Kinetics of carbosulfan hydrolysis to carbofuran and the subsequent degradation of this last compound in irrigated rice fields

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Abstract

The objectives of this work were estimate the reaction rates of hydrolysis of carbosulfan to carbofuran and subsequent degradation of this last compound in irrigated rice fields, and the respective half life, in aquatic environment and soil solution, by mean of numerical solution of differential ordinary linear equations system that describes the kinetics of insecticide concentrations. The results indicated that the carbosulfan and carbofuran have low persistence in water and medium persistence in soil solution of tropical irrigated rice fields. However, both compounds can be found in laminar water and soil solution in concentration above environmental and human safety limits.

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Keywords: Kinetics; Rice; Carbamate; Carbosulfan; Carbofuran; Oryzophagus oryzae; Model

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1. Introduction

Oryzophagus oryzae (Coleoptera: Curculionidae) is a major pest of the irrigated rice crop, commonly known as rice-infesting weevil, which larvae cause severe damage to rice roots after flooding and consequently drastically reducing plant nutrient uptake (Carbonari, 2000). When this pest is not under control losses may reach 40% of the grain yield. One of the control procedures consists on the insecticide application, which is a common practice in Brazil during the later years. Carbosulfan has been the mostly used insecticide and the control procedure is the direct application of granular carbosulfan in sidedressing or in the irrigation water when the presence of weevil larvae is detected. The practice of such verification is done by taking off some plants and shaking them into the water what makes the larvae show up over the water surface (Prando, 2002).

Although carbosulfan shows a good agronomic efficiency, this insecticide has environment restrictions due to the risks of contamination. One problem frequently associated to the carbosulfan is the death of forest animals as the case that came into notice in the State of Virginia observed by Stinson et al. (1994). Dietrich et al. (1995) found similar problems for the carbosulfan granules applied in field crops in Swiss. According to Crepeau and Kuivila (2000), the continuous presence of carbosulfan in water channels and rivers might cause severe, sub-lethal or chronic damages to aquatic organisms. Gupta (1994) observed that carbosulfan is toxic to micro crustaceous and vertebrates of a same food chain. Norberg-King et al. (1991) affirm that carbosulfan is a toxic insecticide to the aquatic wildlife. The use of carbosulfan in agriculture is prohibited in some countries (Anonymous, 1996a; Anonymous, 1996b; James, 1995) due to its eco-toxicity. The carbosulfan persistence in the paddy water and in soil solution has been studied in tablelands and channels, because carbosulfan is degraded mainly by hydrolysis (Seiber et al., 1978; Siddaramappa and Seiber, 1979; Tejada and Magallona, 1985; Jinhe et al., 1989; Mora et al., 1996; Trevizan et al., 2002). However, Chiron et al. (1995) have demonstrated that carbamate insecticide concentrations exceeding 0.5 µg l⁻¹ (limit established by the European Community) are scarcely found in the environment.

The degradation process of carbosulfan (2,3-dihydro-2,2-dimethyl-7-benzofuranol methylcarbamate) molecule (represented as RX) occurs when it reacts with the water molecule originating a new C–N bond and breaking a C–X bond in the original molecule. The net reaction is essentially a direct displacement of X by OH (Seiber et al., 1978; Mabury and Crosby, 1996). Other factors might accelerate the hydrolysis such as high pH (Siddaramappa et al., 1978; Siddaramappa and Seiber, 1979; Chapam and Cole, 1982; Ramanand et al., 1991), the microbial community (Siddaramappa and Seiber, 1979) and light intensity (Seiber et al., 1978; Siddaramappa et al., 1978). The volatilization, photolysis and oxidation are important factors in the process of carbosulfan dissipation (Seiber et al., 1978; Deuel et al., 1979). Tejada and Magallona (1985) and Rouchaud et al. (1990) have observed that the main carbosulfan metabolites are the 3-ketocarbosulfan (2,2-dimethyl-3-oxo-2,3-dihydro-1-benzofuran-6-yl methylcarbamate), carbosulfan-phenol (2,2-dimethyl-2,3-dihydro-1-benzofuran-7-ol) and 3-ketocarbosulfan-phenol (7-hydroxy-2,2-dimethyl-1-benzofuran-3(2H)-one).

Carbosulfan (2,3-dihydro-2,2-dimethyl-7-benzofuranol(di-n-butylaminosulfenyl)(methylcarbamate)) has substituted carbosulfan as insecticide, because of environmental reasons and of its lower persistence. According to Marsden et al. (1982) and Umemu and Fukuto (1982), carbosulfan presents lower toxicity for the aquatic wildlife than carbosulfan. Tejada and Magallona (1985) demonstrated that carbosulfan was not detected in samples of paddy water and soil solution collected few hours after its application. Hydrolysis is the main path of carbosulfan to carbosulfan degradation, its first metabolite, but in some cases, this latter might present longer persistence in a low pH environment (Ramanand et al., 1991). Hydrolysis is the main path of carbosulfan to carbosulfan degradation, its first metabolite, but in some cases, this latter might present longer persistence in a low pH environment (Ramanand et al., 1991). Other environmental factors, such as temperature variation, might directly influence the carbosulfan degradation process (Sahoo et al., 1990). Thus, more information is required about the behavior and destination of carbosulfan and carbosulfan in the environment in Brazilian areas where flooding irrigation is used.

The pesticide persistence in an environment compartment can be characterized by the pesticide half-life in such a compartment. The half-life is a measure of the time required for the pesticide concentration to be reduced to half the original value throughout biological or chemical degradation processes. Some pesticides are found in a specific compartment as a transformation product of another pesticide originally applied or by transport from a compartment to another. In these cases, the original concentration, necessary for the half-life calculation, is obtained by means of a special
transformation kinetics that cannot be described by a first-order kinetics. An example of this situation occurs when calculating the carbofuran half-life in the paddy water and soil solution, because carbofuran is the result of carbosulfan transformation originally applied in the paddy water. Another example is the carbosulfan half-life calculation in the soil solution when diffused from the paddy water. The half-life estimated may be obtained by the maximal pesticide concentration calculation in that compartment in a kinetics described by an equation of the type

\[ C(t) = a \exp(-bt) - \exp(-ct) \]  

in which the initial concentration and the maximum concentrations are given by \( C(0) = 0 \) and \( C_{\text{max}}(t) = C(t_{\text{max}}) \)

where \( t_{\text{max}} = \frac{\ln(\frac{a}{b})}{a-b} \). In this case, half-life can be estimated by \( t_{1/2} = \frac{1}{2} \). Thus, this research aimed at estimating the carbosulfan and carbofuran half-lives in the paddy water and soil solution through the numerical resolutions of a linear system of ordinary differential equations, which describe the insecticide concentrations kinetics in a Brazilian rice field trial.

2. Materials and methods

The field experiment was carried out at “Varjão” Farm, a 200 ha area of irrigated rice crop. The farm is located at Bariri municipal district, State of São Paulo, Brazil (Occidental Planalt, 21°59′47″S and 48°36′41″ LGr). The area was subdivided in 1.5–2.5 ha rice fields that according to the local topography were separated by irrigation and drainage channels. The experiment was carried out in a 2 ha field located at the first water entry to avoid contaminations, so the flooding water enters this area first and afterwards is distributed to the other rice fields. The soil was classified as Gleissolos (Oliveira et al., 1999). Soil samples were collected for analysis of probable pesticide (carbofuran and carbosulfan) residues from previous planting.

The entire area is managed according to usual procedures for irrigated rice crop, initially consisting of pre-sowing irrigation to induce germination of red rice and other weeds. For that, the area is flooded and drained and after weed emergence, herbicides are applied as follows: glyphosate at a rate of 3.3 l ha\(^{-1}\) and 2,4-D at a rate of 0.75 l ha\(^{-1}\) (Foloni, 1999).

Twenty-two days after the post-emergence weed control (November 22nd, 2002), rice (IRGA 420) was seeded with fertilization at a rate of 250 kg ha\(^{-1}\) of a 05-25-25 NPK formulation. One day after sowing, one more herbicide application was made to control weed in pre-emergence, using clomazone at a rate of 0.66 l ha\(^{-1}\). Following, irrigation was applied by fast flooding and draining afterwards, inducing seed germination. Fifteen days after seedlings emergence, the area was flooded again and this paddy water remained in the field up to harvest. Dress nitrogen fertilization was applied using urea at 27 and 45 days after sowing at the rates of 50 and 80 kg ha\(^{-1}\), respectively.

Carbosulfan (Marshal 400 SC) was applied at a rate of 400 g ha\(^{-1}\) of active ingredient, in order to control the rice-inesting weevil. Before application, the water paddy was maintained on the field by keeping closed the water entry and exit for 48 h, after they were open again. Harvest was made 105 days after sowing.

A soil solution sampler was built, consisting of a porous capsule that was attached to a PVC tube (1.27 cm diameter x 30 cm length), two silicone corks (one in a plastic bottle and another in the PVC tube) and a hose. The soil solution was pumped through the hose up to the bottle using a manual pump. Eight samplers were randomly installed in the experimental area, when the soil was dry, 20 cm depth, nine days before rice sowing. The paddy water flow was also collected using plastic bottles and samples were obtained by fast bottle immersion in eight randomly chosen places in the plot. Soon after, temperature and pH were determined in all paddy water and soil solution samples, using a portable pH-meter (PG1400, GENAKA). At the end of sampling, plastic bottles with samples were immediately placed in icebox and transported to freezer, where were maintained at –18 °C.

The time sequence adopted for the paddy water and soil solution sampling was: 0, 24, 48, 96, 192, 384 and 768 h after carbosulfan application. All samples were kept at –18 °C during five months, and thereafter, they were sent to the Laboratory of Pesticide Residues and Chromatographic Analysis of the University of São Paulo (ESALQ, USP). The method of carbofuran and carbosulfan extraction from water was adapted from Leppert et al. (1983) and consisted of 100 ml sample extraction by liquid-liquid partition with three times 50 ml of dichloromethane.

In order to insert and separate sample compounds, a gas chromatography system was used, injecting 2.0 µl aliquot-sample, in “splitless” mode, in a HP-SMS capillary column (length—30 m, diameter—0.25 mm; film thickness—0.25 µm, with oven temperature programmed as follows: initial = 100 °C, for 1 min; slope: 25 °C min\(^{-1}\) up to 280 °C, kept for 2 min 30 s). For residue identification and quantification, a mass selective detector (MSD) was used, coupled to the chromatograph, which was operated in the system of ion monitoring (SIM), analyzing fragments 160 and 164 for the carbofuran and carbosulfan quantification, respectively.

The linear system of ordinary differential equations that describe the kinetics of carbofuran and carbosulfan
The observed average temperature in the plots might have interfered in the carbofuran degradation both by hydrolysis and microbiological processes. As pointed
out by Tejada and Magallona (1985) and Ramanand et al. (1991), carbosulfan was immediately transformed to carbofuran through hydrolysis, with a half-life of 3 days (78 h) in paddy water (Table 1). Similar results were obtained by Tejada and Magallona (1985) (5.8 days). Johnson and Lavy (1995) found half-life of 3 days, meanwhile Nicosia et al. (1991) determined values of 22, 26 and 18 days.

Once carbofuran is a stable compound in acidic environment (Siddaramappa and Seiber, 1979; Ramanand et al., 1991), the carbofuran degradation in paddy water, according to Siddaramappa and Seiber (1979) and Mora et al. (1996), occurs mainly by hydrolysis and was even enhanced by pH. High temperatures might also have contributed for carbosulfan degradation. The carbofuran maximum concentration period and the maximum concentration were 30 h (1.25 day) and 0.2334 mg l$^{-1}$, respectively.

The maximum concentration found in the paddy water is above the value accepted by the American
Environmental Protection Agency (EPA) (<40.0 μg l⁻¹) and the European Community (<0.10 μg l⁻¹). Fig. 2 demonstrates that carbosulfan concentration evolution in paddy water is described by Eq. (8) and does not follow a first-order kinetics.

In the soil solution (0–20 cm layer) the maximum concentration period, maximum concentration and carbosulfan half-life were 3.4 days (78 h), 0.0018 mg l⁻¹ and 21 days (540 h), respectively (Table 1). Soil solution showed an average pH of 6.63 and temperature of 29 °C. However, the carbosulfan half-life was 10 days (240 h), the time period for maximal concentration was 92 h (3.8 days) and the maximum concentration, 0.2476 mg l⁻¹, respectively (Table 1). Figs. 3 and 4 illustrate the carbosulfan and the carbofuran concentrations evolution kinetics in soil solution as described by Eqs. (9) and (10) respectively.

The carbosulfan and carbofuran physicochemical characteristics required for the study of the insecticides behavior and environmental destination are presented in Table 2. The air–water partition coefficient is a pesticide volatilization indicator from the water surface and is given by

\[ K_{aw} = \frac{P_a P_m}{SR(273 + t)} \]

where, \( R = 8.314 \text{ Pa m}^3 \text{ mol}^{-1} \text{ K}^{-1} \) is the gas constant, \( t \) is the atmospheric temperature (25 °C), \( S \) (ml g⁻¹) is the pesticide water solubility, \( P_m \) (g mol⁻¹) is the pesticide molecular weight and \( P_a \) (Pa) is the pesticide vapor pressure.

Pesticides with \( K_{aw} < 4.0 \times 10^{-6} \) are not volatile under atmospheric temperatures. Pesticides with \( 4.0 \times 10^{-6} < K_{aw} < 4.0 \times 10^{-4} \) have volatilization controlled

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Carbosulfan</th>
<th>Carbofuran</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_a ) (g mol⁻¹)</td>
<td>380.55</td>
<td>221.26</td>
</tr>
<tr>
<td>( S ) (ml g⁻¹)</td>
<td>0.3</td>
<td>320.0</td>
</tr>
<tr>
<td>( P_m ) (g mol⁻¹)</td>
<td>5.57</td>
<td>2.32</td>
</tr>
<tr>
<td>( K_{aw} ) (carbon organic partition coefficient, ml g⁻¹)</td>
<td>8500&lt;sup&gt;a&lt;/sup&gt;</td>
<td>22&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>( P_a ) (vapor pressure, Pa)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4.09 × 10⁻⁵</td>
<td>6.5 × 10⁻⁹</td>
</tr>
<tr>
<td>( K_{aw} ) (air–water partition coefficient)</td>
<td>2.06 × 10⁻²</td>
<td>1.23 × 10⁻⁷</td>
</tr>
<tr>
<td>GUS index</td>
<td>0.09</td>
<td>2.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> Tomlin (2000).

<sup>b</sup> Estimated by \( \log K_{aw} = 3.64 - 0.55 \log(S) \) (Kenaga, 1980).

<sup>c</sup> Hornby et al. (1995).

by gaseous diffusion, which is dependent on temperature and moisture and present low air percentage distribution. Pesticides with \( K_{aw} > 4.0 \times 10^{-4} \) are probably volatile and might present high air percentage distribution (Trapp and Matthis, 1998). Under these conditions carbosulfan might be volatile from the water surface and carbofuran does not volatilize both under atmosphere temperatures (Table 2). These results are in accordance with those of Tejada and Magallona (1985) and Deuel et al. (1979) for carbosulfan and carbofuran volatilization, respectively.

The carbosulfan sorption coefficient, \( K_{oc} = 8500 \text{ ml g}^{-1} \), indicates that this compound has high affinity with both organic matter and soil solid particles, while the carbofuran, \( K_{oc} = 22 \text{ ml g}^{-1} \), indicates low affinity with soil solid particles and high affinity with both laminar water and soil solution (Table 2). As in

![Fig. 3. Evolution of carbosulfan concentrations (means and standard mean deviations) in the irrigated rice soil solution at 0–20 cm depth in function of time.](image-url)
et co ndition s, ca r b osulf an and carbofuran concen trati o ns
in paddy water and so il so lution samp les all owed th e
vi ation potential
" A lmeida" Spain
respe ct i vi ty. Furthermore, in studies carried out in the
residues in so il s fr om
solution half - life in Table I and so il sorpti on coefficients
(GUS ;;::,:
(1989). The
GUS
index, calculated departing from soil
lixi­
(1.8
(Gustafson,
The GUS index, calculated departing from soil
solution half-life in Table 1 and soil sorption coefficients
in Table 2, indicate that carbosulfan (GUS = 0.09) do
not lixivate and carbofuran has an indeterminate lixi­
vation potential (GUS = 2.7) (Table 2), even taking into
account that Bosch and Truman (2002) and Cogger
et al. (1998) had detected high amounts of carbofuran
residues in soils from Plains, Georgia and Washington,
respectively. Furthermore, in studies carried out in the
"Almecida" Spain aquifers, Chiron et al. (1995) found
carbofuran concentrations above 0.5 µg l-1.

4. Conclusions

Despite the experiment was carried out under field
conditions, carbosulfan and carbofuran concentrations
in paddy water and soil solution samples allowed the
numerical fitness of kinetic equations that turned possible
to estimate the period of maximum concentration,
maximum concentration and half-life of both pesticides.
The concentration values estimated from field collected
samples indicated that carbosulfan and carbofuran had
low water persistence and medium persistence in soil
solution, however, both can be found in paddy water
and in soil solution in concentrations above the human
and environment safety limits stated by foreign regulat-
ory agencies.

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