

Fachhochschule Köln
Cologne University of Applied Sciences



UNIVERSIDAD AUTÓNOMA DE SAN LUIS POTOSÍ
FACULTADES DE CIENCIAS QUÍMICAS, INGENIERÍA Y MEDICINA
PROGRAMAS MULTIDISCIPLINARIOS DE POSGRADO EN CIENCIAS AMBIENTALES

AND

COLOGNE UNIVERSITY OF APPLIED SCIENCES
INSTITUTE FOR TECHNOLOGY AND RESOURCES MANAGEMENT IN THE TROPICS AND SUBTROPICS

**ASSESSMENT OF GROUNDWATER CONTAMINATION IN THE UPPER BASIN OF RIO GRANDE, RIO DE
JANEIRO, BRAZIL**

THESIS TO OBTAIN THE DEGREE OF

MAESTRÍA EN CIENCIAS AMBIENTALES

DEGREE AWARDED BY

UNIVERSIDAD AUTÓNOMA DE SAN LUIS POTOSÍ

AND

MASTER OF SCIENCE

“TECHNOLOGY AND RESOURCES MANAGEMENT IN THE TROPICS AND SUBTROPICS

FOCUS AREA “ENVIRONMENTAL AND RESOURCES MANAGEMENT”

DEGREE AWARDED BY COLOGNE UNIVERSITY OF APPLIED SCIENCES

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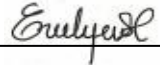
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Abstract

The use of groundwater in Brazil has been growing, specially in rural areas, due to surface water contamination caused by anthropogenic activities; those same activities could also have an impact on groundwater quality. Surface water of the upper basin of Nova Friburgo presents high concentrations of total and fecal coliforms product of waste water management of the region; besides rivers content agrotoxics product of use of pesticides. Despite, water wells, springs and streams supply 100% of the water demand of rural communities located in the upper basin of Rio Grande; any study had been developed to define if the physico-chemical characteristics of those water sources fulfill with the Brazilian legislation for drinking water and if the sources of contamination that impacted surface water, are also impacting groundwater. This study evaluated the water quality of drinking water sources and rivers used for the rural community of the upper basin of Rio Grande.

Possible sources of groundwater contamination were located and the methodology of GOD for determining vulnerability of groundwater contamination were used. Springs, artisan water wells, dug water wells, Rio Grande and its tributaries were sampled during April and May and parameters like total dissolved solids (TDS), dissolved oxygen (DO), nitrate (NO_3^-), electrical conductivity (EC), temperature ($^{\circ}\text{C}$), pH, nitrate, nitrite, total coliforms, thermotolerant coliforms and others were measured. Groundwater flow direction were made to observe the interaction between surface and groundwater.

The author found that the surface and groundwater of the upper basin of Rio Grande exceed the limits of Portaria N $^{\circ}$ 2914 of 2011, WHO and CONAMA Resolution 357 of 2005 for drinking and irrigation water indicating that water should receive at least a simplified treatment (filtration and disinfection) before using it for human consumption. The upper basin of Rio Grande is located in a shallow and vulnerable aquifer where dragging of animal feces, direct discharge of waste water into rivers and bad water well construction are the main causes of water pollution.

Research Agencies of Rio de Janeiro state and programs of Sustainable Agriculture like RIO RURAL should implement measures of water protection like wastewater treatment, provide permanent accompaniment and job training for inhabitants of the upper basin of Rio Grande to prevent problems that threat the water quality and human health but also to improve quality of life of the farmers.

1. Introduction

Groundwater is an important natural resource for the economy and is mainly used in rural and urban environments as water supply for human consumption, agricultural and industrial purposes; besides, it has a role in aquatic systems. In Brazil, 15.6% of the residences use exclusively groundwater for their domestic activities, 77.8% use a water supply network and 6.6% use other supply sources like rivers (IBGE, 2002); but many of the residences with a water supply network also use groundwater (Zoby and OLIVEIRA, 2005). Near 400,000 wells exist in Brazil (Zoby and Matos, 2002), São Paulo counts with 11,000 operation water wells (Martins Netto et al., 2004) and metropolitan region of Recife counts with 4,000 supplying water for 60% of the population (Costa, 2000). Growing of surface water use for power generation and water pollution result in an increase of groundwater use, for that reason, groundwater quality and proper use of the resource are becoming topics of concern of water management in Brazil (Zoby and OLIVEIRA, 2005). However, until now Brazil does not have strong information about the water potential of its aquifers, the exploitation state and far less about water quality.

Brazilian groundwater dependence is growing, specially in rural areas, but as was the case with surface water, human (or anthropogenic) activities could degrade groundwater quality reducing water availability. However, there are also natural sources of contamination that affect water chemistry and disrupt ecological and anthropogenic processes. Natural groundwater contamination is attributed to water-geological formation interaction and seawater intrusion, while anthropogenic contamination includes domestic, agricultural, industrial and municipal wastes (Baba & Tayfur 2011; Price 2003). A better description of the groundwater contamination sources is described as follows (Zoby and OLIVEIRA, 2005):

1. Water well construction: Inadequate perforation of a water well could create a connection between shallow aquifers, more vulnerable to contamination, with deep aquifers, less vulnerable to contamination, jeopardizing groundwater quality. Lack of isolation during drilling, absence of sanitary protection, inadequate height position of well head, proximity with sources of pollution (septic tanks, gasoline station and landfills), lack of disinfection after well construction and lack of cementing into the well bore are some factors that represent a groundwater contamination risk.
2. Sanitation: Only 56.3% of the households in Brazil have sewage system and only 39.0%

of this percentage receives a treatment (SNIS, 2013). Lack of sanitation cause contamination problems not only in surface water but also in groundwater. Leachate from septic tanks can infiltrate through unsaturated zone of the soil and reach saturated zone polluting groundwater.

3. Solid waste management: Urban and rural areas have a serious problem with the disposition and treatment of the solid wastes. 17.4% of rural households and 95.% of urban households in Brazil count with the service of garbage-collection whose destinities are dumps, sanitary landfills and controlled landfills. Heavy metals and acids, product of product of organic matter decomposition, have been found in groundwater at high concentrations (da Costa et al., 2004). Some of them are carcinogenic compound controlled by World Health Organization and Health Ministry of Brazil.
4. Agriculture: This is one of the most common sources of groundwater pollution around the world. The intensification of agricultural practices over the last decades with an excessive use of fertilizers and pesticides, have caused problems including eutrophication of water bodies -due to elevated concentration of nutrients such as nitrogen and phosphorus- and human health issues (Boy Roura, 2013). Nitrate is the compound with higher impact on groundwater quality because of its high mobility. Brazil have a worried situation because forms part of the largest consumers of agrotoxics in the world but whose use is not controlled increasing the risk of groundwater contamination.
5. Industry: This is an activity full of toxic substances that without an adequate management represent a risk for the environment and human health. Many of the pollutant produced by industries reach soil and river and depending on natural factors such as aquifer characteristics, depth to water, type of soils, etc could also reach groundwater. Zoby and OLIVEIRA 2005 highlight that the most contaminant activities are petrochemical, , mineral extraction, steel and agro-toxic production industries.
6. Mining: The impact of mining activities on the environment is known over all the world and include air pollution, deforestation, etc. This activity can also impact groundwater and one of the most sources of pollution are mine tailings; rainwater infiltrate those waste products washing the toxic substances to surface and groundwater resources modifying aquifer recharge mechanisms, changing rate, frequency and water quality (Foster et al., 2002).

In general, the bad management of surface contaminated load generated during the activities at the land surface such as discharge and leaches can threat groundwater quality (Figure 1). Soil and subsoil possess an natural attenuation capacity that through biochemical degradation and chemical reaction eliminate many water pollutants but once the concentration of

Table 1.: Common groundwater contaminants and associated pollution sources. Taken from [Foster et al. 2002](#).

Pollution Source	Type of contaminant
Agricultural activity	Nitrates, ammonium, pesticides, fecal organisms
In-situ sanitation	Nitrates, halogenated hydrocarbons, microorganisms
Gas station and garages	Aromatic hydrocarbons, benzene, phenols, halogenated hydrocarbons
Solid waste disposal	Ammonium, salinity, halogenated hydrocarbons, heavy metals
Meta industries	Trichloroethylene, tetrachloroethylene, halogenated hydrocarbons, phenols, heavy metals cyanide
Pesticide manufacture	Halogenated hydrocarbons, phenols, arsenic
Sewage sludge disposal	Nitrates, halogenated hydrocarbons, lead, zinc
Oil and gas exploration/extraction	Salinity (sodium chloride), aromatic hydrocarbons

components exceeds a certain concentration, groundwater pollution is unavoidable ([Foster et al., 2002](#); [Clarke et al., 1996](#)). Table 1 shows common contaminant compounds found in groundwater and the activities that could generate them.

The upper basin of Rio Grande, Nova Friburgo is located in the mountainous region of Rio de Janeiro, Brazil where 55% of drinking water sources are from wells and springs. However, lack of wastewater treatment system obligate the inhabitants to make septic systems or pit latrines for domestic wastewater disposal. Many studies have demonstrated that the proximity between septic system and water wells increase the potential risk of water supply

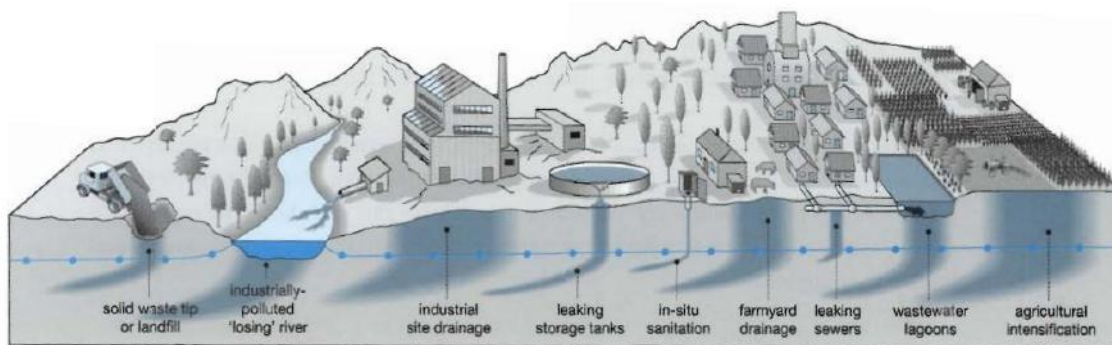


Figure 1.: Common processes of groundwater pollution. Taken from [Foster et al. 2002](#)..

contamination (Gerba and Smith, 2005; Stanford et al., 2010; Carrara et al., 2008; Baba and Tayfur, 2011). Additionally, agriculture is the main economic activity in that rural area which could also impact water bodies due the use of fertilizers and pesticides (Fu et al., 2013; Stamatis et al., 2011; Moss, 2008; Cruz et al., 2013; Baba and Tayfur, 2011).

Despite the high reliance on groundwater in rural areas of Brazil and the fact that the lack of sewerage systems and growing use of agro toxics can cause degradation of water quality (Agência Nacional de Aguas-ANA- 2002), very little is known about the conditions and the behavior of groundwater.

Few researchers have determined water quality of the upper basin of Rio Grande. In 2002, Moreira et al. 2002 sampled monthly for two years the part of Rio Grande which crosses São Lourenço microbasin in order to determine the existence of agrottoxics in the water. They found high levels of anticholinesterasics agrottoxics, even above Brazilian legislation for drinking an irrigation water, during dry season. Besides, they found a pesticide consumption (56 kg/worker/year) higher than national average (12 kg/worker/year). Nevertheless, they did not assess quality of drinking water sources.

Since 2011, the Environmental Monitoring department of the Health Agency of Nova Friburgo collect river samples three times per year in just one point of Barracão dos Mendes microbasin. They analyze physicochemical parameters like turbidity, free residual chlorine concentration, colour and odor, besides fecal coliforms (*E. coli*). The results show that water of Barracão dos Mendes present microbiological contamination, total and fecal coliforms (Segovia Sánchez, 2014).

The institute of environment of Brazil INEA have been monitoring Rio Grande river based on 9 parameters (dissolved oxygen, fecal coliforms, Biochemical Oxygen Demand (BDO), temperature, total nitrogen, total phosphorus, turbidity and total residue) considered indicators of contamination by sewage or industrial activities. According with the results of INEA, Rio Grande need a conventional treatment before using its waters in any human activity (Conejo et al., 2005). Finally, as part of the activities of the international cooperation project INTECRAL (INTECRAL, 2014), the students of IBELGA school, located on São Lourenço microbasin, measured some parameteres on Rio Grande river and found high concentrations of total and thermotolerant coliforms indicatives of fecal contamination. The studies of water quality in the upper basin of Rio Grande has been focused on the river but the nothing has been developed for other water sources.

1.1. Justification

Water wells, springs and streams supply 100% of the water demand of rural communities located in the upper basin of Rio Grande. Agriculture is the main economic activity of the rural area where farmers grown vegetables in order to fulfill local and Rio de Janeiro's city needs. This activity needs a huge quantity and good quality of water because a water quality problem may affect crop production. Additional, water wells and springs are the only drinking water sources of the area indicating that groundwater is an indispensable resource for locals; but until now it is unknown if physical, chemical and biological groundwater characteristics are appropriate for drinking water or irrigation purposes. Besides, existing sources of pollution, like homemade septic tanks, that could be affecting groundwater quality and health of people.

Water quality assessment is an effective way to know the environmental state of a specific area that could be used as a decision making tool to propose changes on the system and mitigation programs. This study propose to evaluate the water quality of drinking water sources and rivers used for the rural community of the upper basin of Rio Grande.

1.2. Objectives

1.2.1. General objective

Evaluate the impact of diffuse pollution sources (agriculture return flow and septic tank effluent) on groundwater resources with combined indicators (nitrogen and phosphorus compounds, microbiological, chloride, total dissolved solids) in the upper basin of Rio Grande, Rio of Janeiro.

1.2.2. Specific objectives

1. Identify the location of groundwater sources.
2. Assess groundwater vulnerability to pollution.
3. Analyze groundwater quality.
4. Determine indicators of contamination and assess its spatial changes.

2. Description of the study area

The upper basin of Rio Grande is located in the 3rd district of Campo do Coelho, municipality of Nova Friburgo, Serrana Region of Rio de Janeiro State, at the north slope of Serra dos Orgãos, between the peaks Três Picos and Pico do Caledônia, and geographical coordinates 22°20.689' and 21°21.226' South Latitude and 42°43.580' and , 42°35.092' West Longitude.

2.1. Climate

A Serra do Mar, a mountainous region of hilly topography, surround the upper basin of Rio Grande. Its orientation WSW-ENE expose the Serra do Mar to humid winds that once hit the hillside and upward movement and condensation occurs precipitating in form of fog or rain (Bohrer and Barros, 2006; Santos, 2011). The Relativity air humidity reaches 83% with an annual median precipitation varying from 1500 to 2400mm concentrated in October and April. Despite less than 10km separated Barracão dos Mendes and São Lourenço micro-basins, precipitation values of 1650 mm and 1900 mm have been registered respectively (Mata Pires, 2006). This could be explained because the pass of humid winds through the Serra do Mar generate a loss of humidity resulting in dry winds flowing above Barracão dos Mendes micro-basin in the direction to the rivers Rio Grande and Paraíba do Sul. Nova Friburgo's climograph shows two functional stations: Humid and hot and dry and cold . November, December, Januar, Februar, March and April are hottest and most humid months, June, July and August are coldest and driest months. The dry season result from the occasional cold fronts(Bohrer and Barros, 2006).

According with de Lima et al. 1997, the upper part of the basin Rio Grande has a humid climate with at least two dry months or high-altitude tropical climate, equivalent to a Cfb climate in the Köpper classification. The mean temperature in São Lourenço and Salinas micro-basins is 16°C with a summer mean temperature of 22°C and winter mean temperature of 11°C but temperatures of 34°C and 2°C has been registered during the period of 1961 to 1990 (Mata Pires, 2006). The micro-basin of Barracão dos Mendes is hotter than the other microbasins with a mean temperature of 18°C, a summer mean temperature of 24°C and

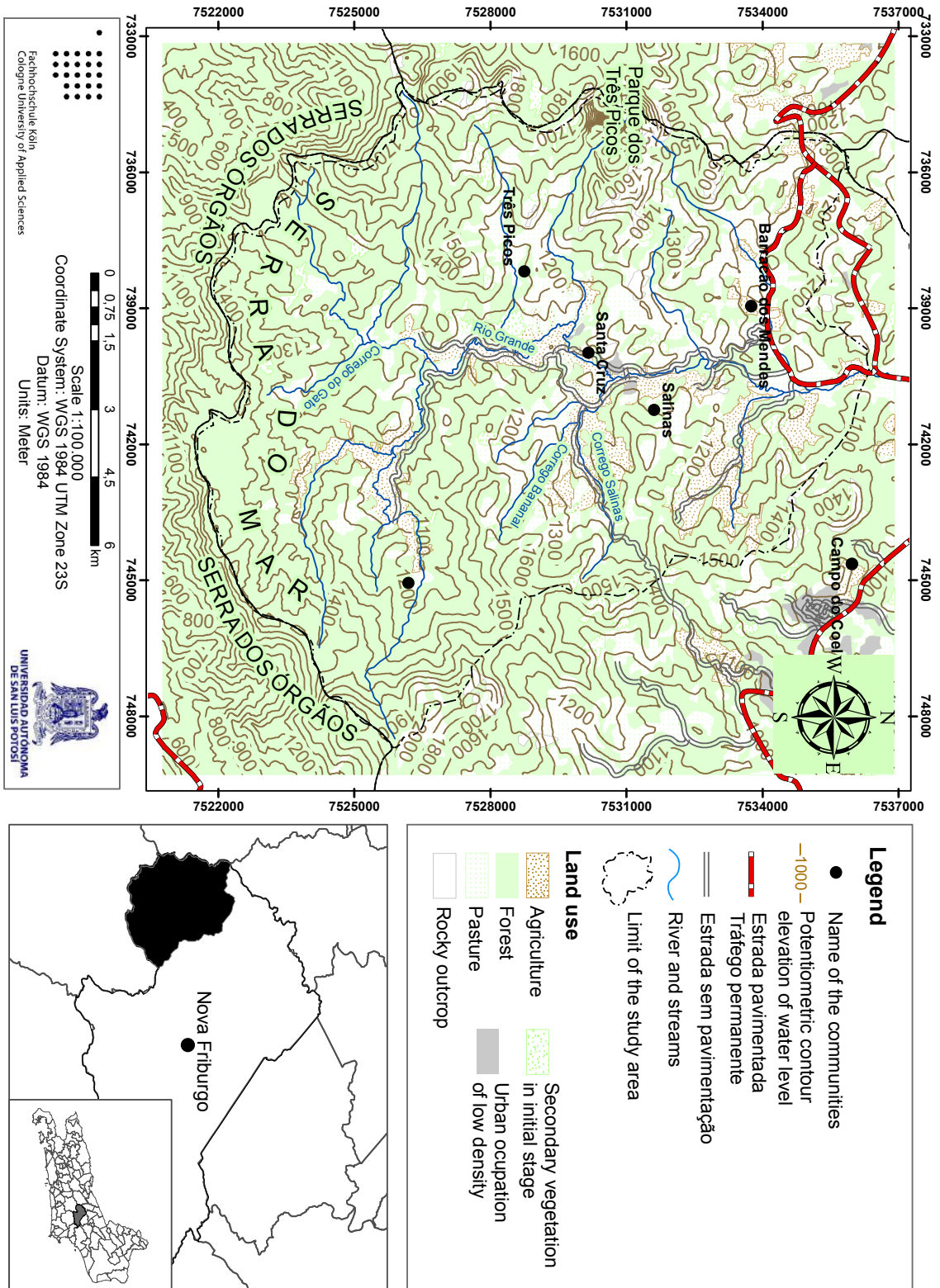


Figure 2.: Location of the upper basin of Rio Grande. Data source: IBGE.

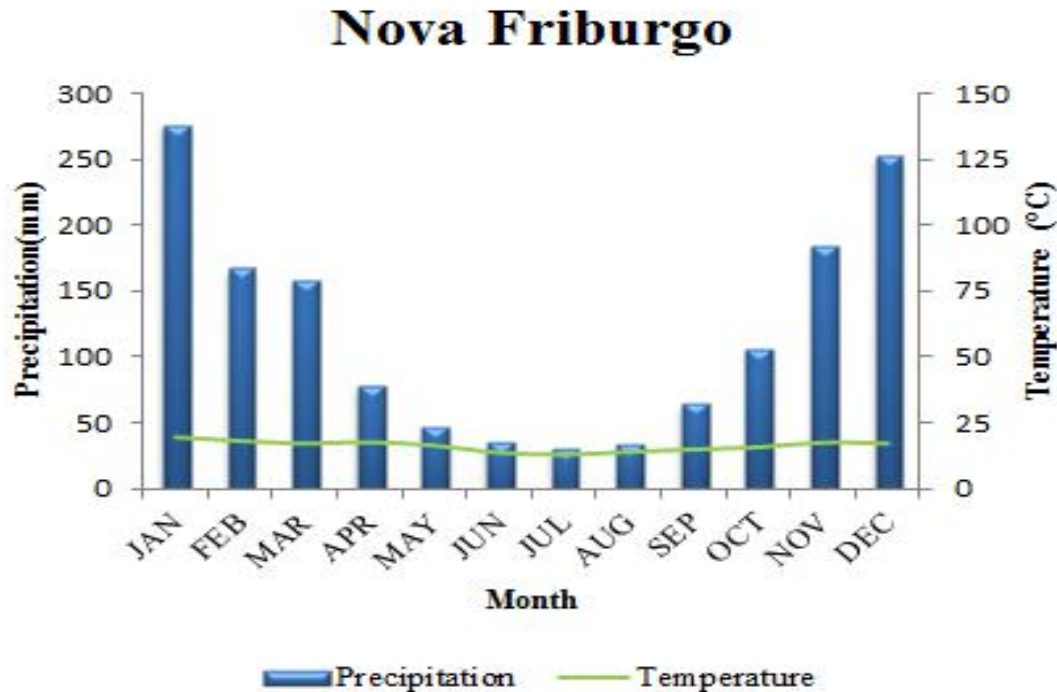


Figure 3.: Climogram of Nova Friburgo.

winter mean temperature of 13°C. In some occasions frost events occurs in lowlands and during summer, rains of hail are common (Alves Filho et al., 1999).

2.2. Soils

The soils of the upper basin of Rio Grande result of a combination between a hilly topography, dense forest cover and the humidic climate which explain the physico, hydrologic (mechanical fixation, filtration, evapotranspiration) and ecologic (organic matter production and nutrient cycling) processes of the region (Bohrer and Barros, 2006). Those are leached soils -soluble constituents of the soils are removed by water action- with a medium fertility, low pH and low nutrient content. In the Embrapa solos' classification three soil types characterize the microbasins: Alic Cambisols, Alic Litolics, and Rocky outcrop (Mata Pires, 2006). Cambisols are shallow soils formed by an association between Distrofic Haplic Cambisols, Latic Red-Yellow Latosols and Red-Yellow Latosols in hilly and mountainous area or with Litolic soils in high relief terrains of Serrana region. A difficult differentiation between soil horizons and an undeveloped B horizon (lay of stone, clay and inorganic materials) are the main characteristics of Cambisols (dos Santos et al., 2006). It has a sand-silt texture with yellowish and brownish tonalities. Its small thickness and occurrence on hilly

topography difficult the vegetable development and favour erosion leading to low use for agriculture activities.

Latosols are generally deep or very deep, with a low capacity of cation exchange resulting in a low natural fertility. However, these are well-drained soils possessing a high permeability and an argillaceous texture. Due to that, latosols have a high surface erosion resistance. Latosols occur on flat or smoothly undulated relief which join with its physical characteristics meet the requirements for agriculture. Most of them are acids, therefore, farm workers have to do an acidity correction. Farmers also use this type of soil as pasture areas.

Alic Litolic soils are shallow underdeveloped soils with an A horizon (mineral water mixed with some humus) direct on the rock or thin B and C horizons, formed by the association of Alic Litolic soils and Alic Cambisol (dos Santos et al., 2006). Rocky outcrop is also associated with Alic Litolic soils. Hydromorphic soils characterized flat areas which favor vegetable farming due soil fertility and water saturation. However, haplic cambisols and red-yellow latosols are the predominant types of soils in the upper basin of Rio Grande . Haplic Camisol soil is poor in organic material with the absence of rock structure and sediments stratification; has a high concentration of lime and oxides and a low capacity of nutriment supply (?). Red-yellow Latosol presents an advances state of weathering without presence of first and second minerals. The soil is deep with a diffuse transition between the horizons; possess a low capacity of cationic exchange, high porosity and high permeability. Sartori et al. 2005 classified Brazilian soils into 4 groups (A, B,C and D) according with their physical properties .

1. Group A: These are soils with low run-off of water but a high infiltration rate ($> 7,62$ mm/h). Sand and gravel are part of this group.
2. Group B: These soils are deep soils of moderate infiltration rate (3,81 - 7,62 mm/h) and with coarse or fine texture.
3. Group C: These soils have a low infiltration rate (1,27 - 3,81 mm/h) formed by layers that inhibit water flow from surface to subsoil. They have a fine texture.
4. Group D: These are soils with a high run-off of water and the lowest infiltration rate ($<1,27$ mm/h) in comparison with soils from the other groups. Clays belong to this group.

The soils of the upper basin of Rio Grande belong to the groups A, B and C.

2.3. Vegetation

Forest remnants and dense forest domains the upper basin of Rio Grande. Veloso et al. 1991 classified the vegetation up to altitudes of 1500m as Ombrofila Dense Mountain Forest and

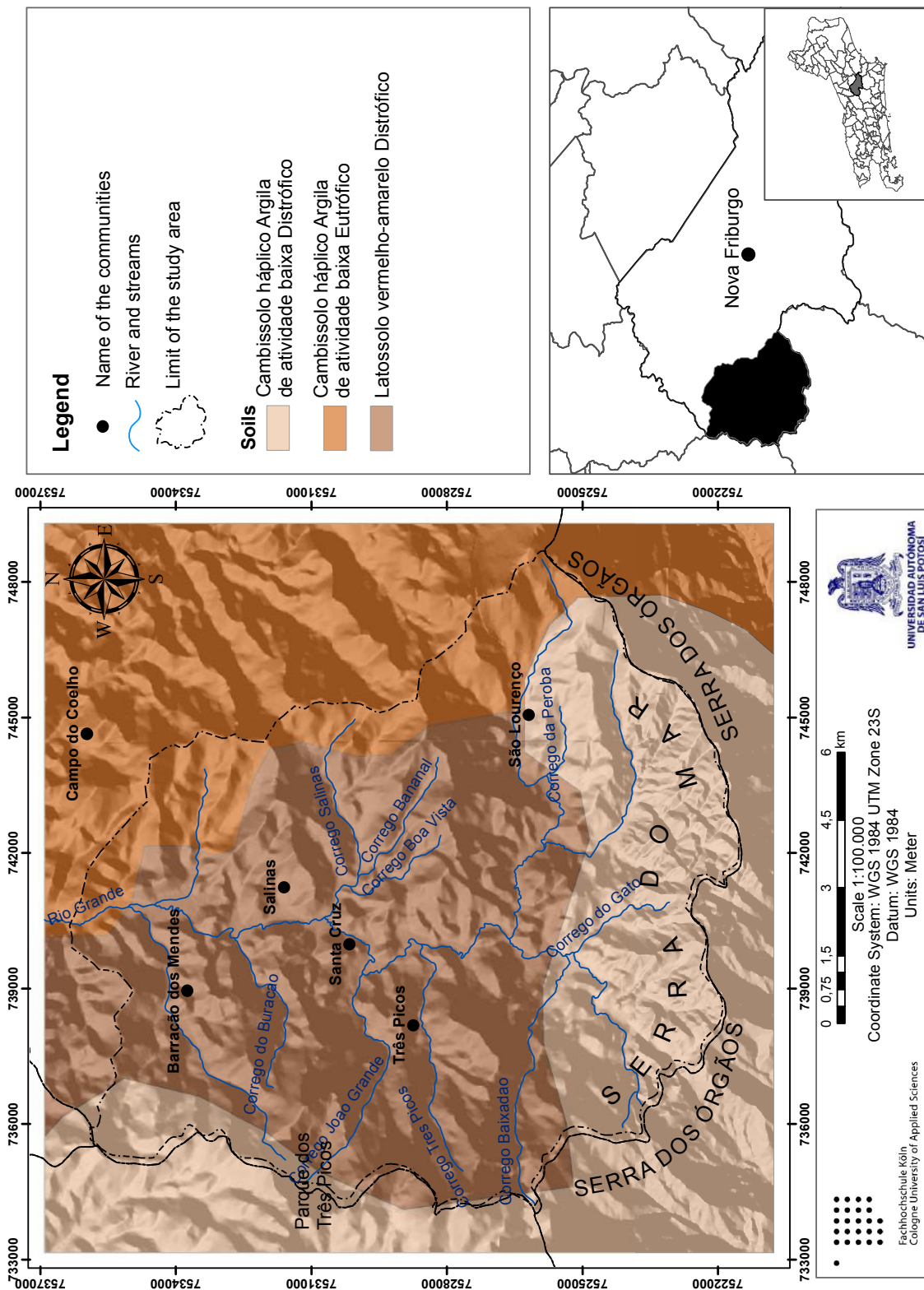


Figure 4.: Type of soils of the upper basin of Rio Grande. Data source: IBGE-EMBRAPA Solos.

Table 2.: Classification of the soils according with their physical characteristics and erosion resistance. Modified from [Lombardi Neto et al. 1989.](#)

Group	Erosion resistance	Depth	Permeability	Texture	Types of soils
A	High	Very deep (>2m) or deep (1 to 2m)	Fast /fast Moderated/fast Fast /fast	Medium/medium Vary clayey/very clayey Sandy/sandy Sandy/medium Sandy/clayey	Red /yellow latosol, red latosol and yellow latosol Yellow latosol and red /yellow latosol , Brun latosol, red nitosol, red argisol
B	Moderate	Deep (1 to 2m)	Fast/moderated Moderated/moderated	Clayey/very clayey Sandy/medium Sandy/clayey Medium/clayey	Argisol, red argisol, red /yellow argisol, cambisol, and haplic cambisol
C	Low	Deep (1 to 2m) to moderately deep (0.5 to 1.0m)	Slow/fast Slow/moderated Fast/moderated	Sandy/medium Medium/clayey Sandy/clayey Sandy/very clayey Variable	Litolic neosol, organosol, rocky outcrop, cambisols, red argisol
D	Very low	Moderately deep (0.5 to 1.0m) or shallow (0.25 to 0.5m)	Fast, moderated or slow		



Figure 5.: *Araucaária angustifolia* Parque Três Picos.

vegetation over 1800m as *campos de altitude* or high-altitude grasslands-mosaic of shrubs and small copses of short trees located on hilltops-. In the Ombrofila Dense Mountain Forest dominate endemic and evergreen tree species and a large quantity of epiphytes such as bromeliads and lians while in the steeper declivities areas, is common to find rocky outcrops covered by gramineae and spread bromeliads. *Campos de altitude* occurs on top of the hills Caledônia and Três Picos where also endemic species can be found (Bohrer and Barros, 2006).

2.3.1. Pico do Caledônia

The vegetation of Pico do Caledônia presents a high grade of conservation. In altitudes of 1500m exists a dense sub-forest with trees that can reach heights of 30m; at lower altitudes is common to find secondary forest in a regeneration state. There are trees of natural occurrence as *Araucaária angustifolia* and introduced species like *Eucalyptus sp.*, grass for pasture areas, vegetables and legumes (INEA, 2009).

2.3.2. Três Picos

Forest typology of Três Picos area is defined as primary forest in the top of the hills and secondary forest of different ecological succession stage in the lowest areas of the zone. Against the forest code (Lei 4.771/65) for the conservation units, pasture areas extend beyond altitudes of 1800m leading to deforestation of native species; but the same difficult of livestock production in those areas had lead to initial state vegetation. Forest fragments immerse in a matrix of vegetables, principal economic activity of the region (INEA, 2009).

2.4. Land use

A total area of 15,572ha cover by natural vegetation, secondary forest, forest planting, agriculture, pasture and low density urban centers represent the upper basin of Rio Grande. Bohrer and Barros 2006 identified five land use and land cover classes:

1. Dense Forest: Correspond to the areas covered with highly opened forest corresponding to primary forest or secondary forest in an advanced state of regeneration and areas covered with trees in medium stage of regeneration, shrub or bush. It covers 63% of the area and locates in the west, south and eastern zones characterized by steeper declivities close to the origin of the streams and the dividers of the Rio Grande basin. The State Park Três Picos (total area of 65.113 ha) is also located in the basin of Rio Grande; it was created in 2002 in order to protect the remaining Atlantic Forest from degradation caused by urban sprawl, tourism and agricultural activities (INEA, 2014).
2. Pasture: Correspond to areas dominated by grasses, with some presence of arboreal species in initial stage and shrubs, devoted to beef, dairy cattle and equines. Covering 21.4% of the study area lying on the lower slopes and flood plains of all the micro-basins.
3. Agriculture: Correspond to agricultural areas where vegetables of short-term cycle mainly in the alluvial terraces. Some crops are cassava, maize and beans covering 9.54% of the study area.
4. Rocky outcrop: Correspond to areas of high declivity and scarce vegetation covering 1% of the micro-basins.
5. Low density urban area: Correspond to small urban centers for residential purposes and small shops.

Despite of the extensive forest area of the upper basin of Rio Grande, natural vegetation and the riparian forest of the water catchment areas are disappearing due the expansion of irrigation areas and pasture (Bohrer and Barros, 2006). The removal of the vegetation and the

improper land use linked with the geology of the place favors erosion process- Plano de Recursos Hídricos da Bacia do Rio Paraíba do Sul classified the municipality of Nova Friburgo with a high vulnerability to erosion-, increasing soil compaction and sediment transport to drainage area, reducing water infiltration and therefore river flow ([Chaboudt Borges, 2005](#)).

2.5. Relevo

The upper basin of Rio Grande is located on the mountainous region of Rio de Janeiro with altitudes varying from 1000m in the valley to 2240m in the highest part of the Pico do Caledônia. [Cunha 1978](#) described three geomorphology units with different topography: A mountain range with steep slopes and rocky outcrops on the periphery of the study area which form water divide; hilly terrains of different altitudes whose gradient decrease in direction to the main valley and the lowest part formed by floodplains that extends from river bank to the less steep hills, allowing agricultural development. presents a tridimensional view of the topography in the study area.

Agriculture and pasture is presented in altitudes between 1000 and 1200m which correspond to 52% of the study area. Pico do Caledônia has altitudes as high as 2300m and possess access roads favoring sightseeing. As well as Pico do Caledônia, Três Picos is a reference point with altitudes also of 2300m and an area that only covers 0.4% of the study area where climbing, hiking and ecotourism are the only allowed activities.

Slopes of the study area range from 0 to 90° but major part of the zone lies on slopes from 0 to 45° . According with the forestry code of Brasil, slopes up to 5° are the areas where agricultural machines can be used and correspond to 18.8% of the total area, slopes between 15 to 25° represent 51.9% of the study area dedicated to perennial crop and agroforestry systems, slopes up to 25° represents 73.3% of the area and are used for agriculture, which correspond to 11,420 ha approximately, finally, slopes from 25 to 45° characterize 24.3% of the study area and have to be only destined for forest management ([Bohrer and Barros, 2006](#)).

2.6. Regional geology

The Ribeira Belt covers an extension of 1400km along the south-southeast costal area of Brazil and is the result of one of the tectonic episodes more important of Brazilian south-east: the collision between the tectonic plates Francisco-Congo and Cratón of Ágola during Brazilian cycle in Neoproterozoic-Cambrian period ([CPRM, 2012](#); [Tupinambá et al., 2012](#); [Heilbron et al., 2008](#)). The increasing of temperature generated by the collision metamor-

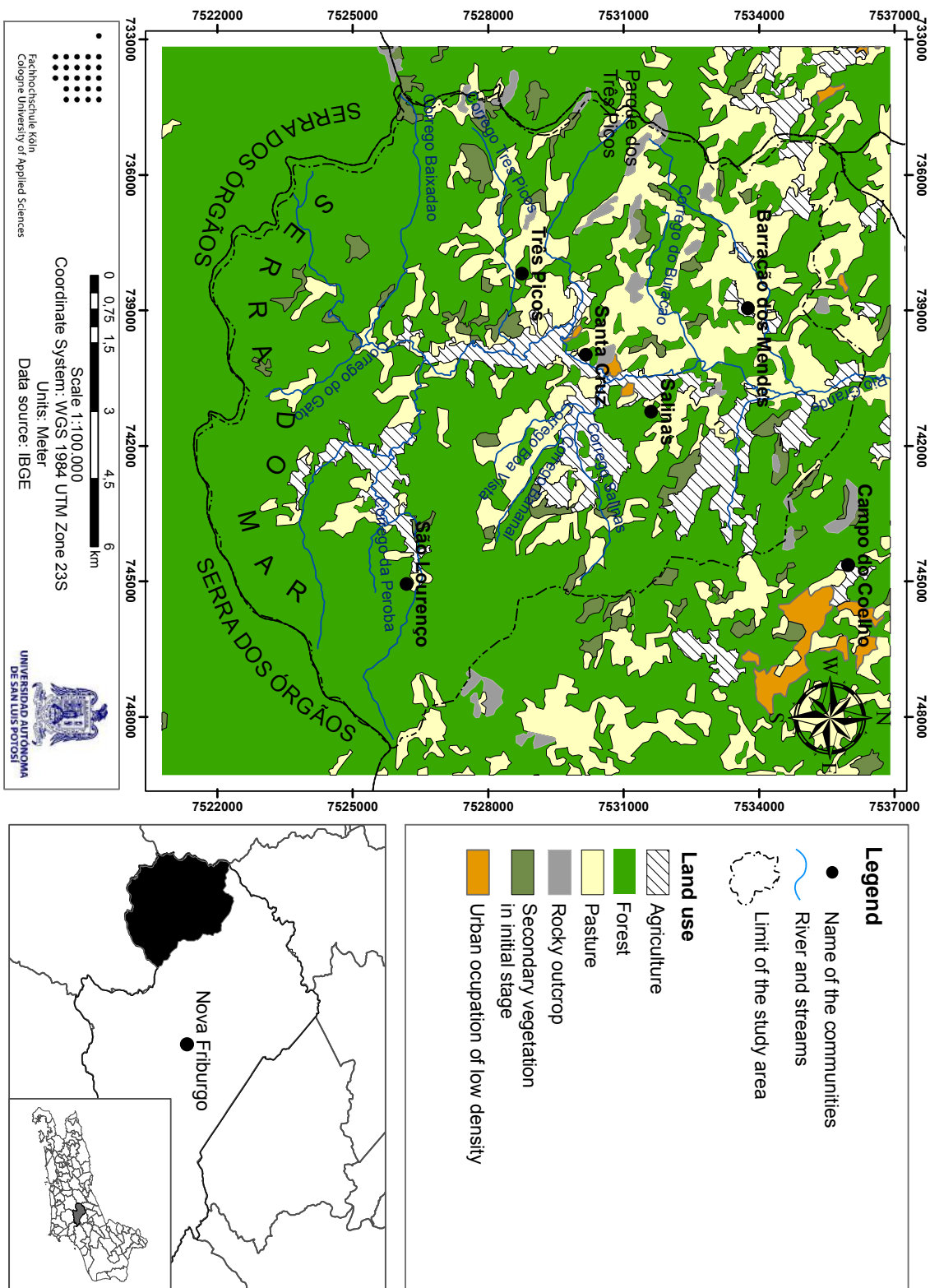


Figure 6.: Land use and land cover upper basin of Rio Grande.

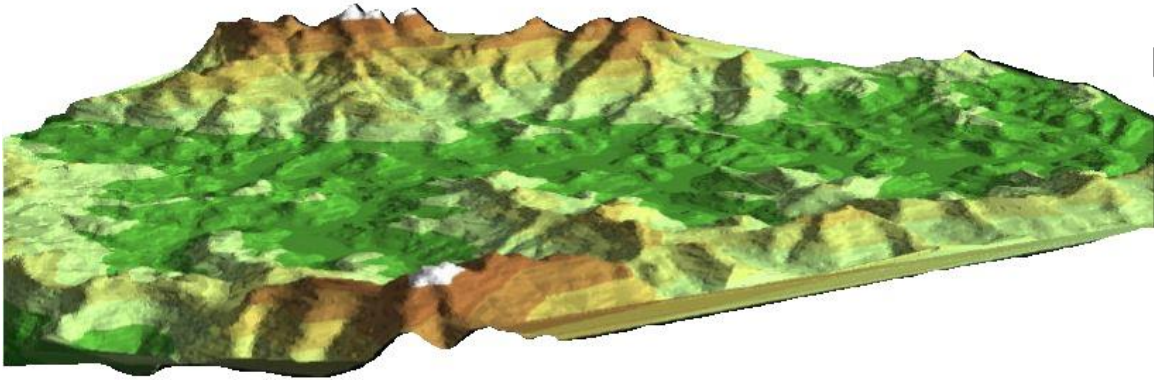


Figure 7.: Topography of the upper basin of Rio Grande in 3D. On the bottom of the image is Três Picos while on the front is Pico do Caledônia.

phosed and deformed igneous and sedimentary rocks giving rise to ortogneisses (gneisses from an igneous rock) such as Complexo Rio Negro, Suíte Cordeiro and Serra dos Orgãos, and paragneisses (gneisses from a sedimentary rock) such as the groups: Italva, São Fidélis and Bon Jesus do Itabapoana. The final of the collision formed granitic gneisses represented by Suíte Nova Friburgo (Tupinambá et al., 2012). The paragneisses are the oldest rocks in the region, product of sedimentary rocks metamorphism between 1000 and 800 Ma. The ortogneisses resulted from the igneous rock metamorphism introducing into sedimentary rock between 630 and 560 Ma (INEA, 2009).

A proportion of paleoproterozoic gneisses divided the Ribeira Belt in East, West, Paraíba do Sul and Cabo Frio territories. West territory involves ortogneisses with anfibolites and granulite rocks (tectonic domain of Andrelândia) and paleoproterozoic ortogranulites (tectonic domains of Juiz de Fora). Paraíba do Sul territory encompasses paleoproterozoic ortogneisses with granitic composition, banded gneisses with marble lenses deposits, and calciosilicatic and gndites rocks that emerge along an isolated fault with NE-SW direction (CPRM, 2012; Andrade Almeida, 2010).

East territory involves Cambuci, Costeiro and Italva domain. Cambuci domain presents a sequence of metasedimentary rocks including sillimanite-biotite-grenade gneiss with intercalations of marble and lenses of calciosilicatic rocks (Heilbron and Machado, 2003). Costeiro domain involves associations of metasedimentary rocks intruded by the magmatic arc Complexo Rio Negro, composed of banded paragneisses with insersions of calciosilicatic

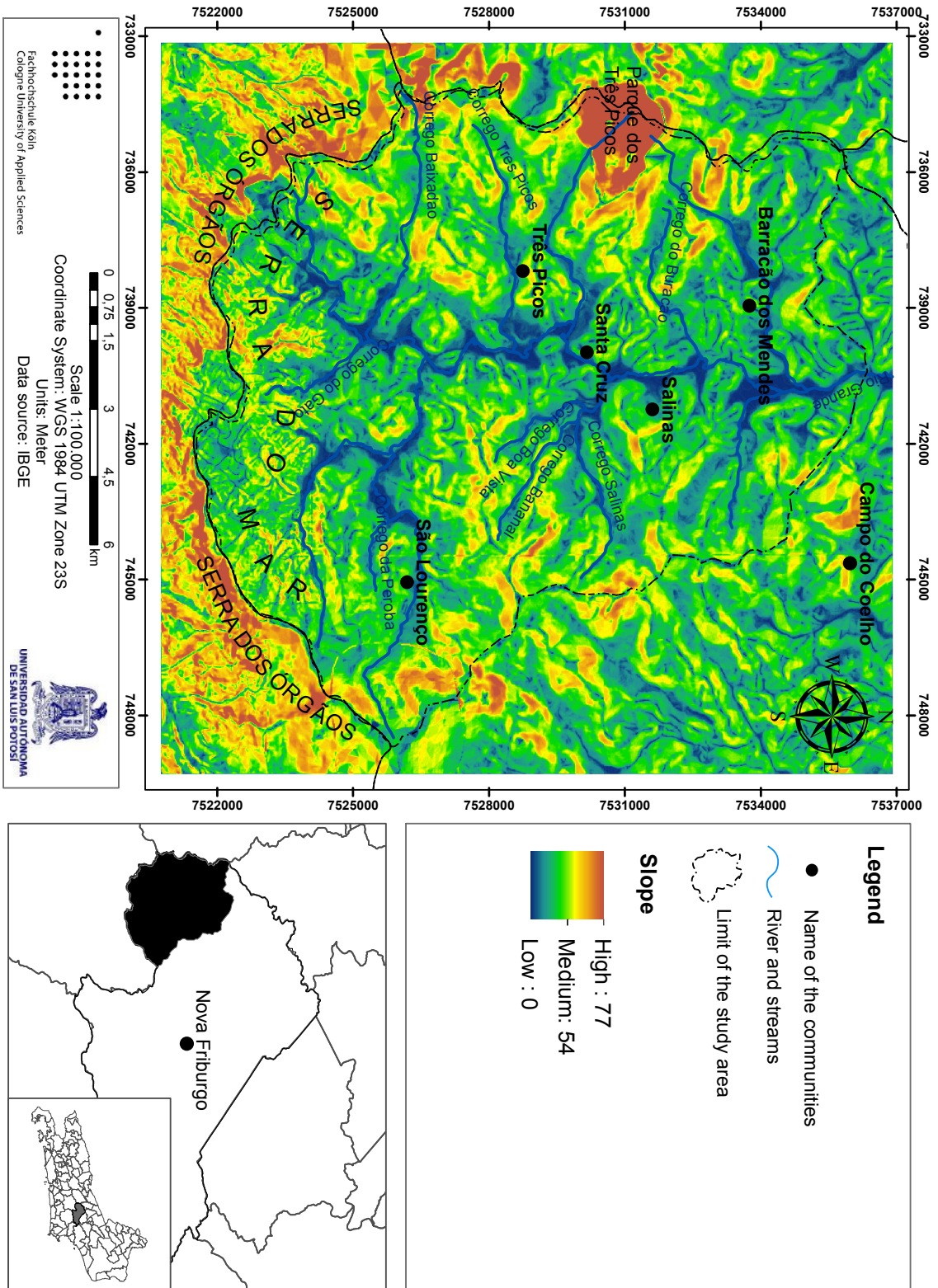


Figure 8.: Slope of the upper basin of Rio Grande.

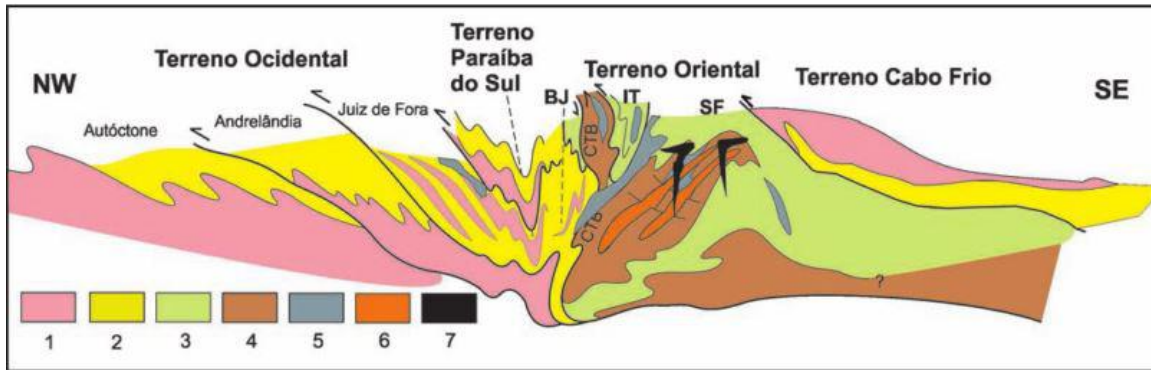


Figure 9.: Tectonic partitioning of Ribeira Belt. 1- Paleoproterozoic basement; 2- Metasedimentary cover; 3- Metasedimentary sequences of the magmatic arc; ITV, Italva klippe; BJ, Bom Jesus do Itabapoana klippe; SF, São Fidélis klippe; 4-Rio Negro Complex, ortogneisses of the Magmatic Arc; 5-granitic leucogneisses of Suíte Cordeiro; 6-Metaluminous gneisses of Suíte Serra dos Orgãos; 7-Granites of Suíte Nova Friburgo. Taken from (?).

rocks and carbonatic rocks (Heilbron and Machado, 2003). Metasedimentary sequence of Italva domain possesses banded garnet-biotite gneisses and calcic marble interspersed with banded amphibolites and hornblende biotite gneisses (metamorphic rock) (Heilbron and Machado, 2003). Finally, Cabo frio territory presents paleoproterozoic orthogneisses with amphibolites intrusions, pelitic paragneisses with amphibolite lenses and calciosilicatic rocks (CPRM, 2012). The formation of this territory was the result of a belated collision (520Ma) (Schmitt et al., 1999).

2.6.1. Stratigraphy

The municipality of Nova Friburgo is part of the Região Serrana Fluminense, located in the east Ribeira Belt, characterized by gneisses, paragneisses and granites (Tupinambá et al., 2012). shows the geology of the study area.

Host rock of Brazilian Magmatism: Silimanite biotite gneiss (Npsfbgn) and Quartzite (NPsfqz)

Tupinambá et al. 2012 represented São Fidelis group like biotite granite gneiss with sillimanite and cordierite, calciosilicatic rock, amphibolites and feldspathic quartz.

The gneisses of this group appears across the fault beginning in the main channel of rio Guapiaçú, going through Serra do Mar, alto do São Lourenço, the east of Maciço de Caledônia and finalizing in the urban area of Nova Friburgo. The unit garnet sillimanite biotite gneiss has a composition tonalite, migmatite, mesocratic of medium grain and in

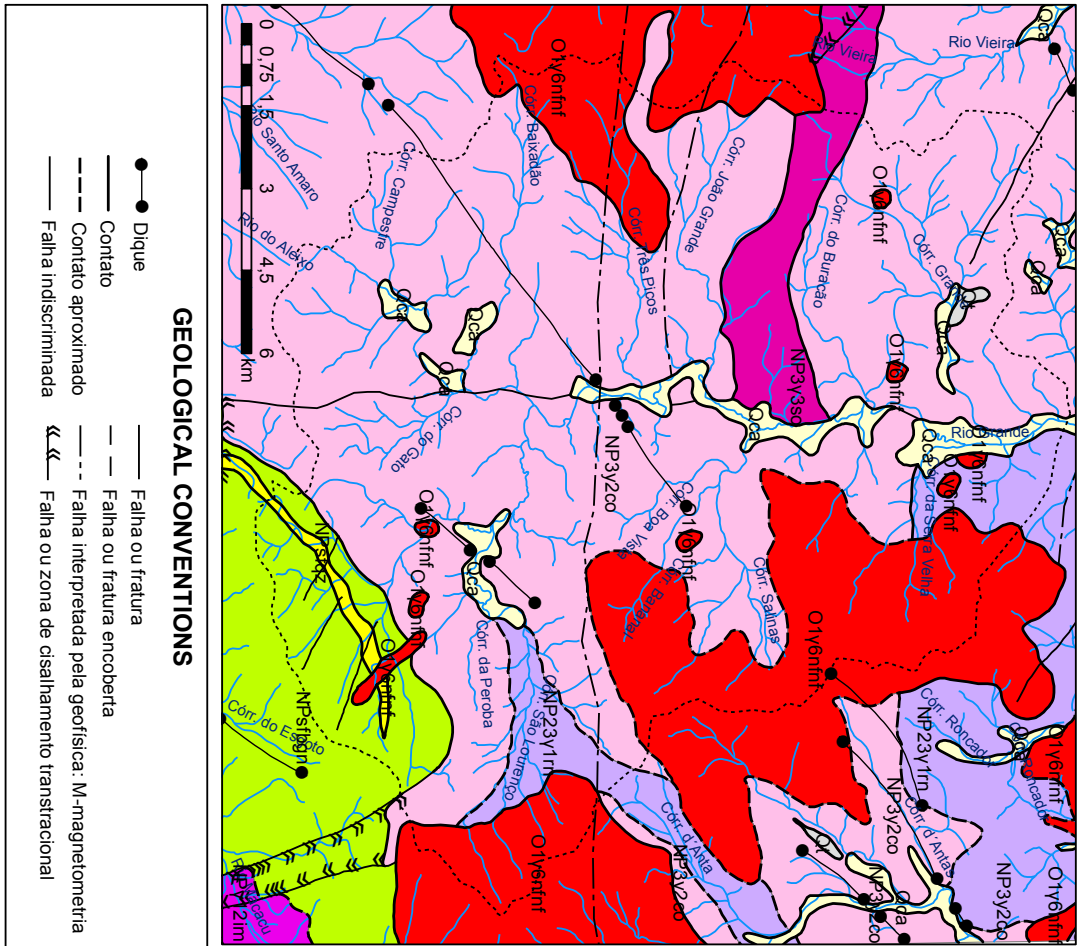


Figure 10.: Geology of the upper Basin of Rio Grande. Data source: CPRM.

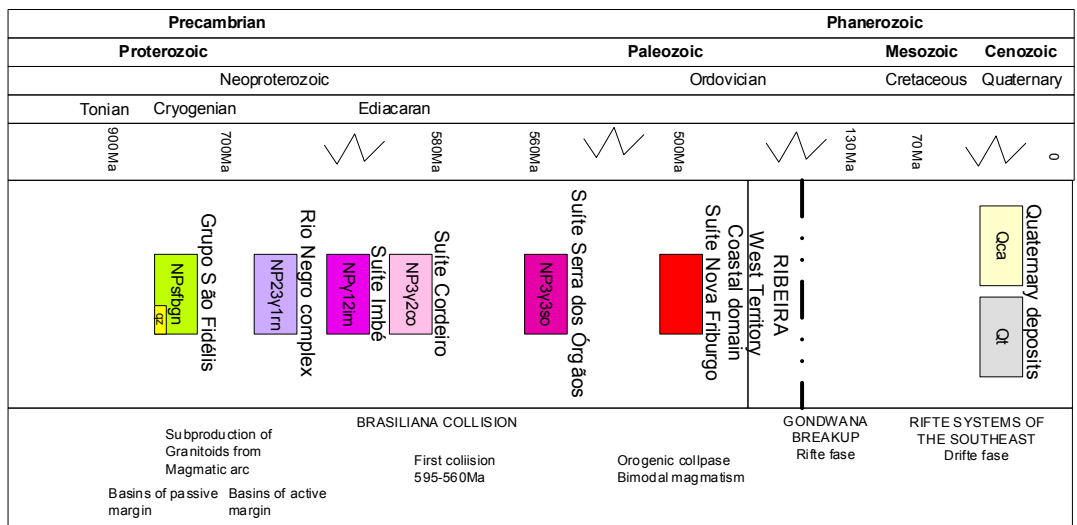




Figure 11.: Aggregates of hornblende and biotite in gneiss of Rio Negro complex. Taken from [Tupinambá et al. 2012](#).

some occasions muscovite can be found. In some places gneisses has a parallel disposition (schistose gneisses) with biotite and garnet but in other places gneisses are interspersed with deformed and recrystallized quartzite (quartzite (NPsfqz)), muscovite and sillimatite ([CPRM, 2012](#)).

Pre-collisional magmatism: Rio Negro Complex (NP23 γ 1rn)

Rio Negro Complex orthogneisses result from the metamorphism of the oldest igneous rocks in Região Serrana Fluminense generated between 630 and 600Ma ([Tupinamba, 1999](#); [Heilbron and Machado, 2003](#)). [Tupinambá et al. 1996](#) redefined Rio Negro Complex like an ortho-derived complex formed by orthogneisses and granitoids (diorite, tonalite gneiss, leucogranite gneiss and porphyroid gneiss).

Big grain size gneisses with discontinuous layering (foliation) of biotite and hornblende characterize Rio Negro Complex ([Tupinambá et al., 2012](#)). Those rocks has a high content of Ca ([Tupinambá et al. 2012](#)) and can be found mainly in Alto de São Lourenço in Três Picos park ([INEA, 2009](#)).

Syn-collisional magmatism: Suíte Cordeiro (NP3 γ 12co)

Suíte Cordeiro occupies the major area of Nova Friburgo geological map. It is distributed along a fault in northeast direction (NE) and surrounded by Rio Negro Complex, especially in northwest direction. The predominant rock of Suíte Cordeiro is a coarse grained leucocratic or hololeucocratic gneiss with a mineral size around 3mm ([CPRM, 2012](#)). The rock presents an alignment with biotite crystal and quartz lenses .

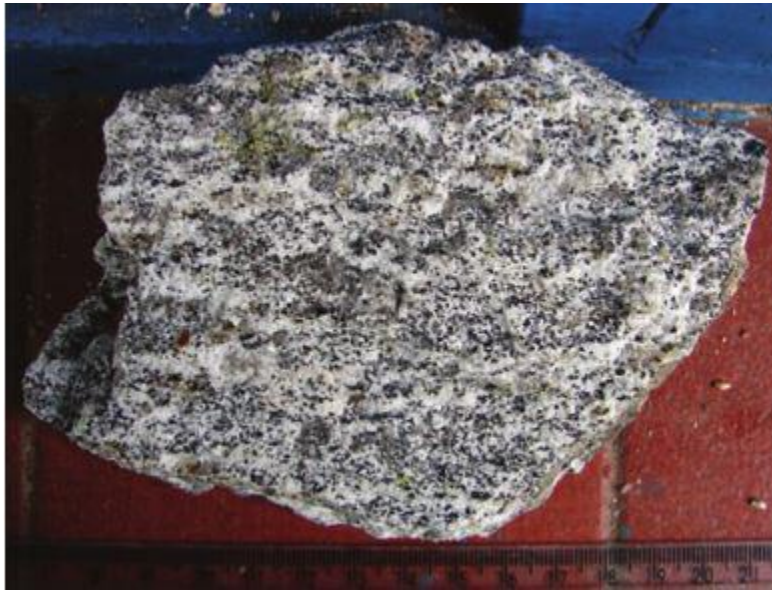


Figure 12.: Alignment of millimeter crystals of biotite and quartz lenses along foliation in leucogneiss of Suíte Cordeiro. Taken from [CPRM 2012](#).

Syn to late collisional magmatism: Suíte Serra dos Órgãos(NP3 γ 3so)

The gneisses of this unit are meso to leucocratic coarse-grained rocks with discontinuous layering (foliation) of centimetric biotite and hornblende, leucocratic garnet and huge crystals of quartz with “drop” form . Suíte Serra dos Órgãos gneisses and Rio Negro Complex gneisses are similar in composition but different in texture. Despite their differences, their distinction in field is difficult ([INEA, 2009](#); [Tupinambá et al., 2012](#)).

Post-collisional magmatism: Suíte Nova Friburgo

Suíte Nova Friburgo is an arrangement of homophonous granites intrusive rocks also found like subhorizontal or subvertical dikes in orthogneisses of Suíte Serra dos Órgãos, Rio Negro Complex and paragneisses of Grupo São Fidélis ([Tupinambá et al., 2012](#)). Rosier 1957 identified two classes of post-tectonic granites: oldest coarse grained intrusive granites and youngest fine grained granites in form of dikes. The magmatism occurred between Cambrian and Ordovician period in two series: the first 511Ma and the second 486Ma ([de Morisson Valeriano et al., 2011](#)).



Figure 13.: Grenade and quartz of Suíte Serra dos Órgãos. Taken from [Tupinambá et al. 2012.](#)



Figure 14.: Contact between equigranular and megaporfiritic faces, Suíte Nova Friburgo. Taken from [Tupinambá et al. 2012.](#)

2.7. Hydrology

Five hydrographic units divide Nova Friburgo municipality: Alto do Rio Grande Basin, Rio Bengalas basin, Dos Riberões São José, de Capitão and São domingos basin and Alto do rio Macaé basin . The zone of study belongs to the Alto do Rio Grande basin (Figure 15) formed by the microbasins of São Lourenço, Santa Cruz and Barracão dos Mendes with an total catchment area of 136.7 km², a perimeter of 72.28 km. and 244 stream segments distributed in 5 orders of magnitude with a pattern of drainage mainly dendritic (found in areas with uniform geologic structure, Gordon et al. 2004). Córrego Baixadão, São Lourenço, Bananal, Boa Vista, Campestre, Fazenda de São Lourenço, da Peroba, Serra Velha, de Buracao, do Gato, Grande, Joao Grande, Salinas and Três Picos are the permanent tributaries of Rio Grande river which cross the main communities of the study area and are used for irrigation. The longest stream of the study area have a length of 20 km and a mean slope of 2.7° characteristic of a stream with a high water velocity. This stream starts on the São Lourenço microbasin and correspond to the source of Rio Grande river. The value of stream slope and the profile of the river (Figure 16) indicate that surface runoff is higher in the steep-slope areas and decrease as the terrain smooths.

All the streams converge in Rio Grande (Figure 17) river which join with Rio Negro river in the northeast of Rio de Janeiro state to form the basin Rio dois Rios and flow into Paraíba do Sul river (Mata Pires, 2006). The upper basin of Rio Grande has a oval-shape suggesting water takes more time to get out the basin, however, looking the slope of the study area water flow is fast in the high areas (Chopra et al., 2005). Drainage density is also a that determines the time of water withing the basin which in humid areas could vary from 0.55 to 2.09 km/km². For the case of the upper basin of Rio Grande, drainage density has a value of 1.308 km/km² characteristic of regions with higly permeable materials and vegetative cover (Chopra et al., 2005). Table 3 summarizes the characteristics of the upper basin of Rio Grande.

2.8. Socio-economic indicators

2.8.1. Population

As it was mentioned before, the upper basin of Rio Grande is divided in tree micro-basins: São Lourenço, Santa Cruz and Barracão dos Mendes. Despite Barracão dos Mendes is the smallest micro-basin (2797.5 ha), it is the most populated with around 445 head of families and 1780 people approximately, Santa Cruz follow in the magnitude order with an average area of (4127.6 ha) and intermediate population with around 300 heads of families and 1200

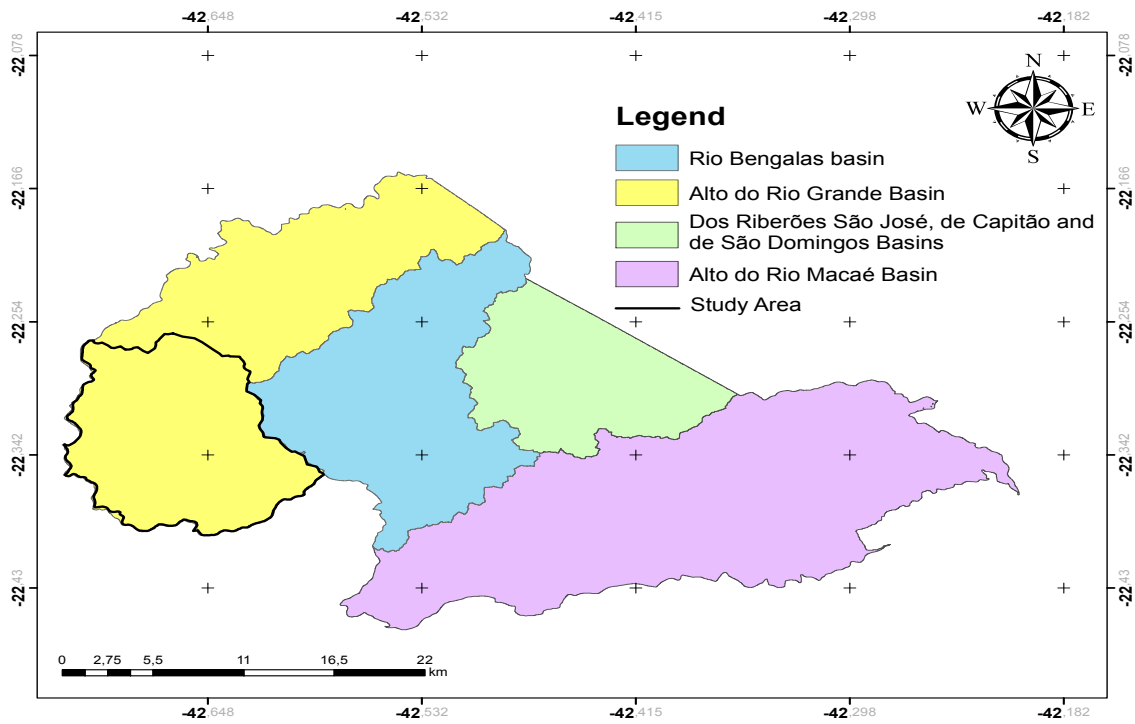


Figure 15.: Hydrographic units of Nova Friburgo.

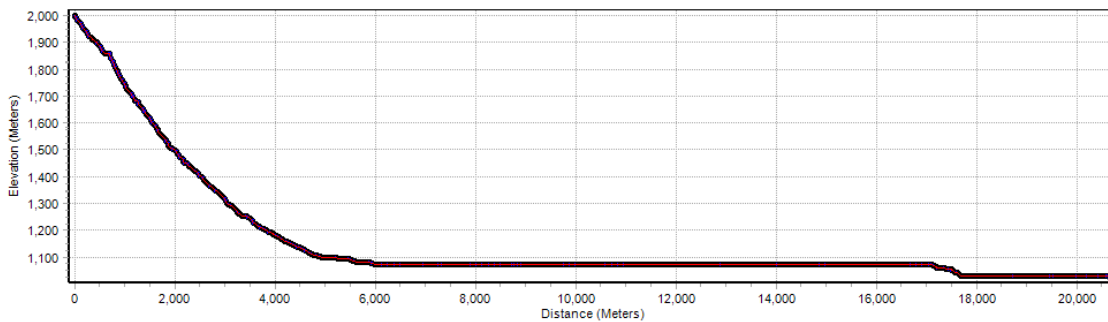


Figure 16.: Profile of the longest stream of the study area.

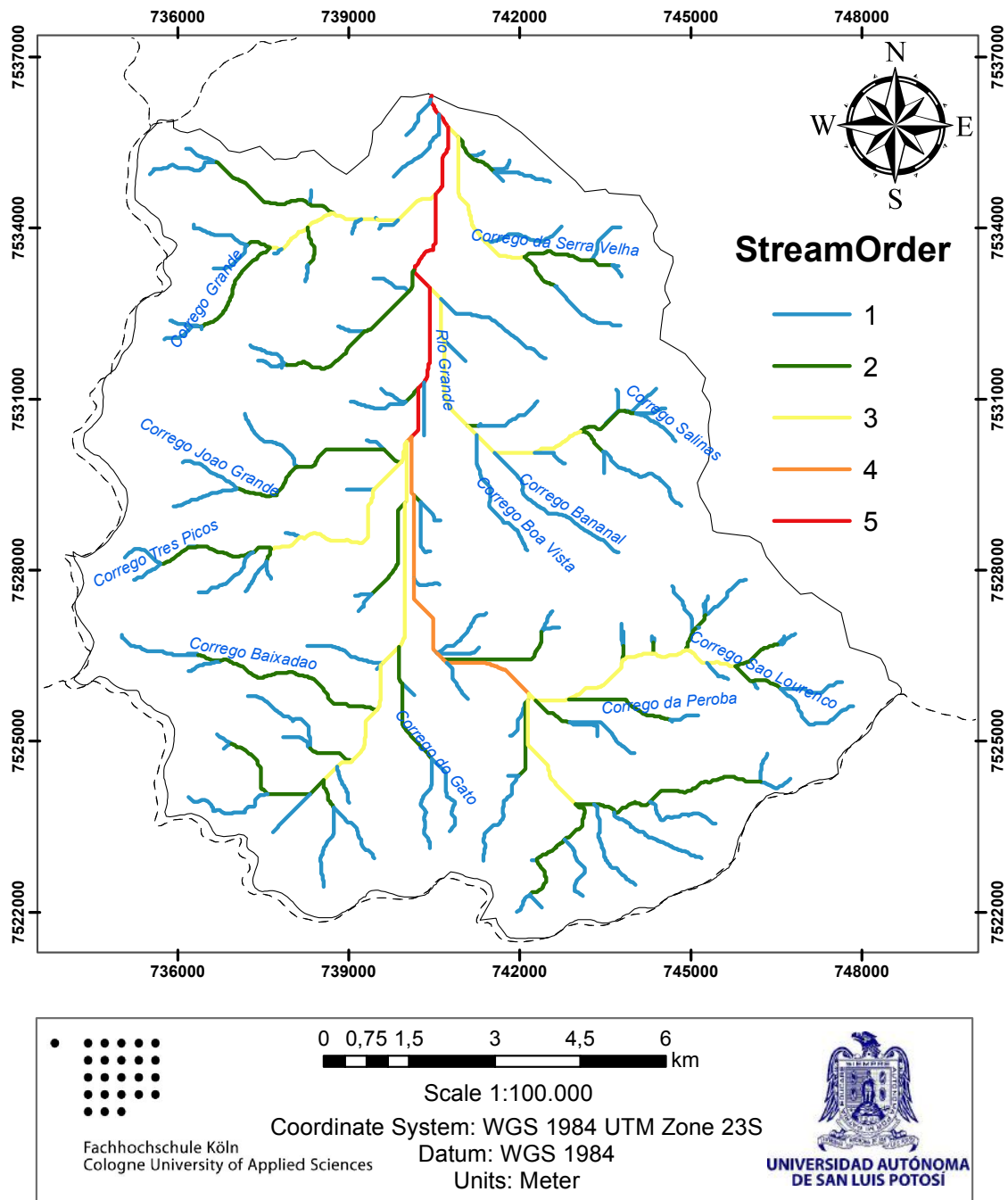


Figure 17.: Streams that form Rio Grande river with their respective order.

Table 3.: Morphometric parameters of the upper basin of Rio Grande.

Physical characteristics	
Drainage area	136.7 km ²
Perimeter	72.3 km
Drainage density	1.308 km/km ²
Stream length	20 km
Mean stream slope	2.7°
Mean catchment slope	1.01°
Maximum elevation	2002 m.a.s.l.
Minimum elevation	1028 m.a.s.l.
Length of the basin	15 km
Drainage basin shape	0.61

Table 4.: Classification of properties based on its area. Taken from (Mata Pires, 2006; Olivieri et al., 2013).

Area of the property	São Lourenço	Santa Cruz/Salinas
<10ha	110	155
11 to 20ha	48	31
21 to 50ha	37	12
51 to 120ha	21	1
121 to 200ha	15	
>201ha	4	
TOTAL	235	199

people in total; finally, São Lourenço is the largest microbasin (7189.8 ha) but it is not as populated as Barracão dos Mendes micro-basin with only 405 heads of families and more or less 1620 people for a total of 4600 people living in the upper basin of Rio Grande (COGEM et al., 2013; Olivieri et al., 2013; Ribeiro Canellas and da Costa Silva, 2013). Most of this people make their living out of agriculture and own lands of no more than 120ha .

Intimate apparel industry is also growing in the region but job positions are not enough for all leading people to migrate to other places. The study area face unemployment problems and the public policies do not promote job generation (COMPERJ, 2011).

2.8.2. Technology and infrastructure

After Green revolution, basic agricultural techniques like use of chemical inputs, mechanization and irrigation, increase land use efficiency converting agriculture in the most profitable economic activity of the study area and improving living conditions of people.

Exist some agriculture techniques that have permitted the growing of agriculture: mechanized soil preparation with micro-tractor, chemical and organic fertilization (but without

soil analysis due to the lack of a full equipped laboratory in the area), pest and diseases control with agrottoxics -with insufficient or non-existent technical advice- and irrigation. Farmers implement conservation practices like planting “cortando as águas” disposed in the form of fish spine in the direction of high declivity. Normally, labor force is familiar with eventual hiring of people for working as day laborers.

The main products of the region are: cauliflower, tomato, parsley, cabbage, broccoli and strawberry which are commercialized either through middlemen or through Mercado Produtor da Região Serrana-CEASA-RJ. The farmer can sell his product to the middleman who is in charge of transporting and selling the production, but under their conditions of low prices and late payments, or can sell it directly to CEASA-RJ, which have more benefits for the farmer because the payment is immediate and at prices of the market of Rio de Janeiro.

2.8.3. Commerce and services

People who does not work in agriculture have bars, small shops and restaurants for supplying the basic necessities of the study area population.

The study area have around 5 or 6 schools for all the grades but one of the most important is the Escola Rei Alberto I or IBELGA school created with funds of Belgium government for young from rural producer’s families with the idea to form agricultural technicians. However, the basin has a percentage of illiterate children younger than 5 years varying from 17.9% to 22.5% (COMPERJ, 2011).

Each micro-basin has a public health unit with a family doctor but works few hours per day. There are insufficient doctors and specialized equipment to fulfill the demand and despite city of Nova Friburgo is close to the micro-basins and people could access to a better health service, the financial resources of population may be insufficient to cover the costs of it.

The micro-basins have electricity and fixed telephony services but there are still some problems with mobile communication and internet connection. Transportation is efficient in the study area, people count with a bus line functioning from 5 to 22 hours.

2.9. Situation of water quality in the basin

Most of the people of the upper basin of Rio Grande are located in rural areas and living on the agriculture. To increase the productivity of the soil, farmers use pesticides and fertilizers that can reach water table and subsequently the river degrading water quality (Moss, 2008; Veiga et al., 2006). In 2013, Instituto Estadual do Ambiente reported that Water Quality Index in the upper part of Rio Grande correspond to class 2 which means that water needs

Table 5.: Percentage of residences with a particular type of sewage system in the upper basin of Rio Grande. . Taken from [ISER 2012](#)

Locality	Rainwater network	Septic tank	Rudimentary septic tank	Discharge into the river	Ditch	Without sanitation
São Lourenço	1.3	5.1	70.5	2.6	17.9	2.6
Santa Cruz/Centenário	2.1	1.1	87.4	0.3	7	2.1
Salinas	3.2	64.3	16.8	5	8.7	2
Barracão dos Mendes	0.3	27.3	55.2	3.7	10.6	2.9

a conventional treatment before using it for public supply. However 7% of the houses in the basin ([ISER, 2012](#)) use the water from Rio Grande for domestic purposes and it is unknown if they do any treatment.

2.10. Water supply and sanitation

The problems with sanitation complement the contamination in the micro-basins. Springs and water wells provide freshwater for 50% of the houses but the lack of sewage systems (Brazilian Institute of Geography and Statistics) lead people to construct rudimentary septic tanks for waste water disposal. 30.7% of the residences in the study area use rudimentary septic tanks and 17.5% of the residences drain sewage directly into the streams ([ISER, 2012](#)). Salinas is the only locality of the study area that count with septic tanks operating in good conditions (63% of the residences have septic tank), the other localities (Santa Cruz, São Lourenço and Barracão dos Mendes) have rudimentary septic tanks consisting, in many cases, of a hole in the soil with a concrete recover ([ISER, 2012](#)). Some studies have demonstrated that these systems can contaminate groundwater ([Gerba and Smith, 2005](#); [Stanford et al., 2010](#); [Carrara et al., 2008](#); [Baba and Tayfur, 2011](#)), jeopardizing water quality and health of people. Parasitic infections are one of morbidity causes in the municipality of Nova Friburgo that can be related with the crisis of the basic sanitation.

3. Methodology



3.1. Election of sampling points

Some sampling points were defined with the help of the members of Clube de Água, a group of high school students from Escola IBELGA created in 2014 to monitoring water quality of Barracão dos Mendes, Santa Cruz and São Lourenço micro-basins. They contacted people from the area to ask permission for sampling their drinking water sources. This points are located in a radio of few kilometers around the Escola IBELGA. Other sampling points were defined by using Google Earth, which was useful to locate some points of interest away from the urban areas unknown for the students of Clube de Água and others points were chosen during informal site visits.

For each sampling, a form (Figure 18) was used to register data of geographical coordinates, municipality, organoleptic and physico-chemical characteristics of the water, use of water, sources of pollution, pumping equipment, observations and telephones of contacts of people. As one of the objectives of the INTECRAL and RIO RURAL project is to know the quality of water consumption, 73% of the sampling points correspond to drinking water sources (springs and water wells). River was also sampled to identify the differences between groundwater and surface water.

3.2. Sample collection and field measurements

Water samples from water wells, springs and rivers were collected in a single sampling campaign during the months of March and May of 2015 in the upper basin of Rio Grande. The SEBA Hydrometrie multiparameter probe MPS-D8 was used for on-site measuring of total dissolved solids (TDS), dissolved oxygen (DO), nitrate (NO_3^-), electrical conductivity (EC), temperature ($^{\circ}\text{C}$) and pH of the first 10 samples. (Table 6) shows the characteristics of the sensors used to measure the parameters on-site. A portable multiparameter bench photometer for aquaculture, HANNA instruments, HI83203 and a dissolved oxygen and temperature portable meter, HANNA HI9146 were used to measure the same physico-chemical properties of the remaining sampling points due to a probe MPS-D8 damage. For water wells the sensors were submerged in a flow-through chamber (Figure 19) -to avoid air

 Fachhochschule Köln Cologne University of Applied Sciences		DADOS FÍSICO-QUÍMICOS DE AGUA SUBTERRÂNEA				
DADOS GERAIS						
Código de identificação						
Coordenadas	X=		Y=			
Datum			Zona UTM			
Elevação (m.s.n.m)						
Município						
Bairro						
Data e hora da coleta						
Litologia Predominante						
Profundidade do nível de água	NE	m	ND	m		
Fonte de água	Poço de água Lago	Poço de água artesiano Rio	Nascimento Canal			
Uso de água	Água de bebida	Atividades domésticas	Industrial			
	Água para animais	Irrigação	Não usado			
Tipo de bomba	Turbina vertical	Submersível	Sem bomba			
	Elétrica	Centrífuga				
Fontes próximas de poluição da água	Fossa séptica	Sumidouro	Vala negra			
	Agricultura					
CARACTERÍSTICAS ORGANOLÉPTICAS						
Color			Olor			
Aparência			Sedimentação			
Turvação			Desgaseificação			
Profundidade Total (m)			Velocidade de extração (l/s)			
PARÂMETROS MEDIDOS NO CAMPO						
Tempo (min)	1	3	5	7	9	
T (°C)						
pH						
CE (microSiem/cm)						
O.D. (%)						
O.D. (mg/l)						
	Nitrato (NO ₃ ⁻)	Nitrito (NO ₂ ⁻)	Amônia (NH ₃)	Fosfato (PO ₄ ³⁻)		
Primeira medição						
Segunda medição						
INFORMAÇÃO COLETA DE ÁGUA						
COMPOSTO	TIPO DE RECIPIENTE	QUANTIDADE	VOLUME	TIPO DE CONSERVAÇÃO	FILTRAÇÃO?	
CATIONS	POLIETILENO	1	125ml	REFRIGERAÇÃO, HNO ₃	SEM	
NITRATES	POLIETILENO	1	125ml	REFRIGERAÇÃO, H ₂ SO ₄	NÃO	
ANIONS	POLIETILENO	1	125ml	REFRIGERAÇÃO	NÃO	
COMENTÁRIOS						

Note: This format was modified from the one that the Department of Ciencias de la Tierra, Universidad Autónoma de San Luis Potosí use for the registration of groundwater samples

Figure 18.: Form for registering characteristics of water source

Table 6.: Measuring ranges and accuracy of Multiparameter probe MPS-D8 sensors

Parameter	Measuring range	Accuracy	Resolution
Temperature	-5-50°C	±0.1°C	0.01°C
Conductivity	0-200mS	±1µS	0.001mS
Oxygen (amperometric)	0.04-40 mg/l	±5%	0.01mg/l
Turbidity	0-1000NTU	±0.3NTU	0.01NTU
pH	0-14	±0.1	0.01
Nitrate (NO ₃ ⁻)	0.4-60,000mg/l	±2mg/l	0.01mg/l
Total Dissolved Solids (TDS)	0-200,000mg/l		

contact and preserve in-situ conditions of the water- and samples were collected after the stabilization of temperature and electrical conductivity.

Clean high density polyethylene bottles of 1l were used for major ions analysis while 60ml of sterile bottles were used for microbiological analysis. The water samples were stored in a portable cooler, filled out with ice and transported right after the sampling to the laboratories of Instrumental analysis and microbiology of PESAGRO-RIO (Centro Estadual de Pesquisa em Sanidade Animal Geraldo Manhães Carneiro) in Niterói where major ions and bacteriological properties of the groundwater and surface water were analyzed. Carbonate and bicarbonate content were estimated by titration with HCl 0.02N according with APHA protocols (Federation et al., 2005); color, turbidity, calcium, magnesium, sodium, sulphate, fluoride and chloride were determined by photometric method with the Portable Datalogging Spectrophotometer HACH DR/2010. The microbiological concentration in the water samples were determined using Colilert[®] test kit based on IDEXX's patented Defined Substrate Technology[®] (DST[®]). The Colilert[®] possess a nutrient-indicator which when total coliform metabolized it, the sample turns yellow and when *E.coli* metabolizes it, the sample fluoresces.

3.3. Electroneutrality condition

Freeze and Cherry 1977 defined that in an electrolyte solution, the sum of the positive ionic charges equals the sum of negative ionic charges, this rule is known as the electroneutrality condition. Normally, the laboratories use this principle and calculate a *charge-balance error* to determined the accuracy of water analysis, considering an acceptable charge-balance error less than 5%.

Table 7.: Methods used for water chemical analysis

Author	Field Parameters				Anions			Cations			Average error	
	E.C	Temperature	pH	HCO ₃	Cl	SO ₄	NO ₃	K	Na	Ca		Mg
This study	Portable conductivity meter, thermometer and pH-meter		Direct Titration			Photometry		ND		Photometry		44.8%±42.92
Boy Roua 2013	Portable conductivity meter, thermometer and pH-meter				Capillary electrophoresis			Inductively coupled plasma optical emission spectrometry (ICP-OES)				0.79%±1.62
Hernández Martínez 2008	Portable conductivity meter, thermometer and pH-meter		Gran Titration on field		Argentometric titration	Turbidimetric method	Brucine sulphate method	Atomic absorption spectrometry				< 5%
HWA and HORA 2009	Portable conductivity meter, thermometer and pH-meter		Direct Titration on field			Ion chromatography		Inductively coupled plasma mass spectrometry (ICP-MS)				2.77%±5.28
Jiang et al. 2009	Portable conductivity meter, thermometer and pH-meter		Direct Titration on field			Ion chromatography		Inductively coupled plasma-mass spectrometry				3.93%±13.23
Yoshimoto et al. 2011	ND		Direct Titration on field					Ion chromatography				1.61%±2.86

ND: Not defined



Figure 19.: Flow-through chamber for groundwater sampling

$$Error(\%) = \frac{\sum cations - \sum anions}{\sum cations + \sum anions} * 100$$

where cations and anions concentration should be expressed in milliequivalents per liter.

Calculated charge balance errors for chemical analysis were ranged between 4 and 82% (A) indicating that the analysis where unacceptable for the purposes of this study. Comparing the water chemical analysis method of in this study with other studies method (Table 7), the author found that the accuracy of the photo-metric method is unsuitable for knowing the real concentrations of major ions in the water. Brown 2011 had already remarked that the results obtained with portable test kits and portable photometers are indicative but its accuracy level and reliability are not comparable with the methods of a certified laboratory. Despite of that, to identify the groundwater and surface water condition, the author selected 14 parameters: field-measured parameters (temperature, pH, electrical conductivity, dissolved oxygen, nitrate, nitrite and phosphate) because they represent the natural condition of the water, microbiological parameters (total and thermotolerant coliforms), and 3 chemical parameters (chloride and sulphate). Chloride was include because is a conservative ion that is not degraded in the environment, tend to remain in solution once dissolved (Valle et al., 2014) and in absence of natural sources indicate anthropogenic contamination. Sulphate

was also used in the analysis because it can be introduced to groundwater by natural or anthropogenic activities.

3.4. Processing of data

With the software IBM SPSS Statistics 21, a correlation analysis was calculated to identify the relationship between all possible pairs of variables and explain this behavior. Additionally, a descriptive statistical analysis was realized with the aid to have a general idea about the process influencing groundwater chemistry. The software ArcGIS 10.0 was used to localize sampling points of the study area and represent spatial variation of the physicochemical parameters.

3.5. Groundwater vulnerability GOD method

The GOD method was used in this study to assess groundwater vulnerability due to its simple and pragmatic structure but also due to the small number of parameters required for the analysis. This method allow a quick assessment of the aquifer vulnerability which fulfill with the requirements of the study area despite of poor data availability. It was developed by Foster 1987 for studying the vulnerability of the aquifer against the vertical percolation of pollutants through the unsaturated zone without considering their lateral migration in the saturated zone (Boufekane and Saighi, 2013). Three parameters are considered: the groundwater occurrence (G), the lithology of the overlying layers (O), and the depth to groundwater (D) (Gogu and Dassargues, 2000). Each parameters is rate between 0 and 1 (Figure 20) and multiplied to obtain the vulnerability index according with equation:

$$I = G \times O \times D$$

The index value vary from 0 to 1 and it is classified into five vulnerability classes: Negligible, low, moderate, high and extreme.

3.5.1. Rating of groundwater occurrence and overlying lithology

The geology map of Brazil at scale 1:100,000 Folha Nova Friburgo SF23-Z-B-II published by CPRM (Serviço Geológico do Brasil) was used to define and the overlying lithology predominating in the study area. The upper basin of Rio Grande is formed by unconsolidated sediments that correspond to the Rio Grande area and igneous rocks that characterize most of study area. According with the GOD method, unconsolidated sediments deserve a rate

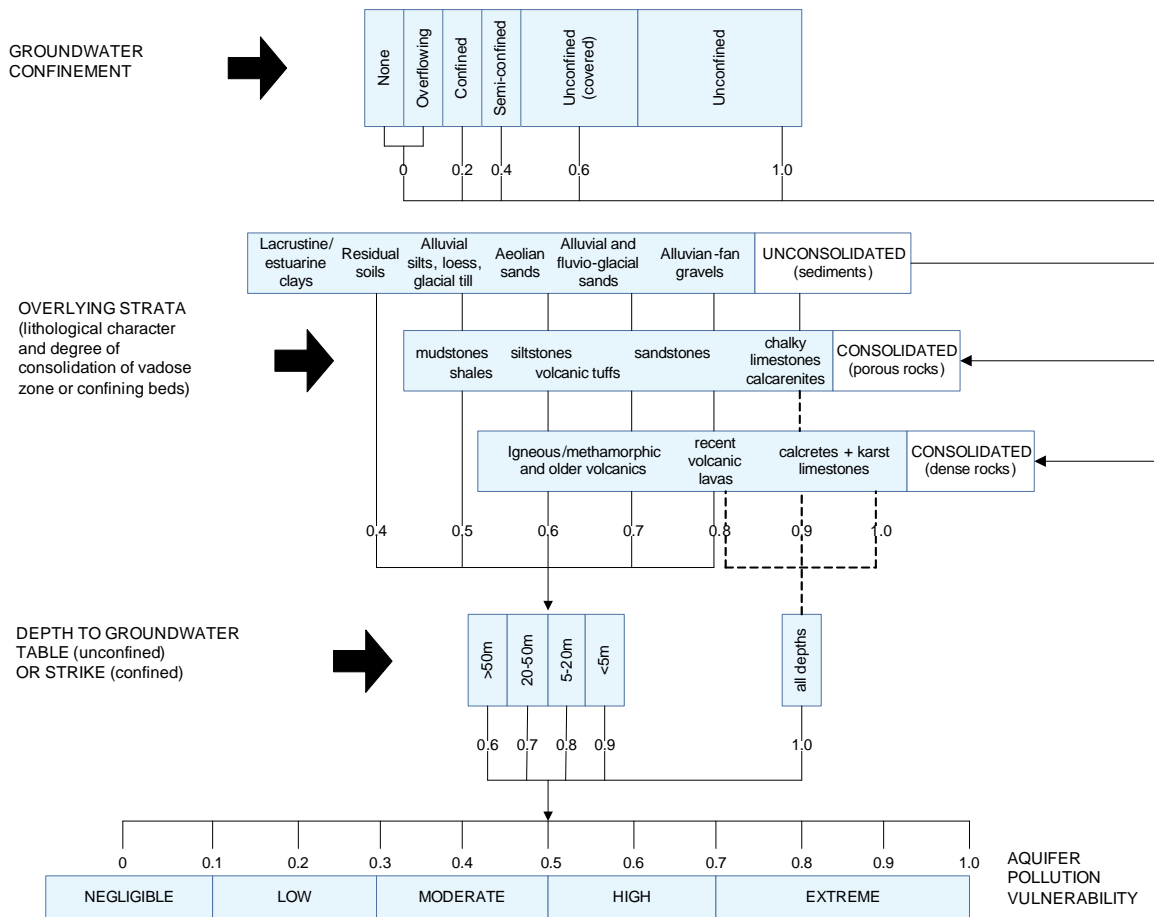


Figure 20.: GOD system for evaluation of aquifer pollution vulnerability. Modified from Foster et al. 2002

of 1 for being the most vulnerable geological unit while igneous deserve a rate from 0.6 to 0.7, the author averaged those values and assigned a rate of 0.675 (Table 8).

Nova Friburgo geology map join with Nascimento 2012 studies and map of hydro-geological favourability of Rio de Janeiro were used to define the groundwater hydraulic confinement. The aquifer of the study area is type unconfined, fractured, heterogeneous and anisotropic, according with this description, “the hydraulic conductivity varies with the direction of measurement at a point in a geologic formation (Freeze and Cherry, 1977)”, in other words geological formations have different hydraulic conductivity, thus, should have a different rating based on GOD method. As a result, the author divided the study in two parts: one correspond to geological formations that combined with soils and slope have highest hydraulic conductivity (map of hydro-geological favourability), considered as unconfined aquifer and rated with 1; the other correspond to geological formations with lower hydraulic conductivity, considered as semi-unconfined aquifer and rated with 0.5 (Table 8).

Table 8.: GOD rating for the hydrogeological parameter settings

GOD Parameter	Characteristics	Rating
Groundwater confinement	Rio negro complex, Nova Friburgo granite, Frades granite and colluvial and alluvial deposits located on flood plains: unconfined	1
	Nova Friburgo granite, Cordeiro, Serra da Onça Granite and São Fidelis units locate on very undulated topography with low permeable soils: unconfined (covered)	0.5
Overlying lithology	Colluvial deposits and alluvial deposits. Unconsolidated sediments	1
	Biotite-gneiss, granite, diorite, orto-gneiss, quartzite and metadiorite. Igenous and metamorphic rocks.	0.65
Depth to groundwater	Unconsolidated sediments	1
	<5m	0.9
	5-20m	0.8

3.5.2. Estimation of depth to groundwater

Due to the lack of tools, the depth to groundwater or water level of artisan and dug water wells was not measured directly. For the artisan water wells, the owners provided an approximate depth to groundwater varying from 6 to 15m. For the dug water wells, its nearness to the river permitted to suppose that their operation is similar to a piezometers whose depth to groundwater should coincide with river water level, therefore, the author assumed that the depth to groundwater of the dug water wells and the river water level had the same values. The depth to groundwater was interpolated with the geostatistic tool technic Kriging of ArcGIS[®] in order to obtained the values for the whole study area. Values between 2 and 3 meters were assigned a rating of 0.9, values of 6 and 7 meters were assigned a rating of 0.8 and values higher than 15 meters were assigned a rating of 0.7 (Table 8). Once the vector maps with their respective ratings where obtained, the union ArcGIS[®] tool was used to join map's features and calculate the vulnerability index.

3.6. Hydraulic head and the direction of groundwater flow

In general terms, the groundwater flow depends on the hydraulic gradient presented when the elevation of the water level or *hydraulic head* varies. Hubbert 1940 defined the *hydraulic head* (h) as a physical quantity, capable of measurement, where the flow occurs from regions with higher h values to regions where h is lower. The hydraulic head is the sum

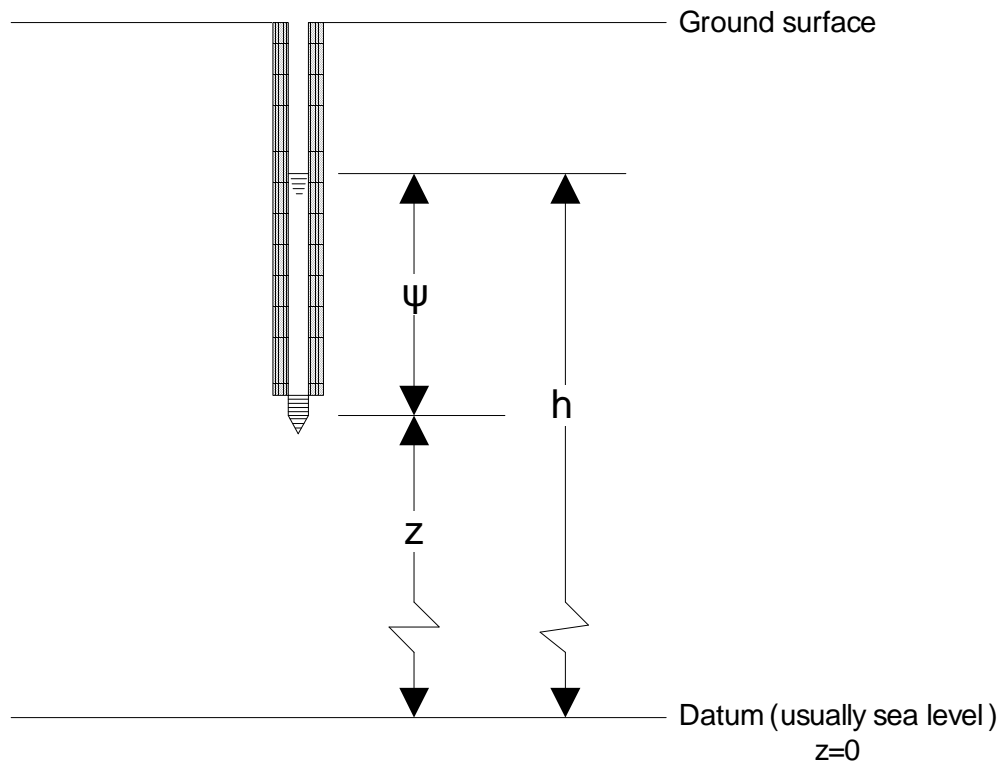


Figure 21.: Hydraulic head h , pressure head ψ , and elevation head z for a field piezometer. Taken from [Freeze and Cherry 1977](#).

of the elevation of the point of measurement, or *elevation head*, z , and the *pressure head* (Figure 21).

In this study, the *hydraulic head* was calculated using two datasets: (1) digital elevation model (DEM) of the study area at a scale of 1:100,00 ([Weber et al., 2004](#)) and (2) depth to groundwater map reflecting March and May 2015 hydrologic conditions. The depth to groundwater map was subtracted from the digital elevation model on a cell-by-cell basis resulting a grid file with the water level for each cell. The positions of equal hydraulic head or *equipotential lines* were contour and the *flowlines* were drawn perpendicular to the equipotential lines from the zone with higher hydraulic head to zones with lower hydraulic head obtaining groundwater flow direction.

4. Results and discussion

4.1. Hydrogeology settings

Alluvium system and fractured crystalline system are the two aquifer systems in the upper basin of Rio Grande (Figure 22). Alluvium system comprises the alluviums from Rio Grande and its affluents, presented in the central part of the study area. It is a free aquifer recharged by river and rain, constituted by sandy sediments that can reach 20m of thickness (CTE, 2009). Time and technical limitations restrained the measurement of water well flow rates but Martins et al. 2006 underline that flow rates are higher than $1.0 \text{ m}^3/\text{h.m}$. The sandy sediments of the alluvium system and its granulometry, facilitate water infiltration to subsoil which give to the aquifer high permeability properties but also high vulnerability to contamination. The same properties favor water extraction through dug water wells of big diameters or shallow wells (CTE, 2009). Shallow and free aquifers have high pollution vulnerability, for that reason it is necessary protect its recharge and influence zones.

Fractures on granites and gneisses define the permeability and porosity of the crystalline system (CTE, 2009). In the upper basin of Rio Grande, fractured crystalline system occupies the south, eastern and western part of the area, formed by the geological units of Suíte Cordeiro, Suíte Serra dos Órgãos and Suíte Nova Friburgo (Figure 10). According with hydrogeological favorability map of Brazil the hydrological potential of this rocks vary depending of the terrain slope, type of soil that covers them and the hydraulic conductivity proper of the geological medium, thus Barreto et al. 2000 divided crystalline aquifer in low hydrogeological favorability and medium hydrogeological favorability.

Domains with slopes higher than 45° (mountaneous areas and scarps) form crystalline systems of low hydrogeological favorability (Figure 22). The aquifer has a low productivity (approx. $1\text{m}^3/\text{h}$, Barreto et al. 2000) because the thin soil cover limit the accumulation of groundwater, however, it can be generalizes that crystalline systems in steep slopes have low productivity because water well yield depend on the existence of fractures in the rock and its connection with the upper soil. On the other hand, domains with slopes lower than 45° , crystalline rocks surrounded by colluvionar deposits, gently hilly area domains and shallow artisan wells for water abstraction, characterize crystalline system of moderate hydrogeological favorability. Those areas have high permeability responsible for the recharge

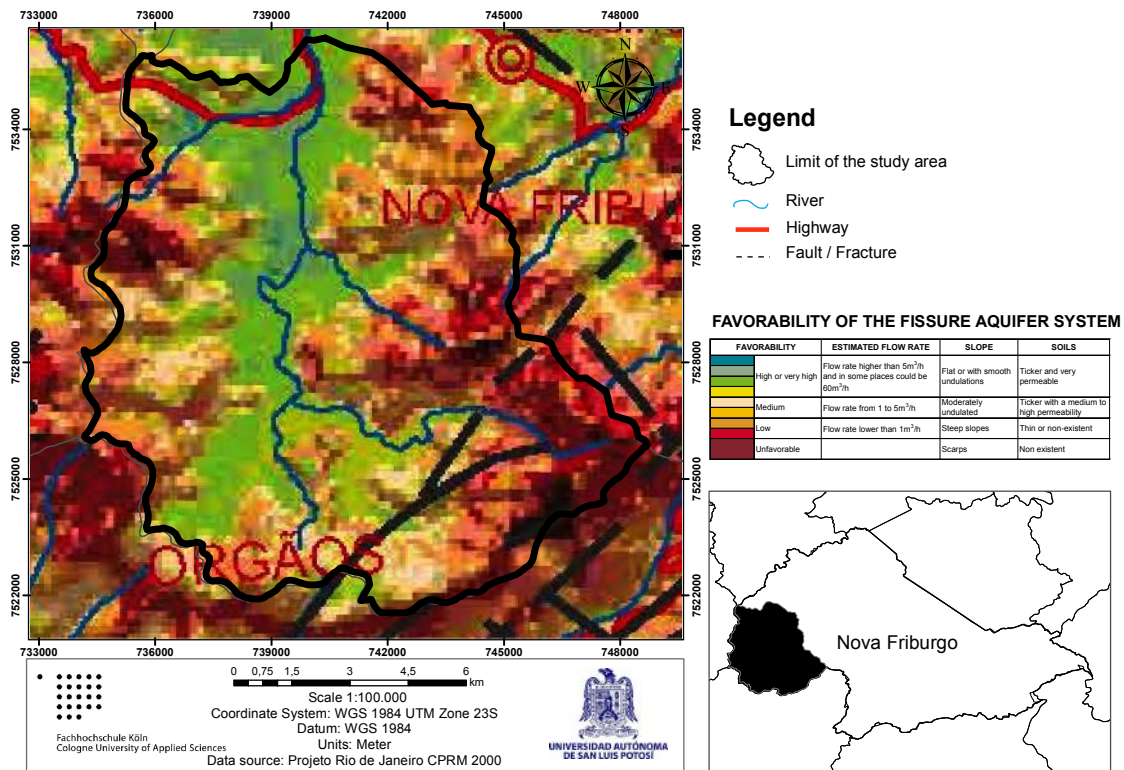


Figure 22.: Hydrogeological favorability of the upper basin of Rio Grande

of fractured crystalline aquifer (Martins et al., 2006).

Shallow groundwater, high precipitation, permanent availability of water of the study area and low electrical conductivity of groundwater (Table 10) indicate that the upper basin of Rio Grande lies on an aquifer with a high recharged rate determined by the infiltration of rainwater in medium and high steep areas as it was indicated by de Oliveira Filho 2003 for an area of similar characteristics to the upper basin of Rio Grande.

The water table generally is not far below the land surface in alluvial valleys. Therefore, vegetation on flood plains, as well as at the base of some terraces, commonly has root systems deep enough so that the plants can transpire water directly from ground water. Because of the relatively stable source of ground water, particularly in areas of ground-water discharge, the vegetation can transpire water near the maximum potential transpiration rate, resulting in the same effect as if the water were being pumped by a well (see Figure 7). This large loss of water can result in drawdown of the water table such that the plants intercept some of the water that would otherwise flow to the river, wetland, or lake. Furthermore, in some settings it is not uncommon during the growing season for the pumping effect of transpiration to be significant enough that surface water moves into the subsurface to replenish the transpired

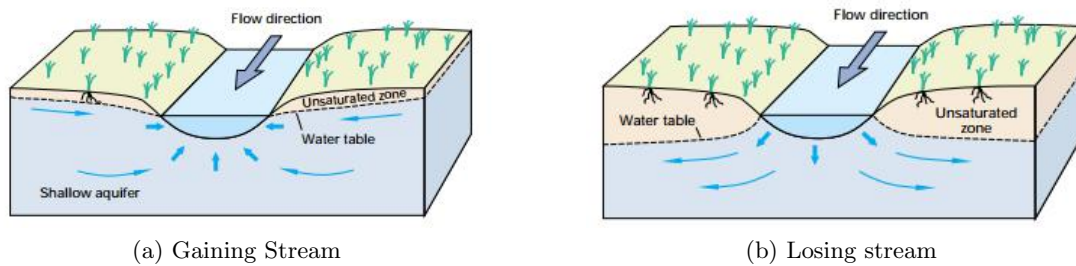


Figure 23.: Interaction of groundwater and streams. (a) Gaining stream receives water from groundwater system and (b) Losing stream loses water to the groundwater system. Taken from [Winter 1999](#)

ground water

Groundwater and surface water interact in three ways: streams gain water from inflow of groundwater through streambed (gaining stream, [Figure 23](#)), stream lose water to groundwater through the streambed (losing stream, [Figure 23](#)) or they do both, in some places they like gaining stream and in other act as losing stream ([Winter, 1999](#)). Based on static water level measured on field, the author identified that contour lines point in the upstream direction following the natural slope of the area which means groundwater recharge Rio Grande([Figure 24](#)). This is possible because, the water table in the vicinity of the river is higher than river-water surface and its tributaries leading to transfer water from the aquifer to the river contributing to increasing river flow.[Mendes da Rocha 2013](#) described the same process for an alluvionar aquifer in São Paulo. However, this interaction may vary in time and space. [Winter 1999](#) defined that flow direction can change as a result of individual storms, transpiration of groundwater by streamside vegetation and pumping groundwater near streams. Withdrawing water from shallow aquifers near surface-water bodies diminish the available surface water and change flow pattern of the river, forcing surface to flow into the aquifer [Figure 25](#). Vegetation on flood plains of a shallow aquifer have the same effect of a pumping water well because its deep roots permit the plants to transpire water directly from groundwater([Winter, 1999](#)).

4.2. Groundwater vulnerability GOD method

4.2.1. Groundwater occurrence

Groundwater occurrence refers to aquifer type: unconfined, unconfined covered, semi-confined, confined, overflowing or none aquifer. According with the classification of [Heilbron](#)

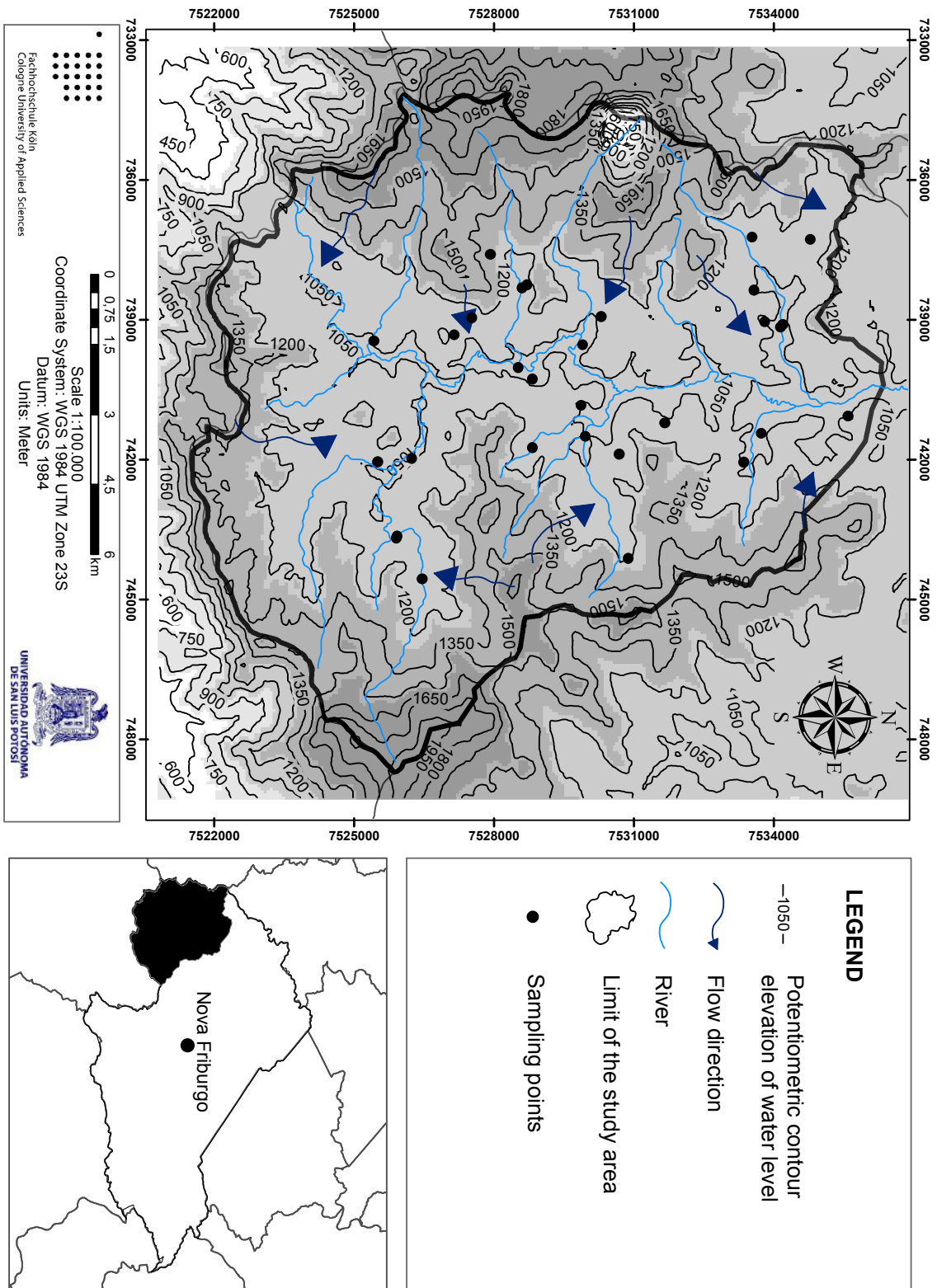


Figure 24.: Groundwater flow direction

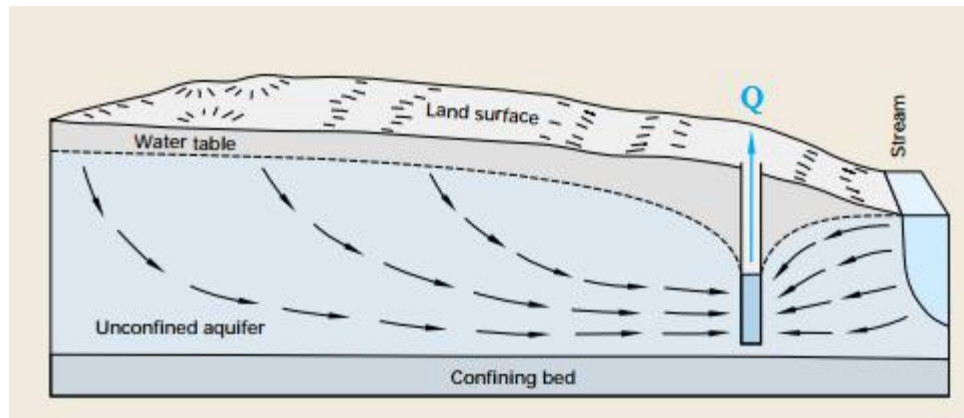


Figure 25.: Hydrologic system during withdraw of a well near surface water body. Modified from [Winter 1999](#).

[et al. 2008](#) and the review of [Nascimento 2012](#), the upper basin of Rio Grande lies on the unconfined aquifer of Complexo Rio Negro-Costeiro. However, from the work of [Tupinambá et al. 2012](#), geological map of Nova Friburgo and the soils type of the study area, the author identified zones of high and medium permeability: colluvio-alluvional deposits and the geological units of Suíte Nova Friburgo, Suíte Serra dos Orgãos and Suíte Cordeiro respectively. As such, the colluvio-alluvional deposits were assigned a rating of 1 because of its high permeability and high infiltration rate while the rest of the area were assigned a rating of 0.5 [Figure 26](#).

4.2.2. Overlying lithology

The knowledge of lithology and stratigraphy of geologic deposits and formations help to understand the distribution of the aquifers ([Dinu, 2004](#)). From litho-stratigraphic map ([Figure 10](#)) the author found that the study area consist of igneous rocks (Complexo Rio Negro, Suíte Cordeiro and Serra dos Orgãos) and unconsolidated sediments. Ratings have a range between 0.6-0.7 or metamorphic and igneous rocks and 1 for colluvio-alluvional deposits [Figure 26](#).

4.2.3. Depth to water table

Depth to water indicates the distance that a pollutant has to travel before reaching the aquifer ([Aller et al., 1987](#)). Shallower water table implies an aquifer more vulnerable to contamination. Depth to water table varies from 0 to 15m in the study area. Northeast and southern zones have the lowest water level between 0.5 and 3.7m but almost all the area falls within shallow groundwater zone [Figure 26](#). The author classified the map into 3

intervals and assigned values from 0.8 to 1; being 1 for shallow groundwater (<2m of depth to water table), the most vulnerable area, 0.9 for deeper water table from 2 to 5m and 0.8 for the deepest water table of the study area (5-10m).

The vulnerability map [Figure 26](#) was classified into four classes: low, moderate, high and extreme vulnerable to pollution. 70% of the study area lies on zone of low or moderate vulnerability where the aquifer is unconfined covered by soils with a medium pollutant attenuation capacity due its low infiltration rate and where steep slopes difficult the development of any productive activity. On the other hand, around 30% of the area correspond high or extreme vulnerability where fine sand constitute vadose zone and saturated zone and where most of people has its crops land increasing the contamination risk.

4.3. Hazard assessment

Vulnerability analysis just gives an idea of the potential pollution areas to groundwater but the absence of factors of risk represent an absence of danger to pollution. For that reason, hazard assessment usually joins vulnerability assessment.

From the annexes of “Programa Estatal de Microbasias Hidrográficas” ([COGEM, 2012a,b](#); [Gomes da Silva and rural do Salinas e Santa Cruz, 2012](#)) the author identified tree possible sources of groundwater pollution: the use of agrotoxics (pesticides and fertilizers) in agricultural areas, the management of its vessels, the use of septic tanks and cesspits for wastewater disposal, and the direct discharge of wastewater into rivers and land. During the field work, other hazards were registered like graveyards, greenhouses and gasoline station but short field time precluded a full pollution sources inventory. The author calculated a hazard index for each source of pollution and divided them into 5 classes: “very low”, “low”, “medium”, “high” and “very high” hazard level.

[Figure 27](#) shows that most of the groundwater pollution factors correspond to a very low or low hazard level. Septic tanks, cesspools, greenhouses, graveyards, waste water discharge into surface water courses and pasture belong to this category. The hazard inventory list and the hazard mapping method of COST Acion 620 are general and unspecific for the characteristics of particular zones ([Werz and Hötzl, 2007](#)), therefore, this methodology omits characteristics that could have higher influence on groundwater pollution and should be include into the hazard index rating. For example, cesspools and septic tanks should have a regular maintenance but according with [Segovia Sánchez 2014](#) this process is inexistent in the microbasins of the upper Rio Grande which could increase the probability of groundwater contamination by septic system leachate.

According with hazard level assessment in the study area, intensive agricultural areas do

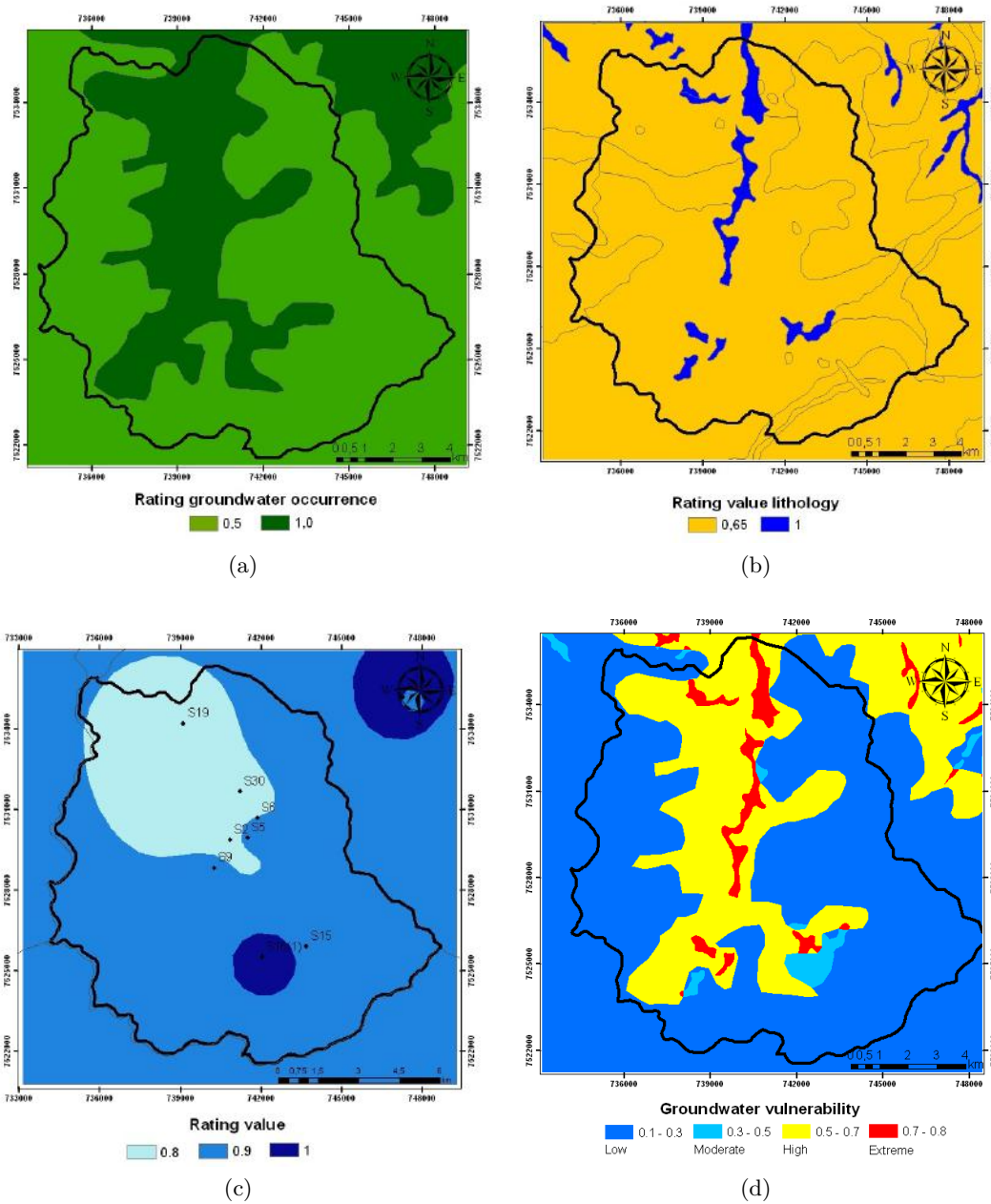


Figure 26.: Factors of GOD method and map of groundwater vulnerability. (a) Groundwater occurrence (G); (b) Overlying lithology (O); (c) Depth to water table (D) and (d) Map of groundwater vulnerability.

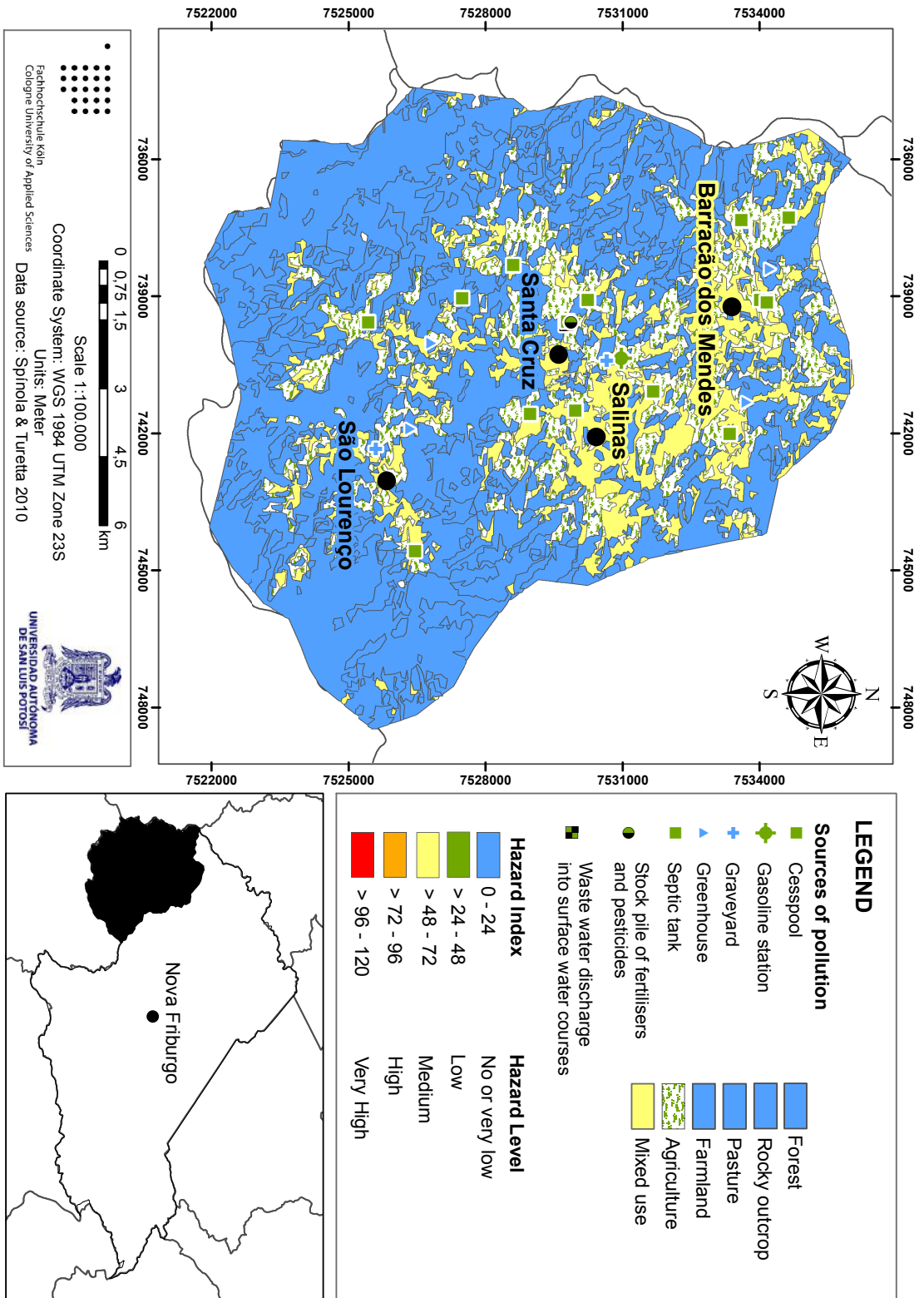


Figure 27.: Hazard index map

not represent a danger for groundwater contamination but some characteristics like the extension of agriculture (17% of the land cover) and the long-term use of agrottoxics in the area, more than 30 years (Peresa et al., 2001), could convert agriculture in a source of groundwater pollution with a higher hazard level than the obtained with COST Action 620 methodology (Zwahlen, 2004). Figure 27 shows that areas of mixed-use (urban areas of low-density associated with self-consumption agriculture) possess a medium hazard level. The situation can be explained for the fact that the greatest number of houses located in those areas, lack wastewater treatment system and rivers, cesspit, septic tank or land are the final destinies of the sewer (COGEM, 2012a,b; Gomes da Silva and rural do Salinas e Santa Cruz, 2012).

The hazard map in combination with groundwater vulnerability map (Figure 28) allowed to identify the zones of high risk intensity because of the presence of pollution sources such as agriculture and houses without sewer system in the most vulnerable areas to groundwater contamination. Those areas should be monitor and controlled in order to protected the main water sources of the upper basin of Rio Grande and avoid public health problems related to groundwater pollution.

4.4. Samplings points location

Precipitation, geology and vegetation of Nova Friburgo favored the presence of rivers, streams lakes and springs, being springs the most important source of drinking water. Only in the microbasin of Barracão dos Mendes unprotected springs correspond to 85% of water sources (Segovia Sánchez, 2014). A similar situation occurs in the microbasins of Santa Cruz and São Lourenço where springs are more than 55% of the water sources. However, the recurrent and long droughts in Brazil for a few years now have dried springs up not only in the upper basin of Rio Grande but also in all the mountaneous region of Rio de Janeiro and have forced people to find other ways of water supply as artisan water wells and dug water wells (Figure 29).

Meanwhile, the lack of water quality information in the study area complements the recent situation of water availability. Residents evaluate water quality based on two physical parameters: odor and color. All of them perceived a good quality of spring water and wells water, but Segovia Sánchez 2014 indicated that any analysis has been done to probe their conclusions and she remarked the necessity of a water quality monitoring program that can evaluate the real state of water. This study tried address this issue not only in the microbasin of Barracão dos Mendes but also in the microbasins of São Lourenço and Santa Cruz.

The author collected information of 11 springs, 8 artesian water wells, 4 dug water wells, 7

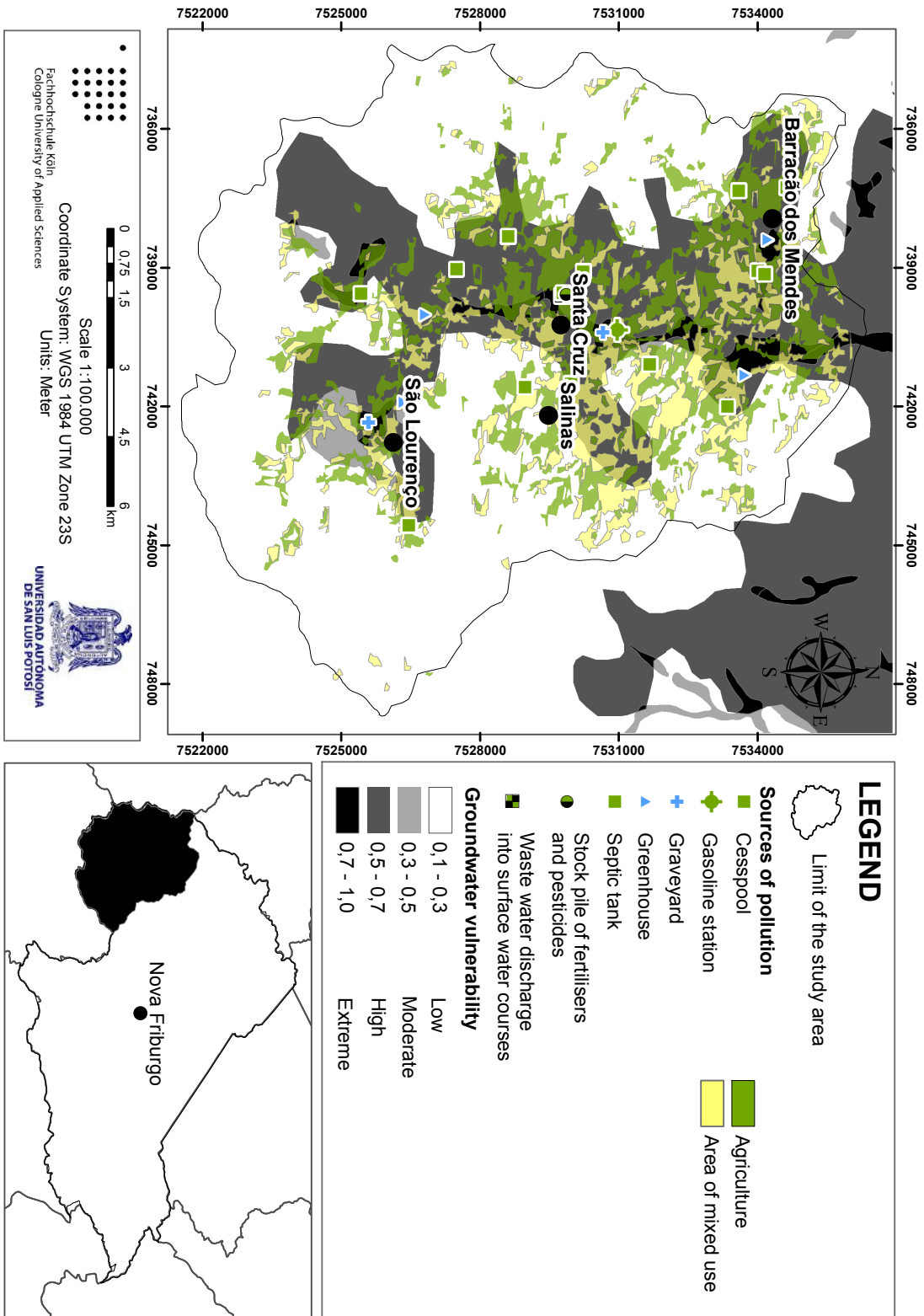


Figure 28.: Risk map



(a) Artisan water well is deeper and has a PVC tube with a small diameter. The water is extracted without a pump.



(b) Dug water well is handmade with a higher diameter and a cover of concrete. The water is extracted with a pump.

Figure 29.: Differences between an artisan water well and a dug water well according with community of the study area..

points along the river Rio Grande and 1 lake (Figure 30) during April and May 2015. All the sampling points are located in the zone of the highest vulnerability and groundwater contamination risk with exception of the samples S1 (spring), S23 (river), S24 (spring) and S30 (artisan water well).

The main use of water sampling sites, with exception of rivers, is domestic consumption, being water wells (39% of sampling points) as important as springs (35% of sampling points) for drinking and irrigation water supply in all the sampling points of the upper basin of Rio Grande (Table 9). Springs are located on mildly hilly or hilly areas with slopes between 3 to 20° surrounded by pasture, some areas of subsistence agriculture and few square kilometers of forest which in the own words of the farmers: “is for protecting the water source and avoid spring drought off”. Dug and artesian water wells are located in mildly hilly areas with slopes of 3 to 8° nearest to the valley of the basin characterized by the huge development of agriculture and the low urbanized areas without wastewater system treatment.

4.5. Physicochemical characteristics of groundwater

The length of time that water is in contact with geological materials and the activities developed in the land surface control water chemistry. Exist chemical reactions that influence the biological and chemical characteristics of groundwater some of them are: acid-base reactions, precipitation and dissolution of minerals, sorption and ion exchange, oxidation-reduction reactions, biodegradation and dissolution and exsolution of gases ; but when the contact time between water and geological medium, like in the case of shallow aquifers, few chemical changes take place in the water (Winter, 1999).

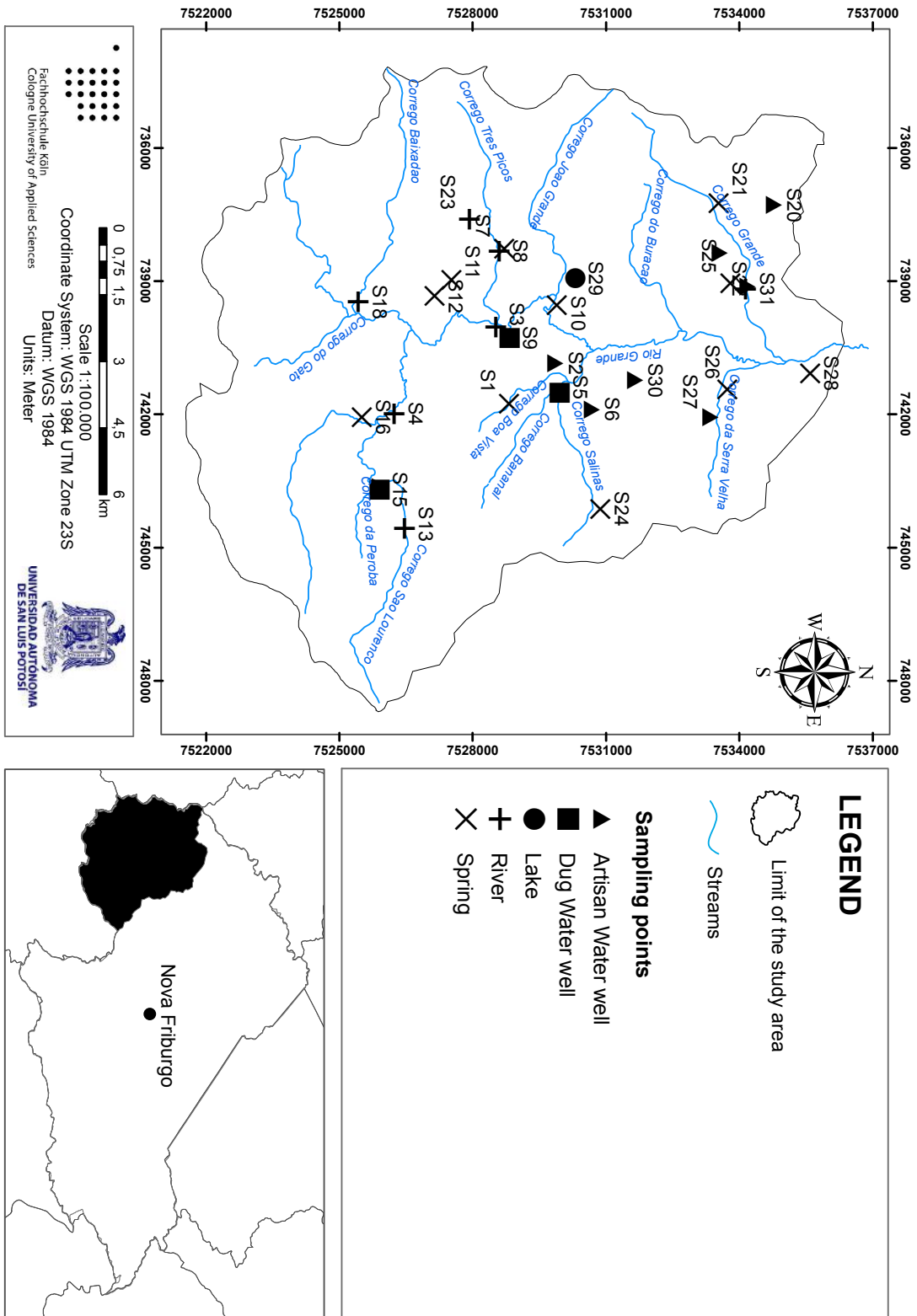


Figure 30.: Sampling points location

Table 9.: Use of water from the sampling points.

UTM_X	UTM_Y	Code	Water source	Use of water
741745.0	7528817.0	S1	Spring	Drinking and domestic
740848.0	7529863.0	S2	Artisan Water well	Drinking and domestic
740033.0	7528512.0	S3	River	Irrigation
741976.0	7526231.0	S4	River	Irrigation and bath
741509.0	7529948.0	S5	Dug Water well	Drinking and domestic
741885.0	7530679.0	S6	Artisan Water well	Drinking and domestic
738254.0	7528704.0	S7	Spring	Drinking and domestic
738319.0	7528591.0	S8	River	Irrigation
740279.0	7528819.0	S9	Dug Water well	Wash vegetables
739545.0	7529891.0	S10	Spring	Drinking and domestic
738960.1	7527516.5	S11	Spring	Drinking and domestic
739330.4	7527136.0	S12	Spring	Drinking troughs
744567.1	7526459.8	S13	River	Irrigation and drinking troughs
743646.4	7525911.1	S14	Artisan Water well	Drinking, domestic, irrigation and drinking troughs
743689.1	7525895.7	S15	Dug Water well	Drinking, domestic and irrigation
742053.1	7525500.3	S16	Spring	No use (little amount of water)
739465.4	7525422.3	S18	River	Drinking troughs
739109.2	7534192.5	S19	Artisan Water well	Drinking, domestic and drinking troughs
737283.0	7534778.0	S20	Artisan Water well	Drinking and domestic
737238.1	7533525.1	S21	Spring	Drinking, domestic, irrigation and drinking troughs
738367.6	7533565.0	S22	Artisan Water well	Drinking and irrigation
737609.4	7527921.3	S23	River	Drinking and domestic
744119.4	7530870.5	S24	Spring	Drinking, domestic and drinking troughs
739055.0	7533792.7	S25	Spring	Drinking and domestic
741444.1	7533726.2	S26	Spring	Drinking and domestic
742062.0	7533349.2	S27	Artisan Water well	Drinking and domestic
741070.9	7535587.6	S28	Spring	Drinking and domestic
738939.4	7530299.3	S29	Lake	Irrigation
741224.8	7531658.0	S30	Artisan Water well	Drinking and domestic
739170.7	7534139.9	S31	River	Irrigation

Table 10.: Variation of physico-chemical and microbial content of sampling points of the upper basin of Rio Grande.

Code	Water Source	Temp (°C)	pH	TDS (mg/l)	E.C. ($\mu\text{S}/\text{cm}$)	D.O. (%)	D.O. (mg/l)	NO_3^- (mg/l)	PO_4 (mg/l)	NO_2 (mg/l)	Total coliforms (MPN/100ml)	Thermotolerant <i>E.coli</i> (MPN/100ml)	Hardness (mg/l CaCO_3)	HCO_3^- (mg/l)	Cl^- (mg/l)	SO_4 (mg/l)
S1	Spring	18.97	8.21	53	79	50.52	4.35	7.531	0.08	0.0006	>23	0	13.4	18.30	3	1
S7	Spring	17.31	6.4	15	23	36.6	3.221	0.85	0.04	0.02	>23	>23	12.8	9.76	1.2	0
S10	Spring	20.03	5.17	58	86	37.248	3.278	74.51	0.06	0.01	>23	3.6	12.6	3.66	8.1	8
S11	Spring	18	6.75	5	5	58.47	4.91	0.443	0	0.01	>23	>23	19.9	7.32	1.1	0
S12	Spring	21	6.5	10	25			8.417	0.18	0.03	>23	>23	8.4	7.32	12.1	0
S16	Spring	21	6.33	5	5	88.38	7.91	0	0.02	0.01	>23	>23	5.0	4.88	1	0
S21	Spring	22.2	6.6	5	5	95.48	8.31	1.0189	0	0	>23	>23	9.0	7.81	0.4	0
S24	Spring	16.75	6.5	5	5	75.55	7.4	0	0.3875	0.044	>23	1.1	8.8	7.32	1.3	0
S25	Spring	19.68	5.2	18	5	25.18	2.29	3.4	0	0.04	>23	1.1	19.9	6.59	3.8	0
S26	Spring	19	6.4	5	5	84.25	7.44	1.3	1.76	0.03	>23	9.2	15.6	7.81	1	0
S28	Spring	18.3	5.7	5	10	75.33	7.04	1.1	0.73	0.02	>23	9.2	12.8	6.83	1.5	0
S5	Dug Water well	21.4	6.12	156	233	2.33	0.186	95.35	0	0.03	>23	0	10.6	31.72	9.9	31
S9	Dug Water well	22.44	5.64	30	83	40.704	3.581	13.55	0.22	0.01	>23	0	14.7	10.98	6.7	6
S15	Dug Water well	21	6.04	30	70	55	4.97	6.645	1.47	0.01	>23	16.1	12.1	15.86	2	8
S2	Artisan Water well	19.75	6.23	54	81	52.75	4.43	6.85	0.01	0.0012	0	0	9.4	2.44	6.3	6
S6	Artisan Water well	22.37	5.74	16	23	61.78	5.436	2.95	0.04	0.03	>23	0	9.6	4.88	1.2	0
S14	Artisan Water well	19	6.4	20	40	66.42	6.19	0.443	0.4	0.01	6.9	2.2	8.1	28.06	1	0
S19	Artisan Water well	20.575	4.8	75	165	35.275	2.9575	65.121	0.09	0.04	>23	3.6	17.1	5.98	11.2	3
S20	Artisan Water well	19	5.9	10	30	82.28	7.65	6.202	0.08	0.05	>23	0	23.9	7.20	1.2	0
S22	Artisan Water well	20.38	6.1	10	30	79.4	7.16	0.7974	0.3	0.01	0	0	11.8	7.56	0.6	0
S27	Artisan Water well	19.7	6	10	5	84.75	7.76	0	0.62	0.01	6.9	0	14.0	7.81	0.9	1
S30	Artisan Water well	19.05	5.6	5	5	77	7.15	5.1	0.49	0.01	16.1	0	11.8	7.20	1.2	0
S3	River	17.32	6.13	16	24	75.02	6.57	26.34	0.12	0.0009	>23	>23	12.4	4.88	2.5	0
S4	River	17.09	6.27	15	22	68.64	6.04	16.44	0	0.0024	>23	>23	11.5	2.44	2.9	0
S8	River	16.51	7.16	15	22	50.5	4.443	3.88	0.52	0.01	>23	>23	11.6	7.32	1.2	0
S13	River	18	6.5	5	5			0.886	0.68	0.01	>23	>23	9.8	6.10	1.2	0
S18	River	17	6.6	5	5	87.2	8.56	0	2.26	0.01	>23	>23	7.8	4.88	0	0
S23	River	15.15	7.1	5	5	93.63	9.41	0.886	0	0.01	>23	16.1	14.1	7.93	1	1
S31	River	19	6.7	20	40			78.8	0.07	0.01	>23	>23	14.1	7.93	3.1	1
S29	Lake	16.5	7.1	5	13	83.88	7.99	4	0.27	0.01	>23	>23	12.6	9.03	1.1	1

Table 11.: Descriptive statistic of springs, dug water wells, artisan water well and river.

	Spring	Artisan water well	River	Dug water well
Temp (°C)	19,29	19,98	17,07	21,61
pH	6,34	5,85	6,70	5,93
TDS (mg/l)	16,73	25,00	10,75	80,33
E.C. ($\mu\text{S}/\text{cm}$)	23,00	47,38	17,00	128,67
D.O. (%)	62,70	67,46	76,48	32,68
D.O. (mg/l)	5,61	6,09	7,17	2,91
NO_3^- (mg/l)	8,96	10,93	16,40	38,52
PO_4 (mg/l)	0,30	0,25	0,49	0,56
NO_2 (mg/l)	0,02	0,02	0,01	0,02
Hardness (mg/l CaCO_3)	12,55	13,22	11,75	12,45
HCO_3^- (mg/l)	7,96	8,89	6,31	19,52
Cl^- (mg/l)	3,14	2,95	1,63	6,20
SO_4 (mg/l)	0,82	1,25	0,38	15,00

table [Table 10](#) shows the results of groundwater samples taking during March and April of 2015. The temperature of springs and artisan water wells is similar to mean air temperature for March and April ([Figure 3](#)) suggesting that time of water retention in the subsoil is short, proper of shallow aquifers recharged by local flow systems ([Hergt et al., 2009](#)). The pH of the springs, dug water wells, artisan water wells and river; suggest a slightly acidic ground and surface water. This may be due to the acidic character of rainwater ([Chapman, 1996](#)) that recharges the shallow aquifer of the study area where the short residence time (from months to some decades) of the groundwater permits to maintain the pH of the rainwater. Total dissolved solids and electrical conductivity tend to increase from the river and its affluent, to springs, to artisan water well and to dug water well ([Table 11](#)). TDS concentration ranged from values lower than 10 mg/l to 156 mg/l but most of the values are below 60 mg/l, characteristic of a low reactive environment and a rapid water flow, indicating the existence of vulnerable aquifer as it was indicated before.

[Hernández Martínez 2008](#) divided the groundwater in four groups based on electrical conductivity: low salinity water, medium salinity water, high salinity water and very high salinity water. Electrical conductivity values lower than $250\mu\text{S}/\text{cm}$ correspond to low salinity water, from 250 to 750 to medium salinity water, between 750 and 2250 to high salinity water and for values higher than 2250 to very high salinity water. The electrical conductivity of the water samplings in the study area belong to the low salinity water proper of a scarcely mineralized groundwater. However, some sampling points exceed mean electrical conductivity ($38.5\mu\text{S}/\text{cm}$). [Table 12](#) shows that total dissolved solids (TDS) and Electrical Conductivity (EC) have a positive and a significant correlation ($p < 0.01$) with NO_3^- , indicating nitrate influence the behavior of those parameters. The highest nitrate concentration,

Table 12.: Correlation matrix of groundwater physicochemical parameters

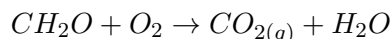
Parameters	Temp	pH	TDS	E.C.	O ₂	NO ₃ ⁻	NO ₂ ⁻	PO ₄	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
Temp	1										
pH	-0.451*	1									
TDS	0.402*	-0.213	1								
E.C.	0.416*	-0.253	0.972**	1							
O ₂	-0.358	0.311	-0.771**	-0.73**	1						
NO ₃ ⁻	0.241	-0.302	0.748**	0.762**	-0.637**	1					
NO ₂ ⁻	0.12	-0.417*	0.121	0.161	-0.204	0.117	1				
PO ₄	-0.155	0.052	-0.24	-0.214	0.322	-0.265	-0.019	1			
HCO ₃ ⁻	0.194	0.209	0.565**	0.542	-0.37	0.265	0.035	-0.007	1		
Cl ⁻	0.427*	-0.372*	0.699**	0.73**	-0.753**	0.646**	0.265	-0.31	0.149	1	
SO ₄ ²⁻	0.349	-0.168	0.901**	0.841**	-0.615**	0.667**	0.094	-0.098	0.609**	0.535**	1

*Significant at 0.05 level

**Significant at 0.01 level

the highest total dissolved solid concentration and the highest electrical conductivity this relationship could explain the difference between water samples. In general, the physicochemical parameters increase from little human activities areas (hilly zones) to valley areas where agriculture and pasture are more developed.

The dissolved oxygen concentration divide the sampling points in two groups: springs, artisan water wells and river with an oxygen content between 62 and 76% characteristic of aerated water in contact with the atmosphere and dug water wells with an oxygen content of 32% characteristic of waters without atmospheric contact or reduced water for oxidation processes (HWA and HORA, 2009). The low oxygen concentration in the dug water wells may be due to the oxidation of organic matter presented in the groundwater, rather than lack of atmospheric contact because the shallow depth to water of S5, S9 and S15 (3m approximately) favor oxygen dissolution into groundwater. Sampling point S5 presents the lowest concentration of dissolved oxygen (0.186 mg/l). Unlike the other dug water wells (S9 and S15), the dug water wells S5 is located inside the garden of a house whose only protection is an unfixed cement slab allowing the entrance of animals, leaves or other residues (Figure 31) which could increase the demand of oxygen, due to the oxidation process of the organic matter, and decrease oxygen availability. The concentration of total coliforms in the water from dug water well S5 support this fact (Table 10). On the basis of these observations, the author concluded that low oxygen concentration on S5 due to oxidation of natural organic matter given by the following reaction:



The sulfate, chloride and bicarbonate concentration of the sampling points correspond to the average composition of rainwater (Nelson, 2002), and are below the guideline standards for drinking water (Table 13); but their concentration is higher on shallow dug water wells than on springs. Taking into account that:



Figure 31.: Sampling point S5 (dug water well)

- There are not natural sources of SO_4^{2-} , Cl^- and HCO_3^- in the study area.
- Domestic and agricultural activities can introduce some Cl^- and SO_4^{2-} in the water supply (Cardona et al., 2008).
- There is a strong relationship between SO_4^{2-} , Cl^- , HCO_3^- and NO_3^- indicative of a same contamination source (Table 12).

The author concludes that waste-water infiltration, irrigation-return effluents and losses from sewer systems could explain the differences between the dug water wells and the other water sources.

4.5.1. Nitrate

Nitrate is the most common contaminant in the groundwater being agricultural activities, sewage effluents and livestock manures the common sources of this compound (Freeze and Cherry, 1977). Looking the results of field and laboratory analysis, the author found that most of the sampling points in the upper basin of Rio Grande (80%) present low nitrate concentration ranging between 0 mg/l and 26.34 mg/l; 23% of the samples have a concentration above 10 mg/l (S10, S5, S19 and S31) which, according to Sener et al. 2009, is the minimum nitrate concentration indicative of contamination from anthropogenic source; and



(a) Agricultural activities around spring water well S10 (b) Water extraction from sampling point S10

Figure 32.: Location of the spring S10 and its surroundings

13% of the samples (S5, S10, S19, S31) exceed 40 mg/l of NO_3^- —maximum permissible limit of nitrate concentration for drinking water established by portario saúde WHO. [Ward et al. 2005](#) reported that the infant ingestion of drinking water with nitrate concentration above 50mg/l could cause methemoglobinemia or the syndrome of “blue baby”.

Springs and artisan water wells show no signs of nitrate contamination, with exception of S5, S10 and S19. This could be due to little agricultural activity in those areas. Despite, the existence of feedlots around these water sources, this activity do not have a big influence on the nitrate level. [Freeze and Cherry 1977](#) state that fertilizers rather than animal wastes, are the primary nitrate source. The sampling point S5 shows the highest nitrate concentration of the area (95.35 mg/l), but the absence of of thermotolerant faecal coliforms indicates that sewage effluents do not influence on the nitrate concentration of sampling point S5, however, its closeness to agricultural areas could explain the nitrate pollution. [Takem et al. 2009](#) defined that the high concentration of nitrate in water without thermotolerant coliforms presence, indicates multiple sources of contamination.

The spring S10 also register a nitrate concentration above drinking water standards (74.51 mg/l). It was located at open-air in the middle of farmland ([Figure 32](#)), which, during the sampling period, was being treated with pesticides twice or more per week, in order to eradicate and prevent the plagues of cauliflower, broccoli and lettuces (seasonal vegetables). [Moreira et al. 2002](#) identified atmospheric contamination with agrotocics during aerial spraying of pesticides, this could explain the nitrate level of the spring S10.

Similarly, the high concentration of nitrate in the artisan water well S19 (65.12 mg/l) may also be due to the proximity with agricultural activities. The water well is located in the center of an agricultural area and only protected with a plastic bag ([Figure 33](#)) which could

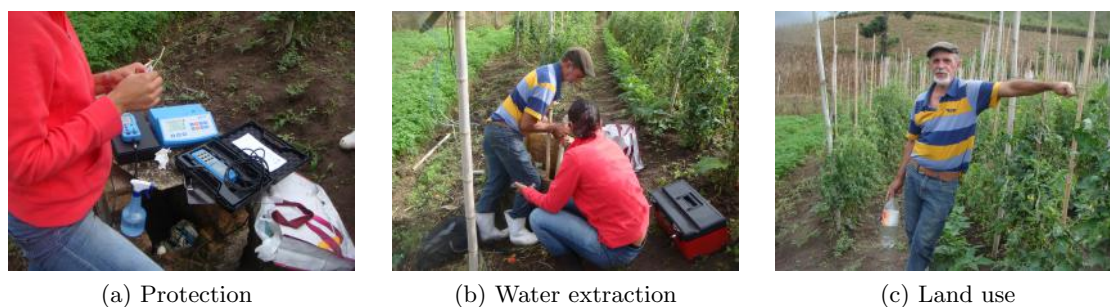


Figure 33.: Conditions of the water well S19

leach nitrate into groundwater. Another possible explanation for high NO_3^- concentration could be the improper construction of the well that facilitates aquifer recharge through lateral river flow introducing septic tank effluents and agricultural chemical on groundwater. This observation is consistent with the results of [Huang et al. 2013](#) who found that lateral flow from rivers and agricultural irrigation are factors that control groundwater chemistry in the river network area.

Samples along Rio Grande and its tributaries show a spatial variation of nitrate concentration. In the upstream points (S23, S21, S18 and S13), characterized for almost nil agricultural activity, the nitrate values lie in the range of 0 mg/l to 3.8 mg/l but as the wastewater discharges and irrigation areas increase along river course, water quality goes in the contrary direction increasing nitrate concentration to values, for example, of 78.8 mg/l in Barracão dos Mendes. [Figure 34](#) shows this quality transition. This studies complement the observations of [Moreira et al. 2002](#) because even though they did not assess nitrate concentration on rivers, they reported high levels of agrottoxics in the microbasin of São Lourenço which confirm that that pesticides and fertilizers play a role in the nitrate pollution of the river Rio Grande.

During informal interviews with members of SINDAF-NF (Sindicato dos Agricultores Familiares de Nova Friburgo) located on the Central Provision of Serrana Region-Nova Friburgo-CEASA-, the author found that farm workers use nitrogen pesticides in excess due the non-existent supervision or technical advice. The structure of those pesticides include nitrogen, chloride, sulfate, manganese and zinc ([Figure 35](#)) that could explain high nitrate concentration as well as high chloride concentration of the sampling points nearby vegetable fields.

The author concluded that the excessive use of agricultural chemicals in the surrounding areas of the sampling points S5, S10 and S19 is the most probably cause of high NO_3^- in the water. However, malfunctioning on-site sewage disposal and improper water sources protection may contribute to this contamination as well. [Barroso et al. 2014](#) highlighted

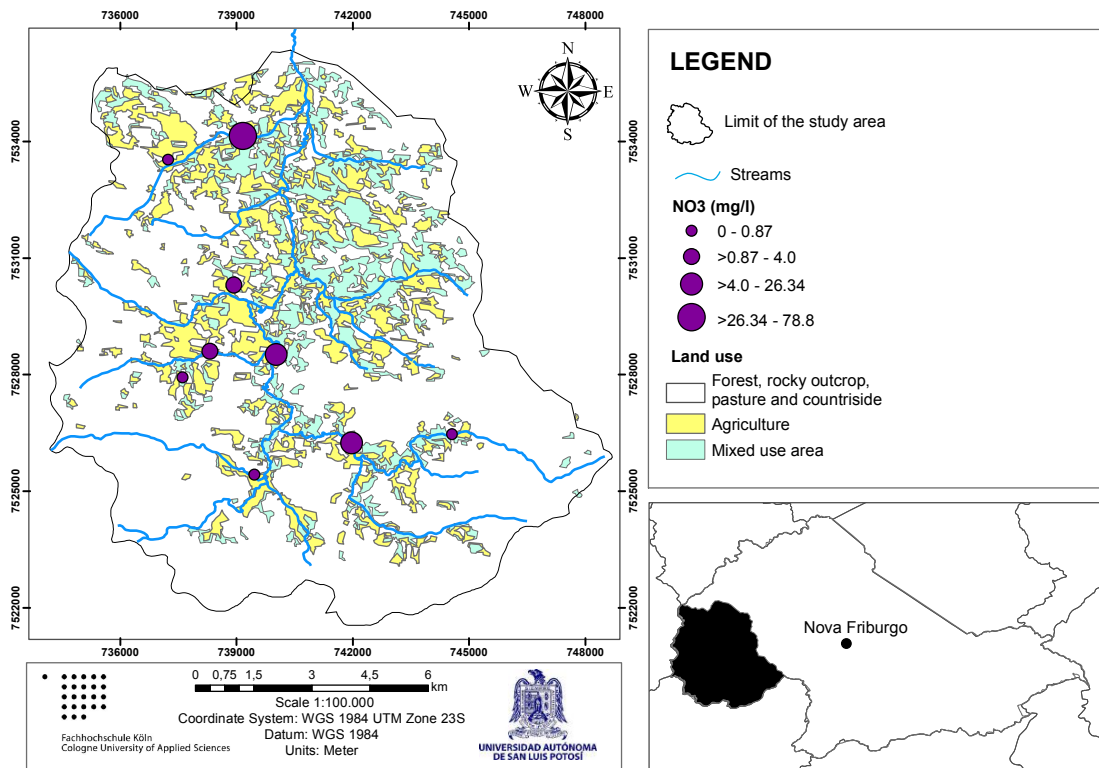


Figure 34.: Variation of Rio Grande quality along its pathflow

something similar for an agricultural peri-urban area of Portugal where farmers use nitrogen fertilizers to increase crop production and discharge nitrogen compounds from on-site sanitation directly to groundwater.

4.5.2. Total coliforms and thermotolerant coliforms (*E. coli*)

Several microorganisms can be found in the groundwater including viral, bacterial and protozoal pathogens, but the presence coliform bacteria like total coliforms and thermotolerant indicate the possible wastewater contamination to groundwater (Cardona et al., 2008). All the water samples of the study area, with exception of S2 and S22, have presence of either total coliform, thermotolerant coliform (*E. coli*) or both of them. 93% of the sampling points show contamination with total coliforms and 70% with fecal coliforms. Based on Brazilian law for drinking water and WHO limit the sampling water sources are inappropriate for human consumption unless water receive a treatment before consumption.

All the springs located in places where pasture dominates land use, show contamination with total or fecal coliforms, indicating that the dragging of animal feces and the pres-

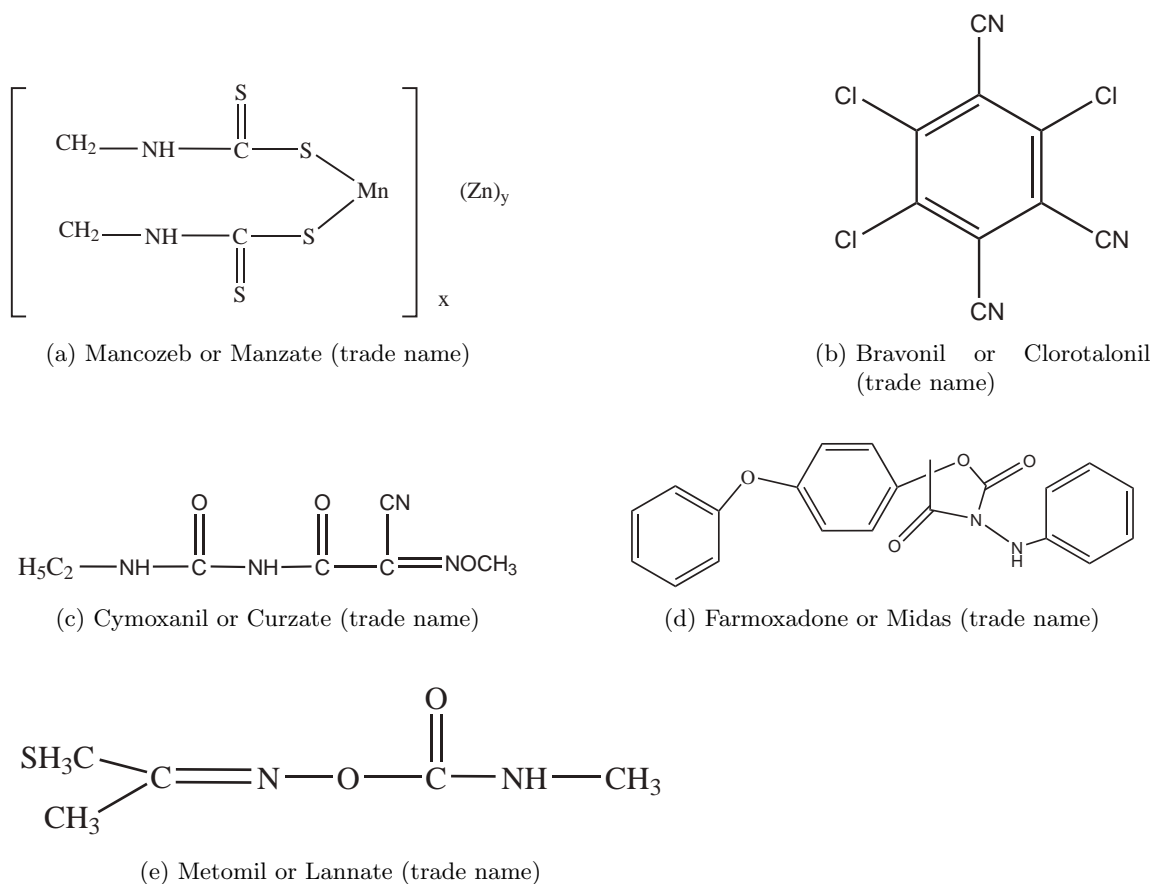


Figure 35.: Most common pesticides used in the upper basin of Rio Grande

ence of organic material like leaves carry out by runoff water are the causes of the high microbiological counts.

The points S14, S15 and S19 also present fecal coliform contamination (Table 10). Since fecal coliform contamination is exclusive condition of these points, the author concluded that the cause of groundwater pollution could be improper construction, maintenance and operation of the wells which could lead the infiltration of septic tanks or cesspools effluents. The health agency of Nova Friburgo has been monitoring a point in micro-basin of Barracão dos Mendes finding presence of total coliforms and *E. Coli* in water samples. Segovia Sánchez 2014 also stated that this could be due to bad operation of cesspit and septic tanks.

High levels of fecal coliforms in Rio Grande and its tributaries are a sign of river pollution (Table 10). The program Participatory Rural Approach of the micro-basins Barracão dos Mendes, Santa Cruz and Salinas and São Lourenço (COGEM, 2012a,b; Gomes da Silva and rural do Salinas e Santa Cruz, 2012) defined that the water quality degradation of Rio

Grande is the result of the wastewater direct discharge into the river without any treatment and the leakage from rudimentary septic tanks and cesspools.

4.6. Drinking water quality

Around 4600 people make up the upper basin of Rio Grande (COGEM et al., 2013; Olivieri et al., 2013; Ribeiro Canellas and da Costa Silva, 2013); all of them with springs or water wells for drinking water supply but anyone with data about the quality of the water they are consuming. The Ministry of Health of Brazil through Portaria N°2914 of December 12th of 2011 and the Water Health Organization described the guidelines that should satisfy a safe drinking water-water does not represent any significant risk to health over a lifetime of consumption (Table 13). The author compared the results of the chemical analysis of water (Table 10) with the Portaria de Saúde and WHO guidelines finding that water from sampling points of the upper basin of Rio Grande, except for water wells S2 and S22, are unsafe for human consumption due to high concentration of total coliforms, thermotolerant coliforms, color and turbidity. Figure 36 shows the spatial distribution of the parameters that exceed maximum permissible concentration limits of WHO and Brazil for drinking water.

The presence of thermotolerant coliforms in the groundwater are associated with badly constructed water wells without casing seal, sanitary seal and protection perimeter and the influence of polluted rivers (Zoby and OLIVEIRA, 2005); while groundwater color and turbidity problems are associated with the inadequate filters in the water well. This situation respect to groundwater quality deserves attention, because unsafe drinking water could reflect problems in the health of the inhabitants of the study area, specially for infants, young children and elderly (constitute around 20% of people of study area), the group with the greatest risk of diseases.

Use of water in the study area includes also irrigation and drinking trough for animals, even in some areas, people use water for fish-farming. Those activities needs water with different quality thus the limits of Portaria N°2914 and WHO are not enough to provide that information. Brazilian legislation took into account those limitations and created CONAMA Resolution 357 of 2005 which classify water bodies according with their use (Table 14) and the quality level (Table 15) that should posses for that specific use.

Based on CONAMA resolution and the results of some measured parameters in the upper basin of Rio Grande (dissolved oxygen, nitrate, pH, turbidity and color) the author found that:

1. Water from 50% of the sampling points correspond to class 1, thus, this water can be

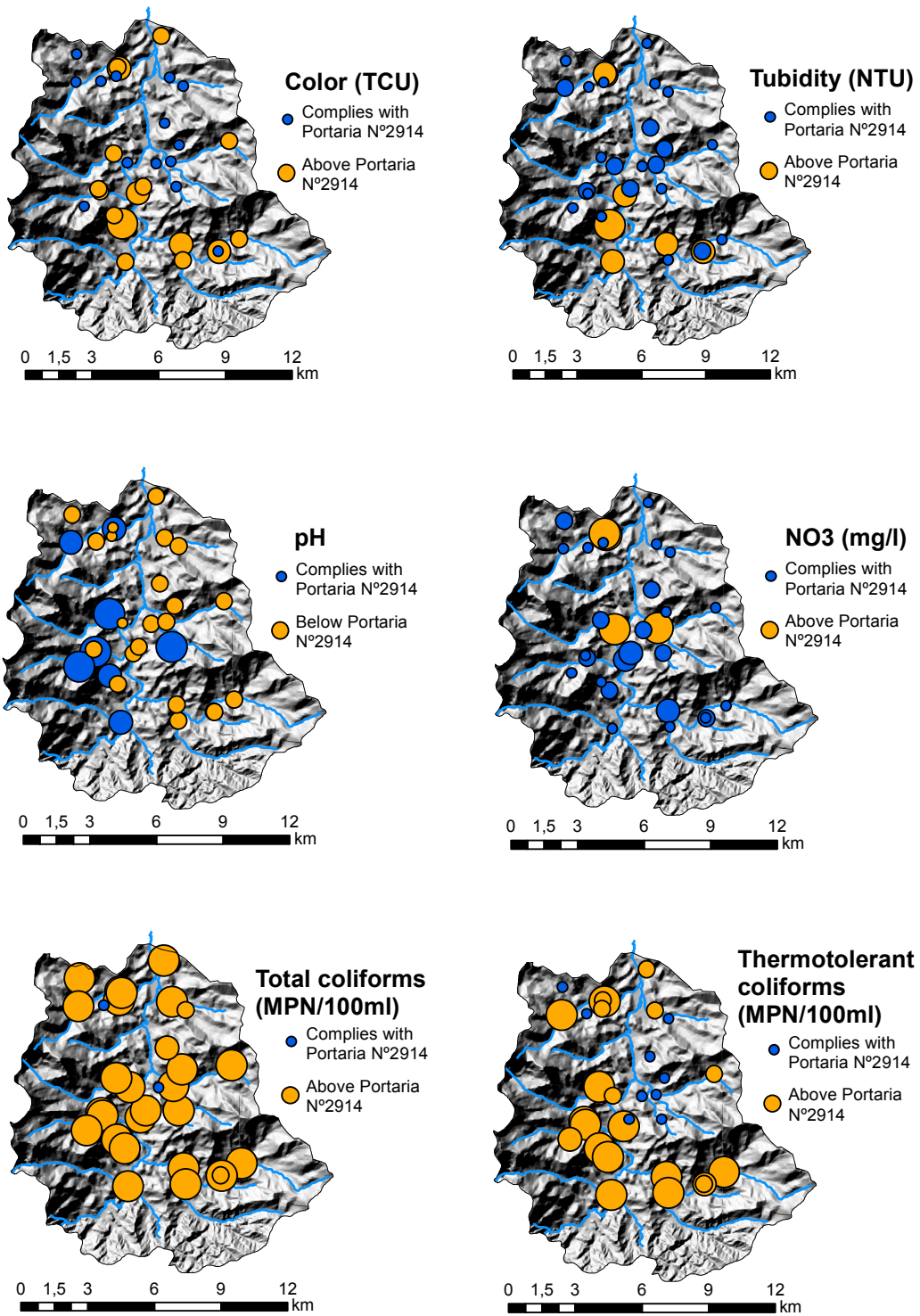


Figure 36.: Spatial variation of parameters above drinking water standards

Table 13.: Standards of safe drinking water.

Constituent	Concentration limit (mg/l) of Portaria N°2914 of December 12th of 2011	Concentration limit (mg/l) of WHO
pH	6,0-9,5	6,5-8,5
Colour	15 TCU	15 TCU
Turbidity	5 NTU	1 NTU
Total hardness (CaCO ₃)	500	500
Total dissolved solids	1000	1000
Sodio (Na ⁺)	200	200
Chloride (Cl ⁻)	250	250
Sulphate (SO ₄ ²⁻)	250	250
Nitrate-nitrogen (NO ₃ ⁻)	10	11 or 50mg/l as nitrate
Nitrite-nitrogen(NO ₂ ⁻)	1	0.9 or 3mg/l as nitrite
Iron (Fe)	0.3	0.3
Manganese (Mn)	0.1	0.1
Mercury (Mg)	0.001	0.006
Copper (Cu)	2	2
Chromium (Cr)	0.05	0.05
Lead (Pb)	—	0.01
Fluoride (F)	1.5	1.5
Total coliforms	Absent in 100ml	Absent in 100ml
Thermotolerant coliforms or <i>E. coli</i>	Absent in 100ml	Absent in 100ml

Table 14.: Classification of freshwater according CONAMA resolution 357 of 2005.

Classes	Use
Special	Preservation of the natural equilibrium of aquatic communities Preservation of aquatic environments in conservation units of integral protection
1	Supply for human consumption, after simplified treatment Protection of aquatic communities Primary contact recreation such as swimming, water skiing and diving, as stated in CONAMA No. 274, 2000 Irrigation of vegetables that are consumed raw and fruits that are full development within the soil and are eaten raw without the peel removal Protection of aquatic communities in indigenous lands
2	Supply for human consumption, after conventional treatment Protection of aquatic communities Primary contact recreation such as swimming, water skiing and diving, as stated in CONAMA No. 274, 2000 Irrigation of vegetables, fruit trees and from parks, gardens, fields of sports and leisure, that general public has direct contact Aquiculture and fishing activities
3	Supply for human consumption, after conventional and advanced treatment Irrigation of the tree crops, cereal and forage Secondary contact recreation Watering animals Recreational fishing
4	Navigational Landscaping

Table 15.: Water quality standards for freshwater according with CONAMA Resolution 357 of 2005.

Parameter		Class 1	Class 2	Class 3	Class 4
Total N	Lentic water	1.27mg/l	1.27mg/l		
	Lotic water	2.18mg/l	2.18mg/l		
Thermotolerant coliforms*		< 200 UFC/100ml	< 1000 UFC/100ml	< 2500 UFC/100ml	
Dissolved oxygen		> 6mg/l	> 5 mg/l	> 4mg/l	> 2mg/l
Turbidity		40 NTU	100 NTU	100 NTU	
Color			< 75 UC	< 75 UC	
pH		6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0
Total hardness		500 mg/l	500 mg/l		
Total dissolved solids		500 mg/l	500 mg/l	500 mg/l	
Total chloride		250 mg/l	250 mg/l	250 mg/l	
Total fluoride				1.4 mg/l	
Total phosphorus		0.025 mg/l	0.,050 mg/l	0.075 mg/l	
Nitrate-nitrogen		10 mg/l	10 mg/l	10 mg/l	
Nitrite-nitrogen		1 mg/l	1 mg/l	1 mg/l	
Total Sulfate		250 mg/l	250 mg/l	250 mg/l	

*in 6 water samples collected in a period of 1 year

used for drinking after a simplified treatment like filtration and disinfection and for irrigation of vegetables that are consumed raw.

- Water from 10% of the sampling points correspond to class 2. The water can be used for irrigation of vegetables and drinking after a conventional treatment that includes not only filtration and disinfection but also coagulation, flocculation and decantation
- Water from 10% of the sampling points correspond to class 3. This water can be used for drinking after an advance treatment including ultrafiltration and/or osmosis.
- Water from 30% of the sampling points correspond to class 4 which can be only used for navigation.

As the community did not know about the importance of a good water quality and the upper basin of Rio Grande does not have a treatment plant that could fulfill the water supply conditions of the Brazilian legislation; the author and Ms. Lilian Santos Carvalho from the laboratory of microbiology of the Agricultural Research Institute of Rio de Janeiro (PESAGRO-RIO) delivered the results of the quality analysis of water to the inhabitants of the basin, explained them the results and gave them a guide to disinfect the water they are consuming and to clean the reservoirs of water (B); actions that could help to diminish organic load of water.

In the case of compounds like nitrate, Jean W H Yong from the Singapore University of

Technology and Design state that “reducing excessive nitrate requires good farm management strategies, design of farmlands in relation to land geomorphology and geology, use of bio fertilizers instead of synthetic fertilizers” and Dr. Monica Vianna from Syndicate of Farmers of Nova Friburgo remarked the necessity of technical assistance, tasks left in the hands of Brazilian Agricultural Research Agency (EMBRAPA), Ministry of Agriculture and programs like RIO RURAL.

5. Conclusions and recommendations

The upper basin of Rio Grande lies on a shallow and vulnerable free aquifer where pollution sources like septic tanks, cesspools, greenhouses, graveyards, waste water discharge into surface water courses, pasture and agriculture could represent a hazard for groundwater contamination at different levels. Although, applied methodology of hazard inventory list gives an idea about the hazard and risk level of pollution sources, the results could be unspecific for the study area because the methodology avoids characteristics that could have higher influence on groundwater contamination, thus it is ideal to create a local hazard mapping method which reflect the specific problems of the region.

Rio Grande river and its tributaries have the highest vulnerability to contamination and according with the water quality results and some previous studies in effect have the highest contamination due to direct discharge of waste water mainly. This river condition affect groundwater quality as a result of mixing occurred during process of groundwater discharge in the vicinity of the river (gaining stream) or aquifer recharge by river (losing stream). Therefore, the processes that affect groundwater quality, indirectly affect river quality and vice versa.

Land use and protection of water sources have an impact on groundwater and surface water quality. The selected sampling points lay in areas with agricultural, forested, urban and pasture areas. Water quality decrease from sampling points located in steep slopes with low agricultural activity -which could coincide with groundwater recharge- to unprotected sampling points located in the valley of basin near agricultural areas and Rio Grande river and its tributaries- which could coincide with groundwater discharge.

The surface and groundwater of the upper basin of Rio Grande exceed the limits of Portaria N°2914 of 2011, WHO and CONAMA Resolution 357 of 2005 for drinking and irrigation water indicating that water should receive at least a simplified treatment (filtration and disinfection) before using it for human consumption. Almost all the water sources of the basin, springs, artisan water wells, dug water wells and rivers, have presence of total and fecal coliforms in different concentrations. Malfunctioning on-site sanitation, dragging of animal feces into water sources, direct discharge of wastewater to river and organic matter decomposition could be the causes of this situation. Despite fecal coliforms constitute a problem for health of the inhabitants of the study, specially for children and elders, a

proper treatment of wastewater and chlorination of drinking water could be a solution for the problem.

Water wells near septic tanks and vegetable fields with an intense use of pesticides present an additional problem with nitrate concentration; but, that punctual condition could be related with the construction, maintenance and operation of wells. The norm ABNT NBR-12.244 of 1990 from Brazilian Association of Technical Norms (ABNT) regulates water wells construction giving the standards of well construction for individuals or enterprises, however, in the upper basin of Rio Grande shortage of skilled labor obligate inhabitants to construct their own wells without the correct specification leading to mentioned problems.

The problems with water in the region not only demonstrate a problem with water wells construction and operation but also with the operating dynamics of the region. High nitrate concentration in groundwater is an indicator of septic tanks, cesspool and wastewater contamination and also pesticides and fertilizers contamination. The author mentioned wastewater contamination could be controlled or avoid with simple actions but pesticides contamination need more time and work.

In the upper basin of Rio Grande, farmers use pesticides in excess for the sole reason of lacking technical assistance. They do not know what is the exact quantity for a determined crop and an effective product for the plague present in their land, it is there where sellers convince farmers “the more, the better”; a philosophy which affect water as well as human health taking into account that agrototoxics (pesticides and fertilizers) relates with cancer and depression ([How et al., 2014](#); [Beard et al., 2014](#)).

As well as quality of water have a spatial change, it also has a change in the time which could depend on fertilization period, rainy season and wet season. Despite, this study did not assess temporal variation of water quality serve as a precedent to differentiate the factors influencing water quality and the behavior of surface and groundwater. Nevertheless, it is necessary a periodic monitoring programs of surface and groundwater sources to determine a trend in the natural environment. With that information, decision makers, Reaserch Agencies of Rio de Janeiro state and programs of Sustainable Agriculture like RIO RURAL could implement water protection measures like wastewater treatment, provide permanent accompaniment and job training for inhabitants of the upper basin of Rio Grande that not only avoiding or preventing problems that threat the water quality and human health but also improving quality of life of the farmers.

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Appendices

A. Percentage of error and electroneutrality condition

UTM_X	UTM_Y	Code	Water source	Na (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	HCO ₃ (mg/l)	Cl (mg/l)	SO ₄ (mg/l)	NO ₃ (mg/l)	Na (mesq/l)	Ca (mesq/l)	Mg (mesq/l)	Fe (mesq/l)	HCO ₃ (mesq/l)	Cl (mesq/l)	SO ₄ (mesq/l)	NO ₃ (mesq/l)	Ycat	Yani	%Error
741745	752817	S1	Spring	4	0.12	3.2	0.04	18.30	3	1	7.531	0.174	0.006	0.283	-0.3	-0.085	0	-0.02	-4.21E-01	0.443	-0.527	-8.62549555
740848.0	7528861.0	S2	Artisan Water well	3	0	2.3	0.05	2.44	6.3	6	6.85	0.130	0.000	0.189	-0.04	-0.178	0	-0.13	-1.10E-01	0.420	-0.453	-17.27036529
740333.0	7528512.0	S3	River	72	1.83	1.92	0.03	4.88	2.5	0	26.34	1.132	0.091	0.158	-0.08	-0.071	0	0.00	-4.25E-01	3.381	-0.575	79.91519409
741976.0	7528231.0	S4	River	120	1.66	1.8	0.02	2.44	2.9	0	16.44	0.220	0.083	0.148	-0.04	-0.062	0	0.00	-2.63E-01	5.451	-0.387	86.74213395
741509.0	752948.0	S5	Dug Water well	6	0.08	2.54	0.02	31.72	9.9	31	95.35	0.261	0.004	0.209	-0.52	-0.279	0	-0.65	-1.54E+00	0.474	-2.983	-72.58027183
741885.0	7530790	S6	Artisan Water well	7	2.02	1.11	0.03	4.88	1.2	0	2.95	0.304	0.101	0.091	-0.08	-0.044	0	0.00	-4.70E-02	0.497	-0.161	50.93503061
728244.0	7528704.0	S7	Spring	30	3.76	0.82	0.06	9.76	1.2	0	0.85	1.305	0.188	0.067	-0.16	-0.044	0	0.00	-1.77E-02	1.560	-0.208	76.51455599
738319.0	7528591.0	S8	River	38	1.5	1.92	0.08	7.32	1.2	0	3.88	1.653	0.075	0.158	-0.12	-0.044	0	0.00	-6.26E-02	1.886	-0.216	79.40843248
740279.0	7528819.0	S9	Dug Water well	60	1.21	2.84	0.08	10.98	6.7	6	13.55	2.610	0.060	0.234	-0.18	-0.189	0	-0.13	-2.19E-01	2.904	-0.713	60.93030228
729445.0	7528881.0	S10	Spring	48	0.32	2.87	0.09	3.66	8.1	8	74.51	2.088	0.016	0.236	-0.06	-0.228	0	-0.17	-1.20E+00	2.340	-1.657	17.08876264
738961.1	7527516.5	S11	Spring	11	5.88	1.28	0.09	7.32	1.1	0	0.443	0.478	0.233	0.105	-0.12	-0.011	-0.001178947	0.00	-7.15E-03	0.877	-0.169	69.18753645
738338.4	7527136.0	S12	Spring	396	2.08	0.82	0	7.32	12.1	0	8.417	17.225	0.180	0.067	-0.12	-0.341	0	0.00	-1.90E-01	17.303	-0.597	93.30194572
741667.1	7528459.8	S13	River	28	2.29	0.99	0.04	6.10	1.2	0	0.886	1.218	0.114	0.081	-0.1	-0.044	-0.035263158	0.00	-1.43E-02	1.414	-0.183	77.03073729
749646.4	7529011.1	S14	Artisan Water well	17	0	1.98	0.02	28.06	1	0	0.443	0.739	0.000	0.163	-0.46	-0.028	-0.017368421	0.00	-7.15E-03	0.902	-0.513	27.53400777
741808.1	752885.7	S15	Dug Water well	65	0.07	2.9	0	15.86	2	8	2.827	0.003	0.239	-0.26	-0.056	0	-0.17	-1.07E-01	3.009	-0.509	67.74225999	
742953.1	7525500.3	S16	Spring	52	0.68	0.8	0.04	4.88	1	0	0	2.262	0.034	0.066	-0.08	-0.028	0	0.00	0.00E+00	2.362	-0.108	91.22748569
739465.4	7525422.3	S18	River	16	1.83	0.79	0.01	4.88	0	0	0	0.696	0.091	0.065	-0.08	0.000	-0.002105263	0.00	0.00E+00	0.852	-0.082	82.4255821
739109.2	7534192.5	S19	Artisan Water well	20	0.07	4.12	0.06	5.88	11.2	3	65.121	0.870	0.003	0.239	-0.088	-0.316	-0.008421053	-0.06	-1.65E+00	1.212	-1.535	-11.74570164
737285.0	7534178.0	S20	Artisan Water well	2	0.21	5.7	0.04	7.20	1.2	0	6.202	0.087	0.010	0.469	-0.118	-0.044	-0.016315789	0.00	-1.00E-01	0.566	-0.268	35.73117631
737238.1	7533525.1	S21	Spring	0	1.22	1.44	0.09	7.81	0.4	0	1.0189	0.000	0.061	0.118	-0.128	-0.011	-0.005789474	0.00	-1.64E-02	0.179	-0.162	5.23424162
738367.6	753565.0	S22	Artisan Water well	8	0.52	2.56	0.1	7.36	0.6	0	0.7974	0.348	0.026	0.211	-0.124	-0.017	-0.015263158	0.00	-1.29E-02	0.585	-0.109	51.1347226
737690.4	7527921.3	S23	River	14	1.74	2.37	0.06	7.93	1	1	0.886	0.609	0.087	0.195	-0.13	-0.028	-0.002631579	-0.02	-1.43E-02	0.891	-0.196	63.93518506
744119.4	7530870.5	S24	Spring	36	1.55	1.2	0.1	7.32	1.3	0	0	1.566	0.077	0.099	-0.12	-0.037	-0.018947368	0.00	0.00E+00	1.742	-0.176	81.8838243
738055.0	7533792.7	S25	Spring	6	1.14	4.15	0.03	6.59	3.8	0	0.4	0.261	0.057	0.241	-0.108	-0.107	-0.001052632	0.00	-5.48E-02	0.659	-0.271	41.72597897
741444.1	7533726.2	S26	Spring	5	2.57	2.23	0.004	7.81	1	0	1.3	0.217	0.128	0.183	-0.128	-0.028	-0.014736842	0.00	-2.10E-02	0.529	-0.192	46.7725753
742062.0	7533149.2	S27	Artisan Water well	0	0.95	2.84	0.06	7.81	0.9	1	0	0.000	0.047	0.234	-0.128	-0.025	-0.012105263	-0.02	-3.77E-02	0.281	-0.222	11.72746918
741076.9	753597.6	S28	Spring	15	1.41	2.27	0.06	6.53	1.5	0	1.1	0.652	0.070	0.187	-0.122	-0.042	0	0.00	-1.77E-02	0.910	-0.172	68.18586139
738938.4	7530299.3	S29	Lake	28	0	3.08	0.05	9.03	1.1	1	4	1.218	0.000	0.253	-0.148	-0.031	-0.013684211	-0.02	-6.45E-02	1.471	-0.278	60.2103522
741224.8	7531658.0	S30	Artisan Water well	5	1.48	1.98	0.04	7.20	1.2	0	5.1	0.217	0.074	0.163	-0.118	-0.044	-0.1473684211	0.00	-8.23E-02	0.454	-1.708	-57.98071746
729170.7	7534139.9	S31	River	38	0	3.44	0.06	7.93	3.1	1	38.8	1.653	0.000	0.283	-0.13	-0.087	0	-0.02	-1.27E+00	1.938	-1.569	12.84822871

B. Indications for cleaning reservoirs of water and disinfecting drinking water

LIMPEZA E DESINFECÇÃO DE CAIXAS D'ÁGUA

- Utilize luvas e botas de borracha (*);
- Feche o registro e esvazie a caixa d'água (abra as torneiras da residência e acione as descargas dos vasos sanitários para agilizar o processo);
- Deixe um pouco de água na caixa para ser utilizado na limpeza;
- Esfregue as paredes e o fundo da caixa utilizando escovas, panos ou esponjas macias (*) (não use sabão, detergentes ou outros produtos de limpeza);
- Retire a água suja da limpeza com balde e panos, deixando a caixa totalmente seca;
- Abra o registro e torne a encher a caixa;
- Acrescente um litro de Hipoclorito de Sódio a 2,5 %, para cada 1000 litros de água;
- Aguarde duas horas para desinfecção do reservatório;
- Esvazie a caixa (esta água servirá para limpeza e desinfecção da canalização);
- Tampe a caixa d'água e anote a data da limpeza;
- Abra o registro de entrada da água;
- Se a água for de poço ou nascente utilizar o tratamento sugerido na tabela abaixo.

(*) – Este material tem que ser usado somente para esta finalidade.

TRATAMENTO DA ÁGUA NA CAIXA

Utilizar o Hipoclorito de Sódio a 2,5%, na proporção abaixo (este produto pode ser adquirido em lojas de venda de produtos para piscina):

Volume de água na caixa	Dosagem	Medida prática	Tempo de contato do produto com a água
1000 Litros	100 mL	2 copinhos de café	30 minutos
150 Litros	15 mL	1 colher de sopa	30 minutos
20 Litros (*)	2 mL	40 gotas	30 minutos
1 Litro (*)	0,1 mL	2 gotas	30 minutos

(*) Se a água estiver turva ferver durante 15 minutos, deixar esfriar e colocar o Hipoclorito de Sódio, dobrando a quantidade da tabela acima.

OBS: Só utilizar água sanitária na total impossibilidade da utilização do Hipoclorito de Sódio, pois não há garantia de que neste produto o teor de cloro seja o desejado.

A água contaminada pode servir de veículo para a transmissão de doenças. Caso apresente sintomas como febre, dores no corpo, diarreia, vômitos, enjôos, tontura, dores de cabeça, calafrios, procurar imediatamente a unidade de saúde mais próxima.

Fonte: Lilian Santos Carvalho/Bióloga/Assistente Técnica/PESAGRO-RIO/CEP-GM/Área de Bacteriologia.