

12. A REVIEW OF ISOTOPE APPLICATIONS IN CATCHMENT HYDROLOGY

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1. Introduction

Isotope methods were introduced into catchment hydrology research in the 1960s as complementary tools to conventional hydrologic methods for addressing questions of where water goes when it rains, what pathways it takes to the stream and how long water resides in the catchment (McDonnell, 2003). Despite slow incorporation into routine research applications, the last decade has seen a rapid increase in isotope-based catchment studies. These have been mainly carried out in small well-instrumented experimental catchments, on the order of 0.01 to 100 km² and located typically in headwater areas (Buttle, 1998). In contrast, little has been done in terms of application and transfer of these concepts and methodologies to large (>100s to 1000s of km²), less instrumented basins. Much potential also waits to be realized in terms of how isotope information may be used to calibrate and test distributed rainfall-runoff models and to aid in the quantification of sustainable water resources management. In this chapter, we review the major applications of isotopes to catchment studies, and address a variety of prospective new directions in research and practice. Our discussion is based primarily on catchments in temperate to wet zones.

2. Review of research

2.1. HISTORICAL OVERVIEW OF ISOTOPES EMPLOYED IN CATCHMENT HYDROLOGY

Natural ^{14}C was discovered in the late 1940s and natural ^3H (tritium) was discovered in the early 1950s (Grosse et al., 1951). Shortly thereafter, atmospheric nuclear weapon tests substantially increased the ^3H content in the rapidly circulated parts of the hydrologic cycle, with the peak around 1963. Tritium was therefore used for the first systematic estimations of water age in catchments (Eriksson, 1963). While bomb spike ^3H is now rarely used for water age-dating, oxygen-18 and/or deuterium (^2H) became and remained common tools for dating waters up to about five years of age, which typically occur in shallow aquifers connected to streams (Epstein and Mayeda, 1953). Noble gases such as ^3He (Torgersen et al., 1979), ^{85}Kr (Rozanski and Florkowski, 1979) and ^{222}Rn (Rogers, 1958), solutes such as ^{35}S (Lal and Peters, 1966), and the anthropogenic compounds, CFC (Thompson et al., 1974) and SF_6 (Maiss and Levin, 1994), date water ages from days up to decades.

In addition to water age dating, hydrograph separation approaches employed tritium (Crouzet et al., 1970) and stable isotopes of ^{18}O and ^2H (Dinçer et al., 1970) in two-component mixing models (Pinder and Jones, 1969). These early studies opened the way for an expansion of studies of runoff generation and runoff components (event vs pre-event water) on experimental hillslopes and in catchments. The paper by Sklash and Farvolden (1979) is a benchmark study that documented the dominant role of the subsurface pre-event water in runoff generation. Solute isotopes such as ^{87}Sr (Stueber et al., 1987), ^{13}C , ^{34}S and ^{15}N (Kohl et al., 1971) have provided important information on biological and geological sources of solutes recharging groundwater and delivery to surface water. Several other cosmogenic (^7Be , ^{10}Be , ^{24}Na , ^{41}Ca) and lithogenic (^6Li , ^{37}Cl , ^{11}B , ^{143}Nd , ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{210}Pb) isotopes have been introduced into catchment hydrology research within the last two decades and many potential applications are yet to be realized.

Thus, the expansion of isotope techniques in catchment hydrology in recent decades generated two major sets of applications: (1) assessment of the temporal variations of the major stocks and flows of water in catchments between events, such as estimation of water residence times and quantification of recharge travel times, and (2) assessment of catchment hydrologic processes, such as quantification of the sources of runoff and delineation of infiltration and exfiltration zones along streams.

2.2. TEMPORAL VARIATIONS OF HYDROLOGIC PROCESSES IN CATCHMENTS

The hydrologic cycle in catchments varies in time (Ohmura and Wild, 2002) and the runoff generation is a complex of highly nonlinear processes (Phillips, 2003). Water infiltrates at different rates, mixes in the subsurface and thus has different travel times to the stream. The mean residence time (MRT) or "age" of water in a catchment is the average time elapsed since a water drop entered the catchment and the time it is observed in the catchment outlet, well or soil depth (adapted after

Yurtsever, 1995). It describes functionally the catchment response to water withdrawals, contamination, or land use changes, and provides a basis for assessing sensitivity to imposed catchment management practices (Alley et al., 1999). To date, stable water isotopes ^{18}O and ^2H have been the dominant age-assessment tool, generally because of the conservative nature of those isotopes and the ease in field and laboratory processing of water samples. Table 1 summarizes recent estimates of the MRT of water exiting a catchment; a few applications have been also carried out also on water exiting a spring (Małozzewski et al., 2002) or the base of a hillslope (Asano et al., 2002). These approaches are typically based on residence time distribution models presented by the pioneers in this field (e.g. Kreft and Zuber, 1978; Małozzewski and Zuber, 1982; Zuber, 1986a). These techniques have been recently formalized into a variety of software packages, such as FLOWPC (Małozzewski and Zuber, 1996), MULTIS (Richter et al., 1993), TRACER (Bayari, 2002), BOXmodel (Zoellmann et al., 2001), and TRANSEP (Weiler et al., 2003). Most of these models combine deconvolution of isotope input (i.e. the isotopic composition of precipitation or throughfall) with a system response function (also called weighting function) to calculate the time of the isotope output (i.e. the isotopic composition of streamwater) from the catchment. Adjusting the response function to optimize the fit between measured and computed streamwater isotope content provides a mean water residence time. Finally, the optimized model parameters provide the distribution of residence times for a designated point on the water flowpath. Other applications of this approach range from simple sine-wave and isotope damping analysis (Burns and McDonnell, 1998; DeWalle et al., 1997; Soulsby et al., 2000; Stewart and McDonnell, 1991 to mathematically more complex approaches such as multi-parameter response function models (Amin and Campana, 1996; Haitjema, 1995; Zuber 1986b). Less common approaches, which require special data or precisely defined boundary conditions, include power spectra techniques (Kirchner et al., 2000; Manga, 1999), direct simulation (Etcheverry and Perrochet, 2000; Goode, 1996), and stochastic-mechanistic models (Simic and Destouni, 1999). Some workers have also tried to define surrogate indicators of water residence times based on the hydraulic and topographic features of the subsurface (Wolock et al., 1998; Vitvar et al., 2002).

In addition to the use of stable isotopes and tritium, other environmental isotopes and anthropogenic tracers have been used as dating tools, including ^{35}S and ^7Be (Cooper et al., 1991), $^3\text{He}/^3\text{H}$ (Solomon et al., 1993), CFCs and SF_6 (Plummer and Busenberg, 2000), and ^{85}Kr (Smethie et al., 1992). The range of potential "datable" ages obtained can vary from a few days (using ^{35}S and ^7Be), up to decades (using ^3H , $^3\text{He}/^3\text{H}$, CFCs and ^{85}Kr). Multitracer studies in shallow aquifers (Ekwurzel et al., 1994; Plummer et al., 2001, Plummer in this volume) estimated the age of groundwaters at different depths. Notwithstanding, the use of noble and atmospheric gases is still limited to groundwater applications, since the interaction of these isotopes with the atmospheric air compromises their use in streamwaters. Schlosser et al. (1988) introduced a method of calculating streambed infiltration velocities using the $^3\text{H}/^3\text{He}$ ratio. These techniques have been suitable in areas of both high and low recharge rates; however, diffusion dominates the ^3He transport in the unsaturated zone and provides little information on vertical transport of water

(Solomon and Cook, 1999). The infiltration velocities obtained by $^3\text{H}/^3\text{He}$ dating are also useful as a calibration tool in numerical 3-D groundwater flow models (Mattle et al., 2001).

The relationship between basin area and baseflow residence time remains equivocal. Though no studies have reported a relation between residence time and catchment size, McDonnell et al. (1999) and McGlynn et al. (2003) found that the internal flowpath composition may be a first-order control on stream baseflow age. Recent ^{18}O and ^2H studies comparing small catchments in Japan and New Zealand by Uchida et al. (2004) show how bedrock permeability may control the direction of water aging. In the impermeable bedrock case (Fig 1a), Stewart and McDonnell (1991) observed a lateral downslope increase in soil water mean residence time. Asano et al (2002) tested this hypothesis on a comparable slope configuration, but with permeable bedrock, and found that water aged vertically through the soil profile, with no evidence of a downslope age increase. In this case, the communication of water vertically between the the soil and underlying bedrock did not “force” a downslope component to soil water age (Fig. 1b).

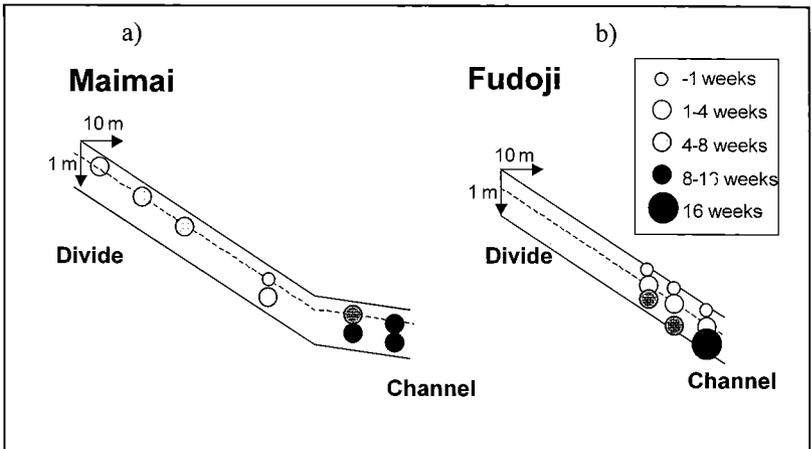


FIG. 1. Comparison of mean water residence times in two small catchments (a) Maimai (New Zealand) and (b) Fudoji (Japan). Differences in runoff generation processes cause increase in mean water residence times along the depth (Fudoji) and distance from the catchment divide (Maimai). Adapted after Uchida et al. (2004).

In most streams, there are two storm hydrograph discharge components: (1) surface and near-surface quickflow in response to rain or snowmelt, and (2) baseflow, which is water that enters from persistent, slowly varying sources and maintains streamflow between water-input events (Dingman, 2002: p. 342). The relative contributions of these sources differ in each watershed, and depend on the physical setting of the drainage basin (topography, soil type, depth to bedrock, vegetation, fractures, etc.), climatic parameters (precipitation amount, seasonal

variations in precipitation, temperature, potential evapotranspiration, etc.), and human activities, such as dams, reservoirs, irrigation usages, clearing of agriculture, channel restructuring, etc. (Kendall and Coplen, 2001). The baseflow runoff component originates predominantly from unconfined shallow groundwater reservoirs, which are less than 50 years old and range in depths between 10 and 100 m (Seiler and Lindner, 1995), and exfiltrate through river banks and the bottom of river beds (Wittenberg and Sivapalan, 1999). Since the late 1960s, ^2H and ^{18}O have been used routinely to delineate the baseflow component of a stormflow event. where event water is represented by the distinct isotopic composition of rainfall/throughfall, and pre-event water is represented by the distinct isotopic composition of pre-storm stream water or adjacent groundwater. This approach has been applied to a large number of studies of stormflow events in small catchments (recent thorough reviews in Genereux and Hooper, 1998; Turner and Barnes, 1998). In general, these studies have revealed a much greater baseflow proportion in the stream discharge hydrograph (theoretical discussion in Kirchner, 2003), which differs markedly from the early conceptual models of streamflow generation and graphical hydrograph-separation analysis (Hewlett and Hibbert, 1967). In almost all cases the mobilized pre-event water accounts for over half, and usually about three-quarters of the runoff and/or peakflow associated with rainstorms (Genereux and Hooper, 1998). These results contradict the traditional engineering assumption of Hortonian overland flow generation (Horton, 1933) as the dominant component of streamflow. A large number of publications describe the subsurface hydraulic mechanisms of rainfall-induced release of the pre-event water; however, comprehensive reviews can be found e.g. in Bonell (1998), for snowmelt-dominated catchments in Rodhe (1998) and for tropical rainforest catchments in Elsenbeer (2001). Hydrograph-separation techniques have evolved and become more sophisticated — adopting methods to quantify errors and uncertainties (Genereux, 1998, Joerin et al., 2002) and incorporating additional solute tracers that separate three or more runoff components (DeWalle et al., 1988). These methods have allowed simultaneous identification of both the origin (pre-event and event water) and the geographical sources (soil, aquifer, riparian zones, hillslopes, etc.) of runoff components.

2.3. SPATIAL DISTRIBUTION OF HYDROLOGIC PROCESSES IN CATCHMENTS

Regardless of the age of streamwater, runoff in streams is generated from a variety of spatial sources and along various flow pathways. This complexity increases with catchment size, so that large rivers often represent highly heterogeneous mixtures of water types. Craig (1961) was among the first to compile water isotope content information in selected rainfall, stream discharge, and groundwaters to demonstrate the effects of evaporative enrichment and water-rock interactions. His work was based largely on the deviations of the stream water isotopic composition from the global meteoric water line. This information and methodology have been further integrated into longitudinal surveys of larger streams, which has allowed the identification of recharge waters isotopically enriched due to evaporative effects in lakes, streams, drainage channels and shallow

river banks (Simpson and Herczeg, 1991; McKenna et al., 1992), and waters isotopically depleted from irrigation use and return in arid areas (Friedman et al., 1992). On a small scale Burns and McDonnell (1998) used this approach to identify how streamwater in a small catchment in the Adirondack Mountains, New York, contained water that was seasonally isotopically enriched due to summer evaporation from the adjacent small beaver ponds (Fig. 2). Lee and Hollyday (1991) determined the location of groundwater recharge to streams using ^{222}Rn .

Table 1. Principal works in peer-reviewed journals on streamflow residence time estimations since 1990. A review of previous works is presented in Herrmann (1997).

Reference	Catchment	Area	MRT	Isotope
Burns et al., 1998	Winnisook, USA	200 ha	330 d 247-319 d	^{18}O ^{35}S
Burns and McDonnell, 1998	two catchments in the Adirondack Mountains, USA	41.3 and 61.2 ha	100 d	^{18}O
DeWalle et al., 1997	three catchments in the Appalachians, USA	34, 39 and 1134 ha	1.4-5 a	^{18}O
Frederickson and Criss, 1999	Meramec River, Missouri, USA	10.300 km ²	100 d	^{18}O
Holko, 1995	Jalovecky potok, Slovakia	23 km ²	31 mo	^{18}O , ^2H
Małozzewski et al., 1992	Wimbachtal, Germany	33.4 km ²	4.1 a 4.2 a	^{18}O ^3H
McGlynn et al., 2003	four nested subcatchments of Maimai, New Zealand	280, 80, 17 and 2.6 ha	1.1-2.1 a	^3H
McGuire et al., 2002	Mahantango, Leading Ridge, Pennsylvania, USA	14ha, 100ha	9.5 mo 4.8 mo	^{18}O

Table 1. (cont.)

Reference	Catchment	Area	MRT	Isotope
Rodhe et al., 1996	Gårdsjön, Sweden	63 ha	7.5 mo	^{18}O
Rose, 1993	three catchments in Piedmont Province, Georgia, USA	347, 109 and 6.5 km ²	15-35 a	^3H
Soulsby et al., 2000	Allt a' Mharcaidh, Scotland	30 km ²	5 a	^{18}O
Stewart and McDonnell, 1991	Maimai, New Zealand		100 d	^2H
Sueker et al., 1999	3 catchments in High Rockies, Colorado, USA	780-1320 ha	200-400 d	^{35}S
Taylor et al., 1992	Wairau, New Zealand	170 km ²	10 a	^3H
Vitvar and Baldeder, 1997	Rietholzbach, Switzerland	3.14 km ²	12.5 mo	^{18}O
Vitvar et al., 2002	Winnisook, USA	200 ha	11.5 mo	^{18}O

In larger drainage basins, the process of infiltration from rivers into river banks can be successfully addressed using isotopic approaches. Schlosser et al. (1988) have quantified this connection using ^3H and ^3He . Ellins et al. (1990) showed how ^{222}Rn could be used for studying leakage of river water into shallow aquifers and delineation of exfiltration and infiltration zones along river reaches. In zones where river baseflow exfiltrates into the adjacent aquifers, recharge velocities and residence times of the recharged water can be obtained by use of $^3\text{He}/^3\text{H}$ techniques (Solomon et al., 1993). Conversely, the source and residence times of groundwater seepage to streams have been evaluated by using chlorofluorocarbons (Modica et al., 1998). These approaches have been further developed in stream recharge studies in urban areas, such as Calcutta (Sinha et al., 2002) and Dhaka (Darling et al., 2002). Several of these studies have documented increased recharge of shallow aquifers in developed areas (Foster et al., 1998), due to leakage from

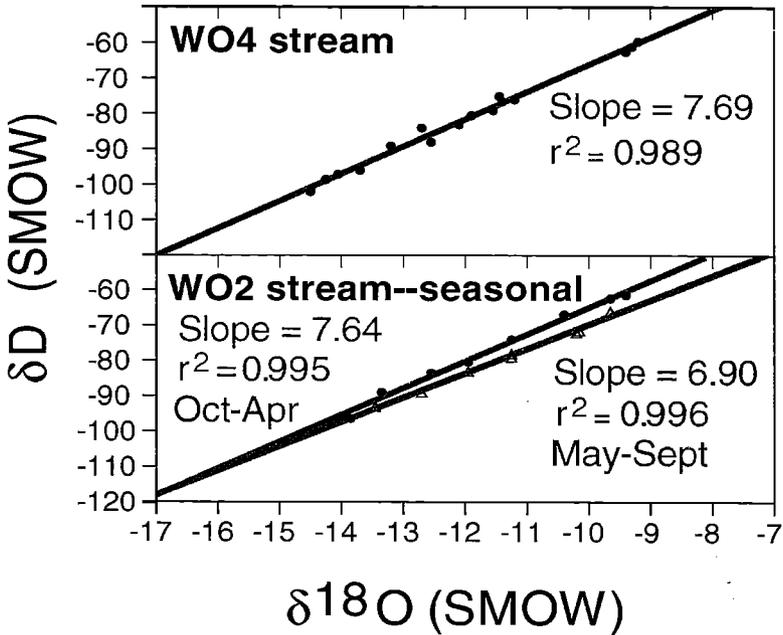


FIG. 2. Relation between ^{18}O and D (or 2H) content in streamwater of two small catchments in the Adirondack Mountains, New York, USA. The stream in catchment WO4 contains no lakewater, whereas the stream in catchment WO2 contains water from beaver pond lakes, isotopically enriched during summer. Adapted from Burns and McDonnell, 1998.

water supply pipes and storm sewers (review in Lerner, 2002), and septic leachfields (Sherlock et al., 2002). These findings apparently contradict the common view of urban catchments as being sources of enhanced rapid runoff on impervious areas (review in Hirsch et al., 1990) and indicate a substantial need for further investigations of processes in developed catchments.

Simultaneous analysis of isotopes and solutes in hillslope and small catchment studies have identified the geographic sources of the subsurface runoff component that had been stored in the catchment prior to the rain event. Buttle (1998) described two principal mechanisms to explain the presence of this "old" water in streamflow: (1) subsurface stormflow, and (2) groundwater ridging. Subsurface stormflow of the "old" pre-event water is explained as macropore flow through large conduits in the soil and "translatory flow", a flux of water stored in soil micropores with soil water contents close to saturation. Groundwater ridging is caused by flux of groundwater to the stream, enhanced by the saturation of the capillary fringe, or tension-saturated zone, during infiltration. These mechanisms, and the presence of "old" pre-event water in streams, have been noted in a number of field and laboratory studies at the plot and hillslope scales (Ward and Robinson, 2000) and identified on the catchment scale through multi-tracer hydrograph-separation techniques (DeWalle et al., 1998).

However, runoff in undisturbed catchments is generated typically through a combination of mechanisms, varying temporally and spatially in each catchment. A large number of isotope-based studies on runoff generation exist; recent comprehensive reviews can be found in publications on well-known leading experimental watersheds, such as Brugga in Germany (Uhlenbrook et al., 2002), Haute-Mentue in Switzerland (Jordan et al., 1994) Panola (Freer et al., 2002), Hubbard Brook (Hogan and Blum, 2003) and Sleepers (Shanley et al., 2002) in the USA, Maimai (McGlynn et al., 2002) in New Zealand, Hydrohill (Kendall et al., 2001) in China and Fudoji (Uchida et al., 2004) in Japan.

The combination of water stable isotopes and selected solutes, such as silica and calcium, has been particularly effective in determining flow sources and flowpaths. Isotope of solutes (for a thorough review, see Lal, Horita, this volume), such as ^{15}N and ^{18}O of nitrate, have been developed and successfully applied on the catchment scale as tracers of nitrate sources in catchments. Böhlke and Denver (1995) showed that in a small catchment draining into Chesapeake Bay the outflowing water continued to be contaminated with nitrates for 2–3 decades after cessation of the N-input. A large number of studies also provided information on the contributions of nitrate from precipitation and from microbial nitrification (Burns and Kendall, 2002), from microbial denitrification in shallow aquifers (Böttcher et al., 1990), from septic tank leakages and animal waste (Aravena et al., 1993), and from natural soil (Kreitler and Browning, 1983). Mayer et al. (1995) used ^{34}S for tracing runoff sources from atmospheric deposition and mineral weathering. A review of studies on nitrogen isotopes is presented in Kendall (1998) and a review of studies on sulphur isotopes can be found in Mitchell et al. (1998).

Isotopes of solutes such as ^{87}Sr and ^{210}Pb have become useful tools for identification of the evolution and origin of river waters via tracing the geochemical reactions along water pathways in the catchment (Bullen et al., 1994; Bullen et al., 1996, Bullen and Kendall, 1998). ^{11}B (Vengosh et al., 1994) and ^{37}Cl (Van Warmerdam et al., 1995) have been used for identification of anthropogenic sources of water pollution, whereas several cosmogenic isotopes, such as ^7Be and ^{10}Be (Brown et al., 1995) have addressed the identification of runoff sources from horizons under strong chemical weathering.

Multi-tracer separation methods of runoff sources have been formalized into the concept of End-Member-Mixing-Analysis EMMA (Christophersen et al., 1990), based on the multivariate statistics and quantification of runoff sources as statistical end-members. EMMA has become a popular technique for interpretation of isotopic (and solute) data, and has great potential in extended future applications (Table 2).

Table 2. Principal works in peer-reviewed journals on the End Member Mixing Analysis (EMMA) in catchments.

Reference	Catchment	Area
Brown et al., 1999	Shelter Creek, USA	161 ha
Burns et al., 2001	Panola, USA	41 ha
Christophersen and Hooper, 1992	Panola, USA, and Birkenes, Norway	41 ha both
Elsenbeer et al., 1995	South Creek, Australia	25.7 ha
Genereux et al., 1993	Walker Branch, USA	97.5 ha
Katsuyama et al., 2001	Matsuzawa, Japan	6 ha
McHale et al., 2002	Archer Creek, USA	135 ha
Mulholland, 1993	Walker Branch, USA	97.5 ha
Soulsby et al., 2003	Newmills burn, United Kingdom	14.5 km ²

One of the lingering challenges in the application of the runoff tracer-based data is in parameterization and calibration of distributed rainfall-runoff catchment models. Although the isotopic investigations on runoff generation substantially changed the conceptualization of the catchment rainfall-runoff process, they have not been widely incorporated into models, model structures and model parameter testing. Thus, while the hydrologic community continues to develop and operate sophisticated rainfall-runoff models (such as those summarized in Beven and Freer, 2001, Döll et al., 2003, Gurtz et al., 2003, and Leavesley et al., 2002), simulated runoff components are rarely calibrated by results of isotopic hydrograph separations. Some recent work has seen calibration of the rainfall-runoff models using the isotopically obtained proportion of runoff components as one of main model parameters. Seibert and McDonnell (2002) showed that although these “soft data” slightly decrease the absolute quality of the fit of the simulated versus measured discharge, they provide a higher quality of the understanding of the runoff components within the model routing procedure. These approaches are considered as a promising way to enhance the relation between isotope-based and conventional hydrologic methods in catchment hydrology (see also Uhlenbrook and Leibundgut, 2002).

3. Future directions

The application of isotopes to track sources and movement of water in catchments over the past 40 years has resulted in a substantial improvement in the understanding of runoff processes. This is especially true in small, dominantly forested humid experimental catchments with a high level of instrumentation and long data records (Burns, 2002). However, moving beyond these traditional catchment types and scale remains a challenge (Gibson et al., 2002). Recent trends indicate a continuously growing interest in isotopic applications to solve practical problems in hydrology and water resources management in large scale catchments.

In particular, application of isotope methods from small catchments to large river basins is a promising area of research. Owing to the ever-decreasing bomb tritium signal in natural systems, development of new methods for tracing older waters (with mean residence time >50 a) is essential. In particular, the use of dissolved gases ^3He and ^{222}Rn , solute isotopes ^{15}N , ^{35}S , ^{87}Sr , ^{208}Pb , ^{41}Ca , ^{11}B and anthropogenic gases CFCs and SF_6 needs to be further investigated and addressed in catchment studies. A movement towards multi-isotope studies is highly desirable; yet, many researchers and sub-communities are still too fixated on one particular isotope. A significant potential also remains in novel applications of isotopes coupled with solutes and artificial tracers in complex approaches such as EMMA or the geochemical model NETPATH (Burns et al., 2003). In addition, calibration and verification of rainfall-runoff catchment models is an area where isotopic applications could aid significantly process and parameter interpretation.

Large basins are very heterogeneous and are typically driven by a large variety of runoff processes. Therefore, methods developed in small natural catchments might be limited in large basins (Blöschl, 2002). Techniques and indicators are required, that describe the principal processes in large catchments without the need of spatially intensive experimental datasets. Large-scale catchment studies may be able to utilize well known isotopic effects (the altitude effect, the continental effect, etc.) to assess gross first order controls on flow generation (Kendall and Coplen, 2001; Schotterer et al., 1993). More attention to the catchment groundwater system and its coupled relation to the large river is required. At larger river basin scales, it is likely that a mean water residence time in the channel is a weak indicator of process. A synoptic survey longitudinally up/down the main channel might better characterize the variety of runoff processes contributing from different catchment positions to streamflow. A more intensive merging of isotopic survey data in rivers with conventional hydrologic data is needed, such as statistical characteristics of stream low-flow and runoff recession, which would help broaden insight into streamwater-groundwater interactions in catchments on different scales. New techniques of storing and presenting isotopic data in catchments should be created, especially those which link monitoring and mapping of isotopic input from the atmosphere (e.g. GNIP) with mapping and monitoring of isotopic content in streamwaters and groundwaters.

Finally, integration of isotope-based solutions of hydrologic problems in catchments into the solutions of water resources sustainability is an essential challenge for the further development of isotopic methods in catchment hydrology. Sustainability indicators of water resources are focused typically on local water scarcity (Atkinson et al., 1997). New approaches should be developed to generate, quantify and integrate indicators of runoff processes in catchments, and evaluate them in terms of potential sustainability.

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