

## Major and trace element geochemistry of water flows: application to a storm hydrograph separation. An example from the Strengbach experimental catchment (Vosges, Eastern France)

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The geochemistry of water flows is a very useful tool to constrain hydrological models when associated with hydrological measurements. The efficiency of such a coupled geochemical/hydrological approach was tested in the small experimental catchment of Strengbach (Vosges, Eastern France) through a multidisciplinary study realized during a storm flow period. Geochemical analysis of sampled flows permitted the characterization of water fluxes from distinct sources. Geochemical data allowed to separate the storm hydrograph in various contributing waters (ground deep waters, subsurface waters, and surficial waters). Another major result of this work is to demonstrate that trace elements concentrations in waters can be used as valuable tracers of hydrological processes.

This study was conducted in the Strengbach experimental catchment located in the Vosges Mountains (Eastern France). This basin was initially equipped to study the problem of forest decline as a result of acid rain inputs (Probst *et al.*, 1990, 1992; Dambrine *et al.*, 1995). This small catchment (0.8 Km<sup>2</sup> square area) has a topographic range from 883 m to 1146 m above sea level with highly incised sideslopes (~15°). The substratum is mainly composed of granitic rocks. At the northern top edge, the granite is in contact with a band of gneiss. The catchment, with the exception of the bottom valley, is completely forested with 75% of Norway spruce. Climate is temperate oceanic mountainous with a mean annual temperature of 6°C and a mean rainfall of 1400 mm. This catchment is characterized by a saturated area representing 3% space of the catchment surface.

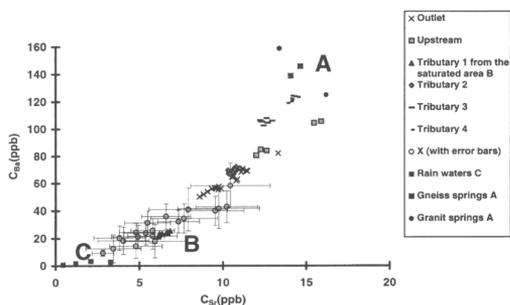
During the stormflow period (18–20 May 1994), various hydrologic flows were collected on the main

stream outlet, upstream, tributaries, open field rain water, throughfall, soil solutions, springs. Hydrological (discharge, water level) and geochemical (stable  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  isotopes, major anions and cations and trace elements) measurements have been performed. The following significant results have been obtained:

The different water samples display distinct geochemical features on major and trace element compositions.

Two main groups of elements could be identified during this storm event according to their chemical behaviour at the mainstream discharge. The first group are those elements which concentration decreases with increasing discharge (Ba, Sr, Rb, Na, Ca, Mg, Cl, Si). The second group of elements are those which concentration increases during the storm event: U, Pb, Al and dissolved organic carbon (DOC). These elements are known to form colloidal complexes with organic matter. These different chemical variations observed in the stream water outlet indicate variable contributions of flows from distinct sources during the storm event.

Mass balance equations relative to discharge flows and element concentrations (equations 1 and 2), in the downstream catchment region, show the significant importance of unsampled hydrologic fluxes. Stream discharge ( $Q_x$ ) and geochemical concentrations ( $C_x$ ) of these unsampled fluxes ( $X$ ) were evaluated from the mass balance equations and using elements that are assumed not to react with solid phases. This type of element will be referred thereafter as conservative.  $Q_x$  is shown to be up to 40% of the outlet discharge at the peak of the storm event.



Mixing diagrams ( $C_i$ ,  $C_j$ ) ( $C_i$ ,  $C_j$ : respective concentrations of assumed conservative elements  $i$ ,  $j$ ), reporting the measured contents of the sampled and unsampled hydrological fluxes ( $X$ ), were used to identify their end-member components. Analysis of these mixing diagrams (Fig. 1) showed that main streamwater, tributaries, and unsampled fluxes ( $X$ ) can be explained mainly by the mixing of three end-members flow components (A, B, C) with the following characteristics: (A) represents waters draining the deep layers of the hillslope (deep-ground water) that corresponds to ground waters which were equilibrated with the substratum rock. They are enriched in  $H_4SiO_4$ , and in many cations such as Ba, Sr, Rb, Na, Ca, Mg. (B) represents subsurface waters found in the upper horizons of the catchment saturated areas. They are particularly enriched in DOC and in elements forming organic complexes (Pb, Al, U). (C) represents rainwater and/or superficial waters which are highly depleted in most measured elements.

An example of such an end-member decomposition is shown in Fig. 1 using Ba and Sr.

The previous end-member decomposition was used to separate step by step the streamflow at the outlet into three main contributing flow components (Fig. 2), according to equations (3) and (4).

For such an event in this catchment, the results indicate that:

(a) The direct contribution of the rain or superficial water is very low (5% maximum). This result is in agreement with  $\delta^{18}O$  and  $\delta^2H$  measurements which indicate a very low percentage of 'new water' (Ladouche, 1997)

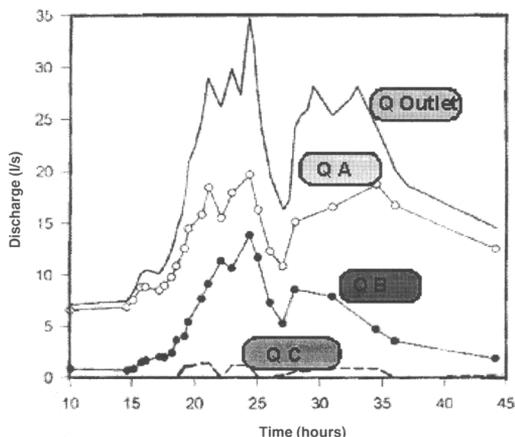


FIG. 2. Hydrograph separation: discharge vs time.

(b) The deep ground waters from the hillslope and the subsurface waters from the saturated areas mainly contribute to the total stream discharge. During the storm event the proportions of waters from the saturated areas display the most significant increase in discharge.

**Appendix**

- (1)  $Q_O = Q_U + Q_{t1} + Q_{t2} + Q_X$
  - (2)  $Q_O \cdot C_O = Q_U \cdot C_U + Q_{t1} \cdot C_{t1} + Q_{t2} \cdot C_{t2} + Q_X \cdot C_X$
- O: Outlet; U: mean upstream; t1: tributary 1 (from saturated area); t2: tributary 2 (left river); X: unsampled flows
- (3)  $Q_O = Q_A + Q_B + Q_C$
  - (4)  $Q_O \cdot C_O = Q_A \cdot C_A + Q_B \cdot C_B + Q_C \cdot C_C$
- Q: Discharge flows; C: element concentrations, A,B,C index: end-member distinguished fluxes.

**References**

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