



## Seasonal assessment of groundwater quality in the cities of Itacoatiara and Manacapuru (Amazon, Brazil)

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### Resumo

Baseado em um ciclo hidrológico, foi desenvolvida uma investigação sobre a composição química das águas subterrâneas em Itacoatiara e Manacapuru que envolve o maior aquífero do mundo (Aquífero Alter do Chão- agora chamado de Sistema Aquífero Grande Amazônia). Para este estudo, amostras de água subterrânea foram coletadas a partir de poços em quatro períodos sazonais em 2012 (junho, setembro e dezembro) e 2013 (abril). As profundidades dos poços variaram entre 100 e 150 m. Para cada amostra de água subterrânea, foram determinados os íons  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  e  $\text{SO}_4^{2-}$ , bem como os valores de pH e condutividade elétrica. As concentrações de íons mudaram ao longo do tempo. No entanto, o efeito de contribuição de chuva sobre as espécies químicas não foi clarificado. A análise PCA mostra uma correlação entre o nitrato e cloreto, o que sugere a influência humana em alguns poços. Os resultados mostraram que alguns poços exibiram uma elevada concentração de  $\text{NO}_3\text{-N}$ , o que sugere necessária manutenção, limpeza e cuidados com tais poços.

**Palavras-chave:** Alter do Chão, SAGA, NBCI, PCA

### Abstract

Based on hydrological cycles, an investigation has been developed on the chemical composition of groundwater in Itacoatiara, and Manacapuru that involves the largest aquifer in the world (Alter do Chão aquifer now called the Large Aquifer System Amazon). For this study, groundwater samples were collected from wells in four periods during hydrological cycles in 2012 (June, September, and December) and 2013 (April). Well depths varied between 100 and 150 m for the samples. For each groundwater sample, the  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  ion concentrations as well as pH and electrical conductivity values were analyzed. The concentrations of ions change over time. However, the effect of rain contribution on the chemical species has not been clarified. PCA analysis shows a correlation between nitrate and chloride, which suggests human influence in some wells. Findings showed that some wells exhibited a high concentration of  $\text{NO}_3\text{-N}$ , suggesting necessary maintenance and cleaning of such wells.

**Key-words:** Alter do Chão, LASA, Nitrate, NICB, PCA

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## 1. Introduction

Rapid urbanization, especially in emerging countries such as Brazil, China, and India, has affected the availability and quality of water. Waterborne disease incidence is on the rise and the amount of time and money from private, mostly poor, residences going into collecting water has been an inefficient use of already scarce resources (CASEY et al., 2006). As a consequence, overexploitation and improper waste disposal, especially in urban areas, are responsible for problems observed in groundwater. According to the World Health Organization (WHO), about 80% of all human diseases have a relation to groundwater contamination. For example, diarrhea occurs worldwide and causes 4% of all deaths (Who, 2009).

Furthermore, nitrate contamination of water is a worldwide environmental problem due to the effects of intensive human activities. Nitrate can reach both surface water and groundwater as a result of agricultural activities (including the excessive use of inorganic nitrogenous fertilizers and manure), wastewater treatment and the oxidation of nitrogenous waste material in human and animal excreta, including septic tanks (Who, 2016). Unfortunately, nitrate is the most ubiquitous chemical contaminant in the world's aquifers, and contamination levels are increasing (SPALDING e EXNER, 1993). Ingestion of nitrate in drinking water causes methemoglobinemia, a disorder in which the ability of blood to carry vital oxygen decreases (SUPER et al., 1981). In most countries, nitrate levels in drinking water exceed 10 mg L<sup>-1</sup>. For example, in European countries, the percentage of the population exposed to nitrate levels above 50 mg L<sup>-1</sup> in drinking water is from 0.5 to 10%, corresponding to nearly 10 million people (WAKIDA e LERNER, 2005). The level of nitrate in drinking water from Brazilian aquifers has risen in all regions (ZOBY e OLIVEIRA, 2005). Additionally, nitrate in groundwater has remained a hot research topic over the past 2 decades (NIU et al., 2014). Indeed, the prospect of groundwater exploitation in the Amazonia region has increased significantly in the Alter do Chão aquifer, now called the Large Aquifer System Amazon - LASA considered by UNESCO as the largest aquifer in the world (AGUIAR e MOURÃO, 2012). In Manaus, which is the largest

city of the Amazon State, there are nearly 15,000 wells with depths ranging from 10 to 240 m, representing 25% of the total local water supply (ROCHA e HORBE, 2006). According to the Mineral Resources Research Company (CPRM), there is a high risk of contamination from several wells which have been illegally drilled. The indiscriminate process of drilling has resulted in the abandoning of several wells (AGUIAR e MOURÃO, 2012). According to the ROCHA and HORBE (2006) report, nitrate levels have reached >10.0 mg L<sup>-1</sup> for wells with a depth of 80 m in Manaus, which could be related to the overexploitation of water supply and landfills in public spaces.

LASA groundwater, formed by conglomerates of interbedded sandstones, mudstones, and siltstones has unconfined (depth 50 m) and confined (depth 430 m) aquifers, distributed throughout the entire region. Water transmissivity is between  $1.5 \times 10^{-3}$  and  $9.1 \times 10^{-3}$  m<sup>2</sup> s<sup>-1</sup> with porosity and an average thickness of rock being 20% and 160 m, respectively. The LASA water supply reserve is greater than 148 km<sup>3</sup> (ROCHA e HORBE, 2006; Da SILVA e BONOTTO, 2014), varying with the hydrological cycle in all aquifers. In the Solimões Formation, the reserve is 25,950 km<sup>3</sup> and the Alter do Chão Formation is 37,900 km<sup>3</sup> (CUNHA et al., 1984). The inflow into the LASA obeys the following order: i) 87% as a result of pluviometrical infiltration ii) 2.4% from the river, iii) 3.5% from constant charge. Rivers and streams in the region receive 78.0% of the water that outcrops from the LASA. Public-supply uses nearly 19% of the water from the LASA (ROSSETTII et al., 2012; PAULIQUEVIS et al., 2012).

Despite the quantity of rainfall in the Amazonia region, the effect of the hydrological cycle on the physical and chemical water properties is low in the LASA (REIS et al., 2006). The Alter do Chão Formation water quality has the following characteristics: pH values between 4.1 and 5.4, electrical conductivity ranging from 15.1 to 82.9 µS cm<sup>-1</sup>, being classified as chlorinated sodium and potassium with some reported evidence of anthropogenic contamination. Whereas, the physical and chemical properties of the Solimões Formation water quality are: pH values ranging from 5.0 to 6.0, electrical conductivity between 12.0 and 100 µS cm<sup>-1</sup>, being classified as bicarbonates-sodium

with concentrations of  $\text{Na}^+$  and  $\text{HCO}_3^-$  being less than 7 and 30  $\text{mg L}^{-1}$ , respectively (REIS et al., 2006).

The aim of this investigation was to assess the groundwater quality in the cities of Itacoatiara and Manacapuru, as well as to contribute to improving on the knowledge of the effects of indiscriminate well drilling in the Amazonas State.

## 2. Material and Methods

### 2.1 Sampling site

The LASA, situated between the sedimentary basins of the Marajo and Acre (Figure 1), receives influences from the following formations: Nova Olinda, Itaituba, Monte Alegre, Curiri, Barreirinha, Irerê, Maecuru, Alter do Chão, Solimões, and Içá (AGUIAR e MOURÃO, 2012). In Itacoatiara and Manacapuru, the water chemical composition of the LASA receives influence from the Alter do Chão and Solimões Formations.

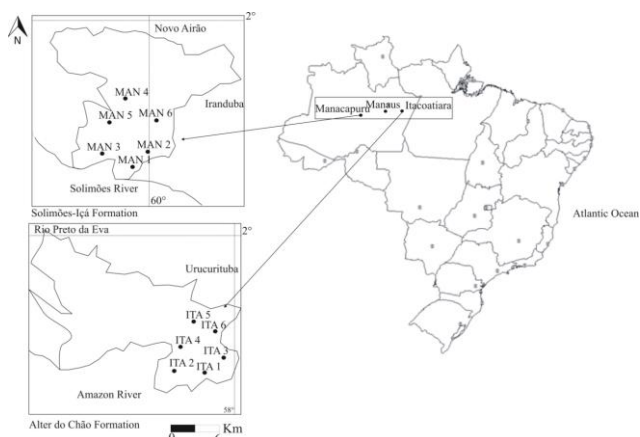


Figure 1. Map of Itacoatiara and Manacapuru showing areas sampled (Amazonas).

The Alter do Chão Formation (Figure 2-A) encompasses an area of 312,574  $\text{km}^2$  and spreads over the western Amazon area. The Alter do Chão Formation is composed of Cretaceous rocks with WE-oriented forms and a superimposed belt of Paleozoic rocks in the Amazon Basin and a variety of igneous and metamorphic Precambrian rocks in the Guianas and the Central Brazilian shields (Figure 2-B). The Solimões Formation encompasses an area of 948,600  $\text{km}^2$ . An area of 576,300  $\text{km}^2$  is underlying the Içá Formation. The remaining area (~372,300  $\text{km}^2$ ) outcrops throughout the Içá Formation sediment (Figure 2-B). The Solimões Formation has crystalline and

Proterozoic rocks divided into two sub-basins (Jandiutuba and Juruá) (CUNHA et al., 1984).

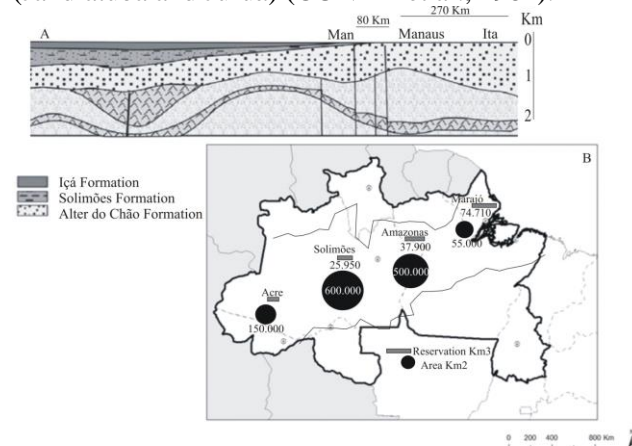


Figure 2. Geological map (A) with area and volume of the LASA (B)

Water was collected from twelve wells, chosen randomly, six being in Itacoatiara (ITA) and the other six in Manacapuru (MAN), all being public wells (Figure 1). The lithology of the wells obeyed the following sequence: mudstone/sandstone/mudstone. Organic soil, coarse sand, loamy sand and laterite were identified in two sampling sites (Aguilar e Mourão, 2012). Manacapuru has 501 wells, and Itacoatiara has 221 wells registered at an official public agency. Both cities have 30 wells registered in the urban area for public supply to 94,175 inhabitants in Manacapuru and 97,122 inhabitants in Itacoatiara. For samples collected in Itacoatiara, well depths varied from between 100 and 150 m. A 0.02 g portion of biocide thymol was added to each collected groundwater sample for conservation and then preserved at 4°C in polypropylene containers (GAILLARDET et al., 1997). Groundwater samples were collected in June (dry season), September (wet season) and December (rainy season) 2012 and April 2013 (wet season), based on the hydrological cycle and annual season (DA SILVA e BONTOTTO, 2015).

### 2.2 Physical and chemical analyses

This work analyzed the following chemical species:  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  using ion chromatography methods, and alkalinity with a titrimetric method using  $\text{H}_2\text{SO}_4$  titrant for all groundwater samples. The analytical instrument used was a Dionex ICS-900 Ion Chromatography system with its detection limit set at 0.0001  $\text{mg L}^{-1}$ . For each analysis, the



reference sample was *ELGA* LabWater's *PURELAB* ultrapure water, and flasks were washed with a solution of 10% nitric acid. Samples contained thymol as a preservative (GAILLARDET et al., 1997) and were chilled for analyses carried out in the Geochemical Laboratory of the Federal University of Amazonas.

Physical analyses consisted of pH and electrical conductivity measurements with values taken in situ. pH measurements were with a Metrohm pH meter model calibrated with buffer solutions of pH 7.0 and 4.0. The conductivity was measured with a digital conductivity meter and KCl solution was used for conductivity calibration (standard conductivity  $12.9 \text{ mS cm}^{-1}$ ).

### 2.3 Applied statistics

Statistical analysis consisted of two unsupervised methods (Hierarchical Cluster Analysis, HCA, and Principal Component Analysis, PCA). The software statistical R (version 2.15) performed all variables standardized by transforming data into Z-scores (i.e.  $(x - x_m)/\sigma$ , where  $x_m$  stands for the average). The Ward method and squared Euclidean distance were the options used to generate dendrograms in PCA.

### 3. Results and discussion

Table 1 shows the average of the ionic concentrations found in the four sampling periods. The high standard deviation values found in the groundwater chemical compositions from Itacoatiara and Manacapuru suggest huge seasonal influence. The phosphate concentration was less than the detection limit. However, the F-test ( $p = 0.95$ ) shows that the hypothesis of equality of variances is true for 4 sampling sites as well as for the comparison between Itacoatiara and Manacapuru ground water, with the exception of  $\text{NO}_3^-$  ( $p = 0.03$ ),  $\text{NH}_4^+$  ( $p = 0.03$ ) and  $\text{SO}_4^{2-}$  ( $p = 3.0 \times 10^{-4}$ ).

The fractional difference between the total cations and total anions calculated by the Normalized Inorganic Charge Balance (NICB), defined as  $(\sum z^+ - \sum z^-/z^+)$  and representing the fractional difference between the total cations and total anions, showed two distinct behaviors.

These findings already suggest the existence of environmental problems with the LASA caused by nitrate introduction in the

groundwater in Itacoatiara and Manacapuru. Commonly, the sources of nitrogen in urban aquifers are a mixture of point sources (e.g., landfills and coal gasification works), and multipoint sources (atmospheric deposits, house construction, and recreational areas). On the account of the number of nitrogen sources in an urban area, it is not surprising to find high nitrogen concentration in urban aquifers (WAKIDA e LERNER, 2005). However, the main source in Itacoatiara and Manacapuru is the septic system which commonly receives domestic waste. Unfortunately, high nitrate level in groundwater has also affected the Guarani aquifer, another important Brazilian groundwater system. Table 2 shows several nitrate levels above  $10 \text{ mg L}^{-1}$  found in groundwater from the Guarani aquifer. The high nitrate level in Guarani aquifer has several causes, such as the indiscriminate use of fertilizers (KIM et al., 2015) urban wastewater present in surface water (MIRLEAN et al., 2005), the high risk of contamination from illegally drilled wells (SOUZA e DEMÉTRIO, 2011), septic and black tanks (BIGUELINI e GUMY, 2012), and infiltration of water from contaminated rivers (GASTMANS e KIANG, 2005). Therefore, the reasons responsible for high nitrate level in groundwater are similar for the Guarani aquifer and the LASA.

The first NICB included  $\text{NO}_3^-$  contents and the second did not (Figure 3). The findings varied according to the nitrate content, for instance, ITA-6 and MAN-6 showed negative NICB values calculated with the addition of nitrate, while only MAN-2 presented a negative NICB value calculated without nitrate. According to Singh et al. (US. EPA, 2012) this charge imbalance, shown in most of the groundwater, points to high organic matter content degraded by biological activity of microorganisms under hot and humid conditions. On the other hand, GAILLARDET et al. (1997) claims that in a tropical region such as the Amazonas region where weathering is higher, nitrate content contributes in counterbalancing the NICB values. Despite observation, the median NICB values for collection showed an error  $< 5.0 \%$ , signifying the lack of alterations caused by anthropogenic or natural activity (KIM et al., 2015). The negative charge reveals sporadic problems of contamination in some wells (SOUZA e DEMÉTRIO, 2011).



Table 1. Groundwater chemical composition (average,  $\pm$  standard deviation in mg L<sup>-1</sup>) and value of Normalized Inorganic Charge Balance – NICB - collected in two studied cities

Variable	Itacoatiara					
	1	2	3	4	5	6
Na <sup>+</sup>	4.00±2.58	6.56±3.67	5.11±1.76	11.3±5.78	22.6±10.36	6.08±6.87
K <sup>+</sup>	6.44±2.98	4.2±0.46	4.78±1.46	3.85±3.31	3.39±0.89	1.05±0.70
NH <sub>4</sub> <sup>+</sup>	12.1±9.25	12.9±8.94	10.4±7.58	9.40±7.93	8.61±7.47	2.93±4.43
Mg <sup>2+</sup>	2.54±2.42	2.18±0.97	2.23±0.60	1.73±2.34	1.2±1.36	0.46±0.66
Ca <sup>2+</sup>	5.69±4.26	4.02±1.64	3.92±1.55	2.06±1.67	1.28±0.93	0.48±0.33
Cl <sup>-</sup>	2.95±3.94	4.12±2.84	1.28±0.93	9.44±5.25	19.8±6.49	4.82±2.45
HCO <sub>3</sub> <sup>-</sup>	23.6±1.19	23.5±0.70	23.6±0.73	17.10±0.89	12.7±8.76	17.3±0.75
NO <sub>3</sub> <sup>-</sup>	0.17±0.32	2.29±0.76	1.93±2.24	17.2±11.82	25.4±9.75	3.42±0.99
NO <sub>2</sub> <sup>-</sup>	3.60±6.03	3.03±4.04	4.7±5.81	0.05±0.09	2.6±3.05	0.07±0.13
SO <sub>4</sub> <sup>2-</sup>	5.22±4.59	1.49±1.08	1.32±1.10	2.41±1.90	4.04±3.71	0.24±0.27
NICB	0.25±0.35	0.20±0.17	0.24±0.11	-0.03±0.12	-0.02±0.47	-0.12±0.29
Variable	Manacapuru					
	1	2	3	4	5	6
Na <sup>+</sup>	14.0±8.2	23.1±6.8	1.83±0.35	3.02±0.68	14.1±3.27	2.69±1.48
K <sup>+</sup>	7.54±3.54	5.96±1.50	9.34±3.02	10.2±4.90	4.10±1.04	5.95±4.94
NH <sub>4</sub> <sup>+</sup>	2.51±3.16	1.51±1.23	0.91±0.88	3.58±4.20	0.58±1.15	0.52±0.77
Mg <sup>2+</sup>	1.80±0.09	1.44±0.45	2.69±0.23	5.87±3.26	1.10±0.73	3.76±3.85
Ca <sup>2+</sup>	5.26±3.00	5.44±0.85	5.25±0.62	14.5±8.92	3.87±1.33	8.49±8.66
Cl <sup>-</sup>	14.8±10.0	25.6±10.4	0.81±0.87	1.23±0.70	16.4±0.72	2.02±0.72
HCO <sub>3</sub> <sup>-</sup>	20.3±2.81	0.01±0.00	23.1±0.56	25.5±0.40	4.23±8.44	25.9±0.31
NO <sub>3</sub> <sup>-</sup>	34.2±20.9	77.4±1.61	0.77±0.14	1.86±1.19	35.1±4.06	1.98±1.23
NO <sub>2</sub> <sup>-</sup>	0.30±0.34	0.30±0.35	0.24±0.27	2.15±3.77	1.91±3.11	1.60±2.48
SO <sub>4</sub> <sup>2-</sup>	0.18±0.10	3.01±1.23	0.11±0.07	20.9±4.94	4.24±2.62	36.5±4.30
NICB	-0.09±0.35	-0.4±0.58	0.38±0.08	0.68±0.80	-0.18±0.20	-0.26±0.87

Table 2. Studies carried out by other authors on the Guarani Aquifer

Author	Country	State	Nitrate level	Year
Gastmans e Kiang	Brazil	Mato Grosso do Sul	32.4	2005
Alaburda e Nishihara	Brazil	São Paulo	46.0	2008
Lourencetti et al.	Brazil	São Paulo	15.0	2015
Montanheiro et al.	Brazil	São Paulo	67.9	2014
Fernandes et al.	Brazil	Rio de Janeiro	145.0	2013
Freitas et al.	Brazil	Rio de Janeiro	43.4	2001
Biguelini e Gumy	Brazil	Paraná	30.8	2012
Zerwes et al.	Brazil	Paraná	41.6	2015
Mirlean et al.	Brazil	Rio Grande do Sul	72.2	2005
Perdomo et al.	Uruguay	San Pedro	93.0	2001
Costa et al.	Argentina	Buenos Aires	32.5	2002
Martinez et al.	Argentina	Buenos Aires	72.9	2014

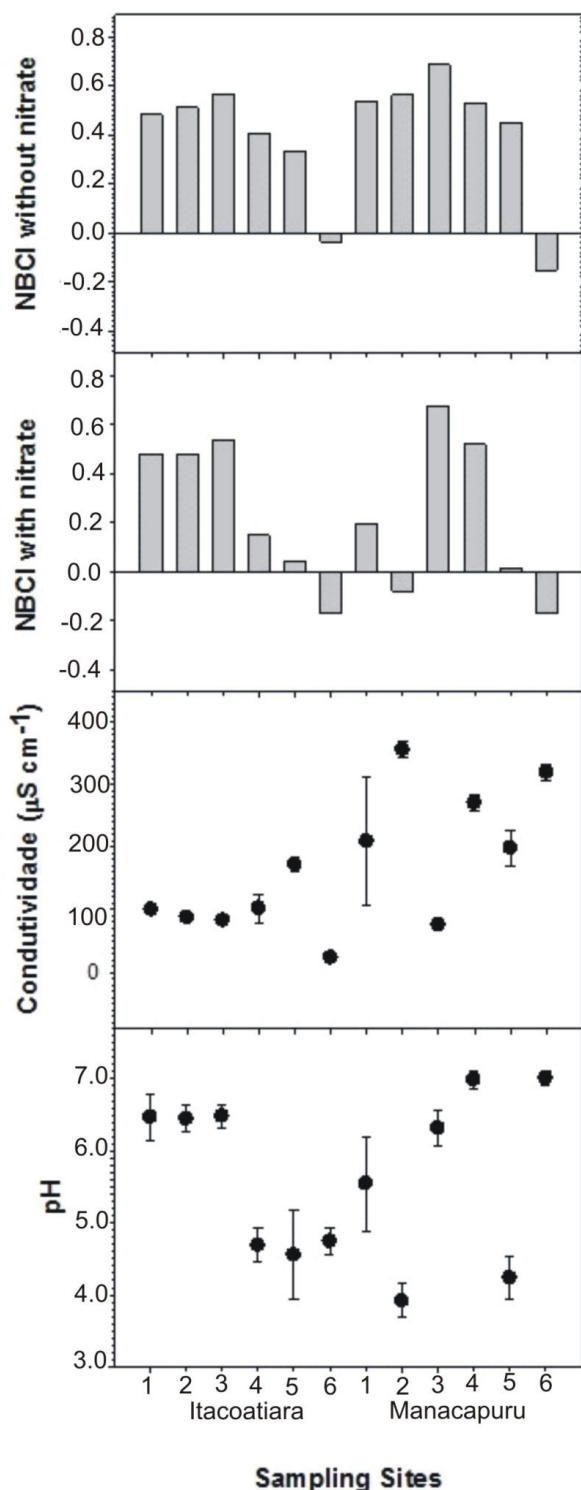


Figure 3. Results of pH, electrical conductivity and NICB obtained for wells in Itacoatiara and Manacapuru (Amazonas, 2012/2013)

The findings show an important relationship between acidity, sampling site, and collection time. The geological formations under highly weathering environmental conditions explain this relationship. It also explains the high

acidity found in the Manacapuru and Itacoatiara groundwater samples (Figure 3). The lowest pH values were found in the water samples collected in September (3.84) and the highest in June (7.12). Regardless of the geological formation, it was possible to observe two groundwater classes: i) the first formed by groundwater presenting pH values  $< 4.00$  and ii) the second with pH values  $> 6.50$ . Furthermore, the electrical conductivity values for Manacapuru and Itacoatiara groundwater varied from 18.4 to 319  $\mu\text{S cm}^{-1}$ . The weathering, environmental and typical high rainfall conditions of the Amazon region explain the fluctuations observed. The distinctive geological differences between the two cities explain their chemical differences, especially the high levels of sulfate in Manacapuru (AGUIAR e MOURÃO, 2012).

Rainfall data from the central Amazon was used to show the influence of rain on the chemical composition of the groundwater in Itacoatiara and Manacapuru in the analyzed wells. The hydrologic cycle influences the chemical composition of the groundwater. The chemical concentration depends on seasonal changes: i) decreasing during the rainy season due to the dilution of ions from the local rainfall, and ii) increasing during the dry season when wells have lower level groundwater. However, the chemical properties of the rainwater itself (ROSSETTI et al., 2012) constituted the only noticeable contribution to enrichment of the groundwater in wells Ita 1 and Man 3, with  $\text{NO}_3^-$  probably associated with biological processes (Figure 4 – A).

Sodium is prevalent in the rainy season, both in Itacoatiara and Manacapuru. There is minimal influence from the hydrological regime on potassium. On the other hand, there is great influence on calcium and magnesium, predominantly during the dry seasons in both cities. The ammonium ion is prevalent in Manacapuru during the rainy season, and in Itacoatiara during the transition period to the dry season. Among the anions, the chloride ion has not proven to be an indicator of climatic influence, while bicarbonate was more concentrated in periods of low rainfall. Similarities were found with nitrite and nitrate. All ions have been analyzed using the current regulations for potable water, except for nitrate (Figure 4 – B) with concentrations being above

the limits set (10.0 mg L<sup>-1</sup>).

Five of the twelve analyzed wells showed anomalous values of nitrate. As the NICB values were all below 1.0, this may suggest anthropic effects in these wells, such as inadequate drilling, proximity to septic tanks or improper cleaning using materials with nitrogen products.

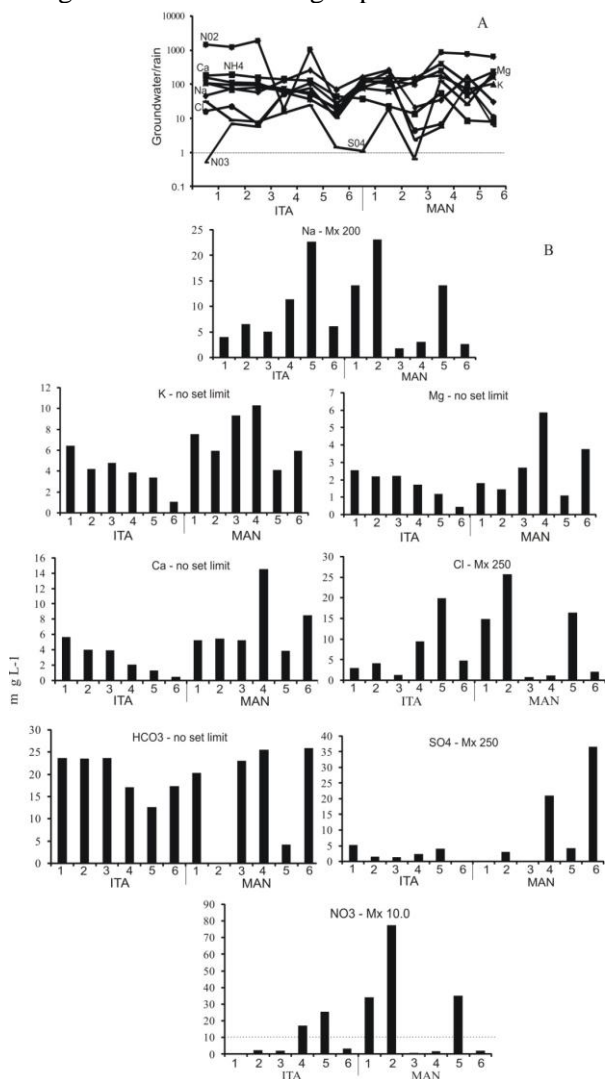


Figure 4. (A) Season influence of rain on groundwater (meq L<sup>-1</sup>) and (B) annual variations in average with the limits of Ordinance 2914 / Health Legislation

The principal components (PC) in this study are composed of the evaluation between the loadings and groundwater chemical composition as well as the collection period. Table 3 shows the summary statistics for the groundwater chemical composition. The criteria used for choosing the number of PCs are: (i) the retaining of principal components describing 90% of the total variance, (ii) the excluding of principal components whose

eigenvalues are less than the average eigenvalues, (iii) the plotting of a graph of eigenvalues versus principal components. That represents a visual inspection in order to find the greatest number of components. The total variance for the first two factors varied from 65.21 to 78.22% for eigenvalues from 1.66 to 1.18. According to criterion 2 above, three components have eigenvalues greater than the average retained. Thus, the total variance for the first two factors is informative to the cluster samples in two-dimensional space.

The distance of how far the variable is from the origin measures the impact of any variable for the entire PCA analysis. Variables that show greater distances have wider impact on the general architecture of the PC-loading than variables with shorter distances. PC-loadings show two variables with shorter distances: NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup> (Figure 5). This result points out contamination from domestic waste in some of the wells studied. We agree because of the lack of NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup> in the chemical-mineralogical composition of the studied region (CUNHA et al., 1984). Additionally, research shows that NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup> are products of organic matter degradation (SOUZA e DEMÉTRIO, 2011). NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> formation generally occur because of microbiological activity that degrades the organic matter.

Depending on the sample, the variable impact varies, for instance, the electrical conductivity (CE), K<sup>+</sup>, and SO<sub>4</sub><sup>2-</sup>. It is clear that most of the variables correlate positively with a stronger impact on the groundwater chemical composition from Manacapuru and Itacoatiara. The Ca and Mg correlates positively and negatively in Dim 1 versus Dim 2, signifying a similar source contribution of these two metals in the water samples. The positive correlation between pH and HCO<sub>3</sub><sup>-</sup> suggests carbonate influence on water acidity.

The water wells have low Na<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> ion concentrations, with values usually between 7 and 30 mg L<sup>-1</sup> and K<sup>+</sup> >5.5 mg L<sup>-1</sup>. Furthermore, the electrical conductivity shows wide variations, from 12 to 100 μS cm<sup>-1</sup> as well as pH values from 4.5 to 8.0 (CUNHA et al., 1984).

Table 3. Principal component analysis for groundwater chemical composition from Manacapuru and Itacoatiara

Eigenvalue	April		
	F 1	F2	F3
Eigenvalue	5.58	3.66	1.18
Variability (%)	46.58	30.54	9.87
Cumulative (%)	46.58	77.12	86.99
June			
	F1	F2	F3
Eigenvalue	5.02	2.81	1.66
Variability (%)	41.83	23.38	13.85
Cumulative (%)	41.83	65.21	79.06
September			
	F1	F2	F3
Eigenvalue	5.25	2.48	1.61
Variability (%)	47.75	22.53	14.63
Cumulative (%)	47.75	70.29	84.92
December			
	F1	F2	F3
Eigenvalue	5.72	3.67	1.47
Variability (%)	47.66	30.56	12.27
Cumulative (%)	47.66	78.22	90.48

observed for the electrical conductivity, as well as the pH values.

#### 4. Conclusion

The work shows that the ion concentration in the groundwater from Itacoatiara and Manacapuru is seasonally influenced by the water cycle. Our results suggest that carbonate influence on water acidity and groundwater occur in the rainy periods. The NICB data show that the charge imbalance is due to nitrate. The PCA analysis confirmed that the discordant species studied in the groundwater is nitrate. The association between ammonium and nitrate suggests human action in some of the wells studied. The nitrate contamination observed in the wells of Itacoatiara and Manacapuru is a result of inadequate drilling, proximity to septic tanks or cleaning of wells with nitrogen products. The hydrologic cycle exerts an inverse function in both cities. Thus, the dilution and concentration factors also take place in reverse order. Both cities have high indices of waterborne diseases, which could be associated with the quality of the wells,

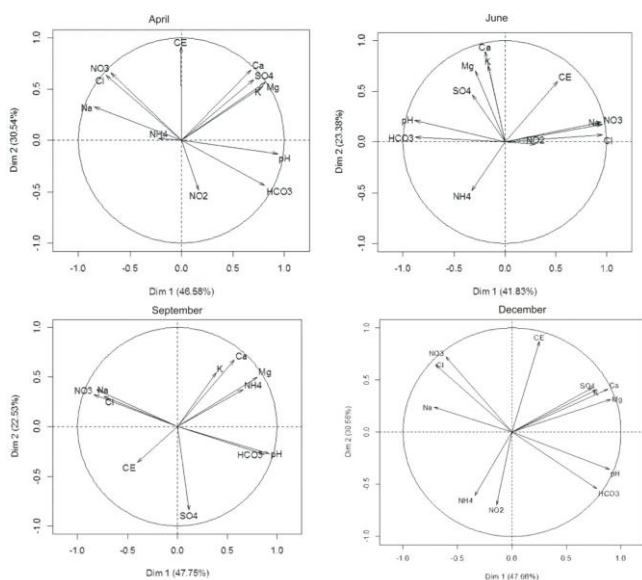


Figure 5. Projection of variables and their correlation in the factor space for groundwater chemical composition from Itacoatiara and Manacapuru.

The correlations between  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$ , mainly in April and December, points to an alteration in the chemical composition of groundwater during rainy periods. This explains the lack of correlation





and high nitrate values. A microbiological study on these waters has been suggested to investigate the level of biological contamination in these wells. Increased surveillance for the drilling of wells and better management of the Alter do Chão- LASA are also necessary.

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