Support method for interpretation of regional groundwater monitoring in urban areas

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Abstract
Urban centers radically alter hydrological cycles, causing unintended consequences for the environment, such as the creation of extensive contamination plumes in unconfined aquifers. The Environmental Agency of the State of São Paulo has observed this issue since 1994. Therefore, this study aimed to create a method using nitrate as an indicator of contamination that permits an assertive interpretation of changes in the groundwater-monitoring network in the State of São Paulo. The method was applied in ten cities with monitoring wells in the Bauru Aquifer System. The results correlated the presence of nitrate with the time and dynamics of land use in the capture zones of the wells over 54 years (1962–2016). In areas with sewer networks installed before 2001 and urban occupation greater than 60% of urban occupation in the capture zones, there was an increase in nitrate concentration of at least 35%. Likewise, extending this new method to other wells will make it possible to identify the causes of nitrate and other contaminants in the groundwater-monitoring network in the State of São Paulo.

KEYWORDS: groundwater; nitrate; aquifer monitoring network; land use and occupation; urban planning.

INTRODUCTION
Cities have radically altered the flow of water, energy, and matter from river basins. Waterproofing the land increases rain interception and runoff and reduces aquifer recharge. Similarly, cities modify the heat flow and, consequently, water evaporation processes and rain patterns. Equally important, various urban activities transfer immense amounts of matter from the atmosphere (Babinski et al. 2003, 2012) and from the surface to the soil (CETESB 2013, Santos Filho et al. 2017, Aranda et al. 2019), rivers (Porto 2003, Xu et al. 2019), and aquifers (Foster and Hirata 1988, DAEE 2012, Cary et al. 2013, Conicelli 2014, Bertolo et al. 2015, Hirata et al. 2015, Petelet-Giraud et al. 2018), sometimes contaminating them. In this urban cycle of water, energy, and matter, one of the rarely researched components is the aquifer (Foster et al. 2011, Hibbs and Sharp 2012, Hirata and Suhogusoff 2019), even in countries in Europe and North America.

In Brazil, in recent decades, cities have faced problems related to drastic increases in the concentration of pollutants in aquifers, including nitrate (Hirata and Suhogusoff 2019, Varnier et al. 2019). The origins of this contaminant in aquifers are associated with poor agricultural practices, including over-application of inorganic fertilizers, infiltration of sewers in urban areas, and extensive industrial activities (Foster et al. 2006, Reynolds-Vargas et al. 2006, He and Wu 2019, Wu et al. 2020). Despite the numerous cases of nitrate described in the State of São Paulo, as in Marília (Varnier et al. 2010), São José do Rio Preto (Barcha 1980), and Bauru (Hirata 2000, Giafferis and Oliveira 2006), this problem remains underestimated by public authorities and even more by groundwater users (Varnier et al. 2019). This issue has been systematically documented in the Environmental Sanitation Technology Company (CETESB) triennial reports — Quality of Groundwater in the State of São Paulo. Nevertheless, no studies have explained the causes behind the increase of nitrate concentrations in the monitoring network over time; and reports have only attempted to describe the problem.

The best way to reduce the nitrate contamination risk in urban aquifers is to construct sewer networks, whose service reaches more than 38 million of the São Paulo population (88.4%) (SNIS 2017). However, leaks from the sewer mains are responsible for extensive contamination in unconfined aquifers (Hirata et al. 2015, Hirata and Suhogusoff 2019, Varnier et al. 2019), which is worrisome, especially when 80% of the state cities state have total or partial public water supply from groundwater, in addition to the existence of hundreds of thousands of private tubular wells that are extensively used.

The presence of nitrate in a specific well, which extracts water from an unconfined aquifer, is a function of contamination sources in its nearby recharge area (Drake and Bauder 2005, Reynolds-Vargas et al. 2006, Xu et al. 2007). These studies maintain that higher nitrate concentrations are associated with sites whose sewage collection network is old, poorly maintained and leaks or contains cesspools and septic tanks to drain domestic effluents (Hirata et al. 2015).
An additional problem related to regional monitoring networks, such as those operated by CETESB, is their low assertiveness levels. Monitoring wells can only assess what is happening in their immediate area (Foster and Gomes 1989), not exceeding a few hundred meters. Also, São Paulo network uses tubular production wells, usually with long screen intervals, which cause a mixture of waters of varying ages and chemical compositions. Generally, deeper levels with clean waters mask shallower portions of the heavily contaminated aquifer.

Therefore, this paper aimed to create a methodology that generates more assertive results obtained by a regional monitoring network, allowing the establishment of a relation between land occupation and deterioration of the quality of aquifers caused by urban sources, using nitrate as a chemical indicator.

**STUDY AREA**

The geological framework of the State of São Paulo allows the aquifers to be divided into two groups: those of primary porosity, represented by sedimentary aquifers (Furnas, Itararé, Aquidauana, Passa Dois, Botucatu, Piramboia, Santo Anastácio, Caiuá, Marília, Adamantina, São Paulo, Litorâneo, and Taubaté) and undifferentiated cenozoic coverings; and secondary porosity aquifers, represented by the fractured Serra Geral and Cristalino (DAEE 2005). These aquifers are aggregated into aquifer systems, namely Cenozoic, Bauru, Serra Geral, Guarani, Aquitarde Passa Dois, Tubarão, Paraná, and Cristalino (Carvalho and Hirata 2012).

The Bauru Aquifer System (BAS), which is the focus of this study, occupies around the Western half of the State of São Paulo, with an area of 96,880 km², as in Fig. 1 (Varnier et al. 2010). It consists of the Bauru Groups rocks, whose continental fluvial...
sedimentation occurred in desert conditions and at a semi-arid climate, providing it lithological heterogeneity. The primary lithologies of this unit are sandstones, clayey sandstones, and siltstones, with or without carbonate cementation, characterized as a predominantly unconfined hydrogeological body that is a locally semi-confined one (DAEE 2005). Due to its extent and good productivity, it is the most intense and extensively explored system and is a water source for most of the municipalities in Western São Paulo.

The aquifers part of the BAS are Marília, Adamantina, Santo Anastácio, and Caiuá (Tab. 1). According to CETESB (2019), its waters are predominant of two hydrochemical types, calcium bicarbonates (43%) and mixed type (37%) and, secondarily, sodium bicarbonates (17%). With the exception of local natural problems of iron, manganese, (more locally) chromium (Bourrotte et al. 2009) and barium (Tavares et al. 2015) anomalies, its water is of excellent quality and is drinkable in more than 95% of the locations.

The BAS has an average saturated thickness of 75 m and can vary from 150 to 200 m in the region of São José do Rio Preto and Presidente Prudente, and to 300 m in the Residual Plateau of Marília. Thickness is influenced by the morphology of the rocky substrate represented by the basalts of Serra Geral Formation. Recharge occurs directly due to rainfall, and the groundwater regional flow takes place towards the main drains of Turvo, São José dos Dourados, Tietê, Aguapeí, Peixe, Santo Anastácio, Paraná, and Paranapanema rivers. The exploitable flow varies from 10 to 120 m$^3$/h per well, with higher potential zones located along the Paraná and Paranapanema rivers.

### MATERIALS AND METHODS

The method to monitor the nitrate concentration in the BAS consisted of two main stages, the selection and mapping of the wells and the comparison and chemical and urban occupation data correlation of the wells (Fig. 2). After selecting the wells, the next step was to map the capture zone for each well. Then, in each capture zone, changes in occupation between the years 1962 and 2016 were identified in the aerial images. The second stage compared and correlated the urban occupation, the sewer network installation year, and chemical data between 1962 and 2016.

### Physical-chemical data of the monitoring network

Groundwater-monitoring network data of the State of São Paulo covered 1994 to 2015 (CETESB 2013, 2016, 2019). Groundwater was collected and analyzed by CETESB and included 67 physical, chemical, and bacteriological parameters (Tab. 2). The monitoring network consists of active tubular water production wells equipped with submerged electric pumps.

The program used for calculating the variation in nitrate concentrations overtime was Microsoft Excel. The groundwater collection frequency was one to three times a year, with sampling carried out according to the hydrological cycle, usually in a dry period (May to October) and a rainy one (November to April). The tubular wells were included in the network at different times, generating varied sampling periods. Given the wealth of chemical data, we sought to associate the various parameters with one another using correlation diagrams for each well. Positive, negative, or null ρ correlations were established according to the method described by Pearson (Freedman et al. 2007), as seen in Equation 1:

$$
ρ = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2} \sum_{i=1}^{n}(y_i - \bar{y})^2}
$$

(1)

The values of ρ are interpreted as follows:

- ρ = 1 means a perfect direct correlation between the two variables;
- ρ = -1 means a perfect inverse correlation between the two variables, that is, if one increases, the other always decreases;
- ρ = 0 means that the two variables do not depend linearly on each other.

### Well identification

Currently, the aquifer-monitoring network of the São Paulo State comprises a total of 313 tubular wells distributed over the main aquifer systems (CETESB 2019). Two public reports were evaluated for this study: CETESB (2013) and CETESB (2016), which highlight the main wells in the State of São Paulo with nitrate concentrations above 5 mg/L N-NO$_3$.

The BAS is the main water unit affected by nitrate in the State of São Paulo (CETESB 2016). Ten wells located in this aquifer system were chosen to correlate land use and nitrate

### Table 1. Hydrogeological parameters of the aquifers of the Bauru Aquifer System in the State of São Paulo.

| Aquifer System | Aquifer       | Description                                         | Area (km$^2$) | Q (m$^3$/h) | n (%) | b (m) | K (m/d) | i | $n_e$ (%) | Recharge (mm/year) |
|----------------|---------------|-----------------------------------------------------|---------------|-------------|-------|-------|---------|---|-----------|-------------------|
| Bauru          | Marília       | Regional extension, granular, free to semi-confined, discontinuous, heterogeneous, anisotropic | 15,000        | 7.5         | 0.13   | 120   | 1       | 0.04 | 0.1       | 250               |
|                | Adamantina    |                                                     | 104,000       | 19          | 0.15   | 130   | 1.5     | 0.03 | 0.1       | 250               |
|                | Santo Anastácio | Limited extension, granular, free to semi-confined, discontinuous, heterogeneous, anisotropic | 67,000        | 35          | 0.25   | 80    | 2       | 0.02 | 0.12      | 250               |
|                | Caiuá         |                                                     | 13,000        | 100         | 0.2    | 100   | 2.5     | 0.01 | 0.15      | 350               |

Q: flow rate (considering 24 hours pumping); n: total porosity; b: saturated thickness; K: hydraulic conductivity; i: hydraulic gradient; $n_e$: effective porosity. Source: modified from Carvalho and Hirata 2012.
concentrations. The selected wells are located mainly in the Adamantina Aquifer, followed by Santo Inácio and Caiuá aquifers.

The information available for the ten selected wells includes:

- increase, decrease, or neutral/stable nitrate concentration overtime;
- location of the wells that allows to make a correlation with the evolution of land occupation;
- complete and reliable construction information;
- consistency in the variation of nitrate concentrations in several campaigns.

The average concentration for two different periods was determined and compared in order to evaluate the changes in nitrate concentration for each selected well: the first six years of well operation and between 2009 and 2015.

Mapping of capture zones in wells

The method used to establish the capture zones (related to recharge) of the well was the calculated fixed radius (CFR), which is defined through the transit time of 50 years, in agreement with the time of comparison between the images of the 60 s and the last collection evaluated in 2016.

The CFR method (Fig. 3 and Eq. 2) is based on a geometric approach that defines a circular area around the well proportional to the volume of water withdrawn in a particular period (USEPA 1994, Carvalho and Hirata 2012). This technique does

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**Figure 2.** Diagram summarizing the methodology.

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**Table 2.** Physical-chemical and microbiological parameters analyzed in the groundwater in the State of São Paulo monitoring network.

| Physical                                      | Chemical                                                                 | Microbiological                           |
|-----------------------------------------------|--------------------------------------------------------------------------|--------------------------------------------|
| Water and air temperature, total dissolved and total solids | pH, alkalinity bicarbonate, alkalinity carbonate, alkalinity hydroxide, electrical conductivity, total hardness, nitrogen nitrate, nitrogen nitrite, ammoniacal nitrogen, Kjeldhal nitrogen, dissolved organic carbon, chloride, fluoride, sulfate, aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, calcium, lead, cobalt, copper, chromium, hexavalent chromium, tin, strontium, iron, lithium, magnesium, manganese, mercury, molybdenum, nickel, potassium, silver, selenium, sodium, titanium, uranium, vanadium, and zinc | Heterotrophic bacteria, *Escherichia coli*, total coliforms, and F-specific bacteriophages |
not consider the conditions of heterogeneity, anisotropy, or direction of aquifer flow, nor other particularities of the outline of wells. The CFR defines a capture zone that corresponds to a very simplified reality; however, the method is quite useful with a first assessment, especially in smooth topographical relief and few geological data (Carvalho and Hirata 2012).

\[
\rho = \sum (x_i - \bar{x}) (y_i - \bar{y}) / n_i = 1 \sqrt{\sum (x_i - \bar{x})^2 / n_i = 1 \sum (y_i - \bar{y})^2 / n_i = 1}
\]

\[
R = \sqrt{\frac{Qt}{\pi H n_{ef}}} \quad (2)
\]

Where:
- \( R \) is the calculated fixed radius;
- \( t \) is the travel time;
- \( Q \) is the pumping rate;
- \( H \) is the thickness of the aquifer saturated zone;
- \( n_{ef} \) is the effective porosity (Fig. 3).

The method applied the information of the following:
- well yield;
- effective porosity;
- thickness of the aquifers saturated zone, which were taken from the construction profiles of the wells, as well as from the geology of the lithostratigraphic units.

The capture zones were calculated using the average effective porosity of the respective aquifers (Tab. 1), and the flow and saturated thickness were obtained from the construction profiles of wells.

Sewer network installation year

The sewer mains in the capture zones of the selected wells were obtained through interviews with the service operators in each city and presented different installation dates, starting in 1962 (Andradina, Flórida Paulista, Inúbia Paulista) until 2000 (Jales and São José do Rio Preto). The other cities had their sewer network installed after 2001; the most recent being Clementina, Nova Independência, and Murutinha do Sul.

Aerial photo analysis and images

The images were manipulated using Google Earth Pro and ArcMap 10.4.1, whose features allowed the integration and comparison between:
- 1:25,000 panchromatic aerial photographs, from an August 1962 aerial photographic survey by the São Paulo State Secretariat of Agriculture (São Paulo 1962), which were kindly provided by the Aerial Photography and Remote Sensing Laboratory (LASERE) of Universidade de São Paulo;
- satellite images from the 2000s onwards from the Landsat program (Land Remote Sensing Satellite), owned by the US government, and extracted from Google Earth Pro.

The comparison between the images determined the evolution and patterns of occupation throughout the extension of the capture zone (Fig. 4). It was possible to establish the variation in occupation, with special attention to the:
- type of land occupation;
- urban occupation density (houses/area of the capture zone), through the counting of roofs;
- presence and assessment of green zones (drainages, rivers, native vegetation).

RESULTS

The analyzed wells are in the urban area of the cities indicated in Table 3. The results revealed three types of behaviors

Figure 4. (A) Scheme for assessing the evolution of capture zone occupation patterns considered the type of land occupation, density of buildings, and recognition of natural zones, based on a comparison of aerial photographs from 1962. The blue color near the surface represents water without the presence of nitrate. (B) satellite images from the 2000s onward. The brown color near the surface indicates the presence of nitrate.
overtime (Tab. 3): three wells with a tendency toward decreased concentration (Cajobi, Murutinga do Sul, and Pompéia); a well showing stable behavior (Inúbia Paulista); and six wells with a tendency toward increased concentration (Andradina, Clementina, Florida Paulista, Jales, Nova Independência, and São José do Rio Preto). The average radius values of the capture zones were 532 m, with highs and lows of 799 (Andradina) and 314 m (Pompéia), respectively (Tab. 4).

Urban occupation (Tab. 5) was estimated by counting buildings (houses or service facilities) located in the capture zone of each well, constituting a relationship between the number of houses or building/km² (Fig. 5). In all the studied cities, the urban density in the capture zone area increased between 132% (Inúbia Paulista) and 730% (São José do Rio Preto).

The highest values of urban density in 1962 were found in places whose age of occupation was older, that is, in the portions close to each city’s center. By contrast, the wells installed in these places showed the smallest increases in urbanization because they were already substantially occupied.

The 2016 images show that the predominant occupation was urban, except in Cajobi and Nova Independência, where there are significant green areas. Urban areas predominated in a large part of the capture zone, with urban occupation rates of 30% in Cajobi and 45% in Nova Independência. The locations of São José do Rio Preto, Jales, and Florida Paulista had 100% urban occupation.

Pearson’s method determined the correlations among the 67 physical, chemical, and bacteriological parameters, and nitrate, seeking to better understand the nitrate origin (Tab. 6). However, although there were some significant direct and inverse correlations with other chemical parameters, few conclusions could be drawn. In Jales, there was a negative correlation ($\rho = -0.7$) between nitrate and hexavalent chromium, as this contaminant has a natural origin. As nitrate is a contaminant of anthropic origin, its concentration is higher in the aquifer’s most superficial portions. On the other hand, the hexavalent chromium is found at aquifer greater depths, denoting a longer water-transit time (Bertolo et al. 2011).

### Table 3. Average nitrate concentration for the first six years of well operation and the 2009–2015 period for the ten selected wells.

| Town                  | CETESB well code | First year of operation | Average nitrate concentrations in the first six years of operation (mg/L N-NO₃) | Average nitrate Concentrations from 2009 to 2015 (mg/L N-NO₃) | Variation of nitrate concentrations | Variation |
|-----------------------|------------------|-------------------------|---------------------------------------------------------------------------------|-----------------------------------------------------------------|------------------------------------|-----------|
| Andradina             | BA0006P          | 1993                    | 8.36                                                                            | 16.20                                                          | +94% Increase                      | Increase  |
| Cajobi                | BA0023P          | 1994                    | 6.32                                                                            | 3.28                                                           | -48% Decrease                      | Decrease  |
| Clementina            | BA0028P          | 1993                    | 3.71                                                                            | 6.58                                                           | +77% Increase                      | Increase  |
| Florida Paulista      | BA0040P          | 1993                    | 1.48                                                                            | 6.31                                                           | +326% Increase                     | Increase  |
| Inúbia Paulista       | BA0052P          | 1992                    | 8.08                                                                            | 7.57                                                           | -6% Stable                          | Stable    |
| Jales                 | BA0059P          | 1993                    | 5.59                                                                            | 7.57                                                           | +35% Increase                      | Increase  |
| Murutinga do Sul      | BA0076P          | 1993                    | 8.30                                                                            | 5.39                                                           | -35% Decrease                      | Decrease  |
| Nova Independência    | BA0079P          | 1993                    | 2.45                                                                            | 5.08                                                           | +107% Increase                     | Increase  |
| Pompéia               | BA0203P          | 1998                    | 7.44                                                                            | 3.80                                                           | -49% Decrease                      | Decrease  |
| São José do Rio Preto | BA0127P          | 1993                    | 2.17                                                                            | 8.79                                                           | +305% Increase                     | Increase  |

### Table 4. Identification of parameters for calculating the capture zones of the selected wells.

| Town                  | Aquifer system | UTM N | UTM E | Well depth (m.b.g.l) | Screen level depth (m.b.g.l) | Static level depth (m.b.g.l) | CFR (50 years) (m) | Q (m³/d) | b (m) | K (m/d) | i | $n_e$ (%) | Recharge (mm/year) |
|-----------------------|----------------|-------|-------|---------------------|-----------------------------|-----------------------------|-------------------|----------|-------|--------|---|-----------|-------------------|
| Andradina             | Adamantina     | 7687350 | 459600 | 105                 | 54–102                      | 26                          | 799               | 1,032    | 94    | 1.5    | 0.03 | 0.1       | 250                |
| Cajobi                | Adamantina     | 7693900 | 729750 | 112                 | 5–112                       | 63                          | 608               | 312      | 49    | 1.5    | 0.03 | 0.1       | 250                |
| Clementina            | Adamantina     | 7615650 | 557350 | 94.5                | 22–84                       | 33                          | 405               | 144      | 51    | 1.5    | 0.03 | 0.1       | 250                |
| Florida Paulista      | Adamantina     | 7609600 | 482350 | 200                 | 81–195                      | 14                          | 450               | 384      | 110   | 1.5    | 0.03 | 0.1       | 250                |
| Inúbia Paulista       | Adamantina     | 7592750 | 504050 | 220                 | 70–204                      | 42                          | 394               | 432      | 162   | 1.5    | 0.03 | 0.1       | 250                |
| Jales                 | Adamantina     | 7759100 | 547675 | 145                 | 36–142                      | 19                          | 593               | 744      | 123   | 1.5    | 0.03 | 0.1       | 250                |
| Murutinga do Sul      | Adamantina     | 7678650 | 471730 | 140                 | 35–130                      | 15                          | 365               | 264      | 115   | 1.5    | 0.03 | 0.1       | 250                |
| Nova Independência    | Santo Anastácio | 7665750 | 449100 | 91                  | 32–86                       | 7                           | 767               | 960      | 79    | 2      | 0.02 | 0.1       | 250                |
| Pompéia               | Marília         | 7555540 | 584827 | 259                 | 52–233                      | 134                         | 314               | 168      | 99    | 1      | 0.04 | 0.1       | 250                |
| São José do Rio Preto | Adamantina     | 7695940 | 668800 | 68                  | 28–68                       | 22                          | 628               | 312      | 46    | 1.5    | 0.03 | 0.1       | 250                |

Q: flow rate (considering 24-hour pumping); b: saturated thickness; K: hydraulic conductivity; i: hydraulic gradient; $n_e$: effective porosity; CFR: calculated fixed radius; UTM: Universal Transverse Mercator Coordinate System.
case of a positive relation between N-Kjeldahl and TDS and chloride in several wells, these results were expected due to the common origin of these compounds.

**DISCUSSION**

This research found that the sewer network (Tab. 5) substantially influences nitrate concentrations; however, not homogeneously. In older occupation areas, where the sewer mains were installed until 2001, nitrate concentrations increased between 1994 and 2016, except in Cajobi, indicating leaks from the sewer network. Sewer mains were constructed in the ceramic material before 1990, which breaks down with age due to the lack of maintenance.

As to Clementina and Nova Independência, whose sewer networks were installed in 2013 and 2011, respectively, there

**Table 5. Urban occupation in capture zones of the well.**

| Town              | Number of buildings (1962) | Number of buildings (2016) | Area (km²) | Urban density-1962 (buildings/km²) | Urban density -2016 (buildings/km²) | Evolution of urban density (%) | Total urban occupation within capture zone in 2016 (%) | Sewer network installation year |
|-------------------|---------------------------|---------------------------|------------|-----------------------------------|------------------------------------|--------------------------------|------------------------------------------------------|-------------------------------|
| Andradina         | 1.321                     | 1.902                     | 2.00       | 660                               | 950                                | +144                           | 85                                                   | < 1962                        |
| Cajobi            | 53                        | 135                       | 1.16       | 46                                | 116                                | +255                           | 30                                                   | 2001                          |
| Clementina        | 125                       | 304                       | 0.51       | 243                               | 590                                | +243                           | 60                                                   | 2013                          |
| Flórida Paulista  | 262                       | 543                       | 0.63       | 411                               | 853                                | +207                           | 100                                                  | < 1962                        |
| Inúbia Paulista   | 337                       | 446                       | 0.48       | 693                               | 917                                | +132                           | 90                                                   | < 1962                        |
| Jales             | 562                       | 817                       | 1.10       | 509                               | 740                                | +145                           | 100                                                  | < 2000                        |
| Murutungu do Sul  | 156                       | 258                       | 0.41       | 373                               | 616                                | +165                           | 50                                                   | 2010                          |
| Nova Independência| 132                       | 488                       | 1.84       | 71                                | 264                                | +264                           | 45                                                   | 2011                          |
| Pompeia           | 63                        | 273                       | 0.31       | 204                               | 882                                | +882                           | 70                                                   | 2005                          |
| São José do Rio Preto | 243                    | 1.775                     | 1.23       | 196                               | 1.435                              | +1.435                         | 100                                                  | < 1995                        |

**Figure 5. Evolution of capture zone occupation patterns.**
was an increase in nitrate due to a large number of buildings (with cesspools and septic tanks) built before the sewage collection network installation. In the future, the nitrate concentration will decrease due to the installation of those new sewer mains and the abandonment of pits.

All cities that tended to show increases in nitrate had direct associations with the number of buildings present within the capture zone in 2016, with greater than or equal to 60% of urban occupation in the capture zone (Fig. 6). If the well location is closer to the city center, that is, in older places, the occupation of the capture zone tends to be more significant.

The well located in Inúbia Paulista center showed stability in nitrate concentrations (6% variation). Since 1962, the site has had a high urban density in the capture zone (693 houses/km² in 1962), reaching 917 houses/km² in 2016. The well was installed in 1992 and had a concentration of 6.34 mg/L N-NO₃ and in 2016, 7.00 mg/L N-NO₃ was measured.

Finally, the wells in the cities of Cajobi, Pompéia, and Murutinga do Sul showed a decrease in nitrate concentrations, although these locations presented an increase in the urban occupation density. In this group, the installation of the sewer mains occurred after 2001, and there was time for the contamination to be reduced, showing that modern

Table 6. Parameters including the main positive and negative values, analyzed according to Pearson’s correlations.

| Nitrate variation of time | Town            | Correlation                      |
|--------------------------|-----------------|----------------------------------|
|                          |                 | Positive                        | Negative                     |
| Increase                 | Andradina       | Total dissolved solids: ρ = 1.0  | Lithium: ρ = -0.9             |
|                          |                 | Total resistivity: ρ = 0.8       | Titanium: ρ = -0.5            |
|                          | Clementina      | Air temperature: ρ = 0.7         | Lithium: ρ = -0.6             |
|                          |                 | Kjeldahl nitrogen: ρ = 0.5       | Uranium: ρ = -0.6              |
|                          | Flórida Paulista| Kjeldahl nitrogen: ρ = 0.5       | Silver: ρ = -0.9               |
|                          |                 | Total dissolved solids: ρ = 0.7   | Bicarbonate alkalinity: ρ = -0.8|
|                          |                 |                                  | Hexavalent chromium: ρ = -0.7  |
| Decrease                 | Jales           | Antimony: ρ = 0.8                |                                  |
|                          |                 |                                  | Silver: ρ = -0.7               |
|                          |                 |                                  | Tin: ρ = -0.7                  |
|                          | Nova Independência| pH: ρ = 0.7                  |                                  |
|                          |                 | Kjeldahl nitrogen: ρ = 0.7       |                                  |
|                          | São José do Rio Preto | Chloride: ρ = 0.7 | Sulfate: ρ = -0.8 |
|                          |                 |                                  |                                  |
| Stable                   | Inúbia Paulista | Total solids: ρ = 0.7            | Lithium: ρ = -0.7              |
|                          |                 |                                  | Titanium: ρ = -0.8             |

Figure 6. Variation of nitrate concentrations according to the evolution of occupation in each analyzed well. The dashed lines in the red color indicate the trends of nitrate concentrations: increase or reduction of concentrations.
and efficient networks are essential to minimize the aquifer contamination.

CONCLUSION

The method applied to the BAS showed a correlation between the urban land use in the well vicinity (capture zone) and changes in the concentration of nitrate in groundwater between 1994 and 2016. In areas with sewer mains built before 2001 and with an urban density greater than 60% of urban occupation in the capture zone, there might have been an increase of at least 35% in the nitrate concentration.

Although the implementation of a public sewage system is the most efficient way to reduce contamination by domestic effluents, the lack of maintenance, mostly of old ceramic networks, has caused leaks that deteriorate the BAS waters.

This study demonstrates that the method established a causal relationship between the history of urban occupation and the nitrate concentration in monitoring wells in an unconfined and sedimentary aquifer, such as the BAS. Thus, it would be desirable to extend the application to all the other wells in the state monitoring network. This method could also be applied to select new locations for future wells that will integrate this network.

The results of such a method could be used by health surveillance agencies, which should pay attention to public-supply wells in areas where urban density is more significant than 60% of urban occupation in the capture zone and sewer networks were built before the 2000s.

Finally, any urban expansion should be preceded with the installation of a sewer network, using materials that are more resistant to time, such as PVC, followed by an efficient and permanent maintenance program, as can be seen in the cities of Murutinga do Sul and Pompeia.

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