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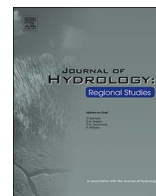
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Hydrogeochemical and isotopic indicators of vulnerability and sustainability in the GAS aquifer, São Paulo State, Brazil

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ABSTRACT

Study region: The Guarani Aquifer System (GAS), São Paulo State, Brazil, an important freshwater resource regionally and part of a giant, transboundary system.

Study focus: Groundwaters have been sampled along a transect. Based on environmental tracers (REEs, Br, B, δ^{11}B, Sr, ^{87}Sr/^{86}Sr) aquifer vulnerability and sustainability issues are identified.

New hydrological insights for the region: For sites near to aquifer outcrop, REE and Sr signatures (and relatively light δ^{13}C) trace possible vertical recharge from flood basalts directly overlying the GAS. This highlights aquifer vulnerability where confined by fewer basalts and/or having cross-cutting fractures. ^{14}C activities for these waters, however, suggest the impact of this recharge is significantly delayed in reaching the GAS. Anthropogenic sources for boron are not currently encountered; δ^{11}B highlights feldspar dissolution, isotopically lighter signatures in the deepest sampled GAS waters resulting from pH/hydrochemical speciation changes downgradient. Br/Cl signatures (and heavier δ^{18}O, δ^{2}H) in these latter samples appear to reflect a past climatic signature emplaced under more arid conditions; carbon isotope systematics (δ^{13}C, ^{14}C) support that these represent fossil waters, and care must be taken in their water resources management in regard to sustainability of abstraction. δ^{18}O, δ^{34}S (sulfate) signatures confirm hydrological arguments that waters leak out of the base of the GAS aquifer in this locality rather than underlying formations with poorer water quality potentially mixing in, although other deep GAS waters in the region do show this inter-aquifer mixing.

1. Introduction and aquifer context

The Guarani Aquifer System (GAS) is an important freshwater resource regionally across São Paulo (SP) State and forms part of a giant, transboundary aquifer system, areally some 1.2 million km^2, within the Paraná sedimentary basin comprising southern Brazil, eastern Paraguay, NW Uruguay and the NE extreme corner of Argentina. The total freshwater availability overall in the GAS based on a depth of abstraction limit of 400 m is estimated as being 2014 ± 270 km^3 (Organization of American States, 2009, their Table 7). However, some areas (near the borders of Paraná and Santa Catarina States and in parts of Rio Grande do Sul in Brazil) are already below this critical 400m depth threshold.

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1.1. Hydrogeological and mineralogical context

The Botucatu (BO) Formation is a well-sorted, aeolian sandstone, deposited (188–177 Ma) under mid-latitude desert conditions (Araújo et al., 1999). This is the principal hydrogeological unit of the GAS. Mineralogically, the GAS is composed of quartz (>90%), detrital feldspars (<10%), mica (<1%) and rock fragments cemented mainly by calcite and dolomite cements (Invernizzi and de Oliveira, 2004). Along with a porosity range 17–30% and depth 4–484 m (Araújo et al., 1999), average aquifer properties are: 138 m (thickness), 8.7 m/d (hydraulic conductivity). Lavas of the Serra Geral (SG) Formation (127–138 Ma) overlie the Botucatu Fm. confining the aquifer except at its outcrop margins. The underlying Triassic, argillaceous, fluvial-lacustrine sandstones of the Pirambóia (PI) Formation occur at depths 25–770 m, are less porous (14–24%) and less well-sorted with average aquifer properties: 139 m (thickness), 1.9 m/d (hydraulic conductivity). These two sandstone formations interdigitate, and are often identified simply as undifferentiated Botucatu- Pirambóia (BP) sandstone in borehole cores. Underlying the GAS in the study area are low-permeability, greatly variable thick-layers of Passa Dois, Tubarão and Paraná Group (Paleozoic) sediments (Bonotto, 2006; his Table 1). The underlying lithologies of the Passa Dois, Tubarão typically are associated with poorer quality, more saline waters with relatively high fluoride content (Hypolito et al., 2010; Montanheiro et al., 2014; Soler i Gil and Bonotto, 2015).

1.2. Flow system and aquifer diagenesis

A conceptual geologic history of the groundwater flow system has been outlined originally by Araújo et al. (1999). For the aquifer system developed in the Botucatu Fm. from initial deposition (188–177 Ma), overlay of lavas of the Serra Geral Formation (127–138 Ma), and precursor uplifting of the Serra do Mar mountains (110–90 Ma), the water in the system was presumed fresh to slightly alkaline and brackish due to the prevailing arid to semi-arid climate. Subsequent fresh water flux through the system effectively has flushed the overlying Botucatu aquifer, whilst brackish waters persisted then in the underlying Pirambóia aquifer of the GAS. Based on statistical analysis of the hydrochemistry of GAS groundwaters, Meng and Maynard (2001) have suggested that in recharge area of the Botucatu sandstone aquifer dissolution of alkali-feldspars is the main reaction observed; this is seen also in secondary porosity development of the Botucatu aquifer, with calcite and feldspar leached from the framework (calcite removed from the aquifer a distance on average some 140 km from outcrop and a burial depth of 250 m) and diagenesis of the original feldspathic sandstone to a quartz arenite at and close to outcrop (França et al., 2003). In the basin interior where Na- and SO_4-facies waters are dominant Meng and Maynard (2001) invoke upward leakage of poorer quality, saline water from underlying formations such as Passa Dois and Tubarão Group, as do as do Kern et al. (2008) and Manzano and Guimareans (2012). However, Sracek and Hirata (2002) suggest instead that a cation-exchange front has developed in the GAS aquifer reaching as far as Águas de Santa Bárbara (ASB) along the given transect, some 50–70 km from the inferred recharge zone, effectively explaining then the downgradient loss of Ca and increasing Na downgradient along the transect from this point. A conceptual framework for the diagenetic evolution (eodiagenesis, mesodiagenesis, teleodiagenesis) of the GAS sediments has been put forward by Gesicki (2007), which is summarised in Hirata et al. (2011; their Fig. 2).

1.3. The strategic nature of the resource

As outlined by Mejía et al. (2012) "The GAS constitutes a strategic reserve for water supply in the face of increasing scarcity and pollution of surface water sources in southern Brazil and parts of Uruguay, Paraguay and Argentina." A Strategic Action Programme (SAP) for the transboundary GAS aquifer gives groundwater abstraction rates of 1.04 km^3/year and suggests natural replenishment rates of 0.4–1.4 km^3/year such that the volume exploited is about the same as the natural recharge rate and therefore considered a safe aquifer yield (Organization of American States, 2009, their Chapter 2); however, it is highlighted also that 90% of the current abstractions occur in Brazil, and the largest number of wells and volumes of water abstracted are in SP State. As pointed out by Rodriguez et al. (2013), whilst in the regional sense the rate of groundwater pumping of the GAS in SP state is well within the rate of aquifer recharge, where pumping is concentrated in heavily-populated and industrialised regions the situation may be less sustainable. Foster et al. (2009) have documented the overdraft of groundwater and decline of the water table in the GAS aquifer due to aquifer overabstraction over several decades around Ribeirão Preto city in the NE of SP State which could then lead to induced vertical recharge from overlying formations and possible aquifer vulnerability. Recent research is also starting to identify structural controls on water quality in the Paraná Basin and GAS (e.g. Ferreira et al., accessed 06/2015; de Barros et al., 2014) which may affect also aquifer sustainability (cf. Dickson et al., 2014). In a stronger sense, for water resources management and sustainability of any aquifer the presumption of equating safe aquifer yield to its natural recharge can be problematic (e.g. Sophocleous, 1997; Elliot et al., 1998, 2001), especially for large transboundary systems (Elliot et al., 2014). All aquifers are effectively distributed flow systems – water coming in at any specific location is flowing somewhere specifically which abstraction wells then intercept. The use of environmental tracers of groundwater flow and residence times and hydrochemical and hydrogeochemical processes, can help identify and characterise e.g. surface-subsurface water interactions, subsurface flowpaths, intra- and inter-aquifer connectivity, and water quality provenance and issues. These should be taken into account for water resources management (Elliot, 2014) as indicators of vulnerability, exposure, and sustainability, and which then may feed into a risk management framework context for the resource (cf. Hall and Borgomeo, 2013). Sindico and Hawkins (2015) and Villar (2016) have highlighted the role of such scientific information particularly in sketching a clearer picture of what needs to be managed; recognising e.g. aquifer response time and renewability is a recommended pathway to improving groundwater governance per se (Groundwater Governance, 2015). Most recently, Hirata et al. (2017) have published a policy briefing promoting the entry into force of the Guarani Aquifer Agreement (signed in Argentina in

2010) as a means to meeting for example the objectives of the 2030 Agenda for Sustainable Development adopted by the United Nations Resolution A/70/1 in 2015 as part of the Paris Agreement of the United Nations on Global Climate Change, for which Goal 6.5 effectively targets international agreements for management of such transboundary aquifers.

Bonotto and Elliot (2017) have recently published original analyses of a suite of rare earth elements (REEs) and also boron (δ^{11}B) and strontium (^{87}Sr/^{86}Sr) isotopic ratios in groundwaters from the Guarani Aquifer System (GAS) in the Middle and Lower Paranapanema Basin in SP State (i.e. Water Resource Management Unit (WRMU) or Unidades Hidrográficas de Gerenciamento de Recursos Hídricos (UGHRI) 17 & 22, respectively) and also a relevant rainwater sample in São Paulo State, Brazil. The current paper places and integrates these environmental tracers and other hydrogeochemical and isotopic signatures then in the context of vulnerability and sustainability issues for this aquifer.

2. Methods

The current paper presents an integration of published and/or accessible grey literature sources of hydrogeological/geohydrological, hydrogeochemical and environmental tracers (including) isotopic data for the GAS aquifer in São Paulo State (Brazil). This study focusses on a particular downgradient section (A-A', Fig. 1) which is considered representative of the regional conceptual model along a direction of groundwater flow. This allows local scale information (including eg borehole construction details) to be embedded in the regional context.

Groundwater have been sampled from ten municipalities along with one rainfall site in SP state: AVR-Avaré; SUT-Sarutaiá; ASB-Águas de Santa Bárbara; BCS-Bernardino de Campos; PPA-Paraguaçu Paulista; PPE-Presidente Prudente; PEO-Presidente Epitácio; SCP-Santa Cruz do Rio Pardo; SPO-São Pedro; ITI-Itirapina; RCL-Rio Claro. The location of the specific sites discussed is shown in Fig. 1. Well details including borehole stratigraphy for the 10 cities sampled for groundwater in SP state are shown in Table 1; full details of the sample analyses (including REEs, bromide, boron, δ^{11}B, strontium and ^{87}Sr/^{86}Sr signatures) are given by Bonotto and Elliot (2017; their Tables 2 & 3). Basalts and diabases of the Serra Geral (SG) Formation overlying the GAS occur in all wells sampled, except at São Pedro (SPO) city. A section along the specific transect A-A' (Fig. 1) in the Rio Paranapanema Basin is shown in Fig. 2. Additional environmental tracer literature (e.g. groundwater age, stable isotopes of water, etc.) is identified, incorporated in summary figures, and interpreted in context in the text and figures as supporting information for the discussion.

3. Results & discussion

3.1. Rainwater sample at recharge (Rio Claro)

Monthly rainfall samples published by the International Atomic Energy Agency (IAEA) for Rio Claro city (IAEA GNIP data, World Meteorological Office (WMO) station code 8374701; Lat. 22°23′57″S, Long. 47°32′37″W) during 2013–14 (Fig. 3) establishes a Local Meteoric Water Line (LMWL) relevant to the GAS recharge zone. Published data for the water stable isotope signatures (δ^{18}O‰, δ^{2}H‰ versus VSMOW) of rainfall for weekly sampling (da Silva, 1983) during December both for Ribeirão Preto city (Lat. 21°10′08″S, Long. 47°49′05″W) in the north-east of the outcrop area and also São Carlos city (Lat. 22°00′00″S, Long. 47°53′38″W) again in the recharge zone of the GAS and lies closer to Rio Claro, and also rainfall event sampling (December 1997) from Campinas city (IAEA GNIP data; World Meteorological Office (WMO) station code 8372901; Lat. 23°00′00″S, Long. 47°07′59″W) again close to Rio Claro, are also shown (Fig. 3). All of these samples taken over shorter sampling intervals than monthly still plot close to the established LMWL. This supports the statement by Bonotto and Elliot (2017) that the single rainwater sample collected at a station located in the GAS recharge beds close to Rio Claro city area, and sampled during the middle of the wet season (December 2009) reflects then modern, pristine rainfall signatures unaffected essentially by e.g. evaporative effects. This is then representative for comparison with groundwater samples in this study. It is noted further that published groundwater GAS signatures for relevant samples in the current study also generally plot then close to this characteristic LMWL for GAS recharge area (Fig. 3) reflecting meteoric waters.

3.2. Downgradient hydrochemical trends for the GAS groundwaters (samples Avaré, Sarutaiá, Águas de Santa Bárbara, Santa Cruz do Rio Pardo, Paraguaçu Paulista, Presidente Prudente, Presidente Epitácio)

The trends downgradient for the GAS groundwaters along transect A-A' (Fig. 4) highlight particularly that: (i) the highest Total Dissolved Solids (TDS, measured by electrical conductivity (EC) as a proxy) and dissolved chlorinity (Cl⁻) occur at Presidente Prudente suggesting the greatest maturity and residence time in the system; (ii) Eh increases downgradient between Bernardino de Campos and Santa Cruz do Rio Pardo (with a coincident dip in alkalinity), but then a possible redox barrier occurs between Santa Cruz do Rio Pardo and Paraguaçu Paulista (negative Eh values occurring at and after Paraguaçu Paulista which gives then the lowest U content at Presidente Prudente); (iii) the influence of a flow direction from the NW at the end of the transect A-A' at Presidente Epitácio (e.g. dilution of chlorinity with e.g. Na, Sr, F, B following sympathetically, but also then increasing dissolved U and also SO$_4$ at Presidente Epitácio), as picked up also by Hirata et al. (2011) using Principal Component Analysis; (iv) an apparent spike of U at Águas de Santa Bárbara, and spikes of Sr at Avaré and Bernardino de Campos and highest concentrations of REEs at Bernardino de Campos. Bernardino de Campos also has the highest dissolved ^{222}Rn activity (Bonotto and Elliot, 2017, their Table 2).
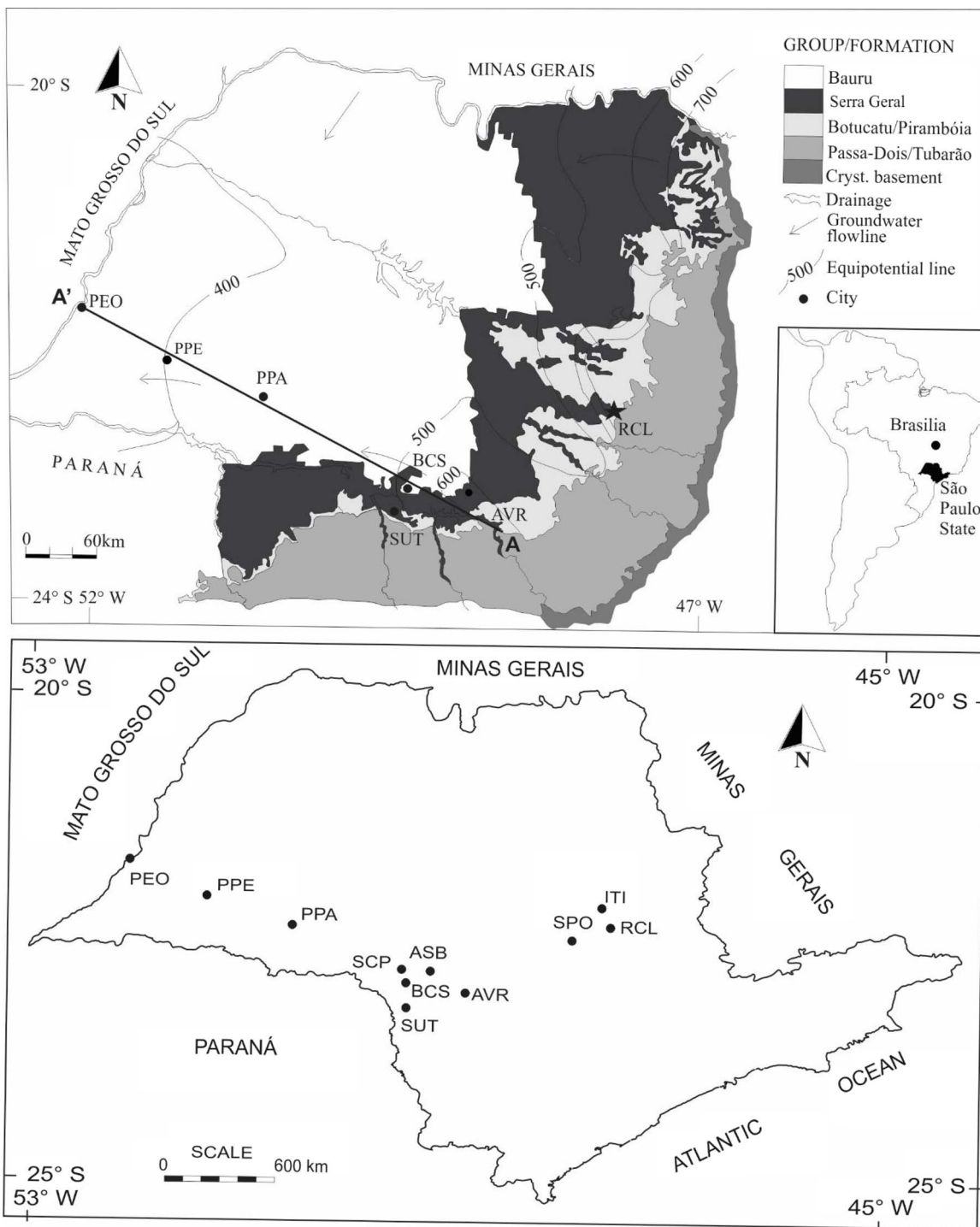
Fig. 1. (top) Simplified map modified from da Silva (1983) showing the outcrop and groundwater flow direction in the GAS, São Paulo State, Brazil, as well the transect AA' from Avaré up to Presidente Epitácio (SE-NW direction); the star symbol indicates the location of the rainwater sampling point (Rio Claro). (bottom) Location in São Paulo State of all sampling sites.

3.3. Dissolved REEs

Since the concentrations of Rare Earth Elements (REEs) typically are at trace levels in rocks, potentially they can be used as sensitive environmental tracers of groundwater flow and water-rock interactions in aquifers (Smedley, 1991; Johannesson et al., 1996, 1997; Tweed et al., 2005; Tang and Johannesson, 2006). Groundwater Rare Earth Elements (REEs) typically reflect those of

Fig. 2. Simplified geological cross-section along transect AA' in the Lower and Middle Paranapanema Basin according to da Silva (1983) showing the depth and stratigraphy of the bores, as well the groundwater flow direction in the GAS. The main lithologies are (Almeida and Melo, 1981): Bauru (B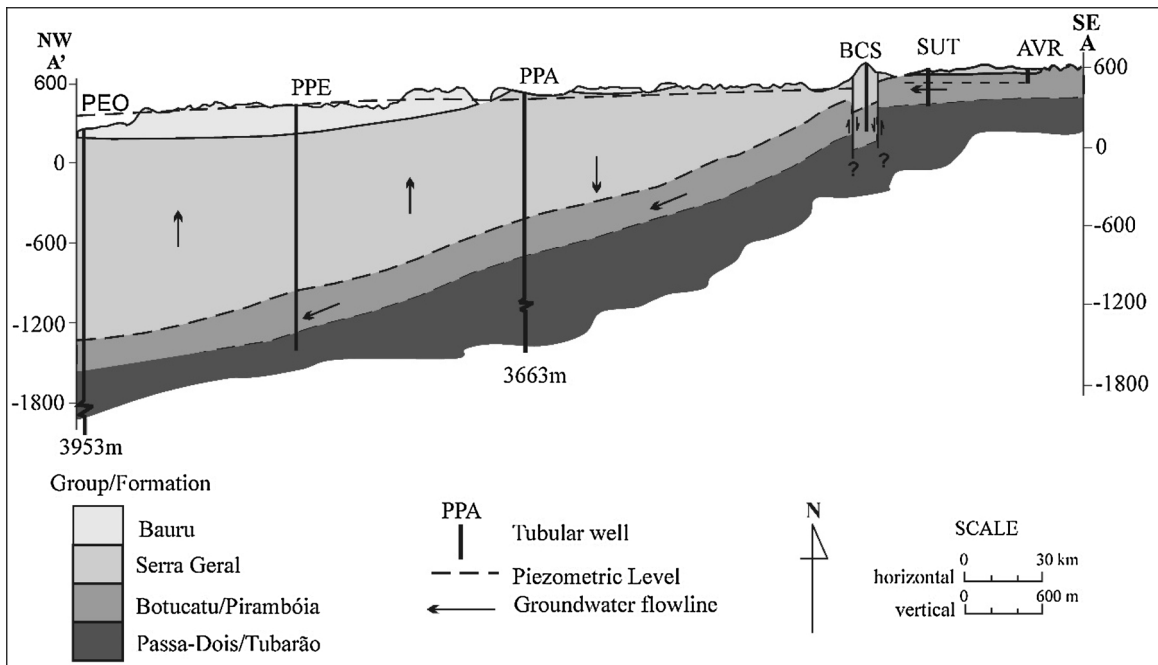A, Cretaceous) = sandstones, siltstones, mudstones, carbonate nodules; Serra Geral (SG, Triassic) = basalts, diabases; Botucatu/Pirambóia (BO/PI, Triassic) = sandstones; Passa-Dois/Tubarão (PD/TU, Palaeoizoic) = sandstones, conglomerates, siltstones, mudstones, shales, limestones, diamictites, tillites, rythmites.
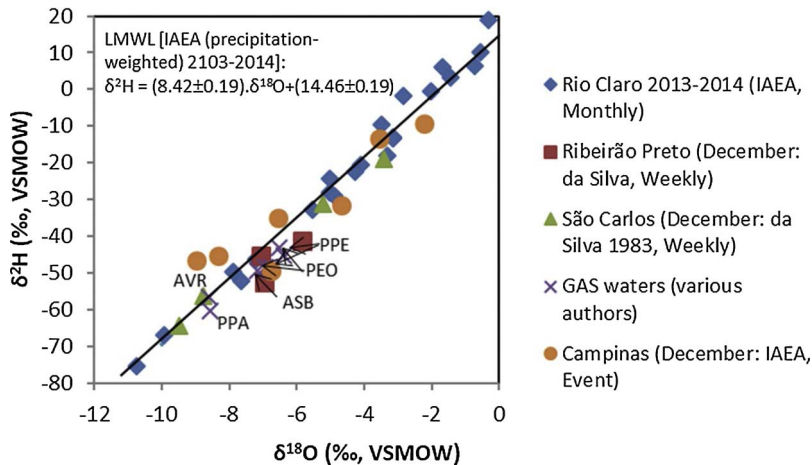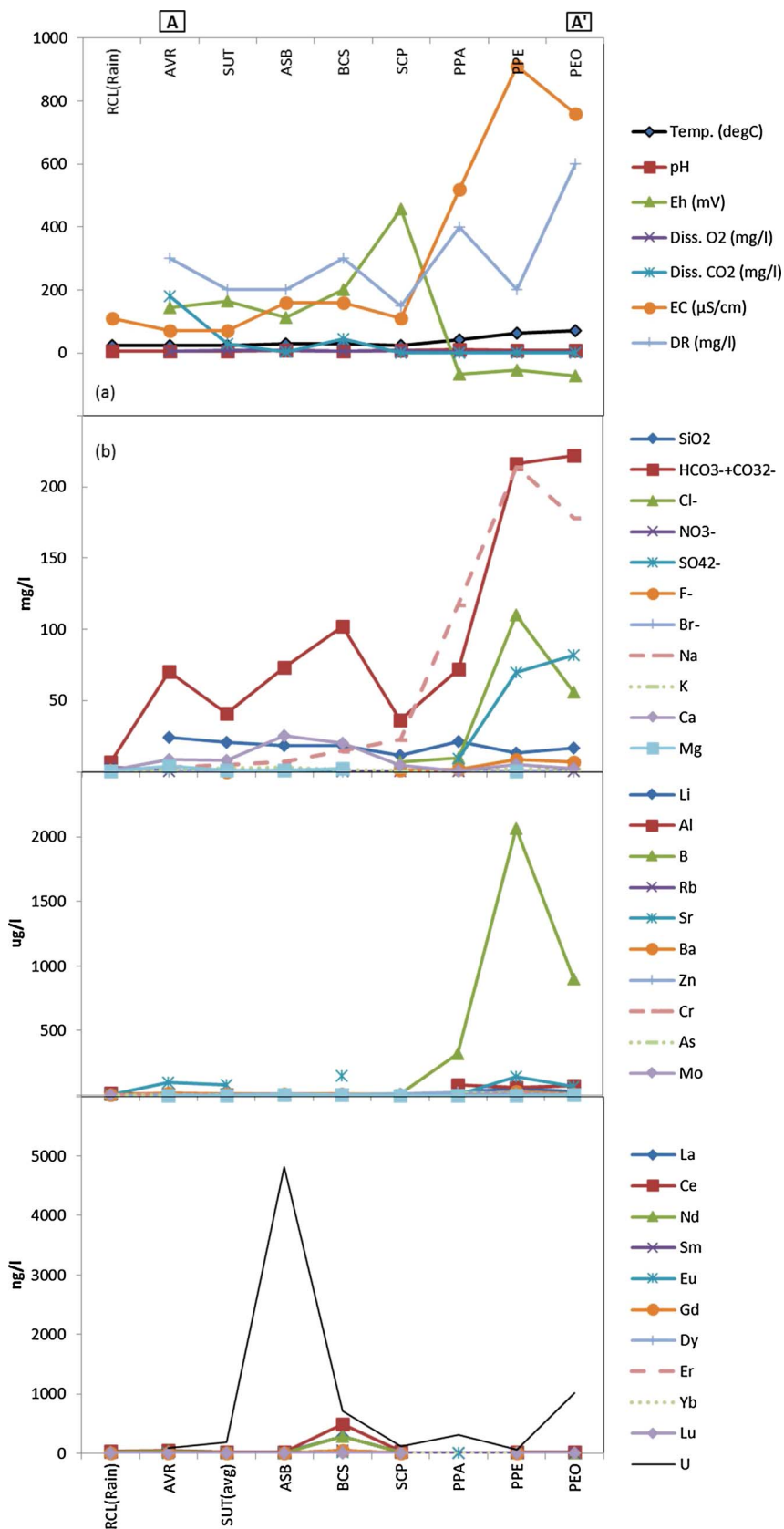

Fig. 3. Stable isotopes of water (‰ δ^2H, $\delta^{18}O$ with respect to Vienna Standard Mean Ocean Water, VSMOW) for monthly rainfall samples (*diamonds*) at Rio Claro (2013–2014) and event waters for December 1997 from Campinas station (*circles*) in São Paulo State. Data are taken from the Global Network of Isotopes in Precipitation (GNIP) database of the International Atomic Energy Agency (IAEA). The Rio Claro data define the precipitation-weighted Local Meteoric Water Line (LMWL). Relevant weekly rainfall samples from Ribeirão Preto (squares) and São Carlos (triangles) (da Silva, 1983) also have been included. Additionally, GAS groundwater signatures (*crossed symbol*) for sites Avaré (AVR), Águas de Santa Bárbara (ASB), Paraguaçu Paulista (PPA), Presidente Epitácio, Presidente Prudente have been included (da Silva, 1983; Kimmelmann et al., 1994; Gastmans et al., 2010a) for comparison.

host aquifer lithologies, and are therefore useful tracers of flow directions where mineralogies of different aquifers vary (Tang and Johannesson, 2006; Tweed et al., 2006).

More or less a full suite (excepting Pr, Pm, Tb, Ho, Tm) of REEs was analysed in the GAS groundwater samples (Bonotto and Elliot, 2017, their Table 3). To eliminate the 'Oddo-Harkins effect' (whereby, as a rule, even-numbered elements are more abundant than their immediate odd-numbered neighbours) and to characterise the REE signatures all concentrations have been normalised both to the C1 chondrite standard and also the NASC (so-called 'North American Shale Composite') standard. Results are plotted in Fig. 5a–c, respectively. Whilst outcrop volcanic rocks of the Serra Geral Formation in São Paulo (SP) State generally have been well-characterised for REEs, signatures for outcrop rocks associated with the Botucatu and Pirambóia Fm. are generally lacking. In Fig. 5b two

(caption on next page)

samples attributed as Botucatu sandstone (sst) are shown for comparison, albeit a sample from Santa Catarina State SW of the study area (Crósta et al., 2012) and one from Rio Grande do Sul in southern Brazil (Gilg et al., 2003) and not SP State itself. Additional data in Fig. 5c shows a representative flow basalt sample (KS 692) of Pitanga-type in the Serra Geral (SG) Formation in the region around the city of Jaú (Squisato et al., 2009). Similar REE signatures are to be found in Serra Geral flow basalt samples found specifically in the vicinity of Bernardino de Campos (BCS; de Assis Janasi et al., 2007, their Table 2).

The REE trends for both Itirapina and São Pedro (although more subdued) suggest a classical W-type tetrad distribution when normalised to C1 Chondrite, indicative of rock dissolution (cf. Takahashi et al., 2002; Fig. 5a). Similar trends can be found in shale-normalised (i.e. NASC) signatures but are generally subtler (Kawabe, 1996). The well descriptions for both sites (Table 1) point to possible water-rock interaction directly with outcrop of the GAS aquifer (undifferentiated Botucatu-Pirambóia Fm; Table 1) in a known area of recharge (cf. Wendland et al., 2007, 2015), with REEs apparently characterised here by positive Eu (Eu/Eu* = 1.7 at Itirapina) and also weaker Gd (1.45 at Itirapina) anomalies when NASC-normalised (Fig. 5b). The singular Botucatu sandstone sample from Santa Catarina State (Crósta et al., 2012) similarly shows a Eu-anomaly and weaker Gd-anomaly. However, the recharge waters potentially feeding the A-A' transect further to the west do not appear to pick up this Gd-anomaly, which could mean that Gd is lost or diluted in flowing westwards or that this is not in fact an identified flow direction for the transect; indeed the Itirapina and São Pedro sites lie in a different WRMU (UGHRI 13) and potentiometric contours around the Itirapina and São Pedro sites suggest their recharge into the GAS in this locality flows instead directly northwards (Fig. 1). An alternative is that source signatures other than from the sandstone predominate for the A-A' transect waters.

For the A-A' transect waters, the Bernardino de Campos groundwater sample itself particularly shows the highest REE concentrations and a predominant characteristic positive Eu-anomaly when NASC-normalised, with only a weak apparent positive anomaly potentially in Nd and a negative weak anomaly potentially in Yb, similar to the identified SG flow basalt sample (Fig. 5c). The samples Avaré, Sarutaiá, Águas de Santa Bárbara show a more subdued version of this same REE distribution. This strongly suggests interaction with or recharge through the SG basalts in the vicinity of Bernardino de Campos for example, and highlights then the possible vulnerability of the GAS waters through SG recharge. The REE signature of a NPK-fertilizer used in Rio Grande do Sul (de Vargas, 2010; their Tables 12 and 20) which also shows a weak positive Eu-anomaly has been added for comparison, but this potential source term is unlikely as there are no concomitant increases in Ca, Mg, K, SO_4, NO_3, etc. in the sampled waters. For recharge waters at the start of the transect A-A' then there appears to be predominantly an apparent (NASC-normalised) Eu-anomaly (cf. 1.42 Avaré, 21.00 Sarutaiá, 1.47 Águas de Santa Bárbara, 1.91 Bernardino de Campos) and a similar Lu-anomaly (Lu/Lu* ~0.2) which may reflect therefore interaction with overlying basalts (Table 1). Gustinelli et al. (2017) have recently developed a protocol for the determination of Eu isotopes ($\delta^{151/153}$Eu) in low-level, natural waters including groundwaters which in the future may provide additional source/process evidence.

The basalts of the Serra Geral (SG) Formation themselves contain an important source of waters for water supply in the southern SP and Paraná States (e.g. Athayde et al., 2012; Gastmans et al., 2013a). Vertical fracturing of the basalts previously has been thought potentially to facilitate waters in the Serra Geral Aquifer (ASG) leaking into and/or recharging the GAS. Wahnfried (2010), in a study aimed at assessing aquifer vulnerability for wellhead protection near Ribeirão Preto city in the north-east of SP State, has suggested limited connection there since the vesicular basalt layers act effectively as stratabound hydraulic barriers. However, a more recent detailed study of cross-cutting tectonic fractures (Fernandes et al., 2016) confirms a potential for vertical groundwater flow This limited hydraulic connection is echoed by Fernandes et al. (2012) for the southern portion of the state relevant to the current study but with the significant caveat for this locality that local strike-slip events where their activity was more intense (cf. Fernandes and Amaral, 2002) and/or where there are fewer flood basalts indeed might allow vertical connection (as suggested also by Rabelo and Wendland, 2009). Fernandes and Rudolph (2001) have related the presence of fracture structures (especially extensional fractures) with enhanced water-well production capacity. In the current study it appears then that the sampled GAS groundwaters (e.g. Bernardino de Campos, Avaré) have indeed picked up characteristic REE signatures from water-rock interaction at recharge or through well construction, discriminating geochemically then that a component of the pumped waters is affected by interaction with basalts of the SG Formation which overlie the Botucatu-Pirambóia Formations.

In the A-A' transect groundwaters, this Eu-anomaly apparently persists as at least as far as Paraguaçu Paulista (Fig. 5c), following this flow direction, beyond which mixing with deeper waters is inferred with the likes of dissolved Eu below detection in the deepest GAS groundwater (Presidente Prudente).

3.4. Other trace/minor elements (Br, B, Sr) and Isotopes ($\delta^{11}B$, $^{87}Sr/^{86}Sr$)

Dissolved major/minor elements such as Na, F, (data not shown) and also trace Br, B and minor Sr all generally plot with linear trends against geochemically conservative dissolved Cl^- (i.e. chlorinity) in the GAS groundwaters. For example, for Na it can be shown (cf Bonotto, 2006) that the deepest groundwaters (including Presidente Prudente, Paraguaçu Paulista, Presidente Epitácio)
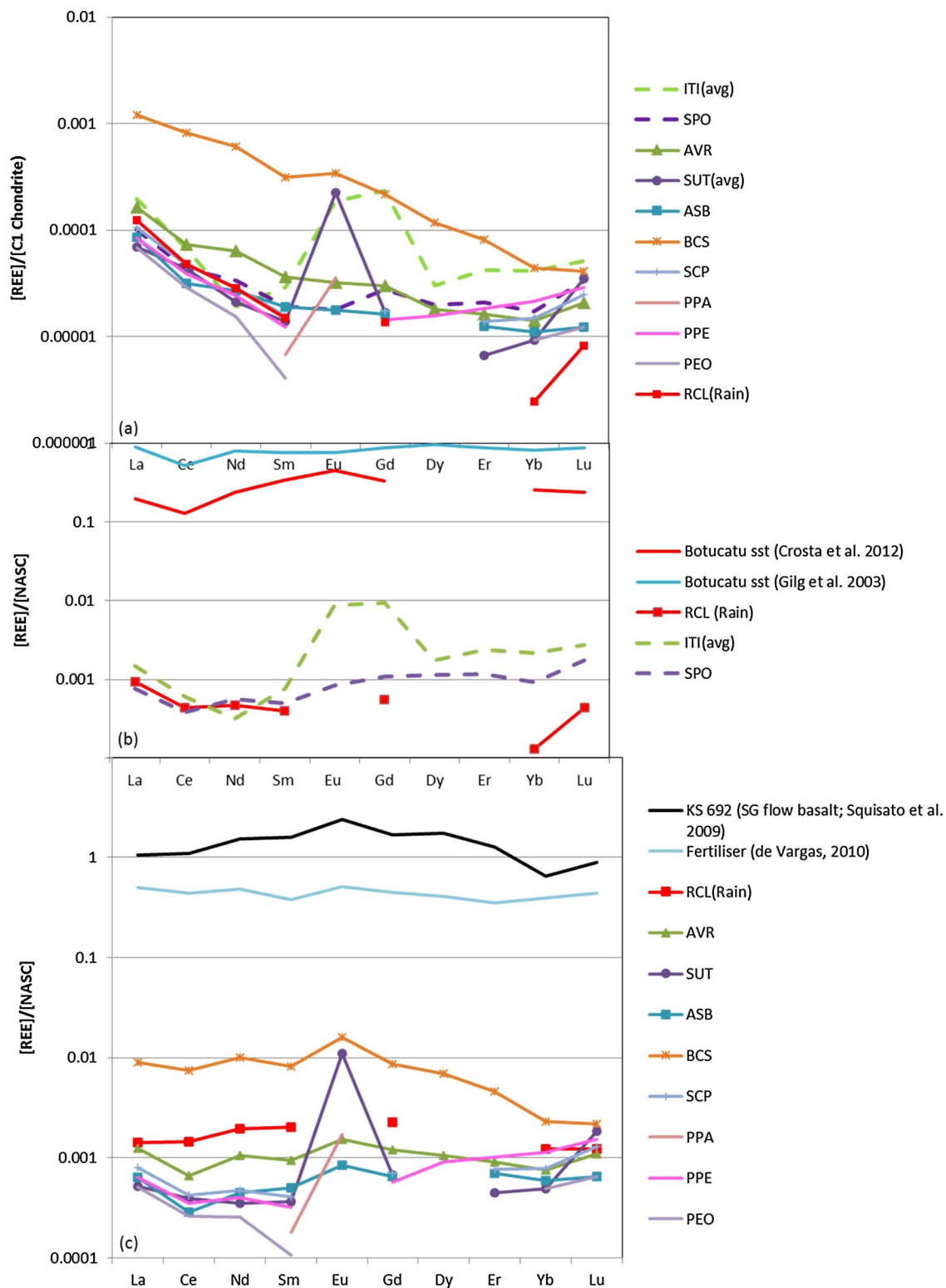
Fig. 5. Dissolved REE concentrations in sampled GAS waters normalised to (a) C1 chondrite (Anders and Grevesse, 1989), (b) and (c) North American Shale Composite (NASC) standard (Gromet et al., 1984). Additional data for comparison shows in (b) REE-signature attributed to the Botucatu Sandstone (sst) (Gilg et al., 2003; Crósta et al., 2012) and in (c) a Serra Geral flow basalt representative of the region (Squisato et al., 2009). Additionally, an NPK- fertiliser sample (de Vargas, 2010) has been included.

TABLE 1

Location and description of the identified tube wells drilled in the GAS-Guarani Aquifer System, São Paulo State, Brazil, whose waters were analysed in Bonotto and Elliot (2017). The Stratigraphic codes are: M = weathered mantle; DI = diabase sill; BA = Bauru Group; SG = Serra Geral Formation; BO = Botucatu Formation; PI = Pirambóia Formation; PD = Passa-Dois Group; TU = Tubarão Group; PA = Paraná Group (Devonian). Particular well construction details can be found in the SIAGAS database (Sistema de Gestão de Informações de Águas Subterrâneas) from the CPRM (Serviço Geológico do Brasil; http://www.cprm.gov.br).

Sample code	Site	SIAGAS[a]	State	Latitude	Longitude	Altitude (m)	Depth (m)	Open or slotted depth	Stratigraphy
ITI	Itirapina	03369	SP	22°15'13"S	47°49'05"W	880	129	69-129	BP (0-60); DI (60-115); BP (115-129)
SPO	São Pedro	04666	SP	22°32'07"S	47°54'33"W	550	150	66-150	BP (0-150)
AVR	Avaré	04786	SP	23°06'46"S	48°54'33"W	640	150	113.8-150	M (0-8); BA (8-12); SG (12-35); BP (35-150)
SUT	Sarutaiá	07845	SP	23°16'03"S	49°29'05"W	750	152	71.5-140.67	M (0-4); SG (4-26); BO (26-145); DI (145-152)
ASB	Águas de Santa Bárbara	10334	SP	22°52'24"S	49°13'38"W	560	120	65-120	SG (0-8); BO (8-56); SG (56-104); BO (104-120)
BCS	Bernardino de Campos	26898	SP	23°01'41"S	49°29'05"W	660	509	25-509	M (0-21); SG (21-327); BO (327-402); PI (402-509)
SCP	Santa Cruz do Rio Pardo	29768	SP	22°54'56"S	49°39'05"W	440	124	18-124	SG (0-114); BO (114-124)
PPA	Paraguaçu Paulista	00019	SP	22°25'21"S	50°33'38"W	474	3663	127-3663	BA (0-64); SG (64-974); BO (974-1250); PD (1250-2050); TU (2050-3554); PA (3554-3663)
PPE	Presidente Prudente	46651	SP	22°06'45"S	51°22'43"W	407	1800	1367.67-1713.74	BA (0-218); SG (218-1440); BO (1440-1570); PI (1570-1730); PD (1730-1800)
PEO	Presidente Epitácio	00015	SP	21°46'29"S	52°05'27"W	258	3953	91.32-3183	BA (0-90); SG (90-1623); BO (1623-1976); PI-PD-TU-PA (?-?)
RCL[b]	Rio Claro	–	SP	22°24'41"S	47°33'41"W	625	–	–	–

[a] SIAGAS number 35000###### (http://siagasweb.cprm.gov.br/layout/).
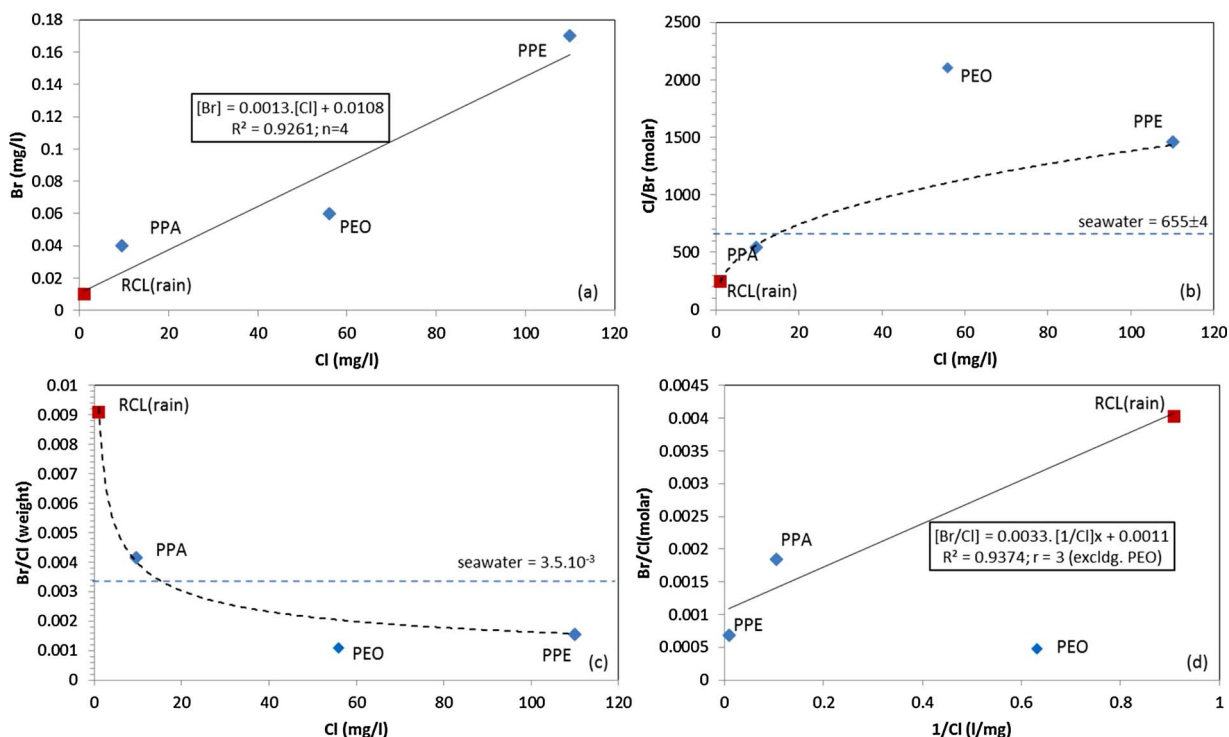
[b] RCL = Rainwater sample.

Fig. 6. Cross-plot mixing diagrams: (a) Br (mg/l) versus geochemically conservative chloride molarity (Cl, mmol/l); (b) Cl/Br (molar) ratio versus chlorinity (weight; Cl, mg/l); (c) Br/Cl (weight) versus chlorinity (weight); (d) Br/Cl (molar) versus reciprocal chlorinity (weight). Particular GAS groundwater and rainfall (Rio Claro) sites are identified. Data are from Bonotto & Elliot (2017).

plot along a linear trend [Na] = 0.96[Cl] + 113.9 with an enhanced intercept for Na at the origin over sampled waters such as Santa Cruz do Rio Pardo close to the recharge zone (Na = 22.6 mg/l), highlighting the lithological imprint of water-rock interaction then downgradient of the recharge area.

3.4.1. Br/Cl ratios

A plot of Br versus Cl also appears to show conservative behaviour with chlorinity (Fig. 6a). The (weight) Br/Cl ratio ~ 0.0013 given by the slope of the Br vs. Cl cross-correlation plot (not shown) is half the characteristic weight ratio (0.0034) of say a modern seawater precluding a saline intrusion source; this also precludes a simple evaporitic source from halides for the deeper waters, halides characteristically showing much smaller Br/Cl ratios than seawater, e.g. 0.000014 for halite mineral (cf. Hounslow, 1995). Alcalá and Custodio (2004, 2008) have shown that on a Cl/Br versus Cl plot geochemical mixing of end-members follows a curve (Fig. 6b, excluding Presidente Epitácio specifically since it is affected by flow from the NW) which transforms to a linear trend in a plot of Br/Cl (molar) versus 1/Cl (l/mg) (Fig. 6d). When molar ratios for Br/Cl are plotted against Cl the GAS samples similarly appear to follow then a mixing curve between a rainfall value (Rio Claro) and Presidente Prudente for a saline end-member with a Br/Cl much less than, for example, seawater (Fig. 6c). Sracek and Hirata (2002) have suggested that the input of Cl⁻ for the deepest waters comes from the diffusion of ions from underlying brackish waters of the Pirambóia aquifer and argue the aqueous diffusion coefficients for Br and Cl are similar (Martin, 1999) such that the Br/Cl of the mixing source should not be affected for relatively low salinity waters. However, chlorinity remains < 150 mg/l even in the deepest water (Presidente Prudente). Instead, the Cl/Br ratio (molar) versus Cl (mg/l) for the deepest sample (Presidente Prudente) plots closest genetically to "coastal arid climate" waters as characterised by Alcalá and Custodio (2004, 2008) for modern coastal groundwaters under arid/semi-arid conditions, indicating a possible characteristic recharge source. Thus, the Br-Cl relationships here potentially reflects mixing between modern rainfall (e.g. Rio Claro) and a stored signature (e.g. Presidente Prudente) emplaced in the aquifer system when the climate was more arid.

3.4.2. Boron and strontium and their isotopes

Both B and Sr (Fig. 7) also appear to plot conservatively against chlorinity, indicating evolutionary trends downgradient.

3.4.2.1. Boron. Negrel et al. (2002) have previously used boron isotopes to highlight water-rock (silicates) interaction in coastal groundwaters of French Guiana. Alongside its trace element abundance in hydrogeological studies, the large natural variation of both boron isotope signatures and also characteristic anthropogenic sources (e.g. synthetic fertilisers, domestic wastewater, washing powders – which would highlight groundwater vulnerability to modern pollution) make boron a useful natural tracer for discriminating sources. A useful collation of boron isotope data is the ISOBORDAT site (http://isobordat.igg.cnr.it/index.php/en;
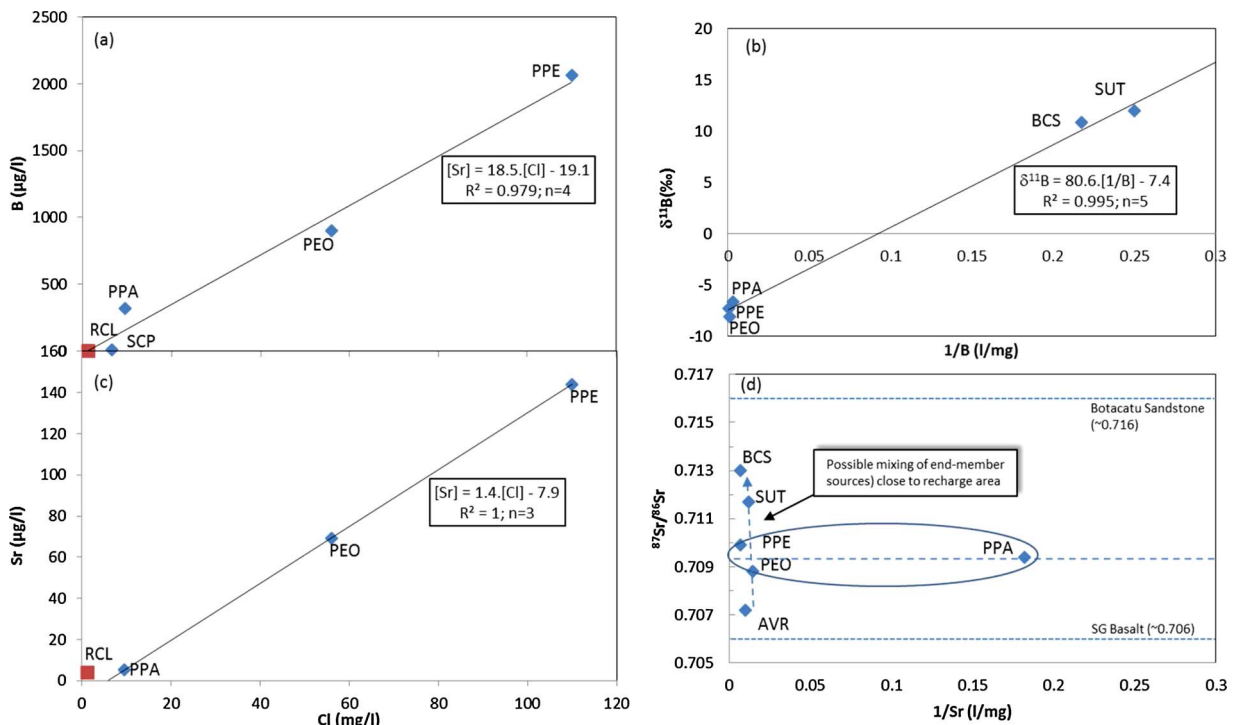
Fig. 7. Cross-plot mixing diagrams: (a) B versus Cl (weight); (b) $\delta^{11}B$ versus reciprocal boron concentration (weight); The boron isotope values are with respect to NIST standard SRM 951; (c) Sr versus Cl (weight); (d) $^{87}Sr/^{86}Sr$ versus reciprocal strontium (weight). Particular GAS groundwater and rainfall (Rio Claro) sites are identified.

Pennisi et al., 2011).

The B/Cl weight ratio in the deepest groundwaters (Paraguaçu Paulista, Presidente Prudente, Presidente Epitácio) is ~0.0185, nearly two orders of magnitude enhanced in comparison to say a modern seawater ratio of ~0.0002. There is a linear trend apparent in both elemental and isotopic signatures between samples close to the recharge zones (e.g. Bernardino de Campos, Santa Cruz do Rio Pardo) with positive (heavy) $\delta^{11}B$ signatures of $+10.9‰$ and $+12‰$, respectively, and these deepest GAS waters along the transect (characterised at Presidente Prudente by negative (light) $\delta^{11}B = -7.3‰$) (Fig. 7a,b).

Detrital tourmaline, a B-bearing mineral, alongside zircon and rutile, is identified in both the Pirambóia and the Botucatu Formation but occurring generally as well-rounded grains characterising these ZTR minerals as resistant to weathering (Wu and Caetano-Chang, 1992; Donatti, 2002). Mica in these formations is principally muscovite; an end-member boromuscovite is a known mineral although only in hydrothermal settings (Jung and Schreyer, 2002; Wunder et al., 2005). In the Pirambóia Formation feldspars occur very frequently – generally orthoclase, microcline, and weathered plagioclase, along with partially and altered kaolinite and/or illite (Wu and Caetano-Chang, 1992). Donatti (2002) particularly demonstrates dissolution features on feldspar samples from the Pirambóia and Botucatu Formations in north Paraná State, close to the current study region. Boron can substitute for Al in the system albite-reedmergnerite (cf. Wunder et al., 2013). Using the WQ4F thermodynamic database (Ball and Nordstrom, 1992) plagioclase feldspar mineral phases such as albite (data not shown) are characterised as undersaturated in all the sampled GAS groundwaters and could provide here therefore a source term for B-mineral dissolution downgradient in line with the diagenetic evolution of the aquifer.

Contaminant sources (cf. Vengosh et al., 1994, 1998) are precluded even for the waters closest to the recharge zone as concomitant enhancement in other characteristic elements (e.g. Na, Br, etc.) is not evident. The heaviest boron isotopic signatures (Bernardino de Campos, Santa Cruz do Rio Pardo) are instead characteristic of freshwater in inland aquifers (Vengosh et al., 1998) and likely relate here to dissolution of nonmarine borate/evaporite minerals (Vengosh et al., 1992). This is likely also for increasing B contents (mineral dissolution) seen in the deepest GAS waters (Paraguaçu Paulista → Presidente Prudente) in the transect. Modern seawater has a $\delta^{11}B = +39‰$ and Chetelat et al. (2005) suggest values closer to $+30‰$ for rainfall associated with the dry season in French Guiana when winds flow from the southeast (i.e. from Brazil), excluding this as predominating marine source influencing the GAS signatures. Chetelat et al. (2005) cite a range of $+2‰$ to $+17‰$ for $\delta^{11}B$ and generally isotopically lighter than marine rainwater in continental locations more in line with the GAS signatures seen then at Bernardino de Campos and Sarutaiá (Fig. 7b). B contents in rainfall (Rio Claro) and Bernardino de Campos and Santa Cruz do Rio Pardo groundwaters are similar (~5 ppb) and these latter have lower dissolved NO_3 concentrations than Rio Claro similar to the deepest GAS waters (Paraguaçu Paulista, Presidente Prudente, Presidente Epitácio) (Bonotto and Elliot, 2017, their Table 2). Boron isotope ($\delta^{11}B$) fractionations however are often controlled by the partitioning between the undissociated boric acid, $B(OH)_3$ (planar trigonal), and the borate anion $B(OH)_4^-$

(tetrahedral), through the equilibrium reaction: $B(OH)_3 + OH^- = B(OH)_4^-$ (Pennisi et al., 2006). Both dissolved species are pH-dependent: at 25 °C and a B concentration of 10^{-3} mol L^{-1}, $B(OH)_3$ is dominant for pH < 9, whereas $B(OH)_4^-$ predominates for pH > 9 (Tonarini et al., 2004; their Fig. 1). At equilibrium the $\delta^{11}B$ signature is $\Delta\delta = 20$‰ lighter for $B(OH)_4^-$ than for $B(OH)_3$, and can be up to $\Delta\delta = 30$‰ less (Pennisi et al., 2006). Boron adsorption also can cause positive isotopic fractionation (enrichment) ~10–20‰, but characteristically alongside decreasing B contents downgradient (Vengosh et al., 1994).

Speciation modelling of boron using the WQ4F programme (data not shown) shows that for the GAS samples in the pH range 5.9–6.6 both the Rain sample (Rio Claro) and GAS samples in the recharge zone (Avaré, Sarutaiá, Bernardino de Campos) show H_3BO_3 as the dominant chemical form (>99.5%) in the groundwater with respect to $B(OH)_4^-$. For Águas de Santa Bárbara (pH = 7.58) and Santa Cruz do Rio Pardo (pH = 8.26) this predominance is 97.6% and 90.3% as $B(OH)_3$, respectively. Thus close to the recharge areas $B(OH)_4^-$ is <10%. In the deepest waters however at higher pH $B(OH)_4^-$ becomes more significant: Paraguaçu Paulista (78.1%; pH = 9.64), Presidente Prudente (39.7%; pH = 8.80), Presidente Epitácio (35.4%; pH = 8.70). These samples show a $\delta^{11}B$ signature $\Delta\delta \sim 17$–20‰ lighter than for the recharge zone waters (Bernardino de Campos, Santa Cruz do Rio Pardo) in line with the evolution of the speciation. The effect at Presidente Epitácio is presumed more likely due to dilution of the chlorinity by flow from the NW which then appears to have an even lighter $\delta^{11}B$ than the source for Presidente Prudente.

Thus, the evolutionary trends for dissolved B appear likely to relate to ongoing diagenesis of mineral sources such as feldspars downgradient, and the apparent mixing line $\delta^{11}B$ relates to the pH evolution of the waters and B-speciation in the groundwaters.

3.4.2.2. Strontium. Strontium and its isotopes have been extensively used in groundwater studies because Sr it is readily soluble as a +II valence ion, behaves geochemically as an alkaline earth metal, and generally retains a signature of its source. Sr concentrations are relatively enhanced close to the recharge area in Avaré, Sarutaiá, Bernardino de Campos (Fig. 4) all having substantial weathered mantle cover at their localities (Table 1), and then again only in the deepest GAS sample (Presidente Prudente). For strontium, there is a clear Sr linear trend with chlorinity in the deeper waters. The isotopic trend also suggests then a downgradient shift from a $^{87}Sr/^{86}Sr$ ratio of, for example, 0.7130 (Bernardino de Campos) to the deepest waters with a ratio ~0.709 (Fig. 7c,d). Sr is not seen in recharge waters Itirapina or São Pedro at outcrop of the GAS Botucatu–Pirambóia (BP) formation, which is likely a consequence of rock diagenesis.

Sample Avaré ($^{87}Sr/^{86}Sr$ = 0.7072; Bonotto and Elliot, 2017) shows the lowest strontium isotope ratio. This $^{87}Sr/^{86}Sr$ signature at Avaré might reflect some contribution locally of recharge from the overlying Upper Cretaceous aquifer of the Bauru Group (BA 8–12 mbgl; Table 1). For the sandstone Adamantina aquifer outcropping around Urânia city in the NW of SP State rock signatures show $^{87}Sr/^{86}Sr$ ratios of 0.71734–0.72172 (3 samples) for silts of the Bauru (BA) Group (da Silva et al., 2006a). Maldaner (2010) and Maldaner et al. (2013) have published preliminary data which show a trend with values in hand dug wells (highest at ~0.7134), rain (~0.7105), tap (0.7089), and waste water (0.7096), but the lowest dissolved ratios then in deeper aquifer waters (BA depths ~40–100 mbgl; $^{87}Sr/^{86}Sr$ ~0.7085) as the deeper groundwater becomes saturated with respect to calcite in the of the Bauru Group which overlies the SG Formation in the locality of Urânia, and similar then to the ratio seen at Avaré with (limited) BA Group. The highest ratios in the shallow, hand dug wells in the (Bauru Group) Adamantina aquifer are attributed by Maldaner et al. (2013) to a surface layer (skin) richer in clayey minerals having enhanced radiogenic ratios of Sr isotopes. It is noted however that Bauru Group natural waters characteristically have enhanced Ba content other regional waters in SP State (Tavares et al., 2015) and in the Adamantina aquifer potentially anomalous hexavalent chromium content (cf. Bertolo et al., 2011), neither of which are seen however at Avaré. An alternative provenance, and more likely, is that the $^{87}Sr/^{86}Sr$ ratio in Avaré instead approaches the mean value of 0.7065 ± 0.0006 reported by Wildner et al. (2006; their Table 5.2.1) for 18 samples of basaltic lavas belonging to the Serra Geral (SG) Formation sampled in the southwest of Paraná State (ranging 0.70587–0.70791 for Pitanga-type), which most likely suggests then water equilibration for the Sr isotopic signature with SG basalts. A range of 0.70548–0.70654 has been reported for 80 samples of Pitanga-type basalts across the Paraná Basin (Metal Mining Agency of Japan, 2003), alongside $^{87}Sr/^{86}Sr$ ranges of 0.70575–0.70590 (4 samples) in unaltered SG basalts of Ametist do Sul (Gilg et al., 2003; average $^{87}Sr/^{86}Sr$, 0.70578; average Sr = 460.7 ppm) and 0.7054–0.7061 (5 samples) in Pitanga-type flow basalts (Rocha et al., 2008). Innocent et al. (1997) have shown that leaching experiments (pH = 5.3) on (high-Ti) basalts from the northern Paraná Basin yield a higher $^{87}Sr/^{86}Sr$ ratio for the leachates (~0.708 versus the parent material ~0.7059). This potentially explains then the $^{87}Sr/^{86}Sr$ signature seen at Avaré.

At Bernardino de Campos (BCS; $^{87}Sr/^{86}Sr$ = 0.7130; Bonotto and Elliot, 2017) the borehole lithology shows no possible contribution of signature from BA (which cannot therefore be an influence on the water signatures at Bernardino de Campos, or indeed Sarutaiá) but instead a relatively thick weathered mantle (0–21 m; Table 1) in comparison to surrounding boreholes and overlying SG basalt directly, which perhaps focusses groundwater flow vertically here and provides also for enhanced solution of e.g. Sr (Fig. 4). The Bernardino de Campos borehole is however fully lined through the thick mantle to 24 m depth, and then is unlined in the SG basalt beyond. The thick SG formation (~300 m) at Bernardino de Campos likely however delays any such vertical recharge reaching the GAS. This suggests the Bernardino de Campos (and Sarutaiá) signatures could reflect recharge in this locality and an influence of the shallow layers somewhat akin to that seen for the Adamantina aquifer (Maldaner et al., 2013) albeit not now involving BA, however the $^{87}Sr/^{86}Sr$ ratios at Bernardino de Campos and Sarutaiá are the most enhanced seen in the GAS waters (Fig. 7d) and unlike the signature for SG basalts (cf. Avaré).

Strontium isotopic signatures attributable to the relevant GAS formations unfortunately are scarce, but Gilg et al. (2003) give two whole rock (sandstone) analyses (their samples #15384, #15380) from the Salto do Jacuí region with ratios 0.71611 (Sr = 342.6 ppm) and 0.71617 (Sr = 189.1 ppm) [with ratios corrected to 0.717662 and 0.71492, for a formation age of 130 Ma]. A sandstone sample from the Tacuarembo Formation (the equivalent of the Botucatu Fm. in Uruguay; Morteani et al., 2010) similarly yields a $^{87}Sr/^{86}Sr$ ratio of 0.71828. Filho (1976) has given a range 0.71490–0.73597 (Sr = 28.8–199 ppm) for specifically silty shales

samples of the Pirambóia Facies from two shallow boreholes in the Botucatu Formation (28.6–54.8 m depth) close to the study area in SP State, and Vieira (1980) has published a ratio of 0.7171 for fine-grained sample from the same depth in the Pirambóia Fm. In the south-southeast of SP State. da Silva et al. (2006a,b) show a range 0.72063–0.72298 for fine-grained sediments from the Santa Maria Fm. in the Paraná Basin. Therefore, alternatively, the limited Sr-isotopic data for the Botucatu/Pirambóia (BP) sandstones here suggests equilibrium ratios $^{87}Sr/^{86}Sr$ ratios (0.7161–0.7171) in sandstones of these formations, similar to the Bernardino de Campos sample which might suggest then a chemical (lithological) overprinting of any recharge through the SG basalts for these waters in relation to the Sr-content of e.g. the Avaré sample. The sample Sarutaiá then shows signature more intermediate between the basalt and sandstone signatures reflecting mixing or partial overprinting of these sources. Strontium signatures show emplacement of Sr in waters likely through recharge interaction with overlying basalts (e.g. Avaré), however the isotopic signatures suggest a lithological overprinting of sources in the GAS aquifer itself (e.g. Sarutaiá, Bernardino de Campos).

There is a further downgradient input of Sr in the GAS starting around Paraguaçu Paulista. The deepest waters downgradient however all show a lower $^{87}Sr/^{86}Sr$ ratio ~0.709, which corresponds approximately then to the value for carbonates in equilibrium with a seawater Sr isotopic ratio in the Jurassic-Triassic (e.g. McArthur et al., 2001; Fig. 7d). Fontboté and Gorzawski (1990) and Moritz et al. (1996) record $^{87}Sr/^{86}Sr$ isotopic ratios ~0.708 for an Upper Triassic-Lower Jurassic carbonate platform (Pucara Group) in central Peru at the western margin of the Brazilian Shield.

3.5. Groundwater ages and residence times

Radiocarbon activities up to 88 pmc and $\delta^{13}C$ as light as −16.4‰ recently have been published (Gastmans et al., 2013a,b; Aggarwal et al., 2014) for recharge waters in the Guarani Aquifer (GAS). Similar isotopically light $\delta^{13}C$ carbon isotopic signatures have also been recorded (Hirata et al., 2011) for Sarutaiá (−18.9‰) and Águas de Santa Bárbara (−15.5‰). A single tritium (^3H) value of 0.6 ± 07 TU was recorded in 1989 at site Avaré (which has BA overlying) by Kimmelmann et al. (1994) alongside a ^{14}C activity here of 7.6 ± 1.6 pmc and $\delta^{13}C = −12.7‰$. This suggests that the Avaré signature itself might in fact reflect delayed recharge through the basalts especially given a recent shallow groundwater sample from the Serra Geral (SG) aquifer with $\delta^{13}C = −19.87‰$ and $^{14}C = 80.37$ pmc (Gastmans et al., 2017). A similar ^{14}C activity of 7.1pmc in GAS groundwater also was sampled in 1982 by da Silva (1983) for Bernardino de Campos, with a $\delta^{13}C$ signature of −18.1‰ reported by Gastmans et al. (2010a,b). Downgradient in the deeper basin, da Silva (1983) found lower ^{14}C activities of 1.3 pmc (Paraguaçu Paulista) and 0.3 pmc (Presidente Prudente), and Hirata et al. (2011) have sampled isotopically heavier $\delta^{13}C$ signatures of −5.4‰ (Paraguaçu Paulista) and −3.9‰ (Presidente Prudente), with a lighter isotopic signature found again however at Presidente Epitácio $\delta^{13}C = −7.3‰$ (in line with a value of −6.5‰ sampled by Gastmans et al., 2010a,b, and −6.3‰ sampled by Kimmelmann et al., 1994). Kimmelmann et al. (1994) sampling three wells at different depths recorded slightly heavier isotopic values for Presidente Prudente around $\delta^{13}C = −5.3‰$ along with much higher ^{14}C (~15 pmc) at depth although also with a substantial ^4He excess from radiogenic accumulation implicating the aquifer waters have significant residence time at odds with this ^{14}C activity. Recently, Aggarwal et al. (2014) have evaluated radiocarbon (^{14}C) model ages alongside ^{81}Kr dating for very old groundwater samples (cf. IAEA, 2013) to derive then flux estimates for dissolved ^4He gas and crustal degassing in the GAS system of SP State, although not for sites directly along traverse A-A'. The closest sites to the transect A-A' are Aggarwal et al. (2014) samples in the vicinity of Jaú ($\delta^{13}C = −10.6$, $^{14}C = 8.2$ pmc) some 80 km NE of Águas de Santa Bárbara with a groundwater residence time (radiocarbon age) of 14ka and Agudos ($\delta^{13}C = −12.4$, $^{14}C = 30.9$ pmc) 50 km NNE of Águas de Santa Bárbara with a groundwater residence time (radiocarbon age) of 4.7ka. Calculated ages for samples with $\delta^{13}C$ heavier than −12‰ and $^{14}C < 5$ pmc typically have radiocarbon ages beyond the limit of the ^{14}C-dating method (>30 ka); these waters also show significant ^{81}Kr ages apparently up to 800 ka (Aggarwal et al., 2015). The nearest site to the deepest sampled GAS waters in the current study is Marilia ($\delta^{13}C = −8.2$, $^{14}C = 1.38$ pmc) 70 km ENE of Paraguaçu Paulista with a groundwater residence time (radiocarbon age) of >30 ka and a ^{81}Kr age of 216 ka.

Relevant published data for $\delta^{13}C$, ^{14}C and [DIC] (usually taken as Alkalinity) for samples along traverse A-A' are collated here alongside the Aggarwal et al. (2014) GAS data and plotted for comparison (Fig. 8) using the graphical method for carbon isotope systematics recently developed by Han et al. (2012). Initial radiocarbon activity at recharge is taken as $^{14}C_0 = 90$ pmc with $\delta^{13}C_0 = −23‰$ (cf. Sracek and Hirata, 2002, p.654). The carbon isotopic systematics are similar to the interpretation presented for Stute and Deak (1989) by Han et al. (2012, their Fig. 10) as an example of the effect of weathering of silicates in the Great Hungarian Plain, and as proposed as a mechanism for the recharge region of the GAS (Meng and Maynard, 2001) although Sracek and Hirata (2002) place greater emphasis on the effect of cation exchange of Ca for Na in the confined aquifer. Without necessarily placing greater emphasis here on the detailed process mechanisms, the comparison for A-A' transect waters highlights two main points: (a) that the carbon systematic signatures for Avaré and Bernardino de Campos appear anomalous with relatively immature (isotopically lighter) $\delta^{13}C$ isotopic signatures although moderately low ^{14}C; (b) that the deepest samples (Paraguaçu Paulista, Presidente Prudente, Presidente Epitácio) follow the carbon isotope systematic trends of plotted data from Aggarwal et al. (2014), indeed the samples along the A-A' transect appear to be isotopically more evolved than all of the Aggarwal et al. (2014) samples suggesting that these deepest samples potentially have residence times (radiocarbon ages) likely >30 ka and are therefore palaeowaters. This interpretation for the deepest GAS waters in the current study is further supported by previous age dating for these particular waters using U-isotope disequilibrium methods (Bonotto, 2006) which suggested residence times of 640ka along the transect Avaré → Presidente Epitácio. The apparently immature $\delta^{13}C$ signature along with the REE evidence at Bernardino de Campos then suggests possible effective recharge through the SG Formation at this point alongside feed in from the recharge beds (e.g. Avaré, Sarutaiá). It is noted also that a study of ^{36}Cl in the GAS groundwaters (Cresswell and Bonotto, 2008) along this transect identifies Bernardino de Campos as having an anomalously high ^{36}Cl level (^{36}Cl atoms = 5×10^{-6}; their Table 4) similar to a rainfall sample taken at São Pedro (^{36}Cl
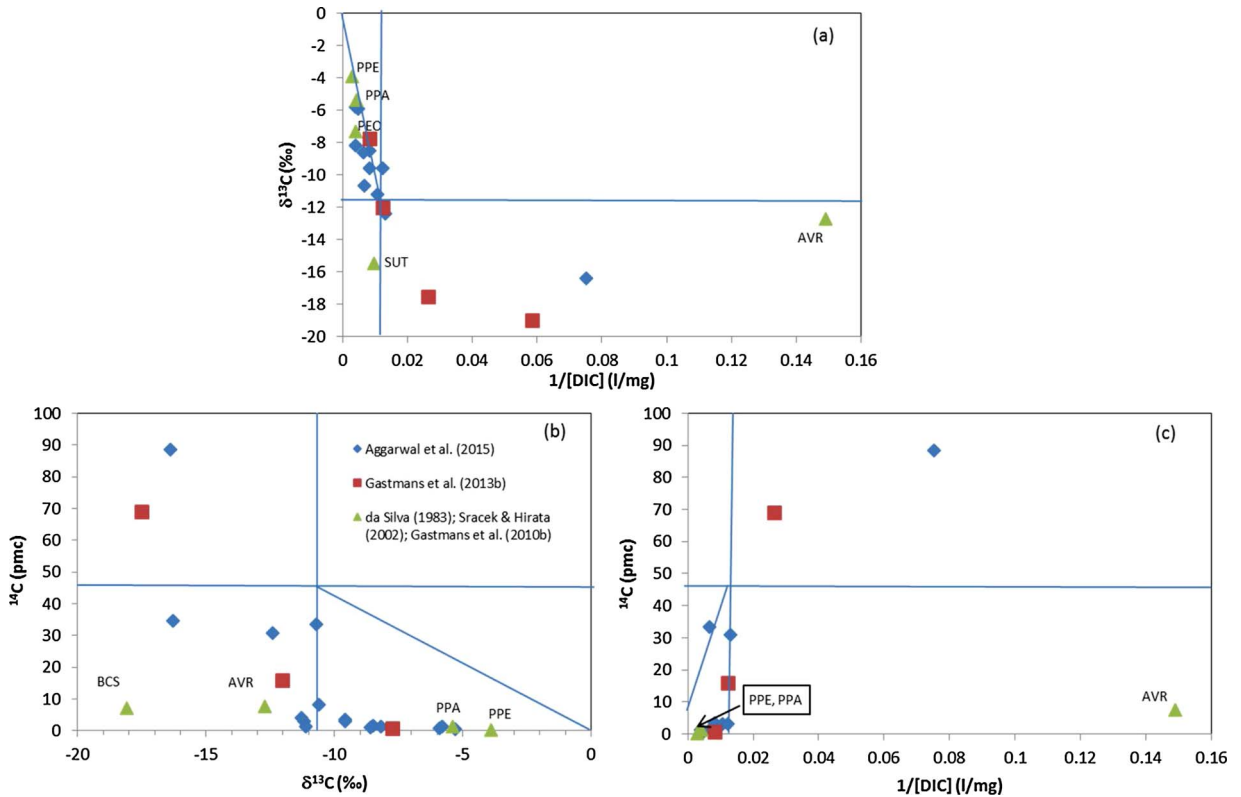
Fig. 8. Graphs for carbon data interpretation following the method of Han et al. (2012). Data presented relevant to sites in the current study are from da Silva (1983), Sracek and Hirata (2002), and Gastmans et al. (2010b). The relevant GAS sites (*triangles*) have been identified. Additional samples for other GAS groundwater in São Paulo State are from Gastmans et al. (2013b; *squares*) and Aggarwal et al. (2014; *diamonds*). δ^{13}C (‰) values are with respect to Vienna Pee Dee Belemnite (VPDB).

atoms = 2.1×10^{-6}; their Table 3) which may suggest a re-evaluation of their published interpretation favouring particularly their Scenario 2 which then implicates a ^{36}Cl groundwater age of 720 Ka for sample Presidente Epitácio and >1 Ma for Presidente Prudente.

3.6. Deep groundwater mixing in the GAS (inter-aquifer mixing)

The signature for GAS waters mixing with deeper Pass Dois/Tubarão aquifer waters is highlighted in recently published sulfur isotope data for dissolved sulfate (Soler i Gil and Bonotto, 2015). For δ^{34}S, samples from Paraguaçu Paulista, Presidente Prudente and Presidente Epitácio clearly lie on a two-component isotopic mixing-line (Fig. 9) between the lightest signature found at Paraguaçu Paulista (+2‰) and the heaviest signature at Presidente Prudente (+6.6‰). If this trend is extrapolated to the *y*-axis then this could suggest a possible 'end-member' of mixing with an isotopic signature δ^{34}S = +7.4‰. Similarly, for δ^{18}O extrapolation of the two-component mixing trend for these three waters characterises an end-member of mixing with an isotopic signature of δ^{18}O = +15.5‰. These two signatures together genetically (cf. Krouse and Mayer, 2000, their Fig. 7.3) identify an evaporitic mineral source for the dissolved sulfate as suggested by Soler i Gil and Bonotto (2015) and implicated also in geochemical models of groundwater evolution in the Guarani aquifer (cf. Sracek and Hirata, 2002). For δ^{34}S, a deep tube-well (Rio Claro, Rio Claro-GW) sampled by Soler i Gil and Bonotto (2015) which intersects Tubarão Group (TU) lithology lie (Fig. 9) within a triangle formed by assuming the Águas de São Pedro (ASP-GIO) sample forms another end-member of mixing. This suggests then a mixing of GAS and TU waters in this well (Rio Claro-GW). The assumed end-member ASP-GIO borehole water (and also ASP-JUV) also intersect the PD/TU and typically provide poor quality waters enriched in dissolved sulfate aquifer (Soler i Gil and Bonotto, 2015, their Table 3). Two deep groundwaters to the north (Aruçatuba – ATA, Três Lagoas – TLG; this latter sample from the deep Paraná Basin in Mato Grosso do Sul state) sampled by Soler i Gil and Bonotto (2015) again reflect apparent mixing between GAS and PD/TU waters (Fig. 9) even though no TU lithology is recorded in their borehole construction. These latter sites are however located closer to an area of upflow of deep waters in the Paraná Basin identified by Pimentel and Hamza (2014). Although the borehole lithology for sample Paraguaçu Paulista apparently also suggests some Tubarão Group (PD/TU) intersection (whereas Presidente Epitácio and Presidente Prudente boreholes record no TU lithology; Table 1) the strong linear trend with Presidente Prudente and Presidente Epitácio samples suggests in fact little impact of TU waters or inter-aquifer mixing here, in line with hydrologic data (e.g. Pimentel and Hamza, 2014) suggesting leakage of waters out from the base of the GAS in this region.
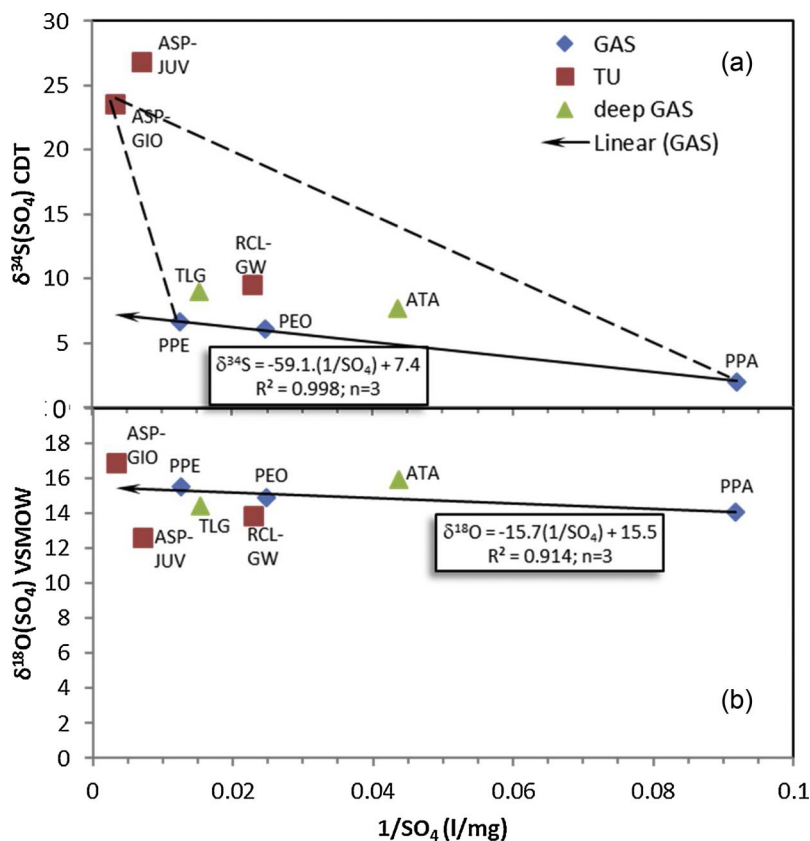
Fig. 9. Two-component mixing diagram (cross-plot) for sulfur isotope systematics ($\delta^{34}S$, $\delta^{18}O$) of dissolved sulfate in the GAS of São Paulo State. (a) $\delta^{34}S$ (‰ with reference to the standard Canyon Diablo Troilite, CDT) versus reciprocal sulfate concentration (weight); (b) $\delta^{18}O$ (‰ with reference to VSMOW) versus reciprocal sulfate concentration (weight). The relevant GAS sites (*diamonds*) have been identified alongside other deep GAS (*triangles*) and TU (*squares*) sites. Data are taken from Soler i Gil and Bonotto (2015). Borehole construction details for other relevant GAS sites are: ASP-JUV: unlined in Sao Bento (0–45 m), PD (45–240 m), TU (240–469) Groups; ASP-GIO: details unknown; TLG lining details are unknown; ATA: unlined through SG (22–957 m), BO (957–1214 m); Rio Claro-GW: unlined through SG (0–62.4 m), PD (62.4–112.0 m), TU (112.0–198.5 m).

4. Conclusions

4.1. Vulnerability and sustainability issues arising for the GAS

From the REE and also Sr signatures (Figs. 4 and 7 d), the possible pathway of interaction with SG basalts e.g. particularly at Bernardino de Campos requires comment. Bonotto (2006; his Fig. 9) previously has noted an elevated piezometric level in the GAS formation at Bernardino de Campos indicating potential recharge contribution here. It is noted from the borehole lithology that Bernardino de Campos has the thickest layer of weathered mantle (0–21 m; Table 1) which might suggest some hydraulic effect focussing recharge in this locality (cf. Chilton and Foster, 1995; Taylor and Howard, 2000; Cho et al., 2003). Since the 1960s there has also been a population shift into the cities in this region as a consequence of agricultural mechanisation on the land with accompanying increased water demand and potentially vertical drawdown (SigRH, 2000). Of particular significance, a geological map of groundwater in the state of São Paulo (DAEE/IG/IPT/CPRM, 2005) further identifies faulting in the locality of Bernardino de Campos. During the Wealden (Lower Cretaceous) and after the volcanic phase of the Serra Geral (SG) Formation tectonically the area was in tension forming for example classical horst and graben features (SigRH, 2000). Normal faulting around Bernardino de Campos is suggested along the SE-NW geological section by da Silva (1983; see Fig. 2). Geological mapping in the region appears to show horst-graben features in the direction NW-SE (DAEE/IG/IPT/CPRM, 2005), with high and low ground oriented approximately NE-SW which is picked out particularly on an aeromagnetic map for the Paranapanema region (CPRM, 2004). This may be associated then with the NW-SE regional trending Guapiara Lineament with possibly reactivated Quaternary normal faulting extending WNW-ESE across the southern part of SP State (Riccomini, 1997; Saadi et al., 2002). More locally, Guedes et al. (2015; cf. their Fig. 9) recently have highlighted the horst-graben structure occurring in the Rio Pardo hydrographic basin north of Bernardino de Campos which encompasses both Águas de Santa Bárbara and Santa Cruz do Rio Pardo. Moreover, Pelaes (2013; e.g. his Fig. 46) provides evidence of possible neotectonic (apparently Neogene to Upper Pleistocene) reactivation of normal faults along the Guapiara lineament, which trend approximately NE-SW affecting both Botucatu sandstone and Serra Geral basalt in the vicinity of Piraju City just 20 km south-

east of Bernardino de Campos. However, a more detailed geology is required at Bernardino de Campos to confirm this conceptual model. Looking to the CPRM (Serviço Geológico do Brasil; http://www.cprm.giv.br) SIAGAS database (Sistema de Gestão de In-formações de Águas Subterrâneas) shows that the well construction for Bernardino de Campos is in fact not lined beyond 25 m depth, and so the water level here is intimately in contact with both SG and GAS formations. Similarly, Águas de Santa Bárbara is lined from 0 to 65 m but not deeper. It is not surprising then that these wells therefore reflect REE signatures of the SG basalt. Closer to the GAS recharge zone, Sarutaiá apparently is fully lined (0.50–71.50 m) into the GAS, as is Avaré (0–133.80 m), but these sites still show the REE signature of SG basalts in the GAS waters at these locations. Fernandes et al. ((2012); their Fig. 9) show direct evidence of vertical seepage across the vesicular basalt of the Serra Geral formation at a site close to Avaré which from the aeromagnetic map again lies close to a horst feature. Both of these sites also however also lie closer to the outcrop of the Botucatu/Pirambóia Formations and suggest the effect of recharge waters directly through the SG Formation and interacting locally or possibly surface runoff from the SG basalt into the GAS outcrop. For Avaré, its Sr-isotopic ratio (0.7072) likely reflects leaching of the SG basalt signature, which for Sr in Sarutaiá and Bernardino de Campos apparently is lithologically overprinted then by a Botucatu sandstone signature in these GAS waters (Fig. 7d). It is suggested then that REEs and Sr-isotopes might prove useful environmental tracers then for vulnerability studies also on the eastern border of the Bauru Basin where SG basalts also outcrop albeit more thinly (cf. Fernandes et al., 2016).

The hydrogeochemical/isotopic signatures therefore for these waters trace interaction with and possibly vertical recharge through the SG basalts indicating therefore a vulnerability to surface recharge in the locality. The relatively light $\delta^{13}C$ signature at Bernardino de Campos (also Sarutaiá, Águas de Santa Bárbara) and Avaré (Fig. 8) apparently also highlights the presence of a geochemically immature water component. Nevertheless, Bernardino de Campos in particular also has a deep (306 m) layer thickness of SG for-mation intervening above the GAS. This suggests that any vertical recharge in this locality could be significantly delayed in reaching the GAS aquifer; published ^{14}C activities ($\sim$7 pmc) for both Avaré and Bernardino de Campos along with a ^{3}H-free signature at Avaré, suggest that the possible vertical recharge reaching these GAS waters is not necessarily immediate but nonetheless a lagged contribution, although inter-aquifer mixing effects would need to be assessed. If taking the depth of sampling (pump placement) in the middle of the slotted/open sections of the GAS boreholes, sampling temperatures for the GAS groundwaters (including Avaré and Bernardino de Campos, but excluding São Pedro and Paraguaçu Paulista) give a temperature-depth relationship of 28.3 ± 1.3 °C/km (R^2 = 0.9873; n = 8; data not shown; SIAGAS database and Bonotto and Elliot, 2017, their Tables 1 and 2) in line with the regional geothermal gradient Paraná basin of 28.14 ± 6.1 °C/km published by Pimentel and Hamza (2014), suggesting that for sampling temperature as a potential heat tracer all of these waters also have had time at least to thermally equilibrate at depth. São Pedro shows an anomalously higher sampling temperature, whereas Paraguaçu Paulista shows a lower than expected sampling temperature suggesting a pump depth set here just at the base of the SG formation in line also with a lower geostatic pressure than expected from comparison with the other GAS wells.

Boron and its isotopic signatures appear to reflect dissolution of feldspars in the aquifer, and even in the sites affected by vertical recharge do not reflect currently an anthropogenic source. Sr-isotopic signatures in the deepest waters (Paraguaçu Paulista, Presidente Prudente, Presidente Epitácio) also appear to reflect a rock/mineral source potentially related to dissolution of carbonates deposited in the Jurassic-Triassic.

The Br/Cl ratios in the deepest waters (Paraguaçu Paulista, Presidente Prudente, Presidente Epitácio) appear to reflect a climate signature emplaced at recharge under more arid conditions. Thus, the Br/Cl ratios in the deepest waters possibly reflect a palaeo-climate signature. The paleoclimate status is supported notionally by water isotope signatures ($\delta^{18}O$, $\delta^{2}H$) published by other authors which (Fig. 3) show that the deepest waters sampled (Presidente Epitácio, Presidente Prudente) whilst clustering still around the Local Meteoric Water Line (LMWL) show isotopically heavier signatures than the other GAS waters suggesting a warmer temperature at recharge. This is in contrast to groundwater samples in the NE Brazil from the (Devensian) Last Glacial Maximum which show cooler recharge temperatures than present (Stute et al., 1995). In support of their palaeoages, a graphical plot (Fig. 8) of the carbon isotope systematics suggests that these deepest sampled waters (Paraguaçu Paulista, Presidente Prudente) may be geochemically more mature than other GAS groundwaters sampled across São Paulo (SP) State which have shown significant ^{81}Kr ages apparently up to 800 ka. This is in line with the original work of Bonotto (2006) which suggested a uranium activity residence time of 640 ka for the section between Avaré and Presidente Epitácio, and a possible >1 Ma from ^{36}Cl dating (Cresswell and Bonotto, 2008). From sulfur-sotopic signatures these waters (Paraguaçu Paulista, Presidente Prudente, Presidente Epitácio) do not show any impact of mixing-in from deeper formations (Fig. 9). As these deepest waters along the transect are likely palaeowaters then care must be taken in their water resources management as regards the current and future sustainability in abstracting these effectively fossil ground-waters (cf Foster et al., 2009; Chang et al., 2013; Elliot et al., 2014).

Conflicts of interest

None.

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