Nitrate in groundwater in a recharge area of Guarany aquifer in Brazil

Antonio L. Cerdeira, Lourival C. Paraíba, Karen Kataguiri, Denizart Bolonhezi, Marco A.F. Gomes, Manoel D. DeSouza, Anderson S. Pereira, Carlos F. Neto, and Marcus B. Matallo
Embrapa-Environment, Brazilian Department of Agriculture
cerdeira@cnpma.embrapa.br

The region of Ribeirão Preto City located in São Paulo State, southeastern Brazil, is an important sugarcane, soybean and corn producing area. This region is also an important recharge area (Espraiado) for groundwater of the Guarany aquifer, a water supply source for the city and region. It has an intercontinental extension that comprises areas of eight Brazilian states, as well as significant portions of other South American countries like Argentina, Uruguay, and Paraguay, with a total area of approximately 1,200,000 Km^2. Due to the high permeability of some soils present in this region, the high mobility of the herbicides and fertilizers applied, and being a recharge area, it is important to investigate the potential transport of applied fertilizers to underlying aquifer. The cultivation sugar cane in this area demands the frequent use of nitrogen as fertilizer. This research was conducted to characterize the potential contamination of groundwater with nitrogen in the recharge area of groundwater. Seven groundwater sample points were selected in the Espraiado stream watershed, during the years of 2005 and 2006. Samples were collected during the months of March, July, and December of each year. Three replications were collected at each site. Groundwater was also collected during the same months from county groundwater wells located throughout the city. The following six wells were studied: Central, Palmares, Portinari, Recreio Internacional, São Sebastião, and São José. Nitrate water samples were analyzed by Cadmium Reduction Method. No significant amount of nitrate was found in the recharge, agricultural, area. However, nitrate levels were detected at concentrations higher than the Maximum Concentration Level (MCL) of 10mg/L in downtown, urban, well located away from agricultural sites with no history of fertilizer or nitrogen application.

Keywords: Groundwater, Nitrate Contamination, Nonpoint Source Pollution, Toxic Substances, Water Quality

Introduction

The region of Ribeirão Preto city, São Paulo State, located in Southeast of Brazil, is an important area for sugar cane production, with high level of herbicide and fertilizer utilization. It is also an important recharge area of the Guarany aquifer ground water, which extends to eight Brazilian states and part of Argentina, Uruguay, and Paraguay, with approximately 1,200,000 km2 (Figure 1). Geological studies in the region have identified a watershed, called Espraiado, with high risk of ground water contamination. Certain areas of the Espraiado watershed are highly permeable sandy soil allowing leaching of agrochemicals applied in crops (Miklós and Gomes 1996).

Several studies conducted in the region have detected low levels of pesticides used in agriculture particularly in groundwater on sugarcane area (Lanchote et al. 2000, Cerdeira et al. 2000, Gomes et al. 2000). One of those studies allowed ranking counties by contamination risk levels, defining priority regions for monitoring programs for nitrates (Rodrigues et al. 1997).

Due to the high permeability of some soils present in this region, the high mobility of the herbicides and fertilizers applied, and being a recharge area, it is important to investigate the potential transport of applied fertilizers to underlying aquifer. This research was conducted in Ribeirao Preto county in Brazil (Figure 2). The cultivation sugar cane in this area demands the frequent use of nitrogen as fertilizer. Nitrate ground water contamination is a frequent problem due to the massive use of fertilizers in agriculture (Rodrigues et al. 1997).

Drinking water and dietary sources of nitrate and nitrite can react in vivo with amines and amides to form N-nitroso compounds (NOC), potent animal carcinogens and nitrate is a widespread contaminant of drinking water supplies especially in agricultural areas (Ward et al. 2007; De Jong et al. 2007). The health effects of contamination are due to the transformation of nitrates into nitrites and possibly the transformation of nitrites into nitrosamines in the stomach.

The risk of methemoglobinemia in infants is due to nitrites contained in the water used to reconstitute milk for feeding (Levallois and Phaneuf 1994; Sacco et al. 2007). The use of nitrate-contaminated drinking water, N0-3-N, to prepare infant formula is a well-known risk factor for infant methemoglobinemia. Affected infants develop a peculiar blue-gray skin color and may become irritable or lethargic, depending on the severity of their condition (Knobeloch et al. 2000). According to a Sao Paulo State law in Brazil, the maximum concentration level (MCL) of nitrates is 6.0 mg/L (Alaburda and Nishihara 1998).
Because of the watershed vulnerability and high imput of nitrogen fertilizer applied, this research was conducted to characterize the potential contamination of groundwater with nitrates in the recharge area of groundwater and its vicinity

Materials and Methods

A survey conducted in the area has indicated that nitrate applied as nitrogen fertilizer, was regularly utilized and it was chosen for this study. Seven groundwater sample locations were selected in the recharge area watershed, during the years of 2005 and 2006. Samples were collected during the months of March, July, and December of each year.
Groundwater was also collected during the same months from five county municipal wells located outside of the watershed at the vicinity of the recharge area in addition to a well located in downtown far away from any agricultural activities (Figure 1). The following six urban wells were studied: Central, Palmares, Portinari, Recreio Internacional, São Sebastião, and São José. Three replications were collected at each site. (Table 1).

Estimation and Analysis of Nitrate Risk

Water samples (1L) were collected and nitrate was analyzed by Cadmium Reduction Method according to Greenberg et al. 1992. Health risk for the population was estimated according to Arumi et al. 2006, combining the following factors expressed as Risk Coefficient (RC), where RC , was function of C, the nitrate concentrations (mg/L) found in each well (Tables 2 and 3), V, Volume of water ingested in L/Day (2.0 for adults and 0.64 for infants), EF, Exposition Frequency in Days/year (350), BW, Body Weight (70 and 4.0 kg for adults and infants, respectively), and RfD, Reference concentration, which is the safe maximum level of exposition that causes no harm. This was obtained from literature from toxicological studies (United States Environmental Protection Agency). In this case, the RfD was 1.6 mg kg–1 day–1.

RC can vary from zero, no-risk, to 1.0, highest risk.

Results and Discussion

Very low amount of nitrates residues were detected in ground water of the recharge, agricultural area, where fertilizer (nitrogen) is applied (Table 2), even though a non-confined superficial water table with depths varying between zero to 20 m (Table 1) and porous sandy soil are found (Miklós and Gomes 1996). Analysis of municipal wells located at the edge of the recharge area have also shown low levels of nitrate (Table 3). However, nitrate levels were detected at concentrations higher than the MCL of 6.0 mg/L in downtown, urban, Central well located away from agricultural sites with no history of fertilizer or nitrogen application (Table 3).

RC Index evaluation has also shown values close to zero for all the wells with the exception to the Central, located in urban, non agricultural area. In this Central well we found RC index of nitrate close to 1.0, maximum, particularly for infants (Figure 2). This was also found in an aquifer beneath the old industrial city of Nottingham, UK, in shallow ground water originated mainly from residential and industrial areas, where high nitrate concentrations probably arising from leaking sewers and contaminated land were detected (Trowsdale and Lerner 2007). Arumi et al. 2006, also found in the Parral region of Chile, nitrate contamination of wells primarily linked to certain factors such as construction practices and the proximity of livestock. These factors affect the quality of drinking water in isolated cases. There was no risk found for the adult population, but there was for infants fed on formula mixed with water coming from the contaminated wells (Arumi et al. 2006). Alaburda and Nishimura, 1998, also found high level of nitrate in the metropolitan area of São Paulo city in Brazil.

Soil samples from the watershed were characterized by the determination of the sand, clay and silt content and texture. The sampled soils were classified as Dusky Latosol (Typic Haplorthox), Structured Dusky Latosol (Typic Eutrorthox), Dark Red Latosol (Quartzipsammentic Haplorthox), sandy loam Red-Yellow Latosol (Quartzipsammentic) and Quartzous Sand (Typic Quartzi-psament). They were submitted to leaching studies in laboratory with samples from the watershed. The data have shown the clayey (Dusky Latosol, structured Dusky Latosol) and sandy loam (Dark Red Latosol and Red-Yellow Latosol) soils with medium infiltration potential of

water as opposed to Quartzous Sand soil, which showed a high infiltration potential (Miklós and Gomes 1996)
As our data have shown, other studies have concluded that the principal cause of groundwater contamination by N0-3-N are the urban and industrial wastes dumped in the environment without treatment, and that contamination by agriculturally related fertilizers is a secondary cause (Schalscha et al., 1979). According to studies conducted by Arumi et al. 2005, contrary to expectations, the aquifers of the Central Valley of Chile also appear free from any significant nitrate pollution from agricultural sources in spite of the high levels of nitrogen-based fertilizers used in the agricultural activity, the irrigation practices and the active surface water-groundwater interactions.
Arumi et al. 2005, concluded that this could be due to a possible dilution effect that the amount of groundwater has on chemicals entering the groundwater system or related to the anion exchange capacity, which is very high in our study area also. Another reason pointed by the Author could be due to denitrification process by the presence of biodegradable organic carbon and presence of denitrifying bacteria, which are usually found in natural systems. The existence of naturally high levels of organic carbon in the soils in our study would contribute to this.
In conclusion, results have shown that nitrate was detected at levels higher than the MCL of 6.0 mg/L in well located in downtown area, which is away from the sugar cane plantations. Risk analysis has shown that the dangerous levels in wells located in down town is a health hazard mainly for infants, reaching the maximum risk levels of 1.0.

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