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## HYDROGRAPH SEPARATION: A COMPARISON OF GEOCHEMICAL AND ISOTOPIC TRACERS

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### ABSTRACT

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A chemical hydrograph separation can be used to study runoff processes on a watershed scale provided the soil kinetics of the geochemical tracer are well documented. To separate streamflow into surface (SF) and subsurface flow (SSF), the supply of the tracer from the soil should be uniform throughout the soil profile and independent of the residence time of the soil/groundwater. This paper examines the use of two weathering products, dissolved silica and magnesium, for separating spring runoff into SF and SSF in small headwater streams on the Canadian Shield. Field observations and leaching experiments in the laboratory suggested that both tracers were released very rapidly from the podzolic soils. Silica allowed a well-defined separation of streamflow into SF and SSF since it is absent in melt/rain water and its concentration varies little throughout the soil profile. Magnesium was used in those streams with wetlands when silica was not behaving conservatively. Both geochemical tracers suggested higher contributions of SSF to total spring runoff (> 90%) than estimates ( $\approx$  72%) based on the stable isotope deuterium. This difference may result from laterally flowing soil-water that did not mix with the phreatic/groundwater reservoir.

### INTRODUCTION

The mechanisms by which snowmelt or rainfall in a basin is transformed into streamflow, i.e. the process of streamflow generation, has been studied extensively to improve storm runoff forecasting and to model changes in stream water quality. The approaches taken range from the intensive monitoring of instrumented plots or hillslopes (e.g. Kirkby, 1980) and the simulation of stream response based on mathematical models (Stephenson and Freeze, 1974) to the use of hydrological tracers, which may be artificially introduced (Pilgrim et al., 1979) or naturally occurring. In the latter case, the supply or application is often basin-wide allowing a separation of basin runoff into components with

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different tracer concentrations (Dinçer et al., 1970). The interpretation of waterflows using a tracer relies upon the distinct uniform signature of tracer in different compartments and the conservative behaviour of the tracer during mixing of the compartments. Flow may originate from many different source areas. However, sources with the same tracer concentration cannot be identified so they are pooled together, often only one tracer is used and a two-component hydrograph separation is performed (Pinder and Jones, 1969):

$$Q_{\text{SSF}} = Q_{\text{T}} \frac{(C_{\text{T}} - C_{\text{SF}})}{(C_{\text{SSF}} - C_{\text{SF}})} \quad (1)$$

and

$$Q_{\text{SF}} = Q_{\text{T}} - Q_{\text{SSF}} \quad (2)$$

where:  $Q$  = discharge;  $C$  = concentration of the tracer; the subscripts T, SF, and SSF refer to the total stream discharge as well as the two runoff components (surface and subsurface flow respectively). The exact definition of the two runoff components depends on the properties of the tracer used. Two commonly used groups of tracers are: (1) stable isotopes of water, oxygen-18 ( $^{18}\text{O}$ ) and deuterium ( $^2\text{H}$  or D) (e.g. Sklash and Farvolden, 1979; Sklash et al., 1986) and (2) weathering products such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  or  $\text{SiO}_2$  (e.g. Pinder and Jones, 1969; Kennedy, 1971).

The fundamental difference between a non-reactive isotope of water and a chemical tracer of water is that the isotopic content changes only as a result of mixing (assuming evaporation is negligible) while the chemical composition changes as a result of interaction with the soil and bedrock. As a result, the interpretation of an isotopic and a chemical hydrograph separation may differ from one another and provide complementary information (e.g. Fritz et al., 1976; Sklash et al., 1976). In general, isotopes trace the source of water whereas chemicals trace the flow paths of water. Isotopic hydrograph separation distinguishes old and new water (Sklash and Farvolden, 1979). However, the flow paths of new water are not known. With the aid of a model it may be possible to further trace that part of melt water that mixes with the saturated (phreatic) zone, or groundwater reservoir (Rodhe, 1987). However, the identification of new water that infiltrates and does not completely mix the groundwater before discharging to the stream is not possible using an isotopic hydrograph separation.

In contrast, geochemical tracers may be used to separate streamflow into runoff components according to their flow paths, independent of their origin (old vs. new) and degree of mixing (soil water vs. groundwater) (Kennedy et al., 1986). The exact definition of the flow paths depends on the source and dissolution rates of the chemical tracer used for separation. In order to avoid speculative interpretation and erroneous conclusions based on chemical hydrograph separation, the soil kinetics of the geochemical tracer must be investigated.

The overall objective of this study was to determine the contributions of subsurface flow to spring runoff in three small streams on the Canadian Shield.

A mixing model and an isotope separation were used to estimate the contributions of all subsurface/groundwater to streamflow that infiltrated the ground and mixed in a groundwater reservoir (Wels, 1989; Wels et al., 1990a). However, this approach may have underestimated the contributions of subsurface flow to streamflow if new water was routed through the soils so that mixing with the pre-storm or pre-melt subsurface water was not complete (e.g. via pipeflow or lateral flow through the top soil layers) (Rodhe, 1987; Wels et al. 1990b).

Chemical hydrograph separation was performed to test the hypothesis that subsurface flow was underestimated by an isotope separation. For this purpose, a geochemical tracer was needed to distinguish surface flow (water that does not infiltrate) from all subsurface flow. Ideally, flow through the various soil layers should have a uniformly high tracer concentration relative to surface flow with very low tracer concentrations. One prerequisite for a chemical hydrograph separation is that the tracer concentration is independent of the residence time of the water, i.e. it is a result of fast equilibrium reactions. Assuming that the chemical tracer does not interact with the stream bed it could be used to separate streamflow into surface flow and subsurface flow using eqn. (1). In order to test the hypothesis that contributions of subsurface flow based on geochemical tracers are greater than those of well-mixed groundwater using isotopic tracers, this paper: (1) evaluates the source and dissolution rates of the weathering products silica and magnesium in the field and laboratory; (2) compares contributions of subsurface flow based on those geochemical tracers (hereafter termed chemical subsurface flow, CSSF) with those of groundwater using isotopic hydrograph separation (hereafter termed isotopic subsurface flow, ISSF).

#### STUDY SITE

The study was performed in the Plastic Lake and Harp Lake watersheds located in the Muskoka-Haliburton area near the southern fringe of the Canadian Shield (Dillon et al., 1987; Wels et al., 1988; Wels, 1989). The study focused on a small first-order stream, Plastic-108, draining the northeastern corner of the Plastic-1 watershed (Fig. 1). The Plastic-1 watershed and the larger Harp-5 sub-basin were studied less intensively.

All three streams are very responsive headwater streams with peak discharges up to  $30 \text{ mm day}^{-1}$  during spring runoff and very little or no flow during the late summer period. The mean annual precipitation depth is  $\sim 1000 \text{ mm year}^{-1}$  (1941-1980);  $\sim 26\%$  ( $260 \text{ mm year}^{-1}$ ) falls as snow (Shibatani, 1988). Spring runoff is the dominant hydrological event in this region. The long-term annual runoff is  $400\text{--}600 \text{ mm year}^{-1}$  with 50-75% occurring during March-April in response to snowmelt (Scheider et al., 1983).

The topography of the Plastic-108 sub-basin is characterized by a relatively narrow valley with steep convex side slopes typical of a fault zone (Fig. 1). Large permanent wetlands do not exist in Plastic-108. Only the valley bottom is commonly saturated during periods of high flow. The surficial deposits vary considerably in depth within this small sub-basin. On the eastern side of the

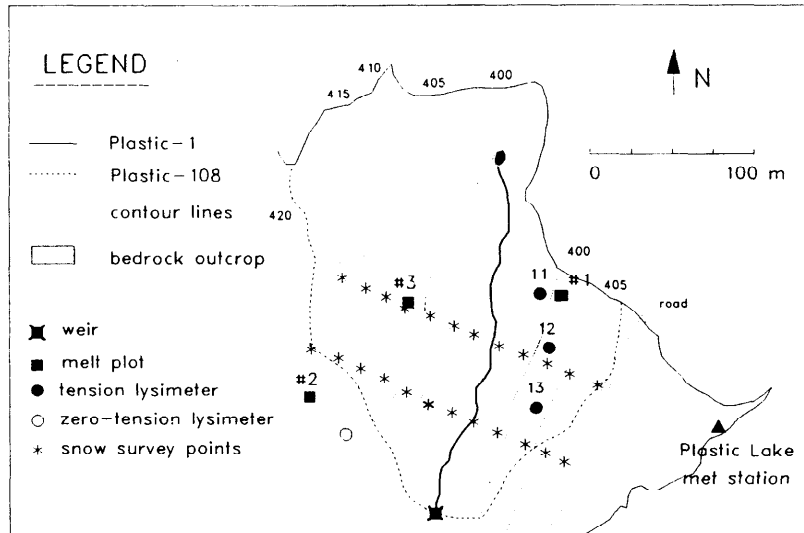


Fig. 1. The location of field instrumentation in the Plastic-108 sub-basin and vicinity. The contour interval is 5 m.

valley the till thickness ranges from 0.3 to 1 m and the podzolic soils sometimes show the development of a C-horizon. The surficial deposits on the western side are much thinner. Here, the B-horizon of the podzolic soil is often absent and the bedrock is covered only by an A-horizon and/or a humus layer (rankar). Hardly any soil and vegetation cover is found on a large bedrock outcrop on the western side of the valley, which comprises  $\sim 10\%$  of the total area of Plastic-108 (Fig. 1). The soils in the stream valley differ from the side slopes. The valley soils are gleysolic soils with a high organic content and are saturated frequently.

The bedrock in the Harp-5, Plastic-1 and Plastic-108 catchments is primarily granitic biotite gneiss with some hornblende gneiss in Harp-5 and hornblende or biotite amphibolite in Plastic-1 and 108 (Jeffries and Snyder, 1983; Kirkwood and Nesbitt, 1989). The soils of all catchments are very sandy (63–86%) with a low clay content (3–5%) and low cation exchange capacity (0.4–1.4 meq per 100 g) typical of podzolic forest soils below the top few centimetres of the LFH and A horizons (LaZerte, unpublished data).

#### METHODS

Stream flow was gauged using a  $90^\circ$  V notch weir equipped with a Stevens water-level recorder (Fig. 1). Stream water samples were collected with ISCO automatic water samplers which were placed in heated weir huts to prevent the suction lines and samples from freezing. Meltwater was sampled at three sites in Plastic-1 (Fig. 1). Two snowmelt lysimeters (Nos. 1 and 2) were installed on the west- and east-facing slope of Plastic-108. A composite meltwater sample

was taken at least once a day. Soil water samples were obtained bi-weekly from three tension lysimeters in the Plastic-108 sub-basin and daily during the major spring runoff period from a zero-tension lysimeter on a south-facing slope just outside the watershed boundaries (Fig. 1).

Dissolved reactive silicate ( $\text{SiO}_2$ ), expressed in  $\text{mg l}^{-1}\text{Si}$ , was determined using colorimetry (blue silicomolybdate complex) (Strickland and Parsons, 1972). The terms 'dissolved silica' or simply 'silica' are also used to describe 'dissolved reactive silicate' throughout this text. Magnesium ( $\text{Mg}^{2+}$ ) was determined by flame atomic absorption using a Varian AA - Series 1275 spectrophotometer (Wels, 1989). Both analyses were very reproducible with mean standard deviations of 0.02 and 0.01  $\text{mg l}^{-1}$  (i.e. coefficient of variation (CV) of 0.5% and 2%) for dissolved silica and magnesium, respectively (Wels, 1989). Samples for deuterium analysis were measured by mass spectrometry at Chalk River Nuclear Laboratories, with a precision ( $1\sigma$ ) of  $\pm 0.3$  ppm, as determined from duplicate analysis (Wels, 1989).

#### DISTRIBUTION OF CHEMICAL TRACERS

Silica occurs in precipitation (snow or rain) only in very small concentrations in the study area (Ontario Ministry of the Environment, unpublished data). In Plastic-108, silica concentrations ( $C_{\text{Si}}$ ) in runoff from the two melt plots were  $< 0.03 \text{ mg l}^{-1}$  throughout spring runoff. In contrast, silica in stream water ranged from a volume weighted mean of  $2.6 \text{ mg l}^{-1}$  during spring runoff in Plastic-108 to  $2.9 \text{ mg l}^{-1}$  in Harp-5. Higher silica concentrations were found in soil water of the mineral horizons of the podzolic soils in Plastic-108 (average  $3.0 \text{ mg l}^{-1}$ ). Apparently, weathering processes within the soil supply large amounts of silica which are exported from the watersheds during spring runoff. This large difference between  $C_{\text{Si}}$  of precipitation and of soil/groundwater suggested the use of silica for separating streamflow into subsurface and surface flow components.

During periods of flow recession, when no melting and/or rainfall takes place, streamflow should be sustained by subsurface flow only. Hence,  $C_{\text{Si}}$  in stream baseflow should be representative of the tracer concentration in the subsurface flow component.  $C_{\text{Si}}$  values in pre-melt and post-melt baseflow were very similar in the small headwater stream Plastic-108 (Fig. 2). Even during daily flow recessions,  $C_{\text{Si}}$  recovered to pre-melt baseflow concentrations, indicating  $C_{\text{Si}}$  is constant in subsurface flow (Wels, 1989). The gradual increase in  $C_{\text{Si}}$  during post-melt baseflow may be a result of longer residence times of water in the soil and/or increased weathering rates as soil temperatures increased. However, for the analysis of the main runoff period this increase in  $C_{\text{Si}}$  of subsurface flow is negligible.

The temporal trends of  $C_{\text{Si}}$  in Plastic-1 differed greatly from those observed in Plastic-108 (Fig. 2). In Plastic-1,  $C_{\text{Si}}$  showed a strong seasonal decline largely independent of changes in flow (Fig. 2). This was probably a result of biogeochemical reactions occurring within the centrally located conifer swamp in

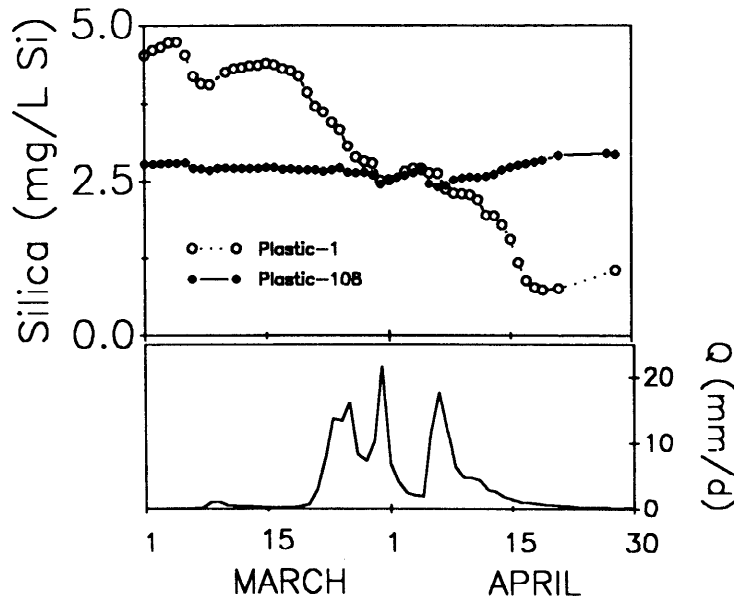


Fig. 2. Temporal trends of silica in Plastic-1 and Plastic-108 during spring runoff 1987. The daily discharge of Plastic-108 is shown below.

Plastic-1 (Wels and Devito, 1988). The swamp acted as a source of silica during pre-melt baseflow and as a sink during the later parts of spring runoff. The seasonal uptake of silica by diatoms may explain the decrease in stream Si in Plastic-1 well below those of Plastic-108 (and other tributaries to the swamp). The same seasonal trends in stream  $C_{Si}$  were observed for Harp-5, which also drains several wetland areas. Therefore, silica was used as a chemical tracer only in Plastic-108 which does not contain any permanent wetlands.

Soil water samples were analyzed in addition to stream water to test whether stream baseflow was representative of all subsurface flow, i.e. whether the tracer concentration was uniform throughout the soil profile. Pronounced differences were observed between soil water Si from the top organic layers (LFH and Ae) and the deeper mineral horizons (Bf and BC) of the soil (Fig. 3).  $C_{Si}$  was low in the top soil layers ( $\approx 0.8 \text{ mg l}^{-1}$ ) suggesting that the infiltrating melt water did not pick up much silica. This could result from short residence times and/or a limited supply of silica. The contribution of this soil water (i.e. shallow subsurface flow SSSF) to streamflow is considered part of surface flow in chemical hydrograph separation. A single silica concentration,  $C_{SF}$ , has to be assigned to the surface flow component for chemical hydrograph separation. Direct inputs of rain/melt water into the stream channel (DPS) should have a silica concentration close to  $0.0 \text{ mg l}^{-1}$  whereas most melt water flowing on the surface and/or through the top layers of the soil will pick up small amounts of silica. The uncertainty that this range of  $C_{Si}$  introduced in estimates of the fraction of subsurface flow ( $X_{CSSF}$ ) was less than 5%, assuming  $C_{SF}$  values

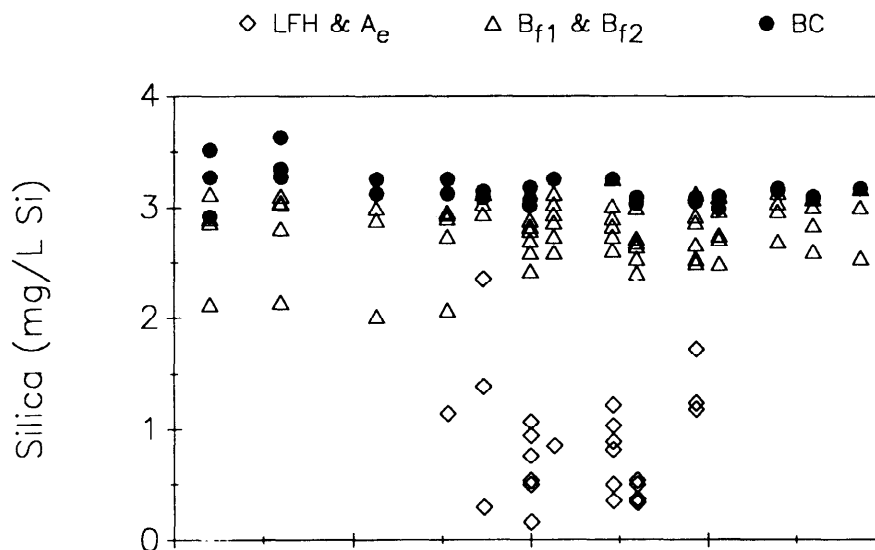


Fig. 3. Temporal trends in soil water silica in Plastic-108. Tension lysimeter samples are grouped into 'near-surface' (LFH, Ae), 'upper mineral' (Bf<sub>1</sub>, Bf<sub>2</sub>) and 'deep mineral' (BC) horizon.

ranging from  $0.0 \text{ mg l}^{-1}$  (silica in DPS) to  $0.8 \text{ mg l}^{-1}$  ( $C_{\text{Si}}$  in shallow subsurface flow). In the present study,  $C_{\text{SF}}$  was assumed to be  $0.3 \text{ mg l}^{-1}$ , i.e. intermediate between Si in precipitation and Si in the top organic soil layers (A<sub>e</sub> and LFH).

Soil-water Si concentrations in the deeper, mineral soil horizons were considerably higher than in precipitation.  $C_{\text{Si}}$  ranged from  $\sim 2.5 \text{ mg l}^{-1}$  in the upper mineral horizons (Bf<sub>1</sub>) to  $3.5 \text{ mg l}^{-1}$  in the deepest soil horizons (BC) (Fig. 3).  $C_{\text{Si}}$  in soil water did not vary much from site to site. Despite the mixing and subsequent displacement of old soil water by infiltrating melt water (Wels, 1989), the soil water  $C_{\text{Si}}$  remained very stable during spring runoff (Fig. 3). This suggests that the uptake of silica by melt water was fast relative to its residence time in the soil. Most of the soil water silica concentrations were consistently higher than the stream water baseflow value ( $\approx 2.8 \text{ mg l}^{-1}$ ) throughout the spring runoff period. This suggests that soil water from the upper mineral horizon (Bf<sub>1</sub>) was contributing to baseflow as well. Alternatively, the deep soil water collected from the three soil pits was not representative of deep soil/groundwater contributing to stream baseflow.  $C_{\text{Si}}$  of stream water baseflow was regarded as the best estimate of the average  $C_{\text{Si}}$  for the subsurface flow component. The uncertainty in estimates of  $X_{\text{CSSF}}$  as a result of variations in the subsurface flow Si of  $0.2 \text{ mg l}^{-1}$  was  $\sim 6\%$ .

The annual volume-weighted, mean magnesium concentration in precipitation (snow and rain) in the studied area was  $0.35 \text{ mg l}^{-1}$  for 1987 (Ontario Ministry of the Environment, unpublished data). However, magnesium concentrations ( $C_{\text{Mg}}$ ) in runoff from the two melt plots in Plastic-108 were generally much lower. Only the first fractions of melt water showed  $C_{\text{Mg}}$  around 0.2–

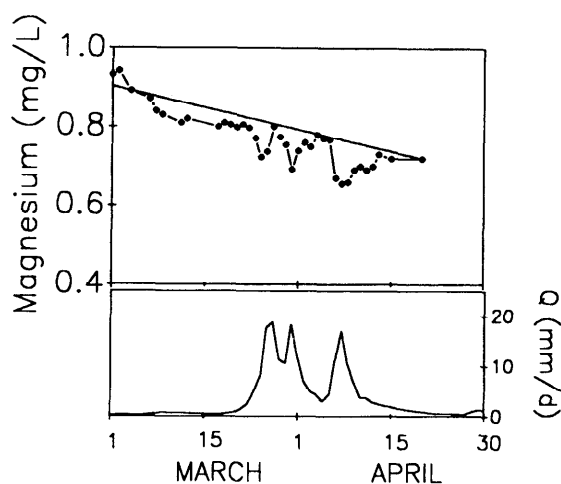


Fig. 4. Temporal trends of magnesium and daily discharge in Harp-5 during spring runoff 1987. The solid line indicates the interpolation used as an estimate for  $C_{SF}$  in chemical hydrograph separation.

$0.3 \text{ mg l}^{-1}$ . During the major runoff period,  $C_{Mg}$  was usually less than  $0.1 \text{ mg l}^{-1}$ . On days of considerable rain inputs,  $C_{Mg}$  in runoff from the plots increased again to  $\sim 0.3\text{--}0.4 \text{ mg l}^{-1}$ .  $C_{Mg}$  in stream water ranged from a volume-weighted mean of  $0.37 \text{ mg l}^{-1}$  in Plastic-1 to  $0.73 \text{ mg l}^{-1}$  in Harp-5 during spring runoff 1987. Differences in tracer concentrations of precipitation and stream water were generally much smaller for magnesium than for silica. Magnesium was used for chemical hydrograph separation only in Harp-5, where silica could not be used, and where stream water  $C_{Mg}$  was considerably higher than  $C_{Mg}$  in precipitation. The temporal trends of stream water magnesium in Harp-5 suggested a seasonal decrease in magnesium of subsurface flow (Fig. 4). The decrease in the magnesium concentrations from pre-melt baseflow ( $0.95 \text{ mg l}^{-1}$ ) to post-melt baseflow ( $0.75 \text{ mg l}^{-1}$ ) could be the result of varying contributions of different soil/groundwater reservoirs. Alternatively, the supply of magnesium in the soils may have decreased over time. In Plastic-108, no significant differences were seen in soil-water Mg concentrations in the soil horizons. No soil-water data were available from the Harp-5 watershed to examine the vertical distribution of  $C_{Mg}$  in the soil profile. Similar to the silica analysis, it was assumed that  $C_{Mg}$  in stream water baseflow represents  $C_{Mg}$  of all subsurface flow. For chemical hydrograph separation,  $C_{SF}$  was found from interpolation from pre-melt baseflow to post-melt baseflow as suggested by Hooper and Shoemaker (1986) (Fig. 4). The average magnesium concentration from the snow melt plots ( $0.2 \text{ mg l}^{-1}$ ) was used for the surface flow component of streamflow. The uncertainty in  $X_{CSSF}$  due to a random error in  $C_{SSF}$  of  $0.1 \text{ mg l}^{-1}$  and in  $C_{SF}$  of  $0.1 \text{ mg l}^{-1}$  was 13% and 8%, respectively.

In conclusion, the first assumption of chemical hydrograph separation, i.e. distinctly different tracer concentration in surface flow and subsurface flow,



was met by dissolved silica and magnesium in the Plastic-108 and Harp-5 watersheds, respectively.

#### RELEASE OF CHEMICAL TRACERS BY SOILS

##### *Field observations*

The consistency in stream water (Fig. 2) and soil-water silica concentrations in Plastic-108 (Fig. 3) during spring runoff are one indication of the rapid release of silica from the soils. A comparison of  $C_{Si}$  and deuterium concentrations (D) in soil water samples obtained from two zero-tension lysimeter pans in the deeper mineral horizon provided the strongest field support for a fast equilibrium reaction of soil water silica. Daily samples were taken over the period of intensive runoff when the soil water ran continuously and discharged several litres per day. Deuterium concentrations in soil water decreased toward the lower melt water concentrations indicating the mixing of old groundwater with infiltrating melt water (Fig. 5). However,  $C_{Si}$  remained almost constant throughout the high flow period despite the infiltration of new melt water (Fig. 5). The melt water must have taken up silica to old soil water concentrations very rapidly, i.e. within several hours. Stream flow rates did not seem to have any effect on  $C_{Si}$  in the soil water lending further support to the hypothesis that silica is readily available at least in the mineral horizon.

Magnesium concentrations in stream water and soil water did not always show the same trends. In Harp-5, stream water Mg was higher during pre-melt than during post-melt baseflow, suggesting a seasonal decrease in soil/groundwater Mg (Fig. 4). However, this seasonal decrease in magnesium of stream baseflow was much less pronounced in Plastic-108 (only  $\sim 0.05 \text{ mg l}^{-1}$  or 10% of pre-melt baseflow). Most water sampled with tension lysimeters in the mineral

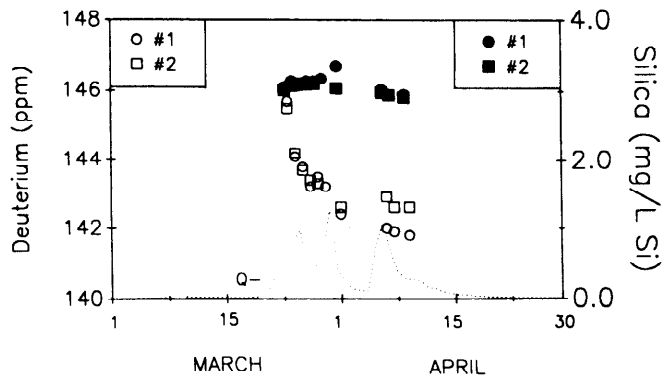


Fig. 5. Temporal trends of silica (solid symbols) and deuterium (open symbols) in the deep mineral horizon and daily discharge (dotted line) during spring runoff 1987. Soil water samples were obtained from two adjacent zero-tension lysimeter pans (Nos. 1 and 2) in the  $Bf_2$  horizon. (For units of discharge see Fig. 2).

horizons also showed a decrease in magnesium over time. However, these changes were generally small ( $< 0.1\text{--}0.2\text{ mg l}^{-1}$ ) relative to the large spatial variability in soil water Mg in the mineral horizons ( $0.4\text{--}0.9\text{ mg l}^{-1}$ ). In contrast, soil water from the zero-tension lysimeter maintained very constant  $C_{\text{Mg}}$  values ( $0.41\text{--}0.45\text{ mg l}^{-1}$ ) over the peak runoff period similar to those shown for silica in Fig. 5. These field data suggest that  $C_{\text{Mg}}$  in soil water was also controlled by a fast equilibrium reaction. However, a seasonal trend in soil and stream water may be present, possibly owing to biological demand during the growing season which starts in early May.

To perform a chemical hydrograph separation into subsurface flow and surface flow, it is assumed that the chemical tracer in stream water does not interact with the stream bed. Two observations suggest that this assumption is valid, at least in the case of silica in Plastic-108. First, no appreciable differences in stream silica concentrations were observed in the stream along longitudinal sampling transects in Plastic-108 and downstream of the swamp in Plastic-1 during pre-melt baseflow. Secondly, the stream channel in Plastic-108 is not deeply incised into the valley gleysol. As a result, the streambed is mainly composed of organically rich soil. The valley gleysol, and particularly the top organic soil layers (LFH), were found to release only small amounts of silica during continuous leaching (see Fig. 8).

Some studies have shown that cations (such as magnesium) may interact with the streambed in small headwater streams. For example, aluminum may be released from stream beds during episodic events (Hall et al., 1980), but may also be retained (Driscoll et al., 1987). Experimental acidification of first to third-order streams also resulted in the release of aluminum, calcium and magnesium from stream sediments (Hall et al., 1987). No field observations were available in this study to exclude the possibility of an exchange of magnesium with the stream bed in Harp-5.

Another uncertainty in chemical hydrograph separation was the release of silica and magnesium from exposed bedrock on the side slopes or within the stream channel. However, water flowing downhill over several meters of exposed bedrock in Plastic-108 picked up only small amounts of silica ( $< 0.8\text{ mg l}^{-1}$ ) and magnesium ( $< 0.06\text{ mg l}^{-1}$ ). This uptake of chemical tracer by flow over exposed bedrock (surface flow) introduced a small, positive bias ( $< 5\%$ ) in the estimates of subsurface flow contributions.

#### *Laboratory observations*

Silica and magnesium concentrations in stream and soil water suggested that they were released by the soils at a rapid rate. Leaching experiments were conducted on soils from the Plastic-108 watershed to test this hypothesis. Soil samples were collected in the field using a metal auger, returned to the laboratory and placed into plexiglass columns (6.3 cm i.d.). In all leaching experiments, double distilled (DD) water was used as an eluent and soil

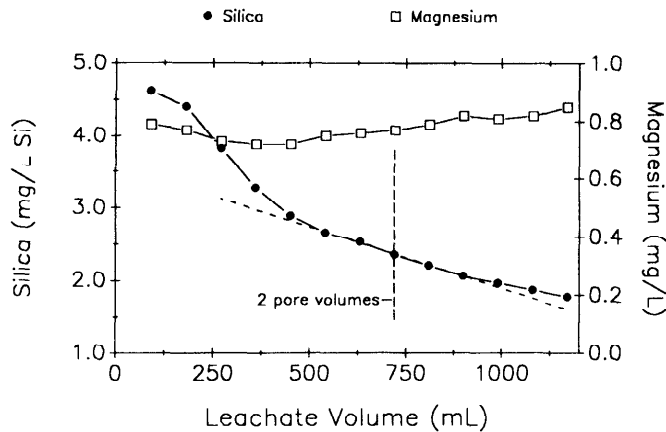


Fig. 6. Silica and magnesium in leachate during continuous leaching of a composite podzol sample. The soil columns were leached with double distilled water. The dashed line shows a rate of Si decrease of  $\sim 0.14 \text{ mg l}^{-1}$  for every 100 ml leachate.

columns were kept in the dark at  $2\text{--}8^\circ\text{C}$  in an attempt to mimic snowmelt runoff conditions (details in Wels, 1989).

First, dissolution rates of a composite sample of podzolic soils were examined. The soil samples were taken at six sites located on a transect running parallel to the stream channel in proximity to the tension lysimeters Nos. 12 and 13 (Fig. 1). Sub-samples of the well-mixed soil were leached continuously over 10–20 h at flow rates of  $1\text{--}2 \text{ ml min}^{-1}$  with  $\sim 3$  pore volumes of DD water. Magnesium concentrations remained almost constant throughout the period of continuous leaching (Fig. 6). The range of magnesium concentrations ( $0.72\text{--}0.85 \text{ mg l}^{-1}$ ) was similar to magnesium concentrations measured in tension lysimeter waters from most deeper mineral horizons of Plastic-108. The small changes in  $C_{\text{Mg}}$  concentrations of the leachate despite the application of large volumes of water (three times the total soil water volume) indicate that an equilibrium reaction must be controlling the  $C_{\text{Mg}}$  in soil water.

In contrast,  $C_{\text{Si}}$  in leachate decreased during continuous leaching which suggests that  $C_{\text{Si}}$  in soil water is not controlled by a single equilibrium reaction only (Fig. 6). Large amounts of silica must have been readily available to the water that originally wetted the soils. The resulting  $C_{\text{Si}}$  in the first leachate ( $\approx 4 \text{ mg l}^{-1}$ ) was higher than observed at any site or horizon in Plastic-108 (see Fig. 3). This suggests an influence of the experimental protocol. Possible reasons for the initially high soil water  $C_{\text{Si}}$  could be: (1) a change in the soil structure owing to mixing of the soils; (2) a concentration of readily available material as a result of air drying; (3) different chemical reactions occurred in the soil since double distilled water was used. However, these factors did not influence  $C_{\text{Si}}$  in soil water in the same way.

Much of the readily available silica was flushed out of the soil column after

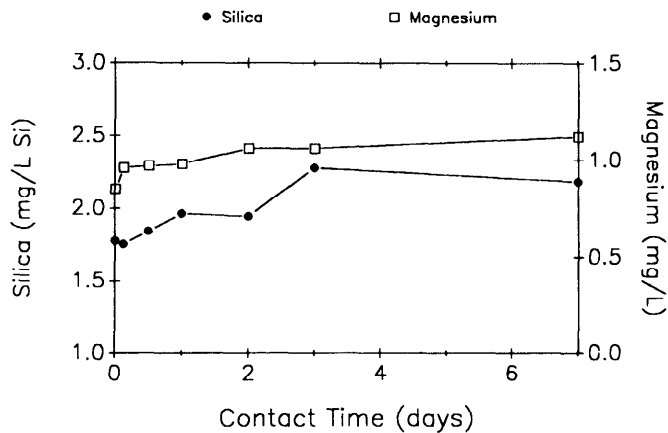


Fig. 7. Silica and magnesium in leachate vs. contact time for a composite podzol sample. Data points were obtained from single leaching of duplicate soil columns.

leaching with  $\sim 450$  ml of water as indicated by the sharp drop in the rate of decrease in leachate Si (Fig. 6). This leaching volume was close to the total pore volume of the column (350 ml). Subsequently,  $C_{\text{Si}}$  in leachate was now in the concentration range ( $\approx 2\text{--}3\text{ mg l}^{-1}$ ) observed in lysimeter samples collected from the mineral horizons (Fig. 3). Although not constant,  $C_{\text{Si}}$  remained very high considering that the contact time of the leachate was limited to its travel time through the column, i.e.  $< 1$  h (Fig. 6). The silica concentration in leachate decreased  $\sim 0.14\text{ mg l}^{-1}$  per 100 ml leachate (dashed line in Fig. 6). This would result in a decrease in soil water  $C_{\text{Si}}$  of only  $0.87\text{ mg l}^{-1}$  assuming that the entire spring runoff 1987 (200 mm) passed through the soil. The decrease in soil water  $C_{\text{Si}}$  should be even smaller in the real field situation where the soils are deeper and contact times are longer during periods of flow recession. When continuous leaching was discontinued after passing 1170 ml of leachate, the estimated equilibrium concentration of  $1.8\text{ mg l}^{-1}$  for continuous flow was still much higher than Si observed in melt water.

In a second experiment, we tested whether longer residence times would increase the soil water concentrations of magnesium and silica. The replicate soil columns that had been leached continuously were saturated and were allowed to equilibrate for different periods of time. The contact times were 3 and 12 h, and 1, 2, 3 and 7 days. The initial concentrations (at  $t = 0$ ) of Si and Mg in the leachates were determined from the continuous leaching experiment. Similar initial concentrations were observed for all replicate soil columns ( $< 10\%$  variation). A consistent increase in soil water  $C_{\text{Si}}$  and  $C_{\text{Mg}}$  with contact time was observed during the first 3 days (Fig. 7). However, the soil water concentration of both chemicals increased by only  $\sim 20\%$  for a contact time of 3 days compared with the concentrations measured after continuous leaching. In other words, 80% of the tracers were released from the soil within less than an hour contact time. Both leaching experiments suggested that silica and

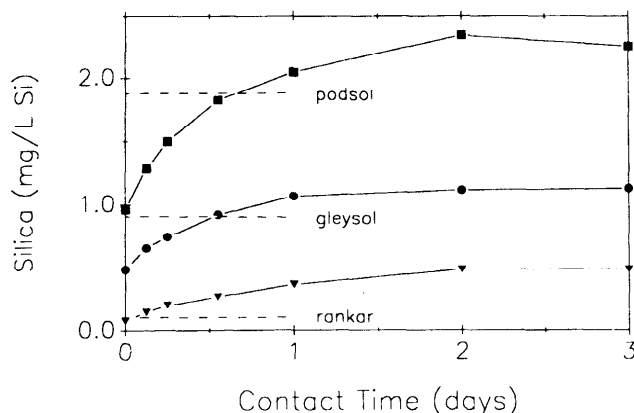


Fig. 8. Silica in distilled water leachate vs. contact time for three soil types. Data points were obtained from multiple leaching of one soil column. Dashed lines indicate the initial concentrations (after continuous leaching) for the three soil types.

magnesium were released rapidly from the soils at rates which were largely independent of the residence time of soil water.

In a follow-up experiment (Fig. 8),  $C_{Mg}$  and  $C_{Si}$  in different soil types were examined to test whether the observed trends in tracer concentrations vs. contact time were generally applicable. To cover the major soil types in the Plastic-108 basin, three soil types were compared: (1) a podzol soil similar to that used in the previous experiment; (2) an organic gleysol from the stream valley; (3) a thin layer (10 cm) of a highly leached mineral horizon overlying bedrock (rankar). The experimental protocol was similar to that described above. However, each individual soil column was leached several times with progressively shorter contact times in order to obtain contact time-concentration relationships. Between each measurement, the soil columns were eluted with 250 ml DD water to flush out as much water from the previous run as possible.

The soil-water silica concentrations for short contact times were lower than previously determined (compare Figs. 7 and 8). However, the trends in concentration vs. contact time were very similar for all three soil types (Fig. 8). In all cases, silica concentrations decreased with decreasing contact time and increasing volume of leachate. Contact times of up to 3 days also did not yield much higher  $C_{Si}$  than during continuous leaching of the organic soil and the rankar (Fig. 8). However, the absolute silica concentrations differed significantly among the three soil types (Fig. 8). The absolute silica concentration was lower in the organic soil since its mineral content was lower than in the podzol. The low silica concentrations in the rankar leachates may result from the leaching that this shallow soil type experiences in situ at its shallow depth. The concentration reached after continuous leaching of this podzol sample ( $1.85 \text{ mg l}^{-1}$ ) was in very good agreement with that obtained in the previous experiment ( $2.1 \text{ mg l}^{-1}$ ; Fig. 7) suggesting that these soil leaching experiments

were reproducible.  $C_{Si}$  in leachate from the podzol experiments decreased about 5% after 2–3 days. Very similar differences between soil types and between multiple and single leaching were observed for magnesium (not shown).

### *Evidence from literature*

The field and laboratory data presented above support the hypothesis that silica and magnesium are released very rapidly from the podzolic soils in the study watersheds. This observation is in general agreement with related studies on subsurface water and stream water chemistry in other environments (Kennedy, 1971). All studies reviewed by Kennedy reported fast rates of silica release from the soil. For example, Bricker and Godfrey (1968) found that only a few hours to a few days were needed for silica to achieve a constant concentration in water recycled through a soil column. Feth et al. (1964) reported that silica is released within a few days to percolating, slightly acidic, snowmelt waters which supply ephemeral springs in the high Sierra Nevada. Kennedy (1971) conducted various soil leaching experiments to establish contact time–concentration relationships. His soil leaching experiments using soil water mixtures gave very similar results to those obtained in the present study using soil columns. Kennedy (1971) concluded from his review that silica could be released or taken up rapidly — i.e. within a few minutes or hours — and that the mechanism is not simply one of solubility.

These findings are further consistent with temporal trends of silica and magnesium observed in many streams (e.g. Johnson et al., 1969; Keller, 1970; Reid et al., 1981). All studies reported that silica and magnesium concentrations remained well above those of precipitation even during periods of peak flow when residence times of subsurface water are generally shorter and precipitation may contribute directly to streamflow. A simple mixing model that conceptualizes stream water as a mixture of subsurface water and melt water demonstrates this point. This model was used to estimate the concentration level which pedologic processes are able to sustain during periods of rapid replacement of soil water by rain or melt water (non-equilibrium soil concentration) (Johnson et al., 1969). Wels et al. (1988) applied the model to Plastic-1 and Harp-4 (a watershed adjacent to Harp-5) and found very similar non-equilibrium soil water silica concentrations of  $\sim 2.1 \text{ mg l}^{-1}$ . This suggests that the rates of silica release from the soils under high flow conditions might be very similar in both catchments. Similar non-equilibrium values for silica were also estimated for headwater streams at Hubbard Brook, NH using several years data ( $1.4\text{--}1.8 \text{ mg l}^{-1}$ ; Johnson et al., 1969) or spring runoff data only ( $1.91 \text{ mg l}^{-1}$ ; Hooper, 1986). Those hypothetical non-equilibrium soil water concentrations were very close to the final concentrations ( $\approx 1.8 \text{ mg l}^{-1}$ ) obtained during continuous leaching of Plastic-108 soils (Fig. 6). Non-equilibrium values determined for magnesium were more variable and ranged from  $0.7 \text{ mg l}^{-1}$  in Harp-4 (Wels et al., 1989) to  $0.36 \text{ mg l}^{-1}$  and  $0.26 \text{ mg l}^{-1}$  for the

long-term and the spring runoff data set in Hubbard Brook, respectively. These magnesium values were of the same order of magnitude but somewhat lower than the soil water concentrations obtained from continuous leaching of the Plastic-108 soils ( $0.85 \text{ mg l}^{-1}$ , Fig. 6).

In conclusion, the second assumption for chemical hydrograph separation, that the tracer concentration is practically independent of the residence time of water in the soil, is supported both by field observations and leaching experiments in the laboratory. These experiments and published literature demonstrate that both tracers are released very rapidly from the podzolic soils.

#### ISOTOPE HYDROGRAPH SEPARATION

We used measurements of the HDO concentration of meltwater, stream water and subsurface water to separate the sources of stream runoff into two components: meltwater and subsurface water inputs. Measurements of water in all reservoirs made prior to freeze-up indicated that the HDO concentration within the catchment was  $147.0 \pm 0.3 \text{ ppm}$ . The HDO concentration in subsurface water in different zones could not be distinguished from stream baseflow at this time. Soil water samples collected in the deep mineral horizon of the tension lysimeter just prior to the melt were isotopically enriched about  $0.4 \text{ ppm}$  compared with stream baseflow. This may indicate isotopic fractionation during the collection of water in the lysimeter or heterogeneity in the distribution of HDO at this time. If this difference exists in situ, it introduces an error of  $< 5\%$  in the estimates of the flow components at peak discharge (Wels et al., 1990a).

During the melt period, conditions for isotopic separation were very favourable because HDO concentrations in meltwater were very distinct from subsurface water ( $136.5\text{--}140 \text{ ppm}$  in all but two samples). Subsurface water and

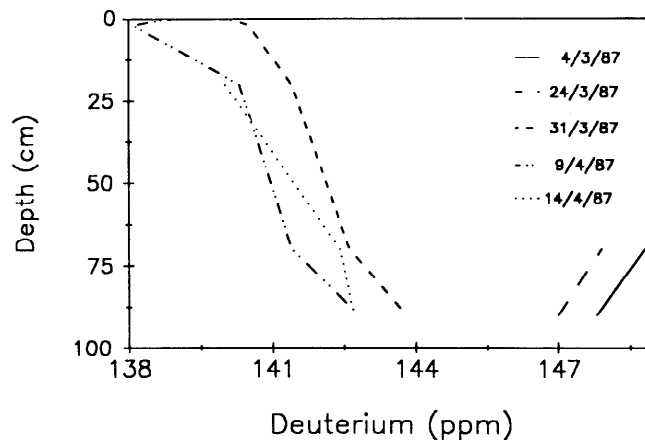


Fig. 9. Vertical deuterium profiles of subsurface water collected from tension lysimeter No. 12 during the spring melt.

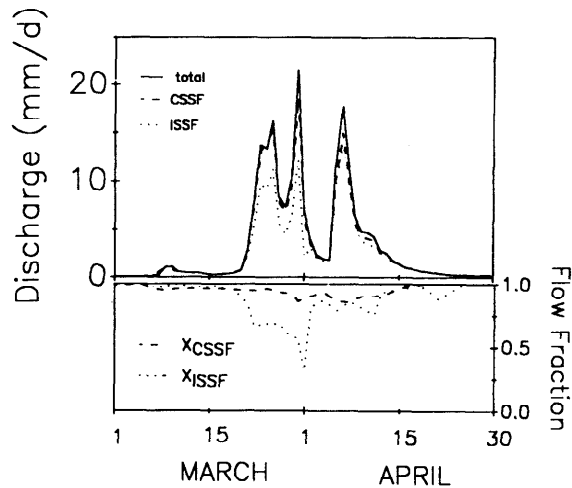


Fig. 10. Chemical and isotopic hydrograph separation of spring runoff 1987, Plastic-108. The contributions of subsurface flow and groundwater to streamflow are shown in the upper panel. The fractions of subsurface flow and groundwater (lower panel) were calculated using a constant  $C_{SF}$  and a time-variable  $C_{GW}$ , respectively.

stream water data indicated that the isotopic composition of groundwater decreased and gradually approached that of new melt water (Fig. 9). This change reflects the recharge of the subsurface water reservoir with infiltrating melt water. This temporal change in the isotopic content of groundwater was simulated using a single reservoir model (method of Rodhe (1987) and Wels et al. (1990a)). Then the daily contributions of melt water and water from the groundwater reservoir were estimated by the two-component hydrograph separation method using eqn. 1 (Fig. 10). Based on this isotopic analysis, the fraction of daily stream flow that was contributed by water flowing through the groundwater reservoir in Plastic-108 was 34 to > 99%. During the period 1 March to 30 April 1987,  $74 \pm 14\%$  of the total stream flow was water that flowed from the groundwater reservoir. We estimated uncertainties of 10–20% in most of the daily estimates of the groundwater contributions. However, on 2 days during rain events the precision decreased to about 40%. A more detailed analysis of the hydrograph separation is presented in Wels et al. (1990a).

#### COMPARISON OF SUBSURFACE FLOW AND GROUNDWATER

The previous sections show that silica and magnesium might be used to separate water contributing to streamflow into overland flow and subsurface flow in our study basins. In contrast, the subsurface flow estimates obtained from isotopic hydrograph separation using a simple mixing model (Rodhe, 1987) represent only phreatic zone (groundwater) from the well-mixed deeper soil horizons. Any lateral flow of water through the soil that bypasses the ground-



water reservoir would not be identified as ISSF. In theory, an estimate of ISSF fractions using isotopic tracers should yield only a lower limit of all subsurface flow that contributes to streamflow. In this section, this assumption is examined by comparing the fractions of subsurface flow and groundwater in spring runoff, in Plastic-108 and Harp-5, and we document a systematic difference in the subsurface flow contributions to the streamflow traced by chemical tracers (CSSF) and groundwater contributions traced by isotopes (ISSF).

The daily contributions of subsurface flow and groundwater to streamflow for the entire spring runoff in Plastic-108 (Fig. 10) are expressed both in terms of discharge (upper panel) and fractions of total flow (lower panel). The subsurface flow fractions are inversely related to total flow. Maximum depressions in  $X_{\text{CSSF}}$  are observed in response to the rain-on-snow event on 30 March (85%) and during peak melt on 6 April (82%) (Fig. 10). Despite the inverse relationship of  $X_{\text{CSSF}}$  with flow, the largest volumetric contributions of subsurface water to streamflow were always observed at days of peak flow (Fig. 10). The relative contributions of the various flow components of streamflow change with flow rate (Wels, 1989). The temporal trends in  $X_{\text{ISSF}}$  clearly contrast with those of  $X_{\text{CSSF}}$ . First, the relative contributions of groundwater are consistently lower than  $X_{\text{CSSF}}$  and correlate poorly with changes in flow (Fig. 10, bottom panel). Furthermore,  $X_{\text{ISSF}}$  exhibited a seasonal trend not observed for  $X_{\text{CSSF}}$ . Estimates of  $X_{\text{ISSF}}$  were lower during the first melt event relative to the second event (Fig. 10, bottom panel). Similar temporal trends were observed in the Harp-5 watershed (not shown).

The contributions of subsurface flow to the individual melt periods and to

TABLE 1

Contributions of subsurface flow and groundwater in spring runoff 1987. Upper values represent Plastic-108; lower values represent Harp-5. The uncertainty in event mean  $X_{\text{CSSF}}$  was estimated to be 6% and 13% for Plastic-108 and Harp-5, respectively; the uncertainty in event mean  $X_{\text{ISSF}}$  was ~14% in both watersheds (Wels, 1989)

Period	Total runoff (mm)	Fractions of		
		Subsurface flow (%)	Groundwater (%)	$(X_{\text{CSSF}} - X_{\text{g}})^1$ (%)
M1 <sup>2</sup>	118	92.3	65.5	28.8
	124	91.8	65.4	26.4
M2 <sup>3</sup>	69	87.4	82.4	5.0
	64	85.6	77.6	8.0
Total <sup>4</sup>	203	91.1	73.6	18.4
	214	90.6	72.7	17.9

<sup>1</sup>Difference of subsurface flow fraction and groundwater fraction.

<sup>2</sup>First melt period (22 March–4 April).

<sup>3</sup>Second melt period (5 March–14 April).

<sup>4</sup>Total spring runoff (1 March–30 April).

TABLE 2

Summary of subsurface and groundwater contributions to streamflow in previous studies

Catchment	$X_{ISSF}^1$	$X_{CSSF}^2$	Event	Area (ha)	Reference
Wilson Creek	90%	65-75	Storm	2200	Fritz et al., 1976
Kenora	40-45	60-100	Storm	180	Fritz et al., 1976
Hubbard Brook	75	75	Melt	42	Hooper and Shoemaker, 1986
Mattole	65-75	75	Storm	62000	Kennedy et al., 1986

<sup>1</sup>Calculated from old water or groundwater estimates using <sup>18</sup>O or D analyses.

<sup>2</sup>Calculated from SiO<sub>2</sub> or Mg<sup>2+</sup> measurements.

total spring runoff were very similar in Plastic-108 and Harp-5 (Table 1). Subsurface flow was the dominant flow component in Plastic-108 and Harp-5 comprising more than 90% of total spring runoff in 1987 (Table 1). The fractions of subsurface flow were consistently higher than those of groundwater for both melt periods and for the total spring runoff (see ( $X_{CSSF} - X_{ISSF}$ ) in Table 1). In both watersheds the difference in estimates of  $X_{CSSF}$  and  $X_{ISSF}$  was ~18% (or 37 mm) of the total spring runoff (Table 1). Since both watersheds gave very similar results, this suggests a systematic difference in subsurface flow contributions traced by chemicals and groundwater contributions traced by isotopes. Our findings are consistent with Rodhe's argument that the use of a simulated value of groundwater concentration ( $C_{ISSF}$ ) for estimates of groundwater fractions can only yield lower limits of all subsurface water (Rodhe, 1987).

Three other studies have used both Si or Mg and isotopic hydrograph separations to determine the origins of stream water (Fritz et al., 1976; Hooper and Shoemaker, 1986; Kennedy et al., 1986). The results of Hooper and Shoemaker and Kennedy et al. (Table 2) do not show a consistent difference between the chemical and isotopic separations as those observed by Fritz et al. and by this study. In other studies using different geochemical tracers, hydrograph separations that use isotopes generally yield larger groundwater fractions than those using chemical tracers (Rodhe, 1987). The lack of a clear pattern between flow fractions defined using chemical and isotopic tracers may reflect imperfections in the data or models used to perform the separations and/or different processes in different basins that influence the behaviour of either the isotopic or geochemical tracer. These alternative hypotheses are evaluated briefly in the following paragraphs.

Although a diversity of events (e.g. precipitation vs. snow melt runoff) and catchments have been studied using hydrograph separations, the fractions separated and the methods used to define the fractions have not been standardized. Therefore, some results may be erroneous, caused by methodological problems in the interpretation of stream water chemistry data or by different definitions of the flow components (Rodhe, 1987). To minimize these possible problems, this synthesis examines only comparisons of Si and isotopic hydrograph separations.

Our analyses do not support the hypothesis that the different separations are caused by the incorrect modelling of the isotopic data. First,  $X_{\text{ISSF}}$  changes by less than 20% if alternative assumptions are used in the simulations (Wels, 1989). Secondly, in this study, the model's simulation of groundwater isotopic content agreed reasonably well with observations of soil water from deeper soil layers throughout the melt (Wels et al., 1989). Finally, the deuterium concentration of the soil water prior to spring melt was constant in all reservoirs within the Plastic catchment (Wels, 1989; Wels et al., 1990a). This minimizes the complexity of the interpretation of the separations and makes water stored in the unsaturated and saturated zones indistinguishable.

The interpretation of hydrograph separations is more complex when using geochemical tracers which may not be uniformly distributed in the ground, or may change in concentration during the discharge event. One way to explain the different separations calculated in different basins, is to postulate that different catchments have either one or two (or more) types of contributing areas or reservoirs in the subsurface with similar isotopic concentrations but different concentrations of geochemical tracers (e.g. wetland and upland areas). If the amount of runoff contributed by different areas changes during the runoff event, the calculated volume of water flowing through the ground will change while the actual volume of subsurface discharge may not change at all. Volumes of subsurface discharge could be underestimated if the concentration of the geochemical tracer in base flow was representative of a much smaller soil reservoir than the average subsurface discharge during the storm or melt event and if this value was used to estimate subsurface flows. If the Plastic, Harp and Kenora catchments have a single dominant Si reservoir while Wilson Creek, Hubbard Brook and Mattole catchments have two or more reservoirs with different Si concentrations, this hypothesis could explain the different results. The spatial and temporal variations in soil and groundwater chemistry observed in contributing areas in some catchments support this concept. However, this hypothesis requires further testing.

In summary, there is no systematic relationship between the isotopic and chemical hydrograph separations reported to date. Most studies reported similar temporal trends in isotopic and chemical tracers. The finding of the present study, that hydrograph separation using isotopic tracers yielded lower estimates of subsurface flow than using chemical tracers was reported in one study on the Canadian Shield (Fritz et al., 1976). The high contributions of subsurface flow in the present study ( $\approx 90\%$ ) are the highest reported to date. This suggests that surface flow is less important in these study basins than in others. However it may also indicate differences in the rate of uptake or release of the chemical tracer in different environments.

#### CONCLUSIONS

The weathering products dissolved silica and magnesium were useful tracers for chemical hydrograph separation in Plastic-108 and Harp-5, respectively.

Field and laboratory observations suggested that both tracers were released very rapidly from the soils. The absence of silica in melt water and its small variability within the soil profile allowed a well-defined separation of streamflow into surface and subsurface flow. Chemical hydrograph separation based on magnesium was less precise due to variability in magnesium concentrations in both runoff components.

Subsurface flow was the dominant flow component in Plastic-108 as well as Harp-5, comprising more than 90% of the total spring runoff. In both basins studied, groundwater estimates using isotopic tracers underestimated subsurface contributions by 18% for the total spring runoff. It is hypothesized that laterally flowing soil water which did not mix with the deep soil/groundwater reservoir, contributed to streamflow. No systematic bias was found in isotopic vs. chemical hydrograph separation in several studies reviewed. However, a comparison of results from chemical hydrograph separations is complicated by the fact that the rate of uptake or release of the chemical tracer may differ in different environments.

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