Nitrate temporal and spatial patterns in 12 water-supply wells, Yucatan, Mexico

Julia Pacheco · Luis Marín · Armando Cabrera · Birgit Steinich · Oscar Escolero

Abstract The nitrate concentration in 12 water-supply wells were monitored for the period April 1992 to March 1993. Each water-supply well was sampled once a month. The nitrate concentrations in the 12 wells ranged from 7 to 156 mg/l. Two water-supply wells (Chacsinkin and Peto) showed concentrations that reached 3.5 times the maximum permissible limit for the Drinking Water Standard (45 mg/l). A third water-supply well (Akil) exceeds the norm for 7 out of 12 months. The use of nitrogen-rich fertilizers are responsible for high nitrate concentrations in groundwater in the southern part of Yucatan, Mexico where intensive agricultural practices exist.

Keywords Agricultural practices · Groundwater contamination · Karst · Nitrate

Introduction

Agriculture can degrade groundwater quality through the use of fertilizers and pesticides. The most common contaminant identified in groundwater is dissolved nitrogen in the form of nitrate (Freeze and Cherry 1979) and the primary origin of the contamination by nitrates is undetermined in most cases (Wells and Krothe 1989). Transport of nitrate ions from their source to the aquifer depends on many hydrogeological factors. Carbonate aquifers have great potential for groundwater contamination because of the presence of numerous fractures and solution cavities that permit rapid infiltration. They also lack physical and chemical attenuation mechanisms commonly associated with laminar granular flow through unconsolidated sediments (Kreitler and Browning 1983).

Agriculture is one of the predominant activities in Mexico. The farming techniques employed throughout the country are divided in two types: highly sophisticated techniques, which include state-of-the-art water distribution systems, and the 'traditional' manual labor-intensive practices from the turn of the century. Both groups, but particularly the latter, have recently discovered the benefits of using pesticides to control unwanted pests and fertilizers to increase crop yields. Little understanding of the limitations of both types of products has resulted in an indiscriminate use of both and, as a consequence, ground and surface waters are being impacted throughout these irrigation districts. In this paper, the authors focus on the latter. The basic idea that farmers have is that the use of fertilizers results in better yields. Thus, if the recommended doses are increased, their yields will increase even more, without realizing that the excess fertilizer is only washed away. Despite the efforts of federal agencies, it has not been possible to convince the farmers in the agricultural districts to reduce their fertilizer loads. Clearly, this also would have an important immediate financial benefit. Reducing the cost of fertilizer use lowers the cost to produce the crops. As a result of this practice, it is expected to find high nitrate concentrations in areas where agriculture is predominant.

The nitrogen cycle has been described extensively in the literature. Thus, it is only briefly discussed here (Freeze and Cherry 1979). Nitrates occur in surface waters, shallow wells, and deep wells: shallow wells, however, usually contain the highest levels because of the heavy concentrations found in runoff and their proximity to living plants that fix nitrogen. Excess nitrogen that is not required by the plants, however, is leached downward into the shallow aquifers by rain water. Additional nitrate and ammonia enter water supplies from runoff and leaching. Ammonia is present as a result of the application of ammonia containing fertilizers and animal waste. Ammonia is a transitory part of the nitrogen cycle. Organic nitrogen breaks down to ammonia by bacterial activity and is then transformed into nitrate (nitrification). Topically applied ammonia fertilizer follows the same steps (Chandler

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1989). Nitrate is stable in groundwater because of the dissolved oxygen (Hamilton and Helsel 1995) and in the study area had an average concentration of 4.89 mg/l (Pacheco 1994), and it is highly mobile because it does not interact with the matrix materials (Bulger and others 1989).

The maximum nitrate level for drinking water established by Mexican standards (Secretaria de Salud 1996) is 45 mg/l as nitrate. High nitrate levels in drinking water are of concern because of an infant disease, methemoglobinemia, commonly known as “infant cyanosis” and human cancer (Vigil and others 1965; Bouchard and others 1992). Doehring and Butler (1974) showed that >60% of the deaths of children under 6 years of age in Yucatan are caused by pathogens transported by groundwater. Untreated sewage in the larger cities in Yucatan is discharged into septic tanks that are finished 3–5 m below the land surface. In the smaller towns, many of the houses do not have any sanitary facilities and defecation occurs out in the open. This untreated sewage typically infiltrates rapidly into the shallow aquifer through joints, conduits and fractures (Pacheco 1994; Marin and Perry 1995). A common approach throughout Mexico is to boil the water to kill pathogens transported in the water. Pacheco and others (1996) have shown that boiling water, while it may kill bacteria, also concentrates the nitrate ions in solution. Since boiled water is used to prepare milk for infants, this practice is also worrisome, and thus, it should be discouraged. The authors suggest both the treatment of water with chlorine, for bacteriological water quality assurance, and the promotion of natural lactation to reduce bottle-fed babies. Alternative techniques such as source replacement, borehole abstraction modification, etc., are expensive to implement.

The land surface of Yucatan is practically flat (30 m difference in elevation in 100 km), the only major relief feature is located in the southern part of the state. A low range of hills, known as the Sierrita de Ticul, extends 120 km from the south-eastern part of the state near to the border of Campeche. Characteristic vegetation is *Simorfia fructicetum* and the soils are relatively thin and overlie the limestone and evaporites of the Paleocene and Eocene age (Velázquez 1986).

The hydrogeology of the eastern coast of the Yucatan Peninsula has been studied extensively by Back and Hanshaw (1970), Weidie (1982), Stoessell and others (1990), Moore and others (1992), and Alcocer and others (1998); but the hydrogeology of the north-western part of the Yucatan Peninsula has received little attention until recently (Perry and others 1989, 1990, 1995; Marin 1990; Marín and others 1990; Steinich and Marín 1996, 1997; Steinich and others 1996). Back and Hanshaw (1970) called attention to important characteristics of the hydrogeology of Yucatan such as the high permeabilities found in this area and the presence of a saltwater wedge that extends tens of kilometers inland. They observed that no integrated drainage system existed in north-western Yucatan, and that no rivers exist in this part of the Peninsula. They inferred a low gradient of the water-table (based on the very low topographic relief), a high permeability of the aquifer, which they suggested probably contains large interconnected openings, they assumed that no confining beds were present (because of the thin fresh water lens) and suggested that groundwater flowed in a north–north-eastern direction. The upper geological section of the northern Yucatan Peninsula consists of nearly flat-lying carbonate and evaporitic rocks and sediments (Lopez-Ramos 1973).

The upper hundreds of meters of rocks consist of almost pure carbonate rocks and evaporites, which when dissolved leave little or no residue. As a result, the aquifer in north-west Yucatan consists of a shallow, thin fresh water lens (less than 45 m), which is underlain by saline water of dual origin (seawater intrusion and dissolution of evaporites), and this penetrates >110 km inland (Perry and others 1995; Velázquez 1995; Steinich and Marin 1996). This aquifer is the sole source of drinking water because no surface drainage exists. The aquifer is unconfined, except for a narrow band parallel to the coast (Perry and others 1989). The potential for contamination of this aquifer is very high since there is a thin to non-existent soil cover (Marin and Perry 1995). High nitrate concentration in shallow groundwater (0–223 mg/l) have been reported just north of Merida (Pacheco and Cabrera 1997). The southern portion of the Yucatan is potentially vulnerable to nitrate contamination because of extensive agricultural activities. Within the southern part of the state lies an important agricultural zone. Crops grown here regularly include citrus fruits, corn and peanuts. The types of fertilizers used in this area are urea, ammoniacal nitrates, and potassium chlorides and sulfates (Pacheco and Cabrera 1996), and are commonly applied during the early growing season, just before the rainy season starts (typically May–June). Excessive applications of fertilizers and pesticides above the amounts needed for plant growth have been used in this area (Cobos 1996), which may increase the nitrate content of groundwater. Animal wastes and leakage from septic tanks are also potential sources of nitrate in this area (Pacheco and Cabrera 1997). The study area (Fig. 1) is located in southern Yucatan, Mexico, in a predominantly rural area. Because of the high permeability of the rocks, the rainfall percolation is rapid resulting in scarce surface runoff. The dominant land use is agriculture and the statistical average annual precipitation is 1200 mm, 50% of which falls during the rainy season from June to early October (INEGI 1996). Groundwater is pumped regularly from October through to May/June, which typically corresponds to the dry season. During the rainy season, no pumping is necessary for agricultural practices because the precipitation is sufficient to meet the crop needs. Because the only source of drinking water for north-west Yucatan is the sole-source aquifer (Marín 1990; Steinich and Marín 1996), and the water-supply wells for the inhabitants of southern Yucatan lie in this zone, we wanted to evaluate the nitrate concentration to determine whether there was a negative impact on the water quality in this zone as a result of the current agricultural practices.

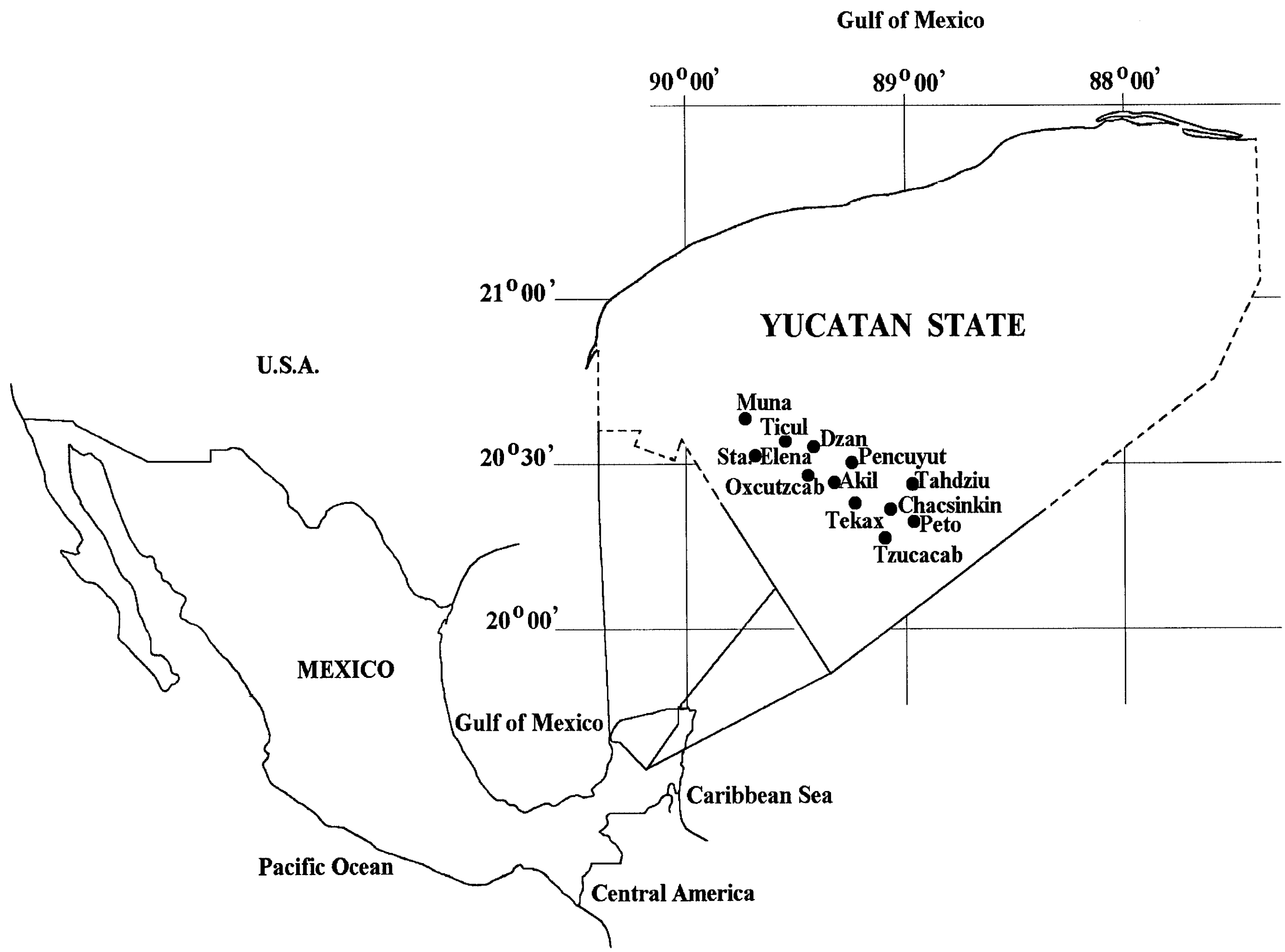

Fig. 1
Map showing study area in Yucatan Peninsula, Mexico

Objectives

The objectives of this study were to (1) elucidate the source of nitrogen in the groundwater in southern Yucatan; (2) determine whether water-supply wells located within the irrigation district were being negatively impacted by nitrogen loading because of the application of fertilizers, and (3) determine the spatial and temporal patterns with respect to nitrate concentrations.

Methodology

Water-supply wells in Yucatan are typically drilled to 50 m below the land surface with a 30-cm inside diameter of screened iron pipe. The unsaturated zone in this area lies within the range of 20–25 m below the land surface. Permission to take water samples on a regular basis was only granted at 12 municipal water-supply wells (Fig. 1, Table 1). Initially, it was decided to collect one set of water samples per month at each of the wells. Out of a possible 144 samples it was only possible to collect 134 (Table 1). This was primarily because of well malfunctions, lack of electricity, or restricted access to the well. Before each sampling event, 1-liter polyethylene bottles were washed with a 5% solution of hydrochloric acid and rinsed gently with tap water, and then finally rinsed with distilled water. Wells were pumped for 10 min so that the water sample was representative of the aquifer and the water samples were collected before the chlorinating system.

Field determinations were: pH, temperature, specific conductivity and dissolved oxygen. During each of the sampling episodes, the samples for nitrate analysis were acidified to a pH of ~2 with sulfuric acid to inhibit bacterial activity. Samples were transported to the laboratory in a cooler and kept in a dark refrigerator at 4 °C until analyzed. The nitrate concentrations were determined in the laboratory using an ultraviolet technique that is suitable for water with a low concentration of organic matter (APHA, AWWA, WEF 1992). In this area, the average concentration for organic nitrogen is 0.66 ± 0.5 mg/l (Pacheco 1994). The ion balance for 125 samples of the total groundwater samples (134) was $<5\%$ and the remainder were between 5–10%.

Table 1
Groundwater nitrate concentrations (mg/l) in the study area. (April 1992–March 1993). *nd* Not determined

Well	April	May	June	July	August	September	October	November	December	January	February	March
Akil	57.2[a]	56.2[a]	54.0[a]	48.0[a]	33.6	37.8	35.8	32.5	48.2[a]	51.4[a]	62.3[a]	65.7[a]
Chacsinkin	131.1[a]	132.0[a]	116.7[a]	109.6[a]	59.4[a]	70.1[a]	28.3	60.7[a]	62.10	64.2[a]	153.8[a]	155.5[a]
Dzan	nd	31.6	24.2	30.1	nd	25.1	29.2	24.5	37.80	40.4	46.7[a]	44.6
Oxcutzcab	22.2	20.3	nd	17.7	11.8	15.0	18.8	16.7	24.50	22.4	25.7	27.1
Pencuyut	45.0	41.7	nd	nd	29.9	32.4	24.8	23.5	45.50	47.2[a]	45.9[a]	54.9[a]
Peto	114.9[a]	111.8[a]	100.4[a]	93.3[a]	54.7[a]	65.6[a]	28.2	60.2[a]	63.90	64.8[a]	136.2[a]	150.2[a]
Muna	25.9	nd	22.1	22.5	15.8	nd	22.3	nd	24.30	26.5	32.7	33.1
Sta. Elena	nd	24.8	21.9	22.0	14.7	17.0	21.3	20.0	24.80	20.6	29.6	31.1
Tahdziu	33.3	31.3	28.10	27.0	18.8	25.0	18.7	30.6	33.60	36.3	35.2	40.7
Tekax	18.5	19.1	15.90	16.4	12.5	7.3	12.4	19.8	19.20	21.8	19.4	25.0
Ticul	30.5	27.0	22.20	23.2	11.8	22.9	22.4	21.0	26.20	29.2	36.9	34.2
Tzucacab	36.5	43.1	33.50	nd	22.6	28.1	20.9	22.6	34.20	37.4	27.2	41.4

[a] Nitrate concentration that exceeded the Drinking Water Standard (45 mg/l)

Results and discussions

In Yucatan, there are two possible main sources of nitrogen. These are untreated domestic and animal sewage, and nitrogen-rich fertilizer. One way to identify the origin of the nitrate is to examine the NO_3/Cl and the K/Cl in the groundwater. The sources in the study area for chloride and potassium are seawater intrusion or anthropogenic sources.

Aquifers contaminated by sewage commonly have a concentration of chloride higher than the water from the potable portion of the aquifer. Linear regression analysis, with a significance level of 5%, were calculated to examine the relationship between nitrate and chloride data from the 12 wells (Table 2). Correlation values above 0.35 indicate that groundwater has been affected by municipal and/or domestic wastes (Piskin 1973; Back and Hanshaw 1974; Ritter and Chirnside 1984). Table 2 shows that three of the water-supply wells had a r^2 value >0.35 (Ticul, Tekax, and Tzucacab; at a significance level of 5%) and the other nine, had values >0.35. Velázquez (1995) showed that the K/Cl ratios in groundwater from north-west Yucatan are similar to those of seawater. The K/Cl ratios for the study area are significantly higher than those for seawater suggesting that there is an additional source of potassium. As the carbonate rocks and evaporites are not a ready source of potassium, an anthropogenic source is a plausible alternative, particularly as potassium is one of the ingredients in fertilizers. The average potassium versus chloride concentrations are shown in Fig. 2. These data were chosen as representative for the whole sampling period. A line was drawn to show the K/Cl for dilute seawater. All samples have ratios that are above the dilute seawater line suggesting that there is another source for potassium. The nitrate versus chloride ratio suggested that in only three of the 12 water-supply wells is there a contribution from sewage. Thus, the authors conclude that the main source for the high nitrate concentrations in groundwater are from the use of nitrogen-rich fertilizers.

Table 2
Statistics summary and linear regression of the nitrate and chloride data

Wells	Nitrate (mg/l)			Chloride (mg/l)			r^2
	Average	Minimum	Maximum	Average	Minimum	Maximum	
Akil	48.56	32.50	65.70	275.31	264.09	294.85	0.17
Chacsinkin	95.29	28.30	155.50	111.52	93.80	125.12	0.00
Peto	87.02	28.2	150.20	294.72	250.14	400.23	0.02
Oxcutzcab	20.20	11.80	27.10	162.53	150.28	177.49	0.19
Tekax	17.28	7.30	25.00	251.84	234.06	271.58	0.55
Sta. Elena	22.52	14.70	31.10	285.49	265.32	390.00	0.17
Tahdziu	29.88	18.70	40.70	128.46	84.46	144.52	0.09
Ticul	25.62	11.80	36.90	229.95	159.59	273.52	0.42
Tzucacab	31.59	20.9	43.1	473.43	435.89	507.26	0.08
Dzan	33.42	24.20	46.70	280.70	266.81	296.79	0.43
Pencuyut	39.08	23.50	54.90	101.25	47.53	127.48	0.18
Muna	25.02	15.80	33.10	450.59	195.86	514.93	0.23

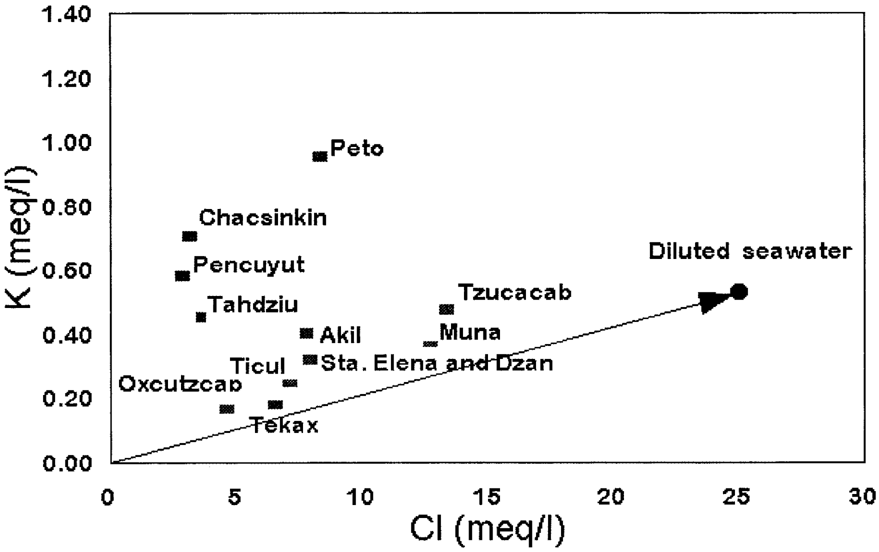

Fig. 2
K/Cl ratio from groundwater samples in the study area

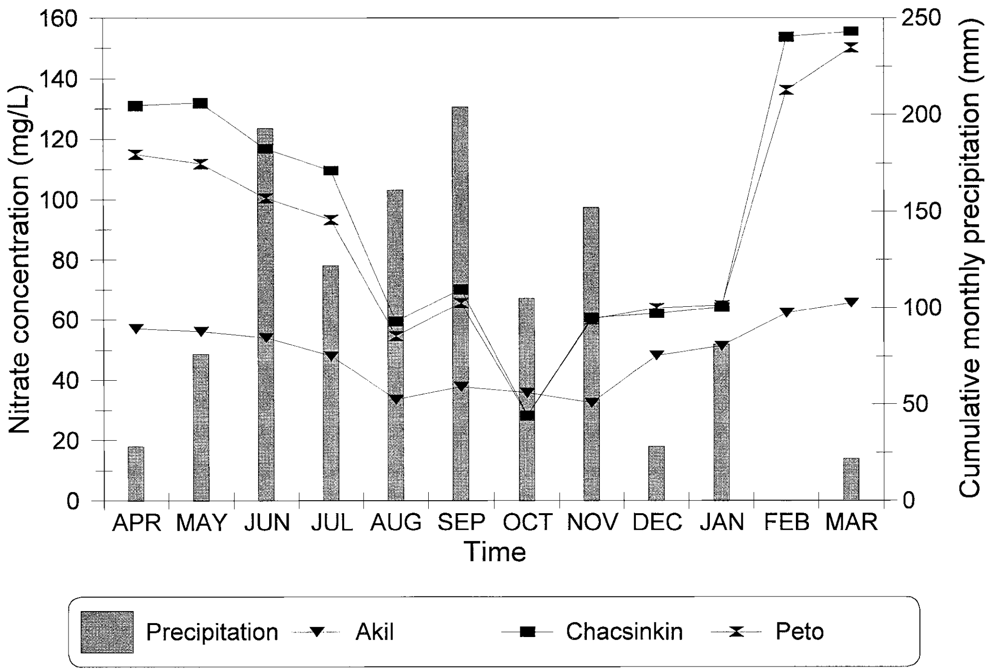

Fig. 3
a Relationship between precipitation and nitrate levels in wells

Nitrate levels ranged from a minimum of 7.43 mg/l in Tekax to a maximum of 156 mg/l in Chacsinkin (Figs. 3 and 4; Table 1). Seven water-supply wells comply with the Mexican Drinking Water Standards (DWS) throughout the year. These are Oxcuztcab, Muna, Santa Elena, Tahdziu, Tekax, Ticul, and Tzucacab. The other five wells: Akil, Dzan, Pencuyut, Chacsinkin and Peto, are out of norm for different periods of time throughout the year (Table 1). Chacsinkin and Peto exceeded the DWS for 11 months (only during October was the nitrate concentration within the DWS).

Seasonal trends in nitrate concentrations showed a strong correlation with precipitation. Two inflection points may be observed in the precipitation versus nitrate concentration plots (Figs. 3 and 4). The first is when the nitrate concentrations start to decrease, corresponding to the month of June, and the second, when the nitrate concentrations start to increase, corresponding to the month of December. Although the wet season is normally considered to be from June to October, the period from the end of October through to February can receive additional precipitation from tropical storms. Thus, for this study, the average nitrate concentration during the rainy season was calculated for the period June through to November and the nitrate concentration for the dry season was calculated for the remaining months (Table 2). The higher

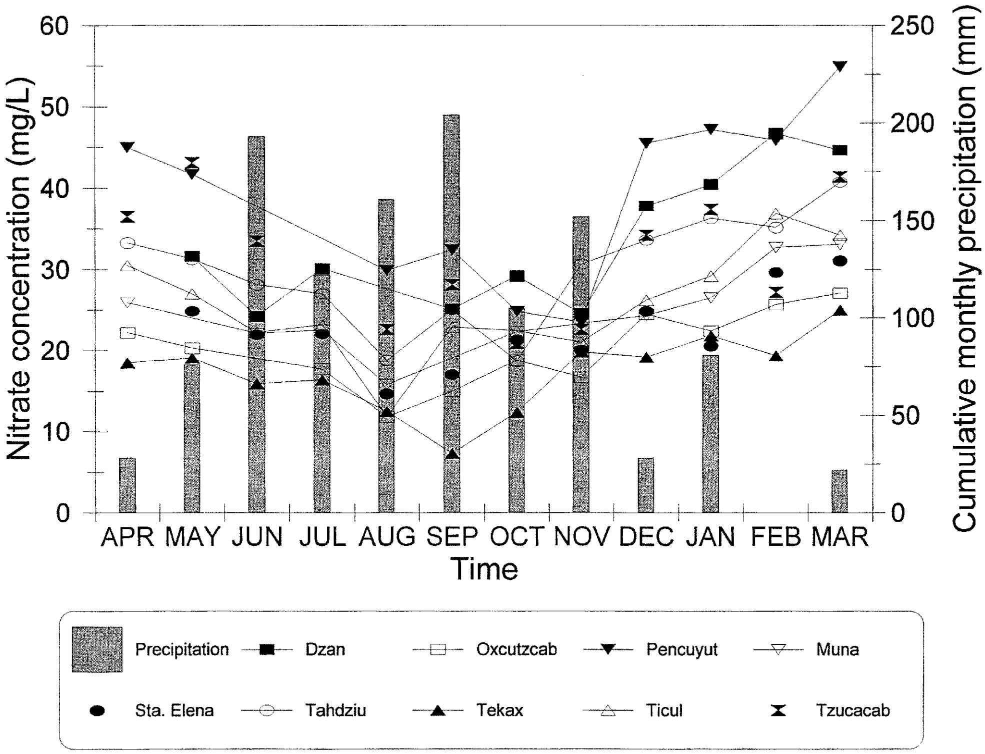

Fig. 4
Relationship between precipitation and nitrate levels in wells

concentrations are found during the period of low rainfall. During the rainy season, nitrate concentration decreased (Figs. 3 and 4) because of a dilution effect. Because of the high permeability of the area, the authors propose that groundwater, rich in nitrate ions is diluted by the low salinity rain water. All 12 sample wells showed an interesting temporal pattern. A dilution/concentration effect could be observed between the nitrate concentrations and precipitation. The aquifers, except for Chacsinkin, Peto, and Akil, are probably in a quasi steady-state situation with regards to the nitrate input/output. During the rainy season, though, the rain water infiltrates into the aquifer, diluting the nitrate present in the groundwater. Two background nitrate levels may be determined for each water-supply well. The two most dramatic cases are the wells from Chacsinkin and Peto (Fig. 3) whose decrease in nitrate concentration between the dry and wet season is dramatic. It varies between 116 and 74 mg/l, and 107 and 67 mg/l nitrate respectively. The other 10 wells show changes that oscillate between the dry and wet seasons from 14 to 20.5 mg/l nitrate (Tekax) and 40 to 57 mg/l (Akil). Table 3 shows the average nitrate concentration for the wet and dry seasons.

Table 3
Average nitrate concentrations for the dry and wet seasons

Well	Dry season	Wet season
Akil	46.91	40.89
Chacsinkin	123.00	66.80
Dzan	35.40	31.74
Oxcutzcab	20.80	18.57
Pencuyut	43.48	35.56
Peto	109.00	63.73
Muna	25.35	22.99
Sta. Elena	24.02	20.90
Tahdziu	30.63	27.66
Tekax	18.11	15.87
Ticul	26.54	22.86
Tzucacab	34.05	28.55

Conclusions

The main sources of nitrate in southern Yucatan are nitrogen-rich fertilizers with a smaller contribution from untreated domestic and animal wastes. Nitrate concentrations in 12 water-supply wells show a temporal pattern in response to the rainy season. A dilution effect is observed by infiltrating rain water as it mixes with nitrate-rich groundwater. Two background nitrate concentrations are observed for the 12 water-supply wells, one for the dry and one for the wet season respectively. The two cases with the highest nitrate concentrations are Chacsinkin and Peto, with the following concentrations: 116–74 and 107–67 mg/l respectively.

Two water-supply wells, Chacsinkin and Peto, show concentrations that are 3.5 times above the maximum permissible limits. A third water-supply well, Akil, exceeds

the maximum permissible concentration for 7 months of the year. This situation is clearly unacceptable. New wells finished at a greater depth are not a viable option because it is likely that it will only draw the contamination deeper into the aquifer.
The authors suggest that an alternative source of water for these towns is needed as well as a continued effort to advise farmers of the proper use of fertilizers.

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