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# Risk Estimate of Water Contamination and Occurrence of Pesticides in the South of Brazil

Sergiane Souza Caldas<sup>1</sup>, Renato Zanella<sup>2</sup> and Ednei Gilberto Primel<sup>1</sup>

<sup>1</sup>*Federal University of Rio Grande (FURG)*

<sup>2</sup>*Federal University of Santa Maria (UFSM)*  
Brazil

## 1. Introduction

Worldwide pesticide usage has increased dramatically during the last two decades, coinciding with changes in farming practices and the increasingly intensive agriculture (Konstantinou et al., 2006). Developing countries represent approximately 30% of the global pesticide consumer market. Within this group, Brazil is the most important individual market, with an estimated 6.5 billion dollars per year spent on pesticides, making the country the second largest consumer of pesticides in the world (Peres et al., 2006). Rio Grande do Sul State, located in the south of Brazil, is responsible for 10.4% of pesticide consumption in Brazil (SINDAG, 2006).

The higher the agricultural productivity, the more contamination with pesticides. Pesticides are a group of artificially synthesized substances which have been used in agriculture to control pests and to increase production. These substances protect the agricultural crops, but overuse and incorrect use can pose risks to human health and the environment (Caldas et al., 2009). The impact of pesticide uses on human health is especially evident in developing countries, where pesticides are widely used in agriculture. According to the 2005 annual report of the Brazilian Toxicopharmacological Information System (Sinitox), 8,000 notifications of cases of human pesticide poisoning had been received annually. The Brazilian Ministry of Health estimates that for each reported case there are at least 50 non-reported ones, it increases the annual pesticide poisoning rates to 400,000 cases per year, with 2,000 deaths (Peres et al., 2006). This human contamination can occur in different ways, and one of them is through contaminated waters.

Brazil has approximately 10% of the world's fresh water, with an annual average river flow of 182,600 m<sup>3</sup> s<sup>-1</sup>. When all areas of the Amazon region are considered, including the territory in neighboring countries, the outflow is around 272,000 m<sup>3</sup> s<sup>-1</sup>. Although Brazil is considered rich in water due to its extensive landmass, there is a high disparity in distribution of this resource among its regions. Moreover, the rapid process of urban development and increases in agricultural productivity in the last few decades have been affecting the quality and availability of water (Marques et al., 2007).

The surface water is considered the water stored or flowing on the earth's surface: natural bodies of water such as rivers, lakes, and wetlands, as well as constructed (artificial) water reservoirs such as canals, man-made lakes, and drainage ditches. The quantity and quality

of surface water is important for many activities: consumption, recreation, transportation, waste assimilation, agricultural production, and industrial use (Whitford et al., 2010).

Groundwater, in the broadest sense, refers to all subsurface water which is also important for many activities, and represents an important source of drinking water supply in many countries.

Pesticide residues reach the aquatic environment through direct run-off, leaching, careless disposal of empty containers, equipment washing, etc; and the water contamination depends on the physico-chemical characteristics of the compound and the interaction of the pesticides with soil, surface water and groundwater.

Moreover, the pesticide fate is controlled by numerous simultaneous biological, physical, and chemical reactions (Whitford et al., 2010). When a pesticide is applied to a field, certain reactions follow. Foliar-applied pesticides stick to leaves, where they are absorbed. But rainfall inevitably washes some of the chemical off the leaf surface onto the soil below; and some may be transformed by sunlight. For instance, pesticides that are tightly sorbed to soil particles have decreased mobility and are less likely to contaminate groundwater. Pesticides strongly sorbed to soil particles may travel primarily with eroded soil and enter surface water, while weakly sorbed pesticides that are more water soluble may be released into soil water solution and enter surface water as runoff (Whitford et al., 2010). Chemicals, which are sufficiently resistant to degradation and are adequately soluble to be transported in water, may reach the water bodies in significant amounts (Konstantinou et al., 2006).

The surface and groundwater contamination by pesticides has been documented in many papers around the world (Carabias-Martínez et al., 2002; Cerejeira et al., 2003; Hernández-Romero et al., 2004; D'Archivio et al., 2007; Baugros et al., 2008; Barrek et al., 2009). In some areas in Brazil, where pesticides are widely used, mainly due to agricultural activities, some pesticides have been found. In Table 1, results from researches that analyzed sample waters in Rio Grande do Sul (RS) State, in the south of Brazil, are shown in a summarized way. All studies found most of the investigated compounds. Normally, the compounds analyzed are used in rice and tobacco cultures. The herbicide clomazone was investigated in all studies and found in all, showing the tendency of this compound to be present in water samples, and the high use of this herbicide in the region. Only one study with pesticides determination in groundwater was found; it emphasizes the need for more studies in this compartment.

The amount of pesticide that will reach the environment compartments varies with environmental changes, and the estimation is difficult. But, because of the lack of analytical facilities and the high cost of analyses, one strategy to identify, from among the long list of chemicals applied to the area, those pesticides which are likely to be present in surface and groundwater is to focus in their physico-chemical properties, using some model environmental partitioning indexes such as Groundwater Ubiquity Score (GUS), the screening criteria recommended by the U.S. Environmental Protection Agency (US-EPA) and GOSS (Cabrera et al., 2008).

## 2. Objective

The aim of this chapter is to present an evaluation of the contamination of surface, drinking and groundwater by herbicides, insecticides and fungicides used in different crop cultures in Rio Grande do Sul State, Brazil.

Table 1. Studies that analyzed pesticides in sample waters in RS state after 2002

Water sample	Compounds	Culture related	Pesticides found (maximum concentration found)
surface	clomazone	rice	clomazone (1.72)
surface	2,4-D, bentazone, clomazone, propanil, quinclorac	rice	2,4-D (>2.0) bentazone (>2.0) clomazone (>2.0 ) propanil (>2.0) quinclorac (>2.0)
surface	atrazine, clomazone, chlorpyrifos, flumetralin, imidacloprid, iprodione, simazine	tobacco	atrazine (0.63) clomazone (2.18) imidacloprid (2.18)
surface and groundwater	atrazine, chlorpyrifos, flumetralin, imidacloprid, iprodione, simazine, clomazone	tobacco	atrazine (ground – 0.69 - surface – 0.69) clomazone(ground – 12.84 - surface – 12.84) chlorpyrifos (ground-0.14 - surface – 0.14) imidacloprid (ground –2.33 - surface – 2.33) simazine (ground – 0.8 - surface – 0.8)
surface	clomazone, propanil, quinclorac	rice	clomazone (8.85) propanil (6.6) quinclorac (6.6)
surface	beta cyfluthrin, carbofuran, clomazone, fipronil, quinclorac	rice	carbofuran (14.99) clomazone (1.14) fipronil (1.14) quinclorac (1.14)
surface	carbofuran 3-hydroxy, carbofuran, clomazone, fipronil, imazapic, imazethapyr, penoxsulam, quinclorac, tebuconazole	rice	carbofuran 3-hydroxy (0.33) carbofuran (1.4) clomazone (1.4) fipronil (3.45) imazapic (0.33) imazethapyr (0.33) Penoxsulam (0.33) quinclorac (0.12) tebuconazole (0.12)
surface	2,4-D, bentazone, carbofuran, clomazone, fipronil, imazethapyr, propanil, quinclorac	rice	2,4-D (3.4) bentazone (3.4) carbofuran (0.8) clomazone (0.8) fipronil (26.2) imazethapyr (5.4) propanil ( 5.4) quinclorac (5.4)

This region has special characteristics because of its agricultural production. Pesticides of different classes are widely used and some of them, due to their physico-chemical properties, can reach the water systems. Firstly, a theoretical evaluation was made using the approaches suggested by US-EPA, the GUS index and the Goss method to estimate the contamination possibilities. Afterwards, a monitoring program was established for the surface and groundwater of the area to investigate the presence of pesticide residues.

### 3. Methods

#### 3.1 Characterization of the physico-chemical properties

The knowledge of most relevant physico-chemical parameters is important to set up the analytical scheme and to understand the environmental behavior of the compounds. It helps in the selection of the analytes that can be present in the area under study, the sample extraction and the technique for the analyses. A review about the physico-chemical characteristics was carried out and all information was based on Barceló & Hennion (1997).

##### 3.1.1 Water solubility

Water solubility is a fundamental, specific chemical property defined as the concentration of a chemical dissolved in water when that water is both in contact and in equilibrium with the pure chemical. Water solubility indicates the tendency for a pesticide to be removed from soil by runoff or irrigation water and to reach the surface water. It also indicates its tendency to precipitate on the surface soil.

##### 3.1.2 Octanol-Water partition coefficient

This parameter is usually reported as a logarithm  $\log K_{ow}$  or  $\log P$ . It is defined as the ratio of the equilibrium concentrations of the two-phase system consisting of water and *n*-octanol. This parameter is characteristic of the lipophilicity of the molecule and gives an indication of the tendency the compound has to accumulate in biological membranes and living organisms. It is generally considered that substances with a  $\log K_{ow}$  value higher than 3 can show accumulation. The polarity of a molecule is strongly related with  $K_{ow}$ . As a rough rule, non-polar analytes are characterized by  $\log K_{ow}$  values above 4.5, whereas polar analytes have  $K_{ow}$  values below 1 or 1.5. Between these two values, compounds are classified as moderately polar.  $K_{ow}$  has proved valuable for prediction of mobility and persistence in soils, and of soil sorption. However,  $K_{ow}$  alone cannot be considered to be an indicator of soil affinity because it merely represents a partition between two well-defined nonmiscible phases, whereas the real soil sorption process involves other mechanisms such as partition, adsorption, ion-exchange, complexation and precipitation.

##### 3.1.3 Acid-base ionization constants

Ionic pesticides behave differently from non-ionic pesticides. It is therefore important to know which pesticides are capable of ionization within the normal soil/water environmental pH range of 5-8. Since soils have a tendency to be negatively charged, anionic compounds may be potential leachers whereas cationic compounds will be strongly retained. This knowledge is also important for perform trace analysis, especially to extractions from water, because it is easier to extract a non-ionic compound than an ionic one. A simple pH adjustment can help greatly in extraction recovery, which requires a knowledge of the ionization constant values. The water solubility of ionic species is always

much higher than that of their non-ionic form. The ionization constant is usually expressed as pKa. The higher the pKa value, the weaker is the acid and the tendency to be ionized.

### 3.1.4 Vapour pressure

The vapour pressure is defined as the partial pressure of a chemical, in the gas phase, in equilibrium, with the pure solid or liquid chemical. Vapour pressures are very temperature-dependent. This parameter governs the distribution between liquid and gas phase or between solid and gas phase.

### 3.1.5 Henry's Law constant

Henry's Law constant, denoted  $H$  or  $K_H$  is a partition coefficient defined as the ratio of a chemical concentration in air to its concentration in water in equilibrium. This parameter is important in several aspects. The tendency for the pesticides to volatilize from water solution into air is largely determined by their  $H$  values, a high value favouring volatilization.

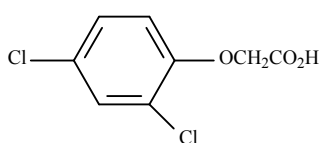
### 3.1.6 Normalized soil sorption coefficient ( $K_{oc}$ )

One of the most critical factors for assessing the potential mobility of most pesticides in the soil compartment is the distribution between the solid and liquid phases of soil. This portioning presents a difficult problem since the types of soil in the environment vary enormously. The first characterization is the measurement of the simple "sorption" coefficient,  $K_d$ , defined as the ratio of the concentration of the chemical adsorbed on soil to the concentration of pesticide in the soil solution. Therefore, taking into account the different soil organic matter or organic carbon content, the adsorption constant is normalized, and  $K_d$  values are expressed per unit of organic carbon as  $K_{oc}$ . They are referred to as "soil organic carbon sorption coefficients" and expressed in  $\text{cm}^3 \text{g}^{-1}$ . The environmental relevance of this parameter is important to the leaching properties in groundwater. Pesticides with  $K_{oc}$  values below 50 are considered to be highly mobile; values of 150-500 signify moderately mobile, and above 2000, slightly mobile compounds.

### 3.1.7 Field half-life

The half-life ( $t_{1/2}$ ) is defined as the time required for the pesticide to undergo dissipation or degradation to half of its initial concentration. However, there is not a single half-life for pesticides, and measurements depend strongly on the environmental conditions (soil, site, climate, soil microbial activity, etc).

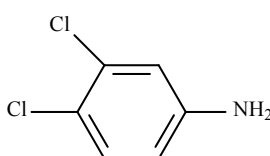
### 3.1.8 Chemical structures of the studied pesticides



Name: 2,4-D

Mw: 221.0

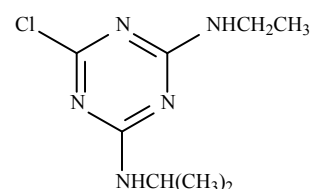
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Name: 3,4-DCA

Mw: 162.0

CAS number: 95-76-1

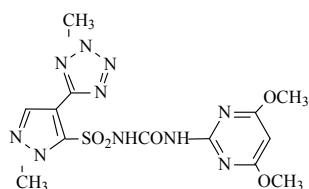


Name: atrazine

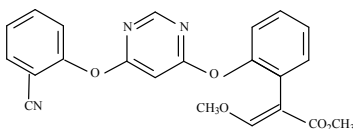
Mw: 215.7

CAS number: 1912-24-9

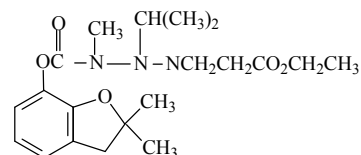




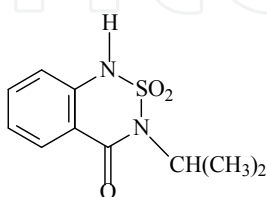
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Mw: 424.4  
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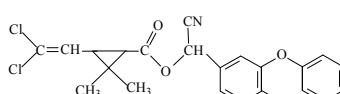
Name: azoxystrobin  
Mw: 403.4  
CAS number: 131860-33-8



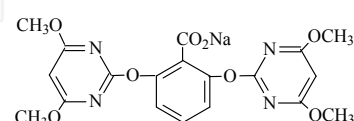
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Mw: 410.5  
CAS number: 82560-54-1



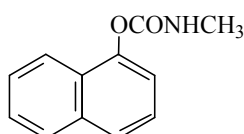
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Mw: 240.3  
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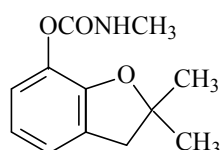
Name: beta-cyfluthrin  
Mw: 434.3  
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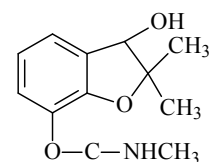
Name: bispyribac-sodium  
Mw: 452.4  
CAS number: 125401-92-5



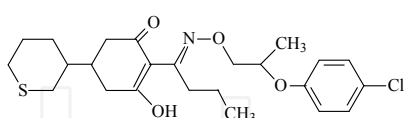
Name: carbaryl  
Mw: 201.2  
CAS number: 63-25-2



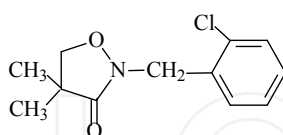
Name: carbofuran  
Mw: 221.3  
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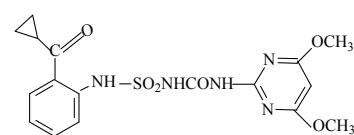
Name: carbofuran 3-hydroxy  
Mw: 237.3  
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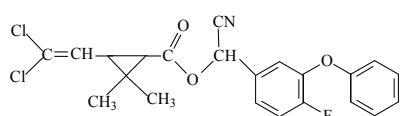
Name: clefoxydim  
Mw: 466.0  
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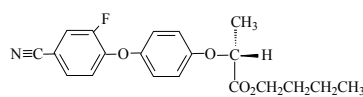
Name: clomazone  
Mw: 239.7  
CAS number: 81777-89-1



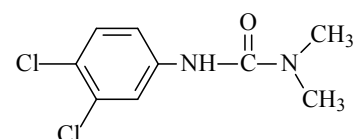
Name: cyclosulfamuron  
Mw: 421.4  
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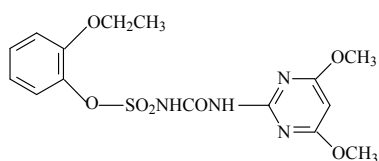
Name: cyfluthrin  
Mw: 434.3  
CAS number: 68359-37-5



Name: cyhalofop-butyl  
Mw: 357.4  
CAS number: 122008-85-9



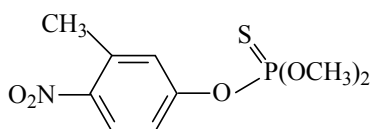
Name: diuron  
Mw: 233.1  
CAS number: 330-54-1



Name: ethoxysulfuron

Mw: 398.4

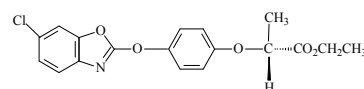
CAS number: 126801-58-9



Name: fenitrothion

Mw: 277.2

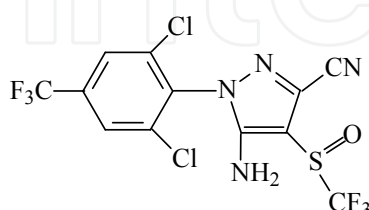
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Name: fenoxaprop-p-ethyl

Mw: 361.8

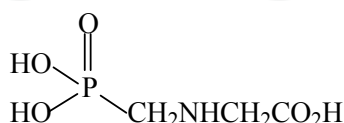
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Name: fipronil

Mw: 437.2

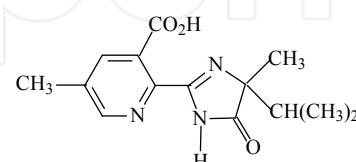
CAS number: 120068-37-3



Name: glyphosate

Mw: 169.1

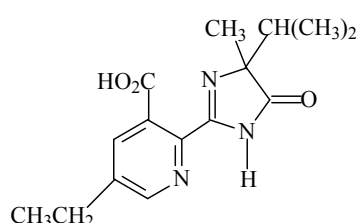
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Name: imazapic

Mw: 275.3

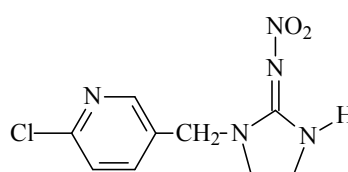
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Name: imazethapyr

Mw: 289.3

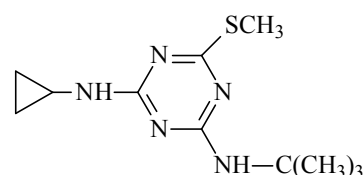
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Name: imidacloprido

Mw: 255.7

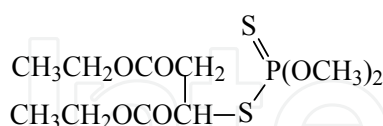
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Name: Irgarol

Mw: 253.4

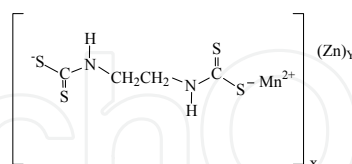
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Name: malathion

Mw: 330.4

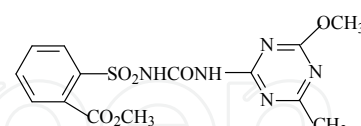
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Name: mancozeb

Mw: 271.2

CAS number: 8018-01-7



Name: metsulfuron-methyl

Mw: 381.4

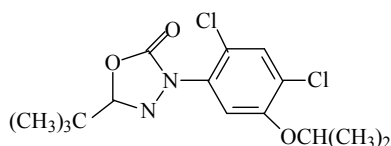
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Name: molinate

Mw: 187.3

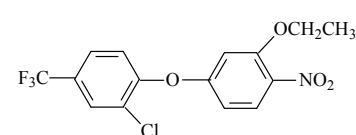
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Name: oxadiazon

Mw: 345.2

CAS number: 19666-30-9

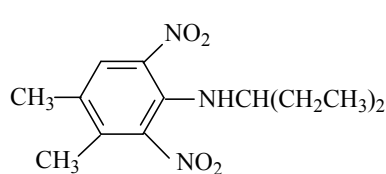


Name: oxyfluorfen

Mw: 361.7

CAS number: 42874-03-3

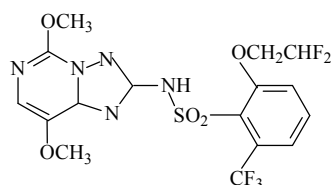




Name: pendimethalin

Mw: 281.3

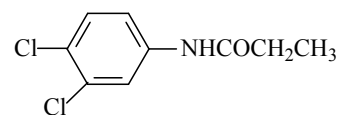
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Name: penoxsulam

Mw: 483.4

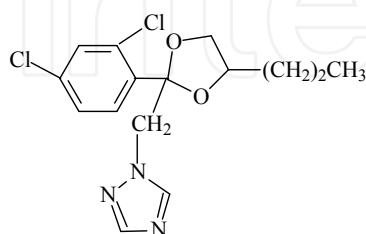
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Name: propanil

Mw: 218.1

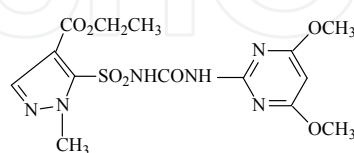
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Name: propiconazole

Mw: 342.2

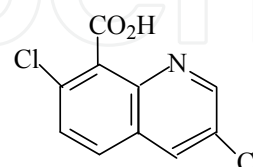
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Name: pyrazosulfuron-ethyl

Mw: 414.4

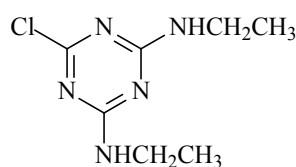
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Name: quinclorac

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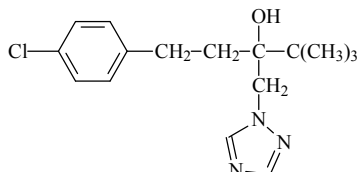
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Name: simazine

Mw: 201.7

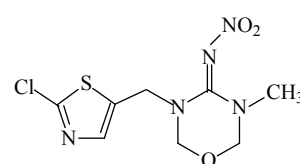
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Name: tebuconazole

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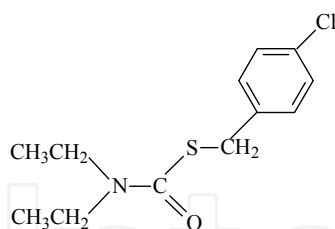
CAS number: 107534-96-3



Name: thiamethoxam

Mw: 291.7

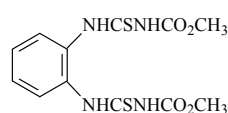
CAS number: 153719-23-4



Name: thiobencarb

Mw: 257.8

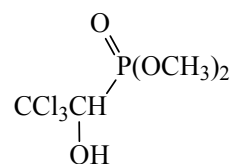
CAS number: 28249-77-6



Name: thiophanate-methyl

Mw: 342.4

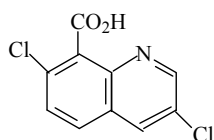
CAS number: 23564-05-8



Name: trichlorphon

Mw: 257.4

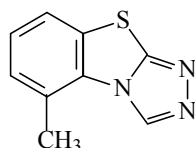
CAS number: 52-68-6



Name: triclopyr

Mw: 242.1

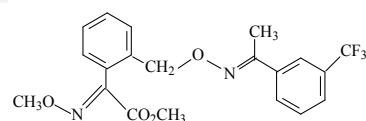
CAS number: 84087-01-4



Name: tricyclazole

Mw: 189.2

CAS number: 41814-78-2



Name: trifloxystrobin

Mw: 342.2

CAS number: 60207-90-1

Fig. 1. Chemical structures, molecular weight (Mw) and CAS number of the studied compounds

### 3.2 Risk Assessment for groundwater

#### 3.2.1 GUS

The leaching potential was determined by calculating the GUS which is based on the partition coefficient between soil organic carbon and water—sorption coefficient ( $K_{oc}$ ) and the half-life ( $t_{1/2}$ ) in soil for each pesticide compound.

The GUS index was calculated according to equation 1.

$$GUS = \log t_{1/2} \times (4 - \log K_{oc}) \quad (1)$$

where  $K_{oc}$  is the soil sorption coefficient ( $\text{mL g}^{-1}$ ) and  $t_{1/2}$  is the half-life in soil (days). GUS values lower than 1.8 and higher than 2.8 indicate, respectively, non-leacher and leacher pesticide compounds; for GUS values between 1.8 and 2.8 the pesticide is considered in a transition zone (Gustafson, 1989).

#### 3.2.2 US-EPA

The US-EPA screening criteria was also used for predicting the leaching potential. It is based on the following: water solubility  $> 30 \text{ mg L}^{-1}$ ;  $K_{oc} < 300\text{-}500$ ; Henry's Law constant -  $K_H < 10^{-2} \text{ Pa m}^3 \text{ mol}^{-1}$ ; speciation - negatively charged (either fully or partially) at room temperature pH (5-8); soil  $t_{1/2} > 2\text{-}3$  weeks; hydrolysis  $t_{1/2} > 25$  weeks; vulnerable field conditions (annual precipitation  $> 250 \text{ mm}$ , aquifer not confined, porous soil).

### 3.3 Risk assessment for surface waters

#### 3.3.1 GOSS

For the evaluation of which pesticides might contaminate the surface waters, a criterion proposed by Goss was used (Goss, 1992).

This criterion considers the half-life in soil ( $t_{1/2}$ ), water solubility and the soil sorption coefficient ( $K_{oc}$ ).

According to this criteria the compounds are divided in groups: High Sediment-Transport Runoff Potential (HSTRP); Low Sediment-Transport Runoff Potential (LSTRP); High Water-Phase-Transport Runoff Potential (HWTRP) and Low Water-Phase-Transport Runoff Potential (LWTRP). The values considered for each parameter are: HSTRP -  $t_{1/2} \text{ soil} \geq 40 \text{ d}$  and  $K_{oc} \geq 1000 \text{ cm}^3 \text{ g}^{-1}$ , or  $t_{1/2} \text{ soil} \geq 40 \text{ days}$ ,  $K_{oc} \geq 500 \text{ cm}^3 \text{ g}^{-1}$  and water solubility  $\leq 0.5 \text{ mg L}^{-1}$ ; LSTRP -  $t_{1/2} \text{ soil} < 1 \text{ d}$ , or  $t_{1/2} \text{ soil} \leq 40 \text{ d}$ ,  $K_{oc} \leq 500 \text{ cm}^3 \text{ g}^{-1}$  and water solubility  $\geq 0.5 \text{ mg L}^{-1}$ , or  $t_{1/2} \text{ soil} \leq 2 \text{ days}$  and  $K_{oc} \leq 500 \text{ cm}^3 \text{ g}^{-1}$  or  $t_{1/2} \text{ soil} \leq 4 \text{ days}$ ,  $K_{oc} \leq 900 \text{ cm}^3 \text{ g}^{-1}$  and water solubility  $\geq 0.5 \text{ mg L}^{-1}$  or  $t_{1/2} \text{ soil} \leq 40 \text{ d}$   $K_{oc} \leq 900 \text{ cm}^3 \text{ g}^{-1}$  and water solubility  $\geq 2 \text{ mg L}^{-1}$ ; HWTRP -  $t_{1/2} \text{ soil} > 35 \text{ d}$ ,  $K_{oc} < 1000000 \text{ cm}^3 \text{ g}^{-1}$  and water solubility  $> 1 \text{ mg L}^{-1}$ , or  $t_{1/2} \text{ soil} > 35 \text{ d}$ ,  $K_{oc} \leq 700 \text{ cm}^3 \text{ g}^{-1}$  and water solubility between 10 and 100  $\text{mg L}^{-1}$ ; LWTRP -  $K_{oc} > 1000000 \text{ cm}^3 \text{ g}^{-1}$ , or  $t_{1/2} \text{ soil} \leq 1 \text{ d}$  and  $K_{oc} \geq 1000 \text{ cm}^3 \text{ g}^{-1}$ , or  $t_{1/2} \text{ soil} < 35 \text{ d}$  and water solubility  $< 0.5 \text{ mg L}^{-1}$ . The compounds which do not meet any of these criteria are considered with medium potential, in other words, Medium Water-Phase-Transport Runoff Potential (MWTRP) or associated with sediment (MSTRP).

### 3.4 Reagents and chemicals

In this study, high purity standards of eighteen pesticides were selected: clomazone, tebuconazole, diuron, irgarol, atrazine, simazine, metsulfuron-methyl, quinclorac, 2,4-D, pyrazosulfuron-ethyl, bentazone, propanil, carbofuran and the two metabolites, 3,4-DCA and carbofuran 3-hydroxy, which derive from propanil and carbofuran, respectively, were

purchased at Sigma Aldrich (São Paulo, Brazil). Imazethapyr, imazapic, fipronil, bispyribac-sodium and penoxsulam were purchased at Dr. Ehrenstorfer GmbH (Augsburg, Germany). Methanol and acetonitrile of chromatographic grade were supplied by Mallinckrodt (Phillipsburg, NJ, USA). Phosphoric acid (85%) and formic acid (98%) of analytical grade were purchased at Merck (Darmstadt, Germany). Ultra pure water was produced by a Direct-Q UV3® system (Millipore, Bedford, MA, USA). The SPE extraction tubes were Chromabond C18ec, 500 mg/3 mL (Macherey-Nagel, Düren, Germany).

### 3.5 Equipment

All analyses were performed on a Waters Alliance 2695 Separations Module HPLC, equipped with a quaternary pump, an automatic injector and a thermostatted column compartment, and detection was carried out on a Quattro micro API (triple quadrupole) mass spectrometer, equipped with a Z-spray electrospray (ESI) ionization source, from Micromass (Waters, Milford, MA, USA), according to previous studies (Caldas et al., 2010; Demoliner et al., 2010).

### 3.6 Sampling

Samples were collected directly in 1 L amber glass bottles in each sampling site. These bottles had been cleaned prior to sampling by rinsing them three times in the water to be sampled. The bottle was filled to the top with as little remaining air as possible, and sealed tightly. All samples were properly labeled with details of the source and sampling date, and stored at 4 °C until the solid-phase extraction, which was carried out on the same day of the sampling.

#### 3.6.1 Groundwater

The studies of groundwater contamination with pesticides were carried out in Quitéria, a rural area located near Rio Grande, a city in the southeast of Brazil that has about 185,000 inhabitants. The region of Quitéria is an agricultural area where there are different kinds of production, mainly onion, fruits and vegetables in general. The intense agricultural production, and consequently the use of pesticides, can cause the contamination of groundwaters.

Samples from drinking water wells (Figure 2) with depths ranging from 2.5 up to 37 m were collected in ten sampling points from September 2007 to August 2008, and analyzed to determine the concentration of carbofuran, 2,4-D, clomazone and tebuconazole. Sampling was carried out once per month in each well.

#### 3.6.2 Drinking and surface water

The sampling of the drinking and surface water was carried out monthly at CORSAN, the Water Treatment Station in Rio Grande, from January, 2008 to April, 2010. Two different samples were collected: a surface water sample, collected at the entrance of the water channel (the São Gonçalo Channel), and a drinking water sample, collected after the water treatment, in the output of the station (Figure 2).

### 3.7 Sample preparation

The samples were acidified at pH 3.0 with phosphoric acid. Afterwards, they were pre-concentrated and extracted by SPE tubes containing 500 mg of octadecylsilane

(Chromabond C18ec) with an average particle size of 45  $\mu\text{m}$ . Cartridges were conditioned with 3 mL of methanol, 3 mL of ultrapure water and 3 mL of ultrapure water pH 3.0, acidified with phosphoric acid 1:1 (v/v). After the conditioning step, aliquots of 250 mL of water samples, acidified at pH 3.0 with phosphoric acid (to increase the pesticide retention) were loaded through the cartridges with a flow rate of 6 mL min<sup>-1</sup>. Then, the analytes were eluted with 1 mL (2 x 500  $\mu\text{L}$ ) methanol, volume adjusted in 1 mL and injected into the chromatographic system. This extraction procedure had been previously developed and optimized in our laboratory (Caldas et al., 2009).

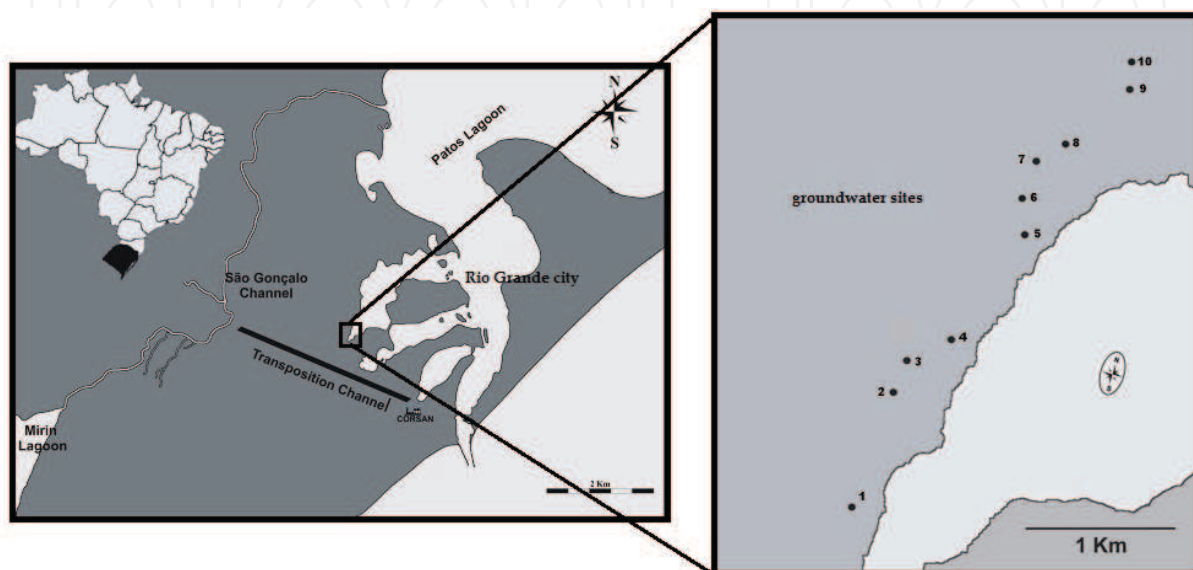


Fig. 2. Regions of surface and groundwater collection

## 4. Results

The pesticides evaluated by Goss, GUS and US-EPA criteria were chosen because of their high use in RS state, mainly in the rice cultivation (Câmara dos Agrotóxicos, 2008; SIA, 2003).

### 4.1 Risk assessment for surface water

The results for the risk assessment for surface water are shown in Table 2. According to the GOSS criteria, regarding the water-phase-transport runoff potential, the compounds fipronil, imidacloprid, propiconazole, atrazine, cyclosulfamuron, diuron, fenoxaprop-p-ethyl, imazethapyr, metsulfuron-methyl, molinate, oxadiazon, triclopyr, glyphosate and thiamethoxam show high potential. Clomazone, imazapic and thiobencarb besides presenting HWTRP showed LSTRP, which is a high indicative that these compounds have good chance to be found in surface waters.

Some compounds such as beta-cyfluthrin, cyfluthrin, thiophanate, cyhalofop-butyl and penoxsulam show LWTRP showing less tendency to be found in surface waters.

Some others due to their physico-chemical properties, presented intermediate probabilities, showing MSTRP and MWTRP. They are benfuracarb, tebuconazole, trifloxystrobin, bispyribac, oxyfluorfen, pendimethalin, quinclorac and simazine.

Among the compounds under study, only carbofuran showed HSTRP.

The contamination potential for the herbicide clefoxidim, mancozeb and tricyclazole was not evaluated because of the lack of data about these compounds.

Fungicides and Insecticides	GOSS classification		Herbicides	GOSS classification	
azoxystrobin	LSTRP	MWTRP	2,4-D	LSTRP	MWTRP
benfuracarb	MSTRP	MWTRP	atrazine	MSTRP	HWTRP
beta-cyfluthrin	MSTRP	LWTRP	azimsulfuron	LSTRP	MWTRP
carbaryl	LSTRP	MWTRP	bentazone	LSTRP	MWTRP
carbofuran	HSTRP	MWTRP	bispyribac-sodium	MSTRP	MWTRP
cyfluthrin	MSTRP	LWTRP	cyhalofop-butyl	LSTRP	LWTRP
fenitrothion	LSTRP	MWTRP	cyclosulfamuron	MSTRP	HWTRP
fipronil	MSTRP	HWTRP	clefoxydim	I	MWTRP
imidacloprid	MSTRP	HWTRP	clomazone	LSTRP	HWTRP
malathion	LSTRP	MWTRP	diuron	MSTRP	HWTRP
mancozeb	I	I	ethoxysulfuron	LSTRP	MWTRP
propiconazole	MSTRP	HWTRP	fenoxaprop-p-ethyl	MSTRP	HWTRP
tebuconazole	MSTRP	MWTRP	glyphosate	MSTRP	HWTRP
thiamethoxam	MSTRP	HWTRP	imazapic	LSTRP	HWTRP
thiophanate-methyl	LSTRP	LWTRP	imazethapyr	MSTRP	HWTRP
tricyclazole	I	I	metsulfuron-methyl	MSTRP	HWTRP
trichlorphon	LSTRP	MWTRP	molinate	MSTRP	HWTRP
trifloxystrobin	MSTRP	MWTRP	oxadiazon	MSTRP	HWTRP
			oxyfluorfen	MSTRP	MWTRP
			pendimethalin	MSTRP	MWTRP
			penoxsulam	MSTRP	LWTRP
			pyrazosulfuron-ethyl	LSTRP	MWTRP
			propanil	LSTRP	MWTRP
			quinclorac	MSTRP	MWTRP
			simazine	MSTRP	MWTRP
			thiobencarb	LSTRP	HWTRP
			triclopyr	MSTRP	HWTRP

Table 2. Goss classification for the compounds under study (HSTRP= High Sediment-Transport Runoff Potential; LSTRP= Low Sediment-Transport Runoff Potential; HWTRP= High Water-Phase-Transport Runoff Potential; LWTRP= Low Water-Phase-Transport Runoff Potential; MWTRP= Medium Water-Phase-Transport Runoff Potential; MSTRP= Medium Sediment-Transport Runoff Potential and I = non-conclusive)



## 4.2 Risk assessment of groundwaters

For the risk of contamination of the groundwater, according to GUS and US-EPA, the herbicides atrazine, bentazone, clomazone, imazethapyr, imazapic, metsulfuron-methyl, quinclorac, simazine and triclopyr, besides the fungicides and the insecticides carbofuran, imidacloprid, thiamethoxam, tricyclazole and trichlorphon are classified as potential contaminants of groundwaters (Table 3) by both methods. The compounds azoxystrobin, benfuracarb, beta-cyfluthrin, cyfluthrin, fenitrothion, malathion, mancozeb, thiophanate, trifloxystrobin, bispyribac-sodium, cyhalofop, cyclosulfamuron, fenoxaprop-p-ethyl and oxyfluorfen did not show any leaching tendency by both methods.

Some compounds show different classifications by the EPA-US and GUS methods, or due to the lack of physico-chemical parameters the prediction was not possible. These compounds were 2,4-D, azimsulfuron, diuron, ethoxysulfuron, glyphosate, oxadiazon, pendimethalin, penoxsulam, pyrazosulfuron, propanil, thiobencarb, carbaryl, fipronil, propiconazole and tebuconazole. These differences between the methods can occur because the methods consider different physico-chemical characteristics.

## 4.3 Surface Waters

### 4.3.1 Choice of the pesticides for the surface waters monitoring

For the surface water monitoring, eighteen pesticides and two metabolites were chosen. The choice was based on the pesticide usage in the region and on the possibility of contamination of the surface water by these compounds. The sources of contamination near the water source were also considered. The company that supplies water for the Rio Grande city takes water from the Sao Goncalo channel. This channel is an important connection between the Patoos Lagoon and the Mirim Lagoon, and in the margins there are many agricultural activities; such as horticultural, grains and rice irrigation, besides the industrial activities and the navigation. The compounds 2,4-D, bispyribac-sodium, propanil, bentazone, carbofuran, pyrazosulfuron-ethyl and quinclorac besides being used for the rice culture showed MWTRP. The compounds atrazine, clomazone, diuron, fipronil, imazethapyr, imazapic, metsulfuron-methyl showed HWTRP and penoxsulam showed LWTRP. Tebuconazole and simazine showed MWTRP. And, besides these compounds, two metabolites (3,4-DCA and carbofuran 3-hydroxy) and the biocide irgarol were also analyzed.

### 4.3.2 Monitoring studies of surface water

In Figure 3, the sum of the monthly results of the monitoring analysis of the surface water from the São Gonçalo Channel and of the drinking water in Rio Grande are presented.

Taking into account the 18 pesticides and 2 metabolites under analysis, concentrations above the LOQ were detectable, at least once, for carbofuran 3-hydroxy, 3,4-DCA, atrazine, clomazone, bentazone, bispyribac-sodium, carbofuran, clomazone, diuron, fipronil, imazethapyr, imazapic, irgarol, pyrazosulfuron-ethyl, propanil, quinclorac, simazine and tebuconazole. It is noticed that, except in February 2009, March and April 2010 the sum of concentrations of pesticides was always lower than  $0.5 \mu\text{g L}^{-1}$ , the value established by the European legislation (EU Council Directives, 1998).

Some compounds were found in more than 60% of the collections. In surface water, they were atrazine, clomazone, diuron, imazapic, imazethapyr, irgarol and tebuconazole; and in drinking waters they were clomazone, diuron, imazapic, imazethapyr and tebuconazole.



The presence of diuron and irgarol in almost all the monitoring period indicates that in the region of the São Gonçalo Channel, concerning the contamination by pesticides, is influenced not only by the agricultural process but also by other sources. The occurrence of diuron can be due to the fact that this herbicide is largely used in other kinds of cultures such as lettuce, citrus fruits, and onion (Camara dos Agrotóxicos, 2008). Besides, diuron and irgarol are used as antifouling in paints for vessels (Buma et al., 2009; Avila et al., 2005). The association of these uses increases the contamination by diuron in waters, especially in portuary regions such as Rio Grande where there is intensive navigation. The presence of 3,4-DCA, the main metabolite of diuron and of propanil, although lower than LOQ, confirms the use of these compounds.

Whereas diuron is used in the culture of rice, the herbicide irgarol is not, but both are used as antifouling (Sapozhnikova et al., 2007), indicating that the contamination by these compounds has the same source, the vessels. The other compounds found in the samples are probably due to irrigated rice, because all compounds are recommended for this culture and this is the agricultural practice that dominates the southern region in RS state, besides the cultures of onion and tomato (Camara dos Agrotóxicos, 2008).

The herbicides imidazolinones analyzed in this study, imazethapyr and imazapic, were detected during all the sampling period, both in the surface water and in potable water. The highest concentrations found for imazapic were  $0.34 \mu\text{g L}^{-1}$  for drinking water and  $0.2 \mu\text{g L}^{-1}$  for surface waters. For imazethapyr the highest concentrations were  $0.27 \mu\text{g L}^{-1}$  for drinking water and  $0.35 \mu\text{g L}^{-1}$  for surface waters. The fact that they are frequently detected in the samples can be explained, for example, by the system of rice cultivation, which works with a variety of rice that is very resistant to the pesticides of the imidazolinones class; they are effective against red rice, the main pest in the irrigated rice plantation (Avila et al., 2005). Most of the time, the compounds were found in the same month probably indicating the use of a mixture, that was sold commercially and is composed by both compounds.

The fungicide tebuconazole and the herbicide atrazine were detected in the sampling in many months. Triazines are used in the world as pre and post-emerging selective herbicides to control weeds in many cultures, such as corn, wheat, sugar cane and barley.

The insecticide fipronil was detected in all samples, since it is recommended for several cultures (agriculture and silviculture). This compound was found in surface waters in RS, in other studies. In the study developed by Marchesan et al. (2010) it was found in concentration until  $26.2 \mu\text{g L}^{-1}$  and with high frequency of detection. The herbicide pyrazossulfuron-ethyl was also detected in some samples since this compound is recommended for rice cultivation.

The detection of the metabolite carbofuran 3-hydroxy, from carbosulfan and carbofuran, indicates that one of these compounds had been used on farms near the São Gonçalo Channel.

The herbicide clomazone was detected in concentrations lower than the LOQ in all samples, except in July, when it was detected in surface and potable waters. Marchesan et al. (2007) detected clomazone in river waters in RS, with high frequency. They comment the relation of the frequency with the rainfall regime and with the rice water management used in the fields.

#### 4.4 Groundwater

##### 4.4.1 Choice of the pesticides for the groundwater monitoring

The selection of the analytes included in this study was based on their extensive use as pesticides in agricultural areas. Moreover, these pesticides are some of the mostly used

pesticides in the area under study; according to the US Environmental Protection Agency (US EPA), they have potential to reach the groundwater systems (Table 3).

Herbicides	US-EPA Criteria						GUS index
	Water solubility	$K_{oc}$	$K_H$	$t_{1/2}$ soil	$t_{1/2}$ water	Result	
2,4-D	A	A	A	N	N	PC	TL
atrazine	A	A	A	A	N	PC	PL
azimsulfuron	A	A	A	A	N	PC	TL
bentazone	A	A	A	A	A	PC	PL
bispyribac-sodium	A	N	N	N	A	NC	IL
cyhalofop-butyl	N	N	A	N	N	NC	IL
cyclosulfamuron	N	N		A	N	NC	IL
clefoxydim	N		N		N	NC	
clomazone	A	A	A	A	N	PC	PL
diuron	A	A	A	A		PC	TL
ethoxysulfuron	A	A	A	A	N	PC	TL
fenoxaprop-p-ethyl	N	N	A	N	N	NC	IL
glyphosate	A	N	A	A	N	PC	IL
imazapic	A	A		A	N	PC	PL
imazethapyr	A	A	A	A	N	PC	PL
metsulfuron-methyl	A	A	A	A	A	PC	PL
molinate	A	A	N	A	A	PC	PL
oxadiazon	N	N	A	A	N	NC	TL
oxyfluorfen	N	N	A	A	N	NC	IL
pendimethalin	N	N	N	A	N	NC	PL
penoxsulam	N	A	A	A	N	PC	TL
pyrazosulfuron-ethyl	N	A		A	N	I	TL
propanil	A	A	A	N	N	PC	IL
quinclorac	N	A	A	A		PC	PL
simazine	N	A	A	A	N	PC	PL
thiobencarb	A	N	A	A	A	PC	IL
triclopyr	N	A	A	A	N	PC	PL
fungicides and insecticides							
azoxystrobin	N	N	A	N	N	NC	IL
benfuracarb	N	N	A	N	N	NC	IL
beta-cyfluthrin	N	N	A	N	N	NC	IL
carbaryl	A	A	A	N	N	PC	TL
carbofuran	A	A	A	A	N	PC	PL
cyfluthrin	N	N	N	A	N	NC	IL
fenitrothion	N	N	A	N	N	NC	IL
fipronil	N	N	A	A	N	NC	PL
imidacloprid	A	A	A	A	N	PC	PL
malathion	A	A	N	N	N	NC	IL

Fungicides and Insecticides	US-EPA Criteria						GUS index
	Water solubility	$K_{oc}$	$K_H$	$t_{1/2}$ soil	$t_{1/2}$ water	Result	
mancozeb	N	N	A	N		NC	IL
propiconazole	A	N	A	A	N	PC	TL
tebuconazole	A	N	A	A		PC	TL
thiamethoxam	A	A	A	A	N	PC	PL
thiophanate-methyl	N	A	A	N	N	NC	IL
tricyclazole	A	A	A	A		PC	PL
trichlorphon	A	A	A	A		PC	PL
trifloxystrobin	A	N	A	N	N	NC	IL

Table 3. Risk assesment of groundwater contamination based on US-EPA criteria and GUS index (US-EPA, N= not meet the criteria; A= meet the criteria; I= non-conclusive; PC = potential contaminant NC = non-contaminant; blank – data not available; GUS IL = not leachable, TL = transition zone and PL= probably leachable)

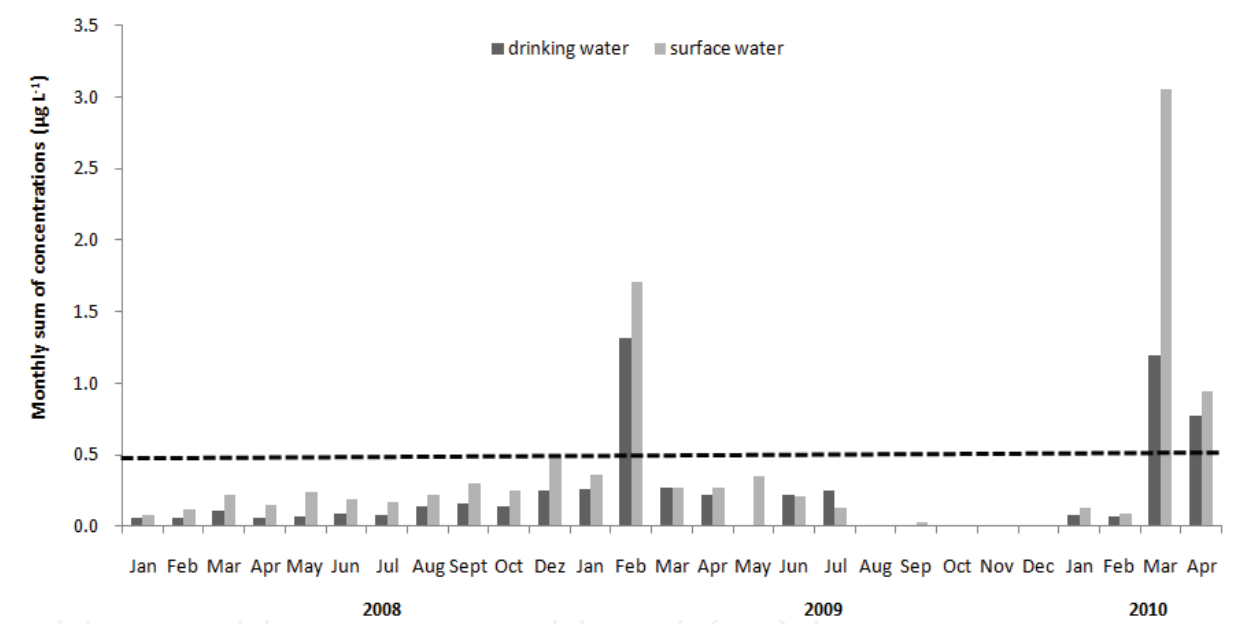


Fig. 3. Sum of pesticide concentrations determined from January 2008 to April 2010.

4.4.2 Pesticide determination in groundwater

Figure 4 show the pesticide levels detected at each location in various sampling campaigns, carried out from September 2007 until August 2008. Results are not surprising at all, since the agricultural practice in the area is intense and has been going on for years. Carbofuran, clomazone and tebuconazole were the compounds found. In general, significant differences were observed in the levels and the profile of the pesticides detected in distinct sampling periods.

The behavior of the samples was strongly different. 2,4-D was the only pesticide that was not detected, probably because it is less used in Quitéria than the others. It is mainly used in the cultures of rice, corn, soy and wheat (Camara dos Agrotóxicos, 2008), which are not raised in Quitéria. This compound has lower half life than others and, moreover, has the

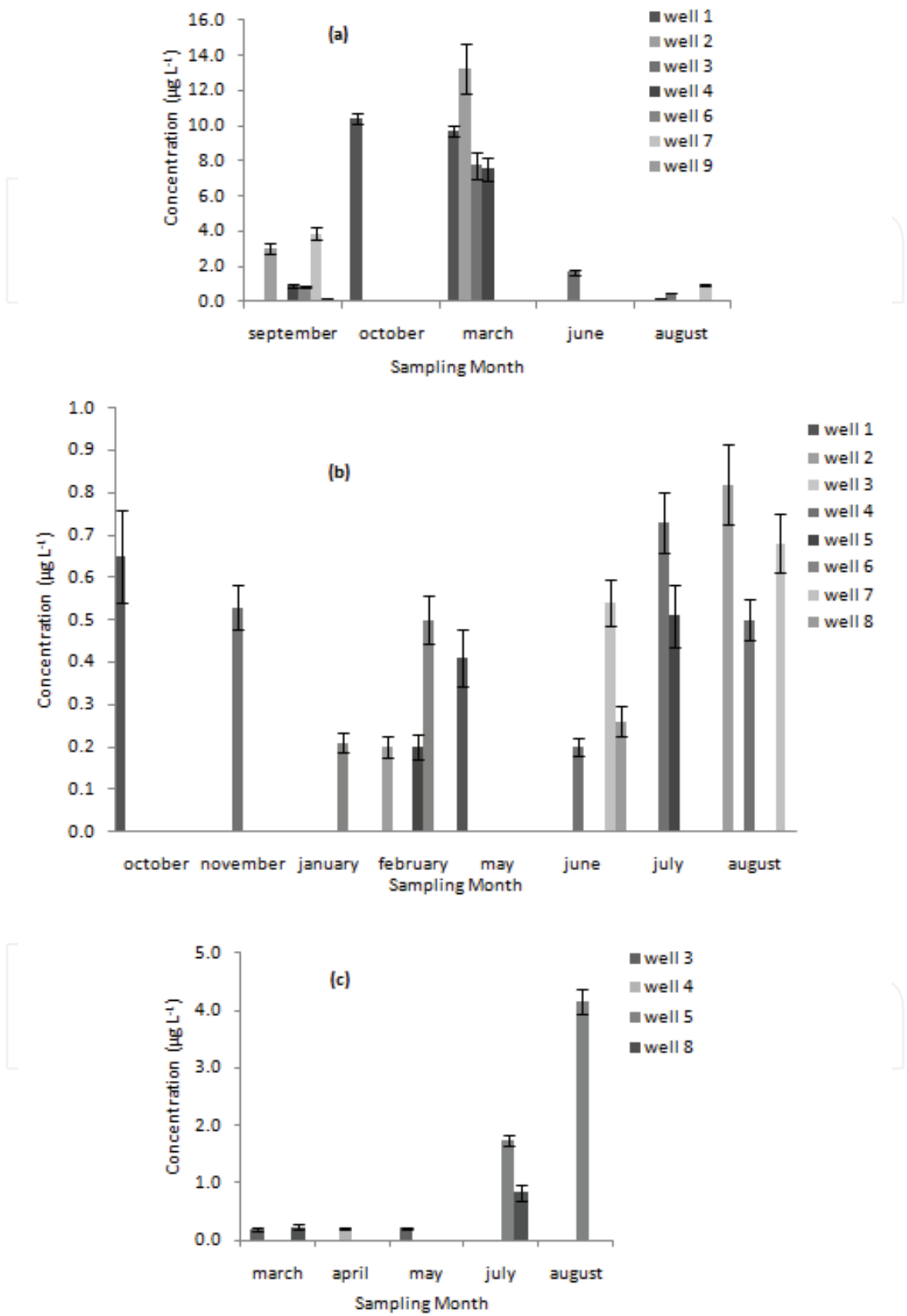


Fig. 4. Concentrations of carbofuran (a), clomazone (b), and tebuconazole (c) (µg L<sup>-1</sup>) in water samples from wells in different months (Caldas et al., 2010)

highest solubility in water and the lowest half life in soil, probably being degraded rapidly before reaching the groundwater. In surface waters, it has been found in many studies (Laganà et al., 2002; Palma et al., 2004; Primel et al., 2005).

The pesticide carbofuran showed the highest concentrations. October and March were the months that showed the highest contamination, 10.4 and 9.75  $\mu\text{g L}^{-1}$ , respectively; exceeding the maximum value permitted by the Brazilian legislation for groundwaters. Wells 1 (9 m) and 2 (37 m) presented the major occurrence. Tariq et al. (2004) detected carbofuran residues in well waters with a detection frequency of 59% in July and 43% in October. This is one of the factors related to the high solubility of the compound in water. The highest concentration was 23.1  $\mu\text{g L}^{-1}$ . Bacigalupo & Meroni (2007) analyzed water from wells in an agricultural area in the south of Milan for 11 months and found residues of carbofuran in 90% of the samples at concentrations below 5.0  $\mu\text{g L}^{-1}$ . Hernández et al. (2001) detected carbofuran in groundwater in around 25% of samples, but never in levels higher than 0.1  $\mu\text{g L}^{-1}$ .

Clomazone has high water solubility and water half life higher than 30 days and showed its highest levels in August in well 2 (9 m), 0.82  $\mu\text{g L}^{-1}$ . The high frequency of contamination of clomazone in groundwaters was detected by Bortoluzzi et al. (2007); they detected the compound in 50% of well samples, at a mean concentration of 6.76  $\mu\text{g L}^{-1}$ . In this study, the herbicide clomazone was detected in 70 % of wells. This is the only work found that analyze pesticides in groundwater in RS state.

The high detection frequency of the pesticides carbofuran and clomazone in groundwater, both in shallow and deep wells can be explained by their high potential for leaching as a result of their low soil sorption coefficient and high solubility in water, as well as relatively high half life in the soil.

The systemic tebuconazole fungicide is used to control a wide range of fungi on fruit and vegetables. The concentrations of tebuconazole were higher in July and August, and well 5 (6 m) showed the highest levels, 1.73  $\mu\text{g L}^{-1}$  in July and 3.65  $\mu\text{g L}^{-1}$  in August.

The compound tebuconazole was detected in wells 29 m deep. Although it has occurred with low frequency, it confirms the high potential for leaching that this compound has. This compound was found in groundwaters by Baugros et al. (2008). The amounts ranged from 0.03 to 0.89  $\mu\text{g L}^{-1}$ .

## 5. Conclusion

The use of models/parameters to predict the pesticide behavior in the environment is important to obtain an estimate about the contamination risk. The evaluation of the data presented in the list of compounds reveals that among the pesticides most commonly used in agriculture in Rio Grande do Sul State, most of those investigated presented mobility in the environment, and risk to contaminate the surface and groundwaters.

The results of the monitoring show that surface and groundwater contamination by agriculture is still an important issue that cannot be ignored.

In an attempt to minimize risks associated with pesticides, technological advances that allow pesticide detections at very low concentrations, combined with research findings help to increase the scientific understanding of the potential of pesticides to contaminate water resources.

The public interest is well served by a cooperative effort among regulators, university researchers, and industry to establish reasonable use restrictions. These efforts should ensure that, when used appropriately, pest control products will not pose a threat to water quality.

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## **Herbicides and Environment**

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Herbicides are much more than just weed killers. They may exhibit beneficial or adverse effects on other organisms. Given their toxicological, environmental but also agricultural relevance, herbicides are an interesting field of activity not only for scientists working in the field of agriculture. It seems that the investigation of herbicide-induced effects on weeds, crop plants, ecosystems, microorganisms, and higher organism requires a multidisciplinary approach. Some important aspects regarding the multisided impacts of herbicides on the living world are highlighted in this book. I am sure that the readers will find a lot of helpful information, even if they are only slightly interested in the topic.

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Unit 405, Office Block, Hotel Equatorial Shanghai  
No.65, Yan An Road (West), Shanghai, 200040, China  
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元  
Phone: +86-21-62489820  
Fax: +86-21-62489821

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