Nitrate-Nitrogen (N-NO$_3^-$) in Ground Waters of Agricultural Zones in Tabasco, México; Risks for Aquatic Life and Human Health

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ABSTRACT

Nitrate nitrogen (N-NO$_3^-$), the most common pollutant in groundwater, is a result of the effect of diffuse sources of pollution like agriculture and animal husbandry intensive. The land use for these economic activities is very common in the Los Ríos sub-region in the state of Tabasco, Mexico, where the Los Ríos and Boca del Cerro aquifers are located. The aim of this research was to assess the concentrations of nitrate-nitrogen (N-NO$_3^-$) in groundwater, determine the quality in agreement with the maximum permissible limits established by national and international regulations, and the risks to the public health and aquatic life. The spatial distribution of N-NO$_3^-$ was determined using the inverse distance weighted (IDW) interpolation technique. The average nitrate-nitrogen concentration was 0.76 mg.L$^{-1}$, while the maximum concentration observed was 3.98 mg.L$^{-1}$. This does not exceed the maximum permissible limit (MPL) established in Mexico for the protection of the life of seawater. Relatively low concentrations of N-NO$_3^-$ have shown to be toxic to certain aquatic organisms, and the aquifers studied discharge a third of the water to the rivers in the area, which flow into the Laguna de Términos Campeche and the Gulf of Mexico. Laguna de Términos Campeche is one of the most diverse and rich environmental systems on earth, where numerous ecosystems converge such as coastal lagoons, wetlands, mangroves, seagrasses, and coral reefs.

INTRODUCTION

Groundwater is the largest reservoir of freshwater that is easily available to humans (Zaporozec 2002). In Mexico, 38.7% of the total volume of water granted for consumptive uses comes from groundwater (CONAGUA 2015). Among the pollutants that affect groundwater, nitrates are important because of their mobility, soluble nature, distribution area, and the risk they pose to human health and the ecosystem (Martínez et al. 2011). Nitrates are converted into nitrites by the action of certain bacteria in the esophagus. This conversion can also occur in other sites, including the small intestine and the colon (Ward et al. 2005). Nitrite is one of the most commonly reported agents causing methemoglobinemia (Basulto et al. 2014), a disease caused by the increase of methemoglobin in the blood. Its effects range from cyanosis (blue discoloration of the skin) to diarrhea, tachycardia, headache, fatigue, lipothymia, nausea, anorexia, and vomiting (Larios 2009). In addition, nitrate is a precursor in the formation of N-nitrous compounds such as nitrosamides and nitrosamines, which are gastric carcinogens produced by the combination of nitrates with amides and amines (Ward et al. 2005).

The enrichment of nutrients (phosphorus and nitrogen, as well as compounds of these elements) in marine and freshwater systems causes eutrophication (Karydis 2009), which affects algal blooms, anoxia, and death of aquatic organisms (Dokulil & Teubner 2010). In addition, the presence of nitrates in water represents a risk for living beings. As with humans, nitrate in aquatic organisms transformed into nitrite reduces the ability to transport oxygen in the blood (Camargo & Alonso 2007). These compounds can be found in groundwater as a result of natural and anthropogenic sources, among latter, agricultural activities represent a serious threat given that the use of fertilizers is not regulated and producers are often in the excessive application of them (Galaviz et al. 2011, Rodríguez et al. 2015).
In recent decades, extensive areas of forests, mangroves, popales, and tulares of the state of Tabasco have been disappearing to give way to a greater number of ejidos dedicated to agriculture and livestock (Munguía 2005). In the region of Tabasco Los Ríos, agriculture and livestock are the most important economic activity, and the use of land is, for the most part, dedicated to cultivated pastures (INEGI 2015). Added to this, in the municipalities that make up the study area, the fertilized surface shows a growth trend. From 2011 to 2016, the fertilized area in the municipalities of Balancán and Emiliano Zapata increased by 95% and 29%. In Tenosique, during the same period, the sown area decreased by 36%, although the fertilized surface increased by 2% (SIAP 2011, 2013, 2016).

Within this region, there are two aquifers, Los Ríos and Boca del Cerro, which are unconfined, with static levels ranging from 30 cm to 20 m and contain sulfated sodium, sodium bicarbonate, sodium chloride, and mixed waters (CONAGUA 2002a, 2002b). No historical data or background of similar studies conducted in these aquifers was found. Therefore, the objective of this study was to assess nitrate-nitrogen concentrations (N-NO₃⁻) in groundwater of the Los Ríos and Boca del Cerro aquifers and compare them with national and international standards to determine if there is contamination that poses a risk to public health and aquatic life.

MATERIALS AND METHODS

The study area covered the municipalities of Tenosique, Balancán, Emiliano Zapata and Jonuta in the state of Tabasco, México in which the Los Ríos and Boca del Cerro aquifers lie (Fig. 1). The predominant climate is humid and warm with abundant rains in summer. The average annual temperature range is 26 to 28 °C and the annual rainfall is 1,500 to 2,500 mm (INEGI 2015, INIFAP 2016).

The information related to the use of soil, surface water, groundwater, and urban and rural localities was taken from the digital repository of the National Institute of Geography and Statistics for its interpretation, modification, and mapping in the geographic information system (GIS), QGIS, version 2.18.2 for Windows.

With the information provided by the State Water and Sanitation Commission (SWSC) from each municipality, the inventory of existing and active wells was carried out. Subsequently, the wells were identified through the GIS and the sampling sites were determined (Fig. 1).

The study was carried out from May to October 2017 in two sampling seasons - the dry season (May-June) and the end of the rainy season (August-October). Thirty wells were sampled, of which eleven are located in the municipality of Tenosique, eight in Balancán, five in Emiliano Zapata, and six in Jonuta. In situ measurements of temperature, electrical conductivity (EC), and hydrogen potential (pH) were made with HACH SENSION + MM 156 multisensor. The laboratory results were reported as nitrate-nitrogen (N-NO₃⁻), and the laboratory analysis of the water samples was carried out by method 353.2 (automated colorimetry) of the EPA (1993).

The statistical analysis was carried out with the STATISTICA v.12 program. Kolmogorov-Smirnov normality tests and non-parametric analysis of variance were performed using the Kruskal-Wallis test to determine the existence of significant differences between the concentrations of N-NO₃⁻ by land use. The N-NO₃⁻ isoconcentration map was developed with the QGIS software, using the interpolation method of inverse distance weighting (IDW).

RESULTS AND DISCUSSION

Results

The maximum concentration of N-NO₃ in the low season was 3,979 mg.L⁻¹ and the minimum concentration was 0.0049 mg.L⁻¹. At the end of the rainy season, in 17 of the 30 sampling sites, the average concentration of N-NO₃ increased to 0.54 mg.L⁻¹, although the increase recorded in the sampling site corresponding to the population of Multé (Balancán) was 3.06 mg.L⁻¹. In eight sites, the decrease of N-NO₃ was on average 0.45 mg.L⁻¹, although the decrease recorded in the sampling site corresponding to the population of Chablé population was 2.07 mg.L⁻¹. In the remaining five sites, it was not possible to determine the difference in concentrations of N-NO₃ because in some seasons the result was less than the detection limit. In the rainy season, the maximum concentration registered
was 3,821 mg L\(^{-1}\) of N-NO\(_3^-\), while the minimum was 0.0027 mg L\(^{-1}\) of N-NO\(_3^-\). The average concentration of N-NO\(_3^-\) (0.872 mg L\(^{-1}\)) was higher at the end of the rainy season than at the beginning of the rainy season. The averages of pH (7.3), EC (96.5), and temperature (29.4) showed high values in the dry season. The standard deviation of the concentrations of N-NO\(_3^-\) was higher in this season (Table 1).

### DISCUSSION

The results obtained are explained by the temporary variability of N-NO\(_3^-\), which in summer show minimum values (Graco et al. 2007) due to the biological demand of vegetation and crops (Nevárez & Flor 2014). The quartiles of the variable N-NO\(_3^-\) took the values of 0.028 (Q1) and 0.892 (Q3) in the dry season, and 0.032 (Q1) and 1.22 (Q3) in the rainy season. 50% of the observations were found between these values for each season (Table 1).

The spatio-temporal distribution of the concentrations of N-NO\(_3^-\) did not follow a normal distribution, which was confirmed by adjustment probability graphs (Fig. 2).

The result of the statistical analysis (Kruskal Wallis H [2,24] = 2.467, p = 0.291) showed that there was no statistically significant differences between the land use categories (grassland, agricultural and human settlement) when comparing the medians of their N-NO\(_3^-\) concentrations. Given that the proximity of the sources of contamination to the sampling sites is the variable most associated with the concentration of N-NO\(_3^-\) (Gallart 2008, Perdomo et al. 2001), it is probable that the results obtained are lower than the concentrations that could be found in areas dedicated to crops where nitrogenous fertilizers are applied (Estrada-Botello et al. 2002, Muñoz et al. 2004).

The spatio-temporal distribution of the concentrations of
N-NO$_3^-$ in groundwater showed slight differences. In the first season (dry season), two areas were detected indicating the sites with the highest concentrations of N-NO$_3^-$, one to the northwest of the municipality of Emiliano Zapata in the town Chablé and another north of Tenosique, in the towns of San Isidro and La Palma (Fig. 3). In the second sampling season (rainy season), concentrations were maintained high in the sites located in the municipality of Tenosique. However, in the Multé population of the municipality of Balancán the concentration of N-NO$_3^-$ increased (Fig. 4). This site showed the greatest variation from one sampling period to another.

The sampling sites with the highest concentrations of N-NO$_3^-$ are far from the sources of point pollution present in the area such as the Azsuremex-Tenosique sugar mill and the final disposal sites for urban solid waste. In these sampling sites, the use of the soil is for the cultivation of pastures (Fig. 5). Wells in Chablé are public-urban use, are more than 100 m deep, and are on the banks of the Usumacinta River. They are from the oldest wells, whose construction dates from the sixties. The uses in Tenosique belong to an ejido (San Isidro) and a Ranchería (La Palma), where the well water is destined for public-domestic use. Its depths are 80 m and 70 m, respectively.

These wells are the closest to the San Pedro River, being the town of La Palma on the banks of this river. The Multé well is on the banks of the Usumacinta River and less than 3 km from the San Pedro River. Its depth is 120 m and is the most recent of all, as it was built in 2014. The results obtained in these areas could be due to contributions from diffuse sources, due to the proximity of areas dedicated to irrigated agriculture (Chablé), and the proximity with the Usumacinta (Chablé, Multé) and San Pedro (San Isidro, La Palma) rivers. Because the wells near rivers obtain their recharge from these rivers and not from the aquifer that overrides them (Agudelo 2005), in this particular case, these rivers could transport nitrogenous compounds that eventually reach the referred aquifers.

The results of N-NO$_3^-$ obtained are below the maximum permissible limits (MPL) for drinking water established nationally and internationally in the official Mexican standard NOM-127-SSA-1994 (DOF 1994) and by the World Health Association (WHO 2011). First, a limit value of 10 mg.L$^{-1}$ (MPL) of N-NO$_3^-$ for water for human consumption, and second, a limit value of 50 mg.L$^{-1}$ of N-NO$_3^-$ equivalent to approximately 10 mg.L$^{-1}$ of N-NO$_3^-$.

The N-NO$_3^-$ concentrations found in this study were also compared with the Ecological Criteria for Water Quality (ECWQ) available in Mexico. The ECWQ establish different levels of concentration according to the minimum quality

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**Fig. 3**: Nitrate-nitrogen (N-NO$_3^-$) isoconcentrations in the study area during the dry season.

**Fig. 4**: Nitrate-nitrogen (N-NO$_3^-$) isoconcentrations in the study area during the rainy season.

**Fig. 5**: Areas with higher concentrations of nitrate-nitrogen (N-NO$_3^-$) and sources of contamination in the study area.
required for the use of it as a source of drinking water (5 mg.L⁻¹ of N-NO₃), livestock use (90 mg.L⁻¹ of N-NO₃), and marine water life protection (0.04 mg.L⁻¹ of N-NO₃) (DOF 1989). The highest concentrations obtained in the present study are close to the established MPL for drinking water, and in 50% of the sampling sites, the concentrations of N-NO₃ exceed the MPL defined for the protection of the life of seawater. The latter is important because the aquifers studied discharge a third of the water to the rivers in the area, which flow into the Laguna de Términos and the Gulf of Mexico (CONAGUA 2002a; 2002b). Laguna de Términos is one of the most diverse and rich environmental systems on earth, where numerous ecosystems converge, such as coastal lagoons, wetlands, mangroves, seagrasses, and coral reefs. The Laguna de Términos stands out among the estuaries and coastal lagoons of Mexico due to its rich fauna, which is estimated at 122 species of ichthyofauna and 174 species of mollusks. Among the most valuable species is the pink shrimp, whose life cycle develops in this area (Toledo 2005).

According to Camargo and Alonso (2007), freshwater species are generally more susceptible to nitrate toxicity compared to marine species. Among the most vulnerable, the authors point to certain crustaceans, insect larvae, and fish. It has been shown, for example, that concentrations above 1.1 and 2.3 mg.L⁻¹ of N-NO₃ have adverse effects on salmonid fingerlings of the species Oncorhynchus mykiss and Oncorhynchus tshawytscha. Likewise, concentrations equal to 2.8, 4.4, and 4.5 mg.L⁻¹ of N-NO₃ are fatal for amphipods Echinogammarus echinotusosus, Eulimnogammarus toletanus, and trichoptera Hydropsyche occidentalis, in that order. Therefore, the N-NO₃ concentrations in the aquifers studied may represent a risk to the ecosystem of the Laguna de Términos and the coastal zone of the Gulf of Mexico.

CONCLUSIONS

Nitrate-nitrogen (N-NO₃) concentrations in the Los Ríos and Boca del Cerro aquifers do not exceed the maximum permissible limits for drinking water established by NOM-127-SSA-1994 and by the World Health Association. Therefore, the water from the Los Ríos and Boca del Cerro aquifers does not represent an immediate risk to public health in terms of the nitrogen content of nitrates. However, the frequent consumption of water from these aquifers could eventually cause, in the long term, a significant accumulation of N-NO₃ and consequently, damage to public health. The concentrations of N-NO₃ exceed the MPL defined by the ECWQ for the protection of the life of seawater. Therefore, it is recommended to conduct studies in the discharge zones towards the Laguna de Términos and the coastal zone of the Gulf of Mexico, to determine if there is indeed damage to these aquatic ecosystems.

ACKNOWLEDGEMENTS

To the National Water Commission (CONAGUA) and to the National Council of Science and Technology (CONACYT) 2014-248265 Project “Evaluation of the effect of diffuse sources of pollution on the quality of the water of the Usumacinta River, in the state of Tabasco. To the Postgraduate College, Veracruz Campus; and the Boca del Río Technological Institute.

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