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Rojas Fabro, AY, Pacheco Avila, JG, Esteller Alberich, MV et al. (2 more authors) (2015) Spatial distribution of nitrate health risk associated with groundwater use as drinking water in Merida, Mexico. *Applied Geography*, 65. 49 - 57. ISSN 1873-7730

<https://doi.org/10.1016/j.apgeog.2015.10.004>

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Spatial distribution of nitrate health risk associated with groundwater use as drinking water in Merida, Mexico

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Abstract

Water containing nitrate levels above 45 mg/l is not recommended for human consumption and its prolonged intake is associated with various health conditions. In Merida city, Mexico, the only source for water supply is a karstic aquifer, but the absence of sewerage and drainage networks makes it highly vulnerable to anthropogenic contamination. In this work, the concentration and spatial distribution of nitrate in the Merida's karstic aquifer were assessed by statistical and geostatistical techniques. The sources of nitrate contamination were tracked by making statistical correlations between nitrate concentrations and key ions; the potential risk to human health was also estimated by using the Hazard Index (HI). A total of 177 groundwater samples were collected from the four water supply systems serving Merida, during 2012 and 2013. Nitrate concentrations from collected samples varied between 15.51 and 70.61 mg/l, with maximum and minimum concentrations per sampling point ranging from 47.47 to 70.61 mg/l and from 15.51 to 17.32 mg/l, respectively. Significant positive correlations ($P < 0.05$) between nitrates and chlorides, sulphates and potassium were found, which may indicate potential contamination from domestic wastewater and agricultural activities. The spatial distribution of nitrate concentrations in the aquifer revealed an increase in nitrates following a trajectory South – North West, towards central and northwestern zones within Merida Metropolitan Area. From the health risk analysis, it was found that infants exposed at current nitrate levels are at a higher risk ($HI_{MAX} = 1.40$) than adults ($HR < 1.0$) and therefore, there is a clear need for implementing effective strategies to protect groundwater quality and to better manage and control nitrate pollution sources.

Key words: Nitrates, groundwater, drinking water, karstic aquifer, spatial distribution, health risks.

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<http://dx.doi.org/10.1016/j.apgeog.2015.10.0041>

1. Introduction

In different regions around the world, environmental or quality-related water shortage is associated to poor water quality caused mainly by rapid economic development and urbanization, which in return affects the possibility to achieve sustainable socio-economic development, particularly in emerging economies and developing countries. In Latin America for instance, 70% of the water supplied to urban settlements returns to the environment without treatment, which affects not only the quality of water in rivers and coastal areas, but also increases public health risks to the resident population (mainly to the poor) and causes billions to be lost in economic activities including tourism and real state revenue (World Bank, 2012). Therefore, there is a clear need for developing science-based strategies integrating the water cycle with sustainable socio-economic development for integrated water resource management and governance.

Mexico has a current population of about 125 million people and it has been predicted that by 2030, communities residing in 12 out of their 13 hydrological-administrative regions (HARs) will be affected by water shortage. (Semarnat and INE, 2006). The Yucatan HAR, comprising the Mexican states of Campeche, Quintana Roo and Yucatan, has a higher availability of water resources (7,603 m³/person/yr) when compared with the national mean (4,210 m³/person/year) (Semarnat, 2008); however, their entire population (aprox. 3.1 million) mainly relies on groundwater as the sole source for water supply (i.e., domestic, industrial and agricultural uses). This aquifer is a coastal and karstic aquifer and hence, it is highly vulnerable to natural and anthropogenic contamination (Gonzalez-Herrera et al., 2014).

In the City of Merida, the capital of the Mexican state of Yucatan, groundwater is extracted from deep wells using pumps installed at 20 to 30m under the water table and conducted to the local water treatment works for disinfection with chlorine gas, as the only treatment process before distribution to the consumers.

The City of Merida lacks of integrated sewerage and drainage networks and wastewater management is mainly provided in-situ or in decentralised wastewater treatment systems, but regardless the alternative, the final disposal is always via a direct or indirect discharge into the aquifer. Urban wastewaters are commonly disposed through privately-owned individual septic tanks followed by infiltration wells causing a scattered contamination of the shallower groundwaters (Graniel et al., 1999); some neighborhoods with large, community septic tanks have added small sewage treatment units to polish the quality of their effluent before discharge into the aquifer (i.e., activated sludge with nitrification and disinfection). There are very few wastewater treatment systems in Merida (i.e., 24 at the most) serving new housing developments mainly located outside the outer ring road of the city, but the majority of them are currently underload and do not make a significant difference considering the fact that there are more than 100 neighborhoods and enclosed urban developments (Seduma, 2010; PIDEM, 2012).

Nitrate is an important parameter in assessing groundwater pollution from diffuse sources and has been used as a surrogate indicator to determine groundwater vulnerability to contamination (Evans and Maidment,

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1995). Nitrates are used in the formulation of industrial fertilizers and can also derive from the oxidation of ammonium and other nitrogen compounds found in wastewaters. They have adverse effects on human health, mainly causing methaemoglobinaemia in infants but also in pregnant women and the elderly (Sajil et al., 2014) and hence, their concentration is limited in drinking water. Besides methaemoglobinaemia, it has been mentioned that the consumption of water contaminated with nitrate may cause gastric cancer, multiple sclerosis, Non-Hodgkin lymphoma and thyroid gland hypertrophy, among other health conditions (Suthar et al., 2009). The World Health Organization (WHO) has set a guideline value for nitrate in drinking water of 50 mg/l as nitrate ion, which is based on epidemiological evidence for methaemoglobinaemia in infants resulting from short-term exposure and aiming at protecting bottle-fed infants and other equally vulnerable population groups (WHO, 2011). In Mexico, the Secretary of Health has issued the corresponding Official Mexican Standard (OMS) limiting the presence of nitrates in drinking water to a maximum permitted value of 10 mg/l as nitrogen-nitrate (N-NO₃⁻) or 45 mg/l as nitrate ion (NO₃⁻) (Secretaría de Salud, 2000).

Nitrates have been previously monitored in the karstic aquifer of the Mexican State of Yucatan. During the period 1983-1986, water samples from eight shallow wells in a rural area of the northern Yucatan Peninsula were collected and processed for nitrate analysis; 56% of the 380 collected samples reported nitrate concentrations above the current maximum permitted value (>45 mg/l), mainly in highly populated areas (Pacheco and Cabrera, 1997). In southern Yucatan, a typical agricultural area, 12 wells used for water supply were also monitored from the period April 1992 to March 1993 (Pacheco et al., 2001). In that study, nitrate concentration ranged from 7 to 156 mg/l and in three particular wells, nitrates concentration was also higher than 45 mg/l, which was attributed to intensive use of inorganic nitrogen fertilizers. Such findings are in line with previous studies reporting that the presence of nitrates in groundwater can be caused by several factors including infiltration of domestic wastewater, the use of chemicals for gardening and the practice of periurban agriculture (Lawrence et al., 2000; Rao, 2006; Obeidat et al., 2007; Martínez et al., 2014). In the Mexican State of Yucatan, several authors studying groundwater quality have also confirmed that nitrate concentrations are caused by similar factors (Gonzalez-Herrera et al., 2014; Graniel et al., 1999; Pacheco and Cabrera, 2013).

Despite previous works reporting nitrate concentrations in the karstic Yucatan aquifer, such information has not been analysed or reported by using Geographic Information Systems (GIS). Groundwater quality studies through GIS constitutes an important tool for data analysis and to effectively communicate research findings not only among those who have the duty of managing water resources and to protect water supply sources, but also to the general public and groundwater users (Hoover et al., 2014).

Considering that the presence of nitrates in water supply sources poses an intrinsic public health risk and that previous research works have identified high concentrations of nitrates in the karst aquifer of Yucatan, this work will be aimed at determining the spatial distribution of the potential human health hazard index

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associated to the consumption of drinking water contaminated with nitrates in the Mexican State of Yucatan and in particular to those residing in the City of Merida. Although this research work is based on existing and well-known methodologies, its novelty comes from coupling environmental groundwater quality data with the assessment of quantitative chemical risks in a vulnerable aquifer in Latin America. It is expected that the outcomes of this work could help to develop effective strategies for integrated water resource management, particularly by providing scientific evidence for decision and management of groundwater sources used for drinking water supply.

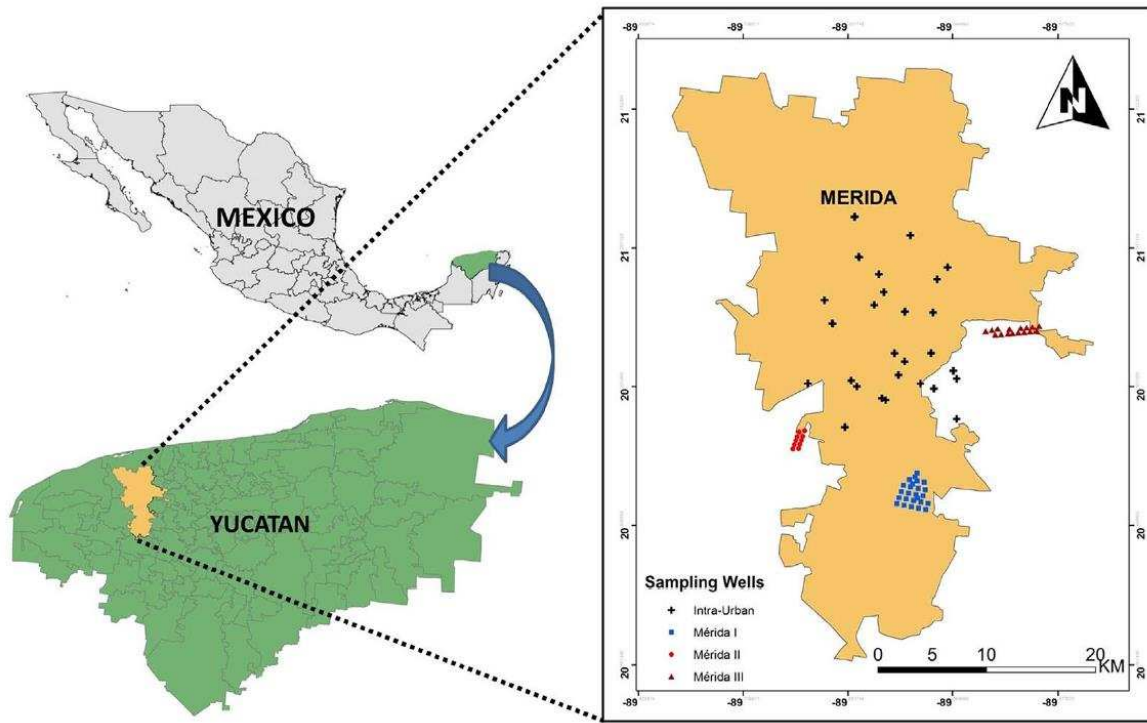


Fig. 1. Map of the study area and location of drinking water supply wells.

2. Materials and methods

2.1 Study Area

The State of Yucatan is located on the Southeast of the Mexican Republic, in the North Central part of the Yucatan Peninsula. It is limited by the parallels $19^{\circ}31'46''$ and $21^{\circ}37'21''$ N and the meridians $87^{\circ}22'08''$ y $90^{\circ}24'22''$ W, with an extension of $43,577 \text{ km}^2$ (INEGI, 2002). The capital city, Merida, is located to the northwest of the Yucatan Peninsula and is 35km far from the coast of the Gulf of Mexico (Fig. 1). Merida's aquifer is highly vulnerable to pollution sources due to its typical hydrological characteristics including: a) free aquifer with a water table depth between 8 and 9m; b) coastal aquifer, with a distance of about 36km

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from the coast to water-supply wells; and c) a karstic underground with abundant cracks, crevices, hollows, caves and sinkholes (Pérez et al., 2008; Herrera, 2012; Sosa, 2014).

The population in the City of Merida has increased from 556,819 inhabitants in 1990 to 777,615 in 2010, following a linear population growth during this period ($r^2=0.9957$; population growth rate of 11,270 hab./year). The increase in population has an impact on the water demand, considering that the average daily water consumption per capita in the City of Merida is 285 liters. For its water supply, the City of Merida has three main water treatment works (Merida I, II and III) and 37 intra-urban wells (see Table 1). These 37 wells are part of a decentralized water supply network (Back-up water supply well system) aimed at distributing drinking water to neighborhoods and suburbs located far from the main water treatment works, where water pressure is too low. The entire water supply system is managed by the Drinking Water and Sewerage Board of Yucatan (JAPAY), which belongs to the Yucatan State Government. In addition, there are 112 privately owned water supply systems serving new housing developments located outside of the outer ring road in Merida (PIDEM, 2012).

Table 1
Characteristics of the water supply system serving the city of Merida.

Water treatment works	Location	Area (Ha)	Number of wells, flow rate (l/s)	Serving area in Merida
Merida I	Southeast Merida, Cuxtal Reserve	625	24 wells, 1200 l/s	Center and South
Merida II	Southwest Merida	72	10 wells, 500 l/s	South and West
Merida III	East Merida	316	4 out of 17 wells, 700 l/s.	North and East
Backup water supply well system (intra-urban wells)	Distributed in the central part of Merida	--	37, Variable flow rate	Center
Independent water supply systems	Recent housing developments (outside of city's outer ring road)	--	112, Variable flow rate	Outside of the city's outer ring road

Source: Modified from PIDEM (2012).

The main zone for groundwater extraction is in the Merida I water treatment works, with a total production rate of 42.3 hm³ per year, which represents 48% of the total groundwater extraction to the City of Merida (Gobierno del Estado de Yucatán, 2011). Merida I has been in operation since 1966 (Irigoyen, 1970). The chemical characteristics of the groundwater extracted from wells within the metropolitan area of the City of Merida have been reported as suitable for water supply, according to the maximum accepted values set by the Official Mexican Standards for drinking water (Secretaría de Salud, 2000), which includes parameter such as total hardness, sodium, chlorides, sulphates, pH and total dissolved solids; although nitrates values have reached a maximum value of 70.61 mg/l, while above the acceptable limit of 45 mg/l. The groundwater also contains carbonate hardness mainly related to calcium bicarbonates or to a mix between calcium and magnesium bicarbonates, with no evidence of salinity due to over exploitation or seawater intrusion (Rojas et al., 2014).

2.2 Groundwater sampling and chemical analysis

Two water quality surveys were conducted, one in 2012 and the other in 2013, which coincided with periods of low water table in the aquifer. Sampling points corresponded to wells located in the three main water

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treatment works (i.e., Merida I, Merida II and Merida III systems) and in the back-up water supply well system (i.e., 177 sampling points in total), see Figure 1 and Table 2. All the selected wells were geographically located using a GPS device (GPSMAP 78S, GARMIN). Groundwater samples were collected at the inlet point of the water treatment works and always before entering the chlorinating system, by keeping the corresponding pump working on its own and by letting the water flow until a representative sample of the aquifer was collected. Water samples for nitrate analysis were preserved on site by adding concentrated sulfuric acid until obtaining a pH lower than 2, and stored at 4°C until the corresponding analysis was conducted. In the laboratory, nitrates and sulfates were determined by using spectrophotometric techniques; bicarbonate and chloride by titration; and calcium, magnesium potassium and sodium by atomic absorption spectrometry techniques. All the analytical methods followed the methodologies described in the Standard Methods for the Examination of Water and Wastewater (APHA et al., 2005).

Table 2
Nitrate concentration in water supply wells: descriptive statistical analysis.

System	Number of samples	Mean, mg/l	Median	Standard deviation	Minimum, mg/l	Maximum, mg/l
Merida I	50	18.97	18.63	1.11	17.32	22.86
Merida II	19	18.92	19.54	2.83	15.59	26.09
Merida III	36	21.57	19.02	7.59	16.04	47.71
Intra-urban	72	36.71	33.47	14.13	15.51	70.61
All systems	177	26.71	20.38	12.77	15.51	70.61

2.3 Statistical analyses

Non-parametric methods were used to prove the hypotheses of evenness among temporal-spatial evaluation for water supply systems given that raw data did not followed a normal distribution. The Kolmogorov-Smirnov test was applied to prove the temporal evenness hypothesis. Based on this result, the nitrate concentration analysis was performed using a non-parametric Kruskal-Wallis Analysis of Variance (ANOVA) for the four water supply systems. The null hypothesis of evenness was rejected if the P-value obtained was lower than 0.05, concluding that there was a statistically significant difference in the median nitrate in each of the systems with a 95.0% confidence level ($\alpha=0.05$). A box and whiskers plot was produced in order to show any statistically significant difference between median values (Miller and Miller, 1988).

2.4 Geostatistical analysis

Geostatistics comprises a series of mathematical and statistical tools to analyze and predict the values of a variable distributed in a continuous form through time or space. This prediction could replace or compensate for the insufficient information from maps (Delgado et al., 2010).

In general, the specific variable is measured through data points, which do not completely cover the study area and an estimate of the unmeasured sites is required. The creation of a continuous surface can be done using various interpolation methodologies, such as deterministic and stochastic interpolation methods. Therefore, it is expected that the values of the studied variables from nearby sites will be more similar than

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the ones from farther sites. In other words, there is a degree of spatial dependency, or self-correlation, and a spatial continuity among neighboring sites (Isaaks and Srivastava, 1989; Burrough, 2001).

An experimental semi-variogram describes the relation between the study variable's variance and the distance between sampling and predicted points (Hernández-Stefanoni, 2006):

The semi-variance's (Eq. 1) according to (Burrough, 2001) is:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \{Z(x_i) - Z(x_i + h)\}^2 \quad \text{Eq. 1}$$

Where $\gamma(h)$ is the semi-variance of the sampling sites separated by a distance h ; $Z(x_i)$ are the sampling values at points x_i with data in x_i and x_i+h ; $N(h)$ is the number of paired data separated by an h distance. The inverse distance method of interpolation combines the notion of vicinity with steady change and integrates the mathematical model (semivariogram), which describes the spatial variation. Using the estimated information (GS+2006), the variable distribution maps were created with Surfer software (Surfer, 2002).

2.5 Nitrate relation with selected hydrochemical parameters

Correlation coefficients between nitrate concentrations and chlorides, potassium and sulphates were calculated to determine the potential pollution sources and factors controlling the presence of high nitrate concentrations in the Merida's aquifer (Sajil, 2014; Rao, 2006; Reddy, 2014). The analytical precision of chemical analyses was verified by conducting a ionic balance in meq/l (Deutsch, 1997); the resulting observed error was lower than 7% for all processed samples.

2.6 Nitrate health hazard assessment in drinking water supply sources

The health hazard assessment consisted of determining the tolerability of the risk faced by the population exposed to nitrate content from groundwater used in supply systems. Hazard characterization consisted of determining the Hazard Index (HI), which is an indicator of the existing risks from consuming a given substance. The individual risk of developing a negative effect becomes higher along the values of HI. This relation is named HI by the Environment Protection Agency (USEPA) (Díaz-Barriga, 1999). The HI is determined based on the Ingested Dose (ID) and the Reference Dose (RfD) (Eq. 2). The latter is defined as the concentration of a substance with no toxic effects on the individual over a determined period of time.

$$\text{HI (Hazard_Index)} = \frac{\text{Ingested Dose (mg/kg/d)}}{\text{Reference Dose (mg/kg/d)}} \quad \text{Eq. 2}$$

The Ingested Dose (ID) of a substance is calculated with Eq. 3 (USEPA, 2001):

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$$ID = \frac{C \times I \times EF \times ED}{BW \times AT} \quad \text{Eq. 3}$$

Where C is the average concentration of a hazardous substance in water (mg/l); I is the water volume daily intake (l/day); EF is the exposure frequency (days/year); ED is the exposure duration (years); BW is the body weight of the exposed individual (kg); and AT is the average time of exposure (ED * 365 days/year).

To apply Equation 3, the exposure duration (ED) was set to be the total time during which the water supply systems have been operating with an exposure frequency of 365 days. As a result, the quotient was equal to one when divided by the average time (Eq. 4), that simplifies Eq. 3.

$$ID = \frac{C \times I}{BW} \quad \text{Eq. 4}$$

Water intake (I) values for adults and bottle-fed infants were assumed to be 2 and 0.64 l, respectively; while body weights (BW) were assumed to be 70 and 4 kg, respectively. ID values were calculated accordingly. In addition, a Reference Dose (RfD) of 1.6 mg/kg/d N-NO₃⁻ equivalent to 7.088 mg/kg/d of NO₃⁻ was used. If the quotient value equals or exceeds the unit, a hazard level of non-carcinogenic toxic effect exists and must be addressed immediately (USEPA, 2013).

3. Results and discussion

The number of samples of groundwater collected from the four water supply systems (Merida I, Merida II, Merida III and Intra-urban) during the two periods (2012 and 2013) were 177 and the resulting descriptive statistical analysis for the corresponding nitrate concentrations are presented in Table 2.

3.1 Nitrate levels in water wells: statistical analysis

The mean, median and standard deviation for nitrates in groundwater samples collected from all sampling points during the two-year period were 26.71, 20.38 and 12.77 mg/l, respectively. The nitrate concentration for all sampling points ranged between 15.51 and 70.61 mg/l. It can be observed from Table 2 that the highest mean and median values were found in the intra-urban wells. Concerning the standard deviation, the most even values occurred in Merida I and II with 1.11 and 2.83 values, respectively. However, processed data from Merida III and the intra-urban wells reported higher variability with corresponding figures of 7.59 and 14.13, respectively. Minimum and maximum values for all the samples (15.51 and 70.61 mg/l NO₃⁻) coincided with figures found in the intra-urban wells, justifying their high variability.

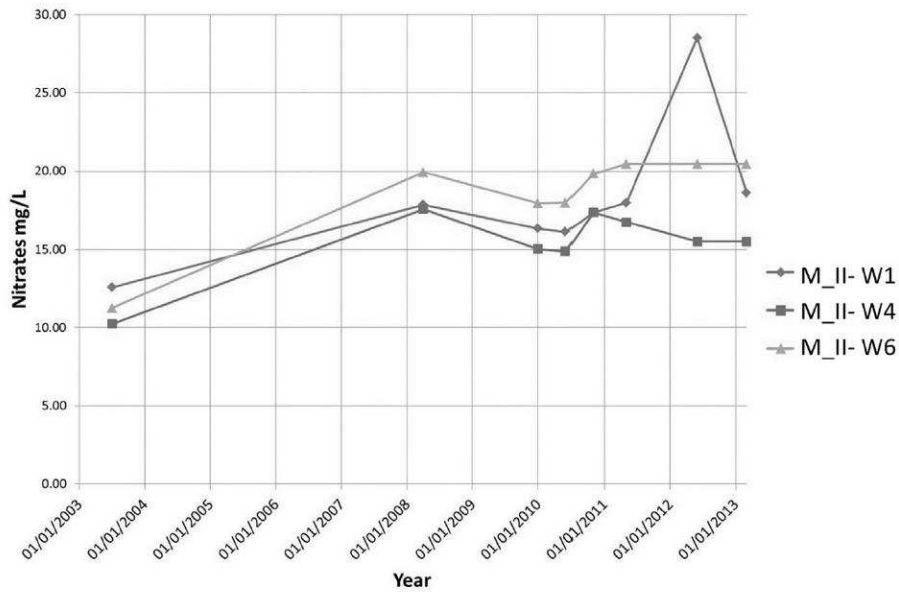
These concentrations indicate the presence of nitrates contamination levels similar to figures reported internationally and in Mexican States (Schmoll, 2006). Nitrate concentrations in non-polluted surface and

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ground- waters vary from 0 to 18 mg/l. In the Yucatan Peninsula, the estimated background value is 13.6 mg/l as mentioned by Torres (2010) and cited by Gonzalez-Herrera et al., (2014).

During the period from 1991 to 1993, a study conducted by the British Geological Survey, the School of Engineering at the University of Yucatan and the National Commission for Water reported that nitrate concentrations in two of the four water supply systems reported in this work (Merida I and II) were lower than 22.15 mg/l. Similarly, shallow wells had nitrate concentrations between 44.3 and 132.9 mg/l in the central part of the City of Merida, corresponding to the most populated area, and values from 17.72 to 44.3 mg/l towards the city's outer ring road (Trafford et al., 1994). In 2003 after hurricane Isidore, nitrate concentrations in supply wells were measured and displayed a concentration range between 10 and 31 mg/l with a mean value of 16.82 mg/l (Pacheco and Cabrera, 2013). Those concentrations found after hurricane Isidore were potentially caused by the recharge of the acquired followed by the corresponding dilution effect due to heavy rainfall (> 353.1 mm of rainfall in 36 hours; GERPY, Personal communication). That masked the potential effect of population growth, discharges from septic tank, nitrogen fertilizer use, and swine and poultry farm discharges.



Data 2003 from Pacheco, A.J. (2004)
 Data 2008 from Pacheco, A.J. (2008)
 Data 2009 to 2011 from Pacheco, A.J. (2013)

Fig. 2. Temporary evolution of nitrates in water well supply.

In order to analyze the temporal behavior of nitrate concentrations (i.e., short-term effect), additional data was gathered from previous studies to represent the period 2003 - 2011 (Pacheco, 2004; 2008; 2013). Nitrates time series shown an increase in the average nitrate concentration for wells 1, 4 and 6 in the Merida II water treatment works which shifted from 10.23 mg/l in 2003 to 19.84 mg/l in 2012-2013 (Fig. 2). In a previous study, Trafford et al., (1994) reported a concentration of nitrogen of 4mg/l in Merida II that clearly

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demonstrates a steady accumulation of nitrate in the Merida’s aquifer at an average rate of 1.6 mg/l/year and supports the hypothesis that anthropogenic activities are consistently impacting groundwater quality in the region. The increasing trend of nitrate concentration in groundwater is also common in other countries like India, Jordan and Palestine, where sanitation and wastewater treatment coverage is poor (Rao, 2006; Obeidat et al., 2007; Anayah and Almasri, 2009).

The frequency distribution of nitrate concentration is presented in Fig. 3. It was found that 56% of the resulting data had values below 22.5 mg/l, 33% were between 22.5 and 45 mg/l and 11% of the samples exceeded the maximum acceptable limit of 45 mg/l. Values from the middle (i.e., 22.5 - 45 mg/l) and high interval (>45mg/l) could indicate a predominant influence of human activity in the region affecting 44% of the tested wells. Regarding the compliance with the OMS (< 45mg/l), 18 intra-urban wells and two wells from Merida III did not meet the water quality criteria for drinking water.

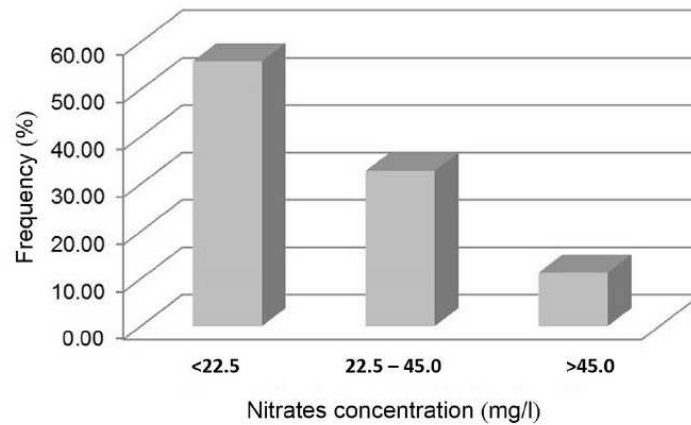


Fig. 3. Frequency distribution for nitrate concentrations during the sampling years 2012 and 2013.

Nitrate concentrations for the two sampling years and for the different supply systems were analyzed with non-parametric techniques because the raw data did not follow a normal distribution. The Kolmogorov-Smirnov test was used to compare the distributions of nitrate concentrations from the different sampling years. The results displayed a P-value of 0.561911, meaning no statistically significant differences between the two distributions with a 5% significance level (Fig. 4).

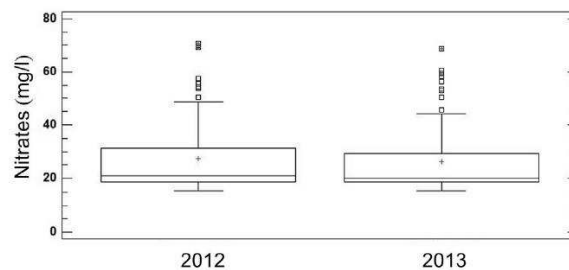


Fig. 4. Box and whiskers diagram for nitrate concentrations during the sampling years 2012 and 2013.

However, the ANOVA analysis showed that there is a significant difference at a 5% significance level between the nitrate concentrations from the water treatment works serving the City of Merida. It was observed that some wells in the intra-urban back-up system and in Merida III reported the highest nitrate concentrations (Fig. 5). These higher concentrations are believed to come from the use of nitrogen fertilizers in agricultural activities, as well as from the discharge of septic tanks, uncontrolled solid waste disposal and swine farming located in Merida and adjacent municipalities (Euán, 2012).

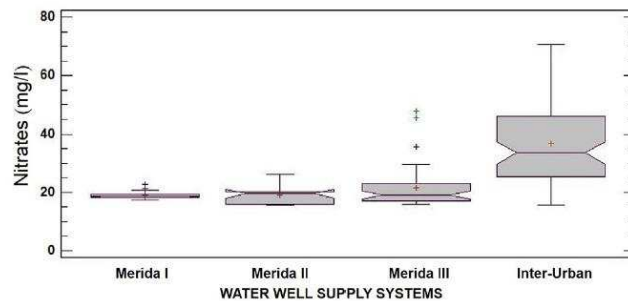


Fig. 5. Box and whiskers diagram for nitrate concentrations in the different water treatment works.

3.2 Geostatistical analysis

A Gaussian model was found to fit the experimental semivariogram and to better explain the spatial autocorrelation currently found from nitrate concentrations in groundwater ($r^2=0.78$). The calculation of iso-concentration contour lines was conducted by using Inverse Distance Weighting (IDW) interpolation based on the theoretical Gaussian model and on the locations of the original data. A cross-validation analysis of the interpolations was applied and resulted in an acceptable r^2 coefficient value (0.713), which means the proportion of the variation is properly explained by the best-fit line. This result was used in creating the iso-concentration contour map for nitrate based on data reported in this study exclusively (i.e., period 2012-2013), in order to reach a good representation of the current situation (Fig. 6).

A large variation in the nitrate concentrations between water treatments works is shown in Fig.6, with the higher concentrations found in the central part of the City of Merida. That corresponds to the oldest part of the city, where all domestic wastewater is directly disposed into the aquifer via sinkholes or caves or through septic tanks. As compared with earlier reports from others regions within in the Mexican State of Yucatan, the nitrate level found was relatively lower in the same region. Pacheco and Cabrera (1997) reported 56% of the total 380 water samples collected from a dug wells in a rural area of Northern Merida, where the nitrate concentrations were above the maximum permissible limits (>45 mg/l). Graniel et al. (1999) reported nitrate concentrations of up to 80 mg/l in the upper layer of the Merida's aquifer from dug wells located in the central zone of the City of Merida. One of the main differences between this actual research and others previously mentioned herein is the study of the spatial behavior of nitrates in groundwater through geostatistical analysis in order to reproduce numerically and graphically, the spatial distribution of nitrate concentrations on the study area.

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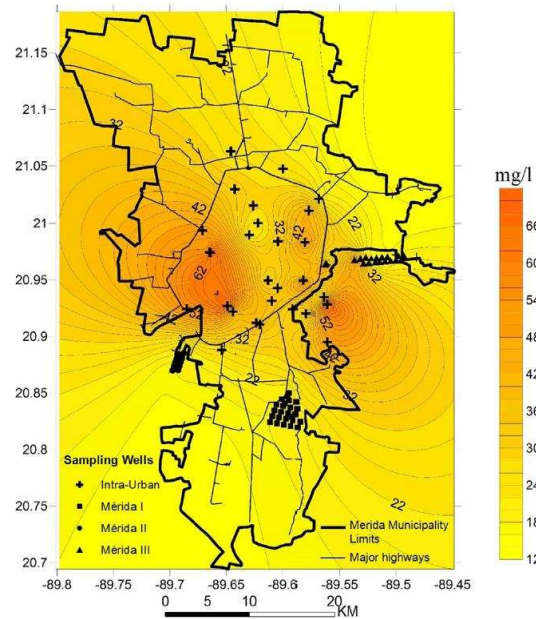


Fig. 6. Nitrate concentration (mg/l) in the study area (2012–2013).

Regarding the water treatment works, it can be observed that some of the wells in the intra-urban back-up system and in Merida II reported the highest nitrate concentrations. This could be explained by the existence of some activities, which potentially discharge nitrates into the groundwater in Merida and its adjacent municipalities, Uman and Kanasin. The nitrogen input caused by the activities in those municipalities has been reported by Euán (2012), who mentioned that the most important nitrogen inputs could come from the use of nitrogen fertilizers in agricultural, as well as from septic tanks, solid waste and farm discharges (Table 3). From the total nitrogen inputs for each of the previously mentioned activities, leachates; agricultural and urban runoff; and dilution due to rainfall infiltration must be considered as the most relevant for the Merida region. As an example, in the case of agriculture in the metropolitan area of Merida, leachates were responsible for 44% of the total nitrogen load fed into the groundwater, resulting in a nitrate concentration diluted by a factor of 12 (Gonzalez-Herrera et al., 2014).

Table 3
Main nitrogen inputs (kg) according to different activities in the study area.

Municipality	Agriculture	Swine farming	Poultry farming	Septic tanks	Solid waste
Merida	319,937	12,463,728	348,976	3,738,294	2,141,198
Uman	146,839	2,675,633	755,420	229,469	131,434
Kanasin	187,297	1,743,569	1,813,246	354,191	202,871

Source modified: Euán (2012).

The areas located north and southeast of Merida have lower nitrate concentrations which could be attributed to lower population densities and smaller scale economic activities as compared to Uman and Kanasin.

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<http://dx.doi.org/10.1016/j.apgeog.2015.10.00412>

3.3 Nitrate correlations with selected water quality parameters

The correlation values calculated for a 5% significance level of NO_3^- against Cl^- ; NO_3^- against K^+ and NO_3^- against SO_4^{2-} were not significant ($r < 0.9$) for both sampling years and all sites. However, as showed in Table 4, there is a certain degree of correlation between nitrate and chloride concentrations in Merida II ($r^2 = 0.59$). This could be explained by several factors which include the presence of septic tanks and swine farm discharges, added to open defecation practices which has been detected in some rural communities in the region (Rao, 2006; McQuillan, 2004).

The positive correlations between potassium and sulphates with nitrates indicate groundwater contamination by industrial nitrogen fertilizers, domestic wastewater and farm discharges (Anayah and Almasri, 2009; Sajil et al., 2014; Suthar et al., 2009; Reddy, 2014). In the study region, positive correlations ($r^2 > 0.5$) of these parameters were found in Merida II and in intra-urban wells, which could relate to the activities developed in the surrounding municipalities.

Table 4
Correlation coefficients (r^2) for nitrates against chlorides, potassium and sulphates.

Supply system	NO_3^- vs. Cl^-	NO_3^- vs. K^+	NO_3^- vs. SO_4^{2-}
Merida I	-0.75	-0.01	-0.27
Merida II	0.40	0.77	0.59
Merida III	-0.39	-0.27	-0.31
Intra-urban	-0.14	0.44	0.52

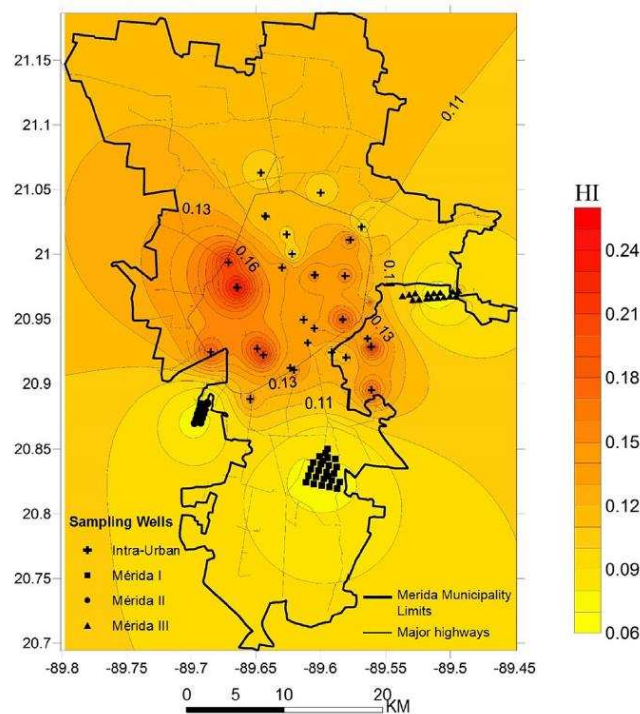


Fig. 7. Hazard Index of nitrates for adults drinking groundwater.

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<http://dx.doi.org/10.1016/j.apgeog.2015.10.00413>

3.4 Hazard characterization

Results indicated that the Hazard Index (HI) calculated for adults was lower than the unit ($HI < 1.0$), meaning no adverse effect to human health by nitrate contamination because it was below the actual safety limit (Bozek et al., 2013; Jamaludin et al., 2013). However the higher levels were located at the central region of the study area which corresponds to Merida's city center (Fig. 7). A similar spatial behavior was found for HI values calculated for bottle-fed infants; nevertheless, values above the unit ($HI > 1.0$) were reached in the central area as well (Fig. 8), indicating a health risk for babies feed with milk formula prepared with this water.

The spatial distribution models (Figs. 7 and 8) showed that the highest values of HI are located in the central part of the City of Merida, which is supplied by wells in intra-urban back-up system. Generally speaking, the lowest values were observed in Mérida I, II and III located on the outskirts of the city. This result shows the need to provide water for human consumption from field water wells at the periphery of the city with the lowest HI to reduce any related public risks, particularly to infants.

4. Conclusions

The nitrate concentrations in the groundwater supply sources serving the City of Merida City were found to be within a range of 15.51 to 70.61 mg/l. In 11% of the collected water samples, nitrate concentrations exceeded the maximum limits allowed by OMS and WHO for human use and consumption. The main contribution of this research work, when compared with others previously reported in the same geographical area, is the study of the spatial behavior of nitrates in groundwater through a robust geostatistical analysis in order to reproduce numerically and graphically the spatial distribution of nitrate concentrations on the study area. The spatial distribution of the nitrate ion showed that the highest concentrations were located in the central and northwest parts of the City of Merida. A positive correlation of nitrates with chlorides, potassium and sulphates in Merida II and in the intra-urban back-up system suggests anthropogenic contamination mainly due to agricultural activities, as well as inadequate discharge of wastewater from farming in the case of Merida II. In the case of the intra-urban system, the use of septic tanks, which could influence the nitrate concentrations in the groundwater, must be considered. In general, there is no health hazard of nitrates for adults, but bottle-fed infants may be under risk if consume water from the inter-urban system.

The spatial distribution of the HI reported in this research provide for the very first time scientific evidence confirming that the aquifer feeding the water treatment works in the periphery of the city (Merida I, II and III), does not pose mayor public health risks due to the presence of nitrates. GIS technology is an essential tool to achieve a better representation of the spatial distribution of chemical contaminants that may affect drinking water supply sources and public health. The present study found that in the City of Merida the current natural solution to nitrate contamination is dilution caused by infiltration of water from rainfall reaching aquifer. However, it must be considered that this scenario is highly vulnerable to long term due to unpredictable changes induced by climate change scenarios and current unsustainable socio-economic

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development in the region, which could reduce the quality of the groundwater, rendering it inadequate for feeding the current water supply system in Merida.

Acknowledgements

The authors wish to thank the National Science and Technology Council CONACYT for the scholarship award granted to Mrs. Annette Y. Rojas for her PhD studies and to the Mixed Funding System CONACYT-GOBIERNO DEL ESTADO DE YUCATÁN for financing this Project (Project Key: YUC-2009-C07-131955).

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