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Hydrogeochemical study of spas groundwaters from southeast Brazil

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ABSTRACT

This paper describes a hydrochemical study focusing spas groundwaters occurring at São Paulo and Minas Gerais states, Brazil, that are extensively used for drinking in public places, bottling and bathing purposes, among other. The water samples (75) for this study were taken from springs and pumped tubular wells drilled at different aquifer systems that are inserted in Paraná and Southeastern Shield hydrogeological provinces. The data acquisition for temperature, electrical conductivity (EC), pH, redox potential (Eh), dissolved gases (O_2, CO_2 and H_2S) and alkalinity was in situ performed for avoiding losses and modification due to transportation. The total dissolved solids (TDS) concentration was evaluated by gravimetry, the major cations and anions, iron and silica by colorimetry/atomic absorption spectrophotometry (AAS), and fluoride by potentiometry. The acquired database allowed establish the principal trends among the parameters analyzed after assuring its consistence from expected relationships found in hydrogeochemical surveys. The groundwaters are reducing (from pH and Eh data), there is a direct TDS-EC relationship, implying on a significant correlation between their ionic strength (IS) and EC. The major ions justifying such trends were sodium, (bi)carbonate, chloride, sulfate and phosphate that also correlated positively with the IS. The spas groundwaters were classified according to the guidelines of the Brazilian Code of Mineral Waters (BCMW) and EU directive for mineral waters. The major hydrochemical facies were also determined, as well the main sources influencing the groundwater composition and possible subsurface temperatures.

1. Introduction

In the last few decades, the consumption of natural drinking water, either spring or mineral (bottled or not), increased in several countries. Despite drinking water has been used mostly as the tap water accessible in every household, many people believe that the naturally occurring waters are healthy and/or can be utilized for health cures, thus, exhibiting better quality than the tap water. Additionally, economic reasons have also favored their use as bottled waters so that the commercialization of mineral waters has widely increased, inclusive in Brazil where circa 20 million consumers are involved (SEBRAE, 2012).

The thermal and mineral waters use in Brazil is not recent due to arrival of European immigrants, mainly from Portugal. The construction of thermal and non-thermal spas for therapeutic and leisure purposes reached a maximum number in the 1930s and 1950s, mainly at São Paulo (SP) and Minas Gerais (MG) states (Mourão, 1992). The Brazilian Code of Mineral Waters (BCMW) was established in this time, under French influence, by Register 7841 published on 8 August 1945 (DFPM, 1966). It classifies the mineral waters for spas and bottling uses, as well the potable waters for bottling, including several parameters like the radioactivity due to dissolved ^{222}Rn and ^{220}Rn (DFPM, 1966; Serra, 2009).

Some hydrogeochemical studies of Brazilian natural mineral waters took into account the BCMW guidelines. For instance, Bertolo et al. (2007) analyzed 303 labels of bottled mineral waters, grouping them according to the total dissolved solids (TDS) concentration. Oliveira et al. (2001) and Godoy et al. (2001) measured ^{226}Ra, ^{228}Ra and ^{210}Pb in 17 and 28 brands of bottled mineral waters, respectively. Szikszay (1981) realized a detailed hydrogeochemical survey at Águas da Prata (SP) spa, whereas Oliveira et al. (1998) evaluated the ^{222}Rn e ^{226}Ra seasonal variation there.

EuroGeoSurveys (The Geochemistry Group of the European Geological Surveys) managed a common European sampling campaign of bottled mineral and spring waters (analysis of 884 samples for >70 chemical parameters in one laboratory) whose results were published in 2010 in the Special Issue "Mineral Waters of Europe" of Journal of Geochemical Exploration (v. 107, pp. 217–422). The hydrogeochemical study held within the framework of the project involved different approaches like analytical techniques, major constituents, trace elements, radionuclides, stable isotopes, mapping, waters classification, statistical treatment of hydrochemical data, human health, etc. Water sources were from Croatia (Peh et al., 2010), Estonia (Bityukova and Petersell, 2010), Germany (Birke et al., 2010a, 2010b), Greece (Demetriades, 2010; Dotsika et al., 2010), Hungary (Fugedi et al., 2010), Italy (Dinelli

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et al., 2010; Cicchella et al., 2010), Norway/Sweden/Finland/Iceland (Frengstad et al., 2010), Portugal (Lourenço et al., 2010), Serbia (Petrović et al., 2010), Slovakia (Dušan et al., 2010), and Slovenia (Brenčič and Vreča, 2010; Brenčič et al., 2010).

DNPM-National Department of Mineral Production manages in Brazil the production and commercialization of mineral waters. The amount of bottled mineral waters at SP in 2007 was higher than 1.5 billion liters (34% of the total in the country) (CPRM, 2012). The actual accentuated consumption of spring and mineral waters for drinking purposes in Brazil requests a better understanding of their composition as the available information is sparse without considering the various lithologies involved and the adoption of standardized procedures for sampling and analyses. They are widely exploited from spas located at SP and MG due to historical reasons and the generation of a consistent database from the use of the same experimental steps allowed new hydrogeochemical insights and a comparison with other water sources occurring elsewhere.

2. Study area

The groundwater samples (75) were taken from springs and pumped tubular wells from 14 spas located in SP and MG (Fig. 1) at various geological contexts: Águas de São Pedro (3), Águas da Prata (7), Águas de Lindóia (7), Serra Negra (8), Lindóia (2), Termas de Ibirá (5), Águas de Santa Bárbara (1), Lambari (6), São Lourenço (8), Cambuquira (6), Caxambu (10), Poços de Caldas (6), Pocinhos do Rio Verde (4) and Araxá (2). The water sources were from different aquifer systems in the Paraná and Southeastern Shield hydrogeological provinces (Table 1).

The spas of Águas de São Pedro, Águas de Santa Bárbara and Termas de Ibirá are in the Paraná basin, a huge sedimentary area of southern Brazil, with extensions into Paraguay, Uruguay and Argentina. The stratigraphical record of this intracratonic basin shows a tendency towards continental depositional systems (Milani, 2004). In the Neo-Ordovician, marine strata deposited from the onset of sedimentation continued throughout the Devonian with oceanic influence up to the Carboniferous (Milani, 2004). From Permian times on, the basin took the form of a large inland sea (Milani, 2004). Eolian sandstone beds came to dominate the Mesozoic scenario and with the break-up of Gondwana, the basin basement was much affected by the intrusion of vast amounts of magma emplaced as dykes and sills between the sedimentary strata as well as flows on the surface (Milani, 2004). The evolutionary history of the Paraná basin closed in the Early-Cretaceous with the deposition of continental sediments over the Serra Geral lavas (Milani, 2004). Different magma eruption rates (~0.1 $km^3\ yr^{-1}$ or ≥2.0 $km^3\ yr^{-1}$) and duration (11 Ma, from 140 Ma to 129 Ma; <1 Ma, began at 134.7 Ma) of the Paraná continental flood basalt (CFB) volcanism have been suggested from $^{40}Ar/^{39}Ar$ geochronology data (Renne et al., 1992; Turner et al., 1994; Thiede and Vasconcelos, 2010; etc.). The main rocks in the Paraná basin are sandstones, conglomerates, diamictites, tillites, siltstones, shales, rythmites, silex, mudstones, limestones, basalts and diabases (IPT, 1981). Deep tube wells have exploited groundwaters of the sampling points at Águas de Santa Bárbara spa (Serra Geral and Botucatu formations) and Águas de São Pedro spa (Tubarão Group) (Kimmelmann et al., 1987).

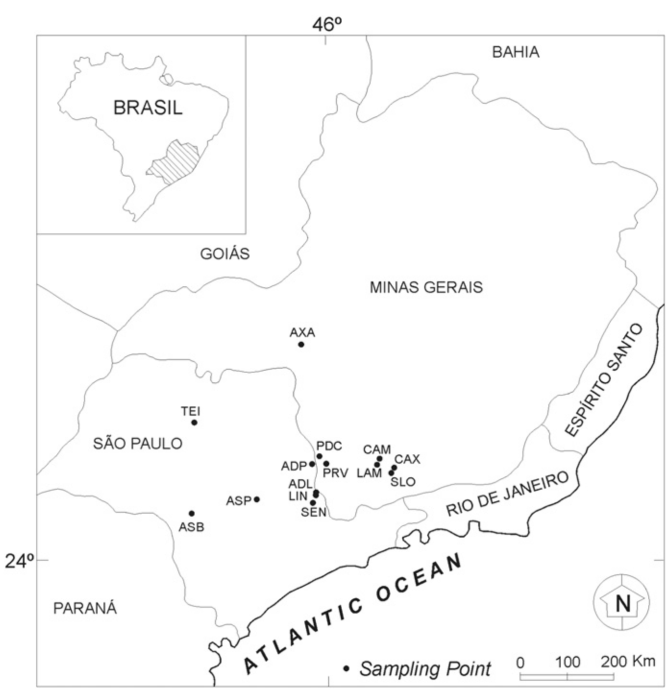

Fig. 1. Sketch map of the research region in Brazil and location of the groundwater sampling points in the following spas of São Paulo and Minas Gerais states: ASP = Águas de São Pedro, ADL = Águas de Lindóia, SEN = Serra Negra, LIN = Lindóia, TEI = Termas de Ibirá, ASB = Águas de Santa Bárbara, ADP = Águas da Prata, PDC = Poços de Caldas, PRV = Pocinhos do Rio Verde, LAM = Lambari, SLO = São Lourenço, CAM = Cambuquira, CAX = Caxambu, AXA = Araxá.

The spas of Águas de Lindóia, Serra Negra and Lindóia are in a region where various phases/cycles involving metamorphic, deformation and magmatic events have acted from the Archean to the Upper Proterozoic times. They have affected rocks of high metamorphic degree, generally of granulite and amphibolite facies (Ebert, 1955; Almeida and Hasui, 1984). The principal rocks occurring there are immature sediments (comprising sand, silt, clays and organic matter), milonites, quartzites, schists, gneisses, anfibolites, migmatites and syntectonic granites (Zanardo, 1987). The groundwater samples at Águas de Lindóia spa provided from fractures/fissures/faults occurring in migmatite (Lindália and Santa Isabel springs), quartzite (Comexim, Curie, Filomena and Beleza springs) and milonite/quartzite (São Roque spring) (del Rey, 1989).

The extensive Early-Cretaceous Paraná CFB province and a number of Early-Cretaceous to Eocene alkaline igneous provinces that surround the Paraná Basin like the Poços de Caldas alkaline massif (PCAM), Alto Paranaíba igneous province (APIP) and minor occurrences have been associated with the thermal and/or chemical influence of mantle-plumes (Tristan and Trindade) impacting on the base of the continental lithosphere (e.g. Gibson et al., 1995a, 1995b; Thompson et al., 1998).

The spas of Águas da Prata, Poços de Caldas and Pocinhos do Rio Verde are located in PCAM that is roughly circular (diameter ~33 km) and covers ~800 km^2. It is a suite of alkaline volcanic and plutonic rocks (mainly phonolites and nepheline syenites) whose evolutionary history starts with major early volcanism involving ankaratrites (biotite-bearing nephelinite), phonolite lavas, and volcano-clastics, followed by caldera subsidence and nepheline syenite intrusions forming minor ring dykes and circular structures and, finally, the intrusion of eudialite-bearing nepheline syenites (Ellert, 1959; Schorscher and Shea, 1992; Ulbrich et al., 2005). The following springs were sampled at Águas da Prata spa: Villela and Boi (discharges into sandstones); Vitória and Prata (discharges through fissures in diabase); Platina, Paiol and Padre (discharges through volcanic tuffs, phonolites and eudialite-bearing nepheline syenites) (Szikszay, 1981). Groundwaters at Poços de Caldas and Pocinhos do Rio Verde spas were from thermal/non-thermal springs discharging in crystalline fractured rocks (Cruz and Peixoto, 1989).

Araxá spa is located at APIP, including the renowned Araxá carbonatite circular intrusion (diameter ~4.5 km) (Traversa et al., 2001). The APIP is one of the world's most voluminous mafic potassic provinces composed of a relatively diverse suite of ultrapotassic-potassic, ultramafic-mafic, silica-undersaturated lavas and hypabyssal intrusions with very high concentrations of incompatible trace elements and strongly enriched in light rare earths relative to heavy rare earth elements (Gibson et al., 1995b; Gomes and Comin-Chiaramonti, 2005). A