Geophysical Research Abstracts
Vol. 12, EGU2010-6936, 2010
EGU General Assembly 2010

Catchment dynamics at Plynlimon, Wales, revealed by high-frequency, long-term time series of tracers spanning the periodic table

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Catchment tracer studies have typically suffered from a stark mismatch of measurement timescales: water fluxes are typically measured sub-hourly, but their chemical signatures are typically sampled only weekly or monthly. More intensive measurement campaigns usually last only for short periods, such as individual storm cycles. At the Plynlimon catchment in mid-Wales, however, precipitation and streamflow have now been sampled every seven hours for nearly two years, and analyzed for water isotopes and more than 40 chemical tracers spanning the periodic table.

Here we explore these unique tracer time series, and compare them to longer-term ($\sim$20 years) but less frequently sampled (weekly) hydrochemical data from the same catchment. The high-frequency sampling reveals clear diurnal cycles in many chemical species, including some that are not normally thought to be biologically controlled. Passive tracers such as chloride and water isotopes are very strongly damped in streamflow relative to precipitation, implying that the catchment stores and mixes volumes of water that are much larger than individual storms, on timescales that are much longer than the intervals between events. However, other chemical species show strong coupling to streamflow on timescales of hours, implying that the catchment can rapidly re-set the chemical signature of "old water" in response to changes in the flow regime. The implications of these observations for catchment flowpaths, runoff generation, and biogeochemical processes will be discussed.