UNIVERSIDADE FEDERAL DE MINAS GERAIS
INSTITUTO DE GEOCIÊNCIAS
PROGRAMA DE PÓS-GRADUAÇÃO EM GEOLOGIA

DISSERTAÇÃO DE MESTRADO

NATURAL BACKGROUND LEVELS OF INORGANIC ELEMENTS IN THE GROUNDWATERS OF THE LAGOA SANTA KARST REGION, MINAS GERAIS, BRAZIL

AUTOR: Frederico Aragão Cardoso

ORIENTAÇÃO: Leila Nunes Menegasse Velásquez
CO-ORIENTAÇÃO: Paulo Henrique Ferreira Galvão

Nº 206

BELO HORIZONTE
DATA (29/08/2019)

Frederico Aragão Cardoso

Natural Background Levels of inorganic elements in the groundwaters of the Lagoa Santa karst region, Minas Gerais, Brazil

Dissertação apresentada ao programa de Pós-graduação em Geologia do Instituto de Geociências da Universidade Federal de Minas Gerais como requisito para obtenção do título de mestre em Geologia

Área de Concentração: Geologia Econômica e Aplicada

Orientadora: Prof. Leila Nunes Menegasse Velásquez

Co-orientador: Prof. Paulo Henrique Ferreira Galvão

Belo Horizonte
Instituto de Geociências da UFMG
Agosto de 2019

A659n Aragão, Frederico Cardoso.
2019 Natural background levels of inorganic elements in the groundwaters of the Lagoa Santa Karst Region, Minas Gerais, Brazil [manuscrito] / Frederico Aragão Cardoso – 2019.
87 f.: il. (principalmente color.)

Orientadora: Leila Nunes Menegasse Velásquez.
Coorientador: Paulo Henrique Ferreira Galvão.
Dissertação (Mestrado) – Universidade Federal de Minas Gerais, Instituto de Geociências, 2019.
Área de concentração: Geologia Econômica e Aplicada.
Bibliografia: f. 61-72.
Inclui apêndices.

1. Hidrogeologia – Teses. 2. Aquíferos – Lagoa Santa (MG) – Teses. 3. Carste – Lagoa Santa (MG) – Teses. I. Velásquez, Leila Nunes Menegasse. II. Galvão, Paulo Henrique Ferreira. III. Universidade Federal de Minas Gerais. Instituto de Geociências. IV. Título.

CDU: 556.3 (815.1)

UNIVERSIDADE FEDERAL DE MINAS GERAIS

PROGRAMA DE PÓS-GRADUAÇÃO EM GEOLOGIA

FOLHA DE APROVAÇÃO

NATURAL BACKGROUND LEVELS OF INORGANIC ELEMENTS IN THE GROUNDWATERS OF THE LAGOA SANTA KARST REGION, MINAS GERAIS, BRAZIL

FREDERICO ARAGÃO CARDOSO

Dissertação submetida à Banca Examinadora designada pelo Colegiado do Programa de Pós-Graduação em GEOLOGIA, como requisito para obtenção do grau de Mestre em GEOLOGIA, área de concentração GEOLOGIA ECONÔMICA E APLICADA.

Aprovada em 29 de agosto de 2019, pela banca constituída pelos membros:

Profa. Leila Nunes Menegasse Velásquez - Orientadora
UFMG

Prof. Julian Cardoso Eleutério
UFMG

Prof. Aníbal da Fonseca Santiago
UFOP

Belo Horizonte, 29 de agosto de 2019.

A **FOLHA DE APROVAÇÃO**, devidamente assinada, fica com o aluno para anexá-la no volume final impresso.

OBS: **DIGITALIZE** a folha de aprovação, pois ela deverá ser incluída na versão do trabalho final **DIGITAL** em formato PDF.

Agradecimentos

A meus pais pelos incondicionais e constantes suporte e preocupação, e a meus irmãos pelo apoio e pela presença.

À Leila Menegasse, pela exímia orientação e pela experiência as quais se traduzem em cada linha deste trabalho. Muito obrigado por me acolher no dia em que bati à porta de sua sala no IGC perguntando por ideias para projeto de Mestrado. O fruto disso está aqui. Ao Paulo Galvão, pela brilhante co-orientação, ilustrada em sua total disponibilidade e agilidade para me ajudar em todos os tipos de dúvidas e anseios, fossem eles grandes ou pequenos. Muito obrigado por acreditar em mim e neste trabalho.

À Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG, processo APQ 02049-14), ao Instituto Chico Mendes de Conservação da Biodiversidade/Centro Nacional de Pesquisa e Conservação de Cavernas (ICMBio/CECAV) pelo apoio financeiro e, finalmente, à Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) pela concessão das bolsas mensais.

Aos responsáveis e integrantes do Projeto de Adequação e Implantação de uma Rede de Monitoramento de Águas Subterrâneas em Áreas com Cavidades Cársticas da Bacia do Rio São Francisco Aplicado à Área Piloto da APA Carste de Lagoa Santa, Minas Gerais. À Companhia de Pesquisa de Recursos Minerais (CPRM), ao Instituto Mineiro de Gestão das Águas (IGAM) e ao Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) pelo apoio e pela disponibilidade de dados.

Ao Rodrigo, pelos constantes conselhos desde o meu ingresso no Mestrado até o dia em que finalizei a dissertação. Você me ajudou demais! Ao Thiago Lucon pela assessoria e pelo suporte com os famigerados NBLs em regiões cársticas. Ao Thiago Tayer pela parceria e pela ajuda à distância que resultou no primeiro capítulo deste trabalho, e à Manuela Corrêa pela boa vontade em me ajudar com seu mapa de Uso e Ocupação do Solo.

A todos os colegas de campo, em especial à Lu e à Carol, pelos dias de coleta que ficaram bem mais leves e divertidos, com incêndios, pneus estourados, tamanduás e bois (pra não dizer tamandubois) suspeitos no meio do mato. Ao Geraldo e ao Pedro pelo essencial suporte também durante esse período! A todos os funcionários do Instituto de Geociências, em especial ao secretário William, pela prontidão e boa vontade em resolver as picuinhas burocráticas. Ao corpo docente do IGC, da Escola de Engenharia da UFMG e da UFOP pelas disciplinas cursadas.

Por fim, obrigado também a todo o corpo discente de pós graduação em Geologia e em especial a seus representantes, pelas presenças em reuniões, reivindicações e melhorias realizadas em nosso favor.

RESUMO

Foram propostos Valores Naturais de Fundo (*Natural Background Levels*, NBLs) para as águas subterrâneas coletadas em poços profundos, surgências e ressurgências da região cárstica de Lagoa Santa, em uma área de 505 km^2. Os metacalcários são de idade do neoproterozóico, de baixo grau metamórfico e pertencentes à Formação Sete Lagoas, constituída de calcários impuros (Membro Pedro Leopoldo) e calcários calcíticos (Membro Lagoa Santa) e pelos metapelitos da Formação Serra de Santa Helena. Feições geomorfológicas típicas mostram um carste evoluído, com grande número de depressões, cavernas, dutos, surgências e ressurgências. O método de cálculo dos NBLs foi a determinação do 90º percentil a partir dos gráficos de distribuição de probabilidade relativos a cada parâmetro. De acordo com o número de amostras com valores acima do limite de quantificação, o estudo foi realizado em duas etapas: na primeira, foram propostos NBLs para íons indicadores de poluição de águas coletadas apenas em poços profundos quanto a $N\text{-}NO_3^-$ (1,0 mg/L), Cl^- (2,4 mg/L), PO_4^{3-} (0,1 mg/L) e SO_4^{2-} (5,3 mg/L); na segunda etapa foram propostos NBLs para águas coletadas de poços e de nascentes apenas para os íons majoritários, respectivamente, Ca^{2+} (96,99 e 91,52 mg/L), Mg^{2+} (4,88 e 2,88 mg/L), Na^+ (6,15 e 3,75 mg/L), K^+ (1,01 e 0,31 mg/L), HCO_3^- (282,52 e 254,55 mg/L), SO_4^{2-} (9,35 e 13,64 mg/L), Cl^- apenas para poço (6,67 mg/L) e Si^{4+} (17.87 e 12.71 mg/L), esta última para distinção das unidades siliclásticas. Quanto aos indicadores de poluição em poços da primeira etapa, os resultados mostraram que, em relação ao nitrato, cloro, fosfato e sulfato, a maioria das áreas que ultrapassaram o NBL estão em porções de vulnerabilidade moderada, indicando impactos antrópicos representados por esgoto doméstico e atividades agrícolas e industriais. E, quanto aos íons majoritários e sílica de poços e nascentes, os resultados mostraram que, para todos os parâmetros, excetuando-se o cloro, as concentrações elevadas, acima do NBL, possuem origem geogênica, influenciadas principalmente pela composição pura calcítica do Membro Lagoa Santa e das intercalações impuras pelíticas do Membro Pedro Leopoldo e da Formação Serra de Santa Helena, enquanto que os altos níveis de Cl^- podem ser devido a esgotos no ribeirão da Mata. Os resultados contribuem para o conhecimento dos níveis hidroquímicos inorgânicos naturais da região e norteia novos estudos em áreas específicas a partir dos parâmetros indicadores de poluição.

Palavras-chave: Níveis Naturais de Fundo, hidroquímica, anomalias geogênicas, aquíferos cársticos, contaminação de águas subterrâneas

ABSTRACT

Natural Background Levels (NBLs) were proposed to the groundwaters sampled from deep tubular wells in the karst region of Lagoa Santa, Minas Gerais, within an area of 505 km². The metalimestones are from the Neoproterozoic age, show a low-grade metamorphism and constitute the Sete Lagoas Formation, which is composed by impure limestones (Pedro Leopoldo Member), calcitic limestones (Lagoa Santa Member) and metapelites from Serra de Santa Helena Formation. Typical geomorphological features illustrate an evolved karst, with an elevated number of depressions, caves, ducts and upwelling zones. The NBLs calculation method was the determination of the 90º percentile from the probability distribution plots, related to each parameter. According to the number of samples with values above the quantification limit, the study was realized in two stages: firstly, NBLs were proposed to ions that are indicative of pollution in the collected waters only from deep tubular wells, for N-NO_3^- (1.0 mg/L), Cl^- (2.4 mg/L), PO_4^{3-} (0.1 mg/L) e SO_4^{2-} (5.3 mg/L); secondly, NBLs were proposed only to major ions, namely, Ca^{2+} (96.99 and 91.52 mg/L), Mg^{2+} (4.88 and 2.88 mg/L), Na^+ (6.15 and 3.75 mg/L), K^+ (1.01 and 0.31 mg/L), HCO_3^- (282.52 and 254.55 mg/L), SO_4^{2-} (9.35 and 13.64 mg/L), Cl^- only for deep tubular wells (6.67 mg/L) and, finally, Si^{4+} (17.87 e 12.71 mg/L), which was used to the distinction of the siliciclastic units. As for the pollution indicators considered in the first stage, results have shown that, for all parameters, the majority of the areas with surpassed NBLs are in moderate vulnerability portions, indicating anthropic impacts represented by domestic sewage and agricultural and industrial activities. And, as for the major ions and silica from deep tubular wells and springs, results have shown that for all parameters, except for chloride, the elevated concentrations above the NBL hold a geogenic origin, influenced mainly by the calcitic pure composition of the Lagoa Santa Member and by the impure pelitic intercalations of Pedro Leopoldo Member and Serra de Santa Helena Formation, whereas the high Cl^- levels might be due to sewage in the Mata river. The results contribute to the understanding of the natural inorganic hydrochemical levels of the region and orientate new studies in specific areas, according to the indicative parameters of pollution.

Keywords: Natural Background Levels, hydrochemistry, geogenic anomalies, karst aquifers, groundwater contamination

Contents

INITIAL CONSIDERATIONS

This dissertation is one of the products derived from the “Project of adequation and implantation of a groundwater monitoring network in areas with karst cavities of the São Francisco river basin, applied to the pilot area of the Lagoa Santa Karst region, which entirely comprehends the Carste Lagoa Santa Protection Unit - CLSPU (Área de Proteção Ambiental - APA Carste Lagoa Santa), Minas Gerais, Brazil”, which in turn composes the “National act plan for the conservation of the speleological patrimony of São Francisco basin karst areas”, under federal responsibility. This project has started in January 2015 and has been developed under a partnership between the Federal University of Minas Gerais (Universidade Federal de Minas Gerais - UFMG) and the Nuclear Technology Development Center (Centro de Desenvolvimento de Tecnologia Nuclear - CDTN) and financed by the National Center of Research and Caves Conservation (Centro Nacional de Pesquisa e Conservação de Cavernas - CECAV). The author’s monthly scholarships were provided by the Coordination for the Improvement of Higher Education Personnel (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES).

The study area has approximately 505 km², from which 377,4 km² (or 74.7 %) area of the APA. It is noteworthy to state the strong dependence on groundwaters resources, as five of the seven municipalities that compose the study area have 100% of their water supply derived from deep tubular wells colleting from the fissured karst aquifer.

The motivation for this study took place in the necessity to understand the regional groundwater hydrochemistry, as it is a basal step for the required future monitoring. Since the study area, as granted by federal legislation, is allowed to undertake anthropic presure, such as limestone mining and steel mill, as well as anthropic occupations, illustrated by the seven municipalities englobed by the APA, an environmental concern regarding the water quality arouse.

In Brazil, the underground water quality reference standards are oriented by the potability thresholds from the Consolidation Ordinance n. 5 of the Health Ministry. This document provides a maximum permitted concentration for a given substance or element, above which the potability is affected. However, since the natural contribution of the aquifer to the concentrations of the considered compounds is not considered in these legislations, there is a gap that can be addressed.

In this regard, the proposal of Natural Background Levels (NBLs) better the comprehension of the origins of a determined substance or element, as it provides an indication of how much of this compound naturally occurs in the hydric bodies, as a result of the complete interaction between the rocks, groundwater, soil, microorganisms and the atmosphere. In case of a determined water sample having parameters with concentrations higher than the proposed NBL, there is an indication of an anomaly, which might be anthropogenic or geogenic. Therefore, the understanding of the regional hydrogeochemistry as well as the urban dynamics of the study area is a must, as it provides the needed means to correctly interpret the laboratory results and consequently indicates the possible origin of the studied substance.

This dissertation is divided into two main chapters composed of scientific articles: the first one, “Natural background levels and validation of the assessment of intrinsic vulnerability to the contamination in the Carste Lagoa Santa Protection Unit, Minas Gerais, Brazil”. The scope of the paper is to propose NBLs for groundwater collected from deep tubular wells for substances that might be indicative of environmental impacts, namely nitrate, chloride, phosphate, and sulfate, as well as to expose areas where those values were surpassed on the reclassified intrinsic vulnerability (COP method) map, in order to understand whether there is a relation between high vulnerabilities and hydrochemical anomalies, finally pointing to anthropogenic inputs. Additionally, it`s noteworthy to state that this article is currently under a revision process, aiming to publication in a scientific journal. In case of acceptance, its content will slightly differ from the herein presented since the reviewers thus the corrections made for this dissertation were not the same than the ones for the journal.

The second chapter, “Natural Background Levels under a hydrogeochemistry analysis in the surroundings of the Lagoa Santa karst region, MG, Brazil”, is currently under the process of its first submission to the Brazilian Journal of Geology. Its goal is to propose NBLs for waters collected from karst deep tubular wells and springs for the parameters calcium, bicarbonate, magnesium, silica, sodium, potassium, sulfate, and chloride, as well as to point the areas where those values were surpassed on the geological map. The regional hydrogeochemistry proved to be the essential means to indicate the origin of those substances, helping differentiate between geogenic and anthropogenic origins.

It is also noteworthy to mention the author’s participation in the XX Congresso Brasileiro de Águas Subterrâneas (XX Brazilian Congress of Underground Waters) in November 2018, Campinas, Brazil, where it was presented and published, in the annals of the Congress, an expanded abstract titled “Metodologia para Determinação dos Níveis Naturais de fundo (NBL) e da Interpolação de Isoconcentrações de Parâmetros Hidroquímicos”, which composes the first solid results of the current research. Finally, the Appendix contains all the laboratory analytical results, including also all the organic parameters that were not discussed due to the fact that all of them showed concentrations below the quantification limit, as well as a photographic catalog which illustrates the sampling process.

Finally, this study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

CHAPTER 1: NATURAL BACKGROUND LEVELS AND VALIDATION OF THE ASSESSMENT OF INTRINSIC VULNERABILITY TO THE CONTAMINATION IN THE CARSTE LAGOA SANTA PROTECTION UNIT, MINAS GERAIS, BRAZIL

Natural background levels and validation of the assessment of intrinsic vulnerability to the contamination in the Carste Lagoa Santa Protection Unit, Minas Gerais, Brazil

Frederico Aragão[1]; Leila Nunes Menegasse Velásquez[1]; Paulo Galvão[1]; Thiaggo de Castro Tayer[1]; Thiago Nogueira Lucon[2]; Úrsula Ruchkys de Azevedo[1]

1. Department of Geology, Federal University of Minas Gerais, Pampulha Campus, Belo Horizonte/MG 31275-035, Brazil
2. Department of Geology, Federal University of Ouro Preto, Morro do Cruzeiro Campus, Ouro Preto/MG 35400-000, Brazil

Corresponding author:
Frederico Aragão Cardoso
Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil
Contact: +5531992317872
Email: aragao.ambiental@gmail.com
ORCID: 0000-0002-7304-9679

Acknowledgements

Special thanks go to the Foundation for Supporting Research of Minas Gerais (FAPEMIG - project APQ-02049-14); to the Geology Postgraduate Program of the Geosciences Institute of the Federal University of Minas Gerais, Brazil; to Chico Mendes Institute for Biodiversity Conservation/Brazilian National Center for Research and Conservation of Caves (ICMBIO/CECAV), and, finally, to the Coordination of Superior Level Staff Improvement (CAPES).

Abstract

The contamination of karst aquifers by anthropogenic activities poses a major issue regarding environmental policies, since they present higher sensitivity influenced by unique features such as dolines, swallow holes, and conduits. This paper focused on the Carste Lagoa Santa Protection Unit (Área de Proteção Ambiental – APA Carste Lagoa Santa), MG, Brazil, with three main goals: to determine the Natural Background Levels of chloride, nitrate, sulfate, and phosphate of waters collected from deep tubular wells; to expose the locations where the concentrations of those parameters exceed the Natural Background Levels in the existing vulnerability map and, finally, to assess the percentage of those areas, according to each of the vulnerability classes (high, moderate, low). Results have shown values (90th percentile) of 2.4 mg/L, 1.0 mg/L, 5.3 mg/L and 0.1 mg/L, for Cl^-, NO_3^-, SO_4^{-2} and PO_4^{-3}, respectively, pointing that for all four parameters there were areas (mainly distributed within moderate vulnerability portions) where the values were surpassed, suggesting anthropogenic contribution due to the presence of urban settlements and agricultural activities. The proposal of Natural Background Levels was therefore essential to further understand the hydrochemistry of the study region.

Keywords: *Natural Background Level; Carste Lagoa Santa Protection Unit; Intrinsic Vulnerability; Karst aquifer; Groundwater contamination.*

1. INTRODUCTION

Aquifer contamination by anthropogenic activities constitutes a major issue regarding environmental policies. Groundwater quality, which is oriented by reference values such as *Drinking Water Standards* or *Environmental Quality Standards*, and usually regulated by Water Authorities, requires a representative surveillance monitoring to assess its chemical status and to comprehend the evolution of its quality, especially in areas where human pressures are present.

Karst aquifers, which are hydrogeological formations composed by calcitic lithologies and capable of storing and transmit water, are important sources of global water supply, accounting for approximately 25% of total global share (Ford and Williams 2007). As this typology is more sensitive to contamination if compared to porous/fractured aquifers due to its varied number of recharge points and to its capability of transmit water with elevated fluxes, it then gains a delicate position in terms of management and strategic use of water resources (Goldscheider and Drew 2007). The storage capacity, which is defined by the maximum volume of water that can be stored in an aquifer (Lóaiciga 2008), is generally low whereas water flow is usually high, in a range from 1 to 10 m/s (Kaufmann et al 2010), in karst aquifer. These two factors combined contribute to a lower effect of interference of natural processes, such as absorption, degradation, and filtration, thus developing a higher risk of contamination propagation (Mudarra and Andreo 2011; Entezari et al. 2016). Additionally, the intrinsic vulnerability, which is the observed, inferred, or suspected degree to which characteristics of the studied area make it vulnerable or resilient to natural or anthropogenic stresses or catastrophes, is mainly justified by the presence of heterogeneity, anisotropy, and conduits where ramified flows are developed, as well as the presence of autogenic (from the karst area itself) and allogenic (from adjacent non-karstic areas) recharge areas (Goldscheider and Drew 2007).

As exposed by Auge (2004) and Tayer and Velásques (2017), most of the intrinsic vulnerability concepts are linked with the capacity of the soil, subsoil, and aquifer on being able to naturally protect groundwater. In this context, current methods based on parametric models through matrix, index or ranking systems were developed to assess intrinsic vulnerabilities. The most applied methods for assessing the intrinsic vulnerability of karst aquifers have shown good results with a low level of subjectivity, as EPIK, which stands for Epikarst, Protective cover, Infiltration conditions and Karst network development (Doerfliger 1996, Doerfliger and Zwahlen 1998, Doerfliger et al. 1999); COP (Concentration of Flow as the *C* factor, Overlying Geological Layers as the *O* factor and Precipitation as the *P* factor) (Vías et. al 2002, 2006 and Zwahlen 2003), and PI (*P* indicating the Protective Cover and *I* the Infiltration conditions) (Goldscheider et al. 2000, Goldscheider 2002).

Another method that can be used in karst areas is the Natural Background Level (NBL). In 2006, following a lack of a consolidated method, the European Union’s Background Criteria for the Identification of Groundwater Thresholds (BRIDGE) was proposed, which turned official the concept of NBL for hydrochemical parameters (BRIDGE 2006, 2009). NBL thus corresponds to the range of concentrations of an element or a substance derived from the interaction between groundwater, surface water, lithologic, biologic and atmospheric components, with no or very small anthropic influence. The eventual interconnection between aquifers, rain and small anthropogenic impacts can influence those values, which might face considerable spatial variations (ISPRA 2009).

In Brazil, karst limestone formations compose between 5% and 7% of total area (425,000 – 600,000 km^2), with the central portion of the country representing the most extensive karstified region (Karmann 1994, Auler et al. 2001). These areas are generally developed on Proterozoic and Lower Cambrian dolostones and limestones (Auler and Farrant 1996), belonging to the Bambuí and Una groups, where states of Bahia and Minas Gerais are located. In this sense, several cities are almost exclusively dependent on groundwater originating from local karst aquifers, such as Montes Claros, Sete Lagoas and Jaíba, in Minas Gerais, and Lapão, Irecê and Desidério, in Bahia. Besides that, ecological and archeological sites and important karst landscapes are common, and therefore should be protected.

To minimize anthropogenic pressures in fragile areas (e.g. karst landscapes), Environmental Protection Units are noteworthy resources of sustainable development. These units are composed by public and private lands, aimed to protect and to preserve both the environment and their natural systems to guarantee life quality and regional ecosystem safety (BRASIL 2012). The Carste Lagoa Santa Protection Unit (CLSPU), situated in the state of Minas Gerais, was implemented in 1990 and it is characterized by a unique karst geomorphology, with poljes, shafts, dolines, caves, ponors, swallow holes and springs. It is in a region where a substantial urban development takes place, especially in southwest and west borders, stimulated by the metropolitan region of Belo Horizonte (Northern vector), the state capital. Despite this urban pressure, up to date, however, there are no studies on NBL determination specifically.

In the CLSPU, the presence of urban settlements, industries and agricultural activities near high intrinsic vulnerability areas poses a constant risk to the quality of groundwater and surface water, as a diverse quantity of effluents and waste is produced and might not receive the adequate environmental treatment (Tayer 2016). However, the distinction between anthropogenic and geogenic origins of a parameter can only be done through the definition of NBL values (Reinmann et al. 2005, Edmunds & Shand 2008, Hinsby et al. 2008).

The main goal of this paper is, firstly, to determine the NBLs of parameters that may also be indicators of human activities, namely nitrate (NO_3^-), chloride (Cl^-), phosphate (PO_4^{3-}) and sulfate (SO_4^{2-}), through the calculation of the 90th percentile of their probability distributions; secondly, to expose where the concentrations (interpolated by geostatistical analyses) of these parameters exceed the NBLs plotted in the reclassified map based on the intrinsic vulnerability map developed by Tayer (2016) and, finally, to calculate the percentage of those areas, according to each of the vulnerability classes, through geoprocessing routines.

2. SITE DESCRIPTION

The Carste Lagoa Santa Protection Unit (CLSPU) (Fig. 1) is located in the state of Minas Gerais, southeast of Brazil. It covers seven municipalities, within an area of approximately 400 km². It is considered part of the upper São Francisco river basin and the Velhas river subbasin, with an altitude range that varies between 620 and 910 m above sea level (IBAMA 1998, Tayer and Velásques 2017).

The most common impacting activities in the region include limestone mining, steel industry, cemeteries, fuel stations, intensive agriculture, urban sites within poor sanitation structures and the Tancredo Neves International Airport, with an annual capacity of 22 million passengers (IBAMA 1998, Tayer 2016 and BH Airport 2019). The land use map (Correa 2018) indicates considerable areas where, notably, agricultural activities and urban uses settlements are frequent (Fig. 1).

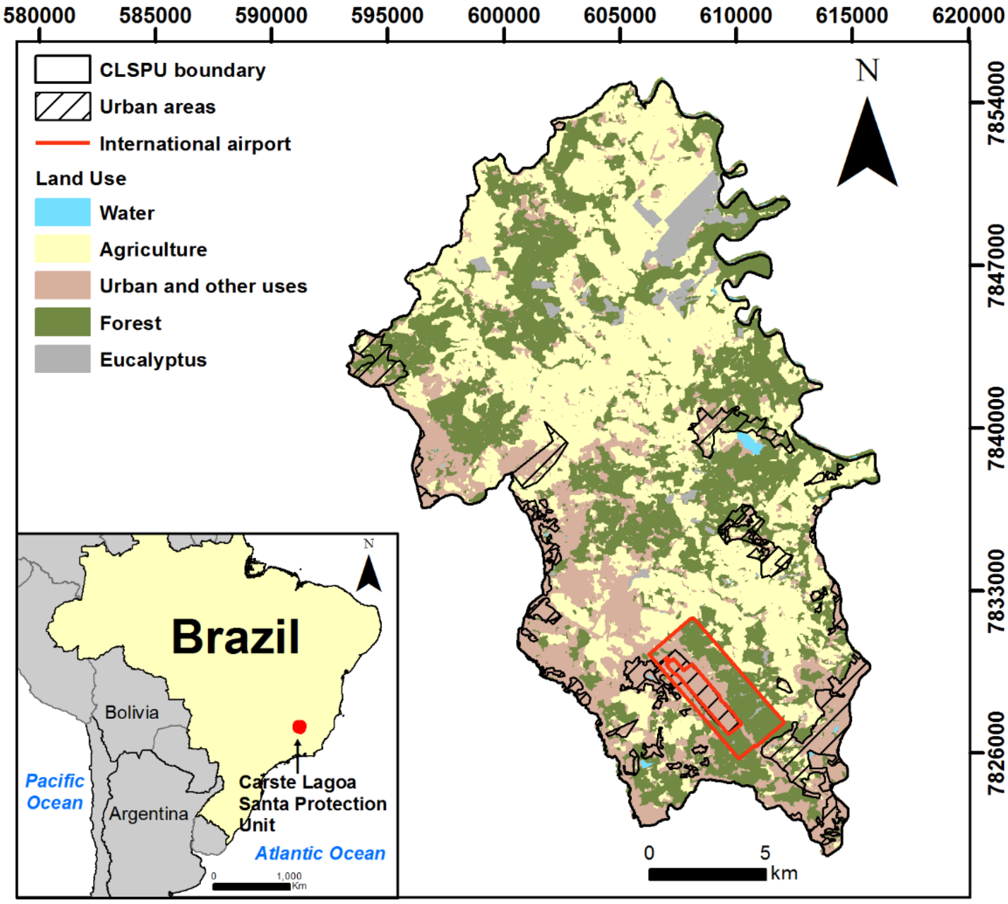

Figure 1 – Location and land use information of the study area (Correa 2018)

Geologically, the area is in the São Francisco Craton, where Neoproterozoic carbonate argillo-arenaceous rocks (Sete Lagoas and Serra de Santa Helena formations) are emplaced as the Bambuí Group. The Archaean basement (Belo Horizonte Complex) is composed of gneiss, migmatites and granitoids (Fig. 2) (Ribeiro et al. 2003, Tuller et al. 2010, Galvão et al. 2016).

The Sete Lagoas Formation is divided in two members (Ribeiro et al.2003): Pedro Leopoldo, at the base, represented by fine limestones, dolomites, marlstones and pelites, with a composition of calcium carbonate between 60% and 90%; and Lagoa Santa Member, on the top, composed of purer medium-grained black limestones (calcium carbonate content > 90%) and with a high degree of karstification (Piló 1998 and Galvão et al. 2016) (Fig. 2a).

The Serra de Santa Helena Formation overlays the Sete Lagoas Formation and it is constituted by slate, marble, siltstone and argillite (Tuller et al. 2010, Pessoa 2005, Galvão et al. 2016). Cenozoic unconsolidated sediments, which covers the Bambuí Group where drainages, meanders of watercourses and low topographic levels are located, are divided in detritus coverage, alluvial terraces and alluvium (Ribeiro et al. 2003, Tuller et al. 2010) (Fig. 2a).

The two main soil typologies present in the CLSPU are Red Latosol and Haplic Cambisol, covering about 45% and 39% of the total area, respectively. Argisol and Gleysol represent a minor extent, with 11% and 6%, respectively (EMBRAPA 2013 and Tayer 2016) (Fig. 2b).

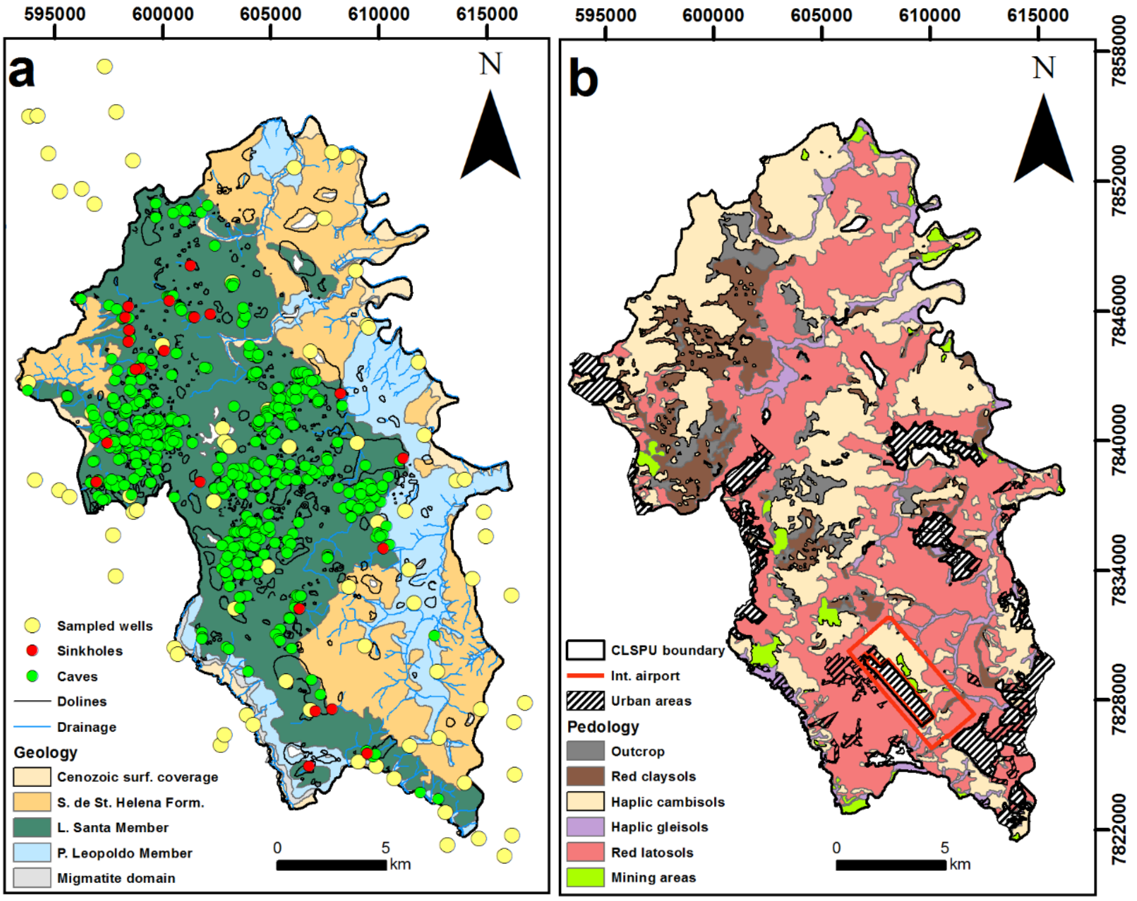

*Figure 2 – **a** Geological map, karst features; **b** Pedological map of the study area (Tayer 2016, CECAV 2014, EMBRAPA 2013 and Ribeiro 2003) and location of sampled deep tubular wells*

Kämpf et al. (2008) proposed a soil classification regarding its resistance to environmental impacts based on the disposal of waste. The following factors were considered on the evaluation: depth, texture, mineralogy, textural gradient, natural drainage, water table, surface water table, flood risk, susceptibility to erosion, local topography and slope. The presence of clay is important to sorption, retention and tamponing of contaminants, with the following classification being used: clayish (clay content higher than 35%), medium (content between 15% and 35%) and sandy (content lower than 15%). Regarding the mineralogy, the presence of kaolinitic clay and iron oxides or expansive clay are also important as they influence the cation-exchange capacity (CEC), which is a notable condition for contamination control. Kämpf et al. (2008) divide soils in four classes (ranging from A to D), with A being the most resistant soil and D being the least. As for the purpose of this study, it is noteworthy that Latosols belong generally to class A, and Cambisols to class B. The amount of organic matter and oxides are also important in the area, as they represent the possibility of, respectively, pesticides complexation and the reaction with some contaminants that pose threat to human health (Ker 1995).

Hydrogeologically, unconfined and semi-confined karst aquifers are predominant, developed upon rocks from the Bambuí Group (Tayer and Velásquez 2017). The Lagoa Santa Member comprehends the carbonate-karst aquifer system, while the Pedro Leopoldo Member forms karst-fractured aquifers, due to the presence of fractures/faults as secondary permeability (Mourão et al. 2001). The Serra de Santa Helena Formation presents a lesser aquifer potentiality because of metapelite influences, working as a local aquiclude. The basement (i.e. Belo Horizonte Complex) acts as a fissured aquifer, in which the groundwater is stored in fractures and faults. The groundwater presented within the Sete Lagoas Karst Aquifer (SLKA) is mostly classified as calcium-bicarbonate type, with a pH between 6.5 and 7.5. Karst conduits in this system store water generally of good quality for human consumption, despite the relatively high hardness (Pessoa 2005, Tayer and Velásques 2017).

The geomorphology is composed by exokarstic shapes, represented by poljes, shafts, dolines, caves, ponors, and springs, with the endokarstic represented mostly by grottos (Ribeiro et al. 2003). The three Great Geomorphological Units that cover the recharge areas are the South American Surface, the Karst covered by sparse paleokarstic features and the Karstic terrain holding a both surface and ground hydric system. On the other hand, the Great Geomorphological Unit, which corresponds to discharge areas, are regions with a higher degree of dissection, below the altitude of 700 m, counting with residual karstic features and expressive uvala systems and a relatively flat terrain.

Finally, the area has two types of recharge: 1) autogenic, when the karst recharges itself from rainwater falling on the aquifer. This direct recharge promoted by the strong interaction between surface water and groundwater eases the pollutant transport due to the rapid water flow within karst conduit without time for absorption, degradation, or filtration. This type of recharge is common where the Sete Lagoas Formation outcrops. 2) allogenic, when adjacent non-karst areas recharge the karst aquifer. These areas have diffuse recharge which is developed through thick lateritic soils, which, in turn, stimulates the pollutants attenuation. These areas are mostly found where Cenozoic unconsolidated sediments and Serra de Santa Helena's rock are located.

3. MATERIALS AND METHODS

3.1 Groundwater sampling for NBL determinations

Between September 2017 and April 2018, groundwater samples were collected in 89 tubular deep tubular wells distributed throughout the study area (Fig. 2). The samples selected belonged only to deep tubular wells extracting water from the SLKA and from the Serra de Santa Helena Formation, comprising about 99% of the area (Ribeiro et al. 2016) due to the need to exclude any granitic lithology influence over water quality.

Deep tubular wells that were not previously pumped had to be purged for a minimum period of 10 minutes before sampling to restore original hydrochemical conditions, avoiding stagnant water inside deep tubular wells. Previously to each sampling, plastic bottles where the collected water was stored were rinsed three times with the sample to equilibrate sampling equipment with the sample environment, as well as to remove possible residues, following standards from USGS (2006). To assure a minimum interference on water quality, samples were collected following a priority order: if present, water should have been directly sampled from the faucet; in case of the absence of it, the sampling should be done through disconnecting the pipe; and, lastly, in case of those two options being not feasible, water was collected right before flowing into the tank.

Samples were stored in a cooler during fieldwork and sent at the same day to the laboratory located in Vespasiano/MG, Brazil, where they were kept at a temperature of 4°C for a maximum of 24 h before the analyses, according to the Sampling and Water Preservation Guide (CETESB 2011). The ionic balance was calculated following the methodology presented in Feitosa et al. (2008), in which the concentrations are converted from mg/L to meq/L (milliequivalent per liter), then the following calculation is to be performed:

$$Ionic\ balance\ error = \{\frac{(\sum cations - \sum cations)}{(\sum cations + \sum anions\ )}\} \text{ x } 100$$

Samples with an error < 13% can be deemed as correct (Feitosa et al. 2008). Only two of them presented such value and therefore were excluded from the analysis. It was also initially considered the sampling of 20 springs, comprehending the same organic and inorganic analyses held for the groundwater samples. These analyses were excluded from the work as none of them indicated traces of contamination, with most of the values being sufficiently low or below the quantification limit.

3.2 Natural Background Levels determination

Due to the dataset size and the current level of the geochemical knowledge, the Preselection Method for the determination of NBLs was chosen as suggested by ISPRA (2009). This method comprises a procedure of excluding samples that might contain any possibility of contamination and ionic balance error of < 13% (Feitosa et al. 2008), as the goal is to determine the natural influence of the aquifer on the concentrations. Additionally, outlier values and samples collected from deep tubular wells located on the Belo Horizonte complex were also excluded, as to provide a more substantial comprehension over the karst aquifers influence on the water quality.

The definition of NBL comprehends the accumulated frequency of the concentrations of the collected samples (ISPRA 2009, APAT-ISS 2006). BRIDGE (2006) proposes three approaches intended to the derivation of NBL, each of them based on the level of geochemical knowledge (low, medium and high) of the groundwater body, with this study fitting the medium one. The Preselection Method, which is based on a medium level of geochemical knowledge and a limited amount of available data, was the chosen one for this study (approximately 0.22 deep tubular wells *per* km²).

Nitrate (NO^{3-})' chloride (Cl^{-}), phosphate (PO_4^{3-}), and sulphate ($SO4^{2-}$) were the main parameters used for this study since they are good indicators of environmental pollution and contamination (Mullaney et al. 2009; Muller 2006; Nolan et al. 1998; Zhang 2018; Toran 1987; USGS 2016; Domagalski and Henry 2012). After performing the Preselection Method, each of those parameters held a different number of usable samples. The most common contamination sources of the four parameters considered and the number of usable samples are exposed on Table 1.

Table 1 – Number of usable samples for each parameter considered in the NBL assessment and their respective generic sources of contamination (Toran 1987; Nolan et al. 1998; Muller 2006; Mullaney et al. 2009; Domagalski and Henry 2012; USGS 2016; Zhang 2018)

Parameter	NO_3^-	Cl^-	SO_4^{2-}	PO_4^{3-}
Number of samples	50	19	35	37
Possible sources	Pesticides, fertilizers, septic systems, airborne nitrogen compounds	Sewage, fertilizer and water softener	Domestic or industrial waste and sulfide oxidation from mining	Chemical fertilizers, manure and composted material

Since the determination of the Natural Background Levels depends on the 90th percentile of probability distribution plots, it is necessary to assess the best statistical distribution for each parameter. As to accomplish that, the "Individual Distribution Identification" tool on Minitab® 17.1.0 was used. It compares sixteen distributions through the Anderson-Darling statistic (AD) and the P-value, in which the combination of the lowest AD and the highest P (at least above 5%) indicates the best fit.

3.3 Isopleth interpolation

Isopleth maps for each parameter were created. Although water samples from the fractured basement aquifer were not taken into account in the NBL calculation, they were considered for the interpolation in order to understand the influence of the granitic lithology on water quality. Additionally, the outliers (determined using the software RStudio, version 1.1.453) were also included in the interpolation due to their significant influence on water quality as they are not computational errors and represent a solid contribution to the understanding of the overall hydrogeochemistry of the region.

For this routine, the Radial Basis method (Completely Regularized Spline function) was used as the interpolation tool, as it is exact, flexible and produces "the best overall interpretations of most data sets" when compared to other interpolation techniques, such as Kriging, Inverse Distance to Power and Natural Neighbor (Golden Software 2017, Gunarathna et al. 2016). A reclassification of the interpolated values was performed, as to simply divide the map in two regions: those with values greater than the NBL and those below it.

3.4 Intrinsic vulnerability reclassification

The intrinsic vulnerability map developed by Tayer (2016) was reclassified and adapted for the needs of the study. The COP method assesses three factors: flow (C), which represents the degree in which the precipitation aims on recharge areas with consequent bypassing of contaminants throughout protective layers; overlying layers (O), which stands for natural protection as the capacity of the unsaturated zone to filter or reduce contamination, minimize the effects of contaminants; and precipitation (P), calculated by the sum of parameters related to the quantity and intensity of rainfall.

The score ranges used in the original map are presented on Table 2. Those values were reclassified also on ArcMap®, through Spatial Analyst tool "Reclassify", with the main purpose of reducing and simplifying the number of classes. The occupied areas by each of these classes was also determined, through the tools "Zonal Geometry as Table" and "Calculate Geometry", shown on Table 2.

Table 2 – Vulnerability classes presented in Tayer (2016) and reclassified values

Tayer (2016) vulnerability classes		Reclassified values for NBL assessment			
Values	Classes	Values	Classes	Area (km²)	Percentage
0 - 0.5	Very High	0 - 2.0	High	122.95	30.2%
0.5 - 1.0	High	2.0 - 4.0	Moderate	237.84	58.9%
1.0 - 2.0	Moderate	4.0 - 6.0	Low	44.65	10.9%
2.0 - 4.0	Low				
4.0 - 15.0	Very Low				

3.5 Determination of areas with high NBL concentrations

Following the reclassification of the intrinsic vulnerability map, the next step was to determine, for each parameter, regions where their values were higher than the Natural Background Levels. Those can be considered sensitive areas as they can work as indicators of possible anthropic contamination. To accomplish this goal, a series of steps on ArcMap® had to be taken. Isopleth interpolations (Radial Basis method) were made, performed with the values distributed throughout the study area. Afterwards, some geoprocessing procedures, such as Conversion Tools and Extract by Mask, present on Arc Toolbox were used, needed to be done in order to produce the final maps. The coordinate system used was Universal Transverse Mercator (UTM) projection, Zona 23, datum WGS 84, with units in meters.

4. RESULTS

The reclassified version of the intrinsic vulnerability map is present on Fig. 3. The original map held 5 classes of vulnerability, ranging from “very high” (with a limit from 0 – 0.5), to “very low”, (from 4 – 15), whereas the new one is presented with 3 classes, namely “high”, “moderate” and “low”, with scores of 0, 2 and 4, respectively, as to simplify the correlation analysis with the NBLs.

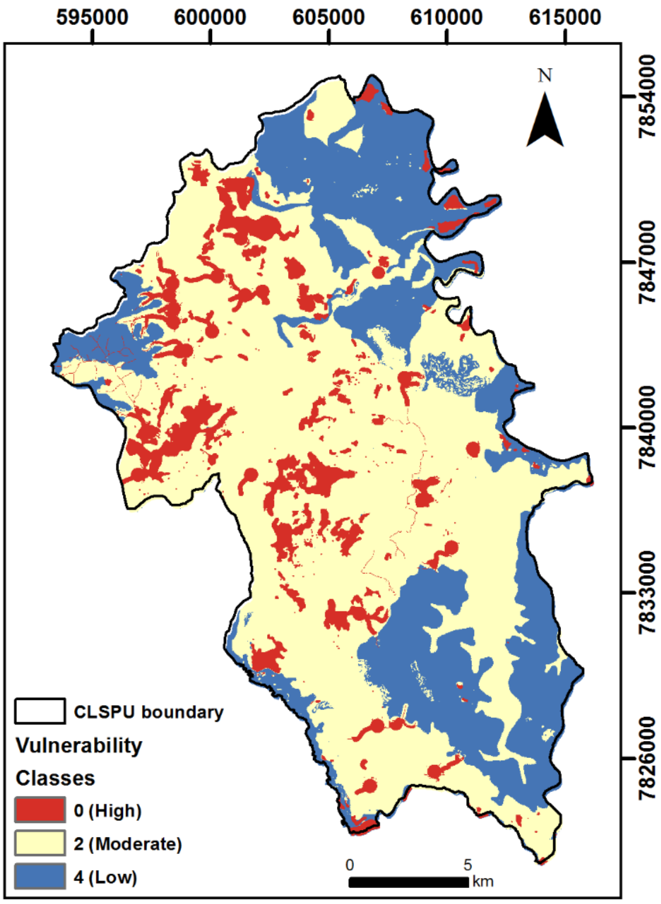

Figure 3 - Reclassified Intrinsic Vulnerability Map (COP Method) of the Carste Lagoa Santa. Adapted from Tayer (2017)

There is a clear predominance of moderate vulnerability. The second most prominent class is "low", identified mostly in the southeast and northeast limits, followed by high vulnerability, distributed within sparse patterns throughout the study area, but with a high feature concentration in the center and southwest. An expressive number of portions showing moderate and high vulnerabilities is coincident with the categories "urban and other uses" in southwest and southeast, and "agriculture", in the mid-north and northwest of the land use map as exposed on Fig. 1.

Chloride, illustrated on Fig. 4a and b, presents areas with concentrations above the NBL in the south, west-center and west. Moderate vulnerabilities represent 66.9% of the study area while 13.8% and 19.4% are covered by high and low vulnerabilities, respectively. According to the probability graph (Fig. 5c), the Natural Background Level is 2.4 mg/L (obtained in the 90th percent) with a maximum value (obtained in the 100th percent) of 4.7 mg/L, and the statistical distribution is the 2-Parameter Exponential.

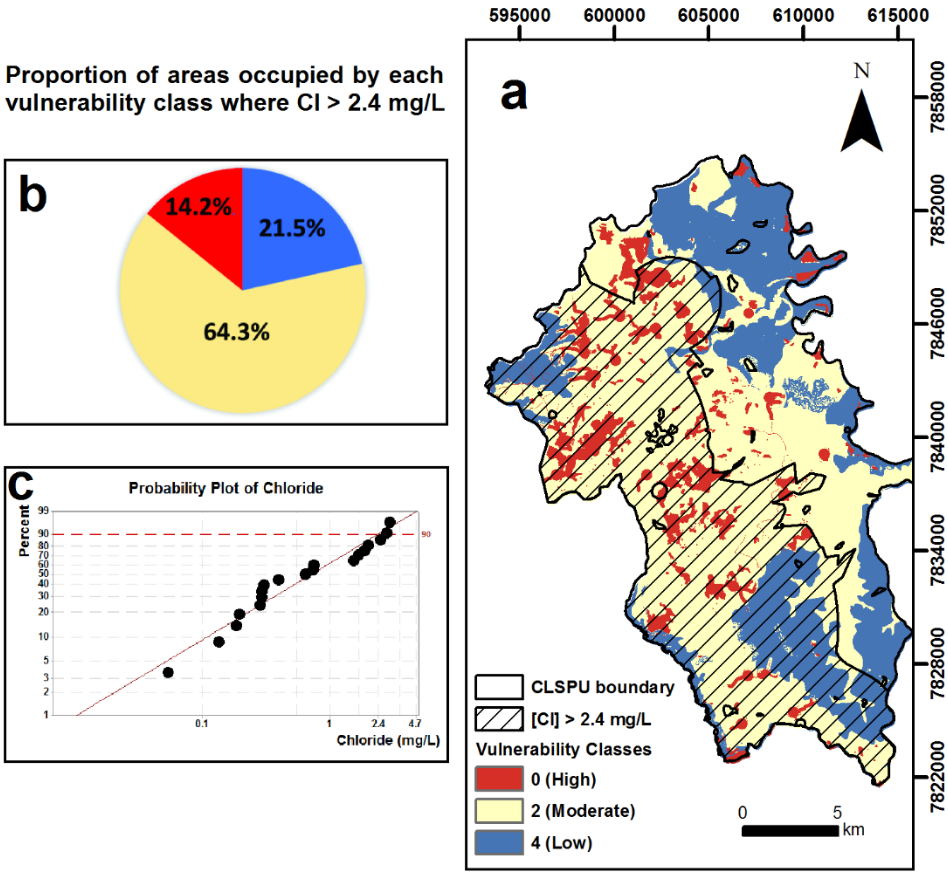

*Figure 4 – **a** Areas where concentrations surpass the Natural Background Levels for chloride; **b** Proportion of surpassed areas; c Probability plot of chloride*

As for nitrate, there are two areas (north and southeast) where the NBL is surpassed (Fig. 5a). The Fig. 5b shows that 49.9% and 46.8% of total nitrate coverage area is related to moderate and low vulnerabilities, respectively, whereas 3.3% is represented by high vulnerability. The Natural Background Level, obtained by the 90 percent of the probability plot (Fig. 5c) is 1.0 mg/L, with a maximum value of 3.0 mg/L, with the Exponential Distribution as the best fit.

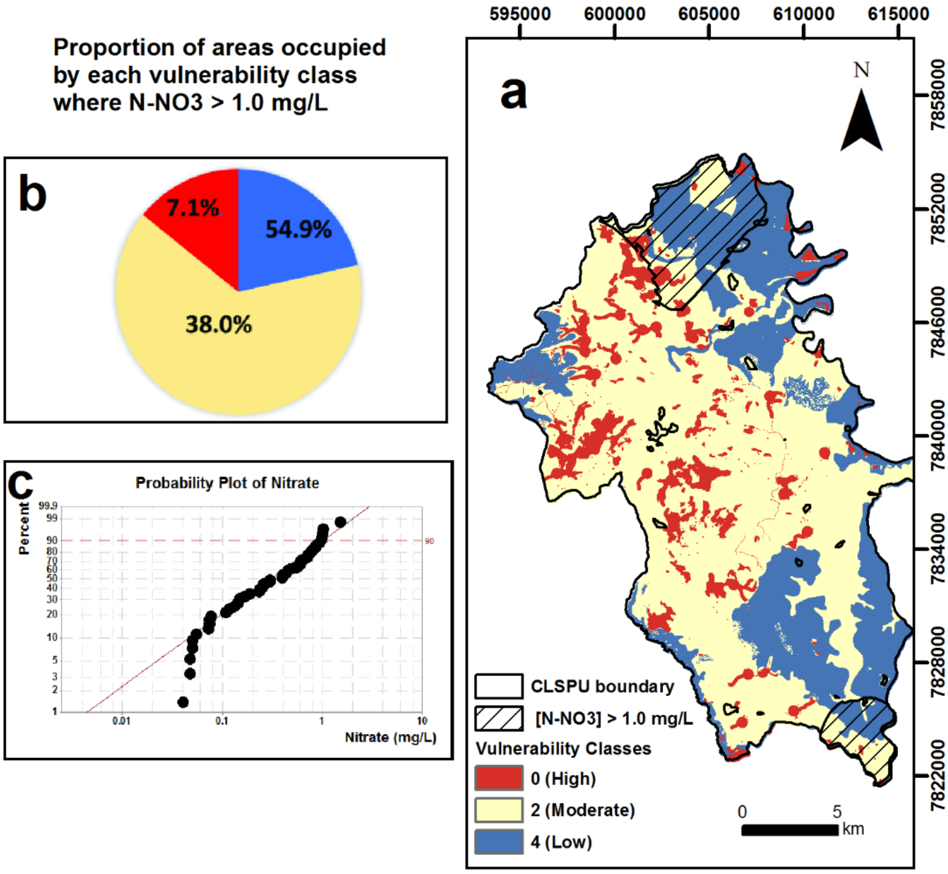

*Figure 5 – **a** Areas where concentrations surpass the Natural Background Levels for nitrate; **b** Proportion of surpassed areas; c Probability plot of nitrate*

Sulfate, shown on Fig. 6a and b, presents one area, in the west center, where the concentrations exceeds the NBL. 73.2% of the surface are in moderate vulnerabilities, 23.7% in high vulnerabilities and 3.0% cover low vulnerabilities. The NBL is, according to the probability graph (Fig. 6c), 5.3 mg/L, with a maximum value of 9.3 mg/L, and the statistical distribution is the Lognormal.

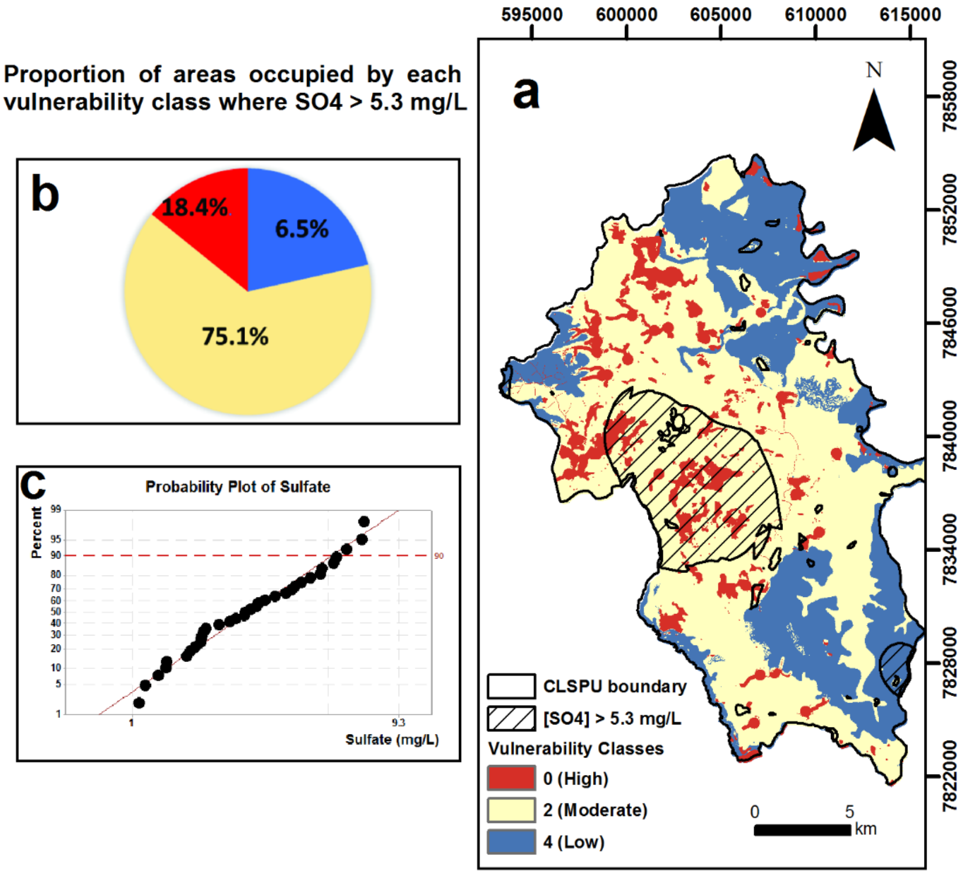

*Figure 6 – **a** Areas where concentrations surpass the Natural Background Levels for sulfate; **b** Proportion of surpassed areas; c Probability plot of sulfate*

Concerning phosphate (Fig. 7a), there are four areas where the NBLs are surpassed. The largest one covers the westernmost portion of the region, extending to the north central and to the east. There is also a part in the southeast and two minor ones surfacing the southernmost field. According to Fig. 7b, 81.4% of the total exceeded area represents moderate vulnerability, whereas 14.5% and 4.1% shows high and low vulnerabilities, respectively. The NBL obtained from the probability plot on Fig. 7c is 0.1 mg/L, with a maximum value of 0.2 mg/L, with 2-Parameter Exponential Distribution as the best fit.

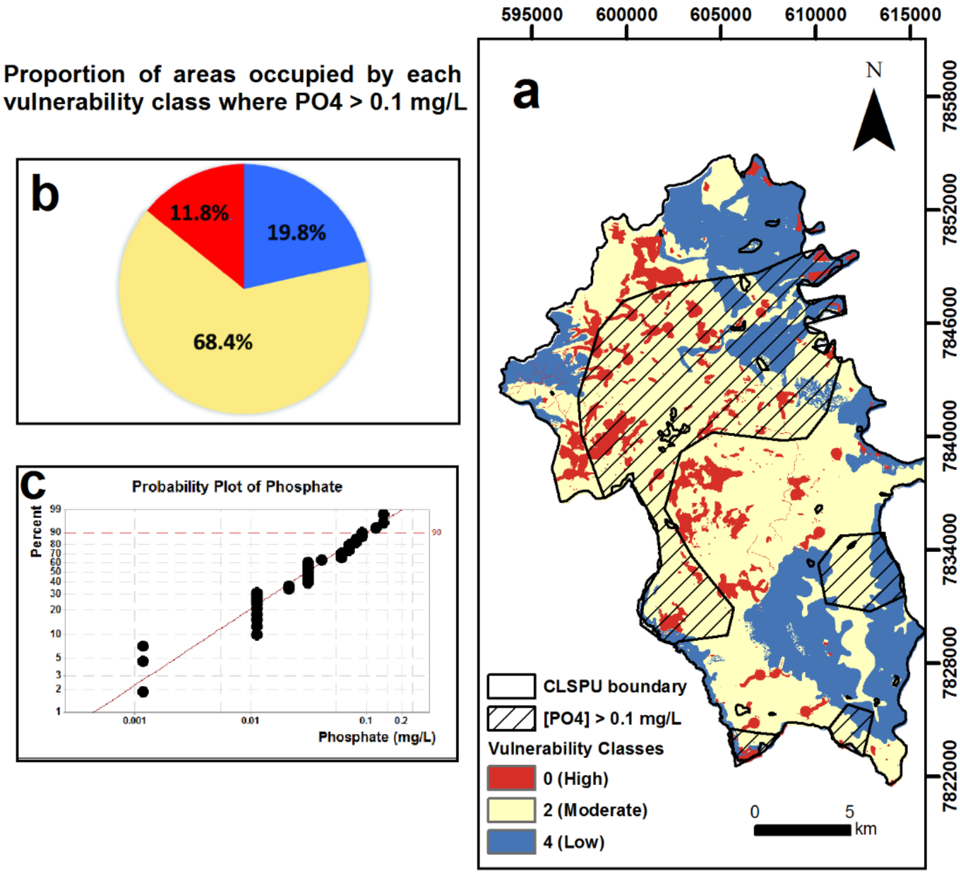

*Figure 7 – **a** Areas where concentrations surpass the Natural Background Levels for phosphate; **b** Proportion of surpassed areas; c Probability plot of phosphate*

Table 3 summarizes, for all parameters, the values of the areas where the NBLs are surpassed and their respective percentage proportions. In terms of total area, chloride covers 33.8 km^2 of the study area, representing the highest coverage among the elements classified as highly vulnerable. In terms of percentage proportion, sulphate presents the greater percentage in comparison with the other elements, with 18.4% representing areas with high vulnerability. Despite that, among the four parameters, moderate vulnerability is the class with the largest representativity, both in terms of total area and of percentage, with nitrate being the only parameter with low vulnerability as the most notable class.

Table 3 – Total surface covered by areas where NBL values are surpassed for chloride, nitrate, phosphate, and sulfate, and their respective percentages

Vulnerability	Chloride		Nitrate		Phosphate		Sulfate	
Class	km²	%	km²	%	km²	%	km²	%
Low	51.2	21.5%	24.7	54.9%	31.3	19.8%	4.1	6.5%
Moderate	153.4	64.3%	17.1	38.0%	108.2	68.4%	47.6	75.1%
High	33.8	14.2%	3.2	7.1%	18.6	11.8%	11.6	18.4%
Total	238.4	100.0%	45.1	100.0%	158.1	100.0%	63.3	100.0%

Table 4 summarizes the results for the analyzed parameters. The NBLs, the Brazilian drinking standards (BRASIL 2017), the descriptive statistics, and the ionic balance errors are represented. As the number of samples is too large to be on a table (especially for nitrate, with 50 deep tubular wells), only the minimum, maximum and average are illustrated for the concentrations and for the ionic balance errors (it is noteworthy to state herein that the Appendix contain all the analyses performed for consultation). None of the parameters had any samples with concentrations above the Brazilian standards. Besides that, the NBLs as well as the maximum values from the probability distributions are quite below those thresholds.

Table 4 – NBLs, descriptive statistics, ionic balance error and Drinking Water Standards (Feitosa et al 2008 and BRASIL 2017)

	NBL (mg/L)	Brazilian drinking water standard (mg/L)	Min. conc. (mg/L)	Max. conc. (mg/L)	Max. value of the prob. distribution (mg/L)	Mean	Median	Std. Dev.	Ionic Balance Error Average (%)	Ionic Balance Error Min. (%)	Ionic Balance Error Max. (%)
Cl	2.4	250	1.2	4.1	4.8	2.2	1.8	1.0	4.6	0.3	12.2
N-NO_3^-	1	10	0.0	1.5	3.0	0.4	0.4	0.4	5.5	0.0	12.2
SO_4^{2-}	5.3	250	1.1	7.0	0.2	3.1	2.6	1.7	4.6	0.0	11.9
PO_4^{3-}	0.1	-*	0.0	0.7	9.3	0.1	0.1	0.0	4.9	0.0	11.6

*-: Threshold not defined in BRASIL (2017)

5. DISCUSSION

As exposed on Fig. 4, chloride is largely distributed where the NBL of 2.4 mg/L is exceeded, covering areas with high vulnerability, as there is a considerable urban use, mainly in the western side of the study area, and agriculture, in the central portion. High concentrations of chloride can be considered a sign of contamination by sewage, fertilizer and water softeners (Mullaney et al. 2009), thus indicating negative anthropic interventions. Lucon et al. (2018) determined NBL for chloride of 0.3 mg/L and 0.63 mg/L for dry and rainy seasons, respectively, in a same hydrogeological context at the São Miguel watershed, distant about 180 km southeast of the study area, pointing anomalies directly related to agricultural activities, hence corroborating this study.

Nitrate surpasses the NBL of 1.0 mg/L in two main regions inside the study area: one in the northeast, occupied mainly by agricultural uses, and another in the southeast, which shows considerable urban settlements. High levels of NO_3^- in groundwater surely indicate anthropic pressure, as suggested by Muller (2006), including agricultural activities (Zhang 2018), fecal contamination by septic systems, lawn fertilizers, and airborne nitrogen compounds produced by automobiles and industries (Nolan et al. 1998). Thus, human impacts in those areas are fairly possible, though there were not sufficient levels to affect the potability.

The geological map in Fig. 2a shows that the two areas with higher nitrate NBLs (Fig. 5) also cover parts where Serra de Santa Helena Formation is located. This one, when compared with the Sete Lagoas Formation, presents fractures zones filled with clayish material (Pessoa 2005), therefore it poses a higher resistance due to possible retention of the contaminants through adsorption on the particles, thus corroborating with the determined low vulnerability. The area in the southeast is densely occupied by urban settlements, so high levels of nitrate on groundwater are possible regardless of the lithology. On the other hand, the area in the northeast is not quite occupied, but as exposed by Vieira et al. (2018, in press), the deep tubular wells located there actually pump water from Pedro Leopoldo Member, even though the outcropped geology shown in Fig. 2a is pelitic. Therefore, the groundwater might have come from a location where there was contamination, flowing through upstream karstic conduits. Besides that, the direction of the water flow in the study area goes from west to east and one of the deep tubular wells (located in the northernmost part) is quite close to the Velhas river, hence there might be a flow reversion which can also derive the contaminant into this well. Additionally, Calijuri et al. (2012) carried out a study in the vicinity of the International Airport present in the CLSPU, pointing to contamination due to domestic sewage from inadequate usage of septic tanks near the collected wells, as well as to the contribution of chemical fertilizers, thus corroborating this study.

Additionally, there are high vulnerability areas where the Sete Lagoas Formation is exposed, which, due to its dissolved carbonatic composition, is more sensitive to contamination. Lucon et al. (2018) suggested NBL for nitrate of 9.25 mg/L for the dry season and 13.7 mg/L for the rainy one, pointing agricultural inputs and thus agreeing with the present study (Table 4). Additionally, Tedd et al. (2017) proposed values of 8.73 mg/L and 1.48 mg/L, for confined and unconfined lithologies, respectively, with the latter being close to the value of 1.0 mg/L from this work.

As for sulfate, it exceeds the NBL of 5.3 mg/L in a single area in the west (Fig. 6a). This portion shows a relative abundance of three major land uses: urban, agricultural and forests, over the more karstified Lagoa Santa Member and, as exposed on Figure 6b, there is a relatively abundance of high vulnerability (23.7%). SO_4^{2-} is present in domestic or industrial waste, as shown by USGS (2016), or indicates contamination by the oxidation of sulfide minerals, as a result, for example, of abandoned zinc/lead mine tailing impoundments (Romero et al 2006), corroborating with the high determined NBLs and therefore indicating possible negative anthropic impacts. Nevertheless, the highest value extracted from the plot on Fig. 6b is 9.3 mg/L, which stands quite below the federal drinking threshold of 250 mg/L, indicating that despite the higher levels of NBL, it is not enough to alter the potability of the water. Lucon et al. (2018) determined a 90th percentile NBL of 17.5 mg/L for dry and of 24.1 mg/L for rainy seasons, respectively, pointing to a geological origin of pyrite and galena intercalated with carbonates.

Phosphate, similarly to chloride, covers a large area throughout the CLSPU, mostly with moderate vulnerability (81.4%), followed by high (14.5%) and low (4.1%) (Fig. 7a, b), where the NBL of 0.1 mg/L is exceeded. The maximum value determined by the probability distribution is 0.2 mg/L (Fig. 7c), and neither the Brazilian federal potability legislation nor state ones, such as CETESB’s, from São Paulo, or COPAM’s, from Minas Gerais, define a potability threshold for phosphate. Additionally, similarly to the other parameters, phosphate’s area is distributed mostly over the Lagoa Santa Member. This parameter can be added to the soil by the usage of chemical fertilizers, manure and composted materials (Domagalski and Henry 2012), therefore it is coherent that the NBL is surpassed in areas where there are agricultural uses. Lucon et al. (2018) indicated NBL of 0.8 mg/L for the dry season, whereas for the rainy one the value is 0.7 mg/L, indicating origin on agricultural dumping and inadequate sewage disposal, endorsing this study. Calijuri et al. (2012) also pointed positive moderate contributions attributed to phosphate in the surroundings of the airport, which are possibly related to anthropic interference at the monitored points, hence corroborating this study.

The soil possibly exerts an important role within this context, constituting an effective filter for any contaminants which might be in contact with the area. As exposed by Kämpf (2008), Latosols, despite holding a lower Cationic Exchange Capacity (CEC), show a higher resistance to environmental impacts due to their elevated physical stability (lower erodibility, better transportability and easiness of manipulation). Also, Latosols hold a high adsorption capacity, mainly for phosphorus, as shown by Leal (1971) and Novais et al. (1991), which may shed light on why phosphate concentrations on groundwater samples are so low in the present study. Cambisols, following the method present in Kämpf (2008), are less resistant than Latosols as they hold a relatively higher sand content when compared to them; nevertheless, Cambisols are the second most resistant ones, also showing high levels of environmental protection capacity. The presence of those two soil typologies, representing 83.6% of total surface of CLSPU, therefore may help on understanding the large extent of moderate and low vulnerability areas in the study region.

The land use map also proved to be essential in this context. It shows urban areas where there are high NBLs, especially for nitrate and chloride in the South, Southeast and West portions, indicating anthropogenic activities. The agricultural inputs are related with high levels of sulfate and phosphate mainly in the central part, with this type of use covering an expressive portion (more than 50%) of the CLSPU area.

Finally, the absence of major anthropic occupations nearby outcrops that constitute sensitive recharge areas (mainly dolines) also contribute to the preservation of the CLSPU, as although there are indications of human impacts because of the surpassed NBLs, none of the parameters showed elevated concentrations.

6. CONCLUSION

This study aimed to determine natural background levels for chloride, nitrate, sulfate and phosphate and to associate the areas where those levels were surpassed on the reclassified intrinsic vulnerability map proposed for The Carste Lagoa Santa Protection Unit, through geoprocessing and geostatistical tools. The used method can be applied to other karst regions considering a careful evaluation of the specificity of each region.

The exceeded values of the Natural Background Levels are consistent with the anthropic inputs associated with urban settlements or agricultural activities. There is a predominance of moderate vulnerability where the isopleth maps surpass the proposed NBLs. Chloride, phosphate and sulfate show, respectively, 64.3%, 68.4% and 75.1% of the total area. Nitrate represents the only exception, holding a major presence of low vulnerability areas (54.9%). Most moderate and low vulnerability fractions can be explained by the role played by the soil depth, in which Latosols and Cambisols pose a high resistance to environmental impacts and because there are no major anthropic occupations, especially nearby sensitive points, such as recharge areas represented by dolines and swallow holes.

Finally, the connection between intrinsic vulnerability and NBLs constitute a powerful tool aimed to the management and protection of water resources. Karst regions are extremely sensitive to anthropic contamination and, especially in Brazil, there is still a lack of knowledge within this field. Therefore, it is recommended by the authors that studies in a detail level should be conducted to improve the environmental understanding of water contamination, background levels and intrinsic vulnerability of karst areas.

CHAPTER 2: NATURAL BACKGROUND LEVELS UNDER A HYDROGEOCHEMISTRY ANALYSIS IN THE LAGOA SANTA KARST REGION, MINAS GERAIS, BRAZIL

Natural background levels under a hydrogeochemistry analysis in the Lagoa Santa Karst region, Minas Gerais, Brazil

Frederico Aragão[1]; Leila Nunes Menegasse Velásquez[1]; Luísa Costa Vieira[1]; Paulo Galvão[1]

1. Departmento de Geologia, Universidade Federal de Minas Gerais, Campus Pampulha, Belo Horizonte/MG 31275-035, Brazil

Corresponding author:
Frederico Aragão Cardoso
Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil
Contact: +5531992317872
Email: aragao.ambiental@gmail.com
ORCID: 0000-0002-7304-9679

Abstract

The identification of an anomaly related to a substance in surface and groundwater represents an important step in water management plans. The Lagoa Santa karst region, despite the fact that it comprehends a very important and unique karst region in Brazil, faces an accelerated urban and industrial development, which potentially may result in alterations in water quality. This paper aims to establish Natural Background Levels for karst springs and deep groundwaters for Si^{4+} and the major main elements Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-}, Cl^{-}, in order to understand sources of possible hydrochemical anomalies to distinguish between geogenic or anthropogenic inputs. The areas where those thresholds were surpassed were compared with regional geological, hydrogeochemical and land use studies. Results have pointed that all the parameters, except for chloride, showed elevated concentrations due to lithologic origin. The Natural Background Levels (90th percentile) for waters collected from wells and springs, respectively, are 17.9 and 12.7 mg/L (silica), 97.0 and 91.5 mg/L (calcium), 4.9 and 2.9 mg/L (magnesium), 6.2 and 3.8 mg/L (sodium), 1.0 and 0.3 mg/L (potassium), 285.5 and 254.6 mg/L (bicarbonate), 9.4 and 13.6 mg/L (sulfate), and for chloride, it was done only for wells, showing 6.7 mg/L. High Cl^{-} levels indicate anthropogenic loads with the presence of domestic sewage delimited by the Mata river. This work was thus important to comprehend the Natural Background Levels of the major elements, point to possible pollution from the Mata river and also to distinguish calcitic carbonate aquifer units to impure ones.

Keywords: *Natural Background Level; karst Lagoa Santa region; Hydrogeochemistry; Karst aquifer; Geogenic Anomalies*.

1. INTRODUCTION

Groundwater quality poses a key role in environmental management studies. Populations often rely upon this resource and therefore a sound monitoring and protection is required. Karst aquifers are important groundwater sources, where more than 20-25% of the entire world depends on water from this hydrogeological feature (Ford and Williams 2007; Chen et al. 2017), and by 2025 it is estimated that this number will increase to approximately 80% (Forti 2002).

Karst aquifers have unique hydrogeological characteristics; the recharges might be autogenic (from the outcrops of rocks) or allogenic (beyond them through sinkholes), and it also may be concentrated or diffuse. Flow velocities can reach high values, up to 2.66 m/d in West Virginia (Jones 1977) or even 5.18 m/d in Herzegovina (Goldscheider and Drew 2007), with a heterogeneous network which allows the integration of the flow path from surface to spring (White 1988; European Commission 1995; Bakalowicz 1995, 2005; Ford and Williams 2007; Mudarra and Andreo 2011).

The heterogeneity constitutes a complex flow behavior, consequently producing a highly variable hydrochemistry. These variations depend on rock mineralogy, residence-time, the reactive processes, as well as flux conditions and on permeability properties. A highly mineralized groundwater composition resulting from paleo-recharge and circulation processes has been studied, whereas others studies pointed weakly mineralized composition couples with fast transfer conditions (Cook et al. 2005; Bucher et al. 2008; Waber and Smellie 2008; Bucher and Stober, 2010; Armandine Les Landes et al. 2014; Roques et al. 2014).

The protection of underground waters in karst aquifers can be achieved through the mapping of the vulnerability of the aquifers to contamination and the study of contaminant load generation. After this, the delimitation of protection and catchment areas of groundwater supply sources, the evaluation of the danger of contamination and the investigation of the activities that generate contaminants should be addressed. Finally, groundwater protection measures, such as control of effluents treatment, the land use and the urban planning are to be done, as to effectively protect the resources (Foster et al. 2006).

A method that can be used to aid the protection of groundwater resources in karst terrains is the determination of Natural Background Levels (NBL) for hydrogeochemical parameters. This concept corresponds to the range of concentrations of a substance or element obtained from the interaction between groundwater, surface water, lithologic, biologic, and atmospheric factors, under little or absent anthropogenic impact. Possible linkage between aquifers, rain and small anthropogenic outputs might influence those values, thus spatial variations are expected (ISPRA 2009). NBLs can therefore indicate whether a value for an element or substance corresponds either to a geogenic or to an anthropogenic origin (Hawkes & Webb 1962, Reinmann et al. 2005, Edmunds & Shand

2008, Hinsby et al. 2008). Based on this, a solid methodology for determining NBLs was developed by the European community in 2006 in the project “Background Criteria for the Identification of Groundwater Thresholds” (BRIDGE 2006, 2009).

In Brazil, 61% of the population is supplied with groundwater (IBGE 2003). However, despite the fact that karst areas in Brazil comprise between 5% and 7% of the national territory (425,000 - 600,000 km^2 – Auler et al., 2001), there are few studies regarding about natural background levels in karst aquifers. Lucon et al. (2018) presented NBL values for calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chlorine, nitrate, and phosphate for the São Miguel watershed, state of Minas Gerais, pointing to anthropogenic impacts for NO^{3-}, PO_4^{3-}, and Cl^-.

The Sete Lagoas Formation, constituted by impure limestones of the Pedro Leopoldo Member and by calcitic limestones of the Lagoa Santa Member, and the Serra de Santa Helena Formation, composed by metapelites, constitute the geology. The metalimestones are from the Neoproterozoic age and show a low-grade metamorphism.

The Lagoa Santa karst region comprehends karst geomorphology features composed of springs, swallow holes, caves, dolines, shafts and poljes. This region faces an uprising urban and industrial development, especially in southwest and west borders. Industries, agricultural and urban settlements take place indicating risks to the quality of groundwater and surface water, since proper treatment is not always present to the effluents and waste that are produced (Tayer 2016).

Due to these features, this paper proposes NBLs for inorganic elements in the groundwaters of the Lagoa Santa karst region. Values were calculated for waters collected from deep tubular wells and from springs for calcium, magnesium, silica, sodium, potassium, bicarbonate, chloride and sulfate. Only samples from Sete Lagoas and Serra de Santa Helena Formations were considered as to understand their influence in the hydrochemistry and water quality of the aquifers.

2. SITE DESCRIPTION

The study area (Fig. 1) is in the southeast of Brazil, in the Minas Gerais state. It includes completely the Carste Lagoa Santa Protection Unit (CLSPU) (Área de Proteção Ambiental - APA) Carste Lagoa Santa and partially seven municipalities, within 505 km^2. It is inserted in the upper São Francisco river basin and the Velhas river subbasin, with an altitude range that varies between 620 and 910 m above sea level (IBAMA 1998, Tayer and Velásques 2017).

The most commonly found activities in the region that pose environmental impacts are fuel stations, steel industry, cemeteries, limestone mining, intensive agriculture and urban sites within poor sanitation structures (IBAMA 1998, Tayer 2016). The land use map (Correa 2018) indicates considerable areas where, notably, agricultural activities and urban uses settlements are frequent (Fig. 1).

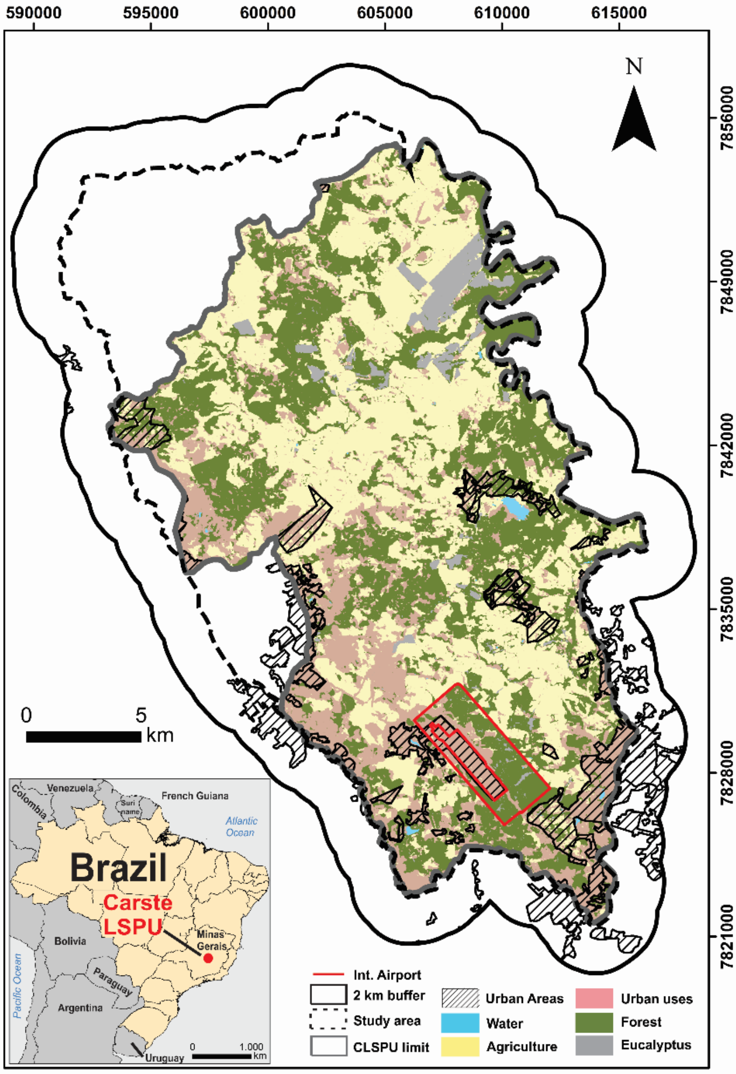

Figure 1 – Location map and land use map extracted from Correa (2018)

Geologically, the area is in the São Francisco Craton, in which neoproterozoic pelite-carbonate rocks from Sete Lagoas and Serra de Santa Helena formations compose the Bambuí Group. The Belo Horizonte complex, which forms the Archaean basement, is composed of gneiss, migmatites and granitoids. Moreover, the Sete Lagoas Formation (SL Fm) is segmented into two members: Pedro Leopoldo, at the bottom, represented by fine limestones, dolomites, marlstones and pelites, showing a calcium carbonate composition between 60% and 90%; and Lagoa Santa Member, at the upper portion, constituted of purer medium-grained black limestones (calcium carbonate content higher than 90%) and with a substantial karstification level. The Serra de Santa Helena Formation covers the Sete Lagoas Formation and it is composed of argillite, siltstone, slate and marble. The Bambuí Group is overlaid by Cenozoic unconsolidated sediments, in which drainages, meanders of watercourses and low topographic levels are located, are divided in detritus coverage, alluvial terraces and alluvium) (Branco and Costa 1961, Oliveira 1967, Schöll and Fogaça 1973, Dardene 1978, Schobbenhaus 1984, Piló 1998, Berbert-Born 2002, Ribeiro et al. 2003, Pessoa 2005, Tuller et al. 2010, Galvão et al. 2016) (Fig. 2).

Hydrogeologically, there is a predominance of unconfined and semi-confined karst aquifers formed over the Bambuí Group (Tayer and Velásquez 2017). The Lagoa Santa Member (LS Mb) constitutes the karst aquifer system, whereas the Pedro Leopoldo Member (PL Mb) composes karst-fractured aquifer, due to the presence of fracture/fault as secondary permeability (Mourão et al. 2001), where both aquifers constitute the Sete Lagoas Karst Aquifer (SLKA – Pessoa 2005, Galvão et al. 2015). The Serra de Santa Helena Formation, due to the presence of metapelite, shows a reduced aquifer potentiality, acting as a aquiclude. The basement Belo Horizonte Complex has groundwater in faults and fractures, acting as a fractured aquifer. The groundwater presented within the SLKA is mostly classified as type, with a pH between 6.5 and 7.5 (Galvão et al. 2017). Karst conduits in this system holds water generally of good quality for human consumption, despite the high hardness (Pessoa 2005, Tayer and Velásquez 2017).

The Lagoa Santa karst region presents two types of recharge: 1) autogenic, in which the karst recharges itself from rainwater that covers the aquifer, most commonly found where the Sete Lagoas Formation outcrops. This direct recharge, due to considerable interaction between surface and groundwater eases the pollutant transport because of the rapid water flow within karst conduit with no time for filtration, degradation or absorption. 2) allogenic, mainly found where Serra de Santa Helena’s rocks and Cenozoic unconsolidated sediments occur, takes places when adjacent non-karst areas recharge the karst aquifer. There is diffuse recharge, developed through thick lateritic soils that arouse the attenuation of pollutants.

As for the hydrochemistry, the waters are classified as predominantly calcium-bicarbonate and, subordinately, mixed bicarbonate, referring to the granite, and sodic, associated to the colluvium. There is a tendency of horizontal compartmentation, illustrated by the increase of Si^{4+} concentration from NW to SE, extending also to NE and followed by Mg^{2+} concentrations. This pattern is developed from the Lagoa Santa Member pure limestones to the impure rock of the Pedro Leopoldo Member, showing an increase of dolomite, mica and chlorite in the east of the region. The Pedro Leopoldo Member’s waters can be divided in 4 hydrochemical types, mainly according to Ca^{2+} and Si^{4+} concentrations and secondly to Mg^{2+} concentrations (types i, ii, iii and iv), and associated to different classifications of rocks through lithochemistry, as proposed by Vieira (2018).

The endokarst is mainly exemplified by grottos, whereas the exokarst features are illustrated as poljes, shafts, dolines, caves, ponors, prings and uvalas (Ribeiro et al. 2003). The discharge areas show a greater level of dissection, below the altitude of 700 m, counting with residual karstic features, substantial uvala systems and a relatively flat terrain.

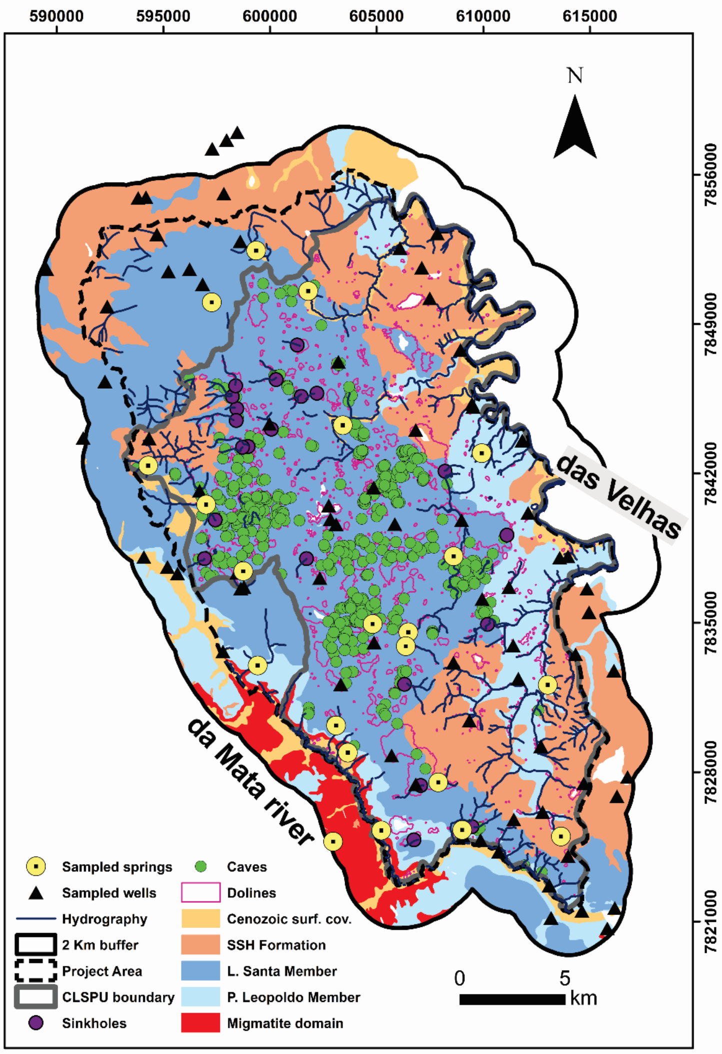

Figure 2 – Geological map including karst features and hydrography

3. MATERIAL AND METHODS

To understand the carbonate and the pelitic lithologies influences over the quality of the groundwater, only deep tubular wells extracting water from Sete Lagoas and Serra de Santa Helena formations were considered, as illustrated by Figure 2. A total of 26 samples were collected from the Lagoa Santa Member, 43 from Pedro Leopoldo Member, 3 from Serra de Santa Helena Formation, and 5 from a mix between Lagoa Santa Member and Serra de Santa Helena Formation. For springs, a total of 21 samples were collected: 13 of them derive water from Lagoa Santa Member, 5 from Lagoa Santa Member, 2 from Belo Horizonte complex basement and 1 from lateritic Cenozoic unconsolidated sediments.

The samples were analyzed at SGS Geosol Laboratórios Ltda. Calcium, magnesium, potassium, sodium and phosphate were determined by the method metals by plasma emission spectroscopy; chloride and sulfate by ions chromatography, bicarbonate by alkalinity and silica by the molibdosilicate method. All the sampling was carried out between September 2017 and April 2018, during the wet season. A stainless-steel bucket was used, which was rinsed three times with the collected water. As for the deep tubular wells, the ones that were not previously pumping were purged for a minimum period of 10 minutes before sampling to restore original hydrochemical conditions and to avoid stagnant water.

Previously to each sampling, the plastic bottles used to store the collected water were rinsed three times with the sample, as to equilibrate sampling equipment with the sample environment and to residues that might be present (USGS 2006). Right after sampling, the bottles were then placed in a cooler and delivered to the laboratory at the same day, where they were kept at a temperature of 4ºC for a maximum of 24 h before the analyses, according to the Sampling and Water Preservation Guide (CETESB 2011). As for the springs, the sampling was carried in the most possible upstream point as to obtain the most preserved physicochemical characteristics. Finally, the values were then compared with the Brazilian Federal drinking standards, present in BRASIL (2017).

3.1 Outliers and non-detect treatment

In the case of having samples with values below the detection (or quantification) limit (DL), it is recommended to convert them to the DL itself to identify a representative value, or it would be shown as "< DL" and therefore it would be impossible to mathematically manipulate them (ISPRA 2009). For instance, two Magnesium samples (deep tubular wells 14212-2010 and N53), in the analysis of Sete Lagoas Formation, were considered with an exact value of 0.25 mg/L. Additionally, in order to avoid the uncertainty which is inherent with the usage of those type of data, it is suggested to use this constant value only when the number of DL samples constitute a maximum of 15% of the entire dataset (EPA 2002).

Moreover, all the samples presented outlier values, which were determined through the algorithm "Boxplot stats", ran on software RStudio®, version 1.1.453. At first, they were not excluded from the analysis; however, if there was any interference within the statistical credibility by producing p-values smaller than 0.05, then an exclusion was considered, as it indicates strong evidence against the null hypothesis, as further explained in the next topic.

3.2 NBL determination, descriptive statistics and maps production

The methodology used for Natural Background Levels assessment was the one suggested by ISPRA (2009), in which the NBL corresponds to the 90th percentile of the probability distribution plot. To that end, it was needed first to determine the best statistical distribution for each parameter, which was done through software Minitab® version 17. Its tool Individual Distribution Identification compares 14 statistical distributions by the Anderson Darling (AD) test, which provides the P and the AD values. The combination of a greater P (with a minimum acceptable value of 5%) coupled with a smaller AD indicates the best fit, as suggested by Minitab Inc (2018). The mean, median and standard deviation were also calculated and the maps showing the areas in which the NBLs were surpassed were produced. To obtain these areas, Radial Basis interpolation method (Completely Regularized Spline function) was used, since it is exact, flexible and produces "the best overall interpretations of most data sets" when compared to other interpolation techniques (Golden Software 2017, Gunarathna et al. 2016). The 2 km buffer was considered in all maps, as to provide a security margin to more assertive interpretations of the analyses.

3.2.1 Groundwater analysis

As for the cationic parameters, Calcium was the only parameter that did not present any samples with concentration below the quantification limit. The tool Individual Distribution Identification suggested the Logistic distribution as the one with a better fit, since its P-value (>25%) and AD value (0.3) was the best combination among the 14 distributions.

Silica, like Calcium, did not have any sample excluded, showing an AD of 0.6 and a p of 13.5%, under 3-Parameter Weibull distribution.

Bicarbonate presented two outliers that needed to be excluded since it was not possible to obtain a minimum p-value acceptable. Therefore, a P-value of 8.1% and an AD of 0.6 were attained, all of them within the Small Extreme Value distribution.

Moreover, Magnesium, by excluding two DLs, showed a satisfiable fit, with $P > 0.5$ and $AD = 0.2$, under the 3-Parameter Weibull distribution; whereas Sodium had 27 DL and two outliers excluded, showing an AD of 0.1 and a P-value of > 50%, within 3-Parameter Weibull distribution.

Finally, Potassium had 34 DLs excluded, under Loglogistic distribution and with AD and p values of 0.6 and 7.8%, respectively.

As for the anions, Chloride presented 60 DL values that needed to be excluded, in order to reach AD and P-values of 0.3 and > 50% under the 3-Parameter Weibull distribution, whilst Sulfate needed to have 39 DLs excluded, to reach AD and p of 0.5 and 27.5%, also under 3-Parameter distribution. Table 1 summarizes those results as well as the descriptive statistics including the mean, standard deviation and median.

Table 1 – Distribution and descriptive statistics for the collected deep tubular wells

Parameter	Distribution	AD	p-value	n final	Mean	Std. Dev	Median
Ca^{2+}	Logistic	0.2	>0.3	77	67.6	26.0	65.7
HCO_3^-	Logistic	0.6	0.1	75	214.2	58.8	211.1
Si^{4+}	3-Parameter Weibull	0.6	0.1	77	13.9	6.4	11.7
Mg^{2+}	3-Parameter Weibull	0.2	>0.5	77	2.7	1.8	2.3
Na^+	3-Parameter Weibull	0.1	>0.5	49	3.1	3.0	2.1
K^+	Loglogistic	0.6	0.1	43	0.7	0.5	0.3
Cl^-	3-Parameter Weibull	0.3	>0.5	22	3.8	4.1	2.3
SO_4^{2-}	3-Parameter Weibull	0.5	0.3	38	4.8	6.1	2.8

3.2.2 Spring analysis

As for the spring cationic parameters, Calcium and Bicarbonate had one outlier excluded in order to reach the statistical significance, both under the Smallest Extreme Value distribution. Ca^{+2} presented an AD of 0.6 and a p of 9.5%, while HCO_3^- showed 0.7 and 7%, respectively. Silica and Magnesium did not have any sample excluded, presenting 0.5 and 19.4% and 0.3 and >25% for AD and p value, under 3-Parameter Weibull and Largest Extreme Value, respectively. Additionally, Sodium needed to have 6 of its LDs excluded, thus presenting an AD of 1.2 and a p of 6.9% under Exponential distribution, whereas Potassium had 5 LDs not considered, showing 0.6 and 10.9%, within 3-Parameter Weibull. Finally, as for the anionic parameters, Sulfate faced an exclusion of 8 DLs, presenting an AD of 1.1 and a p of 8.7% under the Exponential distribution. However, it was not feasible to perform the assessment for Chloride, as too many samples would need to be excluded and the statistical significance would therefore not be attained. Table 2 summarizes the aforementioned analysis as well as the descriptive statistics.

Table 2 – Distributions and descriptive statistics for the collected springs

Parameter	**Distribution**	**AD**	**p-value**	**n final**	**Mean**	**Std. Dev**	**Median**
Ca^{2+}	Smallest Extreme Value	0.6	0.1	20	71.4	21.7	75.8
HCO_3^-	Smallest Extreme Value	0.7	0.1	20	206.1	53.5	219.0
Si^{4+}	3-Parameter Weibull	0.5	0.2	21	11.1	8.6	8.4
Mg^{2+}	Largest Extreme Value	0.3	>0.3	21	1.7	0.9	1.5
Na^+	Exponential	1.2	0.7	21	1.6	2.2	0.9
K^+	3-Parameter Weibull	0.6	0.1	21	0.4	0.2	0.3
SO_4^{2-}	Exponential	1.1	0.1	21	5.9	7.1	2.8

4. RESULTS

4.1 NBLs – Deep tubular wells and springs

Table 3 summarizes the results for the deep tubular wells and the springs, coupled with the maximum values found and the potability drinking standards (Brasil 2017), when defined. The maps that represent areas where the natural background levels are surpassed for each parameter, both for deep tubular wells and springs, can be seen in Figures 3, 4, 5 and 6.

Table 3 – NBLs, maximum values, drinking standards and detection limits

Parameter	**NBL 90 Deep tubular wells (mg/L)**	**Max. Value Prob. Distr. - Deep tubular wells (mg/L)**	**NBL 90 Springs (mg/L)**	**Max. Value Prob. Distr. – Springs (mg/L)**	**Brazilian drinking water standard (mg/L) (Brasil 2017)**	**Detection Limit (mg/L)**
Ca^{2+}	97.0	162.2	91.5	101.0	-	0.3
HCO_3^-	282.5	428.5	254.6	277.5	-	6.0
Si^{4+}	17.9	39.5	12.7	29.2	-	-
Mg^{2+}	4.9	12.1	2.9	4.6	-	0.3
Na^+	6.2	22.2	3.8	7.5	200	0.5
K^+	1.0	2.1	0.3	1.0	-	0.3
Cl^-	6.7	17.9	-	-	250	0.3
SO_4^{2-}	9.4	22.6	13.6	27.3	250	1.2

4.1.2 Calcium and Bicarbonate

Figure 3a, representing the deep tubular wells that collected Calcium, illustrates two main areas in the central-north part and specifically because of two deep tubular wells with 169.0 mg/L also located within Lagoa Santa Member. Figure 3b illustrates the maps where Calcium's NBLs in springs are surpassed. The value of 91.5 mg/L is exceeded only in a central region, due to three springs in which Lagoa Santa Member is predominant. As for the HCO_3^- deep tubular wells, only one point showed a NBL above 282.5 mg/L, located on LS Mb, and it was not sufficient according to the interpolation method to cover a larger area, as shows by 3c. Figure 3d represents, for Bicarbonate, a key area with values higher than 254.6 mg/L, specifically in the central area, coincident with the patterns found for Calcium, due to 2 springs.

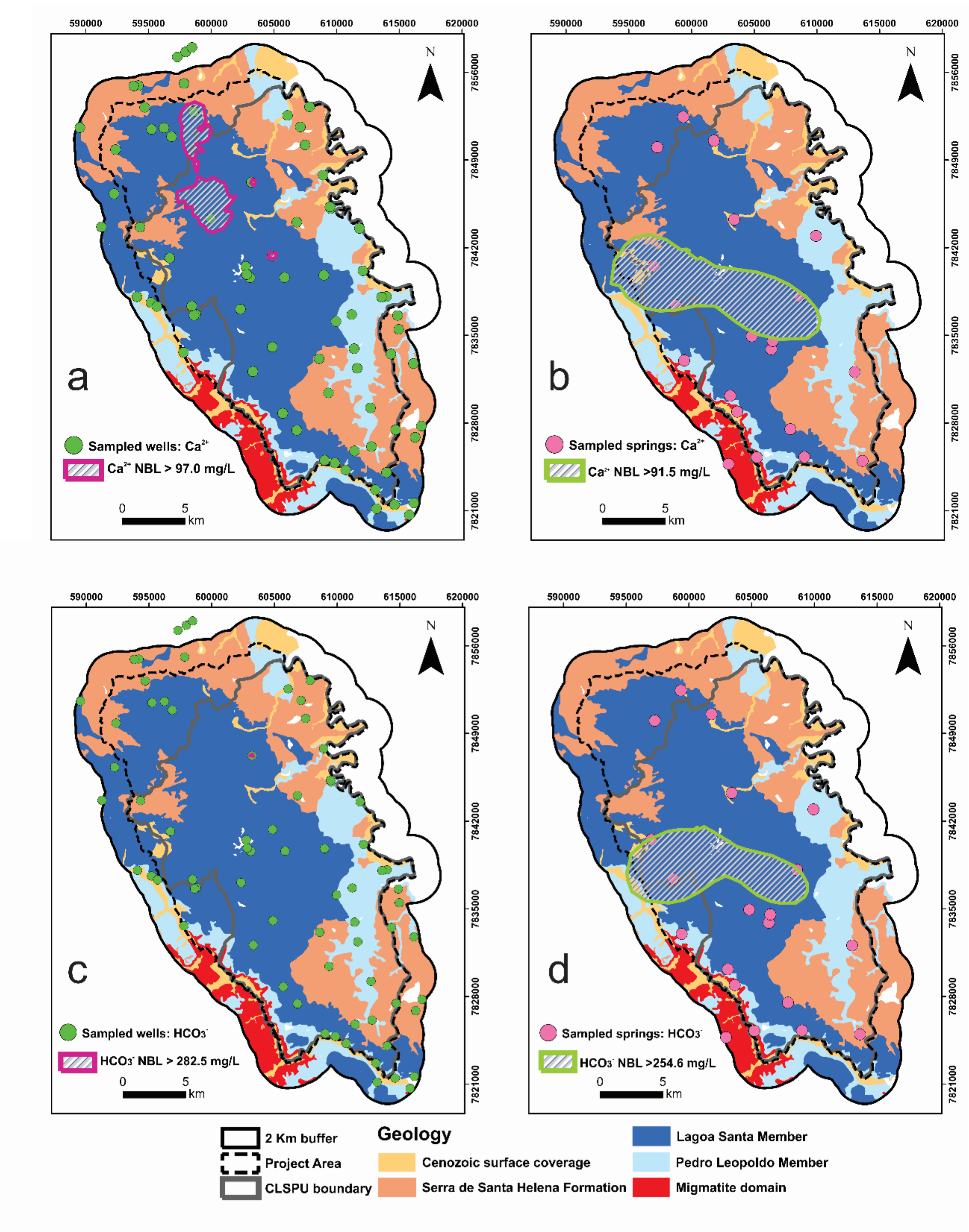

Figure 3a – Areas with surpassed NBLs for calcium collected from deep tubular wells; Figure 3b – Areas with surpassed NBLs for calcium collected from springs; Figure 3c – Areas with surpassed NBLs for bicarbonate collected from deep tubular wells; Figure 3a – Areas with surpassed NBLs for bicarbonate collected from springs;

4.2.2 Silica and Magnesium

Figure 4a illustrates, for silica, an area in the east, as deep tubular wells as isolated points in the south and west and small areas also in the south, center and north due to few collected deep tubular wells. As for the springs, in Fig. 3b, there are two expressive areas with concentrations above 12.7 mg/L, covering the north, east, south and southwest, coincident with the Pedro Leopoldo Member, the Serra de Santa Helena Formation and the granitic complex. In Fig. 3c shows, for Mg^{2+} deep tubular wells, unexpressive portions, with three isolated points with values higher than 4.9 mg/L. On the other hand, Fig. 3d illustrates, for magnesium, only two small areas with concentrations above 2.9 mg/L because of two springs.

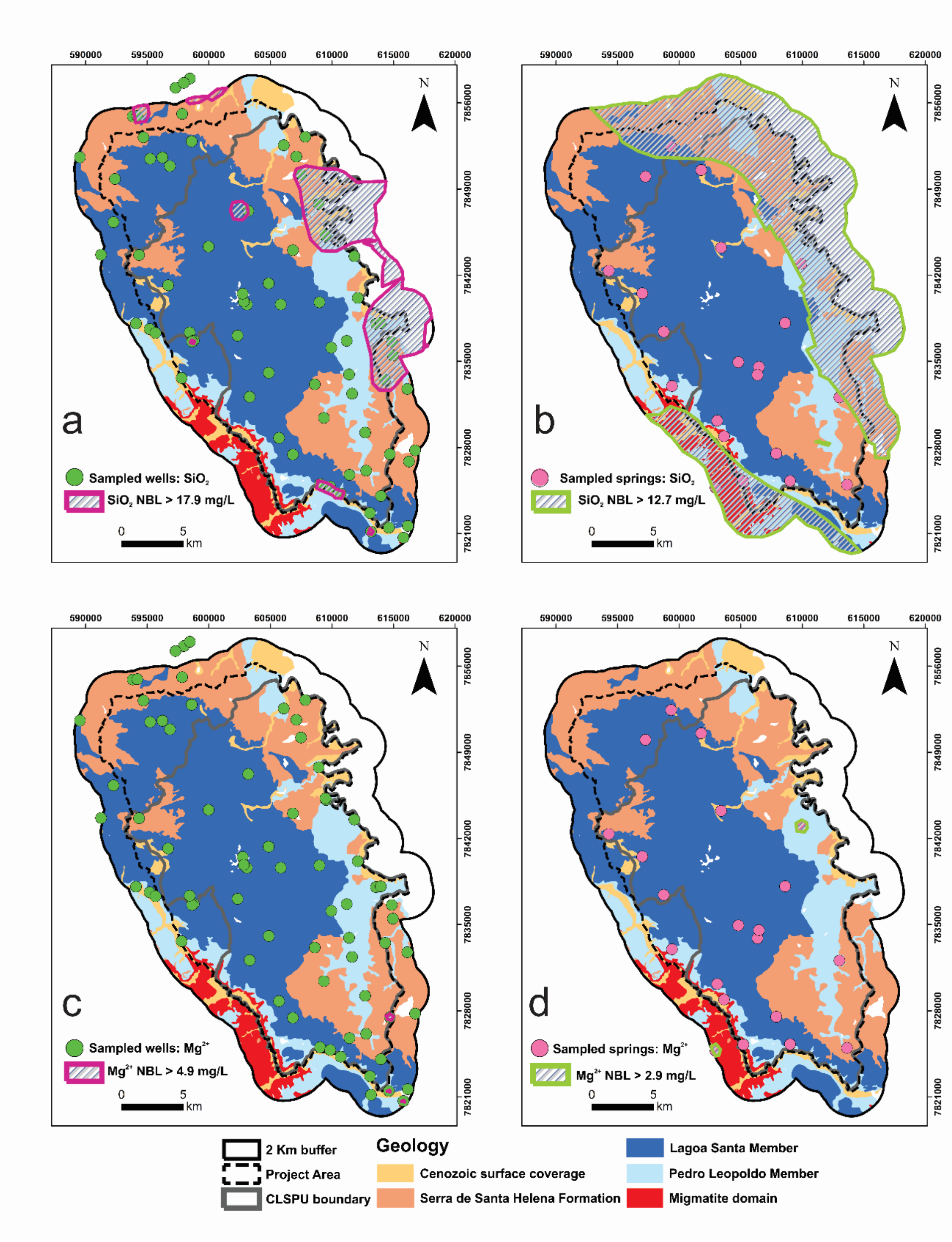

Figure 4a – Areas with surpassed NBLs for silica collected from deep tubular wells; Figure 4b – Areas with surpassed NBLs for calcium collected from springs; Figure 4c – Areas with surpassed NBLs for magnesium collected from deep tubular wells; Figure 4d – Areas with surpassed NBLs for magnesium collected from springs

4.2.3 Sodium and Potassium

As for Sodium deep tubular wells, Fig. 5a represents only four small and isolated points due to the respective deep tubular wells, which were not sufficient for the interpolation to suggest larger portions. As for the springs, Fig. 5b shows an area covering the southwest over the granitic complex because of one sample. As for Fig. 5c, there is only one considerable area in the east for potassium, coupled with three isolated deep tubular wells in the north, west and east, which showed concentrations above 1.0 mg/L. As for the springs, K is the parameter with the largest areas where the NBL of 0.3 mg/L is exceeded, with only the central and east portions being below this threshold.

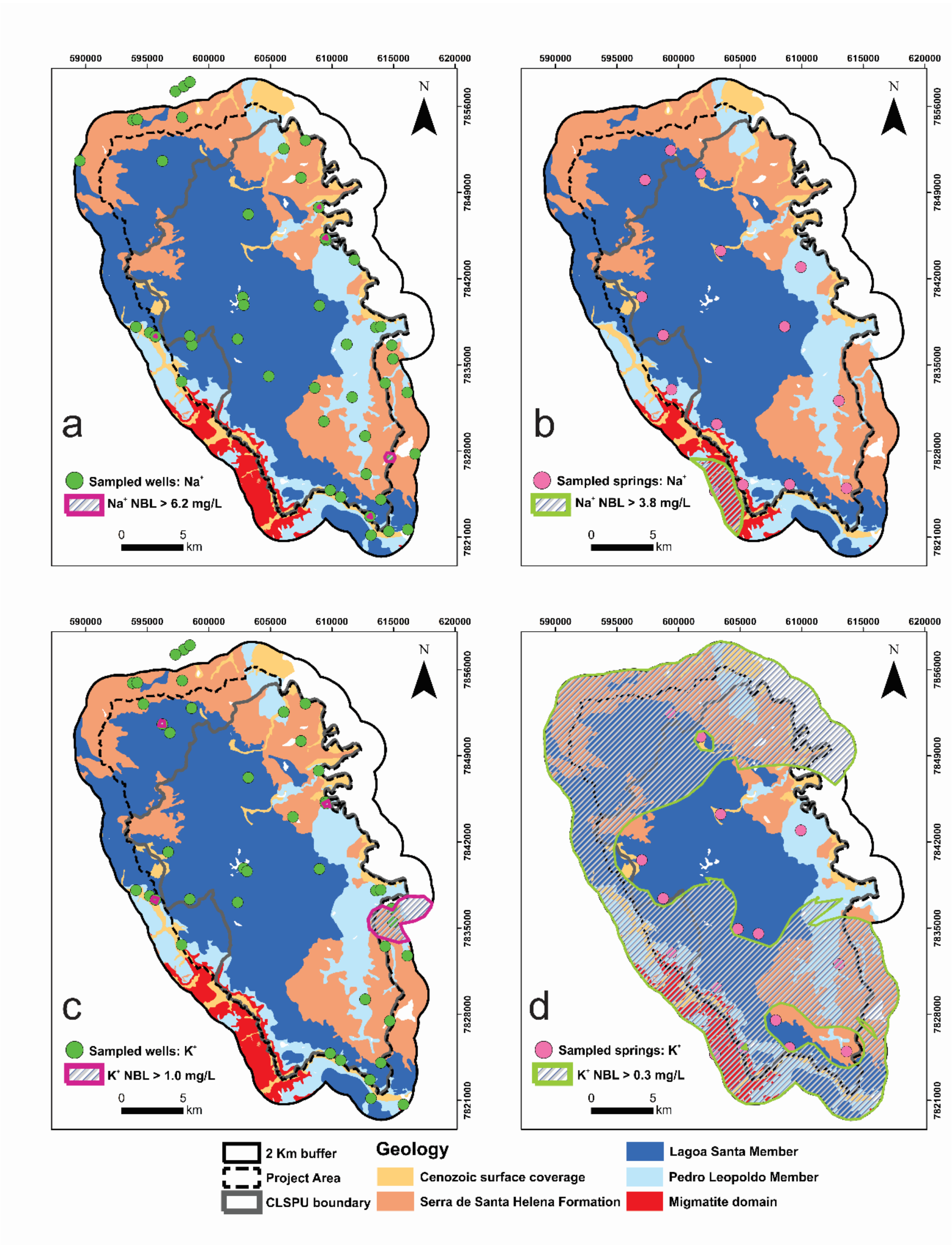

Figure 5a – Areas with surpassed NBLs for sodium collected from deep tubular wells; Figure 5b – Areas with surpassed NBLs for calcium collected from springs; Figure 5c – Areas with surpassed NBLs for potassium collected from deep tubular wells; Figure 5d – Areas with surpassed NBLs for sodium collected from springs

4.2.4 Sulfate and Chloride

Fig. 6a shows a coincident area in the center, coupled with two isolated points where the concentration of 9.4 mg/L is surpassed Additionally, Fig. 6b illustrates only one area in the central part, influenced by three springs located on Lagoa Santa Member with NBL higher than 13.6 mg/L. Due to lack of statistical representativity, it was not possible to create a map for Chloride springs; there were too few points and thus a satisfiable p-value was not reached. However, the map for deep tubular wells was accomplished, which shows a single area in the west influenced by three deep tubular wells and one isolated point in the south, as shown by Fig. 6c.

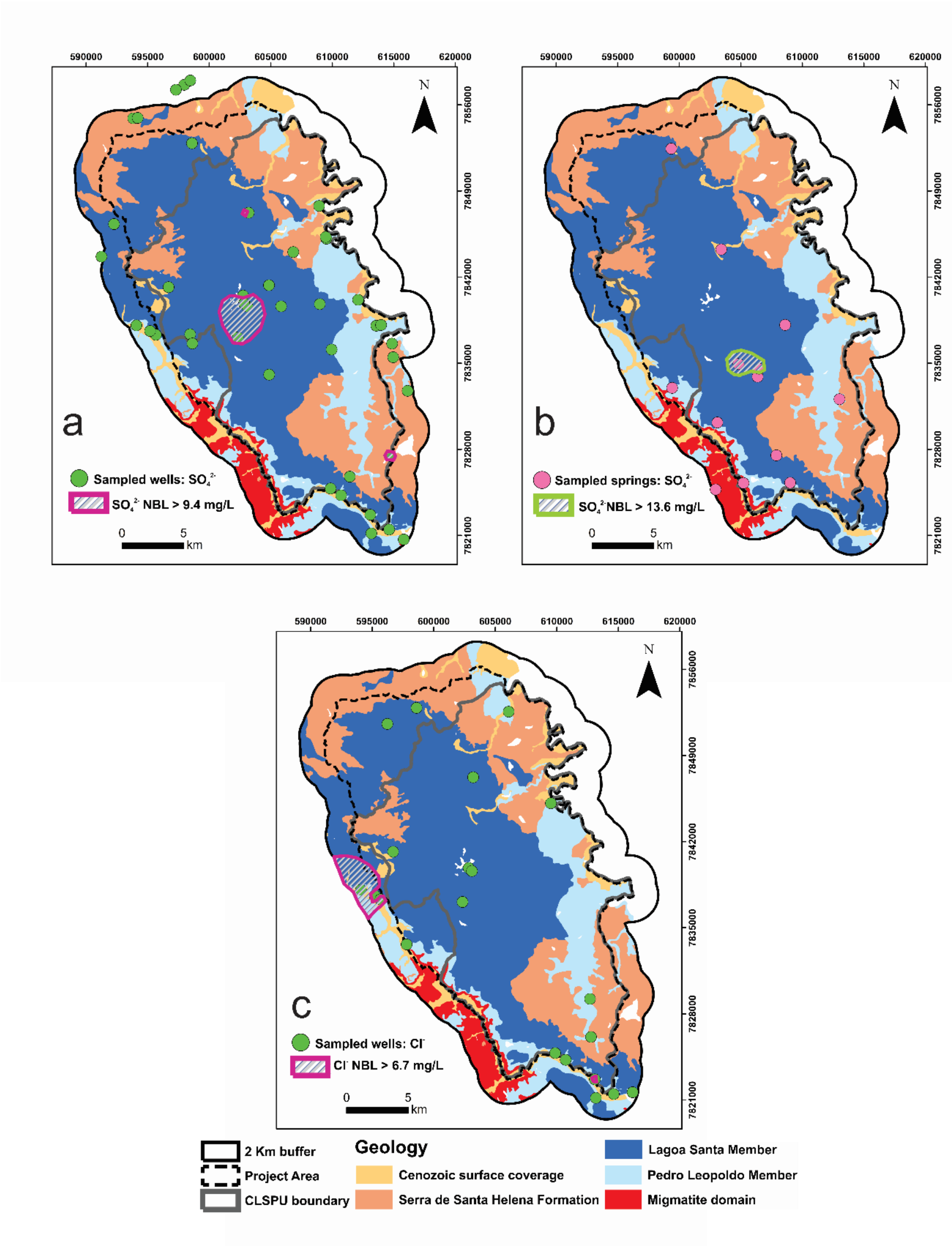

Figure 6a – Areas with surpassed NBLs for sulfate collected from deep tubular wells; Figure 6b – Areas with surpassed NBLs for sulfate collected from springs; Figure 4c – Areas with surpassed NBLs for chloride collected from deep tubular wells

5. DISCUSSION

5.1 Springs

The pattern observed by Calcium and Bicarbonate are coherent with the described geology. The springs that made the NBL to be surpassed are deriving water from Lagoa Santa Member, known for its purer calcitic composition, which contributes to the highest Ca^{2+} and HCO^{3-} concentrations.

As for Silica, the higher concentrations occur due to the granitic lithology of Belo Horizonte Complex and due to Pedro Leopoldo Member. In the east portion, the Pedro Leopoldo Member rocks hold a higher intensity of pelitic intercalation between the carbonate units when compared to the other outcrops, according to field and lithochemical observations presented on Vieira et al (2018). This characteristic influences the chemical composition of the springs in the east of the area and explains the elevated Si^{4+} concentrations.

Likewise, the area where Magnesium shows surpassed NBLs has its origin also in the pelitic composition of Pedro Leopoldo Member, within its magnesian face. The Magnesium concentration is explained by the dissolution of mica, chlorite and dolomite, which is a mineral highly present in the limestones of Pedro Leopoldo Member, as indicated by lithochemistry data and the X-Ray diffraction analysis presented on Vieira (2018).

Sodium, on the other hand, is clearly associated with the granitic basement. However, it is noteworthy that it holds a major relevance regarding the distinction of the waters from Pedro Leopoldo and Lagoa Santa members, as the pelitic intercalations contribute to higher levels of this parameter in the shallow circulation of the aquifers.

As for Potassium, there is an unexpected pattern, in which most of the study area was surpassed with elevated values. This probably occurs due to an influence of the soil, which can release potassium onto the groundwater system and therefore to the springs.

Finally, Sulfate shows its pattern possibly due to the oxidation of sulfides within the rocks, especially pyrite, which is predominantly found in the limestones of Lagoa Santa Member and in the purer portions of Pedro Leopoldo Member rocks.

5.2 Deep tubular wells

The patterns observed for Calcium and Bicarbonate are correlated and indicate the most karstified areas, especially within the Jaguara/Palmeira system, holding a thickness of 30 to 50 m. The NBLs are surpassed due to deep tubular wells exclusively located on the Lagoa Santa Member, with its purer calcitic composition.

As for Silica and Magnesium, their most expressive areas for the surpassing of the NBL correspond to the east limit of the project, close to the Velhas river. These waters belong to Pedro Leopoldo Member and the higher concentrations of these elements are justified by the pelitic intercalations and by the presence of dolomite. The distribution of Si^{4+}, coupled with Ca^{2+} and HCO^{3-} and, to a lesser extent, with Mg^{2+}, enables the identification of four hydrochemical types on the Pedro Leopoldo Member related to different lithofacies (Vieira 2018): firstly, type i, with high concentrations of Ca^{2+} and HCO_3^-, intermediate Mg^{2+} and low Si^{4+}; secondly, type ii, with high concentrations of Ca^{2+}, HCO_3^- and Mg^{2+} and intermediate of Si^{4+}; thirdly, type iii, with low Ca^{2+} and HCO_3^- concentrations, high Si^{4+} and intermediate Mg^{2+} and, finally, type iv, with intermediate and low Ca^{2+} and HCO_3^- concentrations, low Si^{4+} and intermediate Mg^{2+}. Silica has a noteworthy role into the horizontal compartmentation of the aquifers, as its concentration increases from NW to SE, extending alto to NE and followed by Mg^{+2} concentrations. Additionally, Si^{4+} values increase with depth, which is demonstrated by the hydrochemical types of Pedro Leopoldo Member, indicating a vertical compartmentation as well (Vieira 2018).

Magnesium, on the other hand, had its NBL of 4.9 mg/L exceeded due to the impure typology of Pedro Leopoldo Member (group ii, corresponding to dolomitic limestones), with all the three deep tubular wells extracting water from it.

Potassium indicates pelitic intercalations present on Pedro Leopoldo Member on the southeast, with the single well in the north corresponding to the pelite of Serra de Santa Helena formation. As for Sodium, there are two deep tubular wells that are coincident with Potassium (20198-PT and N12074-2009), indicating the influence of feldspar and mica present in the Pedro Leopoldo Member.

Moreover, as for Chloride, the area in the west and the point in the south where the NBL of 6.7 mg/L is surpassed are due to deep tubular wells collecting water from PL Mb.

However, they represent specific points and a large amount of the samples had the concentration deemed as below the quantification limit. Therefore, the high values are possibly due to anthropogenic origin delimited by da Mata river.

As for Sulfate, the central area with the exceeded NBL occurs due to three deep tubular wells extracting water from Lagoa Santa Member, which receives influence from the oxidation of sulfide disseminated on its rocks.

For comparison, Lucon et al (2018) determined Natural Background Levels for Calcium, Magnesium, Sodium, Potassium, Bicarbonate, Sulfate and Chloride, at the São Miguel watershed, located in a similar hydrogeologic context in the Pains Basin, also in Minas Gerais, distant about 260 km southwest from the CLSPU. The values for Ca, Na and K are relatively close to the ones herein determined, thus corroborating this study.

So, the surpassing of NBLs is satisfactorily explained by the geogenic influence for all the parameters, except for Chloride. The purer calcitic composition of the Lagoa Santa Member is expressed by the high levels of Calcium and Bicarbonate, while the pelitic intercalations mainly found in the Pedro Leopoldo Member point to the anomalies found for Silica, Magnesium, Potassium and Sodium. Sulfate, on the other hand, occurs due to oxidation of sulfide minerals. As for Cl, its high concentrations are present because of anthropogenic inputs delimited by da Mata river.

Figure 7 exposes the hydrochemical compartmentation of the aquifers proposed by Vieira (2018). It is mostly marked by Si^{+4} concentrations and by the distribution of the Pedro Leopoldo Member hydrochemical types. The ones with intermediate and high concentrations of Si^{+4} (types ii and iii) are situated in the east and southeast portions, which correspond to the more siliciclastic groups of the Pedro Leopoldo Member and of the granitic basement. Moreover, the map also shows the Stiff diagrams of each aquifer unit, including the water mixes, where it is possible to identify waters with higher Ca^{2+} and HCO_3^- concentrations, corresponding the purer carbonatic lithology, as well as waters with higher Mg^{+2}, K^+ and Na^+, related to carbonatic rocks with more pelitic intercalations, to granitic rocks and to pelitic rocks (Vieira 2018).

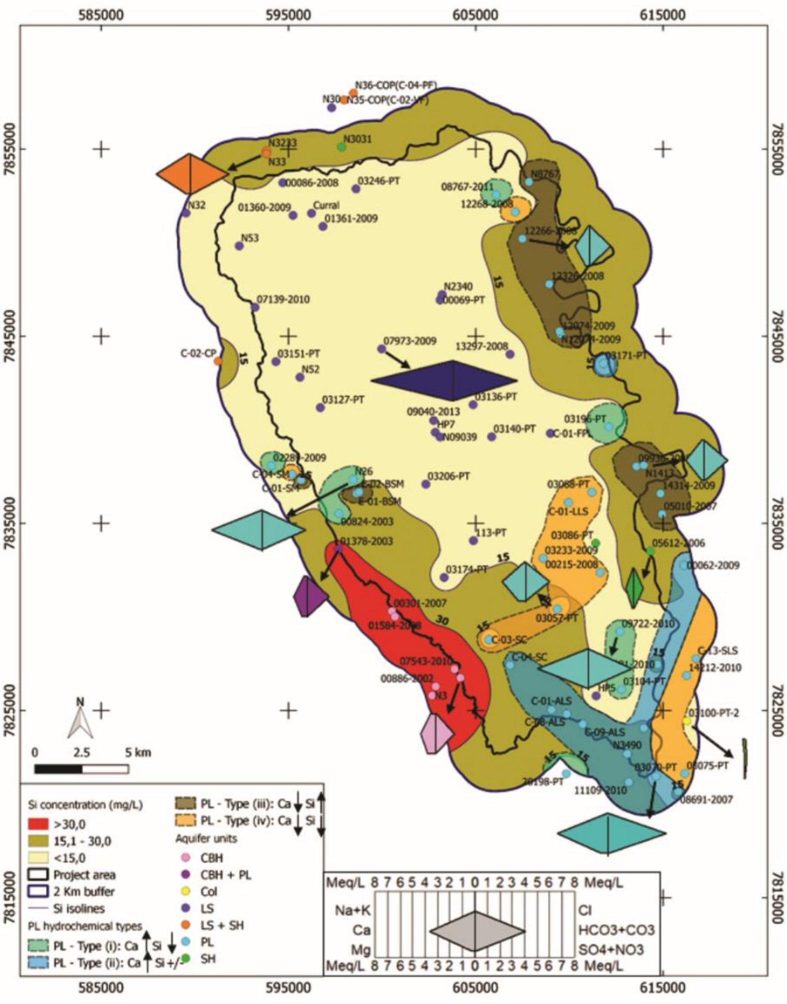

Figure 7 – Hydrochemical map created by Vieira (2018), from Si^{4+} concentrations, showing the Stiff representative composition in the aquifer units. On the Pedro Leopoldo Member four hydric types were determined from isopleth and concentration maps of Ca^{2+} and Si^{4+}:
(i) High Ca^{2+} and HCO_3^- and low Si^{4+} concentrations
(ii) High Ca^{2+}, HCO_3^- and Mg^{2+} and intermediate Si^{4+} concentrations
(iii) Low Ca^{2+} and HCO_3^-, elevated Si^{4+} and intermediate Mg^{2+} concentrations
(iv) Intermediate and low Ca^{2+} and HCO_3^- and low Si^{4+} concentrations

6. CONCLUSION

This paper intended to propose natural background levels in the region of The Carste Lagoa Santa Protection Unit for groundwater collected from deep tubular wells and springs for calcium, bicarbonate, silica, magnesium, sodium, potassium, chloride and sulfate, as well as to understand why those levels were surpassed, in a geochemical context. The study and its method can be used in other karst regions as long as their inherent characteristics, such as lithology, hydrogeology, hydrogeochemistry, pedology, hydrography and land use inputs are taken into account.

The results showed a coherence between the surpassed NBLs and the regional hydrochemistry, under an influence of the geology. Among all the elements, the geogenic influence is clear, except for chloride, for which an anthropogenic input is indicated. Calcium and bicarbonate are most influenced by the purer calcitic composition of Lagoa Santa Member. Magnesium and silica hold their origins in the pelitic intercalations of Pedro Leopoldo Member and its associated dolomites. Moreover, high levels of sodium and Potassium are also associated to the impurities of this Member as well as to the pelites present of Serra de Santa Helena Formation. Finally, sulfate has its exceeded values linked to sulfide which is present in the rocks from both Lagoa Santa and the purer Pedro Leopoldo Members.

The integrated analysis between natural background levels and regional hydrogeochemistry, therefore, compose an important means as to indicate whether high levels of an element or substance are associated to geogenic or anthropogenic origins. Hence, this method substantially contributes to the development of studies in karst regions, which are quite absent in Brazil, with a special focus in the protection of groundwater resources and water quality.

Acknowledgements

Special thanks go to the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG - project APQ-02049-14); to the Programa de Pós-Graduação Instituto de Geociências da Universidade Federal de Minas Gerais, Brasil; to the Instituto Chico Mendes de Conservação da Biodiversidade/Centro Nacional de Pesquisa e Conservação de Cavernas (ICMBIO/CECAV), and, finally, to the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

FINAL CONSIDERATIONS

The proposal of Natural Background Levels for the groundwaters of the Lagoa Santa karst region compose the requirements present for the “Project of adequation and implantation of a groundwater monitoring network in areas with karst cavities of the São Francisco river basin, applied to the pilot area of the APA Carste de Lagoa Santa, Minas Gerais, Brazil”.

As exposed by the first chapter, the high concentrations above the NBLs determined for nitrate, chloride sulfate and phosphate are associated with anthropogenic inputs, such as sewage, agricultural and industrial contaminations. Those values were surpassed mostly in areas where moderate vulnerability was proposed (except for nitrate, for which the major covering was on low vulnerability portions), thus revealing the protective role played by the Latosols and Cambisols, which act as effective filters due to relatively elevated physical stability and adsorption capacity.

Moreover, the thresholds of deep tubular wells and springs for Ca^{2+}, HCO_3^-, Si^{4+}, Mg^{2+}, Na^+, K^+, SO_4^{2-} and Cl^-, as proposed in the second chapter, reveal geogenic origins, except for chloride, hence corroborating with the previous article. Sulfate, therefore, has two possible sources, as it was previously stated that anthropogenic inputs are also possible for this substance. Calcium and bicarbonate hold a deep influence from the Lagoa Santa Member with its essentially calcitic constitution, whereas magnesium, silica, sodium and potassium occur mostly because of the Pedro Leopoldo Member pelitic intercalations, with the two latter elements also having origins in the pelites of the Serra de Santa Helena Formation.

It is also important to highlight the critics and the uncertainties of this dissertation. The statistical approach can and should be improved in a more detailed way for future studies. More sampling campaigns should be carried out, separating at least the rainy and the dry seasons, and more wells and springs could be included as to provide more reliable results. Bacteriological analyses could improve the understanding of the anthropogenic inputs in the water quality. Additionally, more detailed investigations regarding the role played by the soil should be done, as to deeply comprehend the extent of its importance as a contaminant filter. Finally, a more robust geochemical investigation is recommended as well.

The perspective of this dissertation, therefore, is to be a solid reference for further studies regarding Natural Background Levels and underground water quality in karstic regions, as well as for the comprehension between anthropogenic and geogenic origins. It also contributed to the development of the Project of Adequation and Implantation of a Groundwater Monitoring Network in Areas with Karst Cavities of the São Francisco River Basin, Applied to the Pilot Area of the Lagoa Santa Karst region. As the proposal of NBLs in Brazil, especially in the sensitive and complex karst environments, still lack studies and research, this dissertation adds to the improvement of this scientific field. Its importance thus resides as a support to the elaboration of environmental management plans aimed to water resources protection, strongly relying in regional hydrogeochemical and geologic studies and accounting the specificity of each considered scenario.

REFERENCES

Agenzia per la Protezione dell’Ambiente e per i Servizi Tecnici, Istituto Superiore di Sanità (APAT-ISS) (2006) Protocollo operativo per la determinazione dei valori di fondo di metalli e metalloidi nei suoli dei siti contaminati. (Operative protocol for the determination of natural background levels of metals and metalloids in soils of contaminated areas)

Aragão F, Menegasse L, Galvão P, Lucon T (2108) Metodologia para determinação dos níveis naturais de fundo (NBL) e da interpolação de isoconcentrações de parâmetros hidroquímicos. In: Congresso Brasileiro de Águas Subterrâneas, 20., e Encontro Nacional de Perfuradores de Poços, 21

Appelo CAJ, Postma D (2005) Geochemistry, groundwater and pollution. Leiden: A.A. Balkema,558 p

Armandine LLA, Aquilina L, Davy P, Vergnaud V, le Carlier C (2014) Time scales of regional circulation of saline fluids in continental aquifers (Armorican massif, Western France). Hydrol. Earth Syst. Sci. Discuss. 11, 6599–6635

Auge M (2004) Vulnerabilidad de acuiferos (Aquifers vulnerability). Revista Latino-Americana de Hidrogeologia 4: 85-103 <https://revistas.ufpr.br/hidrogeologia/article/download/2652/2193>. Accessed 09 August 2018

Auler A, Farrant AR (1996) A brief introduction to karst and caves in Brazil. Proceedings of the University of Bristol Spelaelogical Society 20: 187-200 <http://www.ubss.org.uk/resources/proceedings/vol20/UBSS_Proc_20_3_187-200.pdf>. Accessed 27 August 2018

Auler A, Rubbioli E, Brandi R (2001) As grandes cavernas do Brasil. Grupo Bambuí de Pesquisas Espeleológicas. Belo Horizonte. 228 p

Bakalowicz M (1995) La zone d’infiltration des aquifères karstiques. Méthodes d’étude. Structure et fonctionnement. Hydrogéologie 4, 3–21.

Bakalowicz M (2005) Karst groundwater: a challenge for new resources. Hydrogeology Journal 13 (1), 148–160.

Berbert-Born M (2002) Carste de Lagoa Santa, MG – Berço da paleontologia e da espeleologia brasileira. Sítios geológicos e paleontológicos do Brasil (Lagoa Santa, MG, Karst – Craddle of Brazilian paleontology and speleology. Geological and paleontological areas of Brazil) http://sigep.cprm.gov.br/sitio015/sitio015.pdf. Accessed 23 Nov 2017

Berg A, Banwart SA (2000) Carbon dioxide mediated dissolution of Ca-feldspar: implications for silicate weathering. Chemical Geology, 163:25-42

BH Airport (2019) Aeroporto Internacional de Belo Horizonte. http://www.bh-airport.com.br/br/p/1/home.aspx. Accessed 16 September 2019

Branco Jr, Costa MT (1961) Belo Horizonte-Brasilia roadmap tour. In: Brazilian Congress of Geology, Brasilia. Radioactive Research Institute, Federal University of Minas Gerais (UFMG), Publication 15, Belo Horizonte, 25 p

BRASIL (2012) Conselho Nacional do Meio Ambiente. Resoluções do CONAMA: Resoluções Vigentes publicadas entre setembro de 1984 e janeiro de 2012. Ministério do Meio Ambiente. (National Environment Council. CONAMA Resolutions. Resolutions published between September 1984 and January 2012) 2. ed. Brasília, DF, 1126 p ISBN: 978-85-7738-168-5

BRASIL (2017) Ministério da Saúde. Portaria de Consolidação n 5, de 28 de Setembro de 2017. Consolidação das normas sobre as ações e os serviços de saúde do Sistema Único de Saúde. (Health Minister. Consolidation Ordinance n 25, September 28 2017. Consolidation of the health regulations and services of the Brazil's Unified Public Health System)
<http://bvsms.saude.gov.br/bvs/saudelegis/gm/2017/prc0005_03_10_2017.html>
Accessed 19 September 2018

BRIDGE (2006) Background Criteria for the Identification of Groundwater Thresholds. Research for Policy Support. http://nfp-at.eionet.europa.eu/Public/irc/eionet-circle/bridge/library?l=/public_information/newsletterbridgemay2006p/_EN_1.0_&a=d>. Accessed 17 November 2018.

BRIDGE (2009) Research for Policy Support. http://nfp-at.eionet.europa.eu/Public/irc/eionet-circle/bridge/library?l=/public_information/newsletterbridgemay2006p/_EN_1.0_&a=d>. Accessed 17 November 2018

Bucher K, Stober I (2010) Fluids in the upper continental crust. Geofluids 10, 241–253.

Bucher K, Zhu Y, Stober I (2008) Groundwater in fractured crystalline rocks, the Clara mine, Black Forest (Germany). Int. J. Earth Sci. 98, 1727–1739

Calijuri ML, do Couto EA, Santiago AF, Camargo RA, e Silva MDFM (2012) Evaluation of the Influence of Natural and Anthropogenic Processes on Water Quality in Karstic Region. Water Air Soil Pollut. 223, 2157–2168. DOI 10.1007/s11270-011-1012-5

Carneiro FA (2013) Modelagem hidrogeoquímica do sistema aquífero pelito-carbonático existente no CNPMS da Embrapa Sete Lagoas, MG, Brasil. Doctorate Thesis, Federal University of Minas Gerais. 338 p.

Castro, E (2011) Estudo hidrogeoquímico ambiental em região cárstica no município Sete Lagoas – Minas Gerais: Investigação da contaminaçãode águas superficiais e subterrâneas por nitrato e atrazina, na área do Centro Nacional de Pesquisa Milho e Sorgo da EMBRAPA. Abr. 2011. 890 p. Tese (Doutorado em Saneamento, Meio Ambiente e Recursos Hídricos) - Programa de Pós-Graduação em Saneamento, Meio Ambiente e Recursos Hídricos, Universidade Federal de Minas Gerais, Belo Horizonte.

CECAV (2014) Base de dados Geospacializados das Cavernas do Brasil (Geospacialized database of Brazil’s caves) (ICMBio). National Center of Caves Research and Conservation. <http://www.icmbio.gov.br/cecav/downloads/mapas.html>. Accessed 17 November 2018

CETESB (2011) Guia Nacional de Coleta e Preservação de Amostras: água, sedimento, comunidades aquáticas e efluentes líquidos (National Guide for Collection and Preservation of Samples: water, sediment, aquatic communities and liquid effluents). Environmental Agency of the State of São Paulo: CETESB, Brasília: ANA, 2011, 326 p

Chen, Z., Auler, A.S., Bakalowicz, M. et al. (2017) The World Karst Aquifer Mapping project: concept, mapping procedure and map of Europe. Hydrogeology Journal. 25: 771. https://doi.org/10.1007/s10040-016-1519-3.

Cook P, Love A, Robinson N, Simmons C (2005) Groundwater ages in fractured rock aquifers. J. Hydrol. 308, 284–301

Correa MCP (2018) The karst under surface analyses: fragility, anthropism and urban and environmental planning in the Lagoa Santa, MG, karstic region. Doctorate Thesis, Federal University of Minas Gerais

Custodio E., Llamas M.R. (Eds.). 2001. Hidrologia subterrânea. (Underground hydrology) Barcelona, Omega, 2350 p

Dardene MA (1978) Synthesis on the stratigraphy of Bambuí Group in Central Brazil. Brazilian Congress of Geology, 30, Recife. Annals Recife: Brazilian Society of Geology, 1978 v.2, pp 597–610

Doerfliger N (1996) Advances in Karst Groundwater Protection Strategy using Artificial Tracer Tests Analysis and Multi-Attribute Vulnerability Mapping (EPIK method). – Ph.D. thesis Univ. Neuchâtel, 308 p

Doerfliger N, Zwahlen F (1997) EPIK: a new method for outlining of protection areas in karstic environment. Rotterdam: in: International symposium and field seminar on karst waters and environmental impacts, pp 117-123

Doerfliger N, Zwahlen F (1998) Groundwater Vulnerability Mapping in Karstic Regions (EPIK), Practical Guide. Swiss Agency for the Environment. Forests and Landscape (SAEFL). Berne

Doerfliger, N., Jeannin, P. Y., and Zwahlen, F. (1999). Water vulnerability assessment in karst environments: a new method of defining protection areas using a multi-attribute approach and GIS tools (EPIK method). Environmental Geology, 39(2), 165-176

Domagalski JL, Johnson H (2012) Phosphorus and Groundwater: Establishing Links Between Agricultural Use and Transport to Streams: U.S. Geological Survey Fact Sheet 2012-3004, 4 p https://pubs.usgs.gov/fs/2012/3004/ Accessed 18 October 2018

Ducci D, de Melo MTC, Preziosi E, Sellerino M, Parrone D, Ribeiro L (2016) Combining natural background levels (NBLs) assessment with indicator kriging analysis to improve groundwater quality data interpretation and management Science of the Total Environment 569: 569-584. doi: 10.1016/j.scitotenv.2016.06.184

Edmunds WM, Shand P (2008) Natural Groundwater Quality. Blackwell Publishing. doi: 10.1002/9781444300345

EMBRAPA (2013) Sistema Brasileiro de classificação de solos SiBCS (Brazilian System of soil classification) (3rd Edition). Brazilian Agricultural Research Corporation. Brasília, Brazil

Entezari M, Yamani M, Aghdam MJ (2016) Evaluation of intrinsic vulnerability, hazard and risk mapping for karst aquifers, Hjorein aquifer, Kermanshah province: a case study. Environmental Earth Sciences 75(5): 435-445. doi: 10.1007/s12665-016-5258-5

European Commission (1995) Hydrogeological Aspects of Groundwater Protection in Karstic Areas. Report EUR 16547 EN, Brussels, 446 p

Feitosa FAC, Manoel Filho J., Feitosa EC., Demetrio JGA. (Eds.) (2008) Hidrogeologia: conceitos e aplicações. (Hydrogeology: concepts and applications) 3. ed. Rio de Janeiro, CPRM, 812 p

Ford DC, Williams PW. (Eds.) (2007) Karst Geomorphology and Hidrology. 2. ed. Chichester, NY, Wiley, 562 p

Forti P (2002) Speleology in the Third Millennium: achievements and challenges. Theoretical and Applied Kartology. 15,7-26

Foster S, Hirata R, Gomes D, D'Elia M, Paris M (2006) Proteção da qualidade da água subterrânea: um guia para empresas de abastecimento de água, órgãos municipais e agências ambientais. Groundwater Management Advisory Team (GW Mate). Banco Mundial, Washington, D.C, 104 p

Fritz P (1997) Saline groundwater and brines in crystalline rocks: the contributions of John Andrews and Jean-Charles Fontes to the solution of a hydrogeological and geochemical problem. Appl. Geochem. 12, 851–856

Galvão PHF (2015) Hydrogeological Conceptual Model of Sete Lagoas (MG) and Associated Implications of Urban Development in Karst Region. Doctorate Thesis, São Paulo University

Galvão P, Hirata R, Cordeiro A, Osório DB, Peñaranda J (2016) Geologic conceptual model of the municipality of Sete Lagoas (MG, Brazil) and the surroundings. Anais da Academia Brasileira de Ciências 88(1):35–53 <http://www.teses.usp.br/teses/disponiveis/44/44138/tde-22092015-151113/pt-br.php>. Accessed 07 July 2017

Galvão P, Hirata R, Halihan T, Terada R (2017) Recharge sourcesand hydrochemical evolution of an urban karst aquifer, Sete Lagoas, MG, Brazil. Environm Earth Sci 76:159

Gascoyne M, Kamineni DC (1994) The hydrogeochemistry of fractured plutonic rocks in the Canadian Shield. Hydrogeol. J. 2, 43–49

Gascoyne M (2004) Hydrogeochemistry, groundwater ages and sources of salts in agranitic batholith on the Canadian Shield, southeastern Manitoba. Appl. Geochem. 19, 519–560.

Golden Software (2017) A Basic Understanding of Surfer Gridding Methods – Part 1. https://support.goldensoftware.com/hc/en-us/articles/231348728-A-Basic-Understanding-of-Surfer-Gridding-Methods-Part-1#. Accessed 30 August 2018

Goldscheider N, Klute M, Sturm S, Hötzl H (2000) The PI method: a GIS-based approach to mapping groundwater vulnerability with special consideration of karst aquifers. Z Angew Geol 46 (3): pp 157-166

Goldscheider N (2002) Hydrogeology and Vulnerability of Karst Systems – Examples from the Northern Alps and Swabian Alp. – PhD thesis, University of Karlsruhe, 229 p.; Karlsruhe. <https://www.researchgate.net/profile/Nico_Goldscheider/publication/36451328_Hydrogeology_and_vulnerability_of_karst_systems_-_examples_from_the_Northern_Alps_and_the_Swabian_Alb_online/links/5716213e08aed2dd5cfceecf/Hydrogeology-and-vulnerability-of-karst-systems-examples-from-the-Northern-Alps-and-the-Swabian-Alb-online.pdf>. Accessed 18 February 2018

Goldscheider N, Drew D (2007) Methods in Karst Hydrogeology: international contributions to hydrogeology, 26. CRC Press, Boca Raton. ISBN: 978-0-415-42873-6

Gunarathna MHJP, Kumari N, Nirmanee KGS (2016). Evaluation of Interpolation Methods for Mapping pH of Groundwater. IJLTEMAS Vol. V, Issue III. ISSN 2278-2540. <https://www.researchgate.net/publication/299562961/download>. Accessed 30 August 2018

Hawkes HE, Webb JS (Eds.) (1962) Geochemistry in mineral exploration. New York, Joanna Cotler Books, 415 p

Hinsby K, Rasmussen ES (2008) The Miocene sand aquifers, Jutland, Denmark. In: Edmunds WM, Shand P (eds) Natural groundwater quality. Blackwell, Oxford, pp 306–334

IBAMA (1998) Série APA Carste de Lagoa Santa—MG (Carste de Lagoa Santa Series). Brazilian Institute of Environment and Renewable Natural Resource. http://www.cprm.gov.br/publique/Gestao-Territorial/Geodiversidade/Apa-Carste-de-Lagoa-Santa-594.html. Accessed 15 March 2015

ISPRA (2009) Protocollo per la Definizione dei Valori di Fondo per le Sostanze Inorganiche nella Acque Sotterranee. (Protocol for the definition of Natural Background Levels of Inorganic Substances in groundwater). Italian Institute for Environmental Protection and Research. <http://www.isprambiente.gov.it/files/temi/fondo-metalli-acque-sotterranee.pdf>. Accessed 10 July 2017

Jones WK (1977) Karst hydrology atlas of West Virginia. Special Publication 4, Karst Waters Institute, Charles Town, West Virginia, 111 p

Karmann (1994) Evolução e dinâmica atual do sistema cárstico do alto vale do rio Ribeira de Iguape, sudeste do Estado de São Paulo. (Evolution and current karstic system dynamic of the valley of Ribeira de Iguape river, southeast of São Paulo state. Doctoral Thesis, São Paulo University. <http://www.teses.usp.br/teses/disponiveis/44/44134/tde-22042013-163755/pt-br.php>. Accessed 18 August 2018

Kämpf N, Giasson E, Junior AVI, do Nascimento PC, Rodrigues ALM, Anghinoni MCM, Ferraro LW, Binotto RB Sanberg JRD (2008) Metodologia para classificação de solos quanto à resistência a impactos ambientais decorrentes da disposição final de resíduos. (Methodology for the soil classification to the environmental impacts resistance from the final solid waste disposal). Fepam em Revista: revista da Fundação Estadual de Proteção Ambiental Henrique Luís Roessler/FEPAM – vol. 1, n.1. ISSN 1982-2162 <http://www.fepam.rs.gov.br/fepamemrevista/downloads/Revista_2008_BAIXA.pdf> Accessed 19 October 2018

Kaufmann G, Romanov D, Hiller T (2010) Modeling three-dimensional karst aquifer evolution using different matrix-flow contributions. Journal of Hydrology, 16(2008): 399-403. doi: 10.1016/j.jhydrol.2010.05.001

Ker JC (1995) Latossolos do Brasil: Uma Revisão. Latosols of Brazil: a revision. Geonomos 5(1):17-40. ISSN 0104-4486 <http://www.igc.ufmg.br/geonomos/PDFs/5_1_17_40_Ker.pdf>. Cited 18 Oct 2018

Leal JR (1971) Adsorção de fosfato em latossolos sob cerrado. Phosphate adsorption in latosols in Cerrado (tropical savanna ecoregion). Master Dissertation, Rural Federal University of Rio de Janeiro

Lóaiciga HA (2008) Aquifer storage capacity and maximum annual yield from long-term aquifer fluxes. Hydrogeology Journal, 16(2008): 399-403. doi: 10.1007/s10040-007-0270-1

Lucon TN, Costa AT, Galvão P, Leite MGP (2018) Natural background levels and seasonal influence on groundwater chemistry of the upper São Francisco karst region, MG, Brazil. Brazilian Journal of Geology XX(X): 1-13. doi: 10.1590/2317-4889201820180071

Mourão M, Cruz W, Gonçalves R (2001) Caracterização hidrogeológica da porção mineira da Bacia Hidrográfica do São Francisco. (Hydrogeological characterization of the mineira portion of São Francisco watershed). In: Bacia do São Francisco: geologia e recursos naturais. SGB-MG, Belo Horizonte, pp 327-349

Mudarra M, Andreo B (2011) Relative importance of the saturated and the unsaturated zones in the hydrogeological functioning of karst aquifers: The case of Alta Cadena (Southern Spain). Journal of Hydrology 397(3-4): 263-280. doi: 10.1016/j.jhydrol.2010.12.005

Mullaney JR, Lorenz DL, Arntson AD (2009) Chloride in groundwater and surface water in areas underlain by the glacial aquifer system, northern United States: U.S. Geological Survey Scientific Investigations Report 2009–5086, 41 p. <https://pubs.usgs.gov/sir/2009/5086/pdf/sir2009-5086.pdf>. Accessed 03 October 2018

Müller D., Blum A., Hart A., Hookey J., Kunkel R., Scheidleder A., Tomlin C., Wendland F. 2006. D18: Final proposal for a methodology to set up groundwater threshold values in Europe. BRIDGE. Available at: <http://cordis.europa.eu/result/rcn/51965_en.html>. Accessed 18 April 2018

Nolan BT, Ruddy BC, Hitt KJ, Helsel DR (1998) Water Conditioning and Purification v. 39, no. 12, pp 76-79. <https://water.usgs.gov/nawqa/nutrients/pubs/wcp_v39_no12/>. Accessed 03 October 2018

Novais RF, Neves JCL, Barros NF (1991) Aspectos físico-químicos envolvidos na fixação de fósforo no solo. (Physicochemical aspects involved in the soil fixation of phosphate) In: Encontro Nacional de Rocha Fosfática, 5, São Paulo pp 133-177

Oliveira MAM (1967) Contribution to the geology of the southern part of the São Francisco Basin and adjacent areas. Collection of Reports Exploration, Rio de Janeiro 1: Petrobras, n.3, pp 71–105

Pessoa, PFP. Aspectos Hidrogeológicos na Região Cárstica de Sete Lagoas - Lagoa Santa, com Enfase a Qualidade das Aguas Subterraneas. In: Simpósio situação ambiental e qualidade de vida na região metropolitana de Belo Horizonte e Minas Gerais, II. 1992. Belo Horizonte. Anais. Belo Horizonte: 1992. p.87-89.

Pessoa PFP (2005) Hidrogeologia dos aqüíferos cársticos cobertos de Lagoa Santa, MG (Hydrogeology of the Lagoa Santa, MG, covered karstic aquifers). Doctorate thesis, Federal University of Minas Gerais. <http://www.bibliotecadigital.ufmg.br/dspace/handle/1843/ENGD-6LBJ3W>. Accessed 07 June 2017

Piló L (1998) Morfologia cárstica e materiais constituintes: Dinâmica e evolução da Depressão Poligonal Macacos - Baú - Carste de Lagoa Santa, Minas Gerais. Dynamic and evolution of Polygonal Depression Macacos – Baú – Lagoa Santa Karst, Minas Gerais. Doctorate thesis, São Paulo University

Reimann C, Filzmoser P, Garret RG (2005) Background and threshold comparison of methods of determination. Science of the total environmental 346(1-3): 1-16. doi: 10.1016/j.scitotenv.2004.11.023

Ribeiro JH, Tuller MP, Danderfer Filho A (2003) Geological mapping of the region of Sete Lagoas, Pedro Leopoldo, Matozinhos, Lagoa Santa, Vespasiano, Capim Branco, Prudente de Morais, Confins and Funilândia, Minas Gerais State, Brazil (scale1:50,000). 2nd ed. Belo Horizonte. 54 p

Ribeiro CG, Meireles CG, Lopes NHB, Arcos REC (2016) Levantamento Geológico Estrutural Aplicado aos Fluxos dos Aquíferos Cárstico-Fissurais da Região da APA Carste de Lagoa Santa, Minas Gerais. Structural Geological assessment applied to Fractured-karstic aquifers flows of Lagoa Santa Karst region, Minas Gerais. Bachelor thesis, Federal University of Minas Gerais. <http://www.igc.ufmg.br/images/igc/biblioteca/TG112.pdf>. Accessed 07 Jun 2017

Romero FM, Armienta MA, González-Hernández G (2006) Solid-phase control on the mobility of potentially toxic elements in an abandoned lead/zinc tailings impoundment, Taxco, Mexico. Applied Geochemistry, 22(2007): 109-127. doi: 10.1016/j.apgeochem.2006.07.017

Schöll WU, Fogaça ACC (1973) Stratigraphy of the Espinhaço in the Diamantina region. In: Symposium on Geology of Minas Gerais State, Brazil, 1. Acts. Belo Horizonte: Brazilian Geology Society, [Bulletin. 1], pp 55–73

Smellie J, Laaksoharju M, Wikberg P (1995) Äspö, SE Sweden: a natural groundwater flow model derived from hydrogeochemical observations. J. Hydrol. 172, 147–169.

Stober I, Bucher K (1999) Deep groundwater in the crystalline basement of the Black Forest region. Appl. Geochem. 14, 237–254

Tayer TC (2016) Avaliação da Vulnerabilidade Intrínseca do Aqüífero Cárstico da APA de Lagoa Santa MG, Utilizando o Método COP. Intrinsic Vulnerability Assessment of Lagoa Santa Protection Unit Karst Aquifer, using COP Method. Master Thesis, Federal University of Minas Gerais. <http://www.bibliotecadigital.ufmg.br/dspace/handle/1843/IGCC-AHENHV>. Accessed 08 September 2018

Tayer TC, Velásquez, LNM (2017) Assessment of intrinsic vulnerability to the contamination of karst aquifer using the COP method in the Carste Lagoa Santa Environmental Protection Unit, Brazil. Environmental Earth Sciences, 76(13): 445. doi: 10.1007/s12665-017-6760-0

Tedd K, Coxon C, Misstear B, Daly D, Craig M, Mannix A, Williams TH (Eds.). 2017. Assessing and developing Natural Background Levels for chemical parameters in Irish groundwater. Wexford, Environmental Protection Agency. 183 p

Toran L (1987) Sulfate contamination in groundwater from a carbonate-hosted mine. Journal of Contaminant Hydrology, 2(1987): 1-29. <https://ac.els-cdn.com/0169772287900027/1-s2.0-0169772287900027-main.pdf?_tid=68212efa-507a-47cb-b049-fbd60c215274&acdnat=1538579849_9e269b5687c057565e5a9a091f869844>. Accessed 03 Oct 2018

Tuller MP, Ribeiro JH, Signorelli N, Féboli WL, Pinho JMM (2010) Sete Lagoas—Abaeté Project, Minas Gerais State, Brazil. 6 geological maps, scale 1:100.000 (Geology Program of Brazil), 160p

USGS (2006) National Field Manual for the Collection of Water-Quality Data. Chapter A4 - Collection of Water Samples. United States Geological Survey. <https://water.usgs.gov/owq/FieldManual/chapter4/pdf/Chap4_v2.pdf>. Accessed 28 Aug 2018

USGS (2016) Contaminants Found in Groundwater. United States Geological Survey <https://water.usgs.gov/edu/groundwater-contaminants.html>. Accessed 03 Oct 2018

Van Beynen P, Townsend K (2005) A disturbance index for karst environments. Environ Manage. Jul; 36(1):101-16. DOI: 10.1007/s00267-004-0265-9

Vías JM, Andreo B, Perles MJ, Carrasco F, Vadillo I, Jiméniz P (2002) Preliminary proposal of a method for contamination vulnerability mapping in carbonate aquifers. In: Carrasco F,Duran JJ, Andreo B (eds) Karst and environment, 2nd Nerja cave geological symposium, Nerja, Spain, pp 75–83

Vías JM, Andreo B, Perles MJ, Carrasco F, Vadillo I, Jiméniz P (2006). Proposed method for groundwater vulnerability mapping in carbonate (karstic) aquifers. Hydrogeology Journal, 14(6) 912-925. doi: 10.1007/s10040-006-0023-6

Vicq R, Matschullat J, Leite MGP, Junior HAN, Mendonça FPC (2015). Iron Quadrangle stream sediments, Brazil: geochemical maps and reference values. Environmental Earth Sciences, 74:4407-4417. doi: 10.1007/s12665-015-4508-2

Vieira LCM (2018) Hidrogeoquímica dos Aquíferos da Região da APA Carste de Lagoa Santa, MG. Master Thesis, Federal University of Minas Gerais

Vieira LCM, Dussin TM, Velásquez LNM (2018). Geoquímica e condições paleoambientais de deposição das rochas carbonáticas da Formação Sete Lagoas na região da Área de Proteção Ambiental Carste de Lagoa Santa, MG. Geochimica Brasiliensis, 31(1) 1-19. doi: 10.21715/GB2358-2812.2018321001

White WB (1988) Geomorphology and hydrology of karst terrains. Oxford Univ. Press, New York. 464 p.

Zhang Y, Wu J, Xu B (2018) Human health risk assessment of groundwater nitrogen pollution in Jinghui canal irrigation area of the loess region, northwest China. Environmental Earth Sciences, 77(273): 445. doi: 10.1007/s12665-018-7456-9

Zwahlen F (ed) (2003) Vulnerability and risk mapping for the protection of carbonate (karst) aquifers, final report (COST action 620). European Commission, Brussels. ISBN: 92-894-6416-X

APPENDIX

Table 1 – Inorganic parameters results for collected deep tubular wells. **Part one** (from Dissolved Ca^{2+} to Cl^{-})

	Point	Dissolv. Ca^{2+}	HCO_3^- Alcalinity	Dissolv. SiO_2	Dissolv. Mg^{2+}	SO_4^{2-}	Cl^-
	Unit	mg Ca/L	mg $CaCO_3$/L	mg SiO2/L	mg Mg/L	mg SO_4/L	mg Cl/L
	Max. Permit (Brasil 2014)	-	-	-	-	250	250
Date	VMP 01*	-	-	-	-	250	250
15/12/17	00062-2009	64.3	205	12.4	2.54	4.90	<1
28/12/17	00069-PT	119	262	5.12	0.49	1.69	<1
19/2/18	00086-2008	92.3	209	13.5	0.91	<1	<1
29/11/17	00215-2008	52.6	152	12.4	4.42	<1	<1
11/10/17	00301-2007	21.2	103	49.9	7.41	<1	<1
19/2/18	00824-2003	77.6	175	11.7	2.02	<1	1.94
24/10/17	00886-2002	15.8	67.8	61.2	5.29	<1	<1
7/2/18	01360-2009	96.7	206	7.75	0.37	<1	<1
7/2/18	01361-2009	91.0	193	10.6	0.81	<1	<1
11/10/17	01378-2003	22.7	87.7	34.5	5.04	<1	<1
12/12/17	01584-2008	20.0	108	32.1	5.54	<1	7.48
6/12/17	02289-2009	65.3	131	5.81	3.17	6.83	18.7
8/12/17	03057-PT	37.4	99.3	14.5	6.35	<1	<1
13/12/17	03070-PT	82.8	238	14.3	6.76	2.26	3.69
15/10/17	03075-PT	34.7	81.7	10.4	1.12	<1	1.38
15/10/17	03086-PT	17.0	57.2	9.54	1.50	<1	<1
6/12/17	03088-PT	27.8	70.2	10.8	2.67	<1	<1
6/12/17	03100-PT-2	0.26	7.0	9.80	<0.25	<1	1.48
1/12/17	03104-PT	62.5	173	8.50	1.05	<1	1.49
13/12/17	03127-PT	80.1	215	6.51	0.61	1.78	1.58
5/12/17	03136-PT	115	227	9.02	0.70	1.11	<1
11/1/18	03140-PT	104	233	8.72	0.64	1.32	<1
12/10/17	03151-PT	79.3	169	9.89	0.97	<1	<1
19/12/17	03171-PT	62.7	177	14.2	4.05	<1	<1
24/10/17	03174-PT	72.4	173	9.54	1.86	<1	<1
5/11/17	03196-PT	88.2	213	10.7	2.08	4.10	<1
12/10/17	03206-PT	79.6	180	8.50	2.82	11.2	1.48
16/11/17	03208-2009	39.2	76.2	28.8	5.34	<1	<1
21/12/17	03233-2009	53.2	156	12.1	3.92	<1	<1
5/2/18	03246-PT	169	358	8.24	0.98	3.80	1.24
19/2/18	03490-PT	101	238	14,4	4,80	4,81	9,09
11/10/17	04493-2008	24.0	80.9	38.8	7.29	3.73	6.44
7/12/17	05010-2007	58.8	168	23.0	5.88	2.82	<1
12/12/17	05612-2006	13.9	37.3	26.2	2.22	<1	<1
25/10/17	07139-2010	81.2	187	9.37	1.23	2.56	<1
24/10/17	07543-2010	15.2	79.4	75.0	6.40	1.39	<1
26/4/18	07973-2009	133	262	6.96	0.50	<1	<1
7/2/18	08691-2007	102	241	15.3	7.12	2.38	<1
5/12/17	08767-2011	65.8	151	10.3	4.78	<1	1.83
26/4/18	09040-2013	80.3	260	10.4	1.31	2.69	<1
22/12/17	09722-2010	81.4	178	9.33	0.89	<1	1.37
9/11/17	09936-2008	44	125	23.6	2.68	3.03	<1
7/2/18	11056-2009	70.7	173	15.3	4.40	<1	<1
13/12/17	11109-2010	73.6	203	18.9	3.24	2.07	3.18
9/11/17	113-PT	74.6	203	6.16	2.91	5.51	<1
5/2/18	12074-2009	65.7	151	25.9	4.52	1.63	1.32
12/1/18	12266-2008	26.0	83.2	23.0	4.71	<1	<1
6/3/18	12268-2008	26.3	72,1	12.3	1.56	<1	<1
5/12/17	12326-2008	63.7	171	26.9	4.11	2.87	<1
15/12/17	13297-2008	65.5	197	10.8	1.15	3.90	<1
1/12/17	14212-2010	39.8	122	5.12	<0.25	<1	<1
29/11/17	14314-2009	75.1	209	21.9	4.21	3.30	<1
22/12/17	15281-2010	61.4	187	16.1	9.93	11.5	<1
13/12/17	20198-PT	77.2	208	10.8	3.73	9.02	7.61
17/12/17	C-01-ALS	59.8	176	18.9	1.68	<1	<1
20/12/17	C-01-FPL	77.9	202	8.85	1.96	1.82	<1
14/12/17	C-01-LLS	59.3	183	11.5	5.02	3.61	<1
15/12/17	C-01-SM	51.5	163	16.5	3.26	1.85	8.25
18/12/17	C-02-CP	66.9	176	18.8	0.53	9.83	<1
14/12/17	C-03-SC	54.7	162	9.98	1.35	<1	<1
17/12/17	C-04-SC	54.5	168	17.5	2.40	<1	<1
15/12/17	C-04-SM	45.7	129	5.64	2.92	2.55	2.87
17/12/17	C-08-ALS	58.6	159	18.6	1.78	1.33	1.47
17/12/17	C-09-ALS	66.1	188	19.3	2.36	6.98	3.97
14/12/17	C-13-LSL	55.1	156	8.24	1.10	<1	<1

7/2/18	Curral	98.9	203	10.4	1.27	<1	3.06
15/12/17	E-01-BSM	53.9	164	19.0	2.34	1.57	<1
15/12/17	E-02-BSM	52.7	153	18.3	1.27	<1	<1
4/12/17	HP5	76.0	176	11.9	2.86	1.06	<1
26/4/18	HP7	102	172	9.75	2.30	33.4	1.92
26/4/18	N09039	42.2	169	9.48	1.48	25.1	2.73
5/2/18	N12074-2009	82.9	210	27.9	5.58	4.45	<1
6/3/18	N12268-2008	25.5	72.8	11.8	1.51	1.69	<1
9/11/17	N1413	31.5	95.9	29.7	2.91	6	<1
5/1/18	N15	<0.25	<6	4.95	<0.25	<1	<1
28/12/17	N2340	88.8	214	5.99	0.86	1.79	4.12
10/11/17	N26	73.3	210	8.59	4.26	1.24	<1
4/12/17	N3	24.9	108	44.2	6.27	<1	<1
2/11/17	N30	72.1	177	12.0	2.14	1.45	<1
2/11/17	N3031	27.1	77.5	17.6	1.67	<1	<1
2/11/17	N32	70.5	173	10.5	1.54	<1	<1
10/11/17	N3233	56.8	165	18.9	2.64	1.77	<1
2/11/17	N33	56.5	158	25.4	4.14	5.39	<1
19/2/18	N3490	97.9	235	16.6	4.65	4.82	9.15
29/11/17	N35-COP	40.6	115	28.8	2.04	1.43	<1
29/11/17	N36-COP	45.2	147	28.0	3.12	2.89	<1
25/10/17	N52	66.1	158	10.2	0.38	<1	<1
29/12/17	N53	62.8	124	7.59	<0.25	<1	<1
25/3/18	N8767	53.9	160	15.5	3.43	<1	<1

Table 1 – Inorganic parameters results for collected deep tubular wells. **Part two** (From Dissolved Na$^+$ to Sample Temperature)

	Point	Dissolv. Na$^+$	NO$_3^-$	PO$_4^{3-}$	Dissolv. K$^+$	Elect. Conduct.	Total Dissolv. Solids	Sample Temp.
	Unit	mg Na/L	Mg NO$_3^-$/L	mgPO$_4^{3-}$/L	mg K/L	µS/cm	mg TDS/L	ºC
	Max. Permit (Brasil 2014)	200	10	-	-	-	1000	-
Date	VMP 01*	-	-	-	-	-	500	-
15/12/17	00062-2009	4.77	<0.1	<0.02	0.44	411	248	24.4
28/12/17	00069-PT	<0.5	3.28	<0.02	<0.25	530	293	24.5
19/2/18	00086-2008	<0.5	0.33	0.06	0.29	400	229	26.4
29/11/17	00215-2008	0.62	<0.1	0.16	<0.25	294	162	24.4
11/10/17	00301-2007	10.3	0.31	0.17	1.02	195	144	24.5
19/2/18	00824-2003	3.18	2.71	0.04	0.29	356	196	23.4
24/10/17	00886-2002	12.7	4.30	0.07	1.45	145	130	23.3
7/2/18	01360-2009	<0.5	0.22	0.05	<0.25	388	220	24.6
7/2/18	01361-2009	<0.5	0.48	0.04	0.50	369	215	24.7
11/10/17	01378-2003	5.75	<0.1	<0.02	0.90	162	93.0	23.5
12/12/17	01584-2008	15.3	0.11	<0.02	1.87	233	148	24.2
6/12/17	02289-2009	3.86	9.40	<0.02	0.68	352	208	27.5
8/12/17	03057-PT	0.58	<0.1	0.03	<0.25	191	113	23.5
13/12/17	03070-PT	2.34	4.46	<0.02	0.25	474	264	24.6
15/10/17	03075-PT	1.03	3.47	<0.02	<0.25	172	95.5	24.3
15/10/17	03086-PT	<0.5	<0.1	<0.02	<0.25	113	63.0	24.1
6/12/17	03088-PT	0.79	0.63	<0.02	<0.25	139	95.0	25.4
6/12/17	03100-PT-2	4.04	1.80	<0.02	<0.25	28.4	18.8	25.7
1/12/17	03104-PT	1.35	2.55	0.08	<0.25	349	202	22.5
13/12/17	03127-PT	<0.5	1.91	<0.02	0.26	427	295	23.4
5/12/17	03136-PT	<0.5	3.16	<0.02	<0.25	434	247	24.5
11/1/18	03140-PT	<0.5	4.13	0.08	<0.25	474	287	25.3
12/10/17	03151-PT	<0.5	0.21	<0.02	<0.25	324	196	25
19/12/17	03171-PT	1.07	0.18	<0.02	<0.25	329	183	26.4
24/10/17	03174-PT	<0.5	0.22	0.14	<0.25	347	191	23.7
5/11/17	03196-PT	<0.5	1.32	0.05	0.25	433	247	23.6
12/10/17	03206-PT	1.13	2.62	0.09	0.53	380	233	25
16/11/17	03208-2009	4.83	<0.1	0.04	0.70	150	132	23.7
21/12/17	03233-2009	0.72	0.34	0.03	<0.25	307	193	24.3
5/2/18	03246-PT	<0.5	8.18	<0.02	0.31	645	371	23.8
19/2/18	03490-PT	12,3	25,9	0,04	1,11	521	277	25,5
11/10/17	04493-2008	8.04	3.49	0.05	1.22	201	133	24.3
7/12/17	05010-2007	3.25	<0.1	<0.02	3.89	323	178	23.9
12/12/17	05612-2006	1.72	0.83	0.11	0.35	81.7	55.0	24
25/10/17	07139-2010	<0.5	1.75	0.05	<0.25	368	219	26.4
24/10/17	07543-2010	7.75	0.22	0.05	1.24	164	134	24.4
26/4/18	07973-2009	<0.5	1.05	<0.02	<0.25	476	272	22.7
7/2/18	08691-2007	<0.5	0.58	0.05	0.37	448	274	23.2
5/12/17	08767-2011	1.53	19.2	<0.02	0.26	331	211	26.5
26/4/18	09040-2013	0.72	2.43	<0.02	<0.25	303	171	24.5
22/12/17	09722-2010	1.56	4.34	0.03	0.27	386	229	25
9/11/17	09936-2008	2.79	<0.1	<0.02	0.49	252	152	23.9

7/2/18	11056-2009	0.55	<0.1	<0.02	0.53	330	186	24.5
13/12/17	11109-2010	2.41	2.87	<0.02	0.35	415	244	24.4
9/11/17	113-PT	0.63	<0.1	<0.02	<0.25	398	220	23.6
5/2/18	12074-2009	4.98	0.74	<0.02	1.44	294	172	24.6
12/1/18	12266-2008	2.79	0.21	<0.02	0.54	173	110	25.6
6/3/18	12268-2008	<0.5	<0.1	0.05	<0.25	135	74.5	24.5
5/12/17	12326-2008	6.74	<0.1	<0.02	0.65	327	241	24.5
15/12/17	13297-2008	<0.5	<0.1	<0.02	0.37	390	216	23.9
1/12/17	14212-2010	<0.5	<0.1	<0.02	<0.25	240	134	24.5
29/11/17	14314-2009	6.41	<0.1	0.02	0.59	297	216	25.6
22/12/17	15281-2010	11.4	<0.1	<0.02	0.50	385	229	26.5
13/12/17	20198-PT	3.98	6.88	<0.02	0.73	445	248	24.2
17/12/17	C-01-ALS	<0.5	1.03	0.03	<0.25	348	192	24.8
20/12/17	C-01-FPL	0.78	4.48	0.10	0.26	385	219	24.8
14/12/17	C-01-LLS	<0.5	0.24	0.03	<0.25	354	195	24.5
15/12/17	C-01-SM	6.32	3.50	<0.02	1.35	377	226	22.7
18/12/17	C-02-CP	<0.5	2.70	0.05	<0.25	387	251	31.1
14/12/17	C-03-SC	<0.5	0.65	0.08	<0.25	309	186	24.9
17/12/17	C-04-SC	<0.5	0.33	0.02	<0.25	338	204	25.2
15/12/17	C-04-SM	3.48	0.32	0.04	1.01	313	181	N.A.
17/12/17	C-08-ALS	0.98	1.31	0.05	0.27	359	217	N.A.
17/12/17	C-09-ALS	2.31	3.77	0.16	0.62	403	234	24.4
14/12/17	C-13-LSL	0.89	1.14	0.05	0.25	320	177	24
7/2/18	Curral	0.72	6.73	0.03	1.53	389	225	25.2
15/12/17	E-01-BSM	1.88	3.08	0.05	<0.25	339	196	25.4
15/12/17	E-02-BSM	<0.5	1.10	0.09	<0.25	315	191	N.A.
4/12/17	HP5	<0.5	<0.1	<0.02	<0.25	337	207	24.6
26/4/18	HP7	1.36	4.30	<0.02	0.53	407	222	24.2
26/4/18	N09039	63.5	3.83	<0.02	0.62	373	245	24.2
5/2/18	N12074-2009	8.22	<0.1	<0.02	0.96	396	267	23.6
6/3/18	N12268-Duplicate	<0.5	<0.1	0.03	0.30	138	83.5	24.5
9/11/17	N1413	4.03	<0.1	<0.02	0.59	201	141	25.5
5/1/18	N15	<0.5	0.45	<0.02	<0.25	11.1	<11	23.3
28/12/17	N2340	1.81	7.47	<0.02	0.56	447	251	25.3
10/11/17	N26	2.09	1.79	<0.02	0.28	406	226	23.4
4/12/17	N3	12.3	0.90	<0.02	0.90	210	147	26.4
2/11/17	N30	1.43	2.08	0.11	0.60	357	196	24.5
2/11/17	N3031	2.26	1.14	0.09	0.98	162	122	24.5
2/11/17	N32	1.14	1.98	<0.02	<0.25	351	194	24.5
10/11/17	N3233	2.32	<0.1	0.19	0.45	311	172	24.1
2/11/17	N33	4.11	<0.1	<0.02	0.68	325	204	25.9
19/2/18	N3490-Duplicate	12.3	26.2	0.03	1.07	528	291	25.5
29/11/17	N35-COP	3.36	0.23	0.18	0.49	223	148	26.1
29/11/17	N36-COP	13.4	<0.1	0.03	0.54	289	172	26.6
25/10/17	N52	<0.5	0.66	0.02	<0.25	314	174	21.5
29/12/17	N53	<0.5	<0.1	0.10	<0.25	239	131	26.8
25/3/18	N8767	1.17	0.51	0.03	0.36	331	196	24.4

Table 2 – Ionic balance and error calculation

Sample	Dissolv. Ca^{2+} (Meq/L)	Bicarbonate (Meq/L)	Dissolv. Mg^{2+} (Meq/L)	Dissolv. K^{+} (Meq/L)	Dissolv. Na^{+} (Meq/L)	Cl^{-} (Meq/L)	SO_4^{2-} (Meq/L)	Cations Sum	Anions Sum	Error (%)
00062-2009	3.209	4.099	0.209	0.011	0.207	0.014	0.102	3.636	4.215	7.375
00069-PT	5.938	5.239	0.040	0.003	0.011	0.014	0.035	5.992	5.288	6.243
00086-2008	4.606	4.179	0.075	0.007	0.011	0.014	0.010	4.699	4.204	5.563
00215-2008	2.625	3.039	0.364	0.003	0.027	0.014	0.010	3.018	3.064	0.748
00301-2007	1.058	2.060	0.609	0.026	0.448	0.014	0.010	2.141	2.084	1.357
00824-2003	3.872	3.499	0.166	0.007	0.138	0.055	0.010	4.184	3.564	7.998
00886-2002	0.788	1.356	0.435	0.037	0.552	0.014	0.010	1.813	1.380	13.553
01360-2009	4.825	4.119	0.030	0.003	0.011	0.014	0.010	4.870	4.144	8.057
01361-2009	4.541	3.859	0.067	0.013	0.011	0.014	0.010	4.631	3.884	8.778
01378-2003	1.133	1.754	0.414	0.023	0.250	0.014	0.010	1.820	1.778	1.173
01584-2008	0.998	2.160	0.456	0.048	0.666	0.211	0.010	2.167	2.381	4.705
02289-2009	3.258	2.619	0.261	0.017	0.168	0.528	0.142	3.704	3.289	5.938
03057-PT	1.866	1.986	0.522	0.003	0.025	0.014	0.010	2.417	2.010	9.189
03070-PT	4.132	4.759	0.556	0.006	0.102	0.104	0.047	4.796	4.910	1.178
03075-PT	1.732	1.634	0.092	0.003	0.045	0.039	0.010	1.872	1.683	5.307
03086-PT	0.848	1.144	0.123	0.003	0.011	0.014	0.010	0.986	1.168	8.475
03088-PT	1.387	1.404	0.220	0.003	0.034	0.014	0.010	1.644	1.428	7.035
03100-PT-2	0.013	0.140	0.010	0.003	0.176	0.042	0.010	0.202	0.192	2.551
03104-PT	3.119	3.459	0.086	0.003	0.059	0.042	0.010	3.267	3.512	3.610
03127-PT	3.997	4.299	0.050	0.007	0.011	0.045	0.037	4.065	4.381	3.742
03136-PT	5.739	4.539	0.058	0.003	0.011	0.014	0.023	5.810	4.576	11.880
03140-PT	5.190	4.659	0.053	0.003	0.011	0.014	0.027	5.256	4.701	5.581
03151-PT	3.957	3.379	0.080	0.003	0.011	0.014	0.010	4.051	3.404	8.681
03171-PT	3.129	3.539	0.333	0.003	0.047	0.014	0.010	3.512	3.564	0.738
03174-PT	3.613	3.459	0.153	0.003	0.011	0.014	0.010	3.780	3.484	4.075
03196PT	4.401	4.259	0.171	0.006	0.011	0.014	0.085	4.590	4.359	2.581
03206-PT	3.972	3.599	0.232	0.014	0.049	0.042	0.233	4.267	3.874	4.821
03208-2009	1.956	1.524	0.439	0.018	0.191	0.014	0.010	2.604	1.548	25.422
03233-2009	2.655	3.119	0.322	0.003	0.031	0.014	0.010	3.012	3.144	2.149
03246-PT	8.433	7.158	0.081	0.008	0.011	0.035	0.079	8.533	7.273	7.972
03490-PT	5.040	4.759	0.395	0.028	0.535	0.256	0.100	5.998	5.116	7.941
04493-2008	1.198	1.618	0.600	0.031	0.350	0.182	0.078	2.178	1.877	7.425
05010-2007	2.934	3.359	0.484	0.100	0.141	0.014	0.059	3.659	3.432	3.194
05612-2006	0.694	0.746	0.183	0.009	0.075	0.014	0.010	0.960	0.770	10.957
07139-2010	4.052	3.739	0.101	0.003	0.011	0.014	0.053	4.167	3.807	4.521
07543-2010	0.758	1.588	0.526	0.032	0.337	0.014	0.029	1.654	1.631	0.699
07973-2009	6.637	5.239	0.041	0.003	0.011	0.014	0.010	6.692	5.263	11.948
08691-2007	5.090	4.819	0.586	0.009	0.011	0.014	0.050	5.696	4.883	7.686
08767-2011	3.283	3.019	0.393	0.007	0.067	0.052	0.010	3.750	3.081	9.784
09040-2013	4.007	5.199	0.108	0.003	0.031	0.014	0.056	4.149	5.269	11.890
09722-2010	4.062	3.559	0.073	0.007	0.068	0.039	0.010	4.210	3.608	7.694
09936-2008	2.196	2.499	0.220	0.013	0.121	0.014	0.063	2.550	2.577	0.522
11056-2009	3.528	3.459	0.362	0.014	0.024	0.014	0.010	3.927	3.484	5.984
11109-2010	3.673	4.059	0.266	0.009	0.105	0.090	0.043	4.053	4.192	1.687
113-PT	3.723	4.059	0.239	0.003	0.027	0.014	0.115	3.992	4.188	2.390
12074-2009	3.278	3.019	0.372	0.037	0.217	0.037	0.034	3.904	3.091	11.625
12268-2008	1.312	1.442	0.128	0.003	0.011	0.014	0.010	1.455	1.466	0.393
12326-2008	3.179	3.419	0.338	0.017	0.293	0.014	0.060	3.826	3.493	4.554
13297-2008	3.268	3.939	0.095	0.009	0.011	0.014	0.081	3.383	4.034	8.778
14212-2010	1.986	2.439	0.010	0.013	0.011	0.014	0.010	2.020	2.464	9.909
14314-2009	3.747	4.179	0.346	0.003	0.279	0.014	0.069	4.376	4.262	1.318
15281-2010	3.064	3.739	0.817	0.013	0.496	0.014	0.239	4.389	3.993	4.730
20198-PT	3.852	4.159	0.307	0.019	0.173	0.215	0.188	4.351	4.562	2.365
C-01-ALS	2.984	3.519	0.138	0.003	0.011	0.014	0.010	3.136	3.544	6.101
C-01-FPL	3.887	4.039	0.161	0.007	0.034	0.014	0.038	4.089	4.091	0.027
C-01-LLS	2.959	3.659	0.413	0.003	0.011	0.014	0.075	3.386	3.748	5.081
C-01-SM	2.570	3.259	0.268	0.035	0.275	0.233	0.039	3.147	3.531	5.738
C-02-CP	3.338	3.519	0.044	0.003	0.011	0.014	0.205	3.396	3.738	4.795
C-03-SC	2.730	3.239	0.111	0.003	0.011	0.014	0.010	2.855	3.264	6.688
C-04-SC	2.720	3.359	0.197	0.003	0.011	0.014	0.010	2.931	3.384	7.171
C-04-SM	2.280	2.579	0.240	0.026	0.151	0.081	0.053	2.698	2.714	0.291
C-08-ALS	2.924	3.179	0.146	0.007	0.043	0.041	0.028	3.120	3.248	2.017
C-09-ALS	3.298	3.759	0.194	0.016	0.100	0.112	0.145	3.609	4.017	5.347
C-13-LSL	2.749	3.119	0.090	0.006	0.039	0.014	0.010	2.885	3.144	4.293
Curral	4.935	4.059	0.104	0.039	0.031	0.086	0.010	5.110	4.156	10.297
E-01-BSM	2.690	3.279	0.192	0.003	0.082	0.014	0.033	2.967	3.326	5.706
E-02-BSM	2.630	3.059	0.104	0.003	0.011	0.014	0.010	2.748	3.084	5.755
HP5	3.792	3.519	0.235	0.003	0.011	0.014	0.022	4.042	3.555	6.400
HP7	5.090	3.439	0.189	0.014	0.059	0.054	0.695	5.352	4.189	12.188
N09039	2.106	3.379	0.122	0.016	2.762	0.077	0.523	5.006	3.979	11.428
N12074-2009	4.137	4.199	0.459	0.025	0.358	0.014	0.093	4.978	4.306	7.237
N12268-2008	1.272	1.456	0.124	0.008	0.011	0.014	0.035	1.415	1.505	3.075
N1413	1.572	1.918	0.239	0.015	0.175	0.014	0.125	2.002	2.057	1.357

N15	0.006	0.060	0.010	0.003	0.011	0.014	0.010	0.031	0.085	46.843
N2340	4.431	4.279	0.071	0.014	0.079	0.116	0.037	4.595	4.433	1.798
N26	3.658	4.199	0.350	0.007	0.091	0.014	0.026	4.106	4.239	1.593
N3	1.243	2.160	0.516	0.023	0.535	0.014	0.010	2.316	2.184	2.937
N30	3.598	3.539	0.176	0.015	0.062	0.014	0.030	3.851	3.584	3.602
N3031	1.352	1.550	0.137	0.025	0.098	0.014	0.010	1.613	1.574	1.218
N32	3.518	3.459	0.127	0.003	0.050	0.014	0.010	3.697	3.484	2.974
N3233	2.834	3.299	0.217	0.012	0.101	0.014	0.037	3.164	3.350	2.861
N33	2.819	3.159	0.343	0.017	0.179	0.014	0.112	3.358	3.286	1.096
N3490	4.885	4.699	0.382	0.027	0.535	0.258	0.100	5.830	5.057	7.096
N35-COP	2.026	2.300	0.168	0.003	0.146	0.014	0.030	2.343	2.343	0.007
N36-COP	2.255	2.939	0.257	0.014	0.583	0.014	0.060	3.109	3.014	1.554
N52	3.298	3.159	0.031	0.003	0.011	0.014	0.010	3.344	3.184	2.449
N53	3.134	2.479	0.010	0.003	0.011	0.014	0.010	3.158	2.504	11.552
N8767	2.690	3.199	0.282	0.009	0.051	0.014	0.010	3.032	3.224	3.070

Table 2 – Organic parameters results for collected deep tubular wells. **Part one** (From 0824-2003 to 03136 LSL)

		Max. Permitted	11/10/17	12/10/17	24/10/17	5/11/17	10/11/17	16/11/17	29/11/17	1/12/17	4/12/17	5/12/17	5/12/17
Parameter	Unit	(BRASIL 2008)	0824-2003	03206-PT	07543-2010	03196-PT	N3233	03208-2009	00215-2008	03104-PT	HP5	12326-2008	03136
1,1,1,2-Tetracloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1,1-Tricloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1,2,2Tetracloroetan	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1,2-Tricloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1-Dicloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1-Dicloroeteno	µg/L	3	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1-Dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2,3Triclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2,3Tricloropropano	µg/L	-	<5	<5	<1	<5	<5	<5	<5	<5	<5	<5	<5
1,2,4Triclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2,4Trimetilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dibromoetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloroetano	µg/L	10	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloropropano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,3,5-Triclorobenzen	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,3,5-Trimetilbenzen	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,3-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,3-Dicloropropano	µg/L	-	<5	<5	<1	<5	<5	<5	<5	<5	<5	<5	<5
1,4-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,2-Dicloropropano	µg/L	-	<1	<1	<5	<1	<1	<1	<1	<1	<1	<1	<1
2-Clorotolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4-Clorotolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4-Metil-2-Pentanona	µg/L	-	<5	<5	<1	<5	<5	<5	<5	<5	<5	<5	<5
Alaclor	µg/L	20	<0.005	<0.005	<1	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Aldrin	µg/L	-	<0.0015	<0.0015	<1	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
alfa-BHC	µg/L	-	<0.1	<0.1	<1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Atrazina	µg/L	2	<0.005	<0.005	<1	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Bentazona	µg/L	-	<0.05	<0.05	<1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Benzeno	µg/L	5	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Benzidina	µg/L	0.001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
beta-BHC	µg/L	-	<0.1	<0.1	<1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bromobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Bromoclorometano	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Bromodiclorometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Bromofórmio	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Bromometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cis-1,2-Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Clordano - alfa	µg/L	-	<0.0015	<0.0015	<1	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Clordano - gama	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Clordano (Isômeros)	µg/L	0.04	<0.003	<0.003	<1	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Cloreto de Vinila	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Clorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Clorofórmio	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Clorometano	µg/L	-	<10	<10	<1	<10	<10	<10	<10	<10	<10	<10	<10
delta-BHC	µg/L	-	<0.1	<0.1	<1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dibromoclorometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dibromometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

Diclorometano	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dieldrin	µg/L	-	<0.0015	<0.0015	<1	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Dissulfeto de C.	µg/L	-	<1	<1	<5	<1	<1	<1	<1	<1	<1	<1	<1
Mirex	µg/L	0.001	<0.001	<0.001	<1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Endosulfan Sulfato	µg/L	-	<0.0015	<0.0015	<1	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endosulfan1	µg/L	-	<0.0015	<0.0015	<1	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endosulfan2	µg/L	-	<0.0015	<0.0015	<1	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endrin	µg/L	0.004	<0.0015	<0.0015	<1	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endrin Aldeido	µg/L	-	<0.005	<0.005	<1	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Estireno	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Etilbenzeno	µg/L	90	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptacloro	µg/L	-	<0.0015	<0.0015	<1	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Hexaclorobenzeno	µg/L	0.0065	<0.005	<0.005	<1	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Hexaclorobutadieno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Isopropilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Lindano	µg/L	0.02	<0.0015	<0.0015	<1	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
m,p-Xilenos	µg/L	300	<2	<2	<1	<2	<2	<2	<2	<2	<2	<2	<2
Metolacloro	µg/L	10	<0.005	<0.005	<1	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Metoxicloro	µg/L	0.03	<0.0015	<0.0015	<1	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Molinato	µg/L	-	<0.005	<0.005	<1	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Naftaleno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
n-butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
n-propilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
o-Xileno	µg/L	300	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
DDT+DDE+DDD	µg/L	0.002	<0.002	<0.002	<1	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Pendimetalina	µg/L	-	<0.005	<0.005	<1	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Permetrina	µg/L	-	<0.5	<0.5	<1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
p-Isopropiltolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Propanil	µg/L	-	<0.5	<0.5	<1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sec-Butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Simazina	µg/L	2	<0.5	<0.5	<1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Temperature(env.)	ºC	-	32.2	32.5	29.6	24.8	22.1	23.3	28.1	N.A.	23	28.8	29
Temperature(sample)	ºC	-	23.5	25	24.4	23.6	24.1	23.7	24.4	N.A.	24.6	24.5	24.5
Terc-butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Tetracloreto de C.	µg/L	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Tetracloroeteno	µg/L	10	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Tolueno	µg/L	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Toxafeno	mg/L	0.01	<0.00001	<0.00001	<0.0001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
Trans - Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Triclorobenzenos	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1	<1	N.A.	<1
Tricloroeteno	µg/L	30	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Trifluralina	µg/L	0.2	<0.05	<0.05	<1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<1	<0.05
Trihalometanos	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<0.05	<1
Xileno	µg/L	300	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

Table 2 – Organic parameters results for collected deep tubular wells. **Part two** (from 03088-PT to C13-LSL)

		Max. Permitted (BRASIL 2008)	6/12/17	6/12/17	6/12/17	7/12/17	8/12/17	12/12/17	13/12/17	13/12/17	13/12/17	14/12/17	14/12/17
Parameter	Unit		03088PT	03100-PT2	02289.2009	05010.2017	03057-PT	05612/2006	03490PT	11/092010	20198-PT	C03SC	C13 LSL
1,1,1,2Tetracloroetan	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1,1-Tricloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1,2,2Tetracloroetan	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1,2-Tricloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1-Dicloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1-Dicloroeteno	µg/L	3	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,1-Dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2,3-Triclorobenzen	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2,3-Tricloropropan	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
1,2,4-Triclorobenzen	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2,4-Trimetilbenzen	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dibromoetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloroetano	µg/L	10	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloropropano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,3,5-Triclorobenzen	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,3,5-Trimetilbenzen	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,3-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
1,3-Dicloropropano	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
1,4-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2,2-Dicloropropano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
2-Clorotolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

4-Clorotolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
4-Metil-2-Pentanona	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Alaclor	µg/L	20	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Aldrin	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
alfa-BHC	µg/L	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Atrazina	µg/L	2	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Bentazona	µg/L	-	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Benzeno	µg/L	5	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Benzidina	µg/L	0.001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
beta-BHC	µg/L	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bromobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Bromoclorometano	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
Bromodiclorometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Bromofórmio	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Bromometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cis-1,2-Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Clordano - alfa	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Clordano - gama	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Clordano (Isômeros)	µg/L	0.04	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Cloreto de Vinila	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Clorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Clorofórmio	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Clorometano	µg/L	-	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
delta-BHC	µg/L	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dibromoclorometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dibromometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Diclorometano	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Dieldrin	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Dissulfeto de C.	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Mirex	µg/L	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Endosulfan Sulfato	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endosulfan1	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endosulfan2	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endrin	µg/L	0.004	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endrin Aldeido	µg/L	-	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Estireno	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Etilbenzeno	µg/L	90	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Heptacloro	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Hexaclorobenzeno	µg/L	0.0065	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Hexaclorobutadieno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Isopropilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Lindano	µg/L	0.02	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
m,p-Xilenos	µg/L	300	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Metolacloro	µg/L	10	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Metoxicloro	µg/L	0.03	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Molinato	µg/L	-	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Naftaleno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
n-butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
n-propilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
o-Xileno	µg/L	300	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
DDT+DDE+DDD	µg/L	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Pendimetalina	µg/L	-	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Permetrina	µg/L	-	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
p-Isopropiltolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Propanil	µg/L	-	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sec-Butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Simazina	µg/L	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Temperature(Env)	ºC	-	29	28.9	28.8	28	23.5	27.8	28.6	21	29	28	28
Temperature(Sample)	ºC	-	25.4	25.7	27.5	23.9	23.5	24	24.6	24.4	24.2	24.9	24
Terc-butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Tetracloreto de C.	µg/L	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Tetracloroeteno	µg/L	10	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Tolueno	µg/L	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Toxafeno	mg/L	0.01	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
Trans-Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Trans-dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Triclorobenzenos	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Tricloroeteno	µg/L	30	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Trifluralina	µg/L	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trihalometanos	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Xileno	µg/L	300	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1

Table 3 – Organic parameters results for collected springs. **Part one** (from Nas-01 to Nas-04)

		Max. Perm.	27/08/2017	27/08/2017	29/08/2017	29/08/2017	30/08/2017	30/08/2017	31/08/2017	01/09/2017
Parameter	Unit	(BRASIL 2008)	Nas-01	Nas-08	Nas-20	Nas-24	Nas-16	Nas-22	Nas-06	Nas-04
1,1,1,2-Tetracloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,1,1-Tricloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,1,2,2-Tetracloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,1,2-Tricloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,1-Dicloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,1-Dicloroeteno	µg/L	3	<1	**<1**	<1	<1	<1	<1	<1	<1
1,1-Dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2,3-Triclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2,3-Tricloropropano	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5
1,2,4-Triclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2,4-Trimetilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dibromo-3-cloropropano	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5
1,2-Dibromoetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloroetano	µg/L	10	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloroeteno (Cis + Trans)	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloropropano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,3,5-Triclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,3,5-Trimetilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,3-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,3-Dicloropropano	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5
1,4-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
2,2-Dicloropropano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
2-Clorotolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
4-Clorotolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
4-Metil-2-Pentanona	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5
Alaclor	µg/L	20	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Aldrin	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
alfa-BHC	µg/L	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Atrazina	µg/L	2	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Bentazona	µg/L	-	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Benzeno	µg/L	5	<1	<1	<1	<1	<1	<1	<1	<1
Benzidina	µg/L	0.001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
beta-BHC	µg/L	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bromobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Bromoclorometano	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5
Bromodiclorometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Bromofórmio	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Bromometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Cis-1,2-Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Cis-1,3-Dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Clordano - alfa	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Clordano - gama	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Clordano (Isômeros)	µg/L	0.04	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Cloreto de Vinila	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Clorobenzeno (Monoclorobenzeno)	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Cloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Clorofórmio	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Clorometano	µg/L	-	<10	<10	<10	<10	<10	<10	<10	<10
delta-BHC	µg/L	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dibromoclorometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Dibromometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Diclorometano(Cloreto de Metileno)	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1
Dieldrin	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Dissulfeto de Carbono	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Dodecacloropentaciclodecano(Mirex)	µg/L	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Endosulfan Sulfato	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endosulfan1	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endosulfan2	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endrin	µg/L	0.004	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endrin Aldeido	µg/L	-	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Estireno	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1
Etilbenzeno	µg/L	90	<1	<1	<1	<1	<1	<1	<1	<1
Heptacloro + Heptacloro Epoxido	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Hexaclorobenzeno	µg/L	0.0065	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Hexaclorobutadieno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Isopropilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Lindano (gama-BHC)	µg/L	0.02	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
m,p-Xilenos	µg/L	300	<2	<2	<2	<2	<2	<2	<2	<2
Metolacloro	µg/L	10	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Metoxicloro	µg/L	0.03	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015

Molinato	µg/L	-	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Naftaleno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
n-butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
n-propilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
o-Xileno	µg/L	300	<1	<1	<1	<1	<1	<1	<1	<1
p,p'-DDT+p,p'-DDE+p,p'-DDD	µg/L	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Pendimetalina	µg/L	-	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Permetrina	µg/L	-	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
p-Isopropiltolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Propanil	µg/L	-	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sec-Butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Simazina	µg/L	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Temperatura Ambiente	ºC	-	28.4	27	27.5	26.8	23.2	27	29	21.8
Temperatura da Amostra	ºC	-	24	23.2	23.1	22.8	20.3	21.3	23.7	22.6
Terc-butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Tetracloreto de Carbono	µg/L	2	<1	<1	<1	<1	<1	<1	<1	<1
Tetracloroeteno	µg/L	10	<1	<1	<1	<1	<1	<1	<1	<1
Tolueno	µg/L	2	<1	<1	<1	<1	<1	<1	<1	<1
Toxafeno	mg/L	0.01	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
Trans-1,2-Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Trans-1,3-dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Triclorobenzenos	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1
Tricloroeteno (1,1,2-Tricloroeteno)	µg/L	30	<1	<1	<1	<1	<1	<1	<1	<1
Trifluralina	µg/L	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trihalometanos	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Xileno	µg/L	300	<1	<1	<1	<1	<1	<1	<1	<1

Table 3 – Organic parameters results for collected springs. **Part two** (from Nas-35 to Nas-40)

		Max. Perm. (BRASIL 2008)	03/09/2017	05/09/2017	07/09/2017	10/09/2017	10/09/2017	12/09/2017	22/09/2017	22/09/2017
Parameter	Unit		Nas-35	Nas-33	Nas-10	Nas-27	Nas-32	Nas-19	Nas-11	Nas-40
1,1,1,2-Tetracloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,1,1-Tricloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,1,2,2-Tetracloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,1,2-Tricloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,1-Dicloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,1-Dicloroeteno	µg/L	3	<1	<1	<1	<1	<1	<1	<1	<1
1,1-Dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2,3-Triclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2,3-Tricloropropano	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5
1,2,4-Triclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2,4-Trimetilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dibromo-3-cloropropano	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5
1,2-Dibromoetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloroetano	µg/L	10	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloroeteno (Cis + Trans)	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,2-Dicloropropano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,3,5-Triclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,3,5-Trimetilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,3-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
1,3-Dicloropropano	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5
1,4-Diclorobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
2,2-Dicloropropano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
2-Clorotolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
4-Clorotolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
4-Metil-2-Pentanona	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5
Alaclor	µg/L	20	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Aldrin	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
alfa-BHC	µg/L	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Atrazina	µg/L	2	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Bentazona	µg/L	-	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Benzeno	µg/L	5	<1	<1	<1	<1	<1	<1	<1	<1
Benzidina	µg/L	0.001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
beta-BHC	µg/L	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bromobenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Bromoclorometano	µg/L	-	<5	<5	<5	<5	<5	<5	<5	<5
Bromodiclorometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Bromofórmio	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Bromometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Cis-1,2-Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Cis-1,3-Dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Clordano - alfa	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015

Clordano - gama	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Clordano (Isômeros)	µg/L	0.04	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Cloreto de Vinila	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Clorobenzeno (Monoclorobenzeno)	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Cloroetano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Clorofórmio	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Clorometano	µg/L	-	<10	<10	<10	<10	<10	<10	<10	<10
delta-BHC	µg/L	-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Dibromoclorometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Dibromometano	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Diclorometano(Cloreto de Metileno)	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1
Dieldrin	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Dissulfeto de Carbono	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Dodecacloropentaciclodecano(Mirex)	µg/L	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Endosulfan Sulfato	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endosulfan1	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endosulfan2	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endrin	µg/L	0.004	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Endrin Aldeido	µg/L	-	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Estireno	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1
Etilbenzeno	µg/L	90	<1	<1	<1	<1	<1	<1	<1	<1
Heptacloro + Heptacloro Epoxido	µg/L	-	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Hexaclorobenzeno	µg/L	0.0065	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Hexaclorobutadieno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Isopropilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Lindano (gama-BHC)	µg/L	0.02	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
m,p-Xilenos	µg/L	300	<2	<2	<2	<2	<2	<2	<2	<2
Metolacloro	µg/L	10	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Metoxicloro	µg/L	0.03	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015	<0.0015
Molinato	µg/L	-	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Naftaleno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
n-butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
n-propilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
o-Xileno	µg/L	300	<1	<1	<1	<1	<1	<1	<1	<1
p,p'-DDT+p,p'-DDE+p,p'-DDD	µg/L	0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Pendimetalina	µg/L	-	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Permetrina	µg/L	-	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
p-Isopropiltolueno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Propanil	µg/L	-	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sec-Butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Simazina	µg/L	2	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Temperatura Ambiente	ºC	-	22.6	23.1	25.3	25.2	28.7	21.9	24.7	24.7
Temperatura da Amostra	ºC	-	19.1	22.3	22.2	23.5	23.9	22.5	24.3	24.3
Terc-butilbenzeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Tetracloreto de Carbono	µg/L	2	<1	<1	<1	<1	<1	<1	<1	<1
Tetracloroeteno	µg/L	10	<1	<1	<1	<1	<1	<1	<1	<1
Tolueno	µg/L	2	<1	<1	<1	<1	<1	<1	<1	<1
Toxafeno	mg/L	0.01	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
Trans-1,2-Dicloroeteno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Trans-1,3-dicloropropeno	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Triclorobenzenos	µg/L	20	<1	<1	<1	<1	<1	<1	<1	<1
Tricloroeteno (1,1,2-Tricloroeteno)	µg/L	30	<1	<1	<1	<1	<1	<1	<1	<1
Trifluralina	µg/L	0.2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Trihalometanos	µg/L	-	<1	<1	<1	<1	<1	<1	<1	<1
Xileno	µg/L	300	<1	<1	<1	<1	<1	<1	<1	<1

PHOTOGRAPHIC CATALOG

Figure 1 – Spring

s

Figure 2 – Sampling at spring

Figure 3 – Sampling

Figure 4 – Collected well

Figure 5 – Sampling from well

Figure 6 – Sampling

Figure 7 – Sampling equipment