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Imidazolinone herbicide dissipation in rice fields as affected by intermittent and continuous irrigation

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Abstract: **Background:** Clearfield® (CL) rice is one of the most successful tools for selective weedy rice control, using imidazolinone herbicides (IMI). However, IMI have residual soil activity and may carryover to non-tolerant crops growing in succession. It is necessary to find options to reduce IMI persistence in paddy rice fields.

Objective: Evaluate the effect of water management on IMI dissipation in rice paddy and its carryover to soybean and non-CL rice.

Methods: The herbicide mixture of imazapyr and imazapic totalizing 147 g a.i. ha^{-1} and 49 g a.i. ha^{-1}, respectively, was applied half in preemergence (S_3 stage – rice spike stage) and the other half in postemergence (V_3-V_4 rice stage). After herbicide application, a total of 21 samples were taken for analysis of residues. Soil samples were air dried and herbicides residues were analyzed using high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS).

Results: Calculated field dissipation half-life ($DT_{1/2}$) of imazapyr was 182.5 and 42.0 days in continuous flooding and intermittent water management, respectively. Imazapic had a $DT_{1/2}$ of 96.3 days on intermittent water management. No adjustment for the dissipation regression parameters was obtained for imazapic in continuous water management. No reduction in yield components was observed in soybean when grown in soil with imidazolinone residues. On the other hand, non-CL rice showed decreased shoot dry weight and stem number.

Conclusion: Imidazolinone herbicides have a longer half-life under continuous rice water management than intermittent. Therefore, growers can use intermittent irrigation in ares prone to IMI carryover and can use soybean in rotation.

Keywords: Residual; Imidazolinone half-life; Carryover; Soil residue

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1. Introduction

The CL rice system is the most successful weedy rice control tool up to date (Avila et al., 2021a). In rice, with the use of IMI herbicide in CL rice system, farmers have the option of using only one herbicide to control weedy rice (*Oryza sativa* L.), *Echinochloa* spp., *Cyperus* spp., *Aeschynomene* spp., *Luziola peruviana* J., *Urochloa plantaginea* L., and other weeds (Avila et al., 2021b; Gehrke et al., 2021). In Brazilian CL system, one of the options is the commercial mixture of imazapyr + imazapic (Kifix™), which has residual soil activity that improves weed control after application and helps to prevent reinfestation (Avila et al., 2021a).

In Brazil, Rio Grande do Sul (RS) State, the top rice producer contributing with 70% of the rice in the country (Sociedade Sul-Brasileira de Arroz Irrigado, 2018), approximately 85% of the area is cultivated with imidazoline-resistant cultivars (Avila et al., 2021b; Instituto Rio Grandense do Arroz, 2019). Although the imidazolinone herbicides (IMI) used in the CL system are highly selective and efficient, these herbicides have high persistence in the soil and can cause crop injury by carryover, affecting the rotational crop or non-CL rice cultivars (Gehrke et al., 2021).

In general, the primary sorption mechanism of IMI in the soil is the hydrophobic partition with the soil organic matter (Gianelli et al., 2014). Therefore, several factors may affect IMI sorption, including soil pH. In low soil pH, these molecules interact strongly with soil particles, slowing the dissipation processes (Gehrke et al., 2021; Su et al., 2019). This fact is due to the amphoteric behavior of IMI, which allows these herbicides to act as weak acids or bases, depending on the pH of the environment in which they are present (Gianelli et al., 2014). Therefore, according to the ionization coefficient (pKa) of the molecules and the pH of the soil, these herbicides may be more associated or dissociated and therefore available in the soil solution (Refatti et al., 2017). Soils with lower pH (more acidic) tend to increase the association of IMI in the soil and, therefore, increase its persistence in the environment (Refatti et al., 2017). In RS State, it is estimated that 50% of the rice soils have natural soil pH between 5-5.4 (Boeni et al., 2010).

Rice is regularly irrigated under flooded conditions, and irrigation management significantly affects the environment in rice fields, including soil pH (Refatti et al., 2017). Therefore, when the crop is cultivated in the irrigated system the herbicide is solubilized, allowing the absorption by the plants and thus affecting the growth of sensitive crops (Agostinetto et al., 2018).

Dissipation is the process of losing the herbicide from the applied site to the environment involving: 1) volatilization, 2) drift, 3) runoff, 4) leaching, 5) degradation, 6) plant metabolization, and others (Farha et al., 2016; Jin et al., 2013). For IMI, the primary process responsible for dissipation is microbial degradation (Gehrke et al., 2021). Microorganisms use the herbicide molecules to modify them into simpler compounds that can be used in their metabolism (Singh, Singh 2016). Although literature reports that imazapyr and imazapic are primarily degraded by aerobic processes (Shaner, 2014), there are some evidences that demonstrates imazapyr degradation in aerobic and anaerobic environments (Wang et al., 2006). Therefore, it is necessary to obtain clearer information on dissipation of these herbicides under rice field conditions.

Another critical aspect that has been neglected is the possibility of mitigating the IMI carryover effect by adequate irrigation management. Intermittent irrigation is a strategy that has been studied and adopted worldwide (Avila et al., 2015; Carracelas et al., 2019; Martini et al., 2013). With this irrigation system, soil aeration may be improved during the rice-growing season favoring IMI degradation. Besides of that, at the moment and to our knowledge, there is no information in the literature demonstrating the relationship of IMI soil residues and intermittent irrigation effects in susceptive crops such as soybean and non-CL rice.

Persistence and phytotoxicity of IMI herbicides in susceptible crops can be a potential problem in areas prompt to carryover, water management may be a strategy to mitigate these effects. Therefore, this study aimed evaluate: 1) the dissipation of the formulated mixture of imazapyr + imazapic in irrigated rice field with continuous and intermittent water management, and 2) the injury to injury of soybean and non-CL rice to these herbicides in the following year.

2. Material and Methods

2.1 Experiment design

A field experiment was carried out at the *Centro Agropecuário da Palma*, at the Federal University of Pelotas, Capão do Leão, RS, Brazil, during two growing seasons. The experiment was divided in two phases (Figure 1): the first, using CL rice genotypes and use of IMI herbicides (2017/18 growing season); and the second, when non-CL rice and soybeans were planted in the area to evaluate potential carryover (2018/19 growing season).

In the first phase, the experiment was set up in a randomized completed block design with four replications. The treatments included irrigation strategies: 1) continuous flooding, and 2) intermittent water management. In the second phase, the experiments were set up in a randomized completed block design with four replications. Non-CL rice and soybean were cultivated in the areas where irrigation treatments were established in the previous year.

2.2 Rice crop management

The CL experiment (2017/18 growing season): Thirty days before installing the experiment, the area was limed using 9,000 kg ha^{-1} of $CaCO_3$. The experiment was sown on November 1, 2017 at 90 kg seeds ha^{-1} of IRGA 424 RI (CL rice). An additional treatment was carried out using the cultivar IRGA 424 (non-CL rice) in the flooding irrigation regime to simulate a condition without IMI herbicides. At sowing, it was applied 330 kg ha^{-1} of N-P-K formulated as 05-20-20. Subsequently, urea was applied twice; the first application of 100 kg of urea (45 kg of N ha^{-1}) when seedlings reached the 3–4-leaf stage (beginning of tillering) and the second also with 100 kg (45 kg of N ha^{-1}) in the stage R_1 (panicle differentiation). The plot measured 6 x 5 m (LxW). Seeding was performed in the middle of the plot using nine rice rows spaced 0.17 m, corresponding an area of 6 x 1,5 m.

Water management for rice in the 2017/18 growing season followed the treatments described in the

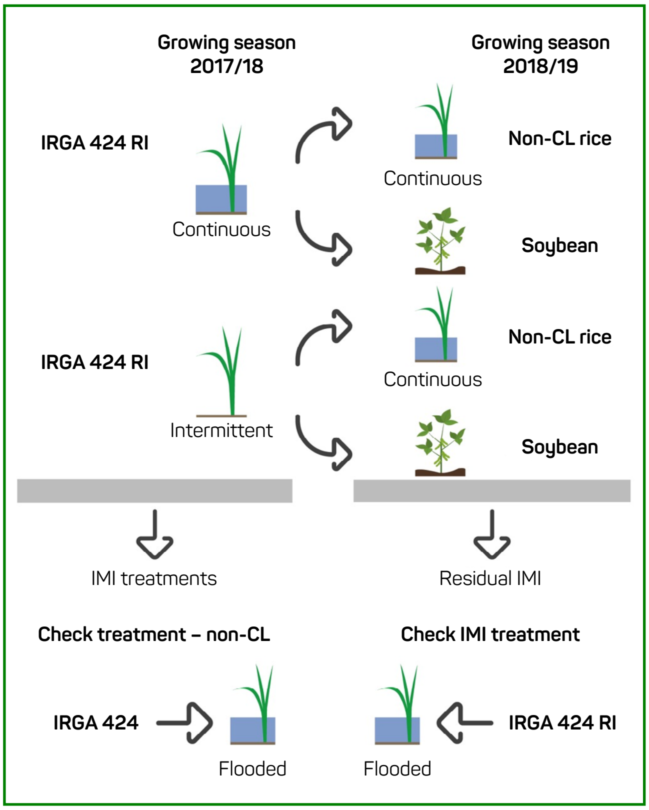

Figure 1 - Treatment application scheme using imazapic and imazapyr on cultivar IRGA 424 RI (CL™) during the growing season 2017/18 and followed by residue effects on cultivar non-CL rice and soybean in growing season 2018/19

experiment design (continuous and intermittent water management). In continuous flooding, a water depth of 10 cm was maintained from the time seedlings reached the 3–4-leaf stage up to 15 days before rice harvesting. In the intermittent water management, the cultivated area was irrigated, and water was maintained for 24 hours. Subsequently, the area was drained until the soil moisture tension reached 50-70 kPa, and then, a new irrigation cycle was performed. Soil physicochemical parameters were determined before the 2017/18 season: 4.4 water pH (1:1), 1.79 % organic matter (O.M.), 50.0% sand, 30.0% silt, 20.0% clay, 14.9 mg dm^{-3} phosphorus (P), 57 mg dm^{-3} potassium (K), 1.9 cmol$_c$ dm^{-3} calcium (Ca), 0.9 cmol$_c$ dm^{-3} magnesium (Mg), 2.2 cmol$_c$ dm^{-3} aluminum (Al). In 2018/19 season: 5.6 water pH (1:1), 1.52% O.M., 18.0% clay, 14.2 mg dm^{-3} P, 62.0 mg dm^{-3} K, 2.7 cmol$_c$ dm^{-3} Ca, 1.6 cmol$_c$ dm^{-3} Mg, 0.1 cmol$_c$ dm^{-3} Al.

Crop management was performed based on regional recommendations for maximum rice yield (Sociedade Sul-Brasileira de Arroz Irrigado, 2018). The plot hosting the CL cultivar IRGA 424 RIwas treated with a formulated mixture of imazapyr + imazapic, with a total rate of 147 g a.i. ha^{-1} + 49 g a.i. ha^{-1}, respectively, in a split application: 1) in the S$_3$ stage (rice spiking) half of the rate was applied tank-mixture with glyphosate at 1,140 g a.e. ha^{-1} and 2) in the V$_3$ stage the other half alone. In the cultivar IRGA 424 (non-CL rice), the herbicide clomazone (Gamit® 360 CS) at 252 g a.i ha^{-1} was applied in the S$_3$ stage tank-mixture with glyphosate at 1,440 g a.e. ha^{-1} on November 10th, 2017. To control weeds in postemergence (POST), cyhalofop-butyl at 360 g a.i. ha^{-1} and penoxsulam at 48 g a.i. ha^{-1} were used just before irrigation establishment. All treatments were applied using a CO$_2$ pressurized backpack sprayer coupled with a four flat-fan nozzles (110-02) boom, spaced at 50 cm, and calibrated to apply the spray volume of 150 L ha^{-1}.

Carryover experiment (2018/19 growing season): The areas where IMI treatments were applied (flooding and intermittent) were divided in half to cultivate a non-CL rice cultivar (non-commercial inbreed line) and soybean. An additional treatment was carried out with the cultivar IRGA 424 RI (CL rice), simulating the CL system.

Rice was sown on October 19th 2018 using 90 kg ha^{-1} of seeds for both genotypes. At seeding, the fertilization consisted of 400 kg ha^{-1} of 05-20-20 (NPK) fertilizer. Topdressing nitrogen fertilization was performed using urea, totalizing 100 kg ha^{-1} of nitrogen throughout the season. Urea was applied as in the 2017/18 growing season. The plot measured 3 x 5 m (LxW) with nine rice rows spaced 0.17 m.

Weed control in the non-CL rice was performed with the application of the tank mixture of clomazone (252 g a.i. ha^{-1}) and glyphosate (1,440 g a.e. ha^{-1}) in preemergence (PRE). Two herbicide applications were performed in POST; the first was carried out on November 16th, 2019 using herbicide penoxsulam and cyhalofop-butyl at 48 g a.i. ha^{-1} and 360 g a.i. ha^{-1}, respectively. The second application was conducted on December, 1st, 2019 using the same herbicides of the first application plus pyrazosulfuron-methyl, at a dose of 20 g a.i. ha^{-1}.

The chemical control of weeds in IRGA 424 RI in PRE was carried out applying glyphosate and imazapyr + imazapic (Kifix™) at the same dose applied in 2017/18 growing season. In POST, the herbicide Kifix™ was applied again using the same dose used in PRE. The herbicides were applied using the same equipment for the 2017/2018 season. The other managements were carried out according to the rice crop recommendation (Sociedade Sul-Brasileira de Arroz Irrigado, 2018).

After flowering, the rice genotypes were eliminated to prevent seed production as inbreed lines were not commercially licensed. The herbicide glyphosate at 2,520 g a.e. ha^{-1} was initially applied at the flowering stage following by application of paraquat (400 g a.i. ha^{-1}) after five days. The following-up application was performed to guarantee that no-seed production would occur and eliminate possible escapes from the first desiccation. After that, all the plants in the experiment were cut, removed from the area, and incinerated.

On October 19th, 2018, soybean was sown using a seed driller with five rows spaced 0.45 m. Each plot consisted of five rows with 6 m in length. The cultivar used was a 6.8 maturation group cultivar (BRASMAX Ícone IPRO) with a density of 13 seeds per meter aiming at the final population of 250,000 plants ha^{-1}. The seeds were treated with Standak Top™ (fipronil + pyraclostrobin + methyl thiophanate) in the dose of 1.5 mL per kg of seed and inoculant symbiotic nitrogen fixation. Base fertilization was used using 400 kg ha^{-1} of 05-20-20 (N-P-K).

Weed management in soybean was carried out using *S*-metolachlor at 1,044 g a.i ha^{-1} and glyphosate at 1,440 g a.e. ha^{-1} in PRE. Besides, glyphosate was applied three times at POST (1,440 g a.e, ha^{-1}) at the following stages: V$_3$ and R$_3$ (when new weeds emerged) and at pre-harvesting. No application of cover fertilization was carried out, considering that the seed inoculation was carried out, and nodules of nitrogen-fixing organisms were found in the roots during the crop growing phase.

2.3 Soil moisture monitoring

Air temperature data were taken from the Agroclimatic Station of Pelotas (31°52’00’’ S and 52°21’24’’ W) (Schöffel et al., 2019). Soil moisture in the intermittent management was performed using five moisture sensors (Watermaker™ electro-tensiometers, Irrometer Company, Riverside, United States of America). The sensors were installed at 7 cm depth allowing analysis of a 15 cm soil layer. The moisture sensors were connected to the datalogger (900M monitor) to record the water tension every six hours automatically.

In the continuous flooding management, monitoring sensors were not placed during the crop cycle, considering that the water layer was stablished in the area when seedlings reached the 3–4-leaf stage to pre-harvest drainage. Therefore, the soil was saturated throughout this period. Due to technical problems with the equipment, the water tension data on the soil was collected until 263 days after irrigation.

2.4 Sampling, sample preparation, and quantification of analytes

Soil was sampled in twenty-one different timing from November 11th, 2017, to June 24th, 2019 (Figure 2). Samples were collected at 1, 8, 15, 22, 29, 36, 50, 64, 78, 92, 123, 153, 184, 214, 245, 276, 306, 337, 386, 500 and 591 days after herbicide application (DAA). The four replications were sampled, and in each plot, four subsamples were collected to compose a sample. The subsamples were collected using a soil sampler probe (2,0 cm of diameter) at a 10-cm soil depth. Samples were placed in identified polyethylene bags and placed in a freezer at a temperature of -4 °C until sample preparation and analysis.

Samples were prepared according to the methodology developed by Kemmerich et al. (2015). Initially, a sample of 5.0 ± 0.001 g was weighed on an analytical balance (Shimadzu do Brazil, São Paulo, Brazil) and placed in a 50 mL polypropylene (PP) tube. Then, 10 mL of the extraction solution (ultrapure water containing ammonium acetate at 0.5 mol L^{-1}) were added to the tube. Afterward, the tube was shaken manually for 1 min and centrifuged for 5 minutes at 3.500 rpm (Megafuge™ 16R Centrifuge, Thermo Scientific, Waltham, MA, USA). After, 1 mL of the supernatant was placed in a 1.5 ml microtube containing 0.625 ± 0.0001 g of PSA (primary secondary amine), then stirred for one minute in a vortex shaker (Phoenix Luferco, São Paulo, Brazil) and centrifuged for 5 minutes at 3.500 rpm. In the end, the supernatant was removed and filtered with a nylon filter (0.2 µm) and analyzed in the HPLC-MS/MS system (model Q-Exactive Focus) containing mass spectrometer Q-Orbitrap with automatic sampler Dionex ultimate 3000, Accucore C18; 2.6 µm analytical column (10 x 21 mm) and Data Acquisition System Trace Finder (Thermo Scientific, Waltham, MA, USA).

2.5 HPLC-MS/MS system for determining imazapyr and imazapic residues in soil

The conditions used in the HPLC-MS/MS system were as follows: column temperature: 40 °C; source of ionization: electrospray; electrospray mode: positive; ionization energy: 10, 20 and 30 eV; capillary temperature: 320 °C; spray voltage: 4.0 kV; sheath gas flow: 30 L h^{-1}; auxiliary gas flow: 10 L h^{-1}; injection volume: 10 µL; resolution: 70,000.

Binary mobile phase was used for edlution in gradient: A) Aqueous ammonium acetate solution (5 mmol L^{-1}) containing 0.1% formic acid, and B) methanol. The mobile phase from 0 to 4 minutes was 10% A and 90% B, then at 4 min was changed to 40% A and 60% B, at 6.6 min was 100% A and 0% B and finally at 9.0 min was returned to the 10% A and 90% B gradient. The total running time was 9 min.

A mixture of the analytes was prepared at a concentration of 1 mg L^{-1} to quantify the compounds used in this study. From this solution, calibration curves were prepared at the final concentrations of 0.5, 1, 2, 5, 10, 20, 50, and 100 µg L^{-1}. Fortified samples were extracted in each batch of analysis at a concentration of 20 µg L^{-1} to assess the accuracy and precision of the method.

The acceptance criteria were linearity (≥0.99), accuracy (70-120% of recovery), and precision standard

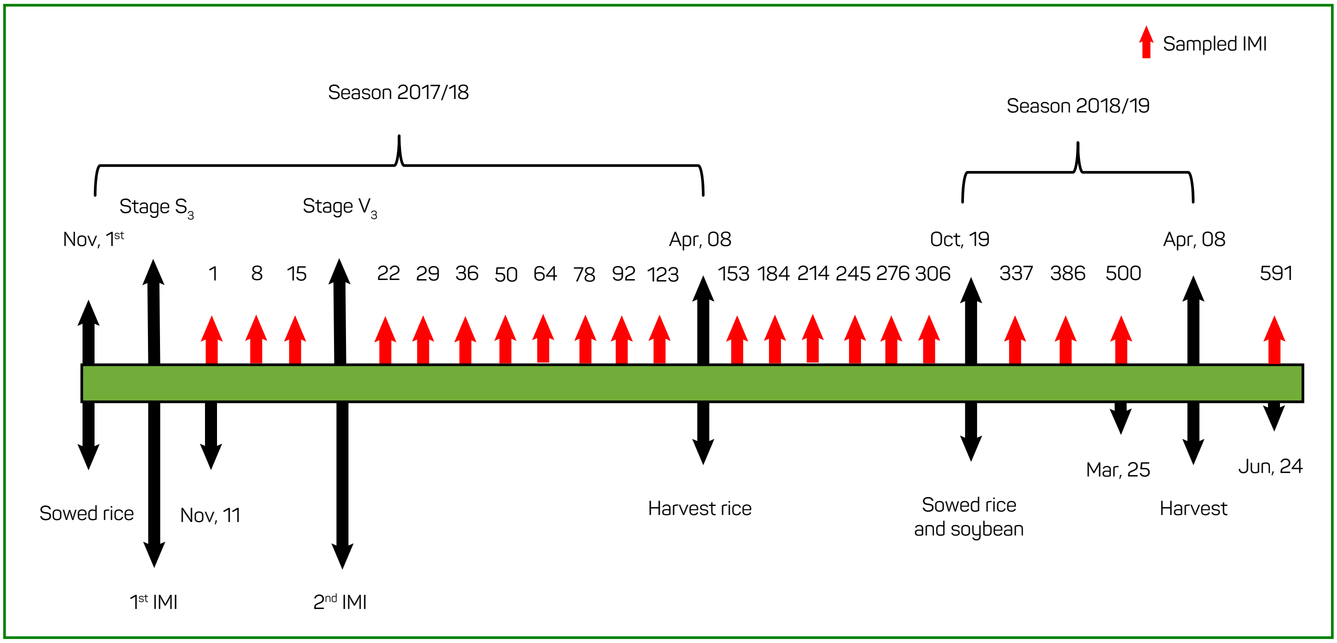

Figure 2 - Soil collection period for analysis of imazapic + imazapyr in growing seasons 2017/18 and 2018/19

deviation (RSD) (≤20%) (INMETRO, 2016). The limit of quantification (LOQ) was estimated as the first dose of the linear working range and the limit of detection (LOD) as LOQ/0.33. Values below LOD are considered not detected (n.d.).

2.6 Rice stem counting and plant dry mass

The number of rice stems was counted in one linear meter within each experimental plot. The rice plant dry mass was obtained by sampling a 0.25 m^2 (0.5 m x 0.5 m) area in each replication. A square metal-framed was placed randomly within the plot, excluding the two lateral rows. Subsequently, the collected biomass was placed in an oven with forced air circulation at 60 °C until it reached constant weight (72 hours). After this period, shoot dry weight was determined using an analytical scale. Soybean plants number was counted in 5 m crop row, and soybean yield was estimated harvesting the three central lines in 5 m long.

The data stems number, shoot dry mass, plants number and yield were compared using the statistical program R Core Team (2018) using the ExpDes.pt package (Ferreira et al., 2014), considering the water management (continuous flooding and intermittent irrigation) and the effect on non-CL crops. Before the analysis of variance (ANOVA), the data were tested for normality. Means of analyzed variables were compared using the 95% confidence intervals. The graphics were performed using SYSTAT (Systat Software, San Jose, CA).

Degradation of imazapyr and imazapic in soil was performed by simple first-order kinetic model, adjusted by linear regression in Equation (1).

$$y = \alpha + \beta x \text{ (1),}$$

where β is the angular coefficient, α is the interception coefficient, x is the days of herbicides in soil and y is herbicides concentration in soil.

The half-life ($t_{½}$) was calculated by Equation (2).

$$t\frac{1}{2} = \frac{\ln 2}{k} \text{ (2),}$$

where *k* is the estimated angular coefficient (β) of the linear regression of the herbicide concentration, which is time-dependent.

3. Results and Discussion

Soil moisture and air temperature for continuous and intermittent water management are shown in Figure 3. In intermittent water management, 22 irrigation cycles were carried out until total irrigation was stopped at pre-harvest. It is observed in Figure 3 that on the 53rd day after herbicide application there was a moisture peak of 120 kPa; it is worth noting that in this period, the average air temperature recorded was 25.1 °C, while the maximum temperature for this day was of 31.1 °C, thus the evapotranspiration was high, causing quick soil moisture reduction. While in continuous flooding management, the water tension remained constant, demonstrating the flooding of the area. During the winter, there was a drought period (20 days), raising the soil tension to approximately 150 and 100 kPa in the areas of intermittent and continuous flooding management, respectively. In the other off-season periods, high soil moisture was maintained in both areas.

3.1 Dissipation of imazapyr and imazapic in the soil (season 2017/18)

After the second application of imazapyr + imazapic in the first season, the dissipation profile of the herbicides was monitored, and the results are illustrated in Figure 3.

In general, the concentration of imazapyr and imazapic residues in the soil decreased more quickly in intermittent management than in continuous flooding for both herbicides. Differences in the initial concentrations of imazapyr in the soil between the irrigation management were detected at the beginning of monitoring. This initial difference at one DAA may be due to the type of irrigation. In continuous flooding, with a water layer in the soil, there was a greater distribution of the imazapic and imazapyr herbicides along the soil profile. During intermittent management, the soil was expected to reach a tension of 70 kPa to start irrigation, which may have resulted in a higher concentration of herbicides on the soil surface. IMI concentrations were higher in the intermittent condition and remained until the sampling at 29 DAA.

The herbicide concentration observed in this study was close to the theoretical concentration calculated based on known parameters. Studies in the literature

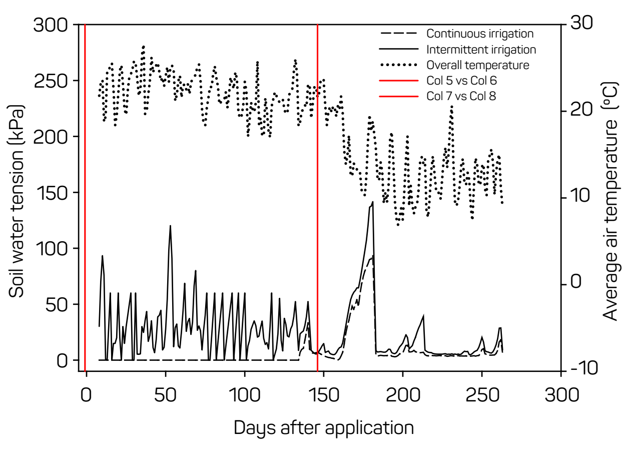

Figure 3 - Soil water tension (kPa) in continuous and intermittent water management and average air temperature at Pelotas agroclimatic weather station during the 2017/2018 growing season. Red lines represent the end of the growing season and the beginning of the fallow

show that the density in floodplain soils is approximately 1.50 g cm^{-3} (Kraemer et al., 2009). Thus, in a 0.10 m layer, the amount of soil would be equivalent to 1,500,000 kg ha^{-1}. Therefore, the theoretical concentration of herbicide in the soil after the second application was estimated to be 84 and 28 µg kg^{-1}, of imazapyr and imazapic, respectively. The mean values of imazapyr concentration one day after starting monitoring were 50.33 and 26.97 µg kg^{-1} in intermittent and continuous watering, respectively (Figure 4). For the herbicide imazapic, these values were 6.90 and 3.64 µg kg^{-1}, in intermittent and continuous water management, respectively.

The leaching of the herbicides imazapyr and imazapic is favored in irrigation management, such as the intermittent system (Bundt et al., 2014). Thus, the movement of herbicides to a lower soil layer, where microbial degradation is lower due to the lower soil temperature, lower organic matter content, low pH, and lesser microorganisms activity (Hoagland et al., 2000; Jin et al., 2013), may favor the persistence of the herbicide in the soil for a longer time, enabling the upward movement during the fallow period.

After harvesting rice at 129 DAA, the plots were drained and maintained in this condition until the following season. As illustrated in Figure 4, an increase in soil concentration of the herbicide in both systems during the off-season was observed. This increase was more pronounced in continuous flooding than intermittent, with peaks at 153 and 184 DAA, for the herbicides imazapyr and imazapic, respectively. During the off-season (winter), IMI move upward from the lower soil layers to the surface (Bundt et al., 2013). Water tension in the soil from 153 to 175 DAA was high (Figure 3). Probably, there was an upward flow of the herbicides imazapyr and imazapic to the superficial layers resulting in a higher herbicide concentration in the sampled layer.

The concentration of imazapyr and imazapic were linearized by logarithmic transformation to identify dissipation rate in intermittent and continuous management irrigation. For the herbicide imazapyr, there was an adjustment of the linearized regression for both managements, while for the herbicide imazapic, the curve was significant only for intermittent management. Based on the slope of the generated linear equations it was possible to obtain the dissipation rate (k). It is important to note that in soil samples collected after 184 DAA in intermittent management, no herbicide was detected with the used methodology. The recorded dissipation was faster in intermittent than in continuous management for the herbicide imazapyr. The estimated half-live (DT$_{½}$) period was 182.4 and 42.0 DAA in continuous and intermittent management, respectively (Table 1).

Imazapic herbicide had a DT$_{½}$ of 96.3 DAA in intermittent management, while for continuous management, there was no linear regression adjustment. It can be seen in Figure 4 that the concentration of imazapic in continuous management was relatively constant over time; the average initial concentration (0 DAA) was 3.64 µg kg^{-1} while at 123 DAA, the concentration was 3.53 µg kg^{-1}, and after this period, there was an increase in the soil concentration evidenced by the herbicide's upward movement. This profile resulted in a lack of adjustment for DT$_{½}$ estimation.

The main dissipation processes for herbicides in the soil are plant absorption, leaching, photolysis, runoff, and biological degradation (Jin et al., 2013; Kraemer et al.,

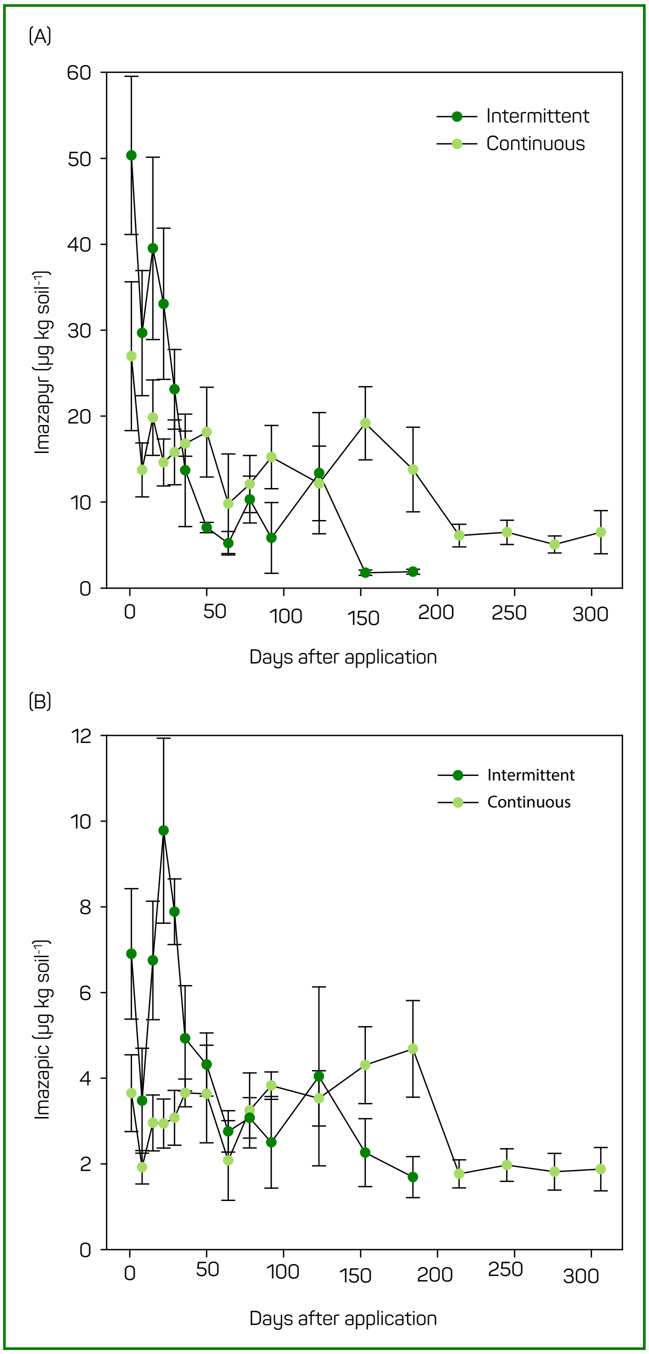

Figure 4 - Imazapyr (A) and imazapic (B) dissipation under continuous and intermittent rice water management. Bars represent confidence intervals at 95% of probability, with four repetitions

Table 1 - First-order rate constant (k), half-life ($t_{1/2}$), 95% confidence intervals (CI) of imazapyr and imazapic, and adjusted coefficient of the determination under continuous and intermittent water management

Herbicide	Management	k ($\|\beta_1\|$)[1]	$t_{1/2}$ (days)	95% de IC (days)	R^2
Imazapyr	Continuous	0.0038	182.4	130.8 – 301.4	0.66
	Intermittent	0.0165	42.0	30.8 – 65.4	0.77
Imazapic	Intermittent	0.0072	96.3	63.6 – 203.9	0.62

[1] k is the estimated angular coefficient of the linear regression (β) of the herbicide concentration, which is time-dependent.

2009). In continuous management, water was removed only in the pre-harvest; therefore, the runoff factor can be disregarded in this system. In intermittent management, the effect of runoff was present as the water was removed frequently and, therefore, herbicides could have been transported by water (data not shown). However, previous studies using intermittent management demonstrated that the decrease in the herbicide concentration is only 3% of the total applied; therefore, the runoff represents only a small part of the total dissipation of the herbicide in the soil (Martini et al., 2013).

Photolysis is another possible dissipation process as IMI herbicides undergo direct and indirect photolysis when dispersed in water (Avila et al., 2006). In soil, photolysis decreases considerably due to the low light penetration, which can be considered effective up to 1 mm in depth (Mallipudi et al., 1991). Due to the irrigation carried out one day after the second application, it is considered that this factor had little influence on the final result of the herbicide concentration.

The main factor responsible for the dissipation of IMI in the field is microbial degradation (Kraemer et al., 2009; Su et al., 2019). The diversity of microorganisms in the soil is vast; therefore, several soil microorganisms can degrade these herbicides. Also, with the constant application of herbicides, some more efficient species may be selected. In a study performed by Huang et al. (2009), a specific group of microorganisms able to degrade imazethapyr was selected, and when the soil was sterilized (all microorganisms eliminated), at 25 DAA, the degradation was only 8.7%. On the other hand, when the soil contained the selected group, degradation increased to 48.8% at 25 days. Comparing aerobic and anaerobic environments, the microorganisms selected in each environment are different, considering that the substrate for the microorganism's metabolism is also different. Degradation of imazethapyr by aerobic microorganisms results in three metabolites while in the anaerobic environment, the transformation occurs in only two routes, one of which is the same as for the aerobic environment (Wang et al., 2006). Demethylation, loss of the isopropyl group, cleavage, and rearrangement of the imidazolinone ring are the main routes of degradation of the herbicide imazapyr (Morrica et al., 2001).

The values obtained from the dissipation rate curves show the actual dissipation values in the field. The values obtained in this study for the herbicide imazapyr differ from previous reports, that showed the $DT_{½}$ of this herbicide ranging from 25 to 142 DAA, and for the continuous management system, the $DT_{½}$ was 182 days; thus the values obtained in this study are higher than that previously reported (Shaner, 2014).

3.2 Dissipation of imazapyr and imazapic in the soil (season 2018/19)

Imazapyr and imazapic concentration in the soil analysis performed on Sept 30th, 2018 (306 DAA), indicated the presence of the imazapyr at 6.49 μg kg^{-1} in continuous management while for intermittent management, the concentration was below the LOQ (Table 2). For imazapic, the concentration was 1.87 μg kg^{-1} in continuous management and not detected for intermittent (Table 3). These data refer to the herbicide residual from the previous season; therefore, the differences are due to the irrigation management treatments conducted during the rice-growing season.

At 337 DAA (Table 2), a difference in the concentration of imazapyr between soybean and rice cultivation areas was detected. Soybean areas showed lower imazapyr concentration (1.53 μg kg^{-1}) than non-CL rice areas (2.97 μg kg^{-1}). In the imazapic analysis (Table 3), no difference between crop was observed in the sampling performed at 337 DAA. In the additional treatment with CL rice (IRGA 424 RI), the management was similar to the 2017/18 season, where sampling at 337 DAA have already received the first imazapyr + imazapic application. In this case, only imazapyr showed a higher concentration (9.34 μg kg^{-1}) compared to non-CL rice crop and soybean.

At 381 DAA, the non-CL rice in continuous flooding had a concentration of 2.42 ± 1.15 μg kg^{-1} for imazapyr, while no herbicide was detected in the soybean treatment. Similar to what observed in the previous growing season, the water layer help to maintain the herbicide residue for a longer period in the soil, reducing the dissipation to the environment. In contrast, in soybean, the herbicide residues were able to dissipate quicker. For imazapic, the quantified residue (1.22 ± 0.04 μg kg^{-1}) was similar to the one found in the previous evaluation. This sampling was performed after the flood had been established in the field, which may have increased the availability, and

Table 2 - Imazapyr concentration (μg kg^{-1}) in soil after growing Clearfield™ rice during 2017/2018. Initial herbicide application occurred in 2017. Data presented here are from soil samples collected in the season 2018/2019

Treatment	Crop	Days after application (DAA) in 2017/18				
		306[1]	337[2]	386	500	591
Intermittent	Soybean	< LOQ[3]	n.d.[4]	n.d.	<LOQ	n.d.
	Non-CL rice	< LOQ	n.d.	n.d.	<LOQ	n.d.
Continuous	Soybean	6.49±2.55[5]	1.53±0.22	n.d.	<LOQ	n.d.
	Non-CL rice	6.49±2.55	2.97±0.29	2.42 ± 1.15	n.d.	n.d.
	IRGA 424 RI	6.49±2.55	9.34±4.77	17.24±1.27	4.02±3.97	6.87±2.01

[1]Soil herbicide residual before sowing crops. [2]New application of imazapyr only occurred in the cv. IRGA 424 RI (CL). At 337 DAA, treatment had received the first application of Kifix™, and at 386 DAA, the first and the second application. [3]Limit of quantification (LOQ). [4]Not detected, i.e. lower than method LOD. [5]Confidence interval (95%).

Table 3 - Imazapic concentration (μg kg^{-1}) in soil after growing Clearfield™ rice during 2017/2018. Initial herbicide application occurred in 2017. Data presented here are from soil samples collected in the season 2018/2019

Treatment	Crop	Days after application (DAA) in 2018				
		306[1]	337[2]	386	500	591
Intermittent	Soybean	n.d.[3]	n.d.	n.d.	n.d.	n.d.
	Non-CL rice	n.d.	n.d.	n.d.	n.d.	n.d.
Continuous	Soybean	1.87±0.84[4]	1.08±0.10	n.d.	n.d.	n.d.
	Non-CL rice	1.87±0.84	1.08±0.10	1.22±0.04	n.d.	n.d.
	IRGA 424 RI	1.87±0.84	1.76±1.02	3.95±1.02	n.d.	0.68±0.42

[1]Soil herbicide residual before sowing crops. [2]New application of imazapyr only occurred in cv. IRGA 424 RI (CL). At 337 DAA, treatment had received the first application of Kifix™, and at 386 DAA, the first and the second application. [3]Not detected, i.e. lower than method LOD. [4]Confidence interval (95%).

consequently, increased the concentration observed in the analysis. For both herbicides, it was observed an increase in the concentration in CL rice after application. The values obtained were 17.24 and 3.95 μg kg^{-1}, for imazapyr and imazapic, respectively. This increase in the area of CL rice was caused by the second application of imazapyr + imazapic, in addition to flooding, which may have increased the availability of herbicides.

When soil sampling in continuous management was carried out at 156 DAA, a concentration of 4.02 μg kg^{-1} was observed in the treatment of CL rice for the herbicide imazapyr. In intermittent management, the imazapyr concentration was below the LOQ. For imazapic herbicide, no herbicide was detected in any of the treatments.

In the last sampling, during the winter at 591 DAA, on June 24th, 2019, no herbicide residues were detected in treatments without imazapyr + imazapic application during the 2018/2019 season. The herbicides imazapyr + imazapic concentration were 8.70 μg kg^{-1} and 0.68 μg kg^{-1}, respectively, in the continuous management treatment for CL rice. As previously mentioned, during the off-season, there may be an upward flow of herbicide in the soil, which may have increased the concentration in the previous analysis (Bundt et al., 2013).

When comparing imazapyr between CL rice crops in the two years, it was demonstrated that during winter 2018 (245 DAA), the concentration was 6.48 ± 1.41 μg kg^{-1} while the concentration in 2019 (591 DAA) was 6.87 ± 2.01 μg kg $^{-1}$. Considering the confidence interval, it is concluded that the two concentrations were similar. Thus, although there was a residual of the herbicide in the soil in the previous year, the concentration of this herbicide returned to the initial residual level after two seasons. The experiment was eliminated immediately after the flowering stage of rice in 2018/19; thus, the total flooding period in the cultivation was 77 days, while in 2017/18, the total period of water management was 115 days. Therefore, the aerobic environment without the water layer favored the dissipation of the herbicide in the second year. Thus, although there was residual herbicide in the soil of previous year, the concentrations obtained at similar times (247 and 591 DAA) did not differ.

On the other hand, for the herbicide imazapic, the concentration of the first year at 245 DAA was 1.97 ± 0.37 μg kg^{-1}, while in the second year, the concentration at 591 DAA was 0.68 ± 0.42 μg kg $^{-1}$, in CL rice. Due to the concentration of imazapic in the field been extremely low, it is difficult to specify the reasons related to the faster dissipation of this herbicide in 2017/18. It stands out that the analysis of the behavior of this herbicide in the field is complex, considering its low concentration in the soil. Furthermore, in the 2017/18 cropping season, it was not possible to adjust the dissipation rate of this herbicide, considering the behavior in the continuous irrigation environment, as it can be seen in Figure 4, the concentration was relatively constant over time, with the maximum 4.68 μg kg^{-1} and a minimum of 1.81 μg kg^{-1} at 184 and 276 DAA, respectively.

Although the concentrations at the beginning of the 2018/19 harvest were relatively low compared to the initial concentration, damage to the plants was observed in the field. The susceptible rice plants had no symptoms before flooding establishment, but after approximately seven days post flood, the herbicide symptoms began to be observed. The symptoms observed were plants with impaired growth, leaves with whitish veins, and roots with the appearance of a laboratory brush.

As shown in Figure 5 for the number of stems, there was no significant difference between the non-CL in intermittent management and the non-CL in the treatment without application of imazapyr + imazapic considering confidence interval. Similar results were observed for shoot dry weight where there was no difference between intermittent and non-application of IMI.

The non-CL rice in the area with CL rice in the continuous system in the previous year was severely damaged with the number of the stem reduced by 67% of the total produced by the system without residual. In the shoot dry weight production, the reduction was 43% comparing to the area without residual; thus, the residual present in this area affected rice growing; although no evaluations of grain productivity were carried out, these reductions are clear indicators that the final yield could be affected.

No differences between intermittent and continuous management in soybeans were detected for number of plants/m and grain yield (Figure 6). The cultivar used is susceptible to the herbicide; however, at the concentration determined in the analysis, no characteristic symptoms of the herbicide were observed in the crop. On the other hand, previous reports show a difference in injury levels between soybean cultivars. The cultivar NA5909RR, susceptible to the IMI herbicide, presents 40.6% phytotoxicity when subjected to the soil with a carryover of 280 g a.i. ha^{-1} of imazapyr + imazapic at 409 DAA, while the cultivar BRS382CV, IMI resistant, had 4.03% phytotoxicity. Also, resistant cultivars could maintain yield in places with residual herbicide (Agostinetto et al., 2018). Soybean cultivars that were affected by the herbicide carryover have higher production of reactive oxygen species (ROS) and, consequently, greater plant damages (Fraga et al., 2019).

Imazapyr dissipation is faster in intermittent water management than in continuous flooding. Therefore, in areas with IMI residual problems, the farmers can use intermittent management to decrease the amount of herbicide in the soil more quickly, resulting in lower crop injury and less problems for the crop. Imazapyr DT½ is 4.3-fold longer in the continuous flooding (182.4 days) than intermittent water management (42.0 days). For imazapic, DT½ was, 96.27 days for the intermittent management.

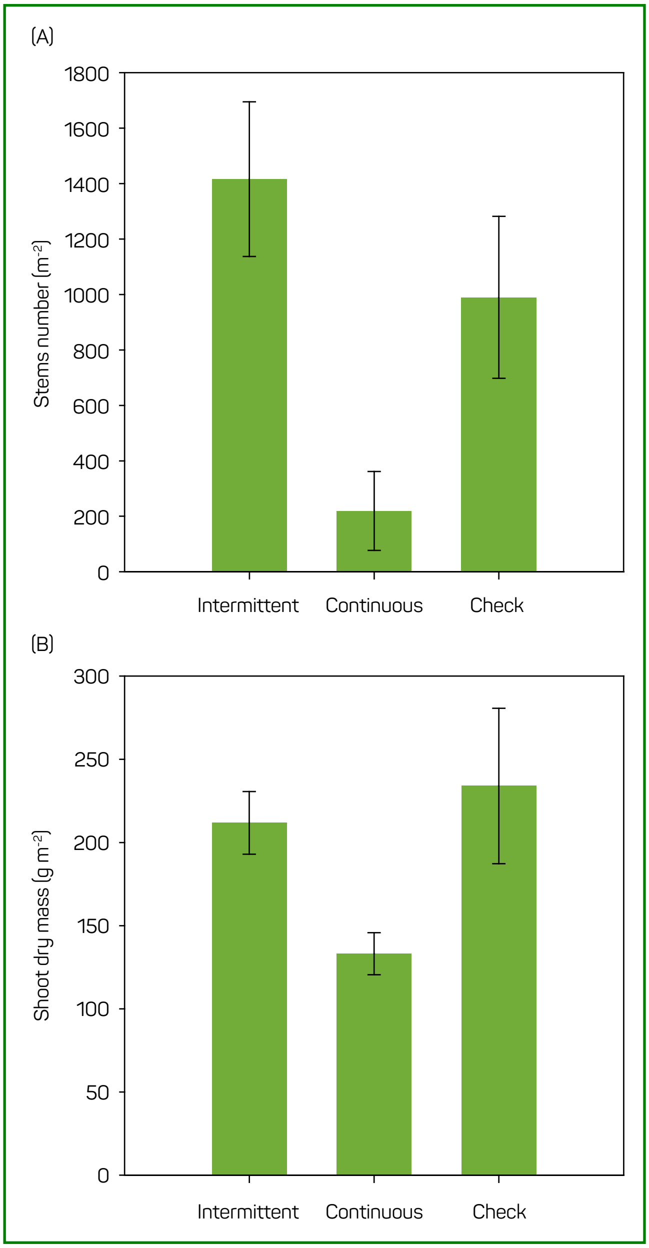

Figure 5 - Number of stems m^{-2} (A) and shoot dry weight (g m^{-2}) (B) in non-CL rice during the 2018/19. Intermittent: water management applied in CL rice in 2017/18; Continuous: water management applied in CL in 2017/18; Check: area without application of imazapyr + imazapic and continuous water management in 2017/18. Bars represent confidence intervals at 95% of probability, with four repetitions

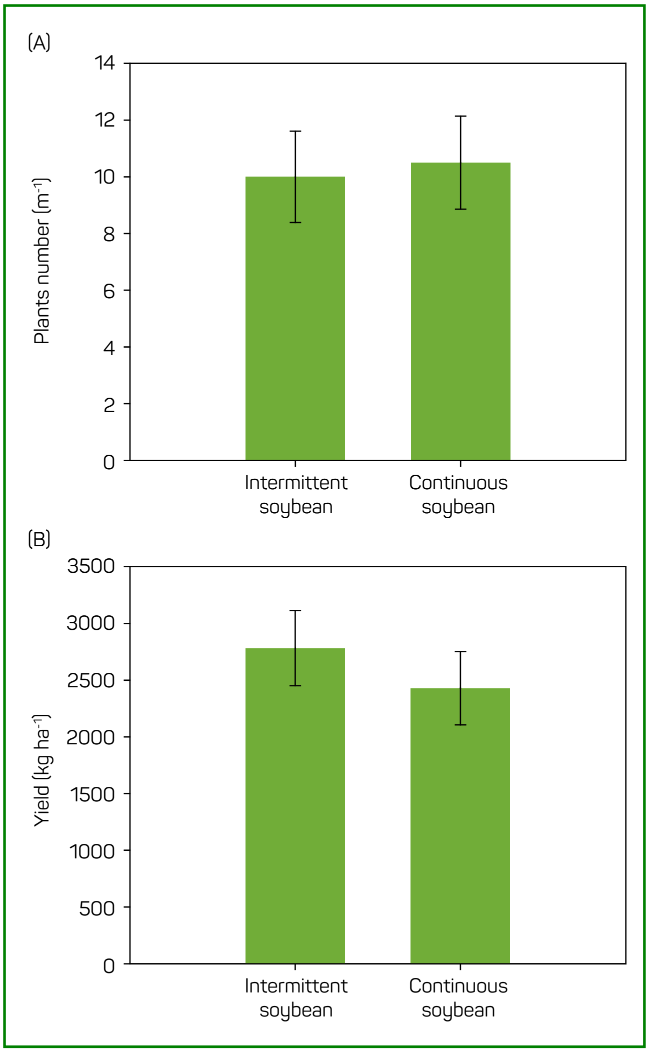

Figure 6 - Number of soybean plants per meter of row (A), soybeans grain yield (B). Bars represent confidence intervals at 95% of probability, with four repetitions

4. Conclusions

Imidazolinone herbicides have a longer half-life under continuous rice water management than intermittent. Soybean is a good alternative to be used after imazapyr and imazapic application as it favors dissipation without affecting grain yield. The non-CL rice is affected by imidazolinone carryover and should not be used in areas where IMI were applied and continuous water management were adopted in the previous year. Therefore, growers can use intermittent irrigation in ares prone to IMI carryover and can use soybean in rotation.

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Authors' contributions

All authors critically revised the manuscript and approved the final version. GVJ, LAA and ERC conceived and designed experiments. GVJ and VRG performed the experiments. GVJ, VRG and MK carried out the lab analyses. GVJ and MVF performed statistical data analyses and prepared the draft of the manuscript.

References

Agostinetto D, Fraga DS, Vargas L, Oliveira ACB, Andres A, Villela FA. Response of soybean cultivars in rotation with irrigated rice crops cultivated in Clearfield® system. Planta Daninha. 2018;36:1-9. Available from: https://doi.org/10.1590/s0100-83582018360100048

Avila LA, Marchesan E, Camargo ER, Merotto A, Ulguim AR, Noldin JA et al. Eighteen years of ClearfieldTM rice in Brazil: what have we learned? Weed Sci. 2021a;69(5):585-97. Available from: https://doi.org/10.1017/wsc.2021.49

Avila LA, Noldin JA, Mariot CHP, Massoni PFS, Fipke M V, Gehrke VR et al. Status of weedy rice (Oryza spp.) infestation and management practices in southern Brazil. Weed Sci. 2021b;69(5):536-46. Available from: https://doi.org/10.1017/wsc.2021.24

Avila LA, Martini LFD, Mezzomo RF, Refatti JP, Campos R, Cezimbra DM et al. Rice water use efficiency and yield under continuous and intermittent irrigation. Agron J. 2015;107(2):442-8. Available from: https://doi.org/10.2134/agronj14.0080

Avila LA, Massey JH, Senseman SA, Armbrust KL, Lancaster SR, Mccauley GN et al. Imazethapyr aqueous photolysis, reaction quantum yield, and hydroxyl radical rate constant. J Agric Food Chem. 2006;54(7):2635-9. Available from: https://doi.org/10.1021/jf052214b

Boeni M, Anghinoni I, Genro Jr. SA, Osório Filho BD. [Evolution of the fertility of soils cultivated with rice in Rio Grande do Sul]. Porto Alegre: Instituto Rio Grandense do Arroz; 2010. Portuguese.

Bundt AC, Avila LA, Agostinetto D, Refatti JP, Cassol L, Rockemback FC. [Imidazolinone leaching in response to different irrigation management on rice cultivated soil]. Cienc Rural. 2014;44(11):1943-9. Portuguese. Available from: https://doi.org/10.1590/0103-8478cr20131216

Bundt ADC, Avila LA, Pinto JJO, Santos TT, Agostinetto D, Martins K. [Upward movement of the formulated mixture of imazethapyr and imazapic in response to height of the water table]. Cienc Rural. 2013;43(9):1597-604. Portuguese. Available from: https://doi.org/10.1590/s0103-84782013005000111

Carracelas G, Hornbuckle J, Rosas J, Roel A. Irrigation management strategies to increase water productivity in *Oryza sativa* (rice) in Uruguay. Agric Water Manag. 2019;222:161-72. Available from: https://doi.org/10.1016/j.agwat.2019.05.049

Farha W, Abd El-Aty AM, Rahman MM, Shin HC, Shim JH. An overview on common aspects influencing the dissipation pattern of pesticides: a review. Environ Monit Assess. 2016;188(12):693. Available from: https://doi.org/10.1007/s10661-016-5709-1

Ferreira EB, Cavalcanti PP, Nogueira DA. ExpDes: an R package for ANOVA and experimental designs. Appl Math. 2014;5(19):2952-8. Available from: https://doi.org/10.4236/am.2014.519280

Fraga DS, Agostinetto D, Langaro AC, Oliveira C, Ulguim AR, Silva JDG. Morphological and metabolic changes in soybean plants cultivated in irrigated rice rotation and as affected by imazapyr and imazapic herbicides carryover. Planta Daninha. 2019;37:1-10. Available from: https://doi.org/10.1590/s0100-83582019370100023

Gehrke VR, Fipke MV, Avila LA, Camargo ER. Understanding the opportunities to mitigate carryover of imidazolinone herbicides in lowland rice. Agriculture. 2021;11(4):1-17. Available from: https://doi.org/10.3390/agriculture11040299

Gianelli VR, Bedmar F, Costa JL. Persistence and sorption of imazapyr in three argentinean soils. Environ Toxicol Chem. 2014;33(1):29-34. Available from: https://doi.org/10.1002/etc.2400

Hoagland RE, Zablotowicz RM, Hall JC. Pesticide metabolism in plants and microorganisms: an overview. In: Hall JC, Hoagland RE, Zablotowicz RM, editors. Pesticide biotransformation in plants and microorganisms. Washington: American Chemical Society; 2000. p. 2–27.

Huang X, Pan J, Liang B, Sun J, Zhao Y, Li S. Isolation, characterization of a strain capable of degrading imazethapyr and its use in degradation of the herbicide in soil. Curr Microbiol. 2009;59(4):363-7. Available from: https://doi.org/10.1007/s00284-009-9442-7

Instituto Rio Grandense do Arroz – IRGA. [Crop results bulletin 2018/19: irrigated rice and soybeans in rotation]. Porto Alegre: Instituto Rio Grandense do Arroz; 2019. Portuguese.

Jin M, Li D, Xi Y. Multi-rate model predictive control to reject periodic disturbance with reduced ripple. IFAC Proc Vol. 2013;46(20):491-6. Available from: https://doi.org/10.3182/20130902-3-CN-3020.00166

Kemmerich M, Bernardi G, Adaime MB, Zanella R, Prestes OD. A simple and efficient method for imidazolinone herbicides determination in soil by ultra-high performance liquid chromatography-tandem mass spectrometry. J Chromatogr A. 2015;1412:82-9. Available from: https://doi.org/10.1016/j.chroma.2015.08.005

Kraemer AF, Marchesan E, Avila LA, Machado SLO, Grohs M. [Environmental fate of imidazolinone herbicides: a review]. Planta Daninha. 2009;27(3):629-39. Portuguese. Available from: https://doi.org/10.1590/S0100-83582009000300025

Mallipudi NM, Stout SJ, Cunha AR, Lee AH. Photolysis of imazapyr (AC 243997) herbicide in aqueous media. J Agric Food Chem. 1991;39:412-7. Available from: https://doi.org/10.1021/jf00002a038

Martini LFD, Mezzomo RF, Avila LA, Massey JH, Marchesan E, Zanella R et al. Imazethapyr and imazapic runoff under continuous and intermittent irrigation of paddy rice. Agric Water Manag. 2013;125:26-34. Available from: https://doi.org/10.1016/j.agwat.2013.04.005

Morrica P, Giordano A, Seccia S, Ungaro F, Ventriglia M. Degradation of imazosulfuron in soil. Pest Manag Sci. 2001;57(4):360-5. Available from: https://doi.org/10.1002/ps.294

R Core Team. R: A language and environment for statistical computing. Vienna: The R Foundation; 2018[access october 10, 2018]. Available from: https://www.r-project.org/

Refatti JP, Avila LA, Noldin JA, Pacheco I, Pestana RR. Leaching and residual activity of imidazolinone herbicides in lowland soils. Cienc Rural. 2017;47(5):1-6. Available from: https://doi.org/10.1590/0103-8478cr20160705.

Schöffel ER, Steinmetz S, Miori LOFL, Silva PRG, Barcelos PR. Estação agroclimática de Pelotas. Boletim Agroclimático. 2019.

Shaner DL. Herbicide handbook. 10th ed. Lawrence: Allen; 2014.

Singh B, Singh K. Microbial degradation of herbicides. Crit Rev Microbiol. 2014;42(2):1-17. https://doi.org/10.3109/1040841X.2014.929564

Sociedade Sul-Brasileira de Arroz Irrigado - Sosbai. [Research technical recommendations for southern Brazil]. Cachoerinha: Sociedade Sul-Brasileira de Arroz Irrigado; 2018. Portuguese.

Su W, Hao H, Ding M, Wu R, Xu H, Xue F et al. Adsorption and degradation of imazapic in soils under different environmental conditions. PLoS One 2019;14(7):1-11. https://doi.org/10.1371/journal.pone.0219462

Wang X, Wang H, Fan D. Degradation and metabolism of imazapyr in soils under aerobic and anaerobic conditions. Int J Environ Anal Chem. 2006;86(8):541-51. https://doi.org/10.1080/03067310500410730