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Spatial analysis of hydrogen and oxygen stable isotopes ("isoscapes") in ground water and tap water across South Africa

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A B S T R A C T

Stable isotopes in water (δ^2H and δ^{18}O) are important indicators of hydrological and ecological pattern and process. δ^2H and δ^{18}O of water are incorporated into geological and biological systems in a predictable manner and have been used extensively as tracers in hydrological, ecological and forensic studies. Physical processes result in spatial variation of δ^2H, δ^{18}O in water across the landscape (so-called "isoscapes") and provide the basis for hydrological, ecological, archaeological and forensic studies. Southern Africa is a globally important meeting point for ocean and climate systems, biological diversity and human societies, yet there is little information on the spatial variability of δ^2H and δ^{18}O in water across this important region. Here we present the first ground water and tap water isoscapes for southern Africa. We compare and contrast these two water resources, and consider how well global models of precipitation isotopes capture isotopic variation across South Africa. Ground water and tap water samples were collected from across South Africa, analysed for δ^2H and δ^{18}O, and used to generate interpolated δ^2H, δ^{18}O and deuterium-excess ($d = \delta^2$H $- 8*\delta^{18}$O) isoscapes. We found coherent spatial structure in δ^2H, δ^{18}O and d of ground water and tap water that could be predicted by a geostatistical model based on simple environmental parameters (elevation, mean annual precipitation, precipitation minus potential evaporation, distance to coast and modeled isotope ratio of precipitation). This spatial structure resulted in considerable differences in isotopic composition of water in many of the major wildlife reserves in South Africa, indicating a good potential for wildlife forensics in this region. δ^2H and δ^{18}O of ground water, and to a lesser extent tap water, reflected the δ^2H and δ^{18}O of long-term weighted annual precipitation at the two GNIP stations in South Africa. However, large discrepancies between modelled isotopic composition of precipitation and our ground water and tap water isoscapes, particularly at higher elevations, highlighted uncertainty in the accuracy of modelled precipitation isoscapes for this region. Increased spatial sampling of precipitation, especially for high elevation regions, and temporal sampling of ground and tap water would considerably aid isotopic studies in this region.

1. Introduction

Stable isotopes in water (δ^2H and δ^{18}O) are important indicators of hydrological and ecological pattern and process (Gat, 1996; West et al., 2006). The stable isotopic composition of water reveals information about the physical processes that lead to its formation and transport (Craig, 1961; Dansgaard, 1964; Gat, 1996). These physical processes result in spatial variation in δ^2H, δ^{18}O and deuterium-excess (defined as $d = \delta^2$H $- 8*\delta^{18}$O,) (Bowen and Revenaugh, 2003; Craig, 1961; Dansgaard, 1964). δ^2H and δ^{18}O of water are incorporated into geological and biological systems in a predictable manner (Ehleringer et al., 2008a; Killingley and Newman, 1982; Roden et al., 2000), allowing extensive use of δ^2H and δ^{18}O as tracers in hydrological, archaeological, ecological and forensic studies (Ehleringer et al., 2008b). Water isotopes

have been used to trace the fate and origin of atmospheric moisture sources (Bowen et al., 2012; Burnett et al., 2004), partition evapotranspiration fluxes from the land surface (Williams et al., 2004; Yepez et al., 2003), trace moisture sources in terrestrial plants (Brienen et al., 2012; Hawkins et al., 2009; West et al., 2007), determine the dependence of vegetation on stream or ground water (Dawson and Ehleringer, 1991; Ehleringer and Dawson, 1992), identify the source of ground water recharge (Harvey and Sibray, 2001), identify region-or-origin on forensic materials (Bowen et al., 2005; Ehleringer et al., 2008b; Hobson, 1999), amongst many other applications.

Increasingly, the stable isotopic composition of water is being measured and modeled on a large and highly resolved spatial scale (Bowen et al., 2007; Wassenaar et al., 2009). These isotopic-landscapes, or "isoscapes" (West et al., 2010b), have considerable utility in that they allow the documentation and visualization of large-scale hydrological processes, on the regional, continental or global scale. A well-supported water isoscape allows interrogation of the hydrological

processes causing the spatial pattern (e.g. seasonal rainfall patterns, precipitation/evapotranspiration ratios, catchment hydrology) (Bowen et al., 2011). It can also provide an isotopic base layer for the development of more complex biological isoscapes, such as leaf water (West et al., 2008), hair (Ehleringer et al., 2008a) and feathers (Cherel et al., 2000). Such isoscapes allow a statistical approach to determining the origin of materials (Neubauer and Shima, 2013). Spatial variation in stable isotopes has been used successfully in revealing patterns of animal migration (Rubenstein and Hobson, 2004) and forensic identification of a wide variety of materials (Ehleringer et al., 2008b).

Global monitoring of water isotopes commenced with the formation of the Global Network for Isotopes in Precipitation (GNIP) in 1961 (IAEA/WMO, 2006a). In many regions of the world, the GNIP dataset has sufficient temporal and spatial density to provide a good basis for spatial modeling (Bowen and Revenaugh, 2003). However, there are many regions where the station density is insufficient (e.g. Wassenaar et al., 2009). South Africa is such an example, where only two GNIP stations (Pretoria and Cape Town) exist in a country of over 1.2 million square kilometers. While good δ^2H and δ^{18}O datasets exist at these locations, there is relatively little data on how these isotopes vary spatially across South Africa. This lack of spatial data limits hydrological, archaeological, ecological and forensic studies in a region that is a globally important meeting point for ocean and climate systems, biological diversity and human societies, as well as under increasing pressure to optimize its scare water resources (New, 2002).

In this study we present the first ground water and tap water isoscapes for southern Africa. We focused on ground water and municipal tap water as two key water resources that are readily measureable and integrate across a variety of disciplinary interests. Ground water is key water resource for vegetation, agriculture and human consumption in many of the more arid parts of the world. The isotopic composition of ground water approximates that of seasonally weighted long-term precipitation inputs, even in some of the most arid regions of the world (IAEA, 2007). As such, ground water may serve as a proxy for precipitation in areas of the world under-represented by GNIP stations (Wassenaar et al., 2009). Municipal tap water is a key deliverable for water resource management, representing the interface between human and hydrological systems, and has a direct effect on human geography and socio-economic development. Tap water has been shown to retain a similar isotopic composition to that of local precipitation (Bowen et al., 2007), although there is considerable potential for evaporative enrichment in surface-stored waters (e.g. reservoirs and dams). Thus, differences between the isotopic composition of ground water, tap water and modelled precipitation provides information on the coupling of water resources to precipitation source and can provide insight into resources that might be vulnerable to changes in climate or excessive exploitation (Bowen et al., 2007). Additionally, drinking water is incorporated into the tissues of consumers and provides an important forensic tracer of location (Ehleringer et al., 2008a; Hobson et al., 1999).

In the interpretation of our water isoscapes, we asked the following questions: 1) Is there a coherent spatial pattern in ground water and tap water isotopes across South Africa that can be geostatisically modeled? 2) What do differences between ground water and tap water isotopes reveal about drinking water resources? 3) Can ground water and tap water isoscapes be used as proxy for precipitation across South Africa? 4) What potential do these isoscapes have for the forensic tracing of wildlife?

2. Methods

2.1. Ground water sample collection

The ground water isotope data were obtained from the National Ground water Quality Monitoring Project (NGwQMP) run by the Department of Water Affairs, South Africa (http://www.dwaf.gov.za/Groundwater/NGQMP.aspx). Ground water samples were collected at

369 monitoring points around South Africa (Fig. 1) between April 2006 and September 2007.

2.2. Tap water sample collection

410 tap water samples were collected from around South Africa during the period April 2009 to December 2010 (Fig. 1). We used two techniques to gather samples. The first technique involved a return mail
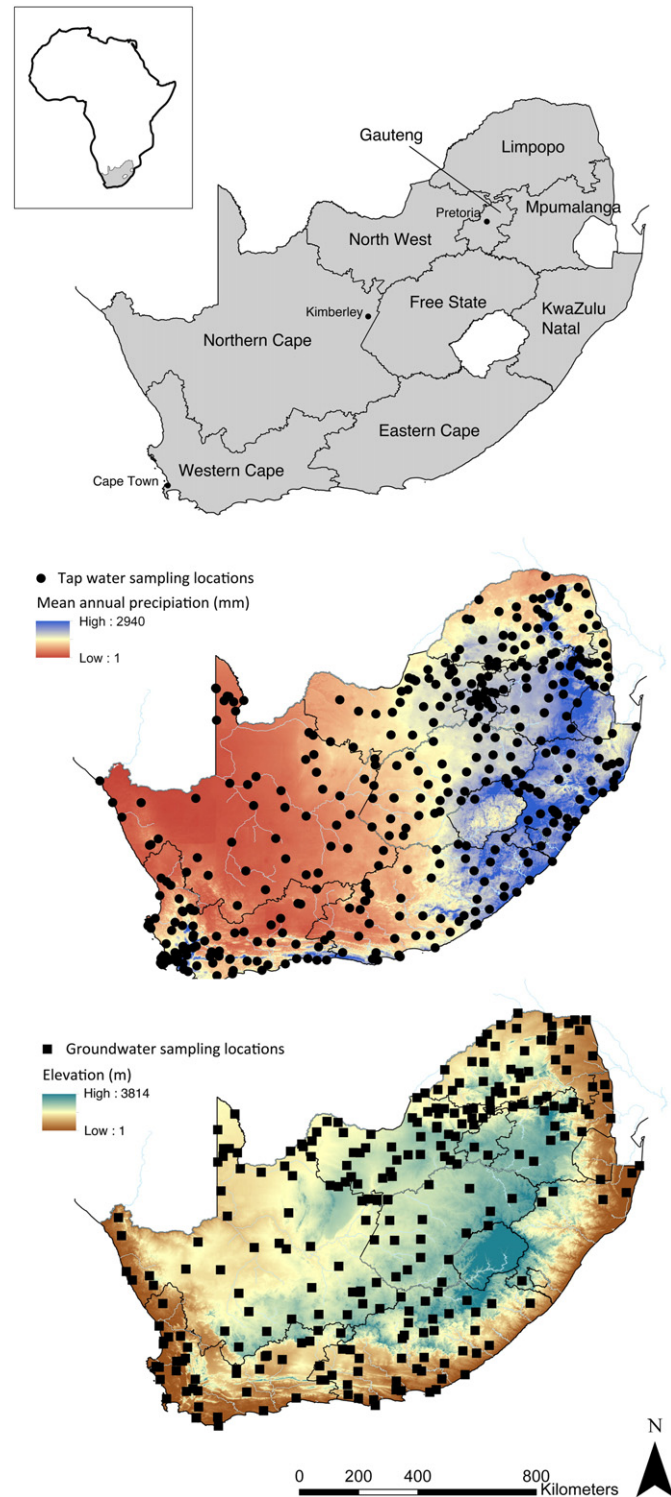

Fig. 1. The provinces of South Africa and sampling locations for tap water and ground water overlaid on mean annual precipitation (mm) and elevation (meters above sea level) respectively.

campaign with the cooperation of the South African Post Office. We sent sample kits to 336 post offices nationally. The sample kit contained a letter stating the purpose of the study together with a brief instruction sheet, two empty vials, some Parafilm® (Bemis Flexible Packaging, Neenah, WI 54956, USA) to seal the vials with and a postage-paid, return-addressed, padded envelope. Of the 336 sample kits sent out, 280 were returned successfully (83% success rate). Returns were only considered successful if: 1) the sample cap was tightly attached and secured with Parafilm®, or 2) in the case where no Parafilm® had been used, the sample vial was completely full, with no headspace. Our high success rate for our sampling campaign suggests this to be an efficient and cost-effective strategy for repeat sampling campaigns. The second sampling strategy involved targeted and opportunistic sampling. Sampling kits were supplied to colleagues visiting specific locations within South Africa, or mailed to colleagues in remote locations. Additionally, the researchers visited some specific locations personally in order to collect samples in poorly sampled areas. Samples were collected in this manner at 130 locations. All tap water samples were collected in 8 ml borosilicate glass vials with rubber-lined screw-top caps (LASEC, South Africa). All filled vials had Parafilm® wrapped around the caps to prevent caps from coming loose and the sample becoming evapoconcentrated.

3. Stable isotope analyses

Ground water samples were analyzed for δ^2H and $\delta^{18}O$ in the laboratory of the Environmental Isotope Group (EIG) of iThemba Laboratories, Gauteng using a PDZ Europa GEO 20-20 gas mass–spectrometer connected to a PDZ water equilibration system, working in dual-inlet mode. Equilibration time for the water sample with hydrogen was one hour and eight hours for CO_2. Laboratory standards, calibrated against international reference materials, were analyzed with each batch of samples.

Tap water samples were analyzed by wavelength-scanned cavity ring-down spectroscopy (WS-CRDS, (Gupta et al., 2009) using a L2120-i (Picarro Inc., 480 Oakmean Parkway, Sunnyvale, California, 94085, USA; www.picarro.com). These analyses were conducted in the Department of Biological Sciences, University of Cape Town. WS-
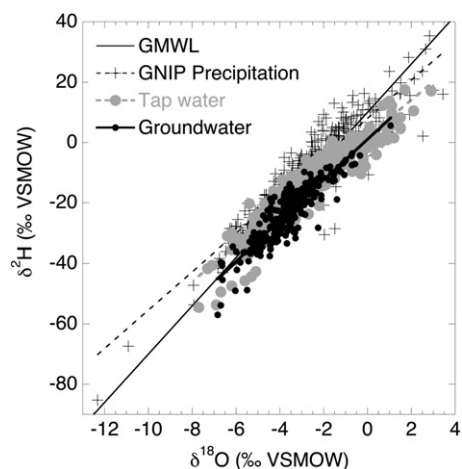

Fig. 2. δ^2H and $\delta^{18}O$ of ground water, tap water and precipitation from the GNIP stations in South Africa.

CRDS measurements have been shown to be susceptible to organic contaminants (West et al., 2010a; Brand et al., 2009). However, spectral analysis software is able to accurately identify problematic samples (West et al., 2011). Following the methodology of West et al. (2011), all WS-CRDS samples were screened post-analysis by Chemcorrect™ version 1.0.0 using analysis file "chemcorrect_inst avg_orgeval_06.csv" (Electronic supplement). As expected, none of the tap water samples were identified as problematic. Nevertheless, selected samples were cross-checked by isotope ratio mass spectrometry (IRMS) to confirm the Chemcorrect™ results. IRMS δ^2H analyses were performed using the closed-tube Zn-reduction method (Coleman et al., 1982). $\delta^{18}O$ was measured using the CO_2-equilibration method (Socki et al., 1992). The isotopic ratio of the H_2 and CO_2 gases was analyzed via dual-inlet on a Finnigan MAT 252 mass spectrometer (Bremen, Germany) in the Archaeometry Laboratory, University of Cape Town, South Africa. All comparisons were within the convolved error of the two analytical methods, indicating that the WS-CRDS and IRMS produced comparable results.

Table 1
Model parameters and goodness of fit statistics for regression models of predictive environmental variables and geostatistical models that included spatial autocorrelation in addition to predictive environmental variables. The model selected to generate a predictive surface is highlighted in **bold**. See methods for further details on model selection.

Layer	Parameters			Regression model				Geostatistical model	
				AIC	MSE	R^2	Rank	AIC	Rank
δ^2H (tap)†	**P-PE**	**elev**	**MAH**	**2867.2**	**93.8**	**0.28**	**5**	**2773.1**	**1**
δ^2H (tap)	PE	elevxtocoast	MAH	2865.8	93.5	0.28	4	2778.6	2
δ^2H (tap)	P-PE	MAH		2865.1	93.8	0.28	1	2779.1	3
δ^2H (tap)	RH	P-PE	MAH	2865.4	93.4	0.28	2	2780.9	4
δ^2H (tap)	P-PE	elevxtocoast	MAH	2865.5	93.4	0.28	3	2792.6	5
$\delta^{18}O$ (tap)†	**P-PE**	**elev**	**MAO**	**1499.9**	**2.77**	**0.14**	**5**	**1428.0**	**1**
$\delta^{18}O$ (tap)	P-PE	elevxtocoast	MAO	1495.8	2.74	0.15	2	1429.0	2
$\delta^{18}O$ (tap)	P-PE	tocoast	MAO	1498.7	2.76	0.14	4	1429.0	3
$\delta^{18}O$ (tap)	PE	tocoast	MAO	1498.5	2.76	0.14	3	1430.2	4
$\delta^{18}O$ (tap)	PE	elevxtocoast	MAO	1494.4	2.73	0.15	1	1430.2	5
δ^2H (ground)	MAP	elev	tocoast	1804.3	59.5	0.24	4	1760.0	1
δ^2H (ground)†	**MAP**	**tocoast**	**MAH**	**1802.0**	**59.0**	**0.25**	**1**	**1761.4**	**2**
δ^2H (ground)	MAP	tocoast	elevxtocoast	1804.7	59.6	0.24	5	1766.8	3
δ^2H (ground)	RH	MAP	tocoast	1804.2	59.5	0.24	3	1766.9	4
δ^2H (ground)	MAP	tocoast		1803.4	59.8	0.24	2	1766.9	5
$\delta^{18}O$ (ground)	MAT	tocoast	elevxtocoast	824.6	1.37	0.06	3	801.6	1
$\delta^{18}O$ (ground)	P-PE	MAO		825.3	1.39	0.05	4	802.5	2
$\delta^{18}O$ (ground)	MAP	MAO		825.5	1.39	0.05	5	802.5	3
$\delta^{18}O$ (ground)	elev	tocoast	MAO	821.4	1.36	0.07	1	803.5	4
$\delta^{18}O$ (ground)	tocoast	elevxtocoast	MAO	822.0	1.36	0.07	2	803.6	5
$\delta^{18}O$ (ground)†	**MAP**	**tocoast**	**MAO**	**826.9**	**1.39**	**0.05**	**9**	**803.6**	**6**

Notes: Model parameters are: **P-PE** – precipitation minus potential evaporation, **MAH** – mean annual precipitation δ^2H, **RH** – relative humidity, **elevxtocoast** – elevation x distance to coast, **elev** – elevation, **MAO** – mean annual precipitation $\delta^{18}O$, **tocoast** – distance to coast, **MAP** – mean annual precipitation, **MAT** – mean annual temperature.
† Model selected to generate predictive layers.

For all methods, isotope ratios are expressed in ‰ as:

$$\delta^N E = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) * 1000 \qquad (1)$$

where N is the atomic mass of the heavy isotope of element E and R is the ratio of the heavy to light isotope (^{2}H/H or ^{18}O/^{16}O). For the WS-CRDS data, precision (1σ) and accuracy (mean absolute difference between measured and known) obtained via quality control standards with identical isotope ratios introduced into every run were 0.2‰ and 1.5‰ for δ^{2}H and 0.07‰ and 0.13‰ for δ^{18}O respectively. For the ground water analyses, the analytical precision was estimated at 0.1‰ for δ^{18}O and 0.5‰ for δ^{2}H.

3.1. Precipitation data

Long-term measurements of precipitation at Pretoria and Cape Town (1961 – 2008) were obtained from the International Atomic Energy Agency's Global Network of Isotopes in Precipitation (GNIP) program (IAEA/WMO, 2006a), using the Water Isotope System for Data Analysis, Visualization, and Electronic Retrieval (WISER) interface (IAEA/WMO, 2006b).

Modeled precipitation layers for South Africa were obtained from the Online Isotopes in Precipitation Calculator (OIPC, http://waterisotopes.org, accessed June 2013). The OIPC calculates long-term average precipitation δ^{18}O and δ^{2}H at specified locations through geostatistical modeling of precipitation isotope data collected from 1960–2004 (Bowen and Revenaugh, 2003; Bowen and Wilkinson, 2002; Bowen et al., 2005).

3.2. Spatial analyses

To develop a spatial model of how δ^{2}H, δ^{18}O and d vary across South Africa, we compiled a matrix of environmental variables that were plausibly related to precipitation, ground water or tap isotope ratios. These were mean annual modeled precipitation isotope ratios for δ^{2}H
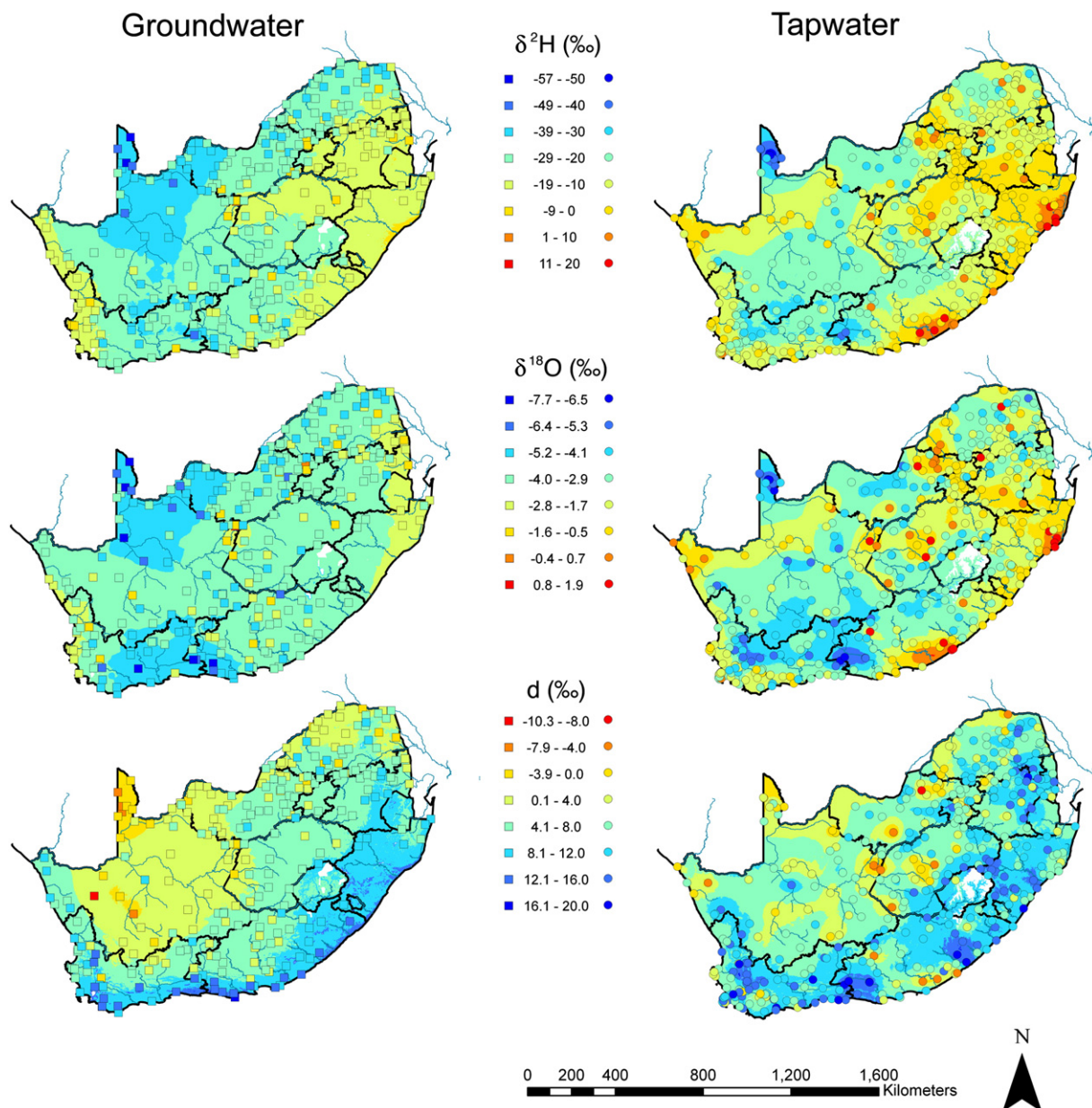

Fig. 3. Measured δ^{2}H, δ^{18}O and d for ground water and tap water sampled in this study (data points) overlaid on a modeled isoscape based on a geostatistical model using simple environmental parameters (see Methods).

(MAH) and δ^{18}O (MAO), mean annual precipitation (MAP), mean annual precipitation minus potential evaporation (P-PE), mean annual temperature (MAT), potential evaporation (PE), shortest path distance to coast (tocoast), elevation (elev), relative humidity (RH). MAP, PE, MAT and RH were obtained from Schulze (2007). We ran a statistical and geostatistical model-fitting algorithm (Bowen et al., 2012) iteratively using all possible linear combinations of these variables to model ground water or tap water values in the dataset. We did not explore non-linear combinations of the variables with the exception of the multiplicative combination of distance to coast and elevation (elevxtocoast), where we suspected a significant non-linear interaction. The result was 129 calibrated linear models for each isotope and water type (ground water or tap water), with a range of goodness of fit statistics for each model. Model residuals were evaluated for normality and were approximately normally distributed, consistent with the assumptions of the statistical models used. We focused primarily on Akaike Information Criterion (AIC) to distinguish between models. For the best linear models, we also fit a geostatisical model (including spatial auto-correlation in addition to predictive environmental variables), getting a second set of goodness-of-fit statistics for these models (Table 1). Within the top tier of models the distinctions in terms of AIC and other metrics were small. We looked for common parameterizations that performed well for both δ^2H and δ^{18}O, since using different parameterizations for the two elements would likely lead to strange artifacts for d-excess in some situations.

4. Results

4.1. Spatial pattern of ground water and tap water isotopes

There was a larger range in δ^2H and δ^{18}O for tap water than ground water across South Africa. As tap water may be composed of evaporated surface water or ground water, and may in some cases reflect a shorter time integration of precipitation, it is expected to be inherently more variable in δ^2H and δ^{18}O than ground water. For δ^2H$_{ground}$, the range was 62.6‰ (-57‰ to $+5.6$‰). For δ^{18}O$_{ground}$, the range was 7.9‰ (-6.8‰ to $+1.1$‰). Ground water deuterium-excess (calculated as $d_{ground} = \delta^2$H$_{ground} - 8*\delta^{18}O_{ground}$) ranged between -10.3‰ and $+16.9$‰. For δ^2H$_{tap}$, the range was 72‰ (-54.5‰ to $+17.5$‰). For δ^{18}O$_{tap}$, the range was 10.6‰ (-7.7‰ to $+2.9$‰). Tap water deuterium-excess (calculated as $d_{tap} = \delta^2$H$_{tap} - 8*\delta^{18}$O$_{tap}$) ranged between -8.2‰ and $+22.7$‰. As revealed in a dual isotope plot (Fig. 2), our ground water and tap water samples were indicative of waters of both meteoric origin (samples close to the Global Meteoric Water Line, δ^2H $= 8 \times \delta^{18}$O $+ 10$) as well as some evaporated surface waters (samples with low d).

Our calibrated geostatistical models were used to generate predictive surfaces of δ^2H, δ^{18}O and d for ground water and tap water (Fig. 3). For ground water, our data were best fit by Mean Annual Precipitation and Distance to Coast (Table 1). For tap water, our data were best fit by elevation, P-PE and modeled isotope ratio of precipitation (Table 1).

A spatially coherent pattern emerged from the ground water and tap water isotope data across South Africa (Fig. 3). For δ^2H$_{ground}$ and δ^{18}O$_{ground}$ the following broad trends could be seen: The most negative values were measured in the Kalahari (northern Northern Cape Province) and the south coast. The most positive values were found on the west coast and the eastern seaboard, extending into northeastern interior. There was a distinct region of more positive values in the central Karoo, surrounding Kimberley, which was also observed in the tap water data.

These trends were largely conserved in the tap water data. As for the ground water, the most negative δ^2H$_{tap}$ and δ^{18}O$_{tap}$ values were measured in the north-west of the country, specifically in the Kalahari and North West Province, and in the southwestern interior and southern Western Cape mountains. Between these two regions was a distinct

band of more positive values, most likely associated with utilization of river water from the Orange River. The western seaboard and south-western Cape were more positive than the interior, and had similar values to the Free State and Limpopo Province. The most positive δ^2H$_{tap}$ and δ^{18}O$_{tap}$ values occurred on the eastern seaboard, and stretched into Mpumalanga and the higher elevations of Gauteng Province.

The spatial pattern of d was very clear and was similar for ground water and tap water. The highest d occurred on the coast, with lower d inland. The lowest values occurred in most arid, northwestern regions of the country (see Fig. 1 for climate overlay).

4.2. Comparison between ground water and tap water

A comparison between the isotopic composition of ground water and tap water revealed extensive areas where ground water and tap water were of similar isotopic composition, as well as several distinct regions of difference (Fig. 4). Below we describe two major features where ground water and tap water differ, giving consideration to the hydrological processes resulting in the formation of ground water and tap water in these regions.
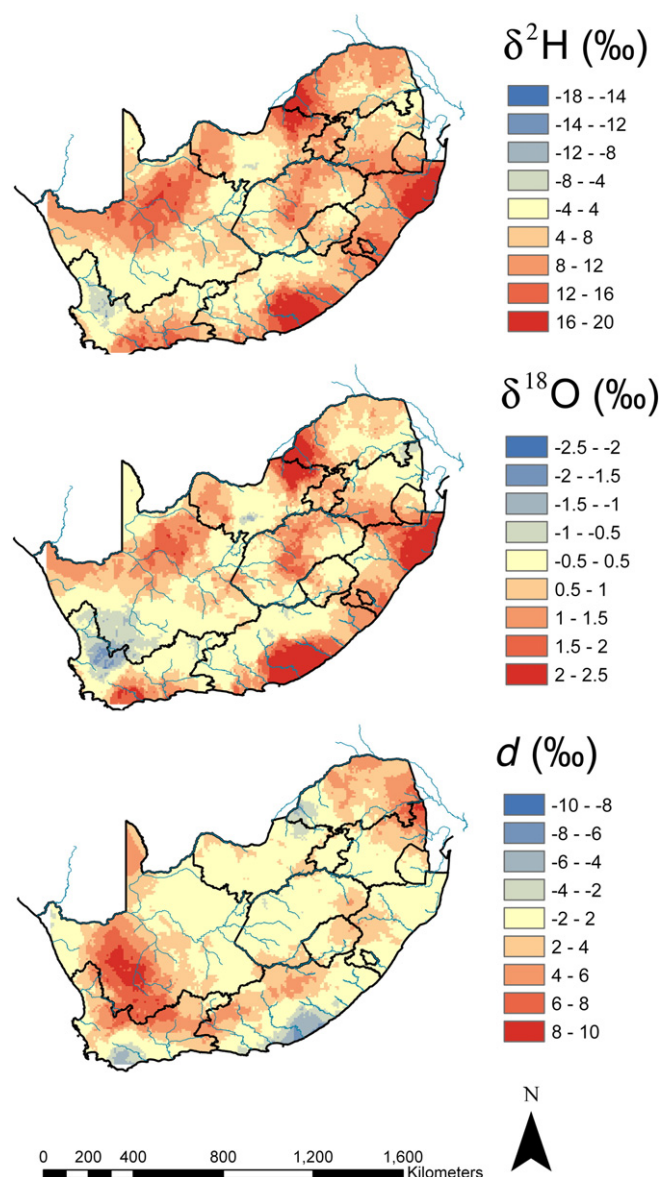

Fig. 4. Difference between δ^2H, δ^{18}O and d of tap water and ground water.

Firstly, in several regions of the country, δ^2H and $\delta^{18}O$ were more positive in tap water than ground water. These regions were the Orange River floodplain in the northwest, the northeastern highveld (Free State, Gauteng, Limpopo), and the south and eastern coastal regions from the Western Cape to KwaZulu-Natal (Fig. 4). There are at least two scenarios that would result in tap water being enriched in ^2H and ^{18}O relative to ground water. Enrichment in tap water relative to ground water could be indicative of a more direct coupling to recent, seasonal rainfall events in the tap water. As tap water was sampled in the summer months, discrepancies between tap and ground water, where d_{tap} and d_{ground} are not different, may reflect a predominant summer precipitation signal in the tap water, compared with a longer-term integration of weighted annual rainfall in the ground water. An alternative explanation for relative enrichment of ^2H and ^{18}O in the tap water is that tap water was exposed to evapoconcentration during surface

storage or transport. This scenario would also result in a $d_{tap} < d_{ground}$, depending on the relative humidity at the time of evaporation (Clark and Fritz, 1999). While the majority of the regions where tap water was enriched relative to ground water had similar d, suggesting the former scenario, there were isolated regions of $d_{tap} < d_{ground}$ along the southern coast of the Western Cape and Eastern Cape Provinces where it is likely that tap water underwent evapoconcentration.

Secondly, there was an extensive region in the southwest of the country (encompassing the Cederberg, Succulent Karoo and Tankwa Karoo) where δ^2H and $\delta^{18}O$ were more negative in tap water than in ground water and $d_{tap} > d_{ground}$ (Fig. 4). It seems probable that the tap water sampled in this region represented recent runoff from rainfall in the mountains, rather than reflecting a longer-term integration of rainfall that the ground water most likely represents. Frontal storm events in the Western Cape can often have a high d (Harris et al., 2010). A
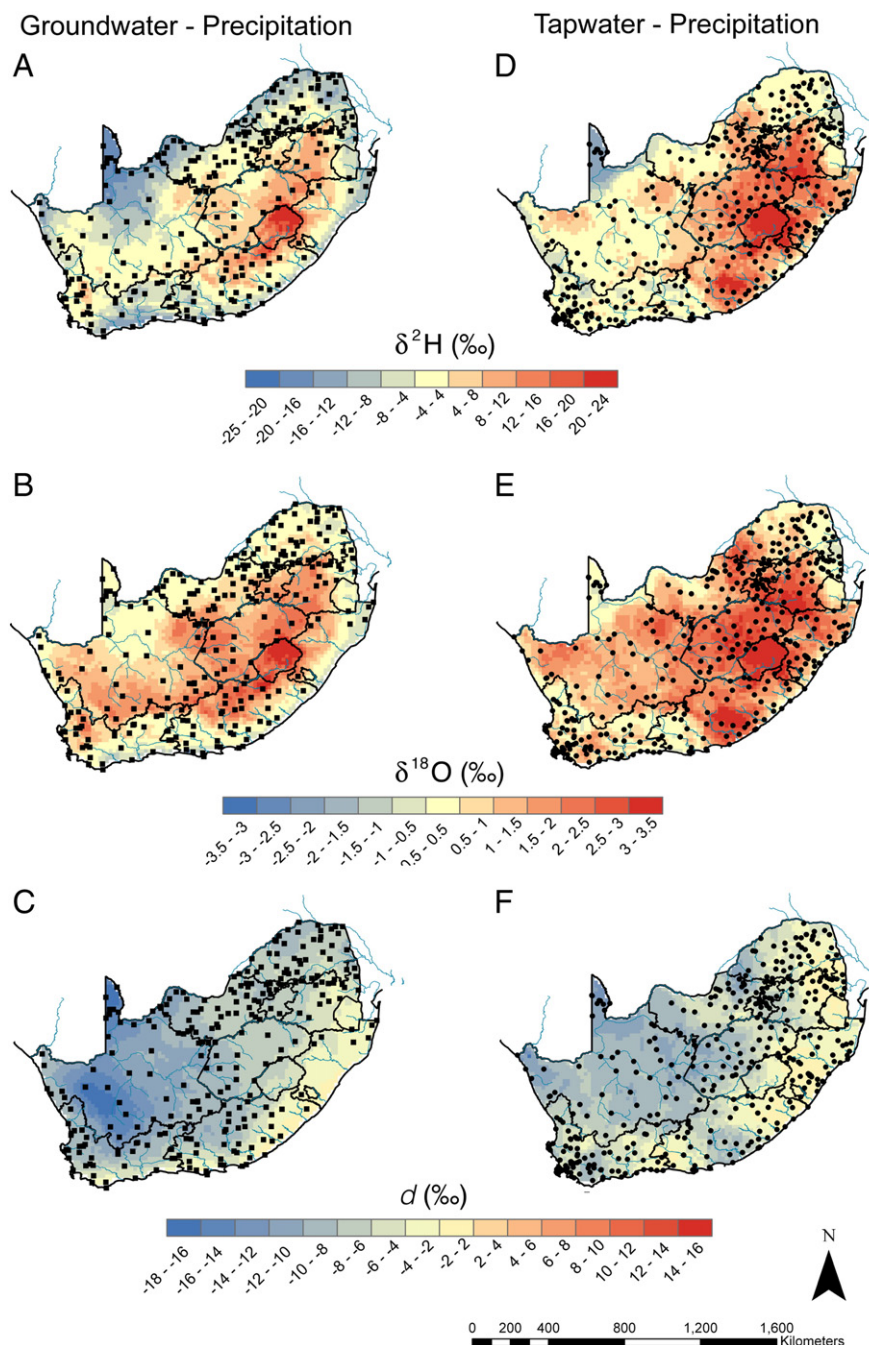

Fig. 5. Difference between ground water and precipitation (left hand panels) and tap water and precipitation (right hand panels) for δ^2H, $\delta^{18}O$ and d.

large frontal storm may contribute to temporal variability in the tap water in this region, but would be attenuated in the longer-term record of ground water, resulting in the pattern we observed.

$d_{tap} > d_{ground}$ was also observed in the Kalahari, and the northeast of the country, including Kruger National Park, despite small differences in δ^2H and $\delta^{18}O$ between the two resources (Fig. 4). The isotopic similarity for the samples is not surprising, as tap water in these regions is primarily obtained from the ground water. The difference in d is harder to explain, but we speculate that it may reflect a mixing of tap water with more recent precipitation, raising d_{tap} relative to d_{ground}.

4.3. Comparison of ground water and tap water with precipitation

The residuals of $\delta^2H_{ground} - \delta^2H_{OIPC}$ (δ^2H of modeled precipitation from the OIPC) indicate that ground water is more enriched in ^2H and ^{18}O than modeled precipitation in the higher elevations or the eastern half of the country (Fig. 5). The Kalahari, southern and eastern seaboard and the northeast interior (Fig. 5A) emerged as distinct regions where δ^2H_{ground} was more negative than δ^2H_{OIPC}. For $\delta^{18}O$, the pattern was similar with the exception that $\delta^{18}O_{ground} - \delta^{18}O_{OIPC}$ was more positive over the majority of the country, in particular the arid west (Fig. 5B).

The above patterns were similar for tap water (Fig. 5D, E), with the exception of more extensive areas where $\delta^2H_{tap} > \delta^2H_{OIPC}$ and $\delta^{18}O_{tap} > \delta^{18}O_{OIPC}$. For both ground water and tap water, there were large areas of negative d residuals ($d_{ground} < d_{OIPC}$ and $d_{tap} < d_{OIPC}$) across most of the country, but particularly in the arid western interior (Fig. 5C, F).

Long-term data from the two GNIP stations in South Africa (Pretoria and Cape Town) were compared with the OIPC model results and sampled ground water and tap water for the two locations. The GNIP data reflects the differences in rainfall seasonality between Pretoria (summer) and Cape Town (winter). Despite differences in the rainfall seasonality (Pretoria – summer, Cape Town – winter), differences in elevation (Pretoria – 1350 m, Cape Town – 40 m), and large seasonal swings in the isotopic composition of rainfall (particularly for Pretoria), the mean annual weighted isotope composition of rainfall is similar between the two stations (Fig. 7). The mean annual weighted isotopic composition of rainfall for the two stations were: Pretoria $\delta^{18}O = -3.8‰$ and $\delta^2H = -16.9‰$, Cape Town $\delta^{18}O = -3.4‰$, $\delta^2H = -13.1‰$. These values are not significantly different to those calculated by the OIPC: Pretoria $\delta^{18}O = -3.9 \pm 0.5‰$ and $\delta^2H = -19 \pm 5‰$, Cape Town $\delta^{18}O = -3.5 \pm 0.1‰$, $\delta^2H = -12 \pm 1‰$ (OIPC, Waterisotopes.org). Despite these limited differences at the station level in South Africa, geostatistical modeling of precipitation isotopes in South Africa predicts some spatial variation (Fig. 6), reflecting the influence of data from outside the country and the globally-calibrated environmental prediction relationships used by the OIPC on the modeled precipitation values.

The isotopic range of ground water samples (averaged within the city limits) was consistent with the weighted annual mean of the precipitation samples for the two GNIP-monitored sites (Fig. 7), indicating that ground water might be a good proxy for mean annual rainfall (Wassenaar et al., 2009). Consistent with our entire dataset across South Africa (Fig. 4), δ^2H_{tap} and $\delta^{18}O_{tap}$ tended to be more positive than δ^2H_{ground} and $\delta^{18}O_{ground}$ and spanned more of the isotopic range of monthly precipitation at the two GNIP stations (Fig. 7). The weighted annual mean of the precipitation samples was at the lower limit of the tap water range with the exception of $\delta^{18}O$ at Pretoria, where $\delta^{18}O_{tap}$ was 1‰ more positive than the weighted annual mean of the measured precipitation (Fig. 7).

4.4. Forensic utility of the isoscapes

As an example of the potential forensic utility of our dataset, we calculated the mean δ^2H and $\delta^{18}O$ for modeled ground and tap water in the major South African National and Provincial Parks. There were considerable differences between many of the major parks for both modeled
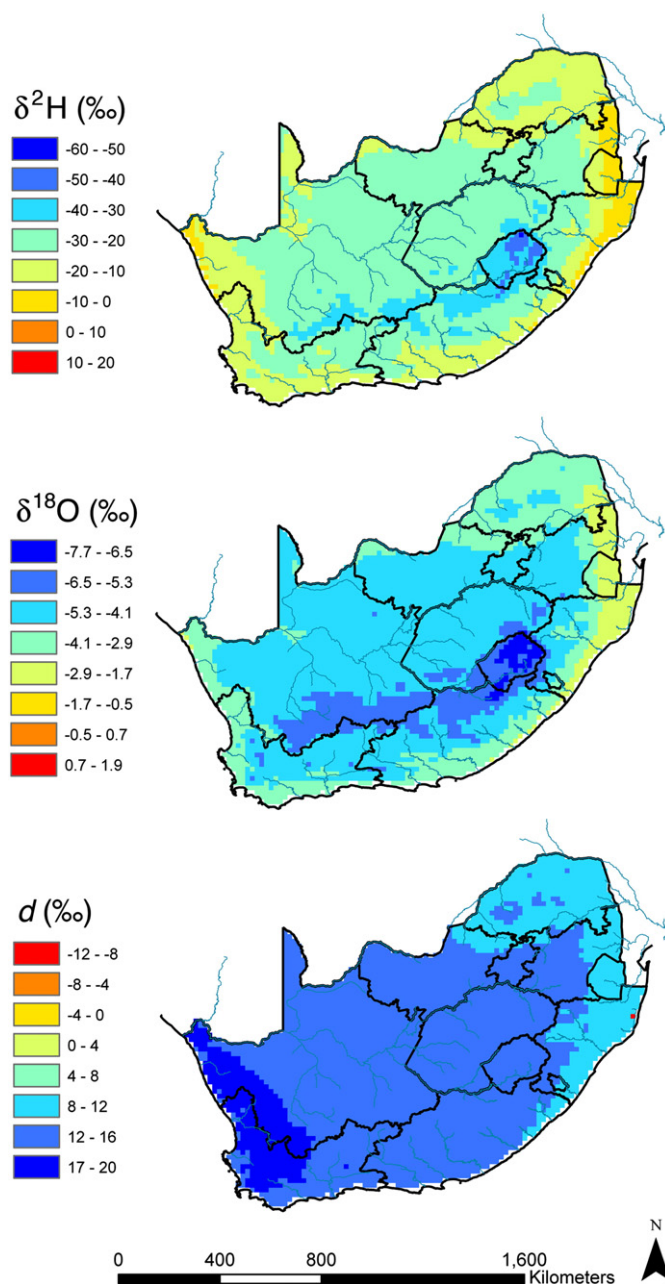

Fig. 6. δ^2H, $\delta^{18}O$ and d of modeled precipitation available from the OIPC (waterisotopes.org).

ground water and tap water (Fig. 8). Tap water isotopic composition showed greater differentiation between the parks than for ground water. This is most likely due to tap water being derived predominantly from surface waters, as well as ground water in the more arid regions, resulting in a greater range of isotopic composition across the country. Thus, the potential for forensic tracing of materials derived from tap water appears promising. As it may not always be possible to know whether a forensic material was derived from surface or ground water, it is useful to examine whether there is still a difference between regions when combining these two sources. When combining the means and errors of ground water and tap water in each park (Fig. 8C), the variance in each park increased substantially, making it difficult to distinguish between many parks (Fig. 8C). However there were still appreciable differences between several parks across South Africa, indicating that there may be potential to forensically trace material even in the absence of information about the water source from which the material was derived.
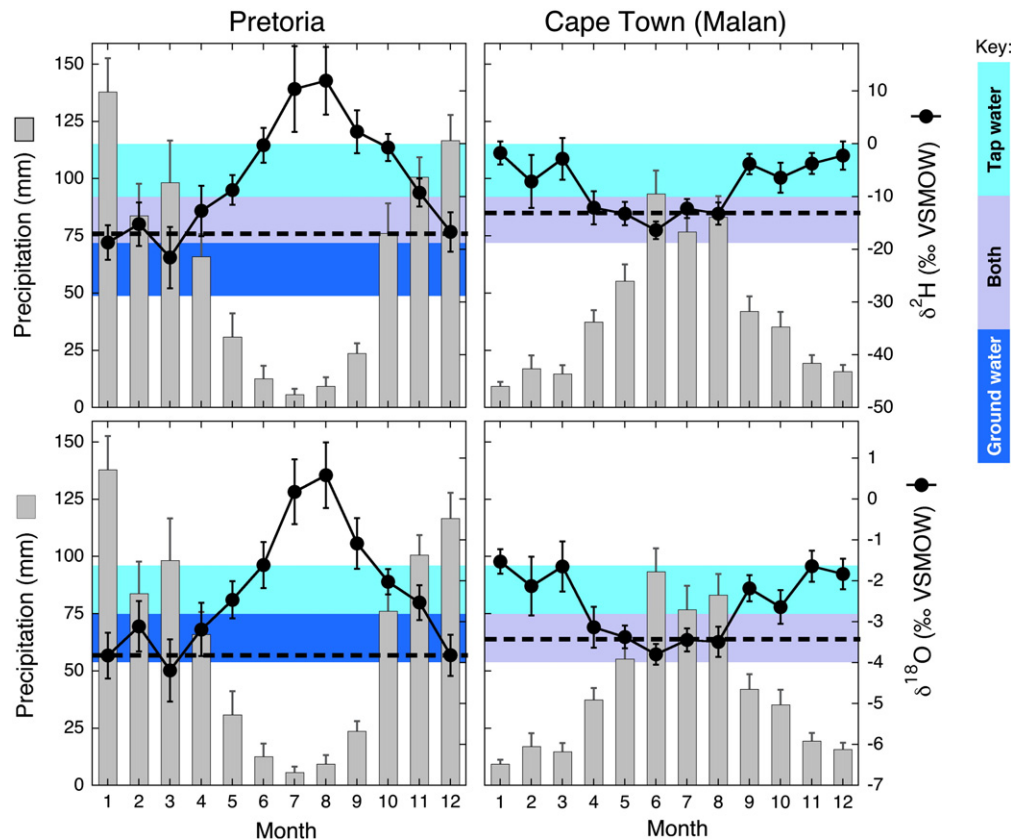
Fig. 7. Long-term monthly precipitation amount and isotopic composition measured at the two GNIP stations in South Africa (Pretoria and Cape Town). Dashed line represents weighted annual mean isotopic composition of precipitation. Colored bars represent the range in tap water and ground water sampled within the city limits of these two locations.

5. Discussion

5.1. Is there a coherent spatial pattern in ground water and tap water isotopes across South Africa?

We documented a spatially coherent pattern in our ground water and tap water isotope data comprising several distinct isotopic regions (Fig. 3). For the purposes of a coarse-scale mapping of water isotopes across South Africa, the spatial pattern observed could be modeled by combination of simple environmental drivers known to affect precipitation isotopes (elevation, distance to coast, mean annual precipitation, potential evaporation). Our geostatistical modeling approach did not incorporate more complex catchment scale modeling (Bowen et al., 2011), nor did we attempt to include information about inter-basin transfer (e.g. the Lesotho Highlands Water Project) into our modeling exercise. These refinements would most likely improve the predictive power and may be an avenue for future modeling work attempting a finer-resolution product. However, at the regional scale, our dataset and modeling approach confirmed the predominance of simple environmental drivers in determining the isotopic composition of these important water resources.

### 5.2. What do differences between ground water and tap water isotopes reveal about drinking water resources?

For extensive regions across South Africa, tap water had a similar isotopic composition to ground water (Fig. 4). In these regions, either the ground water was the source for tap water (in the more arid, or less developed areas of the country) or both tap water and ground water reflected the weighted annual precipitation as seen at the two GNIP stations (Fig. 7). There were also extensive areas where the isotopic composition of tap water was enriched in ^{2}H and ^{18}O relative to ground

water (Fig. 4). The most parsimonious explanations for most differences observed between tap water and ground water are either: 1) evapoconcentration of tap water stored or transported on the land surface (dams, rivers), or 2) shorter-term integration of precipitation into tap water relative to ground water, resulting in tap water reflecting the influence of recent rainfall events that do not recharge the ground water. An examination of the differences in δ^2H, δ^{18}O and d allows inference into which of these hydrological processes might be causing the isotopic difference in these water resources (Fig. 9). These results highlight the need to further resolve the temporal variability in both ground water and tap water across this region.

### 5.3. Can our isoscapes be used as proxy for precipitation across South Africa?

Our isoscapes raise the important question of how well the global precipitation models capture the true isotopic composition of precipitation across South Africa. Global models of isotopes in precipitation predict a depletion of ^{2}H and ^{18}O in precipitation in the interior and high elevations of the country (Fig. 6). Our isoscapes were uniformly more enriched in ^{2}H and ^{18}O than the modeled precipitation in these regions (Fig. 5). Additionally, our isoscapes were more depleted in ^{2}H and ^{18}O than the precipitation in the coastal and northern parts of the country (Fig. 5). The global precipitation models are well supported by the extensive GNIP database (Bowen and Revenaugh, 2003), however there are only two stations in South Africa for ground-truthing their applicability for this region. A direct comparison of δ^2H and δ^{18}O in ground water, tap water and measured precipitation from these two GNIP stations, suggests that ground water, and to a lesser extent tap water, may be a good proxy for weighted annual precipitation (Fig. 7). This is consistent with a similar analysis in Mexico (Wassenaar et al., 2009). If one accepts this assumption, this indicates that current models
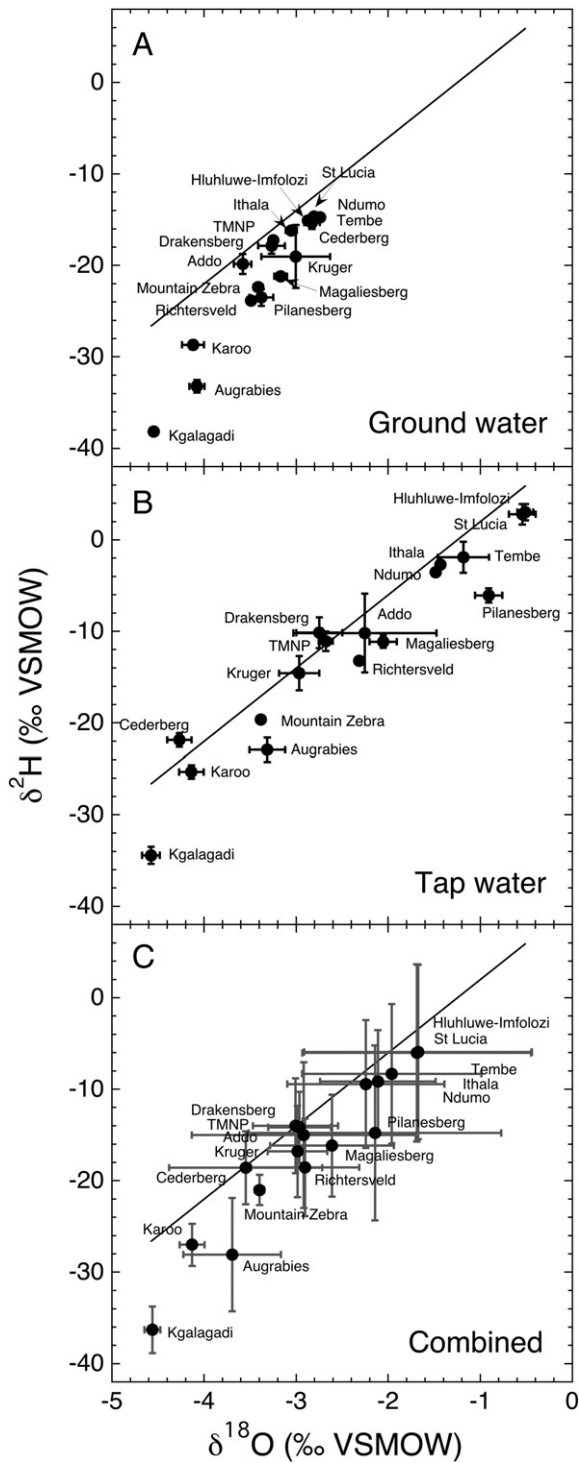
Fig. 8. Mean ± SE isotopic composition of tap water (A) and ground water (B) and combined tap and ground water (C) within major wildlife parks in South Africa. Solid line represents the Global Meteoric Water Line ($\delta^2H = 8*\delta^{18}O + d$). Key to names of parks: Addo - Greater Addo Elephant National Park, Augrabies - Augrabies Falls National Park, Cederberg - Cederberg Wilderness Area, Drakensberg - Ukhahlamba Drakensberg Park, Hluhluwe-Imfolozi - Hluhluwe-iMfolozi Park, Ithala - Ithala Game Reserve, Karoo - Karoo National Park, Kgalagadi - Kgalagadi Transfrontier Park, Kruger - Kruger National Park, Magaliesberg - Magaliesberg Nature Area, Mountain Zebra - Mountain Zebra National Park, Ndumo - Ndumo Nature Reserve, Pilanesberg - Pilansberg Game Reserve, Richtersveld - Richtersveld National Park, St Lucia - Greater St Lucia Wetland Park, Tembe - Tembe Elephant Park, TMNP - Table Mountain National Park.

may not accurately capture the spatial variability of δ^2H and $\delta^{18}O$ in precipitation across South Africa. Unfortunately there are very few data with which to further test this hypothesis at present. Improving our
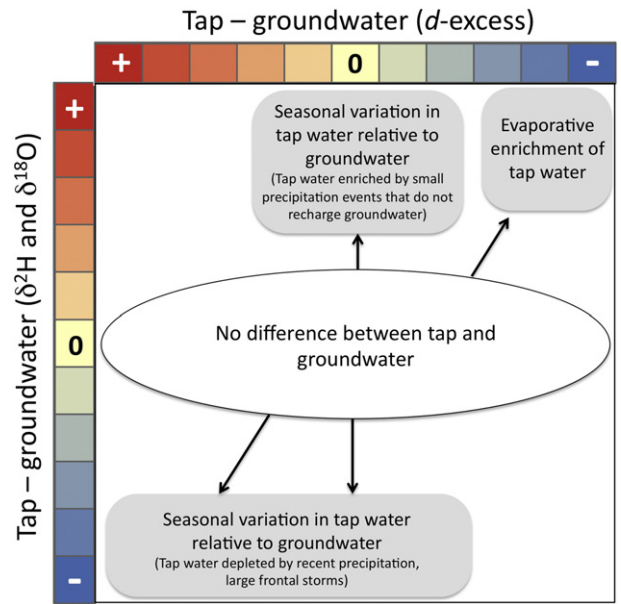
Fig. 9. Conceptual diagram showing interpretation of differences between δ^2H, $\delta^{18}O$ and d of tap water and ground water.

spatial estimation of precipitation isotopes across southern Africa should be a research priority, as a robust precipitation isoscape is of great importance for a variety of applications, including, but not limited to, palaeo-ecological climate reconstruction, migratory wildlife forensics and watershed hydrology.

5.4. What potential do these isoscapes have for forensic tracing of wildlife?

Our analysis of the isotopic composition of ground water and tap water in the major wildlife reserves in South Africa (Fig. 8) illustrates the potential to identify material originating in these areas. As the H- and O-isotopic composition of water is incorporated into plant and animal tissues in a predictable manner (Kahmen et al., 2011; Podlesak et al., 2008; West et al., 2008), forensic identification of illegally traded materials such as rhino horn, ivory, cycads and others from these parks may be possible. This is especially the case in areas where ground water and tap water have similar isotopic composition (Fig. 4). In areas where these water resources are not similar, quantification of temporal isotopic variance may be necessary, and may provide additional information that could be used to identify ecologically relevant seasonal patterns in isotopic composition of water source for plants (West et al., 2007) and animals (Wolf and del Rio, 2000). It is also important to note that surface waters consumed by animals may vary considerably from ground water and tap water as measured in this study. Systematic relationships between $\delta^{18}O$ of tooth enamel in African animals and environmental/meteoric waters have been convincingly demonstrated (Levin et al., 2006). Thus, while our data give a good depiction of the potential regional variability, investigation of additional factors influencing surface waters and plant and animal samples would improve the potential for forensic tracing of wildlife in this region.

6. Conclusion

Our survey of ground water and tap water across South Africa revealed a coherent spatial structure in δ^2H, $\delta^{18}O$ and d, as well as in isotopic offsets between ground water and tap water, that should aid a variety of applications, including hydrological, archaeological, ecological and forensic studies. In particular, the distinct isotopic composition of water resources in the major wildlife reserves across South Africa reveals considerable potential for wildlife forensics. The comparison of our ground water isoscapes to modeled isotopic composition of

precipitation across South Africa highlighted large discrepancies that may have important implications for estimation of precipitation H- and O-isotopes in this region. To what extent these discrepancies are due to the inability of global models to accurately predict the isotopic composition of precipitation across this poorly sampled, but important, region, or to temporal variability in the ground water and tap water, is currently unknown. Additionally, direct comparison between modern precipitation and ground water may be inappropriate in areas where abstraction is from aquifers containing fossil groundwater. Capturing the spatial variability of precipitation isotopes, the temporal variability of ground water and tap water isotopes, and improving estimates of ground water age would be important steps forward in resolving these issues.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.gexplo.2014.06.009. These data include Google maps of the most important areas described in this article.

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