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## Response of emergent behaviour in headwater catchments to environmental change

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Emergent behaviour of hydrological processes at the catchment scale often results in relatively simple and predictable functional characteristics which are underpinned by heterogeneous, complex processes at the small scale. It is unclear how such small-scale processes are affected by long- and short-term perturbations in forcing factors affected by various environmental changes. This leads to uncertainty in how emergent behaviour will change and how hydrology and hydrochemistry will respond at the catchment scale. A powerful resource in improving predictions of such responses is applying advanced statistical analysis to long-term data sets of conservative tracers, particularly in gauged catchments that are subject to marked environmental change. Changes in tracer behaviour can provide an integrated insight into the emergent response of system functioning and its non-linear characteristics.

In this paper, we present the analysis of long-term tracer data collected since 1982 in 2 small (ca. 1km2) experimental catchments in the Scottish highlands. These have been affected by marked change and variability in driving variables of climate, land cover and rainfall chemistry: Annual rainfall ranged between 1490 and 2500mm and an average \$1\deg\$C increase in air temperatures was observed over the monitoring period. In addition, forestry operations resulted in 70\% of each catchment being clear felled. Finally, air pollution legislation targeting acid emissions has improved the quality of precipitation, resulting in a marked reduction in acid deposition. Long-term (20 year, weekly) time-series analyses of two tracers are used to assess changes in emergent catchment behaviour. Chloride input-output time series are analysed using a range of residence time models which highlighted non-stationarity in the catchment mean residence times (which ranged between 2-11 months for individual years) and corresponding residence time distributions. At the catchments scale these were driven mainly by climatic variability and little altered by forestry. The acid neutralising capacity (ANC) of stream waters was also used to examine how the composition and contribution of different hydrological sources changed over the study period in response to reduced climatic variability, forestry and acid deposition. Non-linear curve fitting methods allowed the temporal changes in concentration-discharge relationships to be sufficiently well described to facilitate chemically-based hydrograph separation. This allowed temporal differences in catchment-scale hydrological source contributions (specifically groundwater) to be related, mainly to climatic variability. Impacts of forestry operations were stochastic and depended on the prevailing climatic conditions.