

## **Hydrograph separations based on chemical and isotopic concentrations: a critical appraisal of published studies from New Zealand, North America and Europe**

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### **Abstract**

Chemical and isotopic hydrograph separations of stream discharge are commonly used to determine the fractions of old and new water contributing to streamflow. Isotope tracers ( $^{18}\text{O}$ ,  $^2\text{H}$ ) are assumed to be conservative, while chemical tracers (Cl, Si) are considered to be only quasi-conservative. Any differences between the old water fractions calculated from isotopic and chemical tracers in hydrograph separations are usually attributed to the quasi-conservative behavior of the chemical tracer. We compared old water fraction estimates calculated from both chemical and isotopic tracer separations from 11 published studies from New Zealand, North America and Europe. In studies in which the old water fraction estimates differed between tracers, we attempted to relate the differences to underlying physical or hydrological characteristics of the catchments. Sixteen of the 23 reviewed rain events showed good agreement (<10% difference) between the old water fraction estimates using the two types of tracers in the two-component hydrograph separation model. Four separations were unrealistic (>100% old water fraction) and the remaining three did not agree (>10% difference). The differences between old water fractions estimated by different tracers showed no clear relationships with common catchment features. The differences in old water fractions between tracers could be accounted for by considering analytical uncertainty.

## Introduction

Chemical and isotopic hydrograph separations of stream discharge are commonly used to determine the fractions of old and new water contributing to streamflow. It is often assumed that while isotope tracers ( $^{18}\text{O}$ ,  $^2\text{H}$ ) are conservative, chemical tracers (Cl, Si) are only quasi-conservative. Stable isotope tracers (e.g.  $^{18}\text{O}$ ,  $^2\text{H}$ ) are known to be conservative, and changes in concentration within a hillslope reach occur as a result of mixing (Pearce, 1990). If a chemical tracer is truly conservative, the old water fraction calculated using a two-component storm hydrograph separation (Sklash and Farvolden, 1979) should be the same as that determined from the isotope tracer. Previously, any differences between these estimates have been attributed to geochemical non-conservative behavior (Hooper and Shoemaker, 1986). Notwithstanding, few if any studies have explicitly addressed this problem. The only study to include a rigorous tracer comparison was published by Wels *et al.* (1991a). They found that, for four hydrograph separations using Si and  $^{18}\text{O}$ , there was no significant difference in the estimated old/new water fractions. Alternatively, Pionke *et al.* (1993) suggested that the differences between the old water fractions computed from  $^{18}\text{O}$  and Si that are sometimes explained on a geochemical basis, may be an artifact of the computational method, because of the ranges of tracer concentrations and end-member signatures.

Most hydrograph separations involve the standard two-component model of Sklash and Farvolden (1979), in which the stream water is separated into old (pre-event) and new (event) water components. More recently, soil water has been recognized to be distinct from groundwater and an important contributor to streamflow. This has led to the use of a three-component hydrograph separation model (DeWalle *et al.*, 1988; McDonnell *et al.*, 1991; Pionke *et al.*, 1993) that separates the old water fraction into groundwater and soil water. Ogunkoya and Jenkins (1993) have used a similar three-component separation model employing two tracers. This approach requires that soil water and groundwater are chemically and/or isotopically different.

Whilst several studies have used conservative chemical and isotopic tracers interchangeably in the various two- and three-component models, few attempts have been made to synthesize and compare results from varied catchments. Furthermore, little attempt has been made to relate the separation results to physical and hydrological factors. In this study, we examined published hydrograph separations using different tracers from catchments in New Zealand, North America and Europe. We compared

the old water fraction estimates from both chemical and isotopic tracer separations. In studies where these old water estimates differed, we related the differences to the underlying physical or hydrological characteristics of the catchment. Six factors were examined for each of the reviewed catchments: (1) physical characteristics of the catchment; (2) seasonality; (3) type of runoff event; (4) characteristics of the event (quantity, intensity, duration); (5) differences in behavior of the chemical tracers within the catchment; and (6) the validity of the assumptions used.

## Catchments

We surveyed the literature and found 11 studies where authors reported both chemical and isotopic concentration data or graphical separations. The catchments are mostly small headwater drainages of <100 ha—however some range in size from 700–60,000 ha. They are located in New Zealand, North America and Europe and span a broad range of climatic and hydrogeological conditions (Table 1).

### New Zealand

The Maimai catchment is located in the South Island of New Zealand. The watershed is 3.8 ha, with steep, highly incised side slopes. Soils are generally less than 1 m deep and overlie a firmly compacted conglomerate. Annual rainfall is on the order of 2600 mm and evenly distributed throughout the year. Vegetation consists of regrowth *Pinus Radiata*, planted following a 1980 harvesting of the native beech and podocarp forest cover. Mosley (1979), Pearce *et al.* (1986), McDonnell *et al.* (1990) and McDonnell *et al.* (1991) have described catchment hydrology and soils.

### North America

Several study catchments in Canada were examined. The Wilson Creek Experimental Watershed is 2200 ha and underlain by Cretaceous shale (Fritz *et al.*, 1976). Hummocky glacial deposits of clay-loam till mantle the upper section of the watershed. The middle section has deeply dissected valleys and is differentiated from the upper section by the lack of glacial till. Vegetation is grass, willows and aspen. The lower section has gentle slopes and thick alluvial deposits. Most rainfall occurs during the summer months as heavy showers (e.g. 50 mm/hr). Average annual temperature is -1.1°C and seasonal variations exceed -40 and +35°C. The catchment has also been described in Schwartz (1970) and Bilozar (1972).

The Kenora watershed is 180 ha (Fritz *et al.*, 1976). The soils are

**Table 1** – Concentration data used for two-component separations.

Catchment	Ct		Co		Cn		Tracer Used	Reference
	Isotope (o/oo)	Chemical (mg/L)	Isotope (o/oo)	Chemical (mg/L)	Isotope (o/oo)	Chemical (mg/L)		
Kenora (Oct)	-10.7	4.2	-11.9	6.2	-8.7	0	<sup>18</sup> O, Si	Fritz <i>et al.</i> , 1976
Wilson Creek (Aug)	-16	15	-14.5	22	-19	0.04	<sup>18</sup> O, Na	Fritz <i>et al.</i> , 1976
Mattole (Jan)	-35	2.1	-42	3.2	-19.5	0.02	<sup>2</sup> H, Cl	Kennedy <i>et al.</i> , 1986
Mattole (Jan)	-5.9	8.6	-6.8	11.5	-3.1	0	<sup>18</sup> O, Si	Kennedy <i>et al.</i> , 1986
Maimai (Nov 13 – M8)	-39	3	-38	3.4	-60.7	0.32	<sup>2</sup> H, Cl	McDonnell <i>et al.</i> , 1991
Maimai (Nov 26 – Pit 5)	-40	3.9	-39	4	-65	1.27	<sup>2</sup> H, Cl	McDonnell <i>et al.</i> , 1991
Maimai (Nov 26 – Pit A)	-45	8	-37	6.25	-65	1.27	<sup>2</sup> H, Cl	McDonnell <i>et al.</i> , 1991
Les Cloutasses (Jul 30)	-4.7	0.6	-7	1.3	-2.8	0.01	<sup>18</sup> O, Si	Durand <i>et al.</i> , 1993
Les Cloutasses (Jul 31) <sup>1</sup>	-	-	-	-	-	-	<sup>18</sup> O, Si	Durand <i>et al.</i> , 1993
La Sapine (Jul 30)	-6.2	1.1	-7.5	1.7	-2.8	0.01	<sup>18</sup> O, Si	Durand <i>et al.</i> , 1993
La Sapine (Jul 31) <sup>1</sup>	-	-	-	-	-	-	<sup>18</sup> O, Si	Durand <i>et al.</i> , 1993
Mahantango Cr (May 4)	-7.75	2.3	-7.8	3	-8.3	0	<sup>18</sup> O, Si	Pionke <i>et al.</i> , 1993
Mahantango Cr (May 10)	-9	1.7	-8.2	2.5	-11.15	0	<sup>18</sup> O, Si	Pionke <i>et al.</i> , 1993
Mahantango Cr (May 29)	-10.2	2.25	-8.2	2.6	-18	0.1	<sup>18</sup> O, Si	Pionke <i>et al.</i> , 1993
Mahantango Cr (Jun 18)	-4.3	1.3	-8	2.9	-5.5	0	<sup>18</sup> O, Si	Pionke <i>et al.</i> , 1993
Shaver Hollow (Jun)	-7	23	-7.5	27	-8.3	1.4	<sup>18</sup> O, Cl	Bazemore <i>et al.</i> , 1994
Shaver Hollow (Nov)	-6.6	24	-7	25	-5.3	7	<sup>18</sup> O, Cl	Bazemore <i>et al.</i> , 1994
Mahantango Cr (Oct 19)	-8.1	2.1	-8	3.3	-10.5	0.06	<sup>18</sup> O, Si	DeWalle and Pionke, 1994
Mahantango Cr (Nov 9)	-8.32	2.65	-7.9	3.5	-9.85	0.05	<sup>18</sup> O, Si	DeWalle and Pionke, 1994
Mahantango Cr (Nov 16)	-9	1.1	-8.2	3.2	-8.25	0.05	<sup>18</sup> O, Si	DeWalle and Pionke, 1994
Harp Lake 4-21 (Jun)	-9.5	3.6	-12.43	7.86	-5.78	0.66	<sup>18</sup> O, Si	Hinton <i>et al.</i> , 1994
Harp Lake 4-21 (Oct)	-10	5.68	-11.83	9.08	-6.43	0.66	<sup>18</sup> O, Si	Hinton <i>et al.</i> , 1994
Plastic -108 (May 16)	-10.3	2.5	-11.86	2.84	-5.45	0	<sup>2</sup> H, Si	Buttle <i>et al.</i> , 1997

<sup>1</sup> Concentration data not reported in the literature.

composed of sands, silts and clays of glacio-lacustrine origin, overlying Precambrian granitic bedrock. The average annual temperature is slightly above 0°C with an annual range of -20 to +22°C. Vegetation was a mature forest cover of jack pine, black spruce and white birch, until a large-scale forest fire occurred in 1974.

The Harp 4-21 catchment is 3.7 ha and is located within the Harp Lake catchment in the Muskoka-Haliburton region of central Ontario (Hinton *et al.*, 1994). Soils are Podzolic (predominantly sandy loams) overlying glacial tills. Annual precipitation is c. 1033 mm. Approximately two thirds of annual streamflow occurs during spring snowmelt. Lozano *et al.* (1987) and Hinton *et al.* (1993) provide the physical and chemical characteristics of the catchment.

The Plastic Lake basin 1-08 is 3.22 ha and is located on the Canadian Shield in south-central Ontario. The soils are thin, weakly developed orthic humo-ferric and orthic ferro-humic podzols. The soils overlie a sandy basal till and bedrock composed of granitic gneiss and amphibolite. Soil thickness is highly variable. Annual precipitation is c. 1100 mm (73% falling as rain). High surface runoff occurs during spring snow melt and autumn rains. Vegetation is dominated by white pine, eastern hemlock and white cedar, with some white birch, red oak and striped maple. The catchment has also been described in Wels *et al.* (1991b).

The Mahantango Creek catchment is 19.8 ha and located about 50 km northeast of Harrisburg, Pennsylvania (Pionke *et al.*, 1993; De Walle and Pionke, 1994). The soils are silt loams and contain fragipans and high water tables. The soils range in depth from 750 to 1500 mm and are deepest near streams. Annual precipitation is c. 1160 mm. Surface runoff occurs mostly in spring (April-June) and autumn (September-November). The Mahantango Creek watershed is predominantly agricultural, containing cropland, deciduous forest and permanent pasture.

The Mattole catchment is 62,000 ha and located in Humboldt and Mendicino counties, California (Kennedy *et al.*, 1986). Soils range from gravely to clay loam and overlie folded and faulted sedimentary rocks. The soils vary in depth but can extend to 3 m or more. Extensive logging and road building in the last 25 years have accelerated erosion in the basin. The catchment has low permeability and water-holding capacities. Annual precipitation c. 2340 mm, the bulk of which occurs in the months of November through March. Vegetation consists of grasslands, shrubs and trees.

The Shaver Hollow catchment is 8.2 ha and is located on the western face of the Blue Ridge in Shenandoah National Park, Virginia (Bazemore

*et al.*, 1994). Average slope of the catchment is 57%. Soils are sandy gravelly loam overlying weathered granitic rocks of the Pedlar Formation. Vegetation is a mixed-mesophytic second-growth oak-hickory forest.

## Europe

La Sapine (54 ha) and Les Cloutasses (81 ha) are neighboring catchments in Southern France. Annual precipitation is c. 1950 mm. Precipitation occurs mainly in spring and autumn, with very dry summers. La Sapine is covered with beech coppice and Les Cloutasses is a grassland area. A detailed description of the catchments can be found in Durand *et al.* (1991).

## Methods

The two-component hydrograph separation model is well-known (Pearce *et al.*, 1986):

$$Q_n = Q_t - Q_o \quad (1)$$

$$\frac{Q_o}{Q_t} = \frac{(C_t - C_n)}{(C_o - C_n)} \quad (2)$$

where  $Q_t$ ,  $Q_o$  and  $Q_n$  represent current streamflow, old water (stored subsurface water, including soil water and groundwater), and new water (rainfall or melt water) volumes respectively, and  $C_t$ ,  $C_o$  and  $C_n$  are the corresponding tracer concentrations.

The conditions for the use of environmental tracers in hydrograph separations are (Sklash and Farvolden, 1979): (1) the isotope and chemical content of the new water differs significantly from that of old water; (2) the new water maintains a constant isotopic and chemical content throughout the event or the change throughout the event can be accounted for; (3) groundwater and soil water (which together constitute old water) are chemically and isotopically equivalent, or the soil water contribution to streamflow is insignificant and; (4) surface storage contributes minimally to the runoff event. More recent work has identified additional conditions that must be met (Kennedy *et al.*, 1986; Maule and Stein, 1990), including: (5) no significant spatial variability in soil water or ground water tracer concentration; (6) infiltrating waters equilibrate rapidly; and (7) surface stormflow contains very little tracer.

End-member concentration data from the 11 published studies used in our two-component separations are shown in Table 1. The old water fraction is strongly influenced by the choice of component concentrations used (silica,  $O^{18}$ , etc.) in this model for both isotopes and chemical tracer. An attempt was made to treat all catchments uniformly so that the resulting old water fractions could be compared. The data extracted from the literature included values explicitly tabulated or given in the text and values determined from published graphs. The hydrograph separations and % old/new water values were calculated for peak discharges, because of the limitations of using published results.

Uncertainty was analyzed to determine the accuracy of the old water fraction calculated from the two-component model. This uncertainty analysis was then used to determine if the differences in the old water fraction calculated from the different tracers could be explained by analytical and/or sampling error. The approach of Genereux (1998) was used to calculate the uncertainty in the old water fraction:

$$|\Delta X| = \frac{1}{C_o - C_n} \sqrt{\Delta C_t^2 + \Delta C_n^2 + X^2 (\Delta C_o^2 + \Delta C_n^2)} \quad (3)$$

where:

- $C_o$  = old water concentration
- $C_n$  = new water concentration
- $C_t$  = current streamflow concentration
- $X$  = % old water fraction
- $\Delta C_o$  = error in old water concentration
- $\Delta C_n$  = error in new water concentration
- $\Delta C_t$  = error in stream water concentration
- $\Delta X$  = error in the old water fraction

Equation 3 uses the component concentrations and their errors to determine the uncertainty in the instantaneous old water fraction. The range of values for the old water fraction determined from the uncertainty estimate were then used to compare old water fractions using different tracers. If the ranges of the chemical and the isotope old water fraction overlapped, the difference between the old water fraction estimates were not considered to be significant. Both analytical and sampling errors may be incorporated into the error estimate; however sampling errors due to spatial and temporal variation in component concentrations are generally not well documented in the literature. Uncertainty was analyzed using

analytical error data from: Kenora and Wilson Creek, Canada (Fritz *et al.*, 1976); Mattole, U.S.A. (Kennedy *et al.*, 1986); Maimai, New Zealand, (McDonnell *et al.*, 1991); Mahantango Creek, U.S.A. (Pionke *et al.*, 1993 and De Walle and Pionke, 1994); Shaver Hollow, U.S.A. (Bazemore *et al.*, 1994); and Harp Lake, Canada (Hinton *et al.*, 1994). Hinton *et al.* (1994) included data for spatial variation in groundwater chemistry and temporal variation in throughfall. These data were used to investigate the influence of spatial and temporal variation on the uncertainty of the old water fraction. Error estimates for old water fractions in other catchments incorporated only analytical error.

A dual tracer, three-component model (Dewalle and Pionke, 1994) was used to examine the contributions of soil water and groundwater (both components of old water) to streamflow for the published data:

$$\frac{Q_{se}}{Q_t} = \left[ \frac{\left( \frac{C_{t1} - C_{g1}}{C_{s1} - C_{g1}} - \frac{C_{t2} - C_{g2}}{C_{s2} - C_{g2}} \right)}{\left( \frac{C_{se1} - C_{g1}}{C_{s1} - C_{g1}} - \frac{C_{se2} - C_{g2}}{C_{s2} - C_{g2}} \right)} \right] \quad (4)$$

$$\frac{Q_s}{Q_t} = \left[ \frac{\left( \frac{C_{t1} - C_{g1}}{C_{se1} - C_{g1}} - \frac{C_{t2} - C_{g2}}{C_{se2} - C_{g2}} \right)}{\left( \frac{C_{s1} - C_{g1}}{C_{se1} - C_{g1}} - \frac{C_{s2} - C_{g2}}{C_{se2} - C_{g2}} \right)} \right] \quad (5)$$

$$\frac{Q_g}{Q_t} = \left[ \frac{\left( \frac{C_{t1} - C_{se1}}{C_{s1} - C_{se1}} - \frac{C_{t2} - C_{se2}}{C_{s2} - C_{se2}} \right)}{\left( \frac{C_{se2} - C_{g2}}{C_{s2} - C_{se2}} - \frac{C_{se1} - C_{g1}}{C_{s1} - C_{se1}} \right)} \right] \quad (6)$$

where  $Q_{se}$ ,  $Q_s$ ,  $Q_g$ , and  $Q_t$  represent new water (surface event water), soil water (shallow subsurface), groundwater (deep subsurface) and current



streamflow volumes, respectively.  $C_{se}$ ,  $C_s$ ,  $C_g$ , and  $C_i$  are the corresponding tracer concentrations where subscripts 1 and 2 refer to Tracer 1 and Tracer 2.

In addition to the assumptions for the two-component separation, the two-tracer three-component model requires that the soil water and groundwater components differ significantly in chemical and isotopic content. The shallow and deep water fractions were combined (as the old water fraction) and compared to the old water fraction calculated from the two-component separation.

## Results and discussion

### Comparison of chemical and isotopic two-component hydrograph separations

We examined 23 rain events from the literature that reported, or had enough data to calculate, the old water fraction at peak discharge using the two-component hydrograph separation for both an isotope and a chemical tracer. Individual storm characteristics and the old water fraction results are shown in Table 2. Sixteen of the 23 rain events show strong agreement (<10% difference) between the old water fractions computed by the isotopic and chemical two-component hydrograph separation model; three of the rain events showed disagreement. For four of the rain events, the old water fractions calculated from either the chemical or isotopic concentrations were unrealistic (>100% or negative value).

The isotope separations for Shaver Hollow (June) and Mahantango Creek (May 4) gave unrealistic values for the old water fractions (Table 2). Pionke *et al.* (1993) did not report the same old water fraction for the Mahantango Creek (May 4) as we calculated: this may be because of differences in the end member concentrations used in the hydrograph separation. End member concentrations were not listed in the publication so we digitized values from graphs. Shaver Hollow (June) and Mahantango Creek (May 4) had differences between  $C_o$  and  $C_i$  of only -0.5 ‰ ( $^{18}\text{O}$ ) and -0.05 ‰ ( $^{18}\text{O}$ ). These values are below the analytical error of the measurement technique and therefore cannot be considered different from zero. Since the end member concentrations ( $C_o$  and  $C_i$ ) are not significantly different, the two-component hydrograph separation model is not appropriate. Maimai measurements (Nov 26 – Pit A) resulted in an unrealistic chemical separation. The concentration of Cl increased at this location during this storm, therefore, the two-component mass balance model is not appropriate. At a location farther down the hillslope the Cl

Table 2 – Storm characteristics and results of two-component hydrograph separations.

Catchment	Area (ha)	Total Rainfall (mm)	Avg. Storm Intensity (mm/hr)	Storm Duration (hr)	Peak Storm Intensity (mm/hr)	Peak Flow Discharge (mm/hr)	Increase In Discharge (mm/hr)	Old Water Isotope (%)	Old Water Chemical (%)
Kenora (Oct)	180	50	200	0.25	200	0.450	0.430	62	68
Wilson Creek (Aug)	2200	40	5	8	5	0.075	0.073	67	68
Mattole (Jan – <sup>2</sup> H, Cl)	62000	200	5	42	10	1.742	1.614	69	65
Mattole (Jan – <sup>18</sup> O, Si)	62000	200	5	42	10	1.742	1.614	76	75
Maimai (Nov 13 – M8)	3.8	34	3.6	10	10	1.100	1.000	87	96
Maimai (Nov 26 – Pit 5)	3.8	47	3	24	13	0.660	0.660	96	96
Maimai (Nov 26 – Pit A)	3.8	47	3	24	13	0.660	0.660	71	135
Les Cloutasses (Jul 30) <sup>1</sup>	81	-	-	-	-	-	-	46	43
Les Cloutasses (Jul 31) <sup>1</sup>	81	-	-	-	-	-	-	73	78
La Sapine (Jul 30) <sup>1</sup>	54	-	-	-	-	-	-	85	82
La Sapine (Jul 31) <sup>1</sup>	54	-	-	-	-	-	-	68	64
Mahantango Cr (May 4)	740	18.5	3.9	7	20	0.109	0.073	110	77
Mahantango Cr (May 10)	740	48.2	5	9.7	168	1.460	1.216	73	68
Mahantango Cr (May 29)	740	31	2.8	11	12	0.292	0.243	80	86
Mahantango Cr (Jun 18)	740	58.2	3.2	18	172	2.433	2.433	48	45
Shaver Hollow (Jun)	8.2	108	5.4	20	8.4	1.400	1.400	162	83
Shaver Hollow (Nov)	8.2	61	3.6	16	14.3	0.600	0.600	80	88
Mahantango Cr (Oct 19)	19.8	80	4	20	10	1.364	1.346	96	63
Mahantango Cr (Nov 9)	19.8	8.9	2.8	2.75	3	0.073	0.055	78	75
Mahantango Cr (Nov 16)	19.8	34.3	7.6	4.5	25	0.727	0.059	-	33
Harp Lake 4-21 (Jun)	3.7	36	3.6	10	12	1.460	1.362	56	41
Harp Lake 4-21 (Oct)	3.7	19	2.7	7	5.5	0.243	0.243	65	60
Plastic - 108 (May 16)	3.22	44.5	2.45	18	18.3	0.670	0.670	75	88

<sup>1</sup> Specific event characteristics were not reported in the literature.

concentration for the same event does not increase and the old water fraction is realistic and very similar to the isotope result. Mahantango Creek measurements (Nov 16) resulted in an unrealistic isotopic separation. The concentration of  $^{18}\text{O}$  increased, giving a negative value for the old water estimate, therefore, the two-component mass balance model is not appropriate for this storm.

Substantial differences (>10% difference) in the old water fractions calculated from isotopic and chemical tracers for storm events were found for a June event at Harp Lake (Hinton *et al.*, 1994), an October event at Mahantango Creek (DeWalle and Pionke, 1994) and a May event at Plastic-108 (Buttle *et al.*, 1998). Hydrograph separations using data from Hinton *et al.* (1994), DeWalle and Pionke (1994), and Buttle *et al.* (1998) resulted in differences between  $^{18}\text{O}$  and Si of 15%, 33% and 13%, respectively (Table 2). The sites did not have storm event or catchment characteristics that would explain the lack of agreement between the old water fractions calculated with different tracers.

We used the difference between the old water fraction calculated using the two tracers as the dependent variable in a linear regression model. We regressed independent variables, including catchment area, peak flow discharge, maximum runoff depth, total storm rainfall, average storm intensity, peak storm intensity and storm duration, against our dependent variable. We found no statistically significant relationships. Although Hinton *et al.* (1994) reported a seasonal variation in the old water fraction, we found no consistent relationship between season and old water fraction in our reviewed study areas — possibly because of the varied geographical locations. We could not detect any effects of land use on the differences between tracers.

## Uncertainty in old water fractions

Estimation of uncertainty in the old water fractions provides quantitative support for our findings that old water fractions determined by isotopic and chemical tracers were not significantly different. The uncertainty estimates and related contributing error are shown in Table 3. Contributing error can include analytical error, spatial variability of source water components and sampling error. The contributing error used in the uncertainty estimate in our analysis was based only on analytical error except where otherwise noted. The analytical error was reported in four of the eleven studies examined. The calculated uncertainty is probably underestimated due to the lack of information on other contributing errors, with the exception of data from Hinton *et al.* (1994). Since Hinton *et al.*

(1994) reported both spatial and sampling error, we were able to calculate an uncertainty that included these additional constraints. Sampling errors due to spatial heterogeneity of the old water isotopic signature and changing isotopic signature of the new water increased the uncertainty of the old water estimate by 1-2% when these sampling errors are considered individually and 3-4% collectively for an old water fraction based only on an analytical error of 4-5% (Table 3). This resulted in an old water fraction of  $65 \pm 9\%$ . Incorporating the spatial error in old water Si concentrations greatly increased the error of the Si estimate from 2 to 19% (Table 3). The old water fraction calculated using Si was 60%. The uncertainty estimates of the three events with differences between tracers of  $>10\%$  suggest that only the May event at Plastic-108 is significantly different. However, if spatial variability were considered in the uncertainty estimate, the difference between the tracers probably would not be significant. In addition to showing no significant difference in the old water fraction calculated from chemical and isotopic tracers, this analysis shows that apparent differences between tracers in other catchments may not be significant if sampling and analytical error in the component concentrations is considered.

Estimation of uncertainty in the old water fractions enabled us to examine the strengths and weaknesses of both isotopic and geochemical tracers. Based on analytical error of component concentrations, chemical tracers generally produce a more precise estimate of the old water fraction (Fig. 1). The Maimai catchment, however, showed the opposite: the hydrograph separations based on Cl concentrations had very high uncertainties ( $>20\%$ ) because of high analytical uncertainty. Generally, isotopic hydrograph separation is highly sensitive to the concentration differences between old and new water end members. Uncertainties in the old water fraction were  $>10\%$  when this difference was  $<3\text{‰}$  (for  $^{18}\text{O}$ ). Changes in the new water signature during an event strongly influence the calculated old water fraction and the uncertainty estimate associated with the new water end member. Hydrograph separations using Si are more sensitive to error in the old water end member because Si occurs only in trace concentrations in rainfall. Therefore spatial and temporal variability in the new water concentrations are generally negligible. Notwithstanding, spatial variability of Si within a catchment (old water end member) may be great.

**Table 3** – Results of uncertainty estimate for old water fraction.*Contributing errors are analytical errors, except where indicated (see footnote).*

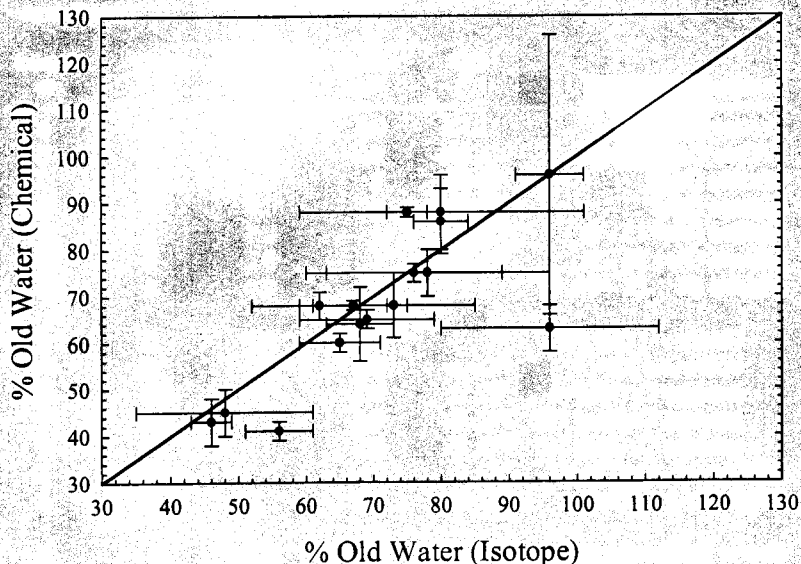
Catchment	Tracer Used	Contributing Error		Uncertainty Estimate	
		$\Delta C_t, \Delta C_o, \Delta C_n$	$\Delta C_t, \Delta C_o, \Delta C_n$	Isotope (%)	Chemical (%)
		Isotope (‰)	Chemical (mg/L)		
Kenora (Oct)	$^{18}\text{O}$ , Si	0.2	0.1	10	3
Wilson Creek (Aug)	$^{18}\text{O}$ , Na	0.2	0.04	8	0
Mattole (Jan)	$^2\text{H}$ , Cl	2	0.3	13	2
Mattole (Jan)	$^{18}\text{O}$ , Si	0.2	0.1	10	2
Maimai (Nov 13 – M8)	$^2\text{H}$ , Cl	1	0.6	6	24
Maimai (Nov 26 – Pit 5)	$^2\text{H}$ , Cl	1	0.6	5	30
Maimai (Nov 26 – Pit A)	$^2\text{H}$ , Cl	1	0.6	4	23
Les Cloutasses (Jul 30)	$^{18}\text{O}$ , Si	0.2	0.1	3	5
La Sapine (Jul 30)	$^{18}\text{O}$ , Si	0.2	0.1	5	8
Mahantango Cr (May 4)	$^{18}\text{O}$ , Si	0.2	0.1	84	6
Mahantango Cr (May 10)	$^{18}\text{O}$ , Si	0.2	0.1	12	7
Mahantango Cr (May 29)	$^{18}\text{O}$ , Si	0.2	0.1	4	7
Mahantango Cr (Jun 18)	$^{18}\text{O}$ , Si	0.2	0.1	13	5
Shaver Hollow (Jun)	$^{18}\text{O}$ , Cl	0.2	0.7	58	4
Shaver Hollow (Nov)	$^{18}\text{O}$ , Cl	0.2	0.7	21	8
Mahantango Cr (Oct 19)	$^{18}\text{O}$ , Si	0.2	0.2	16	5
Mahantango Cr (Nov 9)	$^{18}\text{O}$ , Si	0.2	0.1	18	5
Harp Lake 4-21 (Jun)	$^{18}\text{O}$ , Si	0.2	0.1	5	2
Harp Lake 4-21 (Oct)	$^{18}\text{O}$ , Si	0.2	0.1	6	2
Harp Lake 4-21 (Oct) <sup>1</sup>	$^{18}\text{O}$ , Si	0.2	0.1	8	19
Plastic -108 (May 16)	$^2\text{H}$ , Si	0.12	0.02	3	1

<sup>1</sup> Uncertainty calculation for this event includes the spatial error in  $\Delta C_o$  of 0.5‰ for  $^{18}\text{O}$  and 2.6 mg/L for Si reported in Hinton *et al.*, 1994 in addition to analytical error.

### Comparison of dual tracer, three-component and two-component separations

We carried out dual-tracer, three-component hydrograph separations to examine in greater detail the similarities between tracer old water fractions. This model differentiates the old water component into shallow (soil water) and deep (groundwater) components. Nine of 23 storm events had enough information to calculate the old water fractions using this model (Table 4). The dual-tracer, three-component separation for the rain event at Mahantango Creek (Nov 16) was carried out with two chemical tracers, because of the lack of isotope data.

**Figure 1** – Old water fraction calculated with isotope tracer compared to old water fraction calculated with chemical tracer. Error bars are uncertainty estimates.



Results from the dual-tracer, three-component model using both isotopic and chemical tracers showed strong agreement between the combined soil water and groundwater fractions and the old water fraction calculated using the two-component model (Table 4). For example, the rain event at Maimai (Nov 26 – Pit 5) shows a good agreement between the old water fraction calculated with the two-component model for chemical (96%) and isotope (96%) tracers and the combined shallow and deep old water fraction (95%). In contrast, for the Mahantango Creek (Oct 19) event the old water fractions based on the two-component model did not agree well with total old water fraction estimates from the dual-tracer, three-component model. This may be due to greater soil water contribution to total flow during this event.

Similar patterns were found for the Mahantango Creek (Nov 9) event and for the Shaver Hollow (June) storm; however, no consistent relationship between the two types of models was found for all catchments.

**Table 4** – Results of dual-tracer, three-component separation and comparison with single-tracer, two-component results.

Catchment	Single-Tracer Two-Component			Dual-Tracer Three-Component		
	Old Water Isotope	Old Water Chemical	New Water Surface	Old Water Shallow	Old Water Deep	Old Water Shallow + Deep
	(%)	(%)	(%)	(%)	(%)	(%)
Maimai (Nov 26 – Pit 5)	96	96	5	11	84	95
Mahantango Cr (May 29)	80	86	21	24	55	79
Shaver Hollow (Jun)	162	83	17	45	38	83
Shaver Hollow (Nov)	80	88	5	31	64	95
Mahantango Cr (Oct 19)	96	63	11	59	30	89
Mahantango Cr (Nov 9)	78	75	12	63	25	88
Mahantango Cr (Nov 16) <sup>1</sup>	-	33	59	12	29	41
Harp Lake 4-21 (Jun)	56	41	44	21	35	56
Harp Lake 4-21 (Oct)	65	60	34	8	58	66

<sup>1</sup> Dual-tracer, three-component separation using two chemical tracers.

## Summary

This paper represents one of the first formal comparisons of published isotope and chemical hydrograph separations (and their associated uncertainties) from New Zealand, North America and Europe. The 11 studies reviewed cover catchments with a large range of climate and hydrogeological regimes. Our review and re-calculation of the literature studies suggests that old water fractions calculated using the simple two-component hydrograph separation model with both quasi-conservative chemical and conservative isotopic tracers are surprisingly similar, and differences could usually be explained by analytical error. Although chemical tracers like Si and Cl may be non-conservative in soil water and groundwater on the time-scale of weeks to months, they may behave conservatively on the time scale of a single runoff event. More importantly, our findings indicate that spatial variability in the components may be more important when determining the precision of the old water fraction. Although no relationship was found between catchment or storm event characteristics and the old water fractions, differences in concentration of tracers between old water, new water, and streamflow strongly influenced both the hydrograph separation and the uncertainty in the old water fraction. The old water fractions calculated using two-component and three-component hydrograph separations were generally very similar. In

summary, tracers are a useful tool for determining sources of runoff, and should be considered as a first step in understanding runoff processes. However, without adequate accompanying hydrometric information, interpretations based solely on tracer data may be misleading.

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Manuscript received: 20 March 1997; accepted for publication 15 June 1998.