Effect of Seasonal Variation on the Persistence and Dissipation Behaviour of the Herbicide Mixture of Fomesafen + Quizalofop-Ethyl in Tropical Soybean Agroecosystem and Safety Risk Assessment

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Effect of seasonal variation on the persistence and dissipation behaviour of the herbicide mixture of fomesafen + quizalofop-ethyl in tropical soybean agroecosystem and safety risk assessment

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Abstract

Weeds are the major limiting factor for optimum soybean production in India. The herbicide mixture of fomesafen and quizalofop-ethyl provides effective control of a broad spectrum of weeds, but its fate in the tropical soybean ecosystem is unknown and also the risks involved to the consumer and the environment are still unexplored. Hence, a supervised field trial was conducted following the post-emergence application of fomesafen 12\% + quizalofop-ethyl 3\% in two consecutive seasons. The dissipation of fomesafen followed biphasic double first order in parallel kinetics, whereas quizalofop-ethyl dissipation followed first order kinetics. A significant difference in the persistence of fomesafen was observed due to seasonal variation of meteorological parameters. However, the variation was significant only in plant, but non-significant in soil, in case of quizalofop-ethyl. The overall shorter persistence of both fomesafen and quizalofop-ethyl was recorded in warmer climatic conditions of Season I than Season II. The results thus indicated that care must be taken during application of this herbicide mixture in cold climatic regions, since both the herbicides may exhibit higher stability. The absence of end-point residues at harvest concluded that the formulation is safe for application in tropical agroclimate. The low chronic dietary toxicity and low soil ecological toxicity indicated that the herbicide mixture will offer no threat against consumer health and soil ecosystem. However, there was a concern about the toxicity against soil algal population which needs to be reconfirmed by further studies.

Keywords Fomesafen; Quizalofop-ethyl; LC-MS/MS; GC-MS/MS; Dissipation; Dietary risk; Soil ecological risk

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Introduction

Soybean (Glycine max L.) is considered as the most important seed legume, which occupies one of the largest monocultures in the world. Among all other field crops, it has the highest protein content (40-42%), which is a good substitute of animal protein also and the second highest oil content (18-22%) after groundnut. However, soybean production in India is severely affected by a number of monocotyledonous and dicotyledonous weeds, resulting in almost 50-76% yield reduction (Gharde et al. 2018). To compensate for such a huge yield loss, the herbicide mixture of fomesafen and quizalofop-ethyl has been introduced under the soybean cultivation in India. The mixture formulation (fomesafen 12%+quizalofop-ethyl 3%) controls a broad spectrum of weeds due to multiple modes of action. Fomesafen is a contact herbicide of the nitrodiphenyl ether chemical class. It controls broad leaf weeds by inhibiting the enzyme protoporphyrinogen oxidase (Alves et al. 2018). Quizalofop-ethyl is a systemic post-emergence herbicide of the aryloxy phenoxy propionate chemical family, which controls both annual and perennial grasses by inhibiting the enzyme acetyl coenzyme A carboxylase (Janaki et al. 2018).

Pesticide dissipation expresses a complex correlation with climate, since numerous interacting factors are involved. Meteorological parameters in totality determine the environmental concentration of pesticides by regulating their rate of degradation (Delcour et al. 2015). Besides, climate change is reported to alter the effectiveness and persistence of pesticides (Rhodes and McCarl 2020), often necessitating an increased pesticide application (Noyes et al. 2009). Therefore, conducting dissipation experiments under varying climatic conditions is necessary to predict the fate of pesticides accurately. This is extremely important especially for herbicides, since unlike other agrochemicals they are intended to persist longer in environment and change in climate thus tends to aggravate not only the risk of environmental contamination but also the detrimental effect induced by the herbicides on soil dwelling organisms. Again, the post-emergence herbicides may also contaminate the existing crop in field, making it unfit for domestic consumption as well as for export. Therefore, assessing the risk involved due to field application of herbicides is necessary to ensure the food and environmental safety. However, no information is available regarding the fate of the aforesaid herbicide mixture in soybean and its impact on dietary as well as soil ecological risk.
Therefore, the objectives of the current research are to assess the dissipation dynamics of the herbicide mixture (fomesafen 12%+quizalofop-ethyl 3%) in soybean and the impact of seasonal variation on its persistence. Besides, the risks involved towards soil ecological environment and consumer health are also evaluated.

Material and methods

Chemicals and reagents

The analytical standards of fomesafen and quizalofop-ethyl of >98% purity and their commercial formulation were supplied by Crystal Crop Protection Pvt. Ltd., India. Organic solvents were purchased from J.T.Baker, USA and the salts of ACS grade were procured from Merck Life Sciences Pvt. Ltd, Germany. The dispersive clean up sorbents viz. Primary Secondary Amine (PSA) and C18 were purchased from Agilent Technologies, USA. Graphitized Carbon Black (GCB) was purchased from United Chemical Technology, Bellefonte, PA.

Field experiment

Experimental design

Supervised field trials were conducted on soybean in two consecutive seasons at Jaguli Instructional Farm of Bidhan Chandra Krishi Viswavidyalaya (BCKV), Mohanpur, West Bengal, India (Latitude 22°93´ N, longitude 88°59´ E; altitude 9.75 m). The experimental region was constituted of new alluvial soil and the physico-chemical properties are represented in Table S1. Soybean seeds (variety: Pusa 16) were sown in 5m×4m plots at a spacing of 30 cm×10 cm. The herbicide mixture (fomesafen 12%+quizalofop-ethyl 3%) was applied as post-emergence on 19th May 2017 in Season I and 16th May 2018 in Season II at 225 g a.i. ha⁻¹ (T1 or recommended dose) and 450 g a.i. ha⁻¹ (T2 or double dose) doses. Separate plots were maintained as untreated control (T3) i.e. only water spray. The experiment was designed in randomized blocks, maintaining three replicates for each treatment including control. A total of 72.3 mm and 41.4 mm precipitation was recorded in Season I and II respectively, of which no rainfall was recorded up to 6 days after application of the herbicide mixture. The meteorological parameters were monitored in the regional meteorological station of BCKV (Fig. 1). The solar intensity and UV index were obtained from the Global Land Data Assimilation System and Tropospheric Emission Monitoring Internet Service, respectively (Fig. 1).

Sample collection
Soybean plant and soil samples were collected at an interval of 0 (2 hours after application), 1, 2, 3, 4, 5, 7, 10, 13, 15, 17 and 20 days after application of the herbicide mixture. Besides, soybean oil, deoiled cake and field soil samples were collected at harvest and analyzed separately for fomesafen and quizalofop-ethyl residues.

**Analytical procedures of fomesafen and quizalofop-ethyl**

**Extraction and clean up of soybean plant and soil**

Representative 10 g homogenized plant and soil samples were taken separately in 50 mL polypropylene centrifuge tubes and 10 mL HPLC grade water was added. The extracting solvent was 10 mL acetonitrile for fomesafen, whereas quizalofop-ethyl residues were extracted with 10 mL acetonitrile + 1% acetic acid. A salt mixture of 1.5 g sodium chloride + 5 g magnesium sulphate was added, mixed thoroughly for two minutes and centrifuged at 5,000 rpm for 5 minutes. The supernatant (2 mL) of both plant and soil samples were cleaned up separately by using 50 mg PSA + 25 mg GCB + 150 mg magnesium sulphate and 25 mg PSA + 25 mg C\textsubscript{18} + 150 mg magnesium sulphate clean up combinations, respectively. The extract was filtered with a 0.2 µ membrane filter and analyzed in LC-MS/MS for fomesafen. However, for quizalofop-ethyl, 1.5 mL supernatant was evaporated to dryness after clean up and reconstituted with 1.5 mL ethyl acetate. The extract was filtered and analyzed in GC-MS/MS.

**Extraction and clean up of soybean oil**

A representative 100 g ground soybean seed was extracted with 450 mL hexane in soxhlet apparatus and the solvent was evaporated at 40 °C by using a rotary vacuum evaporator to collect the oil. Representative 2 g oil was dissolved in 20 mL hexane and partitioned thrice with 3x30 mL acetonitrile in a separatory funnel. The combined acetonitrile fraction was concentrated in rotary vacuum evaporator and reconstituted separately with acetonitrile (2 mL) for fomesafen and ethyl acetate (2 mL) for quizalofop-ethyl. Then the extracts were cleaned up by using 50 mg PSA + 50 mg C\textsubscript{18} + 150 mg magnesium sulphate and filtered with 0.2 µ membrane filter before analysis.

**Extraction and clean up of deoiled cake**

The deoiled cake sample (2 g) was taken in a 50 mL centrifuge tube and 10 mL 5 % aqueous sodium chloride solution was added. The mixture was vortexed for one minute. Then 10 mL acetonitrile was added and vortexed again for 2 minutes, followed by rotospin for 15 minutes at 50 rpm. The sample was centrifuged at 10,000 rpm for 5 minutes. Then 6 mL supernatant was evaporated to dryness and reconstituted separately with acetonitrile (1.2 mL) for fomesafen and ethyl acetate (1.2 mL) for quizalofop-ethyl. Then the extracts were cleaned up by using 50 mg PSA + 25 mg C\textsubscript{18} + 150 mg magnesium sulphate and filtered with 0.2 µ membrane filter before analysis.
Instrumental Condition

LC-MS/MS

The analysis of fomesafen was performed with Waters 2695 separation module (Waters, USA) equipped with Symmetry C18 column (5 µm; 2.1×100 mm) and Micromass Quattro Micro API mass spectrometry. Masslynx V4.1 software was used for data acquisition and quantification. The chromatographic separation was performed by using the binary mobile phase viz. mobile phase A (5 mM ammonium acetate + 0.1% acetic acid in water) and mobile phase B (5 mM ammonium acetate + 0.1% acetic acid in methanol) at a flow rate 0.3 mL minute⁻¹. The gradient programming involved: 90% A + 10% B in 0-1 minute, 10% A + 90% B in 1-10 minute and 90% A + 10% B in 10-12 minute. Negative electrospray ionization with multiple reaction monitoring (MRM) scan type was used for analysis. The MRM transitions of fomesafen were: 436.98 > 195.01 (quantifier) with collision energy (CE) 41 eV; 436.98 > 222 (qualifier) with CE 29 eV and 436.98 > 285.9 (qualifier) with CE 22 eV. The other parameters were: capillary voltage (1 kV), cone voltage (31 V), source temperature (120 °C), desolvation temperature (360 °C), desolvation gas (nitrogen) flow (650 L h⁻¹) and collision gas (argon) flow (50 L h⁻¹).

GC-MS/MS

The analysis of quizalofop-ethyl was performed by GC-MS/MS (Agilent Technologies, USA), equipped with 7890A GC, 7000 MS and Masshunter B.05.00 software. GC separation was performed in HP-5 MS capillary column (30 m×0.250 mm×0.250 μm) and helium (purity ≥ 99.99%) was used as a carrier gas at a constant flow of 1 mL minute⁻¹. Splitless injection mode was used to inject 1 µL sample. A constant inlet temperature (285 °C) and auxiliary heater temperature (280 °C) were maintained. The oven temperature programme involved: Ramp 1 (150-220 °C, Rate: 50 °C minute⁻¹, Hold: 1 minute); Ramp 2 (220-250 °C, Rate: 10 °C minute⁻¹, Hold: 2 minutes) and Ramp 3 (250-280 °C, Rate: 5 °C minute⁻¹, Hold: 2 minutes). The mass spectrometry parameters involved electron impact (EI) ionization at -70 eV energy and source temperature of 230°C. The MRM transitions of quizalofop-ethyl were: 372.1 > 299.3 (quantifier) and 299.2 > 91.2 (qualifier) with collision energy 10 and 25 eV, respectively.

Recovery experiment

The recovery experiment was carried out by fortifying all the substrates viz. soil, soybean plant, oil and deoiled cake at 0.01, 0.05 and 0.10 mg kg⁻¹ concentration levels separately for fomesafen and quizalofop-ethyl. An eight point calibration curve involving 0.003, 0.01, 0.02, 0.05, 0.10, 0.25, 0.50 and 1.0 mg kg⁻¹ concentration levels was used for quantification.
Data analysis
The degradation of pesticides is often reported to follow biphasic kinetics in the field (Gluhar et al. 2019). Therefore, the dissipation of fomesafen and quizalofop-ethyl were determined by comparing between two kinetic models as follows:

Single First Order (SFO): $y = ae^{-bt}$ (1)

Double First Order in Parallel (DFOP): $y = ae^{-bt} + ce^{-dt}$ (2)

Where, ‘$y$’ is the concentration (mg kg$^{-1}$) at time ‘t’ (days), ‘$a$’ is the initial concentration at time $t=0$ and ‘$b$’ is the dissipation constant (days$^{-1}$) in SFO. In DFOP, ‘$a$’ and ‘$c$’ are the initial concentrations for two compartments and ‘$b$’ and ‘$d$’ are the respective dissipation constants. The parameters of the kinetic models were estimated by using R Studio version 1.2.5042 (RStudio Team 2020) and associated package \textit{mkin} (Ranke 2020). The best fit model was selected based on $\chi^2$ test as recommended by the FOCUS work group (FOCUS 2006).

Safety evaluation

Dietary risk assessment
The chronic dietary risk quotient (RQ$_d$) was assessed as follows:

$$RQ_d = \frac{\text{Estimated Daily Intake (EDI)}}{\text{Acceptable Daily Intake (ADI)} \times \text{Average Body Weight}}$$ (3)

The estimated daily intake (EDI) was calculated by multiplying the residue levels of fomesafen and quizalofop-ethyl in soybean plant with recommended consumption of soybean per day per person. The National Institute of Nutrition reported an intake of 30g and 75g person$^{-1}$ day$^{-1}$ of pulses for children (4-6 years) and adults (National Institute of Nutrition 2011). The average body weight of an Indian child and an adult are 18 kg and 60 kg (National Institute of Nutrition 2011). The acceptable daily intake (ADI) of fomesafen and quizalofop-ethyl is 0.003 and 0.0013 mg kg$^{-1}$ body weight day$^{-1}$ (PPDB 2021a, b), respectively. The RQ$_d > 1$ signifies high risk for consumption and vice versa.

Soil ecological risk assessment
The soil ecological risk quotient (RQ$_s$) of both fomesafen and quizalofop-ethyl was estimated for algae, earthworm and arthropods following the equation:

$$RQ_s = \frac{\text{Effective Concentration of pesticide (EC)}}{\text{Predicted No Effect Concentration (PNEC)}}$$ (4)
The predicted no effect concentration (PNEC) was obtained by dividing the toxicity value of respective target organism by corresponding assessment factor which was 50 for both the cases. The risk factor is considered high if $\text{RQ} > 1$, moderate for $0.1-1$ and low for $\text{RQ} < 0.1$ (European Communities 2003).

**Results and discussion**

**Method validation**

The analytical methods of fomesafen and quizalofop-ethyl were validated following the SANTE guideline (SANTE 2019). The calibration curves were linear with the coefficient of determination ($R^2$) 0.99 (Figure S1-S2). An average recovery percentage >85% along with repeatability (RSD$_r$) and within-laboratory reproducibility (RSD$_w$) <20% for all the substrates proved that the methods were accurate and repeatable (Table S2). The matrix effect of both fomesafen and quizalofop-ethyl was within ±20% (Table S2) and the specificity of the method was also found to be acceptable as the responses of both the compounds were <30% of the matrix matched standard at the desired retention time in control samples. The limit of quantification (LOQ) of both the molecules was 0.01 mg kg$^{-1}$.

**Kinetics of dissipation of fomesafen and quizalofop-ethyl**

The dissipation of fomesafen in soil and soybean plant followed the biphasic DFOP kinetics (Fig. 2; Table 1). The biphasic degradation of fomesafen involved rapid initial photolysis from both soil and plant surfaces in the first phase. The compound then moved gradually into the soil column or plant matrix, which increased the chance of adsorption with soil colloids or plant cellular components and thereby reduced the rate of soil microbial or chemical degradation as well as the plant enzymatic metabolism. Hence, a slower second phase of fomesafen dissipation was observed. Similarly, Walker and Bond (1977) reported that herbicides dissipated more rapidly from the soil surface than an application incorporated into the soil column. Ugare et al. (2013) reported biphasic dissipation of several pesticides in plants due to adsorption with cellular components. Wu et al. (2014) reported biphasic dissipation of fomesafen in soil, where the rate of degradation decreased due to increased adsorption of the molecule with time.

Unlike fomesafen, the dissipation of quizalofop-ethyl followed SFO kinetics in both soil and soybean plant (Fig. 3; Table 1). A report from the European Food Safety Authority (EFSA 2008) described that the faster rate of deesterification is the reason why quizalofop-ethyl follows simple first order kinetics under field condition. Similarly, Mantzos et al. (2015) also reported SFO kinetics of quizalofop-ethyl decay in both soil and sunflower plant under field experimental condition.
Effect of seasonal variation on dissipation of fomesafen

The average initial concentration of fomesafen in Season I and II ranged between 0.097-0.175 and 0.110-0.190 mg kg\(^{-1}\) in soil (Fig. 2a) and 0.249-0.497 and 0.261-0.509 mg kg\(^{-1}\) in soybean plant (Fig. 2b). A significant variation in the persistence of fomesafen between two consecutive seasons was observed in case of both soil and soybean plant (Table S3). The half-life of fomesafen was found to be lower in Season I (4.23-4.49 days in soil and 2.84-2.89 days in plant) than Season II (5.42-5.62 days in soil and 3.71-3.81 days in plant) (Table 1). A report from the Health Canada Pest Management Regulatory Agency (2018) described fomesafen half-life in soil may vary from less than 1 to more than 4 months depending on the environmental conditions under field condition. The overall shorter persistence of fomesafen in Season I than Season II in our experiment was primarily due to faster rate of photodegradation of the molecule from both soil and plant surface, since the average intensity of UV radiation, total solar radiation and bright sunshine hour (BSSH) were observed to be much higher in Season I along with less cloud coverage (UV index: 12.34, Intensity of total solar radiation: 275.42 Watt m\(^{-2}\), BSSH: 10 hours, cloud coverage: 39.06%) than Season II (UV index: 11.36, Intensity of total solar radiation: 209.24 Watt m\(^{-2}\), BSSH: 5.1 hours, cloud coverage: 78.13%) (Fig. 1). Photodegradation is reported to be the major decomposition pathway of fomesafen under field condition, which readily degrades the molecule even under relatively low sunlight conditions (Ahrens 1994). Besides, both microbial degradation and chemical hydrolysis play an important role in fomesafen dissipation (Das et al. 2020; USEPA 2006) and the rate of degradation increases with an increase in temperature. Hence, higher soil temperature in Season I (34 °C) may also have contributed to some extent to the shorter persistence of fomesafen in soil by decreasing the adsorption of the molecule and augmenting the rate of dissipation as compared to Season II (31 °C) (Fig. 1). Similarly, Rauch et al. (2007) reported that fomesafen dissipation occurs more rapidly under warmer climatic conditions, while cold climatic conditions favour high concentrations.

Effect of seasonal variation on dissipation of quizalofop-ethyl

The average initial concentration of quizalofop-ethyl in soil ranged between 0.034-0.055 mg kg\(^{-1}\) in Season I and 0.035-0.053 mg kg\(^{-1}\) in Season II (Fig. 3a). The half-life of quizalofop-ethyl in field soil was 1.63-1.70 days in Season I and 1.66-1.83 days in Season II (Table 1). The variation in the persistence of quizalofop-ethyl in soil between two consecutive seasons was found to be non-significant (Table S3). The reason underlying the fact is that the deesterification of quizalofop-ethyl to quizalofop acid, which is the major metabolic pathway of aryloxy phenoxy propionate (AOPP) herbicides, occurs rapidly in soil and depends primarily on soil solution pH. It has been
reported that pH is the key determining factor for degradation of quizalofop-ethyl in soil (Mantzos et al. 2017). Besides, Das et al. (2020) described that the rate of deesterification of quizalofop-ethyl reduces at lower pH. The pH of the soil in our experiment was acidic i.e. 6.4 (Table S1). Hence, quizalofop-ethyl showed an overall higher persistence in our experiment with half-life of 1.63-1.83 days in soil (Table 1) than the previously reported half-life of the molecule, which was 0.55-0.68 days (EFSA 2008; Mantzos et al. 2015).

The persistence of quizalofop-ethyl in soybean plant varied significantly between two consecutive seasons (Table S3). The estimated half-life was lower in Season I (1.76-1.77 days) than Season II (1.90-1.96 days) (Table 1). The dissipation of quizalofop-ethyl in soybean plant is represented in Fig. 3b. It has already been reported that the metabolism of AOPP herbicides in tolerant crop like soybean occur through deesterification by carboxy esterase enzyme and aryl hydroxylation by cytochrome P450 monooxygenase or oxidase enzymatic system (Koeppe et al. 1990). The rate of such enzymatic degradation is highly dependent on temperature. A significant reduction of herbicidal activity was observed at higher temperature, which is due to increased metabolism of the compound (Coupland 1989). Refatti et al. (2019) also reported a 3 °C increment in temperature resulted in 30% reduction in cyhalofop-butyl activity due to constitutive upregulation of key genes responsible for detoxification of xenobiotics in higher temperature. In our experiment, higher atmospheric temperature in Season I (30.1 °C) (Fig. 1) thus induced an increased rate of metabolism of quizalofop-ethyl in soybean plant and thereby lower half-life than Season II (26.3 °C).

**End-point residue analysis at harvest**

The interval between the herbicide application and the crop harvest was 100 days. The end-point residues of both fomesafen and quizalofop-ethyl in soil and harvested soybean seed (oil and deoiled cake) were below the quantifiable limit, i.e. 0.01 mg kg⁻¹ (Figure S3-S4). Mandal et al. (2014) also reported that the residues of quizalofop ethyl in black gram were below the quantification limit (0.01 mg kg⁻¹) at harvest. Besides, the residues in harvested crop products were also below the maximum residue limit (MRL) prescribed by the European Union i.e. 0.02 mg kg⁻¹ for fomesafen and 0.2 mg kg⁻¹ for quizalofop-ethyl. Hence, the application of the herbicide mixture in soybean crop was considered safe for consumer health.

**Safety evaluation**

Dietary risk assessment
The dietary risk quotient ($RQ_d$) of fomesafen ranged between 0.010-0.212 for adults and 0.014-0.283 for children (Table 2). The $RQ_d$ of quizalofop-ethyl ranged between 0.018-0.155 for adults and 0.025-0.207 for children (Table 3). Since, the chronic $RQ_d$ of both fomesafen and quizalofop-ethyl on each sampling day were below 1 irrespective of the season and dose, the application of the herbicide mixture was therefore considered to impose no long-term risk of dietary toxicity. Pang and Hu (2020) also reported no dietary toxicity due to fomesafen application in soybean.

### Soil ecological risk assessment

The soil ecological risk quotients indicated that both fomesafen and quizalofop-ethyl are safe towards earthworm and soil arthropods (Table 2-3). However, a high risk for fomesafen and moderate to high risk for quizalofop-ethyl against green algae was observed (Table 2-3). Fomesafen has been reported to be toxic to green algae (Caquet et al. 2005). A moderate toxicity against green algae *Pseudokirchneriella subcapitata* was also reported for quizalofop-ethyl (PPDB 2021b). Therefore, the risk associated with soil algal population due to application of this herbicide mixture can’t be ignored and should be assessed extensively in different agro-climatic zones across the globe in future to establish a conclusive inference.

### Conclusion

The degradation dynamics of the herbicide mixture i.e. fomesafen 12% + quizalofop-ethyl 3% was studied in the soybean ecosystem in two succeeding seasons at two treatment doses. A significant effect of seasonal variation on the dissipation of the herbicide mixture was observed. However, the variation in persistence was observed to be non-significant at two treatment doses irrespective of season. The overall low persistence of both the active ingredients indicated that the formulation is safe for application in the tropical agroclimatic environment and can be used as an alternative to the older molecules which in general leave considerable residues in harvested products. Both fomesafen and quizalofop-ethyl showed low chronic dietary toxicity to the children as well as adults. Besides, the absence of residues at harvest concluded that the harvested soybean products can be consumed safely if the formulation is applied at the recommended dose following good agricultural practices (GAP). However, the risk of acute dietary toxicity was not evidenced in this study. The assessment of soil ecological risk demonstrated that the herbicide mixture was safe towards earthworm and soil dwelling arthropods, whereas a high risk against soil algal population needs to be attended more carefully and sorted out as the future scope of research.
Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

Availability of data and materials
The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interest
The authors declare that they have no competing interests.

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No funding was received for conducting this study.

Authors' contributions
SD developed the experimental design and wrote the manuscript. DS developed and validated the analytical methods. AK conducted the field experiment, collected and prepared the samples. SM performed the statistical analysis and representation of the data generated. AK and AB contributed to the language editing and MK reviewed the manuscript. SR supervised the whole experiment and revised the manuscript for final submission. All authors read and approved the final manuscript.

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**Figure captions**
Fig. 1 The temporal patterns of maximum, minimum and soil temperature; maximum and minimum relative humidity (RH I and RH II); cloud octa; bright sunshine hours; UV index and total solar intensity in Season I (a) and Season II (b)

Fig. 2 Dissipation of fomesafen in soil (a) and soybean plant (b) applied at two treatment doses (T1 and T2) in Season I and Season II

Fig. 3 Dissipation of quizalofop-ethyl in soil (a) and soybean plant (b) applied at two treatment doses (T1 and T2) in Season I and Season II
Figures

Figure 1

The temporal patterns of maximum, minimum and soil temperature; maximum and minimum relative humidity (RH I and RH II); cloud octa; bright sunshine hours; UV index and total solar intensity in Season I (a) and Season II (b)
Figure 2

Dissipation of fomesafen in soil (a) and soybean plant (b) applied at two treatment doses (T1 and T2) in Season I and Season II
Figure 3

Dissipation of quizalofop-ethyl in soil (a) and soybean plant (b) applied at two treatment doses (T1 and T2) in Season I and Season II

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