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Continuous pH, electrical conductivity and temperature measurement at Plynlimon: towards an integrated, reliable and low maintenance instrument system

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Abstract

Water quality data for the Nant Tanllwyth stream, Plynlimon (an acidic upland stream, the waters of which are of such low ionic strength that measurement is difficult), has been recorded using a new integrated field instrument system. The negligible drift of the pH electrode allows the system to operate for extended periods (months) without re-calibration, whilst maintaining a standard deviation of 0.19 pH units between its readings and laboratory reference measurements. Conductivity measurements, although within the sensor manufacturer's specification, did not provide meaningful readings at conductivities below 50 μS cm^{-1}. Using the pH data as a surrogate tracer, a high temporal resolution estimate of the stream dynamics, in terms of the contributions of groundwater and soil-water is presented; the dependence of these relative proportions on instantaneous flow and antecedent conditions is shown. It is concluded that, whilst improvements in instrumentation have been made, greater accuracy is still desirable for some scientific applications and ways forward are described.

Introduction

Water quality data are acquired for many reasons, including measuring the impact of land-use and climate change on water resources and river ecology. For most applications, it is essential that the water quality data are accurate and the instrumentation reliable, but it is often not a straightforward matter to achieve these objectives. In many cases, sensor fouling causes poor performance. In upland regions, the prevalence of low ionic strength waters makes measurement imprecise, a problem often compounded by difficulty of access for maintenance and calibration. This is most unfortunate because the effects of acidification may also be most severe in these regions, causing major environmental concern (UKAWRG, 1988).

Electrical conductivity and pH, two of the most commonly measured water quality variables, have been used in studies of the effects of afforestation on stream and river water quality (Swift et al., 1990) and as indicators to determine the origin and pathways of water within upland catchments (Robson, 1993; Neal, 1990; Hill and Neal, this issue). These variables can also be used as inputs for models to understand the short term dynamics of catchment behaviour (Robson et al., 1993). In many scientific studies of water quality, especially in upland areas, measurements

at least hourly are required to give good temporal resolution (Robson, 1993). This requirement is unlikely to be met by manual or automatic sampling, or by field measurements by personnel. However, since laboratory measurements are usually regarded as being of higher accuracy than those achieved by automatic field instruments, a combination of reliable continuous measurement and the collection of appropriate samples for laboratory analysis provides good temporal resolution and the data quality assurance required for such studies. In particular, for the Nant Tanllwyth catchment, Plynlimon, mid Wales, continuous pH data have supplemented weekly laboratory-measured samples, in the study of changes in water quality since the drilling of an observation borehole close to the stream (Neal et al., 1997a). pH has been used as a surrogate tracer, to estimate the change in the proportion of groundwater contributing to the total flow since drilling of the borehole.

The problems of measuring pH continuously for long periods in natural low ionic strength waters include reduced accuracy, increased response time and sensor drift when compared with measurements of higher ionic strength samples under laboratory conditions. Unless a buffer amplifier is used solutions of low ionic strength present a very high electrode impedance, and erroneous

liquid junction potentials may arise when measuring low ionic strength waters (Davison *et al.*, 1994). There may also be an error related to the flow of water past the electrode (stirring error), when measurements are made under these conditions (Meier *et al.*, 1989). Although many commercial pH sensors rely on a gel reference electrolyte for ease of installation and maintenance, this type of sensor is likely to suffer from these problems more than a sensor with a refillable reference electrolyte, primarily because of the increased likelihood of reference electrolyte contamination. As an alternative to purely commercial instrument solutions, which are necessarily directed at a larger market than that provided by scientific studies, Davison *et al.* (1994) devised a system for recording continuous pH data, particularly for low ionic strength solutions. A very similar sensor arrangement has been used here.

At the Institute of Hydrology, **WISER** (Wallingford Integrated System for Environmental monitoring in Rivers) has been developed to meet continuous water quality measurement and automatic sampling requirements. In the work reported here, the capabilities of WISER for suspended sediment analysis, through turbidity measurements and the collection of automatic river samples (Evans *et al.*, 1997), have been extended to include pH, electrical conductivity and water temperature measurements. The deployment of such a system is described. Continuous measurements of pH and conductivity, over a period of nearly 18 months, have been evaluated against laboratory measurements of samples taken from the stream. The pH and flow data are used to estimate the proportion of flow contributed by waters from different sources (endmembers). Inferences are drawn on the hydrological significance of the varying endmember proportions, with respect to both the instantaneous and antecedent flow conditions, and trends or changes with time are examined.

Equipment and Systems

One WISER system was installed on the Nant Tanllwyth, one of the smaller tributaries of the Upper Severn in mid Wales. This sub-catchment is part of the Plynlimon study area and a description of its hydrogeochemistry has already been given by Neal *et al.* (1997a). The equipment was installed 5 m upstream of one of the Institute of Hydrology's gauging structures (referred to by Neal as the 'Tanllwyth' site), in October 1994, and has been in continuous operation since. Neal *et al.* (1997a) have noted the effect on the stream water chemistry of a borehole drilled about 5 m from the stream in May 1994. This borehole is 45 m deep, 90 mm in diameter, and located about 20 m upstream of the WISER system. Neal *et al.* (1997a) noted, *inter alia*, a continuing marked increase in pH at lower flows, in this, the most acidic tributary of the Upper Severn.

The system installed consisted of an AmpHel pH electrode (Whatman International Ltd.), as used by Davison *et al.* (1994), a model 247 conductivity and temperature probe (Campbell Scientific Ltd., Shepshed, Leicestershire) and a PDCR 830 pressure transducer (Druck Ltd., Groby, Leicestershire) to measure stage. The pH electrode had a built-in buffer amplifier giving a low output impedance ($\sim$10 kΩ), resulting in a high noise immunity. The electrode was of a double junction design. This, combined with a small flow of electrolyte through the refillable electrolyte compartment and junction (Davison *et al.* 1994), minimised contamination of the reference junction and its electrolyte, which is one of the main causes of electrode drift (Meier *et al.*, 1989). All three sensors were interfaced to a Campbell CR10 data logger, to control the system and store the data. Conductivity measurements were corrected for temperature. Data were logged every 15 minutes and were an average of six measurements taken at ten second intervals, immediately prior to logging.

The pressure transducer was installed in a stilling-well in the flume gauging hut (allowing flow to be calculated from stage), which also housed the pH electrolyte reservoir (5 litres of 3.0 molar potassium chloride solution), data logger and 12 V dc battery power supply, the latter charged from a solar panel on the roof of the hut. The cables and the electrolyte feed tube were routed to the sensors in the stream via trunking buried at about 300 mm depth; this gave the electrolyte solution limited protection against freezing, whilst the reservoir maintained a minimum head of approximately 2 m, ensuring a positive, although not constant, pressure of electrolyte at the junction with the stream water. The pH electrode and conductivity cell were mounted in the stream, inside a protective housing; this was an upright length of 300 mm internal diameter PVC water pipe with numerous 25 mm diameter holes drilled in its lower length to ensure good flow around the sensors. The top end of the housing had a lockable cap, allowing the sensors to be withdrawn for maintenance. Fig. 1 is a schematic of the installation and the arrangement used to hold the sensors in place.

Throughout the period of deployment from October 1994 to April 1996, the pH sensor was re-calibrated in the field only on 21st September 1995, using standard buffer solutions. The conductivity cell and pH electrode were checked and cleaned on both 7th May 1995 and 21st September 1995. Manual measurements of water temperature and electrical conductivity were made nearby on a weekly basis and a sample was collected for subsequent laboratory determination of the pH (the reference data). Laboratory pH measurements were made at stream temperature with an accuracy of +/−0.02 pH units. The laboratory combined pH electrode was validated using a standard 10^{-4} N H_2SO_4 solution, which is of much lower ionic strength than standard buffer solutions.

Results

Fig. 2 shows the pH recorded by the WISER system (pH_W) plotted against the laboratory-measured value
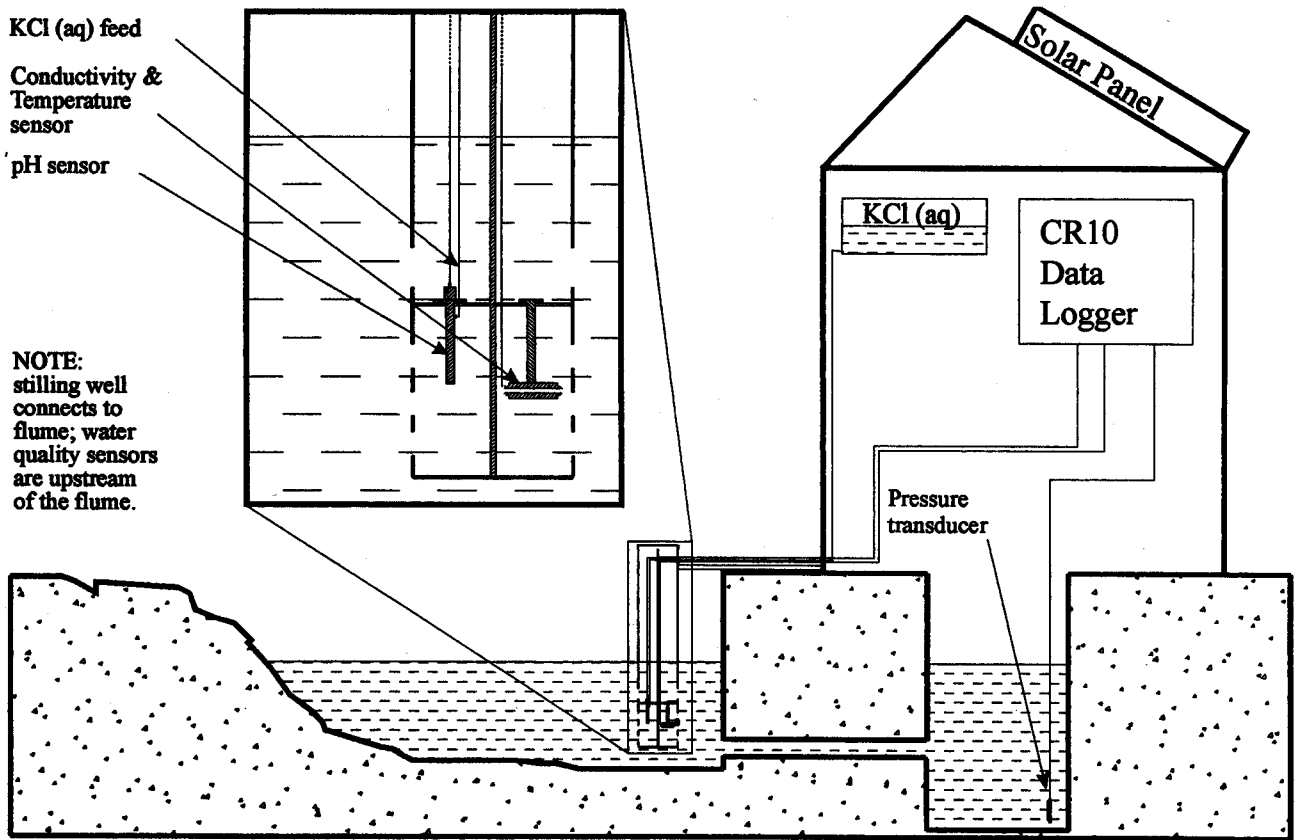
KCl (aq) feed

Conductivity & Temperature sensor

'pH sensor

NOTE: stilling well connects to flume; water quality sensors are upstream of the flume.

Solar Panel

KCl (aq)

CR10 Data Logger

Pressure transducer

Fig. 1. *Schematic diagram of the WISER installation and sensor mountings (insert).*

(pH$_{ref}$) for the period 20th October 1994 to 9th April 1996. All of the continuous pH data has been calibrated using the field calibration of 21st September 1995. The use of a single calibration for the whole dataset allows the instrument performance to be assessed, without the effect of regular changes to its calibration. Over all 74 comparative readings, the standard deviation between the continuous and the reference measurement was 0.19 pH units, with an average bias of −0.13 pH units. This relatively small error spread, compared with the pH range for the waters of 4.2 to 7.5, shows that the use of a single calibration is acceptable for the whole measurement period, whilst the bias shows that it is not the best single calibration available for this dataset. The difference (pH$_W$-pH$_{ref}$) shows no measurable drift with time (Fig. 3), confirming the validity of a single calibration.

The solid line of Fig. 2 shows a linear regression fitted through the whole dataset. This has been used to correct the data for all further analysis.

Fig. 4 shows the continuous pH, conductivity and flow record, for the whole measurement period (the small gaps in the data were due to battery failure). The pH tended towards 7.5 at baseflow; this was slightly seasonally dependent. During a rainfall event and subsequent increase in flow, pH decreased, in extreme cases to as low as pH 4.2,
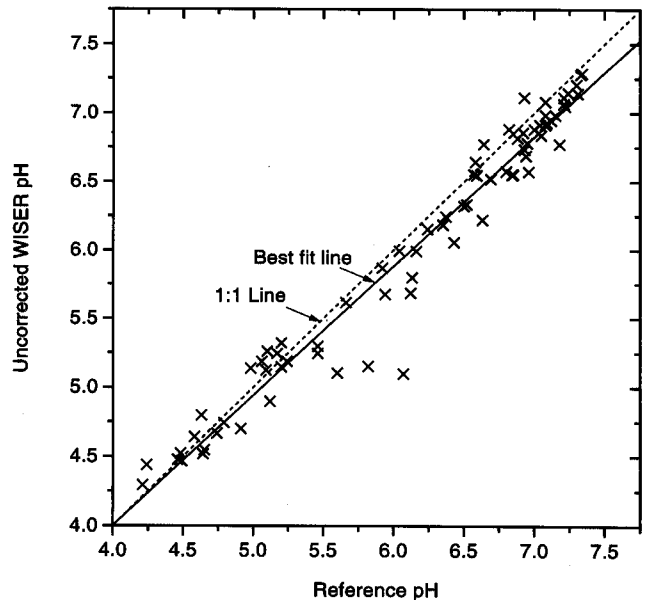

Fig. 2. *Comparison of laboratory-measured reference pH and uncorrected pH measured by WISER in the field. The solid line shows the linear regression for these points, the dashed line shows the ideal relationship.*

characteristic of an upland stream in this area (Neal *et al.*, 1990). The pH is highly correlated with flow because a large proportion of flow during storm events occurs as a result of near surface runoff through highly acidic soils. By contrast, the dominant source of water at low flow is groundwater (Neal *et al.*, 1997a). After a rainfall event, the stream pH recovered slowly, following the receding hydrograph.
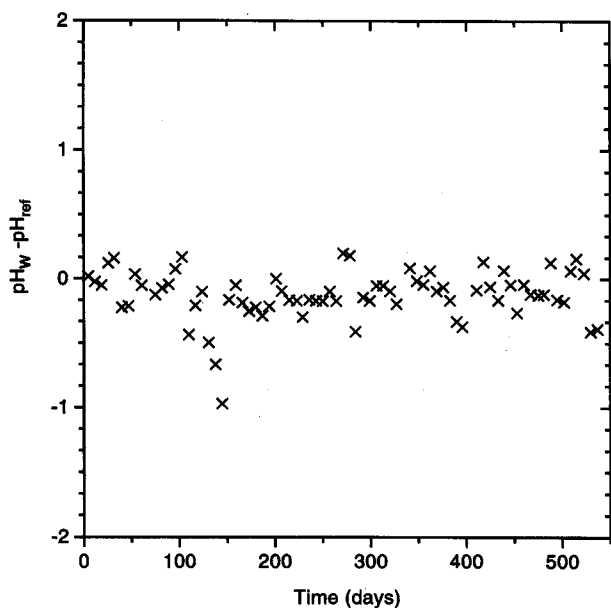

Fig. 3. *Plot of the difference between WISER recorded pH and laboratory reference pH measurements (pH$_W$-pH$_{ref}$) against time, showing no drift.*

Detailed examination of the pH and flow record shows diurnal cycling at periods of low flow (Fig. 5). Flow levels are at their lowest during the day, which is consistent with higher transpiration at such times. pH shows a minimum during the day. The days on which this is most marked show a sharp decline in the recorded pH in the morning, followed by a gradual increase from noon until around dusk. The effects of in-stream biota are unlikely to account for the sharp decline, but may account for the gradual increase. Photosynthesis would be expected to deplete the dissolved CO_2 and carbonic acid levels, increasing the stream pH during the daytime. The observed decrease in pH may be related to the increased transpiration, this requires further investigation.

The reference and continuous electrical conductivity data are compared in Fig. 6. The standard deviation between the two measurements is 10.0 μS cm^{-1} (the mean difference is -5.1 μS cm^{-1}). The data may be clustered into two groups: for reference conductivities greater than or equal to 50 μS cm^{-1}, the mean difference (bias) is -3 μS cm^{-1} (60 readings); for those less than 50 μS cm^{-1}, the

mean difference (bias) is -15 μS cm^{-1} (14 readings). However, the Campbell 247 Conductivity and Temperature Probe is only specified by the manufacturer to operate above 50 μS cm^{-1}, and its accuracy for this range (up to 440 μS cm^{-1}) is quoted as $+/-10\%$, within which all points, except one, lie. The range limitation of this sensor is indicative of the problems in measuring such low electrical conductivities in the field. Fig. 6 shows that, at conductivities less than 50 μS cm^{-1}, the indicated readings from the model 247 conductivity probe rapidly became unreliable.

Continuous electrical conductivity data (Fig. 4) shows the correlation between conductivity and flow. On most occasions, the conductivity decreased when the flow increased, as expected. However, some anomalies occur (minor increases in conductivity as flow increases), but mostly when the conductivity is below the sensor range minimum, so this may not be indicative of a real phenomenon.

Hydrograph Splitting

Splitting of the total stream flow into estimated contributions of deep water and soil-water enables insight into hydrological processes. pH is a non-conservative tracer due to CO_2-degassing, $Al(OH)_3$ precipitation-solution changes and precipitation/solution of H-organic and Al-organic ('humic') substances (Robson, 1993). Despite this, it can be used as a surrogate for the conservative Acid Neutralization Capacity (ANC), following the method of Neal *et al.* (1990). ANC has been estimated from pH using an empirical relationship developed by Robson (1993):

$$ANC = -102 + 113[exp(-0.042[H^+]) + exp(-5.4[H^+])]$$

(1)

where $[H^+]$ is in units of μEq l^{-1}.

For this Tanllwyth site, a soil endmember of -79 μEq l^{-1} has been estimated by Neal *et al.* (1997a), whilst the groundwater endmember was taken as the average baseflow value for this site (109 μEq l^{-1}). Whilst there is considerable uncertainty in these endmember values and there are short term changes in the groundwater endmember (Neal *et al.*, 1997a,b), previous studies have shown (Neal *et al.*, 1990) that the overall temporal pattern of the relative contributions of the endmembers is fairly insensitive to changes in the endmember values. However, the actual magnitude of each flow contribution will be sensitive to the chosen endmember values. Here, the chosen soil endmember was adjusted to -94 μEq l^{-1} since the higher value of -79 μEq l^{-1} leads to negative estimates of the groundwater contribution to total flow. Without any measurement of changes in endmembers over this period, no comment can be made on possible longer term changes in the groundwater contribution.

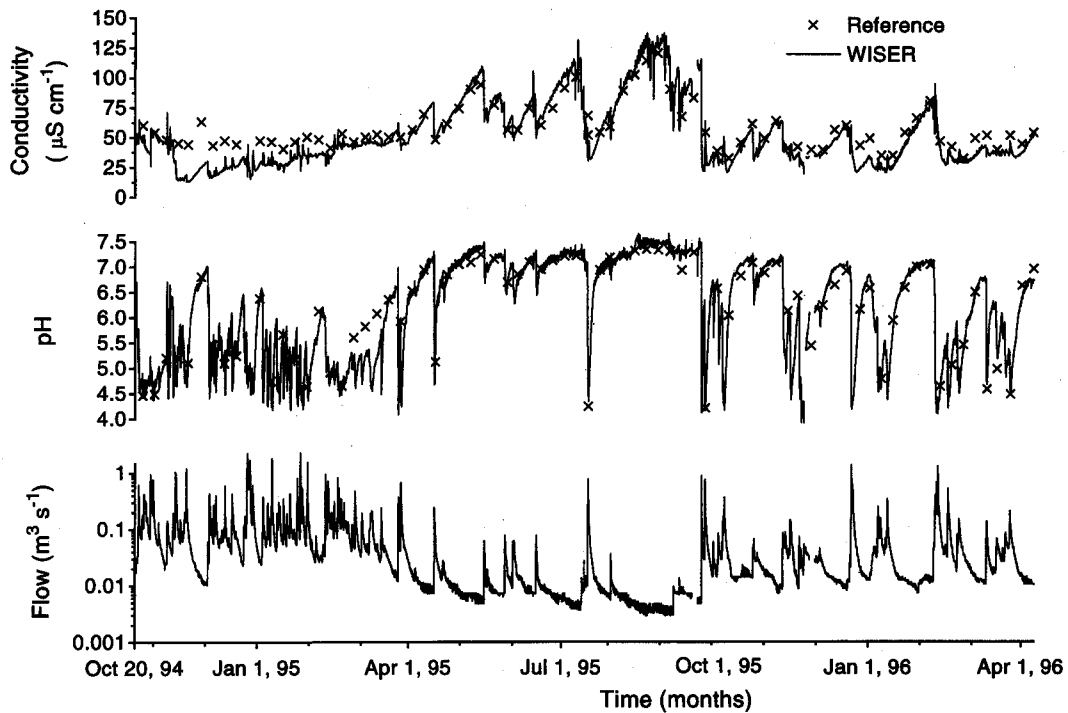The percentage of groundwater at different flows presented here (Fig. 7) follows the pattern already described

Fig. 4. *Continuous conductivity, pH and flow time series for the Nant Tanllwyth stream, for the period 20th October 1994 to 9th April 1996. Conductivity and pH reference measurements are shown by crosses. The continuous pH data has been corrected to best fit the reference measurements.*
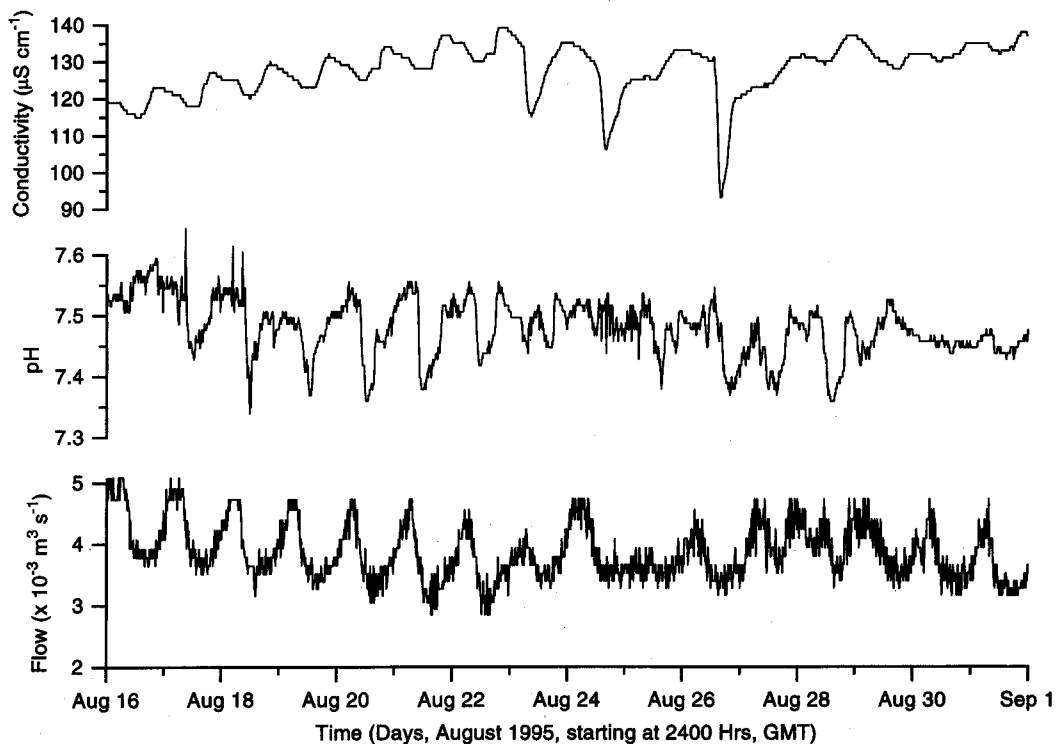

Fig. 5. *Flow, pH and conductivity time series for a short period of low flow (16th to 31st August 1995), showing diurnal cycling.*
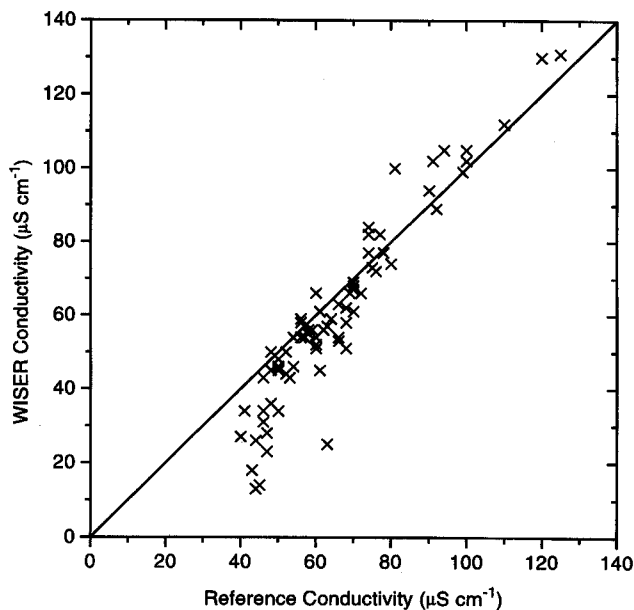
Fig. 6. *Comparison of laboratory-measured reference conductivity and conductivity measured by WISER in the field. The solid line shows the ideal relationship.*

by Neal *et al.* (1997a); groundwater dominates low flows, whilst being much less important at high flows and the actual contribution of groundwater to total flow increases with flow (Fig. 8). The groundwater portion of the flow peaked 1.5 hours before the soil-water component, following low flow conditions (3rd December 1994), and this relatively small storm event was dominated by flow from groundwater. At similar flows, following much larger storm events, but still on the rising-limb of the hydrograph, the soil-water contribution dominated, and the proportion of groundwater flow was lower. Antecedent conditions also affect the time between the two different endmembers reaching their peak flow; this time is reduced following periods of high flow.

Discussion

Continuous pH and conductivity measurements made on the Nant Tanllwyth, compared well with laboratory sample measurements. At very low conductivities, the performance of the conductivity sensor, although within the
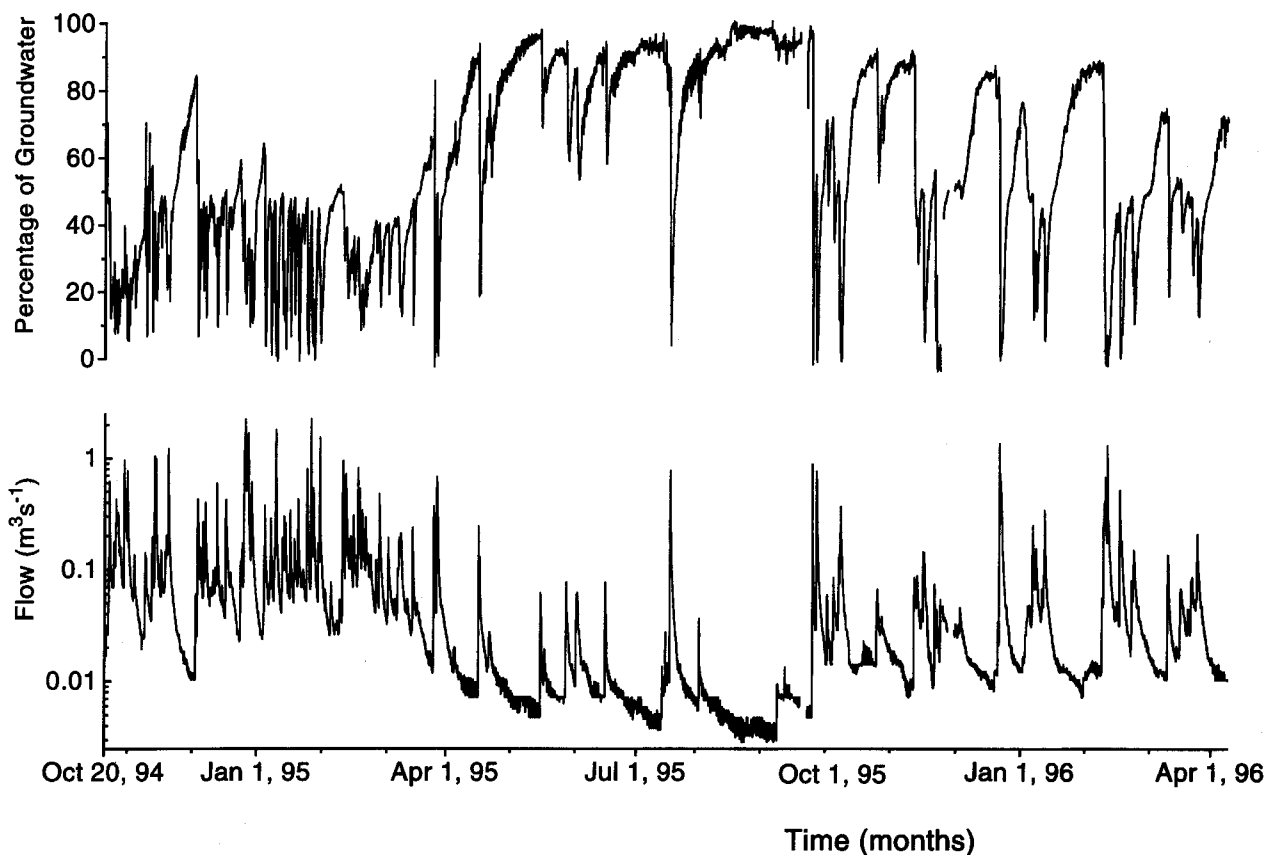

Fig. 7. *Plot of the percentage of groundwater contributing to the total flow, as estimated by the hydrograph splitting, together with the flow record.*
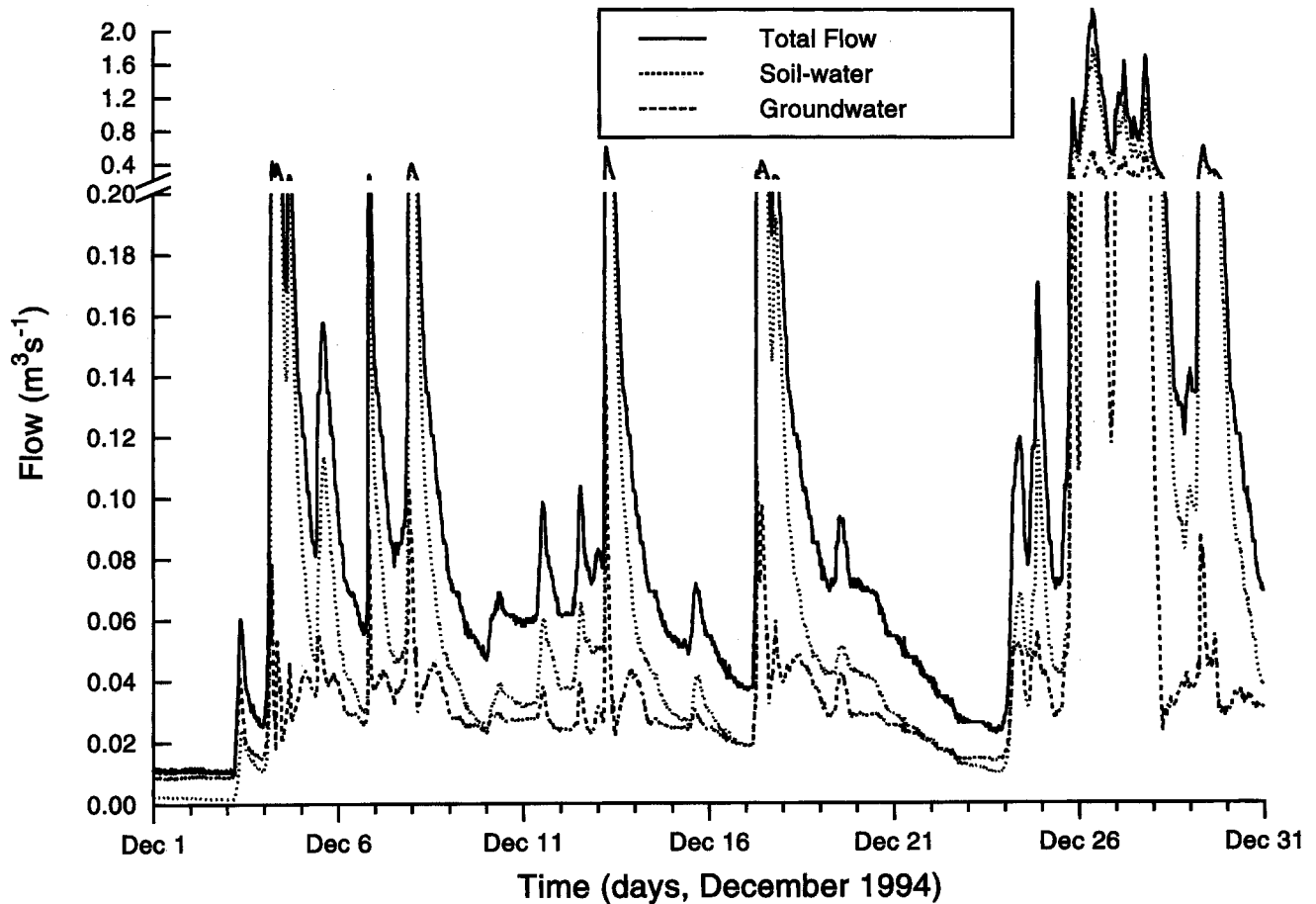
Fig. 8. *Plot of the total flow and the estimated flows attributed to groundwater and soil-water, for the period 1st December to 31st December 1994.*

manufacturer's specifications, was limited by the design of the sensor. The pH electrode was calibrated only once, yet it showed extremely good long term stability so that long term pH monitoring was achieved, without frequent maintenance or calibration, and with an accuracy that compares well with alternative instruments for these measurement conditions.

Reduced accuracy, under field conditions, of the pH electrode is due to a combination of measurement errors associated with the very low ionic conductivity of this stream; this problem is well recognised (Harfst *et al.*, 1995 and Meier *et al.*, 1989). The scatter in the pH data was similar at high and low flows, indicating that other errors are larger than any stirring error; water flow past the electrode may be damped by the protective housing of the installation. There is a possibility of a sampling error, because samples for laboratory measurement are taken at the centre of the stream and the WISER is installed at the side of the stream. However, this error would also be expected to be correlated with flow, since at high flows better mixing is expected; no such correlation is seen, therefore any sampling error is probably insignificant. The

electrode's buffer amplifier prevents the problem of increased signal noise due to the high impedance of low ionic strength solutions, but there remain measurement errors in low ionic strength solutions due to calibration with solutions of high ionic strength (standard buffer solutions), liquid junction potential errors, which are pronounced in low ionic strength solutions and changes in the electrolyte head (pressure).

These errors could not be separated in this study, but future work should look at the significance of each. Calibration could be performed with low ionic strength buffer solutions and, if necessary, the data logger could use different calibrations automatically depending on the measured conductivity. Comparisons should be made between electrodes of the same type but filled with much lower electrolyte concentrations (0.1 M); this should reduce junction potential errors. Finally, a constant electrolyte head could be devised, or the head increased to make the effect of changes in stage less significant.

The application of the hydrograph splitting technique, using the continuous pH data, provides a highly temporally resolved estimation of the stream dynamics, over a

period greater than a year. The varying responses, related to the antecedent conditions, can be used to study the underlying hydrochemical processes. The information is particularly useful for comparing with hydrological model predictions, or indeed as inputs to models. The great benefit of such continuous data has already been expounded upon (Robson, 1993). However, previously, its collection has required intensive maintenance and calibration of equipment. The use of continuous water quality data is made far more efficient by these advances in instrumentation.

Acknowledgements

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