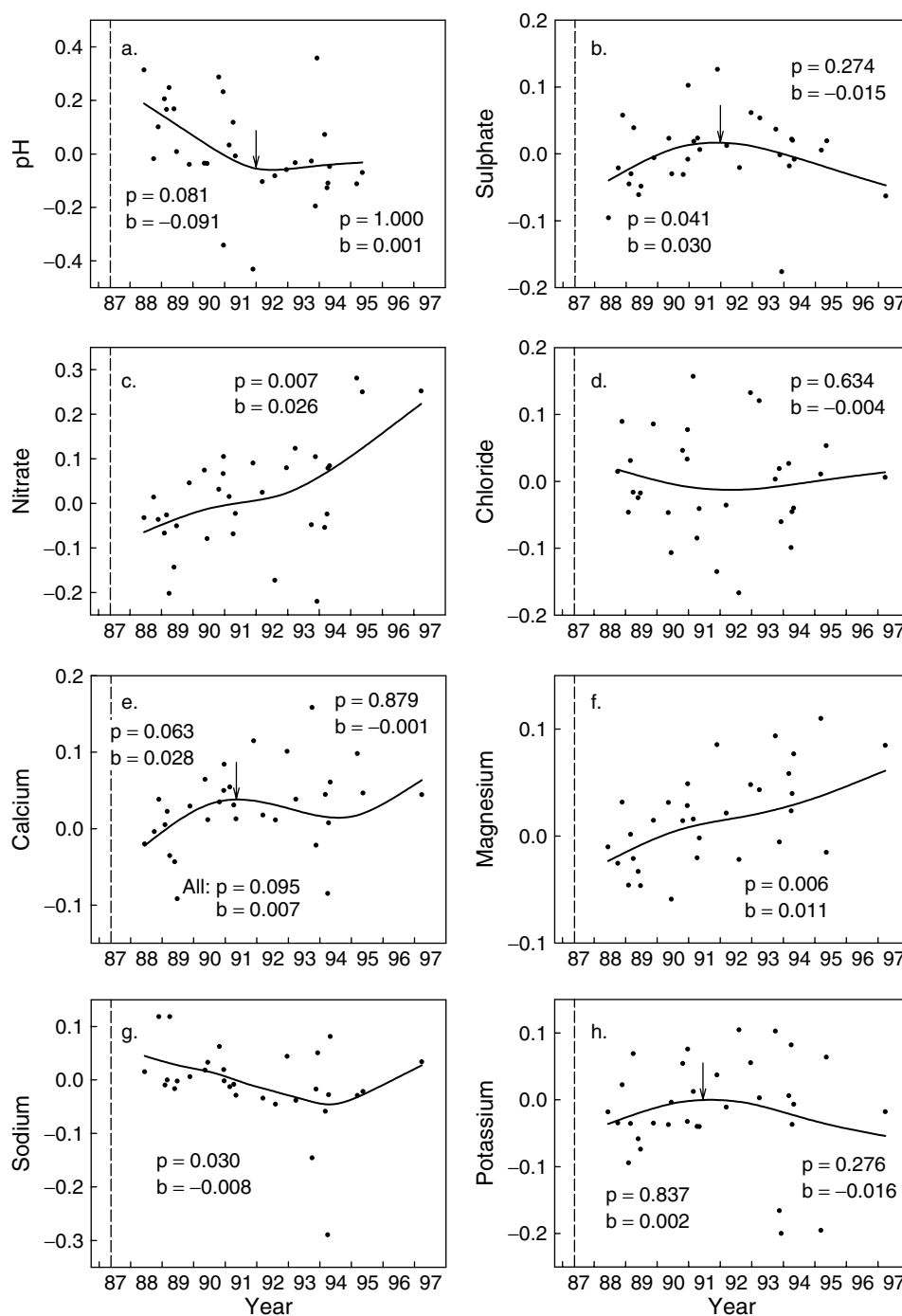
Figure 7. Residuals representing log-transformed peakflow concentration changes over time on WS9 as a result only of the acidification treatment: (a) pH; (b) SO_4; (c) NO_3; (d) Cl; (e) Ca; (f) Mg; (g) Na; (h) K. Trend lines were developed using robust locally weighted regression. The *p*-value is the Mann–Kendall probability of a significant monotonic trend over time, and *b* is the Sen slope estimate of the trend. An arrow indicates where the RLW trend-line changed directions and trend and slope tests were performed on data on either side of the arrow. Treatment began in 1987 (dashed line)

Table V. F-factors for the periods 1982–1986 (pretreatment) and 1989–1994 (treatment); stormflow samples were not collected during pretreatment

Period and Watershed	F_S		F_A	
	Baseflow	Peakflow	Baseflow	Peakflow
Pretreatment				
WS3	1·57	—	1·32	—
WS9	4·86	—	1·07	—
Treatment				
WS3	2·551	1·747	0·558	0·595
WS9	0·105	0·586	0·116	0·388

Almost all WS3 linear regression slopes (Table VI) for baseflow were greater during treatment than before treatment; those involving Ca and Mg had the largest increases in slopes. Those regressions involving K and Na generally had lower slopes during treatment than before, indicating Ca : SO$_4$, Mg : SO$_4$, Ca : NO$_3$ and Mg : NO$_3$ charge pairing became more important on WS3 as a result of the fertilizer additions. With the exception of K : SO$_4$ and Na : SO$_4$, ion charge pairing involving K and Na became less important. Both K : SO$_4$ and Na : SO$_4$ slopes increased as a result of treatment, although the K and Na concentrations associated with the increasing concentrations of SO$_4$ (Figure 4b) were not nearly as large as for Ca or Mg. For example, a 1 unit increase in SO$_4$ resulted in an $\cong 0.8$ unit increase in Ca (i.e. the Ca : SO$_4$ slope) compared with an $\cong 0.1$ unit increase in K associated with each 1 unit increase in SO$_4$ (Table VI).

Although pretreatment peakflow values were not available for comparison, WS3 peakflow and R^2 values during treatment tended to be very similar to those for baseflow. So again, stoichiometrically the Ca and Mg relationships with SO$_4$ and NO$_3$ were more important than those involving K and Na with any anion.

Changes in cation : anion relationships for WS9 between pretreatment and treatment were much less dramatic than those for WS3 (Table VI). For example, the Ca : SO$_4$, Mg : SO$_4$, Ca : NO$_3$, and Mg : NO$_3$ slopes were approximately equal during both time periods. All other cation : anion pair slopes, except Na : NO$_3$, decreased. A strong inverse relationship between Na and NO$_3$ resulted from treatment.

The WS9 peakflow stoichiometric responses of almost all cations to per unit increases in anions were greater, and often substantially greater, than for baseflow. The linear responsiveness also was much greater, especially for pairs involving Ca and Mg. This greater linearity of response between base cations and acid anions helps explain the greater F-factors for peakflow than baseflow (Table V) on WS9 using either C_{SO_4} or C_A.

DISCUSSION

Watershed WS3

The lag in time between treatment initiation and the increases in SO$_4$ and NO$_3$ in baseflow (Figures 4b and 4c) indicates that both were retained in the watershed. Overall ion behaviours suggest anion adsorption was important. Although anion or SO$_4$ adsorption capacities have not been determined for WS3 soils, SO$_4$ and NO$_3$ retention in combination with the immediate loss of Cl suggests that the former two ions were adsorbed preferentially by watershed soils. Chlorine was displaced as a result of its lower affinity for adsorption. Additional evidence of anion adsorption is the sharp increase in NO$_3$ concentrations that occurred about 2 years after the onset of treatment, which was much less steep than SO$_4$ increases that began about the same time (Figures 4c and 4b, respectively). This behaviour suggests additional preferential adsorption of SO$_4$ at the expense of NO$_3$. Preferential adsorption may occur because SO$_4$ is specifically adsorbed (Rajan, 1978), whereas NO$_3$ is only non-specifically adsorbed (Bohn et al., 1985). New sites for SO$_4$ adsorption could have been activated as SO$_4$ concentrations increased with each fertilizer application; SO$_4$ ions displace

Table VI. Linear regression statistics for cation concentrations (y) against anion concentrations (x); pretreatment period is for 1981–1986 and includes weekly samples that are primarily baseflow

Regression pair	Pretreatment						Treatment											
	WS3			WS9			Baseflow						Peakflow					
							WS3			WS9			WS3			WS9		
	Slope	R^2	p	Slope	R^2	p	Slope	R^2	p	Slope	R^2	p	Slope	R^2	p	Slope	R^2	p
Ca:SO$_4$	0.156	0.09	0.0018	0.420	0.30	<0.0001	0.803	0.54	<0.0001	0.463	0.35	<0.0001	0.828	0.59	<0.0001	0.732	0.71	<0.0001
Ca:NO$_3$	0.493	0.28	<0.0001	0.302	0.15	<0.0001	0.512	0.75	<0.0001	0.360	0.22	<0.0001	0.634	0.77	<0.0001	0.713	0.62	<0.0001
Ca:Cl							4.197	0.34	<0.0001	0.414	0.01	0.0528	4.339	0.15	0.0042	3.431	0.22	0.0036
Mg:SO$_4$	0.106	0.08	0.0027	0.270	0.20	<0.0001	0.575	0.45	<0.0001	0.250	0.29	<0.0001	0.519	0.51	<0.0001	0.294	0.43	<0.0001
Mg:NO$_3$	0.380	0.34	<0.0001	0.242	0.16	<0.0001	0.428	0.84	<0.0001	0.206	0.20	<0.0001	0.428	0.77	<0.0001	0.390	0.69	<0.0001
Mg:Cl							3.356	0.32	<0.0001	0.257	0.01	0.0849	2.895	0.15	0.0048	1.923	0.27	0.0011
K:SO$_4$	0.055	0.04	0.0322	0.148	0.16	<0.0001	0.110	0.27	<0.0001	0.009	0.001	0.5019	0.129	0.28	<0.0001	0.100	0.20	0.0014
K:NO$_3$	0.123	0.07	0.0078	0.135	0.13	<0.0001	0.050	0.19	<0.0001	0.065	0.08	<0.0001	0.057	0.12	0.0113	0.077	0.11	0.0228
K:Cl							0.174	0.02	0.0652	0.295	0.06	<0.0001	-0.125	0.003	0.7237	0.554	0.11	0.0455
Na:SO$_4$	-0.013	0.01	0.4424	-0.020	0.002	0.5581	0.049	0.07	<0.0001	-0.033	0.01	0.1652	0.053	0.11	0.0160	-0.048	0.23	0.0006
Na:NO$_3$	0.070	0.05	0.0261	-0.002	0.00	0.9613	0.020	0.04	0.0016	-0.053	0.02	0.0248	0.019	0.03	0.2033	-0.023	0.05	0.1264
Na:Cl							0.088	0.004	0.3252	0.705	0.18	<0.0001	-0.230	0.02	0.3229	0.191	0.06	0.1654

p = probability.

OH^- ions located on neutral sites with increasing SO_4 concentrations (Chao *et al.*, 1962a, b). Additional anion adsorption in the A-horizon also could have been created by decreases in soil pH. Although annual soil pH values are not available, the average soil pH in the A-horizon of WS3 soils decreased from 4·48 before treatment (Table II) to 4·20 in 1994 (unpublished data). Decreasing soil pH results in neutralization of OH^- groups by H^+ (Mattson, 1931; Chang and Thomas, 1963). The resulting H_2O molecule then is replaced by SO_4 (Schofield and Samson, 1954). Soil pH decreases below the A-horizon did not occur so increased adsorption as a result of this mechanism in deeper soils is unlikely. Soil pH values (Table II) and soil water pH values <5 (unpublished data) also suggest that mineral precipitation of aluminum hydroxy sulphates, such as basaluminite, may have provided an additional SO_4 retention mechanism in WS3 soils (Neary *et al.*, 1987; Plumlee *et al.*, 1995), although others (Reuss and Johnson, 1986) have indicated much lower soil pH and quite high SO_4 concentrations are needed for SO_4 mineral precipitation. Some NO_3 almost assuredly also was retained by plant (unpublished data) and microbial assimilation.

The immediate loss of Cl to baseflow in WS3 resulted in a simultaneous immediate increase in Na and K (Figures 4g and 4h), which are easily removed from soil colloids because of their valence and radius characteristics that place them early in the lyotropic series (Bohn *et al.*, 1985). Consequently, they were easily mobilized through charge pairing with anions (including Cl) as anions leached through the soil. Although the trend lines show that K and Na provide the charge pairing cations for the initial increases in Cl concentrations (Figure 4d), over all treatment years Ca and Mg responded to Cl increases to a much larger degree stoichiometrically than either Na or K. Slopes were >3 for Ca : Cl and Mg : Cl regressions, but were <0·2 for K : Cl and Na : Cl (Table VI). As Ca and Mg are higher up the lyotropic series, their release from soil colloids is more dependent upon increasing concentrations of anions, particularly those with greater valence. This explains why losses of Ca and Mg to leaching did not increase until NO_3 and SO_4 concentrations increased. The higher R^2 and slope values for Ca and Mg paired with SO_4 and NO_3 provide further support of the importance of these cation : anion relationships suggested by the trend graphs. For example, for each unit increase in SO_4 or NO_3 during baseflow, Ca and Mg increased by at least 0·4 units (Table VI). This contrasts with much lower R^2 values and < 0·11 unit increases of K and Na with unit increases in SO_4 and NO_3.

Responses of Cl, NO_3 and SO_4 at peakflow probably were the result of the same processes (Figures 5d, 5c and 5b, respectively). Initial SO_4 inputs from the fertilizer were adsorbed preferentially by the soil as Cl was displaced and antecedent NO_3 was displaced and new NO_3 inputs were not adsorbed. Unlike baseflow, the NO_3 concentration increases at peakflow were immediate or nearly immediate (Figure 5c). This suggests much less initial adsorption of NO_3 and more displacement of NO_3 in upper soil layers that contribute to peakflow compared with lower soil layers that contribute to baseflow (Wigington, 1999). However, the slight s-shape on the lower left segment of the NO_3 trend line (Figure 5c) compared with the almost linear response of Cl (Figure 5d) does suggest some limited short-term adsorption of NO_3 at the onset of treatment.

Again, base cations Na and K in peakflow (Figures 5g and 5h) responded immediately to the charge pairing of Cl. The timing and s-shape characteristics of the Ca and Mg trend lines correspond well with the shape and timing of NO_3 increases (Figures 5e, 5f and 5c respectively), so the initial Ca and Mg losses with peakflow appear to be most tied to charge pairing with NO_3.

Earlier pairing of NO_3 with base cations resulted in an increased loss of Ca with each unit output of NO_3 (Table VI). The Mg : NO_3 slope during peakflow was not different than baseflow (Table VI) and apparently not affected by the earlier leaching. This may be because Mg was present in much lower concentrations than Ca in WS3 soils (Table II), so that Ca was involved in most of the additional charge pairing.

As with baseflow, the linear regression results also show the stronger tie between Ca and Mg with SO_4 and NO_3 (Table VI), than Na or K with those anions. Slope values explaining the stoichiometric increases between acid anions and paired base cations were all >0·4 for Ca and Mg with SO_4 and NO_3, but were < 0·1 for Na and K regression pairs.

F-factor results for both baseflow and peakflow indicate that by 1994 the fertilizer treatment had not resulted in creating an ANC sensitive system; F-factors for both flow regimes were $\cong$0·6 (Table V). Pretreatment and

treatment comparisons of baseflow, however, do indicate a reduction in F_A of about 2·5 as a result of induced acidification.

Although they were not yet statistically significant, the downturns in peakflow trend lines for Ca, Mg and Na after several years of fertilization suggest that these ions became more deficient as elevated inputs of SO_4 and NO_3 continued to leach through the soils during storms. If base cation deficiencies are occurring during peakflow, the onset of acid sensitivity during storms could occur quickly, as appears to have occurred for WS9 (described later). The F-factor is only $\approx 0\cdot2$ units above the sensitivity threshold now and with declines in base cation availability coupled with increasing acid anion inputs, a lowering of F_A would occur rapidly.

Acidic inputs affect surface horizons first (Christ *et al*., 1999), so decreases in available base cation supplies first in peakflow are not surprising. Stormflow moves primarily through upper soil layers as evidenced by the flashy responses of this stream (Swistock *et al*., 1997); consequently, depletion of cation reserves would be seen first in stormflow. An increasing deficiency of base cations is not evident in baseflow. Release of cations between storms from weathering, mineralization and other nutrient cycling processes apparently can replenish exchangeable cation supplies in baseflow and baseflow source areas to at least some extent; however, the lower baseflow *F*-factor for 1987–1994 (0·6) compared with pretreatment (1·32) indicates that cation replenishment could not fully meet charge pairing requirements of acid anions because of treatment.

Corroboration that the decreases in Ca and Mg at peakflow (Figures 5e and 5f) reflect actual base cation depletion is available from tree rings. Tree-ring chemistry from *Prunus serotina* on WS3 indicated Ca and Mg mobilization for the first 5 years of treatment (DeWalle *et al*., 1995) followed by Ca and Mg depletion (DeWalle *et al*., 1999). As trees obtain most of their nutrients from upper soil layers, which also correspond to the layers that contribute substantially to stormflow (Wigington, 1999), one would expect tree-ring responses to agree with peakflow responses.

The lag time of 1–2 years between the beginning of treatment and initial treatment responses in baseflow for many of the analytes corresponds well with the 1·6-year mean transit time of baseflow computed for WS3 using seasonal oxygen-18 variations (DeWalle *et al*., 1997). The mean transit time or lag time for precipitation to become baseflow results from the delay in soil water moving downward through the soil profile and then downslope over bedrock to the stream by micropore flow (DeWalle *et al*., 1997). That increases in Na and Cl were observed immediately in baseflow indicates that these ions leached into deep soil layers independent of and at a faster rate than the soil water moving downward that was to become baseflow.

A short mean transit time of stormflow is illustrated by the immediate response of peakflow concentrations to the first fertilizer applications. Thus, different flow mechanisms and paths control stormflow. Although stormflow (i.e. volume above some mathematically defined baseflow separation line (Hewlett, 1982b)) can be composed of a significant portion of groundwater and deep subsurface flow (Swistock *et al*., 1989; Mulholland *et al*., 1990), flashy headwater streams can have substantial shallow-water contributions (Swistock *et al*., 1989). These shallow water contributions provide the mechanism for expressing immediate responses to environmental change. The potential to observe episodic changes soon after an environmental change also should increase as the source area increases, assuming the entire source area has been affected by the environmental change. Large source areas for stormflow are possible because stormflow contributions are not necessarily limited to near-stream source areas; high upslope areas, including ridge tops, can be important contributors to stormflow (Swistock *et al*., 1989; Mulholland *et al*., 1990).

Connections between stream and upslope areas, whether through shallow lateral movement or by vertical and then lateral movement through deep layers, require interconnected flow paths with high hydraulic conductivities to provide quick flow during storm events. These could be in the form of macropore or mesopore flow paths (Luxmoore, 1981). Although the contributions of the two have not been measured or estimated for WS3, we believe that mesopore flow dominates or at least is an important component of stormflow. Drainage through mesopores, which have a pressure range of −0·3 to −30 kPa (Luxmoore, 1981), can occur rapidly (Ritchie *et al*., 1972; Shaffer *et al*., 1979) in vertical and/or lateral directions, particularly

in the non-capillary range of -0.3 to -3 kPa (Nelson and Baver, 1940). Contributing and interconnected mesopore flow also probably means:

1. a greater volume of watershed soil is 'hydrologically active' (i.e. the source areas are more expansive) compared with watersheds dominated by macropores;
2. a greater surface area of soil particles would be in contact with subsurface water in mesopore systems because the pore diameters are smaller than for macropores (ranges suggested by Luxmoore (1981) are $10-1000$ μm for mesopores and >1000 μm for macropores). These greater soil volumes and surface areas associated with mesopores would provide somewhat greater contact times and substantially greater area for contact between soil chemicals and subsurface water than macropores. Thus, the immediate and increasing treatment effect observed for peakflow is explainable if subsurface flow during quick flow is through mesopores. Mesopore flow constitutes a large portion of saturated flow in subdrainages of the Walker Branch watershed (Wilson and Luxmoore, 1988; Wilson *et al*., 1989; Mulholland *et al*., 1990).

Watershed WS9

Many of the ionic responses of WS9 may be attributable to and explainable by past land use on the catchment. The similarities in trends and relatively small treatment effects for both baseflow and peakflow chemistry in WS9 streamflow probably were controlled by the poor nutrient status of watershed soils stemming from abusive farming on the site (Kochenderfer and Helvey, 1989). In addition to depleting soil of nutrients directly, farming resulted in extensive topsoil erosion, which further depleted nutrients (Kochenderfer and Helvey, 1989).

The principal elements added to the soil during fertilization were N and S. Whereas the available N in WS9 soils almost assuredly would have been limiting to native hardwood vegetation, it would not have been limiting to Japanese larch, the dominant tree species on WS9 because it is not an N-demanding species (VanGoor, 1953). Further, S is not a macronutrient nor is it limiting in the eastern USA owing to the elevated atmospheric sulphate deposition (Mitchell *et al*., 1992; Cappellato *et al*., 1998). Because of the general lack of NO_3 and SO_4 uptake by WS9 vegetation, these anions remained mobile and leached with little or no time lag following the initiation of treatment into stream discharge during both baseflow and stormflow periods (Figures 6b, c and 7b, c). This rapid loss indicates that anion retention mechanisms (e.g. microbial immobilization, mineral precipitation, adsorption), were not occurring to a great extent in the watershed at the beginning of the study.

However, the slower rates of NO_3 increases during the first several years following the first treatment compared with later years and compared with those same years for SO_4 (Figures 6c and 6b) suggest that NO_3 was used initially by soil biota, other vegetation competing with the larch, and the native hardwoods in the buffer strip. Preferential adsorption of NO_3 over SO_4 is not possible (Bohn *et al.,* 1985), so the slower initial rate of release of NO_3 must have been by microbial and plant assimilation. As N became less limiting with each fertilizer addition, NO_3 was leached to stream water at an accelerated rate over time (Figure 6c).

Adsorption and/or precipitation of SO_4 must have become more important with time, as evidenced by SO_4 concentration decreases several years after treatment began (Figures 6b and 7b). As on WS3, adsorption apparently was enhanced owing to increased SO_4 concentrations and decreasing soil pH. Evidence for SO_4 adsorption toward the end of the period of record is given by the simultaneous downturn in SO_4 and slight increase in pH in peakflows. A pH increase in soil solution has been documented when OH^- groups are replaced by SO_4 in mineral soils (Chao *et al*., 1965), which could potentially result in less acidic stream water. Again, the low soil pH also may have allowed precipitation of aluminum and hydroxysulphate minerals (Plumlee *et al*., 1995).

The absence of continued base cation leaching increases to baseflow and stormflow as SO_4 and NO_3 increased suggests that WS9 soils were deficient in base cations even at the beginning of the study. Abusive farming is believed to be the agent of the pre-fertilizer nutrient deficiencies. Again, tree-ring chemistry for WS9 supports the claim of initial base cation deficiencies in the soil. *Prunus serotina* tree rings (from trees

sampled in the treated streamside buffer zone) showed little chemical response after 6 years of ammonium sulphate additions. This was attributed to the poor site fertility at the beginning of the study as a result of poor farming practices (DeWalle *et al*., 1995).

The F_A value for baseflow during pretreatment (Table V) did not indicate sensitivity to acidification ($\cong 1\cdot 1$), even though these other measures indicate base cation deficiencies. Although sensitivity and base cation deficiencies are not completely analogous to each other, base cation deficiencies are needed to induce ANC sensitivity. The reason for the apparent inconsistency is not known. However, the rapid decline in the F-factor from ≈ 1 to $\approx 0\cdot 1$ over the treatment period (Table V) illustrates how little the base cation concentrations responded to increasing concentrations of SO_4 and NO_3. If WS9 was not truly cation deficient relative to N and S inputs immediately before treatment, it was at a threshold at which relatively small increases in total N and S inputs could result in large changes in sensitivity to acidification. This behaviour is consistent with the overall lack of change in base cation concentrations (Figures 6e–h and 7e–h) compared with increasing NO_3 and SO_4 baseflow and peakflow concentrations (Figures 6b, c and 7b, c). Pickens *et al*. (1995) showed that aluminum (Al) concentrations in soil and soil water increased over time on WS9; we believe that Al is replacing base cations during charge pairing with acid anions (Edwards *et al*., 1999), and Al is accounting for a much larger part of the soil's cation exchange capacity.

That a larger lag was not observed between the first treatments and the first evidence of chemical changes in baseflow in WS9 was surprising given the physical similarities between WS3 and WS9, e.g. soil and geological types, and their proximity to each other. The rapid expression of a treatment response on WS9 demonstrates that its baseflow has a short mean transit time. The higher mean daily discharge (Table I) and greater discharge volumes for all exceedence values on the flow duration curve (Figure 2) compared with WS3 and WS4 reflect a faster baseflow transit time on WS9. It appears to be much closer to the transit times of 2 weeks to 2 months reported by Turner *et al*. (1987) and Stewart and McDonnell (1991) for small watersheds in Australia and New Zealand, respectively, than to those of WS3.

To have substantially different baseflow response between WS9 and WS3 requires differences in watershed hydrology and possibly soil chemistry. Past erosion from farming along with soil disturbance from raking might have resulted in thinner soils and in current upper and lower soil layers on WS9 being more similar chemically to each other than to the upper and lower soil layers on WS3. Although watershed hydrology of WS9 could have been substantially different than WS3 regardless of site history, a decrease in soil thickness could shorten mean baseflow transit times because there is less material for precipitation to percolate through to reach groundwater. Losses of organic matter and nutrient-rich topsoil would have caused substantial losses in base cation reserves. Because these original reserves accumulated as the result of many years of nutrient cycling processes, it is likely that previous levels would not yet be restored, even considering that larch needle fall can have calcium concentrations as high (Tyrell and Boerner, 1987) as native hardwood vegetation (Adams and Angradi, 1996). If soil chemistry and soil structure are similar throughout the remaining soil profile, similar chemical responses between baseflow and stormflow would be expected.

Sampling implications to detect changes

Both watersheds demonstrated an immediate peakflow response to treatment, but only WS9 also exhibited an immediate baseflow response; WS3 baseflow had a lagged response to treatment. These differences illustrate the need to understand the hydrology and condition of the watershed when attempting to detect changes owing to a particular treatment or to long-term natural or anthropogenic influences. Whether baseflow, stormflow, or a combination of both flow regimes is the best indicator of trends or effects will depend on the hydrology, chemical responses to hydrological variations (e.g. whether chemical concentrations increase or decrease with stormflow) and purpose of the investigation (Rekolainen *et al*., 1991; Brewin *et al*., 1996). However, Wigington (1999) stated that episodic sampling should be included in evaluations of acidification impacts to aquatic ecosystems. The results of this current research indicate that the greatest sensitivity for identifying local ecosystem acidification is through stormflow sampling. In the case of WS3, had only baseflow been

sampled, one would conclude that the treatment had no effect on stream-water chemistry during the first 1–2 years of fertilization, when in fact stormflow chemistry had been affected by the treatment during those initial years. Indeed, when episodes strongly influence chemistry, some level of stormflow sampling is warranted (e.g. Kohonen, 1982; Rekolainen *et al*., 1991; Brewin *et al*., 1996). Christ *et al*. (1999) stated: 'Because acid deposition affects surface horizons first, streamwater chemistry may not be an adequate way to assess nutrient supply of forest soils.' However, their conclusion is based on results from weekly grab sampling. On the basis of our results and because stormflow travels through those initially affected surface soil horizons, Christ and others' conclusion might better be stated: 'Peakflow or stormflow chemistry probably provides a better tool than weekly or baseflow chemistry to assess nutrient supplies.' In large basins where mean transit times may be long (DeWalle *et al*., 1997) and cumulative effects from other sub-basins exacerbate problems associated with identifying trends, stormflow sampling may be the best way to detect ecosystem changes in a timely manner. Formal trend monitoring programmes such as the National Water-quality Assessment Program may limit their own success by minimizing or specifically excluding storm sampling from their protocols (Gerhart and Brakebill, 1996; Robertson, 1998).

CONCLUSION

Chemical data associated with peakflows and baseflows from two nearby watersheds, WS3 and WS9, subjected to induced acidification were analysed. Peakflow chemistry of most major ions increased and pH decreased over time, and the expression of these changes as a result of treatment began almost immediately after the first treatment on both catchments. Baseflow responses on WS3 generally were not affected by the treatment until 1–2 years after the initiation of treatment, whereas a treatment response in baseflow was elicited almost immediately on WS9. The time lag between treatment initiation and the expression of the treatment on WS3 corresponds well to the mean transit time of baseflow, determined previously using oxygen-18 isotope analyses. Chemical changes on WS9 also were less than those on WS3. Smaller responses on WS9 are attributed to the infertile soils caused by a long history of abusive farming. Fewer ions, especially base cations were available for leaching. The rapid treatment response on WS9 suggests that vastly different baseflow pathways or hydrogeology exist on the two watersheds. Differences in hydrological responses for baseflow and stormflow on these two proximate watersheds illustrate that it is essential to understand watershed hydrology when designing a sampling programme to monitor natural or human-caused changes to ecosystems.

REFERENCES

Adams MB, Angradi TR. 1996. Decomposition and nutrient dynamics of hardwood leaf litter in the Fernow whole-watershed acidification experiment. *Forest Ecology and Management* **83**: 61–69.
Adams MB, Angradi TR, Kochenderfer JN. 1997. Stream water and soil solution responses to 5 years of nitrogen and sulfur additions at the Fernow Experimental Forest, West Virginia. *Forest Ecology and Management* **95**: 79–91.

Alley WM. 1988. Using exogenous variable in testing for monotonic trends in hydrologic time series. *Water Resources Research* **24**: 1955–1961.

Bohn HL, McNeal BL, O'Connor GA. 1985. *Soil Chemistry*, 2nd edn. Wiley: New York; 341.

Brewin PA, Reynolds B, Stevens PA, Gee AS, Ormerod SJ. 1996. The effect of sampling frequency on chemical parameters in acid-sensitive streams. *Environmental Pollution* **93**: 147–157.

Cappellato R, Peters NE, Meyers TP. 1998. Above-ground sulfur cycling in adjacent coniferous and deciduous forests and watershed sulfur retention in the Georgia piedmont, USA. *Water, Air and Soil Pollution* **103**: 151–171.

Chang ML, Thomas GW. 1963. A suggested mechanism for sulphate adsorption by soils. *Soil Science Society of America Proceedings* **27**: 281–283.

Chao TT, Harward ME, Fang SC. 1962a. Adsorption and desorption phenomena of sulphate ions in soils. *Soil Science Society of America Proceedings* **26**: 234–237.

Chao TT, Harward ME, Fang SC. 1962b. Soil constituents and properties in the adsorption of the sulphate ion. *Soil Science* **94**: 286–293.

Chao TT, Harward ME, Fang SC. 1965. Exchange reactions between hydroxyl and sulphate ions in soils. *Soil Science* **99**: 104–107.

Christ MJ, Driscoll CT, Likens GE. 1999. Watershed- and plot-scale tests of the mobile anion concept. *Biogeochemistry* **47**: 335–353.

Cleveland WS. 1979. Robust locally weighted regression and smoothing scatterplots. *Journal of the American Statistical Association* **74**: 829–936.

Cleveland WS. 1994. *The Elements of Graphing Data*. Hobart Press: Summit, NJ; 297.

Cleveland WS, Devlin SJ. 1988. Locally weighted regression: an approach to regression analysis by local fitting. *Journal of the American Statistical Association* **83**: 596–610.

DeWalle DR, Tepp JS, Pickens CJ, Edwards PJ, Sharpe WE. 1995. Tree-ring chemistry response in black cherry to ammonium sulphate fertilization at two West Virginia sites. In *Proceedings, 10th Central Hardwood Forest Conference*, Gottschalk KW, Fosbroke SL (eds). General Technical Report NE-197, USDA Forest Service: Radnor, PA; 179–187.

DeWalle DR, Edwards PJ, Swistock BR, Aravena R, Drimmie RJ. 1997. Seasonal isotope hydrology of three Appalachian forest catchments. *Hydrological Processes* **11**: 1895–1906.

DeWalle DR, Tepp JS, Swistock BR, Sharpe WE, Edwards PJ. 1999. Tree-ring cation response to experimental watershed acidification in West Virginia and Maine. *Journal of Environmental Quality* **28**: 299–309.

Edwards PJ, Helvey JD. 1991. Long-term ionic increases from a central Appalachian forested watershed. *Journal of Environmental Quality* **20**: 250–255.

Edwards PJ, Wood F. 1993. *Fernow Experimental Forest Watershed Acidification Project: Field and Laboratory Quality Assurance/Quality Control Protocols*. General Technical Report NE-177, USDA Forest Service: Radnor, PA; 15.

Edwards PJ, Kochenderfer JN, Helvey JD. 1999. Soil water and stream water acidification caused by nitrogen and sulfur amendments. In *The Effects of Acidic Deposition on Pennsylvania's Forests. Proceedings, 1998 PA Acidic Deposition Conference*, vol. 1, Sharpe WE, Drohan JR (eds). Environmental Resources Research Institute: University Park, PA; 91–105.

Edwards PJ, Kochenderfer JN, Wood F. 2001. Using specific conductance to predict stream water chemistry during storms. In *Water Quality Monitoring and Modeling, Proceedings, American Water Resources Association Annual Spring Specialty Conference*. American Water Resources Association: Middleburg, VA.

Gerhart JM, Brakebill W. 1996. *Design and Implementation of a Sampling Strategy for a Water-quality Assessment of the Potomac River Basin*. Water-Resources Investigations Report 96-4034, US Geological Survey: Baltimore, MD; 31.

Gilliam FS, Adams MB, Yurish BM. 1996. Ecosystem nutrient responses to chronic nitrogen inputs at Fernow Experimental Forest, West Virginia. *Canadian Journal of Forest Research* **16**: 196–205.

Helvey JD, Kunkle SH. 1986. *Input–output Budgets of Selected Nutrients on an Experimental Watershed near Parsons, West Virginia*. Research Paper NE-584, USDA Forest Service: Broomall, PA; 7.

Henrikson A. 1982. *Changes in Base Cation Concentrations due to Freshwater Acidification*. Acid Rain Research Report 1/1982 50, Norwegian Institute for Water Research: Oslo.

Herlihy AT, Kaufmann PR, Church MR, Wigington PJ Jr, Webb JR, Sale MJ. 1993. The effects of acidic deposition on streams in the Appalachian Mountain and Piedmont region of the Mid-Atlantic United States. *Water Resources Research* **29**: 2687–2703.

Hewlett JD. 1982a. *Principles of Forest Hydrology*. The University of Georgia Press: Athens, GA; 183.

Hewlett JD. 1982b. Forests and floods in light of recent investigation. In *Proceedings of the Canadian Hydrology Symposium—Associate Committee on Hydrology*. National Research Council of Canada: Ottawa, Ontario; 543–559.

Hipel KW, McLeod AI. 1994. *Time Series Modelling of Water Resources and Environmental Systems*. Elsevier Science: New York; 1013.

Kochenderfer JN, Edwards PJ. 1991; Effectiveness of three streamside management practices in the central Appalachians. In *Proceedings, 6th Biennial Southern Silvicultural Research Conference, vol. 2*, Coleman SS, Neary DG (eds). General Technical Report SE-70; USDA Forest Service: Asheville, NC; 688–700.

Kochenderfer JN, Helvey JD. 1989. Hydrologic impacts of mechanized site preparation in the central Appalachians. In *Proceedings, 7th Central Hardwood Forest Conference*, General Technical Report NC-132, USDA Forest Service: St Paul, MN; 233–289.

Kohonen T. 1982. *Influence of Sampling Frequency on the Estimates of Runoff Water Quality*. Publications of the Water Research Institute, No. 27, National Water Board of Finland: Helsinki; 30.

Lima WP, Patric JH, Holowaychuk N. 1978. *Natural Reforestation Reclaims a Watershed: a Case History from West Virginia*. Research Paper NE-392, USDA Forest Service: Broomall, PA; 7.

Loader CR. 1998. *Locfit for Windows, October 1998 Version*. Bell Laboratories: Murray Hill, NJ.

Losche CL, Beverage WW. 1967. *Soil Survey of Tucker County and Part of Northern Randolph County, West Virginia*. USDA Soil Conservation Service, Forest Service, and West Virginia Agricultural Experiment Station: Washington, DC; 78.

Luxmoore RJ. 1981. Micro-, meso-, and macroporosity of soil. *Soil Science Society of America Journal* **45**: 671–672.

Mann HB. 1945. Nonparametric tests against trend. *Econometrica* **13**: 245–259.

Mattson S. 1931. The laws of soil colloidal behavior: VI. Amphoteric behavior. *Soil Science* **32**: 343–365.

Mitchell MJ, Harrison RB, Fitzgerald JW, Johnson DW, Lindberg SE, Zhang Y, Autry A. 1992. Sulfur distribution and cycling in forest ecosystems. In *Atmospheric Deposition and Forest Nutrient Cycling*, Johnson DW, Lindberg SE (eds). Springer-Verlag: New York; 90–129.

Mulholland PJ, Wilson GV, Jardine PM. 1990. Hydrogeochemical response of a forested watershed to storms: effects of preferential flow along shallow and deep pathways. *Water Resources Research* **26**: 3021–3036.

Neary AJ, Mistry E, Vanderstar L. 1987. Sulphate relationships in some central Ontario forest soils. *Canadian Journal Soil Science* **67**: 341–352.

Nelson WR, Baver LD. 1940. Movement of water through soils in relation to the nature of the pores. *Soil Science Society of America Proceedings* **5**: 69–76.

Pickens CJ, Sharpe WE, Edwards PJ. 1995. The effects of doubling annual N and S deposition on foliage and soil chemistry and growth of Japanese larch (*Larix leptolepis* Sieb. and Zucc.) in north central West Virginia. In *Proceedings, 10th Central Hardwood Forest Conference*, Gottschalk KW, Fosbroke SL (eds). General Technical Report NE-197, USDA Forest Service: Radnor, PA; 131–140.

Plumlee GS, Smith KS, Berger BR, Foley-Ayuso N, Klein DP. 1995. Creede, Comstock, and Sado epithermal vein deposits. In *Preliminary Compilation of Descriptive Geoenvironmental Mineral Deposit Models*, du Bray E (ed). Open File Report OFR-95-0831, US Geological Survey: Denver, CO; 152–161.

Rajan SSS. 1978. Sulphate adsorbed on hydrous alumina, ligands displaced, and changes in surface charge. *Soil Science Society of America Journal* **42**: 39–44.

Rekolainen S, Posch M, Kamari J, Ekholm P. 1991. Evaluation of the accuracy and precision of annual phosphorus load estimates from two agricultural basins in Finland. *Journal of Hydrology* **128**: 237–255.

Reuss JO, Johnson DW. 1986. *Acid Deposition and the Acidification of Soils and Water, Ecological Studies 59*. Springer-Verlag: New York; 119.

Ritchie JT, Kissel DE, Burnett E. 1972. Water movement in an undisturbed swelling clay soil. *Soil Science Society of America Proceedings* **36**: 874–879.

Robertson DM. 1998. *Evaluation of the Surface-water Sampling Design in the Western Lake Michigan Drainages in Relation to Environmental Factors Affecting Water Quality at Base flow*. Water-Resources Investigations Report 98-4072, US Geological Survey: Middleton, WI; 53.

Schofield RK, Samson HR. 1954. Flocculation of kaolinite due to the attraction of oppositely charged crystal faces. *Discussions of the Faraday Society* **18**: 135–145.

Sen PK. 1968. Estimates of the regression coefficient based on Kendall's tau. *Journal of the American Statistical Association* **63**: 1379–1389.

Shaffer KA, Fritton DD, Baker DE. 1979. Drainage water sampling in a wet, dual-pore soil system. *Journal of Environmental Quality* **8**: 241–246.

Stewart MK, McDonnell JJ. 1991. Modeling base flow soil water residence times from deuterium concentrations. *Water Resources Research* **27**: 2681–2693.

Stoddard JL. 1991. Trends in Catskill stream water quality: evidence from historical data. *Water Resources Research* **27**: 2855–2864.

Sullivan TJ, Charles DF, Smol JP, Cumming BF, Selle AR, Thomas DR, Bernert JA, Dixit SS. 1990. Quantification of changes in lakewater chemistry in response to acidic deposition. *Nature* **345**: 54–58.

Swistock BR, DeWalle DR, Sharpe WE. 1989. Sources of acidic storm flow in an Appalachian headwater stream. *Water Resources Research* **25**: 2139–2147.

Swistock BR, Edwards PJ, Wood F, DeWalle DR. 1997. Comparison of methods for calculating annual solute exports from six forested Appalachian watersheds. *Hydrological Processes* **11**: 655–669.

Turner JV, MacPherson DK, Stokes RA. 1987. The mechanisms of catchment flow processes using natural variations in deuterium and oxygen-18. *Journal of Hydrology* **94**: 153–162.

Tyrell LE, Boerner REJ. 1987. *Larix laricina and Picea mariana*: relationships among leaf life-span, foliar nutrient patterns, nutrient conservation, and growth efficiency. *Canadian Journal of Botany* **65**: 1570–1577.

VanGoor CP. 1953. The influence of nitrogen on the growth of Japanese larch (*Larix leptolepis*). *Plant and Soil* **5**: 29–35.

Webb JR, Fitzhugh RD, Furman T. 1997. *The Acid-base Status of Surface Waters in Otter Creek and Dolly Sods Wildernesses*. Report submitted to the USDA Forest Service, Monongahela National Forest and Northeastern Research Station; University of Virginia: Charlottesville, VA; 62.

Wigington PJ Jr. 1999. Episodic acidification: causes, occurrence and significance to aquatic resources. In *The Effects of Acidic Deposition on Pennsylvania's Forests. Proceedings, 1998 PA Acidic Deposition Conference, vol. 2*, Sharpe WE, Drohan JR (eds). Environmental Resources Research Institute: University Park, PA; 1–4.

Wilson GV, Luxmoore RJ. 1988. Infiltration, macroporosity, and mesoporosity distributions on two forested watersheds. *Soil Science Society of America Journal* **52**: 329–335.

Wilson GV, Alfonsi JM, Jardine PM. 1989. Spatial variability of saturated hydraulic conductivity of the subsoil of two forested watersheds. *Soil Science Society of America Journal* **53**: 679–685.