Tracing subsurface water flowpaths by means of dissolved Ba/Sr, Ca/Sr and ^{87}Sr/^{86}Sr ratios

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When studying field weathering processes and catchment mass balances it is of critical importance to know which sources of surface water are the most important. However, despite numerous studies, the origin of stream water is still a matter of controversy. Different runoff mechanisms include Horton overland flow, saturation overland flow, and subsurface flow. The subsurface flow may be dominated either by displacement of old water, or by rapid through-flow emphasizing macropore flow. Stream water during snowmelt or a storm event is often considered a mixture of new water (precipitation) and old water. The old water, or pre-event water, is usually regarded as groundwater. However, recent studies have shown that soil water may also constitute a significant part of the old water component. Both isotopic and chemical tracers have been used in various mixing models in order to trace different water masses. The most frequently used isotopic tracers have been H and O isotopes which provide good information about the new and old water content in a stream, but less information about the subsurface flow paths. The chemical tracers most often employed have been concentrations of various elements. However, in many situations the elemental concentrations in stream water are diluted by precipitation or horton overland flow, which obscures the tracer signals from the subsurface flowpaths. One way to overcome this is to use element ratios as tracers since very dilute components will influence element ratios in a mixture insignificantly compared to components with high cincentrations. Both dissolved and particulate element ratios have been used as tracers in other studies (e.g. Négrel *et al.*, 1993; Ingri and Widerlund, 1994; Ingri *et al.*, 1997; Land and Öhlander, 1997).

In this study we show how Ba/Sr and Ca/Sr ratios can be used to resolve the subsurface flow into three different components: soil water, shallow ground-water, and deep groundwater. In an attempt to validate the results Sr isotopes were also employed as a tracer. The idea behind the use of Ba/Sr and Ca/Sr ratios as tracers is that these elements occur in different minerals with different weathering susceptibility. Usually, Sr substitutes Ca or K, whereas Ba usually substitutes K, and the K-minerals in granitoids are generally more resistant to weathering than the Ca-minerals. As weathering intensity and solution chemistry change along a flow path, the relative importance of different minerals in the weathering process should change. If this is the case, the dissolved element ratios should also change.

This study was performed in a relatively small (9.4 km^2) catchment drained by a first order stream. The peak discharge during snowmelt in early May is about 750 l s^{-1}, while the base-flow discharge during summer is 20–30 l s^{-1}. The catchment is mainly covered by podzolized till (more than 90 % of the area), classified as typic haplocryod. Bedrock outcrops and mires add up to less than 7 % of the area, and there are no lakes in the catchment. The till, supporting mainly pine and spruce forest, is unsorted and consists mainly of granitic material. It is underlain by a 1.8 Ga granite.

The chemical composition of soil water, shallow groundwater and stream water was measured for a period of more than one year, including two snowmelt seasons. In addition a few chemical analysis of precipitatation, throughfall, and deep groundwater were performed. The soil water was sampled by tension lysimeters from four depths: 5 cm (E-horizon), 15 cm (Bs1-horizon), 40 cm (Bs2-horizon), and 100 cm (C-horizon). Shallow groundwater and deep groundwater were sampled in recharge areas at the depths of 2.3−5.2 and 20−25, respectively. The Sr isotopic composition was measured in selected soil water, groundwater and stream water samples.

Results

Both winter and summer precipitation in the area was rather dilute and therefore did not influence the Ba/Sr and Ca/Sr ratios in the stream water significantly, although the concencentrations of Ba, Ca and Sr were influenced. Throughfall on the other hand showed a little higher concentrations of Ba and Ca. During snowmelt the soil water was diluted. However, the dilution decreased with depth, and in the C-horizon the concentrations remained relatively constant throughout the study period. Also the concentrations in the shallow groundwater remained constant throughout the study period. The deep groundwater was sampled only once, but it is not likely that the temporal variation in this water was larger than in the shallow groundwater. In the stream water the concentrations of most major elements as well as Sr decreased during snowmelt. In contrast to the major elements and Sr, the concentration of Ba increased in the beginning of the snowmelt. Generally, the dissolved Ba/Sr ratio decreased with depth in the ground, whereas the Ca/Sr ratio increased with depth. The Ba/Sr ratios in soil water, shallow groundwater and deep groundwater were approximately 0.87, 0.18 and 0.05, respectively, and the Ca/Sr ratios were approximately 120, 110 and 330, respectively. In the stream water the the Ba/Sr ratio varied between 0.15 and 0.57. There was a positive correlation between the Ba/Sr ratio and discharge, indicating an increased contribution from soil water during high discharge events. In accordance with this the Ca/Sr ratio decreased during high discharge, and increased during base flow (the Ca/Sr ratio varied from 160 to 205). On the basis of these results a simple mixing model was developed.

Calculations show that the fraction of deep groundwater in the stream water varied between approximately 5 and 20% with the highest values during base flow. It should be recognized, however, that even though the relative proportion of deep groundwater decreased during high discharge, the absolute discharge increased. During base flow the discharge of deep grondwater was approximately 3 l s^{-1}, whereas during snowmelt the deep groundwater discharge was about 35 l s^{-1}. Soil water dominates during snowmelt seasons, whereas during base flow it is the least important fraction. The fraction of shallow groundwater varied between 0 and 80% with the lowest values during peak discharge.

The validity of the model was evaluated by comparing the measured $^{87}Sr/^{86}Sr$ ratios in the stream water with the $^{87}Sr/^{86}Sr$ ratios predicted by the model. During base flow in September the measured $^{87}Sr/^{86}Sr$ ratio in the stream water was 0.7381. On this occasion the calculated fractions of soil water, shallow groundwater and deep groundwater were 11%, 75%, and 14%, respectively. With Sr concentrations of 11.5, 20.0, and 52.2 μg l^{-1}, and with $^{87}Sr/^{86}Sr$ ratios of 0.7259, 0.7266, and 0.7605 in soil water, shallow groundwater and deep groundwater, respectively, the model predicts a $^{87}Sr/^{86}Sr$ ratio of 0.7371. During snowmelt the model is somewhat less accurate. The measured and modelled $^{87}Sr/^{86}Sr$ ratios in the stream water were 0.7387 and 0.7347 at peak discharge 1994, 0.7388 and 0.7348 at early snowmelt 1995, and 0.7386 and 0.7342 at peak discharge 1995, respectively. There is a systematic underestimation of the $^{87}Sr/^{86}Sr$ ratio which may reflect an overestimation of the soil water fraction by the model (soil water has the lowest $^{87}Sr/^{86}Sr$ ratio). However, considering the large variation in $^{87}Sr/^{86}Sr$ ratios between the end members, the differences between measured and modelled $^{87}Sr/^{86}Sr$ ratios in the stream water are relatively small.

This study shows that element ratios can be useful as chemical tracers when the geochemistry of streams or rivers is to be interpreted. The developed model using Ba/Sr and Ca/Sr ratios as tracers is able to predict $^{87}Sr/^{86}Sr$ ratios in stream water that are well in accordance with measured values. It is shown that soil water can be a significant constituent of stream water at high discharge events such as spring flood during snowmelt. It is also shown that deep and relatively old groundwater contributes to stream water (5−20%) throughout the year. However, during base flow shallow groundwater is by far the most important stream water component.

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