Hydrobiologia **179**: 97–102, 1989.

Nutrient concentration-stream discharge relationships during storm events in a first-order stream

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Received 21 October 1987; in revised form 30 March 1988; accepted 15 May 1988

Key words: nutrients, trajectories, hydrology, storms, stream, discharge, pollution source determination

Abstract

The relationship between nutrient element concentration and stream discharge during storm events was studied in a nutrient-rich first order stream. Stream concentrations of NO_3-N, phosphate-P, Ca, and Mg were determined during the course of and following thunderstorms. Nutrient element trajectories were constructed for the elements monitored and some recognizable and reproducible patterns in nutrient concentrations emerged. NO_3-N and phosphate-P generally increased in concentration during the early stages of increasing stream discharge resulting in a general clockwise trajectory. Ca and Mg consistently showed decreases in concentration during rising water, but the pattern of the trajectories was less constant. The patterns seen for NO_3-N and phosphate-P suggest surface run-off as their origin while the patterns for Ca and Mg reflect their primary origin in groundwater. The ability to detect these differences from the analysis of nutrient trajectories suggests the use of this technique for determining the source of other elements in streams.

Introduction

Nutrient element dynamics in watersheds have been the focus of a number of studies in recent years. In particular valuable information has arisen from studies conducted in small controlled watersheds during which relatively long-term input, retention, and release of nutrient elements have been emphasized (e.g., Bormann & Likens, 1967, 1970; Vitousek, 1977; Johnson & Swank, 1973; Swank & Caskey, 1982). A number of these studies have focused on seasonal fluctuations in selected nutrients and have formulated annual nutrient budgets, sometimes comparing disturbed and undisturbed watersheds (Bormann *et al.*, 1968; Likens *et al.*, 1970; Webster & Patten, 1979). Although this previous work recognized the potential importance of stream discharge rate on the concentration of certain elements in the watershed (Johnson *et al.*, 1969; Likens, 1967), few studies have made the relationship of discharge to element concentration the primary focus of the study. Bond (1979) appears to be one of the first to do so, specifically attempting to identify the presence of trends or patterns in the dynamics of nutrient concentrations as related to seasonal changes in stream discharge. In this study there were two objectives: to examine the relationship between rate of discharge and the concentrations of certain nutrient elements in a small stream during storm events; and to establish whether or not recognizable and predictable patterns exist with regard to element concentration-discharge rate relationships.

Materials and methods

The system studied

The project was carried out on a small stream on the Bucknell University Natural Area in Montour County, PA. The stream is first order, nutrient-rich and arises from a small eutrophic spring-fed farm pond. pH's typically found for the stream are slightly alkaline, ranging between 7.0 and 8.0. The drainage basin is approximately 60 ha and is comprised largely of fallow fields in various stages of succession underlain at the upper reaches by limestone. The sample site was located approximately 300 m below the farm pond where a weir is in place across the stream. The weir creates a small pool of water approximately 2 m in length. The pool is not unlike other naturally-occurring pools in the stream which in its upper reaches contains alternating riffles and pools. The sample probe was placed on a concrete slab just beneath the V-notch of the weir. Hence minimal sedimentation occurred around the probe. Water flow is permanent even during drought conditions although baseline flow is small during most of the year – as little as 0.1 l/s.

Seven storm events were monitored during the summers of 1984–85. All were thunderstorms. Rates of stream discharge were calculated from continuous recordings of stream level changes at the weir site. Samples were collected at one-hour intervals during the course of the storm events using a Sentry Model 505 sequential composite water sampler set up at the weir site. Samples were taken to the laboratory within 24 h of collection, filtered through 0.45 μm membrane filters, and either analyzed immediately or frozen for subsequent analysis.

NO_3-N and phosphate-P (S.R.P.), were measured using automated analysis (Technicon AA and A.P.H.A., (1980). Ca and Mg were analyzed using atomic absorption spectrometry (Instrumentation Laboratory aa/ae spectrophotometer).

Data collected from storm events were used to construct nutrient element trajectories by plotting concentration vs. discharge and connecting points in a time sequence (Bond, 1979). A trajectory has two limbs: ascending (stream discharge increasing) and descending (stream discharge decreasing). Theoretically these trajectories may be clockwise or counterclockwise with varying degrees of limb separation.

Results

Typical trajectories for the four elements monitored are shown in Fig. 1. Generally, NO_3-N and phosphate-P showed clockwise trajectories with considerable limb separation. The highest concentrations of these elements occurred very early in the storm event and concentrations were diluted as the stream reached higher rates of discharge. Concentrations near pre-storm levels were seen as stream levels fell toward baseline. In contrast, the concentrations of Ca and Mg were diluted immediately with increasing rate of discharge and generally reached minimum concentrations at or near the maximum rates of discharge. Both clockwise and counterclockwise trajectories were seen for these although the limb separation was so small that the direction of the trajectory was usually difficult to determine. Considerable storm-to-storm variability was seen in the pattern of all the trajectories. This was not surprising since storm intensity and precipitation amount also varied. The measured rainfall during events reported here ranged from 12.5 to 25 mm.

Data from these storm events were combined and analyzed in an attempt to establish the existence of predictable patterns in the behavior of the elements studied. Figure 2 shows the results of this effort. For each storm event, changes in concentration for a given element were divided by the maximum concentration change measured and plotted against changes in stream discharge divided by the maximum rate of change in discharge seen. This was done in order to combine data from several storms since high variability existed among storms with regard to such parameters as initial element concentrations, initial stream discharges, maximum concentrations and discharges reached, and duration and severity of the storm. As can be seen from this analysis,

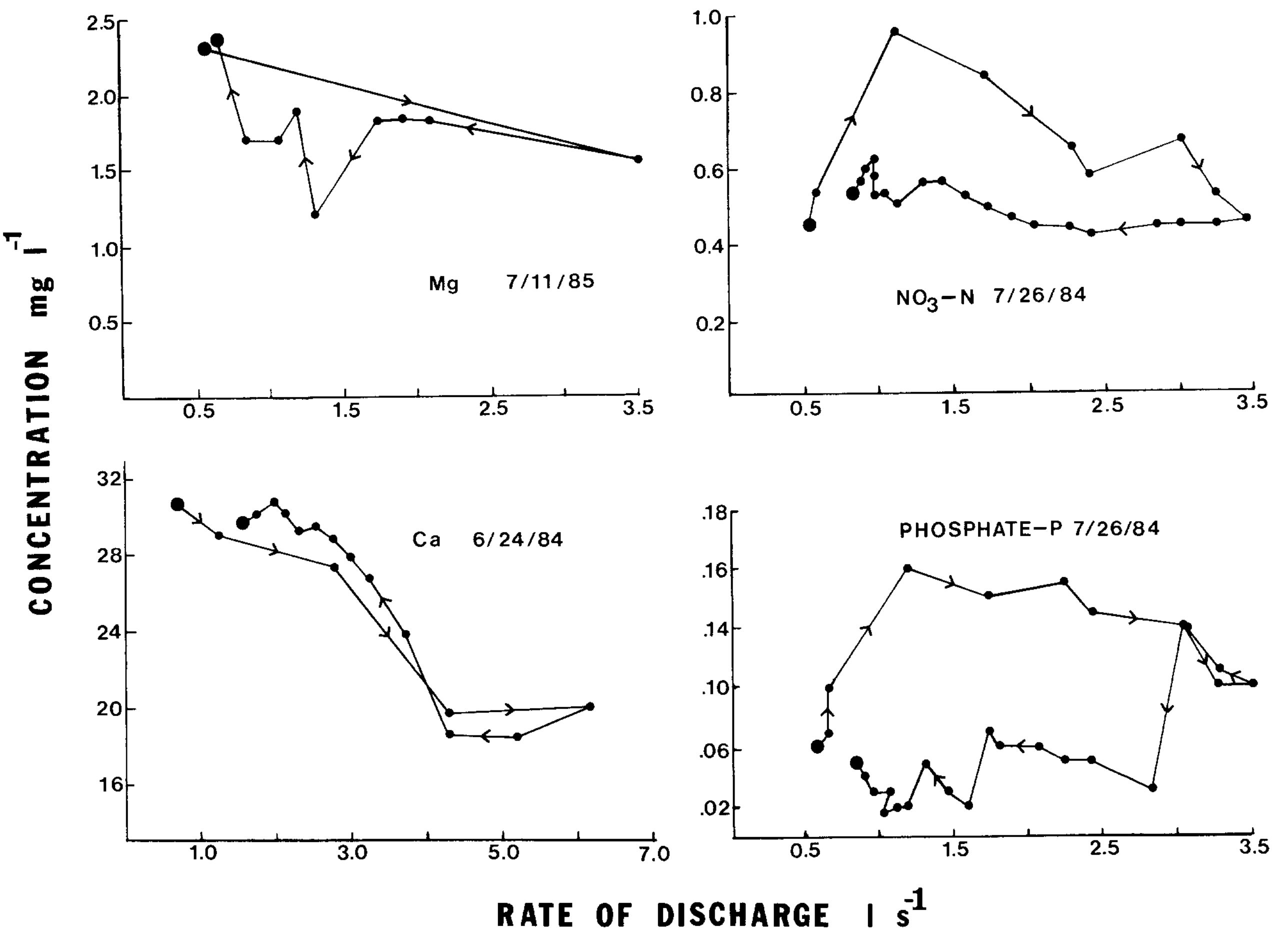

Fig. 1. Representative nutrient element trajectories.

significant negative correlations were found between changes in concentrations of Ca and Mg and changes in flow rate whereas NO_3-N and phosphate-P showed significantly positive correlations. In an effort to correlate the behavior of elements with one another as well as with flow rate, Pearson Correlation Coefficients were calculated and are shown in Table 1. All of the elements showed statistically significant correlations with flow – and in addition, the behaviors of Ca and Mg were positively correlated as were the behaviors of NO_3-N and phosphate-P. The only other statistically significant correlations appeared to occur between Mg and NO^{-3}. However, when the correlations were controlled for flow and partial correlation coefficients were calculated, no significant relationship was evident for any combination other than Ca-Mg and NO_3-N – phosphate-P (Table 2). Indeed, when these pairs were analyzed separately highly significant partial correlations were found.

Discussion

Although statistically significant correlations with discharge were found for all elements monitored, those for NO_3-N and phosphate-P were not strong ones. The concentrations of both tended to fluctuate considerably and were almost certainly influenced by a variety of factors in addition to discharge. For example, the length of time between storm events and the amount of precipitation would contribute significantly to the varia-

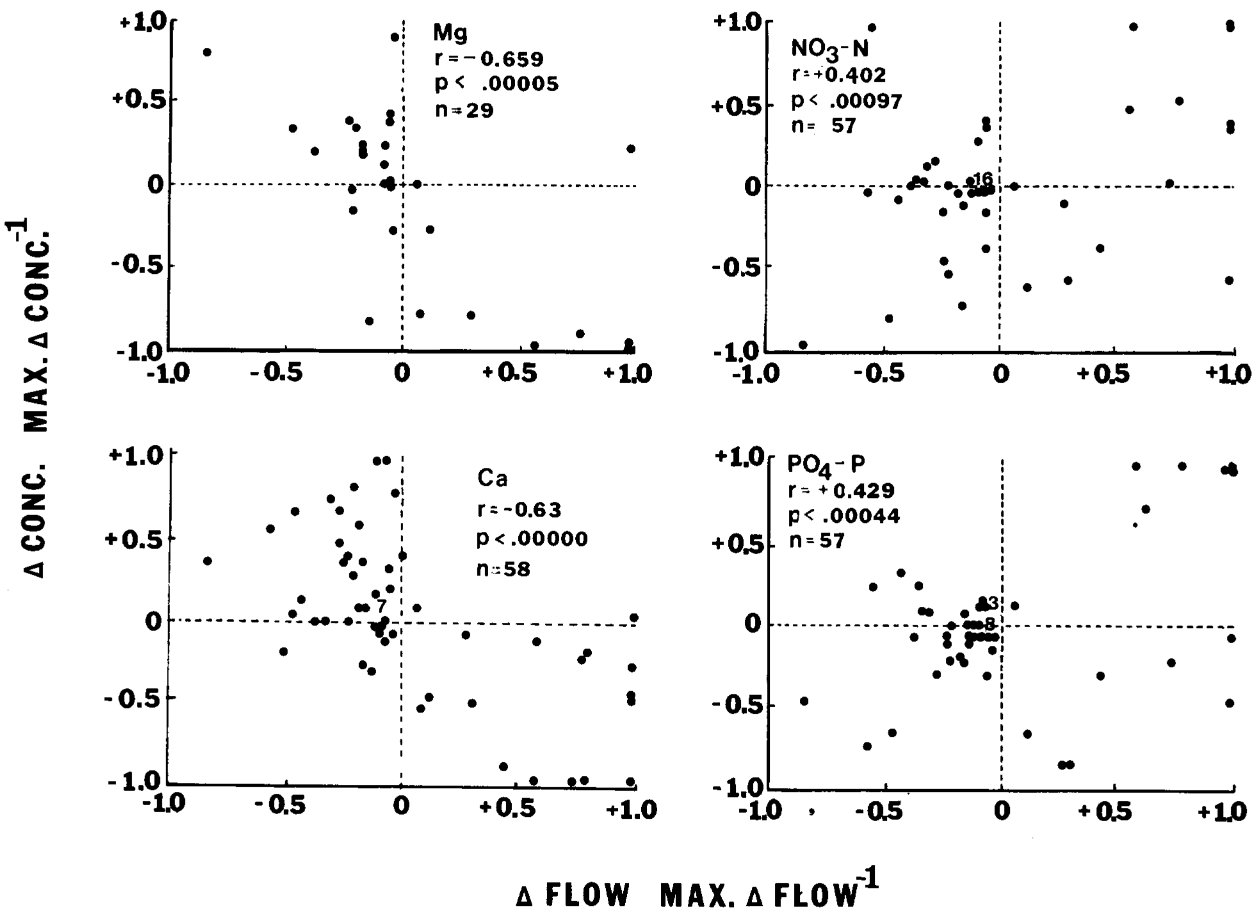

Fig. 2. The relationship between changes in nutrient element concentration and changes in rate of stream discharge. Change in element concentration between consecutive sample times is determined during each storm event and divided by the maximum change observed during the event. Similar calculations for flow data.

Table 1. Pearson Correlation Coefficients. Sample size in parentheses and levels of statistical significance shown.

	Flow	Ca	Mg	NO_3-N
Ca	− 0.62 (58) p = .000	–	–	–
Mg	− 0.66 (58) p = .000	0.74 (29) p = .000	–	–
NO_3-N	0.40 (57) p = .002	− 0.24 (31) p = .190	− 0.59 (18) p = .011	–
phosphate-P	0.43 (57) p = .001	− 0.24 (31) p = .202	− 0.45 (18) p = .068	0.72 (57) p = .000

Table 2. Partial correlation coefficients. Effects of flow are controlled (n = 15), levels of statistical significance are shown.

	Ca	Mg	NO_3-N
Mg	0.48 p = .05	–	–
NO_3-N	− 0.28 p = .281	0.10 p = .703	–
phosphate-P	− 0.12 p = .661	0.03 p = .914	0.58 p = .014

	NO_3-N		Ca
phosphate-P	0.67 (54) p = .000	Mg	0.66 (26) p = .002

bility in concentration of these forms of elements. In addition, considerable input of NO_3-N may come from precipitation itself. Our own data indicate concentrations in the range of 0.5 to 2.6 mg/l in composite rainwater samples. Indeed the input of NO_3-N in precipitation in central Pennsylvania is among the highest in the world (Galloway *et al.*, 1987). The concentrations of both NO_3-N and phosphate-P were undoubtedly influenced by inputs from surface run-off, interflow, throughfall, and metabolic activity in the stream and the surrounding watershed. A number of authors have reported high variability in the concentrations of these ions in solution with little of the variability accounted for by stream discharge (Bond, 1979); e.g., Meyer & Likens (1979) reported no significant changes in the concentration of dissolved P with changes in stream discharge in a stream draining a forested watershed. On the other hand, Singer & Rust (1975), working in a mixed deciduous forest, found P concentrations to be related to precipitation and runoff in the watershed. Clearly the nature of the watershed must be an important factor influencing concentrations of these forms of dissolved N and P.

Also contributing to the low correlation coefficients for NO_3-N and phosphate-P with stream discharge was the fact that the highest concentrations of both forms occurred early in a storm event, usually before maximum flow occurred (Fig. 1). Later in the storm event, they were diluted so that low concentrations were seen over a wide range of flow rate. This resulted in highly variable data and weak correlation coefficients.

The negative correlation coefficients with discharge shown by Ca and Mg are much stronger than the coefficients seen for NO_3-N and phosphate-P. This should not be surprising since the major source of Ca and Mg is assumed to be groundwater which is not immediately affected by surface phenomena. These elements were diluted by the flush of surface run-off early during a storm and their concentrations increased towards baseline levels as groundwater again became the significant component of stream discharge.

Despite the variability in element trajectories produced by the variable nature of storm events, some predictable patterns in the behavior of certain elements seem likely. Although an element may show storm trajectories which are not unique for that element, nonetheless certain groups of elements will probably behave differently from other groups. Hence Ca and Mg concentrations vary in similar fashion during storm events due to their common origin in groundwater but their patterns are quite different from those of NO_3-N and phosphate-P, which themselves behave similarly (Table 2) and may be associated with surface runoff and/or rain.

The use of this technique, i.e., the analysis of element trajectories, suggests the possibility of identifying the sources of many elements in solution in a watershed. An analysis of limb separation and direction of the trajectory may give a clue as to whether an element is available primarily in surface runoff or in groundwater. For example, large limb separation, clockwise trajectories, and a positive correlation with discharge suggest runoff as a primary source whereas little limb separation and a negative correlation with discharge suggests groundwater as a primary source.

However, many questions remain. In this study, data from storms of only one type have been examined, i.e., thunderstorms where the entire hydrological event was completed in a matter of a short period of time. Rain events of longer duration where precipitation is spread out over longer periods of time need to be examined. Furthermore, it is likely that a given element will behave differently in different watersheds. This study was carried out in a nutrient-rich watershed dominated by an early successional terrestrial community. It is very likely that different patterns would emerge for elements in relatively nutrient-limited watersheds such as a mature forest. Patterns are also likely to differ on a seasonal basis. All data reported here are from events monitored primarily during warm weather. Ecosystem dynamics obviously change seasonally and can be expected to strongly influence at least some solute relationships in the watershed.

References

American Public Health Association, 1980. Standard methods for the Examination of Water and Wastewater. 15th Ed. APHA. 1134 pp.

Bond, H. W., 1979. Nutrient concentration patterns in a stream draining a montane ecosystem in Utah. Ecology 60: 1184–1196.

Bormann, F. H., G. E. Likens, D. W. Fisher & R. S. Pierce, 1968. Nutrient loss accelerated by clear-cutting of a forest ecosystem. Science 158: 882–884.

Bormann, F. H., G. E. Likens, T. G. Siccama, R. S. Pierce & J. S. Eaton, 1974. The effect of deforestation on ecosystem export and the steady-state condition of Hubbard Brook. Ecol. Monogr. 44: 255–277.

Galloway, J. N., Zhao Dianwu, Xiong Julling & G. E. Likens, 1987. Acid rain: China, US and a remote area. Science 236: 1559-1562.

Johnson, N. M., G. E. Likens, F. H. Bormann, D. W. Fisher & R. S. Pierce, 1969. A working model for the variation in stream water chemistry at the Hubbard Brook Experimental Forest, New Hampshire. Water Resour. Res. 5: 1353–1363.

Johnson, P. L. & W. T. Swank, 1973. Studies of cation budgets in the southern Appalachians on four experimental watersheds with contrasting vegetation. Ecology 54: 79–80.

Likens, G. E., F. H. Bormann, N. M. Johnson & R. S. Pierce, 1967. The Calcium, Magnesium, Potassium, and Sodium Budgets for a Small Forested Ecosystem. Springer-Verlag, New York, New York, USA.

Likens, G. E., F. H. Bormann, N. M. Johnson, D. W. Fisher & R. S. Pierce, 1970. Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbart Brook Watershed-ecosystem. Ecol. Monogr. 40: 23–47.

Meyer, J. L. & G. E. Likens, 1979. Transport and transformation of phosphorus in a forest stream ecosystem. Ecology 69: 1255–1269.

Singer, M. J. & R. H. Rust, 1975. Phosphorus in surface runoff from a deciduous forest. J. Envir. Qual. 4: 307–311.

Swank, W. T. & W. H. Caskey, 1982. Nitrate depletion in a second-order mountain stream. J. Envir. Qual. 11: 581–584.

Vitousek, P. M., 1977. The regulation of element concentrations in mountain streams in the northeastern United States. Ecol. Monogr. 47: 65–87.

Webster, J. R. & B. C. Patten, 1979. Effects of watershed perturbation on stream potassium and calcium dynamics. Ecol. Monogr. 19: 51–72.