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Deuterium Variations in Storm Rainfall: Implications for Stream Hydrograph Separation

J. J. McDONNELL,[1,2] M. BONELL,[3] M. K. STEWART,[4] AND A. J. PEARCE[5]

Isotopic variation in storm rainfall is an important consideration in hydrograph separation using the mass balance approach but is rarely considered when determining the accuracy of old water estimates. Study of a small watershed on the South Island of New Zealand in which new water is a major component of the storm hydrograph shows that, in addition to the within-storm isotopic variations themselves, rainfall weighting techniques may substantially influence estimates of old/new water as a function of both total runoff and total quick flow production. Two incremental approaches to rainfall weighting are presented. Results show that within-storm incremental weighting is better than the standard weighting technique, which imposes a total storm rainfall value exogenously on the mass balance equation.

1. INTRODUCTION

1.1. *Hydrograph Separations Based on Deuterium Concentrations*

Recent studies in humid temperate, moderate rainfall [*Fritz et al.*, 1976; *Sklash et al.*, 1976; *Sklash and Farvolden*, 1979; *Bottomley et al.*, 1984; *Kennedy et al.*, 1986], seasonally arid [*Turner et al.*, 1987], and high rainfall [*Pearce et al.*, 1986; *Sklash et al.*, 1986] environments have utilized the natural stable isotope variations (either deuterium (D) or oxygen 18 (^{18}O) in water to determine the "old" water (groundwater and soil water) versus "new" water (rainfall) components in storm runoff. Since oxygen 18 and deuterium concentrations are linearly related, they may be used interchangably. For the purpose of this study we have used deuterium concentrations only. Hydrograph separations are based on the simple mass balance equation:

$$Qo = [(Cs - Cn)/(Co - Cn)]Qs \quad (1)$$

$$Qn = Qs - Qo \quad (2)$$

where Q is the stream discharge and C expresses the deuterium or oxygen 18 concentration of stream s, the old water o, and the new water n. Deuterium concentrations are generally expressed as δ values which are per mil (‰) variations with respect to Standard Mean Ocean Water [*Craig*, 1961]. The use of equations (1) and (2) requires that old and new water have distinct isotopic signatures. Further assumptions usually made are that (1) old water (often identified as groundwater) has a constant isotopic composition, which is the same as that of base flow immediately preceding the runoff event, and (2) new water (rainfall generating the event) can be characterized by the isotopic composition of the bulked storm rainfall.

Limitations of both of the latter assumptions have been recognized. For example, the effect of including vadose water contributions in the old water component of streamflow is discussed by *Kennedy et al.* [1986]. Although previous authors have been aware that considerable variations of the isotopic composition of rainfall can occur, no previous attempts have been made to account for such variations in isotopic separation studies of individual storm events. We present alternative weighting techniques for incrementally collected storm rainfall in order to increase awareness of rainfall isotopic variations and the applicability of different weighting techniques for varying hydrological situations. These techniques are applied to isotopic data from a small New Zealand catchment where new water dominates the storm hydrograph.

1.2. *Potential Problems of δD Rain Variations*

Large variations in the isotopic compositions of precipitation over short periods of time (hours or days) at individual locations are commonly observed. Factors influencing rainfall isotopic compositions are temperature of condensation [e.g., *Dansgaard*, 1964; *Hartley*, 1981], origin of air mass vapor [*Gat and Dansgaard*, 1972], and evaporation and isotopic exchange between falling raindrops and surrounding water vapor [*Ehhalt et al.*, 1963; *Stewart*, 1975]. Recently, *Heathcote and Lloyd* [1986] observed large variations in rainfall isotopic composition on a time scale of a few days, which showed no seasonal dependence nor any clear relationship with daily mean air temperature. Fractionally collected rainwater was also analyzed by *Matsuo and Friedman* [1967], who showed that storm rainfall isotopic contents varied with time, especially at the beginning of showers when the precipitation intensity is low. Constancy of the isotopic composition was observed only during high-intensity rainfall.

In most storm isotopic separations, bulk storm rainfall is collected and analyzed to yield a single isotopic input value. When several rainfall samples have been collected during a storm, a weighted mean value for the storm rainfall has been computed as

$$\delta D = \sum_{i=1}^{n} Pi\delta i \Big/ \sum_{i=1}^{n} Pi \quad (3)$$

[1]Universities Space Research Association, NASA Marshall Space Flight Center, Earth Science and Applications Division, Huntsville, Alabama.
[2]On leave from Watershed Science Unit, Department of Forest Resources, Utah State University, Logan.
[3]Department of Geography, James Cook University of North Queensland, Townsville, Australia.
[4]Institute of Nuclear Sciences, Department of Scientific and Industrial Research, Lower Hutt, New Zealand.
[5]Forest Research Center, Christchurch, New Zealand.

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TABLE 1. Deuterium Variations for 5 mm Sequentially Collected Glendhu 2 Storm Rainfall, February 23, 1988

Time	δD, ‰
1040	−94.8
1235	−92.2
1320	−93.8
1400	−77.0
1455	−76.0
1545	−76.9
1645	−68.0
2030	−61.9

where Pi and δi denote fractionally collected precipitation depth and δ value, respectively. This weighted mean represents the average isotopic composition of the new water input to the catchment but does not address the within-storm isotopic variability or the time response of the catchment to new water.

2. METHODS

2.1. *Sequential Rainfall Sampler*

A modified version of a *Kennedy et al.* [1979] sequential rainfall sampler was used to sample discrete rainfall increments during individual storm events. Rain samples were collected using a 0.39-m-diameter plastic funnel connected to individual 300 and 600 ml sample bottles, representing 2.5 and 5.0 mm increments, respectively. Glass fittings were arranged such that each bottle was filled before rain flowed into the next bottle in the sequence. An air outlet tube prevented siphoning from bottle to bottle and eliminated any cross contamination within the sequence. A tipping bucket rain gauge was located within 1 m of the sequential sampler to enable sample volume to be related to rain intensity and time of rainfall burst.

Water samples were removed from the bottles within 1–3 days and analyzed for deuterium composition. Samples were housed in cool shaded areas in sealed full bottles to prevent any fractionation prior to analysis. Water samples for deuterium analysis were prepared by the zinc reduction method [*Stanley et al.*, 1984], and analyses were run on a V. G. Micromass 602 mass spectrometer.

2.2. *Additional Weighting Techniques*

The time or distribution of time required for rainfall incident on the catchment to reach the stream sampling point determines the appropriate weighting to be applied to the composition of fractionally collected rainfall during an event.

In addition to the standard mean weighting (equation (3)), two other weighting techniques were employed: incremental mean and incremental intensity mean. On the simplest level the incremental mean technique proposed is merely a refinement of the standard weighted mean and uses equation (3) to adjust δD so that the bulk composition of rainfall from the beginning of the event to the time of stream sampling (or to a specified time prior to sampling) is calculated. In this way, rain that has not yet fallen is excluded from the δD estimate, unlike the standard mean weighting approach which uses the bulk composition of rainfall for the entire storm. The incremental mean technique then removes one source of obvious error (inclusion or rainfall that has not yet fallen) but is not entirely correct, as rainfall falling at one time will most likely contribute more strongly to the streamflow than rainfall at other times. A good knowledge, however, of the runoff-generating mechanisms within a catchment would be required to predict the correct weighting required. On the other hand, a detailed study of the response of stream water to a strongly varying rainfall composition, on the proposed

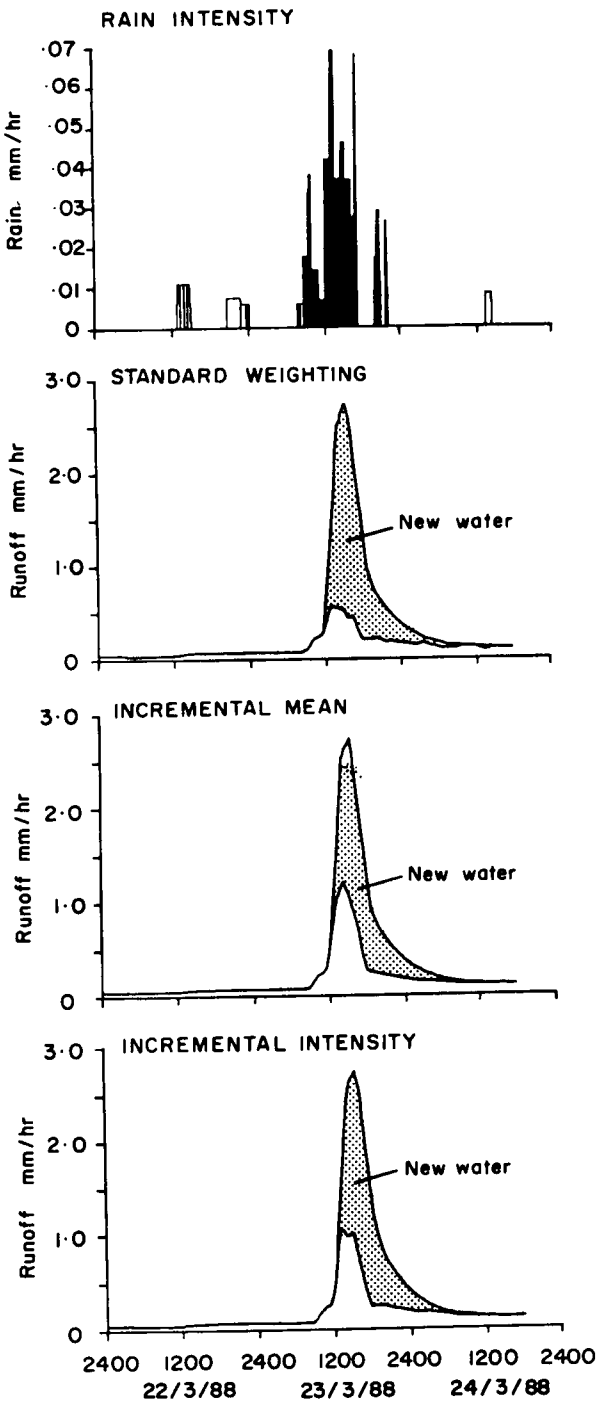

Fig. 1. Glendhu 2 response to the February 23, 1988, storm event showing effect of weighting techniques on hydrograph separations.

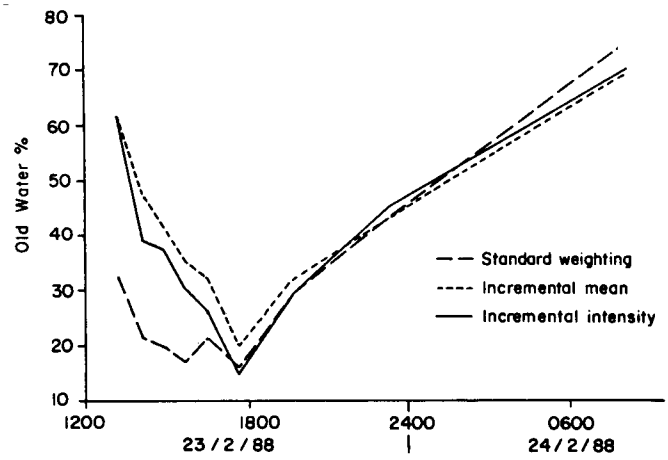

Fig. 2. Old water percentage estimates for the Glendhu 2 February 23, 1988, storm event.

lines, may reveal aspects of the catchment time response to new water.

Mechanisms by which new water finds its way to the event runoff include channel precipitation, saturation overland flow, Horton overland flow, and through flow (as defined by *Kirkby* [1978]). The catchment time response will be different for each mechanism. The incremental mean assumes that all of the rainfall during the event contributes equally to the streamflow. A second approach, the incremental intensity mean, includes another relevant factor, that is, the rainfall intensity. Higher intensity rainfall is more likely to cause rapid rise of water tables to the surface to produce saturation overland flow or to exceed infiltration capacities causing Hortonian overland flow, thereby allowing these flow path contributions to the stream hydrograph. The incremental intensity mean therefore includes a weighting according to rainfall intensity and is based on the rationale that higher intensity rain produces more runoff under many circumstances and thus should be weighted accordingly. The procedure is similar to the incremental mean but modifies equation (3) to give

$$\delta D = \sum_{i=1}^{n} Ii\delta i \Big/ \sum_{i=1}^{n} Ii \qquad (4)$$

where Ii is the average millimeters per hour rainfall intensity during the sampling increment. In this way the isotopic signatures of high intensity bursts assume a greater influence on the average storm isotopic weighting.

3. Results and Discussion

Weighting technique effects on storm hydrograph isotopic separation are presented for a small catchment on the South Island of New Zealand. Glendhu 2 is a moderately responsive catchment (310 ha) with rolling side slopes (average 28°) and wide concave valley bottoms. Annual precipitation is 1303 mm and quick flow production averages 30% of the total runoff and 20% of the total precipitation [*Pearce et al.*, 1984].

A 45.1-mm rain event on February 23, 1988, showed a 32.9‰ range in δD values (Table 1) with a weighted mean (equation (3)) of −80.3‰. Peak catchment specific discharge was 2.72 mm hr^{-1}, with the proportion of total runoff in the form of quick flow (QF/*R*) = 86.9%, and the quick flow response ratio (QF/*P*) = 35.2%. Hydrograph separations using the three weighted mean approaches are shown in Figure 1. Peak old water specific discharges for the standard, incremental mean, and incremental intensity were 0.56, 1.19, and 1.06 mm hr^{-1}, respectively. The percent old water versus time is shown in Figure 2 and clearly demonstrates the dependence on the method of rainfall weighting used. In this storm "relative to the standard weighting method" the amount of new water entering the stream was overestimated by up to 30%, with the highest differences being encountered during the rising limb of the hydrograph.

Large variations in rain δD, as shown above, are common across the South Island. In a similar study at Maimai, *McDonnell* [1989] reported an average within-storm rain δD range of 34‰ (standard deviation = 27) for 17 events (15–105-mm gross rain) monitored during 1987.

Tabulation of quick flow characteristics (Table 2) as a function of new water volumes shows clear differences in the ratio of new water to gross precipitation (*Qn*/*P*) and total quick flow (*Qn*/*QF*). Standard rainfall weighting produced 14.5 and 10.7% overestimates of new water volumes in quick flow against the incremental mean and incremental intensity approaches, respectively.

Less difference is found between calculations from incremental *Pi* and *Ii* in this event because of persistent low rain intensities of similar magnitude between increments. Greater differences may occur in high-rainfall areas such as tropical rain forests [*Bonell et al.*, 1981] or mid-latitude convective thunderstorm events. The differences that do occur in the Glendhu example are largest during the rising limb of the hydrograph. Each of the methods should and do merge toward a single value toward the end of the storm, once all the rainfall samples have been included into the cumulative mean.

Yet another rainfall "weighting" technique may be appropriate under certain conditions. For example, a heavy 10 min burst of rainfall may occur within a protracted low-intensity rain event, producing a large and rapid hydrograph response. If widespread saturation overland flow was occurring, as in the case of a semiwetland [e.g., *Jackson*, 1987] or a high rainfall, high-relief tropical rainforest catchment [e.g., *Bonell et al.*, 1981], only the 10-min burst could be realistically linked with the resulting sudden hydrograph rise. In this case, weighting rainfall to values that fell several hours previous to the intense burst or giving them any weighting at all would be unrealistic. Here again, if total storm rainfall was simply bulk collected and used in the mass balance separation, major errors could occur if rain varied isotopically.

4. Conclusions

Peak specific discharge of "new" water at Glendhu 2 for the February 23 storm is higher than most previously re-

TABLE 2. Weighting Technique Comparisons for the Glendhu 2 February 23, 1988, Storm Event

Method	*QF*, mm	*Qo*, mm	*Qn*, mm	*Qn*/*P*, percent	*Qn*/*QF*, percent
Standard	15.9	3.8	12.1	26.8	76.1
Incremental mean	15.9	6.1	9.8	21.7	61.6
Incremental intensity	15.9	5.5	10.4	23.1	65.4

ported values in other catchments. Details of the runoff production processes are given elsewhere [*Bonell et al.*, 1990]. Clearly, rainfall weighting techniques can make a large difference to old water computation if rainfall isotopic variability is high. Conclusions drawn from this note are

1. Deuterium concentration in storm rainfall can vary significantly and therefore should be sampled sequentially during storm events if hydrograph separation is to be conducted. Single measurements on the total event rainfall could conceal large variations in isotopic composition.

2. The standard weighting technique employed in most isotopic hydrograph separations is unrealistic if the rainfall composition varies because it uses rain isotopic signatures for the entire event for point separations within the event. Therefore old water estimates at any point before the end of the event are affected by the isotopic composition of rain that has not yet fallen, rendering the technique physically incorrect.

3. An incremental mean approach overcomes the above problem 2 by computing a running mean through an event and using this value in the mass balance separation.

4. The more difficult problem of determining the weighting that should be applied to the event rainfall to reproduce the isotopic composition of new water appearing in the stream requires knowledge of the time response of the catchment to new water. This depends on the nature of the catchment, the rainfall variation, etc. We suggest that the incremental mean technique is the most appropriate starting point in most situations. The incremental intensity mean approach is likely to be more useful in conditions of variable rainfall intensities, for example, mid-latitude continental areas or the humid tropics, where bursts of intense rainfall are interspersed with lower-intensity periods. Use of individual sequential values through an event (or a single value within the event) may be appropriate when a very high intensity burst is isolated within a protracted low-intensity period, particularly for a highly responsive catchment where saturation overland flow is produced over large portions of the watershed.

Finally, we do not suggest that these additional weighting techniques are the only ones to consider or that they solve specific hydrograph separation problems. We merely wish to highlight the variability in rainfall deuterium composition and its implication for hydrograph separation.

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M. Bonell, Department of Geography, James Cook University of North Queensland, Townsville, Queensland 4811, Australia.

J. J. McDonnell, Universities Space Research Association, NASA Marshall Space Flight Center, Earth Science and Applications Division, ES42, Huntsville, AL 35812.

A. J. Pearce, Forest Research Center, P.O. Box 31-011, Christchurch, New Zealand.

M. K. Stewart, Institute of Nuclear Sciences, Department of Scientific and Industrial Research, Private Bag, Lower Hutt, New Zealand.

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