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Hydrograph separation and scale dependency of natural tracers in a semi-arid catchment

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Abstract

A solid understanding of the hydrological processes in a catchment is important in order to guarantee appropriate management of the available surface and groundwater resources, both in terms of quality and quantity. In order to achieve this, insights in the behaviour of the water fluxes and the interaction between groundwater and surface water is of utmost importance.

This paper discusses the applicability and constraints of using hydrochemical and isotope tracers in identifying the runoff contributing sources at different scales in a semi-arid catchment in Tanzania. The hydrograph separation techniques shows that at the smallest scale (0.3 km²), for all types of tracers, the pre-event contribution is between 74–82%. At the larger scale (26 km²), two sub-catchments contribute to the flow at the weir site in Bangalala. Using the hydrochemical tracers the calculated contributions for the sub-catchments are in agreement with the catchment size and rainfall contributions over these two catchments. This showed that at the weir site 20% of the total flow comes from event water (of which 2% from Vudee sub-catchment and 18% from Ndolwa sub-catchment). The large difference is mainly due to preceding wetness conditions.

However, with the isotope tracers no unambiguous results could be obtained. Two end members have been investigated to account for the ambiguous nature of the isotopic concentrations. The rainfall analysis shows that during the season the isotopic concentration changes, with a clear distinction between the two seasons. In addition, within one event the isotopic concentrations vary substantially within the area. The spring analysis also shows substantial temporal and spatial variation.

The research therefore shows that the assumption of stable isotopic end-members was not met in our study. At the smaller scale the spatial variability could be neglected and the hydrograph separation technique could be applied, although for each event, end member concentrations needed to be collected to account for the temporal variability.

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1 Introduction

A solid understanding of the hydrological processes in a catchment is important in order to guarantee appropriate management of the available surface water and groundwater resources, both in terms of quality and quantity. In semi-arid populated environments in sub-Saharan Africa (SSA), this is probably even more essential since both floods and droughts can result in severe crop loss (e.g. Mul, 2009; Rockström et al., 2004). A good insight into the hydrology of a semi-arid catchment can help to increase the productivity in smallholder farms and to sustain long-term food security. In order to achieve this, insights in the behaviour of the water fluxes and the interaction between groundwater and surface water is of utmost importance. This includes the quantification of the spatial-temporal variability of the water fluxes and responses to extreme climatic conditions. Much experimental work on understanding hydrological processes has been done in humid climates using either a single approach or multi-method approach (e.g. Blume et al., 2008; Uhlenbrook et al., 2002, 2008; Wenninger et al., 2008). However, experimental hydrology in sub-Saharan Africa is not that widespread (Kongo et al., 2007).

Hydrograph separation is more and more used in understanding hydrological processes in SSA and semi-arid areas. Mul et al. (2008, 2009) applied two-component hydro-chemical hydrograph separation on a relative small flood in 2005 (10 mm d^{-1}) and an extreme event in 2006 ($75\text{--}100 \text{ mm d}^{-1}$) in a sub-catchment (26 km^2) of the Makanya catchment, Tanzania. Discharge was separated into surface and sub-surface runoff contributions. For the small event, more than 95% of the total runoff originated from sub-surface water. The large flood showed 50% of the peak flow to originate from direct surface runoff, whereas the recession was mainly fed by groundwater (90%). However, the assumption that surface water quality is equal to that of rain water was questioned. This was illustrated by a concentration rise of some of the hydro-chemical parameters during the rising limb of the hydrograph. Hence, the suggestion was made to perform a hydrograph separation based on isotope tracers, which are assumed to

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behave conservatively when it comes to separation between event and pre-event water.

The objective of the paper is to show the applicability of isotopic tracers in order to obtain improved understanding of the hydrological processes in a small-scale, semi-arid catchment. Furthermore, the paper discusses the scale limitations of isotope tracers in semi-arid environments. Therefore, several field experiments in the experimental Makanya catchment have been conducted during the two rainy seasons of the 2007/2008 hydrological year: (a) monitoring the main climatic parameters (e.g. rainfall, temperature, soil moisture), (b) measuring stream discharge at different spatial scales, (c) sampling of stream water prior and during two events at different scales, (d) sampling of spring water throughout the seasons at different places throughout the catchment and (e) analyzing the stream and spring water samples on hydrochemical and isotopic composition.

2 Material and methods

2.1 Site description

The Makanya catchment is a 300 km^2 catchment in the South Pare Mountains, in northern Tanzania (Fig. 1). Approximately 35 000 people are living in small villages throughout the catchment, mainly living from small scale subsistence agriculture. The altitude ranges from 600 to 2400 m, where the lower parts mainly consist of alluvial deposits and the higher regions are characterized by steep slopes, often with shallow soil coverage.

The catchment is named after the Makanya village, at the outlet of the catchment. In the past, the Makanya river drained towards the Pangani river, but nowadays this is only the case during extreme floods (Mul et al., 2006). The climate is characterized by two rainy seasons, locally called the *Vuli* season (October till December), followed by a short dry period (January and February) and the second rainy season, *Masika* (March till May). Total annual rainfall averages 550 mm a^{-1} in the lower regions up to

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800 mm a⁻¹ in the higher regions.

This study focuses on two catchments within the Makanya catchment, located in the upper mountainous regions, the Ndolwa catchment (8.4 km²) and the Vudee catchment (14.2 km²) (Fig. 1). Both catchments are characterized by steep slopes, shallow soil coverage and numerous rock outcrops. Besides, both catchments are mainly cultivated agricultural land with sparse terraces. Some parts are still forested, either primeval/pristine forest or replanted in the beginning of the 20th century by German missionaries.

Furthermore, within the Vudee catchment, a nested catchment (0.3 km²) has been intensively monitored, the Mataini catchment. Besides meteorological data, runoff is measured and a piezometer was installed. This catchment is mainly forested, the source area is a flat and swampy area surrounded by small farm plots where people grow maize, further downstream this turns into a steeper section with many rock outcrops and large trees rooting in the riparian zone.

2.2 Experimental set-up

Rainfall amounts have been measured at different places in the catchment both automatically (4 times) at 1-h intervals by tipping bucket rain gauges (Campbell Scientific, TE525WS, 20.3 cm diameter) and manually (12 times) at 09:00 a.m. every day. Ten different rain stations throughout the Makanya catchment have been selected for sampling precipitation to be analyzed for isotopic composition. Since automatic samplers were not available, the people responsible for the gauge readings took samples manually after reading a rainfall depth larger than 10 mm over the previous 24 h. Discharge has been measured at two points in the catchment: (a) at Bangalala, 1 km downstream of the Vudee and Ndolwa rivers junction (drainage area 25 km²), and (b) at the outlet of the small forested catchment. V-notches have been constructed and pressure transducers measured the hydraulic head at 15-min intervals which is converted into stage and subsequently into discharge using the rating curve for 90° V-notches and rectangular

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notches (Hudson, 1993). Calibration has been done using the salt dilution method. A large flood in December 2007 caused a lot of damage throughout the catchment. Both V-notches got destroyed, therefore the runoff monitoring was interrupted between December 2007 and March 2008. On 9 April, the reconstruction of the Bangalala weir was finished and a new pressure transducer was installed.

Stream water samples have been collected in plastic bottles during both low flows and events. Local people living close to the measuring points have been employed to do the sampling manually. Low flow (pre-event) samples have been collected every morning at 09:00 a.m. During events, stream water samples have been taken when a pre-defined water level was exceeded (10 cm at Mataini catchment, equivalent to about 5 l s⁻¹ and 30 cm at Bangalala weir, equivalent to about 70 l s⁻¹), with an interval of 1 to 2 h. Samples have been analyzed for hydrochemical (SiO₂, HCO₃⁻, Ca²⁺ and Mg²⁺) and isotopic (oxygen-18 and deuterium) composition. Electrical Conductivity (EC) and pH have been measured in the samples, shortly after the sampling.

Throughout the Makanya catchment, but mainly in the Vudee catchment area, more than 20 groundwater springs have been selected in order to monitor the spatial variability and seasonal dynamics of spring water quality. Most places were visited 3 times, at the beginning of the *Vuli* season, at the end of the *Vuli* season and during the *Masika* season. Temperature, pH and EC have been measured in-situ, and hydrochemical and isotopic composition have been analyzed in the lab.

A piezometer has been installed at the upper part of the Mataini catchment, near the springzone (Fig. 1). From this piezometer, groundwater level has been measured manually twice a day and groundwater samples have been taken twice a week. A 4-days stay in the Mataini catchment has been done to take in situ frequent measurements (e.g. EC, pH and temperature) and to take stream water, surface runoff, rain and groundwater samples during and just before an event.

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2.3 Chemical and isotopic analyses

Stream water and groundwater samples have been analyzed for hydrochemical parameters including: dissolved silica (SiO_2), Ca^{2+} , Mg^{2+} and HCO_3^- . The analyses have been done in a field lab using Hach (digital) titration field kits for Ca^{2+} , Mg^{2+} (both using EDTA) and HCO_3^- (using H_2SO_4), with an accuracy of 1%. SiO_2 has been analyzed using the spectrophotometric Silicomolybdate method with a precision of 1.0 mg l^{-1} (standard deviation). Samples have been analyzed within 2 days after they had been taken.

After collection in the field, samples have been filtered using $0.45 \mu\text{m}$ nitrocellulose filters and stored in glass vials. A part of these samples have been analyzed for the isotopes oxygen-18 (^{18}O) and deuterium (^2H) using a water isotope analyzer (Los Gatos Research, model 908–0008) in combination with a CTC LC-PAL liquid autosampler. For operational details, the reader is referred to Lis et al. (2008); Baer et al. (2002); Paul et al. (2001). A precision higher than 0.2‰ for $^{18}\text{O}/^{16}\text{O}$ and higher than 0.6‰ for $^2\text{H}/^1\text{H}$ was reached. Post-processing has been performed according to the IAEA standard (Newman et al., 2009).

2.4 Hydrograph separation

Hydrograph separation is a method to separate the runoff during floods in two or more components (end-members), based on the mass balances for tracer fluxes and water. Pinder and Jones (1969) were among the first to use the technique in order to quantify groundwater and direct runoff contributions to total runoff from chemical characteristics of stream water and its assumed components. Abundant studies, carried out in different and hydrogeologically diverse watersheds, concluded groundwater contributions to storm runoff to be a dominant process especially during moderate intensity storms in humid temperate (Pinder and Jones, 1969; Sklash and Farvolden, 1979). The driving process behind the rapid mobilization of subsurface flow is still discussed in hydrology

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(e.g. ground water ridging (e.g. Gilham, 1984), translatory or piston flow (e.g. Rodhe, 1987), transmissivity feedback (e.g. Bishop, 1991), macropore flow (e.g. McDonnell, 1990), saturation overland flow including return flow Dunne and Black, 1970, pressure waves (Torres et al., 1998), kinematic waves (e.g. Nolan and Hill, 1990), and the fill and spill hypothesis (Tromp-van Meerveld and McDonnell, 2006). Recently, Jones et al. (2006); Renaud et al. (2007) discussed the influence diffusive processes have on tracer exchange between runoff components disguising discharge generating processes, causing the interpretation of hydrochemical tracer information being more complicated.

Three studies have used the hydrograph separation technique in semi-arid areas with varying results (McCartney et al., 1998; Sandström, 1996; Wenninger et al., 2008). Groundwater contributions vary between 30 and 90%, mostly dependent on the rainfall intensities, groundwater contributions increased several times the base flow contributions. McCartney et al. (1998) is the only study using isotopes. Mul et al. (2008) used a two-component hydrochemical hydrograph separation in the Makanya catchment, which showed that during a small flood more than 90% of the total runoff came from sub-surface flow, during an extreme event this reduced to about 50% (Mul et al., 2009). However, this still meant that the groundwater contribution increased a number of times during the event.

The mass balance equations used for hydrograph separation can be written as follows:

$$Q_{\text{total}} = Q_1 + Q_2 + \dots + Q_n \quad (1)$$

$$c_{\text{total}}^{t_i} Q_{\text{total}} = c_1^{t_i} Q_1 + c_2^{t_i} Q_2 + \dots + c_n^{t_i} Q_n \quad (2)$$

Where Q denotes discharge and c for the concentration of the considered tracer t_i . Subscripts 1,2,.. n indicate the assumed end-members and total represents the stream runoff, which is the sum of all end-members. Separating runoff into n different component requires $n - 1$ tracers to solve the linear mixing equations.

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Sklash and Farvolden (1979); Buttle (1994) discussed the assumptions on which hydrograph separation using isotope tracers is based. Hoeg (2000) generalized these assumptions to the use of both hydrochemical and isotope tracers:

- 5 . there is a significant difference between the tracer concentrations of the different components;
- . the tracer concentrations are constant in space and time, or any variations can be accounted for;
- . contributions of an additional component must be negligible, or the tracer concentrations must be similar to that of another component;
- 10 . the tracers must mixed well and conservatively; and
- . the tracer concentrations of the components are not correlated.

Isotope tracers are often believed to meet these assumptions better than hydrochemical tracers. However, the concentration of isotopes in rainfall is temporally variable, within a storm and during a season. In addition, isotope concentrations are also spatial variable, related to distance to the sea and topography (Kendall et al., 1998). In the following, we will assess the impact of these variations on the robustness of the hydrograph separation method in semi-arid areas.

3 Results and discussion

3.1 Hydrograph separation

20 3.1.1 Hydrograph separation at the Mataini catchment (0.3 km²)

The tipping bucket rain gauge near the source recorded a seasonal total of 296 mm (13 March till 30 April), while the downstream gauge recorded 259 mm. More than 50% of

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the total rainfall amount fell in a 1 week period (22–28 March). Daily totals for both stations correlate well ($r = 0.92$), hourly values are less correlated ($r = 0.83$).

During the investigation period, ten different events could be distinguished. Table 1 gives the main characteristics of the events. During events 1, 2, 3, 5 and 7 stream water samples were collected. Figure 2a shows the rainfall, runoff and the behaviour of the EC, the silica concentrations and the isotopic contents (δD [‰]) during the investigation period. Figure 2b displays the observations during the 4 days continuous survey of 25–28 March.

Three 2-component “event–pre-event” (indicated by Q_e and Q_p , respectively) separations of the 27 March hydrograph were done using δD , SiO_2 and EC as tracers (Fig. 3). A bulk rain sample integrating over the whole event was taken as representative for event water, the pre-event stream water sample was taken 1.5 h before the event started. All tracers show a large contribution of pre-event water (74–82%). During peak flow, just 30 min after the event started, up to 55% of the flow consisted of pre-event water. 3 h after the peak flow, tracer concentrations have almost returned back to pre-event values, indicating no event water contribution during the later recession.

The groundwater levels in the piezometer near the spring source showed an increase of 1 m during this event. The groundwater samples, taken before and after the event, do not show large differences in both EC and SiO_2 . It is remarkable that the groundwater sample after the event is slightly enriched ($\delta D_{\text{before}} = -19.5\text{‰}$, $\delta D_{\text{after}} = -16.5\text{‰}$), whereas the event rain sample (bulk) is much lighter ($\delta D_{\text{rain}} = -30.3\text{‰}$).

3.1.2 Hydrograph separation at Vudee/Ndolwa catchment (26 km²)

Vuli '07 season (October–December)

25 Seasonal rainfall totals between 450 mm (Ndolwa) and 500 mm (Vudee) were recorded during the Vuli '07 season. Most of the rainfall (85–88%) was recorded between mid November and mid December. Daily and hourly rain data of the two stations

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correlate well ($r_{\text{daily}} = 0.94$, $r_{\text{hourly}} = 0.82$). Table 2 presents the main hydrological characteristics of 9 different events and the contributions of the Ndolwa and Vudee catchments to the total runoff during the events by hydrograph separation. Figure 4 shows the hydrographs and chemographs of the Ndolwa and Vudee catchments from 12 November 2007 till 12 December 2007. Figure 4b shows an enlargement of Fig. 4a for the period 18–25 November.

Masika '08 season (March–May)

Table 2 shows the rainfall and runoff characteristics of 4 events monitored during the Masika '08. Figure 5 shows the EC-values of the base flow samples. During events the EC drops, due to dilution of the relative high-EC pre-event water with low-EC event water. The recession shows an opposite trend. This can be attributed to either a decrease of low-EC event water contribution in the late recession, or to the longer contact time with soil minerals of the recharged water which results in higher dissolved mineral concentrations, represented by higher EC values.

Figure 5 (middle figure) shows the groundwater levels which were monitored in the Mataini catchment (Fig. 1). After events 2, 3 and 4 clear groundwater level jumps (>10 cm) can be seen, followed by a smooth decline. These jumps occur around 24 h after the last recorded rainfall of the preceding events 2, 3 and 4.

On 28 April, the sampling threshold of 10 cm was exceeded and samples were taken during 16 h. During the event, a rainfall depth of 30 mm in 6 h was recorded in both Vudee and Ndolwa catchment. The peak discharge was 660 l s^{-1} and the runoff coefficient was around 7%, which is significantly higher than for all events recorded in the smaller Mataini catchment (Table 1).

Figure 6 shows the hydrochemical and isotopic behaviour during the storm and the early recession. The hydrochemical parameters EC and SiO_2 show a similar behaviour, a sudden drop in both the Vudee and the Ndolwa catchment followed by a smooth recession towards background concentration. The tracer concentrations at the weir in

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Bangalala behave as expected: both silica and EC values plot in-between concentrations of both contributing sub-catchments, thus indicating conservative mixing.

The isotope tracers behave less unambiguous (Fig. 6); the concentrations at the weir in Bangalala, which is assumed to be a linear mix of the two upstream components of the Vudee and Ndolwa catchments, do not plot in-between the two end-member tracer concentrations. This could indicate a third component/contribution in the 1 km stretch between the confluence of the two catchments and the weir in Bangalala. The isotopic values of the pre-event samples (taken on 28 April at 09:00 a.m., during base flow) also indicate this. However, discharge measurements by means of salt dilution during base flow at the 3 sampling spots do not show this possible third component, since the discharges from Vudee and Ndolwa sum up to the discharge at the weir in Bangalala. The isotope dynamics within the two catchments are consistent again; the storm runoff concentrations (indicated by the red and green lines) plot mainly in-between the rain (event) samples (indicated by the dots) and the base flow (pre-event) samples (the start values of the lines).

Silica concentrations were used to quantify the contributions of the two catchments based on (a) the measured discharge at the weir in Bangalala, and (b) the concentrations at this point and upstream of the confluence for each sample moment. The discharge distribution over the event was then integrated over time. The total runoff volumes were used to express the relative total contributions of both catchments. This resulted in a 46% contribution by Vudee river and 54% by Ndolwa river. At first a look, the contribution of Ndolwa is quite high compared with Vudee's larger catchment size (14.2 km^2 vs. 8.4 km^2) and larger rainfall depth (23 mm vs. 19 mm). Similar events during the Vuli '07 season (Table 2) show much higher relative contributions from Vudee.

The quantification of the catchment contributions was then separated into event and pre-event contributions per time-step using deuterium as tracer. The results are presented in Fig. 6 in the upper figure. From the total runoff volume at the weir in Bangalala, 2% was contributed by event water from Vudee, 18% by event water from Ndolwa, and 44% and 36% by pre-event water from, respectively Vudee and Ndolwa.

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Preceding conditions can explain the difference of the two sub-catchment responses. During the 4 weeks before 28 April, Ndolwa received 88 mm of rain, whereas in Vudee between 47 and 81 mm was recorded. This is confirmed by a higher base flow contribution by Ndolwa before 28 April, indicated by Fig. 5 (the lower figure), where the EC at the weir plots closer to the Ndolwa concentration.

3.2 Stability of end-members

The validity of the assumptions, especially assumption 1 and 2, of the hydrograph separation technique mentioned in paragraph 2.4, has been investigated by comparing the temporal and spatial variability of the different tracers in rain water and groundwater.

3.2.1 Precipitation

Figure 7 shows the δD and $\delta^{18}O$ isotopic values of 33 rain water samples taken at 2 different locations (Mwembe and Ndolwa) in the period October 2007 till April 2008. Both the slope and the intercept of the constructed Local Meteoric Water Line (LMWL, $\delta D = 7.86 \delta^{18}O + 11.1\%$ VSMOW) coincides with the Global Meteoric Water Line (GMWL, $\delta D = 8.13 \delta^{18}O + 10.8\%$ VSMOW) (Clark and Fritz, 1997). The weighted-mean values for δD and $\delta^{18}O$ for the total period and combining the 2 stations is -14.7% and -3.4% , respectively. Separating values for both stations results in $\delta D = -12.8\%$ and $\delta^{18}O = -3.2\%$ for Mwembe station and $\delta D = -16.2\%$ and $\delta^{18}O = -3.5\%$ for the 500 m higher located Ndolwa station.

A clear clustering can be seen between the rains falling during the two rainy seasons. The *Vuli* '07 season mainly contains isotopically enriched precipitation ($\delta D = -7.5\%$ and $\delta^{18}O = -2.6\%$), whereas the rains during the *Masika* '08 season were isotopically depleted ($\delta D = -26.4\%$ and $\delta^{18}O = -4.7\%$). In January and February, normally a short dry period, 3 rain events >10 mm were sampled. Consistently, these rains do not plot clearly in one of the two clusters¹.

¹A possible explanation of the clear clustering can be the origin of the rain during the two

During two rain events in the *Vuli* season (21 November and 12 December), rain-water samples were obtained at several locations, which show the spatial variability in isotopic composition in the Makanya catchment. The rainfall was sampled at 5 stations for the November event, and at 8 stations after the December event. During the 21 November event, the rainfall depth varied between 7 and 20 mm for the different rain stations and during the 12 December event the variation was much larger, between 8 and 180 mm. For both events a large spread in isotopic content (both δD [between -12 and 5%] and $\delta^{18}O$ [between -3.2 and 5%]) between the different locations was measured.

3.2.2 Springs

Figure 8a and b show the seasonal variation in spring water quality. 21 springs throughout the catchment were sampled and analyzed on EC, SiO_2 , Mg^{2+} , Ca^{2+} and HCO_3^- . The springs which were sampled three times, were also analyzed on isotopic content. Figure 8a shows the behaviour of both SiO_2 and $\delta^{18}O$. Silica shows relatively little variation per spring between the seasons, although, the absolute concentration differences between the different springs are large. Similar behaviour applies to the other hydrochemical parameters. Oxygen-18 shows an opposite behaviour. The relative variation between the different samples is not as large as for hydrochemical parameters, but

rainy seasons. Nieuwolt (1973) and Sumner (1982) reported about prevailing wind directions during *Vuli* and *Masika*. During *Vuli* season a clear sea breeze from the Indian ocean develops, from east and northeast direction. During the *Masika* season however, a south-easterly wind parallel to the coastline is prevalent. When assuming that the moisture transport follows these prevailing wind directions, the moisture during *Vuli* season travels a significantly shorter distance over land than the moisture during *Masika*. These different prevailing wind directions and rain cloud origins during these seasons are in line with the information of the local population. The travel distances of the moisture over land can be linked with the continental rain out effect, described by Clark and Fritz (1997). Longer travel distances over land result in isotopically lighter rains.

within each spring larger variations are visible. For all samples, an isotopic enrichment can be observed between December (end of *Vuli* season) and April (middle of *Masika* season). The October samples represent the pre wet season conditions (end of long dry period). In this series the largest variation in isotope composition is visible.

5 Figure 8b shows how the spring water samples plot to the LMWL, using the same scale as Fig. 7. The blue and red dots represent the weighted means of the isotopic fractions for rains during both seasons. Most of the spring samples plot below the LMWL and they are more enriched in $\delta^{18}\text{O}$ than in δD . This indicates evaporation of the recharge water before reaching the groundwater system or evaporation of the
10 shallow groundwater system.

4 Conclusions

The hydrograph separation technique has been applied to two different, nested catchments (0.3 km^2 and 26 km^2) in a semi-arid catchment in Sub-Saharan Africa. Hydro-metric observations were combined with tracer studies during two field campaigns in
15 2007 and 2008.

At the small scale catchment the method is clearly able to separate event and pre-event water using hydrochemical and isotope tracers. Pre-event water contributed up to 82% of the total runoff volume. Even at peak flow, 55% of the runoff consisted of old water.

20 At the larger scale the same technique was used for one rain event of 25 mm in 3 h during the *Masika* season, the runoff increased from 50 l s^{-1} to 660 l s^{-1} . Hydrograph separation based on hydrochemical parameters showed high pre-event contributions (80%) during this storm, similar values were observed during two other events (Mul et al., 2008, 2009). However, hydrograph separation based on isotopes gave inconclusive
25 results. Using the tracers for runoff separation based on geographic sources, we found that the 20% of event water originated for only 2% of the total runoff volume from the Vudee catchment and 18% from Ndolwa. This result is in contrast with the observed

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rainfall differences and size of the two catchments, but is most likely attributed to the different antecedent precipitation in the two catchments.

At the larger scale (26 km^2) isotope tracers proved to be less reliable than hydrochemical tracers. Two end-members have been investigated, the rain water and the
5 groundwater, and showed large spatial and temporal variability. The assumption that the end-member concentrations are constant over time and in space was not met at the larger scale.

Not only the spatial and temporal variability in rainfall amount is high, but also its isotopic content is highly variable unlike the hydrochemical parameters. There appears to
10 be a clear clustering of the rain during the two wet seasons. The *Vuli* season contains the isotopically enriched events ($\delta D = -7.5\text{‰}$ and $\delta^{18}\text{O} = -2.6\text{‰}$), whereas *Masika* is the season with lighter rains ($\delta D = -26.4\text{‰}$ and $\delta^{18}\text{O} = -4.7\text{‰}$). The clustering can be attributed to the different origin of the atmospheric moisture during these seasons.

The groundwater springs also showed spatial variability in hydrochemical characteristics and both spatial and temporal variability in isotopic content. Especially the spatial
15 variability of the different groundwater springs in the catchment can obscure the results of the hydrograph separation technique. The pre-event sample taken at the outlet of the catchment is a weighted average of all groundwater spring contributions. The assumption that the relative contribution of these different springs remains constant during a runoff event has to be questioned.
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In conclusion, this analysis shows that the assumption of stable isotopic end-members was not met in our study for both the groundwater samples and the rain water samples. At the smaller scale the spatial variability could be negligible and the technique became better applicable, although for each event, end member concentrations
25 needed to be collected to account for the temporal variability.

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References

- Baer, D., Paul, J., Gupta, M., and O'Keefe, A.: Sensitive absorption measurements in the near-infrared region using off-axis integrated-cavity-output spectroscopy, *Appl. Phys. B-Lasers O.*, 75(2), 261–265, 2002. 1349
- Bishop, K. H.: Episodic increases in stream acidity, catchment flow pathways and hydrograph separation, PhD thesis, Cambridge Univ., Cambridge, UK, 241 pp., 1991. 1350
- Blume, T., Zehe, E., Reusser, D. E., Iroume, A., and Bronstert, A.: Investigation of runoff generation in a pristine, poorly gauged catchment in the Chilean Andes I: A multi-method experimental study, *Hydrol. Process.*, 22(18), 3661–3675, doi:10.1002/hyp.6971, 2008. 1345
- Buttle, J.: Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins, *Prog. Phys. Geog.*, 18(1), 16–41, 1994. 1351
- Clark, I. and Fritz, P.: *Environmental Isotopes in Hydrogeology*, CRC Press, 1997. 1355, 1356
- Dunne, T. and Black, R. D.: Partial area contributions to storm runoff in a small New England watershed, *Water Resour. Res.*, 6, 1296–1311, 1970. 1350
- Enfors, E. and Gordon, L.: Analysing resilience in dryland agro-ecosystems: a case study of the Makanya catchment in Tanzania over the past 50 years, *Land Degrad. Dev.*, 18(6), 680–696, 2007.
- Gilham, R. W.: The capillary fringe and its effect on watertable response, *J. Hydrol.*, 67, 307–324, 1984. 1350
- Hoeg, S., Uhlenbrook, S., and Leibundgut, C.: Hydrograph separation in a mountainous catchment – combining hydrochemical and isotopic tracers, *Hydrol. Process.*, 14 (7), 1199–1216, 2000. 1351
- Hudson, N.: Field measurement of soil erosion and runoff, *FAO Soils Bulletin*, 139 pp., 1993. 1348
- Jones, J., Sudicky, E., Brookfield, A., and Park, Y.: An assessment of the tracerbased approach to quantifying groundwater contributions to streamflow, *Water Resour. Res.*, 42(2), 2006. 1350
- Kendall, C., and J. J., McDonnell (Eds.): *Isotope Tracers in Catchment Hydrology*, Elsevier Sci., New York, USA, 839 pp., 1998. 1351
- Kongo, V. M., Kosgei, J. R., Jewitt, G. P. W., and Lorentz, S. A.: Establishment of a catchment monitoring network through a participatory approach in a small rural catchment in South Africa, *Hydrol. Earth Syst. Sci. Discuss.*, 4, 3793–3837, 2007, <http://www.hydrol-earth-syst-sci-discuss.net/4/3793/2007/>. 1345
- Lis, G., Wassenaar, L., and Hendry, M.: High-Precision Laser Spectroscopy D/H and 18 O/16 O Measurements of Microliter Natural Water Samples, *Anal. Chem.*, 80(1), 287–293, 2008. 1349
- McCartney, M. P., Neal, C., and Neal, M.: Use of deuterium to understand runoff generation in a headwater catchment containing a dambo, *Hydrol. Earth Syst. Sci.*, 2, 65–76, 1998, <http://www.hydrol-earth-syst-sci.net/2/65/1998/>. 1350
- McDonnell, J. J.: A Rationale for Old Water Discharge Through Macropores in a Steep, Humid Catchment, *Water Resour. Res.*, 26, 2821–2832, 1990. 1350
- Mul, M. L., Savenije, H. H. G., Uhlenbrook, S., and Voogt, M.: Hydrological assessment of Makanya catchment in South Pare Mountains, semiarid northern Tanzania, *IAHS Publication*, 308, 31–37, 2006. 1346
- Mul, M. L., Mutibwa, R. K., Uhlenbrook, S., and Savenije, H. H. G.: Hydrograph separation using hydrochemical tracers in the Makanya catchment, Tanzania, *Phys. Chem. Earth*, 33(1–2), 151–156, 2008. 1345, 1350, 1357
- Mul, M. L., Savenije, H. H. G., and Uhlenbrook, S.: Spatial rainfall variability and runoff response during an extreme event in a semi-arid catchment in the South Pare Mountains, Tanzania, *Hydrol. Earth Syst. Sci.*, 13, 1659–1670, 2009, <http://www.hydrol-earth-syst-sci.net/13/1659/2009/>. 1345, 1350, 1357
- Mul, M. L.: Understanding hydrological processes in an ungauged catchment in sub-Saharan Africa, PhD thesis, 130 pp., UNESCO-IHE Delft, The Netherlands, 2009. 1345
- Newman, B., Tanweer, A., and Kurttas, T.: IAEA Standard Operating Procedure for the Liquid-Water Stable Isotope Analyser Rev.11. IAEA Water Resources

- Programme, http://www-naweb.iaea.org/naweb/ih/document/Laser%20Spectroscopy/laser_procedure_rev11.pdf, last access: 8 January 2010, 2009. 1349
- Nieuwolt, S.: Breezes along the Tanzanian east coast, *Theor. Appl. Climatol.*, 21(2), 189–206, 1973. 1356
- 5 Nolan, K. M. and Hill, B. R.: Storm-runoff generation in the Permanente Creek drainage catchment, west central California – an example of flood-wave effects on runoff composition, *J. Hydrol.*, 113, 343–367, 1990. 1350
- Paul, J., Lapson, L., and Anderson, J.: Ultrasensitive absorption spectroscopy with a high-finesse optical cavity and off-axis alignment, *Appl. Optics.*, 40(27), 4904–4910, 2001. 1349
- 10 Pinder, G. and Jones, J.: Determination of the Ground-Water Component of Peak Discharge from the Chemistry of Total Runoff, *Water Res. Res.*, 5(2), 438–445, 1969. 1349
- Renaud, J., Cloke, H. and Weiler, M.: Comment on “An assessment of the tracer based approach to quantifying groundwater contributions to streamflow”, edited by: Jones, J. P., Sudicky, E. A., Brookfield, A. E. and Park, Y. J., *Water Resour. Res.*, 43(9), W02407, 2007. 1350
- 15 Rockström, J., Folke, C., Gordon, L., Hatibu, N., Jewitt, G., Penning de Vries, F., Rwehumbiza, F., Sally, H., Savenije, H., and Schulze, R.: A watershed approach to upgrade rainfed agriculture in water scarce regions through Water System Innovations: an integrated research initiative on water for food and rural livelihoods in balance with ecosystem functions, *Phys. Chem. Earth*, 29(15–18), 1109–1118, 2004. 1345
- 20 Rodhe, A.: The origin of streamwater traced by oxygen-18, Doctoral Thesis, Department of Physical Geography, Uppsala University, Sweden, 260 pp., 1987. 1350
- Sandström, K.: Hydrochemical deciphering of streamflow generation in semi-arid East Africa, *Hydrol. Process.*, 10, 703–720, 1996. 1350
- 25 Sklash, M. and Farvolden, R.: The role of groundwater in storm runoff, *J. Hydrol.*, 43(1/4), 45–65, 1979. 1349, 1350
- Sumner, G.: Rainfall and wind circulation in Coastal Tanzania, *Meteorol. Atmos. Phys.*, 30(1), 107–125, 1982. 1356
- Torres, R., Dietrich, W. E., Montgomery, D. R., Anderson, S. P., and Loague, K.: Unsaturated zone processes and the hydrologic response of a steep, unchannelled catchment, *Water Resour. Res.*, 34, 1865–1879, 1998. 1350
- 30 Tromp-van Meerveld, H. J. and McDonnell, J. J.: Threshold relations in subsurface stormflow 2., The fill and spill hypothesis, *Water Resour. Res.*, 42, W02411, doi:10.1029/2004WR003800,

1361

2006. 1350
- Uhlenbrook, S., Frey, M., Leibundgut, C., and Maloszewski, P.: Hydrograph separations in a mesoscale mountainous basin at event and seasonal timescales, *Water Resour. Res.*, 38(6), 1–13, 2002. 1345
- 5 Uhlenbrook, S., Didszun, J., and Wenninger, J.: Source areas and mixing of runoff components at the hillslope scale – a multi-technical approach., *Hydrolog. Sci. J.*, 53, 4, 741–753, doi:10.1623/hysj.53.4.741, 2008. 1345
- Wenninger, J., Uhlenbrook, S., Lorentz, S., and Leibundgut, C.: Identification of runoff generating processes using combined hydrometric, tracer and geophysical methods in a headwater catchment in South Africa, *Hydrolog. Sci. J.*, 53(1), 65–80, 2008. 1345, 1350
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Table 1. Rainfall and Runoff events during *Masika*'08 season in the Mataini catchment.

Event Number	Start		Rainfall Event			Runoff event	
	Date	Time	Average depth (mm)	Duration (min)	Peak Rate ($l s^{-1}$)	Total Runoff (mm)	Runoff Ratio (%)
1	13/3	17:00	10.5	120	5.3	0.04	0.4
2	15/3	17:00	11.2	120	9.6	0.08	0.7
3	21/3	16:00	32.3	1080	67.6	0.29	0.9
4	24/3	01:00	33.9	720	26.1	0.26	0.8
5a	26/3	04:00	8.0	180	7.8	0.05	0.6
5b	26/3	12:00	78.5	1980	60.1	1.83	2.3
6	5/4	22:00	7.8	180	3.6	0.04	0.5
7	9/4	11:00	16.6	180	14.0	0.09	0.6
8	10/4	11:00	8.1	700	5.0	0.07	0.9
9	18/4	12:00	7.5	180	5.0	0.04	0.5
10	28/4	11:00	24.2	360	33.1	0.44	1.8

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Table 2. Rainfall and Runoff events during *Vuli*'07 and *Masika*'08 season in the Vudee and Ndolwa catchment.

Event Number	Date	Rainfall Depth		Duration (hr)	Peak rate ($m^3 s^{-1}$)	Runoff Contribution by		
		Vudee (mm)	Ndolwa (mm)			Runoff coef (%)	Vudee (%)	Ndolwa (%)
<i>Vuli</i> '07								
1	19/11	24	21	4	0.2	0.8	66	34
2	20/11	25	30	12	0.6	4.5	47	53
3	21/11	6	9	2	0.3	3.2	56	44
4	23/11	45	39	4+3	0.7	4.1	65	35
5	30/11	28	20	6	1.0	10.4	–	–
6	5/12	17	21	3	0.6	3.6	–	–
7	6/12	22	5	4	0.4	3.4	–	–
8	8/12	48	38	3	6.1	2.9	–	–
9	11/12	110	62	4	>27	–	–	–
<i>Seasonal total</i>		500	450					
<i>Masika</i> '08								
1	10/4	10	15	3	0.5	6.0	–	–
3	28/4	23	19	3	0.7	6.6	46	54
4	1/5	14	8	2	0.3	7.3	–	–
<i>Seasonal total</i>		280	320					

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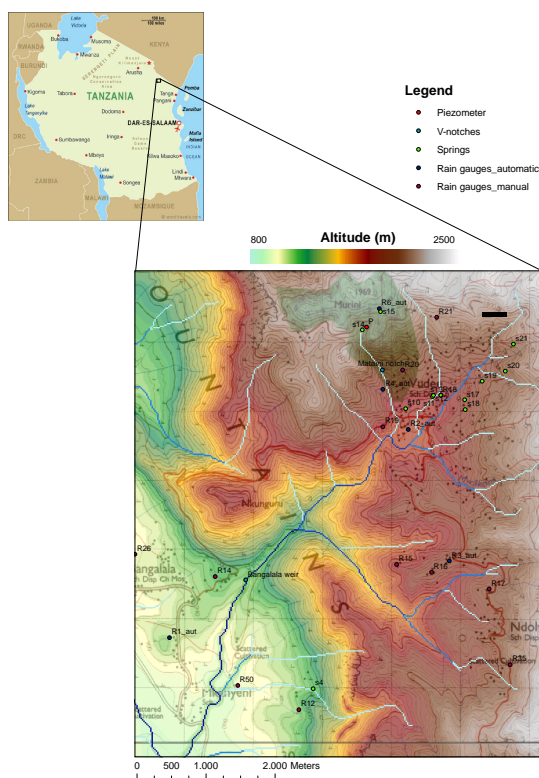


Fig. 1. Location of the study area and instrumentation network.

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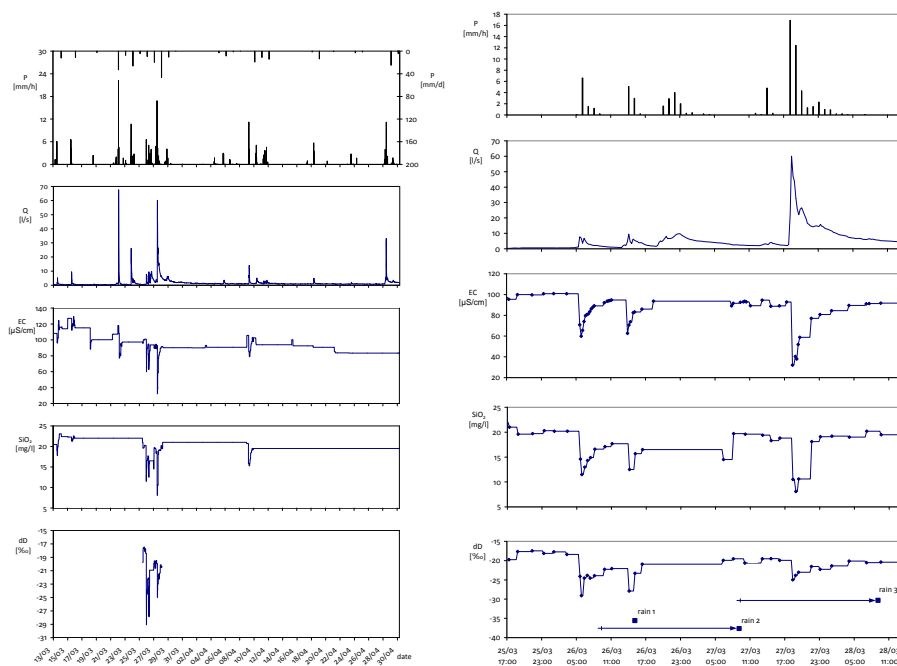


Fig. 2. Time series of precipitation [mm h^{-1} and mm d^{-1}], discharge [l s^{-1}], EC [$\mu\text{S cm}^{-1}$] and SiO_2 [mg l^{-1}] concentration and δD [%] content in runoff for Mataini catchment, 12 March–30 April 2008 and 25–28 March 2008.

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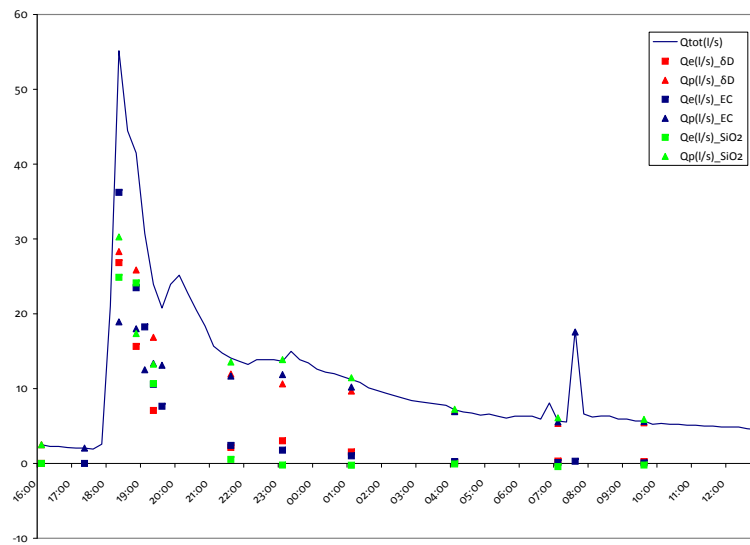


Fig. 3. Hydrograph separation between event (Q_e) and pre-event (Q_p) discharge of the 27 March 2008 event based on δD , EC and SiO_2 in Mataini catchment.

1367

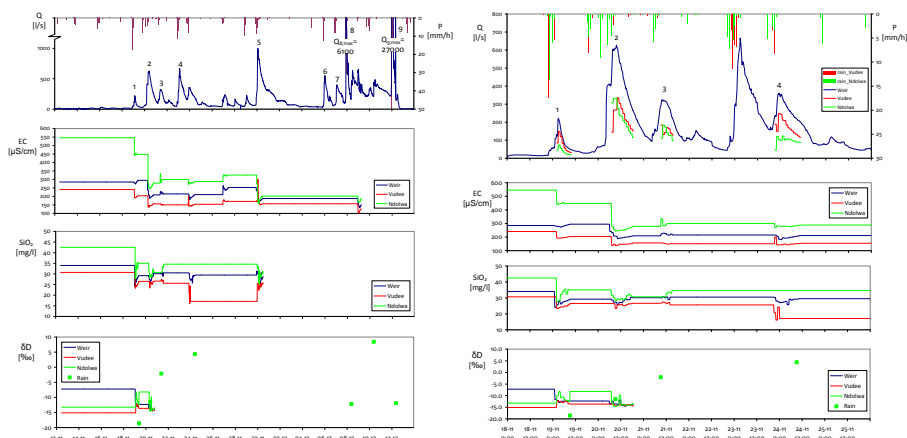


Fig. 4. Time series of precipitation [$mm\ h^{-1}$], discharge [$l\ s^{-1}$], EC [$\mu S\ cm^{-1}$], SiO_2 [$mg\ l^{-1}$] concentration and δD [%] content at the weir site in Bangalala and Vudae and Ndolwa catchments for the Vuli '07 season and 18–25 November 2007 events.

1368

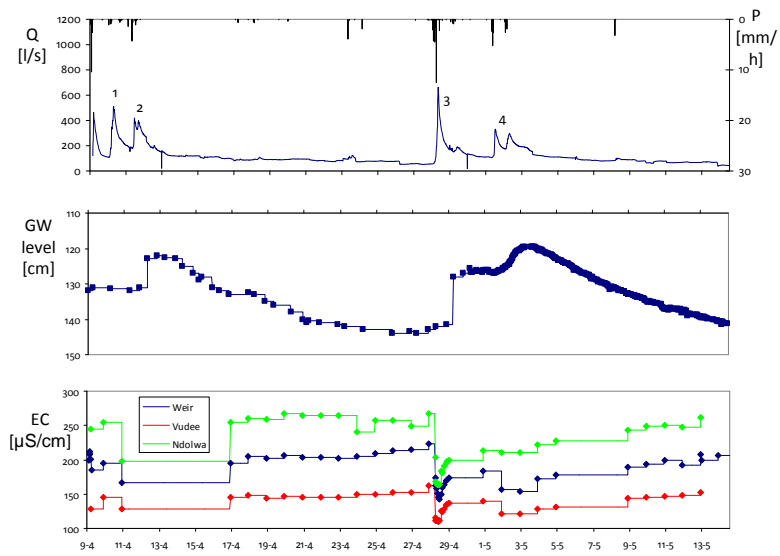


Fig. 5. Time series of precipitation [mm h^{-1}], discharge [l s^{-1}], EC [$\mu\text{S cm}^{-1}$], SiO_2 [mg l^{-1}] concentration and δD [‰] content at the weir site in Bangalala and Vudee and Ndolwa catchments for the *Masika*'08 season.

1369

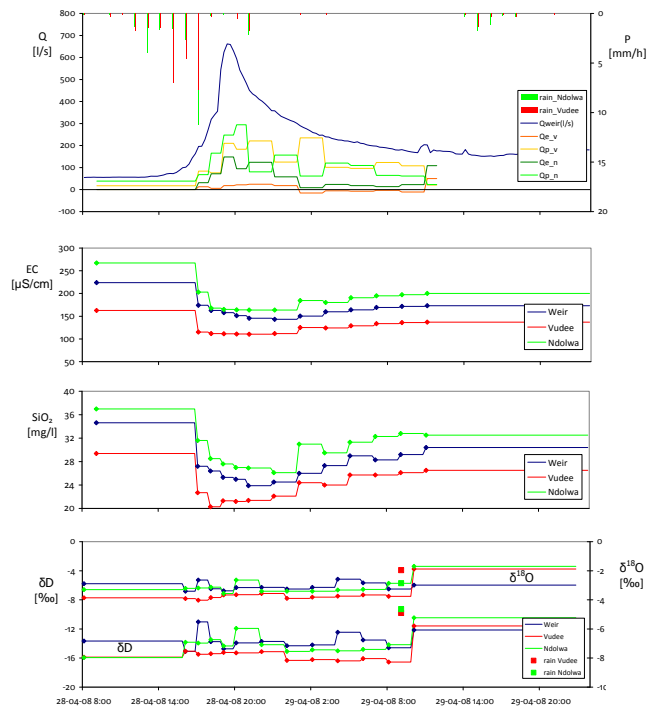


Fig. 6. Time series of precipitation [mm h^{-1}], discharge [l s^{-1}], EC [$\mu\text{S cm}^{-1}$] and SiO_2 [mg l^{-1}] concentration and δD [‰] content in runoff at the weir and Vudee and Ndolwa catchments, 29 April 2008 event.

1370

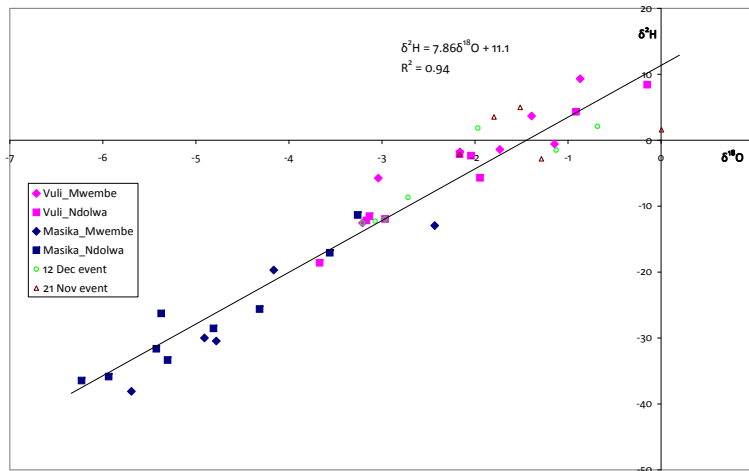


Fig. 7. Seasonal variation in isotopic composition of rainfall, based on measurements at 2 stations and during two events (21 November and 12 December 2007).

1371

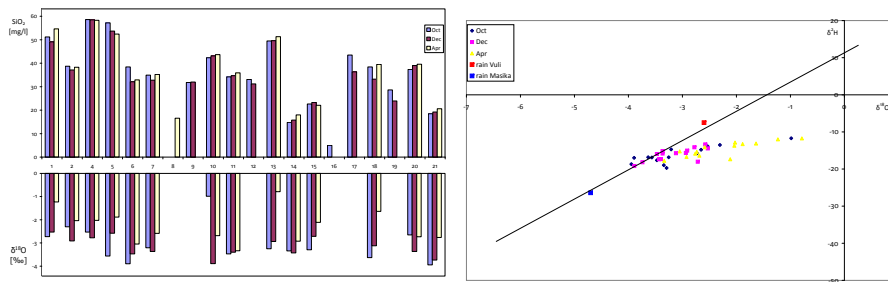


Fig. 8. Inter-seasonal variations of SiO_2 [mg l^{-1}] concentrations and $\delta^{18}\text{O}$ [‰] content in selected springs (see Fig. 1 for locations).

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