# RESIDUES OF CHLORANTRANILIPROLE AND THIAMETHOXAM IN RICE GRAINS

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#### INTRODUCTION

The use of pesticides in irrigated rice has been intensified in recent years due to higher incidence of foliar diseases and pests at the economic injury level. In many cases, the appearance of pests occurs near harvest. Therefore, the use of pesticides is characterized as an essential management practice to ensure agricultural yield and food quality. However, the presence of residues of these substances in food is a major public health concern and industrialized or fresh food must be analyzed for the presence of pesticide residues (UDDIN et al., 2011).

Overall, the results of several studies show variation in the presence of pesticide residues in rice grains. In India, a study was conducted with the insecticides thiamethoxam and lambda-cyhalothrin, the insecticides were applied at 1 and 2-fold of the recommended rate in the rice shoots. The study did not detect any residues in grain (BARIK et al., 2010). Chen et al. (2007) highlight that organochlorine insecticides used during and at the end of the cycle of the rice crop in China resulted in quantification of pesticide residues in polished rice grains (0.039 mg/kg) and rice bran (0.057 mg/kg).

The use of chlorantraniliprole and thiamethoxam insecticides has been important on controlling pests in rice. Therefore, the objective of this study was to analyze residues of these insecticides in hull, bran and rice grain.

# MATERIAL AND METHODS

The first phase of the experiment was conducted during the summer period of 2012 at the David R. Wintermann Rice Research Station at Texas A&M University near Eagle Lake, TX. The rice was planted in May  $5^{th}$ , 2012, using the cultivar Presidio. The seeding rate was 90 kg/ha. Each plot had seven rows spaced at 0.19 m from each other and measuring 4 m long. The management practices were conducted according to the technical recommendations for the crop. The insecticides applications were performed at different timings using 1x and 2x the recommended rate. The experiment was conducted in a randomized complete block design with four replications.

The applications were made at 5, 15, 25 and 35 days after flowering (DAF) using the rate of 30 g a.i.  $ha^{-1}$  of chlorantraniliprole and 30 g a.i.  $ha^{-1}$  of thiamenthoxam (recommended rate), and 60 g a.i.  $ha^{-1}$  of chlorantraniliprole and 60 g a.i.  $ha^{-1}$  of thiamenthoxam (double rate). In two treatments a sequential application using the recommended rate was conducted at 5 and 25 DAF, and at 5, 25 and 35 DAF.

For quantification of residues in grains, rice plants were harvested when the average moisture content reached 22% on the area of 4.76 m<sup>2</sup> (4.0 x 0.95 m) in each plot. After grain harvesting, a homogeneous sample of 2 kg was separated. This process was followed by cleaning and drying with forced air ventilation at  $35\pm2$  °C until reaching an average moisture content of 11%. After that, the samples were stored at -20 °C.

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Insecticides residues were quantified using several different types of rice samples: rice hull removed from the rice processing carried out in a rice testing machine, rice bran and polished grain obtained with the polishing process in a rice processing machine.

The samples were subjected to residues extraction using an accelerated solvent extraction (ASE) with the following equipment configurations: extraction solvent – acetonitrile; cell size - 22 mL; extraction temperature for the hull - 75 °C, extraction temperature for bran and grain - 100 °C; system extraction pressure - 1500 kPa; with two cycle. Afterward the samples were analyzed using ultra performance liquid chromatography (UPLC) with detection limit of 0.01 ng/g.

# **RESULTS AND DISCUSSION**

The results showed residues of chlorantraniliprole and thiamethoxam in hull, bran and polished grains. Pesticides residues were quantified in rice hull (Figure 1) for all analyzed treatments. On overage residues of chlorantraniliprole were quantified in concentrations 68% greater than thiamethoxan in rice hulls. The results showed that greater concentration of chlorantraniliprole were observed for the sequential applications at 5, 25 and 35 DAF. Figure 2 shows the results regarding the analysis performed in rice bran. Residues of both insecticides were detected independent of the application timing and rate. The highest concentrations were observed for chlorantraniliprole when applications were conducted 25 DAF and with sequential applications.

With respect to the analysis conducted in polished grains (Figure 3) residues of both insecticides were not quantified for the applications using the recommended rate performed at 5 DAF. However, for all the other treatments residues were detected for chlorantraniliprole. It was observed that in general applications with 2x the recommended rate showed the highest amounts of chlorantraniliprole residue, even in comparison to subsequences applications. Thiamethoxam residues were not detected for the applications conducted at 5 and 15 DAF, however, for the other applications, insecticide residues were quantified.

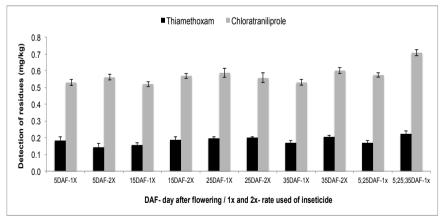


Figure 1- Quantification of chlorantraniliprole and thiamethoxam residues in rice hull. Insecticides were applied at different moments after rice flowering using 1x and 2x the recommended rate.

In summary, the chlorantraniliprole shows the highest levels of residue compared to thiamethoxam for all analyzes performed (hull, bran or rice grain). The highest concentrations observed were obtained in hull and in rice bran, characterized as a physical

barrier in relation to rice grain, because the composition of the hull and the rice bran shows lipophilic characteristics, which can promote the adsorption of some pesticides (DORS et al. 2011).

Similar tendencies in residue concentration detected in hull, bran and rice grain were observed by Pareja et al. (2012). The authors evaluated several pesticides used in irrigated rice, and the results observed are similar to the results observed in this study, with the highest concentration detected in hull and rice bran. The same study evaluated the response and distribution of thiamethoxam in the rice field, where residues were detected in hull (0.032 mg/kg) and in rice bran (0.02 mg/kg), in rice grains residue was not quantified regardless of the beneficiation form, brown rice and polished rice. Barik et al. (2010) showed that the application of the insecticides thiamenthoxam and lambda-cyhalothrin in rice shoots were not detected in the polished rice grains.

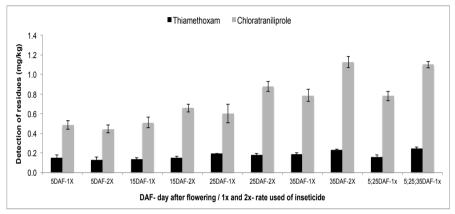


Figure 2- Quantification of chlorantraniliprole and thiamethoxam residues in rice bran. Insecticides were applied at different moments after rice flowering using 1x and 2x the recommended rate.

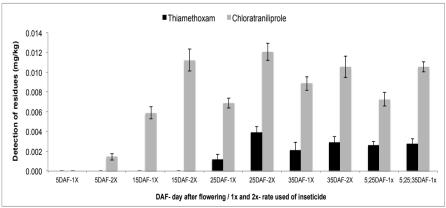


Figure 3- Quantification of chlorantraniliprole and thiamethoxam residues in rice grain. Insecticides were applied at different moments after rice flowering using 1x and 2x the recommended rate.

It is important to note that for the insecticide chlorantraniliprole, the highest concentrations were observed in rice bran. The available literature presents several hypotheses of the factors that may impact the concentration of pesticide residues in the ecosystem of irrigated rice crop, and many of these are not fully understood because of the numerous aspects involved. Uptake, translocation and persistence of pesticides in plants may be interfered by application time, application rate, weather conditions, characteristics of the pesticide (JURASKE et al., 2009), matrix chemical composition, pesticides lipophilicity, and action mode (CHAMPAGNE, et al., 2004).

The values detected in rice grains in this study are below of the Maximum Residue Limit (MRL) set by Agência Nacional de Vigilância Sanitária (ANVISA). The MRLs in rice grains for chlorantraniliprole is 0.2 mg/kg and for thiamethoxam is 1.0 mg/kg.

# CONCLUSION

Residues of chlorantraniliprole and thiamethoxan applied in rice were detected in hull, bran and rice grains, and the quantified values were higher in hull and in rice bran.

The values detected in rice grains are below the Maximum Residue Limit (MRL) set by Agência Nacional de Vigilância Sanitária (ANVISA).

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