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Desorption Kinetics of Tricyclazole and Isoprothiolane in Biochar-Amended Paddy Soils and Implications for Pesticide Bioavailability

Linda Klamann [1,2,*], Yousra Khatib [1], Snežana Maletić [3], Alexandra Axt [4], Khoi Chau Minh [5] and Lutz Weihermüller [1]

[1] Agrosphere Institute (IBG-3), Forschungszentrum Jülich GmbH, 52428 Juelich, Germany; y.khatib@fz-juelich.de (Y.K.); l.weihermueller@fz-juelich.de (L.W.)
[2] Institute of Crop Science and Resource Conservation, Soil Science and Soil Ecology, University of Bonn, 53115 Bonn, Germany
[3] Department of Chemistry, Biochemistry and Environmental Protection, Faculty of Sciences, University of Novi Sad, 21000 Novi Sad, Serbia; snezana.maletic@dh.uns.ac.rs
[4] Institute of Thermoprocesses and Emission Control in Waste Management and Recycling Teaching and Research Unit, RWTH Aachen University, 52062 Aachen, Germany; axt@teer.rwth-aachen.de
[5] College of Agriculture, Can Tho University, Can Tho 900000, Vietnam; cmkhoi@ctu.edu.vn
* Correspondence: l.klamann@fz-juelich.de

Abstract

Assessing pesticide bioavailability in paddy soils is critical for understanding environmental fate and potential food safety implications. This study investigated the desorption and immobilization of isoprothiolane and tricyclazole in a clay- and organic-rich Mekong Delta paddy soil, comparing Tenax and XAD-4 as extraction agents and assessing the effect of biochar amendment, using a two-compartment desorption model. Although both compounds fall below the ISO 16751:2020 criterion for Tenax (log Kow > 3), Tenax and XAD-4 did not differ significantly for the moderately hydrophobic isoprothiolane, whereas for the more polar tricyclazole, Tenax yielded a significantly lower fast-desorbing fraction, despite efficient sorption in matrix-free tests. Both pesticides exhibited high fast-desorbing fractions despite the soil's high clay and TOC content, consistent with their predominantly neutral form at the soil's low pH; nevertheless, a considerable slowly desorbing fraction of tricyclazole indicates interactions beyond hydrophobic partitioning. Biochar amendment had compound-specific, opposing effects: it significantly reduced the fast-desorbing fraction of tricyclazole at the applied, above-field concentration, whereas it increased that of isoprothiolane without significantly affecting its remaining fraction in soil. Residues of both fungicides were detected in regional rice grain, but could not be directly linked to the laboratory-derived parameters.

Keywords: tricyclazole; isoprothiolane; XAD4; Tenax; bioavailability; biochar amendment

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Academic Editor: Gian Franco Capra

Received: 17 September 2026
Revised: 28 October 2026
Accepted: 31 October 2026
Published: 4 November 2026

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1. Introduction

Rice (*Oryza sativa* L.) is the most important staple food worldwide, feeding approximately half of the world's population [1]. While wheat and maize supply around 19 and 5% of the world's dietary energy, respectively, rice is providing over 20% of the world's dietary energy and up to 76% of the calory supply in Southeast Asian countries [1,2]. While the world population continues to grow to an estimate of 8.5 billion by 2030 and further 9.7 billion by 2050, the global rice demand is estimated to increase to approximately 30% by

2050 [2,3]. Five Asian countries account for more than 71% of the global rice production with Vietnam ranking fifth in rice production and third in rice exports [4]. The increasing demand for rice production has put more pressure on rice farmers, especially in the top-producing countries and has driven a shift towards agricultural intensification with high synthetic fertilizer inputs and more frequent cropping cycles, resulting in increased pest pressure and a higher demand for pesticides [5]. Additionally, climate change aggravates environmental stress of increased heat, drought, and flooding events, leading to an increase in bacterial, fungal, and viral infections as well as insect and pest infestation [6].

The rice blast disease, caused by *Pyricularia oryzae*, is widely recognized as the most critical fungal disease in rice cultivation, causing annual yield losses of 10–30%, with high risks to complete crop loss under favorable conditions [7]. While there are different methods such as biological control, breeding of disease-resistant varieties, and cultivation management to control the disease, chemical fungicides remain the main choice to protect plants from diseases [8]. Among the variety of different fungicidal compounds, tricyclazole and isoprothiolane are commonly used compounds for effectively preventing rice blast infection across rice growing countries such as Japan, China, South Korea, and Vietnam [9]. Both are systemic fungicides which are taken up via the roots and foliage and translocated within the plant. Tricyclazole acts by inhibiting the melanin biosynthesis in the fungal appressorium, while isoprothiolane disrupts the phospholipid metabolism [8,10]. In the Vietnamese Mekong Delta specifically, tricyclazole and isoprothiolane rank among the most frequently used fungicides [11]. Reflecting the widespread use of these fungicides, a recent field survey (2023–2024) of paddy soils from three provinces in the Mekong Delta detected both compounds across all sampled sites. Tricyclazole residues reached a concentration of up to 227.3 μg kg^{-1} dry soil, while isoprothiolane was detected at up to 39.1 μg kg^{-1} dry soil [11]. These concentrations, especially for tricyclazole, raise concerns regarding accumulation in the soil and potential transfer to the rice grain, given that both compounds were detected as the most prevalent fungicides in recent studies across the Mekong Delta [11,12].

As Vietnam ranks as among the world's leading rice exporters, the presence of these residues in paddy soils is of particular relevance for food safety compliance. Isoprothiolane is not included in the EU list of approved active substances (Commission Implementing Regulation (EU) No 540/2011 [13]) under the current Regulation (EC) No. 1107/2009 [14], and is subject to a maximum residue limit (MRL) of 6 mg kg^{-1} rice under Regulation (EU) No. 2019/552 [15]. Tricyclazole is not approved under the Commission Implementing Regulation (EU) 2016/1826, in accordance with Regulation (EC) No. 1107/2009 and subject to an MRL of 0.01 mg kg^{-1} in rice under Commission Regulation (EU) 2017/983, a threshold that Vietnamese rice exports have occasionally been found to exceed [14,16–19]. Overall, total soil concentrations alone do not allow conclusions about the fraction of these compounds that are available for plant uptake and subsequent transfer to the grain. The ecotoxicologically and regulatorily relevant fractions of a compound are the freely dissolved or rapidly desorbing concentrations accessible for root uptake [20]. Whether the detected soil concentrations translate into grain residues exceeding EU MRLs therefore cannot be assessed from total residue soil concentrations alone but requires explicit assessment of compound bioavailability.

The sorption behavior of pesticides is defined by their physicochemical properties, particularly hydrophobicity (log K_{ow}) and soil sorption affinity (K_{oc}). Tricyclazole and isoprothiolane differ notably in their physicochemical behavior. With a log K_{ow} of 1.4 [10], tricyclazole shows comparatively low hydrophobicity. Reported K_{oc} values for tricyclazole in rice-growing region soils range from 376 to 1122 mL g^{-1}, depending on soil type and organic amendment [21]. Field dissipation studies report DT_{50} values of 45–85 days under field

and up to 197 days under laboratory conditions [22]. Further, the persistence of tricyclazole varies by soil moisture regime. Thus, the dissipation of the compound is the slowest under dry conditions (DT_{50} up to 334 days) and faster under flooded conditions (DT_{50} up to 177 days) [23]. While tricyclazole dissipates relatively quickly from paddy water (DT_{50} 5.47 days, [23]), it predominantly retains in the soil-bound fraction, suggesting limited bioavailability. However, strong sorption does not necessarily imply permanent unavailability. Given its high persistence, a fraction of soil-bound tricyclazole may become bioavailable over time, potentially contributing to long term soil residues and repeated exposure in intensively cultivated paddy systems. In comparison, isoprothiolane is considerably more hydrophobic (log K_{ow} = 2.8, [10]) but with similar K_{oc} values (196–2300 mL g^{-1}, [24]). Taken together, the available data do not allow a reliable assessment of bioavailability.

To understand the fate and effects of contaminants such as tricyclazole and isoprothiolane, desorption-based passive sampling can be applied. This method consists of a polymer sorbent phase, which quantifies the labile fraction of contaminants to estimate bioaccumulation and toxicity [25]. Therefore, Tenax® TA (further described as Tenax) and XAD-4 have been widely adopted to assess the bioavailable fraction of organic contaminants. Both materials function as infinite sinks, driving desorption of the rapidly desorbing fractions from soil into the aqueous phase, thereby mimicking the thermodynamic conditions of root-zone uptake [26]. Tenax and XAD-4 are non-polar, hydrophobic styrenedivinylbenzene copolymers, which have been most extensively validated for hydrophobic organic contaminants such as PAHs, PCBs, and organochlorine pesticides, where the rapidly desorbing fraction has shown strong correlations with biological accumulation [26,27]. Although both polymers are well studied on highly hydrophobic compounds, their suitability for more polar pesticides such as tricyclazole remains insufficiently characterized. In addition, rice grain samples from conventionally and organically managed fields in the same province were analyzed to assess the occurrence of both compounds in rice under field conditions. As a potential to mitigate pesticide bioavailability and plant uptake, biochar has been proposed as a low-cost soil amendment [28]. Maletić et al. (2022) [29] showed that biochar has decreased the bioaccessibility of organic contaminants. Despite the documented prevalence of isoprothiolane and tricyclazole in Vietnamese paddy soils and rice, systematic studies comparing the performance of Tenax and XAD-4 as bioavailability proxies for these two contrasting fungicides are lacking. Furthermore, the potential of low-dose biochar amendment (0.5% w/w) to reduce fungicide bioavailability in flooded paddy soils has not been evaluated for these compounds. In our study, we are (i) comparing Tenax and XAD-4 as passive sampling surrogates for isoprothiolane and tricyclazole bioavailability in Vietnamese paddy soil under controlled laboratory conditions, (ii) contextualizing polymer-based bioavailability estimates against fungicide residues analyzed in rice grain samples and (iii) evaluating the effect of biochar amendment on compound sorption and bioavailability.

2. Materials and Methods

In this study, we evaluated in a laboratory experiment the bioavailability of pesticides in paddy soils, both unamended and amended with biochar. Isoprothiolane and tricyclazole were chosen as model pollutants due to their frequent application in paddy rice farming systems across Vietnam and Southeast Asia. Information on the physicochemical characteristics of the pesticides can be found in Table 1. XAD-4 and Tenax were selected as extraction agents due to their different physicochemical properties (Table 2), allowing the potentially bioavailable fraction to be estimated under different sink strengths. The immobilization of isoprothiolane and tricyclazole in paddy rice soils was evaluated by applying biochar.

Table 1. Physicochemical properties of studied pesticides.

	Tricyclazole [1]	**Isoprothiolane** [1]
Pesticide category	Systemic fungicide	Systemic fungicide and insecticide
Common application/ pest controlled	Paddy rice/rice blast	Rice/rice blast, rice stem rot, fusarium leaf spot, planthoppers
Water solubility (20 °C, pH 7) mg L^{-1}	596	48.5
Soil adsorption coefficient K_{oc} L kg^{-1}	~376–1122 [2]	196–2300 [3]
n-octanol-water partition coefficient log K_{ow}	1.4	2.8
Half-life in soil DT_{50} av. days	130 (field)	78
GUS leaching potential index	3.89	1.64

[1] Source: PPDB (pesticide properties database) [10], last update tricyclazole: 20.05.2026, isoprothiolane: 10.05.2026). [2] [21]. [3] [24].

Table 2. Physicochemical characteristics of extraction agents (manufacturer data).

	Tenax	**XAD-4**
Size particle (mesh)	60–80	20–60
Density (g cm^{-3})	0.25	1.02
Pore volume (mL g^{-1})	2.4	0.98
Pore size (nm)	200	10
Surface area (m^2 g^{-1})	35	750

2.1. Chemicals

The following chemicals were used for the experiments: tricyclazole and isoprothiolane standards with a purity > 97% were purchased from LGC Standards (LGC Standards, Wesel, Germany), Tenax resins from (Sigma, Darmstadt, Germany), XAD-4 from (Sigma, Darmstadt, Germany), $CaCl_2$ (Merck, Darmstadt, Germany), K_2CO_3 (Merck, Darmstadt, Germany), and $HgCl_2$ (Thermo Fisher Scientific, Darmstadt, Germany). As $HgCl_2$ is highly toxic, it must be handled with appropriate protective measures, and all resulting wastes must be safely disposed of as hazardous waste according to institutional and national regulations. Organic solvents acetonitrile (CAS: 75-05-8) and water (CAS: 7732-18-5) for experiments, extractions, and analysis were of LC-MS grade and purchased from VWR, Darmstadt, Germany.

2.2. Pesticide Analysis

Standard pesticide solutions were prepared in H_2O:MeOH (3:1, *v*/*v*) and kept dark at −20 °C. Pesticide analyses were carried out on a Waters ACQUITY UPLC system (binary pump, autosampler) coupled to a Waters Xevo TQ-S triple quadrupole mass spectrometer (Waters Technologies Corp., Milford, MA, USA) driven in the positive electrospray ionization (ESI) mode. Sample injections were 10 µL and the chromatographic separation was achieved on a reversed-phase C-18 column (Nucleoshell RP18, Macherey-Nagel (100 mm × 4.6 mm, 2.7 µm)). The column oven temperature was 40 °C. Gradient elution was performed at a flow rate of 1.0 mL min^{-1}. Gradient conditions started at 30% mobile phase B and increased to 100% over 14 min, then returned to 30% at 14.1 min and held for 2 min. The total run time was 16 min with a post-run of 2 min, with 70% mobile phase A and 30% mobile phase B. For each pesticide, monitoring conditions were individually

optimized for the multiple reaction monitoring (MRM) mode, including the selection of precursor and product ions, collision energy, cone voltage, and retention time windows (for details see Table S1). Furthermore, the capillary voltage was set to 2.5 (ESI+), the gas flow to 1000 L h^{-1}, and desolvation temperature at 600 °C. Measurements affected by matrix effects, as indicated by unacceptable deviation between injection replicates, were excluded prior to data analysis.

2.3. Evaluation of the Sorption Performance of Extraction Agents

The extraction agent XAD-4 was purified by Soxhlet extraction with ultra-pure water; methanol; mixture of hexane/acetone 1:1; methanol and finally ultra-pure water as suggested in Spasojević et al. (2015) [27]. Each extraction step was carried out for 6 h. Tenax was directly used for extraction. Prior to the soil extraction experiments, the sorption performance of XAD-4 and Tenax toward the target pesticides was evaluated to verify their suitability as sink materials for the subsequent bioavailability assessment. The experiment was designed to confirm both that the extraction agents effectively sorb isoprothiolane and tricyclazole from the aqueous phase and that the amount of sorbent used provides sufficient capacity to avoid saturation under the experimental conditions. Ensuring efficient pesticide uptake and sufficient sorption capacity of the extraction agents is essential to maintain sink conditions during soil extraction and to avoid underestimating the fraction of pesticide released from the soil. For the evaluation of the maximum sorption capacity of the extraction agents, 0.2 g of the extraction agent was added to 40 mL water containing 200 and 2000 µg L^{-1} isoprothiolane and tricyclazole, respectively. These concentrations were selected based on soil residue data from Mekong Delta paddy fields, which consistently showed substantially higher tricyclazole than isoprothiolane concentrations [11]. Further, spiked concentrations were set above the expected range to account for the unknown background contamination of the soils used in the subsequent desorption experiment, thereby testing extraction agent capacity under conservative (worst-case) loading conditions. Then, samples were shaken vigorously at 20 °C. Separate samples were prepared for each time point and aqueous phase pesticide concentrations were analyzed after 1, 2, 4, 24, and 48 h contact time using LC-MS/MS. All experiments were conducted in triplicates. The fraction of pesticide remaining in the aqueous phase at each time point was calculated relative to the initial concentration at $t = 0$ h.

2.4. Paddy Soil Preparation

Background concentrations of 92.3 ± 3.8 µg kg^{-1} tricyclazole and 9.5 ± 0.4 µg kg^{-1} isoprothiolane were determined in the dried, sieved soil prior to spiking. For the biochar treatments, the dried soil was first amended with 0.5% (w/w) biochar and the unamended soil was treated identically without biochar addition. Biochar was also added to an unspiked control soil. Subsequently, unamended and biochar-amended soils were spiked with isoprothiolane and tricyclazole reaching a final concentration of 60 and 1300 µg kg^{-1} including background, respectively. To this end, the pesticides were dissolved in acetone and added to 7.5 g of silica sand, where the solvent was allowed to evaporate. Then, the sand was transferred to the soil and mixed with a rotary mixer for 24 h as suggested by Mukherjee et al. (2016) [30]. Deionized water was then added to adjust the gravimetric water content to 40% (based on dry soil mass), and the samples were aged for 100 days at 4 °C in the dark. The temperature was chosen to minimize pesticide degradation. After the aging period, the samples were dried again at 40 °C. The initial concentrations were verified by solvent extraction of 1 g soil with 10 mL acetonitrile–water (4:1, v/v), shaking for 2 h at 150 rpm, centrifugation at 19,000 RCF for 2 min, and LC-MS/MS analysis of the

supernatant, which confirmed the nominal concentrations and no losses were observed during aging [30].

2.5. Physical and Chemical Characteristics of the Paddy Soil and Biochar

For this study, a paddy soil sample was collected in Vĩnh Long province, Vietnam (10°01′47″ N, 106°11′00″ E) from topsoil (0 to 15 cm) using a stainless-steel auger. The field was used as a rice monoculture and farmed conventionally with two cropping cycles per year. After sampling, the soil was dried at 40 °C, then ground and sieved at <2 mm. The soil's pH was determined in a 0.1 M $CaCl_2$ solution and was 3.8 (22.8 °C). Total organic carbon (TOC) was determined with a soli TOC cube (Elementar Analysensysteme GmbH, Langenselbold, Germany) using the temperature ramp method according to DIN EN 17505:2024-04 [31]. The TOC of the paddy soil was 4.16%. Soil texture was analyzed in the laboratory according to DIN ISO 11277 (2002) [32] by wet sieving and sedimentation using the PARIO (Meter, Munich, Germany) system. Prior, organic carbon was destroyed by boiling the sample with H_2O_2. Note, that the sand fraction was determined at 63 µm according to WRB [33]. Note the soil fractions of sand (2000–63 µm), silt (63–2 µm), and clay (<2 µm) content of 0.85, 46.6, and 52.6%, respectively The high organic carbon content indicates a strong potential for pesticide sorption, while the predominantly fine-grained nature of the sediment (>99% of particles <63 µm) may further contribute to pesticide retention by providing a large specific surface area and additional sorption sites.

The biochar used in this study was produced from *Miscanthus* feedstock through slow pyrolysis at 600 °C at the Technical University Aachen (RWTH), Germany. The total organic carbon content of the biochar was 76.8% and had a pH of 9.5. More details on the biochar used can be found in Tenodi et al. (2026) [34], Gross et al. (2026) [35], and Table S2.

2.6. Sorption Experiment from Paddy Soils

The method to estimate the bioavailability of the pesticides followed the procedure described by Beljin et al. 2025 [36], whereby a multistep extraction over 192 h at intervals of 2, 4, 6, 24, 48, 96, and 192 h was performed. For the assessment of the bioavailability 1 g of biochar-amended or unamended soil, each spiked and unspiked (control) was placed in a 40 mL amber glass vial. For each sampling time, individual vials were prepared in triplicates yielding 21 vials (7 sampling times with 3 replicates) for each pesticide soil or soil/biochar-amendment, respectively. To prevent microbiological degradation of the fungicides during the experiment, 1 mL $HgCl_2$ (300 mg L^{-1}) was added to the soil and mixed with 20 mL of 50 mM $CaCl_2$ solution (see Section 2.1 for safe handling and disposal of $HgCl_2$). Vials were shaken horizontally at 150 rpm min^{-1}, and samples were collected at the predefined contact times listed above. To assess isoprothiolane and tricyclazole in each of the three fractions (liquid, soil, extraction agents), the fractions were first separated through centrifugation at 3270 RCF for 5 min. Then, the extraction agents floating on top were picked-up with a spatula and transferred into a new vial for extraction. An aliquot of the water phase was taken and directly injected into the LC-MS/MS. The pesticides sorbed on the soil fraction and the extraction agents (Tenax and XAD-4) were extracted as prior described and then analyzed using LC-MS/MS. The following Equation (1) describes the distribution of pesticide residues among the soil fractions at a given sampling time.

$$F(t) = \frac{S_t}{S_0} = \frac{c_t}{c_0} \quad (1)$$

where S_t and S_0 (ng g^{-1}) represent the amount of isoprothiolane or tricyclazole in the soil at time t (h) and at $t = 0$, c_t is the pesticide concentration measured in the soil at time t and c_0 is the initial soil concentration, calculated as the sum of the spiked and the background concentration. $F(t)$ is dimensionless but values in the text are given in % ($F(t) \times 100$). The

potentially bioavailable fraction at time t was operationally defined as the proportion of pesticide no longer detected in the soil, $1 - F(t)$. This definition assumes that residues leaving the soil phase were transferred to either the aqueous and/or the extraction agent (Tenax/XAD-4) fraction, which expected to act as an infinite sink. This assumption is supported by mass balance data from the biochar-amended XAD-4 experiment, in which all three fractions (soil, water, extraction agent) were successfully quantified. Their sum approximated 100% without an apparent systematic trend, suggesting that losses due to degradation or other processes were of minor relevance within the studied timeframe. Pairwise comparisons of the pesticide fractions desorbed from soil were conducted separately for each compound using Welch's t-test (function t.test(); $n = 3$ independent vials per group; $\alpha = 0.05$), with p-values adjusted according to Benjamini–Hochberg (BH). Tenax and XAD-4 were compared at $t = 192$ h (BH correction over 2 comparisons), and biochar-amended and unamended soil (both with XAD-4) were compared at $t = 2$, 48 and 96 h (BH correction over 6 comparisons).

2.7. Desorption Kinetics and Statistical Analysis

To describe the desorption of isoprothiolane and tricyclazole in paddy soils from the partial extraction, a two-compartment kinetic model according to Cornelissen et al. (1997) [37] was fitted to $F(t)$:

$$F(t) = \frac{S_t}{S_0} = F_{fast} \times e^{-k_{fast} \times t} + F_{slow+very\ slow} \times e^{-k_{slow+veryslow} \times t} \quad (2)$$

where F_{fast} and $F_{slow+veryslow}$ (dimensionless, 0–1) are the fast and slow-desorbing fractions and k_{fast} and $k_{slow+veryslow}$ (h^{-1}) the corresponding first-order rate constants. Data processing was performed in RStudio (R version 4.4.0).

Three independent replicates were destructively sampled at each timepoint. As each sample represents a separate vessel, desorption curves can only be randomly assigned. Therefore, the two-compartment model (Equation (2)) was fitted to the pooled measurements of all replicates of each treatment. For isoprothiolane $n = 2$, samples had concentrations below the limit of quantification (LOQ) and were substituted by LOQ where included in the model fits (tricyclazole: LOQ = 2.1 ng g^{-1} (i.e., 0.2% of initial concentration); isoprothiolane: LOQ = 2.6 ng g^{-1} (i.e., 4.3% of initial concentration)). Some Tenax extracts yielded unstable technical replicates, likely due to matrix effects. Owing to these analytical challenges, a wider acceptance criterion was applied, and data points were excluded when technical replicates exceeded an RSD of 30% and re-analysis was not possible. For the retained data, RSD was typically below 5%. As exclusion was based on replicate agreement rather than on the measured concentration, and excluded data points occurred at both low and high concentrations, missing values were assumed to occur at random. In total, 15 and 17 out of 21 data points could be used for kinetic modeling for isoprothiolane and tricyclazole, respectively. Kinetic model fits were based on measured data only. For the following analysis, a synthetic data point at $t = 0$ ($F(t) = 1$) was not included, as the model equation yields $F(0) = 1$ for any parameter set. The model was fitted with and without this data point and yielded identical parameter estimates (Table S3). The samples for the biochar-amended experiment were collected at the same time points as in the unamended experiments, but only up to 96 h. To ensure comparability between the experiments, data from the hours of 2–96 h were used for the following analysis and discussion. However, because a longer experimental duration can increase the certainty of information about the slow desorption process [38], the model was also fitted for the time range 0–192 h for unamended soil experiments and can be found in Table S3.

Non-linear least-squares fitting was performed with the nls() function (port algorithm) with the bounds $0 \leq F_{fast} \leq 1$, $0 \leq k_{fast} \leq 50\ h^{-1}$ and $0 \leq k_{slow+veryslow} \leq 1\ h^{-1}$. Fits were started

from 96 combinations of start values, and the solution with the lowest residual sum of squares (RSS) was retained, requiring $k_{fast} \geq k_{slow+veryslow}$.

To assess the identifiability of k_{fast}, RSS profiles were used [39]. Therefore, k_{fast} was fixed at 40 different log-spaced values starting from 0.05 up to 50 h^{-1}. The remaining parameters (F_{fast} and $k_{slow+veryslow}$) were then re-estimated. Values of k_{fast} were considered compatible with the data if RSS $\leq$ RSS_min $\cdot$ [1 + F_0.95(1, n − p)/(n − p)], with n the number of measured data points and $p = 3$ the number of model parameters. This corresponds to the RSS-based confidence criterion described by Baty et al. (2015) [40], applied to a single profiled parameter. In cases, where the compatible range extended to the upper bound, only a lower bound of k_{fast} is reported (Figure S1 and Table S4).

As initial pesticide compounds differ, isoprothiolane and tricyclazole were not compared with each other. To enable comparisons within compounds, the model was kept uniformly within each compound. For isoprothiolane, k_{fast} was identifiable in biochar-amended soil and a fixed k_{fast} was not compatible with these data. Therefore, all parameters were estimated across isoprothiolane experiments. For tricyclazole, k_{fast} was not identifiable in any treatment and the fit with all parameters estimated did not converge for unamended soil with XAD-4. Therefore, k_{fast} was fixed at 10 h^{-1} for all tricyclazole experiments, which was compatible with the RSS profiles of all treatments. F_{fast} and $k_{slow+veryslow}$ were identical for k_{fast} = 5, 10 and 50 h^{-1} (Table S5).

Parameter uncertainty was estimated using a residual bootstrap method (999 iterations). For this, the residuals of the pooled data points were centered. New synthetic datasets were generated by resampling residuals with replacement and adding to the modeled data points. The model was refitted for each synthetic dataset. Following, 95% confidence intervals were derived as percentiles of the bootstrap estimates. Non-converged iterations were discarded but at least 90% of the iterations had to converge. The pooled residual bootstrap assumes constant variance across sampling times. Given the small number of replicates per sampling time ($n = 3$), the confidence intervals in should be regarded as approximate. Goodness of fit is given as root-mean-square error (RMSE) of the measured data points, and residuals were inspected graphically.

Differences between treatments (biochar vs. control and Tenax vs. XAD-4, each within compound) were assessed for F_{fast} and $k_{slow+veryslow}$ from independent bootstrap distributions of both treatments (4999 iterations each). $F_{slow+veryslow}$ ($=1 - F_{fast}$) was not tested separately, and k_{fast} was not tested because it was not identifiable for most treatments. For the resulting 8 tests, Bonferroni-adjusted confidence intervals of the differences (99.375%) were calculated. Differences were considered significant if this interval excluded zero. Bonferroni adjustment was used because inference was based on confidence intervals, whereas the Benjamini–Hochberg procedure applied to the Welch's *t*-tests (Section 2.6) requires *p*-values.

The R code for the kinetic analysis was revised with the assistance of generative AI tools (Claude Opus 5.5, Anthropic, San Francisco, CA, USA). The revised code was reviewed by the authors, and the results were verified for plausibility, including consistency checks between fitting approaches, time windows and RSS profiles.

2.8. Pesticide Extraction from Rice Grain

Rice grain samples were obtained from experimental fields located near the field where the soil samples were taken. Until November 2023, these fields had been managed conventionally, including the application of pesticides. In November 2023, they were converted to organic management, and no pesticides were applied thereafter. Rice was cultivated under transitioning management for three consecutive cropping seasons, and grain from the third season was harvested and analyzed in November 2024. The experimental fields directly border conventionally managed rice fields and share the same irrigation system.

In addition, rice grain was sampled from a neighboring conventionally managed field. This field was managed by local farmers and was not part of the experimental design; therefore, no information on the type, amount, or timing of pesticide applications was available. After harvest, the rice was threshed and dehulled to obtain unpolished rice. Seven samples each from conventionally and organically (under transition) managed fields were analyzed as unpolished rice ($n = 14$). Of these, three samples per management system were additionally polished and analyzed as polished rice ($n = 6$), resulting in a total of 20 analyzed rice samples. For pesticide extraction, a modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction method based on AOAC 2007.01 and DIN EN 15662:2018 was used [41,42]. Firstly, 5 g milled rice sample was hydrated with 10 mL of water for 30 min. Afterwards, 10 mL of acetonitrile and QuEChERS salts (6 g MgSO4 + 1.5 g NaOAC) kit (QuEChERS extraction kit, Thermo Fischer, Darmstadt, Germany) were added to the hydrated sample and subsequently shaken vigorously for 1 min. For purification, 1 mL of supernatant was transferred to a 2 mL tube with 50 mg PSA + 150 mg $MgSO_4$ mixture (QuEChERS dispersive SPE, Thermo Fischer, Darmstadt, Germany). Then, the sample was shaken for 30 s, followed by centrifugation at 1500× *g* for 1 min. The sample was then analyzed for isoprothiolane and tricyclazole by LC-MS/MS (LOQ and Recovery of pesticides from rice extraction see Table S6 and analytical parameters see Table S1).

3. Results and Discussion

3.1. Sorption Capacity of Tenax and XAD-4

In order to confirm the ability of Tenax and XAD-4 acting as infinite sinks for isoprothiolane and tricyclazole, the sorption capacity of both extraction agents was evaluated in a matrix-free control experiment for 48 h (Figure 1).

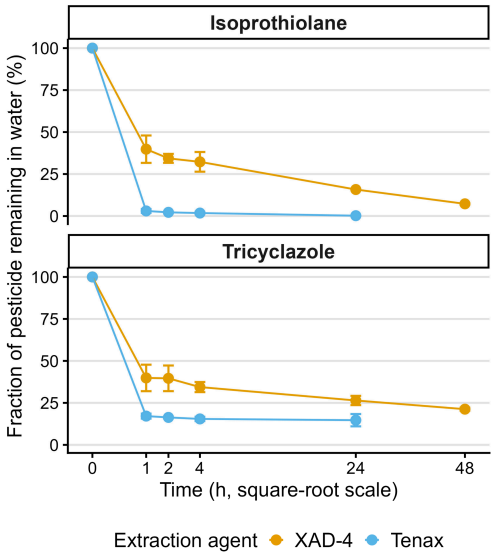


Figure 1. Fraction of isoprothiolane and tricyclazole remaining in the aqueous phase (%) over time during matrix-free sorption capacity experiments with XAD-4 and Tenax extraction agents. Compounds were tested over a contact time of 24 h (Tenax) and 48 h (XAD-4) after contact times of 0, 1, 2, 4, 24, and 48 h. Data points represent mean values of triplicate measurements; error bars indicate standard deviation.

For isoprothiolane, Tenax showed fast and near-complete sorption, with 3.0 ± 1.2% of the pesticide remaining in the water phase after 1 h and below LOQ after 24 h contact time. In contrast, XAD-4 showed a more gradual but continuous decrease in pesticide concentrations in the water, reaching 15.8 ± 0.01% after 24 h and 7.3 ± 0.5% after 48 h

contact time. For tricyclazole, both extraction agents showed fast initial sorption within the first hour, followed by a plateau at approximately 15% for Tenax extraction, while XAD-4 showed a more continuous decrease throughout the experiment reaching 21.3 ± 0.9% after 48 h. In the matrix-free test, pesticide uptake was higher for Tenax than for XAD-4 for both compounds, with Tenax removing nearly all isoprothiolane and approximately 85% of tricyclazole from the aqueous phase, compared to approximately 93% and 79% for XAD-4, respectively.

The results confirm that both XAD-4 and Tenax can act as an effective sorption sinks for isoprothiolane and tricyclazole extraction from aqueous phase, supporting their applicability for the subsequent desorption experiment from the spiked soils. Because tricyclazole was tested at a tenfold higher initial concentration than isoprothiolane (2000 vs. 200 $\mu g\ L^{-1}$), it is not possible to disentangle from the present data whether the residual aqueous fraction of tricyclazole reflects its lower sorbent affinity, consistent with its higher polarity compared to isoprothiolane, or a capacity limitation of the sorbent at this loading level. Distinguishing between these two mechanisms would require testing tricyclazole at the same initial concentration as isoprothiolane, or across a range of concentrations, and is recommended for future work. Notably, in the subsequent soil experiment (60 $\mu g\ kg^{-1}$ isoprothiolane, 1300 $\mu g\ kg^{-1}$ tricyclazole; 1 g soil in 20 mL $CaCl_2$ solution), even assuming 100% desorption into the aqueous phase, the maximum concentrations would reach approximately 3 $\mu g\ L^{-1}$ for isoprothiolane and 65 $\mu g\ L^{-1}$ for tricyclazole. Both concentrations would substantially be below the concentrations used in the capacity test. The extraction agent capacity was therefore evaluated under considerably higher pesticide loading than expected in the soil desorption experiment, supporting the suitability of the selected extraction agent amount, as further confirmed by the results presented in Section 3.2 and confirms that Tenax and XAD-4 are suitable extraction agents.

3.2. General Shape of Desorption Curve of Isoprothiolane and Tricyclazole

The two extraction agents Tenax and XAD-4 were used to assess the total amount of desorbed isoprothiolane and tricyclazole to further investigate the bioavailability. Figure 2 shows the desorption of isoprothiolane and tricyclazole over the timespan of 192 h at seven sampling points (2, 4, 6, 24, 48, 96, and 192 h contact time).

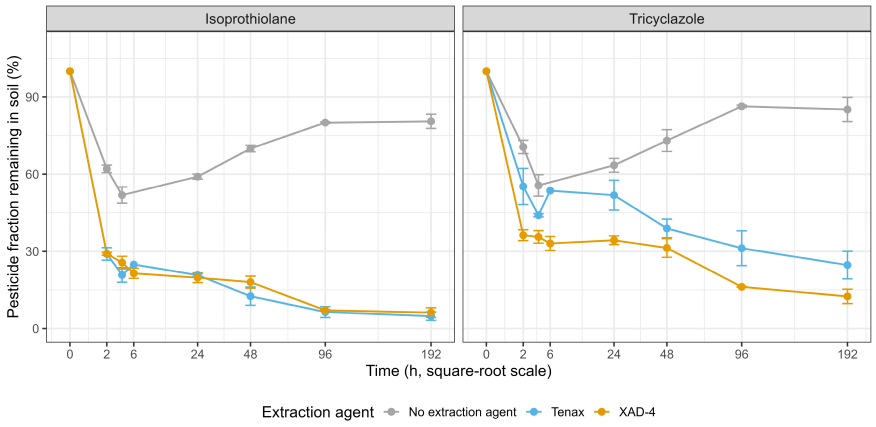


Figure 2. Desorption of isoprothiolane and tricyclazole from the paddy soil over the course of 192 h contact time without extraction agents and using XAD-4 and Tenax as extraction agents. Concentrations remaining in the soil were normalized to initial pesticide concentrations at time zero ($t = 0$) and expressed in %. Shown are the mean values for the triplicates and error bars indicate the standard deviation. The pesticide fraction in the soil without extraction agents reflects the approach to sorption equilibrium between soil and water, stabilizing after approximately 96 h. The additional decrease in the presence of XAD-4 and Tenax reflects the enhanced desorption induced by the extraction agents.

The results show that the pesticide fraction sorbed to the soil decreases over time for both systems where extraction agent (XAD-4 or Tenax) was added, whereby desorption followed an exponential pattern with fast desorption and a levelling out after 96 h. For both pesticides and extraction agents, the fast desorption phase occurred within the first 2 h. The experiment without added extraction agent showed an initial decrease in the sorbed fraction to 52 and 56% of isoprothiolane and tricyclazole, respectively, at 4 h, followed by a partial increase, indicating that sorption equilibrium between soil and water was not fully reached before approximately 96 h, after which the sorbed fraction stabilized at 80 to 85% for isoprothiolane and tricyclazole, respectively. As the soil was dried prior the experiment, the addition of water in the experiment represented a rewetting of the dried soil. The initial decrease in the sorbed fraction in the control without extraction agents may therefore be attributed to this rewetting of the dried soil, which can release dissolved organic carbon (DOC) together with associated pesticide residues into the aqueous phase [43]. This may be relevant for the studied paddy fields, which remain dry after harvest and are reflooded at the beginning of the next cropping season, as this rewetting could remobilize pesticide residues under field conditions, especially shortly after reflooding. A direct comparison between the two compounds is limited, as initial soil concentrations of isoprothiolane and tricyclazole were different (60 and 1300 µg kg^{-1}, respectively). At the higher loading, high-affinity sorption sites may have been saturated to a larger extent, which can affect the partitioning between fast- and slow-desorbing fractions. Differences between the two compounds were therefore not evaluated statistically and are not interpreted in terms of compound properties. For both compounds, the fraction remaining in the soil decreased only continuously in the presence of an extraction agent. For tricyclazole, a difference of the fraction removed from the soil was observed between the two extraction agents, with lower pesticide desorption with Tenax than with XAD-4, whereas for isoprothiolane, Tenax and XAD-4 yielded nearly identical results. The fraction of pesticides desorbed from the soil at the end of the experiment (t = 192 h), was 87.6 ± 4.8 and 75.3 ± 9.3% for tricyclazole (with XAD-4 and Tenax extraction, respectively), and 94.5 ± 4 and 95.2 ± 2.8% for isoprothiolane (with XAD-4 and Tenax extraction, respectively). Although the in soil remaining fractions of tricyclazole were approximately two-fold higher after Tenax extraction compared to XAD-4 extraction, no statistical difference was detected between the two extraction agent types for either tricyclazole (Welch t-test, p = 0.275, Table S7) or isoprothiolane (Welch t-test, p = 0.609, Table S7), likely reflecting the limited statistical power at n = 3 per group. Further fluctuations in the isoprothiolane and tricyclazole fraction sorbed to the soil were observed for contact time from 2 to 6 h in the Tenax treatment. However, the results of the sorption capacity test for the extraction agents without soil confirmed monotonic dissipation of both pesticides for Tenax extraction. We suggest that these fluctuations reflect the transient soil–water dynamics observed in the experiment without extraction agent, where the rewetting of the dried soil at the start of the experiment led to a minimum of the sorbed fraction at 4 h, followed by a subsequent increase. As Tenax represents a weaker sink for the more polar pesticides, these dynamics may have been less effectively buffered than with XAD-4. In addition, competition of DOC for the limited surface area of Tenax (35 m^2/g vs. 750 m^2/g for XAD-4, Table 2) cannot be excluded. Overall, the fractions removed from the soil by Tenax appear to be affected by compound polarity. Tricyclazole desorption from soil tended to be especially lower for Tenax than for XAD-4 (75.3 ± 9.3 vs. 87.6 ± 4.8%), which may be explained by the low affinity for polar compounds of Tenax. For this, ISO 16751:2020 specifies Tenax applicability for nonpolar compounds with log $K_{ow} > 3$ and aqueous solubility < 100 mg L^{-1} [44], while tricyclazole with a log K_{ow} of 1.4 and a solubility of 596 mg L^{-1}, is rather a polar compound, and does not meet the criteria of ISO 16751:2020 [10,44]. In contrast, isoprothiolane (log K_{ow} = 2.8; solubility = 48.5 mg L^{-1})

is closer to the ISO 16751:2020 criteria [44], although its log K_{ow} remains slightly below 3. This is consistent with the nearly identical results obtained with Tenax and XAD-4 for this compound. Although XAD-4 is also a hydrophobic polymer which is expected to have a weaker affinity to polar compounds, we suggest that XAD-4 can compensate through its much larger surface area (Table 2).

3.3. Desorption Kinetic Modelling

The desorption of pesticides from soils is generally kinetically controlled by either the release from sorption sites or diffusion through the soil matrix into the liquid phase [45]. Thereby, the soil characteristics such as TOC and clay content play a dominant role in this process. On the other hand, the physicochemical properties of the pesticides such as water solubility and hydrophobicity can limit or facilitate desorption [27,46].

To describe the desorption behavior of isoprothiolane and tricyclazole, the two-compartment model [37] was used, which describes this behavior by dividing the soil-sorbed pesticides into a fast-desorbing fraction (F_{fast}) that desorbs rapidly with a fast rate constant (k_{fast}), and a slowly desorbing fraction ($F_{slow+veryslow}$) with a slow rate constant ($k_{slow+veryslow}$), where $F_{fast} + F_{slow+veryslow} = 1$ (Equation (2)). The rate constants k_{fast} and $k_{slow+veryslow}$ (h^{-1}) characterize the speed of desorption from each compartment, with higher values indicating faster desorption. The two-compartment model was fitted to the pooled replicates of each treatment for the period 2–96 h (Figure 3).

Deviations between model and measured data were small for isoprothiolane and for tricyclazole with XAD-4 (RMSE = 0.031–0.043, Table 3), and larger for tricyclazole with Tenax (RMSE = 0.082) and in biochar-amended soil (RMSE = 0.099). In these two treatments, the residuals mainly reflected variability between replicates at the same sampling time (Figure S2). For all treatments except isoprothiolane in biochar-amended soil, the fast-desorbing fraction had fully desorbed before the first sampling time at 2 h (Figure 3). Consequently, k_{fast} could not be determined for these treatments, and only lower bounds (0.3–1.2 h^{-1}) are given (Table 3). Extending the observation period to 192 h (XAD-4 and Tenax treatments) hardly affected F_{fast} (difference $\leq$ 0.011), whereas $k_{slow+veryslow}$ was 8–20% lower, albeit within the confidence intervals (Table S3). In the following, kinetic parameters are discussed for the unamended treatments, results for biochar-amended soils are addressed in Section 3.5.

The fast-desorbing fraction (F_{fast}), shown in Table 3, for isoprothiolane was comparable between both extraction agents (XAD-4: 0.748 [0.722–0.775]; Tenax: 0.755 [0.717–0.804]), and the difference was not significant (0.007 [−0.061; 0.082], Bonferroni-adjusted 95% CI, Table S8). The slow desorption rate constants ($k_{slow+veryslow}$, XAD-4: 0.0104 [0.0067–0.0137] h^{-1}; Tenax: 0.0129 [0.0070–0.0191] h^{-1}) did not significantly differ either (0.002 [−0.007–0.013], Bonferroni-adjusted 95% CI, Table S8). For both extraction agents, the fast-desorbing fraction had largely desorbed before the first sampling time, so that only a lower bound of k_{fast} (>1.0 h^{-1}) can be given. The model was nevertheless fitted with all parameters estimated for isoprothiolane, as k_{fast} was identifiable for isoprothiolane in biochar-amended soil and the model was kept uniform within each compound. The uncertainty in k_{fast} did not affect F_{fast} and $k_{slow+veryslow}$ beyond their reported confidence intervals (Table S5). Samples analyzed from the Tenax extraction experiments were affected by matrix effects, resulting in an insufficient number of usable data points (n = 12 out of 18), which is also reflected in wider confidence intervals (Figure 3). Overall, XAD-4 and Tenax yielded consistent desorption parameters for isoprothiolane.

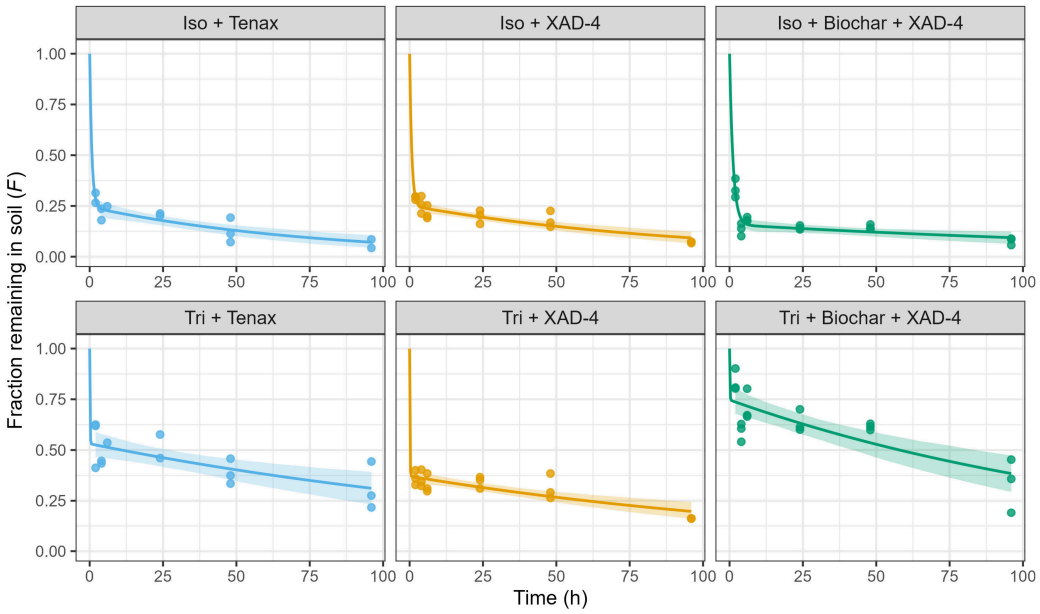


Figure 3. Desorption kinetics of tricyclazole (Tri) and isoprothiolane (Iso) in unamended paddy soil with Tenax or XAD-4 as extraction agent and biochar-amended paddy soil with XAD-4 extraction agent. Points show the measured pesticide fraction remaining in the soil (F) at six time points (t = 2, 4, 6, 24, 48, and 96 h). Lines show the two-compartment model [36] fitted to the pooled replicates (2–96 h). Curves are shown from $t = 0$ for illustration ($F(0) = 1$ by definition of the model), but the curve shape for t < 2 h is not constrained by experimental data. For Tri, k_{fast} was fixed at 10 h^{-1}, as it was not identifiable from the data, while for Iso, all parameters were estimated. Shaded areas show the pointwise 95% bootstrap confidence band of the fitted curve from the first sampling time (2 h) onwards. The confidence band reflects the uncertainty of the fitted mean curve rather than the spread of individual measurements.

Table 3. Kinetic parameters of the two compartments desorption model [37] for isoprothiolane and tricyclazole in unamended paddy soil with Tenax or XAD-4 as extraction agent and biochar-amended paddy soil with XAD-4. The model was fitted to the pooled replicates of each treatment (measured data, 2–96 h), whereas n denotes the number of analyzed and fitted data points. Values are given as point estimate [95% confidence interval (CI)], obtained by residual bootstrap (999 iterations). $F_{slow+veryslow} = 1 - F_{fast}$. RMSE: root-mean-square error of the measured data points (fraction of initial concentration). Biochar: +, with biochar amendment; −, without biochar amendment.

Compound	Extraction Agent	Biochar	Model Fit	n	F_{fast} [95% CI]	k_{fast} (h^{-1}) [95% CI]	$k_{slow+veryslow}$ (h^{-1}) [95% CI]	RMSE
Iso	XAD-4	−	all parameters estimated	18	0.748 [0.722–0.775]	>1.0 [b]	0.0104 [0.0067–0.0137]	0.031
Iso	Tenax	−	all parameters estimated	12	0.755 [0.717–0.804]	>1.0 [b]	0.0129 [0.0070–0.0191]	0.035
Iso	XAD-4	+	all parameters estimated	18	0.841 [0.810–0.872]	0.83 [0.71–1.03]	0.0055 [0.0012–0.0115]	0.034
Tri	XAD-4	−	k_{fast} fixed [a]	18	0.629 [0.597–0.656]	>1.2 [b]	0.0066 [0.0041–0.0091]	0.043
Tri	Tenax	−	k_{fast} fixed [a]	14	0.469 [0.403–0.526]	>0.6 [b]	0.0056 [0.0027–0.0091]	0.082
Tri	XAD-4	+	k_{fast} fixed [a]	18	0.253 [0.190–0.322]	>0.3 [b]	0.0069 [0.0043–0.0102]	0.099

[a] k_{fast} fixed at 10 h^{-1} (not identifiable; results identical for 5–50 h^{-1}, Table S5). [b] lower bound from RSS profile (Figure S1); upper bound not constrained by data.

With Tenax extraction of tricyclazole, the model parameters for F_{fast} were significantly lower than with XAD-4 (0.469 [0.403–0.526] vs. 0.629 [0.597–0.656], Table 3; difference −0.160 [−0.257; −0.065], Bonferroni-adjusted 95% CI; Table S8). In contrast, $k_{slow+veryslow}$ did not differ significantly between the two extraction agents (Tenax: 0.0055 [0.0027–0.0090] h^{-1}; XAD-4: 0.0066 [0.0041–0.0090] h^{-1}; Table S8). The Tenax data also showed a larger variability between replicates at the same sampling time (RMSE = 0.082 vs. 0.043 for XAD-4; Figure S2). Due to matrix effects during sample analysis, only 14 of 18 data points were available for Tenax extraction. As for isoprothiolane, the fast-desorbing fraction of tricyclazole had largely desorbed before the first sampling time with both extraction agents (Figure 3), so that k_{fast} could not be determined and was fixed for the model fit (lower bounds > 0.6 and >1.2 h^{-1} for Tenax and XAD-4, respectively). As k_{fast} could not be determined, F_{fast} for tricyclazole with Tenax may be underestimated. Across the range of k_{fast} compatible with the data, F_{fast} reached up to 0.55 (Table S4), which is still below the lower confidence limit for XAD-4. Although Tenax sorbed tricyclazole as effectively as XAD-4 under matrix-free conditions, the significantly lower F_{fast} obtained with Tenax in soil suggests that its limited affinity for polar compounds reduced its effectiveness as a sink in competition with the strongly sorbing soil matrix, rather than its sorption capacity. This is consistent with ISO 16751:2020 [44], which restricts the applicability of Tenax to compounds with log K_{ow} > 3 and aqueous solubility < 100 mg L^{-1}, criteria that tricyclazole does not meet (log K_{ow} 1.4; 596 mg L^{-1}; Table 1).

Overall, the kinetic parameters show, that the fast-desorbing fraction of isoprothiolane and tricyclazole are rapidly released upon contact with the extraction agent, indicating a readily bioavailable pool that could be quickly taken up by soil organisms, roots, or lost via leaching [47]. In unamended soil with XAD-4, a slow-desorbing fraction ($F_{slow+veryslow}$) of 0.371 [0.344–0.403] was obtained for tricyclazole and 0.252 [0.225–0.278] for isoprothiolane, indicating that a considerable proportion of both compounds remained strongly sorbed and is therefore less bioavailable. A direct comparison between the two compounds is, however, limited by the different spike concentrations, as saturation of high-affinity sorption sites at the higher loading may have affected the partitioning between the fast- and slow-desorbing fractions, and the different fitting approaches (Section 2.4 and Table 3). The high fast-desorbing fractions (F_{fast}) for both compounds with XAD-4 (0.748 and 0.629 for isoprothiolane and tricyclazole, respectively; Table 3) are particularly interesting given the clay-rich nature and high TOC of the paddy soil used (52.6% clay, 99.2% clay and fine silt, high TOC of 4.16%). Clay minerals typically provide abundant sorption sites and create tortuous diffusion pathways that should restrict pesticide desorption [27], primarily through a range of mechanisms, including electrostatic interactions, hydrogen bonding, surface complexation, and hydrophobic association [48]. Based on these soil properties, strong sorption and correspondingly limited desorption, a low potentially bioavailable fraction therefore would be expected. However, isoprothiolane (diisopropyl 1,3-dithiolan-2-ylidenemalonate) contains only ester and thioether groups, which do not dissociate in the environmentally relevant pH range. It therefore remains in its neutral form at the soil pH of this study. Tricyclazole is a weak base (pKa = 1.6 [49]) and is therefore also predominantly present in its neutral form in solution at the soil pH of this study (pH 3.8). For neutral organic compounds in wet soils, sorption occurs mainly by partitioning into soil organic matter, whereas clay surfaces are of minor importance as they preferentially interact with water [50]; accordingly, non-ionic pesticides were reported to sorb only to external clay surfaces, as the hydrated interlayers are not accessible [51]. This limits the potential for strong binding to clay surfaces and favoring weak, reversible interactions and is consistent with the high fast-desorbing fractions observed [52]. In addition, the high F_{fast} values may partly reflect the aging conditions. The spiked soil was aged for 100 days at 4 °C

to minimize degradation, whereas field residues in Mekong Delta paddy soils age at higher temperatures under alternating flooded and dry conditions and over longer periods. As the slowly desorbing fraction increases with contact time [37] and slow desorption is strongly temperature dependent [53], sequestration into less accessible domains was probably less advanced in our experiment than in field-aged residues. The F_{fast} values determined here are therefore likely to overestimate the fast-desorbing fraction of field-aged residues.

Nevertheless, a considerable fraction of tricyclazole desorbed only slowly ($F_{slow+veryslow}$ = 0.371 [0.344–0.403] with XAD-4), consistent with reported K_{oc} values of 376–1122 mL g^{-1} for tricyclazole in rice-growing region soils [21]. As sorption of neutral organic compounds to soil organic matter by hydrophobic partitioning increases with log K_{ow} [50], the comparatively low log K_{ow} of tricyclazole (1.4 [10]) suggests that these K_{oc} values cannot be explained by hydrophobic partitioning alone. Weber (1982) [49] found that the sorption of tricyclazole to soil organic matter and soil increased with decreasing pH, and postulated that part of the sorbed tricyclazole was bound ionically, i.e., as the protonated species via cation exchange or by association with H^+ at the surface of organic matter, and was therefore less readily desorbed by water. Weber (1982) [49] further suggested that protonation at clay surfaces may exceed that expected from the pH of the bulk solution. In addition, the planar, fully aromatic structure of tricyclazole [51,54], may enable interactions of its π-electron system and the lone electron pairs of the sulfur atom with clay surfaces [51]. Such mechanisms could explain the slowly desorbing fraction of tricyclazole at the acidic pH of the studied soil, although they were not directly assessed in this study. A direct comparison with isoprothiolane is limited by the different spike concentrations.

3.4. Implications for Pesticide Bioavailability and Rice Grain Residues in the Mekong Delta

The paddy soil used in this study was collected from Vĩnh Long province in the Mekong Delta, where isoprothiolane and tricyclazole are among the most frequently detected pesticides in paddy soils and surface waters [11]. In our study, the rapidly desorbing fraction of both compounds was relatively high with F_{fast} values of 0.748 [0.722–0.775] and 0.629 [0.597–0.656] for isoprothiolane and tricyclazole, respectively (XAD-4; Table 3). Such rapidly desorbing fractions have been shown to correlate with groundwater leaching and bioavailability to aquatic organisms [55,56]. This suggests that a large share of both compounds could be readily released into the soil solution, where it may become available for transport and potentially for root uptake. However, F_{fast} was determined under laboratory conditions on spiked soil after 100 days of aging, and its transferability to field-aged residues remains uncertain. Residues of isoprothiolane were also detected in polished and unpolished rice grain samples from conventionally and organically (under transition) managed fields in the same province (20 samples, Table S9). In conventionally grown samples, isoprothiolane concentrations where in the range of 0.48–2.42 mg kg^{-1} in unpolished samples (n = 7), with approximately 70% lower concentrations in polished samples. All values were below the EU maximum residue limit (6 mg kg^{-1} rice [15]). In organically grown unpolished samples, isoprothiolane concentrations (n = 7) were approximately 15-fold lower than in conventionally grown samples. Tricyclazole was below LOQ in organically grown rice, while in conventionally grown rice, five of seven unpolished samples exceeded the EU maximum residue limit (0.01 mg kg^{-1}, [17]), with concentrations of 0.013 to 0.028 mg kg^{-1}. These findings demonstrate that both compounds reach the rice grain under field conditions. However, the grain samples were not collected from the same field as the soil used in this study. They therefore indicate the occurrence of both compounds in rice, but do not allow a quantitative link to the F_{fast} values determined here. While isoprothiolane and tricyclazole are not applied on the organically managed fields, their detected concentration may originate from either residual concentrations accumulated

in the soil prior to the transition (since November 2023), or through cross-contamination via spray drift or shared irrigation water from neighboring conventionally managed fields as pointed out by Klamann et al. (2026) [11]. Overall, paired measurements of soil residues, desorbable fractions, and grain concentrations at the plot scale would be required to assess whether F_{fast} can serve as an indicator of pesticide uptake in paddy soil–rice systems.

3.5. Reduction of Pesticide Bioavailability Through Biochar Treatment

Biochar was added, to assess the possibility to reduce bioavailability of isoprothiolane and tricyclazole in paddy soil. Pesticide immobilization efficiency was assessed through multistep desorption with XAD-4 resin, which was suitable to be used for both isoprothiolane and tricyclazole. In different studies, biochar has shown a strong potential in reducing contaminant desorption in sediments but also in improving soil health and increasing soil pH in field trials, as well as water retention and crop productivity on degraded lands [36,57,58]. Furthermore, Beljin et al. (2025) [36] investigated biochar amendment dosages ranging from 0.5 to 10% (w/w) for reducing contaminant bioavailability and demonstrated that even low dosages were sufficient. Considering field feasibility, biochar associated costs, and amendment effectiveness, 0.5% of biochar was used in our experiments. A decrease in desorption is the desired outcome for pesticide immobilization, and therefore, a reduction in environmental mobility, toxicity, and bioavailability.

Figure 4 shows the remaining fraction of isoprothiolane and tricyclazole in unamended and biochar-amended paddy soil samples after 2, 48, and 96 h of contact time. The remaining fraction of tricyclazole in biochar-amended paddy soil was significantly higher than in unamended soil at 2 and 48 h ($p < 0.05$, Welch's t-test, BH correction, Table S10), whereas the difference at 96 h was not significant. Consistent with these findings, F_{fast} of tricyclazole was significantly lower in biochar-amended soil (F_{fast} = 0.253 [0.190–0.322], Table 3) than in unamended soil (F_{fast} = 0.629 [0.597–0.656]; difference −0.376 [−0.476; −0.270], Bonferroni-adjusted 95% CI; Tables 3 and S8) whereas $k_{slow+veryslow}$ did not differ significantly. In biochar-amended soil, F_{fast} (0.253) exceeded the fraction desorbed after 2 h (0.162), as measured and fitted values deviated more strongly for this treatment (Figures 3 and S2). The F_{fast} comparison therefore underestimates the effect of biochar observed in the measured remaining fractions. Biochar amendment thus reduced the rapid desorption of tricyclazole from soil.

The fast (F_{fast}) and slow ($F_{slow+veryslow}$) desorbing fraction of the two-compartment model are associated with binding sites that require distinct activation enthalpies, ranging from near zero for rapidly accessible (fast-desorbing) to 60–100 kJ mol^{-1} for more strongly bound (slow-desorbing) sites [37]. As biochar was added before spiking and aged together with the pesticides, the smaller F_{fast} in biochar-amended soil indicates that part of the tricyclazole was retained by the biochar as an additional, strongly sorbing phase. The planar, fully aromatic structure of tricyclazole favors interactions with aromatic biochar surfaces via its π-electron system [54], which may explain its strong retention by biochar. The pH of the biochar-amended soil was not measured. However, an increase in pH due to the alkaline biochar (pH 9.5) cannot explain the reduced F_{fast} of tricyclazole, as its sorption to soil organic matter and soil decreases with increasing pH [49]; a pH increase would therefore be expected to increase rather than decrease F_{fast}. According to the model, the larger slowly desorbing fraction results in a higher remaining fraction of tricyclazole at 96 h in biochar-amended than in unamended soil (0.38 vs. 0.20), which is consistent with the measured mean values (0.334 ± 0.133 vs. 0.162 ± 0.002). The non-significant difference at this time point therefore likely reflects the high variability between replicates in biochar-amended soil (n = 3) rather than a convergence of desorption. The concentration of tricyclazole in our experiment exceeded realistic field concentrations. As high-affinity sorption sites on biochar

are limited [59], they may have been partly saturated at this loading, so that the effect of biochar may be larger at field-relevant concentrations. Thus, our study indicates that biochar reduces the fast-desorbing, and thus potentially bioavailable, fraction of tricyclazole. This may indicate an ecologically relevance for short term leaching events directly after pesticide application such as heavy rainfalls or flooding, where a reduction in the fast-desorbing fraction may reduce the immediate loss of tricyclazole to the surrounding water.

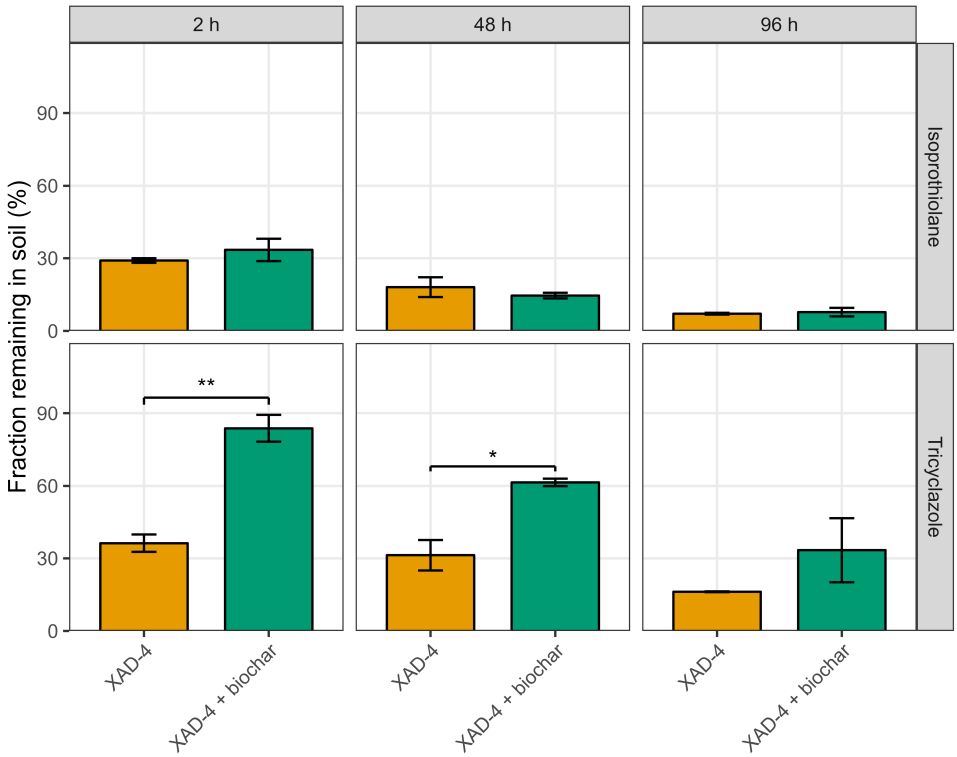


Figure 4. Remaining concentration of isoprothiolane and tricyclazole in paddy soil (% of initial spike) over time (2, 48, and 96 h) in the presence of an XAD-4 sorbent, with and without biochar amendment (XAD4 vs. XAD4 + bc). Bars represent mean values ± SD ($n = 3$). Statistical significance was tested between XAD4 and XAD4+bc treatments (Welch's *t*-test, Benjamini–Hochberg-corrected; * $p < 0.05$, ** $p < 0.01$).

In contrast, F_{fast} of isoprothiolane increased significantly under biochar amendment ($p < 0.05$), suggesting that a larger proportion of isoprothiolane was rapidly desorbed than in unamended soil ($F_{fast} = 0.841$ [0.810–0.872] and $F_{fast} = 0.748$ [0.722–0.775], respectively, Table 3). Nevertheless, the remaining fractions of isoprothiolane did not differ significantly in the soil at 2, 48, and 96 h (Figure 4, Table S10). In general, isoprothiolane already shows a comparatively high fast-desorbing fraction in unamended soil ($F_{fast} = 0.748$ [0.722–0.775]), with nearly complete desorption observed after 96 h contact time (~ 92.9 ± 0.4%). A comparable effect on the increase in F_{fast} in amended soil was shown by Cabrera et al. [60], who found that biochar amendment decreased the sorption of the highly mobile herbicides bentazone and aminocyclopyrachlor relative to unamended soil, which they attributed to the competition between biochar-derived DOC and the pesticide for soil sorption sites [60]. A similar DOC-mediated mechanism may explain the increased F_{fast} of isoprothiolane in our study, although DOC was not measured. Unlike tricyclazole, isoprothiolane lacks an extended aromatic system, so that strong π-interactions with biochar surfaces are less likely, which may explain why biochar did not retain isoprothiolane but rather increased its desorbable fraction. Although, the increase in F_{fast} indicates a larger initially desorbable fraction under biochar amendment, this was not reflected in the remaining soil fraction at

any of the measured time points (2, 48, or 96 h). This apparent discrepancy may be related to the slower fast desorption in biochar-amended soil: k_{fast} was identifiable for isoprothiolane in biochar-amended soil (0.83 [0.71–1.03] h^{-1}), whereas it exceeded 1.0 h^{-1} in unamended soil (lower bound from the RSS profile). A slower release from the fast-desorbing fraction may have partly offset its larger size during the first hours, although k_{fast} was not compared statistically. Overall, biochar amendment at 0.5% (w/w) reduced the fast-desorbing fraction of tricyclazole, whereas it increased that of isoprothiolane, without a significant effect on the remaining fraction of isoprothiolane in soil. The effect of biochar on pesticide desorption is therefore compound specific.

4. Conclusions

This study provides a comprehensive approach to assessing the fate of isoprothiolane and tricyclazole in contaminated, acidic, clay, and TOC-rich paddy soil from the Mekong Delta, Vietnam, using different extraction agents (Tenax and XAD-4) and immobilization strategies by biochar amendment. XAD-4 and Tenax resin desorption were applied to quantify potentially bioavailable fractions of isoprothiolane and tricyclazole to evaluate the performance of both extraction agents for polar pesticides.

For isoprothiolane, the desorption parameters obtained with both extraction agents did not differ, indicating that both extraction methods are suitable for isoprothiolane and that extraction method choice has limited influence on estimated potentially bioavailable fractions for this compound. For tricyclazole, in contrast, Tenax yielded a significantly lower fast-desorbing fraction than XAD-4, which, as the stronger sink, is therefore the more suitable extraction agent for determining the potentially bioavailable fraction of this compound in this soil.

Regarding immobilization, biochar amendment exerted compound-specific, opposing effects on the fast-desorbing fraction. Biochar amendment reduced tricyclazole's fast-desorbing fraction significantly at a dosage of 0.5% (w/w) during the first 96 h. This indicates a reduction of the potentially bioavailable tricyclazole fraction, particularly relevant for short term leaching events following pesticide application, such as heavy rainfall or flooding, potentially reducing immediate losses of tricyclazole to surrounding water bodies. For isoprothiolane, biochar increased the fast-desorbing fraction without significantly changing the fraction remaining in soil, possibly due to a slower release from this fraction. An increase in the fast-desorbing fraction is therefore unlikely to translate into a proportionally higher environmental risk.

Our findings contribute to advancing pesticide bioavailability assessment and remediation strategies for rice paddy soils, particularly for frequently detected fungicides such as isoprothiolane and tricyclazole. Moreover, the observed efficacy of a low biochar dosage (0.5%, w/w) for tricyclazole suggests that biochar amendment may offer a practical remediation approach, given the potential for producing biochar from locally available biomass. These findings are based on a single clay-rich, acidic paddy soil from Vĩnh Long province in the Mekong Delta, Vietnam. As sorption and desorption of both pesticides and the effect of biochar depend on soil properties such as organic carbon content, texture, and pH, their transferability to other paddy soils remains to be tested. Moreover, tricyclazole was applied at concentrations approximately six times above reported field levels, at which high-affinity sorption sites of biochar may be partly saturated; this effect represents a conservative estimate and needs to be confirmed at field-relevant concentrations and under field conditions. Future studies should additionally incorporate bioaccumulation tests in model organisms to validate and complement laboratory derived bioavailability data, providing a more holistic understanding of pollutant bioavailability. Furthermore, sampling before 2 h would allow the fast desorption rate to be determined, and paired field measurements of soil residues

and rice grain concentrations would help to evaluate whether desorption kinetics can serve as an indicator of pesticide uptake.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/land15112105/s1: Table S1. MRM parameters for the LC-MS/MS quantification of tricyclazole and isoprothiolane; Table S2: Elemental and proximate analysis of biochar; Table S3: Kinetic parameters of the two-compartment desorption model for three time windows; Figure S1: RSS profiles for the fast desorption rate constant kfast of the two-compartment desorption model (2–96 h); Table S4: Range of the fast desorption rate constant kfast compatible with the data, for the 2–96 h window; Table S5: Sensitivity of the two-compartment model parameters to the fixed value of kfast; Table S6: Routine limit of quantification (RLOQ) and recovery rate (%) for QuEchERS extraction of pesticide residues from rice grain; Table S7: Comparing pesticide fraction desorbed from soil at t = 192 h with Welch's *t*-test with BH correction; Table S8: Pairwise comparisons of the kinetic parameters Ffast and kslow+veryslow between treatments within each compound; Figure S2: Residuals of the two-compartment desorption model versus time; Table S9: Concentrations of isoprothiolane and tricyclazole (mg kg^{-1}) in rice grain samples from conventionally and organically (under transition since November 2023) managed fields in Vĩnh Long province, Mekong Delta, Vietnam; Table S10: Results Welch *t*-test (*p*_value) with Benjamini–Hochberg correction (grouped by compounds, p_adjusted) comparing remaining pesticide fraction in amended and unamended soil.

Author Contributions: Conceptualization, L.K. and L.W.; methodology, L.K.; L.W. and S.M.; validation, L.K.; formal analysis, L.K.; investigation, L.K. and Y.K.; resources, L.W.; data curation, L.K.; writing—original draft preparation, L.K.; writing—review and editing, L.K., L.W., S.M., K.C.M., Y.K. and A.A.; visualization, L.K.; supervision, L.W.; project administration, L.W. and K.C.M.; funding acquisition, L.W. and K.C.M. All authors have read and agreed to the published version of the manuscript.

Funding: The bilateral OrganoRice project, from which this paper emerged, is funded by the German Federal Ministry of Research, Technology and Space (BMFTR) within the "CLIENT II-International Partnerships for Sustainable Innovations" funding initiative, funding code 01LZ1806A and by the Vietnamese Ministry of Science and Technology (MOST), funding code NĐT/DE/22/29.

Data Availability Statement: The desorption data supporting the findings of this study are provided in Appendix A. The R code used for model fitting and statistical analysis is available from the corresponding author upon request.

Acknowledgments: The authors would like to express their gratitude to Björn Thiele who provided support and guidance throughout the laboratory work and preparation of this manuscript. The authors gratefully acknowledge the financial support of the Bioeconomy Science Center (BioSC). This work was funded by the Ministry of Culture and Science of the German State of North Rhine-Westphalia (MKW NRW) as part of the BOOST FUND 2.0 project NewBIAS (New Biochars for the Improvement of Agricultural Soils). During the preparation of this study, the authors used Claude, Anthropic for the purposes of code revising the R code for the kinetic analysis. The authors have reviewed and edited the output and take full responsibility for the content of this publication.

Conflicts of Interest: Authors Linda Klamann, Yousra Khatib, and Lutz Weihermüller were employed by the company Forschungszentrum Jülich GmbH. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

DOC	Dissolved Organic Carbon
EU	European Union
GUS	Groundwater Ubiquity Score

LC-MS/MS	Liquid Chromatography-Tandem Mass Spectrometry
LOQ	Limit of Quantification
MRL	Maximum Residue Limit
PAH	Polycyclic Aromatic Hydrocarbons
PCB	Polychlorierte Biphenyle
TOC	Total Organic Carbon
QuEChERS	"Quick, Easy, Cheap, Effective, Rugged and Safe"

Appendix A

Table A1. Experimental data given as pesticide fraction in the soil (%) relative to initial pesticide concentration.

Sampling Time (h)	Tri Fraction in Soil (%)	Tri Fraction in Soil with XAD-4 (%)	Tri Fraction in Soil with Tenax (%)	Tri Fraction in Biochar-Amended Soil with XAD-4 (%)	Iso Fraction in Soil (%)	Iso Fraction in Soil with XAD-4 (%)	Iso Fraction in Soil with Tenax (%)	Iso Fraction in Biochar-Amended Soil with XAD-4 (%)
2	65.4	32.8	62.6	80.3	61.6	29.6	26.5	29.3
2	73.4	36.0	61.9	80.8	64.8	28.0	31.4	32.6
2	72.9	40.0	41.2	90.2	59.8	29.6	no data	38.5
4	63.9	32.3	no data	60.6	50.4	21.3	no data	13.9
4	51.2	34.2	44.7	62.8	47.3	25.7	23.6	16.3
4	51.7	40.3	43.4	54.1	57.9	29.8	18.0	10.1
6	no data	31.1	no data	67.2	no data	20.0	no data	17.9
6	no data	38.5	no data	66.5	no data	25.3	no data	17.5
6	no data	29.7	53.6	80.2	no data	19.1	24.9	19.5
24	65.5	31.0	46.0	70.1	57.3	16.2	20.2	15.4
24	58.1	35.3	no data	61.4	59.3	20.4	no data	13.4
24	66.6	36.6	57.6	60.1	60.5	22.7	21.3	14.0
48	64.9	38.4	45.8	61.6	70.1	22.6	19.2	13.6
48	75.1	26.4	37.5	62.9	72.1	14.7	11.3	14.2
48	79.2	29.1	33.5	59.9	67.7	16.8	7.2	15.9
96	87.1	16.1	27.6	19.1	79.9	6.7	no data	5.7
96	86.4	16.4	44.3	45.3	80.7	7.3	8.5	8.7
96	85.5	16.1	21.7	35.8	79.5	7.3	LOQ	8.9
192	92.1	7.3	14.3	no data	85.6	LOQ	1.7	no data
192	87.1	16.9	27.6	no data	80.0	9.9	5.6	no data
192	76.3	13.3	32.1	no data	76.0	4.4	7.2	no data

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