

Monitoring of N-Methylcarbamates and some of metabolites in water the lake the Furnas, Minas Gerais, Brasil

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Abstract – The lake of Furnas, the largest manmade in Brazil, is officially designated by the State of Minas Gerais as and important role economic, supply energy electric long of the to attend activity fishing and water has been at source irrigation annual the potato, corn, bean, coffee and sugarcane intensive agriculture. The purpose of this study was to determine aldicarb, aldicarb sulfone, carbaryl, carbofuran, 3-hydroxycarbofuran and methomyl in surface water. Water samples were taken for the period from October 2003 to March 2004 to describe and compare the occurrence and distribution of pesticides in agricultural area. Water samples were most frequently contaminated by carbofuran and 3-hidroxicarbofuran compounds, carbaryl, methomyl, aldicarb and aldicarb sulfone, although in low ($0.1 \mu\text{gL}^{-1}$) concentrations. However, the January through March samples exhibited of all pesticides and metabolites, with concentrations to 0.10 to 120.00 ngL^{-1} . These results underscore the need to improved environmental protection measures.

Key-words – water analysis; environmental monitoring; environment contamination.

I. INTRODUCTION

The reservoirs include on na área of around of the 1.500 Km^2 of the surface, storing a total capacity of around 768 m and perimeter the 3.500 km . Within this region are located 34 city of the population 800.000 in live. The lake de Furnas is the largest manmade in Brazil. Because of these multiple uses, insecticides contamination lake de Furnas may adversely impact both the natural and social ecosystems of the study area. The purpose of this study was to evaluate insecticides N-methylcarbamates and some of their metabolites concentrations in surface water from the lake Furnas.

The experimental site ($21^\circ 35' 8''$ southern latitude, $46^\circ 10' 5''$ western longitude) is situated about south of state Minas Gerais in the south-east of Brazil (Fig. 1). Its climate is of the tropical type, with a distinguished rainy (september – march) and dry period (april-august).

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The mean annual precipitation is ca. 1500 mm , and annual is 20°C temperature and 65% humidity. A confirmation residue was performed with LC-MS/MS (API 4000- Applied Biosystems/MDS Sciex, Concord, CA, Agilen. 1100 series, injection automatic, ionization TurbolonSpray, software Analyst 1.3.2. The results are expressed as mean \pm standard deviation. The data were tested for homogeneity of variances at significant level of $p < 0.05$.

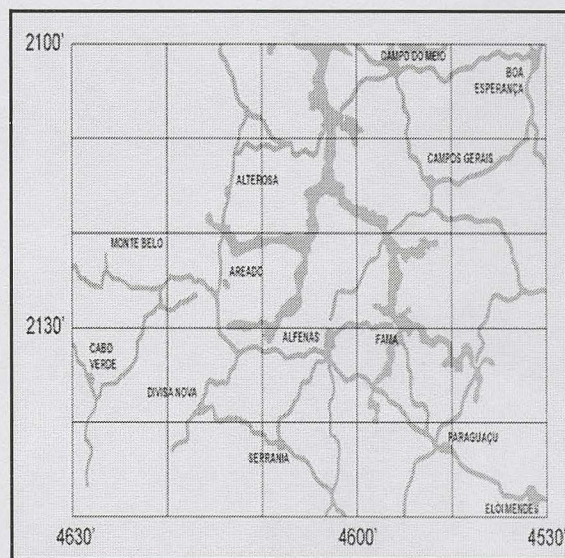


Fig. 1. Location of the studied field sites in Lake Furnas.

II. RESULTS AND DISCUSSION

Lake water samples of months the october until december generally did not contain significant amounts residues of the all pesticides and the suspended sediments, although turbidity in these lake is known to increase strongly during rain events [1]. We attributed this finding to the fact that most the lake banks in the study area were covered by swampy grassland, which accompanied the lake in 5 to 50 m wide strip. Thus a continuous input of soil particles to the water body by surface runoff was present, during heavy storm events these months. The concentrations of individual pesticides measured in surface water of the study area of the never exceeded $0.1 \mu\text{gL}^{-1}$ (established limit by laws of the European Community and for drinking water by the [2]). The The variability in

concentration rates for N-metycarbamates in the October until December samples suggests that differences in other parameters, such as microbial populations or water chemistry, could be responsible for the variance. In the period was detected at low concentrations of (0.02 at 8.80 ngL⁻¹) the all pesticides; its parent compounds could not be detected any more above their limit of quantification. However, in comparison with data from sampling sites lake de Furnas, some pesticides occurred at similar at slightly higher concentrations in the region de study (methomyl, carbofuran). Possibly, the main riverine flux of these pesticides, which are applied at the very beginning of the rainy season (October to December), carried on to the lake Furnas study of in the area. Carbofuran was applied in the study onto bean, potato, sugarcane, corn field by plane, which presumably accounts for the frequent detection in water samples. Factor that might explain these results include concentration the pesticide probably, surface runoff lake bank vegetation caused a major part of the observed contamination. Carbofuran compound studied pesticides in water resources, except for some formerly used organochlorine pesticides was detected most frequently in the lake of Furnas throughout the study period with maximum concentration of 0.10 and 8.80 ngL⁻¹. Our results compare well with water concentrations of the carbofuran detected of the 1μL⁻¹ was found in streams in the USA [3] in the USA ranged from 1 to 30 μgL⁻¹ [4]. The frequent detection of polar like methomyl, carbaryl and aldicarb at low concentration throughout the study period points to a continuous input of pesticides subsurface flow from fields to the surface water. Probably, spray drift and wash-off from lake bank vegetation caused a major part of the observed contamination. A general knowledge has been investigated soil properties and sorption of the compounds. For transformation product, the degradation in soils or sediments depends on the pH. The aldicarb at neutral pH, the degradation half-life is < 7 the 11 days, while at a slightly acid pH (<6.2) the degradation half-lives increase to 1300 days [5]. These assumptions were supported by finding that these pesticides were detected in water samples free of suspended sediment, indicating that surface runoff from fields did not contribute to the measured contamination of lake with pesticides in this case. In contrast, readily degradable substances, such as aldicarb sulfone and 3-hidroxicarbofuran, have were below limit of quantification. In general, the measured pesticide concentrations in lake were low 0,02 ngL⁻¹ at a carbaryl. In general, the measured pesticides concentrations in lake no period at a October and December were between 2,44 and 0,02 ngL⁻¹. A smaller number of pesticides were detected in lake water (4 different compounds and metabolites) we attributed this findings to an elimination of easily degradable substances such aldicarb, carbofuran [6] the riverine transport, or to dilution effects (e.g., methomyl, carbaryl). Different pesticides pose varying degrees and types of risk to water quality. To predict the leaching potential of pesticides in soils, various coefficients involving the key parameters key parameters $t_{0.5}$ and K_{oc} of pesticides have been proposed [7]. We conclude that risk-assessment tools, yet (GUS>2.8), transitional (1.8 <GUS.2.8), and nonleacher (GUS<1.8) compounds [7]. The,

we conclude that interpretation of results the pesticides used in the area under investigation is possible leaching in soils. The ranking results are in agreement with the findings of many field studies from temperature regions reporting that in spite of preferential flow transport of pesticides, the total amounts leached correlated to mobility characteristic (e.g., soil sorption coefficient, water solubility of pesticides [8]. In contrast, with lake water monitoring studies from the January until March at 2004 shown were contaminated by pesticides, with up to all compounds present in one sample. The all frequently detected insecticides were carbofuran, methomyl, carbaryl, aldicarb and metabolites aldicarb sulfone, 3-hidroxicarbofuran. Of all samples taken, 100% were contaminated by pesticides, with up to six compounds present in one sample. The most frequently detected insecticides and metabolites were carbofuran and 3-hidroxicarbofuran and carbaryl. It is noteworthy that also the aldicarb, aldicarb sulfone and methomyl were detected in more than of the analyzed samples. The frequent detection of carbofuran at high concentrations in lake water. The high detection frequency and high concentrations of carbofuran in lake water samples at the all sites was attributed to the regionally intense cultivation of sugarcane, coffe, corn, bean and potato in the upper basin of the lake of the Furnas. There, carbofuran was exclusively used in larged-sized sugarcane plantations, where it was also applied in direct vicinity to the lake banks. The frequent detection of 3-hidroxicarbofuran at high concentration in month February e march in monitoring studies. These results corroborated the finding of that generally higher intermediate concentrations of pesticides carbofuran [9]. Yet, also a more intensive use of these pesticide in other subcatchments of the greater lake watershed than in the sampled ones can explain our results. Otherwise, the pesticides spectrum at the all sites was characterized by the frequent detection smaller of the carbaryl. A smaller concentration of pesticide was detected in lake water we attributed to the regionally used only of the potato culturerb sulfone at high concentrations in all sites was attributed of easily degradable do carbaryl at the lake Furnas was sampled once of the month. Aldicarb sulfone was shown to be second metabolite of aldicarb degradation in aquatic systems [10]. In comparison with monitoring studies from temperate regions [11], measured mean concentrations in tropical samples water 5 to 10 fold lower for many compounds. This may be attributed to a generally higher land-use intensity in such agricultural centers of temperature and rains regions, like the upper lake de Furnas (Fig. 2). The relatively frequent detection of polar pesticides aldicarb, methomyl and, in comparison with the one of carbofuran and carbaryl, in tropical lake points to an increased dispersion of these more low adsorption coefficient, high water solubility, low vapor pressure, in the studied tropical environment. Yet, their relative intensity of use, as well as their application mode in granular, aerially application of insecticides in the study region, may also play an important role in this respect. Attention must be taken to the case of samples water with high level of N-methylcarbamates during certain periods of the year (beginning of January until the end of March). In the site of water samples contained detectable residues, mostly in

higher concentration. In particular, the dominance of carbofuran, 3-hydroxycarbofuran and carbaryl were detected in the smaller 3.28 ngL⁻¹ at higher 120.00 ngL⁻¹ of the 3-hydroxycarbofuran metabolite. Carbofuran was detected at concentrations (11.2 at 115.00 ngL⁻¹); it parent compounds were detected more often and at similar or higher

concentrations in water samples. Its is very difficult to compare our results with those of other monitoring programs from other countries because the range pesticides losses predicted from this procedure reflect only the relative ability of the soil to retain the pesticides at the point of application.

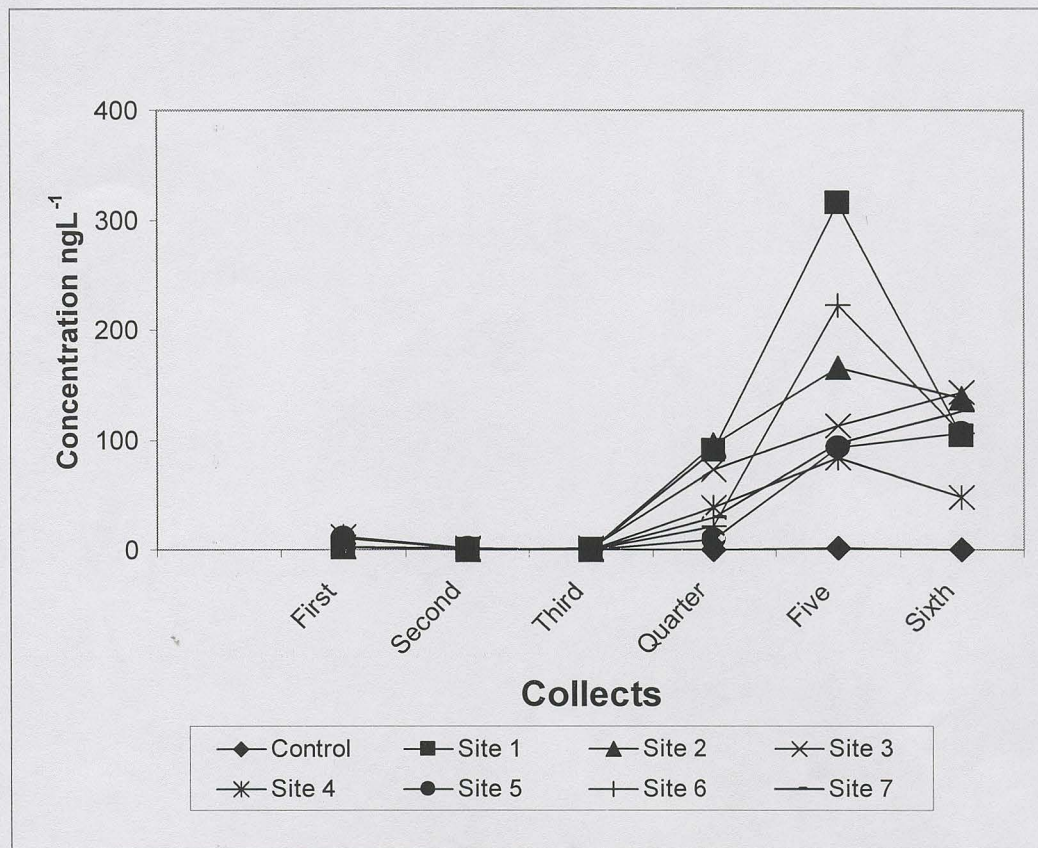


Fig. 2. Detection frequency, concentration (ngL⁻¹) of the N-Methylcarbamates and some of metabolites in water of lake Furnas (sampling period October 2003 to March 2004).

As already noted for [12], the interplay of climate and application method determined whether the leaching or surface loss potentials are reached in a given area. However the results our study showed concentration rates reported of the sites, and evidence of the exposed wide variety of nontarget animais, plants, and microorganisms are affected by N-methylcarbamates exposure. Although, for water, a general concentration of 0.1 ppb was determined by European Union Legislation with the extra restriction that the total amount of all pesticides may not exceed 0.5 ppb. In this our study, 100% of the cases smaller than 0.1 ppb samples water all sites. However, studies from temperatures regions [13], [14], a testing program for potable near potato fields reported mean of the 7µg/L of the samples water. It is evident that among various factors regulating behaviour of pesticides in soils, waters, quantity and quality organic matter and

climatic conditions are very important. Both of these soil properties waters, quantity and quality organic matter and climatic conditions are very important. Both of these soil properties vary significantly between different agroclimatic regions. Other items of special interest or importance were during the of decades of using pesticides the main problem was the risk of acute intoxication among people occupationally exposed to them. With the decrease of acute toxicity of improved pesticides, attention was turned to chronic intoxication and environmental contamination. The toxic effects of pesticides can occur through residues in drinking and surface waters and in the food we eat – fruits, vegetables, bread, meat, fish, cereals and processed foods made from them. Although these residues are consumed only in small amounts, there are certain circumstances and practices that will increase consumption. Pesticides use is

controlled by national regulation, generally a system of registering each pesticide, formulation for a specific use and crop. Approvals are based on evaluation of efficacy, user and consumer safety, and environment impact. Most industrialized countries have also established laws setting the Maximum Residues Levels (MRLs) that are permitted in food, and which apply to food produced domestically and imported. Moreover, the of result the our study suggest to consider the potential health risk that dietary pesticides poses to consumers, should be evaluated: the local diet, the residues in food, the maximum residue level permitted (MRL) and the accepted daily intake (ADI) for the pesticide [15], [16]. In addition, similarlies studies [17] of N-methylcarbamates compounds in vegetables, fruits with 0.37 ppm median concentration. Generally the use of a pesticide will lead to residues in food and provided the pesticide is use according to the manufacture's label directions and Good Agricultural Practice (GAP), regulators calculate the residue should be within the MRL and ADI. Throughout the world, the heavy use of pesticides is causing millions of human poisonings and several thousand deaths each year, especially in developing countries. Thereby pesticides appear to have a greater impact on human health and the environment. Governments and the public policy makers must therefore find ways to protest human health and the stability of the environment from the pollution created by the heavy use of agricultural chemicals.

III. CONCLUSION

Our monitoring study showed evidence of the distribution of a broad spectrum of pesticides in the lake de Furnas. Of the 4 pesticides and 2 metabolites investigated of the october the 2003 at march at 2004 were detected in environmental samples water: aldicarb, aldicarb sulforne, methomyl, carbofuran, 3-hidroxicarbofuran and carbaryl. Generally the concentrations were not of concern, the percentage distributions of the carbofuran, methomyl and carbaryl compounds were detected in october until december the 2003. Although the amounts of carbofuran in water samples mean 8.80 ngL^{-1} , were not found concentration by metabolites. However, water samples in the januaire until march the concentration of the all pesticides (0.10 to 120 ngL^{-1}) were detected at all sites in the lake Furnas. Higher concentrations for three pesticides (carbofuran, methomyl and carbaryl) include of the 3-hidroxicarbofuran metabolite were detected in water samples. The concentrations were not of concern, but did demonstrate different distributions reflecting differing agricultural usage in the region. The concentration of the carbofuran and metabolite ranged from 115 and 120 ngL^{-1} , respectively, with the highest amounts in the region of lake Furnas. Pesticides applied in agriculture may lead to the occurrence of transformation products in aquatic ecosystems with a potential our actual similar or higher risk than their parent pesticide. There is considerable public concern about potential adverse impacts of pesticide used on ecosystem and human health. It is evident that among

various factors regulating behaviour of pesticides in soils, waters, quantity and quality organic matter and climatic conditions are very important. Both of these soil properties vary significantly between different agroclimatic regions. Management decisions encouraged increasing levels of artificial fresh-water recharge and use for drinking purposes at expense of agricultural, recreation and natural environment enhancement. These results underscore the need to improved environmental protection measures in order to reduce the exposure and to evolve a strategy to manage the hazards due to theses group of pesticides.

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