Stream hydrograph separation on two small Guianese catchments

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Abstract Intensive sampling of runoff was carried out in a tropical forest on two small but highly responsive catchments (Saint Elie’s track, French Guiana). After deforestation, one of them is now a meadow, while the other is still a primary forest. A hydrograph separation, based on $^2$H, $^{18}$O, and hydrochemical tracers, has been performed to separate streamflow into subsurface quick flow, mixing zone and groundwater slow flow contributions. Nevertheless, soil water (surface and deep layers) plays a significant role in the generation of stream water chemistry. Applying some reasonable assumptions at different steps of storm flow generation, a two, then a three, and finally, a two-component model recognizing contributions from different compartments can explain the temporal variation of the geochemical tracers observed in the streamflow response in the study area.
INTRODUCTION

The hydrograph separation in different components (direct runoff on ground surface, subsurface interflow and groundwater outflow) is classically undertaken from a graphical decomposition method (Barnes, 1939). The excessive use of this method has largely fed the debate around the status and the future of hydrology (Beven, 1987). Especially, the graphical separation method can largely overestimate the contribution of direct runoff to the stream. This problem remains relatively secondary when the aim is the reconstitution or the prediction of the streamflow rate. It becomes an important problem when the aim is the reconstitution or the prediction of the stream water quality (Hubert, 1989).

In order to allow more specific and realistic separation of stream hydrograph sources, different hypotheses have suggested that precipitation moving rapidly overland or through soils dominates storm flow (DeWalle et al., 1988):
(a) overland flow (Horton, 1933),
(b) partial-area overland flow (Betsen, 1964; Ragan, 1968),
(c) saturation overland flow (Beven, 1978; Dunne & Black, 1970a,b),
(d) macropore flow (Jones, 1971; Beasley, 1976; Pilgrim et al., 1978; Mosley, 1982).

The application of isotopic methods as a tool for tracing water movement is able to provide an interpretation for the origin of water within and/or at the inflows/outflows of the catchment under study. In association with hydrochemical studies, it is therefore usable at the catchment scale within the framework of hydrograph separation (Sklash & Farvolden, 1979; Kennedy et al., 1986; Rodhe, 1987; Wels et al., 1990; Wels et al., 1991; McDonnell & Kendall, 1992). However, the use of these two tracers families allows identification of the origin of water in simple cases (Hubert, 1989). When the reality is complex (for example, a molecule of water from precipitation that has first been intercepted by vegetation, then has become overland flow, then has percolated into the soil to participate in the subsurface outflow before rejoining the groundwater outflow to finally discharge into the stream), one can reasonably doubt the quality of information on the different parts of the molecule history discovered by the geochemical method.

EXPERIMENTAL SITE DESCRIPTION

This study was conducted on two catchments in the North of French Guiana (Saint Elie’s track, near Sinnamary, Fig. 1). The ECEREX experimental catchments have been monitored since 1977 (Sarailh, 1990; Fritsch, 1990). After deforestation, one ("A") of the basins is now a meadow (1.3 ha), the other ("B") is still a primary forest (1.6 ha). These two catchments, without permanent flow, have been retained because they present similar characteristics for soils, slope steepness and rainfall input. They differ only by their canopy: grass on catchment "A", dense primary forest on catchment "B". Mean annual precipitations range from 3500 to 3900 mm (Roche, 1982).

The soil characteristics (Grimaldi et al., 1990) show essentially the existence of a clayey horizon situated at varying depths (from −0.30 m to −1.00 m). During events, this horizon limits the rainwater infiltration and can constitute the floor of a temporary groundwater. This saturation, associated with a slope effect (15 to 20%), provokes lateral flow through the macroporosity along the slope from the upper part of the
catchment to the stream (Grimaldi & Boulet, 1989). According to the depth of this layer, two families of soils can be characterized by the nature of their drainage (Boulet, 1990):
- soil with deep and free vertical drainage (10% of the soil area, in the upper part of the catchment covered in a primary forest),
- soil with deep but delayed vertical drainage (100% of the grass area, and 90% of the primary forest area).

HYDROGRAPH SEPARATION METHOD: GENERALITIES

At the outlet of the catchment, the isotopic compositions ($^{18}$O, $^2$H, $^3$H) and the chemical concentrations of an element are imposed by a mixing of waters with different origins and different histories. Chemical and isotopic characteristics of water sampled at the outlet will depend therefore on the proportions of the mixing between "ancient" waters (anterior to the event) and "new" waters (brought by the event). This allows one to write a two-component mass balance equation: one for water flow and one for isotope or chemical tracer:
\[ Q_{\text{discharge}} = Q_{\text{event}} + Q_{\text{preevent}} \]  
(1)

\[ C_{\text{discharge}}Q_{\text{discharge}} = C_{\text{event}}Q_{\text{event}} + C_{\text{preevent}}Q_{\text{preevent}} \]  
(2)

where \( Q \) and \( C \) are flow and isotopic compositions and/or chemical concentrations of the natural tracers (discharge, new and old water).

The stream water level has been measured and converted into a flow rate. One can therefore determine \( Q_{\text{preevent}} \) and \( Q_{\text{event}} \). But this approach requires different assumptions (Sklash & Farvolden, 1982):

1. the content in heavy isotopes of the considered event has to be significantly different from that of ancient water (Crouzet et al., 1970);
2. the content in heavy isotopes of the intrastorm rainfall does not present spatial and temporal variations;
3. the content in heavy isotopes of the ancient water remains constant during the flood; and
4. the ancient water has the isotopic composition of the baseflow.

Assumption (1) is often verified but has to be nevertheless controlled by an adapted sampling (Kennedy et al., 1986). Assumption (2) has to be imperatively rejected: the isotopic composition of the rainwater evolves over very short time periods (Dansgaard, 1964; Jouzel, 1986; McDonnell et al., 1990; Kendall & McDonnell, 1993). Assumption (3) is not always verified. The isotopic composition of the fraction of groundwater that discharges into flood can be modified by the infiltration of precipitated water with a different isotopic signature. However, this case has been only rarely observed in the literature (Kennedy et al., 1986). On the other hand, the isotopic composition of the soil water (temporarily and/or non-saturated layers) is strongly modified by the infiltration of precipitations with an isotopic time-space evolution. Assumption (4) is generally justified: baseflow coming from groundwater does not generally offer geochemical discontinuity.

The geochemical analysis of the hydrograph separation, taking into account the age of the water ("ancient" and "new"), reveals generally a strong "old" water contribution to a flood. In this case, the runoff contribution does not exceed some percentage of the total volume measured at the outlet (Crouzet et al., 1970).

**SAMPLING, METHODS AND TECHNIQUES**

On 24 May 1992, water sampling was undertaken between 06.00 h and 23.00 h as described below:

(a) stream water samples were collected continuously (5 to 15 minute intervals) at the gauging station (catchment outlets). Stream discharge were recorded at a V-notch weir at the catchment outlet;

(b) 15 minute rainfall intensities and precipitation samples were collected in nonrecording gauges (eight on basin "A", 31 on basin "B");

(c) water from infiltration ditch at different depths on basin "B".

Tensiometer measurements were realized throughout the experiment on basin "A" (3 stations) and basin "B" (3 stations). The day before the experiment, soil waters were taken at different depths near the six tensiometer stations in order to characterize an initial isotopic state of the water in the soil.
RESULTS AND DISCUSSIONS

The isotopic composition of precipitation

During rainfall, the liquid fraction is enriched in heavy isotopes as compared to the residual vapour phase. Evolution of isotopic compositions of water vapour in the clouds and of the resulting precipitation is most often interpreted through the model of Rayleigh distillation (Dansgaard, 1964). On 24 May 1992, from 04.00 h to 14.30 h, four (basin "B") or five (basin "A") distinct rainy events composed the rainfall (Figs 2 and 3). Rainfall amounts were respectively 53.8 mm (throughfall, basin "B") and 56.7 mm (open area, basin "A"). The difference between these two values represents a 5.6% loss due to rain interception by the canopy.

Fig. 2 Rainfall depth and isotopic composition of precipitation ("A" catchment, 24 May 1992).

Fig. 3 Rainfall depth and isotopic composition of precipitation ("B" catchment, 24 May 1992).
Small differences appeared between the isotopic composition of the intercepted and rain fractions because evaporation occurs in an atmosphere with a high relative humidity (Gat & Tzur, 1967).

The isotopic composition of the rainwater varied very slightly in the space (Figs 2 and 3) on the two catchments and appears to be independent of rain amount.

Under primary forest, 31 raingauges were randomly distributed along a line parallel (100 m) to the stream channel in order to study the organization (decametrical scale) of the throughfall samples. The variograms thus determined were of a pure random type with an important nugget effect. The throughfall process has therefore to be considered as a discontinuous phenomenon, without spatial organization. The variograms relative to the isotopic composition of the rainwater under the canopy did not demonstrate the existence of a spatial structure and confirmed therefore the independence of the raingauge device. So, the isotopic composition of rainwater appeared to be independent of raingauge location.

The isotopic composition of stream water

A complex shower caused two successive floods. During the first flood (07.58 h-10.08 h), the stream rate was not substantially affected by the shower intensity. The second flood began during the third rainy event (11.35 h). The three peaks (especially, the main peak recorded at 12.35 h) correspond to the higher intensity values of the rainfall (Figs 4 and 5).

The isotopic composition of the water sampled at the outlet of the catchments tended toward that of the rainwater without ever reaching it (Figs 4 and 5). This could be attributed to:
(1) A spatial variability of the isotopic composition of the rain at the scale of the catchment which would question the representativity of the raingauge and of the

Fig. 4 Total stream discharge ("A" catchment, 24 May 1992). Stream $\delta^{18}$O and initial $\delta^{18}$O soil water are presented elsewhere.
isotopic signature of the rain thus determined. But another experiment (15 May 1993) revealed an absence of $\delta^{18}$O spatial evolution along the stream (Fig. 6) which demonstrates that only the temporal evolution of isotopic signatures of rainwater and temporarily saturated soil layers cause that of the stream water.

(2) Mixing between rainwater and pre-event old water in the soil with a different isotopic composition. It is to be noted that the temporal variability of the isotopic signature of the rainwater covers the spatial variability (vertical profile) of the initial isotopic signature of the soil water (Figs 4 and 5).

**Meteoric water line and evaporation line**

The meteoric water line characterizes the isotopic composition of precipitations that have escaped to evaporation during their fall in the atmosphere. So the $\delta^{18}$O of rainfall is
linked to that of $\delta^2$H by the following empirical relationship (Yurtsever & Gat, 1981):

$$\delta^2 H = (8.17 \pm 0.08)\delta^{18}O + (10.6 \pm 0.6) \quad (3)$$

Values of the meteoric water line parameters only depend on the atmospheric humidity deficit value that governs the ocean evaporation (Merlivat & Jouzel, 1979). Laws that govern the fractionation process during evaporation produce an identical effect on the two stable isotopes of water. This effect tends to concentrate in $^{18}$O and in $^2$H the residual water of a reservoir (surface water body, soil, leaf...). Different studies (Craig, 1961; Craig & Gordon, 1965; Gat, 1971) showed that points that represent the evolution of the isotopic composition of a water submitted to evaporation are all situated under the meteoric water line in a diagram $\delta^2$H-$\delta^{18}$O.

During this experimentation, the representation of the isotopic composition of water (rain, soil and stream water samples) in a diagram $\delta^2$H-$\delta^{18}$O (Fig. 7) revealed the absence of:

- an evaporation line in the case of the soil water; and
- a mixing line between the different components of the stream discharge.

All these points were linearly related following a meteoric water line [$\delta^2H = 6.3 (\pm 0.3) \delta^{18}O + 5.7 (\pm 0.7)$]: the isotopic compositions of waters sampled at the catchment outlet were governed only by the condensation process in the clouds. During infiltration, rainfall (new water) only displaced stored soil water (from ancient events without loss by evaporation). New addition of rain in the soil displaced an approximately equivalent amount of old water (Hewlett & Hibbert, 1967). The non-evaporation of the soil water under these canopies was equally confirmed by micro-meteorological and physiological measurements realized during the dry season (Fig. 8).

The initial isotopic composition of the soil water

The different isotopic profiles realized in the soil (upper, middle and lower parts of the catchment "A") presented a similar trend (Fig. 9). The absorption root and capillary rise
Fig. 8 Evapotranspiration flux (trees and underwood, "B" catchment).

did not provoke isotopic fractionation (Zimmermann et al., 1967). In the absence of evaporation, these results allow one to characterize a succession of precipitations infiltrated in the soil. Isotopic compositions of these ancient precipitations were different and more or less homogenized by the transfer process in the soil (rapid infiltration in

Fig. 9 Initial values of the isotopic composition of the soil water (3 stations) measured before the event ("A" catchment, 24 May 1992). The initial values of the isotopic composition of the soil water (4 stations on "B" catchment) are presented elsewhere.
upper horizons, slower infiltration in deeper horizons). On catchment "B" (Fig. 9), isotopic profiles of the soil water presented a comparable evolution to that of profiles measured on catchment "A". These profiles can therefore be interpreted in an analogous manner: infiltration more or less rapid at the surface accompanied by a mixing more or less complete along the profile. On the other hand, the profile realized in the upper part of this catchment presented a good $\delta^{18}O$ homogenization probably linked to its situation in a free vertical drainage area.

Analysis of the evolution of water potentials in the soil (catchment "B")

The three stations retained on this catchment presented a different hydrodynamical behaviour during the shower. The soil reacted very superficially to the shower (Fig. 10) in the case of the station closest to the stream channel (B1). Only the upper horizons (from 0 to $-0.4$ m) reached or had a tendency to reach the saturation state when the
main stream peak was recorded (12.35 h). Then, water potentials of these horizons remained constant. Between -0.50 m and -0.80 m, the potential variations remained weak. Beyond -1.00 m, variations of potential were non-existent.

With a soil profile nevertheless similar, the station B3 reacted very differently (Fig. 11). At first (06.00 h-11.00 h), the water potential presented small variations whatever the horizons. Only the horizon at -0.15 m was then saturated. Between 11.00 h (superficial layers) and 13.00 h (deeper layers), water potentials increased strongly, except for the deepest horizons (-2.00 m). These potentials stabilized between 13.00 h and 16.00 h, then decreased slowly beyond 18.00 h. At the peak of stream (12.35 h), the saturation in the soil was reached to -1.40 m: the infiltration therefore rapidly reached the deepest layers.

From 08.00 h, the soil of the station B4 was saturated up to -0.40 m (Fig. 12). Then subsequently, the water potential of superficial horizons increased very feebly. On the other hand, the intermediate horizon potential (from -0.60 m to -1.00 m) increased only from 12.00 h. These horizons saturated at 17.00 h. Between -1.00 and -2.00 m, variations of potential were gradually lessened and saturation was never reached. In a quantitative manner, and despite a great variability of hydrodynamical properties of the soil layers, some results may be noted:

- There was a reduction of one to two orders of magnitude in hydraulic conductivity between superficial horizons and deeper ones. The existence of a "less permeable barrier " seems therefore confirmed.
- The drainage at the profile base was negligible (inferior to 1 mm).
- The water recharge of the soil profile was only 10 to 20 mm at the different sites: an important amount of the rain was deflected laterally and was available for lateral flow in the soil profile.

In conclusion, the soil layers of the B catchment could be described as being the superposition of 3 horizons:

- upper soil horizon with a high infiltration rate flow (from 0 to -0.40 m);
- intermediate horizon less permeable (above the red clayey horizon); and
- deep soil horizon (under the red clayey horizon).
Relationship between isotopic composition of stream water and stream discharge

The compartmentalization of water which reaches the stream channel influences the isotopic evolution of stream water (Herrmann & Stichler, 1981). This compartmentalization can be approached through the relationship established between the content in heavy isotopes of the stream water and the outflow. This relationship can present an hysteresis loop, attributed by Sklash & Farvolden (1979) to a mixing among three components, with different isotopic compositions (rainwater, soil water, groundwater), and temporal contributions evolving to the stream discharge. The experimentation realized on these two catchments confirmed the existence of this hysteresis loop relationship (Fig. 13). However, this relationship can equally be explained by the isotopic evolution of the rain water during time in the case of a simple two-component mixing model.

![Fig. 13 δ¹⁸O stream water versus stream discharge ("A" and "B" catchments, 24 May 1992).](image)

Relationships between isotopic and hydrochemical tracers

The use of the relationships between chemical and isotopic tracers allows one to clarify the analysis of the different components that contribute to stream discharge (Maule & Stein, 1990). The isotopic method allows one to distinguish new waters from old waters when their contents in heavy isotopes are significantly different. It allows one equally to characterize waters in the soil affected by mixing (old waters "contaminated" by new waters during the infiltration of the rain) and whose isotopic composition is therefore intermediate between those of old and new waters.

The hydrochemistry method allows one to distinguish waters that have preserved the character of new waters (without chemical exchange with the soil layers) from those that have lost it (chemical exchanges with an organic or mineral horizon). Naturally, this last hypothesis has to be adapted according to the nature of the mineral horizon and the canopy (leaching process).

From a geochemical diagram (Maulé & Stein, 1990), different components can be thus distinguished:
(1) Recent waters *s. s.* , situated above the soil-atmosphere interface (direct rain, direct runoff), whose isotopic composition is imposed by the rain and that are not marked by a chemical tracer. However, no direct runoff is observed on studied catchments.

(2) Recent waters *s. l.* (subsurface flow), situated under the interface ground-atmosphere, that present the isotopic composition of the precipitation and that are marked by a chemical tracer (chemical exchanges with the litter and the first mineral horizons). By reason of a limited mixing between the infiltrated rain and the ancient water present in superficial layers of the soil one can consider that these waters circulate rapidly in zones temporarily saturated.

(3) Mixing water ("intermediate waters") which present an isotopic composition intermediate between that of the rain and that of deep waters are marked by a chemical tracer. Due to the fact of important mixing of waters between the rain and the old water in the soil, one can suppose that these waters circulate more slowly.

(4) Ancient waters *s. s.* , which present the isotopic composition of the saturated zone ("ancient waters ") and that are marked by a chemical tracer.

It is of interest, therefore, to find the chemical tracers allowing one to characterize the different reservoirs. In general, geochemical elements in the soil can be divided into two groups (Hirata & Muraoka, 1993): those (silica, sodium, chloride...) that are not essential to the development of vegetation and whose concentration increases with depth, and those (nitrate, potassium, calcium...) that are essential to vegetation, and have a tendency to concentrate at the soil surface.

These general observations are clearly to be adapted to the mineralogical nature of studied soils and to the influence of the local climate on the alteration of the soil. In the case of these catchments, one can observe that (Grimaldi, 1988):

- Contamination in chloride or in sodium of the soil solution does not exist during the alteration of minerals; these elements are not present in the minerals. These elements are necessarily brought by rain. The ions are very little absorbed by the vegetation (notably Cl⁻) and are going therefore to concentrate in deep old waters.
- Potassium and the calcium are weakly created by the soil (very slow dissolution of muscovite). They are equally liberated during the decomposition of the litter or by canopy leaching, but are very rapidly absorbed by the vegetation (especially K⁺). K⁺ and Ca⁺⁺ are going therefore to be found essentially in superficial new waters.

Fig. 14 Chloride and potassium concentrations versus δ¹⁸O (stream water, 24 May 1992, "B" catchment).
Thus, on these catchments, superficial waters will be characterized by high concentrations in potassium and very low in chloride. An opposite phenomenon will characterize deep waters.

The diagram "deep water chemical tracer (Cl\(^-\))-isotopic tracer (\(^{18}\)O)" demonstrates the existence of a hysteresis loop relationship between these two tracer families (Fig. 14):

- the downward part of the hysteresis loop (rising limb of the hydrograph) is imposed by an isotopic depletion linked to the fall of this signal in precipitations and to the arrival of water from superficial soil layers weakly marked in Cl\(^-\); and
- the climbing part of the hysteresis loop (falling limb and baseflow recession) is created by the rain stopping and the arrival of deeper water at the outlet which is concentrated in Cl\(^-\) and more isotopically enriched.

This hysteresis loop relationship disappears in the case of the diagram "superficial water chemical tracer (K\(^+\))-isotopic tracer (\(^{18}\)O)" (Fig. 14): the observed relationship is essentially imposed by isotopic depletion in precipitation mentioned above. At the outlet, the arrival of deep water weakly concentrated in potassium no longer modifies this relationship.

Mass balance equations (water, chemical and isotopic tracers) may be used for separating the stream hydrograph in different components. This allows therefore to determine qualitatively the water origin and quantitatively the different component contributions.

So as to be able to determine the respective contribution (Figs 15 and 16) from the soil (subsurface waters, intermediate waters above the red clayey horizon, deep waters) susceptible to reach the stream, the parameters used were:

- average $\delta^{18}$O in precipitations, after having regrouped successive weak events;
- initial average $\delta^{18}$O in the soil water, after having regrouped successive horizons with similar isotopic compositions;
- average $\delta^{18}$O in the infiltration ditch water; and
- associated chemical concentrations (K, Cl).

This decomposition obtained revealed an important contribution from intermediate zones of the soil, above the red clayey level.

On catchment "B", the subsurface flow contribution to the hydrograph peak was important (70\%). During the falling limb and baseflow recession, the contribution from the deep water increased gradually to reach 93\% to 22.00 h.

![Fig. 15 Geochemical stream hydrograph separation (24 May 1992, "A" catchment).](image-url)
On catchment "A", the stream discharge was mainly insured by the superficial soil layers (70%). During the baseflow recession period, the contribution from the temporary groundwater did not cease to increase and finished by reaching similar values to those calculated during the beginning of the flood.

The percentage of the volume of water flowing to the outlet compared with precipitation is 41% on catchment "A" against 28% in the case of catchment "B". This difference cannot be entirely attributable to losses due to interception since according to calculations, that was only 5%. These differences of hydrological behaviours are probably attributable to the nature of the canopy and to the action of the vegetation on the soil porosity. Indeed, the deforestation process causes an increase in the volume of rain arriving at the ground and an increase in the volume of water contained in the soil (Sklash et al., 1986).

CONCLUSION

This study showed clearly the interest of the simultaneous use of chemical and isotopic information for the hydrograph separation.

The analysis of stream water by the isotopic method showed that a flood is a mixture of water from different soil layers. However, the isotopic tool alone is insufficient to appreciate the depth of the water mobilized in the soil. Indeed, on the catchments studied, the temporal variability of the isotopic signal of the rainwater was very similar to the spatial variability of the isotopic signal of the soil water. Soil water in catchments is not submitted to evaporation: the isotopic composition of the soil water is governed by successions of infiltrated anterior rainwater.

The use of chemical tracers provided valuable information for the characterization of the soil layers. Thus, the use of combined chemical and isotopic information provided the identification and the quantification of the different component contributions (subsurface flow, intermediate and deep waters).

Contents in $^{18}$O and $^2$H of rain water have a strong temporal evolution, but a weak variation in space, by reason of the small catchment areas. This temporal variability indicates not to use an average isotopic signal during the calculation of the contribution of the component "new water".
Further fieldwork is now necessary to study the spatial and the temporal evolution of geochemical tracers in soil water.

REFERENCES


