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# Source-to-stream connectivity assessment through end-member mixing analysis

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SUMMARY

Streamflow sources across various hydrologic conditions were examined in a 5.1 ha temperate humid forested catchment (Laurentians, Canada). In that system, the relationship between rainfall and runoff is nonlinear, thus hinting towards complex processes involving critical, transient source areas and a changing catchment internal state of connectivity. Multiyear daily stream chemistry data were broken down into several hydrologic scenarios reflecting different conditions with respect to stream discharge and antecedent catchment wetness. End-member mixing analysis and mass balance calculations were performed to: (1) compare the dimensionality of the mixing spaces (i.e. the number of streamflow sources) obtained under 64 different hydrologic scenarios; (2) screen independently sampled end-members (i.e. the nature of sources) to assess catchment connectivity from a spatial perspective; and (3) estimate the relative contributions of end-members to streamflow to characterize hydrological connectivity from a volumetric standpoint. Mixing space dimensionality did not vary significantly among the tested hydrologic scenarios, as three end-members were generally required to account for most of the variance in stream geochemistry. Differences were significant in the ability of the tested end-members to fit in mixing spaces; for instance, throughfall and organic soil water end-members better fitted in mixing spaces associated with high rather than low discharges. The relative contributions of end-members to streamflow were highly variable in time. Scenarios involving low discharges and dry antecedent conditions were mostly associated with baseflow, while scenarios involving high discharges and wet antecedent conditions were associated with increased proportions of throughfall and organic soil water from downstream downslope and downstream upslope areas. These results suggest a cautious evaluation of the predictive power of one single mixing space with regards to the nature of streamflow sources across hydrologic conditions.



## 1. Introduction

The establishment, maintenance and disruption of catchment-wide hydrologic connectivity have been associated with critical runoff production processes and precipitation or moisture thresholds above which stormflow generation is favored (Weiler et al., 2005; Tromp-Van Meerveld and McDonnell, 2006a; James and Roulet, 2007; Lehmann et al., 2007). Dimensions and controlling variables of connectivity are, however, multiple, thus leaving the door open for a large number of definitions, interpretations and approaches of the concept. Following the work of Bracken and Croke (2007), a recent review of the literature led to a classification of hydrologic connectivity definitions into four categories of increasing preciseness (Ali and Roy, 2009). The definitions classified as the "most specific" directly refer to flow processes that allow a rapid, threshold-driven hydraulic connection between landscape units, and they suggest the necessity to investigate processes like subsurface flow or translatory (piston) flow acting above an impeding soil layer.

In order to look into subsurface stormflow, several studies have been conducted using trench excavations (Dunne and Black, 1970a,b; Woods and Rowe, 1996; Tromp-Van Meerveld and McDonnell, 2006a,b), but this technique is not widely used because it generates hydraulic artifacts and since it cannot be deployed over the whole catchment area in order to fully capture triggering processes and their scaling properties. An alternate way to investigate subsurface stormflow is the study of active and maybe connected flow sources using the geochemical signature of stream and soil waters (Bazemore et al., 1994; Weiler et al., 2005). Indeed, the conditions encountered by water originating from different catchment sources while *en route* to the stream control biogeochemical transformations that ultimately determine stream water chemistry (Bishop et al., 1990; Mulholland et al., 1990; Bonell, 1993; Jenkins et al., 1994; Brown et al., 1999; Hill et al., 2000; McClain et al., 2003). As a result, mixing models relying on natural tracers (i.e. chemical elements) have been shown to be effective for stormflow

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generation hypotheses testing; they assume that stream water is a mixture of discrete "source" solutions that have extreme solutes concentrations in comparison to streamflow (Christophersen et al., 1990; Christophersen and Hooper, 1992). Traditional end-member mixing analysis (EMMA) models, based on principal component analysis (PCA), were first introduced in the 90s and require not only knowledge of the stream chemistry but also the explicit identification of potential end-members (i.e. streamflow sources) (Christophersen et al., 1990; Christophersen and Hooper, 1992). Hooper diagnostic tools for mixing models of stream chemistry were formally defined a decade later (Hooper, 2003), thus providing a more general mathematical formulation in which eigenvector and residual analyses of observed stream water chemistry are performed to estimate the appropriate number of contributing end-members. End-members sampled in the field are then screened for their ability to fit into the mixing space, i.e. the multidimensional space obtained from the PCA of observed stream water chemistry (Hooper, 2003; James and Roulet, 2006).

Mixing models are especially useful as they allow inferring and quantifying the relative contributions of different sources to streamflow by using small-scale, internal catchment measurements (e.g. groundwater and soil water chemistry) to explain the integrated, large-scale response at the catchment outlet (Genereux and Hooper, 1998; Hooper, 2001, 2003; James and Roulet, 2006). However, one challenge associated with mixing models is the large spatial and temporal variability of stormwater flow paths. Active flow paths and contributing water sources to streamflow depend on the interaction between rainfall intensity and amount (Dunne, 1978), antecedent catchment conditions (Elsenbeer et al., 1994), soil depth (Ross et al., 1994) and surface or bedrock topography (Brammer and McDonnell, 1996; Brown et al., 1999). These catchment properties are also thought to control hydrologic connectivity, making it difficult to build a simple conceptual model of catchment hydrological behavior. A thorough literature review by Brown et al. (1999) reveals that most studies conducted in temperate forested catchments have focused on streamflow generation processes that take place when prior catchment conditions are wet and soil moisture deficits are low, or in high rainfall areas. Meanwhile, mechanisms that control soil water and groundwater routing to the stream when catchment antecedent conditions are dry or transitional are much less investigated and understood. When the aim is to get some insight into variable contributing areas and periods in a specific catchment, event-based geochemical data associated with a wide range of hydro-meteorological conditions are required. When such data are unavailable, another approach that consists in breaking down a multiyear stream chemistry dataset into multiple sub-datasets associated with different hydro-meteorological conditions should be privileged as it can reveal temporal changes in the nature and/or the number of contributing streamflow sources. Mixing models rely on the premise that the geochemical signatures of end-members are time-invariant (Hooper, 2001; James and Roulet, 2006). They assume that only the presence and the mixing of end-members in streamflow vary with time, and such an approach is consistent with hydrologic connectivity definitions that usually imply an increased contribution of stormflow from source areas, both quantitatively (number of contributing areas) and volumetrically (importance of individual contributions).

Following a recommendation of Liu et al. (2008), we use a combination of Hooper diagnostic tools and end-member mixing analysis in a headwater, temperate humid, forested catchment. Liu et al. (2008) argued that such a combination of methods reinforces the assumptions of mixing models and enhances their results, especially if chemical data are limited. In this paper, a 11-year stream chemistry dataset has been broken into 64 different hydrologic scenarios in order to test for the variability of controlling end-members across a range of hydrologic conditions. Sub-datasets were discriminated from one another with respect to stream discharge at the catchment outlet, and as a function of 2-day or 7-day antecedent precipitation values. Cumulative precipitation values were used as surrogates for catchment antecedent conditions over the short- and the medium-term. Justification for the chosen hydrologic scenarios lies in the fact that strong nonlinearities and threshold-like dynamics affect headwater catchments, a phenomenon that has been observed at the study site (Ali et al., 2010). Examining such a complex internal catchment dynamics from the point of view of stream chemistry is the main contribution of this paper. The objectives of the study are to:

(1) assess the number of streamflow sources needed to explain the Hermine catchment dynamics under several dozens of different hydrologic scenarios;
(2) examine how the relative contributions from some sources (11 potential) vary with each hydrologic scenario in order to assess catchment connectivity from a spatial (horizontal or vertical) perspective; and
(3) estimate scenario-dependent relative contributions of discrete sources to streamflow to characterize catchment connectivity from a volumetric standpoint.

## 2. Data collection

### 2.1. Field site

We examined the hydrological behavior of a 5.1 ha headwater forested catchment, the Hermine, located at the Station de Biologie des Laurentides (SBL) of the Université de Montréal. It is situated on the Canadian Shield, in the Lower Laurentians about 80 km north of Montréal, Québec, Canada (45°59′N, 74°01′W, elevation c. 400 m) (Fig. 1A). The Hermine has a difference in elevation of 31 m between the outlet and the highest point in the catchment. Fig. 1B) and is drained by an ephemeral stream that runs east to west (Fig. 1C). The maximum daily average temperatures are observed in July (+25 °C) while daily minima (−30 °C) occur in January. The total annual precipitation averages 1150 mm (±136 mm) for the last 30 years, of which about 30% falls as snow (Biron et al., 1999).

Soils are developed over a relatively thin sedimentary cover composed of a glacial till. The bedrock is an igneous and impervious feldspar-rich Precambrian anorthosite of the Morin series. Till mineralogy is rather heterogeneous. Soils are mostly classified as 1–2 m deep sandy orthic, gleyed humo-ferric or ferro-humic Podzols (Turmel et al., 2005); they present a discontinuous, compact and impervious layer at a depth of about 50–75 cm (Fig. 1D) that restricts root penetration, slows water infiltration and enhances the probability of rapid lateral subsurface flow. The canopy of the Hermine is dominated by sugar maple (*Acer saccharum* Marsh., 78% of total basal area), American beech (*Fagus grandifolia* Ehrn., 9%) and yellow birch (*Betula alleghaniensis* Britton, 6%) with the accompanying species balsam fir (*Abies balsamea* (L.) Mill.), white birch (*Betula papyrifera* Marsh.), trembling aspen (*Populus tremuloides* Michx.) and large-toothed aspen (*Populus grandidentata* Michx.) (Courchesne et al., 2001). Floristic composition is not uniform throughout the catchment, as pioneer species (e.g. trembling and large-tooth aspen, white birch) tend to concentrate in upslope areas while non-pioneer species (e.g. sugar maple, yellow birch) rather cluster in downslope areas. Transpiration is minimal between October and April, so that changes in soil moisture and water table height during that period are mostly governed by downslope drainage movement. The interception capacity of the forest canopy and the high infiltration potential of soils, combined with high summer evapotranspiration, reduce the likelihood of surface runoff except during heavy rainstorms or spring snowmelt.