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REMOVAL OF DIURON AND HEXAZINONE FROM GUARANY AQUIFER GROUNDWATER

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Abstract - The economy of many communities in southeastern Brazil is based on agroindustry, particularly the sugarcane industry. Recent studies have found increased use of herbicides in this type of agriculture, among which diuron and hexazinone are the most widely used. The water supply for some communities is derived entirely from the Guarany Aquifer (the world's largest transborder underground freshwater system), and some wells are located in recharge zones, which makes the groundwater more vulnerable to contamination. In this study, we monitored some of the wells located in the recharge area. We studied the removal of diuron and hexazinone from synthetic water prepared in the laboratory by preoxidation with chlorine and chlorine dioxide, as well as adsorption with granular activated carbon (GAC). The saturation time of GAC in tests with preoxidation with both oxidants was shorter than the saturation time in the test without preoxidation, possibly due to the formation of by-products that competed for the adsorption of the herbicides. The conclusion was that the use of activated carbon is important for removing the herbicides in question, as well as the by-products produced by these oxidants.

Keywords: Diuron; Hexazinone; Granular activated carbon; Groundwater; Guarany Aquifer.

INTRODUCTION

Driven by the need to reduce greenhouse gas emissions, Brazil has invested successfully in ethanol production from sugarcane, as ethanol is one of the few economically and environmentally sustainable alternative fuel sources. Ethanol accounts for approximately fifty percent of the green fuel that powers Brazilian vehicles and has the advantage of producing less carbon dioxide than gasoline, a substantial part of which is reabsorbed by subsequent sugarcane crops.

The region of Ribeirão Preto, located in the state of São Paulo in southeastern Brazil, is the country's largest producer of sugarcane-based ethanol. According to Cerdeira *et al.* (2005), in the last decade, atrazine, simazine, ametryn, tebuthiuron, diuron, 2,4-D, picloram, and hexazinone have been the main herbicides used in this area. This region is also an important recharge zone for groundwater replenishment of the Guarany Aquifer. Figures 1 and 2 show schematic maps of the Guarany Aquifer. The recharge area and the predominant land use in this area are highlighted in the maps.

Currently, one hundred percent of Ribeirão Preto's urban population (approximately 620,000 people) is supplied with water from the Guarany Aquifer through 100 artesian wells, some of which are located at aquifer recharge points and close to the sugarcane plantations. The vulnerability is further aggravated by the high permeability of some of the soils in this region and the high mobility of herbicides and fertilizers.

Several research studies have been performed to verify the presence of the pesticides ametryn, atrazine, simazine, tebuthiuron, and diuron in the recharge zone of the Guarany aquifer (Cerdeira *et al.*, 2005; Lanchote *et al.*, 2000; Cerdeira *et al.*, 2004

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*To whom correspondence should be addressed and Cerdeira *et al.*, 2007). None of these studies found evidence for residues of the aforementioned pesticides in samples collected from the Guarany aquifer. However, in all of the studies, the authors emphasized that there was a potential risk of contamination. The Ribeirão Preto recharge area, in particular, was classified as a high risk location due to the large quantities of pesticides used in the region (Cerdeira *et al.*, 2005). Table 1 summarizes the technical information for diuron and hexazinone.

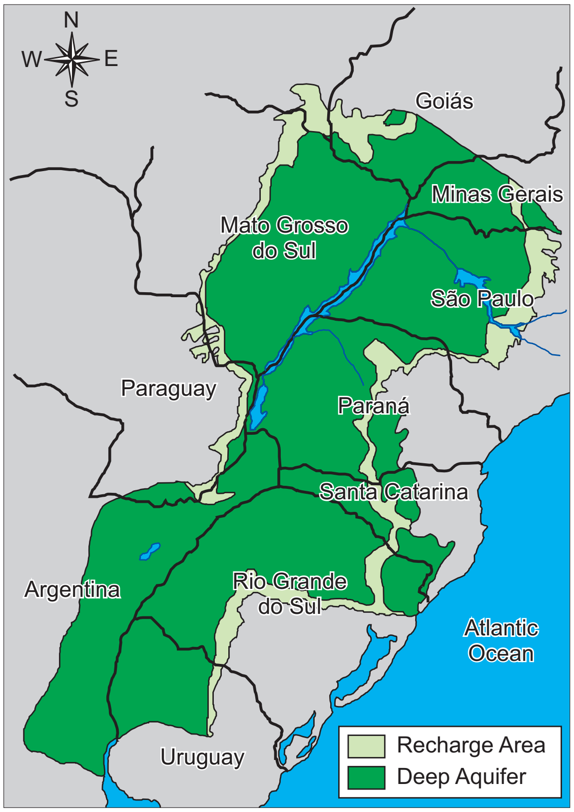


Figure 1: Map of the recharge area in the Guarany Aquifer (Borghetti and Borghetti, 2004)

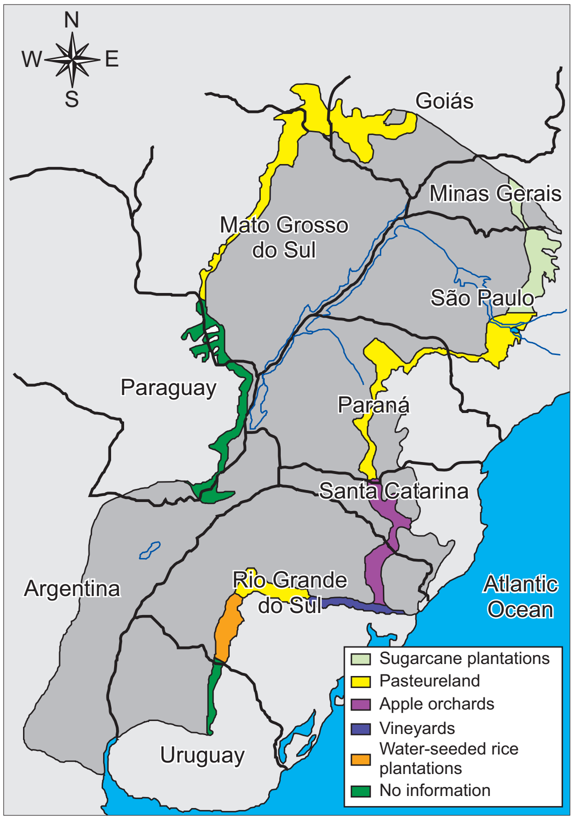
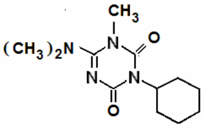
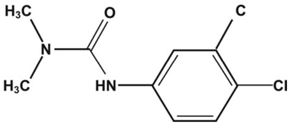


Figure 2: Map of the predominant agricultural activity in the recharge areas of the Guarany Aquifer (Borghetti and Borghetti, 2004)

Table 1: Technical information for diuron and hexazinone

	Hexazinone	Diuron
IUPAC	3-ciclohexyl-6-dimethylamino-1-methyl-1,3,5-triazina-2,4(1H,3H)-dione	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Formula	$C_{12}H_{20}N_4O_2$	$C_9H_{10}Cl_2N_2O$
CAS	51235-04-2	330-54-1
Activity	herbicides (triazine herbicides) pre- and post-emergence control of grassy weeds in sugarcane plantation	algicides and herbicides (phenylurea herbicides) Pre- and post-emergence control of grassy weeds in cotton, coffee, sugarcane and citrus plantations
Toxicity classification (ANVISA, 2008)	Class III - slight toxicity	Class IV - low toxicity
Structure		
Solubility in water	29.8 $g.L^{-1}$	42 $mg.L^{-1}$

Directive 518, which is Brazil's standard for acceptable contaminant levels for drinking water (Brazilian Health Department, 2004) does not establish a limit for the use of the herbicides diuron and hexazinone. However, several international regulations and standards limit the maximum concentration of these herbicides in treated water. For example, Canadian standards allow a maximum diuron concentration of 150 $\mu g.L^{-1}$ and Australian regulations allow a maximum admissible hexazinone concentration of 300 $\mu g.L^{-1}$ (Hamilton *et al*., 2003). Diuron is classified as a "known/likely" human carcinogen, and it is on the United States Environmental Protection Agency's Contaminant Candidate List (U.S. EPA, 1998). According to the Council of the European Union (Directive 98/83/EC, 1998), the maximum admissible concentration for either pesticide is 0.1 $\mu g.L^{-1}$ and the overall concentration allowed in drinking water is 0.5 $\mu g.L^{-1}$.

According to Chen and Young (2008), diuron is one of the most widely used herbicides in California, USA, and it has frequently been detected in the water supply of this state. Their study suggested that diuron may be a precursor in the formation of nitrosodimethylamine (NDMA). NDMA is a compound in a family of N-nitrosamines, which have high carcinogenic potential. Shwarzenbach *et al*. (2006) reported that several technologies have been used for the removal of micropollutants in the presence of organic and inorganic matrices in water, including chemical oxidation, adsorption, sedimentation, and filtration. Chiron *et al*. (2000) concluded that the degradation products formed during advanced oxidation processes (AOPs) of hydrophobic pesticides are often more polar and more bioavailable than the original contaminants. Because a treatment is usually not considered to be acceptable until it achieves complete compound mineralization, there is a need to couple AOPs to biodegradation or other suitable processes to completely eliminate the contaminants. Activated carbon adsorption is a technology that has been successfully used for the removal of pesticides according to studies carried out by Najm *et al*. (1991), Petrie *et al*. (1993), Pelekani and Snoeyink (1999) and Matsui *et al*. (2002).

In this context, a question arises regarding the extent to which the production of sugarcane-derived ethanol can be expanded without impacting natural resources. In the present study, we monitored water quality in four wells in Riberao Preto over a one-year period, two of which were located in recharge areas close to sugarcane plantations. We measured amounts of hexazinone and diuron in the water and also evaluated the removal of these herbicides from laboratory-prepared water using granular activated carbon adsorption and preoxidation with chlorine and chlorine dioxide.

EXPERIMENTAL

The herbicide used to prepare the contaminated water was the commercial product Velpar K WG (DuPont Brasil Produtos Agrícolas). The herbicide contains both diuron (46.8% wt/wt) and hexazinone (13.2% wt/wt) as well as inert compounds. Two analytical techniques were used to measure this product as described below.

In the preliminary tests to select the best GAC for adsorbing the herbicide Velpar, the residue was measured with spectrophotometry. To construct the calibration curve, a solution was prepared with a concentration of 25 $mg.L^{-1}$ of the commercial herbicide. The solution was scanned in the ultraviolet region (200 to 350 nm) in a Varian, model Cary 1E spectrophotometer. The calibration curve was constructed using the wavelength that resulted in the maximum adsorption (λ = 250 nm).

In the other tests, the compounds diuron and hexazinone were quantified by using a gas chromatograph/nitrogen phosphorus detector (GC/NPD). The method we employed was adapted from the U.S. EPA (1995).

The halogenated organic by-products (HOB) were determined by using gas chromatography with electron capture detection, following the technique recommended by the U.S. EPA (1995). The following by-products were investigated: (i) trihalomethanes: chloroform, bromodichloromethane, dibromochloromethane, bromoform; (ii) haloacetonitriles: dichloroacetonitrile, trichloroacetonitrile, dibromoacetonitrile, tribromoacetonitrile, bromochloroacetonitrile; (iii) halopicrines: chloropicrine; (iv) haloacetones: 1,1-dichloropropanone, 1,1,1-trichloropropanone; and (v) trichloroacetaldehyde or chlorine hydrate.

The monitored wells were selected with guidance from the Ribeirão Preto Water and Sewage Department. Four wells were evaluated twice a week for a ten-month period. The monitored wells were identified as: Well 1 – located in a recharge zone in an area without sugarcane plantations; Well 2 – located in rock close to a sugarcane plantation; Wells 3 and 4 – located in a recharge zone close to a sugarcane plantation.

Adsorption studies were carried out using commercial granular activated carbon from three sources (coconut, wood and babassu palm) to select the most efficient source for hexazinone and diuron removal. Activated carbon samples were obtained from conventional carbonization and activation with steam at high temperatures (Bansal and Goyal, 2005; Bandosz, 2006).

The carbon samples were characterized in terms of pH and iodine number. Carbon samples with grain sizes smaller than 325 mesh were chosen for this study. The iodine number was determined according to the standard test JIS K 1474 from the Japanese Industrial Standards (1991).

For the preliminary adsorption tests, ten samples of each GAC were weighed (1, 2, 3, … 10 mg) and placed in ten glass flasks. Then 10 mL of phosphate buffer solution (pH = 7.0) and 40 mL of deionized water were added to the flasks. These samples were placed in a vacuum for 3 h. Following this step, 50 mL of a 50 $mg.L^{-1}$ solution of commercial herbicide were added to each flask, resulting in 25 $mg.L^{-1}$ in the solution. The flasks were placed on a laboratory shaker operating at 160 rpm for 2 h. All the experiments were carried out at a constant temperature (25 ± 1^oC). Once the adsorption tests were completed, the samples were filtered through Whatman 40 paper and through 0.45 μm membranes. The final concentrations of the commercial herbicide were determined by spectrophotometry. The GAC used in the pilot unit (PU) was selected based on these results.

The synthetic water for the pilot installation was prepared by mixing water from the artesian well located at UNAERP (Guarany Aquifer) with 50 $mg.L^{-1}$ of the commercial product Velpar (23.4 $mg.L^{-1}$ of diuron, 6.6 $mg.L^{-1}$ of hexazinone and 20 $mg.L^{-1}$ of inert compounds).

Preliminary tests were performed to determine the dosages of chlorine and chlorine dioxide to use for the preoxidation process. The preoxidation tests with chlorine and chlorine dioxide were carried out with a contact time of 30 min and the dosages ranged from 0.1 to 2.5 $mg.L^{-1}$ of chlorine (calcium hypochlorite solution) and 0.25 to 1.5 mg L^{-1} of chlorine dioxide (which was generated from sodium chlorate, hydrogen peroxide and sulfuric acid).

The residual oxidant value used for selecting the chlorine and chlorine dioxide dosages was approximately 0.10 $mg.L^{-1}$. This value was selected to avoid interference from residual oxidants during the adsorption of the herbicides onto activated carbon. The residual chlorine and chlorine dioxide was measured using a spectrophotometric method with DPD (N,N-diethyl-p-phenyldiamine). Glycine was also added to determine the residual chlorine dioxide. The concentration of chlorite in the water after preoxidation with chlorine dioxide was measured with the iodometric titration method.

A pilot unit (PU) was built, consisting of a water storage tank (60 L), a dosing pump to pressurize the water supplied to the PU, a preoxidation chamber with a mechanical shaker and a GAC column (a photo and a diagram of the PU are shown in Figure 3). The GAC column was mounted inside a glass column with an internal diameter of 2.0 mm and the effective height of GAC was set at 20 cm. The preoxidation chamber was made of acrylic resin with a mean retention time of 45 min for the study flow, which was set at 2.0 $L.h^{-1}$. The fluxes of chlorine and chlorine dioxide solutions (oxidants) were established from the results of the demand tests.

Three tests were carried out according to the specifications listed below:

- Test 1 (GAC adsorption): water flow: 2.0 $L.h^{-1}$; duration of the test: 54 h; control parameters: concentration of diuron and hexazinone in the effluent of the GAC column.
- Test 2 (preoxidation with chlorine and adsorption on GAC): chlorine solution flow: 0.3 $L.h^{-1}$; water flow: 2.0 $L.h^{-1}$; duration of the test: 24 h; control parameters: residual chlorine and HOB in the preoxidation chamber effluent as well as diuron, hexazinone and HOB in the effluent of the GAC column.
- Test 3 (preoxidation with chlorine dioxide and adsorption on GAC): chlorine dioxide solution flow: 0.3 $L.h^{-1}$; water flow: 2.0 $L.h^{-1}$; duration of the test: 14 h; control parameters: residual chlorine dioxide and HOB in the preoxidation chamber effluent, and diuron, hexazinone, chlorite and HOB in the effluent of the GAC column.

RESULTS AND DISCUSSION

Traces of diuron were detected in the water during the month of May, 2007, and traces of hexazinone were detected in May, 2007, and February, 2008. The concentrations ranged from 0.26 to 7.12 $\mu g.L^{-1}$ in the samples collected from Well 3, which was located in a recharge zone close to a sugarcane plantation. The concentrations of diuron and hexazinone that were found during monitoring were low and the values were below those recommended by international standards for drinking water. However, the values that were found indicated that contamination of the aquifer may occur when wells are located in recharge areas.

Figure 4 shows the UV adsorption spectrum for the Velpar K WG solution and the calibration curve for the commercial herbicide at $\lambda = 250$ nm.

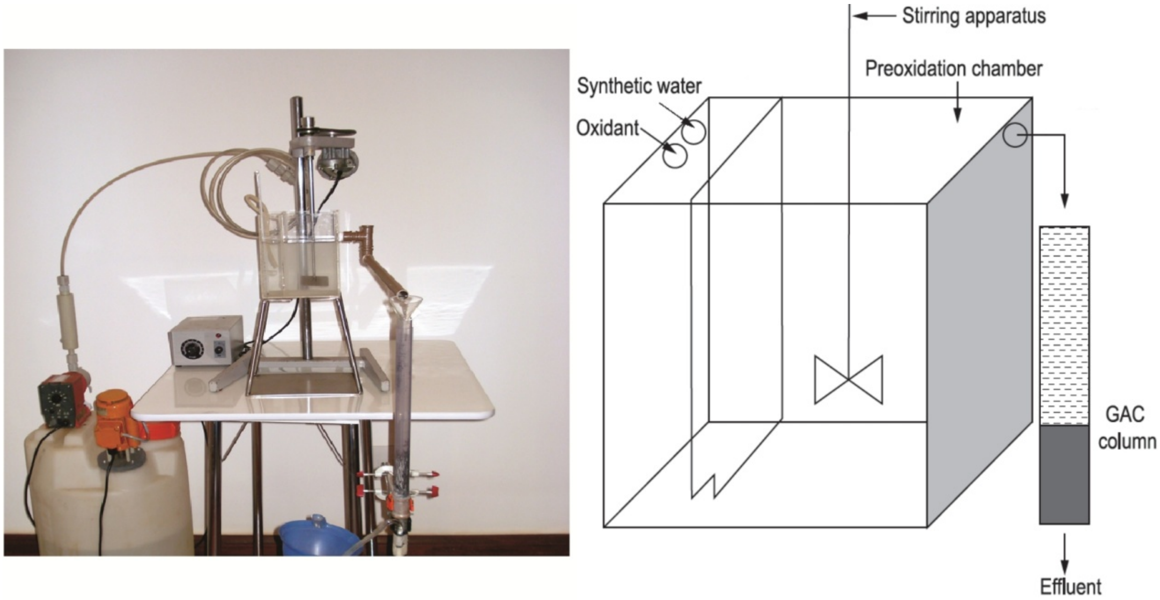


Figure 3: Photo and diagram of the pilot unit (PU).

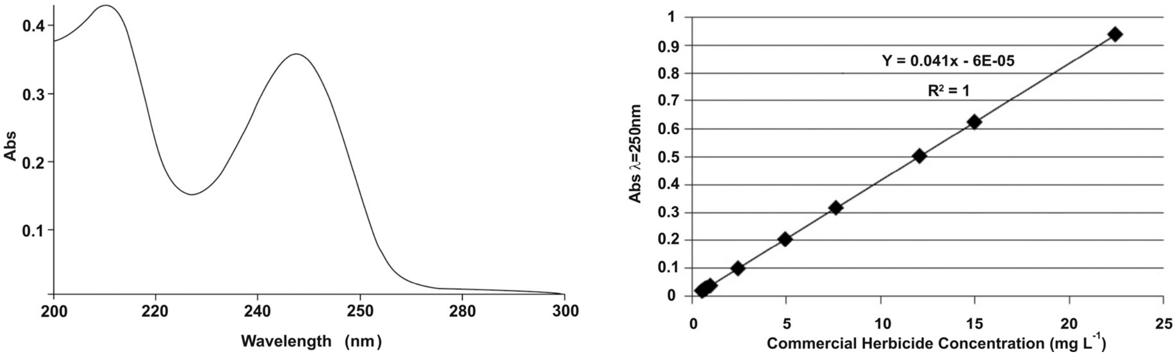


Figure 4: Spectrum in the ultraviolet region used for the spectrophotometric analysis of Velpar K WG and the calibration curve for Velpar K WG.

The iodine number is widely used to represent the amount of micropores that are present in carbon samples. According to Baçaoui *et al*. (2001), the iodine molecule is easily adsorbed on activated carbon due to its small size (approximately 0.27 nm), which allows iodine to penetrate the micropores of activated carbon. The minimum iodine number recommended by the American Water Works Association (2005) for the removal of compounds of low molecular weight using activated carbon is 500 mg.g^{-1}. Babassu GAC yielded the highest iodine number. The pH value is also a very important parameter, and it has a significant effect on the adsorption characteristics of the substrate because it influences electrostatic interactions. In other words, the pH of the solution determines carbon surface charge and electrolyte dissociation. The following results were obtained from the characterization of the commercial GAC samples:

- Coconut GAC:
  pH = 8.72 and Iodine number = 889 mg.g^{-1}
- Wood GAC:
  pH = 8.80 and Iodine number = 988 mg.g^{-1}
- Babassu GAC:
  pH = 9.55 and Iodine number = 1029 mg.g^{-1}

Our results indicate that the carbons we studied have alkaline properties. Figure 5 shows the results of the preliminary adsorption tests using synthetic water contaminated with 25 mg.L^{-1} of the commercial herbicide. Based on the results obtained in the preliminary adsorption tests, the babassu GAC was selected for further testing because only small residual amounts of the herbicide remained after various amounts of babassu GAC were studied. This result is compatible with the iodine number because the babassu GAC had the highest iodine number, which indicated a high adsorption probability for smaller molecules such as diuron and hexazinone.

Figure 6 presents the residual amounts of chlorine and chlorine dioxide from the preoxidation of the synthetic water after a 30 min contact time. The chlorine and chlorine dioxide dosages that were established for the tests in the PU were 0.3 mg.L^{-1} and 0.5 mg.L^{-1}, respectively, and, in both cases, the residual oxidant was about 0.1 mg.L^{-1} (detection limit of such oxidants) in order to avoid interference from the residual oxidants on the adsorption of the herbicides onto activated carbon. The chlorite concentration after preoxidation with chlorine dioxide was 0.20 mg.L^{-1}, which was lower than the maximum value of 1.0 mg.L^{-1} that is allowed by the EPA and equal to the maximum value of 0.20 mg.L^{-1} that was established by Directive 518 (Brazilian National Health, 2004).

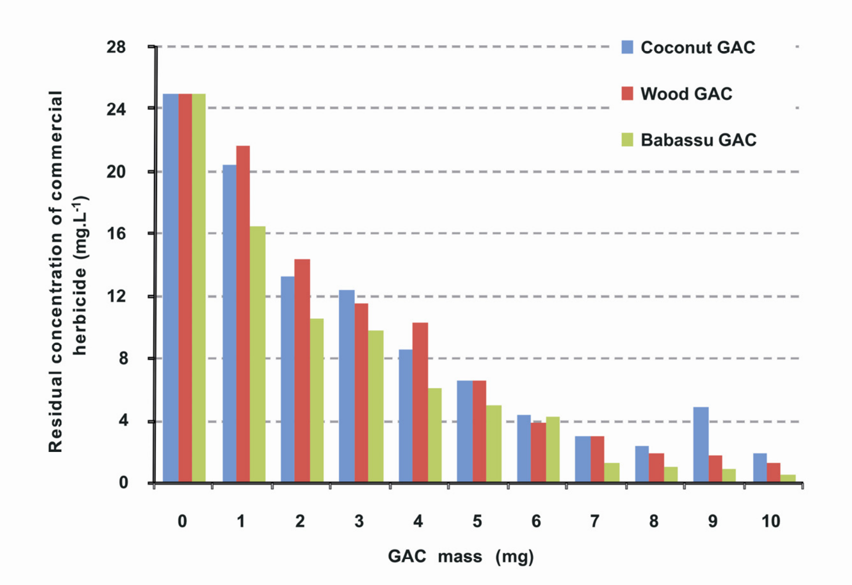


Figure 5: Residual concentration of commercial herbicide in preliminary adsorption tests with synthetic water as a function of the mass of three different GAC for a contact time of 2 h.

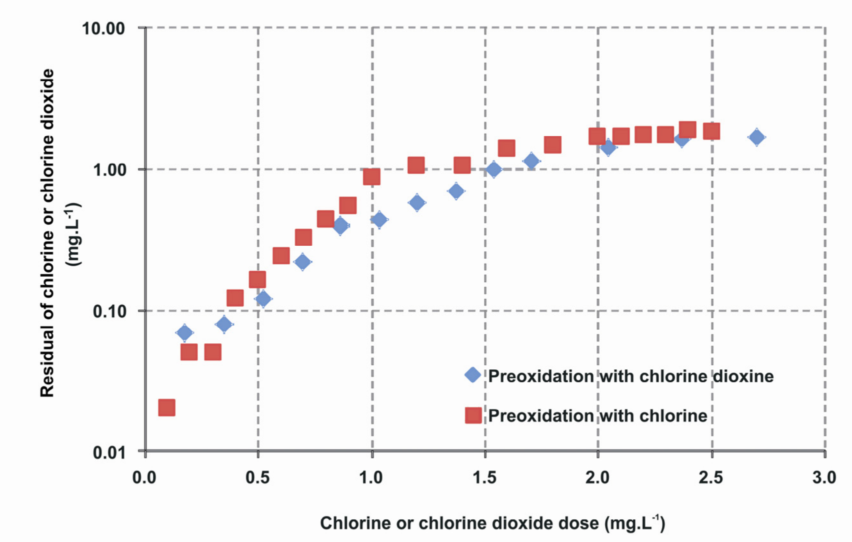


Figure 6: Residual concentrations of chlorine and chlorine dioxide as a function of the oxidant doses for the preoxidation of synthetic water for a contact time of 30 min.

Figures 7, 8 and 9 depict the results of PU tests 1, 2 and 3, respectively. These figures highlight the breakthrough time in the GAC column for each herbicide. Breakthrough was defined as a continuous increase in the concentration of a contaminant in the effluent from the GAC column, which indicated that the column was saturated.

As indicated by the results in Figure 7 (which shows only GAC adsorption), the hexazinone breakthrough time occurred around 18 h before the diuron breakthrough (which occurred between 24 and 30 h). These results indicate the GAC had a greater affinity for diuron adsorption.

As Figure 8 indicates, the breakthrough of both diuron and hexazinone in test 2 (which involved preoxidation with chlorine and GAC adsorption) occurred before the times recorded for test 1. The breakthrough times for test 2 occurred around 14 h for hexazinone and 16 h for diuron. These results demonstrate that water preoxidation with chlorine reduced the GAC adsorption efficiency, which indicates that the by-products from diuron and hexazinone oxidation or the residual chlorine may be competing for GAC active sites.

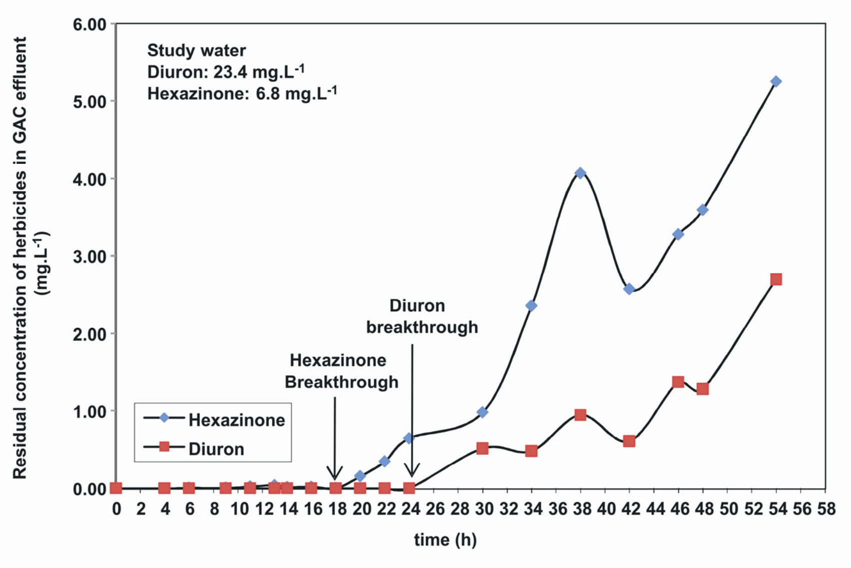


Figure 7: Residual concentrations of diuron and hexazinone in GAC column effluent during the run – results of Test 1 in the PU (without preoxidation).

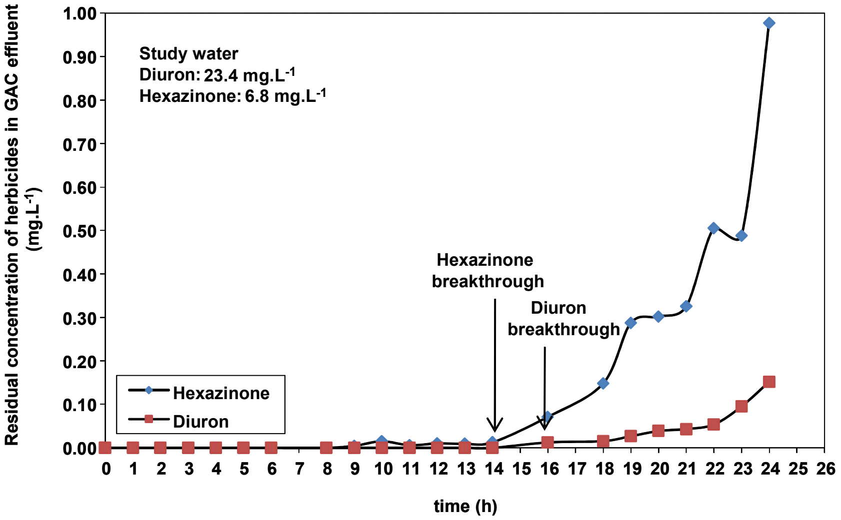


Figure 8: Residual concentrations of diuron and hexazinone in GAC column effluent during the run – results of Test 2 in the PU (preoxidation with chlorine).

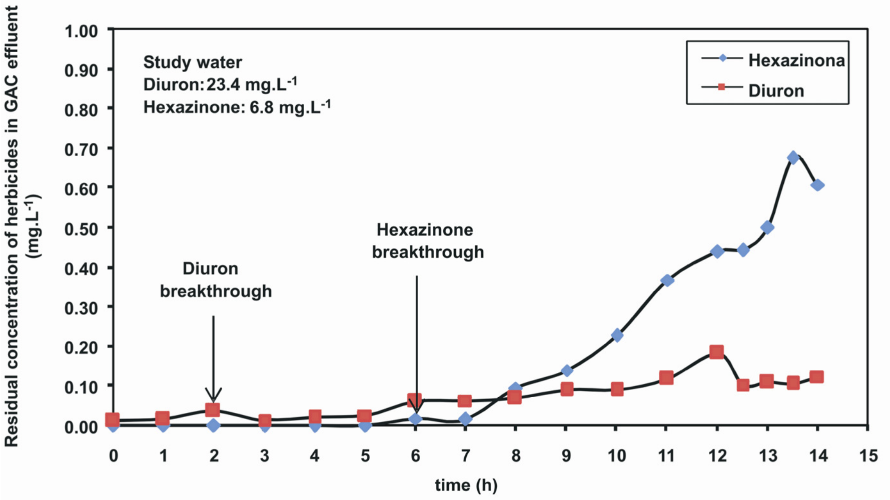


Figure 9: Residual concentrations of diuron and hexazinone in GAC column effluent during the run – results of Test 3 in the PU (preoxidation with chlorine dioxide).

The results of test 3 indicate that preoxidation with chlorine dioxide reduced the efficiency of GAC adsorption even more. Hexazinone breakthrough occurred at approximately 6 h and diuron breakthrough occurred at approximately 2 h (Figure 9). In addition to the effect of the by-products formed by oxidation of the herbicides with chlorine dioxide, the decrease in the GAC efficiency may be due to the presence of chlorite because no chlorite was detected in the effluent from the adsorption column. According to Collivignarelli *et al*. (2006), the removal of chlorite by GAC takes place in two stages: adsorption of chlorite at the GAC sites and reduction of chlorite into chloride.

In the test with preoxidation using chlorine (test 2), 90 µg.L^{-1} of HOB formed in the preoxidized water and there was a predominance of chloroform (63 µg.L^{-1}). After GAC adsorption, the total HOB concentration fell below the detection limit (0.10 µg.L^{-1}). In test 3, involving preoxidation with chlorine dioxide, there was no formation of HOB.

Other by-products likely form when chlorine and chlorine dioxide are used in water samples containing diuron and hexazinone, as reported by Chiron *et al*. (2000) and Chen and Young (2008).

CONCLUSIONS

There has been concern about the groundwater quality in the Guarany Aquifer due to the cultivation of sugarcane in Brazil, particularly in the state of Sao Paulo where many cities are supplied with groundwater. A one-year investigation of a well in the water supply system for the city of Ribeirão Preto, which is located in the recharge zone of the Guarany Aquifer and is close to a sugarcane plantation, revealed concentrations of hexazinone and diuron of up to 0.26 mg.L^{-1} and 7.12 mg.L^{-1}, respectively.

Among the GAC studied, babassu GAC had the highest iodine number (1029 mg.g-1) and yielded the smallest residual amounts of the herbicide in preliminary adsorption tests. The babassu GAC was selected for further study in the pilot unit. Up to the breakthrough points for hexazinone and diuron, the effluent contained levels of the herbicides that were lower than the values recommended by Canadian standards, which establish a maximum diuron concentration of 150 µg.L-1, and Australian regulations, which have a maximum admissible hexazinone concentration of 300 µg.L-1.

Preoxidation with chlorine and chlorine dioxide produced earlier breakthrough times for hexazinone and diuron compared to the times that were obtained when the influent was not oxidized.

Some of the findings of this research clearly underline the importance of investigating diuron and hexazinone in the groundwater of regions where sugarcane cultivation is predominant. We conclude that the use of activated carbon is important for the removal of the pesticides studied in this investigation, as well as for the removal of the by-products from the use of oxidants. Based on our research, we recommend the use of a GAC column in certain wells of the municipal water system in Ribeirão Preto to guarantee the distribution of water without diuron and hexazinone.

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