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Stable isotope hydrology in fractured and detritic aquifers at both sides of the South Atlantic Ocean: Mar del Plata (Argentina) and the Rawsonville and Sandspruit river catchment areas (South Africa)

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ABSTRACT

The aim of this work is to characterize the isotope composition of water (^{2}H and ^{18}O) in order to establish the relationship between fractured and detritic aquifers in similar hydrological environments located at both sides of the Atlantic Ocean. The Mar del Plata zone, placed in the Argentine Buenos Aires province in South America, and the Rawsonville and Sandspruit river catchment areas, situated in the Western Cape province in South Africa were compared. Rainwater and groundwater samples from fractured and detritic aquifers were analyzed through laser spectroscopy. In both Argentina and South African study sites, stable isotopes data demonstrate an aquifers recharge source from rainfall. For the Mar del Plata region, two different groups of detritic aquifer's samples with distinct recharge processes can be identified due to the close relationship existing between the present hydrogeological environments, the aquifer's grain size sediments and the isotopes contents: one representing rapid infiltration in aquifer sediments of the creeks' palaeobeds and hills zones (sandy or silt sandy sediments) and the other with slow infiltration of evaporated water in plain zones with an aquitard behavior. In the last group, the evaporation process occurs previous infiltration or in the aquifer's non-saturated zone, because of the existence of very low topographic gradients and fine-grained sediments. The evaporation phenomenon is not evident in the Sandspruit river catchment site's detritic aquifer, because its sandy composition allows a faster infiltration rate than in the loess that compounds the Pampeano aquifer in the interfluves zones of the Argentinian study area.

1. Introduction

Mar del Plata and Cape Town cities, located to the southeast of the Buenos Aires province, Argentina Republic, South America and to the southwest of the Western Cape Province, South Africa Republic, Africa, respectively (Fig. 1), are two of the sites that were linked 200 million years ago within the Gondwana supercontinent (Suess, 1875; du Toit, 1937; Scotese and McKerrow, 1990; among others). These areas and their surroundings share some hydrological similarities and their geological setting, which determines the existence of detritic aquifers in modern sedimentary covers lying on and juxtaposed to fractured aquifers formed by quartzite rocks, as well as climatic regimes due to their latitudinal location on the Atlantic coast and a correlated effect from the sea temperature at the Southern Atlantic and Indian oceans (Fauchereau et al., 2003). Nevertheless, recent studies indicate the importance of the precipitation type on the isotope composition of precipitation, which can be the source of differences between locations (Aggarwal et al., 2016).

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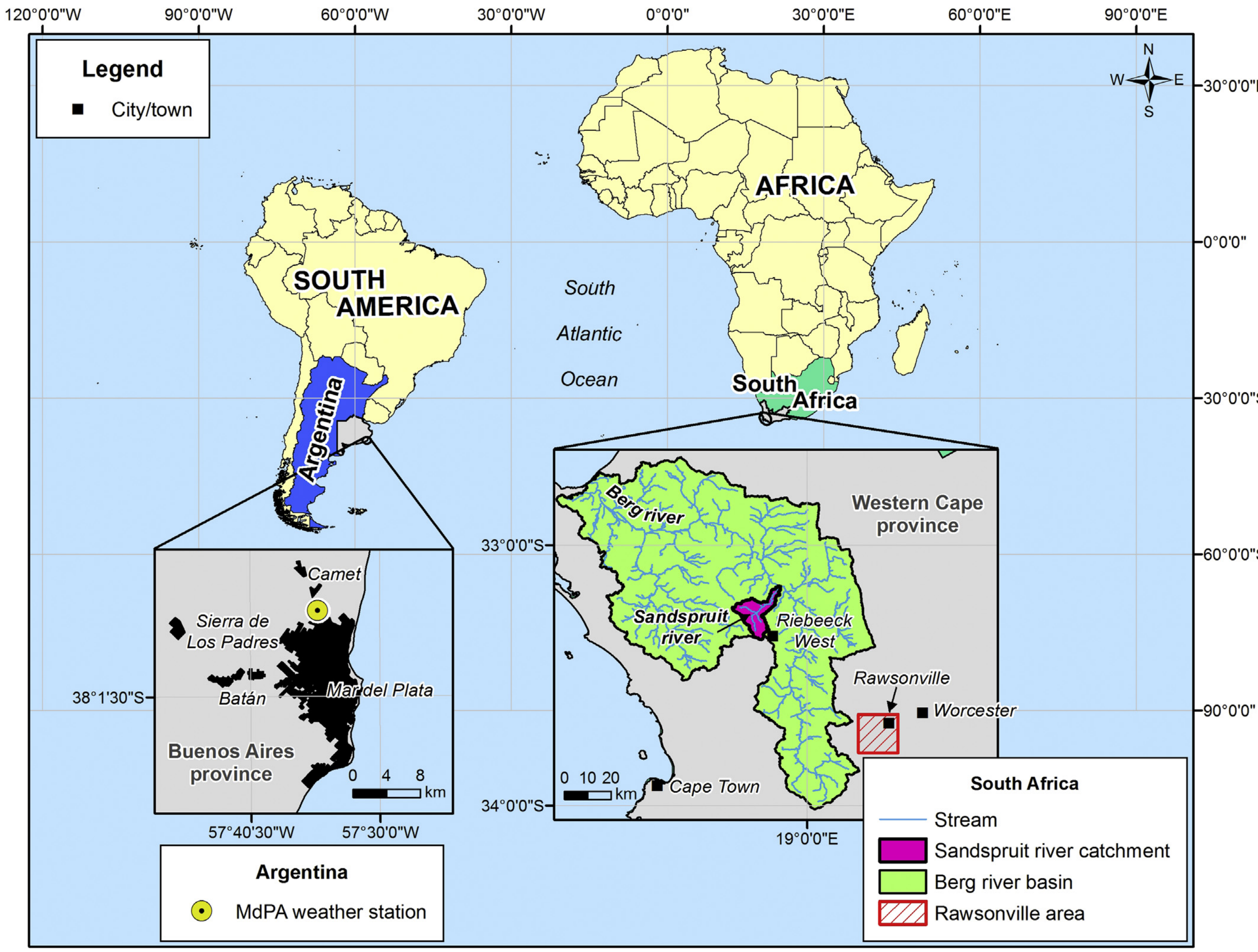

Fig. 1. Location map (MdPA weather station: "Mar del Plata Aeropuerto" weather station).

The lithological composition at both sides of the South Atlantic Ocean shows a similarity in its hydrogeological behavior, some units also showing an age correlation. Granitoids that are intruding the metamorphic rocks of the *Buenos Aires Complex* (Marchese and Di Paola, 1975a) and the *Malmesbury Group* (Hartnady et al., 1974), apart from their similar lithological behavior as impermeable basement, were emplaced in the Proterozoic Eon (Paleoproterozoic and Neoproterozoic, respectively). Regarding the *Balcarce Formation* (Ordovician-Silurian?) (Amos et al., 1972; Dalla Salda and Iñiguez Rodríguez, 1979) and the *Table Mountain Group* (TMG) (Ordovician-Devonian) (Rust, 1967; Visser, 1974), their quartzites rocks constitute the fractured aquifers of the Argentinian and South African areas, besides their depositional ages are the same (Middle Paleozoic Era, Phanerozoic Eon). Finally, the *Pampeano* and *Post-Pampeano sediments* (Frenguelli, 1950) and the *Springfontyn Formation* (Rogers, 1980) are Quaternary sedimentary sequences mostly composed by loess (Mar del Plata; Pliocene-Holocene) and sands (Cape Town zone; Pleistocene) deposits, forming the unconfined detritic aquifers of these sites, which are semiconfined and confined in parts in the Mar del Plata (*Pampeano aquifer*; Auge, 2004) and Cape Town (Rogers, 1980; Flugel, 1991) zones, respectively (Fig. 2).

The relationship between fractured and detritic aquifers is not well known in many areas, and sometimes the hard rock formations are considered just as hydrological basement. Nevertheless, being these two types of aquifers in contact, water transferences must be considered. Taking into account that the infiltration rate conditions, permeability and dispersivity in fractured and detritic aquifers are different, it can be assumed that evaporation during infiltration and mixing physical processes affect the stable isotope (deuterium, ^{2}H, and eighteen oxygen, ^{18}O) contents in rainwater and thus the groundwater isotope fingerprint during the aquifers' recharge. Most of the investigations on groundwater isotope composition indicate that, in temperate climates, it is close to the average rainfall composition because of a well-mixed system (Gat and Tzur, 1967). However, it can be expected a different isotope content comparing detritic and fractured aquifers' porosity (primary porosity versus secondary porosity). The aim of this paper is to verify that hypothesis through the stable isotopes characterization of water in both systems and to establish the relationship between fractured and detritic aquifers belonging to similar hydrogeological environments, situated on both sides of the South Atlantic Ocean. These are the Mar del Plata zone and two areas located around 90 km from Cape Town city: Rawsonville and Sandspruit river catchment (Fig. 1).

Isotopic techniques are a very useful tool for the understanding of groundwater dynamics in hydrologic systems. Physical processes and climate phenomena, responsible both for water transport in the different phases of the hydrologic cycle, produce an isotope fractionation that can be used to obtain conclusions about its

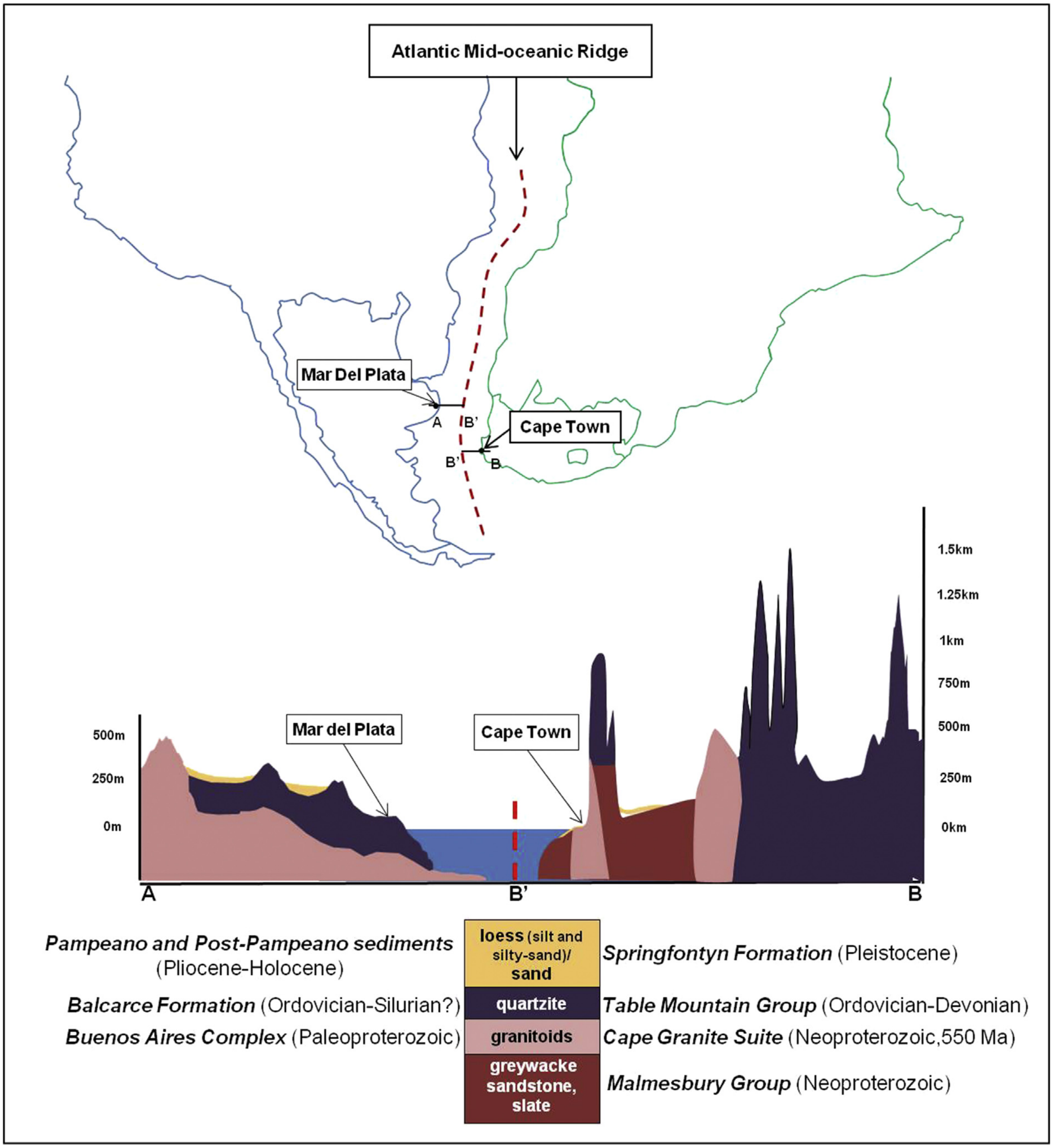

Fig. 2. Lithological (and age) correlations between the Mar del Plata and Cape Town areas.

source and behavior. In that way, the analysis of the isotopic fingerprint of the different hydrological cycle components may have a number of further applications such as recharge and discharge estimations, as well as the interpretation of groundwater-surface-water relationships, flow lines, water residence times in aquifers, evaporation rates, waters mixture and salinization processes, among others (Clark and Fritz, 1997; Kendall and McDonnell, 1998; Cook and Herczeg, 1999; Geyh, 2000).

Some contributions exist as background related to the stable isotope hydrology aspect that is considered in the present work. Bocanegra et al. (2013a,b) and Martínez et al. (2014) performed an isotopic characterization of the Mar del Plata area, as well as Demlie et al. (2011), Jovanovic et al. (2011), Bugan (2014) and Naicker and Demlie (2014); and on the other hand, Siwawa (2012), made the same for the Sandspruit river catchment and the Rawsonville area, respectively. In this way, an isotopic contrast among the same two types of aquifers (fractured and detritic) present at both sides of the Atlantic Ocean in the Southern Hemisphere can be a useful and interesting issue for future researches relating to hydrogeology topics.

2. Description of the study areas

2.1. Mar del Plata area, Argentina Republic

Mar del Plata city is the main Argentine seaside resort on the Atlantic coast (Fig. 1). It has a population of more than 600,000, and a tourist population that exceeds about two million visitors along the summer. Groundwater pumped from about 280 extraction

wells is the only available water resource for drinking, agricultural, and industrial use. This city is located on the northeastern side of the Tandilia System (Teruggi and Kilmurray, 1975, 1980; Dalla Salda et al., 2006; and references therein), which has a maximum altitude in the Mar del Plata area around 400 m above sea level (masl). This is a mountain range in blocks lined up according to three Tertiary faulting systems with directions NW-SE, NE-SW and E-W, producing horst and graben structures. Those blocks are formed by Precambrian crystalline basement rocks that conform the Buenos Aires Complex (Marchese and Di Paola, 1975a, b; Teruggi and Kilmurray, 1980), and Eopaleozoic orthoquartzites of the Balcarce Formation (Amos et al., 1972; Dalla Salda and Iñiguez Rodríguez, 1979) (Fig. 3).

The igneous-metamorphic Buenos Aires Complex consists mainly of granitic-tonalitic gneisses, migmatites, amphibolites, some ultramafic rocks, and granitoid plutons. This is partially covered by the Balcarce Formation, a marine platform sedimentary unit, both being the impermeable basement's components of the area. This last crops out along the southern edge of Tandilia from Olavarría (36° 54' S, 60° 20' W) to Mar del Plata at the Atlantic coast (Fig. 3). Though generally considered impermeable, the joints of these orthoquarzites produce a secondary porosity which is negligible as an aquifer with regard to the overlying detritic aquifer. Thereby, the Balcarce Formation constitutes the fractured aquifer in this study area.

The Pampeano aquifer is formed by an Upper Tertiary-Quaternary sequence of continental sediments, which lies sometimes directly over the Balcarce Formation and others over the Miocene deposit of marine green clays of the *Paraná Formation* (compounding the "Paraniana section" of Sala, 1975) (Groeber, 1954; Ruiz Huidobro, 1971). It comprises the Pampeano sediments "sensu strictu" (Lower Pliocene-Pleistocene) and the Upper Pleistocene-Holocene loessic sediments known as Post-Pampeano sediments (Frenguelli, 1950), which occupy the plain environment in this zone (Fig. 3). The first are loess-like sediments, although similar physically to loess, are mostly reworked loess, having been transported and deposited by streams. This multi-layer aquifer's thickness varies from a few meters to more than 100 m, and its grain size is variable, between sand and silt and with clay intercalations.

The phreatic level in the Mar del Plata area varies between 1 masl and 15 masl (Bocanegra and Custodio, 1994). The permeability of the detritic aquifer have been estimated at 10 m/d–15 m/d (Bocanegra et al., 1993), with transmissivities between 600 m^2/d and 800 m^2/d in urban areas and 1000 m^2/d and 1400 m^2/d in rural zones, because of variations in its thickness (Martínez and Bocanegra, 2002). Aquifer recharge is direct infiltration of rainwater (Martínez and Bocanegra, 2002; Massone et al., 2005; Quiroz Londoño et al., 2008; Glok Galli et al., 2014; Glok Galli, 2015) and it is around 150 mm/year (Bocanegra et al., 2001). The natural discharge is toward the sea, but surface streams are discharge areas for shallow groundwater. Regarding the groundwater ionic composition, this is of $Ca^{2+}+HCO_3^-$ type in the recharge zone (hilly area), and becomes $Na^++HCO_3^-$ type towards the discharge area (Martínez and Bocanegra, 2002).

The climate of the Mar del Plata region is temperate-humid with strong oceanic influence (Barry and Chorley, 1976), also called "Cfb" according to the Köppen climatic classification. Data collected from the "Mar del Plata Aeropuerto (MdPA)" (Airport of Mar del Plata city; 37° 56' S, 57° 35' W, 13.3 masl; Fig. 1) weather station indicate that the average annual rainfall is 930.6 mm/year (1970–2007). The warm season (October–March) is usually rainy and the highest precipitation occurs in December (101.5 mm/month). The cold season (April–September) has low rainfall and the lowest rainfall takes place in July (53.1 mm/month). Daily minimum and maximum temperature values are 5.6 °C (July 2007) and 22.7 °C (January 1983) in winter and summer, respectively (1971–2007). According to the Thornthwaite's method (Thornthwaite, 1948), the evapotranspiration for the period 1971–2007 is 732.1 mm/year. The excess of this one over rainfall is 197.6 mm/year, which occurs between April and November (Glok Galli, 2015).

2.2. Sandspruit river catchment area, South Africa Republic

The Sandspruit river catchment is located in the Western Cape province, near the town of Riebeeck West and is around 90 km to the northeast of Cape Town city. This catchment covers 152 km^2 and is a sub-catchment of the Berg river basin, the Sandspruit river

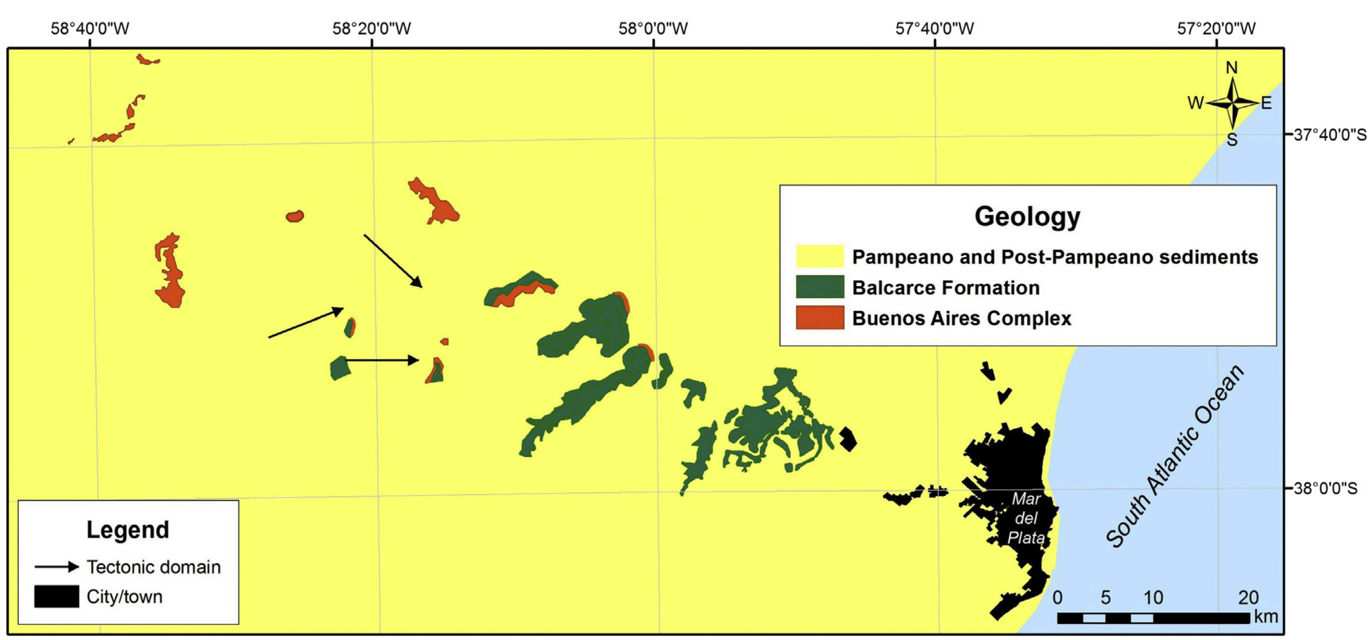

Fig. 3. Simplified geological map for the Mar del Plata study area.

being its main water body (Flugel, 1991) (Fig. 1). It has a gentle hilly topography, with the Eopaleozoic sandstones of the TMG (Rust, 1967; Visser, 1974) reaching an altitude of 700 m. The rest of the area has an altitude between 100 m and 200 m. Surface water and groundwater are primarily utilized for agriculture. Most of the natural vegetation in the area has been cleared for agricultural purposes, and the only natural remaining vegetation is mountain veld (Demlie et al., 2011). The primary land use practices are dryland farming with wheat being the predominant crop, livestock farming, and grapes farms for wine production. Other land uses include the growing of halophytic crops utilized for grazing (Flugel, 1991).

As can be seen in Fig. 4 (A, B), the geology is composed mainly of the Malmesbury Group (Hartnady et al., 1974), which covers about 90% of the Sandspruit river catchment site (Demlie et al., 2011). This Neoproterozoic age (575–540 Ma) sequence is the oldest rock formation and constitutes the basement of the zone, consisting of low-grade metamorphic rocks, with alternating layers of dark grey fine-grained greywacke sandstone and slate (Hartnady and Rogers, 1990; Theron et al., 1992). These were intruded at about 550 Ma by the *Cape Granite Suite* (Burger and Coertze, 1973) (see also Fig. 2), which occupies 1% of the total catchment's area. Though initially intruded at great depth, prolonged erosion eventually exposed the Cape Granite at surface and it now forms a basement upon which younger sedimentary rocks of the TMG were deposited about 450 Ma years ago. This covers 4% of the total catchment's area (Demlie et al., 2011) and is the oldest lithostratigraphic unit of the siliciclastic Paleozoic *Cape Supergroup* (Tankard et al., 1982). The TMG is mainly characterized by thick packages of medium to coarse-grained quartz-arenites, conglomerates and subordinate fine-grained lithologies (Rust, 1973). Much of the sandstone in this group recrystallized to quartzite during the Cape Orogeny (250 Ma; Hälbich, 1992). Movement of water through rocks of the Cape Supergroup is, therefore, primarily via these fractures because cementation destroyed the primary porosity (Diamond and Harris, 2000). Accordingly, the TMG constitutes the fractured aquifer in the Sandspruit river catchment zone.

The post-Paleozoic erosion has removed the TMG and the Cenozoic (recent) sediments that have been deposited cover approximately 6% of the catchment's area. These constitute the Springfontyn Formation (Early to Middle Pleistocene) (Fig. 4A and B), consisting of reddish to grey, unconsolidated quartzose aeolian sands, which are muddy and peaty in places (Rogers, 1980), alluvium and silcrete/ferricrete deposits. The coarse grained nature of the sands leads to a primary aquifer of significant exploitation potential (Maclear, 1995), thereby conforming the detritic aquifer of the study site.

Estimated recharge rates vary between 8 mm/yr and 70 mm/yr in the Sandspruit river catchment (Naicker and Demlie, 2014). Groundwater in this zone is highly saline due to the weathering of the Malmesbury shales which are saline in nature. As was mentioned above, groundwater occurs under both confined and unconfined conditions within this study area. Confined conditions are only present in the upper to middle catchment due to the presence of mud and peat layers. The mud and peat allow for the presence of a perched aquifer only during the rainy season (Flugel, 1991).

The climate is Mediterranean with warm dry summers and cool wet winters (semi-arid) (Bugan et al., 2009), typical of the Western Cape. Rainfall is generally in the form of frontal rain approaching from the North-West, extending normally over a few days with significant periods of clear weather in between, and occurs mainly in winter (from April until October). The mean annual rainfall varies from 300 mm/year to 500 mm/year (Jovanovic et al., 2011). The average annual evaporation is approximately 2200 mm, exceeding the average precipitation. Annual daily mean temperatures range between 8 °C–11 °C and 24 °C–31 °C in winter and summer, respectively (Naicker and Demlie, 2014).

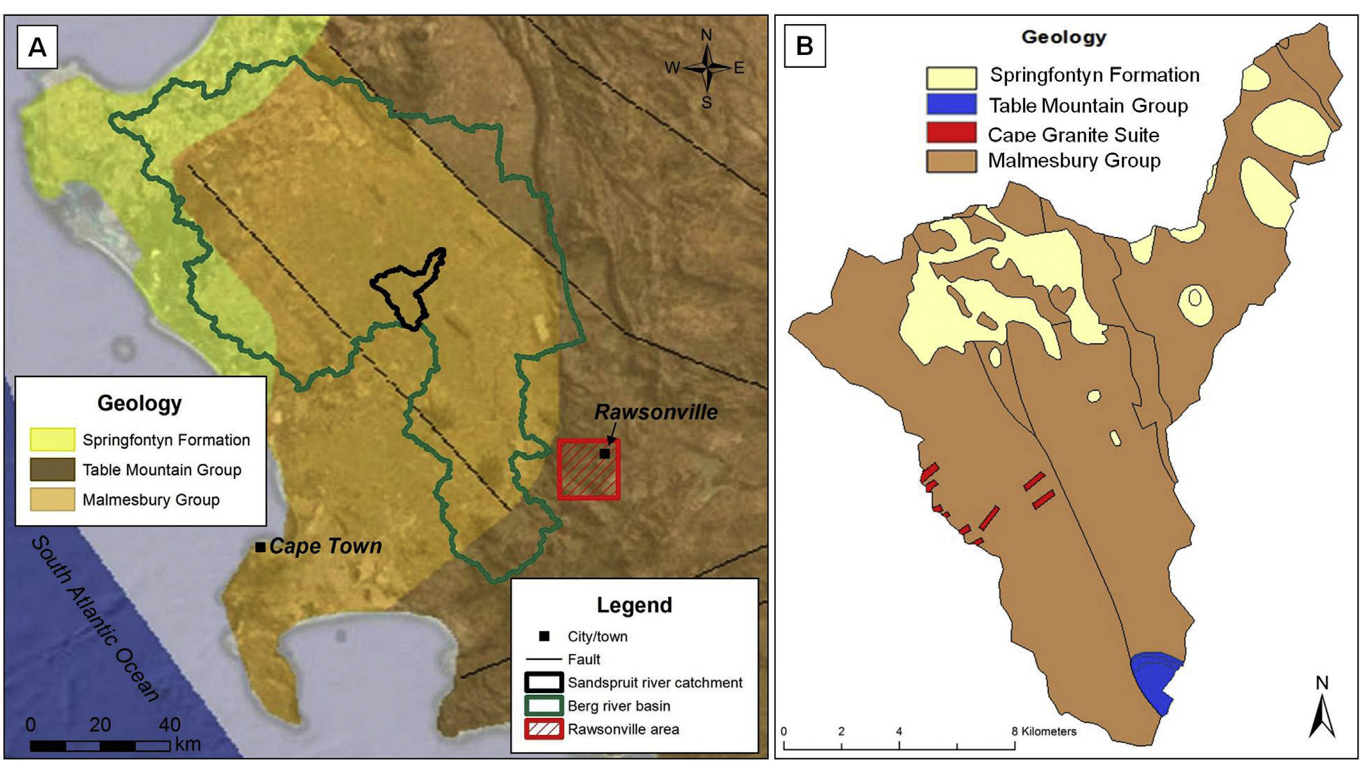

Fig. 4. A. Simplified geological map for the South African study areas **B**. Detailed geological map for the Sandspruit river catchment site (modified from Jovanovic et al., 2011).

2.3. Rawsonville area, South Africa Republic

The town of Rawsonville, Western Cape province, is approximately 90 km to the east of Cape Town city and the southeast of Riebeeck West town, and 15 km to the southwest of Worcester city (Fig. 1). In the area, groundwater is the most important source of fresh water supply for both domestic and agricultural uses, being abstracted principally from the TMG fractured aquifer. The topography is mostly mountainous with gravels, soils and alluvium covering the valley floors. The zone is renowned for its wine industry as agriculture (viticulture in particular) is the major land use type (Siwawa, 2012).

The geology of Rawsonville comprises rocks from the Cape Supergroup, with the main group being the TMG (Fig. 4A). The fractured aquifer permeability values are between 0.04 m/d–0.08 m/d, and the transmissivity ranges from 6.1 m^2/d and 14.7 m^2/d (Lin, 2008). Groundwater composition is dominated by a mixture of Na-K-Cl ions and classified as $Cl^- + SO_4^{2-}$ water type (Siwawa, 2012).

The climate is typically Mediterranean with some possible oceanic influences, characterized by the occurrence of warm, dry summers and mild and wet winters (occurrence of winter rainfall). Sometimes winters are frosty with heavy snowfalls at high altitudes. The average annual rainfall varies from 200 mm/year in the low lying areas and 1595 mm/year in the mountainous areas (Lasher, 2011). The highest rainfall is recorded during the months of July and August with the least rainfall occurring during the months of January and February. Daily minimum and maximum temperatures are 6 °C–7 °C and 20 °C in winter and 15 °C–18 °C and 35 °C in summer, respectively (Siwawa, 2012).

3. Materials and methods

A stable isotope characterization (^{2}H and ^{18}O) of precipitation and groundwater of the study areas were made. An orthogonal regression analysis was used to develop the Local Meteoric Water Lines (LMWLs; IAEA, 1992) that were compared to the Global Meteoric Water Line (GMWL; Craig, 1961) in conventional diagrams δ^2H versus δ^{18}O. In the case of the Argentinian side, the LMWL was taken from that obtained by Martínez et al. (2011), which includes data between 1986 and 2011 and was completed with new information until 2015, getting a total of 85 rainwater monthly composite samples. These belong to the rainfall station "LMP" ("Mar del Plata Rainwater"), located at the "Facultad de Ciencias Exactas y Naturales", Mar del Plata University, Mar del Plata city (Table 1 and Fig. 5). With regard to groundwater in this zone, 18 samples from the fractured aquifer taken in 2010, 2011 and 2013 from wells situated in the surroundings of Batán and Sierra de los Padres localities were used. For the detritic aquifer, 131 groundwater samples collected in 2009 and 2010, which correspond to extraction wells placed in the sub-urban and urban areas of Mar del Plata and near Camet town, were considered (Fig. 1).

On the other hand, being that the amount of precipitation samples collected in South Africa for the present study (26 monthly composite samples from the Rawsonville area) are not enough to obtain a LMWL of this zone, this was calculated from data available in the "Global Network of Isotopes in Precipitation (GNIP)" (IAEA/WMO, 2006) and in the work of Harris et al. (2010), from the Cape Town city International Airport ("CTA") and the Cape Town University ("CTU"), respectively, two stations located approximately 90 km from the Sandspruit river catchment and the Rawsonville study sites. For the first, 236 isotopes analyses for the period 1961–2012 were used, while for the CTU, 150 analyses for 1996–2008 were taken into account, having a total of 386 rainwater monthly composite samples. The Rawsonville area's data (taken from June to September of 2011) were plotted together with these samples, and correspond to 9 rainfall stations situated at different altitudes (Table 1 and Fig. 5). With regard to the groundwater isotope composition, 30 and 107 groundwater samples of the Rawsonville and Sandspruit river catchment areas' fractured aquifers, respectively, were used; the first collected in 2011. Meanwhile for the detritic aquifer, 28 groundwater samples of the Sandspruit river catchment were considered. In this study area, these last and the samples corresponding to the fractured aquifer were taken in 2013 and 2014 (Fig. 1).

All rainwater and groundwater samples were collected in 50 mL or 100 mL plastic bottles during sampling campaigns for posterior analyses. These were performed through laser spectroscopy methods (Lis et al., 2008) as prescribed by the International Atomic Energy Agency (IAEA, 2009), using a DLT-100 Liquid-Water Isotope Analyzer, Automated Injection, developed by Los Gatos Research. For Argentina, analyses were carried out at the Hydrochemistry and Isotope Hydrology Laboratory belonging to the "Instituto de Geología de Costas y del Cuaternario", Mar del Plata University. In the case of South Africa, these were realized at the Department of Earth Sciences of the University of the Western Cape in Cape Town. The results were expressed as δ values in permil (‰), defined as: $\delta = 1000\ (Rs\text{-}Rp)/Rp$ ‰, where δ is the isotopic deviation in ‰, s is the sample, p is the international reference, and R is the isotopic ratio (^{2}H/^{1}H, ^{18}O/^{16}O). The standard is Vienna Standard Mean Ocean Water (V-SMOW; Gonfiantini, 1978), and the analytical uncertainties were ±1‰ for δ^2H and ±0.3‰ for δ^{18}O.

4. Results

Precipitation and groundwater isotope data (δ^2H and δ^{18}O) of

Table 1
Locations (***Latitude*** and ***Longitude***), altitudes (*masl*: meters above sea level), obtained precipitation samples number (**n**) and sampling time periods for the rainfall stations of the Argentinian and South African study areas (**MDP**: Mar del Plata, **R**: Rawsonville, **CTA**: Cape Town Airport, **CTU**: Cape Town University).

Study area		Rainfall station	Latitude	Longitude	Altitude masl	n	Sampling time period
Argentina	MDP	LMP	38°0′20.3″ S	57°34′16.0″ W	15.1	85	1986–2011 + 2015
South Africa	Cape Town	CTA	33°58′10.0″ S	18°35′50.0″ E	44	236	1961–2012
		CTU	33°57′27.0″ S	18°27′38.0″ E	105	150	1996–2008
	R	R1	33°44′4.6″ S	19°14′33.7″ E	702	3	2011
		S1	33°43′52.7″ S	19°14′39.1″ E	650	3	(June to September)
		S2	33°43′28.9″ S	19°14′51.0″ E	570	2	
		S3	33°43′14.2″ S	19°14′59.4″ E	434	3	
		S4	33°43′3.0″ S	19°14′48.4″ E	291	4	
		S5	33°43′57.0″ S	19°17′7.5″ E	695	2	
		S6	33°43′30.0″ S	19°17′22.8″ E	594	3	
		S7	33°43′12.0″ S	19°17′26.0″ E	512	4	
		S8	33°42′35.6″ S	19°17′29.3″ E	395	2	

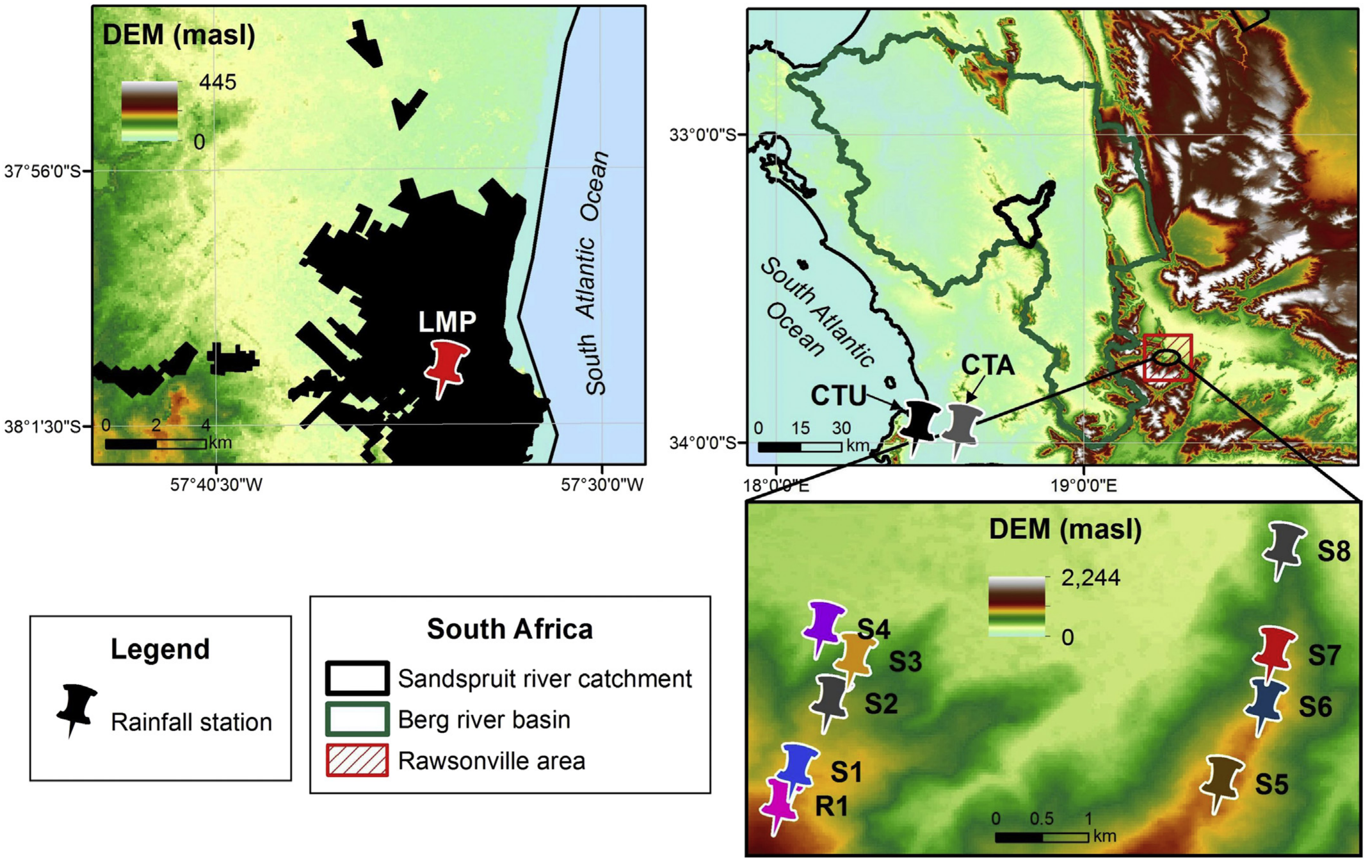

Fig. 5. Rainfall stations' locations for the Argentinian and South African study areas [**DEM (masl)**: Digital Elevation Model (meters above sea level), **LMP**: Mar del Plata Rainwater, **CTA**: Cape Town Airport, **CTU**: Cape Town University].

the Argentinian and South African study areas are presented in a "Supplementary Table" ("Supplementary Material"). The statistical parameters referred to the rainwater (weighted averages) and fractured and detritic aquifers' isotope composition located on both sides of the South Atlantic Ocean are shown in Table 2 and Fig. 6.

4.1. Mar del Plata area

As can be seen in Fig. 7, the LMWL (modified from Martínez et al., 2011) is given by the equation δ^2H ‰ = (7.95 ± 0.26) $\delta^{18}O$ + (11.26 ± 1.50) ‰ ($R^2 = 0.91$). Most of groundwater samples of both fractured and detritic aquifers appear grouped showing an isotope composition that approximates the average isotope composition of rainfall in the region. Some detritic aquifer's samples are arranged in a lesser slope line, with more enriched values (Table 2 and Fig. 6).

4.2. Sandspruit river catchment and Rawsonville areas

As is shown in Fig. 8, the LMWL for the Cape Town area is represented by the equation δ^2H ‰ = (6.37 ± 0.20) $\delta^{18}O$ + (8.45 ± 0.62) ‰ ($R^2 = 0.78$). Groundwater sampling points of the fractured and detritic aquifers in the two South African study areas show similar ^2H and ^{18}O contents to individual rainfall of the Rawsonville area, as well as to the mean isotope composition of the Cape Town zone (CTA + CTU) precipitation (Table 2 and Fig. 6).

In particular, the isotope composition of the Sandspruit river catchment's detritic aquifer is relatively more enriched and similar

Table 2
Statistical parameters related to the isotope composition of rainwater (weighted averages) and groundwater of the fractured and detritic aquifers of the study areas (**ARG**: Argentina, **SA**: South Africa, **MDP**: Mar del Plata, **CTA**: Cape Town Airport, **CTU**: Cape Town University, **R**: Rawsonville, **SRC**: Sandspruit river catchment, **RW**: rainwater, **FA**: fractured aquifer, **DA**: detritic aquifer, ***Min***.: minimum, ***Max***.: maximum, ***SD***: standard deviation, ***n***: samples number).

Study area		Type of water/Type of aquifer	δ^2H ‰				$\delta^{18}O$				n
			Min.	Max.	Mean	SD	Min.	Max.	Mean	SD	
ARG	MDP	RW	−103	0	−32	20	−13.7	−0.4	−5.4	2.5	85
		FA	−32	−22	−27	2	−5.7	−4.2	−5.1	0.4	18
		DA	−30	−13	−25	4	−5.8	−2.4	−4.7	0.7	131
SA	CTA+ CTU	RW	−41,6	44,8	−13	11	−6.8	13.6	−3.4	2.0	386
	R	RW	−27.7	1.7	−15.0	8.8	−5.96	−2.21	−3.90	1.11	26
	R	FA	−25	−19	−22	2	−5.3	−3.4	−4.3	0.5	30
	SRC	FA	−24	−10	−16	3	−4.5	−2.7	−3.7	0.4	107
	SRC	DA	−20	−8	v14	3	−3.9	−3.0	−3.5	0.2	28

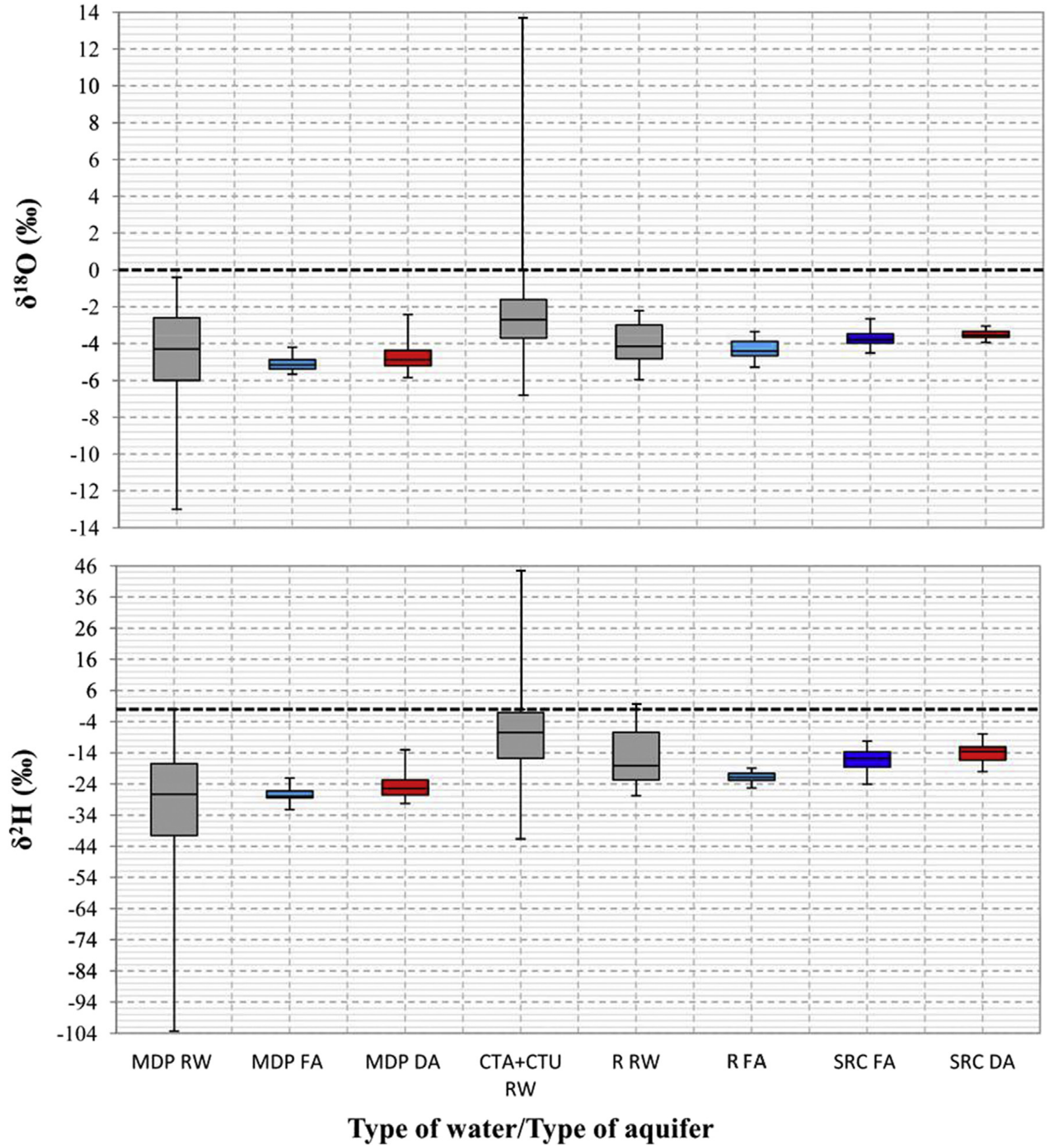

Fig. 6. Box-and-Whisker diagrams for the isotope composition (δ^2H and δ^{18}O) of rainwater and groundwater of the study areas (MDP RW: Mar del Plata rainwater, MDP FA: Mar del Plata fractured aquifer, MDP DA: Mar del Plata detritic aquifer, CTA + CTU RW: Cape Town Airport and Cape Town University rainwater, R RW: Rawsonville rainwater, R FA: Rawsonville fractured aquifer, SRC FA: Sandspruit river catchment fractured aquifer, SRC DA: Sandspruit river catchment detritic aquifer).

to that in the fractured aquifer of this site. As for the Rawsonville area's fractured aquifer, this shows more depleted ^{2}H and ^{18}O contents (Table 2 and Fig. 6), with a few samples plotted just under the GMWL and away from this cluster.

5. Discussion

At both sides of the South Atlantic Ocean, there exist similarities either in the hydrogeological behavior and the geological ages of the Mar del Plata and the Sandspruit river catchment and Rawsonville study areas' lithology. Isotopic signals are controlled by climatic processes, this being the basis for a comparison tending to identify differences in the isotope composition of fractured and detritic aquifers.

The more depleted δ^2H and δ^{18}O weighted mean values of rainfall in Mar del Plata (Table 2 and Fig. 6) can be related to the colder climatic conditions in this area due to the effect of the “Malvinas” Current on the Atlantic Ocean temperature, this being around 5 °C–10 °C lower on the southwestern Atlantic than in the southeastern Atlantic. These values could also be a consequence of the water vapor entry from the Equatorial Atlantic through the trade winds, which form part of the Hadley cell circulation transporting heat from equatorial to subtropical areas replacing hot air with colder air from higher latitudes, and generate convective rains that result in a more depleted rainwater average isotope composition for Argentina (Millero, 2013).

The average values of δ^2H and δ^{18}O for groundwater samples of the fractured and detritic aquifers in the area of Mar del Plata

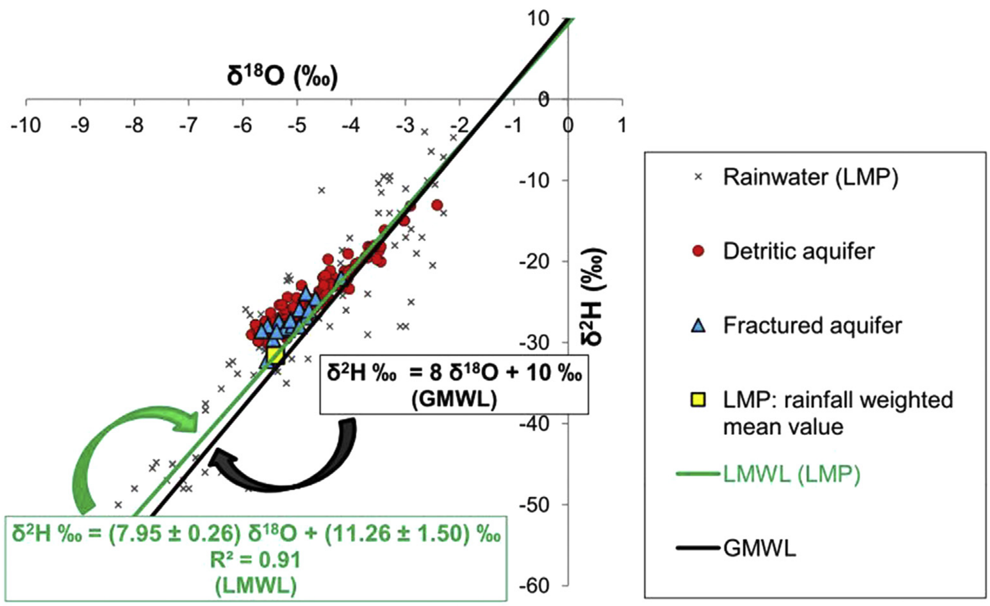

Fig. 7. Isotope composition (δ^2H and δ^{18}O) of precipitation and groundwater samples of fractured and detritic aquifers of the Argentinian study area (**LMP**: Mar del Plata Rainwater, **GMWL**: Global Meteoric Water Line, **LMWL**: Local Meteoric Water Line).

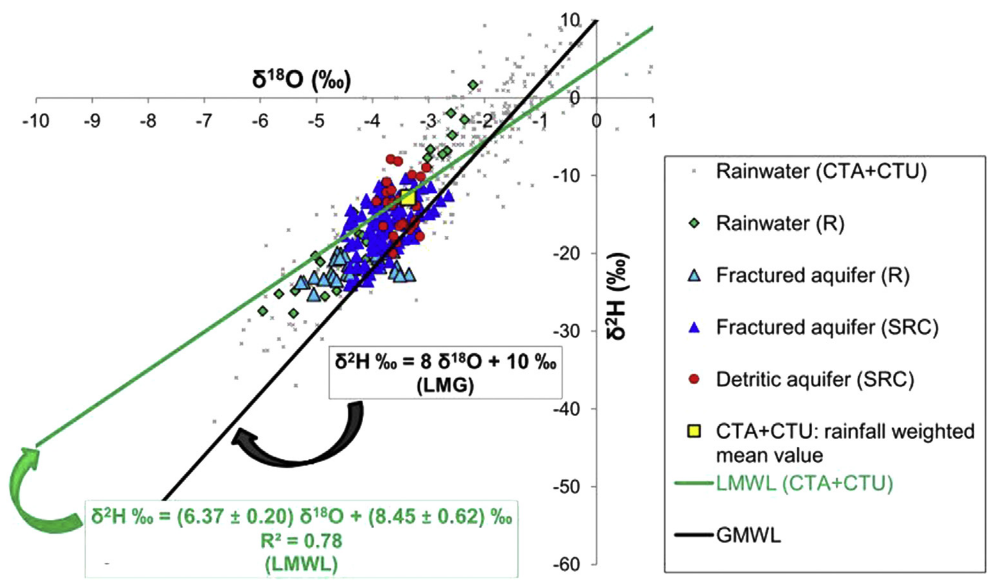

Fig. 8. Isotope composition (δ^2H and δ^{18}O) of precipitation and groundwater samples of the South African study areas (**CTA**: Cape Town Airport, **CTU**: Cape Town University, **R**: Rawsonville, **SRC**: Sandspruit river catchment, **GMWL**: Global Meteoric Water Line, **LMWL**: Local Meteoric Water Line).

generally approximate the mean isotope composition of rainfall in the region (Table 2 and Fig. 6). This fact supports that these aquifers have their recharge source from rain infiltration. Some detritic aquifer's samples are arranged in a lesser slope line, with a more enriched composition (Fig. 7), thus existing two groups of detritic aquifer's sampling points. Although in general this aquifer's wells depths are not different, an isotope composition's zonation existence was previously demonstrated by Bocanegra et al. (2013a,b) for the Mar del Plata zone. Only a few samples correspond to domestic wells are probably shorter in depth, but these do not have different isotopes contents (these are characterized by depleted δ^2H and δ^{18}O values). These authors have performed an integrated analysis of the hydrogeological environment present in this region, such as the hilly area and the plain area that comprises interfluves and palaeobeds, in relation to the distribution of δ^{18}O (and δ^2H). Close to the creeks' palaeobeds and the hills, where sediments are sandy or silt sandy, isotopes values were depleted which imply rapid infiltration, whereas in the interfluves, with a sequence of clayed silt sediments, values were enriched due to evaporation previous infiltration or in the aquifer's non-saturated zone, because of the existence of very low topographic gradients (Glok Galli et al., 2014) and fine-grained sediments, that minimizes surface runoff and favors soil waterlogging. In that way, the close relationship between the hydrogeological environments, the detritic aquifer's grain size sediments and the isotopes contents allows the identification of different processes of recharge: rapid infiltration in aquifer sediments in palaeobeds and hills zones and slow infiltration of evaporated water in plain zones with an aquitard behavior.

Finally, the isotope composition of the Mar del Plata's fractured aquifer is similar to that of the detritic aquifer with depleted values because a typical faster infiltration along the fractures and the possibly existence of water transfer between them (hills area).

On the other hand, similarities between the stable isotopes composition in precipitation (Rawsonville + CTA + CTU) and the fractured and detritic aquifers of the two South African study zones (Table 2 and Fig. 6) indicate that groundwater was recharged also by direct infiltration of rainwater. Additionally, the evaporation at the non-saturated zone phenomenon previously named for the Mar del Plata's interfluves zones is not evident in the detritic aquifer of the Sandspruit river catchment site, probably because its lithological composition (sands) allows the occurrence of a faster infiltration rate avoiding this process apparition.

In the case of the Rawsonville area, the depleted δ^2H and $\delta^{18}O$ values characteristic of this zone's fractured aquifer (Table 2 and Fig. 6) could be due to the aquifer recharge during winter months (seasonal effect; Dansgaard, 1964). Nevertheless, is premature to perform an adequate interpretation because the short rainwater record presented in the site. This can also be accompanied by the amount effect (Dansgaard, 1964), being that the average annual rainfall in Rawsonville is around 1600 mm/year in the mountains areas (Lasher, 2011) where the rainfall stations are located, against the mean annual precipitation value of approximately 350 mm/year of the Sandspruit river catchment (Naicker and Demlie, 2014). That is probably the reason because the isotope composition of the Rawsonville fractured aquifer does not match with that of the Sandspruit river catchment area's detritic aquifer. Finally, those Rawsoville fractured aquifer's sampling points plotted just below the GMWL and away from the cluster may be due to the occurrence of winter snowfalls at high altitudes. In this case, various post-depositional processes, such as melting and subsequent infiltration of surface layers and evaporation, may alter the isotopic content of the snowpack, often leading to meltwater δ^2H and $\delta^{18}O$ values that become progressively enriched (deuterium excess < 10) (Stichler, 1987).

6. Conclusions

In the Argentinian and South African study zones, the average isotopes compositions of groundwater and precipitation are similar, supporting the aquifers recharge source from rain infiltration and the possibly existence of water transfer between the two types of aquifers (fractured and detritic) in both cases. Otherwise, the main difference between these environments is given by the distinct grain sizes that conform their detritic aquifers. In sites where the grain size is fine sand or smaller like in the Mar del Plata interfluves zones (where, in addition, the topographic gradients are very low), detritic aquifers tend to have a more enriched isotope composition than fractured aquifers because of the time lag in the non-saturated zone allowing some evaporation. On the other side, where the grain size is over medium sand, i.e., the creeks' palaeobeds and hills areas of Mar del Plata and the Sandspruit river catchment, the faster infiltration rate avoids this process occurrence.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jsames.2016.12.006

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