



Addressing the Old Water Paradox using tritium

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The paradox that much of the water that contributes to streams during high flow events appears to be derived from relatively old stores in catchments has been of interest to hydrogeologists for several decades. It is a common observation that stream chemistry varies less than would be expected if simple dilution of groundwater inflows by event water occurred during storm events. However, it is not clear to what extent this observation reflects displacement of water from the soils or the regolith vs. enhanced discharge of older groundwater into the stream. Here we use tritium in conjunction with major ion and stable isotope tracers to assess the sources of water in high flow events in streams in southeast Australia.

The concentrations of most of the major ions and EC values either remained relatively constant during the high flow events or displayed non-systematic variations with respect to flow. Oxygen isotopes do vary systematically during the events, but the magnitude of the variation is $<1\%$. By contrast, there is a notable systematic increase in the nitrate concentrations and a decrease in silica concentrations during the events. Tritium activities increased from 1.4 to 1.5 TU to up to 2.4 TU close to the peak in streamflow and then decline over several days to pre-high flow levels. The peak tritium activities in the stream are lower than the tritium activity of the rainfall that generated the high flow events (2.7 to 2.8 TU) but within the range of tritium activities commonly recorded in soil water in southeast Australia (2.0 to 2.6 TU).

The combined geochemical data imply that there is significant input from water stores other than groundwater during the high flow events. This is most likely to include a significant component of water displaced from the soils or regolith that typically has a residence time of 1 to 5 years. The major ion geochemistry of this water, especially its nitrate concentrations, is distinct from both groundwater and rainfall reflecting biogeochemical reactions in the soil zone/regolith. More generally, this study illustrates that since catchments contain multiple stores of water, including intermediate stores such as soil water, interflow, and water in the regolith, a multi-tracer approach is required to apportion the contribution of water from these stores during high flow events. Most of the major ions and EC were not useful in determining the changing water stores and the variation in stable isotopes was minor. Tritium provides the opportunity to directly assess how the average residence time of water varies across the flow event and through this address some aspects of the old water paradox.