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## Boron water quality for the Plynlimon catchments

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### Abstract

Boron concentrations in rainfall, throughfall and stemflow for Spruce stands, mist, streamwater and groundwater are compared with chloride to assess atmospheric sources and catchment input-output balances for the Plynlimon catchments. In rainfall, boron concentration averages about  $4.5 \mu\text{g-B l}^{-1}$  and approximately two thirds of this comes from anthropogenic sources. In throughfall and stemflow, boron concentrations are approximately a factor of ten times higher than in rainfall. This increase is associated with enhanced scavenging of mist and dry deposition by the trees. As the sampling sites were close to a forest edge, this degree of scavenging is probably far higher than in the centre of the forest. The throughfall and stemflow concentrations of boron show some evidence of periodic variations with time with peak concentrations occurring during the summer months indicating some vegetational cycling. In mist, boron concentrations are almost twenty times higher than in rainfall and anthropogenic sources account for about 86% of this. Within the Plynlimon streams, boron concentrations are about 1.4 to 1.7 times higher than in rainfall. However, after allowance for mist and dry deposition contributions to atmospheric deposition, it seems that, on average, about 30% of the boron input is retained within the catchment. For the forested catchments, felling results in a disruption of the biological cycle and a small increase in boron leaching from the catchment results in the net retention by the catchment being slightly reduced. Despite the net uptake by the catchment, there is clear evidence of a boron component of weathering from the bedrock. This is shown by an increased boron concentration in a stream influenced by a nearby borehole which increased groundwater inputs. The weathering component for boron is also observed in Plynlimon groundwaters as boron concentrations and boron to chloride ratios are higher than for the streams. For these groundwaters, increases in boron concentrations are matched linearly by increases in the concentration of the principal base cation weathering component in the bedrock, calcium. However, the bedrock weathering term is not uniform as the ratio of boron to calcium concentration varies for the different boreholes sampled.

### Introduction

As part of the Institute of Hydrology's long term research studies into UK upland water quality issues, major, minor and trace element studies have been undertaken to provide information on atmospheric inputs and runoff chemistry for forested and moorland sites at Plynlimon in mid-Wales (Neal *et al.*, 1986, 1990, 1992, 1994a, 1997a–c; Durand *et al.*, 1994). Within the study, a unique, wide-ranging data set of water quality information has been collected over the past 13 years using accurate and consistent chemical methodologies. These data are of strategic value in developing an overview of element pollution from the atmosphere for one key area of the UK, a rural upland site over 100km from major industrial centres, where industrial pollution from the atmosphere can still occur given particular meteorological patterns.

The distribution of boron within UK riverine environments and the relative contributions of natural and anthro-

pogenic sources is poorly understood even though boron is both a micro-nutrient and a pollutant (Price *et al.*, 1972; Lindsay, 1972; Neal *et al.*, 1996, 1997d). Atmospheric inputs of boron to catchments potentially come from both maritime (sea-salt) and pollution sources such as those associated with fly ash (Neal *et al.*, 1997d; Wilkinson *et al.*, 1997). However, there is little information available for atmospheric boron deposition loadings from the catchment to the basin and regional scales. Within UK river systems, boron pollution occurs for lowland industrial and urban impacted basins due to runoff associated with detergents, drainage from disused coal mines and leaching of tips and land-fill from the mining industry (Neal *et al.*, 1997d). While there is limited information for lowland rivers (Neal *et al.*, 1996, 1997d,e; Robson and Neal, 1997), information for upland rivers is even rarer (Neal *et al.*, 1997a).

In this contribution, new information is provided for boron in rainfall, forest throughfall and stemflow,

streamwater and groundwater. This is undertaken to assess atmospheric and chemical weathering sources and within-catchment regulation of boron. The paper is provided to give the first detailed inventory for boron in an upland UK environment and a much needed backdrop to set against lowland studies where (a) pollution from urban and industrial areas can be high and (b) little background information is available on atmospheric and geological sources (Neal *et al.*, 1996, 1997d).

## Study Area

The Plynlimon catchments are located on the eastern edge of Pumlumon Fawr in mid-Wales, some 30 miles inland from the Atlantic Ocean. The work relates to the catchments of the Afon Hafren, Afon Hore and Nant Tanllwyth which form the main head water drainage of the River Severn in mid-Wales.

Bedrock geology consists of fractured lower Palaeozoic mudstones, greywackes, sandstones and grits. The predominant soil is a stagnopodzol, but peat, brown earth and stagnogley soils also occur within the catchments. The stagnopodzols are typically 70 cm thick, with organic-rich 'L' and 'O' horizons (3 to 10 cm). The lower soils consist of a leached 'E' horizon (10 to 20 cm) and a fine textured podzolic 'B' horizon (about 40 cm thick) merging into a stony 'C' horizon. At the top of the Hafren and Hore catchments, acid *Nardus* and *Agrostis* species grassland is dominant but there are also important areas of acid peats where *Eriophorum* species predominate. On the lower parts of these catchments, plantation forestry (predominantly Sitka spruce, *Picea Sitchensis*) was introduced in various phases between 1937 and 1964, onto acid moorland. Apart from minor 'thinning' of the forest stand, harvesting did not begin until late spring 1985 when clear felling of the lower half of the Afon Hore commenced. This felling took 3 years to complete. In the process, extensive brash and tree stumps were left to decompose in situ. Soon after harvesting, replanting of the slopes with juvenile Sitka spruce (<1 M high) proceeded. For the Afon Hafren catchment, no felling other than tree thinning has taken place up to present. In the case of the Nant Tanllwyth, this forms a small downstream and downslope sub-catchment of the Hafren. The catchment is completely forested and the soils are mainly impermeable gleys and stagnopodzols.

Rainfall averages about 2518 mm/yr with evapotranspirational losses of about 500 to 700 mm/yr. The rainfall is typical of the upland UK and it is relatively unpolluted except for moderate, long distance transport of acidic oxides. For all the streams, the flow responses to storm events are very flashy. For example, the Afon Hafren and Afon Hore have flows which vary from about 0.01 m<sup>3</sup>/s after dry antecedent conditions to 4.5 m<sup>3</sup>/s following major rainfall events.

In brief, the stream water chemistry changes in relation

to the dissimilar chemistry of the soils and shallow groundwaters (Neal *et al.*, 1988, 1990, 1992). The acidic soils are aluminium enriched and they are depleted in base cations and alkalinity. In contrast, the shallow groundwaters are less acidic, aluminium depleted and enriched in base cations and they are bicarbonate bearing (Neal *et al.*, 1997a,f). Consequently, stream chemistry fluctuates in response to changing hydrology. For example, stream pH changes from around 7 at baseflow, when groundwater sources predominate, to about 4.5 under storm conditions when contributions from soil waters become much more important.

## Sampling Programme

Since May 1983, weekly sampling of rainfall and Afon Hafren and Afon Hore stream water has been undertaken for detailed chemical analysis. Stream water was collected by 'grab sampling', while rainfall was represented by combining samples taken from two 'bulk precipitation gauges' spanning the altitude range for the catchments. The bulk precipitation gauges were 'open' collectors and so the rainfall determination comprised both wet and dry deposition components. Initially, the Afon Hafren stream was monitored to provide a control for the study of deforestation on the Afon Hore catchment. Unexpectedly, small differences in the degree of calcium carbonate mineralisation in the bedrock led to important hydrochemical differences between the two streams (Reynolds *et al.*, 1986; Neal *et al.*, 1990). In particular, the Afon Hore has higher pH (typically by 0.5 pH units) and base cation concentrations (a factor of about 4). Thus, the Afon Hafren proved to be inappropriate as a control. So, the Afon Hore was sampled at a second point, above the harvest area, to act as a substitute control. This upper Hore site is about half way between the top of the catchment and the lower Afon Hore monitoring point. Monitoring of this extra site began in September 1984.

Further extensions to the monitoring scheme have also been introduced over the years and these extra data are also presented. These extensions were—

- (1) stemflow and throughfall samples were collected to allow a more complete assessment of atmospheric inputs to the catchment (1984 to 1992);
- (2) Afon Hafren stream water was collected upstream of the forest area (upper Hafren). This stream was monitored (a) to obtain hydrochemical data for future comparison with the lower Afon Hafren stream chemistry when felling occurred and (b) to provide new information on an acid moorland stream (from May 1990 onwards);
- (3) a small tributary of the Afon Hore was sampled (south2Hore). This provided information, from April, 1988 onwards, on the chemical variations occurring before, during and post felling, for an area draining

- podzolic forest soils with minimum groundwater inputs (Neal *et al.*, 1994a);
- (4) to allow assessment of occult deposition (from February 1989 onwards), fine mist was collected near the top of the Severn catchment using a system designed by the Institute of Terrestrial Ecology (Edinburgh);
- (5) to monitor groundwater sources, a series of exploratory boreholes were introduced in 1994 to 1996 across the Hafren catchment (Neal *et al.*, 1997b,c).

Details of the characteristics of the streams sampled are given in Table 1.

Table 1. Catchment details of streams sampled: \* indicates catchment fully felled during the sampling period.

Catchment	Area (ha)	Altitude range (M)	% forest	% peat and moorland
Upper Hafren	117	535–690	0	100
Afon Hafren	347	350–690	52	48
Nant Tanllwyth	97	350–620	100	0
Upper Hore	178	405–738	56	44
Afon Hore*	335	339–738	78	22
South2Hore*	14	360–440	100	0

## Analysis

All the rainfall, stemflow, throughfall, cloud and stream waters sampled were filtered with 0.45  $\mu\text{m}$  membranes and 2  $\mu\text{m}$  glass fibre filters either in the field or soon after return to the laboratory. Samples were stored prior to analysis in the dark at 4°C in 10% acid washed polyethylene bottles for trace element analysis (the 0.45  $\mu\text{m}$  membrane filtrates) and in chromic acid washed glass bottles for major anion, nutrient and dissolved organic carbon (the 2  $\mu\text{m}$  glass fibre filtrates). For the trace element analyses, samples were acidified with high purity concentrated nitric acid to 1% v/v on return to the laboratory. This acidification minimized adsorption and precipitation reactions. Analysis involved inductively-coupled-plasma optical emission (ICPOES) and mass (ICPMS) spectrometry techniques. From May 1983 to January 1988, ICPOES analysis was made on twenty fold pre-concentrated samples. From January 1988 to November 1992 both ICPOES and ICPMS analyses were undertaken. The changeover was made to reduce analytical times; the ICPMS did not require a pre-concentration step due to much greater analytical sensitivity. The overlap period ensured a rigorous test for the method reproducibility and excellent results were obtained. With each batch of samples for ICPOES and ICPMS analysis, the Institute of Hydrology's own quality control standards were included. For the major

anion and nutrient analysis, colourimetric techniques were used. For dissolved organic carbon, an aqueous carbon analyzer was used. General methodologies are provided in Neal *et al.*, 1990.

## Results

Table 2 provides a summary of the salient features for boron distributions in the various water types sampled. Within the table, data for chloride has also been included as this component is derived essentially from the atmosphere. Being chemically conserved in solution at the low concentrations observed at Plynlimon, chloride concentrations provide a chemical marker for the atmospheric maritime influence. Further, by comparing chloride input-output relationships and the boron to chloride ratios, the influence of evapotranspiration on boron concentrations in the streams and groundwaters can be gauged.

Within the tables and for the remaining text, boron to chloride ratios are expressed in  $\mu\text{g-B l}^{-1}:\text{mg-Cl l}^{-1}$  units. These ratios have been calculated using flow weighted values of boron and chloride. This is appropriate as reference is given to boron fluxes through the catchment. The only exception is for the boreholes where there is no available data on flow: in this case, an arithmetic average has been calculated.

Boron concentrations vary by an order of magnitude in rainfall, throughfall, stemflow, stream water and groundwater (Table 2). Considering the atmospheric and canopy inputs, stream water and groundwater components separately, the following basic characteristics are observed.

### ATMOSPHERIC INPUTS

Boron concentrations vary in the order rainfall < throughfall = stemflow < cloud water as the influence of dry and mist capture becomes of increasing importance. For rainfall, concentrations are typically around 4.5  $\mu\text{g-B l}^{-1}$  but there is high scatter. A plot of boron concentration against chloride concentration in rainfall indicates two atmospheric sources (Figure 1). Firstly, rainfall is strongly influenced by maritime salt inputs when the wind direction is mainly from the North Atlantic. At such times, high chloride concentrations are observed and chloride and boron are linearly correlated with a gradient corresponding to the sea water boron to chloride ratio of 0.24 (Rosler and Lange, 1972). Thus, under these weather conditions, boron is overwhelmingly of marine origin. For low chloride concentrations, air trajectories are much more complex and involve air-mass movement over the industrial areas of north and south Wales as well as north and central England. At such times, boron concentrations are much higher than the marine line and pollutant sources are indicated which mirror patterns observed for pollutants such as heavy metals, nitrate, ammonium and sulphate (Neal *et*

Table 2. A summary of boron and chloride variations in rainfall, throughfall, stemflow, mist, stream water and groundwater. In the table \* notes the sites affected by felling, \*\* indicates average data for four boreholes and \*\*\* indicates data for the Nant Tanllwyth downstream of the borehole influence on streamwater chemistry.

Location	Flow weighted average boron concentration ( $\mu\text{g-B l}^{-1}$ )	Flow weighted average chloride concentration ( $\text{mg-Cl l}^{-1}$ )	Boron to chloride ratio ( $\mu\text{g-B l}^{-1}:\text{mg-Cl l}^{-1}$ )
Rainfall	3.2 (0-99.4)	4.4 (0.3-44.0)	0.72
Throughfall	33.4 (9.3-128.6)	31.6 (4.3-194.0)	1.06
Stemflow	34.6 (9.4-112.3)	33.8 (3.4-144.0)	1.02
Cloud water	79.1 (0-4930)	45.7 (1.7-740)	1.73
Upper Afon Hafren	3.46 (0.8-7.5)	5.5 (3.5-10.2)	0.62
Lower Afon Hafren	4.63 (0-71.4)	7.31 (3.9-12.2)	0.63
Nant Tanllwyth***	5.61 (2.5-23.1)	8.5 (4.8-14.0)	0.66
Upper Afon Hore	4.6 (0-63.0)	7.5 (3.8-20.0)	0.61
Lower Afon Hore*	5.5 (0.1-66.5)	7.2 (3.8-21.8)	0.76
South2Hore*	5.4 (1.5-67.3)	7.0 (2.9-18.8)	0.77
Hafren boreholes**	9.9 (3.0-37.9)	10.7 (5.6-14.0)	0.93

*al.*, 1990; Wilkinson *et al.*, 1997). The boron to chloride ratio in Plynlimon rainfall is about 0.72. Thus, it seems that two thirds of the boron in rainfall comes from atmospheric pollutant sources.

In stemflow and throughfall, boron averages about ten times the rainfall value. However, the sampling points are relatively close to the edge of the Hafren forest and this almost inevitably has resulted in enhanced mist collection (as shown by the elevated chloride concentrations): cf. Neal *et al.*, 1994b. For the throughfall and mist, the boron to chloride ratio is about 1.05 and it seems that the capture has increased pollutant boron in rainfall from 67 to 77%. However, there may also be a vegetation cycling term as concentrations are at their highest during the summer months (Figure 2). With regards to the patterns of behaviour between boron and chloride concentrations, the straight line observed at high chloride concentrations in rainfall is not observed as the influence of mist deposition and possibly vegetation cycling becomes dominant.

In the cloud water, concentrations of both boron and chloride are over an order of magnitude higher than in

rainfall. The boron to chloride ratio of 1.73 indicates that about 86% of the boron in mist comes from pollutant sources.

#### STREAM OUTPUTS

On average, boron concentrations in the streams are about 1.4 to 1.7 times higher than those in rainfall (Table 2). This increase is similar to that for chloride. Boron concentrations in the streams show marked fluctuations with time although, except for a few anomalous points, the scatter is lower than for rainfall reflecting the degree to which the rainfall signal is damped (Figure 3a,b). There were marked spikes in the data for the streams during 1988 and 1989 (up to about  $70 \mu\text{g-B l}^{-1}$ ) when major storm events led to significant rainfall event inputs (rather than the usual displacement of water residing in the catchment prior to the event). Other than for these spikes in the data, concentrations are generally much lower and there is some evidence of periodicity with higher values occurring during the summer months (Figure 3a,b). Examination of the

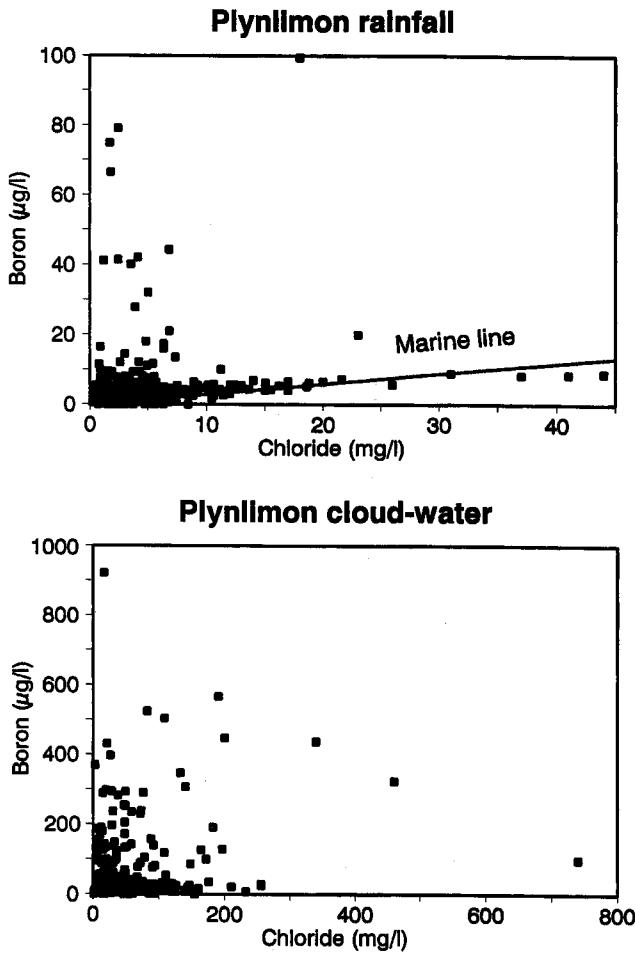


Fig. 1. Boron versus chloride concentrations in rainfall and mist.

relationships between boron and both chloride and flow reveal no significant patterns either statistically ( $r^2 < 0.022$ ,  $N > 250$ ) or visually.

The influence of rainfall on boron concentrations in the streams can be gauged using information on the boron to chloride ratio. To do so, the boron to chloride ratio in the net atmospheric input needs to be assessed to allow for the mist contribution in addition to that of the rainfall input. For the calculation a mist and dry deposition input of 20% of the chloride is taken, based on the detailed flux estimations given by Durand *et al.* (1994). On the assumption that the boron to chloride ratio in mist and dry deposition is the same, the boron to chloride ratio for the atmospheric input is computed to be 0.92 (ie close to that observed in both stemflow and throughfall). In general, the boron to chloride ratio in stream water is similar for all the streams although there is a minor but systematic variation from unperturbed moorland and forest catchments (about 0.63) to felled areas (about 0.76). These ratios are lower than the atmospheric input and this corresponds to about a 30% loss of the boron input to the stream.

Despite the net catchment loss, there is a weathering

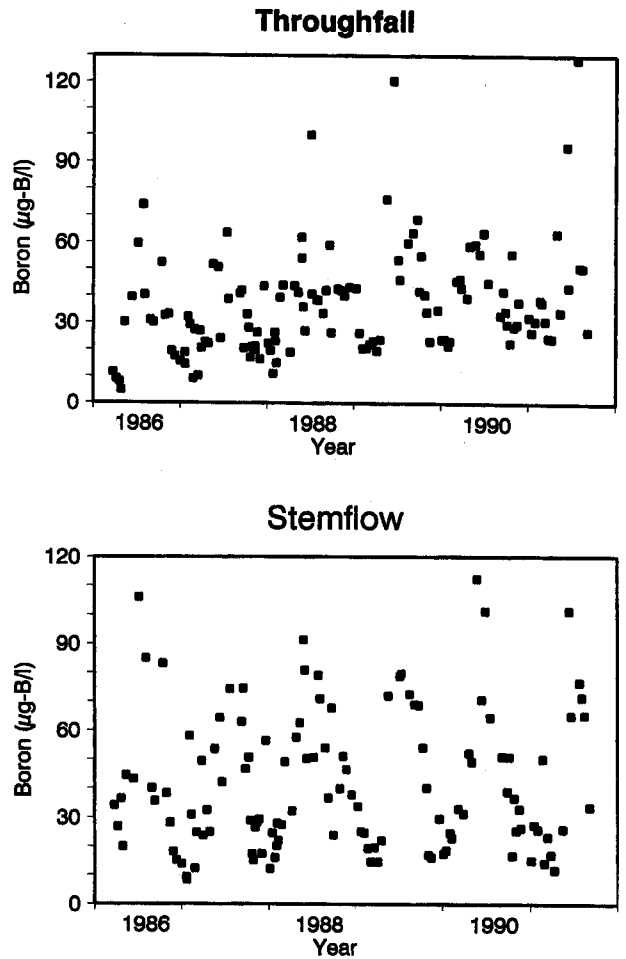


Fig. 2. Boron concentration variations with time for throughfall and stemflow.

source for boron. This in part is indicated by the seasonal patterns observed in streams when, during the summer, the baseflow component associated with bedrock weathering becomes higher—but the lack of a relationship with flow may well indicate that other processes, such as vegetational cycling and seasonal variations in evapotranspiration, are occurring. However, there is one clear indication of a weathering source and this relates to information for the Tanllwyth catchment. At this site, a borehole was introduced in 1994 which increased the input of groundwater and changed the character of the stream water quality to one with much higher calcium and alkalinity concentrations and higher pH (Neal *et al.*, 1997b,c). Following the introduction of this borehole, boron concentrations increased by up to a factor of two compared to earlier years (Figure 4). An additional monitoring point just upstream of the borehole was introduced to gauge to what degree it was the borehole and not some other factor that was causing the change. Comparisons between these two data sets show that the discrepancy is due to the borehole and that the major discrepancy occurs under baseflow conditions when the input of weathering-derived solutes is

at its highest. Under stormflow conditions, the main component of runoff in the stream comes from the gley soils and the effects of the borehole are swamped out. The influence of the weathering effect for the Nant Tanllwyth is illustrated by the linear pattern observed between boron and the major cation associated with mineral weathering, calcium ( $r^2 = 0.735$ ,  $N = 344$ ; Figure 5). For the Nant Tanllwyth, the boron to chloride ratio prior to the borehole introduction was 0.62, which matches the other Plynlimon

streams where felling of the catchment has not taken place. For the period during and subsequent to the borehole introduction, this ratio increased to 0.77. The difference in ratio implies an increased input of weathering-derived boron of about 25% due to the borehole increasing the net contribution of groundwater. This difference is small compared to the factor of two difference in concentration observed, but the main concentration differences are at low flow when flux contributions are also small.

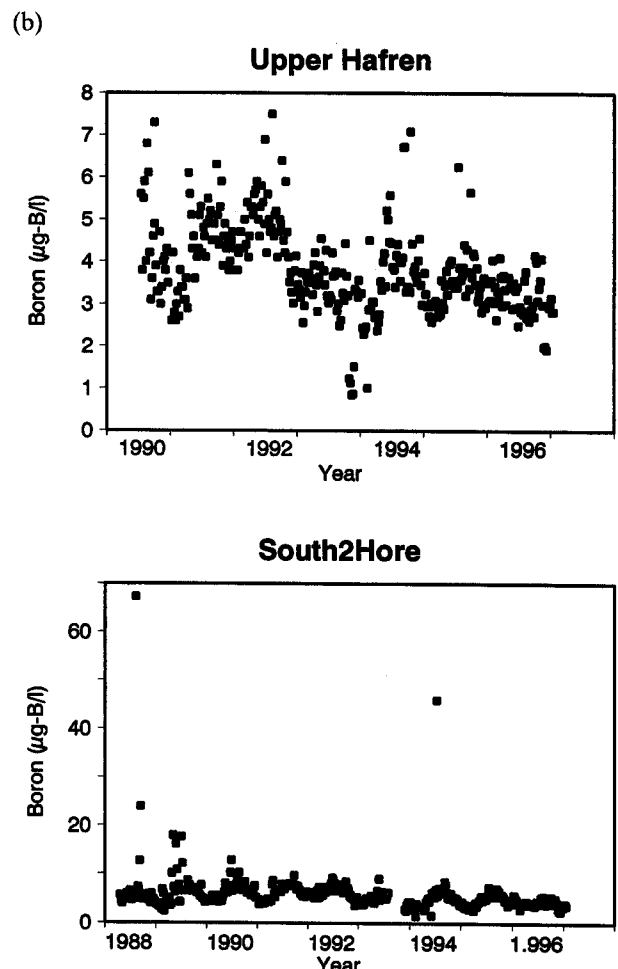
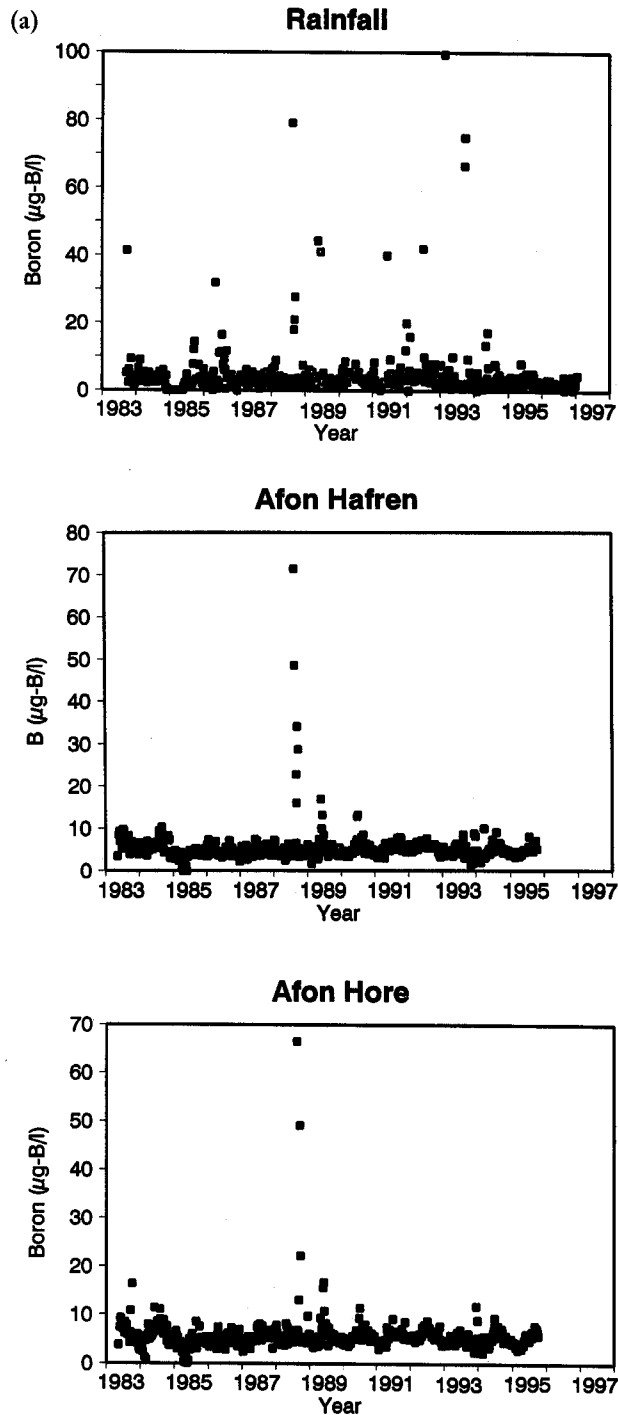


Fig. 3(a) Variations in boron concentration with time for the lower Afon Hafren and the lower Afon Hore. (b) Variations in boron concentration with time for the upper Afon Hafren and south2Hore.

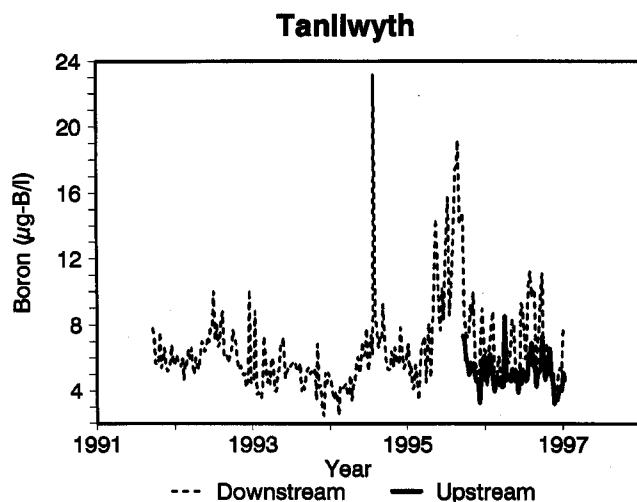


Fig. 4. Variations in boron concentration with time for the Nant Tanllwyth. The dashed lines refer to a sampling point just downstream of a borehole which affected the stream water quality. The solid line refers to a sampling point just upstream of the borehole influence.

GROUNDWATER

Data for four boreholes sampled over a two year period (fortnightly sampling) show not only temporal variations for boron as large as the stream, but average values almost twice those of the stream. These boreholes can have high alkalinities of up to 500  $\mu\text{Eq l}^{-1}$  and the bedrock weathering term is clearly much higher than for the streams (Neal *et al.*, 1997b,c). This increased weathering results in a marked boron release as shown by the higher boron concentrations and the high boron to chloride ratio (about 1.4 times the stream water values). The influence of weathering rate is also clearly indicated when the boron concentrations are plotted against the weathering indicator

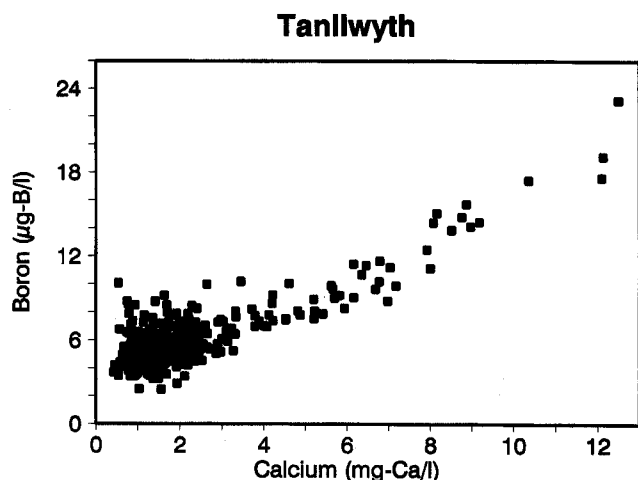


Fig. 5. A plot of boron versus calcium concentration for the Nant Tanllwyth sampled downstream of the borehole groundwater input.

calcium (Fig. 6). However, it seems that there is a variable boron weathering rate across the area as there are at least two distinct lines to the boron-calcium relationship for the individual boreholes.

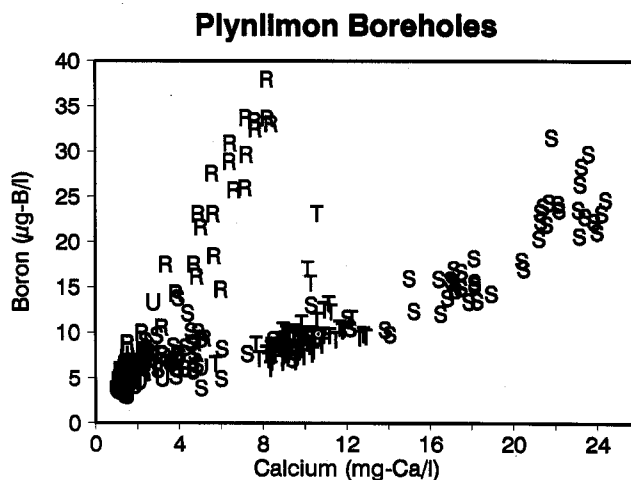


Fig. 6. A plot of boron versus calcium concentrations for groundwater sampled at four boreholes (two in the Tanllwyth catchment—sites S and U: two towards the bottom end of the Hafren catchment—R and T).

DISCUSSION

Boron concentrations in the Plynlïmon streams are relatively low compared to many lowland rivers where there is contamination from urban and industrial wastes. For example, boron concentrations in the Plynlïmon streams, which average about 5  $\mu\text{g-B l}^{-1}$ , are about a half to a thirtieth those for relatively clean to polluted lowland UK rivers entering the North Sea (Neal *et al.*, 1996, 1997d,e). The values are also low compared to regions with high weathering sources of boron and hydrothermal activity where values averaging over a 1000  $\mu\text{g-B l}^{-1}$  can occur (Christ and Harder, 1978). The concentrations encountered in the Plynlïmon streams are not of environmental concern as for example the annual averages set within European directives for the protection of freshwater life is 1000  $\mu\text{g-B l}^{-1}$  (Gardener and Zabel, 1991).

The influence of anthropogenic atmospheric emissions are observed at Plynlïmon and for boron over two thirds of the input seems to come from such sources even in a less polluted region of the UK. As boron is an essential micro-nutrient, (Price *et al.*, 1972), boron inputs at Plynlïmon probably fertilize the catchments. Within the Plynlïmon catchments, boron probably undergoes cycling through the vegetation and soils thus attenuating the rainfall signal on transfer to the stream. Because of the interactions with vegetation, the disruption of the biological cycle during felling leads to a release of boron to the stream.



There are clearly potential weathering sources for boron within the bedrock as the stream and groundwater data show. This occurs because the bedrock is comprised of Palaeozoic slates and shales of marine origin. However, the overall flux relationship indicates a net uptake of atmospherically derived boron of about 30%. This uptake probably relates not only to interactions with the vegetation but also to inorganic adsorption processes as borates (the principle form of boron in solution) are known to adsorb onto iron and aluminium oxides and clays within soils (Lindsay, 1972).

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