Guarani aquifer system (GAS): geothermal spa balneology assessment

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Abstract
Among the geothermal energy direct-uses categories, bathing and tourism applications (balneotherapy, health, well-being, recreation, and swimming pool) correspond to almost all installed capacity in Brazil; where the best quality resources with the highest thermal power range occur in the Guarani Aquifer System (GAS). In a comprehensive international project on the use and protection of this transboundary aquifer, it is recommended to evaluate the potential uses and characteristics of its geothermal resources. Through the hot/mineral springs are developed resorts, water parks, SPAs, bath centers, and wellness destinations, with recognized economic benefits and inducers of sustainability. Thus, this work compiles physicochemical data (temperature, TDS, pH, SO_4^{-2}, HCO_3^-, Cl^-, F^-, Na^+, Ca^{+2}, Mg^{+2}, Si, B^{-3}, Fe, Li^+, Mn^{+2}, Zn^{+2}) from 85 hydrothermal wellsprings located in GAS (Brazil, Argentina, Uruguay and Paraguay), where tourism activities related to balneology are observed. The values obtained are compared with minimum levels of beneficial bioactivities, literature referenced to balneotherapy. The results indicate potential biologically active components (BAC) present in most of the sites, fountains and thermal/mineral waters evaluated here, through baths to experiences of SPA, relaxation, skincare, well-being or thermal medicine, according to the forms and the continuity of the expositions. It is expected to contribute to regional tourism development and marketing, as well as the promotion of related biomedical research.

Key words: spa town, healthy city, health resort, natural therapeutic factors NTF, medicinal mineral water, thermal spring, balneotherapy, complementary alternative integrative medicine CAIM, thermal medicine, medical geology, health tourism, guarani aquifer system GAS

Sistema acuífero guaraní (GAS): evaluación geotermal de los recursos balneológicos

Resumen
Entre las categorías de usos directos de la energía geotérmica, aplicaciones para baños y el turismo (hidro-balneoterapia, salud, bienestar, recreación y piscina) representan casi la

totalidad de la capacidad instalada en Brasil; donde los recursos mejores y con mayor capacidad termal se encuentran en el Sistema Acuífero Guaraní (SAG). En un extenso proyecto internacional sobre el uso y la protección de este acuífero transfronterizo, se recomienda evaluar los posibles usos y características de sus recursos geotérmicos. Por medio de los manantiales de aguas termales se desarrollan, resorts, parques acuáticos, SPA, balnearios y estancias; con beneficios económicos reconocidos e inductores de la sostenibilidad. Este trabajo recopila datos fisicoquímicos (temperatura, STD, pH, SO_4^{-2}, HCO_3^-, Cl^-, F^-, Na^+, Ca^{+2}, Mg^{+2}, Si, B^{-3}, Fe, Li^+, Mn^{+2}, Zn^{+2}) de 85 fuentes termales situadas en el SAG (Brasil, Argentina, Uruguay y Paraguay), donde se observan actividades turísticas relacionadas o no con la balneología. Los valores obtenidos se comparan con los niveles mínimos de bioactividades beneficiosas que se hace referencia en la literatura para la balneoterapia. Los resultados indican potenciales compuestos biológicamente activos (BAC), presente en la mayoría de las fuentes y manantiales de aguas minerales termales aquí evaluados; a través de experiencias SPA, baños, relajación, cuidado de la piel, el bienestar o medicina termal, y de acuerdo con las formas y la continuidad de las exposiciones. Se espera contribuya al desarrollo y promoción del turismo regional, así como, para inspiración y fundación en investigaciones conexas.

Palabras claves: villa termal, ciudad saludable, balneario, factores terapéuticos naturales FTN, agua minero medicinal, fuente termal, balneoterapia, medicina integrativa complementaria MIC, medicina termal, geología médica, turismo de salud, sistema acuífero guaraní GAS

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INTRODUCTION

Geothermal energy is the heat that coming from the internal Earth planet generated by several phenomena, environments, and material combinations. A geothermal system is any localized geologic setting where portions of the Earth's thermal energy may be extracted from a circulating fluid and transported to a point of use. A geothermal system for the formation of a geothermal resource is necessary to include fundamental elements and processes, such as: (i) heat source, (ii) reservoir (i.e., aquifer, caprock or seal), and (iii) fluid (i.e., thermal water or steam) as a heat carrier (fluid flow pathways); it comprises the entire hydrogeological connected area with the recharge zone, reservoir aquifer and outflow zone (Moeck, 2014). The geothermal resources (rock, magma, gas, steam, water) are differentiated by economic applications: direct-use of heat or electric power generation. Many times, direct-use and electric generation are combined where intermediate or high enthalpy boundaries (> 75ºC) occur.

Direct-uses are the oldest, most versatile, common forms and the higher installed capacity geothermal energy utilization; some countries consider such activities to be of historical and heritage geothermal interest. These mainly used categories are for: ground sourced heat pumps, space heating, greenhouses and open ground heating, aquaculture pond and raceway heating, industrial process heating, snow melting and cooling, agricultural drying. Currently, geothermal energy direct-use related to aquatic recreation, wellness, balneology, SPA centers, leisure resorts, and health tourism; is the second mainly world consumption segment (as 20.2% total). Almost every country has these types of activities and the largest reported annual developments are in China, Japan, Turkey, Brazil, and, Mexico (Lund & Boyd, 2016).

The oldest geothermal resources known applications are hot waters for bath and have been an orthodox remedy since the Hippocrates days, including religious faith. The main benefits of geothermal springs (or wells) lie in their therapeutic and curative value for medical treatments. Scientists worldwide have long researched the connection between using natural therapeutic factors (NTF) to developing the bath cure concept (Erfurt-Cooper, 2010).

Balneotherapy is treatments of diseases, injuries and other ailments with bathing; often in the mineral waters with different temperatures, prescribed in some countries as a complement to modern medicine. More commonly mineral and thermal waters are considered to contribute to wellbeing through relaxation from recreational use (swimming pools and water parks) and to health SPA; people will travel many miles for authentic natural experiences. Throughout history, they have influenced and shaped different cultures, the community's growth and development, and contributed to their health and wellness. Despite many changes over time, they continue to play a significant role in society. Some have been afforded special conservation status by being designated as UNESCO World heritage sites and others protect it, specifically under European directives. It is very clear that the importance of these natural features will continue to be valued by society, protected and will provide enjoyment for generations to come (EuroGeoSurveys, 2015).

The thermal/mineral springs industry amount establishments as revenue-earning businesses associated with the wellness, recreational and therapeutic (curative) use of waters with special properties; released globally by 27,507 facilities built around 109 countries, with businesses annual (2015) revenues up to US$ 51 billion. When their establishments indirect and induced economy-wide impact account, estimated values up to US$ 159 billion and 3.9 million jobs. This important wellness economy sector includes the following types of establishments: swimming pool, water park, water bath, hot spring SPA, Onsen, health resort and sanatoria (GWI, 2017).

BRAZILIAN GEOTHERMALISM

The total installed capacity of geothermal systems under economic exploitation in Brazil represents just a 0.5% World rate. Due to its geologic site, where recent tectonic and magmatic activities are scarce, also occur exclusively low-temperature geothermal systems and low enthalpy geothermal resources with similar features (heat and depth) at almost all territory (Dos Anjos, 2018). The national geothermal energy total base resource estimated is 2.4 x 10^{25} J, with its largest fraction (44.3%) on the Phanerozoic sedimentary basin geological environments, a great geothermal potential is found in many little exploitation plants and special characteristics of elements and processes involved in each geothermal system (Rabelo et al., 2002).

Large thicknesses of sedimentary strata are present in the central parts of Amazon, Parnaiba and Paraná basins regions; which are considered as suitable targets for the exploitation of geothermal resources (Hamza & Carneiro, 2004). Despite their classifications as low enthalpy amagmatic geothermal resources, some peculiar characteristics like large geographic and depth dimensions, high water volume presence, and heat flow capacity; these types of geothermal systems become economically interesting. Especially at inter-stratified large igneous provinces (LIP) occurrences, when the aquifer confinement can generate geopressurization, as the Paraná sedimentary basin case, where Guarani Aquifer System (GAS) is inserted (Lazzerini & Carneiro, 2012).

This country totals geothermal energy installed capacity and production are represented by 98% to bathing, therapeutic, tourism, recreation and swimming direct-use category. Where your thermal/mineral springs locations have become popular tourist attractions over the last few decades and the healing water powers gained legitimacy since 1818. Currently, such small-scale SPA places are visited by an estimated 1.5 million tourists per year. This, in turn, has spurred considerable local economic activity. The emphasis at these SPA towns and wellness/health tourism destinations is on entertainment and physical conditioning under programs for revitalizing the body in a relaxing environment, along with modern/thematic thermal water parks. The main thermal/mineral springs geographic distribution shows a relatively high concentration on southern (63.3%) and south-central (15%) parts (Vieira et al., 2015).

Brazilian thermal/mineral springs industry enfolds 147 establishments (1,567 SPA), with annual revenues US$ 526.1 million income, total 22,653 SPA jobs employments and being the 12th global market. An expected solid growth trajectory to next 5 to 10 years, due: growing desire for people to reconnect with their heritage and experience the therapeutic and wellness-enhancing properties of what nature has to offer; accessibility of thermal/mineral spring bathing experiences to all ages citizens, people who may be new or inexperienced with wellness and SPA sense; ease to the bath participating as a complementary option to other recreational, cultural, and leisure activities during travel (GWI, 2017).

These related segments are addressed to the national level by health policies on complementary alternative integrative medicine (CAIM), where social thermalism/crenotherapy services have an incentive to implementation with partnerships that allow access to preventive, therapeutic and health maintenance purposes (BRASIL, 2006). Since 1945, hot/mineral springs are provided with federal mining legislation as ore, and potential water cure classification follows physicochemical specific compositions. Groundwater, as a natural hydrologic resource to general applications, is States grants subject. The health and wellness tourism segments are guided by the Ministry of tourism issues (where hydromineral SPA towns – "estancias" are foreseen).

NATURAL THERAPEUTIC FACTORS (NTF) TO SPA, WELLNESS AND HEALTH TOURISM INDUSTRY

Based on natural therapeutic factors (NTF) physicochemical properties, diversity, organizational form, and spatial distribution; these local pieces of knowledge found destination SPA point creation, support performance of the SPA services and employ methods for sustainable natural endowment (resources and environments) utilizations. When NTF expressive inventory is evaluated, keep enough features to the wellness and health tourism attractiveness, with 'value- adding' to the visitor expectations (Erfurt-Cooper, 2010). It also optimizes the bases to SPA town, resort installations and planned distinct tourism types facilities. Certain traditional health resort medicine countries (Russia, Ukraine, Romania, Serbia, and Czech Republic) endue specific legislation on NTF rational exploitation, health-promoting potential, protection and patrimony/heritage value (Lazzerini, 2019). A similar quality criteria approach adopts the European SPA Association (ESPA, 2006).

Prospects for a balneology development analyze the main NTF, balneological treatment methods and their applications have created a program for further Russian SPA resorts settlement. It is events such as: conduct NTF inventory in order to create a single database, reassess reserves of medicinal mineral waters, carry out geological studies to identify promising therapeutic areas, develop a strategy to the sanatorium and tourism industry installation, rate investment attractiveness factors for resort or recreation business, create a data bank for potential investors, develop a clear legislative and regulatory framework for therapeutic areas with federal heritage significance to the health/wellness tourism; and including a controlled clinical studies guidance (Prokhorova, 2016).

Mineral waters, therapeutic peloids, favorable landscapes, and climatic conditions make up the main basis for the creation and development of the health resort business. The NTF territories suitable for the organization and realization of health-promoting activities, setting up new SPA and health resort facilities are highly vulnerable to any external impact (Munteanu et al., 2013). The Russian geological survey possesses a scientifically grounded and practice-proven method for the search, prospecting, practical development and medical utilization of various NTF as well as technologies for their conservation, restoration, protection from damages and overexploitation (Adilov et al., 2016).

GEOTHERMAL WATERS PHYSICOCHEMISTRY IN HYDROTHERAPY

Each hot/mineral spring water has its own distinctive remedial power, depending on specific peculiarities; i.e.: environment outcrop, discharge generosity flow, temperature, chemical structure, ionic features, inorganics, organics, trace elements, gases and other natural characteristics (NTF) that will influence the bioactivity effect (BAC) on their potential health benefits. These healing properties have been noticed a long time ago, many illnesses can be treated with good rates of success using various water types and to the potential evaluation of water cure through the ingestion, inhalation or bath; their physicochemical compositions are assigned key roles criteria indications (Erfurt-Cooper, 2010; Kosic et al., 2011).

Thermal and mineral water types or names are defined by their physical characteristics, general chemical compositions, macro components ratio, and specific thermal medicine potential contents; according to requirements normative documents at many countries standard legislation (Iordache et al., 2016).

The chemical composition of geothermal water often represents a crucial factor to their origin determination, as a hydrotherapy potential indicator, and to the regional resources valorization. A fastened development of both wellness and SPA concepts, as basic goals for this health tourism sector, has led to establishing an entire range of new methods that are deployed to define SPA-hotel enterprise locations in a qualitative way. Thus, being the baths practices increasingly required in these segments, a special significance to studying these balneological active components (BAC) is ascribed to the mineral groundwater curative properties (Milenic et al., 2015).

There are several publications found, which aim to evaluate regional endowment of springs, wells, aquifers, and others NTF to this geothermal direct-use assessment (balneotherapy, recreation, SPA, tourism, wellness or health); through their hydrochemistry groundwater knowledge, i.e.:

- Recreational use of geothermal water in Visegrád Group countries (Poland, Czech Republic, Slovakia, and Hungary) agrees they're direct effects on the human body due to unique properties such as high water temperature and mineral compounds (including curative potential). Thermal/mineral spring waters are valuable natural resources. In general, thanks to their health, economic and social significance is considered an important part of national natural heritage. Their chemical composition and physical properties are important distinctive features, which differentiate them from ordinary water (Dej et al., 2013).
- Utilization and tourism valorization of geothermal waters in Croatia. In the safeguard interest of this valuable resource, it is important to plan sustainable uses for each phase of the geothermal site development cycle and fully implement joint management principles of transboundary geothermal aquifers including neighboring countries (Borović & Marković, 2015).

- Balneological properties of the geothermal water in Latvia (Skapare et al., 2003). Balneological studies based on the hydrogeochemical aspects of the sulfate springs water, Hit–Kubaiysa region, Iraq (Al Dulaymie et al., 2011). Balneological evaluation of the Tafadek Spring, Agadez Region, Niger Republic (Nghargbu et al., 2012). Determination of hot springs physicochemical water quality potentially uses for balneotherapy in Malaysia (Hamzah et al., 2013). Insights into the factors responsible for the curative effects of Aab-E-Shifa Spring Hasan, Abdal, Pakistan (Rahman & Bilal, 2017).

GUARANI AQUIFER SYSTEM (GAS) GEOTHERMAL BALNEOLOGY PREVIOUS KNOWLEDGE

The Environmental Protection and Sustainable Development to the Guarani Aquifer System Project - GASP, implemented jointly by the 4 countries included in it, with World Bank partial financing; highlights as one of its 7 main objectives the geothermal energy potential use development in the GAS transborder region. Preliminary data and estimates about this potentiality should be presented as studies and survey results to this aquifer geothermal characteristic as a means to the tourism development, facilitating their hydrothermal SPA resorts and water parks installations (Rabelo et al., 2002; OAS, 2005).

Since then, mainly Argentina and Uruguay governments relieve these hot waters importance and promote the SPA touristic centers around their sources. The basement of integrated study and the recognized economic success of these activities, result in rapid regional growth. The establishment of therapeutic (i.e. NTF) and recreational facilities contribute considerably to the local property (Pesce, 2003; 10).

These groundwaters physicochemical characterization, grounds applied research and its availability should be of singular importance to its user management object, from different angles: spending regulation, public health, territorial ordering, and leisure tourism promotion. Establishing a "baseline" to the water quality, identifying different recreational thermal environments, helping competent agencies to establish periodic monitoring of their quantity and quality, strategic planning, new wells grants and cross-border international relations (Carrión & Massa, 2010; Manzano & Guimaraens, 2012).

It is observed that all literature cited in this work, publications related to the GAS, notes these geothermal energy direct-uses categories. Although, no research papers were found with geothermal waters physicochemical analysis compiled database, from GAS SPA towns; as well as with its focus on their balneological potential. Thus, this study does a literature review about hydrogeology, geothermalism, balneology BAC, and compile mineral/hot spring waters physicochemical analysis for GAS potential hot spring SPA towns; to allow further comparisons data level for balneotherapy applications through their specifics BAC, like NTF.

METHODOLOGY

Initially, for the basic descriptions about GAS, a literature review in the digital databases (scholar.google.com, and periodicos.capes.gov.br) applying the key-words: GAS (and Parana sedimentary basin, and hydrogeology, and water resource, and groundwater, and geothermal energy, and hydrothermalism).

To the aims of this study making about the balneology specific therapeutic role of mineral elements and other chemical compounds of mineral waters, searched databases (scholar.google.com, ncbi.nlm.nih.gov/pubmed, cochranelibrary.com, and tripdatabase.com/search); using the following keywords: balneotherapy (and mineral water, and SPA water, and inorganic elements, and skin permeation, and percutaneous absorption, and biologically active components - BAC).

To the GAS hot springs (or geothermal wells) occurrences compilation, previous information published by (Lazzerini, 2005) is used; added to Paraguay locations found through keywords: GAS (and hydrogeochemistry and Paraguay). Among these results, just SPA towns are selected, seeking each site possible tourism or wellness activities related to the thermal/mineral water; with (google.com) the keywords: PLACE NAME (and SPA, and balneario, and estancia, and termas, and parque, and aguas).

This studied approaches a comparative criterion to evaluate the physiological bioavailability of electrolytes in water through balneotherapy, to select chemical elements with potentially therapeutic bioactivities (BAC), their minimum activity levels and their health indications through the baths. Thus, also here, previous information published by (Lazzerini, 2013) is used, where more detailed literature references it.

These selected waters physicochemical parameters to quantitative level comparison are searched for each GAS geothermal water located before; and a database grouped using digital sources (scholar.google.com, periodicos.capes.gov.br, and nlm.nih.gov/mesh), with keywords: GAS hydrochemical or hydrogeochemical or physicochemical (and COUNTRY OR REGION NAME).

GUARANI AQUIFER SYSTEM (GAS)

The Guarani Aquifer System (GAS) it's inserted into the Paraná sedimentary basin, with an outcrop area 30% minor than all this intracratonic basin of elliptical form, with the larger axle with direction NE-SW, coinciding, approximately, with the current course of the Paraná river and with 900 km of width. This sedimentary sequence, developed on the continental crust, practically is not tectonically disturbed, presenting weak dip in the direction to the center of the basin. Located normal faults can have served as main canals during the lava pills. They are rocks predominantly terrain, being the greater part recovered essentially by basaltic lava and cut by its dikes. Consist of Triassic-Jurassic eolian-fluvial-lacustrine sandstone confined by Upper Jurassic-Late Cretaceous basalt flows (Lazzerini, 2005).

Considered the largest transboundary confined aquifer system and groundwater reservoirs in the World. The GAS water volume stored (permanent reserves = Vsat x Vpress) is estimated at 50,000 km^3 (equivalent more than 100 years cumulative flow in the Paraná river) and the natural recharges on the river base flow data are estimated at 234 km^3 per year (OEA, 2001).

Possess about 90% of its area covered by the most extensive spills of volcanic basaltic rocks on the Earth occurrence, which was originated in this region during the Upper Jurassic and Lower Cretaceous. About 70% of its confined area has artesian conditions. A thick basaltic package (up to 1,500 m) overlies this aquifer, reducing its exposed sites to only 10% of its total size. The deposits thus formed, reach already perforated thicknesses with more than 8,000 m. Basaltic rocks, on a regional scale, are considered impermeable and fractures with little or no contribution in the interconnection between the GAS and overlapping units. However, it is recognized that basalt locally fracture at greatest aquifer confinement regions where GAS water percolation it presents natural artesian discharges (Rebouças & Amore, 2002; Foster et al., 2009).

Corresponding to a total area of 1,195,500 km^2, being distributed among Brazil (71%), Argentina (19%), Paraguay (6%), and Uruguay (4%). At the Brazilian States encompassing Mato Grosso do Sul-MS (17.8%), Rio Grande do Sul-RS (13.2%), São Paulo-SP (13%), Paraná-PR (11%), Goiás-GO (4.6%), Minas Gerais-MG (4.4%), Santa Catarina-SC (4.1%), and Mato Grosso-MT (2.2%). However, the main recharges areas that must be preserved are in this last State. Approximately 24 million people live in the area delimited by the GAS boundaries and a total present population of 90 million in areas that directly or indirectly influenced it, including large cities (Foster et al., 2009).

Thus, it is estimated that about 25% total annual groundwater recharge could be extracted from the GAS, meaning about 68 km^3/year, or an amount sufficient to the 68 million populations, with per capita annual consumption rate 1,000 m^3/year - domestic, industrial and irrigation (Rebouças & Amore, 2002). Currently, there are more than 2,000 wells drilled in the Brazilian GAS, with depths between 100 to 300 m, and a few hundred others in their confined domains, with depths between 500 to 2,000 m. Some capable production bigger than 500 m^3/hr but less when only the ‘overflow yield' is utilized and as regards actual average abstraction less than 20% of the total are producing more than 100 m^3/hr. Suggesting these waters minimal exploitations yet, compared to its potential (Manzano & Guimaraens, 2012).

The deep waters confined areas evolution, generates as a result, elevated pH and higher temperature; however, all respond to a normal geothermal gradient, which is typical of tectonic stable zones. The influences of this upstream flow of pre-GAS rocks change the water chemistry into the GAS, mainly in the central portion of the basin. A temperature effect on the aquifer's hydraulic conductivity (permeability) may be expected as a result of changing kinematic viscosity. The highest geothermal values are located within Brazilian territory; where about 65% of the GAS has temperatures between 25 to 45 ºC (Tallbacka, 2001).

Previous studies indicate a meteoric origin to the GAS waters and relatively low kinematics of its flow system. The gradual flows increased from the basin edges to the center part, as well as several parameter variations: water temperature, alkalinity (pH: 5.36 to 9.62), sodium content, total dissolved solids (TDS: 37 to 540 mg/l), and apparent ages ranging between 480 to 38,825 years old (Amore & Surita, 2002).

A full inventory of production boreholes in the GAS which indicates current resource exploitation to total 1.04 km^3/year (2,847,013 m^3/day), with 94% in Brasil (of which about 80% is in São Paulo State), 3% in Uruguay, 2% in Paraguay and 1% in Argentina. For all GAS area, some 66% of the total is used for public water supply, 16% for industrial processes, 13% by geothermal recreation SPA and 5% to rural supply. In Brazil, some 80% of the total is used for public water supply, 15% for industrial processes and 5% by geothermal SPAs. While Argentina consumption is only concerned with the geothermal recreation SPA (OEA, 2010).

GAS - HYDROTHERMALISM

The Paraná sedimentary basin, where GAS inserted, is considered the best quality geothermal resources and with the highest heat power evaluated on different Brazilian geologic regions (2,350 to 2,450 KWt). Also, there are medium enthalpy resources excellent futures potential, deeper than 5 km at the basin bottom parts (Dos Anjos, 2018).

Besides GAS large water amount with excellent quality (potable suitable), this hydrologic reserve also represents another important endowment: the geothermal energy potential through hydrothermalism special hot waters flow (Rodrigues & Arruda, 2006). The heat direct-use is an extractive low cost compared to the domestic or industrial heating and is especially recommended to recreational, tourism and balneology activities; reducing other electrical energy sources consumption (Cernuschi, 2014). Although, this last geothermal direct-use category represents more than 98% of all applications in Brazil, on this country GAS region, recreational, tourism and balneology activities cited above, being just 5% of total groundwater exploitation (Hamza & Carneiro, 2004; Foster et al., 2009).

In a preliminary assessment, the GAS geothermal function utilization would represent an energy economy estimated 11,000 MW, which is equivalent to all currently installed Paraná river hydroelectric power potential. The GAS total heat-in-place valued at 41,000 EJ, corresponding to approximately 1,000 billion tons of fuel oil equivalent (toe). A technical reserve power assessment estimates the total GAS geothermal energy between 12,300 to 33,210 x 10^{18} J (EJ), being calculated equivalent between 300 to 810 x 10^9 ton of fossil fuel or economic value nearby range US$ 29,000 to 36,000 billion; only considering at the 40 °C isotherm as mapped at the top aquifer level Brazil's part increases from 71% to 81% (16.4% Argentina, 2% Uruguay, and 0.6% Paraguay). At the 60 °C and higher isotherms the geothermal energy potential is entirely confined within Brazilian territory, which makes it an important energy power source (Tallbacka, 2001; Amore & Surita, 2002; Rabelo et al., 2002; Rebouças & Amore, 2002).

The temperatures increase as a depth function terrestrial average valued 1 °C/34 m (29 °C/km), i.e., the water temperature increases by 1 °C every 34 meters. Geothermalism, the terrestrial Globe's internal heat, manifests itself in the Paraná sedimentary basin because it has permeable rocks in great depth and is overlaid by an impermeable cover that prevents the loss of heat by convection of fluids to the surface, occurrence of hot water is not due to the existence of magmatic chambers (Rodrigues & Arruda, 2006). The presence of hot waters in the aquifer is related to the natural geothermal degree of the Paraná basin and the depth of the underground catchment. The confined GAS waters average temperature at overpressured deep: ~45 ºC at ~1,000 m (Cernuschi, 2014).

These sedimentary basin resources were evaluated with geothermal gradients, varying from 16 to 46 °C/km and the heat flows reaches to 100 MW/m² (Gomes, 2009). Geothermal anomalies are related to the convective movements towards the GAS, being classified as a low enthalpy geothermal system (40 to 90 ºC - widely exceeding 40 °C and locally reaching 60 °C), with stored energy per aquifer unit area calculated at 280 MW year/km^2 (OEA, 2001). However, they usually respond to the normal geothermal gradient, when increase the confinement, geothermal gradient grows to over 35 ºC/km (OEA, 2010).

In function of the great reached depths (almost 2,000 m) and the pilling up of basalt that overlaps itself (thick confining basaltic cover), the water stored in the GAS is relatively hot (50 to 90 ˚C), reduced viscosity and with elevated pH (Foster et al., 2009). The basalt low thermal conductivity from Paraná LIP (large igneous province), comparing others, makes them act as aquifers heats insulators, accentuating regional geothermal gradient and raising their temperature average. It is possible that this gradient decreases at greater depth since there would be heating transmission by convection of groundwater in the GAS and under aquifers, which contributes to the rock thermal conductivity increase, while there is only conduction in the basalts of low thermal conductivity (Cernuschi, 2014).

MINERALS BALNEOLOGY

To the balneotherapy title searched database results (23/08/2018) at PubMed: 184, cochranelibrary.com: 198, and tripdatabase.com: 161. Balneotherapy is a medical hydrotherapy technique, practiced through immersion bath (general, partial or specialized) in to mineral water or mud, hot or cold; comprising aquatic moving massage, wrapping in towels soaked with clay, peat or other organic material, rubs pressure applications, sheets, and compresses (Jonker, 2016). The balneotherapy involves multiple action mechanisms related to the geothermal or mineral-medicinal water factors: mechanical, thermal, chemical, kinetic bioactivity, psychotropic, and general unspecified (Farcas, 2005; Maján et al., 2017).

Almost all water types can be drunk and almost all thermal stations offer treatments that combine external and internal water cures (Morales, 2004). Despite the medicinal SPA waters, in many countries, receive their classifications based on mineral contents; when related to the baths (topical external applications) some authors question its physiological effects. But, according to the medical balneotherapists, even very small amounts of biologically active inorganic and organic substances absorbed through the skin into the body, get curative value. In vitro and in vivo studies have established that some water-soluble minerals are able to permeate human skin and seem to be the key mechanism responsible for the improvement in some clinical outcomes, in both balneotherapy and mud therapy, thus implying that those beneficial effects are not exclusively linked to the heat action (Rahman & Bilal, 2017).

Even so, this increasing evidence, it is difficult to analyze the specific effects of each mechanism and each chemical component separately. It is known that, generally, different diseases require agents with different chemical compositions to attain therapeutic results. However, the exact components that are the most suitable for each pathology and the ideal concentration of each element that is necessary for obtaining optimal biological and clinical outcomes have not yet been completely elucidated. It is plausible to think that the mechanism of action probably results from a complex synergistic combination of several factors (Gálvez et al., 2018).

The healing effect of spring water is mostly due to the chemical influence of minerals which are transferred to the skin and the bloodstream by the process of osmosis and promote healthy skin. The physical effects of spring water are owing to the water temperature, which facilitates the dilation of skin for oxygen flows in the tissues that are being treated. The movement towards water into and out of the body during the mineral water bath is dependent upon the osmolality of the bath and individual fluid condition. Thus, minerals are either absorbed or pulled from the body. Dermatological curative effects of these elements appear due to a local interaction between mineral water and skin surface (Rahman & Bilal, 2017).

The thermal and mechanical water actions do not only dilate the tissular irrigation, but also paralyze vasoconstrictive responses. In this case, the dermal assimilation of these mineral elements will depend on the skin thickness, vascularization, exposure form, contact length, application rate, means of ensuring the cutaneous absorption, pressure, temperature, pH, osmotic quality, ion exchange capacity (free ion content), particle size, chemical speciation, and potential redox from environment. They act upon the osmosis and diffusion processes, surface tension, cells electric charge, and metabolic process (Morales, 2004).

Double-blind randomized clinical trials seem to be the key to studying the mineral elements and other chemical compounds roles, observing enough consistency to demonstrate better and longer improvements for mineral waters or derived compared to tap water (Morer et al., 2017). The low mineralization doesn't decrease the pharmacodynamic value of its elements (Maján et al., 2017).

Employing the radioactive isotope technique, the therapeutic interest components of mineral-medicinal water percutaneous absorption can be determined. Thus, it has been found that dissociated organic ions and inorganic salts have the lowest absorption rates, while gases such as carbon dioxide, radon, and hydrogen sulfide have good skin penetrability. It is estimated, in each bath, approximately 20 ml of water with its entire corresponding dissolved substances pass through the cornea layers entire body surface. And higher concentrated these bathwater substances are, greater will be deposited in the stratum corneum. In addition to the bioactivity at this absorption process, the so-called "post-resorption" or subsequent resorption of the deposits that have been stored in the skin occurs and the following 100 hours after the bath keep going (San Martín & San José, 1989).

The penetration of substances through the skin is produced by the essential mechanisms: transcellular, intercellular and through the annexes. The percutaneous absorption types =.Penetration into the skin when substance disappears on the dermal surface, one part disappears by permeation through the skin and the other part is absorbed into; .Permeation through the skin when substance crosses the skin, permeation amount could be measured below the skin; .Absorption in the tissue when a substance is stored in a part of it, the absorbed amount could be measured in the tissue (Pratzel & Schnizer, 1987).

The mainly biochemical effects through the baths (target diseases): .direct to the skin (dermatology), .indirect by skin stimulation to the general system (chronically inflammatory), .by percutaneous absorption to elimination by the respiratory system (pneumology), .by percutaneous absorption effect on the general systems (circulatory and central nervous) (Pratzel & Schnizer, 1987).

The benefits of balneotherapy are related to its positive effects on the endocrine and metabolic homeostasis. Thus, it contributes to enhancing the natural mechanisms of defense, balance and organic adaptation. Mineral waters influence the level of cells and tissue reactivity (the capacity of changing the conditions of vital activity under the influence of different environmental factors). Baths have been long used for helping to relax, heal wounds, and improve dermatologic treatments, bone traumatism, and rheumatic processes. Its mechanic and thermic action improve the affections of the locomotor system while the absorption of the minerals by the skin is also beneficial (Morales, 2004).

Other chemical elements ways of exposure may bind externally to the hair during bathing, although occasional bathwater ingestion or steam inhalation of a small amount (Lowney et al., 2005). Nanoparticles generated by natural nanosizing are therefore not uncommon in our environment, a good example can be found like some inorganic elements ($CaSO_4$, SiO_2, S, Se) diluted at mineral spring/well waters. Besides, "simple" physical and chemical events more controlled particle generating processes, often based on spontaneous oxidation. Despite their a rather poor quality, polydisperse, not perfectly shaped and also not entirely pure either; some scientific explanations issues related their potential bioactivities at medical or healing applications for dermal expositions balneotherapy performed (Griffin et al., 2018).

DATA COLLECTION RESULTS

This literature review about GAS physicochemical groundwaters properties levels did not find a public free article containing an integral database analyzed on any of these 4 countries, a total of dozen results at database searched with the keywords described at methodology this. In order to obtain an initial collection encompassing geothermal sites, the following publications are used: a database with 525 Brazilian hydromineral sources (Lazzerini, 2013; plus Freitas, 2016), research referring to Argentina and Uruguay (Silva, 1999; Pesce, 2002; Pesce, 2003; Lazzerini, 2005; Gastmans et al., 2010), and about Paraguay (Farina et al., 2004).

Thus, being found and enumerated a total of 85 cities possessing hot/mineral water. Among these, 72 locations are selected due to the observation of activities involving aquatic recreation, SPA, balneology, water park, thermalism or tourism. It is situated, total 9 in Argentina, 6 in Uruguay, 4 in Paraguay, and 53 in Brazil (States: 3-GO, 2-MT, 2-MS, 1-MG, 12-SP, 12-PR, 10-SC, and 11-RS) (Table 1 and Figure 1).

However, to the potential SPA town (healthy city, wellville, “estancia”) designation, it is necessary to have a more detailed observation of many specific characteristics in these places; i.e., good urban infrastructure, local community quality of life, tourism vocation, preserved environments, and others distinguish NTF (ESPA, 2006; Iordache et al., 2016; Lazzerini, 2019).

Most of the presented places occur at a topographic height below than 400 m (above sea level), predominantly bordering main regional drains, with common natural upwelling, large discharges flow, and hot waters. Such features may be related to the coincident locations of main GAS hydrothermal tourism destinations (Tallbacka, 2001). By observing the geographical distribution obtained (Figure 1), 8 geothermal SPA regions can be differentiated according to these principal hydrographic basins:

- I. River Aporé
- II River São Lourenço
- III Rivers Grande/Paraná
- IV River Paranapanema
- V River Piquiri
- VI Rivers Iguaçu/Paraná
- VII Rivers Uruguai/Iraí
- VIII Rivers Uruguay/Dayman.

Table 1 - Selected cities, referring thermal mineral SPA places at GAS occurrences and hot spring/well water temperatura (Silva, 1999; Pesce, 2002; Farina et al., 2004; Lazzerini, 2005; Gastmans et al., 2010; Lazzerini, 2013)

	CITY	LOC	SPA	°C
1	Cachoeira Dourada	GO	Yquara Termas	**39.0**
2	Jataí	GO	Thermas Jatahy and Bonsucesso	**33.5**
3	Lagoa Santa	GO	Thermas Lagoa Santa	31.5
5	Jaciara	MT	Balneário Paraíso	**40.0**
6	Juscimeira	MT	Thermas Marihá	**39.0**
7	Dourados	MS	Parque Termal Vila Vargas	**37.0**
10	Tres Lagoas	MS	Água do Palmito	**46.0**
11	Conceição das Alagoas	MG	Ubatã Thermas	**36.4**
13	Araçatuba	SP	Balneário Termas da Noroeste (close)	**42.0**
14	Barretos	SP	Barretos Country Thermas Acquapark	**48.0**
15	Fernandópolis	SP	Agua Viva Thermas	**58.7**
16	Jales	SP	Grandes Lagos Thermas (S.C. D'Oeste)	**52.0**
17	Lins	SP	Blue Tree Park	**41.2**
18	Olímpia	SP	Thermas dos Laranjais	**47.0**
19	Paraguaçu Paulista	SP	Resort Água das Araras	**48.0**
20	Pereira Barreto	SP	Thermas Pereira Barreto (close)	**45.4**
21	Piratininga	SP	Novo Thermas de Piratininga	**39.5**
23	Presidente Epitácio	SP	Balneário Thermas de Epitácio (close)	**70.0**
24	Presidente Prudente	SP	SESC Thermas	**63.0**
25	São José do Rio Preto	SP	Thermas Internacional de Rio Preto	**44.0**
26	Bandeirantes	PR	Termas Yara (close)	32.0
29	Cornélio Procópio	PR	Aguativa Golf Resort	**45.0**
30	Coronel Vivida	PR	Águas Minerais Santa Rosa	31.6
31	Foz do Iguaçú	PR	Recanto Cataratas - Thermas Resort	**39.0**
32	Francisco Beltrão	PR	Anila Thermas	**45.0**
33	Iretama	PR	Termas de Jurema	**37.0**
34	Itaipulândia	PR	Itaipuland Hot Park. Resort & SPA Thermal	**41.0**
35	Jardim Alegre	PR	Public Supply	32.0
36	Londrina	PR	Águas Termais de Londrina	**44.8**
39	Maringá	PR	Solar das Águas Quentes	**54.0**
42	Sulina	PR	SESC Thermas de Sulina	**33.1**

Table 1 – *Cont.*

	CITY	LOC	SPA	°C
43	Verê	PR	Águas do Verê Termas	**36.1**
44	Águas de Chapecó	SC	Termas Águas de Chapecó	**36.5**
45	Caibi	SC	Parque da Água Mineral	31.8
46	Itá	SC	Itá Thermas	**33.0**
47	Ouro	SC	Thermas de Ouro	32.9
48	Palmitos	SC	Balneário de Ilha Redonda	**38.0**
49	Piratuba	SC	Termas de Piratuba	**39.0**
50	Quilombo	SC	Balneário de Quilombo	**37.0**
51	São Carlos	SC	Pratas Thermas Resort & Convention	**38.0**
52	São João do Oeste	SC	Termas São João	**53.0**
53	Treze Tílias	SC	Parque Águas Tirolesas	32.0
54	Catuípe	RS	Balneário Águas de Santa Tereza	20.0
55	Caxias do Sul	RS	Thermas Clube	32.0
57	Erechim	RS	Águas Termais da Cascata Nazzari	**38.0**
58	Ijuí	RS	Parque da Fonte Ijuí	21.3
59	Iraí	RS	Balneário Oswaldo Cruz	**33.0**
60	Machadinho	RS	Machadinho Termas	**42.0**
61	Marcelino Ramos	RS	Balneário Marcelino Ramos	**36.7**
63	Nova Prata	RS	Complexo Hidrotermal Caldas de Prata	**44.0**
64	Tres Arroios	RS	Termas de Tres Arroios	32.0
65	Veranópolis	RS	Termas dos Capuchinhos	**33.0**
66	Vicente Dutra	RS	Termas Minerais Águas do Prado	**34.0**
67	Chajarí	ARG	Complejo Termal de Chajarí	**38.0**
68	Colón	ARG	Complejo Termal de Colón	**34.1**
69	Concordia	ARG	Termas Concordia	**46.0**
70	Federación	ARG	Termas Federacion	**43.0**
71	Gualeguaychú	ARG	Complejo Termal de Gualeguaychú	30.0
72	La Paz	ARG	Complejo Termal de La Paz	**40.0**
73	Maria Grande	ARG	Complejo Termal de Maria Grande	**40.0**
74	San José	ARG	Complejo Termal de San José	**37.0**
75	Villa Elisa	ARG	Termas Villa Elisa	**41.0**
76	Almirón	URU	Termas de Almirón	**34.0**

Table 1 – *Cont.*

	CITY	LOC	SPA	°C
77	Arapey	URU	Termas del Arapey	**38.0**
78	Dayman	URU	Termas del Dayman	**45.0**
79	Guaviyú	URU	Termas de Guaviyú	**40.0**
80	Salto Grande	URU	Termas de Salto Grande	**56.0**
81	San Nicanor	URU	Termas de San Nicanor	**44.0**
82	Ciudad Del Este	PAR	Hotel Austria	30.0
83	Santa Fé del Paraná	PAR	Hotel Estancia Laura	29.0
84	Mingá Guazú	PAR	Geothermal well - recreative potential	32.0
85	Alto Paraná	PAR	Geothermal well – Puerto Palma	**34.0**

LOC = between # 1 to 66 are Brazilian States. **Temperature °C =** positive potential biologically active components (BAC) level.

Clusters, not necessarily related to the geology structural constraints, such as the Ponta Grossa Arch or the Rio Grande-Assunção Ridge, which can, however, directly influence the groundwater flow characteristics. This specific GAS grouping may also be influenced by economic factors or by wells drilling regional density of knowledge.

The listed waters temperatures range from 20 to 70 ºC. When the heat is higher than 33 ºC, amenable applications are known as an isothermal bath, or minimum potential biologically active component (BAC) to the balneotherapy (Lazzerini, 2013). Being 57 places owned by this property, see ***bolded and underlines*** values (Table 1).

The hydrochemical parameters selected for this assessment are present in most groundwaters compositions, their contents are commonly analyzed (satisfactory quantification level) in specialized laboratories, with properties generally surveyed at hydrologic researches and water solution related bioactivities evaluated by various scientific areas.

Besides the temperature, physicochemical data compile basic water properties pH and total dissolved solids (TDS or mineralization), and 6 macroelements (SO_4^{-2}, HCO_3^-, Cl^-, Na^+, Ca^{+2}, Mg^{+2}), and 7 trace elements (F^-, Si, B^{-3}, Fe, Li^+, Mn^{+2}, Zn^{+2}). The lack of information about trace element values in some locations is evident, yet (Table 2). These parameters are potential biologically active components (BAC) to the balneotherapy and mineral waters classifications. See ***bolded and underlines*** tips at locations (Table 2) where parameter values are higher than minimum balneological BAC levels (Lazzerini, 2013).

Figure 1 – Schematic map of the Guarani Aquifer System GAS (72 geothermal spring/well SPA locations). Adapted OEA, 2001

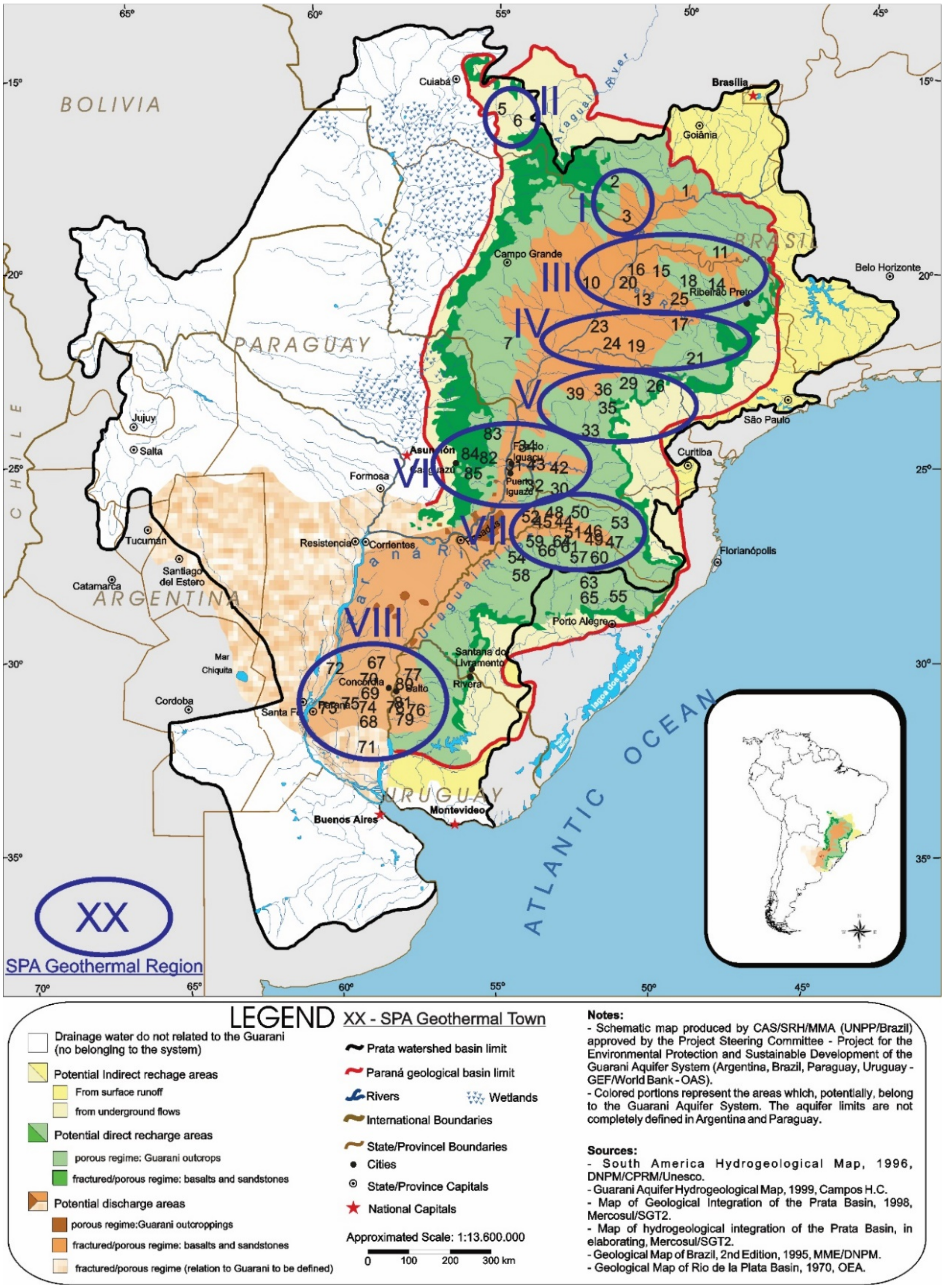

Table 2 - GAS thermal mineral SPA places (#) with physicochemical waters selected parameters (p), comparative minimum BAC content (mg/l) to potential balneotherapy direct-uses (Silva, 1999; Pesce, 2002; Farina et al., 2004; Lazzerini, 2005; Gastmans et al., 2010; Lazzerini, 2013; Freitas, 2016)

p	**pH**	**TDS**	**SO_4^{-2}**	**HCO_3^-**	**Cl^-**	**F^-**	**Na^+**	**Ca^{+2}**	**Mg^{+2}**	**Si**	**B^{-3}**	**Fe**	**Li^+**	**Mn^{+2}**	**Zn^{+2}**
BAC>	***8.5***	***444.0***	***408.0***	***196.6***	***1171.0***	***2.40***	***725.0***	***256.0***	***121.6***	***25.3***	***1.300***	***0.840***	***0.680***	***0.230***	***0.043***
1	8.2	**10343.0**	**5348.0**	**261.0**	**1434.0**	0.70	**3200.0**	146.0	41.0	6.7	0.002	0.002	**1.700**	0.001	**0.080**
2	**8.6**	**473.9**	188.0	180.8	3.0	0.14	97.2	3.6	0.7	8.9		0.030		0.004	0.029
3	7.2	139.0	1.7	53.7	0.6	0.10	11.1	15.7	3.6	6.4		0.005	0.016	0.005	0.011
5	7.9	**478.0**	82.9	**328.0**	8.8		184.0	11.0	3.0	**29.0**		0.040			0.020
6	7.3	59.0	1.0	63.3	0.1		11.9	3.2	1.9	9.1		0.005			0.017
7	8.1	153.0	0.6	54.0	0.2	0.02	14.8	18.6	1.9	9.7	0.005	0.007		0.005	0.020
10	**9.2**	**623.0**	77.0	**204.7**	84.0	1.40	196.0	1.2	1.7	14.4	0.310		0.065		0.006
11	8.2	86.0	2.0	84.2	0.3	0.30	12.3	12.5	1.3	8.5					
13	**9.5**	286.0	26.0	170.0	23.0	0.80	102.0	0.9	0.1	14.2	0.110		0.021		**0.041**
14	**9.4**	220.0	8.3	105.0	1.6	0.77	63.0	1.3	0.1	13.0			0.013		0.021
15	**9.5**	400.7	34.3	92.0	38.0	0.84	100.0	1.4	0.1	17.7	0.160	0.040	0.022		**0.055**
16	**9.0**	327.0	27.0	140.0	21.0	0.90	92.0	1.0	0.4	19.2		0.010	0.020		**0.035**
17	**9.7**	400.3	14.1	**255.0**	6.7	1.00	122.0	3.4	0.7	18.1	0.190	0.010	0.017		**0.041**
18	**9.8**	286.0	14.0	149.0	7.0	0.92	77.0	0.8	0.2	17.4		0.010	0.021		**0.046**
19	**9.6**	**447.7**	10.0	**241.0**	16.4	1.30	117.0	0.5	0.1	**23.1**	0.280	0.160		0.070	0.004
20	**8.7**	**464.6**	68.0	**202.2**	40.0	0.80	119.3	5.7	0.2	13.6		0.070	0.074	0.010	**0.049**
21	8.1	**10700.0**	**5320.0**	**236.0**	896.0	1.80	**3400.0**	**218.5**	39.0	10.0	0.070	0.280	**1.090**	0.120	0.007
23	**8.5**	**657.0**	76.0	**266.0**	51.0	**5.80**	191.0	5.4	0.2	16.9	**1.400**	0.080	0.120	0.020	0.024
24	**8.8**	**615.0**	104.0	**200.0**	189.0	**8.40**	308.0	4.7	0.7	14.3	**2.230**	0.300	0.069		0.013
25	**9.7**	310.0	13.0	162.0	13.0	0.42	91.0	3.0	0.2	14.4	0.133	0.060	0.020		**0.041**
26	**9.3**	**766.0**	232.0	175.1	103.5	**6.10**	305.0	1.0	0.1	**33.3**	0.007	0.010			

Table 2 – *Cont.*

p	pH	TDS	SO_4^{-2}	HCO_3^-	Cl^-	F^-	Na^+	Ca^{+2}	Mg^{+2}	Si	B^{-3}	Fe	Li^+	Mn^{+2}	Zn^{+2}
BAC>	***8.5***	***444.0***	***408.0***	***196.6***	***1171.0***	***2.40***	***725.0***	***256.0***	***121.6***	***25.3***	***1.300***	***0.840***	***0.680***	***0.230***	***0.043***
29	**9.9**	371.0	35.0	**184.0**	12.8	1.15	113.0	0.9	0.3	**23.5**	0.120	0.010			0.004
30	**9.6**	152.0	27.5	61.7	2.5	0.85	68.0	1.0	0.1	15.1		0.010			
31	**8.7**	**2051.0**	**695.0**	**210.0**	497.0	**8.50**	**712.0**	28.0	11.0	20.7		0.180			
32	**9.5**	259.0	43.0	104.0	7.8	0.05	63.0	4.0	0.7	21.8					
33	**8.8**	395.0	12.0	**232.0**	24.0	1.80	143.0	0.6	0.1	17.3	0.150	0.040	0.019	0.001	0.001
34	**8.5**	**2208.0**	**944.1**	**313.2**	448.0	**5.60**	**756.0**	12.8	2.9	15.3	**2.400**	**1.030**	**0.520**	0.022	**0.039**
35	**9.7**	**1046.0**	**672.0**	6.1	337.0	1.70	430.0	192.0	0.5	14.1					
36	**9.8**	**1169.0**	**438.0**	52.0	270.0	**2.25**	368.0	8.2	1.7	22.2	0.160	0.010			0.005
39	**8.9**	**1280.0**	**580.0**	**234.1**	123.0	1.60	242.0	4.0	1.2	13.3	0.660	0.020			0.008
42	**9.0**	**509.0**	77.0	**199.0**	99.2	1.24	190.0	1.8	0.5	17.6		0.050	0.060		0.020
43	**9.2**	370.0	24.0	161.7	28.5	0.06	110.0	1.2	0.4	14.8	0.082	0.010	0.017	0.001	
44	**8.9**	**860.0**	318.0	**194.9**	151.5	1.85	268.0	3.2	0.9	7.1	0.480	0.005	0.064	0.005	0.009
45	8.3	**1731.0**	**808.3**	143.7	304.9	1.42	**727.2**	24.1	10.2	12.0	0.930	0.008	0.149	0.010	0.010
46	**9.1**	**678.0**	201.2	**183.2**	110.4	1.31	260.0	3.5	0.5	7.7	**1.640**	0.032	0.143	0.010	0.013
47	**9.6**	254.0	44.5	157.6	26.2	1.15	94.3	0.8	0.0	10.8	0.160	0.017	0.026	0.005	**0.045**
48	**8.6**	**1133.0**	**380.6**	174.7	224.8	1.76	400.0	7.1	0.9	9.8	0.650	0.079	0.083	0.011	**0.053**
49	**8.6**	**905.0**	159.0	**422.8**	127.0	**2.34**	340.0	3.2	0.0	9.5	0.390	0.005	0.055	0.005	0.007
50	**8.8**	**472.0**	95.7	118.8	87.9	1.64	140.0	4.8	0.0	9.6	0.320	0.076	0.032	0.005	0.015
51	**9.0**	**887.0**	345.0	164.6	141.7	1.80	280.0	4.8	0.0	7.3	0.560	0.005	0.052	0.005	0.009
52	8.1	**2440.0**	**1270.8**	58.4	**1544.0**	1.28	**980.0**	**273.8**	45.4	18.6	0.560	0.060	0.002	0.120	**0.094**
53	**9.5**	306.0	27.0	150.3	28.4	1.00	56.6	2.4	0.1	11.5	0.180	0.005	0.023	0.005	0.010
54	**9.2**	**435.0**	201.0	44.9	25.7	**2.47**	146.8	3.4	0.0	12.5	0.630	0.013	0.033		
55	**9.4**	281.0	82.0	147.7	27.2	0.60	96.0	21.0	4.0	19.7			0.015	0.020	0.012

Table 2 – *Cont.*

p	pH	TDS	SO_4^{-2}	HCO_3^-	Cl^-	F^-	Na^+	Ca^{+2}	Mg^{+2}	Si	B^{-3}	Fe	Li^+	Mn^{+2}	Zn^{+2}
BAC>	***8.5***	***444.0***	***408.0***	***196.6***	***1171.0***	***2.40***	***725.0***	***256.0***	***121.6***	***25.3***	***1.300***	***0.840***	***0.680***	***0.230***	***0.043***
57	**8.8**	**1238.0**	257.0	**617.0**	119.0	**5.90**	474.0	1.1	1.5	15.4	0.410	0.104	0.079	0.010	0.024
58	**9.6**	323.0	116.4	73.9	1.0	1.15	113.0	0.3	0.0	19.9		0.011		0.030	
59	**8.6**	**1237.0**	373.6	**256.6**	259.0	**2.90**	400.0	5.6	5.3	8.5	0.560	0.005	0.089	0.005	0.008
60	**8.7**	**918.0**	141.8	**596.0**	49.5	**6.00**	340.0	2.4	0.0	9.9	0.380	0.005	0.073	0.010	0.013
61	**8.6**	**829.0**	132.5	**510.1**	87.1	**4.83**	300.0	2.4	0.5	7.6	0.380	0.040	0.069	0.010	0.011
63	**8.9**	**487.0**	201.0	44.0	26.0	**2.47**	147.0	2.8	0.1	12.5	0.630	0.013	0.033	0.001	
64	8.4	**1203.0**	286.0	**381.2**	195.4	**3.35**	460.0	7.9	0.0	10.3	0.610	0.005	0.106	0.020	0.020
65	8.1	371.0	25.0	128.7	14.4	0.10	47.0	44.0	6.4						
66	**8.9**	**2572.0**	**1137.5**	**186.9**	522.8	**2.76**	**720.0**	90.2	9.6	**24.5**	0.190	**0.936**	0.058	**0.180**	**0.037**
67	8.2	**476.0**	37.3	**269.0**	111.0	0.83	154.0	12.0	4.2		0.200	0.010		0.040	
68	**8.5**	**620.0**	74.0	**318.0**	105.0	**3.10**	235.0	1.4	0.5	**26.8**	**1.400**	**2.400**	0.030	**0.880**	0.010
69	**8.5**	300.0	8.4	**290.0**	21.0	0.70	118.0	4.6	1.8	9.6	0.210	0.011	0.020	0.009	0.010
70	**8.5**	**698.0**	92.0	**236.0**	199.0	0.76	240.0	16.0	5.8	7.9	0.310	0.011	0.040	0.040	0.003
71	**8.5**	**10144.0**	**2281.0**	55.0	**3408.0**	0.80	**3341.0**	152.0	23.0	13.2	**2.450**	0.486	0.050	0.081	**0.072**
72	**8.6**	**82369.0**	**8761.0**	**195.2**	**43164.0**	**2.50**	**28992.0**	**1136.0**	**431.0**	8.7	**8.800**	0.100		**0.493**	**0.329**
73	7.6	**104600.0**	**5168.0**	43.0	**54831.0**	1.57	**40604.0**	**1287.0**	33.0		**167.600**				
74	**9.0**	**764.0**	123.0	**345.0**	140.0	**3.40**	308.0	12.1	0.3		**1.260**	**1.200**		0.010	0.020
75	7.7	**14500.0**	**4800.0**	98.0	**5070.0**	1.10	**4900.0**	**191.0**	70.0	15.0	**4.980**	0.550	**0.470**	0.123	**0.050**
76	7.2	**8044.0**	**1215.0**	37.0	**2933.9**		**2000.0**	**233.0**	2.9					**2.900**	
77	8.4	297.0	20.0	**310.0**	33.0	0.20	98.0	17.4	13.4	**42.3**		0.280		**1.300**	0.011
78	8.0	**485.0**	81.0	**313.0**	55.6	0.83	159.0	6.4	2.4	**52.2**		0.100	0.080	0.040	0.010
79	**9.1**	**750.0**	75.0	**450.0**	101.0	0.80	274.0	1.5	2.7	**48.9**		0.600		**0.950**	0.003
80	8.0	**770.0**	69.7	**320.0**	85.0	1.10	163.0	8.3	7.4			0.300		0.040	

Table 2 – *Cont.*

p	pH	TDS	SO_4^{-2}	HCO_3^-	Cl^-	F^-	Na^+	Ca^{+2}	Mg^{+2}	Si	B^{-3}	Fe	Li^+	Mn^{+2}	Zn^{+2}
BAC>	***8.5***	***444.0***	***408.0***	***196.6***	***1171.0***	***2.40***	***725.0***	***256.0***	***121.6***	***25.3***	***1.300***	***0.840***	***0.680***	***0.230***	***0.043***
81	7.9	**580.0**	36.0	**314.0**	57.2	1.10	152.0	4.5	5.0	**45.6**		0.400		**1.730**	**0.040**
82	8.3	**2657.0**	**1088.0**	180.0	445.0	**7.40**	**885.0**	9.7	3.4	12.5					
83	6.8	171.0	3.1	115.0	6.0	0.60	11.6	29.8	1.3	8.4					
84	**8.5**	**2180.0**	**810.0**	**224.0**	359.0	**3.90**	**733.0**	4.3	1.2	6.7					
85	8.3	**2180.0**	**873.0**	**208.0**	348.0	**3.60**	**734.0**	6.6	1.5	7.7					

Content = positive potential biologically active components **(BAC)** level

The selected physicochemical hot spring water data, their minimum balneological BAC levels cited in (Chebassier et al., 2004 and Lazzerini, 2013), the number of localities where these parameter values are higher than enough BAC and to related healing indications; see (Table 3).

Noteworthy is the finding to only 2 locations with none BAC, and observed 2 other cases with unique one BAC (temperature) occurrences. It also seems clear, where mineralization is high; the other parameters tend to exceed the minimum adopted bioactivities levels. However, this TDS minimum BAC level (> 444 mg/l) can be considered relatively low, since international standards indicate the 1,000 mg/l as limited TDS value. Thus, their 48 localities with BAC levels should be only 22 occurrences.

In this way, the most prominently highlighted physicochemical GAS parameter is the high pH, despite its high minimum BAC alkaline level (> 8.5), are 50 occurrences superior values; and just one place where pH has less than 7.0.

The anion of prominence is HCO_3, although the SO_4^{-2} is in higher concentrations when waters elevated mineralization (TDS). The clearly predominant cation is the Na^+, as well as, the low Mg^{+2} levels are constant.

One of the main findings is the constant presence of high F^- levels, often higher than the BAC minimum value. And others signify trace element concentrates at these groundwaters are Zn^{+2} and B^{-3}. With the F^- exception, for the other trace elements, it is evident the difficulty in obtaining their analyzed contents published. However, the Si and Mn^{+2} elements appear to demonstrate significant occurrences, when considering their fewer data obtained, high minimum BAC level, and relative importance to the skincare applications benefits.

Table 3 - Physicochemical parameters (p) selected to minimum content (mg/l) BAC for balneolgy evaluations at thermal mineral SPA places, total positive results (N) and healing indications (Chebassier et al., 2004; Lazzerini, 2013)

p	BAC>	N	INDICATIONS
Place	SPA town	72	Health-enabling, physical, mental and social wellbeing.
ºC	33.0	57	Inflammation, stress-related pathologies, facilitates skin permeation, suitable for hygiene, cleaning and underwater exercises.
pH	8.5	50	Positive dermatologic effects, facilitate cutaneous permeation, softens the epidermis and increases skin elasticity.
TDS	444.0	48	Freshness, lightness, softness, malleability and skin comfort.
SO_4^{-2}	408.0	19	Antioxidant effects, skincare, rheumatology.
HCO_3^-	196.6	37	Antioxidant effects, skincare, rheumatology, sedative.
Cl^-	1.171.0	7	Exciting and resolute action, cellular stimulants blood and lymphatic circulation, skincare, rheumatology.
F^-	2.40	21	Dilate vascular skin vessels and internal organs, stimulate secretion of tissue hormones, antiseptic, and skin moisturizing and elasticity action.
Na^+	725.0	15	Major bath skin permeability, cell renewal and moisturizing.
Ca^{+2}	256.0	6	Sedative, dermatitis, rheumatology.
Mg^{+2}	121.6	1	Major aqueous dermal absorption rate.
Si	25.3	10	Anti-inflammatory action, adsorption potentiate, sedative, emollient, skincare.
B^{-3}	1.300	10	Cell renewal and wound healing, changes in cognitive functions, ophthalmic benefits, and rheumatology.
Fe	0.840	4	Skin permeation power, against acne and eczema, astringent properties, alopecia, catalase (anti-free radicals) action, immunity system, synthesis, and regeneration dermal macromolecules (lysine, collagen).
Li^+	0.680	4	Fell calmer and happier, stimulation the immune system.
Mn^{+2}	0.230	7	Cell renewal, wound healing, bactericide and skin barrier recovery, outstanding cutaneous permeation power, dermal macromolecules glucosamine glicanase and tyrosinase synthesis participation, being an enzymatic activator and immunological functions.
Zn^{+2}	0.043	17	Cell regeneration, adaptation reactions in the post-stress period, anti-inflammatory, immunosuppressive, involvement in nucleic acid synthesis, metabolism of vitamins, antioxidant action, strengthening defence system against free radicals, good ability to penetrate psoriasis.

CONCLUSIONS

The GAS is an important geothermal energy reserve to low-medium enthalpy resources direct-uses explorations, due to its dimensions, water abundance, geo-pressurized system (many wells observed with more than 10,000 l/hr) and MERCOSUR transboundary economic region.

There is more than 313 BAC in the 72 potential hot spring SPA towns from this GAS research, grouped in 8 geothermal SPA regions with potential balneological applications, through skin permeation in controlled immersion baths. Inserted at salutogenic environments, getting well-being, healing practices, longevity promotion, and attractiveness to the sustainable development. Once included in local and regional inventories as potential NTF to the health/wellness tourism.

Due to observed main balneotherapy potential indications, resumed: dermatology, immune system, nervous system, rheumatology, and antioxidant actions. To this balneology suggested in this study, it relies upon their potential applications to the CAIM, SPA, wellness, beauty (aesthetics, cosmetics), recreation, health resort, tourism, water parks, and others correlated geothermal energy direct-use category

Potentially toxic (natural or pollutants) water constituents (heavy metals, pesticides, plastics, pharmaceuticals) assessments are necessary; even if their exposures are only external and sporadic. In this study, dissolved or emanated gases were no observed, such as: oxygen, nitrogen, methane, carbon dioxide, hydrogen sulfide, radon, and thoron. However, this can be very important to the mineral water classifications and physiologic indications; because they possess a high skin permeability and internal bioactivity.

Other water analysis which can be recommended, due to the feasible BAC: organic compounds, algae, rare elements (germanium, rubidium), and nanoparticles; in addition to the NAI (negative air ions) measures at the fountain sources and visitation sites, like therapeutic landscapes.

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