Rapid communication

The correct use of Sr isotopes in river-groundwater mixing models: A Breede River case study

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Abstract

Stable isotopes are used extensively in hydrology as a means of establishing the contribution of different reservoirs and sources to the water budget. If the information contained in stable isotope data is to be used in a quantitative sense, appropriate mass balance equations have to be used. Specifically, differences in the equations used for isotopes such as $^{87}Sr/^{86}Sr$ associated with minor water constituents, and the isotopes associated with the water molecule itself, i.e. $^{18}O/^{16}O$ and D/H, has to be recognised. Failure to do so, as illustrated by a re-analysis of a published Breede River study, may lead to significant errors in the inferred magnitude of groundwater contribution to river flow and misleading assertions in regards to the cause of salinisation of river systems.

Keywords: strontium, isotope hydrology, Breede River, salinisation

Introduction

The variable strontium isotopic composition ($^{87}Sr/^{86}Sr$) of water reservoirs in contact with lithologies of different ages and types provides a potentially powerful method in hydrological studies in South Africa (De Villiers et al., 2002). It can, for example, be used to determine the relative contribution of groundwater to river flow (Faye et al., 2005; Negrel et al., 2005). In $^{87}Sr/^{86}Sr$ water mass balance studies the end-members are typically:

(i)   An upstream river water sample with negligible groundwater input
(ii) Groundwater
(iii) A downstream river water sample that is a mixture of (i) and (ii).

If the groundwater $^{87}Sr/^{86}Sr$ (R_{GW}) is measurably different from that of the upstream river water sample (R_{UP}), it will produce a downstream sample with an isotopic composition (R_{DOWN}) intermediate between that of the upstream sample and groundwater. This is because $^{87}Sr/^{86}Sr$, unlike the isotope ratios $^{18}O/^{16}O$ and D/H also used in hydrology (Gat and Tzur, 1967), is conservative during mixing and not affected by processes such as evaporation.

Another important difference between $^{87}Sr/^{86}Sr$ and the lighter isotopes $^{18}O/^{16}O$ and D/H is that Sr is a minor or trace constituent of river water and that as a result, mass balance equations also have to take into account the Sr concentration ([Sr]) of the water masses undergoing mixing. In the case of $^{18}O/^{16}O$ and D/H it is the isotopic composition of the water molecule H_2O itself that is measured and the concentration of water is not a factor. In the case of $^{87}Sr/^{86}Sr$, however, the end-members invariably have different [Sr] and $^{87}Sr/^{86}Sr$ compositions. Also, both [Sr] and $^{87}Sr/^{86}Sr$ can reasonably be assumed to behave con-

servatively during mixing and to be relatively unaffected by precipitation/dissolution processes while in transit. [Sr] will only behave non-conservatively in freshwater systems in the case of, for example, excessive evaporation leading to super-saturation with respect to mineral phases such as celestite ($SrSO_4$) and the removal of dissolved Sr from solution (Flecker et al., 2002).

Recommendation

In the case of $^{87}Sr/^{86}Sr$ applications in hydrology two mass balance equations therefore have to be satisfied in a typical mixing scenario between a fraction f of groundwater with Sr concentration = $[Sr]_{GW}$ and $^{87}Sr/^{86}Sr = R_{GW}$ and a fraction (1-f) of upstream water with $[Sr]_{UP}$ and R_{UP}, to produce a downstream sample with composition $[Sr]_{DOWN}$ and R_{DOWN}:

Sr mass balance:
$$f[Sr]_{GW} + (1-f)[Sr]_{UP} = [Sr]_{DOWN} \quad (1)$$

Sr isotope mass balance:
$$f[Sr]_{GW}R_{GW} + (1-f)[Sr]_{UP}R_{UP} = [Sr]_{DOWN}R_{DOWN} \quad (2)$$

Of these parameters $[Sr]_{UP}$, $[Sr]_{DOWN}$, R_{UP} and R_{DOWN} are easily measured and quantified. In order to calculate the fractional contribution of groundwater, that is f, either $[Sr]_{GW}$ or R_{GW} also has to be known. Constraining average values for these groundwater characteristics is often problematic, because groundwater from compositionally different reservoir may contribute to river flow. An example, a compilation of [Sr] and $^{87}Sr/^{86}Sr$ values for upstream, downstream and groundwater from different reservoirs in the Breede River area, is given in Table 1 (all data from Kirchner, 1995). It can be seen that $^{87}Sr/^{86}Sr$ values for river water at the downstream site are higher than those at the upstream site and lower than those of the groundwater samples. The downstream increase in $^{87}Sr/^{86}Sr$ therefore suggests groundwater penetration along the river flow path. The question then is: how important is the overall groundwater contribution?

The data compilation in Table 1 suggests that although the $^{87}Sr/^{86}Sr$ composition of groundwater from different reservoirs

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TABLE 1
Strontium and ^{87}Sr/^{86}Sr of river and groundwater in the Breede River area (all data from Kirchner, 1995)

Sample location	[Sr] in μg/ℓ	^{87}Sr/^{86}Sr
Upstream (H4H017)	83	0.716595
Downstream (H5H004)	394	0.717141
TMS* groundwater	80 (avg)	0.724181 - 0.729259
Witteberg groundwater	347 (avg)	?
Malmesbury groundwater	1 320 - 1 366	0.726278 - 0.722166
Bokkeveld groundwater	963 (avg)	?
Average groundwater		0.72533
*TMS = Table Mountain Sandstone		

Figure 1
Calculated fractional groundwater contribution (f) to river strontium budget as a function of [Sr]$_{GW}$

falls within a narrow range, the Sr concentration of groundwater from different reservoirs varies by more than an order of magnitude. If the downstream increase in [Sr] is assumed to result from groundwater penetration, the mostly likely source is groundwater from the Sr-rich Malmesbury and Bokkeveld formations. If the average groundwater ^{87}Sr/^{86}Sr value proposed by Kirchner (1995) is adopted, then Eq. (2) can be used to calculate the fractional groundwater contribution to river flow (f) as a function of [Sr]$_{GW}$. The result of this calculation is illustrated in Fig. 1.

Conclusions

For [Sr]$_{GW}$ values of 500 to 1 500 μg/ℓ, i.e. bracketing values measured in groundwater from the Malmesbury and Bokkeveld formations, the implied groundwater contribution is in the order of 20 to 70%. This is a very significant figure and much higher than the 6.7% calculated (Kirchner, 1995) without appropriate consideration of [Sr] in the mass balance equations. The total groundwater contribution to Breede River flow may be even higher than these calculations suggest, considering that the low [Sr]$_{GW}$ of groundwater from the TMS formation will have a diluting effect. If TMS groundwater contributes to Breede River flow, then an even larger contribution of groundwater from the more Sr-rich Malmesbury and Bokkeveld formations would be required to account for the downstream increase in [Sr] and ^{87}Sr/^{86}Sr.
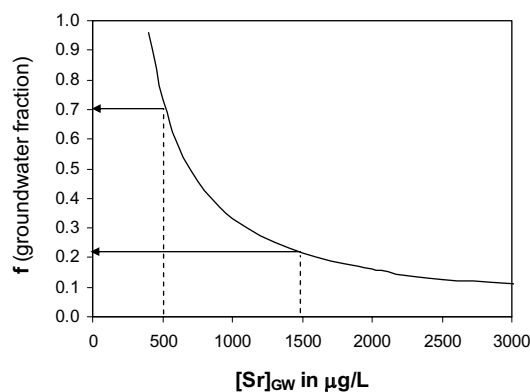
In the context of understanding processes of salinisation in systems such as the Breede River, this is a significant result and suggests an **urgent re-evaluation** of similar studies and the interpretation of [Sr]-^{87}Sr/^{86}Sr data sets.

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