# **1** Understanding Runoff Processes in a Semi-Arid

# 2 Environment through Isotope and Hydrochemical

- 3 Hydrograph Separations
- 4

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#### 12 Abstract

13 The understanding of runoff generation mechanisms is crucial for the sustainable management 14 of river basins such as the allocation of water resources or the prediction of floods and 15 droughts. However, identifying the mechanisms of runoff generation has been a challenging 16 task, even more so in arid and semi-arid areas where high rainfall and streamflow variability, 17 high evaporation rates, and deep groundwater reservoirs may increase the complexity of 18 hydrological process dynamics. Isotope and hydrochemical tracers have proven to be useful in 19 identifying runoff components and their characteristics. Moreover, although widely used in 20 humid-temperate regions, isotope hydrograph separations have not been studied in detail in 21 arid and semi-arid areas. Thus the purpose of this study is to determine if isotope hydrograph 22 separations are suitable for the quantification and characterization of runoff components in a 23 semi-arid catchment considering the hydrological complexities of these regions. Through a 24 hydrochemical characterization of the surface water and groundwater sources of the catchment and two and three component hydrograph separations, runoff components of the 25 26 Kaap Catchment in South Africa were quantified using both, isotope and hydrochemical 27 tracers. No major disadvantages while using isotope tracers over hydrochemical tracers were

1 found. Hydrograph separation results showed that runoff in the Kaap catchment is mainly 2 generated by groundwater sources. Two-component hydrograph separations revealed groundwater contributions between 64% and 98% of total runoff. By means of three-3 4 component hydrograph separations, runoff components were further separated into direct 5 runoff, shallow and deep groundwater components. Direct runoff, defined as the direct 6 precipitation on the stream channel and overland flow, contributed up to 41% of total runoff 7 during wet catchment conditions. Shallow groundwater defined as the soil water and near-8 surface water component (and potentially surface runoff), contributed up to 45% of total 9 runoff, and deep groundwater contributed up to 84% of total runoff. A strong correlation for 10 the four studied events was found between the antecedent precipitation conditions and direct 11 runoff. These findings suggest that direct runoff is enhanced by wetter conditions in the 12 catchment which trigger saturation excess overland flow as observed in the hydrograph 13 separations.

# 14 **1** Introduction

15 Understanding runoff processes facilitates the evaluation of surface water and groundwater 16 risks with respect to quality and quantity (Uhlenbrook et al., 2002). It assists in quantifying 17 water resources for water allocation, hydropower production, design of hydraulic structures, 18 environmental flows, drought and flood management, and water quality purposes (Blöschl et 19 al., 2013). The need for understanding runoff processes has led to the development of tools 20 such as hydrograph separation techniques that identify runoff components in stream water, 21 flowpaths, residence times and contributions to total runoff (Klaus and McDonnell, 2013; 22 Hrachowitz et al., 2009; Weiler et al., 2003). Several hydrograph separation studies using 23 environmental isotopes and geochemical tracers have been carried out in forested, semi-24 humid environments which have led to new insights of runoff processes in these areas (e.g. 25 Pearce et al., 1986; Bazemore et al., 1994; Tetzlaff and Soulsby, 2008; Uhlenbrook et al., 26 2002; Burns et al., 2001). But, there is still a need for understanding runoff generation 27 mechanisms in tropical, arid and semi-arid areas as they were much less investigated (Burns, 28 2002).

Studying runoff processes in arid and semi-arid regions may be a challenging task due to the high temporal and spatial variability of rainfall, high evaporation rates, deep groundwater resources, poorly developed soils, and in some cases the lack of surface runoff (Blöschl et al., 2013; Hrachowitz et al., 2011; Wheater et al., 2008). Although these challenges may not be applicable in various instances (e.g. a reduced vegetation cover results in less importance of the interception process), arid and semi-arid regions may still face extra difficulties due to their remoteness and financial constraints.

Arid and semi-arid regions are characterized by its sporadic, high-energy, and low frequency 6 7 precipitation occurrence (Camarasa-Belmonte and Soriano, 2014; Wheater et al., 2008). Dry 8 spells can last for years, and rain events may vary from a few millimeters to hundreds of 9 millimeters per year. High intensity storms may generate most if not all the season's runoff (Love et al., 2010; Van Wyk et al., 2012). These events can also increase erosion, reduce soil 10 11 infiltration capacity and enhance surface runoff (Camarasa-Belmonte and Soriano, 2014). On 12 the contrary, the lack of precipitation may result in reduced to non-existent groundwater 13 recharge. Compared to humid regions, where evaporation is generally limited by the amount 14 of energy available, evaporation in arid and semi-arid areas is usually limited by the water 15 availability in the catchment (Wang et al., 2013). Evaporation becomes the dominant factor in 16 driving the hydrology of arid and semi-arid areas. Understanding the impact of evaporation on 17 stream runoff processes becomes more complex due to the spatial variability of vegetation. An increase in vegetation cover due to a wetter rainfall season may result in higher 18 19 evaporation rates, reduced streamflow and increased soil infiltration capacity (Hughes et al., 20 2007; Mostert et al., 1993). Transmission losses through the stream channel bed may also 21 reduce the total runoff and increase the volume of recharged groundwater. This occurrence is 22 evident in the overall Incomati Basin, where downstream areas (e.g. Mozambique) benefit 23 from transmission losses and return flows of upstream areas (Nkomo and van der Zaag, 2004; 24 Sengo et al., 2005).

This paper explores the runoff processes, including surface-groundwater interactions in the Kaap Catchment, South Africa by: describing the spatial hydrochemical characterization of the catchment, separating the runoff components through isotope and geochemical tracer analysis, and determining the suitability of isotopic tracers for the characterization of runoff components in the catchment.

#### 1 2 Study Area

The Kaap catchment is located in the northeast of South Africa in the Mpumalanga province and has an area of approximately 1,640 km<sup>2</sup> (Figure 1). Nelspruit, the provincial capital, and Barberton are the closest urban areas to the Kaap with populations of approximately 125,000 and 35,000 inhabitants, respectively (GRIP, 2012). The study area is predominantly located in the low elevation sub-tropical region of South Africa, Swaziland and Mozambique known as the Lowveld region, with elevations ranging from 300 m to 1,800 m above sea level. The average slope is 18%.

9 The geology dates back to Archean times. Biotite granite is the predominant formation in the 10 valley (Figure 2C). Headwater streams originate on the weathered granite, which felsic properties indicate high concentrations of dissolved silica. Surrounding granite, lava 11 12 formations or Onverwacht formations contain basaltic and peridotitic komatiite, which are 13 low in silicates and high in magnesium. The Onverwatch formation is one of the oldest 14 formations in the area. Formed in an ocean, it is rich in quartz, volcanic rocks and chert 15 horizons (Wit et al., 2011). Sandstones and shales are found in closer proximity to the Kaap 16 River and at the Southern section of the catchment. In addition to the gneiss formation 17 observed near the outlet, other formations include ultramafic (high in iron and low in silicates) 18 rocks, quartzite and dolomite (Sharpe et al., 1986). Borehole logs near the upper Suidkaap and Noordkaap tributaries displayed a top layer of weathered granite (approximately 25 to 37 m in 19 20 depth) followed by a thinner, less fractured granite layer and hard rock granite. Borehole logs 21 analyzed in closer proximity to the catchment outlet presented more diverse formations 22 including layers of clay, sand, greywacke and weathered shale.

Bushvelds and grasslands are the predominant land cover types in the Kaap Valley covering up to 68% of the catchment (Figure 2B). In the upstream region (western part of the catchment), approximately 25% of the total catchment consists of pine and eucalyptus plantations used for paper and timber production. Sugar cane, citrus trees, and other cash crops are found in the downstream region where many diversion channels for irrigation are present. Irrigation demand in the Kaap catchment is approximately 56 mm a<sup>-1</sup>(Mallory and Beater, 2009).

The climate is semi-arid with cool dry winters and hot wet summers. Precipitation ranges 1 from 583 to 1243 mm a<sup>-1</sup> (WRC, 2005) with an average annual precipitation of 742 mm a<sup>-1</sup>, 2 3 and mean annual runoff coefficient of 0.14. Between 2001 and 2012, recorded minimum and 4 maximum daily air temperatures at the Barberton meteorological station ranged from 3°C to 5 42°C, with a long-term average of 20°C (SASRI, 2013). The wet season lasts typically from 6 October to March as shown in Figure 3 where the climate diagram shows the monthly 7 averages (from 2001 to 2012) of precipitation, pan A evaporation from four weather stations 8 (X1E006, X1E007, Barberton, and Malelane) and maximum and minimum temperatures at 9 the Barberton station. A dry season is observed from May to September. Class-A-pan 10 evaporation rates largely exceed precipitation during most parts of the year. The range of long-term potential evapotranspiration (PET) shown in Figure 2F for the catchment (1950-11 2000) is between 1500 to 1900 mm  $a^{-1}$  (Schulze, 1997). The PET data shows that most of the 12 catchment is semi-arid, according to UNEP definition (UNEP, 1997), as illustrated on Figure 13 2E (Aridity Index = Mean Anual Precipitation / Mean Anual Potential Evaporation). 14 15 However, according to the Köppen-Geiger classification the catchment is sub-tropical.

16 The Kaap catchment contains three main tributaries; the Queens, the Upper Suidkaap and the 17 Noordkaap. The highest monthly average flow during the year occurs in February with an 18 average of 9.2 m<sup>3</sup> s<sup>-1</sup>. The lowest monthly flow during the year occurs at the end of the dry 19 season in September, reaching an average of 0.8 m<sup>3</sup> s<sup>-1</sup>. Minimum and maximum daily 20 average flows recorded between 1961 and 2012 at the Kaap outlet range from 0 to 483 m<sup>3</sup> s<sup>-1</sup>. 21 The long term mean flow at the outlet is 3.7 m<sup>3</sup> s<sup>-1</sup>, which is equivalent to 55 mm a<sup>-1</sup>.

22 Although analytical methods for hydrograph separation have been carried out in the the Kaap 23 River, no accurate estimations of runoff components were retrieved in the area. Thus, this 24 paper also provides a baseline for understanding surface and groundwater dynamics in the 25 Incomati trans-boundary River system. The Kaap River is a major contributor of flow to the 26 Crocodile River which flows into the Incomati trans-boundary River. The Incomati waters are 27 shared by South Africa, Swaziland and Mozambique where tensions related to the 28 management of water resources have led to the development of water-sharing agreements 29 such as the Tripartite Interim Agreement on Water Sharing of the Maputo and Incomati 30 Rivers (Van der Zaag and Carmo Vaz, 2003). The need for reliable data and understanding of 31 the hydrological functioning of the system has been highlighted in these agreements (Slinger et al., 2010). In addition, the Kaap River and the neighboring catchments have experienced
 devastating floods in February 2000 and March 2014 with return periods exceeding 200 years
 (Smithers et al., 2001).

# 4 **3** Data and Methods

#### 5 3.1 Long-term datasets

Hydrological data in the catchment, including precipitation, evaporation, streamflow and
groundwater records, were collected from the Department of Water Affairs (DWA), the South
African Weather Service (SAWS), the South African Sugarcane Research Institute (SASRI),
and the firm In-Situ Groundwater Consulting (http://www.insituconsulting.co.za). Geological,
topographical and land use GIS (Geographic Information Systems) data were obtained from
the Water Research Commission 2005 study (WRC 2005).

The average catchment precipitation was obtained by studying seven weather stations with daily rainfall data from 2001 to 2012. Only four stations were selected based on data availability and proximity to the catchment. These stations were X1E006, X1E007, Barberton and Malelane (Figure 1). Missing rainfall values for Barberton (2%) and X1E007 (33%) were estimated by regression analysis. Malelane and X1E006 did not contain missing data. Using a Thiessen polygon distribution, the average rainfall was calculated for the catchment.

18 Average actual evaporation was calculated from daily Class A pan evaporation values from 19 the Barberton and Malelane stations and daily Class S pan evaporation from X1E006 and 20 X1E007 stations from 2003 to 2012. Daily pan evaporation values were aggregated to 21 monthly pan evaporation values. Class S pan evaporation was converted to Class A pan 22 evaporation following the Water Resources of South Africa 1990 study WR90 (Midgley et 23 al., 1994). Class A evaporation was converted to reference evaporation using the guidelines 24 for crop water requirements (Allen et al., 1998) and reference evaporation was corrected for the specific land uses using data from the land satellite imagery collected from the Incomati 25 26 Water Availability Assessment Study (Mallory and Beater, 2009). Using a long term water 27 balance from 2003 to 2012, actual mean evaporation rates were found.

To analyze the stream flow response at the outlet and tributaries, daily discharges at X2H022
(Outlet), X2H008 (Queens), X2H031 and X2H024 (Suidkaap) and X2H010 (Noordkaap)

stream gauges were obtained from the DWA. The locations of the stations are shown in
 Figure 2A.

## 3 3.2 Field and Laboratory Methods

#### 4 General

A field campaign from November 20, 2013 to February 4, 2014 was carried out to obtain an
overview of the hydrochemistry of the catchment prior to the rainy season and to collect data
for hydrograph separation studies.

8 Stream discharge collected from DWA data loggers (water levels converted to stream 9 discharge using DWA rating curve) were retrieved at the outlet with a frequency of 12 10 minutes (0.2 hours) from October 30, 2013 to February 17, 2014. Hourly precipitation rates 11 were obtained from the Incomati Catchment Management Agency (ICMA) rain gauges at 12 Roffiekultuur, Nelshoogte Bos, Satico, and Josefdal Boarder from October 1, 2013 to 13 February 28, 2014 (see locations on Figure 2A).

## 14 Water Samples

Water samples were collected from the tributaries, main river, one spring, and two drinking water wells as shown in Figure 2A. Each location was sampled twice during dry weather conditions. Each sample of approximately 250 ml was collected in polyethylene bottles, rinsed three times before the final sample was taken to avoid contamination, and refrigerated for sample preservation. Electrical conductivity (EC), pH and temperature were measured insitu using a WTW conductivity meter.

#### 21 Rain Sampling

To obtain the isotopic and hydrochemical reference of rainfall, bulk rain samples were collected in the upstream and downstream part of the catchment. The rain samplers were constructed according to standards of the International Atomic Energy Agency (IAEA) to avoid re-evaporation (Gröning et al., 2012). Thus an average of upstream and downstream samples per rain event was used for the rainfall end member concentrations for each hydrograph separation. 1 Rainfall characteristics, including duration, total rain amount, maximum and average 2 intensity, and antecedent precipitation index were estimated for each rain event. A rainfall 3 event was defined as a rainfall occurrence with rainfall intensity greater than 1 mm hr<sup>-1</sup>, and 4 intermittence less than four hours as observed in a similar study in a semi-arid area by 5 Wenninger et al. (2008). The Antecedent Precipitation Index (*API*) for *n* days prior the event 6 were calculated using equation (1):

$$API_{-n} = \sum_{i=1}^{7} P_{(-n-1+i)}(0.1i)$$
[1]

8 where *P* in (mm h<sup>-1</sup>) stands for precipitation and *i* is number corresponding to the day of 9 rainfall. For this study, API indexes were calculated for the seven, fourteen and thirty days 10 prior to the event. Peak flow, runoff depth, and time to peak were determined for each event.

### 11 Automatic Sampler

7

12 During the rainy season 2013-2014, four events that occurred on December 12-13 (Event 1), December 28-30 (Event 2), January 13 (Event 3) and January 30-31 (Event 4) were sampled 13 using an automatic sampler manufactured by the University of KwaZulu-Natal (UKZN). The 14 15 first two events were sampled on a volume basis obtaining 22 samples for Event 1, and 5 samples for Event 2 (a smaller number of samples were obtained for Event 2 due to photo 16 17 sensor failure in the automatic sampler). Events 3 and 4 were sampled using a time based 18 strategy obtaining 13 samples for Event 3, and 36 samples for Event 4. A total volume of 19 approximately 100 ml was obtained for each sample.

## 20 Chemical Analysis of Water Samples

All samples were refrigerated, filtered, and analyzed for HCO3 and Cl using a Hach Digital Titrator, and SiO2 using a Hach DR890 Portable colorimeter within 48 hours. Then, samples were transported to the UNESCO-IHE laboratory in the Netherlands for further chemical analysis. The samples were analyzed for major anions, cations and stable isotopes as listed in Table 1.

#### 1 3.3 Data analysis

#### 2 3.3.1 Groundwater Analysis

Groundwater chemical data for 240 boreholes and 18 borehole logs were obtained from InSitu Groundwater Consultants covering the different geological formations (granite, lava,
arenite, and gneiss). For 27 out of the 240 boreholes, pH, CaCO<sub>3</sub>, Mg, Ca, Na, K, Cl, NO<sub>3</sub>-N,
F, SO<sub>4</sub>, SiO<sub>2</sub>, Al, Fe, and Mn data were available. The remaining boreholes had only
information on EC, static water table depth, and physical characteristics of the borehole.

Borehole chemical data was classified according to the geological formations. The classified
data distribution was observed using GIS, and basic statistical analysis was carried out to
determine the control of geology over the hydrochemistry of groundwater.

11 To gain better insights with regard to groundwater flow, groundwater contour lines were 12 created using an Inversed Distance Weighted (IDW) interpolation of the static water tables 13 from the boreholes.

14 3.3.2 End Member Mixing Analysis (EMMA)

Suitable parameters for hydrograph separation were identified by creating mixing diagrams of 15 EC ( $\mu$ S cm<sup>-1</sup>), SiO<sub>2</sub>, CaCO<sub>3</sub>, Cl, SO<sub>4</sub>, Na, Mg, K, Ca (in mg l<sup>-1</sup>) and  $\delta^2$ H and  $\delta^{18}$ O 16 (%VSMOW). Parameters were plotted against discharge to observe dilution and hysteresis 17 18 effects. A principal component analysis was carried out based on the method described by 19 Christophersen and Hooper (1992). Only not statistical correlated parameters were used. From 20 these, the possibility of three end members was explored. The three runoff components 21 identified were direct runoff, deep groundwater and shallow groundwater. Direct runoff was 22 defined according to the conceptual model by Uhlenbrook and Leibundgut (2000) where 23 direct runoff (or quick runoff component) was generated from direct precipitation on the 24 stream channel, overland flow from sealed and saturated areas and from highly fractured 25 outcrops. The deep groundwater component was considered to be the portion of runoff 26 generated from deeper highly weathered granite aquifers, and the shallow groundwater 27 component was considered to be the intermediate component from perched groundwater 28 tables.

The mixing plot for  $\delta^2 H$  and K is presented in Figure 11. The direct runoff end member was 1 2 characterized by the upstream and downstream rain samples. Potassium was used as an 3 indicator of the shallow groundwater component due to the main sources of potassium, which are the weathering of minerals from silicate rocks, application of fertilizers, and the 4 5 decomposing of organic material. The mobilization of potassium is linked to the flushing of the soil and shallow subsurface layers of vegetated areas. This was also observed by Winston 6 and Criss (2002). The direct runoff samples had a low K average (0.5 mg  $l^{-1}$ ) and depleted 7  $\delta^{18}$ O and  $\delta^{2}$ H values (-4.8‰ for  $\delta^{18}$ O; -27.5‰ for  $\delta^{2}$ H). A spring sample was used to 8 9 characterize the deep groundwater component which contained more enriched  $\delta^{18}$ O and  $\delta^{2}$ H values (-0.9‰ for  $\delta^{18}$ O; -2.2‰ for  $\delta^{2}$ H) and low K concentration (0.7 mg l<sup>-1</sup>). The shallow 10 groundwater end member was estimated considering the high K concentrations (4 mg  $1^{-1}$ ) and 11 slightly less depleted  $\delta^{18}$ O and  $\delta^{2}$ H (-3.5% for  $\delta^{18}$ O; -7.0% for  $\delta^{2}$ H) observed in the stream 12 samples. The error interval for the direct runoff in Figure 11 is  $\pm$  the standard deviation of the 13 rain samples. For the groundwater end members, the error intervals were estimated as  $\pm 10\%$ 14 of the measured values. While these errors are arbitrary, they were chosen as they are more 15 conservative than the alternative analytical errors of  $\pm 0.2 \text{ mg l}^{-1}$  for K and  $\pm 1.5 \%$  for  $\delta^2 \text{H}$  and 16 because there were no additional samples from which to derive the standard deviation. 17

## 18 3.3.3 Hydrograph Separation

19 Isotope and hydrochemical data were combined with discharge data to perform a multi-20 component hydrograph separation based on steady state mass balance equations as described, 21 for instance, in Uhlenbrook et al. (2002). The number of tracers (*n*-1) was dependent on the 22 number of runoff components (*n*). Equations (3) and (4) were applied in dividing the total 23 runoff,  $Q_T$ , into two and three runoff components.

24

$$Q_T = Q_1 + Q_2 \dots + Q_n \tag{3}$$

25

$$c_{\rm T} Q_{\rm T} = c_1 Q_1 + c_2 Q_2 \dots + c_n Q_n \tag{4}$$

26 Where  $Q_1$ ,  $Q_2$  and  $Q_n$  are the runoff components in m<sup>3</sup> s<sup>-1</sup> and  $c_T$ ,  $c_1$ ,  $c_2$  and  $c_n$  are the 27 concentrations of total runoff, and runoff components.

#### 1 3.3.4 Uncertainty Estimation

2 Uhlenbrook and Hoeg (2003) showed that during the quantification of runoff components, 3 uncertainties due to tracer and analytical measurements, intra-storm variability, elevation and 4 temperature, solution of minerals, and the spatial heterogeneity of the parameter 5 concentrations occur. For the Kaap river hydrograph separations, these uncertainties were accounted by the spatial hydrochemical characterization of the catchment and by sampling 6 7 rainfall during each event and at different locations. Moreover, tracer end-members and 8 analytical uncertainties were estimated using a Gaussian error propagation technique and a 9 confidence interval of 70% as described by Genereux (1998) and Liu et al. (2004).

10 
$$W = \left\{ \left[ \frac{\partial y}{\partial x_1} W_{x1} \right]^2 + \left[ \frac{\partial y}{\partial x_2} W_{x2} \right]^2 + \dots + \left[ \frac{\partial y}{\partial x_n} W_{xs} \right]^2 \right\}^{\frac{1}{2}}$$
 [5]

11 *W* is the estimated uncertainty of each runoff component (e.g. direct runoff, shallow and deep 12 groundwater components).  $W_{x1}$ , and  $W_{x2}$ , are the standard deviations of the end-members..  $W_{xs}$ 13 is the analytical uncertainty and the partial derivatives  $\frac{\partial y}{\partial x_1}$ ,  $\frac{\partial y}{\partial x_2}$  and  $\frac{\partial y}{\partial x_n}$  are the 14 uncertainties of the runoff component contributions with respect to the tracer concentrations.

15 4 Results

### 16 **4.1** Hydrology, hydrogeochemistry and Groundwater Flow

One of the characteristics of semi-arid areas is the high variability of flows. This large variability is observed at the Kaap outlet and tributaries (Table 2) where the highest and lowest flows recorded at the Kaap outlet are 483 and 0 m<sup>3</sup>s<sup>-1</sup> respectively. Pardé coefficients (Figure 4) reflect the seasonal flow behaviour showing the dominance of one rainy season per hydological year with the largest flows occurring in February. Moreover, the flat slopes observed at the upper end of the Flow Duration Curves (Figure 5) are evidence of groundwater storage areas located in the upstream part of the catchment.

The variability of the catchment's groundwater quality parameters was studied from borehole data. Electrical conductivities in the granite region had the lowest electrical conductivity (EC) values (average 383  $\mu$ S cm<sup>-1</sup>), while the gneiss formation, near the outlet, had the largest EC average of 1140  $\mu$ S cm<sup>-1</sup>. Lava and arenite formations had mean EC values of 938 and 525  $\mu$ S cm<sup>-1</sup>, respectively. The gneiss and lava formations had higher concentration averages of chloride and calcium carbonate than the granite and arenite formations. These can be seen in the box plots in Figure 6.

Groundwater contour lines followed the topographical relief. The highest water tables were observed at the north boundary of the catchment with water tables up to 1,150 m (Figure 2D). From the groundwater contour map, it was observed that groundwater moves toward the stream indicating a gaining river system. Time series data from boreholes did not show a significant change in water tables due to seasonal or long-term changes.

## 10 **4.2** Spatial hydrochemical characterization

11 The upstream rain samples average had a more depleted isotopic signature (-5.1‰ for  $\delta^{18}$ O; -12 30.2‰ for  $\delta^{2}$ H) than the lower elevation rain samples average (-4.4‰ for  $\delta^{18}$ O; -24.7‰ for 13  $\delta^{2}$ H). Upstream and downstream delta deuterium values ranged from a minimum of -30.2‰ 14 to a maximum of -21.8‰ and delta oxygen-18 ranged from -5.14‰ to -3.72‰. Baseflow at 15 the catchment outlet (X2H022) was characterized by analyzing DWA long-term water quality 16 data and by field sampling prior to the rainy season 2013-2014. Results from the field 17 sampling are shown in Table 3.

18 The upper section of the catchment, mainly dominated by granite, is characterized by low to 19 moderate electrical conductivities. Long-term mean electrical conductivities (sampled 20 monthly by the DWA from 1984 to 2012) for the Upper Suidkaap and Noordkaap tributaries 21 were 75 and 104  $\mu$ S cm<sup>-1</sup>, respectively. On the contrary, the catchment outlet had a higher 22 long-term average EC of 572  $\mu$ S cm<sup>-1</sup> (DWA long-term monthly average from 1977 to 2012).

### 23 **4.3 Rainfall-Runoff Observations**

Table 4 summarizes the rainfall-runoff observations for the four studied events. The events had distinctive characteristics showing large variability in peak flows, Antecedent Precipitation Index (API), rainfall duration, rain depth and maximum and average intensities. Event 1 had the highest peak flow at 124 m<sup>3</sup> s<sup>-1</sup> while Event 3 had the smallest peak flow at 6.5 m<sup>3</sup> s<sup>-1</sup>. API indices, especially API.<sub>7</sub>, differed from very wet conditions during Event 1 (39 1 mm) to very dry conditions (1 mm) during Event 2. Event 1 was a relatively short event (7 2 hrs) with high antecedent precipitation conditions and high rain intensities generating the 3 largest amount of runoff at the outlet. In contrast, Event 3 was a short event with average rain 4 intensity that generated the lowest peak flow.

### 5 4.4 Response of Isotopes and Hydrochemical Parameters

6 During the storm events, most hydrochemical parameters (EC, Ca, Mg, Na, SiO<sub>2</sub> and Cl) and water isotopes ( $\delta^2$ H and  $\delta^{18}$ O) showed dilution responses except for potassium (Figure 7). The 7 first flood was the largest event sampled reaching a peak flow of 124 m<sup>3</sup> s<sup>-1</sup> where a larger 8 9 contribution of direct runoff was observed. In this event, a larger degree of dilution of the 10 sampled hydrochemical parameters is also observed. The following events had smaller peak flows of 27.6, 6.5 and 7.1 m<sup>3</sup> s<sup>-1</sup> for events 2, 3 and 4 respectively. Thus, smaller dilution 11 effects were observed for events 2, 3 and 4. The smaller peak flows and lower direct runoff 12 contributions for the latter events may explain the temporal variability observed in the 13 increased concentrations of the hydrochemical parametters over time. During Event 1, EC's 14 initial value of 317  $\mu$ S cm<sup>-1</sup> decreased to 247  $\mu$ S cm<sup>-1</sup> during peak flow. Similarly, CaCO<sub>3</sub> and 15 SiO<sub>2</sub> decreased from 115 to 82 mg l<sup>-1</sup>, and 21.1 to 19.6 mg l<sup>-1</sup>, respectively.  $\delta^{18}$ O (-2.9‰) and 16  $\delta^2$ H (-7.0%) decreased to -3.2% and -12.6%, respectively. Potassium concentrations 17 increased from 1.3 to 2.8 mg l<sup>-1</sup>. For Event 2, a smaller number of samples were collected due 18 19 to malfunctions of the automatic sampler. However, dilution of SiO<sub>2</sub> and Cl, and an increase in potassium concentrations were observed. Event 3 and 4 were smaller events, but a smaller 20 21 sampling interval showed the same dilution behavior of the sampled parameters and the 22 increase in potassium concentrations.

#### 23 **4.5 Two-Component Hydrograph Separation**

Event and pre-event components were separated using  $\delta^{18}O$  and  $\delta^{2}H$ , and direct runoff and groundwater were separated using EC, SiO<sup>2</sup>, CaCO<sub>3</sub>, and Mg. For simplicity, the two component hydrograph separation components in this study are referred as direct runoff and groundwater components. Direct runoff (quick flow component) defined in the methods section as the portion of direct precipitation and infiltration excess overland flow was characterized using the rain samples collected upstream and downstream inside the 1 catchment. Groundwater end members were obtained from the initial stream water samples

- 2 before the rainfall started. Events 1 and 4 had the largest contributions of direct runoff among
- 3 the four events accounting for 29% in case of Event 1 and up to 36% for Event 4 (Table 5).
- 4 Events 2 and 3 had lower direct runoff contributions ranging from 5% to 13% for Event 2 and
- 5 2% to 12% for Event 3. Figure 8 shows the two component hydrograph separations for the
- 6 four events.

#### 7 **4.6** Isotope hydrograph separation vs. hydrochemical hydrograph separation

8 Hydrochemical tracers usually separate runoff from source areas while isotopes generally 9 separate old water from new water. The definition of Klaus and McDonnell (2013) given in 10 was used for this study stating that pre-event water (or old water as referred in this section of 11 the study) is the water stored in the catchment before the rainfall event. This component may 12 not be representative of deep groundwater sources but it may be water stored from the same rainfall season but from previous rainfall events. Thus, a comparison between "old" and 13 14 "groundwater" components obtained during the four events was carried out to investigate to 15 what extend these components are similar. This allowed us to determine the suitability of 16 isotopic hydrograph separations versus hydrochemical separations for semi-arid 17 environments. Figure 9 presents the percentages of groundwater and old water contributions using environmental isotopes ( $\delta^2$ H and  $\delta^{18}$ O) and hydrochemical (EC, SiO<sub>2</sub>, CaCO<sub>3</sub> and Mg) 18 19 tracers for the four investigated events. It is noted that Events 1 and 4 have smaller 20 contributions of groundwater than Events 3 and 4. During events Event 4 and Event 2 old 21 water resembles groundwater. The data points above the line present instances where old 22 water is not necessarily groundwater but water stored before the event. No major differences 23 are observed from using hydrochemical or isotope tracers for the hydrograph separation.

#### 24 4.7 End Member Mixing Analysis (EMMA)

To further differentiate the runoff components, a Principal Component Analysis (PCA) was carried out on twelve solutes (EC, SiO<sub>2</sub>, CaCO<sub>3</sub>, Cl, NO<sub>3</sub>-N, SO<sub>4</sub>, Na, Mg, K, Ca,  $\delta^{18}$ O and  $\delta^{2}$ H) using the statistical software R (R Development Core Team, 2014). The correlation matrix was used for the PCA. Results indicated that 90% of the variability is explained by two principal components (*m*). Thus, the number of end-members (*n*) can be chosen as (*n*=*m*+1)

leading to a three component hydrograph separation (Christophersen and Hooper, 1992). 1 2 Figure 10 shows the biplot of principal components where the orthogonal vectors indicate no dependency between parameters. This is observed for  $\delta^{18}O$ ,  $\delta^{2}H$ , K, and NO<sub>3</sub>. The clustering 3 of the hydrochemical parameters reveals the strong correlation between these parameters 4 5  $(SiO_2, CaCO_3, Ca, EC, Mg, Na, Cl, and SO_4)$ . Potassium shows a negative strong correlation 6 with the clustered parameters but not with the water isotopes and NO<sub>3</sub>. Thus for the three 7 component hydrograph separations, orthogonal vectors with weak Pearson correlations were selected. These are K and  $\delta^{18}$ O (r = -0.28) and K and  $\delta^{2}$ H (r = 0.45). Nitrate was not selected 8 9 due to its non-conservative properties. Potassium was identified as a useful tracer due to its 10 increasing concentrations during runoff peaks. This high potassium concentration suggested the presence of soil water influenced by mobilization of fertilizer and/or organic material. To 11 12 account for additional near surface water, this component is referred as the shallow 13 groundwater component during this study. It is important to note that the shallow groundwater 14 component could be a mix of surface runoff and near-surface water since potassium was used 15 as an indicator of shallow groundwater and this element can also be found in surface runoff.

### 16 **4.8** Three-Component Hydrograph Separation

Direct runoff contributions obtained during the 3-component hydrograph separations (Table 6 and Figure 12) concur with the 2-component hydrograph separations. Events 1 and 4 were characterized by higher contributions of direct runoff than events 2 and 3. Moreover, Event 1 also had a higher contribution of shallow groundwater that peaked during the total runoff peak. Events 2, 3 and 4 had higher deep groundwater contributions. Uncertainties for the 3component hydrograph separations can be seen in Table 6.

23 **5 Discussion** 

#### 24 **5.1** Runoff Processes in the Kaap Catchment

From the mixing diagrams, groundwater analysis and spatial hydrochemical characterization of the catchment, the runoff components were identified and characterized. The groundwater analysis suggested two sources of groundwater of different ionic content at the upper and lower sections of the catchment. In the upstream area, granite is the dominant formation

1 explaining the lower ionic content in groundwater in contrast to the downstream areas where 2 geologically diverse formations and land use increase the ionic content of groundwater. The 3 weathered granite layer allows rain to infiltrate to the deeper groundwater reservoir through 4 preferential flow paths with less contact time for weathering processes to occur. This explains 5 the hydrochemical signature of the deep groundwater component, which is characterized by 6 its moderate electrical conductivities, moderate to high dissolved silica, lower ionic content 7 and low potassium concentrations. The chemical signature of the shallow groundwater 8 component is characterized by the high electrical conductivities, alkalinity, sulphates, 9 potassium, and nitrates which are washed from top geological layers with large ionic content 10 and land uses such as agriculture and mining which are more predominant in the downstream 11 region of the catchment.

12 The three-component hydrograph separations suggest that the shallow groundwater 13 component (potentially including surface runoff) is quickly activated during rainfall events 14 and its contribution increases as the antecedent precipitation increases as observed during 15 Events 1 and 4 where the shallow groundwater contributions were 45% and 20-21% 16 respectively. Moreover, a connection between surface and groundwater is evident from the 17 groundwater countour map (Figure 2D) which shows a gaining river system, and from the 18 flow duration curves, which indicate exfiltrating groundwater storages to the streams. Further 19 literature (Hughes, 2010) suggests that most of South Africa's groundwater is stored in 20 secondary aquifers and that surface flow may be nourished by lateral flow from semi-21 saturated fracture systems after storm events.

22 Other studies (Petersen, 2012) in the nearby Kruger National Park (KNP) have shown that 23 groundwater recharge occurs mostly during the wet season and groundwater flow travels in 24 accordance with the topographical relief. Petersen (2012) studied a granite dominated area 25 and a basaltic rock dominated area, approximately 30 km east from the Kaap outlet. The study 26 found that the granite region was mainly characterized by the steep topography which favors 27 overland flow which infiltrates through depressions, cracks and fractures by preferential 28 pathways while the south basaltic section with a flatter topography showed piston flow 29 processes to be more predominant. Petersen (2012) findings, covering studies of 30 approximately 1011 boreholes in KNP, support the findings in the Kaap catchment where

high fracturing in the granite section allows recharge of deeper groundwater reservoirs
 through preferential flow paths.

It is important to note that the inferences drawn from this study are based on four events sampled during the wet season 2013-2014 but supported by historical meteorological, hydrological and water quality data, groundwater analysis and a spatial hydrochemical study of the catchment. In addition, Table 7 shows runoff studies with similar number of events studied.

### 8 5.2 Catchment's Response Dependency on Antecedent Precipitation

9 Hydrograph separation results suggested that there is a direct runoff contribution (2-36%) to 10 total runoff during storm events for the Kaap River. Similar results have been obtained for 11 other catchments in semi-arid areas. For instance, Hrachowitz et al. (2011) in their study in 12 four nested catchments in Tanzania found event runoff coefficients of 0.09. Similarly, 13 Munyaneza, et al. (2012) found groundwater contributions up to 80% of total runoff in the Mingina catchment in Rwanda during the two and three-hydrograph separations in a 258 km<sup>2</sup> 14 15 catchment. The importance of sub-surface flow in semi-arid catchments is also illustrated in 16 Wenninger, et al. (2008) in the Weatherley catchment in the Eastern Cape in South Africa.

From the several variables considered such as geology, topography and rainfall characteristics studied for the four events, the direct runoff component was most sensitive to the antecedent precipitation index. This is observed during Events 1 and 4 where APL<sub>7</sub> values are the largest among the four events and direct runoff contributions are also the largest for these events. The relationship between APL<sub>7</sub> and direct runoff generation is supported by a strong Pearson correlation (0.76-0.94). This suggests that direct runoff is enhanced by wetter conditions in the catchment due to saturation in the subsurface triggering saturation overland flow.

### 24 5.3 Complexities of Runoff Processes Understanding in Semi-arid Areas

The combination of climatic and hydrological processes influenced by topography, geology, soils and land use make catchments complex systems. Although the opposite may be true for particular situations, in general, catchments become more non-linear as aridity increases and runoff processes become more spatially and temporally heterogeneous than in humid regions (Blöschl et al., 2013; Farmer et al., 2003). Thus, understanding hydrological processes in arid
catchments becomes more difficult due to high variability of rainfall and streamflow, high
evaporation losses, long infiltration pathways, permeable stream channel beds and often deep
groundwater reservoirs (Hughes, 2007; Trambauer et al., 2013).

5 The high variability of rainfall enhances the difficulties of runoff prediction by triggering 6 different runoff responses. For instance, high intensity storms tend to generate overland flow 7 in the form of infiltration excess overland flow (Smith and Goodrich, 2005), while high 8 antecedent precipitation conditions enhance saturation excess overland flow. This effect is 9 visible in this study during Event 1 where the high antecedent precipitation index suggested 10 saturation of the subsurface, thus reducing the infiltration capacity and enhancing saturation 11 excess overland flow. The opposite is observed for Events 2 and 3 where the low soil 12 moisture conditions allow more rainfall to infiltrate activating other runoff processes such as 13 preferential vertical flow.

14 Although not included in this study, inter-annual variability, evaporation, hydraulic 15 connectivity, permeable stream beds and interception have shown to change the behavior of 16 runoff processes in arid and semi-arid areas. For instance, inter-annual rainfall variability is 17 closely related to high evaporation losses. Mostert et al. (1993) study in a Namibian Basin 18 found that during wetter seasons, vegetation cover and total evaporation increased, thus 19 reducing the amount of runoff reaching the outlet. Similarly, hydraulic connectivity in arid 20 environments is limited by the reduced soil moisture conditions in these areas leading to 21 reduced groundwater recharge. Other fluxes such as interception and flow through permeable 22 stream beds pose a greater challenge to the understanding runoff processes in semi-arid areas. 23 Interception can further decrease the hydrologic connectivity breaking the link between 24 meteoric water and groundwater as observed in the Zhulube catchment in Zimbabwe where 25 interception accounted up to 56% of rainfall during the dry season (Love et al., 2010). 26 Similarly, transmission losses due to the high degree of fracturing of stream beds can 27 significantly reduce streamflow but increase recharge of groundwater systems.

28 Thus, this study illustrated the effects of temporal rainfall variability during the wet season 29 suggesting the influence of antecedent precipitation conditions on direct runoff generation. 30 However, studying the effects of spatial and inter-annual rainfall variability, high evaporation and transpiration (from unsaturated zones, alluvial aquifers, riparian zones) fluxes, the spatial variability of vegetation, and deep groundwater resources on streamflow generation is still required for the better understanding of runoff processes in semi-arid areas. More monitoring of groundwater levels and aquifers would assist in bridging this gap of knowledge, such as in Van Wyk et al. (2012). An emphasis is made into studying the region during dry weather for further understanding of evaporation and transpiration from deeper layers of soil moisture that in some cases can reach even into groundwater systems (e.g. eucalyptus trees).

## 8 6 Conclusions

9 The Kaap catchment has suffered devastating floods that affect greatly the trans-boundary 10 Incomati basin, in particular downstream areas in South Africa, Swaziland and Mozambique where recent floods have caused significant economic and social losses. Runoff processes 11 12 were poorly understood in the Kaap catchment limiting rainfall-runoff models to lead to better 13 informed water management decisions. Through hydrometric measurements, tracers and 14 groundwater observations, runoff components and main runoff generation processes were 15 identified and quantified in the Kaap catchment for the wet season 2013-2014. The suitability 16 of isotope hydrograph separation was tested by comparing it to hydrochemical hydrograph 17 separations showing no major differences between these tracers. Hydrograph separations 18 showed that groundwater was the dominant runoff component for the wet season 2013-2014. 19 Three component hydrograph separations suggested a third component that we addressed as 20 shallow groundwater component. However, further research is still necessary to make a clear 21 distinction between surface runoff and shallow groundwater. A strong correlation between 22 direct runoff generation and antecedent precipitation conditions was found for the studied 23 events. Direct runoff was enhanced by high antecedent precipitation activating saturation 24 excess overland flow. Similar groundwater contributions have been observed in other studies 25 in semi-arid areas (Hrachowitz et al., 2011; Munyaneza et al., 2012; Wenninger et al., 2008). 26 The understanding of runoff generation mechanisms in the Kaap catchment contributes to the 27 limited number of hydrological processes studies and in particular hydrograph separation 28 studies in semi-arid regions for the proper management of water resources. Moreover, this 29 study was carried out during the wet season, and in order to gather a better undertanding of 30 the hydrological system, further studies focusing on the dry season are still needed, 31 particularly on the dependency of runoff generation on soil moisture and vegetation.

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## 1 Table 1 UNESCO-IHE laboratory equipment used in chemical analysis of Kaap catchment samples

	Parameter(s) analyzed	Equipment	Number of samples	Preservation method	Analytical uncertainty $(\sigma)$
Environmental Isotopes	<sup>18</sup> O, <sup>2</sup> H	Isotope Analyzer LRG DLT- 100	116	None	±0.2, ±1.5 (‰)
Cations	Ca <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> , K <sup>+</sup>	Thermo Fisher Scientific XSeries 2 ICP -MS	116	Nitric acid (HNO <sub>3</sub> )	$\pm 0.2 \ (mg \ l^{-1})$
Anions	Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> -N, SO <sub>4</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup>	Dionex ICS-1000	116	Refrigerated at < 4 °C	$\pm 0.2 \ (mg \ l^{-1})$

Table 2 Physical and hydrological characteristics of Kaap tributaries and outlet

Tributary Name	Kaap Outlet	Queens	Upper Suidkaap	Noordkaap
Station ID	X2H022	X2H008	X2H031	X2H010
Reach Length (km)	45.7	41.2	42.5	57.5
Sub-basin Area (km <sup>2</sup> )	1640	291	256	315
Data analyzed	1961-2012	1949-2012	1967-2012	1970-2012
Period (years)	51	63	45	42
% Data missing	5%	0%	3%	6%
Highest flow measured HHQ $(m^3 \cdot s^{-1})$	483	96	123	28
Lowest flow measured NNQ $(m^3 \cdot s^{-1})$	0	0	0	0
Mean of yearly highest flows MHQ $(m^3 \cdot s^{-1})$	65	13	19	6
Mean of yearly lowest flows MNQ $(m^3 \cdot s^{-1})$	0.4	0.1	0.3	0.2
Mean flow MQ $(m^3 \cdot s^{-1})$	3.6	0.6	1.1	0.6
Variability Ratio	180	186	65	31
Specific discharge $(L \cdot s^{-1} \cdot Km^{-1})$	3.0	2.2	4.2	1.9
Maximum and average days of no flow per year	139, 8	12,1	23,1	17,1

	Location						
Parameter	Suidkaap	Queens	Noordkaap	Outlet			
EC ( $\mu$ S cm <sup>-1</sup> )	84.0	128.7	92.9	443.0			
$SiO_2 (mg l^{-1})$	22.4	17.0	20.9	24.1			
$CaCO_3 (mg l^{-1})$	38.5	59.5	41.3	154.0			
$\operatorname{Cl}(\operatorname{mg} \operatorname{l}^{-1})$	3.8	3.6	2.8	15.5			
$SO_4 (mg l^{-1})$	1.8	4.1	1.6	47.2			
Na (mg $l^{-1}$ )	7.5	7.1	7.3	29.3			
Mg (mg $l^{-1}$ )	2.8	7.4	3.7	25.3			
$Ca (mg l^{-1})$	7.9	9.1	6.8	27.6			
$\delta^2$ H (‰ VSMOW)	-12.1	-12.4	-12.7	-8.9			
$\delta^{18}$ O (‰ VSMOW)	-3.2	-3.1	-3.5	-2.7			

## 1 Table 3. List of mean values of hydrochemical parameters obtained during field campaign 2013-2014

Table 4. Rainfall-runoff relationships observed during wet season 2013-2014 for Kaap catchment at outlet (X2H022 stream gauge) and average precipitation from Roffiekultuur, Nelshoogte Bos, Satico, and Josefdal Boarder rain stations

		Event 1	Event 2	Event 3	Event 4
Runoff	Peak flow time & date	Dec-13-13 18:24	Dec-30-13 6:12	Jan-16-14 3:48	Jan-31-14 17:00
	Maximum river depth (m)	2.0	1.0	0.5	0.5
	Peak flow $(m^3 s^{-1})$	124.0	27.6	6.5	7.1
	Runoff Volume (mm)	3.2	2.6	0.1	0.4
	Time to peak after rainfall started (hrs)	24.4	31.2	60.8	22.0
Rainfall	Rain start date & time	Dec-12-13 18:00	Dec-28-13 23:00	Jan-13-14 15:00	Jan-30-14 19:00
	Rain duration (hrs)	7	39	7	26
	Rain depth (mm)	24	78	17	20
	Average rain intensity (mm hr <sup>-1</sup> )	3.4	2.0	2.5	0.8
	Maximum rain intensity (mm hr <sup>-1</sup> )	9.8	12	5	10
	Antecedent Precipitation Index API <sub>-7</sub> (mm)	38.7	1.3	7.8	24.9
	API <sub>-14</sub> (mm)	118.1	12.8	20.0	67.9
	API-30 (mm)	390.2	220.8	192.4	223.8

1 2 Table 5. Percentages of direct runoff [DR] and groundwater [GW] contributions and 70% uncertainty percentages [W] from 2-component hydrograph separations for wet season 2013-2014 Kaap catchment, South Africa.

Tracer		Event	1		Event	2		Event	3		Even	t 4
	DR	GW	W	DR	GW	W	DR	GW	W	DR	GW	W
EC	22	78	6.8	5	95	7.9	6	94	7.0	27	73	4.2
SiO <sub>2</sub>	21	79	2.6	6	94	2.5	12	88	2.2	21	79	2.6
CaCO <sub>3</sub>	29	71	6.3	9	91	6.9	6	94	6.8	24	76	4.6
Mg	22	78	5.6	13	87	6.0	8	92	5.3	24	76	4.0
<sup>18</sup> O	23	77	8.6	8	92	3.3	10	90	3.1	36	64	12.4
$^{2}\mathrm{H}$	19	81	5.6	5	95	15.0	2	98	19.4	21	79	24.9

Table 6. Direct runoff [DR], shallow groundwater [GW<sub>S</sub>], and deep groundwater [GW<sub>D</sub>] contributions in (%) and 70%

uncertainty of 3-component hydrograph separations in (%)

Tracers	Event 1			Event 2			Event 3			Event 4		
	DR	GWs	$\mathrm{GW}_\mathrm{D}$	DR	GWs	$\mathrm{GW}_\mathrm{D}$	DR	$\mathrm{GW}_{\mathrm{S}}$	$\mathrm{GW}_\mathrm{D}$	DR	$\mathrm{GW}_{\mathrm{S}}$	$\mathrm{GW}_\mathrm{D}$
K & <sup>18</sup> O	28	45	26	7	19	74	16	6	78	41	21	37
70% uncertainty (%)	7.2	5.3	5.8	7.4	3.2	5.1	5.3	3.0	3.9	7.9	6.2	5.8
$K \&^2 H$	22	45	33	14	19	67	11	5	84	37	20	42
70% uncertainty (%)	4.8	6.6	6.4	3.8	3.9	5.5	3.0	2.8	4.0	6.3	6.2	7.6

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#### Table 7. Runoff studies with number of events studied

Study name	Reference	Number of events
Hydrograph separation using stable isotopes, silica and electrical conductivity: an alpine example	Laudon and Slaymaker (1997)	5
The role of soil water in stormflow generation in a forested headwater catchment: synthesis of natural tracer and hydrometric evidence	Bazemore et al. (1994)	2
Quantifying contributions to storm runoff through end-member mixing analysis and hydrologic measurements at the Panola Mountain Research Watershed (Georgia, USA)	Burns et al. (2001)	2
On the value of combined event runoff and tracer analysis to improve understanding of catchment functioning in a data-scarce semi-arid area	Hrachowitz et al. (2011)	28
Quantifying uncertainties in tracer-based hydrograph separations: a case study for two-, three- and five-component hydrograph separations in a mountainous catchment	Uhlenbrook and Hoeg (2003)	4
Hydrograph separations in a mesoscale mountainous basin at event and seasonal timescales	Uhlenbrook et al. (2002)	2
Identification of runoff generation processes using combined hydrometric, tracer and geophysical methods in a headwater catchment in South Africa	Wenninger et al. (2008)	3
Runoff generation in a steep, tropical montane cloud forest catchment on permeable volcanic substrate	Muñoz-Villers and McDonnell (2012)	13
Quantifying the relative contributions of riparian and hillslope zones to catchment runoff	McGlynn and McDonnell (2003)	2
Dynamics of nitrate and chloride during storm events in agricultural	Kennedy et al. (2012)	2

catchments with different subsurface drainage intensity (Indiana, USA)		
Investigation of hydrological processes using chemical and isotopic tracers in a mesoscale	Marc et al. (2001)	3
Mediterranean forested catchment during autumn recharge		



Figure 1. Location of the Kaap catchment in the Incomati basin displaying nearby cities, and DWA and SAWS rain gauges



Figure 2. A) DEM of Kaap catchment with sampling locations and stream and rain gauges locations, B) Land use map, C) Geological map, and D) Contour map of static groundwater levels E) Aridity index (< 0.03 hyper arid, 0.03-0.2 Arid, 0.2-0.5 Semi-arid, 0.5-0.65 dry sub-humid, >0.65 humid) F) Long-term mean potential evapotranspiration (PET). GIS layers are courtesy of Water Research Commission, 2005 South Africa.



Figure 3. Average monthly precipitation, pan A evaporation (from stations: X1E006, X1E007, Barberton and Malelane), and maximum and minimum temperatures at Barberton station from 2001 to 2012



Figure 4. Annual flow regimes at: X2H022 (Outlet) X2H008 (Queens), X2H031 and X2H024 (Suidkaap) and X2H010 (Noordkaap) based on long-term flow data



Figure 5. Flow duration curves for: X2H022 (Outlet) X2H008 (Queens), X2H031 and X2H024 (Suidkaap) and X2H010 (Noordkaap) based on long-term flow data



Figure 6.Boxplots of borehole water quality parameters at different geological locations in the Kaap catchment.



Figure 7. Kaap catchment a) average precipitation in mm d<sup>-1</sup>, b) discharge at the outlet in m<sup>3</sup> s<sup>-1</sup> and electrical conductivity  $\mu$ S cm<sup>-1</sup>, c) delta deuterium and delta oxygen-18 in ‰ VSMOW, d) calcium, magnesium, sodium and silica concentrations at the outlet in mg l<sup>-1</sup>, and e) chloride and potassium concentrations at the outlet in mg l<sup>-1</sup>.



Figure 8. Two component hydrograph separations using electrical conductivity as a tracer. Event 1 and 4 had larger direct runoff contribution coinciding with the total runoff peak. Event 2 and 3 had smaller direct runoff contribution



Figure 9. Percentages of groundwater and old water contributions using environmental isotopes ( $\delta^2$ H &  $\delta^{18}$ O) and hydrochemical (EC & SiO<sub>2</sub>) tracers



5 Figure 10. Biplot of principal components generated during PCA analysis of stream water samples using EC, SiO<sub>2</sub>, CaCO<sub>3</sub>,





7 8 Figure 11. Mixing diagram of  $\delta^2 H$  and K showing stream water samples at outlet for four rain events during wet season 2013-2014.



2 Figure 12. Three-component hydrograph separations using K and <sup>2</sup>H.