

**GROUNDWATER NITROGEN POLLUTION BY
CONVENTIONAL HORTICULTURAL PRODUCTION
IN KARST AREAS OF THE STATE OF PARANÁ,
BRAZIL**

*Elenice Fritzsos
Luiz Eduardo Mantovani
Ernani Rosa Filho*

INTRODUCTION

During the last century the green revolution turned up in a worldwide significant increase in food production, especially in developing countries though the environmental consequences, including pollution by agricultural chemicals and deforestation have become quite noticeable.

Nitrogen is one of the macro-nutrients included in commercial fertilizers that has the most pronounced and fastest effect on plant growth, but with excessive use it causes water pollution, and associated with phosphorus, it stimulates the eutrophication of lakes and reservoirs. Cases of nitrate pollution in waters that were beyond the limits recommended by the World Health Organization (50 mg-NO₃ L⁻¹) have been reported in many countries. Thus, excess of nitrate in surface water and groundwater has become a great environmental problem.

Nitrate in agriculture is a kind of nonpoint source pollution and its control involves an adaptation of the management system concerning also the land use planning. This is especially important in karst areas due

to the vulnerability the aquifer shows to surface pollution. According to the Kentucky Geological Survey (2009), this vulnerability is due to several factors: *"recharge to karst aquifers bypasses the filtering capability of soil through macropores and swallow holes; groundwater flows through conduits so that there is little opportunity for filtration or sorption of contaminants onto aquifer material; the movement of pollutants cannot be directly observed as in a surface-flowing stream; flow paths may take routes that are not apparent from the topography or slope of the land; flow velocities in karst aquifers are fast compared to velocities in granular aquifers, allowing little time to warn downstream users following a reported spill; flow is in converging conduits; therefore pollutants are not diluted through dispersal"*.

In karstic aquifers, nitrogen is highly soluble and stable in water in its nitrate form, and removing it in water treatment is not easily done, so it can threaten human health. The source of nitrate in groundwater originates from three main sources: a) the application of nitrogen fertilizers, inorganic and also organic, such as those from animal manure on cropland, b) atmospheric deposition, c) domestic sewage deposited into septic systems (Baird, 2002).

The area where this work was carried out has a strong agricultural activity focused on horticultural crops with intensive inputs. Moreover, it is potentially rich in groundwater and alkaline mineral waters from karst aquifers.

The objective of this study is to analyze the impact caused by horticultural systems to groundwater, considering nitrate pollution. For this, it was necessary to quantify the net result of nitrate input in the basins, i.e., we calculated the input of nitrogen introduced by the agricultural system, the nitrogen produced by rural housing and the output by the harvest of crops. This study was developed initially by Fritzsons, 1999.

MATERIAL AND METHODS

The watershed studied represents the general situation of land use over a geological substrate formed by marbles and metadolomite rocks present in the karst region of the Paraná's Atlantic Paranaense in Southern Brazil. The area is called Karst Paranaense Aquifer System, which consists of discontinuous layers of calcium carbonate and dolomitic marbles interlayered into packages of silicate rocks consisting of phyllites and quartzites. All these lithologies are strongly folded and fractured.

The karst is a network of underground drainage that is recharged by water precipitated and infiltrated through the soil or directly drove by dolines (Fig. 1) and fractures. In addition, the karst areas have a geotechnical high fragility, with the presence of collapsing soils, land subsidence, settlements of foundations and groundwater contamination, which may impose restrictions on the legal land use permissions (COMEC, 2009).

Figure 1. Doline present in the area.



The watersheds that were studied, named Ribeirão das Onças and Fervida, are two basins at adjacent areas with of 13.15 km² and 3.53 km², respectively, located at

latitude $25^{\circ} 15' 25^{\circ} 17'$ (S) and longitude $49^{\circ} 9'$ to $49^{\circ} 14'$ (W) . Altitude ranges from 916 to 975 m, with a subtropical highland climate, Cfb in the Köppen's classification. The difference between average precipitation and evapotranspiration is estimated in 955.7 mm per year.

The natural vegetation corresponds to the original area of Araucaria forest (Mixed Ombrophylous Forest) or forest with Araucaria (*Araucaria angustifolia*). Today we have Bracatinga reforestation (*Mimosa scabrella*) and pine (*Pinus sp*), the latter with little expression and situated in small plots.

In hydrograph terms, the watersheds are located in the headwaters of the Capivari River, which is part of the great basin of the coastal river Ribera de Iguape. This area is situated at south of Brazil.

The main economic activities are the extraction of non-metallic minerals (mainly dolomitic limestone for soil liming and burnt lime or quicklime by calcination) and horticulture, which is currently practiced intensively in small farms that have an average size of around 5 ha (Birth, 1997). (Figure 2). There are also corn and beans crops, these existing since 1952 (Klein, 1962) and they are kept up to the present days (Figure 3).

Figure 2. Horticulture areas.



For this work, the amount of nitrogen incident in watersheds was estimated by the total added by cultivated areas through fertilization, besides the amount of nitrogen that came from the houses together with the effluents. For this it was necessary to make a land use map to quantify horticulture areas and to analyze the quantities of incident nitrogen and organic chemicals that were input into the watershed, as well as to estimate the number of inhabitants living in that area.

Figura 3. Agricultural landscape



The land use map

This map was produced in a 1: 10,000 scale, based on the interpretation of aerial photographs (1:60,000 scale, in digital format, obtained in 1996), which were later expanded into a single charter (approximately 1:8,000 scale). We did field visits to verify the different land uses.

Nitrogen input estimation from house effluents

We estimated the resident population over the area in 1,200 inhabitants. This estimate was based on the

number of households seen in aerial photographs totaling 400 edifications, and considering 3 people per residence. This relative low number of inhabitants per house was to balance the counting of halls, small rural schools, stores, etc., i.e., non-residential buildings that are very difficult to separate from home buildings only by phointerpretation. With this demographic estimation we assess the total nitrogen input from human sources. This formula assumes that, on average, a person removes 13.2g of nitrogen per day, including urine and feces (Gloyna, 1973).

Estimation of nitrogen introduced by agricultural activities

It was possible to estimate the amount of nitrogen introduced into the area by agricultural activities through chemical fertilization (NPK formulation) and organic fertilization too, considering data from a survey carried out by EMATER, PR, in 1996, with 28 horticulturists that were representative of the area.

All the cultures kept over a period of one year were recorded and to calculate the nitrogen export, were considered: the productivity of individual producers, the number of crops per year and by bibliographical references, the average extractions of different cultures, in kg / ha or units / ha.

The source of organic nitrogen used was poultry litter (chicken manure with rice straw), which all farmers usually use. It contains an average of 3% nitrogen and 70% dry matter (Comitê de Fertilidade do Solo, 1977). It is necessary to keep in mind that organic nitrogen is not all readily available in the first year of implementation, but only after the second and third years. However, as the use of organic fertilizer occurs all years, it was considered 100% available.

The nitrogen surplus was weighted against the surface of each farm, also considering the fallow land areas and estimating the average values in kg / ha / year

that were obtained. These values were multiplied by the total cultivated area in the watershed, given by the interpretation of aerial photos.

Thus, the difference between the nitrogen added and extracted by crops is the total amount of nitrogen that may show retention, gaseous losses, erosion and leaching into groundwater.

RESULTS AND DISCUSSION

The following main types of land use are present: forests, agriculture, bracatinga reforestation and others uses (Pinus reforestation, araucaria woods with grass fields, secondary forest succession, pastures, mining and housing) (Table 1).

We can observe the large percentage of forested areas, including reforestation (about 45% of the total) with Bracatinga, and some areas with pine. These areas, in addition to presenting an ecological significance, are places where nitrogen pollution is negligible and, at the same time, areas that can be cleared and transformed into agricultural areas. This has been going to replace bracatinga areas by agricultural areas.

Considering the typologies that were found, agriculture and housing areas were considered places where nitrogen entries occurred effectively into the soil / water. An aggravating factor for nitrogen entry in soil/ water is that horticulture crops have very short cycles (2 to 3 months) and require high amounts of soil amendments. Thus, there are several different crops per year over the same field, exporting the added nutrients through leaves, tubers, flowers, lixiviation or gaseous losses. Moreover, there are frequent irrigations, even during rainy periods, once these shallow root crops are strictly dependent on water. Since fertilizers with nitrogen in nitrate form are highly soluble they can easily penetrate the wet soil and reach the aquifer and furthermore, the efficiency of nitrogen fertilizer is low and highly variable,

with around a 50% recovery of nitrogen fertilizer, while the remainder is lost by percolation, leaching and gaseous losses (The Fertilizer Institute, 1976).

Table 1. Area distribution according to typologies

| LAND USE | AREA (ha) | AREA (Km ²) | % TOTAL AREA |
|-------------|-----------|-------------------------|--------------|
| FORESTS | 643,8 | 6,44 | 38,6 |
| AGRICULTURE | 460 | 4,60 | 27,5 |
| BRACATINGA | 271,3 | 2,71 | 16,3 |
| OTHER USES | 293,3 | 2,93 | 17,6 |
| TOTAL | 1.668 | 16,68 | 100 |

The purpose of using organic fertilizers is to give the soil structure, improving its physical characteristics. However, considering calculate of nitrogen surplus, we realize that organic nitrogen, despite representing just 3% in litter, exceeded the amount added, via chemical fertilizers in 26 out of 28 estates. Some producers even add to the soil an amount of 15,000 kg / ha / year of organic matter, which is too much.

As a result the net average amount, weighted against the area of each producer, by acreage, was 207 kg / ha / year or 20.7 grams of nitrogen / m²/year. In Slovenia, Maticic, 1999, it was found that the net balance for the cultivated areas is less than 100 kg N / ha with an average of 56 kg N / ha, and in regions with high levels of livestock, the net excess in average 80 to 90 kg N / ha. The total nitrogen added by household effluents was estimated at 5,781.6 kilograms / year (13.2 g x 365 days x 1,200 inhabitants). Therefore, the total of nitrogen added by cultivated areas results in an annual addition of 101,000 kilograms over the basin.

From this value and assuming a specific average inter-annual flow rate of 9.0 l / s km² (Fraga, 1994), we can estimate the amount of potential (total) nitrogen that is being diluted in water. Within one year, a total of 4,735,310 m³ of water could potentially dilute 101,000 kilograms N per year in the 16.68 km² area of the river

basin. So, a concentration of 21.3 mg / L of nitrogen (NO₃-N) would be expected, which may add up to 94.2 mg / L of nitrate (NO₃) in groundwater.

This estimated value is very high, lying above the potability limit recommended by WHO (1992), which is 50 mg / L nitrate (10mg / L NO₃-N), and may have impact over the aquifer in terms of water quality . However, the nitrogen applied to soil can be absorbed by soil components such as: clays, organic matter, aluminum, iron sesquioxides, also lost through evaporation or be incorporated as organic N, and can also be liable to losses in soil erosion. More specific studies over the karst region focusing the behavior of nitrogen in the soil should better estimate the importance of each process. However, this work takes the following assumptions in terms of percentage of nitrogen converted to nitrate and leached into the soil, as shown in Table 2.

Table 2. Estimates of nitrate concentration in water related to various differential percentages of nitrogen transformation to nitrate

| % Nitrogen transformed into Nitrate and reaching the aquifer | Equivalent nitrogen (mg/L) | Equivalent Nitrate (mg/L) |
|--|----------------------------|---------------------------|
| 100% | 21,32 | 94,23 |
| 50% | 10,66 | 47,12 |
| 25% | 5,33 | 23,56 |
| 20% | 4,26 | 18,85 |

However, the analysis of waters sampled from springs in the karst region shows concentrations ranging from 2.19 to 8.97 mg / L NO₃, a level under the recommended restrictions for potability and well below the estimates in this work, even for an assumption of 20% nitrogen converted to nitrate and reaching the groundwater.

Rosa Filho et al. (2009) worked with the O18 isotope in a neighbor watershed and they observed that some of the springs had nitrate levels (NO₃) greater than 10 ppm, but in most cases the concentrations of this parameter vary from 2 to 6 ppm.

Despite the excellent quality of the aquifer waters, the intensification of agricultural use in this region may cause delayed effects if we consider the long permanency time. In assessments based on tritium, Rosa Filho *et al.* (2009) showed that the average residence time for underground waters there is not short, i.e. not smaller than 5 years.

Some considerations can be made to explain the large discrepancy between the amounts of expected nitrate contents and the nitrate really measured in the water. These differences may reveal an accumulation of nitrogen in the aquifer itself, a fact many authors observed, bound to be perceived in the future. Hrkal and Trouillard (1994) attested the stability of nitrate and the resulting accumulation of this element in the karst environment. For this verification, the mean water residence time throughout the aquifer, the amount of stored water, and the soil nitrogen storage should be known with respect to nitrogen.

The soil purification capability is a very important parameter, especially regarding its texture, as is well demonstrated by Beaudoin *et al.*, 2005. Also, differences in substrate are essential because the studied karst region is not homogeneous and in areas dominated by carbonate rocks, the aquifer's vulnerability is greater than others and also, the risk of groundwater contamination is higher. The study area has been mapped by COMEC – Curitiba Metropolitan Planning Agency (2009) and the most vulnerable areas were identified and mapped. Where the risk of groundwater contamination is greater, soil use for agriculture and urban-industrial purposes is not recommended. This study, established in GIS (Geographic Information System), is an important benchmark because it provides a subsidy for land use planning for others karst watersheds exploited for drinking water. Another factor to be considered is the partitioning of the karst's structures, the geological barriers represented by the dikes

that can concentrate pollutants in one place, or structural cells with aquiclude walls, as defined by Bonacim and Lisboa (1995), a study in the same region.

The impact caused by effluents from households, although resulting in 6% of the amount per volume of all the nitrogen introduced through organic and chemical fertilizers, is qualitatively very important because it is a punctual contamination, acting differently from agricultural contamination, which is non punctual, because the incidence of concentrated pollution reduces the chances of filtering by the soil. A problem is that these effluents are released into the soil by septic tank systems, which in karst areas are potentially harmful because the karst system has faults, fractures, ditches, sinks and some pits are near or over one of these configurations, soil depuration capacity becomes minimal or absent, so the generated pollution can reach the groundwater or the aquifer without prior purification, contaminating it with pathogens and nitrogen forms. This type of organic pollution is worse in this area due to the high prevalence of houses arranged next to each other, coming to form small linear villages along rural dirt and paved roads.

CONCLUSION

According to this work, the horticultural system employed in High Capivari watersheds has a large potential impact in terms of nitrate pollution. This kind of system requires frequent fertilization, due its continuous export represented by various crops harvested throughout the year, the excessive use of organic material and the need for frequent irrigation.

The rural domestic sewage, though on the whole less impressive when compared to agricultural systems, can be introduced through trenches, directly into the aquifer, with little chance of clearance, especially when the karstification starts close to the surface. Also, it is very important when they are situated in the landscape's

most vulnerable areas (uncovered karst). Thus, the active conservation of forest fragments becomes critical.

Measures to mitigate pollution from agricultural areas should involve some alternative land use management issues, including selection of cultural programs, irrigation, fertilization, organic matter management and other agricultural practices. Transforming horticultural conventional systems into agroecological systems could be a way to keep the rural population in the countryside with low impact over the productive activities.

Although the primary data used in this work were obtained before 1997, there was no substantial change in today's land use, even regarding the agricultural system practices. Therefore, we must consider that suburban areas still spread out and take over farmlands, which can be worse than only keeping horticultural activities.

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AUTHORS

Elenice Fritzsos

Agronomist, doctor in Forest Engineering. Researcher at Embrapa Florestas. Email elenice@cnpf.embrapa.br

Luiz Eduardo Mantovani

Geologist, doctor in Sedimentary Geology. Professor Federal University of Parana. Email lem@ufpr.br

Ernani Rosa Filho

Geologist, doctor in Hidrogeology. Professor Federal University of Parana. Email ernani@ufpr.br



Baixada Maranhense - Maranhão - Brazil

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