

This is the accepted manuscript version of the contribution published as:

Cendón, D.I., Haldorsen, S., Chen, J., Hankin, S., **Nogueira, G.E.H.**, Momade, F., Achimo, M., Muiuane, E., Mugabe, J., Stigter, T.Y. (2020):
Hydrogeochemical aquifer characterization and its implication for groundwater development in the Maputo district, Mozambique
Quat. Int. **547** , 113 – 126

The publisher's version is available at:

<http://dx.doi.org/10.1016/j.quaint.2019.06.024>

Hydrogeochemical aquifer characterization and its implication for groundwater development in the Maputo district, Mozambique

Dioni I. Cendón^{1,2}(corresponding author), Sylvi Haldorsen³, Jianjiao Chen⁴, Stuart Hankin¹, G.E. H. Nogueira⁵, Fátima Momade⁶, Mussa Achimo⁷, Elonio Muiuane⁷, João Mugabe⁷, Tibor Y. Stigter⁸

¹Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia.

²Connected Waters Initiative, School of Biological, Earth and Environmental Sciences, The University of New South Wales, Sydney, Australia.

³University of Life Sciences, Faculty of Environmental Sciences and Natural Resource Management, N-1433 AAs, Norway.

⁴Guangdong Key Laboratory for Urbanization and Geo-simulation, School of Geography and Planning, Sun Yatsen University, Xingang Xi Road 135, Guangzhou 510275, China.

⁵Helmholtz Zentrum für Umweltforschung - UFZ, Hydrogeology Department, Permoserstrasse 15, 04318, Leipzig, Germany.

⁶Southern Petroleum, Zedequias Manganhela Av., 1390, Maputo City, Mozambique.

⁷Eduardo Mondlane University, Department of Geology, P.O.Box 257, Av. de Moçambique Km 1.2, Maputo, Mozambique.

⁸UNESCO-IHE, Department of Water Science and Engineering, Delft, The Netherlands.

KEYWORDS:

Quaternary sand dune aquifers; Groundwater residence time; Radiocarbon; Tritium; Maputo; Mozambique.

ABSTRACT

Quaternary sand dunes and underlying Pliocene-Oligocene materials host the key groundwater resources that provide the only source of drinking water to a large proportion of Maputo district (Mozambique). These resources are at risk due to potential over exploitation, pollution and salinization. Few hydrogeochemical studies have been conducted with generally poor quality assurance and availability of the datasets. This study provides the first isotopic results to calculate groundwater residence times in the region. All new data is complemented with other quality-curated datasets, providing a general review of shallow groundwater processes in the Maputo district. Groundwater samples were obtained from multi-level monitoring piezometers constructed and maintained by the local water administrator (ARA-Sul). Analysis in monitoring bores included major ions, selected minors and traces, water stable isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$), carbon stable isotopes in dissolved inorganic and organic carbon ($\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{DOC}}$), strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$), radiocarbon ($^{14}\text{C}_{\text{DIC}}$) and tritium (^3H). Other groundwater samples from drinking bores and rainfall samples were analysed for water stable isotopes.

The Quaternary sand dunes, where present, act as recharge “windows” along elevated areas parallel to the coast. Recharged water evolves from a Na-Cl-type to Na-HCO₃-type groundwater with depth interacting with carbonate cements in underlying calcarenites and being subjected to ion exchange

processes following a freshening trend (uptake of Ca, release of Na). The absence and/or thickness of underlying clay-rich layers control flow into deeper aquifers as well as vulnerability to transport of pollutants. Recharge is controlled by major rainfall events with smaller rains showing strong evaporation effects on water stable isotopes and limited or no influence on recharge. Groundwater residence times within Quaternary sand dunes are of a few decades as supported by measurable tritium. Deeper portions of the semi-confined aquifer (e.g. 23PZ) have no tritium and could have residence times of up to 1000 yr. Groundwater recharged through Quaternary sand dunes north of Marracuene show low major ion concentrations, low dissolved organic carbon and low nitrate concentrations suggesting a fairly healthy groundwater system. However, closer to the city center the combined effect of large pollution sources and thinner or absent confining layers have exposed sections of the semi-confined aquifer to nitrate levels above international guidelines.

1. INTRODUCTION

Despite efforts to increase drinking water supply in Maputo (Mozambique) only 45-62% of households, mostly in centric areas, have access to the piped-water network (Gumbo, 2004; Matsinhe et al., 2008). The limitations of surface water infrastructure have been known for decades (Bosazza, 1954; BURGEAP, 1962; Freitas, 1962; Romano, 1964). However, as the Maputo conurbation grew, population was forced to access groundwater to satisfy human drinking water demands. Increasing numbers of bores were dug particularly since the mid-1980's, resulting in many areas of the city fully relying on small-scale independent groundwater providers (Matsinhe et al., 2008). Mozambique and the Maputo province in particular, with a current population of ca 2.5 M inhabitants, have one of the highest population growth-rates in Africa at 3.5 % (INE, 2017). Population pressure, rising temperatures, droughts and sea-level rise associated to climate change projections (NCFEA, 2015) will increase pressure on secure water resources and particularly groundwater.

Groundwater in the Maputo district is mostly sourced from Quaternary sand dune systems with shallow phreatic aquifers. Sanitation in these peripheral populated areas often relies on in-situ pit latrines and septic tanks (Muchimbane, 2010). Current practices make groundwater in Quaternary sand sediments vulnerable to pollution. Efforts to ensure a safe groundwater supply have concentrated in the deepening of bores, tapping into underlying semi-confined aquifers, where variable thickness of clay form a protective layer to underlying aquifers. However, even in inland portions of the semi-confined aquifer, groundwater shows high salinities locally, related to mixing with trapped seawater. The proximity to low coastal areas further raises the concern of seawater intrusion. Both inland and coastal processes limit the availability of safe groundwater (Nogueira, 2017).

The local government through the Southern Regional Water Authority (ARA-Sul) has invested in groundwater characterization programs and installed a network of monitoring bores that aims to improve management of groundwater resources (Hydroconseil and WE Consult, 2011). However, little quality-assured information is available to understand the origin, interactions and vulnerabilities of these key groundwater resources. Even less hydrochemical or isotopic studies are available that could help to characterise groundwater residence times as well as major processes in the coastal quaternary sand dunes aquifers of Maputo district.

Environmental isotope techniques have been widely used to characterize interactions within coastal aquifers (Böhlke and Denver, 1995; Akouvi et al., 2008; Currell et al., 2013; Cendón et al., 2014; Lee et

al.. 2016 amongst many others). However, their application is lagging behind in developing countries such as Mozambique. The work presented was developed under the auspices of a UN project (IGCP-618) “*Palaeoclimate information obtained from past-recharged groundwater*”. Initially, designed as a training sampling, the quality of the data obtained, its combination with pre-existing studies and uniqueness in the region afforded the opportunity to review the behaviour of groundwater in shallow Quaternary aquifers. The isotopic data presented, albeit limited in number, provides regional groundwater interpretations of value to local managers, in a traditionally data poor region. Similar approaches could be implemented in many data-poor regions worldwide, with economically affordable, quality proven small isotopic data sets providing the bases for interpretations. The aims of the study are to: A) provide a quality-checked review of all hydrogeochemical information available in groundwater from Maputo district shallow aquifers; B) provide, to our knowledge, the first detailed multi isotopic work including determination of groundwater residence time in the Maputo district; C) explore links between local geology and the observed hydrochemical evolution of shallow groundwater; and finally D) provide a methodological benchmark that serves future sampling in the region and other data-poor locations.

2 STUDY SITE BACKGROUND

2.1 CLIMATE

Mozambique has a tropical to subtropical climate with maximum rainfall during the months of October to March. The region around Maputo features a tropical savanna climate, characterised by two well defined seasons. The wet season concentrates about 60% of all rainfall, coinciding with the summer. The dry season extends through the rest of the year with both wet and dry extremes separated by a sort transitional period generally in September and April respectively. The average rainfall (1966-1996), for the three meteorological stations covering the study area is similar with a small rainfall increase towards the north and values of 829 mm in Maputo city, 877 in Marracuene and 891 mm in Manhiça (Westerink, 1996). The average calculated potential evapotranspiration (Penmann-Montheite method) is very similar in the whole study area and has an average of 1450 mm (Westerink, 1996). Rainfall is ultimately linked to the positioning of the Intertropical Convergence Zone and its south displacement with potential wetter or drier years than average being frequent. The Maputo district has a relatively cool climate averaging 22.8 °C. The hottest month is January with mean temperature 27 °C, while the coolest month July has a mean temperature around 19 °C.

2.2 GEOLOGY

The Rovuma basin in the north and the larger Mozambique Basin in the south are the two main sedimentary basins in Mozambique (Fig. 1). The Mozambique Basin extends from the Zambezi River in the north to the South African border in the south, where it continues into the KwaZulu-Natal Province. The southern part of the Mozambique Basin borders the Jurassic volcanic rocks in the west, the same rocks forming the basement of the sedimentary basin. The Maputo district is situated in the southern part of the Mozambique Basin. A variety of Cretaceous rocks, gently dipping eastwards, form the lowest part of the basin’s sedimentary complex. Its lowest part is predominantly coastal and shallow water conglomerates and marls, grading upwards into fine-grained arenaceous sands and shales. The upper Cretaceous consists of an intercalation of quartzitic sandstone and dark argillites (Lächelt, 2004). The Cretaceous is overlain by Cenozoic sediments, which consist of a wide-spread variety of limestones, clayey marls and sandstones.

Several Mesozoic and Cenozoic transgressions have been identified along the southern African coast, the last during the Miocene into the Middle Pliocene. Rocks formed during this transgression are found up to more than 200 m altitude (Siesser and Dingle, 1981) and are overlain by Quaternary sediments in most of the Maputo district.

Aeolian and alluvial sedimentation has dominated after the Pliocene regression. The aeolian sediments consist of fine sand, and represent the main surface sediment in the Maputo district. The alluvial deposits are found along rivers, like the Incomati (Fig. 1) and consist of different sediments from clay to gravel. The Quaternary landforms are characterised by plains alternating with dunes. The youngest sediments are located close to the coastline, where the aeolian processes are active today (Momade et al., 1996). Detailed descriptions of the Quaternary sand dune systems, particularly in the Inhaca barrier island (Maputo Bay) and northern KwaZulu-Natal Province, South Africa can be found in Peché (2012) and Botha and Porat (2007) respectively. South African highstand shorelines during both MIS substages 5c and 5e appear to reach about 4 m amsl. The Holocene sea-level record in South Africa indicates a maximum highstand of ca. 3.5 m amsl (Ramsey and Cooper, 2002). It has been assumed that this was also the Holocene highstand on the Inhaca island in the Maputo Bay (Været et al., 2012), and thus also in the Maputo district.

Bouman (1985) distinguishes four lithological domains in the study area: a) Modern coastal dunes expanding north, parallel to the coast and the Incomati River (these are made out of fine clear sands); b) Alluvial valley, clayey sediments following the Incomati, Matola and Infulene Rivers; c) Inland dunes also named as “old dunes” or “red sand dunes” (Ponta Vermelha Fm) extending to the coast bordering Maputo city and made of ferruginous coated sands intercalated with some clay beds with clay content increasing to the north-west.

2.3 HYDROGEOLOGY OF THE MAPUTO DISTRICT

Several hydrogeological units are described in the area. Freitas (1962) differentiates three simple units: modern coastal sands, older inland sand and underlying sandstones. Bouman (1985) with improved drilling records differentiates several units from older to younger sediments. The Upper Cretaceous Grudja Formation, composed of clay and fine sands is generally regarded as an aquitard (Smidt et al., 1989). The overlying Salamanga Formation of Oligocene age is made out of calcareous sandstones in the eastern and western areas with higher clay content in the central part of study area. Above the Salamanga Formation particularly to the north, Miocene deltaic deposits have been described (Bouman, 1985). A widely distributed clay rich confining-layer separates the Salamanga Fm from the overlying Upper Pliocene-Quaternary aeolian sand dunes, its age is not well defined and in some areas more than one layer has been intersected during drilling. Apart from the Incomati River valley, composed of Quaternary alluvium, Quaternary Inland dunes have a ferruginous semi consolidated aspect on the surface passing gradually into yellow and white sand with depth (Momade et al., 1996). Holocene Coastal dunes are mostly formed of white sands (Cooper and Pilkey, 2002).

The above hydrogeological units have been simplified as phreatic and semi-confined aquifers (Bouman, 1985; Hydroconceil and WE consult 2011; Nogueira 2017). These terms are loosely defined and aquifer assignments are based on driller assessments. Phreatic aquifer refers to shallow groundwater within Quaternary dunes (inland and coastal) and alluvial materials along the Incomati River valley. The semi-confined aquifer corresponds to mostly deeper Paleogene (Salamanga Formation) and Neogene materials of Miocene to Pliocene age. Transmissivity values obtained from pumping tests between

Maputo city and Bobole range from 120 to 722 (m²/d) for the sands in the phreatic aquifer to 250 to 1660 (m²/d) in the sandstone/calcarenite (semi-confined) aquifer (Bouman, 1985).

In 2010 a drilling program carried out by ARA-Sul (Administração Regional Águas do Sul) installed 25 new monitoring bores (PZ series). At most locations, two piezometers were installed, generally one in the upper phreatic aquifer and one in the lower confined or semi-confined aquifer (Hydroconseil and WE consult, 2011). Final bore depths vary from 7 to 63 m. During the drilling program it was found that the confining layer varies in thickness being 0-10 m in the south and northeast and up to 60 m in the north west (Hydroconseil and WE Consult, 2011, p. 99).

In general groundwater shallow systems recharge in the elevated sand dunes and groundwater in both phreatic and semi-confined units flow towards the river valleys and the ocean (Smidt and de Sonnevile, 1990). Numerous springs have been identified along the Incomati River valley (Bouman, 1985). Despite concerns, no direct evidence of seawater intrusion has been identified as yet. However, indications of an abstraction cone in a heavily irrigated area were identified in 1960 between Mannhiça and Xinavane (Bouman, 1985).

2.4. PREVIOUS HYDROGEOCHEMICAL STUDIES

Early lithological information and geochemical data were reported by Bosazza (1954) for southern Mozambique. Only total dissolved solids and selected elements were analysed (Cl, SO₄, SiO₂, Na, Ca, Mg). Samples were collected during drilling or soon after. Anomalous high pH's (>9) were probably related to well construction reactions or mixing with drilling fluids. For example the same bore sampled in the Matola area varied in chloride and sulfate concentrations from 178 mg/L (Cl) and 41 mg/L (SO₄) in the first sample to 28.4 mg/L and 4.9 mg/L respectively for a second sample collected during a pumping test conducted four months later. No data is available on sampling depths or how samples were collected or analysed in most cases. Freitas (1962) provides a summary of lithological and hydrological information in the Maputo district. His work links high total dissolved solids (TDS) values to inland older Quaternary sand-dunes, and interestingly rules out the presence of nitrites in groundwater samples obtained from sands and sandstones in the city during the late 1950's.

In the mid-1980's several investigations were summarised in several reports (De Sonnevile, 1984 and Bouman, 1985). Groundwater from the semi-confined aquifer in Maputo district was analysed and reported in Piper diagrams (Smidt and de Sonnevile, 1990), unfortunately we had no access to the original raw data for reprocessing and quality assurance. More recently several studies have been carried out and details are provided in following sections.

3. FIELD AND LABORATORY METHODS

A total of four monitoring wells from ARA-Sul were accessed for groundwater collection during October 2013. All monitoring wells have PVC casing and are screened at specific depths (Table 1). Unlike other studies where groundwater was manually bailed out, we retrieved samples with a low flow bladder pump connected to a small portable compressor and controller purposely designed and constructed for this sampling. No drawdown was detected during conditioning or during sampling, ensuring representative samples were obtained from the screened intervals. Physico-chemical parameters were

monitored within an in-line flow cell fitted with a multi parameter probe. Specific conductivity (SC), dissolved oxygen (DO), temperature, pH and Eh were monitored. Bores were pumped until parameters stabilized, typically within 1-2 hours, then the flow cell was by-passed and samples were collected from an in-line 0.45 µm high capacity filter minimizing atmospheric contact. A further five production wells fitted with in-situ hand pumps were also sampled but not to the same detail due to the uncertainty on their total depth and construction details.

Further information on bottle preparation, field collection, sample preservation and analytical techniques can be found in Cendón *et al.* 2014, 2015. In brief, total alkalinity was determined in the field by direct titration using a digital titrator and standardised H₂SO₄ acid at 0.1600 N (± 0.0008 N). Ion Chromatography (IC) was used to analyse major anions. Major cations and select minor elements were characterised by inductively coupled plasma atomic emission spectroscopy (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS) (Table 1). Selected elements were analysed with a pre-concentration Sea-Fast system attached to the ICP-MS, this included uranium concentrations. Water stable isotopes (δ²H and δ¹⁸O) and carbon δ¹³C for both dissolved inorganic and organic carbon were determined by isotope ratio mass spectrometry (IRMS). The ratio of radiogenic to stable strontium isotopes (⁸⁷Sr/⁸⁶Sr) was determined by thermal ionization mass spectrometry (TIMS). Radioactive ³H and ¹⁴C_{DIC} measurements were done via electrolytic enrichment followed by liquid scintillation and by accelerator mass spectrometry (AMS) respectively.

Calculations necessary to assess electrical neutrality, dissolved element speciation, and saturation indices for common mineral phases were undertaken using the WATEQ4F thermodynamic database in the PHREEQC program (Parkhurst and Appelo, 1999). These calculations formed the bases for quality assurance of all available major ion analysis. Samples with charge balance >10% were rejected and are not included in this study. Three additional studies provided the bulk of major ion information with 10 samples incorporated from Muchimbane (2010) of a total of 20 analyses; 21 analyses were incorporated from Adonis (2007) of a total of 32 analyses; and a total of 50 samples from Nogueira, (2017) for a total of 60 groundwater analyses. Out of the 86 samples used in this paper, 22% had CBE% between 5 and 10%. Other major ion data sets were assessed but rejected due to incomplete analysis or missing information (location of sampled bores, units and/or analytical methods). The relatively high number of rejected samples is probably due to the challenge associated to sample preservation and availability of analytical facilities.

The inverse modelling code NETPATH (Plummer *et al.*, 1994) was used to correct ¹⁴C data. Details on the input parameters for calculations are discussed below.

4. RESULTS

New results are briefly presented with comparison to other data sets, if available. Sampled groundwater is circumneutral in pH with electrical resistivity <500 µS/cm. This is similar to results from the same or closely located piezometers (Nogueira, 2017). A higher electrical conductivity is observed in samples reported by Adonis (2007). This is due to all samples being recovered just above the intertidal zone or in the barrier islands off the main coast with some bores reaching the fresh-salt water interface.

Groundwater in the phreatic aquifer tends to be of the Na-Cl-type (i.e. 5PZ), while groundwater in the semi-confined aquifer is generally of the Na-HCO₃-type (i.e. 3PZ, 4PZ and 23PZ). Bicarbonate concentrations are low in the phreatic aquifer (i.e.: 5PZ, HCO₃=43 mg/L) and increase in deeper

groundwater sampled from the semi-confined aquifer (i.e.: 4PZ, $\text{HCO}_3^- = 172 \text{ mg/L}$). This is also confirmed in results reported by Adonis (2007) and Nogueira (2017). Groundwater obtained from private wells in populated areas show variations in the main cations, changing from Na to K or Mg (Muchimbane, 2010). NO_3^- and NO_2^- concentrations above the detection limit have only been detected at Manhiça (23PZ) with a concentration, well below guideline/trigger values of 50 and 3 mg/L respectively (WHO, 2011). Cl/Br ratios are close to those expected from marine derived rainfall (Cl/Br=650) in two samples (23PZ, 4PZ) while the other two (5PZ, 3PZ) show higher ratios suggesting minor dissolution of halite along the flow path. Despite a limited number of samples this is also observed in data from Nogueira (2017).

No minor or trace elements have been reported before (Table 2). Uranium concentrations are one order of magnitude lower at 5PZ and 3PZ (25 ng/L) compared to 23PZ and 4PZ (308 and 415 ng/L respectively), suggesting the interaction with marine derived carbonates in some samples.

Groundwater stable isotope results are assessed together with those obtained by Nogueira (2017). In general, values follow the Global Meteoric Water Line (Craig, 1961). At present, the available Local Meteoric Lines (LMWL) rely on a one year record (Haldorsen et al., 2013) or correspond to an incomplete two year record in Central Mozambique 850 km to the north (Steinbruch and Weise, 2016). In view of the available rainfall and groundwater samples and considering the limited time-record available and distance to other LMWLs, these are only used as a reference. There is a tendency to enriched values for groundwater obtained from the phreatic aquifer with an average of $\delta^2\text{H} = -14.6 \text{ ‰}$ and $\delta^{18}\text{O} = -3.5 \text{ ‰}$ ($n = 34$), while samples in the semi-confined aquifer show slightly more depleted average values $\delta^2\text{H} = -17 \text{ ‰}$ and $\delta^{18}\text{O} = -3.7 \text{ ‰}$ ($n = 29$). Rainfall samples collected during sampling show important evaporation and recycling of rainfall moisture during those particular events. D-excess, as defined by Dansgaard (1964), does not show any difference between phreatic and semi-confined groundwater samples with an average of 13‰.

Dissolved organic carbon concentrations (DOC) and their $\delta^{13}\text{C}$ isotopic ratios were determined in four samples. DOC was higher in the shallower sample (5PZ=1.9 mg/L) screened between the phreatic and semi-confined than in deeper samples recovered from the semi-confined (Table 2). Remarkably, $\delta^{13}\text{C}_{\text{DOC}}$ values were quite depleted in three of the samples ranging between -32.3 and -29.1‰. Only sample 3PZ with a $\delta^{13}\text{C} = -25.6 \text{ ‰}$ had values as those expected for DOC derived from C3-type vegetal organic matter.

Carbon isotope values were also measured in dissolved inorganic carbon. Values ranged from $\delta^{13}\text{C}_{\text{DIC}} = -7.85$ to -15.77 ‰ . Interaction with marine derived carbonates is partly responsible for the $\delta^{13}\text{C}$ enrichment observed.

Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) values ranged between 0.713046 and 0.719421. Sample 5PZ showed the more radiogenic values and 4PZ the less radiogenic. Franzese et al. (2009) report $^{87}\text{Sr}/^{86}\text{Sr}$ values from Holocene and LGM terrigenous sediments transported by the Agulhas current. The northernmost values (Lat: -29.93 to -29.07) show an average of 0.73021 ($n=8$). Assuming these transported sediments could have contributed to the sand dune building along the coast they would provide a radiogenic component. However, the importance of coastal sea spray (Whipkey et al., 2000) providing Sr of modern marine ratio (0.7092) and the interaction with marine Oligocene calcarenites of the Salamanga Fm in depth -assumed to reflect partially Oligocene seawater- could explain the tendency to lower Sr isotope ratios observed with depth.

Environmental radioactive isotopes of tritium (^3H) and radiocarbon ($^{14}\text{C}_{\text{DIC}}$) were analysed in groundwater samples. Tritium was above quantification limits (0.14 TU) for two samples (Table 2). The sample with higher activity (0.48 TU) was 5PZ, screened in the transition between the phreatic and semi-confined materials. Sample PZ23 had no quantifiable ^3H and sample 4PZ was close to quantification limits. Radiocarbon results show two types of values, groundwater in the phreatic aquifer have ^{14}C of 92.54 pMC (Table 2). Samples screened in the semi-confined aquifer have values ranging between 54.67 and 56.56 pMC, consistent with higher bicarbonate concentrations and dissolution of carbonates.

5. DISCUSSION

5.1 Geological controls on recharge and hydrochemistry

The separation between the phreatic and semi-confined aquifers, introduced by Bouman (1985) and Smidt and de Sonnevile (1990), provides the basic framework to characterise shallow groundwater geochemical processes in the Maputo district. The phreatic aquifer is basically formed by Quaternary sand dunes. The semi-confined aquifers are formed by undifferentiated Late Paleogene to Pliocene materials.

Fig 2 shows four cross sections approximately perpendicular to the coast. The thickness of the Quaternary sand dune systems is considerable to the south (40-50 m), while the clay-rich confining layer is absent (Smidt and de Sonnevile, 1990). This exposes the underlying semi-confined aquifer to direct recharge from the sand dunes, precisely in the most densely populated areas of Maputo city where risks of pollution are higher. The confining layers increase in thickness to the north and to the west, eventually outcropping (Fig 2-A and B). The Quaternary sands are absent in the NW and concentrate closer to the coast. The complexity of the clay-rich layer/s to the NW, with more than one clay layer identified, probably affects groundwater movement and potentially favours a slow recharge and higher evapotranspiration, leading to higher electrical conductivity values in groundwater at those locations (Nogueira, 2017).

Coastal and inland sand dunes systems act as "windows" for recharge, both parallel to the Incomati River valley. Clay-rich layers to the north attenuate the vulnerability of the underlying semi-confined units and total recharge. Groundwater recharged through the Quaternary sands is generally of the Na-Cl type with minimum water-rock interaction. As groundwater flows deeper, it generally evolves into Na- HCO_3 -type water. Silicate weathering, as suggested by SiO_2 concentrations and radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ values, combines with interaction with dispersed clay minerals in the semi-confined units. The overall results is a freshening-up trend, as observed in other sand dominated coastal aquifers (Andersen et al., 2005). The ion-exchange process could be triggered by the lowering of sea-levels following the Holocene highstand (ca. 3.5 m). In areas where seawater has been totally flushed, silicate weathering and ionic exchange are responsible for the observed Na- HCO_3 -type waters. The uptake of Ca further reduces calcite saturation, enhancing further dissolution of the calcareous sandstones. In areas where deeper piezometers are screened within sand dunes (19PZ), confining units are thin (1PZ) or the sand dunes disappear (8PZ), the Na-Cl-type water is prevalent (Fig. 3).

The Na:Cl and Mg:Cl ratios (Fig 4-A) show the main source of ions is derived from the ocean via rainfall, sea spray or dry deposition while K is enriched compared to K:Cl seawater ratios. The slightly radiogenic nature of Sr-isotope results, compared to seawater, and SiO_2 concentrations of up to 29 mg/L suggest weathering of K-rich silicates derived from the Quaternary sands. Calcium appears generally enriched

with respect to Cl, with groundwater approaching calcite saturation towards deeper samples in the semi-confined aquifer. A large number of samples approach the 1:2 (Ca:HCO₃) ratio (Fig. 4-E). These, together with the abundance of calcareous materials in the sand-dunes (Peché, 2012) and underlying sandstones (Bouman, 1985), demonstrate the active dissolution of carbonates by recharging waters. The potential of groundwater to further interact with carbonates in the semi-confined aquifer is enhanced by the positive feed-back of ion-exchange that uptakes Ca, releasing Na and controls the resulting Na-HCO₃-type water chemistry. Mg is not enriched compared to Cl, while Fe concentrations are quite low, suggesting calcite and not dolomite or siderite is the main carbonate phase interacting with groundwater.

Sulfate concentrations are generally near seawater ratios, but lower in some semi-confined samples, suggesting sulfate reduction with depth (3PZ). Some coastal samples near the tidal zone (Adonis, 2007) show an increase in Cl compared to marine ratios. These samples are consistent with dissolution of gypsum, as their Ca:SO₄ ratios approach unity. These features and the high conductivity of the same samples suggest the dissolution of evaporites (halite and gypsum) rather than mixing with seawater or trapped seawater. On the other hand, Nogueira (2017) suggests mixing with trapped seawater, rather than halite dissolution, as one of main causes for observed high salinities in groundwater to the west of the study area (Matola). Brackish/salt water samples from these areas present Na:Cl and Cl:Br ratios, near seawater ratios, corroborating the suggested hypothesis.

5.2 Estimation of recharge processes

Groundwater water stable isotope values obtained from the phreatic aquifer tend to be slightly enriched ($\delta^2\text{H} = -14.6 \text{ ‰}$ and $\delta^{18}\text{O} = -3.5 \text{ ‰}$, $n = 34$) compared to those in the semi-confined aquifer ($\delta^2\text{H} = -17 \text{ ‰}$ and $\delta^{18}\text{O} = -3.7 \text{ ‰}$, $n = 29$) (Fig 5). Given the generally short residence times of groundwater (presented below) this suggests that depleted, probably more intense rainfall events, control recharge over a decadal time scale. Rainfall samples collected during Oct 2013 show a high deuterium excess (D-excess) with an average of 20.5 ‰ ($n=4$) different to that obtained from gw samples with an average of 13‰. ($n=70$). There are no differences between D-excess in samples from the Phreatic or Semi-confined aquifers, suggesting that overall rainfall dynamics have been similar during the groundwater residence times represented. The D-excess results also suggest recharge takes place mostly during intense rainfall periods and not during small events. Evaporation and evapotranspiration of low intensity rainfall in Maputo is high, and in some cases only events above 25 mm/day contribute to recharge (Andreetta, 2018). This is similar to recharge dynamics observed in other semi-arid locations (Iverach et al., 2017; Hollins et al., 2018).

The chloride mass balance (CMB) is a widely used method to estimate recharge in arid and semi-arid regions (Davis and Crosbie, 2018). This method can be applied assuming: Cl is conservative, contributed from meteoric input, surface runoff is neglected and recharge can be approximated by one dimensional piston flow (Wood and Sanford, 1995). Recharge through sand dunes approximates the above assumptions. De Sonneville (1984) reports a Cl concentration analysis of rainfall collected in Maputo city during 1983. A value of 7 mg/L is provided for a total rainfall of 394 mm. Unfortunately no details are provided to ascertain if this measurement is a cumulative rainfall sample or which months it may represent. Weaver and Talma (2005) report yearly weighted rainfall Cl concentrations of 14 mg/L in South Africa east coast (George). This value is twice that reported for Maputo city. However, water stable isotopes suggest that larger rainfall events provide the bulk of the recharge over 100-1000 yr time

scales represented. Large rainfall events generally have lower Cl concentrations (Duce et al., 1969). Moreover, chloride inputs can change widely based on localised conditions, wind speed and direction (Davis and Crosbie, 2018). We adopt the Maputo rainfall chloride concentration as an approximation and applied to chloride data from the PZ-well series (Nogueira, 2017). Recharge values of 8 to 370 mm are obtained representing between 1 and 43% of rainfall. Figure 6, despite contouring limitations, shows that high recharge areas are localised parallel to the coast following the inland and coastal sand dunes. The northern part of the study area (Fig. 2-A) showing the highest recharge rates along coastal sand dunes.

5.3 Residence time of groundwater

This work represents the first attempt to isotopically characterise groundwater residence time in the Maputo district. Despite the limited number of samples these are quite significant as groundwater can integrate geochemical information along the flow path to the sample collection point. The presence of ^3H in three of the four analysed samples highlights the decadal residence time scale of groundwater in the shallow Maputo district aquifers, even in portions of the semi-confined aquifer. To assess ^3H residence time we need to know the rainfall input. The only available rainfall ^3H analysis corresponds to a sample collected in Maputo city in 1959-60 and reported in Taylor (1966) with a rainfall activity of 1.5 TU (± 0.6), interpreted to represent oceanic contributions. McNaughton and Wurzel (1972) recorded ^3H in rainfall in neighbouring Zimbabwe (Harare) for most of the 1960's. Values recorded were similar to those found in Perth (Australia) during the same time. In recent years ^3H levels in Perth's rainfall have returned to background levels or pre-nuclear testing values (Tadros et al. 2014). All the above suggest that modern rainfall tritium values in Maputo district (at similar latitude than Perth) could be in the order of 1.5 to 2 TU. The presence of ^3H and the large transmissivities reported (up to 1660 m²/d) suggest a relatively fast renewal of groundwater with decadal time scales (Table 3).

Radiocarbon measurements can further inform about water-rock interaction processes and providing all carbon sinks/sources are considered, residence time of groundwater on centuries to millennia time-scales. Initially we attempted a geochemical inverse modelling scenario where geochemical processes necessary to replicate a final groundwater composition can be calculated with Netpath (Plummer et al., 1994). The initial groundwater composition selected was that of Maluana (5PZ) screened between the phreatic and semi-confined aquifer (Table 2). This sample has the highest ^3H activity (0.48 TU) and an elevated ^{14}C concentration (92.5 pMC) and is therefore a close representation of modern recharge groundwater. The final point along the flow path is represented by the sample collected at Manhiça (23PZ), with no quantifiable ^3H and a ^{14}C of 56.6 pMC (Table 2). However, chloride concentrations are higher in the initial sample (5PZ). Assuming a generally conservative behaviour of Cl in groundwater and the connection between the two aquifers, Cl concentrations have increased in more recent times and sample 5PZ is therefore not representative of long-term groundwater recharge. Taking into account the limited data set and the spatial/temporal variability in recharge concentrations we did not have a representative sample of recharge that could be used to calculate residence time along a flow path using Cl as one of the constraints. Therefore we assessed groundwater ^{14}C residence times on an individual basis following a "single well" approach, with interpretations reported in Table 3.

The effect of carbonate dissolution or incorporation of "dead" carbon (devoid of ^{14}C) must be considered when assessing ^{14}C residence times. Peché (2012) reports $\delta^{13}\text{C}$ values for carbonates dispersed within the Quaternary sand dunes in Inhaca Island. The materials including calcareous quartz

arenites, rhizomorphs and shell fragments of either marine or lacustrine organisms have $\delta^{13}\text{C}$ values ranging from -10.8 to 3.2‰ and an average of -4.7‰. Due to the recent age of the Quaternary sediments of either marine or terrestrial origin, recharged groundwater can incorporate measurable ^{14}C concentrations as it dissolves dispersed carbonates. Peché (2012) reports radiocarbon ages for the same type of materials analysed for $\delta^{13}\text{C}$ values with an average pMC of 48.6 (n=7). This relatively high ^{14}C concentration can be incorporated into recharged groundwater. This is expected to affect very shallow groundwater with its effects attenuating as groundwater flows into older sediments containing lower or no ^{14}C .

Another source of ^{14}C can derive from the oxidation of organic matter. Generally, groundwater reflects the average organic carbon isotope values of the local decomposing plant material (Deines, 1980). Considering the relative importance of C4 native grasses and crops in the area (corn, sorghum and sugarcane) we further assess the dissolved organic carbon (DOC) in groundwater. The shallow sample is relatively high 1.9 mg/L with isotopic $\delta^{13}\text{C}_{\text{DOC}}$ values of -32.3 ‰. Concentrations in the down flow sample are lower (0.8 mg/L) with isotopic $\delta^{13}\text{C}_{\text{DOC}}$ slightly more enriched -29.1‰ but still relatively depleted compared to values in Pazimane (3PZ) with a value of -25.6 ‰. Sample 3PZ is located in a natural setting, further inland and away from roads and human settlements. The depleted $\delta^{13}\text{C}_{\text{DOC}}$ values (Table 2) could be linked to decomposition of organic rich sediments (Fernandez et al., 2003), deposited in alluvial or lake deposits. No interaction or supply from C4 vegetation seems likely for the observed values when compared to C4 influenced values reported in Madagascar (Ralison et al., 2008).

The incorporation of ^{14}C via carbonate dissolution or DOC oxidation hinders ^{14}C calculations. Groundwater residence time for 23PZ represents an upper approximation, with real values probably being lower, but still beyond ^3H range. Calculated ^{14}C ages mostly result in modern residence times (M in Table 3), consistent with presence of ^3H .

5.4. Implications for groundwater use and planning

Sanitation in peripheral populated areas of Maputo district often relies on in-situ pit latrines and septic tanks. Furthermore, household waste is disposed of in illegal dumps or concentrates in Hulene rubbish tip (Bocario). The Hulene tip extends over 17 ha with waste heights between 6 and 15m. This is the only tip in Maputo city (~2.5 million inhabitants). Located 10 km from the city centre it has been in operation over 50 years, is uncovered (Allen and Jossias, 2011) and presumed unlined. Taking into account the large recharge rates through the Quaternary sands and the thinning or disappearance of confining layers to the SE (Fig 2-A), continued point source pollution is a concern. This is evidenced by concentrations above WHO (2011) guideline values of 50 mg/L NO_3 in the Hulene area as well as other areas in Maputo city and Matola (Muchimbane, (2010); ARA-Sul (2011)).

According to Freitas (1962), analysis of groundwater in the city centre in bores tapping into the sands and underlying sandstones had no trace of nitrites, no mention to nitrates is made. Analysis reported in Hydroconceil and WE consult (2011) show concentrations of 38.5 and 12.3 mg/L NO_3 in 1PZ and 2PZ respectively. Similarly, Matsinhe et al. (2008) reports values of up to 32 mg/L in densely populated areas to the north of the city centre. Maximum values of above 250 mg/L NO_3 are reported by Juízo (1995) and Marques Arsénio et al. (2018) for areas around the city centre while Muiuane (2007) reports concentrations above 50 mg/L for nine centric suburbs.

In general, this demonstrates that nitrate has moved into deeper portions of the aquifers. This coincides with times scales of potentially <50 years, and concurs with the presence of ^3H at 3PZ within the semi-confined aquifer. Nitrate concentration decreases to the north with lower population density and thicker confining layers, as observed in analyses in Table 1 and reported by Nogueira (2017). The only concentration above detection limit in our sampling was detected in Manhiça (23PZ) at 57 m depth. Given the absence of ^3H , larger residences and depleted $\delta^{13}\text{C}_{\text{DOC}}$ we cannot rule out interaction with organic matter as a source of the nitrate and nitrite at the site rather than fertilizer inputs (Scheiber et al. 2016).

The potential for seawater intrusion and risks to groundwater quality in coastal areas is a well-known problem (Mtoni et al. 2013; Comte et al. 2016). Whether the increased salinity is driven by mixing with modern seawater (Bryan et al. 2017) or seawater trapped from former highstands (Lee et al. 2016), the effects on groundwater quality are similar. In the case of Maputo salinization has been raised as a limitation to groundwater abstractions, mostly from the semi-confined aquifer. Two areas are particularly sensitive. Inland, the proximity to the surface or outcrop of clay-rich layers/lenses (Fig 2-C-D) enhances evaporation processes and salt accumulation. The presence of trapped seawater within clay lenses, rather than halite or gypsum dissolution, leads to local high salinities (Matola River) in both deep groundwater and also surface waters (Nogueira 2017). Near the coast, Smidt et al. (1989) reports on vertical electrical sounding investigations along the coastal fringe of Maputo and situates the toe of the fresh/salty water interface about 500 m from the coast. Adonis (2007) characterised groundwater in a multilevel piezometer 10 km south of Marracuene (Lago Sangué) within meters of the tidal zone. Three samples were collected at different depths and months. The deeper sample at 43 m, reached chloride concentrations close to seawater, it then decreased substantially in a further sampling four months later. This provides direct evidence of a dynamic fresh/salt water interface and seasonal fluctuations at that location. The approximate 3.5 m sea-level drop since the Holocene highstand and modern freshening-up ion-exchange processes, suggest very fragile coastal aquifers at great risk if sea-levels rises. However, the lack of contrasted hydrogeochemical time series makes any interpretations difficult at present.

6. CONCLUSIONS AND PERSPECTIVES

This work presents the first attempt to characterise groundwater residence time within the coastal aquifers of Maputo district (Mozambique). This region relies heavily on groundwater to satisfy the increasing demands of one of the fastest growing cities in Africa. Despite the restricted data set, the combination of new data and a review of previous data provide new information on recharge processes, groundwater hydrochemical variations and a basic assessment of vulnerability in the aquifers for this data-poor region of Mozambique.

Quaternary sand dunes systems (phreatic aquifer) capture recharge during the wet season with groundwater dominated by oceanic derived solutes and Na-Cl-type waters. Underlying these, clay-rich materials form a confining layer of irregular distribution. The absence or thickness of this layer outlines the semi-confined aquifer, characterised by Na-HCO₃-type groundwater. Groundwater in general evolves from Na-Cl-type to Na-HCO₃-along the flow path, suggesting a freshening-up chemical trend, as ionic exchange favours uptake of Ca and release of Na with simultaneous dissolution of carbonates dispersed in the aquifer. The freshening trend, it is hypothesised, could be associated with the chemical

changes triggered after the ca. 3.5 m lowering of sea-levels, following the Holocene highstand. While seawater has been totally flushed, ionic exchange persists, ultimately favouring Na-HCO₃-type waters.

Water stable isotope values for groundwater obtained from the phreatic aquifer show more enriched average values ($\delta^2\text{H} = -14.6 \text{‰}$ and $\delta^{18}\text{O} = -3.5$), while samples in the semi-confined aquifer show slightly more depleted average values ($\delta^2\text{H} = -17\text{‰}$ and $\delta^{18}\text{O} = -3.7$). This suggests that depleted, probably more intense rainfall events, control recharge over the decadal time scales observed in groundwater. Modern rainfall tritium values in Maputo district have been estimated to be in the order of 1.5 to 2 TU based on regional characteristics. The presence of ³H and the large transmissivities reported in the sand dunes (up to 1660 m²/d) suggest a relatively fast renewal of groundwater with decadal time scales. Groundwater residence times based on radiocarbon analysis have also been assessed with careful reconstruction of sinks and sources of carbon. Geochemical corrections have been applied to account for the addition of dead carbon. Results show modern groundwater, consistent with the presence of ³H. Only a deeper sample in the northern part of the Maputo district, devoid of ³H, had a corrected residence time of 1000 yr. Overall, groundwater residence times in the shallow systems of the Maputo district show a very active and modern system.

The thickness of the confining layer between the Quaternary sand dunes and the semi-confined aquifer thins to the south and under Maputo city. This makes Maputo city especially vulnerable to point source pollution. The presence of tritium and high NO₃ concentration further demonstrates decadal time scales in the transfer of pollutants into deeper portions of the aquifer under the city. The modern residence times also suggest that in the event of sea-level rise aquifers would respond fast, making groundwater resources in the Maputo city very vulnerable to salinization, even if no particular signs of salinization are identified at present.

ACKNOWLEDGEMENTS

We would like to acknowledge the International Council of Science, the International Geoscience Programme (IGCP-618 project), the International Union of Geological Sciences, the International Union for Quaternary Research and GRAPHIC (Groundwater Resources Assessment under the Pressures of Humanity and Climate Change) for their economic support that allowed a number of researchers to attend our training activities in Bobole (Mozambique). Thanks to Chris Dimovski, Barbora Gallagher, Robert Chisari, Henri Wong and Vlad Levchenko from ANSTO for their constant logistic and analytical support. Thanks to Holger Treidel (formerly with GRAPHIC) for his encouragement and organisational support. Also, our thanks to the Mozambique government Ministry of Mineral Resources and personnel from the Eduardo Mondlane University that took us to the field. Particular thanks to Lizete Dias (Ara-Sul), Egídio Govate (National Directorate of Water), Simplicio Roseiro (Universidade Eduardo Mondlane). Also, thanks to all the attendees to the course that contributed to fruitful discussions and help in the field: Seifu Kebede (Ethiopia), Chikira Mejema (Tanzania), Jodi Miller (South Africa), Ali Mohsen (Egypt), Jean-Robert Mweze (DR Congo), Niels Schrøder (Denmark), Randy Stotler (USA), Henri Totin (Benin).

REFERENCES

Adonis, S., 2007. The hydrochemical characteristics of groundwater in the Incomati estuary, Department of Chemistry. University of the Western Cape, p. 85.
<http://etd.uwc.ac.za/xmlui/handle/11394/2196> (accessed July 2018)

Akouvi, A., Dray, M., Violette, S., de Marsily, G., Zuppi, G., 2008. The sedimentary coastal basin of Togo: example of a multilayered aquifer still influenced by a palaeo-seawater intrusion. *Hydrogeology Journal* 16, 419-436.

Allen, C., Jossias E., 2011. Mapping of the Policy Context and Catadores Organizations in Maputo, Mozambique. WIEGO Organizing Brief No. 6
http://www.wiego.org/sites/default/files/publications/files/Allen-Jossias_WIEGO_OB6.pdf Accessed on 8/08/2018.

Andersen, M.S., Nyvang, V., Jakobsen, R., Postma, D. 2005. Geochemical processes and solute transport at the seawater/freshwater interface of a sandy aquifer. *Geochim. Cosmochim. Ac.* 69, 3979-3994.

Andreetta, R., 2018. Impact of climate change on groundwater recharge in the Great Maputo Aquifer, Mozambique. MSc thesis, UNESCO-IHE, Delft, The Netherlands.

ARA-Sul, 2011. Boletim de avaliação de agua subterrânea N. 1. 9 pp (in Portuguese).

Böhlke, J.K., Denver, J.M., 1995. Combined Use of Groundwater Dating, Chemical, and Isotopic Analyses to Resolve the History and Fate of Nitrate Contamination in Two Agricultural Watersheds, Atlantic Coastal Plain, Maryland. *Water Resources Research* 31, 2319-2339.

Bosazza, V.L., 1954., Estudos geoquímicos das águas superficiais e subterrâneas das rochas sedimentares do sul do Save. *Serie de Geologia e Minas- Memórias e comunicações* 14, 7-44. (in Portuguese)

Botha, G., Porat, N., 2007. Soil chronosequence development in dunes on the southeast African coastal plain, Maputaland, South Africa. *Quaternary International* 162-163, 111-132.

Bouman, D., 1985. Hydrogeology of the medium lower Incomati between Magude and Marracuene: an analysis of existing borehole data. *Direcção Nacional de Águas. DEP/S. de Geohidrologia, Maputo, Mozambique.* 41 pp.

Bryan, E., Meredith, K.T., Baker, A., Post, V.E.A., Andersen, M.S., 2016. Island groundwater resources, impacts of abstraction and a drying climate: Rottnest Island, Western Australia. *Journal of Hydrology* 542, 704-718.

BURGEAP, 1962. Hydrogeologie du sud du Save. *Serie de Geologia e Minas- Memórias e comunicações* 30, 3-27. (in French and Portuguese).

Cendón, D.I., Hankin, S.I., Williams, J.P., Van der Ley, M., Peterson, M., Hughes, C.E., Meredith, K., Graham, I.T., Hollins, S.E., Levchenko, V., Chisari, R., 2014. Groundwater residence time in a dissected and weathered sandstone plateau: Kulnura-Mangrove Mountain aquifer, NSW, Australia. *Australian Journal of Earth Sciences* 61, 475-499.

Cendón, D.I., Hughes, C.E., Harrison, J.J., Hankin, S.I., Johansen, M.P., Payne, T.E., Wong, H., Rowling, B., Vine, M., Wilsher, K., Guinea, A., Thiruvoth, S., 2015. Identification of sources and processes in a low-level radioactive waste site adjacent to landfills: groundwater hydrogeochemistry and isotopes. *Australian Journal of Earth Sciences* 62, 123-141.

Comte, J.-C., Cassidy, R., Obando, J., Robins, N., Ibrahim, K., Melchioly, S., Mjemah, I., Shauri, H., Bourhane, A., Mohamed, I., Noe, C., Mwega, B., Makokha, M., Join, J.-L., Banton, O., Davies, J., 2016. Challenges in groundwater resource management in coastal aquifers of East Africa: Investigations and lessons learnt in the Comoros Islands, Kenya and Tanzania. *Journal of Hydrology: Regional Studies* 5, 179-199.

Cooper, J.A.G., Pilkey, O.H., 2002. The Barrier Islands of Southern Mozambique. *Journal of Coastal Research* 36, 164-172.

Craig, H., 1961. Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. *Science* 133, 1833-1834.

- Currell, M., Cendón, D. I., Cheng, X., 2013. Analysis of environmental isotopes in groundwater to understand the response of a vulnerable coastal aquifer to pumping: Western Port Basin, south-eastern Australia. *Hydrogeology Journal* 21, 1413-1427.
- Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus* 16, 436-468.
- Davies, P.J., Crosbie, R.S., 2018. Mapping the spatial distribution of chloride deposition across Australia. *Journal of Hydrology* 561, 76-88.
- De Sonnevile, J.L.J., 1984. The groundwater resources of Mozambique, an inventory of existing data. Department of Study and Planning, National Directorate of Water, Maputo, Mozambique, 22pp.
- De Sonnevile, J.L.J. (1985) Project proposals: 1979-1985, Mozambique. In: *Groundwater in Mozambique*. Ed J.L.J. de Sonnevile (in Portuguese).
- Deines, P., 1980. The isotopic composition of reduced organic carbon. In: P. Fritz and J.Ch. Fontes (Eds.), *Handbook of Environmental Isotope Geochemistry*, Vol. 1. Elsevier, New York, pp. 329-406.
- Duce, R.A., Y-B. Seto, Moyers, J.J., 1969. Variation of sodium and chloride concentrations in rainfall intensity in Hawaiian trade wind showers. *Pacific Science* 23, 483-495.
- Farr, T.G., Rosen, P.A., Caro, E., Crippen, R., Duren, R., Hensley, S., Kobrick, M., Paller, M., Rodriguez, E., Roth, L., Seal, D., Shaffer, S., Shimada, J., Umland, J., Werner, M., Oskin, M., Burbank, D. and Alsdorf, D., 2007, The Shuttle Radar Topography Mission. *Reviews of Geophysics* 45. RG2004, doi:10.1029/2005RG000183
- Fernandez, I., Mahieu, N., Cadisch, G., 2003. Carbon isotopic fractionation during decomposition of plant materials of different quality. *Global Biogeochemical Cycles* 17.
- Franzese, A.M., Hemming S.R., Goldstein S.L., 2009. Use of strontium isotopes in detrital sediments to constrain the glacial position of the Agulhas Retroflexion. *Paleoceanography* 24, PA2217, doi:10.1029/2008PA001706, 2009
- Freitas, F., 1962. Condições hidrogeológicas de abastecimento de águas subterrâneas a Lourenço Marques e arredores. *Boletim da Sociedade de Estudos de Moçambique* 31, 119-138. (in Portuguese)
- Gumbo, B., 2004. The status of water demand management in selected cities of southern Africa. *Physics and Chemistry of the Earth, Parts A/B/C* 29, 1225-1231.
- Haldorsen, S., Numme A.M., Kelbe, B., Taylor, R., Cendón, D.I., 2013. Oxygen and hydrogen isotopes in the Greater St Lucia Wetland Park. NE South Africa, precipitation and groundwater. Is this relevant to paleoclimatic studies? In: Haldorsen S. Momade, F.J., Achimo, M., Mugabe J. and Cendón D.I.: *Groundwater and Global Palaeoclimate Signals G@GPS Africa: Long-term recharge of large groundwater basins Proceedings of the 2nd G@GPS Workshop in Bobole, Mozambique 2013*, 50 pp. <http://www.gw-gps.com/events-newsletter/>
- Hollins, S.E., Hughes, C.E., Crawford, J., Cendón, D.I., Meredith, K.M., 2018. Rainfall isotope variations over the Australian continent - Implications for hydrology and isoscape applications. *Science of The Total Environment* 645, 630-645.
- Hydroconceil and WE consult, 2011. Sustainable management of the groundwater resources in the Maputo Metropolitan area. ARA-Sul Administração Regional de Águas do Sul Ministério de Educação 1986: Atlas Geográfico, volume 2.
- INE-Instituto Nacional de Estatística, 2017. Censo 2017, IV Recenseamento Geral da população e habitação. Accessed on line <http://www.ine.gov.mz/operacoes-estatisticas/censos/censo-2007/censo-2017/divulgacao-os-resultados-preliminares-iv-rgph-2017> (in Portuguese)
- Iverach, C.P., Cendón, D.I., Meredith, K.T., Wilcken, K.M., Hankin, S.I., Andersen, M.S., Kelly, B.F.J., 2017. A multi-tracer approach to constraining artesian groundwater discharge into an alluvial aquifer. *Hydrology and Earth System Sciences*. 21, 5953-5969.

- Juízo, D., 1995. Modelação Inversa para a Determinação da Recarga dos Aquíferos a Norte de Maputo, Bachelor-thesis report, Eduardo Mondlane University- Maputo, Mozambique., 19 pp. (in Portuguese)
- Lächelt, S., 2004. Geology and mineral resources of Mozambique. Direcção, Nacional de Geologia Moçambique.
- Lee, S., Currell, M., Cendón, D.I., 2016. Marine water from mid-Holocene sea level highstand trapped in a coastal aquifer: Evidence from groundwater isotopes, and environmental significance. *Science of The Total Environment* 544, 995-1007.
- Marques Arsénio A., Câmara Salim, I., Mingming Hu, Matsinhe, N.P., Scheidegger R., Rietveld, L., 2018. Mitigation Potential of Sanitation Infrastructure on Groundwater Contamination by Nitrate in Maputo. *Sustainability* 10, 858, doi:10.3390/su10030858
- Matsinhe, N.P., Juízo, D., Rietveld, L.C., Persson, K.M., 2008. Water services with independent providers in peri-urban Maputo : challenges and opportunities for long-term development. *Water SA* 34, 411-420.
- McNaughton, D.L., Wurzel, P., 1972. Tritium in rain as an indicator of air mass source. *Tellus* 24, 255-259.
- MCAA-Ministério para a Coordenação da Acção Ambiental, 2013. Estrategia Nacional de Adaptacao e Mitigacao das Mudancas Climaticas. Maputo.Moçambique. p. 71 (in Portuguese).
- Momade, F.J. and Olivera, J.T., 1996. Notícia explicativa da carta Geológica 2532 D3 Maputo, escala 1:50.000 . República de Moçambique. 32 pp.(in Portuguese)
- Muchimbane, A.B.A.A., 2010. Estudo dos indicadores de contaminação das águas subterrâneas por sistemas de saneamento "in-Situ"- Distrito urbano 4, Cidade de Maputo, Moçambique, Instituto de Geociências. - Universidade de São Paulo, Biblioteca Digital-USP. Teses e Dissertações, p. 131. (in Portuguese).
- Muiuane, E., 2007. The Quality of Groundwater in and around Maputo City, Mozambique, Universidade Eduardo Mondlane; Maputo, Mozambique.
- Mtoni, Y., Mjemah, I.C., Bakundukize, C., Van Camp, M., Martens, K., Walraevens, K., 2013. Saltwater intrusion and nitrate pollution in the coastal aquifer of Dar es Salaam, Tanzania. *Environ Earth Sci* 70, 1091-1111.
- NCFEA- Netherlands Commission for Environmental Assessment, Dutch Sustainability Unit, 2015. Climate Change Profile: Mozambique. Accessed on line: https://ees.kuleuven.be/klimos/toolkit/documents/689_CC_moz.pdf 20 pp.
- Nogueira G. E. H., 2017. Tracing the hydrochemical water types and salinization mechanisms in the Great Maputo area as a function of groundwater recharge, hydrogeological properties and human activities MSc Thesis: UNESCO-IHE, Institute for Water Education WSE-Groundwat CH. 123 pp.
- Parkhurst, D., Appelo, C., 1999. User's guide to PHREEQC (version 2)- a computer program for speciation, batch-reaction, one dimensional transport, and inverse geochemical calculations. *Water Resources Investigation Report U.S. Geological Survey* 99, 4259.
- Peché M., 2012. Geology of the KaNyaka barrier island system, Maputo Bay, Mozambique. M.Sc. Thesis Faculty of Geology, University of Johannesburg. 257 pp.
- Plummer, L.N., Prestemon, E.C., Parckhurst, D.L., 1994. User's guide to NETPATH- A computer program for mass-balance calculations: An interactive code (NETPATH) for modelling NET geochemical reactions along a flow PATH- Version 2.0. *USGS Water Res. Invest. Rep.* 94-4169.
- Ramsay, P.J., Andrew, J., Cooper, G., 2002. Late Quaternary Sea-Level Change in South Africa. *Quaternary Research* 57, 82-90.
- Ralison, O.H., Borges, A.V., Dehairs, F., Middelburg, J.J., Bouillon, S., 2008. Carbon biogeochemistry of the Betsiboka estuary (north-western Madagascar). *Organic Geochemistry* 39, 1649-1658.

Romano, M.P., 1964. The water resources of the Maputo (Southern Mozambique). *South African Journal of Science* 60, 245-251.

Scheiber, L., Ayora, C., Vázquez-Suñé, E., Cendón, D.I., Soler, A. and Baquero, J.C. (2016) Origin of high ammonium, arsenic and boron concentrations in the proximity of a mine: Natural vs. anthropogenic processes. *Science of The Total Environment* 541, 655-666.

Siesser, W.G., Dingle, R.V., 1981. Tertiary sea-level movements around Southern Africa. *Journal of Geology* 89, (4), 523-536.

Smidt, E.H., Chutumia, I.I., Egidio, N.M., Haas, P., 1989. Groundwater Exploitation in the Area of Maputo, Mozambique, in: Custodio, E., Gurguí, A. (Eds.), *Developments in Water Science*. Elsevier, pp. 581-591.

Smidt, E.H., de Sonnevile J.L.J. (1990) *Águas subterrâneas*. Ministério da Construção e Águas, Direcção Nacional de Águas. (in Portuguese).

Steinbruch, F., Weise, S.M., 2016. Characterization of the Rainfall of Central Mozambique Based on Isotopes of Water, Geostatistical and Geospatial Approaches for the Characterization of Natural Resources in the Environment. Springer International Publishing, Cham, pp. 321-325.

Tadros, C.V., Hughes, C.E., Crawford, J., Hollins, S.E., Chisari, R., 2014. Tritium in Australian precipitation: A 50 year record. *Journal of Hydrology* 513, 262-273.

Taylor, C. B., 1966. Tritium in Southern Hemisphere precipitation 1953-1964, *Tellus*, 18:1, 105-131, DOI: 10.3402/tellusa.v18i1.9177

Været, L., Leijnse, A., Cuamba, F., Haldorsen, S., 2012. Holocene dynamics of the salt-fresh groundwater interface under a sand island, Inhaca, Mozambique. *Quaternary International* 257, 74-82

Weaver, J.M.C., Talma A.S., 2005. Cumulative rainfall collectors –A tool for assessing groundwater recharge. *Water SA* 31(3), 283-290.

Westerink, R.M., 1996. Evaluation of monthly precipitation data of Mozambique, *Série Terra e Água*. Instituto Nacional de Investigaçao agronómica, Maputo, p. 156. Accessed on-line: https://library.wur.nl/isric/fulltext/ISRIC_22741.pdf (July 2018).

Whipkey, C.E., Capo, R.C., Chadwick, O.A., Stewart, B.W., 2000. The importance of sea spray to the cation budget of a coastal Hawaiian soil: a strontium isotope approach. *Chem. Geol.* 168, 37-48.

WHO, 2011. Nitrate and nitrite in drinking water- World Health Organisation. WHO/SDE/WSH/07.01/16/Rev/1. http://www.who.int/water_sanitation_health/publications/en/ Accessed on-line (July 2018).

Wood, W.W., Sanford, W.E., 1995. Chemical and Isotopic Methods for Quantifying Ground-Water Recharge in a Regional, Semiarid Environment. *Ground Water* 33, 458-468.

Figure headings

Fig. 1 a) Location map of Mozambique and neighbouring countries, showing the main sedimentary basins of Mozambique and Rovuma (modified from MCAA, 2017).

Fig. 2. Location of the ARA-Sul PZ-series monitoring bores (Hydroconceil and WE consult, 2011). Only bore numbers are indicated. Three cross sections (A, B and C) have been constructed based on drilling reports and sections from Hydroconceil and WE consult (2011), section D is constructed from data in de Sonnevile (1985). All cross sections profiles are based on the SRTM digital elevation model (Farr et al., 2007).

Fig. 3. Piper diagrams for groundwater samples with CBE% <10%. A) Sources of the different datasets. B) Samples represented in four electrical conductivity ranges for the same samples

Fig. 4. Bivariate cross plots with selected elements. ARA-Sul PZ-series monitoring bores are separated into PA: Phreatic and SC: Semi-Confined.

Fig 5. Groundwater and rainfall stable isotopes results for all available data. The LMWL-St Lucia is: $\delta^2\text{H}=7.78618\text{O}+11.8$ (Haldorsen et al., 2013). The LMWL-Chitengo is: $\delta^2\text{H}=8.95618\text{O}+15.7$ (Steinbruch and Weise, 2016)

Fig 6. Schematic contouring showing recharge (R%), based on chloride mass balance calculations in the phreatic aquifer. Assignment to the phreatic aquifer has been done based on drilling records (Hydroconceil and WE consult, 2011). For example 19PZ, 20 and 21 are logged as sand materials to completion therefore no separation between phreatic or semi-confined is warranted. (see Table S1 for details).

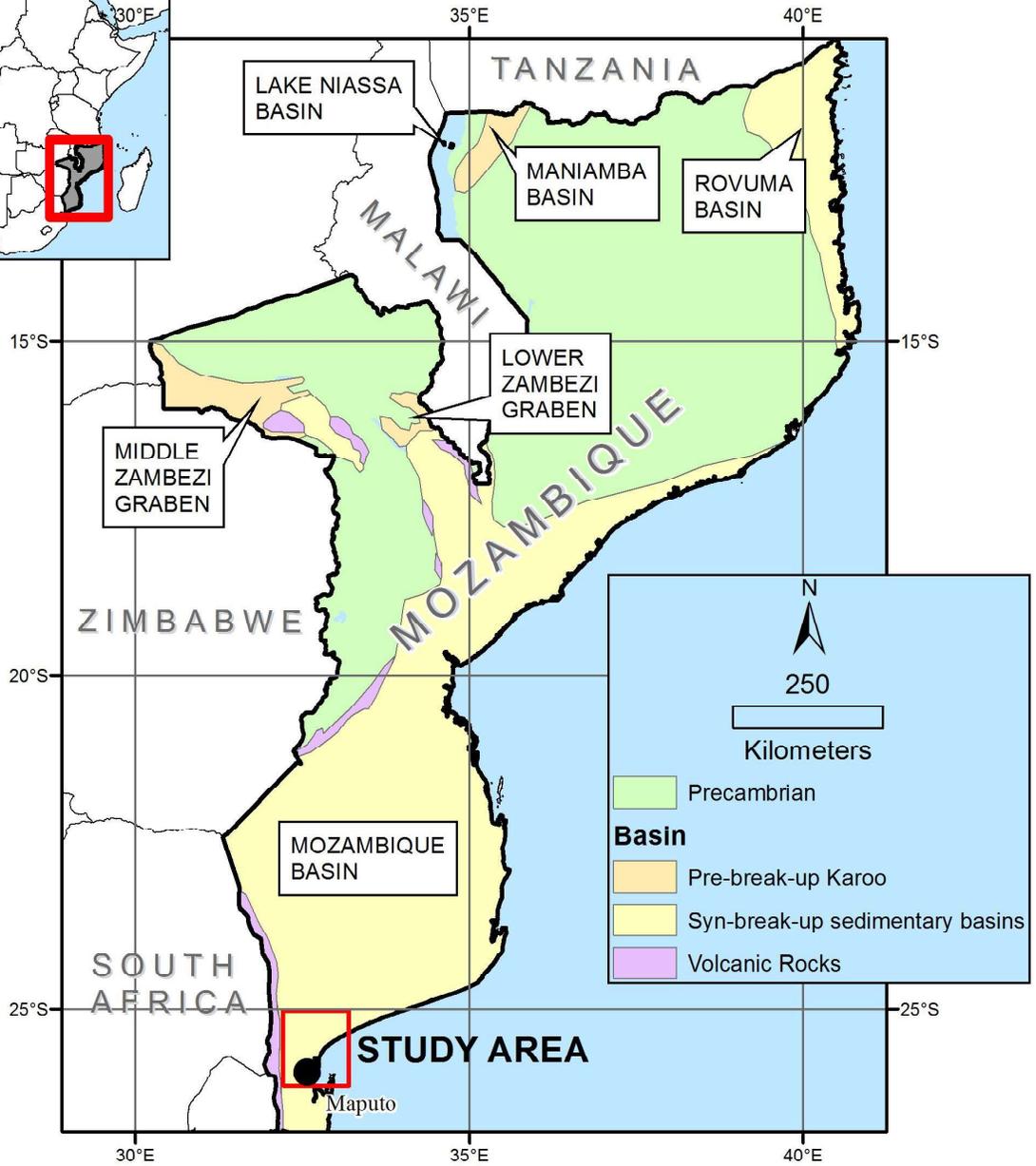
Table headings

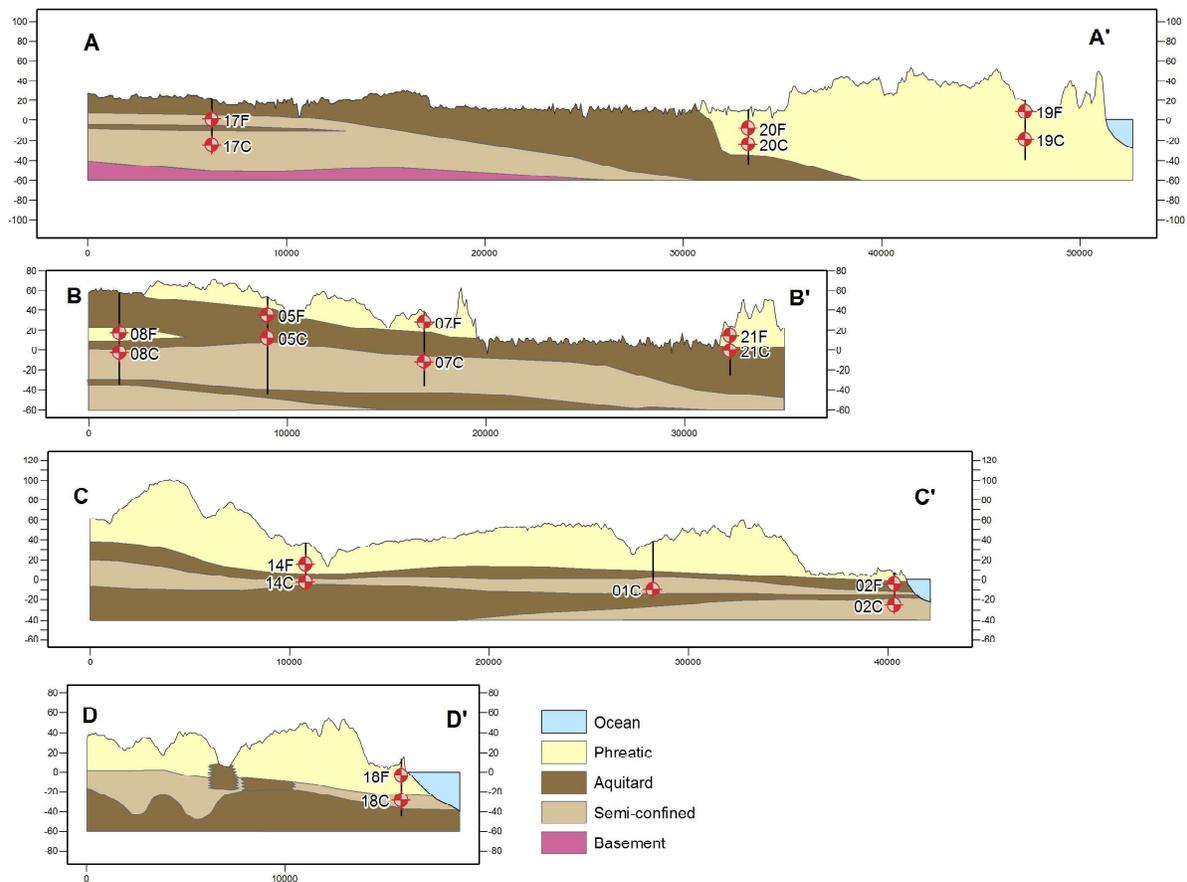
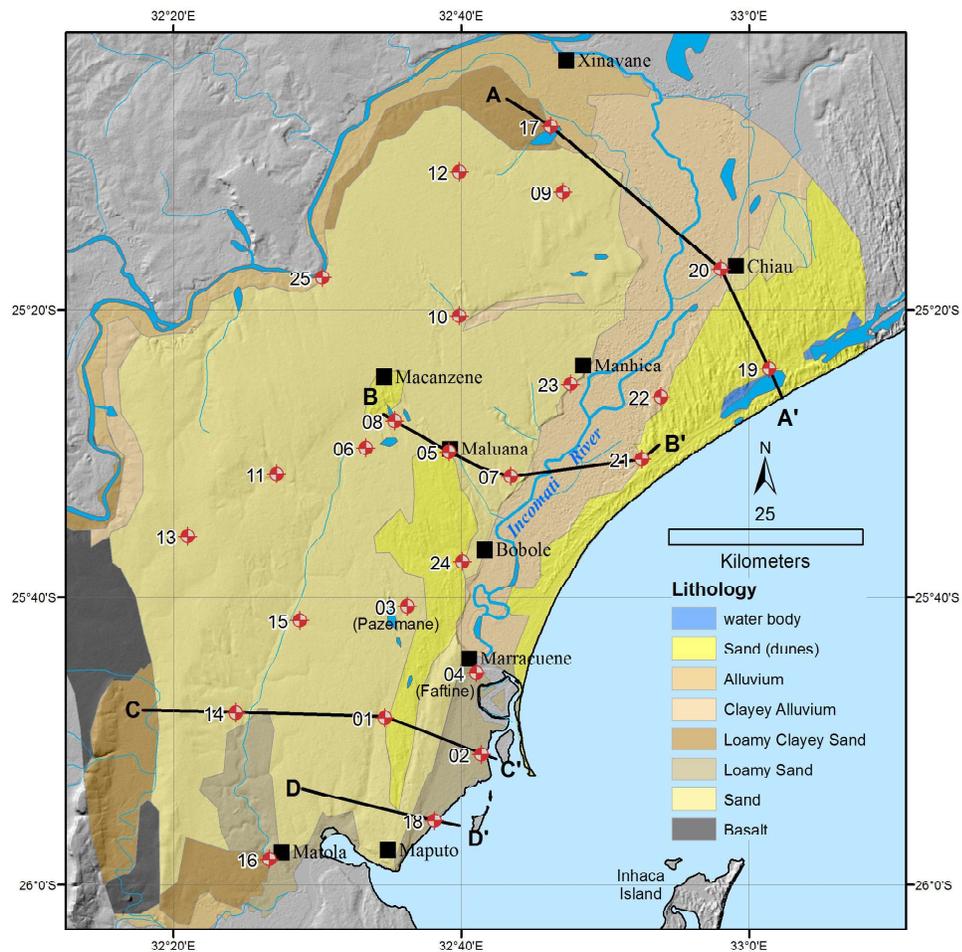
Table 1. Chemical compositions of groundwater (mg/L) in PZ-series and production bores. %CBE (charge balance error) and saturation indices with respect to Cal=calcite, Gyp=Gypsum and Sid=Siderite.

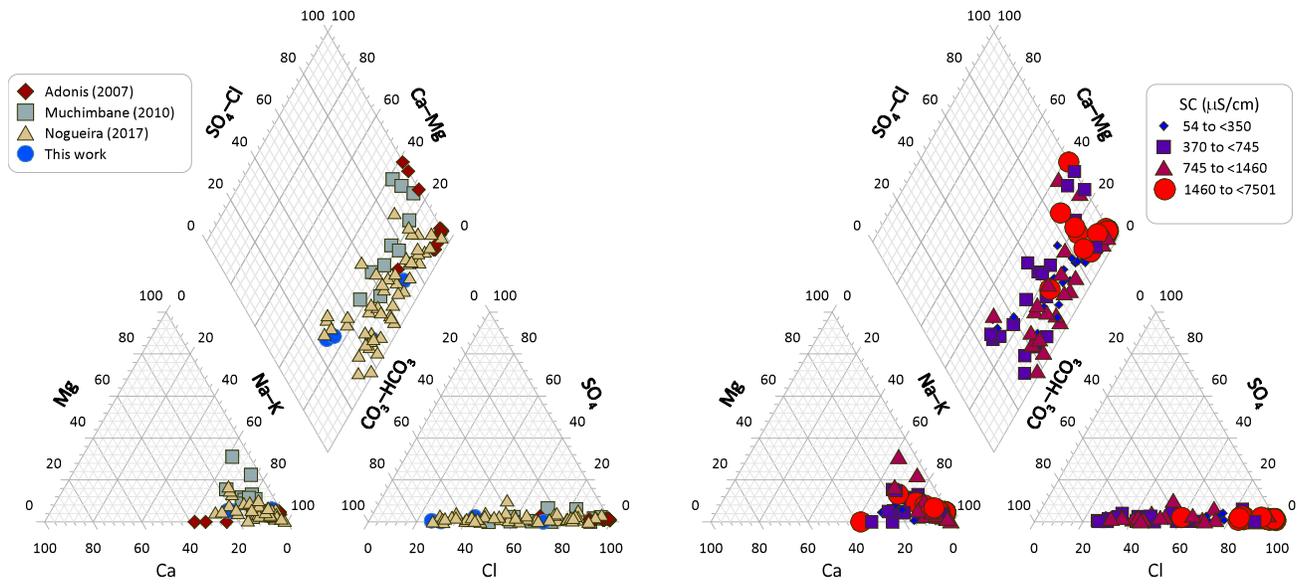
Table 2. Isotopic compositions of groundwater and rainfall samples, DOC and select trace elements.

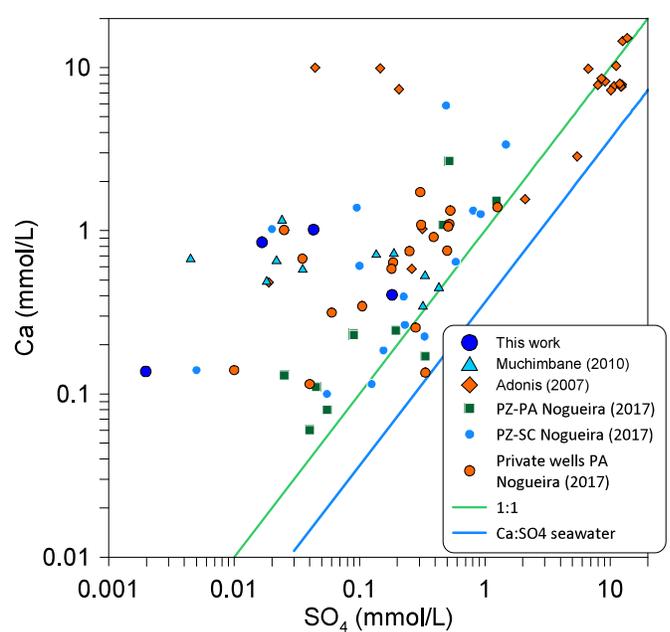
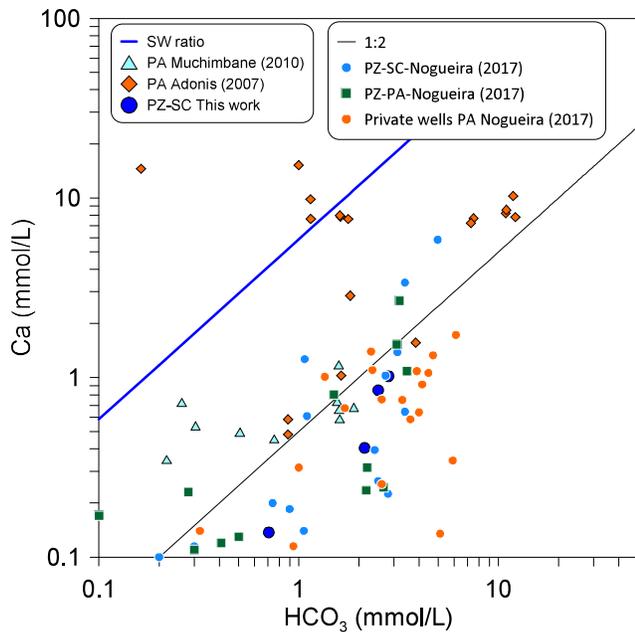
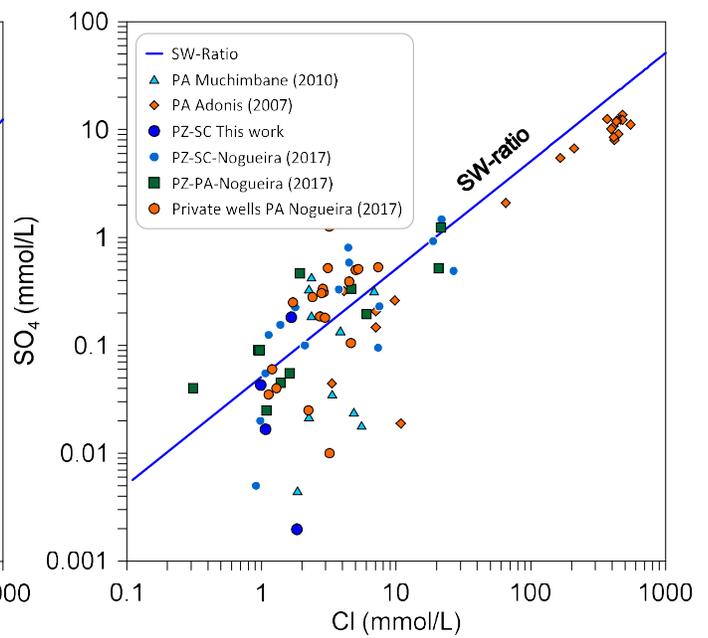
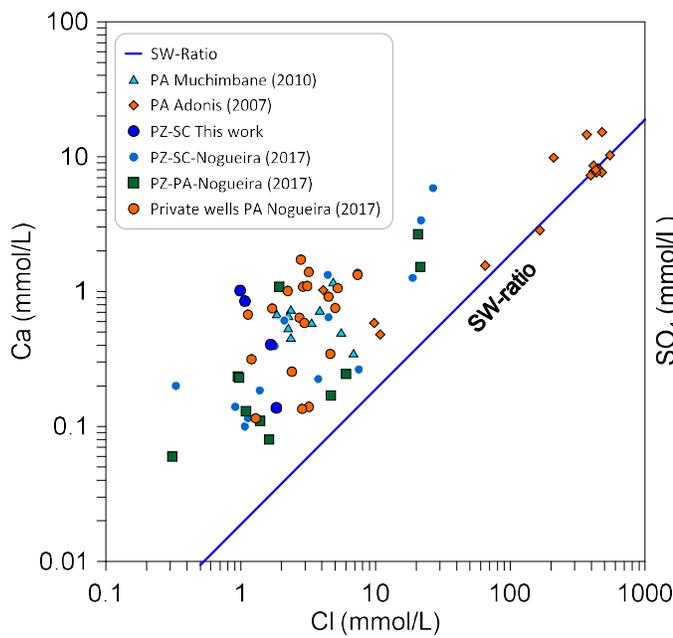
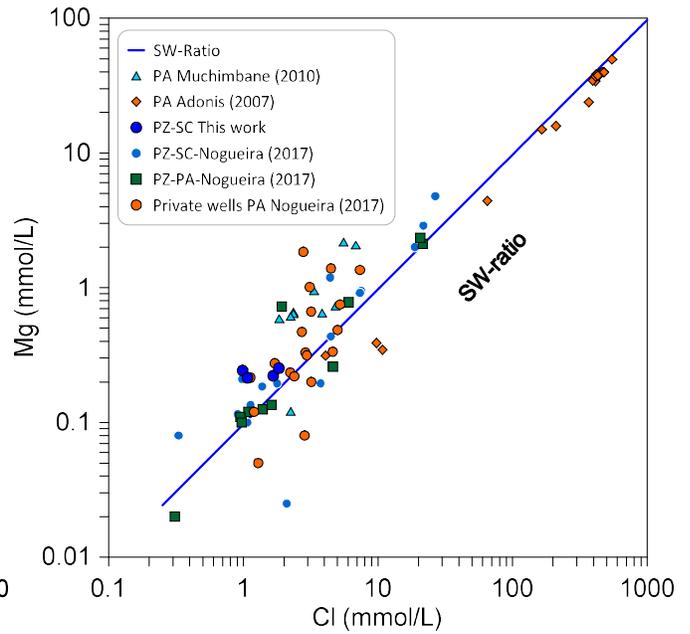
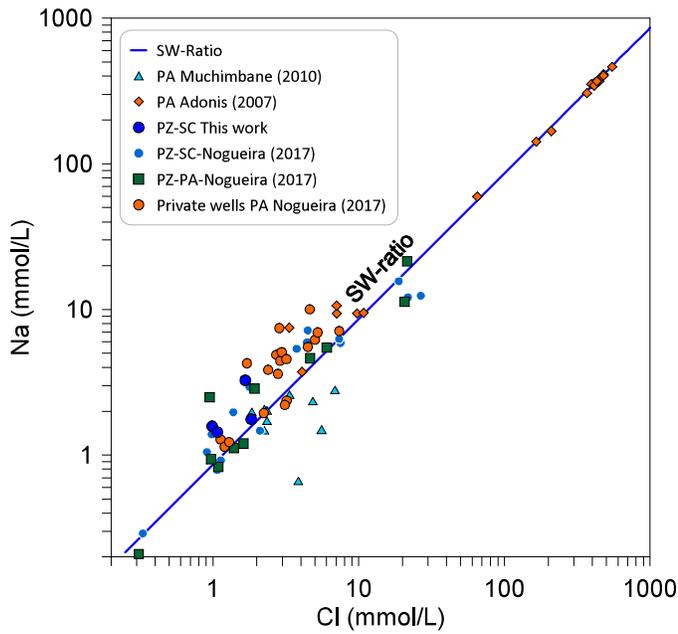
Table 3. Calculated $^{14}\text{C}_{\text{DIC}}$ residence times for groundwater (yr) based on a “single well” approach and for four usual geochemical correction schemes (Cendón et al., 2014). Proposed residence times are either an average of radiocarbon calculated values (Manhiça) or are estimated from ^3H considering an initial 2 TU in rainfall. M= modern.

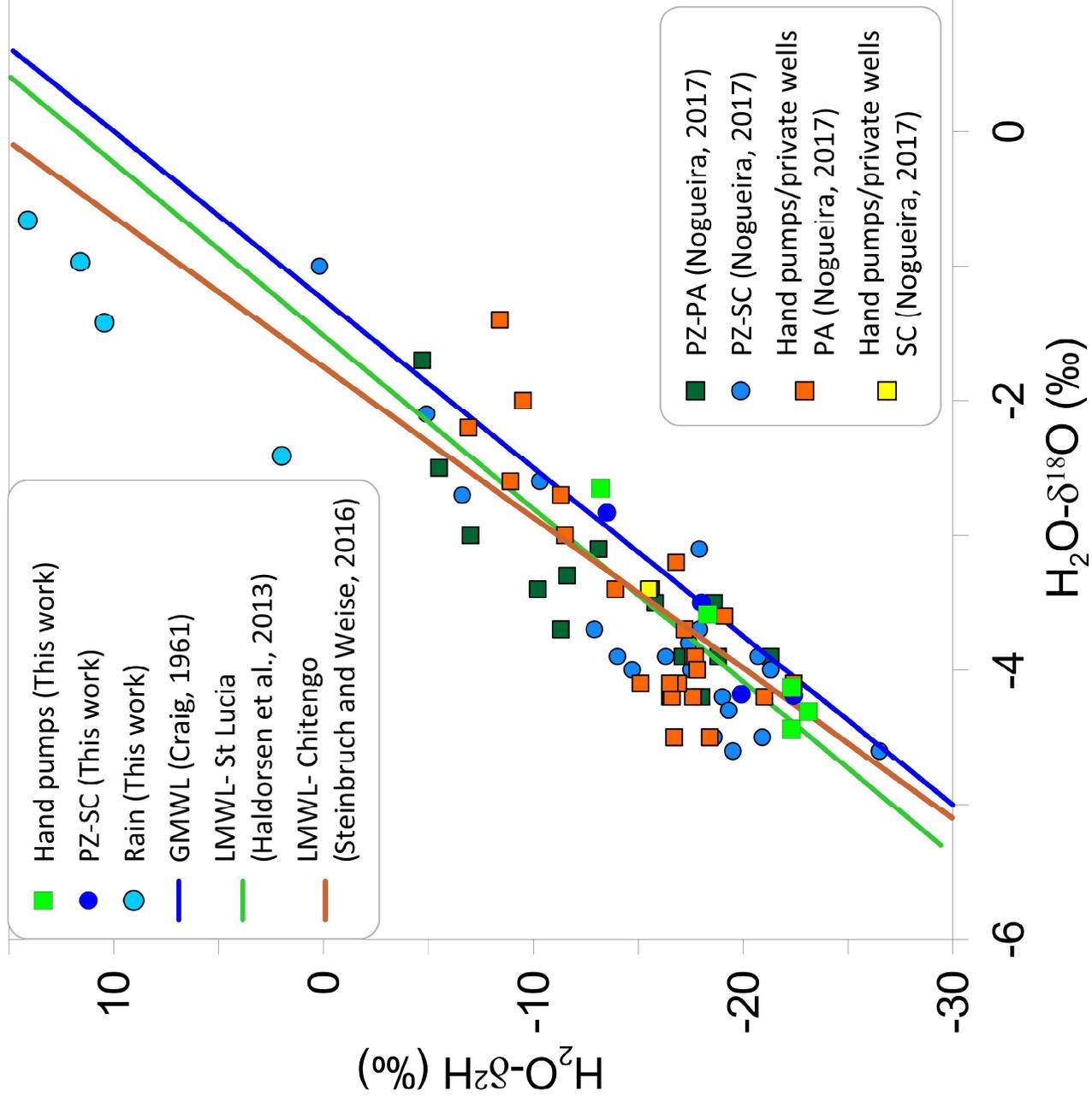
Table S1 (Supplementary data) Calculated recharge (mm) and % of rainfall based on a chloride mass balance. The rainfall used is an average of Maputo city, Marracuene and Manhiça (866 mm). The rainfall chloride composition used is 7 mg/L (De Sonnevile, 1984). In bores where no confining layer is present results for both pipes have been averaged (#). Values were calculated from chloride concentrations reported by Nogueira (2017).

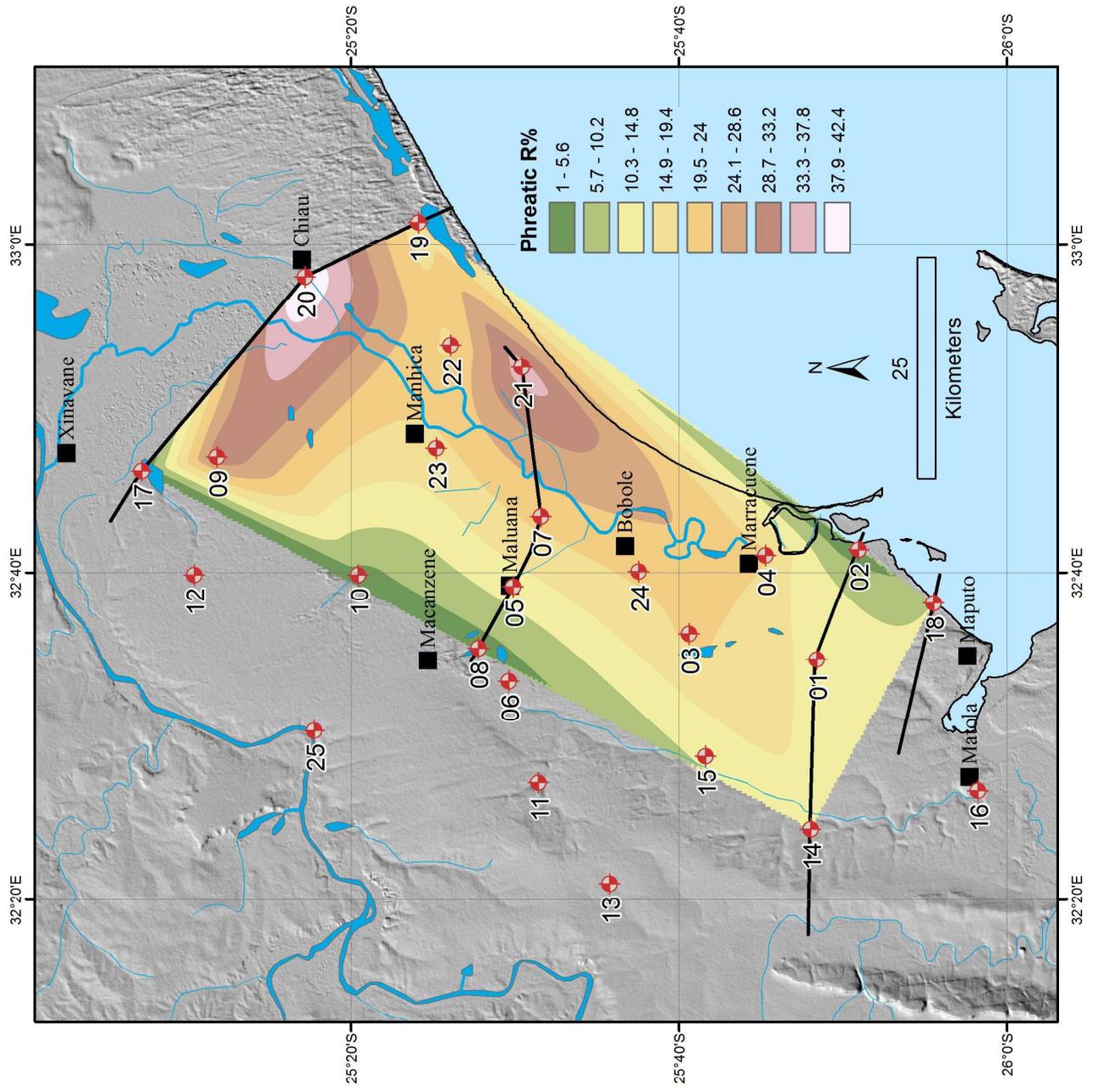












	Tamers	Ingerson and Pearson	Fontes-Garnier	Revised F-G solid	Proposed residence time (yr)
Manhiça (23PZ)	1600	900	900	600	1000
Maluana (5PZ)	M	M	M	M	40
Faftine (4PZ)	800	M	M	M	50
Pazimane (3PZ)	900	M	M	M	40

Bore	Recharge (mm)	% of rainfall
2PZ F	8	1
3PZ F	176	20
4PZ F	180	21
8PZ F	28	3
9PZ F	280	32
10PZ F	37	4
14PZ F	115	13
17PZ F	8	1
18PZ F	89	10
19PZ(#)	141	16
20PZ(#)	370	43
21PZ(#)	313	36
22PZ F	157	18