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EFFECT OF INTRASTORM ISOTOPIC HETEROGENEITIES OF RAINFALL, SOIL WATER, AND GROUNDWATER ON RUNOFF MODELING

CAROL KENDALL
Water Resources Division, U.S. Geological Survey, Menlo Park, California 94025, USA
JEFFREY J. McDONNELL
Watershed Science Unit, Department of Forest Resources, Utah State University, Logan, Utah 84322, USA

ABSTRACT Isotope hydrograph separations determined by simple 2-component conservative-mixing models have shown in a wide variety of climatic and hydrogeological environments that streamflow generated during rainfall or snowmelt is supplied largely by water stored in the catchment prior to the event, but with some combination of event and pre-event water. Nevertheless, considerable debate still surrounds the questions of whether spatial and temporal variations in the compositions of water components are negligible, and whether simple mass balance models realistically portray basin hydrology. Data from four study regions in the USA, New Zealand, and China provide examples of the spatial and temporal isotopic heterogeneity of rainfall, throughfall, soil water, and groundwater. In general, the smaller the catchment and the smaller the ground-water component, the greater the effect of spatial and temporal isotopic variability on modeling of runoff components. Implications for runoff modeling are discussed.

INTRODUCTION

The use of isotopic techniques in runoff studies requires several assumptions (Sklash & Farvolden, 1982):

1. Groundwater and baseflow can be characterized by a single constant isotopic composition.
2. Rain or snowmelt can be characterized by a single constant isotopic composition, or the variations are documented.
3. The isotopic composition of rain water is significantly different from that of groundwater/baseflow.
4. Contributions from soil water are negligible, or the isotopic composition is identical to that of groundwater.
5. Contributions from surface-water bodies (such as ponds) are negligible.

If these assumptions are valid, then one can write two mass balance equations for the composition of stormflow at any time, one for water flux and one for isotope flux:

$$Q_s = Q_n + Q_o \text{ and } Q_s\delta_s = Q_n\delta_n + Q_o\delta_o \tag{1}$$

where Q is streamflow; δ (Delta) is the D or ^{18}O content defined as $\delta = (Rx/Rs-1)/1000$, where Rx is the ratio of D/H or $^{18}O/^{16}O$ of the sample and Rs is the comparable ratio for the standard VSMOW; and the subscripts s, n, and o represent the stream, new rain, and old groundwater, respectively. These equations can then be solved for the amounts of stream water contributed by rain and groundwater (i.e., new versus old water).

The utility of these equations for any particular storm event is a function mainly of the magnitude of (δ_o - δ_n) relative to the analytical error, and the extent to which the aforementioned assumptions are indeed valid (Pearce *et al.*, 1986). Clearly the ratio of new to old water in streamflow are affected by many environmental parameters, such as soil thickness, ratio of rainfall rate to infiltration rate, steepness of the watershed slopes, vegetation, antecedent moisture conditions, lateral permeability of the soil, amount of macropores, and storage capacity of the catchment.

In the last decade, the validity of several of the simple assumptions for the use of the isotope hydrograph separation technique has been evaluated by a number of investigators, including Sklash & Farvolden (1979), Kennedy *et al.* (1986), Rodhe (1987), McDonnell *et al.* (1991), Bishop (1991) and McDonnell & Kendall (1992). Although none of these re-evaluations of the assumptions behind the use of the hydrograph separation method has caused any significant change in the basic conclusion of most isotope and chemical hydrograph studies to date--namely, that most stormflow is old water (Bishop, 1991)--there clearly is a need to address the potential effect of natural isotopic variability on the use of isotopes as tracers of water sources. This paper focuses on the question of how much spatial and temporal variability there can be in the isotopic compositions of new and old water in small catchments (basins), how this variability "violates" the above classic assumptions behind isotope hydrograph separations, and how this variability affects our ability to model how catchments "work". Examples are primarily drawn from four study regions (Maimai, New Zealand; Panola Mountain, Georgia and Huntsville, Alabama, USA; and the Hydrohill experimental catchment, Chuzhou, China).

VIOLATION OF ASSUMPTIONS

Intrastorm variability in rain and throughfall

Although it has long been realized that there are large variations in the isotopic composition of precipitation over short time scales (Dansgaard, 1953), there have been surprisingly few studies of **intrastorm** variations. Intrastorm rainfall compositions have been observed to vary by as much as 90‰ in δD at Maimai (McDonnell *et al.*, 1990), 16‰ in $\delta^{18}O$ in Pennsylvania, USA (Pionke & DeWalle, 1992) and 15‰ in $\delta^{18}O$ at Panola Mountain (Kendall, 1993). At Maimai, McDonnell (1989) examined seven rain events, where mean intrastorm variability of rainfall collected at 5 mm increments was -34‰ ± -27‰. Variations in sequential rainfall δD were strongly correlated with air mass trajectory. At Panola, all the winter convective storms studied showed monotonic decreases in isotopic composition during the storm, whereas summer frontal storms showed monotonic decreases only during intense rainfall; otherwise, all summer storms were characterized by oscillations in composition related to successive fronts.

Sequential throughfall samples at Panola were generally enriched in ^{18}O and D relative to sequential rain samples for the entire storm, especially at the end and for throughfall under coniferous canopy (Kendall, 1993). The isotopic composition of throughfall under deciduous trees, especially during the winter when the trees are bare, is usually similar to that of rain.

Spatial variability of rain and throughfall

As storms move across the continent, rain-out causes successive showers to become isotopically more depleted. Studies of the changes in the isotopic composition of rain with elevation are common but little is known about small-scale (<1 km^2) spatial variations during storms. Spatial variations in the $\delta^{18}O$ of event rainfall of up to 5‰ were observed in a 2500 km^2, 35-gauge network in Alabama. The $\delta^{18}O$ of rain appeared to be independent of rain amount and location. No correlations were found between isotopic composition and rainfall amount, sampling elevation, latitude or longitude for six monitored events. For example, a 25-mm event with rain intensity of 4.8 mm h^{-1} over 7 h, showed a 4.5 to 7.5‰ range in $\delta^{18}O$ over 17 active sampling locations.

Studies of fractionation of rain due to interception with the tree canopy are rare. Gat & Tzur (1967) estimated that enrichments in ^{18}O of recharge waters because of evaporation of rain water on tree canopy probably do not exceed 0.5‰. Saxena (1986) measured the amounts and $\delta^{18}O$ values of rain and throughfall during summer storms in a pine forest in Sweden and found that throughfall was generally enriched in ^{18}O by a few tenths of a permil relative to the original rain for interception losses of about 40%; however, a few storms showed comparable isotopic depletions. Kendall (1993) studied the spatial and intrastorm variability of $\delta^{18}O$ and δD of rain and throughfall for some 30 storms at Panola Mountain, and found that for an average interception loss of 15%, volume-weighted average throughfall was enriched by 0.5‰ in ^{18}O and 3‰ in D relative to rain collected in open areas. For almost all storms, throughfall was enriched relative to rain, with maximum observed enrichments for bulk event throughfall of 0.9‰ for $\delta^{18}O$ and 8.1‰ for δD. Therefore, the isotopic composition of rain collected in open areas at Panola is not representative of the actual recharge water in forested areas.

Site-specific differences in canopy density and micro-climate resulted in an average $\delta^{18}O$ spread of 0.5‰ among 32 throughfall collectors distributed over an area of 0.04 km^2 for the same storm, with a maximum range of 1.2‰. On average, there was a persistent 0.1‰ enrichment in ^{18}O of throughfall at conifer sites relative to deciduous sites, and throughfall at specific sites may be consistently enriched or depleted in ^{18}O by 0.1 to 0.2‰ relative to the average; however, on a storm by storm basis, the enrichments were erratic. Therefore, a single throughfall collector is inadequate to characterize the composition of intercepted water in forested areas. A better solution in mixed forests is to put out several collectors under different trees and combine the collected waters for isotopic analysis as is done by DeWalle *et al.* (1988). If only one small collector is to be used, putting it in the open and *correcting* for canopy effects rather than using a single collector under a tree is probably safer. This is most critical during summer storms when throughfall enrichments and/or depletions can be especially erratic.

Spatial and temporal variability in soil water and shallow groundwater

Intrastorm variability of soil water of up to 1.5‰ in $\delta^{18}O$ was observed during several storms at Panola and a 15‰ range in δD was seen during a single event at Maimai. Analysis of over 1000 water samples at Maimai (McDonnell *et al.*, 1991) showed a systematic trend in soil water composition in both downslope and downprofile directions. Multivariate cluster analysis also revealed three distinct soil water groupings with respect to soil depth and catchment position, indicating that the soil water reservoir is poorly mixed on the timescale of storm events.

The Hydrohill artificial catchment is an ideal location to study the development of isotopic heterogeneity in shallow groundwater because: (1) the catchment is very small (< 490 m^2); (2) there is only 1 m of silty loam above the cement aquiclude; (3) these soils drain rapidly between storms and no groundwater was present before the storm studied; and (4) there are 22 wells in this small catchment. For a 12-cm storm in July 1989, the newly developed groundwater showed considerable spatial and temporal variability in $\delta^{18}O$, with values ranging from -12‰ to -6‰; the average compositions of rain and prestorm soil water were -11.3‰ and -6‰, respectively. Thus, the percent of groundwater derived from pre-event soil water ranged from 0 to 100% at different times and locations.

To illustrate the spatial and temporal evolution of the isotopic compositions of groundwater during the storm, the $\delta^{18}O$ values for groundwaters collected at three times during the storm are contoured and plotted in Fig. 1. At the end of the storm, the $\delta^{18}O$ values of groundwater showed a 4‰ range in composition; hence, the soil waters at the start of the next storm would likely have a similar range of compositions. The range of compositions during the storm appears to be caused by the combined effects of intrastorm variation in rain $\delta^{18}O$ and spatial and temporal variability in subsurface *flowpaths* (i.e., because of the relative importance of downward displacement of prestorm water versus delivery of new water to the aquiclude via macropores (Kendall & Gu, 1992)).

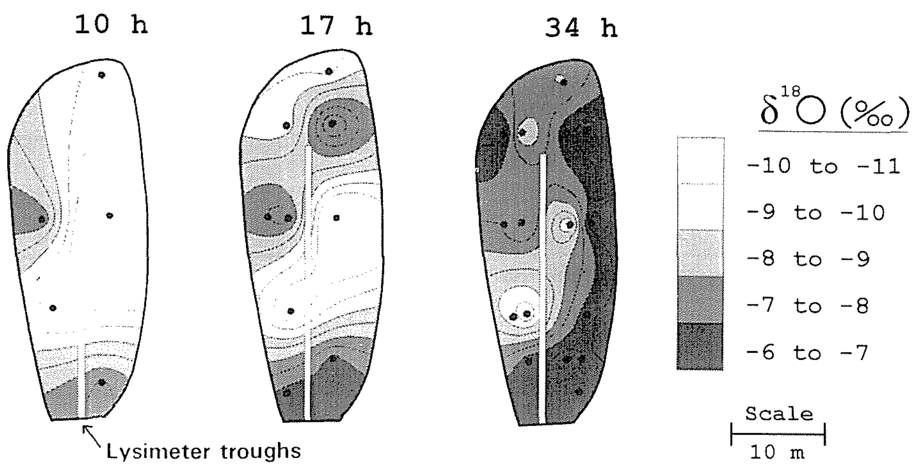

Fig. 1 Contour diagrams of $\delta^{18}O$ in groundwater at the Hydrohill experimental catchment, China, at three sampling times. The solid dots indicate where $\delta^{18}O$ values were available.

Surface water held in storage

If surface water bodies contribute significantly to basin runoff, 3-component models are required for hydrograph separations. Buttle & Sami (1992) show an example of a catchment showing rapid changes in snowmelt runoff despite relatively constant ratios of new and old water in streamflow. Use of a simple 2-component model resulted in hydrologically unrealistic fluctuations in discharges of pre-event water from the catchment. As an alternative explanation, they proposed that discharge of stored water from a wetlands with an isotopic composition intermediate between that of event and pre-event water could explain both the hydrological observations and the stream isotopic compositions.

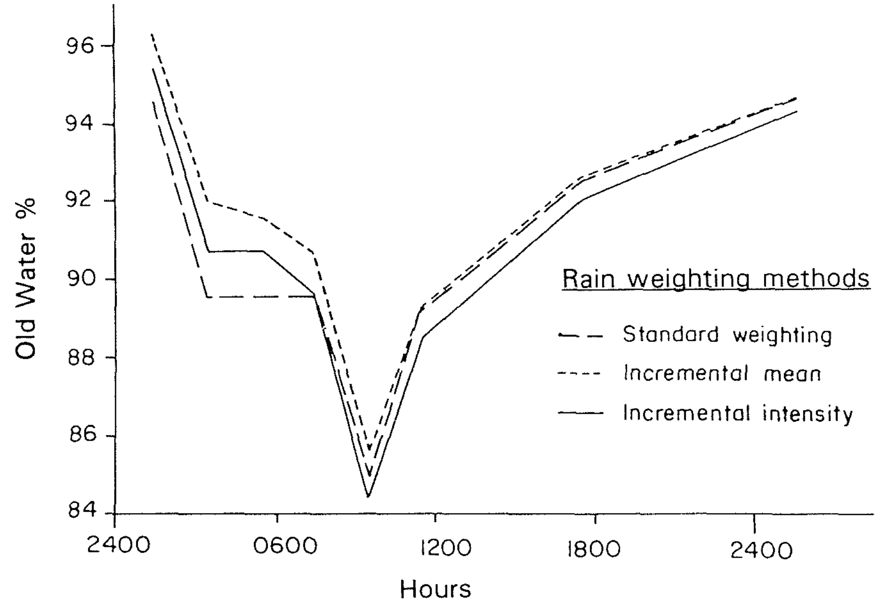

Fig. 2 Estimates of old water percentage at Maimai, New Zealand, using standard (bulk) weighting, incremental mean and incremental intensity weighting schemes (modified from McDonnell et al., 1990).

IMPLICATIONS FOR RUNOFF MODELING

Effect of different rainfall weighting methods

Different rainfall weighting methods can substantially affect estimates of new/old waters in storm runoff in basins with large contributions of new water (McDonnell *et al.*, 1990). Use of the bulk composition of rain for separations is unacceptable because it ignores the presence of rain variability that may be seen in runoff and because it includes the effect of late-storm rain prior to the time when this rain actually fell. Use of various types of cumulative running averages can cause 30% higher estimates of new water than use of the bulk value (Fig. 2); the discrepancies between the different weighting methods are greater on the rising limb of the hydrograph (McDonnell *et al.*, 1990).

The estimated amounts of new water in subsurface flow at Hydrohill (Kendall & Gu, 1992) during the first part of the storm, are higher by 5 to 20% if volume-weighted cumulative rain $\delta^{18}O$ values are used instead of sequential rain values (Fig. 3). After 15 h, when a period of low-intensity rain allowed soils to drain, amounts of new water are higher when sequential rain values are used instead. As noted by McDonnell *et al.* (1990), use of sequential rain values is probably the best choice in very responsive catchments (such as Hydrohill) or ones with high proportions of overland flow. When rain intensities are low and soils drain, current rain may not infiltrate very rapidly and thus use of the cumulative approach is probably more realistic.

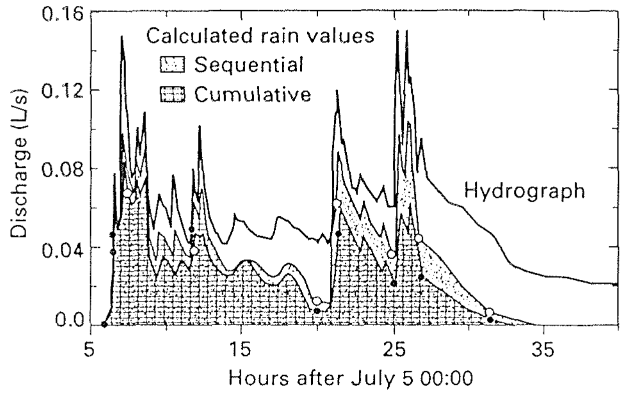

Fig. 3 Estimates of the percent of subsurface flow at the 100-cm lysimeter at Hydrohill that is derived from rain as calculated using sequential and cumulative weighting methods for rain (modified from Kendall & Gu, 1992).

Effect of pre-event old water selection

Eleven storms were monitored at Maimai in 1987 by McDonnell *et al.* (1991). They showed little new water (1 to 25%), and in many cases stream δD values following the onset of rainfall could not be distinguished from baseflow compositions. This situation resulted in some uncertainty associated with the hydrograph separation because the composition chosen for pre-storm had a large effect on the old/new ratio. A ±1‰ change in the δD of δ_o can cause as much as a 20% change in the estimated amount of pre-storm water at peak flow, although most estimates are within ±5% of the original values (McDonnell *et al.*, 1991); unrealistic values of the δ_o can result in calculated amounts of pre-storm water to be either less than 0 or greater than 100% of the streamflow.

Preferential storage of rain fractions

Preferential storage of different time-fractions of rain in the shallow soil-zone is very important because of the *large* amounts of rain potentially going into storage; for a 12-cm storm at Hydrohill, 45% of the total rain went into storage (Kendall, 1993). The amount going into storage varies during the storm, with almost 100% of the rain in the first 3 h of the storm (a total of about 20 mm of rain) going into storage before runoff begins. The volume-weighted $\delta^{18}O$ value of the first 20 mm of rain is enriched relative to the rest of the storm; if this water goes into storage and is not displaced to form discharge by later rain, the $\delta^{18}O$ values of the "residual" or mobile cumulative rain are 0.2 to 0.5‰ depleted relative to the comparable *total* cumulative rain $\delta^{18}O$ values. Incorporation of an apparent storage of initial isotopically enriched rain water for this storm resulted in a decrease in the calculated amounts of new water in total storm discharge by 3 to 7%.

Use of isotopic variability in runoff modeling

Although isotopic variability may complicate the interpretation of the relative amounts of new and old water during storms, this same variability can sometimes prove useful for tracing intrastorm infiltration or modeling of longer-term soil water and groundwater residence times. For example, the simple V-shaped pattern of rain $\delta^{18}O$ for a storm at Hydrohill allowed tracing the infiltration of successive fractions of rain into the subsurface and estimation of transit times despite multi-peak subsurface hydrographs (Kendall & Gu, 1992); if the intrastorm variation had been erratic, such detailed monitoring would not be possible.

Stewart & McDonnell (1991) made use of a nearly sinusoidal pattern of the rainfall δD variation during 24 storms over a 14-week period at the Maimai catchment. Taking advantage of this variable input signature, three approaches to determining mean soil water residence time were investigated: steady-state, non-steady state and dispersion models. The δD values of soil water collected from 11 suction lysimeters over a 14-week period were compared with those of rainfall for the same period. The δD variations in the suction lysimeters were considerably delayed and diminished compared with rainfall, indicating significant storage times and mixing with soil water. Soil water at shallow levels ($\approx$ 200 mm depth) in unsaturated soils was relatively responsive to fresh water input, but deeper water and water near the stream subject to occasional water-table rises showed much less variation. Steady-state and non-steady state exponential models gave similar mean residence times, ranging from 12 to more than 100 days for different locations. A dispersion model yielded the most accurate mean residence times; 13 days for shallow soil, 42 days for soil at 400 mm depth and 63 days for soil at 800 mm depth near the stream. Capillary flow was important for the unsaturated shallow soil, while hydrodynamic dispersion (mixing) was dominant for the periodically saturated and the generally saturated soils.

REFERENCES

Bishop, K.H. (1991) *Episodic Increases in Stream Acidity, Catchment Flow Pathways and Hydrograph Separation*, Ph.D. Thesis, Univ. of Cambridge, Dept. Geol., Jesus College, Cambridge, 246 pp.

Buttle, J.M., & Sami, K. (1992) Testing the groundwater ridging hypothesis of streamflow generation during snowmelt in a forested catchment, *J. Hydrol.* **135**:53-72.

Buttle, J.M. (1993). Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins. *Prog. in Phys. Geog.*, in press.

Dansgaard, W. (1953) The abundance of O^{18} in atmospheric water and water vapour. *Tellus* **5**:461-469.

DeWalle, D.R., Swistock, B.R. & Sharpe, W.E. (1988) Three-component tracer model for stormflow on a small Appalachian forested catchment. *J. Hydrol.* **104**:301-310.

Gat, J.R. & Tzur, Y. (1967) Modification of the isotopic composition of rainwater by processes which occur before groundwater recharge. In: *Proc. 2nd IAEA Symposium on Isotopes in Hydrology*, 49-60, IAEA, Vienna.

Kendall, C. (1993) *Impact of Isotopic Heterogeneity in Shallow Systems on Modeling of Stormflow Generation.* Ph.D. Thesis, Dept. of Geol., Univ. of Maryland, USA, 390pp.

Kendall, C. & Gu, W. (1992) Development of isotopically heterogeneous infiltration waters in an artificial catchment in Chuzhou, China. In: *Isotope Techniques in Water Resources Development.* 61-73, IAEA, Vienna.

Kennedy, V.C., Kendall, C., Zellweger, G.W., Wyermann, T.A. & Avanzino, R.A. (1986) Determination of the components of stormflow using water chemistry and environmental isotopes, Mattole River Basin, California. *J. Hydrol.* **84**:107-140.

McDonnell, J.J. (1989) *The Age, Origin and Pathway of Subsurface Stormflow in a Steep, Humid Headwater Catchment.* Ph.D. Thesis, Dept. of Geog., Univ. of Canterbury, Christchurch, New Zealand, 270pp.

McDonnell, J.J. (1990) A rationale for old water discharge through macropores in a steep, humid catchment. *Wat. Resour. Res.* **26**:2821-2832.

McDonnell, J.J., Bonell, M., Stewart, M.K. & Pearce, A.J. (1990) Deuterium variations in storm rainfall: Implications for stream hydrograph separation. *Wat. Resour. Res.* **26**:455-458.

McDonnell, J.J. & Kendall, C. (1992) Stable isotopes in catchment hydrology. *EOS, Trans. Am. Geophys.Un.* **73**:260-261.

McDonnell, J.J., Stewart, M.K. & Owens, I.F. (1991) Effect of catchment-scale subsurface mixing on stream isotopic response. *Wat. Resour. Res.* **27**:3065-3073.

Pearce, A.J., Stewart, M.K. & Sklash, M.G. (1986) Storm runoff generation in humid headwater catchments 1. Where does the water come from? *Wat. Resour. Res.* **22**:1263-1272.

Pionke, H.B. & DeWalle, D.R. (1992) Intra- and inter-storm ^{18}O trends for selected rainstorms in Pennsylvania. *J. Hydrol.* **138**:131-143.

Rodhe, A. (1987) *The Origin of Stream Water Traced by Oxygen-18.* Ph.D.Thesis, Uppsala University, Sweden, Dept. Phys. Geog., Div. Hydrol. Rep Ser. A., No. 41, 260 pp.

Saxena, R.K. (1986) Estimation of canopy reservoir capacity and oxygen-18 fractionation in throughfall in a pine forest. *Nordic Hydrol.* **17**:251-260.

Sklash, M.G. & Farvolden, R.N. (1979) The role of groundwater in storm runoff. *J. Hydrol.* **43**:45-65.

Sklash, M.G. & Farvolden, R.N. (1982) The use of environmental isotopes in the study of high-runoff episodes in streams. In E.C.Perry, Jr. & C.W. Montgomery, eds., *Isotope Studies of Hydrologic Processes.* N. Ill. Univ. Press, Dekalb, Ill., 65-73.

Stewart, M.K. & McDonnell, J.J. (1991) Modeling baseflow soil water residence times from deuterium concentrations. *Wat. Resour. Res.* **27**:2681-2694.