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Review Paper

Hydrograph separation using stable isotopes: Review and evaluation

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SUMMARY

The separation of storm hydrographs using stable isotope tracers dates back to the late 1960s. These studies ushered in a paradigm shift in how hydrologists conceptualized runoff generation as most showed a large preponderance of pre-event water in the storm hydrograph, even at peak flow. This forced a fundamental re-examination of the processes of water delivery to streams during rainfall and snowmelt events. Whilst the simplicity of the two-component hydrograph separation was a powerful tool for showing the importance of stored water effusion, the assumptions implicit in the two-component model have now become limiting for further advancement of the approach. Here we review the use of stable isotopes for hydrograph separation with particular reference to studies completed since the last comprehensive review of the subject in 1994. We review critically the contributions to new field knowledge gained by isotope hydrograph separation applications. We focus specifically on the current issues regarding the limitations of the two-component approach. We examine the role of soil water as a contributor to channel stormflow and the issues raised by differences in the soil water and groundwater signatures at the watershed scale. Finally, we offer ideas on how to overcome the limitations of the two-component approach and present a vision for future directions for isotope based hydrograph separation. These future directions are focused on high frequency analysis of rainfall-runoff structures and dual isotope analysis of catchment end-members including comparison of lysimeter-based soil water sampling of mobile soil water versus cryogenic and vapor-based analysis of tightly bound water.

Contents

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1. Introduction

Storm hydrograph separation using stable isotope tracers has resulted in major advances in catchment hydrology in the past 40 years. Its use as a tool beginning in the late 1960s (Hubert et al., 1969; Crouzet et al., 1970; Dinçer et al., 1970; Martinec et al., 1974; Martinec, 1975) ushered in a paradigm shift in the way that runoff generation was conceptualized. Existing theories that focused on rainfall translation to streamflow as overland flow (e.g. Dunne and Black, 1970) and rainfall translation to streams via lateral preferential flow (e.g. Mosley, 1979) required significant revision once isotope-based hydrograph separations (IHS) showed that stored, pre-event water dominated the storm hydrograph in most natural, humid systems (Sklash et al., 1976). Even today, high frequency event-based isotope data are challenging our process understanding of streamflow generation. Recent field-based laser spectrometer deployments show that some forested catchments with runoff ratios above 50% may display no detectable rainfall in channel stormflow, even at the peak of the storm hydrograph (Berman et al., 2009).

The last major review of isotope hydrograph separation was made by Buttle (1994) with minor updates along the way since then by Genereux and Hooper (1998), Richey et al. (1998), Buttle and McDonnell (2004), and McGuire and McDonnell (2007). Since 1994, well over 100 papers have been published using the technique. Beyond the case studies of hydrograph components, IHS now influences the development of rainfall-runoff model structures (e.g. Vache et al., 2004) and *a posteriori* model testing and calibration (Stadnyk et al., 2005; Vaché and McDonnell, 2006). Notwithstanding these developments, the assumptions implicit in the technique are still problematic and several papers continue to gloss-over assumptions and limitations associated with the technique. Moreover, while the initial IHS results shifted process thinking away from event water dominance, IHS studies in the past two decades have been less influential in changing process thinking. Rather than IHS results informing new process behaviors, current field-based process studies take pre-event water dominance as 'a given' and seek to show the mechanisms of stored water mobilization, connectivity, and threshold response to precipitation inputs (Tromp-van Meerveld and McDonnell, 2006a,b; Klaus et al., 2013). Consequently, IHS is now not leading new process insights (as it did when it was first introduced) and appears now rather out of step with cutting edge runoff theory development. With fundamentally new insights from continued application of IHS being rare, it seems that we have exhausted easy-to-discover insights from the technique, leading some to ponder if the thrill with isotope hydrograph separation is indeed, gone (Burns, 2002).

Here we provide a comprehensive review and evaluation of storm hydrograph separation using stable isotopes with the following goals:

1. To review, comprehensively, the progress made in IHS and update the last comprehensive review paper by Buttle (1994).
2. To re-evaluate the assumptions and limitations of the technique, especially considering the findings made in the last two decades.
3. To identify and outline what can still be done with IHS and where opportunities for innovation still exist.

We begin this review with a historic overview of the early development of different methods to separate streamflow. Next we present a comprehensive review of the achievments in the last 20 years. We follow this with a section that outlines several of the concerns that arise from current practice and where the underlying assumptions of IHS are not met. Finally, we end with a vision on ways to go forward with the technique.

2. Hydrograph separation: Historical developments

Graphical, hydrometric-based separation of storm hydrographs dates back over 50 years (see early review in Linsley and Köhler (1958)). Many of the early approaches involved simple graphical separation of the hydrograph into fast and slow components, often equated to storm rainfall and groundwater. These approaches, while still used today in engineering practice, have been widely criticized, with Beven (2001, p.32) noting that "the best method of dealing with hydrograph separation is to avoid it all together" and Brutsaert (2005, p.441) equating attempts to separate the storm hydrograph into different components trying to "unscramble the omelette".

The introduction of water isotopes as a tool for separation of the storm hydrograph into time source components of event and pre-event water was a quantum leap in watershed hydrology. Unlike the graphical techniques, IHS was measureable, objective and based on components of the water itself, rather than the pressure response in the channel. The first isotope-based hydrograph separation that we are aware of was published by Hubert et al. (1969) using environmental tritium. Since then, about 200 published journal articles have used naturally occurring stable isotopes of water (Oxygen-18 (^{18}O) and Deuterium (^{2}H)) to define the event and pre-event water components of flow in a wide range of climate, geology, and land use conditions (Fig. 1). Pinder and Jones (1969) were among the first that separated flow components based on a mass balance approach. They used the total sum of various solutes to separate the storm hydrograph in a direct flow and groundwater flow component. Their concept, and the one still used today, is the complete mixing of pre-event with event water in the stream during the storm hydrograph event. While many early studies employed environmental tritium as a hydrograph separation tracer (e.g. Dinçer et al., 1970), most IHS studies after the early 1970s used either ^{18}O or ^{2}H, with important early work using ^{18}O by Mook et al. (1974), Fritz et al. (1976), and Sklash et al. (1976) and ^{2}H by Hermann et al. (1978), and Herrmann and Stichler (1980). Today most of the studies apply either ^{18}O or ^{2}H.

If the two end-members have a distinct difference in their isotopic signature, the stormflow hydrograph can be separated in their contributions based on a mass balance approach:

$$Q_t = Q_p + Q_e \tag{1}$$

$$C_tQ_t = C_pQ_p + C_eQ_e \tag{2}$$

$$F_p = \frac{C_t - C_e}{C_p - C_e} \tag{3}$$

where Q_t is the streamflow, Q_p the contribution from pre-event water, Q_e the contribution of event water, C_t, C_p and C_e are the δ values of streamflow, pre-event water and event water, and F_p is the fraction of pre-event water in the stream. Abundance of stable water isotopes is based on the isotopic ratios ($^{18}O/^{16}O$ and $^{2}H/^{1}H$). The abundance is reported in the δ notation and often expressed as parts per thousand (‰ or per mil).

$$\delta^{18}O \text{ or } \delta^{2}H = \left(\frac{R_{Sample}}{R_{St}} - 1\right) \times 1000$$

where R_{Sample} is the respective $^{2}H/^{1}H$, or $^{18}O/^{16}O$ ratio, and R_{St} the Vienna Standard Mean Ocean Water (absolute VSMOW ratio is $^{2}H/^{1}H = 155.76 \pm 0.05 \times 10^{-6}$ and $^{18}O/^{16}O = 2005.2 \pm 0.45 \times 10^{-6}$).

The contributions of event and pre-event water can be determined based on Eqs. (3) and (4). The equations are constrained so that C_t falls between C_p and C_e and that Q_p and Q_e are between

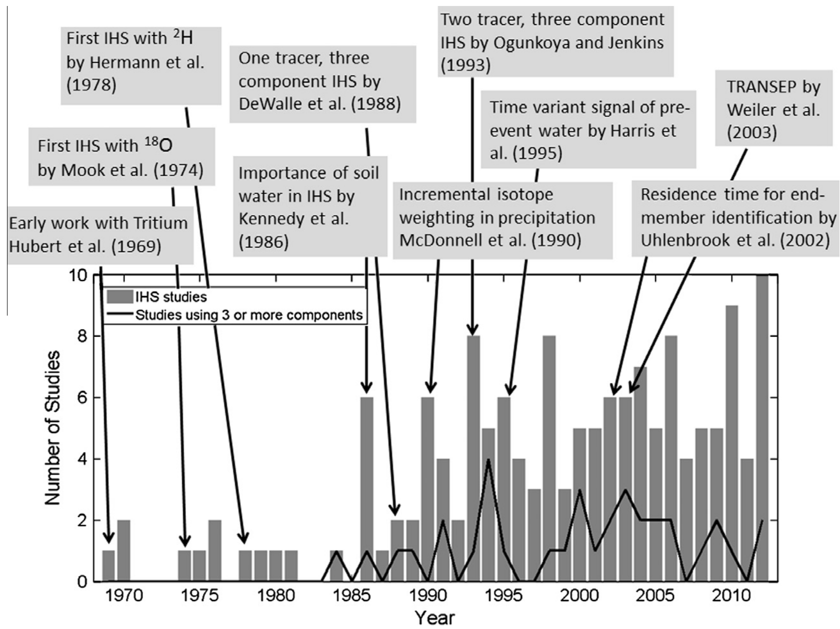

Fig. 1. Timeline of Benchmark paper in Isotope Hydrograph Separation (IHS) method development, number of IHS studies, and number of IHS studies using three (or more) end-member.

zero and Q_t. Several assumptions underlie Eqs. (1) and (2). Sklash et al. (1976) and Sklash and Farvolden (1979) provided the first, clear exposition of the main underlying assumptions implicit in the technique (initially four), which were later refined and extended to five underlying assumptions (e.g. Moore, 1989; Buttle, 1994):

1. The isotopic content of the event and the pre-event water are significantly different.
2. The event water maintains a constant isotopic signature in space and time, or any variations can be accounted for.
3. The isotopic signature of the pre-event water is constant in space and time, or any variations can be accounted for.
4. Contributions from the vadose zone must be negligible, or the isotopic signature of the soil water must be similar to that of groundwater.
5. Surface storage contributes minimally to the streamflow.

We examine these assumptions critically later in this review. For now, it is important to note that early IHS work also assumed that the pre-event water could be described by a single isotopic value of water in the stream prior to the event; describing in essence, a single, integrated pre-event water signal that is assumed to be representative of the entire stored water that may contribute to stormflow (Sklash and Farvolden, 1979). A number of follow-on studies to the early two-component IHS used a multi-component approach to account for additional contributing end-members. In such cases, the standard mixing Eqs. (1) and (2) were extended as follows:

$$Q_t = Q_1 + Q_2 + Q_3 + \cdots + Q_n \quad (4)$$

$$C_tQ_t = C_1Q_1 + C_2Q_2 + C_3Q_3 + \cdots + C_nQ_n \quad (5)$$

where Q_n is the discharge of a particular runoff component and C_n the tracer concentration of a particular runoff component. In the case of three flow components, a second tracer or a measurement of one flow component was required. Most commonly, a stable isotope tracer was combined with a geochemical tracer (e.g. Wels et al., 1991), but sometimes a second stable isotope was used (e.g. Rice and Hornberger, 1998).

Within this paper we define pre-event water (often called old water) as water that is stored in the catchment prior to the streamflow generating precipitation event, while the event water (often called new water) is the water from the current precipitation event. During snowmelt conditions, event water is melt water from the snowpack and possibly falling rain during rain-on-snow conditions, while pre-event water is water that is stored in the catchment below the snowpack at the beginning of the experiment.

3. Review of the main achievements in IHS in the last 20 years

3.1. Use of hydrometric techniques with IHS to constrain process conceptualization

Buttle (1994) observed in his review that isotopic response during storm events can be generated by various alternative processes. Subsequent work showed that inferring runoff generation processes and the water flow paths in hillslopes and catchments based solely on hydrograph separation methods are often inconclusive (Rice and Hornberger, 1998). As such, several studies have recognized that "combining isotopic and hydrometric information, however, opens possibilities for defining mechanisms of runoff generation that would not be otherwise possible" (Laudon et al., 2004, p. 7). Indeed, an early review by Bonell (1993) called for combined hydrometric and isotopic approaches as a way forward in process conceptualization.

Interpreting IHS results together with observed discharge data and detailed precipitation records has been the most common approach for constraining process conceptualizations. The partitioning between event/pre-event water has been evaluated together with the catchment's runoff coefficient (e.g. Brown et al., 1999; James and Roulet, 2009; Hrachowitz et al., 2011) or with recession analysis (Hangen et al., 2001) to gain a better insight on runoff generation processes under different boundary conditions. The link to runoff ratio has been proven to be very helpful in inferring the physical process linked with the event water percentage. For example, when runoff ratios have been very low and event water percent has been very high, then inferences of near-stream overland-flow control on the hydrograph volume have been made (Brown et al., 1999; Muñoz-Villers and McDonnell, 2012).

Frequently used hydrometric data include near stream water table information (Waddington et al., 1993), groundwater well transects (Jordan, 1994; Laudon et al., 2004), water table at the soil–bedrock interface of hillslopes (Brown et al., 1999), or bedrock groundwater on hillslopes (Iwagami et al., 2010). This link between well data with IHS has taken rather different forms. For instance, Blowes and Gillham (1988) and Cey et al. (1998) used measured groundwater level to explain the varying event/pre-event water partitioning between events based on initial groundwater tables and their variations. Waddington et al. (1993) used groundwater data to infer the mechanism of pre-event water delivery to the stream. They found that the near stream response of the groundwater was too small to account for the amount of pre-event water in the stream. They found that soil pipes contributed to the pre-event water amount in the channel (Waddington et al., 1993). This followed earlier calculations elsewhere by McDonnell (1990) who showed that the volume of pre-event water in a near-stream discharge position was insufficient to account for the observed pre-event water fraction in the storm hydrograph.

Various studies have used well data to investigate the role of hillslopes in the delivery of event and pre-event water. Bazemore et al. (1994) observed a transient saturated zone in hillslopes consisting of pre-event soil water that contributed to stormflow. This was similar to the observations of Carey and Quinton (2005) on permafrost slopes. Their shallow water table data suggested that the hillslopes with their transmissive organic soils, supply much of the stormflow. Contrastingly, Brown et al. (1999) observed the development of a groundwater table on the soil–bedrock interface contributing to their relatively high event water fractions in stormflow. Ocampo et al. (2006) used well levels to justify the use of a two-component hydrograph separation. Their well data suggested that only one subsurface storage (the near stream zone) was active during events justifying the use of only one pre-event end-member in their analysis of a Western Australia agricultural watershed (Ocampo et al., 2006).

Buttle and Peters (1997) and McGlynn and McDonnell (2003) used hillslope flows observed in soil trenches together with IHS to infer runoff sources in their study areas. The latter illustrated clear rainfall thresholds for hillslope water contributions to channel stormflow at the Maimai watershed in New Zealand. The work also showed strong hysteresis between riparian and hillslope contributions to the storm hydrograph, where water in the riparian zone alluvial aquifer controlled the rising limb of the hydrograph, while the hillslope flux dominated the falling limb of storm hydrographs. A precipitation threshold of c. 20 mm was necessary to initiate hillslope flow (McGlynn and McDonnell, 2003). Ladouche et al. (2001) used a combination of well data and soil lysimeter data to support the results of IHS and determine flowpath dynamics. They were able to explain the pre-event water transport from hillslopes by a piston flow mechanism, and showed – based on the soil water balance – that the parts of the catchment with coarse soils failed to generate discharge during their observation period.

Hinton et al. (1994) used measurements of the hydraulic gradient at the interface between glacial till and the overlying soil to show that there was no flow from the tills to the soil during events; that the soil was frequently recharged by till waters between events, and that this process controlled the isotopic signal during stormflow. The use of soil data has helped to constrain flow processes at a variety of other sites and helped to explain the link between runoff mechanisms and initial moisture conditions. For instance, Hangen et al. (2001) used a soil survey to infer the flow paths as linked to the results of IHS. They did not directly measure the internal hillslope dynamic, but found hydromorphic characteristics in the soil that helped them to identify the important, controlling end-members. More recently McGuire and McDonnell (2010) found that soil moisture shifts from dry to wet states influenced the composition of channel stormflow, although with less fidelity than measured shallow groundwater and resulting hillslope trenchflow.

3.2. Development of hydrograph separation models that go beyond two-components

Early IHS work by Kennedy et al. (1986) showed that soil water can contribute significantly to channel stormflow. DeWalle et al. (1988) later showed that soil water and groundwater can have distinct isotopic signals and that the isotopic composition of streamwater moves in the opposite direction of the observed event water. These two findings violate, of course, two of the core assumptions in the technique. A standard IHS approach in such systems can result in unrealistic component mixtures that sometimes exceed 100% or fall below 0% (e.g. McDonnell et al., 1991; Blume et al., 2008). Such results led early onto the use of three-component hydrograph separations (DeWalle et al., 1988; Swistock et al., 1989; Wels et al., 1991; Ogunkoya and Jenkins, 1993). Research in the past 20 years has accounted for other geographic source components (as opposed to the original two-component *time-source* component approach) such as snow, rain, and subsurface water (e.g. Sueker et al., 2000), pre-event hillslope, pre-event riparian zone, and event water (McGlynn and McDonnell, 2003), and specific geomorphological units (Hoeg et al., 2000) up to and including five different geographic source components (Uhlenbrook and Hoeg, 2003). Iwagami et al. (2010) showed one of the most compelling examples for the need for a three-component hydrograph separation at the hillslope scale. They noted that while hillslopes have a reduced complexity compared to catchments and are thus a good test scale for process research, they found three distinct components formed hillslope runoff at their site: event water, bedrock groundwater, and the soil water. Other recent work has suggested the importance of similar compositional blends in steep, humid catchments (McGuire and McDonnell, 2010).

Table 1 summarizes multi-component hydrograph separations using isotopes and presents the scale of application, the method and tracer used, and the resultant end-members, demonstrating the wide range of application. Hydrograph separation with various end-members is usually based on the same mass balance approach as the original two-component hydrograph separation. Recently, some authors (e.g. Liu et al., 2004; Williams et al., 2006) have used isotopes as one of several tracers in end-member mixing approaches building upon the foundational end-member mixing analysis (EMMA) work of Hooper et al. (1990). To use a three-component mass balance approach, either one of the flow components must be known or an additional tracer must be used. DeWalle et al. (1988) assumed in their original three-component hydrograph separation that event water was supplied to the stream solely by direct channel precipitation onto the channel area; an area that itself changes with stream discharge. They developed a relationship between discharge and the area of direct precipitation that was then used to describe the event water component for storms. This assumption was used subsequently by Swistock et al. (1989) and McDonnell et al. (1991). Wels et al. (1991) were the first to use an additional tracer (in their case silicate), to calculate the fractions of three components. Wels et al. (1991) used a two-step approach performing two, two-component hydrograph separations; one with deuterium to determine the pre-event and event fractions and one with silicate to determine surface and subsurface contributions. They subtracted the pre-event water component from the subsurface component and could thus determine contributions from pre-event subsurface water, event subsurface water, and event surface water. Ogunkoya and

Table 1
Summary of studies that account for more than two different end-members in hydrograph separation, while using at least one isotopic tracer. The scale, calculation method, type of end-members, and used tracer are reported. ^{2}H is Deuterium, ^{18}O is ^{18}Oxygen, EC is electric conductivity, SumCat a parameter that summarizes various cations.

Scale	Method	Number of components	End-member	Tracer	Source
0.246 km^2	Two tracer mass balance	3	Groundwater, soil water, event water	^{2}H and EC, ^{18}O and EC	Muñoz-Villers and McDonnell (2012)
Hillslope	Two tracer mass balance	3	Bedrock groundwater, soilwater, event water	^{18}O, silicate	Iwagami et al. (2010)
0.07–1.47 km^2	Two tracer mass balance	3	Shallow groundwater, deep groundwater, throughfall	^{18}O, DOC	James and Roulet (2009)
6.64 km^2	Two tracer mass balance	3	Baseflow, snowmelt, rainfall	^{18}O, Na^-	Williams et al. (2009)
Karst spring	Two tracer mass balance	3	Precipitation, upper unsaturated zone, deep phreatic zone	^{18}O, DOC	Trček et al. (2006)
203–2050 km^2	Two-step approach, based on two-component separation, second step is separation of baseflow in GW and surface waters different for different seasons	3	Snowmelt, baseflow (groundwater + surface water)	^{18}O, ^{2}H	St. Amour et al. (2005)
6 km^2	Two tracer mass balance	3	Precipitation, groundwater, soil water	^{18}O, DOC, EC	Carey and Quinton (2005)
0.21 km^2	Two tracer mass balance	3	Rainfall, snowmelt, pre-event water	^{2}H, Silicate, SumCat	Wenninger et al. (2004)
0.08 and 2.25 km^2	Mass balance EMMA	3	Snowmelt, baseflow (or soil water) Soil water, snowmelt, baseflow	^{18}O (plus various Ions)	Liu et al. (2004)
0.026 km^2 and hillslope	Mass balance, 2 tracer, 2 and 3 component	3	Event water, hillslope water, riparian zone water	^{18}O, Silicate	McGlynn and McDonnell (2003)
0.118 km^2	Two-step mass balance, two-component separation, and three component Sr-basedmass balance	3	Event-preevent, and soilwater, deep groundwater, channel precipitation	^{18}O and $^{87}Sr/^{88}Sr$	Hogan and Blum (2003)
18.4 km^2	Mass balance, informing three-component based on results of two-component (two step), and combining that with information of new and old water	3, 5	3 Component: surface runoff, runoff from the upper debris and drift cover and shallow ground water and soil water, runoff from the lower (deeper) drift cover and the crystalline hard rock aquifer and deep ground water; 5 component, using event and preevent water in each component	^{18}O, Silicate	Uhlenbrook and Hoeg (2003)
1.35 km^2	Two tracer mass balance	3	Throughfall, groundwater, soil water	^{18}O, Cl^-	McHale et al. (2002)
0.093 km^2	Two tracer mass balance	3	Throughfall, soil water, groundwater	^{18}O, Silicate	Hangen et al. (2001)
0.33 km^2	Two tracer mass balance	3	Bog/deep hillslope water, shallow groundwater, rain/througfall	^{18}O, ^{2}H, ^{2}H – excess	Gibson et al. (2000)
18.4 km^2	Two tracer mass balance	3	Different geomorphological units	^{18}O, Silicate	Hoeg et al. (2000)
6 WS (780–104.49 km^2)	Two tracer mass balance	3	Snowmelt, rainfall, subsurface waters	^{18}O, Na^+	Sueker et al. (2000)
7 Nested WS (0.08–1.61 km^2)	Two tracer mass balance	3	Throughfall, water from soil's O-horizon, groundwater	^{18}O, DOC	Brown et al. (1999)
0.98 km^2	Two tracer mass balance	3	Throughfall, soil water, groundwater	seven combinations with solute tracer: ^{2}H, ^{18}O, Cl^-, Na^+, silicate	Rice and Hornberger (1998)
0.273 km^2	N/A	3	Event water, soil water, groundwater	^{18}O	Buzek et al. (1995)
9.98 km^2	Two tracer mass balance	3	Event water, soil water, groundwater	^{2}H, Cl^-	Jenkins et al. (1994)
0.082 km^2	Two tracer mass balance	3	Throughfall, soil water, groundwater	^{18}O, Cl^-	Bazemore et al. (1994)
3.7 km^2	Two tracer mass balance	3	Event water, pre-event soil water, and pre-event till water	^{18}O, Silicate	Hinton et al. (1994)
0.198 km^2	Two tracer mass balance	3	Event water, deep subsurface water, shallow subsurface water	^{18}O, Silicate	DeWalle and Pionke (1994)
9.98km^2	Two tracer mass balance	3	Event water, soil water, groundwater	^{2}H, Cl^-	Ogunkoya and Jenkins (1993)
0.038 km^2	One tracer mass balance and determination of channel precipitation	3	Channel precipitation, groundwater, soil water	^{2}H	McDonnell et al. (1991)
0.033 km^2	Two step mass balance one tracer, substracting old water amount from the subsurface amount	3	Premelt subsurface flow, new water subsurface flow, surface new water	^{2}H, Silicate, Mg^{2+}	Wels et al. (1991)
2.08 km^2	One tracer mass balance and determination of channel precipitation	3	Channel precipitation, soil water, groundwater	^{18}O	Swistock et al. (1989)
2.08 km^2	One tracer mass balance and determination of channel precipitation	3	Channel precipitation, soil water, groundwater	^{18}O	DeWalle et al. (1988)

Jenkins (1993) introduced a three-component two tracer mass balance approach for hydrograph separation using deuterium and chloride as a second tracer. This approach has proven to be the most popular approach in recent years (James and Roulet, 2009; Iwagami et al., 2010), combined with various other tracers (Table 1).

Table 1 presents a compilation of studies that have used ^{2}H or ^{18}O with an additional tracer in multi-component mixing models,

Table 2
Summary of IHS studies that go beyond temperate forest catchments. This table sumarizes chatchment characteristics, catchment size and location, topography, the type of event (melt, rain storm), range of event water fractions, per catchment, or event.

Landscape	Catchment size (km^2)	Location	Topography	Type of event	Event water fraction	Source
Sub arctic mountains, 30% glaciated	21.7	Sweden	980–2097 m.a.s.l.	2 Summer season	11% and 22% in average	Dahlke et al. (in press)
Discontinuous permafrost	7.6[a]	Yukon Territory, CAN	1310–2250 m.a.s.l.	Melt	22–26% (in three years), 13% in another year	Carey et al. (2013)
Agriculture (>90%)	129.3 257.4	Rwanda	1375–2278 m.a.s.l.	Storm	20% (Average) 40% (Average)	Munyaneza et al. (2012)
Agriculture (>90%)	5.6 9.3	Indiana, USA	low gradient (<10 m)	Storm	50% (At peakflow) 12% (At peakflow)	Kennedy et al. (2012)
Tropical cloud forest	0.246	Mexico	2020–2280 m.a.s.l., steep slopes	Storm	6–99% (At peakflow), increasing with antecedent moisture	Muñoz-Villers and McDonnell (2012)
Rubber Plantation	0.193	SW China	Hilly	Strom	62–69% (At peakflow)	Liu et al. (2011)
(Sub)urban area (20% paved)	27	Toronto, CAN	80 m Gradient	Storm	87% (Mean)	Meriano et al. (2011)
Mountains, semi-arid forest and agriculture	0.3 25.1	Tanzania	700–2400 m.a.s.l.	Storm	44% (Peak), 27% (volume) 59% (Peak), 37% (volume)	Hrachowitz et al. (2011)
Tile drained site	0.061	Indiana, USA	Flat field	Storm	21–32% (mean) 34–48% (max)	Vidon and Cuadra (2010)
Discontinuous permafrost	7.6[a]	Yukon Territory, CAN	1310–2250 m.a.s.l.	Melt	30% (Mean)	Boucher and Carey (2010)
Urban agriculture	11 45	Appalachians, USA	Hilly	Storm	16–100% (Peak) 1–21%(Peak)	Buda and DeWalle (2009)
High alpine	6.64	Colorado, USA	3000 m.a.s.l.+	Melt	73% (Mean)	Williams et al. (2009)
Residential (72%), forest (14%)	4.1	Massachusetts, USA	N.N.	Storm	Event 1:25% (Volume) Event 2: 65% (Volume)	Pellerin et al. (2008)
Mine reclamation	0.01	Alberta, CAN	Hillslope	Melt	20–80% (Over melt season)	Kelln et al. (2007)
Alpine badlands, bar soil (68%, 54%, 79%)	0.86 0.08 0.001	France	846–1259 m.a.s.l., steep	Storm	Mainly event water	Cras et al. (2007)
Forest, meadows, livestock	24	Western Australia	Hilly	Storm	Mainly below 30% (volume)	Ocampo et al. (2006)
Rangeland, 30% woodland, 20% mixed oak savanna, and 45% grassland	0.19	Texas, USA	Hilly	Storm	Winter: 41% (peak), 46% (volume) Summer: 20% (peak), 16% (volume)	Huang et al. (2006)
Bog and fen, discontinuous permafrost	203–2050	NW Territory, CAN	Low gradient	Melt	Bog dominated: 39% (mean) fen dominated: 26% (mean)	St. Amour et al. (2005)
Discontinuous permafrost	6[a]	Yukon Territory, CAN	1310–2250 m.a.s.l.	Storm	Event 1: 7% (volume), 18% (peak) Event 2: 9% (volume), 19% (peak)	Carey and Quinton (2005)
Alpine, 20% vegetation cover, debris	0.08 2.25	Colorado, USA	3250–4000 m.a.s.l.	Melt	82% (Volume) 36% (Volume)	Liu et al. (2004)
Fen, wetland, discon. permafrost	152	NW Territory, CAN	240–290 m.a.s.l.	Melt (2 years)	Year 1: 30–40% Year 2: 40–50%	Hayashi et al. (2004)
Alpine, berdock outcrops, poorley developed soils	1.2 1.65 19	California, USA	2600–3300 m.a.s.l.	Melt	80–90% (Volume)	Huth et al. (2004)
Discontinuous permafrost	6[a]	Yukon Territory, CAN	1310–2250 m.a.s.l.	Melt	21% (Volume), 44% (maximum)	Carey and Quinton (2004)
Forest, lowland, fen, permafrost	2.4	Manitoba, CAN	253–276 m.a.s.l.	Melt Storm	59–78% (At peak melt) 10%, 2%, 23% (Peak)	Metcalfe and Buttle (2001)
Mediterean forest, coarse soils, mountains	0.54	Cevennes, France	1160–1395 m.a.s.l.	Storm	Event 1: 22% (volume) Event 2: 33% (volume) Event 3: 100% (volume)	Marc et al. (2001)
Subtropical wetland forest, suburban	215 135	Florida, USA	Low gradient	Storm	24% (Volume) 50% (Volume) (suburban)	Gremillion et al. (2000)
Mountains, forest, tundra, unvegetated area	7.8–104.99	Rocky Mountain National Park, Colorado	2500–4500 m.a.s.l.	Melt	Subsurface > meltwater > rain in 6 of 7 catchments	Sueker et al. (2000)
Agricultural	0.06	Ontario, Canada	Low gradient	Storm	Event 1:20%(volume), 33% (peak) Event 2: 36% (volume, 45% (peak)	Cey et al. (1998)
Grassland, wetland (36%)	3.33	Zimbabwe	1611–1654 m.a.s.l.	Storm	34% (Before saturation), 70% (after)	McCartney et al. (1998)
Alpine, subalpine (bare soil, shrubs)	0.29 0.07 (nested)	British Columbia, CAN	1525–1950 m.a.s.l.	Storm	60–75% 10–40%	Laudon and Slaymaker (1997)

Arctic, permafrost, tundra	2.2	Alaska, USA	880–950 m.a.s.l.	Storm	19% (Volume)	McNamara et al. (1997)
Peat, low forest cover	3.9	Plynlimon, UK	hilly, 380–730 m.a.s.l.	Storm	0–10%	Sklash et al. (1996)
Sub-humid mediterrean, 81% agriculture	1	France	75–125 m.a.s.l.	Storm	80% (Peak)	Ribolzi et al. (1996)
Suburban (64% residental, 32% open)	1.066	Ontario, CAN	N.N.	Storm	55–63% (Peak) 48–58% (Volume)	Buttle et al. (1995)
Peatland	9.98	Scotland, UK	325–1111 m.a.s.l.	Storm	18–36%	Jenkins et al. (1994)
Agricultural	0.198	Pennsylvania, USA	220–270 m.a.s.l.	Storm	10% (volume), 26% (maximum)	DeWalle and Pionke (1994)
Peatland	9.98	Scotland, UK	325–1111 m.a.s.l.	Storm	Volume: 19% (fixed end-member), 15% (time variant)	Ogunkoya and Jenkins (1993)
Wetland, permafrost, partly forest	N.N.	NW Territory, CAN	N.N.	Melt	40–50% (Peak), 25–30% (volume)	Gibson et al. (1993)
Crop (57%), forest (35%), pasture (8%)	7.4	Pennsylvania, USA	240–460 m.a.s.l.	Storm	Highly variable between methods	Pionke et al. (1993)
Tundra	2.2	Alaska, USA	880–950 m.a.s.l.	Melt	86% (Peak)	Cooper et al. (1991)
Forest, grassland	10.6	California, USA	120–850 m.a.s.l.	Storm	60% (Maximum) but old water dominated	Nolan and Hill (1990)
Uranium tailing, partly grassland	0.0075	Ontario, CAN	Gentle slopes	Storm/melt	Event 1: 55% (peak), 50% (volume) Event 2: 90% (peak), 78% (volume) Melt: 85% and 60%	Blowes and Gillham (1988)
Clearcut forest	0.038	South Island, NZ	Steep slopes, 34 degree	Storm	3% (Maximum)	Pearce et al. (1986)
Forest recovering from clearcut	0.038	South Island, NZ	Steep slopes, 34 degree	Storm	20% (Mean)	Sklash et al. (1986)
Permafrost, tundra	60	Baffin Island, Canada	Smoothed bedrock hills	Melt	50% (Peak), 40% (volume)	Obradovic and Sklash (1986)

[a] Labels the same catchment with different catchment size reporting.

and shows that silica has been the most popular accompaniment to a single stable isotope, but that chloride has also been widely used. DOC has been used effectively to trace the contributions from organic soil layers as well as sodium and electrical conductivity (EC) for various potential end-members (see Table 1 for references). The combination of ^{2}H and ^{18}O has only rarely been used (Rice and Hornberger, 1998; Burns and McDonnell, 1998; Gibson et al., 2000) since it is often assumed that both tracers supply the same information, although differences were found by Lyon et al. (2009). As we discuss later in the paper, future use of both isotopes is an important way forward for characterizing vadose zone water and its contribution to streamflow generation.

Other variations to three-component hydrograph separation have been developed. Hogan and Blum (2003) used a two-step procedure with a two-component approach based on ^{18}O, which informed a three-component separation based on $^{87}Sr/^{88}Sr$ as a tracer. St. Amour et al. (2005) also used a two-step procedure to separate snowmelt contributions from pre-event water in a permafrost catchment. St. Amour et al. (2005) first separated event snowmelt water and pre-event water with a simple two-component isotope mass balance approach. They then separated the pre-event water component into groundwater and surface water contributions. Their separation method was informed by their unique process understanding of their permafrost catchment. Uhlenbrook and Hoeg (2003) used process insights from their study watershed to derive five components of flow to the stream, using a hydrograph separation approach with ^{18}O and silicate.

Early work showed that the calculated proportions of each end-member in the stream was tracer-specific. For instance, Rice and Hornberger (1998), used ^{2}H combined with ^{18}O, chloride, DOC, and sodium in a three-component hydrograph separation and for several storms found large differences (>50%) in computed component amounts when different tracer combinations were used. Conversely, Carey and Quinton (2005) reported similar event and pre-event water ratios when using different tracers. Nevertheless, the fraction of their two pre-event water end-members differed by up to 20% when using different solute tracers in combination with ^{18}O. These findings support the idea that different tracers may describe different end-members. For example, while chloride is better suited to account for the difference of pre-event and event water (a time source separation), silicate can be a label for a geographic source component activation or a flowpath that traverses a zone with elevated silicate. Of course, solute tracers are not truly conservative (as shown early on for EC by Pilgrim et al. (1979)) and the comparison studies in hydrograph separation support this assertion.

Several studies compared the results of two- and three-component separation. Carey and Quinton (2005) and Muñoz-Villers and McDonnell (2012) showed similar event water between two- and three-component hydrograph separations. Wenninger et al. (2004) showed a difference of 10% in pre-event water contributions between the two methods. In their case, the three-component separation accounted for snow and rain inputs together while the two-component IHS accounted for rain inputs only. McHale et al. (2002) neglected direct inputs of throughfall in a two-component IHS (with soil water and groundwater) since there was no evidence of channel precipitation or saturation area runoff. When using a three-component separation, their throughfall accounted for 38% of flow in the stream, mainly at the expense of the groundwater end-member. This shows that end-members have to be chosen carefully and they can strongly interact.

3.3. Application of IHS outside of humid, upland forested environments

Buttle (1994) review included catchments predominately located in humid temperate forest regions (mainly in southern

Canada, and central and northern Europe with some catchments in the more humid regions of Australia, New Zealand, and the USA). In the intervening years, there has been a large increase in IHS applications in 'new' climate zones. Indeed Burns (2002) made a plea to the IHS community to apply the method to catchments with different climates and landuse types to gain a better insight into runoff generation processes. Buttle and McDonnell (2004) also outlined the need for IHS applications in tropical catchments to investigate the impact of forest disturbance, suburban development, and to quantify where mixing of water occurs in the landscape.

Significant progress has been made on a diverse array of landuse and landcover, and climate where IHS has now been applied (Table 2). The earliest example of work outside forested catchments is that of Obradovic and Sklash (1986) in permafrost terrain. They determined that snowmelt accounted for 40% of the total annual discharge of the Apex River on Baffin Island, Canada. There have been similar follow-on IHS findings in the Canadian tundra and (discontinuous) permafrost catchments focussed on the Spring freshet (Gibson et al., 1993; Carey and Quinton, 2004; Hayashi et al., 2004; St. Amour et al., 2005; Boucher and Carey, 2010; Carey et al., 2013) where about 20–50% of melt water contribution to the total hydrograph were observed over various catchment scales (see Table 2). Metcalfe and Buttle (2001) used IHS to compare two freshet periods in a low relief fen-dominated forested catchments with discontinuous permafrost in Manitoba, Canada. They found a significant difference in the snowmelt contribution to peak discharge (78% vs. 27%) and attributed the difference to varying active layer thickness between the two years. High snowmelt contributions to streamflow in a tundra catchment were also observed by Cooper et al. (1991). They found that 86% of the observed peak discharge was contributed from recent snowmelt in the Imnavait creek catchment in northern Alaska.

While most studies have focussed on long-term sampling of snowmelt in permafrost catchments, McNamara et al. (1997) and Carey and Quinton (2005) investigated runoff generation processes during rainstorms in catchments with discontinuous permafrost. Both studies found that summer stormflow was dominated by pre-event water. McNamara et al. (1997) found that the storm hydrograph in the Imnavait creek watershed consisted of 19% event water compared to 86% during freshet, based on the previous findings of Cooper et al. (1991). This was similar to the findings of Carey and Quinton (2005) who found 7% and 9% event water contributions to channel stormflow for two summer rainstorms, while the freshet-period hydrograph derived from snowmelt was 21% (based on their earlier work reported in Carey and Quinton, 2004). This shows the differences in runoff generation and sources of streamflow during different catchment states.

The application of IHS in various alpine catchments in the western United States has also had a strong focus on snowmelt. These catchments are often characterized by low vegetation cover, steep gradients, poorly developed soils or no soil coverage, and discontinuous permafrost. Liu et al. (2004) compared the runoff generation processes of two high altitude catchments (3500–4000 m.a.s.l.) in Colorado, USA, during snowmelt. They could explain the different contributions of event water during freshet (82% and 36% in total) based on different geological catchment structures and storages. In a nearby catchment, Williams et al. (2009) found that melt water contributed 74% of the measured hydrograph over their observation period, with a constant decrease in event water importance through the water year. Sueker et al. (2000) and Huth et al. (2004) both investigated a set of high mountain catchments. Huth et al. (2004) found that all of their catchments showed 80–90% of snowmelt contribution to discharge independent of the annual snow accumulation. Sueker et al. (2000), showed with a combination of two and three end-members, that the difference between event and pre-event components was controlled by the interplay between precipitation, snowmelt, and subsurface waters. The importance of the event water changed from month to month and catchment to catchment, but six of the seven catchments showed that pre-event water (subsurface waters) were the dominant source waters followed by direct snowmelt and, to a lesser extent, precipitation. Recently, isotopes were used to quantify the interplay of different end-member in glaciated catchments for longer time periods (monthly) and/or larger catchment areas (>1000 km^2) (Cable et al., 2011; Kong and Pang, 2012; Pu et al., 2012), but is beyond the scope of this work. Isotope hydrograph studies with a focus on precipitation events in glaciated catchment are rare. Dahlke et al. (in press) measured streamflow isotopes during various precipitation events in a glaciated mountainous catchment in Sweden. They found that event water (precipitation) comprised for 22% and 11% in two different years, while event water contributions were higher for particular events.

Dense temporal sampling of storm hydrographs is often challenging especially at remote locations. Therefore studies that investigate runoff generation during rain storms in alpine catchments based on IHS are rare. Laudon and Slaymaker (1997) compared the runoff sources in a nested catchment at an alpine and a pre-alpine sub-catchment in British Columbia, Canada. They found a significant difference in the water sources at each stream gauge. While event water dominated the alpine part of the catchment (60–75% during the course of the hydrograph), the stream showed large fractions of pre-event water downstream in the subalpine area. This shows the importance of the landscape structure on hydrograph components since the two sub-catchments differed in their soil development and topographic gradients. This is consistent with the work carried out by Cras et al. (2007) who determined the sources of storm water in three flash flood dominated alpine badland catchments in southern France. There, poorly developed soils together with the lack of storage in the catchments led to a dominance of event water during storms. At peak flow nearly 100% of the hydrograph was comprised of event water; during hydrograph recession pre-event water contributions increased to 40% and up to 90% of streamflow volume.

Table 2 lists a number of more recent papers that have been conducted in urbanized catchments. Following the early findings of Buttle et al. (1995), who tested the applicability of IHS to urban catchments and found high fractions of event water in channel stormflow (often >60% at peak flow), more recent work has extended this to larger scales (Pellerin et al., 2008; Buda and DeWalle, 2009; Meriano et al., 2011) and suburban environments in subtropical regions (Gremillion et al., 2000). A characteristic response, not surprisingly, in each of these studies is the high contribution of event water due to increased impervious surfaces and overland flow runoff dominance.

Although agricultural catchments are prominent in several regions throughout the world, only a few studies have applied the IHS approach to those catchments. Pionke et al. (1993) were among the first to report IHS results from an agricultural dominated catchment. They showed that for a 7.4 km^2 watershed three of four monitored storms were dominated by pre-event water (55–94% in total). The exact contribution was dependent on the way the end-members were described. In a smaller catchment (0.198 km^2) storm runoff was also dominated by pre-event water contributions; 90% over the course of the hydrograph (DeWalle and Pionke, 1994). These high fractions of pre-event runoff sources were also found in other studies in humid agricultural catchments, independent of scale. Cey et al. (1998) found 80% pre-event water contributions to channel stormflow with 67% during peak flow in a 6 ha catchment. For a 45 km^2 catchment, Buda and DeWalle (2009) found more than 80% pre-event water in channel stormflow. A similar range of pre-event water contributions (80%, 60%) was reported by Munyaneza et al. (2012) for two meso-scale catchments (129.3 km^2, 257.4 km^2) in Rwanda. Kennedy et al. (2012) showed the importance of human modification in agricultural catchments. They found that tile drain density in two agricultural catchments in Indiana, USA, was strongly influencing the event water fraction during peak catchment discharge, with 80% event water during peak flow at a catchment where 60% of the soils are drained and only 12% event water with half of tile drained area (Kennedy et al., 2012). The runoff partitioning in agricultural catchment is strongly influenced by the forcing climate, especially when leaving humid regions. For instance, Ribolzi et al. (1996) found only a 20% contribution of pre-event water during storm events in a sub-humid catchment in southern France. Hrachowitz et al. (2011) also showed much lower percentages of pre-event water in a set of four semiarid catchments with forest and agricultural cover (Table 2). This work was consistent with Marc et al. (2001) who showed that channel stormflow was comprised almost entirely of event water following long dry periods in a sub-humid forest catchment in southern France.

Several studies have applied IHS to catchments influenced in various degrees by grassland or meadows in different parts of the world. In general, pre-event water has been found to dominate discharge in these systems, be they mixed landuses of forest and grassland (Nolan and Hill, 1990), grassland-savannah-woodlands (Huang et al., 2006), meadow and forest (Ocampo et al., 2006). In an African wetland dominated grassland, McCartney et al. (1998) identified a threshold process that switched the runoff generation from pre-event water dominance to event water dominance after the storage of the dambo (an African wetland type) was exceeded. Bonell et al. (1990) found similar behavior for a tussock grassland watershed on the South Island of New Zealand.

Early work in peat dominated catchments by Ogunkoya and Jenkins (1991) used a two-component IHS to investigate runoff mechanisms in the peat dominated Allt a′ Mharcaidh catchment in the UK. They showed the dominance of pre-event water in channel stormflow with event water percentages on the order of 15–37%. Later work by Sklash et al. (1996) showed that event water contributions in the peat dominated Plynlimon were found to be below 10%, despite considerable pipeflow (as described in early hydrometric work at the site by Jones (1971)).

In terms of landuse change, Gremillion et al. (2000, p. 1486) noted that "whereas the long-term geochemical and ecological effects of changing hydrologic pathways (associated with landuse change) may be unclear, methods to characterize flow components have been thoroughly investigated". Indeed since then, several papers have used IHS to quantify changes in streamflow composition between different landuses or after human modification of catchments. Liu et al. (2011) compared runoff sources in two tropical catchments in south-west China. One of the catchments was a largely undisturbed tropical rain forest while the second catchment was dominated by rubber plantation. While peak flow for two monitored events in the rain forest catchment was dominated by pre-event water (71% and 69%), event water dominated peak flow in the plantation catchment (62% and 69%). Liu et al. (2011) explained this difference by the change in soil properties that reduced the mixing of waters in the plantation catchment. The role of forest harvesting on runoff sources was investigated by Pearce et al. (1986) and Sklash et al. (1986) in the Maimai watershed in New Zealand. Pearce et al. (1986) found a maximum instantaneous contribution of event water of 3% in one storm after the clear cut, and thus no change in runoff sources compared to the catchment with intact forest cover. Sklash et al. (1986) compared two of the Maimai catchments, one was undisturbed and one was logged approximately four years before event sampling. Sklash et al. (1986) found a large dominance of pre-event water (around 90%) with no clear difference between the two catchments during two storms.

One last important human influenced landscape where IHS has been applied recently are mined- and mining reclamation sites. Only two studies that we are aware of have applied IHS to such catchments. Kelln et al. (2007) determined the streamflow sources during snowmelt in a mine reclamation site in Alberta, Canada. Kelln et al. (2007) found that event water contributions decreased from 80% at the beginning of the melt period to 20% later in the spring. Earlier work by Blowes and Gillham (1988) investigated runoff sources during a long rainfall with high intensity, a short term event with high intensity, and during the melting period in a 0.75 ha catchment dominated by uranium tailings in Ontario, Canada. They reported a smaller contribution of event water during the longer rainfall event (55% at peak, 50% in total) compared to the short duration rainfall event (90% and 78%) controlled by the initial water table depths and the subsequent water table development.

3.4. Towards a better description of the event- and pre-event water end-members

The accurate identification of end-members has often been challenging because of the spatial variability of defined end-members (Uhlenbrook et al., 2002). Liu et al. (2004) have shown clearly that the choice of end-member influences the calculated event/pre-event water fractions. Bivariate mixing diagrams have been used to determine the potential end-members based on two different tracers. While stream geochemical approaches were introduced in the 1980s (Christophersen et al., 1990; Hooper et al., 1990), Ogunkoya and Jenkins (1993) were among the first who plotted the deuterium-chloride values of groundwater, soil water, precipitation, and stormflow to determine if those end-members then bounded the resulting stormflow samples. This was also done by Bazemore et al. (1994) with ^{18}O and chloride, whose data we present in Fig. 2. These data show the two-dimensional mixing space of soil water, groundwater, and event water.

The implications of compositional differences in soil and groundwater isotopic concentrations are shown in Fig. 3. Here we use a virtual hydrograph separation. The contributions of soil water, groundwater, and event water to the total discharge are defined *a priori* (Fig. 3d), as the "observed" isotopic signal and discharge in the stream (Fig. 3a). While the three endmembers enclose the isotopic values of streamflow (Fig. 3b), the three endmembers are not all the meteoric water line. The soil water endmember plots below the line, indicative of evaporative enrichment. A two-component separation with ^{2}H or ^{18}O leads to

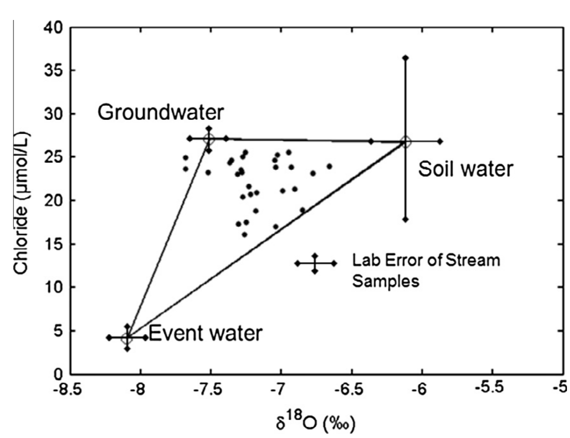

Fig. 2. Dual tracer diagram of ^{18}O and chloride. The observed pattern of streamflow samples (black dots) can only be explained when the soil water signal is taken into account. Then, the samples are within the dual tracer mixing space. Reprinted from Bazemore et al. (1994), with permission from Elsevier.

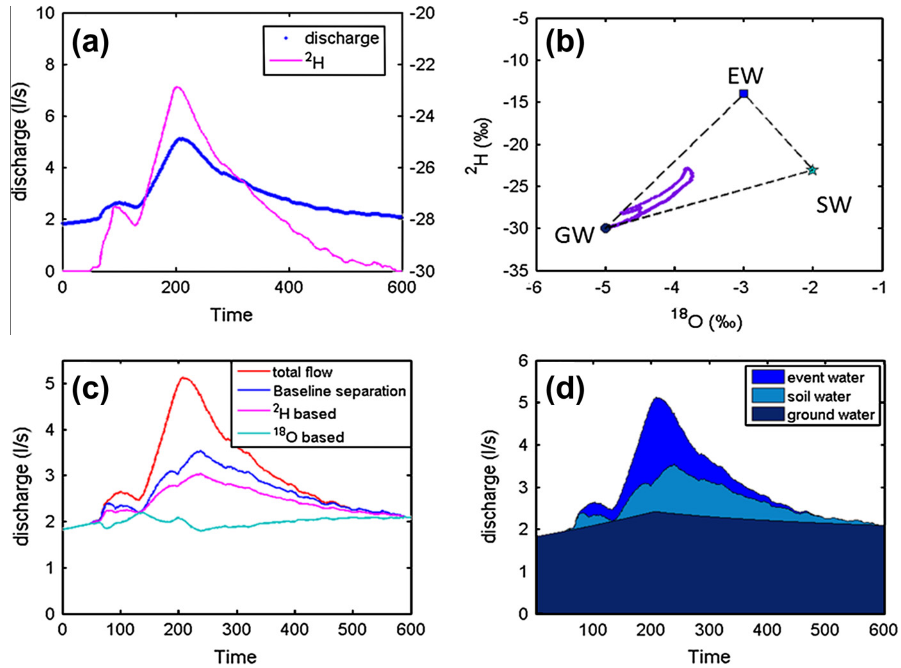

Fig. 3. Conceptual summary of different effects arising during hydrograph separation based on a virtual approach where event water, soil water, and groundwater contribute to stormflow. (a and b) are presenting the virtual data used in the separation: (a) is the hydrograph and temporal behavior of ^{2}H (while ^{18}O is also known but not shown). (b) Presents the isotopic composition of end-member and the temporal development of the streamflow isotopic composition in a bivariate mixing diagram. (c) Presents hydrograph separation results based on a two-component separation using pre-event baseflow (groundwater) and event water as end-member. Different results are gained from the use of ^{18}O and ^{2}H that are different to the known pre-event water fraction (baseline separation). (d) Presents the results of a three component separation, which is the baseline case of (c).

clear differences in the resulting event/pre-event water fractions (Fig. 3c). The baseline separation is the known pre-event water fraction that includes both, soil and groundwater. The results of the two-component separations based on ^{2}H and ^{18}O illustrate the differences in estimated source fractions due to the effect of evaporated soil water and its differential impact on ^{2}H and ^{18}O signatures and underline the need of a careful assessment of potential endmembers.

Bivariate mixing diagrams (Figs. 2 and 3b) were also used by Hangen et al. (2001) to decide which type of different soil waters they should use as an end-member in their hydrograph separation. Williams et al. (2009) used a bivariate mixing diagram based on ^{18}O and sodium to define snowmelt and baseflow as end-members in a two-component IHS. This data-based approach of end-member determination is a less ad hoc way to define end-members, compared to *a priori* end-member determination in a traditional, simple, two-component hydrograph separation.

One area where end-member discrimination has been important in IHS has been the separation of event water in rain and snowmelt. Many studies have defined event water as rainfall, melt water, or both. While end-member determination and sampling of rain, melt, and rain-on-snow events is challenging (Buttle et al., 1995) some studies have overcome this issue with the use of snow lysimeters and discrete sampling and characterization of event water components (McLean et al., 1995). Early work defined the snow end-member with melted snow cores analyzed as a depth integrated sample (Dinçer et al., 1970; Rodhe, 1981; Bottomley et al., 1986; Moore, 1989; Cooper et al., 1991). This method is limited since the isotopic signal of snow shows depth stratification (Huth et al., 2004) and fractionation processes occur during snowmelt (Taylor et al., 2001, 2002; Feng et al., 2002; Unnikrishna et al., 2002), resulting in a characteristic and progressive shift from light to heavy isotopic composition through the melt (Shanley et al., 2002). While Sueker et al. (2000) used snow cores in their IHS, they introduced an adjusted isotopic composition for their new water component but it did not account for temporal changes. To overcome this, several authors have used snow lysimeters or melt plots that give a spatially limited, but useful instantaneous event water signal inputs (Hooper and Shoemaker, 1986; Moore, 1989; Maulé and Stein, 1990; Wels et al., 1991; Buttle et al., 1995; Mast et al., 1995; Laudon et al., 2002; Liu et al., 2004; Williams et al., 2009). Such an approach does not only account for the fractionation process in the snow cover but also for rain-on-snow contributions. McLean et al. (1995) showed that rainfall could account for up to 23% of snow lysimeter outflow.

In forested watersheds, fractionation processes linked to throughfall (Saxena, 1986) can introduce additional temporal and spatial complexity to the IHS procedure. Gibson et al. (2000) showed an enrichment of ^{18}O of up to 2.9‰ but concluded, based on a longer sampling period, that there was no statistically significant difference at their site between the isotopes in throughfall and open range precipitation. Kubota and Tsuboyama (2003) showed an enrichment of up to 8.5‰ for ^{2}H. On average they found 2.8‰ enrichment in throughfall and 2.9‰ enrichment in stemflow compared to ambient rainfall. ^{18}O also showed enrichment effects in their study. Kubota and Tsuboyama (2003) found a corresponding error in the event fraction of their IHS on the order of 5–10% when using open precipitation as end-member. Spatial variability of the isotopic signal in throughfall and its representation in an IHS is an even bigger issue. Studies have shown large spatial differences in isotopic composition with varying distance from the tree below the crown (Brodersen et al., 2000) and between different tree species (DeWalle and Swistock, 1994; Brodersen et al., 2000). The spatial variability in throughfall was investigated by Allen (2012) in a more systematic manner. Within a single plot, the span of variation between throughfall collectors could exceed 2‰

δ^{18}O (mean range was 1.6‰ over 11 collections periods) and variation between throughfall collectors usually exceeded the difference between throughfall and rainfall (Allen, 2012). Although patterns of throughfall depth have been observed to be temporally stable (Keim et al., 2005), patterns of relative differences in isotopic compositions were not stable (Allen, 2012).

When performing IHS in forested watersheds, the methodology of sampling the event water signal has varied widely. Some studies have used open precipitation collectors (e.g. Buttle and Peters, 1997; Metcalfe and Buttle, 2001; Uhlenbrook et al., 2002), some have collected bulk throughfall (e.g. Bazemore et al., 1994; Burns et al., 1998) and others have used incremental sampling of throughfall (e.g. Hill and Waddington, 1993; Brown et al., 1999). These methodological differences complicate the comparison of different studies and the summarization of controlling factors in event/pre-event water partitioning in forested watersheds.

An important question asked in hydrograph separation is how to respond to the event water issues related to space and time, rain and melt and throughfall? Early work by McDonnell et al. (1990) presented two incremental weighting techniques and compared the results to the results of a weighted mean value. Their incremental weighting accounted only for the precipitation at one fixed site. Their intensity based incremental weighting was based on the idea that higher intensity rain produced more runoff than lower intensity rain. The McDonnell et al. (1990) precipitation weighting procedure has frequently been applied for IHS (Ogunkoya and Jenkins, 1993; Jenkins et al., 1994; Brown et al., 1999; Uhlenbrook et al., 2002; Renshaw et al., 2003; McGlynn and McDonnell, 2003). A more sophisticated method, called TRANSEP, which accounts for time variance in the isotopic precipitation signal was introduced by Weiler et al. (2003). The TRANSEP method combines a transfer function for runoff, event and pre-event water by fitting these to the observed data. Weiler et al. (2003) demonstrated its use with various types of transfer functions. Based on the fitting procedure, the fractions of each end-member can be identified. The TRANSEP method has since been successfully applied in various studies to hydrograph separation problems (e.g. Lyon et al., 2008, 2009; McGuire and McDonnell, 2010; Roa-Garcia and Weiler, 2010). Cras et al. (2007) also used a transfer function approach (with reduced complexity compared to Weiler et al. (2003)). They convolved the isotopic input signal with a dispersion model and were able to apply it to several events in two French badland catchments and found clear differences compared to the incremental methods. Nevertheless, their transfer function approach did not work consistently well for all events (Cras et al., 2007).

In snowmelt studies Mast et al. (1995) have used volume weighted average values from snow lysimeters for melt-based IHS. Other authors have used the measured isotopic composition of the meltwater for every time step in the IHS (e.g. Hooper and Shoemaker, 1986; Maulé and Stein, 1990). The former method is limited since it does not consider temporal changes in the snowmelt signature; whereas the latter does not account for storage and longer transit times of melt water within the system. This is especially important since snowmelt applications of IHS usually extend over several weeks. Laudon et al. (2002) presented the run-CE method (runoff-corrected event water approach) that accounted for temporal variability of the isotopic melt signal and temporary storage of meltwater in the catchment. The method was further applied in various snowmelt studies (Beaulieu et al., 2012; Laudon et al., 2004, 2007; Petrone et al., 2007; Carey and Quinton, 2004).

Spatial variability of the isotope signal during snowmelt shows ambiguous results. Work of Moore (1989) and Laudon et al. (2007) showed no statistically significant difference between the isotopic signals of outflow from different snow lysimeters, while Unnikrishna et al. (2002) showed considerable spatial variability on the order of meters. Recently, Beaulieu et al. (2012) found considerable spatial variability in snowpack drainage based on daily to bi-daily sampling at four 6 m^2 snow lysimeters in British Columbia, Canada. Elevation explained much of the variance observed in δ^{18}O. Gustafson et al. (2010) concluded in their study of spatial variablity of δ^{18}O in snow that tracer studies have to account for the spatial variations in the bulk snow composition before the snowmelt to achieve an appropriate result in hydrograph separation studies.

Beyond the issue of event water end-member characterization, the determination of the pre-event water end-member has been very challenging due to its high spatial and temporal variability. Various potential pre-event end-members have been considered. Most studies have used a groundwater component and determined its isotopic composition based on the baseflow or the pre-event streamflow signal (e.g. Blume et al., 2008; Lyon et al., 2008), the average low flow signal over several years (Onda et al., 2006) or actual observed well data (e.g. Iwagami et al., 2010). The soil water component has been sampled in different ways. Zero tension lysimeters (e.g. Hinton et al., 1994; Williams et al., 2009), tension lysimeters (e.g. Bazemore et al., 1994; Burns et al., 1998; Hill et al., 1999; Iwagami et al., 2010), boreholes (e.g. Kelln et al., 2007) and suction cups (e.g. Hangen et al., 2001) have been used to determine the isotopic composition of soil waters.

An important question when sampling soil water is: what soil water is being sampled? Non-suction methods usually sample only mobile water and this is often influenced by event water contributions; thus contaminating a pure soil water end-member. Tension lysimeters and suction cups may bias the sampling towards water that is stored in a distinct soil pore class. Leaney et al. (1993) argued that suction lysimetry predominantly samples water from larger pores. DeWalle et al. (1988) found no significant difference in the isotopic composition of water collected from soil water samplers or pan lysimeters. Figueroa-Johnson et al. (2007) found clear differences in the isotopic signal of soil water based on the applied sample method: suction lysimeters, centrifugation, and azeotropic distillation. This is supported by previous findings of Kelln et al. (2001) that found slightly differences in ^{18}O depending on the sampling method of clay water. This was especially important in well-structured soils. Soil water has also been shown to exhibit depth-dependent signals (Blowes and Gillham, 1988; Königer et al., 2010). Burns et al. (2001) suggested that ‘soil water’ be sampled in throughflow trenches to avoid preferential sampling of soil water types. The drawback is that this might already include event water. Hangen et al. (2001) outlined a strategy based on a bivariate mixing diagram and chose the soil water end-member that allowed the discharge water to be enclosed within the bivariate mixing diagram.

The only work that we are aware of that has incorporated both time-variant event and pre-event end-members in a numerical scheme is Harris et al. (1995). The variable source area concept underpinned their approach and dictated that the pre-event water derives exclusively from the near-stream saturated zone. This near stream zone could then be recharged by lateral influx from unsaturated hillslope water that itself changes its isotopic composition by mixing with the incoming precipitation water (Harris et al., 1995). Their so-called ‘continuous open system isotope mixing approach’ also accounted for the storage volume of the saturated and unsaturated zone. Ogunkoya and Jenkins (1993) compared the results of IHS with constant and changing end-member composition. They interpolated the ground and soil water end-member between the known concentrations at the beginning and the end of an event. Ogunkoya and Jenkins (1993) calculated, based on the fixed end-member approach, a contribution of soil water to the storm hydrograph of 28% and a groundwater contribution of 53%. Using time-variant end-members they calculated 19% and 66%, respectively.

Lastly, uncertainty in IHS as linked to end-member characterization has been an ongoing issue and point of discussion. Errors can be separated into 'statistical uncertainty' based on spatial and temporal variability of the end-member values and the laboratory error and into 'model uncertainty' based on the violations of the underlying assumptions (Joerin et al., 2002). Usually the statistical uncertainty is evaluated and model uncertainty is mainly ignored, although Moore (1989) evaluated the violations of the underlying assumptions qualitatively and Joerin et al. (2002) introduced a method to account for uncertainty formally within the IHS. Rodhe (1981) was the first to introduce an uncertainty assessment of the IHS results. He used ±0.5‰ variations in pre-event water (groundwater) values of ^{18}O and ±1‰ in the event water (melt water). This led to an accuracy of ±15% in the groundwater contribution to streamflow (Rodhe, 1981). Similar approaches were followed by Hooper and Shoemaker (1986) and McDonnell et al. (1991) who found uncertainties of ±10% and ±5% in the end-member contribution of two-component IHS. Bazemore et al. (1994) used a Monte Carlo approach to assess uncertainty in IHS. For every streamflow sample they used 50,000 calculations and evaluated the error based on the analytical error and the spatial variation of the end-members based on their standard deviation (Bazemore et al., 1994). Similar Monte Carlo approaches were followed by Ribolzi et al. (1996) and Rice and Hornberger (1998). Genereux (1998) introduced a Gaussian error propagation approach for his IHS. The input to this approach were spatial and laboratory uncertainties. This approach is now the state-of-the-art approach (e.g. James and Roulet, 2009; Boucher and Carey, 2010; Muir et al., 2011; Meriano et al., 2011). Kubota and Tsuboyama (2003) quantified the effect of using the isotopic signal of rainfall instead the one of throughfall in forested catchment IHS studies. The error can be 15% in event/pre-event water fraction.

Uhlenbrook and Hoeg (2003) used the approach of Genereux (1998) and estimated the uncertainty in a three-component hydrograph separation with ^{18}O and silicate based on variable potential error sources: the error in tracer and discharge measurement, intra-storm variability of ^{18}O, elevation effect, solution of minerals during the runoff process, and spatial variablity of tracer concentrations. The relevance of each error source changes during events. Uhlenbrook and Hoeg (2003) identified the spatial variability of tracers the most critical error source and suggest a targeted sampling strategy. This is consistent with the suggestion of Machavaram et al. (2006) that the problem of spatial variablity of tracer concentration can be overcome by intensive sampling. Uhlenbrook and Hoeg (2003) noted that, due to the mentioned problems, hydrograph separation results at meso-scale catchments (18.4 km^2 in their case) can only be seen as qualitative results.

3.5. Synthesis of factors controlling hydrograph components

An open question in hydrology is how catchment characteristics influence runoff generation and thus the partitioning between event and pre-event water. Based on the IHS studies published to date, five broad characteristics have been especially important in this context: catchment size, landscape organization, landuse, initial system state, and storm characteristics.

3.5.1. Catchment size

Since the initial work of Sklash et al. (1976) who examined scale influences on pre-event water fractions, many studies have examined such relations, but often with equivocal or contradictory results. Gomi et al. (2010), like Sklash et al. (1976), found increasing pre-event water contributions with increasing catchment size for seven small catchments (0.0019–0.0485 km^2). By contrast, Shanley et al. (2002) and Brown et al. (1999) found increasing event water contributions with increasing catchment size in nested catchment systems. Other authors found no catchment size effects over various catchment areas and event types: James and Roulet (2009) at catchments between 0.07 km^2 and 1.47 km^2 during storm events, Laudon et al. (2007) at 15 catchments between 0.03 km^2 and 67 km^2 during snowmelt, McGlynn et al. (2004) at five small catchment (<0.28 km^2), Sueker et al. (2000) at six high alpine catchments during snowmelt (0.78–104.49 km^2), and Wels et al. (1990) at three catchments (0.033–1.95 km^2).

Didszun and Uhlenbrook (2008) observed threshold behavior in the scaling effect of event and pre-event water partitioning. While they did not observe a pattern of event/pre-event water partitioning below 1–2 km^2, they observed little differences in the runoff generation for catchments between 1–40 km^2, while catchments larger than that were then influenced by further urbanization and thus the runoff generation changed towards surface components (Didszun and Uhlenbrook, 2008). Shanley et al. (2002) explained their increase of event water contributions with catchment size by rationalizing that the catchment's topography led to increasing percentage of surface saturation, due the larger upslope contribution area and flatter slopes, with increasing catchment size, and thus larger event water fractions. Overall we cannot find unequivocal results in the effect of catchment size, since it is clearly overlay by landuse and topography effects.

3.5.2. Landscape organization

James and Roulet (2009) linked the fraction of valley bottom area at their catchment to an increase in event water contributions during dry catchment conditions. Another topographic catchment characteristic, the average slope, was observed to be negatively correlated to the amount of subsurface flow with possible consequences for event/pre-event water proportions (Sueker et al., 2000).

The effect of wetlands in event/pre-event water partitioning has also been observed. While studies have shown that wetlands have an effect, the direction of the wetland effects are contradicting. On the one hand Roa-Garcia and Weiler (2010) showed that a wetland dominated catchment reduced the fraction of event water during several events compared to a grassland and a forest dominated catchment (they showed somewhat similar event/pre-event water proportions). On the other hand findings by Petrone et al. (2007) and Laudon et al. (2007) showed higher event water contributions in catchments containing wetlands compared to solely forested catchments, the latter study during snowmelt.

The underlying geology has also been found to have an impact on the delivery of event water, at least at the hillslope scale. Onda et al. (2006) compared two hillslopes with underlying granite and more permeable shale bedrock. They found that the hillslope runoff from the granite slope had a higher fraction of event water, since water flux was through the soil layer while the shale hillslope showed deep bedrock dominated flow paths (Onda et al., 2006).

3.5.3. Landuse

Natural and human induced landuse changes are expected to change hydrological behavior significantly and are thus a major concern for water quality and quantity. The IHS approach is thus an excellent tool to detect changes in, or the influence of landuse types on hydrology. Buttle (1994) summarized pre-event stormflow contributions in relation to landuse. He found that pre-event water was most important in forested catchments and less important in urban areas with agricultural sites in between. In the last 20 years the number of studies and the number of investigated landuse types have increased. Buda and DeWalle (2009) compared catchments with different human activity. They examined nitrate dynamics in an urban, an agricultural, and a forested catchment and used IHS to compare those catchments. Buda and DeWalle

(2009) found that the urban catchment produced the highest amount of event water, while the agricultural catchment produced the lowest. Liu et al. (2011) showed the differences in event/pre-event water fraction between a plantation and tropical forest. While these two studies investigated human changed landuse, Schwarze and Beudert (2006) investigated the effect of the bark beetle on runoff generation. They compared two forested catchments with different amounts of forest damage by bark beetle. They found that the catchment with the most damaged forest showed 45% pre-event water during events while the lesser damaged forest showed 55% pre-event water (Schwarze and Beudert, 2006). However, the study was limited in that there were no data on the catchment pre-event water proportions before the bark beetle attack, so the effect of the bark beetle remains speculative. These newer results mainly confirm the summary of Buttle (1994) in that the effect of landuse is mainly clear. Forest catchments with high infiltrability and canopy effects reduce the event water fraction, while the event water fraction is increasing from agricultural to urban areas by reducing infiltration.

3.5.4. Initial system state

Beyond the effect of stable or slow changing catchment properties, the system state and the nature of the input have also been shown to significantly affect the partitioning of event/pre-event water. Various studies have shown a link between the initial catchment state, or storage before the storm event, with the resulting event/pre-event water fraction, quantified using soil moisture (e.g. Casper et al., 2003), antecedent streamflow (e.g. Pellerin et al., 2008), or water levels (e.g. Cey et al., 1998), as a descriptor of catchment state. Most studies have found increasing event water contributions with increasing dryness (Marc et al., 2001; Casper et al., 2003; Cras et al., 2007; Blume et al., 2008; Pellerin et al., 2008; James and Roulet, 2009). Casper et al. (2003) explained this correlation, conceptually via connectivity, where increasing connectivity led to more contributing areas, thereby increasing the role of stored pre-event water. Additionally, very dry catchments were simply not able to supply pre-event water to discharge (Marc et al., 2001) or can be dominated completely by surface runoff generation processes.

Marc et al. (2001) found 100% event water contributions to channel stormflow after a long dry period in southern France. Alternatively a few studies have found decreasing event water contributions with increasing dryness (Cey et al., 1998; McCartney et al., 1998; Ocampo et al., 2006). These opposing results appear to be explained by specific catchment conditions. In the work of Ocampo et al. (2006) increasing catchment storage led to more saturation excess and thus more event water contributing to streamflow. McCartney et al. (1998) carried out a study in a catchment containing a dambo. Before the storage of this dambo was full, storm discharge and event water contributions were reduced; as soon the storage capacity was exceeded event water contributions increased (McCartney et al., 1998). The effect of storage on the event/pre-event water proportion can also be more complex. Hinton et al. (1994) found that wet conditions led to higher event water contributions during peak flow, but to less event water contributions over the course of the storm event. All this shows the strong influence of the initial state of the catchment prior to a precipitation event, but that the effect of storage is then linked to catchment structure and probably also to storm characteristics.

3.5.5. Storm characteristics

The influence of the characteristics of a precipitation event have also been shown in various studies. James and Roulet (2009) and Segura et al. (2012) showed that total storm size with related increasing percentages of throughfall, increased the amount of event water in storm runoff. The positive correlation between precipitation amount and event water contribution was reported by Pellerin et al. (2008), and in the case of throughfall, by Brown et al. (1999). Contrary to these findings, Renshaw et al. (2003) reported increasing pre-event water contributions with increasing storm size, but only during peak discharge. They attributed this to changing flow paths during the event. Increasing event water contributions with increasing rain intensity was observed by Kværner and Kløve (2006), who found that event water dominated channel stormflow during intense rainstorms, whereas pre-event water dominated during moderate-intensity rainstorms. The effect of input intensity and amount has also been observed for snow-driven systems. Moore (1989) found that event/pre-event water partitioning was controlled by the daily pattern of snowmelt intensity. Most work linked the event/pre-event water fractions with the rainfall and melt characteristics. Rodhe (1989) showed that the pre-event water fraction decreased with the maximum specific discharge ($\mathrm{l\,s^{-1}\,km^{-2}}$) during rainfall and snowmelt events in 10 Swedish catchments.

3.6. Why we use isotopes in hydrograph separation

Despite several limitations, isotopes continue to be the best conservative tracer for water among those currently available. The isotopes of the water molecule are an ideal, conservative tracer since they are part of the water molecule, added naturally during precipitation events and once free from evaporative exposure, are only subject to changes due to mixing (Kendall and McDonnell, 1998). Despite this, many two-component IHS continue to be substituted with solutes; for ease of use and field/lab practicalities. Early work by Obradovic and Sklash (1986) noted that EC and magnesium underestimated the pre-event water fraction during snowmelt compared to ^{18}O. Other work in the 1980s by Pearce et al. (1986) showed significant differences in hydrograph separation in the Maimai catchments in New Zealand with EC-based two-component separations versus IHS. Going forward, there may be usefulness in combined tracer usage, to extend hydrograph analysis in time and place. There will be some places and instances where solutes can in fact be a useful proxy for isotopes. For instance, recent work by Pellerin et al. (2008) found that while the pre-event water contributions were partly overestimated using EC, EC was a good surrogate for ^{2}H in urban catchment settings. Others have also found similarities between EC and water isotopes in a two-component hydrograph separation (McNamara et al., 1997; Cey et al., 1998). Blume et al. (2008) investigated two storm events and found that EC overestimated the pre-event water clearly in one event, and gave similar event/pre-event water proportions compared to ^{2}H in a second event. Vidon and Cuadra (2010) found that using EC led to 5–15% higher pre-event water contributions than when using ^{18}O at a tile-drained field site. Laudon and Slaymaker (1997) compared hydrograph separation based on EC with IHS in a nested catchment approach and found a completely different behavior in the upper catchment, but a similar behavior in the lower catchment, with a difference that still reached 20% in water fractions. Laudon and Slaymaker (1997) concluded that alternative tracers to isotopes can be used but that this must be verified for each catchment.

Differences of EC compared to ^{18}O and ^{2}H during snowmelt were observed by Hayashi et al. (2004) that found that the maximum upper limit of meltwater based on ^{2}H is the lower limit of meltwater contributions based on EC. The conclusion of various other studies using different solutes and their comparison to water isotopes are differing. Turner et al. (1987), Leaney et al. (1993), Ribolzi et al. (1996), and Brown et al. (1999) found similar results (less than 10% difference) in chloride based hydrograph separation and IHS. Differences found by Blowes and Gillham (1988) in the total contributions over three events can reach nearly 30% and even the direction of the difference can change from event to event. Monteith et al. (2006) found instantaneous differences of up to 40%, but also some similarities between chloride and isotopes in a two-component hydrograph separation. The results for other solutes show ambiguous results. There are studies confirming similarities between silicate and isotopes (Hooper and Shoemaker, 1986; Durand et al., 1993; Pionke et al., 1993) and others showing differences (Nolan and Hill, 1990). This can also be found for alkalinity (Durand et al., 1993; Ribolzi et al., 1996) and sodium (Pionke et al., 1993; Sueker et al., 2000). All those results show that besides the differences in hydrograph separation based on ^{2}H and ^{18}O, the results based on solutes are often significantly different than results obtained by isotope based hydrograph separation. Two important things have to be kept in mind. First different tracer can have a different information content (Ladouche et al., 2001). This allows use of, for example, silicate as a flow path tracer and the isotopes as a time-source tracer (e.g. Hoeg et al., 2000), or sodium as a reactive tracer (e.g. Sueker et al., 2000). In these cases the results of a two component hydrograph separation should be different. Second, the behavior of solute tracer can be non-conservative. Hill (1993) showed that calcium, magnesium and sodium ions were similar to ^{18}O as long as the event water contributions were below 25%, above this figure the ions became reactive. Such a study shows the clear limitations of solute tracers and should motivate to use the isotopes of the water molecule in hydrograph separation studies.

4. Conclusions and way forward

In many ways, the current limitations associated with IHS are the same issues of the 1970s: the assumptions implicit in the technique. Of the five underlying assumptions (Buttle, 1994), the first assumption ‘that the isotopic content of the event and the pre-event water are significantly different’ is still a rather critical factor for any IHS. Similarly, the fifth assumption that ‘surface storage contributes minimally to the streamflow’ is also rather obvious, although past work has shown that one can use such surface water storage contributions to ones advantage to determine wetland (Burns and McDonnell, 1998) and lake (Bottomley et al., 1984) contributions to runoff, and relative percentage of peatland water to flow across a gradient of wetland dominance (Laudon et al., 2007).

Problems still surround the second assumption that “the event water maintains a constant isotopic signature in space and time, or any variations can be accounted for”. This is essentially a question of how ‘ideal’ water isotopes are for watershed-scale IHS. While various methods can account for the temporal variability in the isotope signal of rainfall and snowmelt, which we have reviewed in detail above, quantifying the spatial variability in the signal is still a large source of IHS uncertainty. This is especially true in larger catchments, catchments with complex topography, for snowmelt events where inputs are highly non-uniform, or where vegetation plays a role in forming complex patterns of throughfall input (notwithstanding associated evaporative enrichment possibilities therein).

The third assumption that ‘the isotopic signature of the pre-event water is constant in space and time, or any variations can be accounted for’, continues to challenge current work, with few if any studies quantifying these patterns and effects. We continue to work on the early assumption that the δ-value of pre-event streamflow integrates the near-stream groundwater that is most likely to contribute to stormflow during events. Baseflow samples continue to be used to describe the isotopic composition of the pre-event water end-member. While some early studies indeed reported a close link between (shallow) groundwater and baseflow δ-value (Hill and Waddington, 1993; Turner et al., 1987) several other studies have shown clear differences between the isotopic signal of near-stream groundwater and the baseflow signal (Buttle et al., 1995; Bonell et al., 1998; Burns and McDonnell, 1998). We also know that in several instances this shallow groundwater can be poorly mixed (Kendall et al., 2001; Rademacher et al., 2005). McCallum et al. (2010) showed how using baseflow to describe the pre-event water can lead to an overestimation of the pre-event water end-member. We need new work that goes after the spatial patterns of pre-event water concentration: from tackling patterns of mobile soil water to distinguishing the patterns of soil water from transient groundwater (that may drive channel stormflow) to quantifying and differentiating the patterns of mobile versus poorly mobile soil water. As shown recently by Klaus et al. (2013), some distinct soil layers with distinct isotopic characteristics may in fact dominate hillslope response and channel stormflow signatures.

The fourth assumption that “contributions from the vadose zone must be negligible, or the isotopic signature of the soil water must be similar to that of groundwater” continues to be problematic. Based on findings in the past 20 years, it is clear that a better assumption is that soil water contributes significantly to channel stormflow unless there is evidence to the contrary. The findings of Rice and Hornberger (1998) are still a useful cautionary tale where they found instantaneous soil water contributions in channel stormflow of up to 90%, linked with antecedent conditions and event characteristics. Here again, the issues highlight how inter-related the assumptions are; soil water differs isotopically from groundwater and varies with depth in the profile. New work is clearly needed to understand the interplay of deep and shallow soil water and how storm- and seasonally-variable soil waters influence the resulting groundwater signature and blend of stormflow components.

With the advent of laser spectrometers and the now-standard dual isotope reporting of ^{18}O and ^{2}H, embracing a dual approach in IHS seems to be an obvious way forward. It is worth noting that this was inconceivable (due to time, energy and expense) just five years ago. Of course, an advantage of including both ^{18}O and ^{2}H together in an attempt to separate the sources of water in the storm hydrograph is when there is deflection off the meteoric water line of at least one end-member. Until very recently, most studies, particularly in humid regions, assumed that ^{18}O and ^{2}H would plot together on local meteoric water line. While this is indeed the case for mobile waters extracted from soils via low tension suction lysimeters (Muñoz-Villers and McDonnell, 2012), recent work has shown clearly that sampling ‘less mobile water’ in the subsurface via vapor equilibrium (Koehler et al., 2000; Kelln et al., 2001) or cryogenic extraction (Brooks et al., 2009; Goldsmith et al., 2012) can reveal evaporated water that plots below the meteoric water line (e.g. Klaus et al., 2013). Of course, the same is true for lakes and wetlands that usually show a deviation from the local meteoric water line or even summer low flows as shown some time ago by Turner et al. (1987). Following this water in the runoff stream will be a boon to new process insights in terms of addressing some of the outstanding assumptions regarding mixing, spatial stability, and soil water participation.

Laser spectrometers also enable high frequency observation of ^{2}H and ^{18}O in streamflow and input components. We see the potential for new breakthroughs in understanding of time source components in flow at high frequency, as linked to the rich structure of the precipitation input when sampled in high frequency. Berman et al. (2009) showed how a laser spectrometer could be deployed in the field to collect streamflow samples every 15 min for ^{2}H and ^{18}O through multiple storm events. High frequency samples can of course be gained by manual sampling or automatic water sampling devices, but the amount is then limited by labor costs of collection or by capacity of the water sampler device. Koehler and Wassenaar (2011) and Herbstritt et al. (2012) have paved the way for the development of even more reliable high frequency isotope observations in streams, yet these methods have only yet been applied at laboratory conditions thus far. Much potential exists for innovation and discovery for IHS in high frequency. The benefits of high frequency sampling relate directly to the identification of process thresholds (Klaus et al., 2013), better insight into short term catchment processes (Kirchner et al., 2004), and appropriate description of the different components in hydrograph separation that are masked by current low frequency approaches. Birkel et al. (2010) suggested that high-resolution input data is very important for the conceptualization, calibration, and performance of accurate isotope tracer models. Short term processes, such as threshold exceedance can thus change the number of contributing end-members, or their isotopic composition, and require adjustment to the chosen separation model during the course of the storm event. In summary, classical two-component hydrograph separation has contributed crucially to new process understanding in hydrology. It can continue to be a valuable tool to understand new aspects of the hydrological cycle. Using a dual isotope approach combined with three-component separation and hydrometric observations opens a window of opportunities in hydrological research by reducing limitations that arise from the two-component approach. This can enhance our understanding of hydrological processes.

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