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Weed Management in Rice

RESEARCH ARTICLE

Potential reduction of non-imidazolinone rice grain yield by imidazolinone soil residual activity

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Abstract: Background: Imidazolinone (IMI) soil residual activity can carryover and affect non-tolerant rice growth and grain yield. **Objective:** This study aimed to determine the IMI soil residual concentration that can potentially reduce non-IMI rice plant height (PH) and grain yield (GY). **Methods:** Two field experiments in a randomized complete block design were performed to estimate the D_{10} value (herbicide rate that reduces the rice plant height or grain yield by 10%). The factorial arrangement comprised: A) non-IMI rice (Provisia™, IRGA 417, and IRGA 424); B) rates of imazapyr + imazapic: 0 to 0.25x (x = 147 + 49 g ai ha^{-1}) applied 28 days before non-tolerant rice sowing. IMI concentration analyses were performed through high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS) using soil samples from the 0-20 cm depth on the day of rice sowing. The data (concentration of imazapyr, imazapic and imazapyr + imazapic in the soil) were analyzed via linear regression. The means of imazapyr + imazapic were used to fit PH and GY by a nonlinear mixed-effects model. **Results:** Imazapyr + imazapic soil concentration ranged from 0 to 10.08 μg kg^{-1} (Year 1) and 0 to 20.11 μg kg^{-1} (Year 2). D_{10} values for PH were 5.20, 4.03, and 4.07 μg kg^{-1}, while D_{10} values for GY were 4.55, 2.76, and 3.84 μg kg^{-1} for Provisia™, IRGA 417, and IRGA 424, respectively. **Conclusions:** The soil concentration of imidazolinones at rice sowing that can reduce grain yield is 2.8 to 4.5 μg kg^{-1}, close to the field applied doses of 3–6%, depending on various environmental and soil factors.

Keywords: Carryover; Clearfield®; Imazapyr; Imazapic; HPLC-MS/MS

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1. Introduction

Imidazolinones (IMI) are one of the five chemical groups of acetolactate synthase (ALS)-inhibiting herbicides in plants and provide a broad control spectrum (grasses, sedges, and broadleaf weeds) at low application rates (Wendeborn et al., 2012; Yu, Powles, 2014). With the launch of IMI-resistant Clearfield® (CL) rice (*Oryza sativa* L.) in the early 2000s (Sudianto et al., 2013), the use of IMIs became almost essential for rice cultivation (Menezes et al., 2013). The IMI herbicides used in the CL system allowed for selective post-emergence weedy rice control (*Oryza* spp.) (Burgos et al., 2021), which is one of the most troublesome and persistent weeds in direct-seeded paddy rice fields in America, Asia and Europe (Zhang et al., 2014; Merotto et al., 2016; Dai et al., 2017). However, the evolution of IMI-resistant weedy rice is the primary concern in CL rice fields (Avila et al., 2021).

Currently, IMI-resistant weedy rice occurs in all the main rice-producing countries (Heap, 2024), causing widespread abandonment of paddy fields (Merotto et al., 2016). Herbicide-resistant weeds make chemical control nonviable (Busi et al., 2013). Provisia™ rice (PV) was recently released as an alternative, or supplemental technology, to CL rice to sustain rice production (Dauer et al., 2018; Camacho et al., 2019). PV was developed through a mutation in the *acetyl coenzyme-A carboxylase* (*ACCase*) gene, which confers resistance to quizalofop-p-ethyl (QPE) (Dauer et al., 2018; Camacho et al., 2019). QPE effectively controls IMI-resistant weedy rice (Lancaster et al., 2018; Rustom et al., 2018). However, PV rice is highly sensitive to residual activity of IMI in soil (Junkes et al., 2022).

IMI residual activity depends mainly on the sorption-desorption process (which affects bioavailability and phytotoxicity) and the persistence of these compounds in the environment (Liu et al., 2018; Marinho et al., 2019; Su et al., 2019). The most widely used IMIs in CL rice include imazethapyr (Fish et al., 2015) and the premix formulation of imazapyr + imazapic (Dilipkumar et al., 2018). The long persistence of these IMIs in the soil matrix (Gianelli et al., 2014; Su et al., 2019) can affect the growth and development of sensitive plants (carryover), reducing the grain yield of non-IMI crops sowed in succession or rotation (Bundt et al., 2015). In fact, up to one year after application, IMI can reduce the grain yield (or yield components) of non-IMI rice by 50% (Marchesan et al., 2010; Junkes et al., 2022).

Herbicide persistence is desired when it results in longer weed control, but it is undesirable when it damages crops sown in succession/rotation (Santos et al., 2014). Thus, the risk of carryover can preclude the direct transition from CL to PV

(Junkes et al., 2022). An alternative to avoid IMI carryover in non-IMI rice is to plant tolerant crops in rotation, such as soybean [*Glycine max* (L.) Merr.] (Dauer et al., 2018; Agostinetto et al., 2018). However, lowland soils, where rice is typically grown, are not entirely conducive to soybean cultivation due to factors such as soil relief and hydromorphism (Sartori et al., 2016), which can hinder the implementation of this strategy. In this case, it is necessary to adopt some agronomic practices that can increase IMI dissipation in the soil (Gehrke et al., 2021) and mitigate non-CL rice damage (Junkes et al., 2022).

Dissipation of IMI herbicides in soil is affected by several factors, such as photodegradation, chemical degradation, hydrolysis, and microbial activity (Refatti et al., 2017). Thus, the IMI half-life (time required for 50% of the herbicidal molecules to dissipate) is variable, ranging from 72–257 days for imazethapyr (National Center for Biotechnology Information, 2023); 37–182 days for imazapyr (Gianelli et al., 2014; Junkes et al., 2022); and 138–364 days for imazapic (Su et al., 2019). These values vary according to the soil clay content, initial concentration, temperature, moisture, pH (Gianelli et al., 2014; Su et al., 2019), and management of the field (Gehrke et al., 2021; Junkes et al., 2022). The half-life of imazapyr, for example, can be as long as 6 months or as short as 42 days in continuous flooding and intermittent water management, respectively (Junkes et al., 2022). Thus, as much as 25.0% or as little as 0.4% of the applied dose can be present in the soil in the following sowing season. However, no research has linked IMI soil concentrations to grain yield reduction in non-IMI rice and the acceptable loss.

Considering that the evolution of IMI-resistant weedy rice has caused the abandonment of some rice fields and assuming a 10% overall crop yield reduction due to weed management failures (Chauhan, 2020), this value may be a plausible loss due to herbicide residue in soil during the transition from CL to PV. However, due to low application rates and its sorption in the soil, it is difficult to extract and quantify the residual IMI. The analysis of IMI in soil at low limits of detection (LOD) and quantification (LOQ) is complex (Ramezani et al., 2010). However, the use of extraction techniques optimized for the analyte and matrix, combined with sensitive and robust analytical instrumentation has shown potential for the determination of IMI waste in the soil (Kemmerich et al., 2015). The development of a QuEChERS (quick, easy, cheap, effective, rugged, and safe) extraction method, using high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) has enabled advances in IMI analyses and can be used for this purpose (Kemmerich et al., 2015; Marinho et al., 2019).

This work aimed to evaluate the IMI soil residual concentration that can reduce non-tolerant rice plant height and grain yield by 10%.

2. Material and Methods

During the growing seasons 2021-2022 (Year 1) and 2022-2023 (Year 2), field experiments in adjacent areas (Capão do Leão, RS, 31°48'30.8" S, 52°28'50.2" W; and 31°48'27.3" S, 52°28'51.4" W, respectively) were conducted at *Centro Agropecuário da Palma*. The soil in the area is classified as Haplic Planosol (Empresa Brasileira de Pesquisa Agropecuária, 2013), a silty-loam soil type, with the following chemical properties: water pH = 5.2, ECEC = 5.3 cmolc dm^{-3}, organic matter= 1.79%, clay content = 22%, phosphorus (P) = 8.5 mg dm^{-3}, potassium (K) = 31 mg dm^{-3} (Year 1); and water pH = 4.9, ECEC = 5.2 cmolc dm^{-3}, organic matter = 1.93%, clay content = 25%, phosphorus (P) = 5.7 mg dm^{-3}, potassium (K) = 35 mg dm^{-3} (Year 2).

2.1 Dose-response curve

The experiment was performed in a randomized complete block design with four replications – with each plot having 10 m^2 (2 x 5 m). The factorial arrangement comprised: 1) non-IMI rice (Provisia™, IRGA 417, and IRGA 424); 2) rates of imazapyr + imazapic (Kifix, 525 + 175 g ai Kg^{-1}, WG): 0, 3.06, 6.12, 12.25, 24.50, and 49 g ai ha^{-1} (or 0, 0.015, 0.031, 0.062, 0.125 and 0.25x; x = 147 + 49 or 196 g ai ha^{-1} – maximum field rate), with adjuvant addition of 0.5% (v/v) (Dash® HC, 933 g L^{-1}, EC). The treatments were applied 28 days before rice sowing with a CO_2 pressurized sprayer equipped with flat fan nozzles (XR 110.015 model, 0.5 m apart). The application was performed at 250 kPa pressure, delivering 150 L ha^{-1} of carrier volume. Nozzles were positioned at 0.5 m above the soil surface. The environmental conditions were monitored during applications using a Kestrel® 4500 weather meter.

Rice was planted in both years (2021 and 2022) in November as recommended for the region, by direct dry seeding with a nine-row seeder spaced at 0.17 m. For IRGA 417 and IRGA 424, 90 kg ha^{-1} of seeds were used; for Provisia™, 45 kg ha^{-1} of seeds were used. In both cases, 250 kg ha^{-1} of a 05-20-20 N-P-K fertilizer was applied at rice sowing. Subsequently, 110 kg ha^{-1} of nitrogen (N) was applied as urea; the first application (50%) was done when seedlings reached the 3–4-leaf stage, and the second (50%) at panicle differentiation (R1). Before rice emergence, pendimethalin at 1,365 g ai ha^{-1} (Prowl H_2O, 455 g ai L^{-1}, CS), glyphosate at 1,500 g a.e. ha^{-1} (Zapp QI 620, 500 g a.e. L^{-1}, SL) and penoxsulam at 48 g ai ha^{-1} (Ricer, 240 g ai L^{-1}, CS) were applied. When rice was at 3-4 leaf stage, permanent flood was established. From plant establishment to harvest, the field was inspected, and if necessary, weeds were hand-pulled.

At 35 days after flooding, plant height (PH) was measured from the base to the apex of the completely distended leaf. Rice grains were harvested (area of 3 m^2) when grain moisture reached 23%. The samples were threshed and weighed, and a portable device was used to determined grain moisture (Gehaka Agri, G650, Brazil).

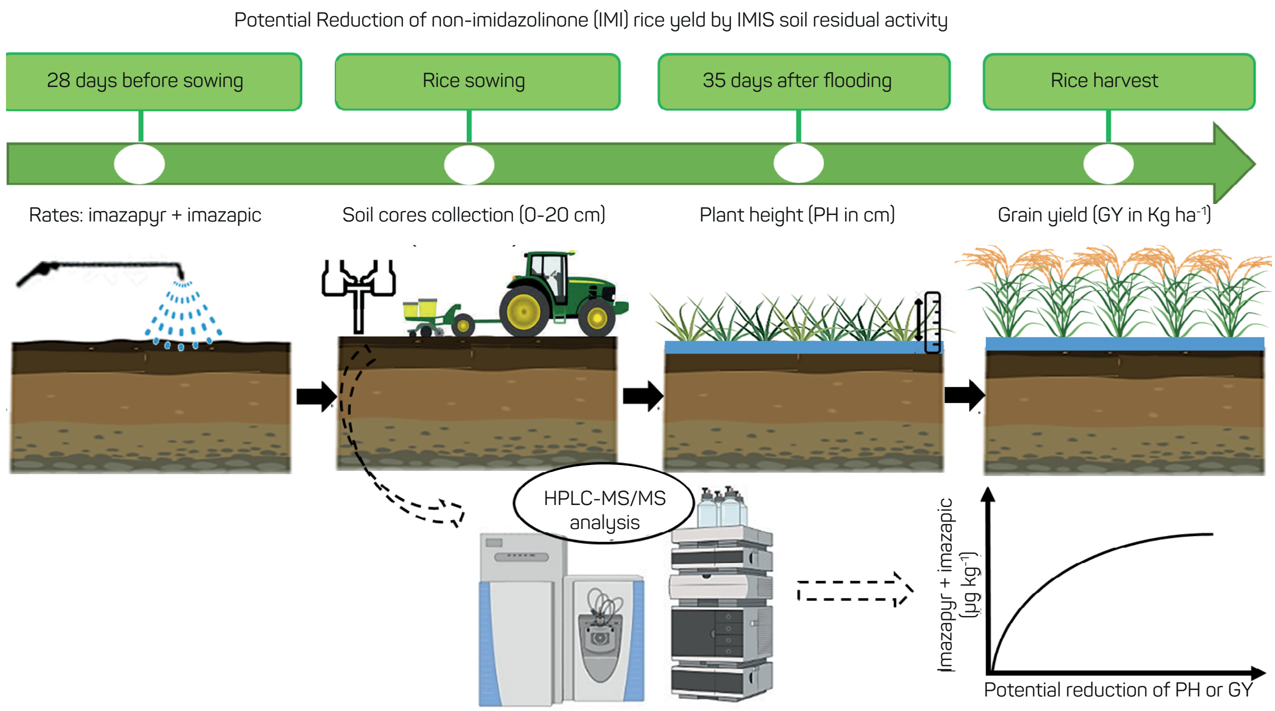

Figure 1 - Scheme to evaluate the potential reduction of non-IMI rice (Provisia™, IRGA 417, and IRGA 424) grain yield by imazapyr + imazapic soil residual activity

The rice grain yield (GY) was corrected to 13% moisture and then converted to kg ha^{-1} (Figure 1).

2.2 Soil sampling and extraction of IMI from the soil

On the day of rice sowing, four soil cores of 0–20 cm depth (Bundt et al., 2010) were randomly collected for each treatment. The subsamples were homogenized into a composite sample. Each composite sample was placed in a forced-air oven set at 60 °C for 96 h. The soil samples were passed through a 2.38 mesh sieve in the next step. The samples were stored in polyethylene bags and kept at -4 °C until IMI extraction.

The IMI extraction was performed according to the procedure developed by Kemmerich et al. (2015), with some adaptations. Initially, 5 g of soil was weighed in a 50 mL polypropylene tube, by adding 10 mL of extracting solution (ultrapure water containing 0.5 mol L^{-1} ammonium acetate at pH 8.5, adjusted with ammonium hydroxide). The tubes were shaken (vortex mixer – Phoenix Luferco, AP 56, Brazil) for 1 min and then kept in an ultrasonic bath (QuIMI, 03350, Brazil) for 15 min. Subsequently, the tubes were kept in the dark under agitation (orbital shaker – Novatecnica, NT50, Brazil) for 24 h.

Next, the tubes were centrifuged (Heraeus Megafuge 16R, Thermo Scientific, USA) for 7 min (5,000 rpm) at 10 °C. An aliquot of 1.4 mL was transferred to a microcentrifuge tube (1.5 mL) containing 62.5 mg of primary secondary amine (Supelclean™ PSA SPE, Supelco, USA), shaken for 1 min and centrifuged for 5 min (3,500 rpm) at 10 °C. The extract was filtered using a nylon filter syringe with 0.22 µm mesh, 1 mL was transferred to glass vials, and the pH was adjusted to 3.0 with hydrochloric acid (HCL, 6 mol L^{-1} – approximately 83 µL).

2.3 Parameters for detection and quantification of IMI by HPLC-MS/MS

The IMI levels in the soil were determined by high-performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS), with a Dionex UltiMate 3,000 automatic sampler coupled to a Q-Exactive™ Focus hybrid Quadrupole-Orbitrap mass analyzer and the data acquisition system using the Trace Finder 4.1 software (Thermo Fisher Scientific™, USA). The herbicide was separated in an Accucore™ C18 column (100 mm x 2.1 mm – particle size of 2.6 µm, Thermo Fisher Scientific™, USA). The mobile phases were: A) an aqueous solution of ammonium formate (5 mM) and formic acid (0.1%); and B) HPLC-grade methanol. The percentage of organic solvent (methanol) was changed: 0.5 min (5%), 2.5 min (100%), 3.0 min (100%), 3.5 min (5%), and 6.0 min (5%); with a flow rate of 0.3 mL min^{-1} and total chromatographic run time of 6 min. The injection volume was 10 µL, and the column temperature was 40 °C.

The conditions used in MS/MS were electrospray ionization (ESI) in positive mode; ionization energy of 20, 40, and 60 eV; capillary temperature of 350 °C; spray voltage of 4.0 kV; sheath gas flow of 40 L h^{-1}; auxiliary gas flow of 12 L h^{-1}; and resolution of 70,000. For imazapyr, the precursor ion was 262.11862 m/z; and the product ions were 220.07161, 217.09714, 202.06107, and 86.09635 m/z. For imazapic, the precursor ion was 276.13427 m/z, and the product ions were 234.08737, 231.11288, 216.07684, and 86.09639 m/z. The retention time and fragmentation profile were used to confirm the IMI compounds in the soil samples.

For IMI quantification, a calibration curve with analytical standards (Sigma-Aldrich) for imazapyr (99.5% purity – CAS number 81334-34-1) and imazapic (99.9% purity – CAS number 104096-48-8) were used at 0.1, 0.2, 1.0, 5.0, 10.0, 15.0, 20.0 and 25.0 μg L^{-1} (using soil extract without herbicide – blank soil sample) – equivalent to 0.2, 0.4, 2.0, 10.0, 20.0, 30.0, 40.0, and 50.0 μg Kg^{-1} (conversion factor of 2x). Linearity was evaluated with an acceptance coefficient of determination (r^2) ≥ 0.99. Accuracy was determined by recovery assays (acceptability of 70–120%), by spiking blank soil samples at 0.3, 0.5, 5.0, and 10.0 μg Kg^{-1} with three replicates (n = 3), and the precision was evaluated through the relative standard deviation (RSD% ≤ 20). The LOQ was obtained by the lowest fortified concentration that presented acceptable accuracy and precision values. The limit of detection (LOD) was obtained by dividing the LOQ by 3.33 (Kemmerich et al., 2015).

2.4 Statistical analyses

The field data were analyzed using the R program (R Core Team, 2019). Each IMI (imazapyr or imazapic) individually and their sum (imazapyr + imazapic) were evaluated. A mixed-effects multi-factor ANOVA model (with blocks as random effects) was used to distinguish doses, non-IMI rice, and years using the *lme4* package. The homogeneity of variance and normal distribution of the measurement errors were graphically evaluated by plotting the distribution of residuals against the fitted value and by normal q-q plot, illustrating whether the residuals were normally distributed, respectively. The *lmer* and *Anova* functions indicated the interaction between doses and years (F *test* < 0.05) – data not shown. Thus, the IMI was fitted by doses and years (joining rice data) via linear regression (Equation 1). The *summary* function was used to assess whether parameters were significant (P < 0.05) and to estimate the standard errors and the adjusted r-squared (r^2) (Kniss, Streibig, 2024).

$$Y = a + bx \quad \text{(Eq. 1)}$$

where Y is IMI soil concentration (μg Kg^{-1}); *a* is the intercept of the regression line (predicted value when x = 0); *b* is the slope of the regression line; x = IMI soil applied (g ai ha^{-1}).

The mean values of imazapyr plus imazapic (μg Kg^{-1} – Year 1 and Year 2) were used to fit the raw data of PH and GY. The *medrc* and *drc* packages were used to adjust dose-response curves by the nonlinear mixed-effects (NLME) model, assuming a three-parameter log-logistic equation with a separate set of *b*, *d*, and D_{50} for each non-IMI rice variety (Equation 2). Individual effects were included in these parameters by the *metadrm* function – cid2 (individual curves) and ind (as a factor containing the between-curve grouping of the data).

$$Y = \frac{d}{1 + exp\,\{b\,(log\,log\,(x) - log\,log\,(D_{50}))\}} \quad \text{(Eq. 2)}$$

where Y is the PH (cm) or GY (kg ha^{-1}) reduction; D_{50} is the dose that causes 50% PH or GY reduction; *d* is the upper limit; and *b* is the slope around *e* (Ritz et al., 2019).

The *metadrm* (*drm* and *summary* functions) estimated the parameters, their standard errors, and the parameters' significance (P < 0.05). D_{10} (the dose that causes 10% in PH or GY reduction) was estimated by *ED* function (95% confidence intervals). The variance homogeneity and normally distributed errors were evaluated as mentioned above. We fit a joint model based on the entire dataset (% relative to the untreated control) to create the figures and test the model's goodness of fit (when not significant, the regression describes the variation of data similar to ANOVA).

3. Results and Discussion

3.1 Parameters for detection and quantification of IMI by HPLC-MS/MS

The extraction method and analysis by HPLC-MS/MS were efficient for determining the IMI content in the soil (Figure 2). Proper separation with retention times of 3.52 min and 3.70 min was achieved for imazapyr and imazapic, respectively (Figure 3). Linearity showed acceptable values (r^2 ≥ 0.99) in all analyses, in the range of 0.1-25 μg ai L^{-1} (data not shown). Furthermore, the recovery assays resulted in acceptability values (70-120%) for each compound, with RSD ≤ 20% (Figure 4). Thus, the LOQ obtained was 0.3 μg Kg^{-1}, and the LOD was 0.09 μg Kg^{-1}.

Liquid chromatography with tandem mass spectrometry is a viable technique for the analysis of residual compounds due to its sensitivity and robustness (Martins et al., 2014; Marinho et al., 2019). Because it can separate and identify the analytes present in the sample and subsequently quantify even very low concentrations. HPLC-MS/MS has been increasingly used in different areas of science (Snyder et al., 2010; Coskun, 2016). Despite the analytical advantages of this technique, factors such as the extraction process and the sample matrix effect during the analysis were limited to obtaining low LOQ/LOD. The IMI extraction process requires using a suitable soil extract, clean-up, and alkalinization of the extraction solution (Kemmerich et al., 2015).

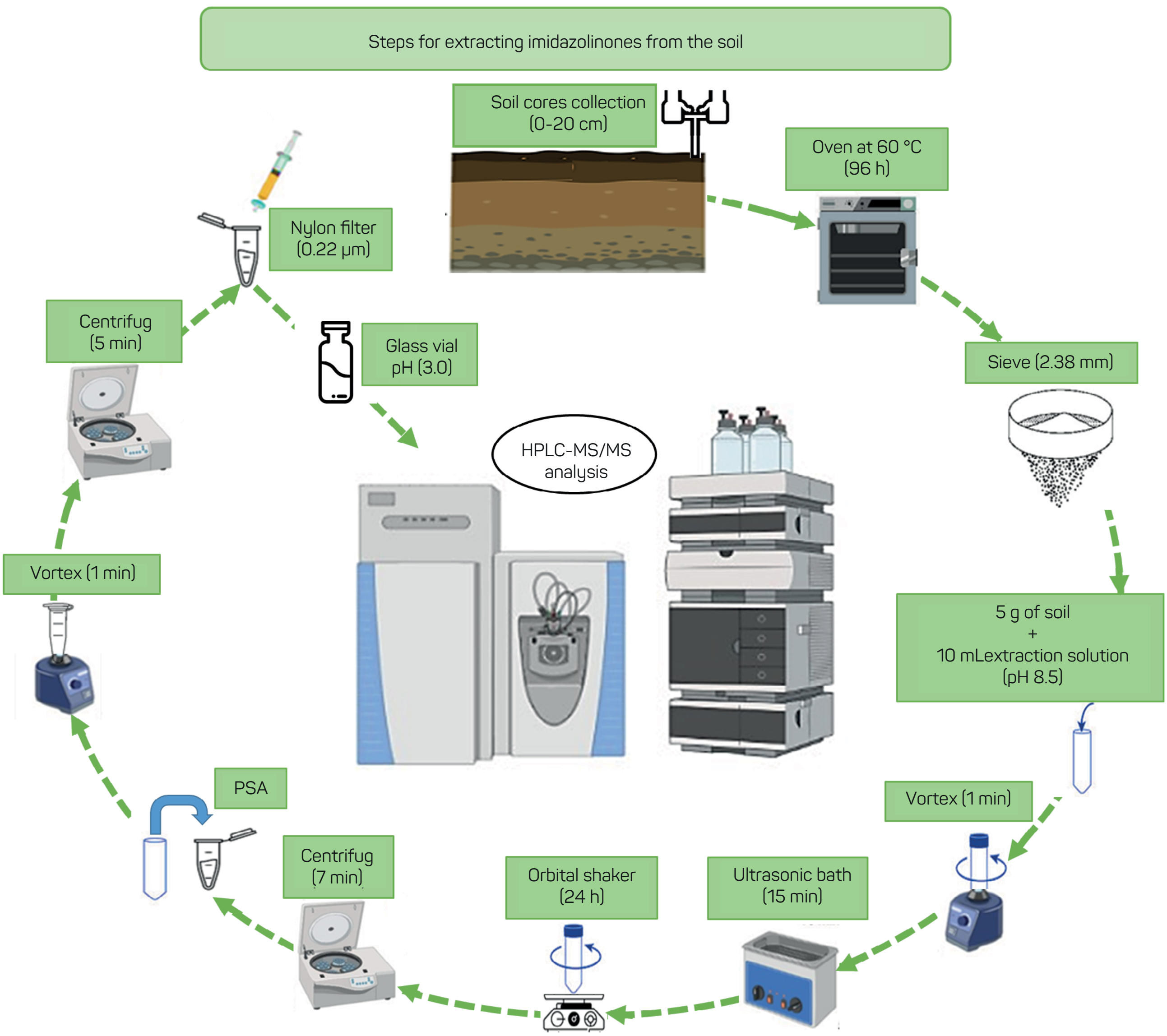

Figure 2 - Extraction method and analysis by HPLC-MS/MS of imidazolinone soil concentration

The alkalinization of the extraction solution is due to the adsorption of herbicides on soil particles, which determines their distribution in the solution and the soil matrix (Wauchope et al., 2002). Most agricultural soils have a net negative charge, resulting in repulsive forces and low adsorption of anions (Reginato et al., 1997). Imazapyr and imazapic are weak acids and have a carboxylic functional group (COOH) (Tan et al., 2005; Kemmerich et al., 2015). The acid dissociation constant values (pKa, which represents the pH-value at which 50% of the molecules are in the molecular form and 50% in the dissociated form) of these herbicides are 3.6 (imazapyr) and 3.9 (imazapic). Depending on the pH of the medium, they occur in cationic or anionic forms (Kemmerich et al., 2015). At pH values greater than 6.0, both imazapyr and imazapic are predominantly anionic (COO^-) (Kraemer et al., 2009). In the present study, alkalinization was carried out with a buffer of 0.5 mol L^{-1} of ammonium acetate at pH 8.5 for the effective extraction of IMI strongly adsorbed to the soil.

Rice fields have a more acidic soil pH (Junkes et al., 2022) and thus allow for greater adsorption of imidazolinone herbicides, due to the occurrence of the molecular form (COOH) in these soil pH conditions. Indeed, in the present study, the soil pH values were 5.2 (Year 1) and 4.9 (Year 2). Thus, adjusting the extraction solution to pH 8.5 enables the alkalinization of the medium, favoring the extraction of IMI for more assertive quantification. This occurs because these herbicides are repelled by the negative charges of the soil in anionic form (COO^-) and remain in higher concentrations in the solution (Aichele, Penner, 2005; Kraemer et al., 2009).

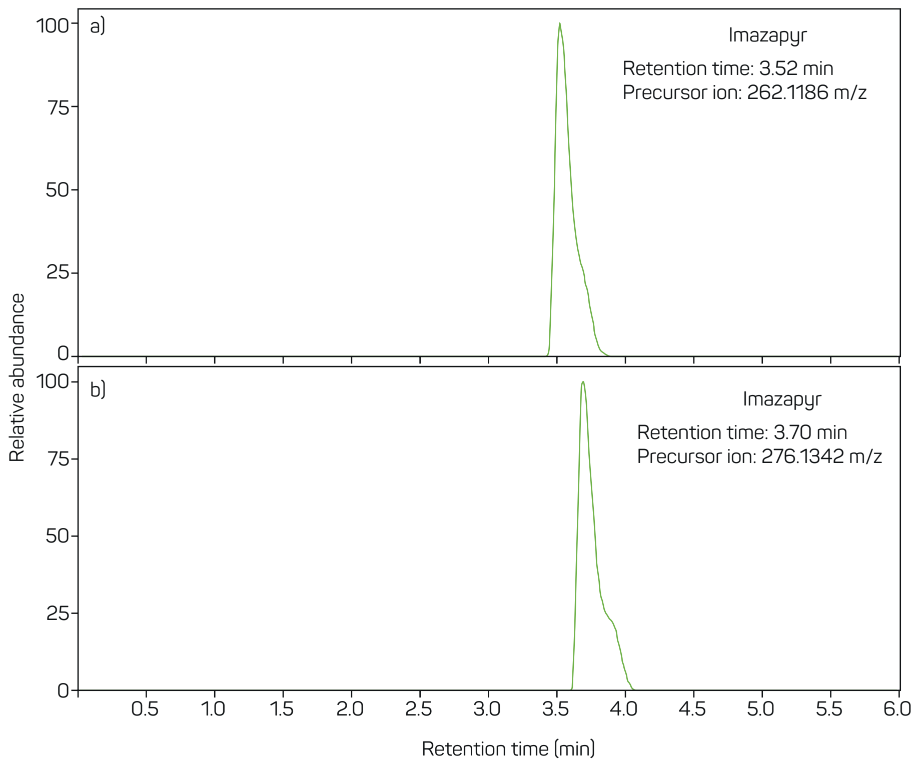

Figure 3 - Chromatogram of imazapyr (a) and imazapic (b) of a standard solution at 5 µg L^{-1} by HPLC-MS/MS, with retention time (min) and precursor ion (m/z)

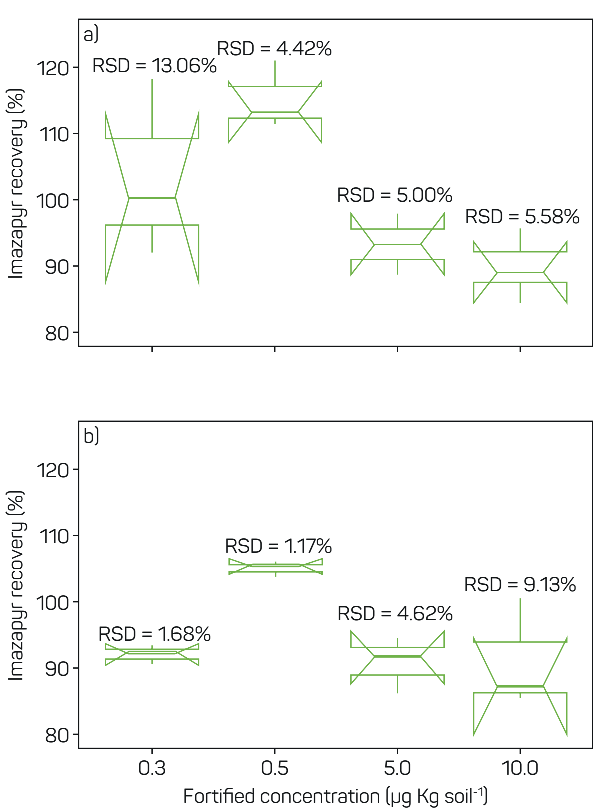

Figure 4 - Recovery and relative standard deviation (RSD%) for "blank" samples spiked with imazapyr (a) and imazapic (b) at 0.3, 0.5, 5.0, and 10 µg kg soil^{-1} (n = 3)

Another factor that enabled the analysis of very low concentrations of IMI in the soil was the increase in proportion between extraction solution:soil (2:1) and the incubation time with agitation (24 h). Water is a competitor for soil adsorption site, and the chemicals are released when the soil is re-wetted, but time is required for molecules to diffuse either toward or away from the soil surface (Wauchope et al., 2002). Thus, using instrumentation with high resolution and sensitivity combined with adopting QuEChERS methods has enabled advances in IMI analyses (Martins et al., 2014; Kemmerich et al., 2015; Marinho et al., 2019). Consequently, it was possible to obtain LOQ and LOD values at low levels, such as those found in this study.

3.2 Concentration of IMI in the soil

The low values of LOQ and LOD obtained using the HPLC-MS/MS method allowed us to evaluate the IMI rates (sub-doses) applied in the field. The IMI (imazapyr or imazapic, and the sum of both) concentrations in the topsoil (0-20 cm depth) profile (µg Kg^{-1}) differed between years and increased linearly in response to soil application rates (Table 1). For imazapyr, the mean values ranged from 0 to 8.33 µg Kg^{-1} and 0 to 16.74 µg Kg^{-1} in year 1 and year 2, respectively (Figure 5a). For imazapic, the mean values ranged from 0-1.75 µg Kg^{-1} (year 1) and 0-3.37 µg Kg^{-1} (year 2) (Figure 5b). Thus, the mean values for the sum of imazapyr plus imazapic were 0-10.08 μg Kg^{-1} and 0-20.11 μg Kg^{-1} for years 1 and 2, respectively (Figure 5c).

One day after application of imazapyr plus imazapic (147 + 49 g ai ha^{-1}) in CL rice, we found up to 50.00 and 6.90 μg kg^{-1} (sum of 56.90 μg kg^{-1}) of these compounds in the soil profile, respectively (Junkes et al., 2022). These values are close to the inter-year average rate of 25% (or 15.09 μg kg^{-1}) applied in the present study. Differences in environmental conditions and soil properties can explain the differences between the doses across years. IMI is mainly degraded by soil aerobic microbial activity (Gehrke et al., 2021), which is directly associated with soil conditions and adsorption process (Su et al., 2019), which in turn affect the bioavailability of these compounds (Liu et al., 2018; Marinho et al., 2019). Thus, depending on the environment and the management of the field, the IMI half-life can vary by more than 400% (Junkes et al., 2022). Furthermore, imazapic can reach deeper into the soil profile (Bundt et al., 2014), explaining the non-ratio of 3:1 found in the 0-20 cm layer.

3.3 Dose-response curve

The PH and GY reductions showed sigmoidal behavior as a function of increasing concentrations of imazapyr + imazapic in the soil, indicating no differences among rice cultivars. The D_{10} values for PH were 5.20, 4.03, and 4.07 μg kg^{-1} for Provisia™, IRGA 417, and IRGA 424, respectively (Table 2; Figure 6). For grain yield, these values were 4.55, 2.76, and 3.84 μg kg^{-1} for Provisia™, IRGA 417, and IRGA 424, respectively (Table 3, Figure 7).

Table 1 - Estimated parameters (*a* and *b* _with standard error in parentheses) and adjusted r-squared (r2) by linear regression [1], based on the soil concentration of imazapyr, imazapic and imazapyr + imazapic (μg Kg $soil^{-1}$) as a function of imazapyr + imazapic soil applied (g ai ha^{-1}) on the rice sowing day.

Herbicide	Parameters	Year 1	Year 2
Imazapyr	*a*	0.78*** (0.19)	0.62* (0.31)
	b	0.21*** (0.01)	0.43*** (0.01)
	Residual standard error	0.70	1.14
	Degrees of freedom	69	69
	R^2	0.94	0.96
Imazapic	*a*	0.14** (0.04)	0.24* (0.09)
	b	0.15*** (0.01)	0.29*** (0.01)
	Residual standard error	*0.16*	0.33
	Degrees of freedom	69	69
	R^2	0.93	0.92
Imazapyr + imazapic	*a*	0.92***(0.22)	0.86* (0.34)
	b	0.19*** (0.01)	0.39*** (0.01)
	Residual standard error	0.80	1.22
	Degrees of freedom	69	69
	R^2	0.94	0.97

[1] Y = a + b * x. *** (p≤0.001); ** (p≤0.01); * (p≤0.05).

As discussed before, the adsorption process also influences the IMI phytotoxicity (Gianelli et al., 2014; Liu et al., 2018). At typical soil pH values (Gianelli et al., 2014), these compounds are in anionic forms (around 94% at pH 5 – a pH value close to the present study), are weakly adsorbed in the soil and can be translocated easily in plants (Sondhia et al., 2015). Indeed, the IMI phytotoxicity to rice increases as soil pH increases, indicating that the adsorption process is the main factor (Liu et al., 2018). Furthermore, when the rice crop is grown in continuous flooding conditions, the herbicide is solubilized, i.e., optimizing uptake by the plants (Junkes et al., 2022).

In the soil, IMI can be absorbed by plant roots via ion trapping, translocated to the shoot (Little et al., 1994), and interfere with the ALS activity of susceptible plants. ALS is the first enzyme in the biosynthesis route of branched-chain amino acids (BCAAs – valine, leucine, and isoleucine) (Garcia et al., 2017). In susceptible plants, the IMI binds to a domain that crosses the entrance of the catalytic site, preventing the substrate from connecting to it and interfering with amino acid synthesis (Duggleby et al., 2008). Multiple hypotheses have been proposed for the mechanism of susceptible plant mortality by ALS-inhibiting herbicides. However, it is known that BCAA depletion causes a decline in protein synthesis, which in turn affects cell division (mitosis) and DNA synthesis (Zhou et al., 2007) and interferes with regular plant growth and development (Bzour et al., 2018).

Our findings corroborate the factors mentioned above, revealing a reduction in the PH of non-IMI rice as a function of increased soil concentrations of imazapyr + imazapic. Ruzmi et al. (2020) reported that only 1.7 nM is needed to achieve 50% inhibition of rice ALS activity *in vitro* for both herbicides – i.e., IMI can affect the rice plant growth even at low concentrations. For rice, certain agronomic traits, such as PH, influence grain yield (Zhang et al., 2017; Li et al., 2019). Indeed, to reach high crop yields, a proper plant architecture is required, often defined by PH (Xue et al., 2008). PH is closely related to biomass production and directly impacts rice grain yield (Zhang et al., 2017). Thus, the observed reduction in plant height can also explain the grain yield reduction found in this study.

In a previous study of a Clearfiled® rice system 306 days after application of imazapyr + imazapic (147 + 49 g ai ha^{-1}), imazapyr concentrations of 6.49 μg kg^{-1} and 1.87 μg kg^{-1} of imazapic were detected (Junkes et al., 2022). That study considered only 0-10 cm layer of soil. About one year after application, the IMI may have leached into the soil profile (Refatti et al., 2017). Damage to rice typically occurs IMI residue at depths up to 20 cm below the soil surface (Bundt et al., 2010). The said study confirmed that residual activity exists and that the sum of imazapyr + imazapic (8.36 μg kg^{-1}) can reduce non-IMI rice grain yield components, including the number of stems (67%) and the shoot dry weight (43%), compared to plants grown in an area without herbicide residue (Junkes et al., 2022). Thus, residual IMI herbicide in soil is a hidden threat to yield of susceptible rice.

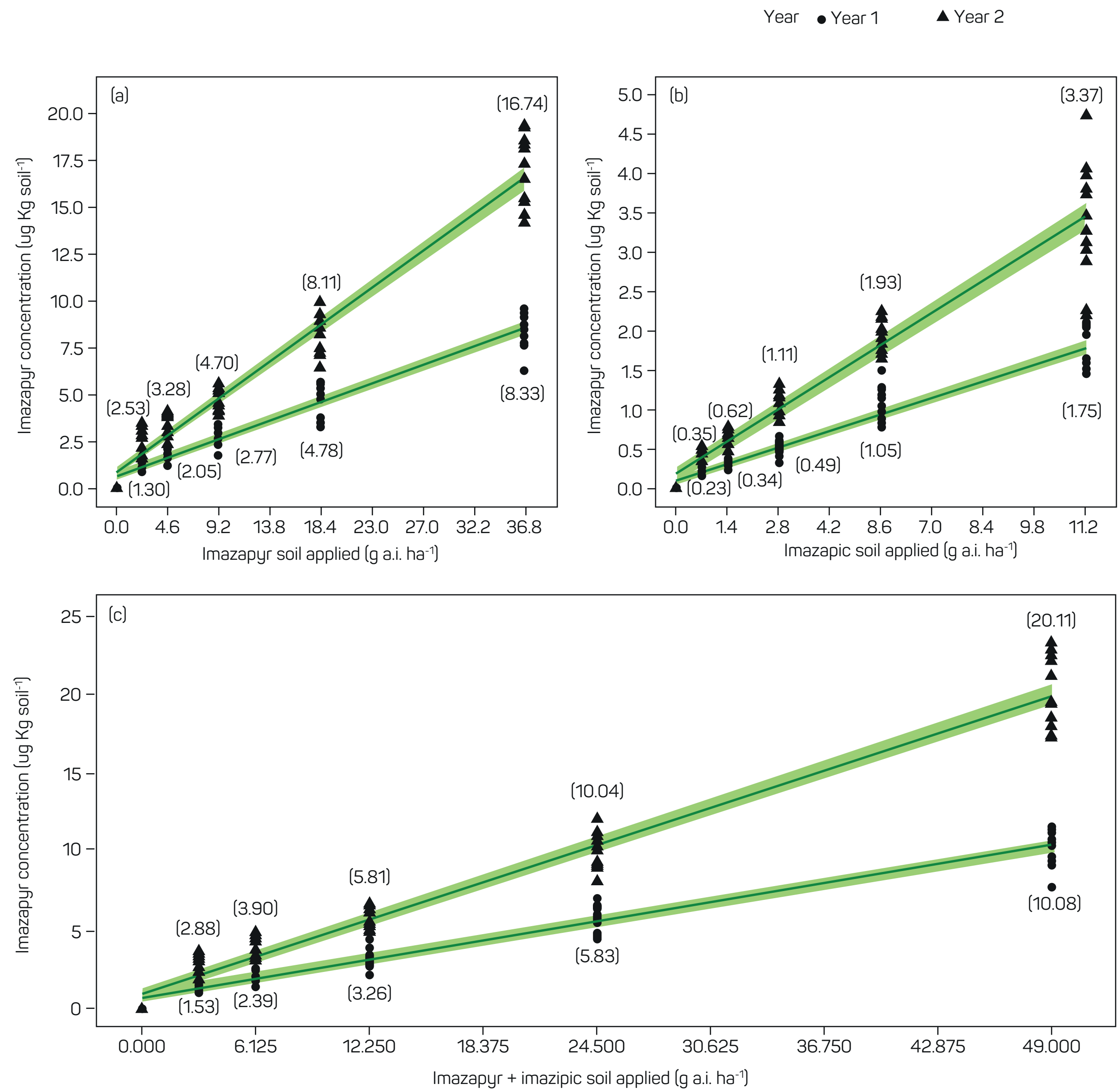

Figure 5 - Observed (● and ▲) and predicted (line) values for the soil concentration up to 20 cm depth (μg Kg soil^{-1}) of imazapyr (a), imazapic (b), and imazapyr + imazapic (c) as a function of imazapyr + imazapic soil applied (g ai ha^{-1}) on the rice sowing day. Values in parentheses are the averages of each rate (n = 12)

The IMI fate (sorption-desorption, bioavailability, phytotoxicity, and persistence) in the soil is mainly determined by soil pH (Aichele, Penner, 2005; Kemmerich et al., 2015; Sondhia et al., 2015; Liu et al., 2018; Marinho et al., 2019; Su et al., 2019). The adsorption process depends on several other factors, such as organic matter, soil texture (clay content), moisture, and temperature (Kraemer et al., 2009; Gianelli et al., 2014; Su et al., 2019; Gerhke et al., 2021). Thus, the potential damage that soil residual activity of IMI can cause to non-IMI crops is environment-specific. In the present study, the potential to reduce non-IMI rice grain yield by 10% occurred at 2.8 to 4.5 μg kg^{-1}, close to the applied doses of 3-6%. The IMI residue that can remain in paddy rice field (Junkes et al., 2022) is above the acceptable reduction and should be avoided in areas where residual activity occurs.

It is known that some agronomic practices can increase the degradation of IMI in the soil, such as drainage, liming, soil tillage, use of cover crops (Gehrke et al., 2021), and intermittent flooding (Junkes et al., 2022). These factors can mitigate damage to the susceptible crop. Thus, having a reference concentration value for the potential damage that the IMI residual activity can cause to rice is fundamental. However, organic chemicals, in general, are absorbed by plant roots from

Table 2 - Estimated parameters (b, d, D_{50}, and D_{10} – with standard error in parentheses) by the nonlinear mixed-effect equation[1], based on plant height (raw data in cm), for non-IMI rice (Provisia™, IRGA 417, IRGA 424), 35 days after flooding.

Parameters	Non-IMI rice		
	Provisia™	IRGA 417	IRGA 424
b	1.53*** (0.28)	1.31*** (0.22)	1.30*** (0.26)
d	71.69*** (5.97)	67.30*** (5.96)	55.75*** (5.98)
D_{50} (µg Kg soil^{-1})[2]	21.83*** (2.81)	21.47*** (2.86)	21.97*** (3.51)
D_{10} (µg Kg soil^{-1})[2]	5.20 (1.66)	4.03 (1.37)	4.07 (1.64)

[1] $Y = d/(1+\exp[b(\log(x) - \log(e))])$; [2] The value is the sum of imazapyr + imazapic (µg Kg soil^{-1}); *** ($p \le 0.001$).

Table 3 - Estimated parameters (b, d, D_{50}, and D_{10} – with standard error in parentheses) by the nonlinear mixed-effect equation[1], based on grain yield (raw data in Kg ha^{-1}), for non-IMI rice (Provisia™, IRGA 417, and IRGA 424)

Parameters	Non-IMI rice		
	Provisia™	IRGA 417	IRGA 424
b	1.35*** ± 0.24	1.20*** ± 0.20	1.17*** ± 0.22
d	8,115.61*** ± 632.88	7,296.49*** ± 642.39	7,721.63*** ± 639.05
D_{50} (µg Kg soil^{-1})[2]	23.11** ± 4.90	17.11** ± 4.50	25.25** ± 5.66
D_{10} (µg Kg soil^{-1})[2]	4.55 ± 1.32	2.76 ± 0.80	3.84 ± 1.36

[1] $Y = d/(1+\exp[b(\log(x) - \log(e))])$; [2] The value is the sum of imazapyr + imazapic (µg Kg soil^{-1}); ***($p \le 0.001$); **($p \le 0.01$).

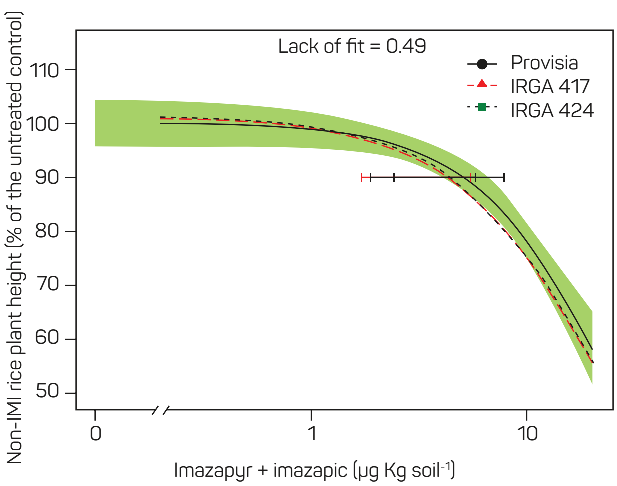

Figure 6 - Adjusted values (% relative to untreated control) for non-IMI rice plant height (Provisia™ (●), IRGA 417 (▲), and IRGA 424 (■)) as a function of imazapyr + imazapic (µg Kg soil^{-1}) soil concentration up to 20 cm depth, with confidence interval by the joint model based on the entire dataset. The horizontal bar represents the 95% confidence interval to obtain 10% plant height reduction (D_{10})

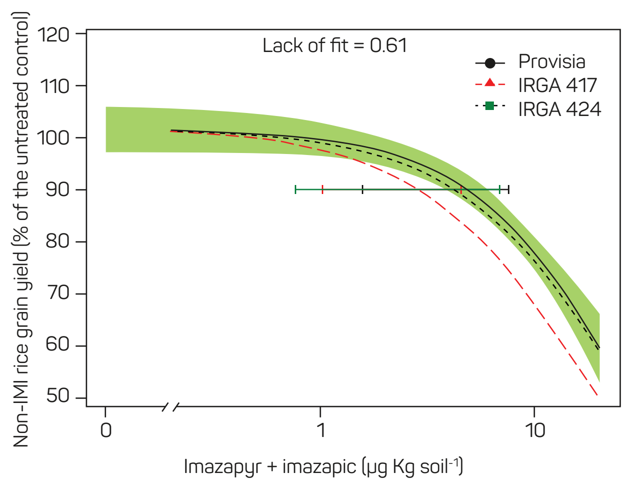

Figure 7 - Adjusted values (% relative to untreated control) for non-IMI rice grain yield (Provisia™ (●), IRGA 417 (▲), and IRGA 424 (■)) as a function of imazapyr + imazapic (µg Kg soil^{-1}) soil concentration up to 20 cm depth, with confidence interval by the joint model based on the entire dataset. The horizontal bar represents the 95% confidence interval to obtain 10% grain yield reduction (D_{10})

water in soil pores, and bioavailability has been estimated using pore water concentrations, which are the effective soil concentrations (Liu et al., 2018). The alkaline method used to extract IMI did not allow us to evaluate the bioavailability, and the low application rates made this task almost impossible.

In our research, we developed and validated a robust analytical technique for assessing the presence of imidazolinone (IMI) herbicides in soil at very low concentrations, which was not tenable previously. Further, we evaluated the impact residual IMI herbicides on the productivity of non-IMI rice. The methods introduced in this study offer validated tools for the precise analysis of IMI levels in soil, facilitating improved monitoring and research in rice-producing areas. These advancements enable the immediate tracking of IMI residual concentrations following application and especially following harvest. Specifically, our methods 1) support residual monitoring in Clearfield (CL) rice cultivation areas with varying histories of IMI use, 2) allow for pre-planting soil analysis to assess potential productivity losses in non-IMI rice, and 3) aid in decision-making for transitioning from CL to non-IMI rice cultivation.

4. Conclusions

Our results demonstrated that the concentration of IMI in soil at rice sowing that can reduce grain yield by 10% was above 2.8 µg kg^{-1}.

Authors' contributions

All authors read and agreed to the submitted version of the manuscript. All authors: conceptualization of the manuscript and development of the methodology. BCA, DMC, LB, and BN: data collection and curation. LAA, and ERC: data analysis and interpretation: all authors; funding and resource acquisition. LAA, and ERC: project administration: all authors; supervision. DMC: writing the original draft of the manuscript. All authors: writing, review, and editing.

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