

Seasonal hydrology of oxygen-18 in the Allt a' Mharcaidh, Scotland: implications for water movement and residence times

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Abstract The seasonal variation of oxygen-18 has been observed in precipitation, groundwater and streamwater in the Allt a' Mharcaidh catchment, Cairngorm mountains, Scotland. Precipitation showed strong seasonal variation in its isotopic signature over the 1995–1998 study period. As anticipated, such variation was substantially damped in groundwater and surface water. Nevertheless, ^{18}O proved a useful tracer, indicating the influence of spring snowmelt events and summer rainfall on stream waters. Detailed examination of the seasonal variation in $\delta^{18}\text{O}$ levels in various catchment waters provided an insight into mixing processes and a first approximation of mean residence times. Preliminary estimates for the latter are <180 days for (inferred) near-surface soil water and storm runoff, 2.5 and >5 years for shallow and deeper groundwater respectively. These longer-term data sets demonstrate the ability of the catchment to effectively mix new precipitation with resident soil and groundwater over the hydrological year. This implies that the influence of groundwater on the hydrology and hydrochemistry upland catchments has been underestimated.

INTRODUCTION

Stable isotopes have been extensively used to independently test hypotheses of hydrological processes developed from hydrometric and water quality observations (Kendall *et al.*, 1995). Such studies have often led to the revision of hypotheses relating to hydrological processes in many catchments that were believed to be well understood conceptually (McDonnell *et al.*, 1991; Hooper *et al.*, 1998). Most applications of isotope hydrology relate to short-term studies over individual storm episodes in an attempt to establish the relative importance of event and pre-event water in generating storm runoff (McDonnell *et al.*, 1991; Neal *et al.*, 1997). More recently, the advantages of examining isotope behaviour over longer time periods, such of one or more hydrological years have become apparent (Dewalle *et al.*, 1997).

In this paper we examine the behaviour of stable oxygen isotopes in precipitation, groundwater and stream waters over a three-year period in the Allt a' Mharcaidh

catchment in the western Cairngorm region, Scotland. The hydrology and hydrochemistry of the catchment have been extensively studied over the last decade and the hydrological behaviour of the catchment is reasonably well understood in a qualitative sense; storm runoff processes have been hypothesized (Wheater *et al.*, 1993; Jenkins *et al.*, 1994) and recent work has examined the influence of deeper groundwater on the quantity and quality of streamflows (Soulsby *et al.*, 1998). The behaviour of ^{18}O in the catchment over a three-year period has been analysed to test some of these hypotheses relating to the catchment hydrological response. The aims of the paper are; (a) to characterize the temporal and spatial variation in isotope signatures in precipitation, groundwater and surface waters, (b) to examine differences in the seasonal variation of ^{18}O levels as a basis for understanding the mixing processes operating at the catchment scale, and (c) estimating the mean residence times of water within the catchment.

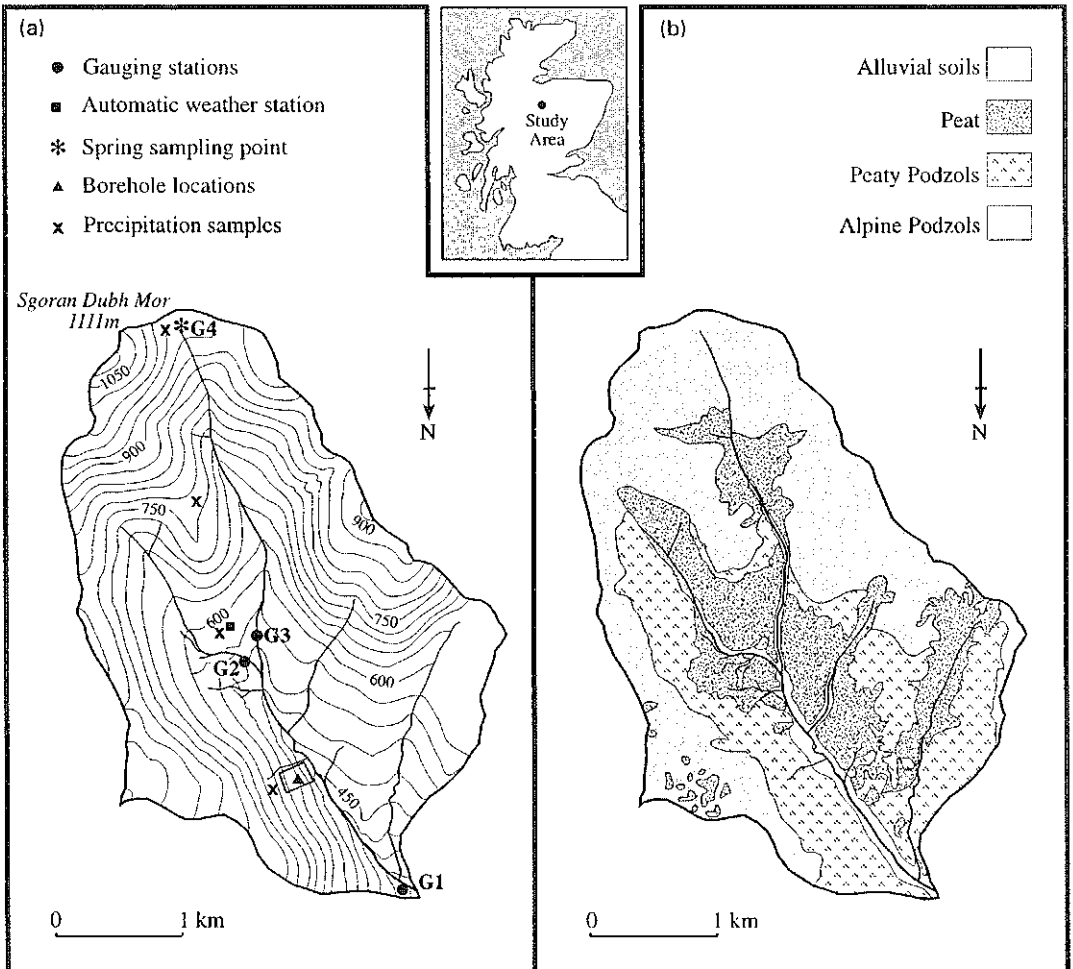


Fig. 1 Allt a Mharcaidh catchment showing (a) main topographic features and sampling locations and (b) distribution of main soil types.

STUDY AREA

The catchment covers an area of 10 km² and spans an altitudinal range of 300–1111 m (Fig. 1). It lies on the western edge of the Cairngorm mountains, an upland area of international conservation importance (Gordon *et al.*, 1998). The catchment is underlain by granite and has been subject to glaciation; thus the solid geology is covered by a range of superficial drift deposits with reasonable aquifer properties (Soulsby *et al.*, 1998). Three main soil–vegetation units occur, at the higher altitudes (*c.* >800 m) freely draining alpine soils have formed with related sub-arctic vegetation communities. On steeper sloping areas up to 800 m, humus–iron podzols support *Calluna* dominated moorland. On gentler slopes near the valley bottom, deep peats support blanket bog communities dominated by *Molinia*. The catchment is subject to a sub-arctic climate. Mean annual precipitation totals 1200 mm, with over 30% of this falling as snow in the winter months. Mean annual evaporation is around 350 mm. The Allt a' Mharcaidh stream has a mean annual flow of 0.25 m³ s⁻¹, though flood flows can exceed 15 m³ s⁻¹ and summer baseflows can fall below 0.1 m³ s⁻¹.

METHODOLOGY

To characterize the $\delta^{18}\text{O}$ signatures of precipitation inputs, a seasonally varied sampling strategy was used. During the summer period (May–October), isotope samples were collected from four rain collectors in the catchment; during the winter (November–April), surface snow samples were collected from four locations. The samples were collected at fortnightly intervals, though on occasion snow sampling from the upper catchment was frustrated by severe weather or avalanche risk. The precipitation sampling points spanned the altitudinal range of the catchment.

Streamwater samples were collected from the catchment outlet (G1) and the outlets of the two major subcatchments (G2 and G3). Samples from G1 were collected at twice-weekly intervals, whilst the G2 and G3 samples were weekly. Groundwater was sampled in two locations: a perennial spring in the catchment headwaters (G4) was sampled weekly (though this was sometimes disrupted by severe winter weather). In addition sporadic samples were taken from a riparian borehole in the lower catchment. All samples were collected according to standard procedures and taken to the laboratories of the Macaulay Land Use Research Institute in Aberdeen. Isotope concentrations are expressed in delta units (‰, parts per mille) defined in relation to SMOW (standard mean ocean water). The analytical precision of $\delta^{18}\text{O}$ analyses was approximately 0.1‰.

Regression analysis was carried out to determine seasonal oxygen-18 trends in precipitation, groundwater and stream baseflows for the period October 1996 to September 1997. Details of the background theory are described by Dewalle *et al.* (1997) and the full methodology is described in Soulsby *et al.* (under review). Periodic regression analysis was used to fit seasonal sine wave models to ^{18}O variations as:

$$\delta^{18}\text{O} = X + A[\cos(ct - \theta)] \quad (1)$$

where $\delta^{18}\text{O}$ is the predicted oxygen-18 level in ‰, X is the mean annual value in ‰, A is the $\delta^{18}\text{O}$ annual amplitude in ‰, c is the radial frequency of annual fluctuations,

t is the time in days after 1 October 1996, and θ is the phase lag or time of the annual peak oxygen-18 values in radians.

Mean transit times for water to move through the subsurface system were also calculated using a simple steady-state, well-mixed model in which precipitation is assumed to mix with all water in the soil reservoir. Sine waves are fitted to input and output water tracer concentrations and an exponential distribution of transit times is assumed. Mean residence time (T) of water leaving the system (in year⁻¹) is computed as:

$$T = c^{-1}[(Az2/Az1)^{-2} - 1]^{0.5} \tag{2}$$

Where $Az1$ is the amplitude of the initial water and $Az2$ is the amplitude of the resulting water.

RESULTS

Hydrogeochemistry of oxygen-18 in the Allt a' Mharcaidh

Figure 2 shows the mean and range of $\delta^{18}\text{O}$ levels in different waters within the Allt a' Mharcaidh. Spatially averaged $\delta^{18}\text{O}$ values in precipitation (individual collectors showed no consistent altitudinal variation) exhibited clear seasonality with summer rainfall having a more enriched $\delta^{18}\text{O}$ signature than winter snow. Both precipitation types exhibit marked variations in maximum and minimum values, which largely reflects the seasonal variation in evaporation rates in precipitation source areas. Soil water (estimated from high flows) shows much more limited variation in comparison

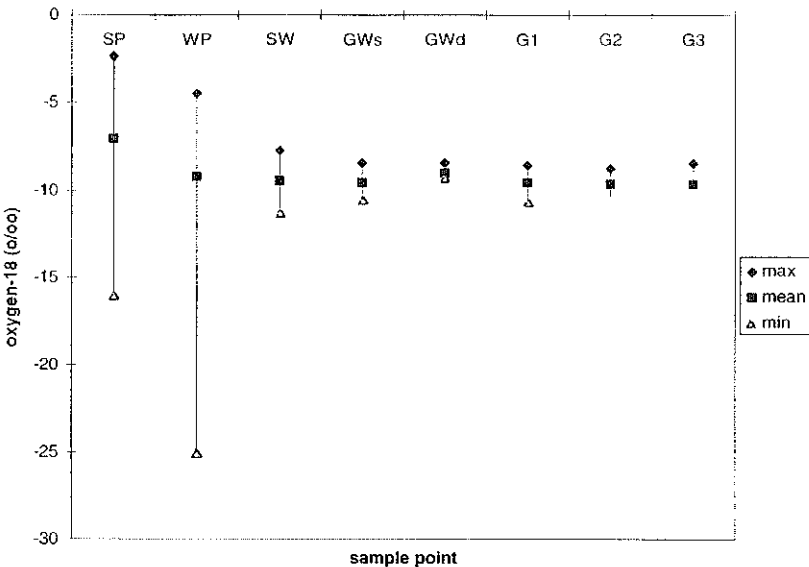


Fig. 2 Mean and range of oxygen-18 in various source waters within the catchment; where SP is summer precipitation, WP is winter precipitation, SW is soil water, GWs is shallow groundwater from the spring site, GWd is deeper groundwater from boreholes and G1, G2 and G3 are stream-water sampling points.

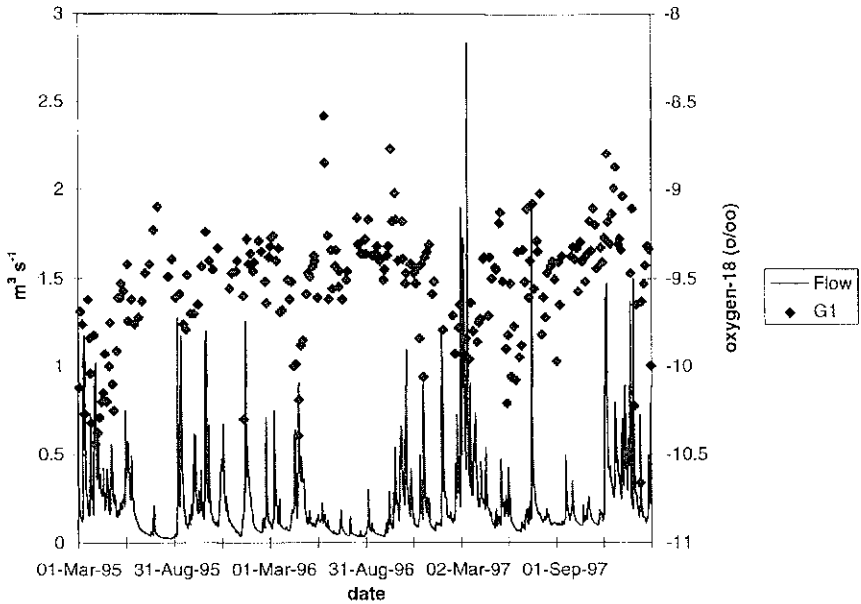


Fig. 3 Temporal variation in ^{18}O levels and flows in the Allt a' Mharcaidh stream at G1 (1995–1998).

with precipitation, suggesting that mixing processes within the soil rapidly damp down variations in input waters. However, higher values tend to occur in summer and lower values in winter in response to variations in precipitation. The variation of groundwater in both shallow springs and deeper boreholes is extremely damped in comparison to both precipitation and soil water, indicative of even more thorough mixing. In addition, the mean values tend to be much closer to those of winter snow rather than summer rainfall, implying that greater recharge occurs during the winter months. Stream waters at both G1 and the two tributary streams are also damped though less so than groundwater.

Despite the limited variation in isotope signatures compared to precipitation, it is clear that when stream water values are plotted on a more appropriate scale, significant variations do occur. Figure 3 shows how the $\delta^{18}\text{O}$ levels in the Allt a' Mharcaidh varied over the sampling period in relation to stream flows. It is clear from this that streamflows can be viewed as a very stable baseflow end member, which mixes with a seasonally variable stormflow end member. In winter this end member is generally characterized by relatively low $\delta^{18}\text{O}$ values in stream water, particularly when snowmelt events occur (generally in March–April). In contrast, during the summer, more enriched storm runoff predominates, albeit in events that are generally relatively small. Conceptually this is consistent with a well-mixed groundwater store providing baseflows from the catchment, whilst storm runoff sources are more responsive to recent precipitation.

Use of oxygen-18 isotopes for seasonal analysis and estimating residence times

Figure 4 shows the results of sine wave regression analysis to fit curves to seasonal variation in isotopic signatures for the 1996–1997 hydrological year. The differences in the amplitude of different curves and the timing of phase shifts can be used to

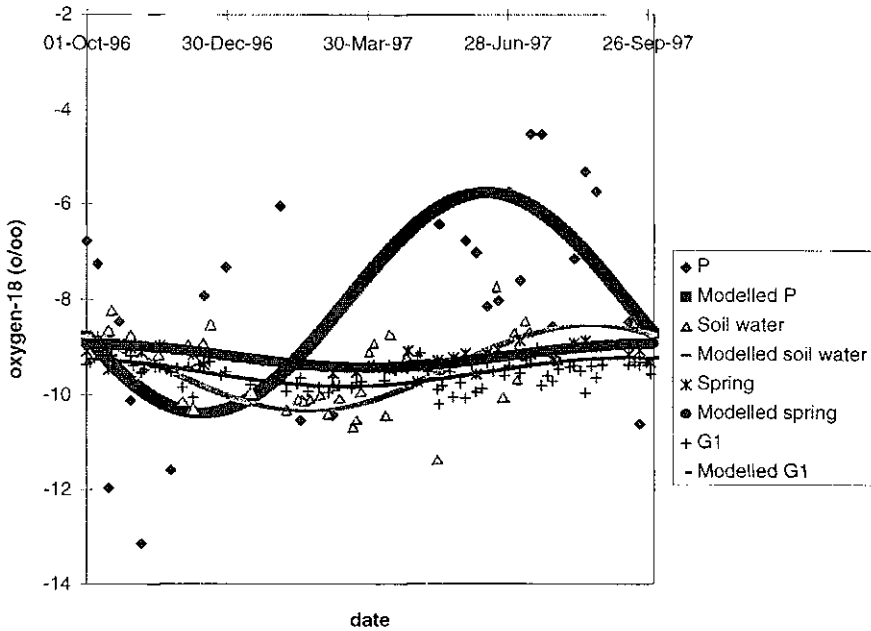


Fig. 4 Fitted regression models to precipitation, soil water, spring water and baseflow in the 1996–1997 hydrological year.

examine patterns of water movement and estimate mean residence times of different catchment source waters (DeWalle *et al.*, 1997). The clear seasonality of precipitation inputs is apparent when rain and snow data are combined to show a pattern of low oxygen-18 values in winter snow and more enriched water in the summer. The damped and lagged response of soil water to these inputs is also clear, whilst groundwater and baseflow damping results in curves of very low amplitude.

Residence times of soil water, spring waters and baseflows were estimated using the model described by DeWalle *et al.* (1997) for well mixed reservoirs. Although the model is obviously a first approximation only, it was developed for unconfined aquifers and the behaviour of soil water, spring water and baseflows in the Allt a' Mharcaidh can all reasonably be viewed as unconfined aquifers. The preliminary analysis for the 1996–1997 hydrological year shows that soil water has a mean residence time of <180 days, whilst spring water is around 2.75 years and baseflows are in excess of 5 years (Table 1). This implies that the superficial drift deposits in the catchment act as substantial aquifers that are able to mix input waters and sustain flows for prolonged periods.

Table 1 Mean oxygen-18 levels, modelled amplitude of seasonal regression model and approximate mean residence times in various stores in the Allt a' Mharcaidh.

| | Mean $\delta^{18}\text{O}$ (‰) | Amplitude $\delta^{18}\text{O}$ (‰) | Mean residence time (year^{-1}) |
|---------------|--------------------------------|-------------------------------------|--|
| Soil water | -9.45 | 0.807 | <0.5 |
| Spring water | -9.59 | 0.138 | 2.75 |
| Baseflow (G1) | -9.39 | 0.091 | >5 |
| G1 | -9.58 | 0.192 | 2 |

DISCUSSION

The analysis of longer-term isotope data in the Allt a' Mharcaidh catchment has complemented both hydrometric (Jenkins *et al.*, 1994; Wheater *et al.*, 1993) and short-term tracer studies (Jenkins *et al.*, 1994) in providing insight into hydrological processes. In contrast to traditional views of upland catchments in the British Isles being characterized by flashy hydrological responses from saturated soils and impermeable bedrock, it is clear that catchments like the Allt a' Mharcaidh have large stores of water in the bedrock, glacial drift and deep peat soils. The isotope results confirm indications from earlier hydrogeochemical analysis which suggested that these large stores allow extremely effective mixing at the catchment scale and thus produce a very constant oxygen-18 signature in baseflows (Soulsby *et al.*, 1998). Nevertheless, it is clear that a responsive hydrological store, probably in the saturated peat soils that characterize the valley bottom areas, has a variable isotopic signature that evolves on a seasonal basis in response to precipitation inputs. Tracer experiments during individual storm events indicate that "new" water in rainfall and snowmelt events mainly displaces "old" pre-event water from saturated and near-saturated source areas in the catchment soils, though a limited amount of "new" water contributes to the storm hydrograph (Jenkins *et al.*, 1994; Soulsby *et al.*, 1997).

Conceptually, the view of catchment behaviour emerging from the isotopic studies lends itself to the application of open-ended mixing techniques as advocated by Harris *et al.* (1995). The relative contribution of water from these two main stores, plus at times the addition of precipitation (event water) at high flows can be modelled using isotope behaviour as a basis for hydrograph separation with open-ended end member mixing analysis (EMMA). The utility of this approach is that it would allow an independent check that the structure of conceptual models and any numerical models to simulate catchment hydrology are correct (Wheater & Beck, 1995). This has obvious advantages when numerical models are being used to simulate the effects of environmental change (Neal, 1997).

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