



Research paper

Fate of selected agrochemicals in a tropical karst aquifer: A five-year study



T.R. Aguiar Jr.^{a,b,c,e,*}, F.R. Bortolozo^a, E.F. Rosa Filho^a, L.M. Parron^c, L.D. Luz^e, A.G. Brito^d,
M.T. Ferreira^b

^a University of Lisbon, School of Agronomy, Department of Natural Resources, Environment and Landscape, Tapada da Ajuda, 1349-017 Lisboa, Portugal

^b Federal University of Paraná, Hydrogeological Research Laboratory, Centro Politécnico, 81990-551 Curitiba, Paraná, Brazil

^c Brazilian Agricultural Research Corporation - EMBRAPA, Forests Department, 83411-000 Colombo, Paraná, Brazil

^d University of Lisbon, School of Agronomy, Department of Biosystems Sciences and Engineering, Tapada da Ajuda, 1349-017 Lisboa, Portugal

^e Federal University of Bahia, Environmental Engineering, Centro Politécnico, 40210-630 Salvador, Bahia, Brazil

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ABSTRACT

Water contamination by agricultural pollutants is one of the major environmental problems for terrestrial and aquatic life on earth. Recent studies have demonstrated the contamination of karst aquifers by pesticides and agricultural nutrients. However, the predominant research does not adequately address the main destination of these compounds. Also, research is targeted primarily towards Europe and North America. The objective of this study is to assess the fate of selected pesticides along the saturated layers of a karst aquifer, located in a tropical area. During a five-year period, 48 monthly collections were conducted by extracting samples from 24 shallow wells (8–9 m depth) and 24 deep wells (55–60 m depth). A total of 2880 samples were obtained. For all samples physical-chemical and pesticide analyses were performed. We found the presence of atrazine, lambdacyhalothrin, lactofen, fluzifop-p-butyl, chlorpyrifos, nitrate and nitrogen agricultural nutrients. The wells with 8–9 m depth had the highest concentration of the compounds studied in relation to deeper wells at 55–60 m. A significant difference was found regarding the types of pesticide ($p < 0.05$) when comparing shallow and deep wells. Nutrients were also monitored and a decrease in the total nitrogen concentration between the wells with a lower depth (42.9 mg L^{-1}) and the deepest wells (1.2 mg L^{-1}) is observed along the period 2008–2013.

1. Introduction

Technological advances in the agricultural sector have provided many gains in crop production over the last decades (Chen et al., 2005). However, the intensive use of fertilizers and pesticides became a leading cause of groundwater and river ecosystems contamination, followed by domestic sewage discharges (Borin et al., 2005; Butler et al., 2008). This chemical contamination occurs in many regions of the world and it has been increasingly significant in fast growing countries where agriculture is an important basis of their economy and environmental controls are limited (Laabs et al., 2002). In general, compounds are transported via surface and groundwater flows, both in soluble form and adsorbed in colloidal particles (Chesnaux and Allen, 2008). The transport of colloidal particles depends on soil conditions and use of the soil (Einsiedl et al., 2005). High concentrations of nutrients in groundwater are directly related to vertical transport, especially in geological formations where the water circulation is made throughout fractures and other discontinuities. Such preferential flowpaths can result from carbonate dissolution by water (Kevin and Victor, 2014). These characteristic geostructures are named karst aquifers and reveal a

high conductivity through perpendicular fractures (Chesnaux and Allen, 2008). In Brazil, as in many other regions, farming production is very dependent on water abstracted from wells, frequently located in zones where pesticides are intensely applied (Laabs et al., 2002; Chesnaux and Allen, 2008). In addition, leaching to the aquifers is amplified due to the precipitation regimen in such areas (Kevin and Victor, 2014).

Among the most used biocides for plant protection and agricultural production, these ones can be emphasized: atrazine, glyphosate, 2,4-D fluzifop-p-butyl, lactofen, lambdacyhalothrin and lactofen. The fluzifop-p-butyl is a herbicide used for post-emergence control of wild oats and cereals, as well as annual and perennial grassy, rape, beet, stone fruit, vines, alfalfa, ornamental plants and other broad-leaved crops. The fluzifop-p-butyl persistence depends on soil moisture. Laabs et al. (2002) reported that only 8% of fluzifop-butyl remained after 48 h in wet soil conditions, while over 90% remained in dry soils. Fluzifop-p-butyl has a relatively low toxicity to birds and mammals, but can be highly toxic to fish and aquatic invertebrates, especially when associated with other herbicides (Borin et al., 2005). Fluzifop-p-butyl is hydrolyzed to fluzifop-acid, which is stable in water and is highly

* Corresponding author at: University of Lisbon, School of Agronomy, Department of Natural Resources, Environment and Landscape, Tapada da Ajuda, 1349-017 Lisboa, Portugal.
E-mail address: terenciojunior@gmail.com (T.R. Aguiar).

toxic. Lactofen is an herbicide from the chemical group diphenylether. It has low persistence in most types of soil, with a half-life ranging from 1 to 7 days. It also has low degradability by hydrolysis and photolysis but high microbial degradability (Borin et al., 2005). Lactofen is strongly adsorbed by organic and mineral colloids and has a low leaching capability in the soil profile and can be very toxic to fish and invertebrates (Aguiar et al., 2015). Lambda-cyhalothrin is an insecticide of the pyrethroid group with lipophilic properties. It is used to control a broad spectrum of organisms, such as aphids, bugs, thrips, larvae of Lepidoptera and Coleoptera in soil, or foliage including several crops types, ornamentals and woods. Lambda-cyhalothrin becomes easily adsorbed in the sediment and has low mobility in the soil profile (Ramsey et al., 2005). Chlorpyrifos is an insecticide from the organophosphates group and tends to adsorb and become immobile in the soil, but is also prone to bioaccumulation (Foster et al., 2002). Atrazine is used in pre-emergence situations. It has a high persistence in the environment along with the ability to interfere with the neuroendocrine and reproductive system, presenting carcinogenic potential (Johnson et al., 2000), inducing prenatal anomalies (Foster et al., 2002). Degradation is controlled by hydrolysis and by microorganisms' activity and occurs at a higher rate in strong acidic (Laabs et al., 2002).

Several authors (Putnam et al., 2003; Einsiedl et al., 2005) have shown the potential of the saturated soil zone to mitigate contamination due to chemical and physical interactions and biological degradation. However, in karstic aquifers the residence time is mostly short and contamination risks are more significant. Consequently, long term monitoring in karstic zones where tropical agriculture practices occur is necessary in order to assess contamination risks and to define better remediation strategies. Therefore, the goal of the present study is to assess the fate of pesticides atrazine, lambda-cyhalothrin, lactofen, fluzifop-p-butyl and chlorpyrifos along the saturated zone of a karst aquifer located in a tropical area. The monitoring sampling was carried out over a five-year period, at two soil depths in 48 wells.

2. Material and methods

2.1. Climatic and geological context

The study area is located in southern Brazil, in Ribeira and Capivari river basins and has a total area of 85 km² (Fig. 1). The area is occupied by Atlantic forest and according to the Koeppen climate system, it is characterized by temperate rain, and an annual average temperature of 16.9 °C (maximum average 28.9 °C and minimum average 10.8 °C) (Aguiar et al., 2014). Mean annual rainfall is approximately 1400 mm. Rainy season is concentrated in December, January and February months, while the driest months are June, July and August.

The region is dominated by metamorphic rocks of the Açungui Group, formed in the upper Proterozoic and constituted by the formations: Capiru, Votuverava, Antinha, Itaiacoca and Abapã (Bigarella and Salamuni, 1956). The Capiru formation, in particular, consists of dolomitic marbles, phyllite, quartzite, metasilstone, meta-argillite and metarenite (Bigarella and Salamuni, 1962). Groundwater is stored in karst structures that were developed in carbonate rocks with intrusion of diabase dykes. The carbonate rocks are represented by a metasedimentary sequence consisting of calcite marble and dolomite rocks intercalated silicate composition as phyllite and quartzite (Bigarella and Salamuni, 1956). The diabase dikes are several hundred meters deep and are practically impervious (Einsiedl et al., 2005). The top layer of the carbonate rocks of the aquifer (near the relief) marks the transition between those and silicate rocks, being covered by colluvial soils and formations, whose thickness and hydraulic conductivity are respectively in the order of 15 m and $1 \times 10^{-9} \text{ m s}^{-1}$ (Bigarella and Salamuni, 1962). In the most recessed portions of the land, sinkholes occur and coalesce to the point that in some situations, there is a direct recharge of the aquifer structures by rainwater (Bigarella and Salamuni, 1956).

2.2. Sampling and analysis methods

Along the 2008–2013 period, 48 monthly campaigns were carried out. The spatial sampling scheme was comprised by 24 shallow wells (8–9 m in depth) and 24 deep wells (55–60 m in depth). This totaled 2880 water samples collected. Some physical-chemical parameters were monitored in-situ by using a multi-parameter AP-7000 AquaProbe: pH, dissolved oxygen, electrical conductivity, Oxidation-Reduction Potential (ORP), salinity and temperature. The water samples were stored in polypropylene bottles and preserved at 4 °C. The following parameters were assessed in the laboratory: nitrogen (N), phosphorus (P) potassium (K⁺), nitrates (NO₃-), nitrite (NO₂-) and phosphate (PO₄³⁻), total alkalinity (CaCO₃), total hardness (CaCO₃), free carbon dioxide (CO₂), total dissolved solids, acidity, bicarbonates (HCO₃⁻), carbonates (CO₃²⁻), chloride (Cl⁻), fluoride (F⁻), sulfates (SO₄²⁻), calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺) and dissolved silica (SiO₂). Analyzes were performed according to Standard Methods (APHA et al., 2005). Pesticides residues were extracted using method proposed by Lacorte et al. (2000) modified by Aguiar et al. (2015) and in compliance to the SANCO/10232/2006 EU protocols. The physical and chemical properties of pesticides are described in Table 1.

2.3. Statistical analysis

Hypothesis testing of different samples was employed using analysis of variance (ANOVA) and mean values were compared by least significant difference (LSD) at the 5% level using the Origin Pro 9.0 (OriginLab Corporation, USA).

3. Results

3.1. Hydrochemical characteristics

Taking into consideration the composition of the Karst aquifer, a classification using the Piper diagram was used as a model for the sampling points. In the 55–60 m deep wells, samples were classified as bicarbonate-calcium-magnesium type water HCO₃²⁻. The predominant anions were observed at concentrations between 219 and 439 mg L⁻¹. The average hardness values were 205.1 mg L⁻¹ (± 7.6); which corresponds to moderately hard water. The average flow in these wells was 90 m³ h⁻¹. The water samples present in the wells with a depth 8–9 m had low mineralization HCO₃²⁻ with concentrations between 19 and 69 mg L⁻¹, and were classified according to Piper diagram as soft water from the zone saturated soil.

Despite the fact that sampling was carried out during rainy and drought periods, the rainfall index was similar along such periods. Results indicated an index ranging from 30 to 80 mm in the rainy season to 28–75 mm in the dry season. There was no significant difference between the two periods ($p > 0.05$). However, there were significant differences ($p < 0.05$) between physical-chemical results of the collection points located at depths of 8–9 m and the ones at 55–60 m for conductivity ($\mu\text{S cm}^{-1}$ at 25 °C), total hardness (CaCO₃), nitrates (NO₃-), bicarbonates (HCO₃-), calcium (Ca²⁺) magnesium (Mg²⁺), sodium (Na⁺) (Table 2). There were no significant differences ($p > 0.05$) for the nutrients potassium (K⁺), fluor (F), chlorine (Cl), phosphate (PO₄-3), total iron (Fe), and nitrites (NO₂) (Table 2).

A decrease in the total nitrogen concentration from the wells with the lower depth (42.9 mg L⁻¹) to the deepest wells (1.2 mg L⁻¹) is observed in Fig. 2 and Table 3. This reduction also occurred for the nitrate ion where concentrations fell. The first ones fell from 17.1 mg L⁻¹ down to 3.1 mg L⁻¹. In the latter ones for ammonia nitrogen, there was a reduction of 0.76 concentrations to 0.03 mg L⁻¹.

A significant difference was found regarding the types of pesticides ($p < 0.05$) when comparing the shallow and deep wells and along the period 2012–2013. Indeed, there was a pesticide concentration increase over the years. In Fig. 3 shows the pesticide removal percentage between the shallow and deep wells.

The fluzifop-p-butyl and chlorpyrifos pesticides maintained similar

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