

The ‘hidden streamflow’ challenge in catchment hydrology: a call to action for stream water transit time analysis

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INTRODUCTION

The transit time distribution of streamflow is a fundamental descriptor of the flowpaths of water through a catchment and the storage of water within it (Soulsby *et al.*, 2009; McDonnell *et al.*, 2010). These qualities along with interactions within the catchment control its response to landuse change, diffuse or point-source chemical pollution, ecological degradation, and climate change (Kendall and McDonnell, 1998; Hamilton, 2011; Rinaldo *et al.*, 2011). Significant time lags in the responses of streams to these stressors and their amelioration or restoration have been recently documented (e.g. Worrall *et al.*, 2009; Howden *et al.*, 2010), and memory in the system – as quantified via stream water transit time – appears to be an exciting new research direction in hydrology.

The transit time distributions of water through catchments have been estimated using isotopes (McGuire and McDonnell, 2006) or conservative chemicals (Kirchner *et al.*, 2010). However, Stewart *et al.* (2010) recently demonstrated that there are distinct differences between transit time distributions derived from tritium (³H) on the one hand and those from stable isotopes and conservative solutes (¹⁸O, ²H, Cl) on the other. These differences are caused by their different methods of age determination, radioactive decay with half-life of 12.3 years in the case of tritium and smoothing of seasonal or other variations in the input water for stable isotopes. Use of tritium often reveals substantial proportions of much older water (with transit times of decades or more), which is not shown by the stable isotope methods because they cannot ‘see’ water older than about 4 years (Stewart *et al.*, 2010). This difference presents a major challenge in catchment hydrology: that of characterizing the effects of ‘hidden streamflow’ (i.e. old water hidden from view in traditional stable isotope-based analysis). This is a problem because catchment hydrologists currently focus solely on stream water transit time deduced from stable isotope and solute variation studies (see McGuire and McDonnell, 2006 for review), and these have truncated our view of stream water transit time distributions and potentially skewed our understanding of how catchments store and transmit water. This truncated view of stream water transit time is now being used in the development of relationships between catchment characteristics and stream water transit time (e.g. McGuire *et al.*, 2005; Soulsby and Tetzlaff, 2008; Hrachowitz *et al.*, 2009). The many new model approaches that include representations of transit time for model testing and development (Vaché *et al.*, 2004; Vaché and McDonnell, 2006; Fenicia *et al.*, 2010) will be similarly truncated.

Although such hidden streamflow is, in theory, present in all catchments, it is expected that some streams would have greater age dichotomy than others. Indeed, our work at the Maimai watershed in New Zealand suggests that there may only be some months of difference between stable isotope-based stream water mean transit time (MTT) (Pearce *et al.*, 1986)

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and tritium-based MTT (McGlynn *et al.*, 2003). This is probably true for other poorly permeable, highly responsive sites with little seasonality of precipitation (like some of the Scottish catchments reported by Hrachowitz *et al.*, 2010 and 2011). However, for catchments with more permeable bedrock and more seasonality, transit time schizophrenia (in the sense of the stream having two or more major age-components) may be the norm rather than the exception (e.g. Maloszewski *et al.*, 1983; Uhlenbrook *et al.*, 2002; Stewart *et al.*, 2007; Stewart and Thomas, 2008; Stewart and Fahey, 2010; Pfister *et al.*, 2002). In addition to streamflow containing greater contributions of old water than expected from stable isotope-based analysis, it is also becoming clear that the transit time distribution can often vary with the timing of precipitation input (Sayama and McDonnell, 2009; Morgenstern *et al.*, 2010; Rinaldo *et al.*, 2011). In a possibly extreme example, Morgenstern *et al.* (2010) found that the MTT of stream water in the Toenepi watershed in New Zealand increased from 4 to 155 years between high baseflow and extreme low baseflow. Although in this case, the old baseflow component did not contribute much to the total annual flow volume, it is still important because it controls the stream water quality during 2–4 months of low flow in summer.

With water bodies being increasingly ‘at risk’, as a direct consequence of anthropogenic contamination sources, the European Commission has recently called for support from the scientific community (EC report COM/2010/0047, 2010). A better understanding on water and pollutant sources and flowpaths will eventually lead to a significant improvement in both the elaboration and implementation of surface and groundwater quality protection policies, as advocated in the European Water Framework Directive.

So what is the way forward? Here, we make a case for the routine use of tritium in stream water analysis to overcome the underappreciated importance of older groundwater contributions to streams. This approach is meant to complement the current hydrometric analyses of the role of bedrock groundwater (e.g. Kosugi *et al.*, 2008), new field approaches to its characterization (e.g. Gabrielli and McDonnell, 2012) and new model analyses of its role in the headwaters (e.g. Ebel *et al.*, 2008; Ferguson and Maxwell, 2009) – all of which are helping to improve the understanding of the role of old, bedrock groundwater at the catchment scale. In this commentary, we outline three important points for moving forward with such a tritium-based agenda: (i) the ‘low hanging fruit’ that exists in the Southern Hemisphere for quantifying and demonstrating the differences between stable isotope-derived transit times and tritium-derived transit times; (ii) the opportunities that we see in the Northern Hemisphere; and (iii) the requirements for tritium analyses, especially the critical

importance of measurement accuracy in a post bomb world. We hope that this commentary will serve the dual purpose of encouraging others to consider using tritium in their work and to propagate analyses in laboratories that are suitable for the work worldwide.

OPPORTUNITIES IN THE SOUTHERN HEMISPHERE: A SINGLE SAMPLE COULD BE ENOUGH!

Although early studies in the Northern and Southern Hemispheres exploited the tritium bomb peak around 1965 for stream water residence time analysis (e.g. Crouzet *et al.*, 1970; Martinec *et al.*, 1974), tritium was used less after the 1970s because of the interpretative difficulties associated with the gradual passing of bomb tritium from the atmosphere. Bomb tritium has now almost disappeared from the atmosphere (WISER database, IAEA) but can still be present in hydrological systems and cause ambiguous age interpretations, especially in the Northern Hemisphere where the bomb peak was much higher. In the Southern Hemisphere, the remaining bomb tritium has declined to very low levels. Consequently, catchments in the Southern Hemisphere represent the ‘lowest hanging fruit’ for MTT characterization using tritium. In many cases, a single streamflow sample taken during baseflow can be enough to give an estimate of the stream MTT at that time. If the MTT varies with flow (as observed by Stewart and Thomas, 2008, and Morgenstern *et al.*, 2010), a series of tritium measurements taken at different streamflows will give the relationship between flow and age. This is because tritium concentrations can correlate uniquely with MTT for appropriate flow models (see below).

To demonstrate the current situation for tritium dating, Figure 1 shows representative tritium records for precipitation in the Northern and Southern

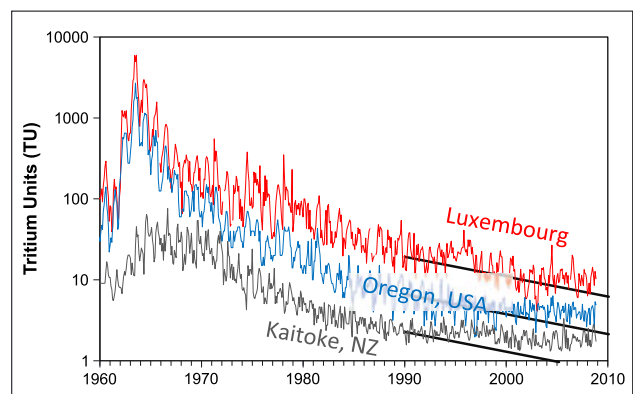


Figure 1. Tritium concentration in precipitation at Luxembourg and Oregon, USA (Northern Hemisphere), and Kaitoke, New Zealand (Southern Hemisphere). Tritium concentrations are expressed as tritium units (TUs) with one TU corresponding to a ratio of tritium/total hydrogen = $T/H = 10^{-18}$. The straight lines show the effects of radioactive decay of tritium in groundwater recharged in 1990

Hemispheres. The main features in the curves are the pronounced bomb peaks because of nuclear weapons testing mainly in the Northern Hemisphere during the 1950s and 1960s. The peak was much higher in the Northern Hemisphere than in the Southern Hemisphere. Since then, there has been a steady decline because of leakage of tritium from the stratosphere into the troposphere from where it is removed by rainout, together with radioactive decay of tritium. Difficulties with using tritium for dating have resulted from the similarity in slope of the decline to the decrease from radioactive decay of tritium. The straight lines in Figure 1 illustrate tritium decay in groundwater recharged in 1990.

However, it can be seen that the remaining bomb tritium in groundwater has now declined close to or below the level of current natural cosmogenic tritium. In the Southern Hemisphere (Kaitoke record), the maximum tritium concentration in bomb tritium-containing groundwater assuming realistic flow models has declined below the cosmogenic tritium concentration in the rain since 1995 (straight line falls below the tritium concentration in the rain). This allows young and older groundwater to be distinguished, and the situation will improve in time with further decay of the small amount of remaining bomb tritium. This means the small amount of remaining bomb tritium does not interfere with the age interpretations anymore resulting in a monotonously decreasing curve with MTT in the tritium output of a catchment (Figure 2, Kaitoke). Consequently, every measured tritium concentration in stream water can now be related to a unique MTT for the Kaitoke curve in Figure 2 based on the exponential piston flow model.

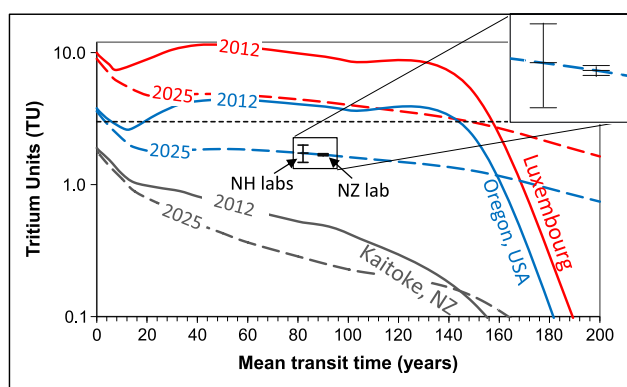


Figure 2. Tritium concentrations predicted in groundwater after applying an exponential piston flow model with exponential fraction 70% to the tritium inputs shown in Figure 1 for sampling at present (2012 curves) and in the future (2025 curves). Two or more mean transit times (MTTs) are indicated for a single tritium value when the curves rise or are level [e.g. a tritium value of 3 TU (fine dotted line) intersects the 2012 Oregon curve at MTTs of 6, 18 and 127 years – only one of these can be correct]. The error bars on the 2025 Oregon curve (and expanded in the inset) show the average measurement error (one sigma) of the ten best Northern Hemisphere laboratories (Groening *et al.*, 2007) and the New Zealand laboratory (Morgenstern and Taylor, 2009)

A RESEARCH AGENDA FOR NORTHERN HEMISPHERE CATCHMENTS

The Northern Hemisphere tritium records shown in Figure 1 are for Luxembourg and Oregon, USA (these sites are chosen because tritium studies have been initiated in catchments there). The Luxembourg record (based on those of nearby Trier, Germany, and for early years from Vienna, Austria, both from the WISER database of the IAEA) shows that tritium in Central Europe has not completely declined back to natural pre-bomb levels because of industrial tritium sources. Good agreement between the records from Ottawa and Vienna prior to local industrial influences shows that records from measured stations not impacted by local tritium sources can be used as tritium input in distant sites with appropriate scaling (Michel, 2006). The Oregon record is based on measurements at Portland, OR, fitted with a scaled correlation of Vienna data by Michel (2006). Oregon has considerably lower tritium levels than Luxembourg.

Figure 2 shows the tritium concentrations predicted in groundwater at Luxembourg and Oregon after applying an exponential piston flow model with exponential fraction of 70% (Maloszewski and Zuber, 1982). Present-day (2012) outputs are shown together with outputs expected in 2025 to demonstrate the changing situation with regard to age interpretations because of the waning interference of bomb tritium. The Southern Hemisphere already shows a monotonous decline of tritium with MTT, which enables unique MTTs to be determined (and in principle, for single tritium measurements to yield unique MTTs, as discussed above). In the Northern Hemisphere, the much larger input of bomb tritium to hydrological systems still causes ambiguous MTT interpretations, that is, two or more possible values of MTT for some tritium values (see, for example, in Figure 2, how a tritium concentration of 3 TU for Oregon groundwater yields three possible MTTs: 6, 18 or 127 years; only one of these can be correct). This situation is not as dire as it appears because some possible MTT values can usually be ruled out from other data. However, the remaining bomb tritium is expected to decrease in the future, resulting in monotonously declining tritium outputs within a few years (see the 2025 outputs). Despite the ambiguous ages because of bomb tritium at present, collecting tritium data now will be valuable for dating in combination with future samples. Time series tritium data at intervals of 2–3 years from the tail of the bomb tritium will produce the most accurate MTTs. In addition, these data will allow establishment of the transit time distribution, which will not be possible when the bomb tritium has completely decayed.

Our recommendation for a research agenda for Northern Hemisphere catchments is to start tritium measurements now to investigate the long tails of transit time distributions in catchments. We recommend

sampling at high and low baseflows because it is probable that transit time distributions will vary with flow. Such sampling will enable a fresh look at geological and geographical controls on runoff mechanisms. Accumulating tritium data also will allow better model testing and development in relation to climate change, landuse change/chemical pollution and ecological degradation where catchment storage plays an important role.

ON THE CRITICAL IMPORTANCE OF TRITIUM MEASUREMENT ACCURACY

In both hemispheres, tritium concentrations in groundwater and stream water are close to natural levels, and dating now requires measurements with high sensitivity and accuracy. Therefore, only high accuracy tritium measurements can be used to determine the ages and amounts of hidden water. The NZ laboratory error bar in Figure 2 illustrates the current measurement precision in New Zealand (Morgenstern and Taylor, 2009). The high precision is sufficient to constrain robust age interpretations with 2–3 years' accuracy in SH systems. However, Figure 2 shows that slopes in NH systems will be mild for a number of years even when the hump caused by bomb-tritium disappears. The error bar for the ten best NH tritium laboratories (deduced from Groening *et al.*, 2007) shows that their measurement accuracy is not yet sufficient for accurate age dating and needs to be improved. Measurement accuracies similar to those reported by Morgenstern and Taylor, (2009, laboratory ID #3 in Figure 15) are required. Therefore, one needs to be extremely careful about tritium measurement quality in relation to the objectives of the study. Key questions for a laboratory to which one might send a sample are as follows: what is the error of the measurement? How does the laboratory perform in international intercomparison exercises?

SUMMARY

Distinct differences between tritium-based transit time computation *versus* stable isotope-based computation of stream transit time highlight a major challenge in catchment hydrology: characterizing the amount of hidden streamflow, that is, water hidden from view in traditional stable isotope-based analysis of water source and transit time. This is a problem because hydrological researchers currently focus solely on stream water transit time deduced from stable isotope studies, which have, in many cases, truncated our view of stream water transit time and skewed our understanding of how catchments store and transmit water. We need to start a concerted community effort to gather high-quality tritium measurements in streams to determine

the realistic pathways and flow rates of water through catchments. Although the cost of individual high-precision measurements is relatively high, the method only needs measurements at long intervals, so the number of samples required is low and overall cost inexpensive (depending on the objectives of the study). Sample collection is straightforward and best coordinated with on-going streamflow and geochemical measurements.

Our six-point call to action for the catchment community and for stream water transit time analysis is as follows:

1. Start making tritium measurements now!
2. Use a high-precision laboratory for analyses. Figure 2 shows that only tritium data with the smallest error bars allow for sufficiently accurate determination of MTT.
3. Sample low and high baseflow conditions to identify the multiple characteristic old water contributions in catchments.
4. Take samples across a wide spectrum of catchment characteristics in the Southern Hemisphere (where a single sample can be used to quantify baseflow MTT) to define relationships between catchment characteristics and MTT.
5. Begin a multi-year program in the Northern Hemisphere to realize the agenda set forth in the IAEA workshop described in McDonnell *et al.* (2010).
6. Begin this tritium-based work with catchments that already have stable isotope-based MTT estimates. We are doing this now ourselves, at the Maimai Catchment in NZ, the Alsea Watershed in Oregon and the Attert Catchment in Luxembourg. This will allow us to establish both the young and the old MTT water components for building new dynamic catchment models that account for the young and old water and changes in MTT.

Embracing this proposed research agenda will represent a 'meeting in the middle' with the new wave of hydrometrically based deep bedrock groundwater studies currently underway. It will ultimately facilitate a much better dialog between surface water and groundwater hydrologists and usher in a more holistic view of water cycling in catchments beyond the largely soil-mantle-centric view that exists today in catchment hydrology.

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