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Isotope Tracers in Hydrology

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A major uncertainty in hydrologic and chemical modeling of watersheds has been the quantification of the contributions of water and solutes from various hydrologic pathways. Hydrologic models exist that can reproduce the timing and quantity of the hydrograph, but when chemical data are coupled with these physical models, they do not accurately reflect the streamwater chemistry. Therefore, it has been concluded that either the hydrologic pathways are represented inaccurately in the models or the processes affecting the water chemistry are not well understood.

Isotope tracers have been used to address these concerns in a wide variety of climatic and hydrogeologic environments. Isotope hydrograph separations determined by simple two-component, conservative-mixing models have shown repeatedly that streamflow generated during rainfall or snowmelt is supplied largely by water stored in the catchment prior to the event, but with some mix of event and pre-event water. Nevertheless, considerable debate still surrounds the processes responsible for rapid contributions of "old water" to channel stormflow, whether isotope tracers actually behave conservatively, whether the spatial and temporal variation in the compositions of water components are negligible, or whether simple mass-balance models realistically portray catchment hydrology.

To provide a forum for a critical evaluation of the use of isotope tracers in catchment hydrology, a special session of AGU's 1991 Fall Meeting in San Francisco, "Evaluation of Streamflow Generation Using Isotope Techniques," was convened. It was organized and co-chaired by Jeff McDonnell and Carol Kendall.

Two invited papers opened the oral session. M. Sklash (University of Windsor) provided a thorough review of environmental isotope studies of runoff generation and the simple mass-balance approach. He then outlined some difficulties associated with the simple two-component approach and new sensitivity analyses to determine the effectiveness of appropriate approaches. J. Buttle (Trent University) presented the second invited paper and summarized the five major mechanisms for rapid delivery of pre-event water to stream channels, including translatory flow, macropore flow, groundwater ridging, extension of saturated conditions in more conductive near-surface layers, and return flow. In addition to commenting on the roles of these different mechanisms in different environments, Buttle advocated more complete integration of environmental isotope studies with the appropriate hydro-metric measurements than has been achieved previously.

C. Kendall (U.S. Geological Survey) and associates compared a unit hydrograph model with hydrograph separations made using  $\delta^{18}\text{O}$ , Si, and Cl at a small artificial catchment in China and found that almost all the flow was quickflow, which the  $\delta^{18}\text{O}$  values indicated was mainly new water. Although the relative amounts of quick and slow flow closely matched the amounts of new and old water determined with  $\delta^{18}\text{O}$ , the Si and Cl separations, although similar, both indicated much larger old-water contributions to flow. J. Dowd (Polytechnic South-west, U.K.) and associates investigated the representativeness of lysimeter samples by adding tracers to intact soil cores and then comparing the compositions of lysimeter samples and matrix water. Lysimeter tracers to the applied concentrations, differed from the matrix waters, which were similar to the initial soil water. P. Addison and associates (Polytechnic Southwest, U.K.) presented results of an isotope tracer experiment in mole drains on a drained grassland soil in Britain, highlighting implications for the old/new-water controversy. They showed that the  $\delta^{18}\text{O}$  composition of drainage water was similar to the background concentration in the soil. This result led them to assume that conventional explanations for large amounts of displaced old water relative to new water were not sustainable for their system.

L. Cooper (Oak Ridge National Laboratory) and associates combined [0012]1000c[00d4] the use of  $\delta^{18}\text{O}$  and physical measurements to monitor snowmelt and streamflow in an Arctic watershed. Their isotope work showed a much greater mixing of melt waters from snow and soil ice than was indicated by physical measurements, but it was also consistent with significant fractionation during snowmelt. The apparent fractionation included a complex pattern of preferential melt and refreezing, combined with evaporative effects. T. Bullen and C. Kendall (USGS) examined the use of  $\delta^{7}\text{Sr}/\delta^{86}\text{Sr}$  and  $\delta^{13}\text{C}$  as tracers of water flowpaths at two streams at Catoctin Mountain, Md. Both tracers showed rapid and highly correlated instream oscillations in composition, indicating deep and shallow flowpaths contribute from deep and shallow flowpaths contributing rapid changes in the amounts of water from deep and shallow flowpaths contributing to streamflow. Interstream differences

primarily reflect differences in the amounts of carbonic acid weathering in the watershed. D. Genereux and associates (Massachusetts Institute of Technology) presented information concerning the use of  $^{222}\text{Rn}$  and Ca as tracers in a three-component mixing-model for streamflow generation at the Walker Branch Watershed, Tenn. Their measurements of naturally occurring  $^{222}\text{Rn}$  and Ca suggest that a simple three-component mixing model is appropriate for streamflow generation over a wide variety of conditions. In this case, bedrock groundwater was distinguished from the two soil end-members on the basis of its high Ca content, and  $^{222}\text{Rn}$  was used to distinguish between unsaturated zone water (low  $^{222}\text{Rn}$ ) and soil groundwater (high  $^{222}\text{Rn}$ ). R. Bassett and associates (University of Arizona) ended the oral session with a look at isotopic and chemical indicators of flow pathways at a field site in Arizona in fractured unsaturated tuff. The work focused on the relations among flowpath, isotopic signature, travel time, fracture recharge, perched water zones, and surface drainage. Isotope tracing revealed the presence of two interconnected flow systems of fluid entering an ore haulage tunnel of a copper mine.

Poster presentations included several interesting summaries of isotopic research. D. Burns (USGS) examined the use of  $\delta^{18}\text{O}$  composition of stream water to determine sources of peak flow in two Adirondack, N.Y., watersheds. Both soil and groundwater showed large spatial variability in  $\delta^{18}\text{O}$  signatures. He showed that meltwater events contained large amounts of old water (55-95% of peak flow); different amounts would be calculated if base flow rather than groundwater had been used as the "old" end-member. K. Ellins and associates (University of Florida) presented work demonstrating the use of  $^{222}\text{Rn}$  and introduced  $\delta^{18}\text{O}$  to determine groundwater gains and streamflow losses along stream reaches in karst terrain in central Florida. They demonstrated that  $^{222}\text{Rn}$  is useful for mass-balance separations of streamflow components, provided that the concentration in groundwater is known and the gas transfer rate from the stream to the atmosphere is measured to correct for loss of  $^{222}\text{Rn}$  from the stream. M. Hinton and associates (University of Waterloo) examined groundwater contributions to a headwater stream in Ontario using isotopic, chemical, and physical measurements. Use of both  $\delta^{18}\text{O}$  and Si showed that old-water contributions to peak flow were high (40-85%). Because large spatial variations in Si concentration were observed in groundwater, they advocated the use of a three-component model with shallow and deep groundwater sources. Physical measurement of groundwater flux could not account for their observed old-water volumes in the stream, due in part to underestimation of old-water flux through highly conductive shallow soil horizons. K. Rice and O. Bricker (USGS) presented  $\delta\text{D}$  and  $\delta^{18}\text{O}$  data from Catoctin Mountain in north central Maryland. They showed that soil water was an integrant of more than one storm, indicating ex-

tensive mixing in the unsaturated zone. Although minor spatial variation in soil-water isotopic composition was observed, soil-water chemistry was spatially variable, indicating chemical reactions during unsaturated flow. J. Waddington and N. Roulet (York University) examined groundwater-surface water mixing during storms for a small wetland-dominated watershed. Although saturation overland flow appeared to dominate runoff production,  $\delta^{18}\text{O}$  and LiBr tracers indicated that prestorm water dominated stormflow during artificial sprinkling events. The apparent dichotomy was resolved by rapid mixing of rainwater and emerging groundwater. D. Wenner and associates (University of Georgia) investigated the changes in the  $\delta^{18}\text{O}$  content of recharge waters in Georgia. Although the rain was variable in isotopic composition, this variability was significantly dampened in shallow soil waters due to mixing between new rain and older immobile water. Waters collected from zero-tension lysimeters were intermediate in composition between matrix water and tension lysimeter waters.

The underlying theme of most of the pre-

sentations was that the isotopic compositions of rain, throughfall, soil water, and groundwater are commonly variable in time and space. The general consensus was that if such variability is significant at the catchment scale, then simple two- or three-component, constant-composition end-member mixing models (that is, the "classic" isotope hydrograph-separation technique) may not provide realistic interpretations of the system hydrology. The various presentations provided novel ways of confirming or refining hydrologic models derived largely from oxygen and hydrogen isotope data by combining these data with other approaches, including applying tracers to the system, integrating isotope hydrograph models with appropriate hydrometric measurements, trying other isotope tracers (strontium, carbon, and radon isotopes), combining chemical and isotopic data, and using multicomponent, end-member mixing models.

A panel discussion at the end of the morning session raised several questions regarding the use of isotope tracers in hydrology. A major concern was how to separate old- and new-water components or gain information on the relative movement of wa-

ter along various flowpaths when the isotopic compositions of the water sources are so often variable in composition. Several presenters and audience participants are actively trying to demonstrate the nature of this variability at different spatial and temporal scales. Several unanswered questions were raised, including: Are multicomponent old-water models warranted; Why do  $\delta^{18}\text{O}$ , Cl, and Si separations often agree, despite the obvious lack of conservativeness displayed by Cl and Si in shallow and deep systems; Is there still a rationale for studies making the assumption that rainfall has a constant isotopic composition; and Have hydrologists ignored important evaporative effects in snow, soil water, and throughfall in small watershed tracing studies? We hope that many of the remaining questions will be addressed at the "Tracers in Hydrology" session at the International Association of Hydrological Sciences meeting to be convened July 11-23, 1993, in Yokohama, Japan.—*Jeffrey J. McDonnell, Utah State University, Logan; and Carol Kendall, U.S. Geological Survey, Menlo Park, Calif.*