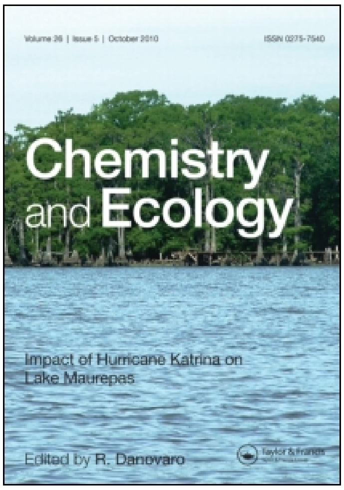
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Experimental Investigation of Potassium and Nitrate Dynamics in A Headwater Stream in Mid-Wales

P. J. Chapman[a]; B. Reynolds[b]; H. S. Wheater[c]
[a] Macaulay Land Use Research Institute, Aberdeen, U.K [b] Bangor Research Unit, Institute of Terrestrial Ecology, Wales, U.K [c] Department of Civil Engineering, Imperial College of Science, Medicine and Technology, London, U.K.

To cite this Article Chapman, P. J. , Reynolds, B. and Wheater, H. S.(1996) 'Experimental Investigation of Potassium and Nitrate Dynamics in A Headwater Stream in Mid-Wales', Chemistry and Ecology, 13: 1, 1 — 19
To link to this Article: DOI: 10.1080/02757549608039098
URL: http://dx.doi.org/10.1080/02757549608039098

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Chemistry and Ecology, 1996, Vol. 13, pp. 1–19
Reprints available directly from the publisher
Photocopying permitted by license only

© 1996 OPA (Overseas Publishers Association)
Amsterdam B.V. Published in The Netherlands under
license by Gordon and Breach Science Publishers
Printed in Malaysia

Downloaded At: 13:57 15 January 2011

EXPERIMENTAL INVESTIGATION OF POTASSIUM AND NITRATE DYNAMICS IN A HEADWATER STREAM IN MID-WALES

P. J. CHAPMAN[a], B. REYNOLDS[b] and H. S. WHEATER[c]

[a]*Macaulay Land Use Research Institute, Craigiebuckler, Aberdeen, AB9 2QJ, U.K;*
[b]*Institute of Terrestrial Ecology, Bangor Research Unit, UWB, Deiniol Road, Bangor, Gwynedd, LL57 2UP, Wales, U.K;*
[c]*Department of Civil Engineering, Imperial College of Science, Medicine and Technology, London, SW7 2UB, U.K.*

(Received 26 February 1996)

Potassium and nitrate were added experimentally to a small moorland stream in the headwaters of the River Wye, mid-Wales, during summer and winter low-flow conditions. Nutrient losses at three downstream sampling locations were calculated using concentrations of an added bromide tracer to correct for dilution effects. During the summer experiment, approximately 18% of the added nitrate and 58% of the potassium were removed from the stream water between the point of addition and the catchment outlet. During the winter experiment, nitrate depletion was not observed and the added nitrate travelled along the stream at the same rate as the bromide tracer, while approximately 93% of the added potassium passed through the stream but, at a slower rate than the bromide and nitrate. The results show that in-stream processes, probably related to biological activity of macrophytes and microflora, can regulate stream water concentrations of nitrate and potassium in the summer under stable flow conditions. During the winter, no removal of nitrate or potassium was observed but ion exchange processes involving biofilms, *Sphagnum* and/or stream sediment may explain the temporary retention of potassium within the stream channel. If similar ion exchange processes operate at high flows, they may account for the hysteresis relationship observed between potassium and discharge during storm events in many upland streams.

Keywords: Nitrate; potassium; in-stream; tracer; uptake; retention; addition experiment

Downloaded At: 13:57 15 January 2011

INTRODUCTION

In natural upland ecosystems nutrients are tightly cycled within the organic soil/vegetation system (Edwards *et al.*, 1985), and consequently streams draining upland catchments have low concentrations of nutrients. However, agricultural improvement and conifer afforestation of natural upland grasslands has added fertilizers to nutrient poor, acid soils, increasing their potential for nutrient leaching and thus a deterioration in upland water quality (Roberts *et al.*, 1984).

Various studies have indicated that a combination of physical, chemical and biological processes occuring within the stream channel are important in regulating nutrient concentrations in stream water. Summer losses of nitrate in headwater streams have been attributed to uptake by macrophytes and microflora (HowardWilliams *et al.*, 1982; Cooke and Cooper, 1988), whilst denitrification within stream sediments may also be important in some systems (Hill, 1979; Swank and Caskey, 1982). Triska *et al.* (1989) found that storage within the hyporheic zone was important in the retention and subsequent biotic uptake for nitrate added to a third-order stream. Mulholland (1992) observed high rates of immobilization of inorganic nitrogen and phosphorus from late autumn to spring which was attributed to microbial and algal uptake. 'Whilst the importance ascribed to each process varies with site conditions (Munn and Meyer, 1990), they all represent major pathways for the depletion of nitrate from stream water (Kaushik *et al.*, 1983).

Stream channels may act as both nutrient sinks and sources depending on the hydrological conditions, season and previous nutrient loadings. Depletion of these nutrients is usually associated with periods of biological uptake at low flows as the benthic microorganisms involved are susceptible to scouring at high flows (Williamson and Cooke, 1985). Whereas denitrification will permanently deplete the stream channel of nitrogen, nutrients immobilised during low flows may be released when environmental conditions change, such as during storm events or following the mineralization of accumulated organic matter. The immobilization capacity of the stream channel may become exhausted following periods of prolonged inputs. Mass balances of stream segments in second and third-order streams in the Hubbard Brook catchment, New Hampshire, USA, have indicated prolonged periods of net in-stream retention of nutrients followed by large net losses during storms (Meyer and Likens, 1979). Conversion of dissolved nutrients from inorganic to organic or particulate forms or vice versa, can also occur (Meyer and Likens, 1979), but will generally result in little change in the total loadings in the stream. However, any transformations that alter the bioavailability of nutrients will have an important impact for water quality.

Pronounced seasonal cycles in stream water nitrate and potassium concentrations, with winter maxima and summer minima have been reported previously for upland, acid grassland catchments in mid-Wales (Reynolds *et al.*, 1989;1992; Neal *et al.*, 1990; Roberts *et al.*, 1984). These fluctuations have been attributed to both the seasonal availability of nutrients to soil water and biological and chemical processes within the stream channel. Decreases in potassium and nitrate concentrations along the stream channel of a small headwater catchment were observed during summer storms but not during late autumn and winter events (Chapman *et al.*, 1993). As these observations could not be explained by dilution, Chapman *et al.* suggested that rapid biological uptake within the channel accounted for the stream response. The potential for this process will be at its maximum in the summer and might help to account for the absence of potassium and the low concentrations of nitrate in summer base-flow. This present study was therefore undertaken to investigate the potential importance of instream processes for regulating stream water nitrate and potassium concentrations in upland, semi-natural acid grassland catchments.

Downloaded At: 13:57 15 January 2011

MATERIALS AND METHODS

Study Site

The study catchment is located in a remote, upland area of mid-Wales (52°26′N, 3°44′W) approximately 24 km east of the Irish Sea. The catchment is underlain by Silurian mudstone and the major soils are acid, nutrient-poor stagnopodzols and peats. Vegetation consists of an acid grassland dominated by *Nardus* and *Festuca* species with *Eriophorum* sp. on the peats. The stream draining the catchment is a first order tributary to the River Cyff and forms part of the headwaters of the River Wye, which drains the eastern slope of the Plynlimon massif. The catchment has an altitude range of 400-510 m above sea-level, an area of just over 4 ha and an annual rainfall of approximately 2500 mm. The catchment has no history of agricultural improvement by liming or fertiliser addition but it supports low density sheep grazing (1 to 2 ewes ha^{-1}) for most of the year.

The stream rises within a small hollow dominated by *Juncus* sp. and flows northnortheast along a steep-sided valley for approximately 135 m before reaching a 90° V-notch weir at the catchment outlet. The stream channel is narrow at low flows and consists of a series of shallow pools connected by channels containing exposed bedrock. Vegetation, dominated by *Juncus* sp and *Sphagnum* spp, grows in both the pools and the channels. During storm events, the stream expands to cover a larger area of vegetation but the riparian area on either side of the stream channel is small due to the steepness of the adjacent slopes (25-30°).

Downloaded At: 13:57 15 January 2011

Experimental Approach

Two nutrient addition experiments were performed under summer and winter baseflow conditions on the 17 August and 8 December 1992. A solution of potassium nitrate was added to the stream near its source in order to raise the concentration of both solutes to amounts seen during storm events (Chapman *et al.*, 1993). The removal of each nutrient from the water was determined by monitoring the downstream decrease in solute concentration at three sampling points. The effects of dilution due to any down-stream increase in stream discharge was assessed by monitoring the change in concentration of a relatively inert tracer, bromide, which was added to the potassium nitrate solution as sodium bromide. The expected concentrations of nitrate and potassium, assuming no removal or addition within the stream channel (i.e. conservative behaviour), were calculated by multiplying the bromide concentration in the sample by the nitrate:bromide and potassium:bromide ratios in the added solution. Observed values of potassium and nitrate lower than the expected values are assumed to represent removal from the stream by one or more of the following processes: adsorption, ion-exchange, uptake by stream biota, transformation to another form, and for nitrate, denitrification and fixation. The higher than expected values would reflect production within the stream or release from the stream substrate.

Experimental Procedure

Solutions of sodium bromide and potassium nitrate were prepared in stream water taken from near the source of the stream on the day of the experiment. The solution was released into the stream from a mariotte bottle at a continuous rate for 3-4 hours (Table I) at a point 30 m below the stream source where the water was shallow and fast flowing. This ensured thorough mixing upstream of the first sampling point which was 16 m below the point of addition. Experimental conditions during each addition experiment are presented in Table I.

Samples of the concentrated solution were taken at the beginning of each experiment to determine the exact concentrations of the added potassium, nitrate and bromide (Table I). Stream water samples were collected in polypropylene bottles above (background samples) and at each of three sampling locations 16 m, 54 m and 105 m below the point of addition. Samples were collected at 15 minute intervals, by hand, at location 1 and at 15 and 30 minute intervals, by automatic water samplers, at locations 2 and 3. Samples were immediately returned to the laboratory for filtration. Nitrate and bromide were analysed by ion chromatography using a Dionex 2000i IC system and potassium was determined by flame atomic emission spectroscopy using a Perkin Elmer 280 atomic absorption spectrophotometer.

Downloaded At: 13:57 15 January 2011

TABLE I Summary of experimental conditions during the summer and winter addition experiments.

	August 1992	*December 1992*
Flow at catchment outlet ($l\ s^{-1}$)	1.8	3.0
Watertemperature (°C)	12.5 – 13.8	4.1 – 4.3
K added ($mg\ s^{-1}$)	2.37	2.42
NO_3 added ($mg\ s^{-1}$)	4.27	4.13
Br added ($mg\ s^{-1}$)	1.46	0.57
Amount of solution added (l)	76	67.8
Duration of addition (min)	194	182
Rate of injection ($ml\ s^{-1}$)	6.5	6.2
Total K added (g)	27.6	26.4
Total NO_3 added (g)	49.7	45.1

Downloaded At: 13:57 15 January 2011

RESULTS

Nitrate

In the summer experiment, the observed and expected concentrations at sampling location 1 were very similar (Fig. 1a). This indicated that the added solution had completely mixed with the stream water. At locations 2 and 3, observed concentrations were lower than the expected values (Fig. 1b, c).

All of the added nitrate was removed from stream water during the initial rise in nitrate concentration at locations 2 and 3 (Fig. 2). The percentage loss rapidly decreased at both locations 2 and 3, as the nitrate concentration increased, but only until the observed concentration reached 1.0 mg l^{-1} at location 2 and 0.84 mg l^{-1} at location 3. Above these concentrations, the efficiency of nitrate removal remained at between 16% and 17% at both locations 2 and 3, even though the nitrate concentration rose to over 1.5 mg l^{-1} and 1.1 mg l^{-1}. Although the largest percentage loss of nitrate occurred at the beginning of the experiment, the actual amount of nitrate retained within the stream channel was small. As nitrate concentrations increased, the amount of nitrate retained within the stream also increased (Fig. 2).

During the winter experiment, observed nitrate concentrations at locations 1 and 2 were essentially the same as the expected values. At location three, observed concentrations during the plateau were slightly greater than expected (Fig. 3). The coincidence of expected and observed concentrations indicated that no nitrate was retained within the stream channel and that nitrate travelled down the stream at the same speed as the bromide tracer.

By comparing the areas under the graphs of expected and observed concentrations for each site, it is possible to determine the amount of solute that has passed through a sampling location and hence the amount of nutrient removed (Table II). For the winter experiment, all of the added nitrate passed through locations 1 and 2, whereas 7% more nitrate passed through location 3 than expected, indicating that a small quantity of nitrate may have been released from the lower channel. In the summer experiment, sampling was stopped prior to concentrations returning to pre-experimental conditions due to a failure in the automatic sampler, and full integration could not be

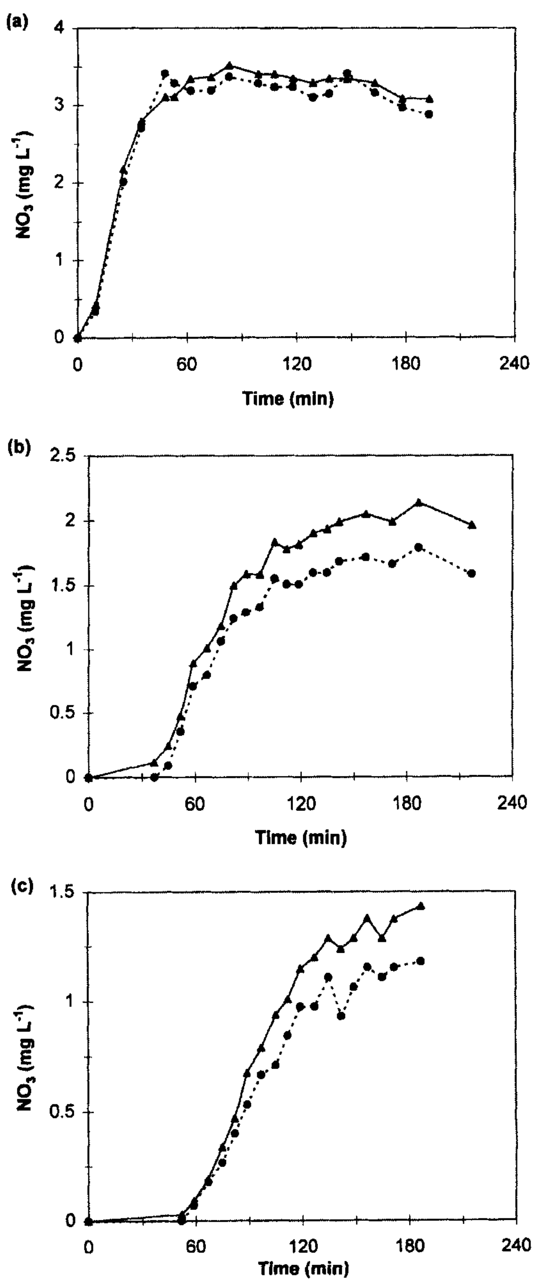


FIGURE 1 Observed (●) and expected (▲) stream water nitrate concentrations at sampling location (a) 1 (b) 2 and (c) 3 during the summer experiment.

Downloaded At: 13:57 15 January 2011

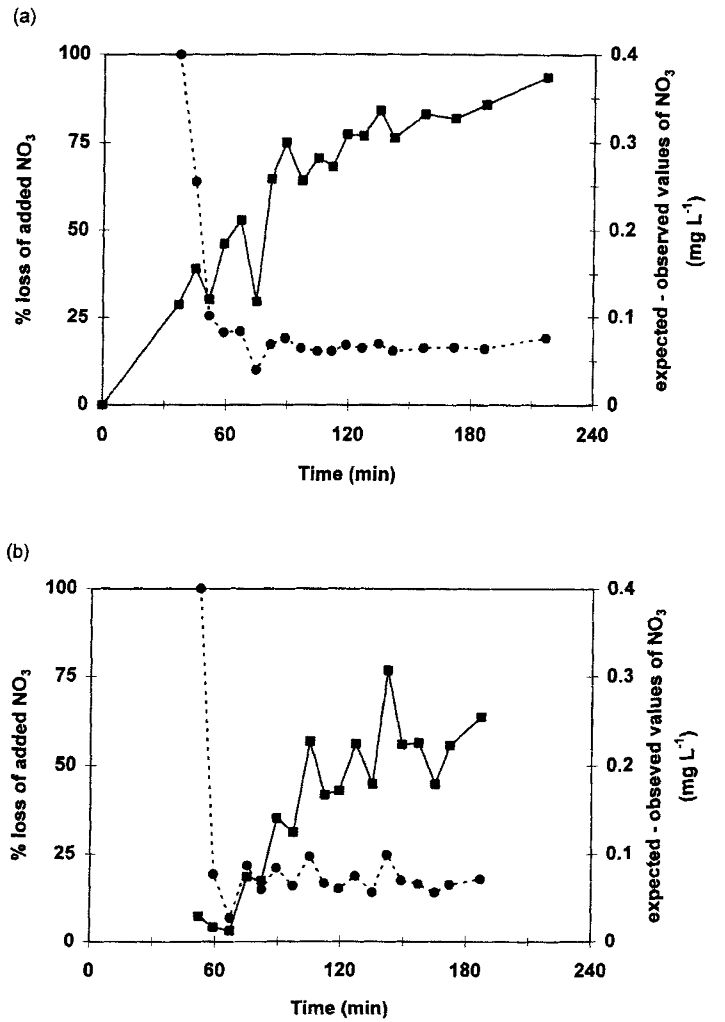


FIGURE 2 Calculated percent loss (●) of injected nitrate and difference between expected and observed nitrate values (■) at (a) location 2 and (b) location 3 during the summer experiment.

applied. However, partial integration of the observed and expected concentrations indicated that 82% of the added nitrate passed through location 2 and 3. All loss of nitrate along the stream reach occurred over a distance of 38 m, between locations 1 and 2.

Downloaded At: 13:57 15 January 2011

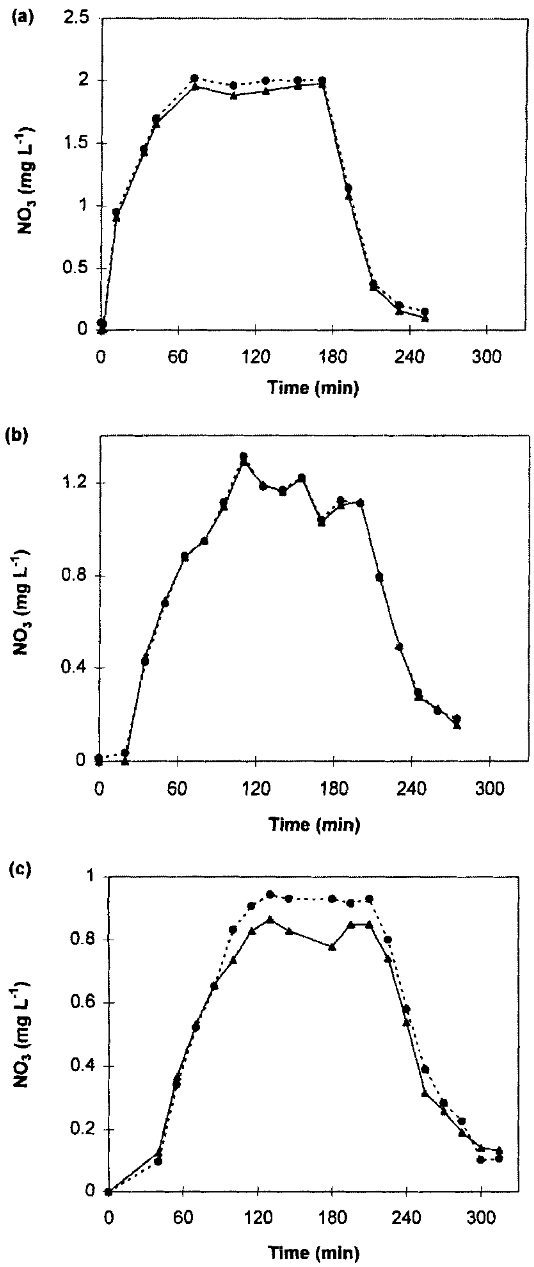


FIGURE 3 Observed (●) and expected (▲) stream water nitrate concentrations at sampling location (a) 1 (b) 2 and (c) 3 during the winter experiment.

Downloaded At: 13:57 15 January 2011

TABLE II Percentage of potassium and nitrate retained within (−) or released from (+) the steam channel during the summer and winter experiment.

		17 August 1992	
Sampling location	*Distance below addition point (m)*	*Potassium (%)*	*Nitrate (%)*
1	16	0	0
2	54	−25	−18
3	105	−58	−18
		8 December 1992	
Sampling location	*Distance below addition point (m)*	*Potassium (%)*	*Nitrate (%)*
1	16	0	0
2	54	0	0
3	105	−7	+7

Downloaded At: 13:57 15 January 2011

Potassium

In the summer at sampling location 1, observed values of potassium were lower than expected values as concentrations in stream water increased, but were greater than expected values when potassium concentrations reached a plateaux (Fig. 4). At locations 2 and 3, observed concentrations were considerably lower than expected values.

In the winter, observed concentrations were lower than expected values as potassium concentrations increased, but greater than expected values as stream water concentrations returned to pre-addition values at all sampling locations (Fig. 5). However, while all the added potassium passed through locations 1 and 2, only 93% of that added was accounted for at location 3. This indicates that a small proportion of the added potassium was retained between locations 2 and 3 (Table II). The results also indicate that the added potassium was delayed relative to the speed at which bromide was transported along the stream.

The difference between expected and observed potassium concentrations at locations 2 and 3 are plotted against time in Figure 6 for the summer and winter experiments. An initial increase in the relative difference was observed as potassium concentration increased, this was followed by a decrease to zero while stream water potassium concentrations were at a maximum. As stream water concentrations

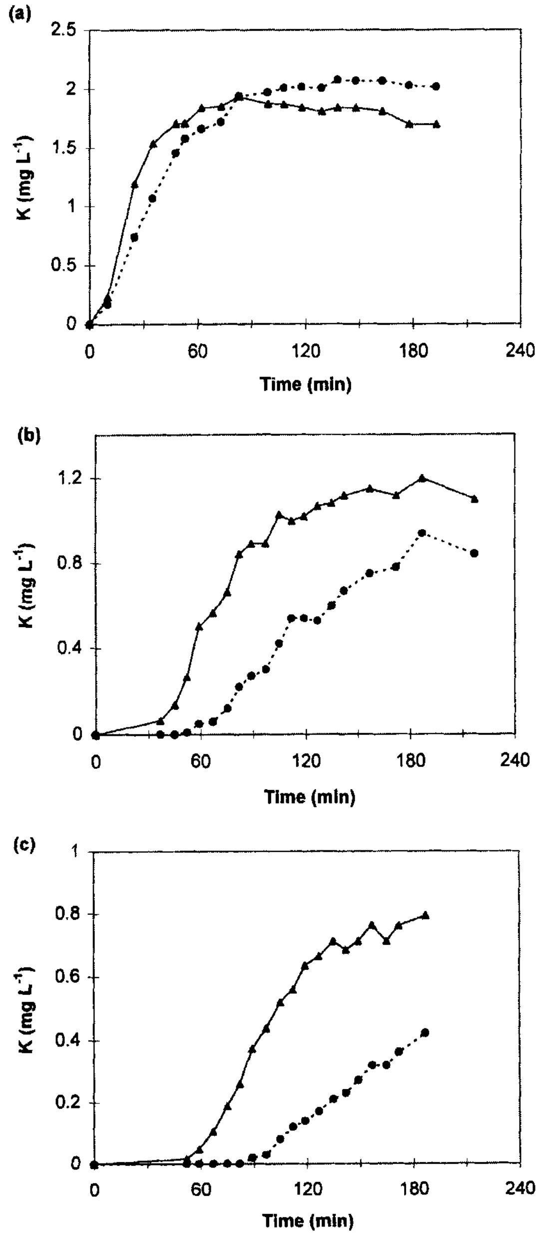


FIGURE 4 Observed (●) and expected (▲) stream water potassium concentrations at sampling location (a) 1 (b) 2 and (c) 3 during the summer experiment.

Downloaded At: 13:57 15 January 2011

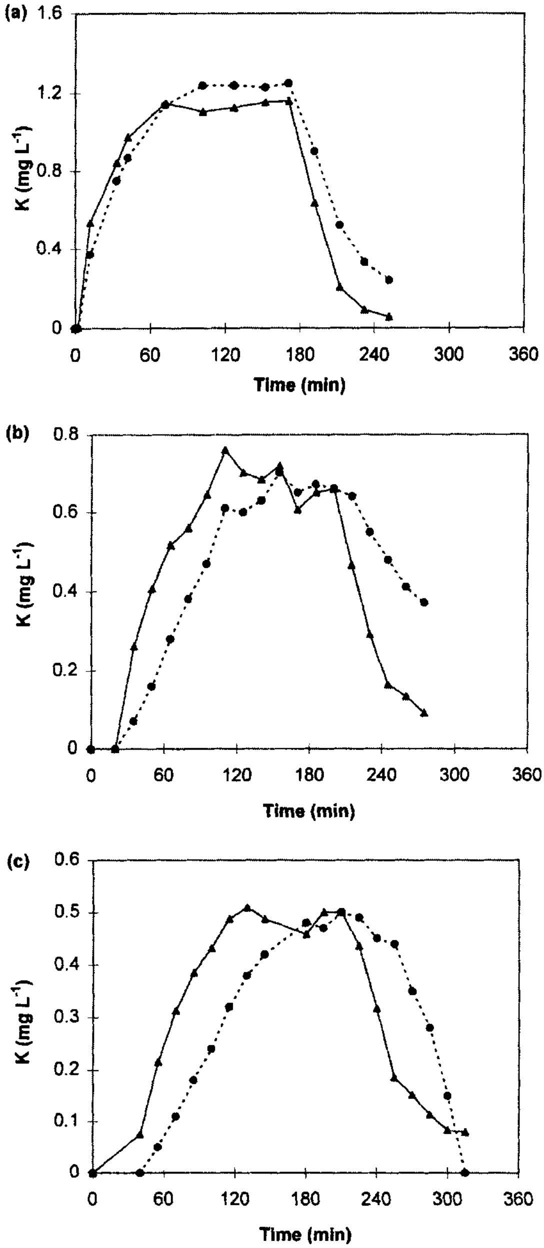


FIGURE 5 Observed (●) and expected (▲) stream water potassium concentrations at sampling location (a) 1 (b) 2 and (c) 3 during the winter experiment.

Downloaded At: 13:57 15 January 2011

Downloaded At: 13:57 15 January 2011

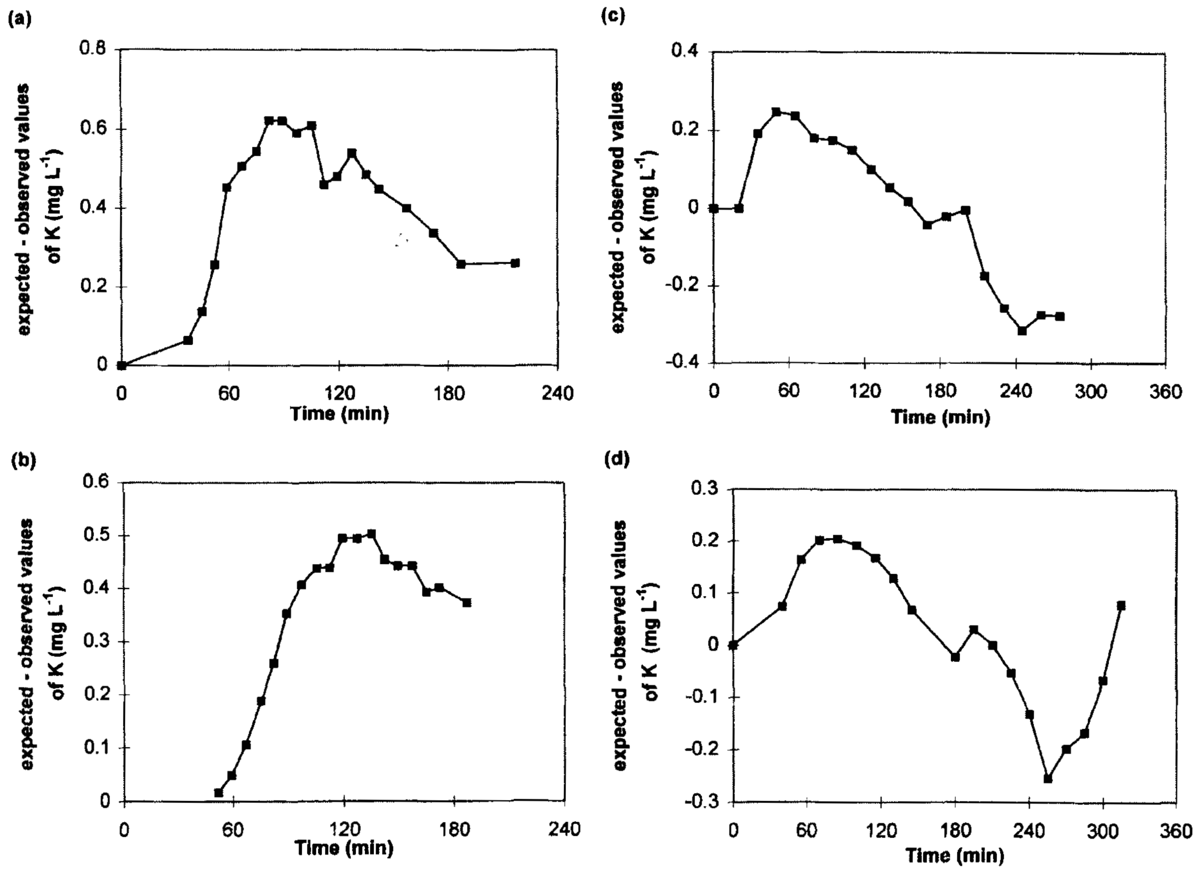


FIGURE 6 Difference between expected and observed potassium values during the summer experiment at (a) sampling location 2 and (b) sampling location 3 and the winter experiment at (c) sampling location 2 and (d) sampling location 3.

decreased in the winter experiment, observed concentrations exceeded expected values, indicating release of potassium from the stream substrate. However, as potassium concentrations in stream water fell, the rate of release of potassium also decreased. This shows that potassium which was retained within the stream as stream water concentrations increased, was subsequently released as stream water concentrations decreased.

To determine the extent to which any of the added potassium was permanently retained in the summer experiment, a correction factor was applied, based on the winter data set, to allow for the delay between the times when the bromide and potassium passed the sampling points. Following this correction an estimated 25% of the added potassium was retained by the stream substrate between locations 1 and 2, and a further 33% between locations 2 and 3 (Table II). Therefore, 58% of the added potassium was estimated to have been retained within the stream in the summer experiment.

Downloaded At: 13:57 15 January 2011

DISCUSSION

Nitrate

Nitrate depletion along the stream channel was only observed in the summer, probably as a result of biological uptake by stream biota (macrophytes, algae, biofilms etc.) and/or denitrification. For the latter to occur, there must be appropriate bacterial populations, an organic carbon substrate, suitable pH conditions and stream bed zones depleted in oxygen in which organisms utilise nitrate ions as electron acceptors rather than oxygen molecules. Organic carbon will be present in the fine sediment of the stream pools and within the root zones of the stream vegetation. Even under stormflow conditions, the stream pH in summer rarely falls much below 5 (Chapman *et al.*, 1993) so that acidity is unlikely to be a limiting factor. Denitrification rates are affected by temperature, with most rapid losses occurring in warm conditions during the summer. However, denitrification can still occur at temperatures of 0–5°C (Wild, 1988) and results presented by Haycock and Burt (1993) suggest denitrification can operate throughout the winter, although the rate of denitrification would be lower than in the summer. If denitrification is the major process responsible for controlling nitrate depletion along the stream channel, loss of nitrate would be expected to occur in both the summer and winter experiments, which was not the case.

The major loss of nitrate occurred between locations 1 and 2, which coincided with the length of stream occupied by dense vegetation, particularly *Sphagnum*. Plant growth and abundance, and hence nutrient demand is at a maximum in the summer and this might explain the seasonal differences in the experimental results. Other studies, particularly in New Zealand, have also observed the dominance of plant uptake as a nitrate depletion mechanism in streams (Howard-Williams *et al.*, 1982; Cooper, 1990). However, other studies have reported that denitrification (Hill, 1979; Swank and Caskey, 1982) is largely responsible for nitrate retention within the stream channel, while others have reported the importance of algal communities (Sebetich *et al.*, 1984; Mulholland, 1992). In upland ecosystems, the growth of vegetation and algal communities are considered generally to be nitrate and phosphorus limited. Therefore any nitrate added into a nitrogen deficient stream, as in this experiment, would be rapidly sequestered by plants and algae, particularly in the summer when plant growth is at a maximum and warm temperatures, light conditions and low flows enhance the growth of algae. Furthermore, the microorganisms involved in depleting nutrients may be lost from the stream bed during storm events. Such events are more frequent in winter, which together with low temperatures and shorter days will restrict re-colonisation during this period. Nutrient uptake by algae will therefore be proportionally greater during the summer.

Downloaded At: 13:57 15 January 2011

Approximately, 16.7 g of the added nitrate should have passed sampling location 3 194 minutes after start of experiment on 17 August based on tracer bromide data. In fact, only 13.8 g or 82% of the added nitrate was accounted for. The nitrate depletion rate by the stream channel was estimated as 946 mg NO_3 h^{-1} or 214 mg NO_3- Nh^{-1} which given an approximate stream channel area of 105 m^2, converts to an average areal rate of 2 mg NO_3-N m^2 h^{-1}. However, as most of the nitrate retention occurred between sampling locations 1 and 2, a distance of only 38 m, the nitrate depletion rate for this reach of the stream channel was estimated as 5.6 mg NO_3-N m^2 h^{-1}. This is considerably higher than the nitrate depletion rate of $0.34 mgNm^2h^{-1}$ reported by Cooper (1990), who estimated the nitrate depletion rate from stream water nitrate concentrations collected over a year, rather than from a short pulse addition of nitrate as in this study.

Potassium

Most studies of stream water nutrient dynamics have concentrated on nitrate and phosphorus but much less work has been reported on the stream transport of potassium. Results from the winter experiment showed that potassium was temporarily retained within the stream channel before being exported from the catchment. This may have been due to ion exchange processes. *Sphagnum* (Clymo, 1963), biofilms (Costerton *et al.*, 1987), which coat every wetted surface within aquatic systems (Lock, 1993), and clay minerals are all known to possess ion exchange surfaces. The experimentally induced increase in potassium concentrations may have caused potassium to be temporarily retained on these surfaces and then released as stream water concentrations returned to pre-experimental conditions. After accounting for the effect of this temporary retention, further losses of potassium occurred along the stream channel in the summer experiment. This was probably due to biotic uptake by plant and algae communities, which are at a maximum in the summer.

In addition, the experimental results help to explain the response of potassium during storm events. An increase in stream water potassium is commonly observed during storms in upland catchments (Chapman *et al.*, 1993; Giusti and Neal, 1993; Muscutt *et al.*, 1990; Reid *et al.*, 1981). However, concentration generally increases more rapidly on the rising limb of the hydrograph and decreases more slowly on the recession limb (e.g. Chapman *et al.*, 1993). This is known as hysteresis, and has been reported for other solutes such as aluminium, iron, dissolved organic carbon and pH, as well as potassium. The results from the winter experiment, which show that potassium is temporarily retained within the stream channel as concentrations increase and then released as concentrations decrease, may also occur during storm events and thus account for the observed hysteresis effect. However, there may be significant kinetic restraints on ion exchange mechanisms during storms as stream discharge will determine the water residence time within the stream channel and hence the time available for ion exchange processes to operate. However, Chapman (1994) showed that rapid ion exchange reactions were re-

Downloaded At: 13:57 15 January 2011

sponsible for changes in the chemical composition of runoff along stormflow pathways.

CONCLUSIONS

The behaviour of the injected nitrate and potassium were quite different; nitrate travelled along the stream at the same rate as the tracer, whereas ion exchange processes involving a combination of biofilms, *Sphagnum* and clay minerals may explain the temporary retention of potassium within the stream. In the winter, no uptake or permanent loss of nitrate or potassium was observed. In contrast, 18% of the added nitrate and 58% of the added potassium was retained within the stream channel during the summer experiment. This retention of nutrients is probably related to biological activity of macrophytes and microflora, which is at a maximum in the summer. The results also show that in-stream processes can regulate stream water concentrations of nitrate and potassium in the summer under low-flow conditions and that rapid ion exchange processes within the stream channel may explain the hysteresis response of potassium during storm events.

Irrespective of the mechanism, the experiments have shown that nutrient retention and/or removal within the stream channel can potentially contribute to the strong seasonal cycle in stream water nitrate and potassium concentrations observed in upland catchments. Additional experimental work would be required to quantify the relative importance of stream channel depletion versus soil nutrient availability and leaching as controls on these seasonal cycles. A better understanding of the processes which control the pattern of nutrient loss and their chemical form is needed, as exports of nutrients from upland streams represent the inputs to higher order streams, lakes and estuaries. Any retention of nutrients by the stream ecosystem and/or any transformations which alter their biological availability will effect the nature of these inputs.

Downloaded At: 13:57 15 January 2011

Acknowledgements

This work was partly funded by the Natural Environment Research Council. The authors thank Mike Hutchins for his invaluable help in the field, Mr S. BennettEvans for permission to work on his land and Dr A. C. Edwards for helpful comments on the text.

References

Chapman, P. J. (1994) *Hydrochemical processes influencing episodic stream water chemistry in a small headwater catchment, Plynlimon, Mid-Wales.* Ph. D Thesis, University of London. pp. 416.

Chapman, P. J., Reynolds, B. and Wheater, H. S. (1993) Hydrochemical changes along stormflow pathways in a small moorland headwater catchment in Mid-Wales, UK. *J. Hydrol.*, **15**, 241–265.

Clymo, R. S. (1963) Ion exchange in *Sphagnum* and its relation to bog ecology. *Annals of Botany*, **106**, 309-324.

Cooke, J. G. and Cooper, A. B. (1988) Sources and sinks of nutrients in a New Zealand hill pasture catchment. 111. Nitrogen. *Hydrol. Proc.*, **2**, 135–149.

Cooper, A. B. (1990) Nitrate depletion in the riparian zone and stream channel of a small headwater catchment. *Hydrohiologia*, **202**, 13–26.

Costerton J. W., Cheng, K. J., Geesey, G. G., Ladd, T. I., Nickel, J. C., Dasgupta, M. and Marrie, T.(1987) Bacterial biofilms in nature and disease. *Ann. Rev. Microhiol.*, **41**, 435–464.

Edwards, A. C., Creasey, J. and Cresser, M. S. (1985) Factors influencing nitrogen inputs and outputs in two Scottish upland catchments. *Soil Use and Management*, **1**, 83–87.

Giusti, L. and Neal, C. (1993) Hydrological pathways and solute chemistry of storm runoff at Dargall Lane, South West Scotland. *J. Hydrol.*, **142**, 1–27.

Haycock, N. E. and Burt, T. P. (1993) The role of floodplain sediments in reducing the nitrate concentration of subsurface runoff: A case study in the Cotswolds, England. *Hydrol. Proc.*, **7**, 287–295.

Hill, A. R. (1979) Denitrification in the nitrogen budget of a river ecosystem. *Nature*, **281**, 291–292.

Howard-Williams, C., Davies, J. and Pickmere, S. (1982) The dynamics of growth, the effects of changing area and nitrate uptake by water cress *Nasturtium of licinale* R. BR. in a New Zealand stream. *J. Appl. Ecol.*, **19**, 589–601.

Kaushik, N. K., Robinson, J. B., Stammers, W. N. and Whitely, H. R. (1983) Aspects of nitrogen transport and transformation in headwater streams. In M. A. Lock and D. D. Williams (eds), *Perspectives in Running Water Ecology.* Plenum, New York, pp. 110–117.

Lock, M. A. (1993) Attached microbial communities in rivers. In T. E. Ford, (ed.) *Aquatic Microbiology-An Ecological Approach.* Blackwell, Oxford, pp. 113–138.

Meyer, J. L. and Likens, G. E. (1979) Transport and transformation of phosphorus in a forest stream ecosystem. *Ecology*, **60**, 1255–1269.

Mulholland, P. J. (1992) Regulation of nutrient concentrations in a temperate forest stream: role of upland, riparian and in-stream processes. *Limnol. Oceanogr.*, **37**, 1512–1526.

Munn, N. L. and Meyer, J. L. (1990) Habitat-specific solute retention in two small streams: an intersite comparison. *Ecology*, **71**, 2069–2082.

Muscutt, A. D., Wheater, H. S. and Reynolds, B. (1990) Stormflow hydrochemistry of a small Welsh upland catchment. *J. Hydrol.*, **116**, 239–249.

Neal, C., Smith, C. J., Wallis, J., Billingham, P., Hill, S. and Neal, M. (1990) Hydrochemical variations in Hafren Forest stream waters, Mid-Wales. *J. Hydrol.*, **116**, 185–200.

Reid, J. M., Macleod, D. A. and Cresser, M. S. (1981) Factors affecting the chemistry of precipitation and river water in an upland catchment. *J. Hydrol.*, **50**, 129–145.

Downloaded At: 13:57 15 January 2011

Reynolds, B., Hornung, M. and Hughes, S. (1989) Chemistry of streams draining grassland and forest catchments at Plynlimon, mid-Wales. *Hydrol. Sci. J.*, **34**, 667–686.

Reynolds, B., Emmett, B. A. and Woods, C. (1992) Variations in streamwater nitrate concentrations and nitrogen budgets over ten years in a headwater catchment in Mid-Wales. *J. Hydrol.*, **136**, 155–175.

Roberts, G., Hudson, J. and Blackie, J. R. (1984) Nutrient inputs and outputs in a forested and grassland catchment at Plynlimon, Mid-Wales. *Agric. Water Manage.*, **9**, 177–191.

Sebetich, M. J., Kennedy, V. C., Zand, S. M., Avanzio, R. J. and Zellweger, G. W. (1984) Dynamics of added nitrate and phosphorus compared in a northern California woodland stream. *Water Resour. Bull.*, **20**, 93–101.

Swank, W. T. and Caskey, W. H. (1982) Nitrate depletion in a second order mountain stream. *J. Environ. Qual.*, **11**, 581–584.

Triska, F. J., Kennedy, V. C., Avanzino, R. J., Zellweger, G. W. and Bencala, K. E. (1989) Retention and transport of nutrients in a third-order stream in northwestern California: Hyporheic processes. *Ecology*, **70**, 1893–1905.

Wild, A. (1988) Plant nutrients in soil: nitrogen. In Wild, A. (ed.) *Russels Soil Conditions and Plant Growth*, Longmans Scientific and Tech., pp. 652–694.

Williamson, R. B. and Cooke, J. G. (1985) The effect of storms on nitrification rates in a small stream. *Water Res.*, **19**, 435–440.

Downloaded At: 13:57 15 January 2011